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Mathematical modeling of air sparging for subsurface remediation: state of the art

John E. McCray *

International Ground Water Modeling Center, Department of Geology and Geological Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401-1887, USA

Abstract

A review of published mathematical models used to simulate air sparging is provided. Applicability of the models, efforts to test the models using experimental data and contributions of modeling efforts to the practice of air sparging are also discussed. Compartmentalized lumped-parameter models and multiphase flow models have dominated air-sparging modeling efforts. In essence, each class of models requires the assumption of a continuum over some model domain. Each approach has significant benefits as well as some inherent disadvantages. Based on the literature, both lumped-parameter modeling and multiphase-flow modeling have been successful in improving our theoretical understanding of the air-sparging process and in facilitating practical development of sparging systems. Lumped-parameter models are simpler to use, and can lend considerable insight to sparging operations. Multiphase flow models have the potential to offer a more realistic simulation of the airflow process, but may require a considerable amount of data collection for model input. The literature suggests that for any air-sparging model to be useful for field applications, detailed model calibration is necessary. It is recommended that models incorporate, in some fashion, the diffusion and dispersion of contaminants to macro-scale air channels, and nonequilibrium interphase mass transfer of contaminants. These mass-transfer-limited processes are frequently listed as causes for the ‘‘tailing’’ of vapor-extraction effluent contaminant concentrations that are frequently observed during field applications. However, time-varying mixing of relatively clean and contaminated vapors in the extraction system may also explain this tailing. Geophysical imaging techniques and inverse modeling combined with air-sparging pilot tests and measurement of traditional hydrogeologic parameters may allow for successful modeling efforts. © 2000 Elsevier Science B.V. All rights reserved.

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* Tel.: +1-303-384-2181; fax: +1-303-273-3859; e-mail: jmccray@mines.edu

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1. Introduction

Air sparging is a remediation technology used frequently for subsurface removal of dissolved volatile organic contaminants (VOCs) and nonaqueous phase liquid (NAPL) contaminants (e.g. gasoline, jet fuel and chlorinated solvents). Air sparging involves injection of air into the subsurface below the water table. The airflow is controlled by the forces of buoyancy and capillarity, and by the influence of permeability. Dissolved or NAPL-phase organic contaminants partition to the air phase and are carried to the vadose zone, where the vapors are typically collected by a soil vapor extraction (SVE) system. Airflow generally occurs in small air channels at the pore scale, although bubble flow is possible in well-sorted, coarse-grained media (e.g. gravel).

While air sparging is becoming a common technique, there is much to learn about the physical flow behavior and air–water chemical partitioning related to this multiphase process. The use of air-sparging technology is growing more rapidly than the theoretical and design knowledge associated with the technique. Mathematical models have long been used to analyze the observed behavior of biophysicochemical systems in order to gain a better theoretical understanding of these systems. However, air-sparging models are in the early stages of development. Published descriptions of the first air-sparging models became available in the early to mid-1990s. As expected for a young research topic, our understanding regarding the proper application of these models is not fully developed.

Excellent reviews of air sparging for groundwater remediation have been offered previously [1–3]. However, these reviews included very little information on mathematical modeling. The aim of this paper is to present a state-of-the-art review of published air-sparging models. Air-sparging models generally fall into two categories: (1) compartmentalized, lumped-parameter models and (2) multiphase fluid flow models. First, a brief discussion on the airflow processes that occur during sparging is offered because an understanding of this topic is critical for successful use and development of air sparging models. Next, generalized mathematical formulations for the two categories of models, a review of the published models, applicability of the models, published efforts to test these models using experimental data, and contributions of modeling efforts to the remediation practice are discussed. Finally, recommendations are offered regarding issues that should be addressed to advance the state-of-the-art.

2. Sparging airflow mechanisms

The first conceptualizations of airflow during air sparging were of bubbles rising in the saturated zone. It is now generally accepted that airflow occurs in discrete air channels for most porous media, and that bubble transport is applicable in gravel or perhaps in coarse, well-sorted sands [4–7]. However, because the porous media at some contaminated sites is primarily gravel [8], bubble-flow conceptual models should not be discarded.

The laboratory experiments of Ji et al. [4], Reddy and Adams [9], and Semer et al. [7] demonstrated that airflow in coarse or sandy porous media exhibits small-scale fingering. Clayton [6] determined from analysis of numerous field and laboratory data that channeling is ubiquitous at the pore scale. However, based on this analysis, he contends that formation of widely spaced air channels in homogeneous media is unlikely. Other authors have also contended that capillarity and relative-permeability heterogeneities appear to be the primary cause of air channels at macroscopic and larger scales [2,4].

At smaller scales, air channels may be closely spaced relative to the representative elementary volume (REV) of a typical model, and thus the assumption of an air–water continuum may be appropriate within a zone of soil with relatively homogeneous hydrogeologic properties. This latter issue has been a topic of considerable debate associated with the use of multiphase-flow models, and will be discussed in more detail in the forthcoming section on these models. Regardless of the causal mechanisms, however, it is clear that air channels will form at various scales during in situ air sparging. Thus, models should be developed to account for the associated fluid-flow and mass-transfer processes at scales relevant to the problem of interest and research goals of the investigator.

3. Compartmentalized and lumped-parameter models

Compartmentalized air-sparging models are based on the assumption that fluid phases or biophysicochemical processes may be separated into compartments. These models are also called ''reactor models'', and generally relate the quantity of mass removed to the volume of fluid circulating through the contaminated zone (Rabideau et al. [22]). Lumped-parameter models attempt to simulate the desired mass-transfer processes by ''lumping'' these processes into bulk parameters. Compartmentalization and lumping techniques are attractive because they often simplify the mathematics of the air-sparging process, which inherently involves multiphase flow and multiple mass-transfer processes. Lumping allows investigators to describe mathematically several processes that are difficult to measure.

3.1. General mathematical formulation

A conceptual schematic for a compartmentalized, lumped-parameter, air-sparging model is illustrated in Fig. 1. Most models described in the literature are based on

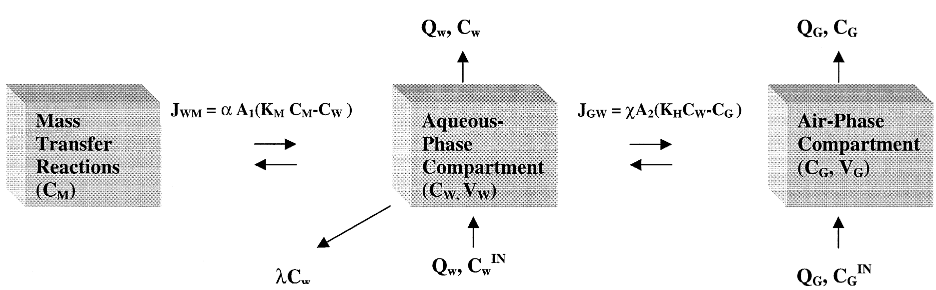

Fig. 1. Generalized lumped-parameter conceptual model for the air-sparging process. J_{WM} and J_{GW} (M/T) represent the mass flux of contaminant between the phases (compartments). The other terms are defined in the text and are associated with Eqs. (1)–(3).

similar conceptual models. Fundamentally, the figure illustrates a three-compartment model where the compartments represent the aqueous phase, the air phase, and a third-phase mass-transfer domain. The third phase is often incorporated to account for nonequilibrium mass-transfer processes such as sorption/desorption to the soil phase, dissolution of a NAPL phase, or diffusion-limited mass transport of aqueous contaminant to an air channel. For most published model formulations, mass transfer between the air and water phases is generally assumed to follow equilibrium behavior according to Henry's Law, although rate-limited mass transfer across the air–water interface may also be included, as shown in the figure. Note that the equations shown for rate-limited mass transfer are merely examples. Many different expressions for mass transfer are possible. For example, a linear, first-order driving force model is illustrated for mass transfer. However, a diffusion-based formulation may be used to model mass transport from a contaminated-water phase (C_M) that is not in contact with an air channel to a water zone (C_W) that interacts directly with an air channel.

The number and type of compartments can vary from those shown in the figure. For example, separate compartments could be provided for the many possible nonequilibrium mass-transfer processes associated with the aqueous phase. However, to date, the model formulations available in the literature lump all such mass-transfer processes into a single compartment. In addition, models are typically developed for either aqueous- or gas-phase transport depending on the desired application of the model, and the measurable parameters associated with the applicable flow process. Thus, two compartments are frequently used to model mass transport in either the aqueous or the vapor phase. For the reasons described above, most air-sparging models of this type in the literature are termed ''two-compartment models''. Note that if the rate-limited mass transfer expressions were reduced to equilibrium expressions (as for the mass-loss term, λC), then a ''single-compartment'' model could be developed for either the aqueous or gas phase.

The contaminant mass balance for the air-phase compartment model illustrated in Fig. 1 may be given as:

$$V_G \partial C_A / \partial t = Q_G \left(C_G^{IN} - C_G \right) + \chi A_2 \left(K_H C_W - C_G \right). \tag{1}$$

Where V_G is the volume of the gas phase, Q_G is the flow of air through the compartment (assuming incompressible flow), C_G is the vapor contaminant concentration, C_W is the aqueous contaminant concentration, K_H is the dimensionless Henry's constant, χ is the air–water mass transfer rate coefficient (L/T), and A_2 is the interfacial area (L^2) between the gas and aqueous phases. For the water phase, the following equations may be written:

$$V_W \partial C_W / \partial t = Q_W \left(C_W^{IN} - C_W \right) - \chi A_2 \left(K_H C_W - C_G \right) + \alpha A_1 \left(K_M CM_W - C_W \right) - \lambda V_W C_W. \tag{2}$$

Where C_M is the concentration of the contaminant in the third phase, K_M is the equilibrium partitioning coefficient of the contaminant between the third phase and the aqueous phase, α is the third phase-water mass transfer rate coefficient (L/T), A_1 is the interfacial area (L^2) between the aqueous phase and the third phase, and λ is a mass-loss rate coefficient (T^{-1}) (e.g. for biodegradation). Finally, for the third phase,

$$V_M \partial C_M / \partial t = -\alpha A_1 \left(K_M C_M - C_W \right). \tag{3}$$

For each equation above, the mass transfer coefficient and interfacial area is often combined into a lumped mass-transfer coefficient because the interfacial area is difficult to measure. Ideally, the flow rates, mass-transfer coefficients, and equilibrium partitioning coefficients can be measured, and Eqs. (1)–(3) have three unknowns (C_W, C_M, C_G). However, mass-transfer coefficients are generally considered to be fitting parameters. Thus, the several unknowns are typically obtained by solving the governing equations iteratively using numerical techniques. The models in the literature do not follow the above formulation exactly. The formulation above is provided for background and to facilitate the subsequent discussions of the published models.

3.2. Bubble-flow models

Sellers and Schreiber [10] offered a lumped-parameter, single-compartment analytical model for predicting cleanup rates for ground water VOC contamination. The model assumes that mass transfer of water to air is diffusive-flux-limited because the residence time of air in the ground water does not allow equilibrium. This conceptual model considers transfer of dissolved contaminants into rising air bubbles completely surrounded by ground water under conditions of complete mixing. The analytical solution is a simple exponential increase of concentration over time. Wilson et al. [11] offered a modification of the Sellers–Schreiber model for calculation of bubble-rise velocities.

3.3. Models that account for air-channels or nonequilibrium mass-transfer phenomena

Many compartmentalized models have been developed to address the impact of air channeling on contaminant mass removal. The purpose of these models is to account for the impact of mass-transfer limiting diffusion of aqueous-phase contaminants to the air channel, and/or non-equilibrium mass-transfer across the air–water interface. Other nonequilibrium mass transfer processes may also be incorporated.

Wilson [12] developed a simple analytical air-sparging model for estimating transit times of dissolved VOC in a nearly stagnant aquifer for transient conditions. The model is based on two well-mixed water compartments whereby contaminated water flowing through one compartment may exchange mass (by advection) with another compartment, which is being sparged. Transfer of contaminant from the sparged-water compartment to the air phase is modeled as an equilibrium mass transfer process according to Henry's Law. Wilson et al. [11] developed a numerical model that incorporated the processes of VOC transport to discrete air channels by aqueous dispersion and by air-induced circulation of the water in the vicinity of the sparging well. The authors used the lumped-parameter approach to simulate dispersion of aqueous-phase contaminant to an arbitrary number of uniform, evenly spaced air channels.

To simulate injection of air into a one-dimensional column of saturated porous media, Chao et al. [13] assumed that a certain fraction of the saturated media was considered to be a ''mass transfer zone'' (MTZ), while the remaining ''bulk water'' was assumed to be unaffected by sparging. In the MTZ, contaminants diffuse to and across the air–water interface. In the ''bulk water'' the impact of the air channels on mass transfer was assumed to be negligible. These authors developed a lumped-parameter model by writing mass-balance equations for the advecting air phase and stationary MTZ. The nonequilibrium mass transfer across the air–water interface was modeled using the linear first-order driving force approximation (e.g. Ref. [14]). The equations were solved numerically, and the values used for the mass-transfer coefficient and the fraction of the saturated porous media comprised by the MTZ were calibrated so that the model results matched the laboratory-column data. In a companion paper, Braida and Ong [15] used a model similar to that described above, except that diffusion from the bulk water phase to the MTZ was included as well as nonequilibrium volatilization at the air–water interface. This model was designed to simulate a laboratory experiment mimicking flow in a single-air-channel.

Wilson et al. [16] included the conceptualization of randomly spaced air channels in their model. The numerical model is similar to their previous work [11], except that a random generator determined the spatial coordinates of air channels. The authors formulated the physics and chemistry associated with each air channel based on a lumped-parameter approach.

Few lumped-parameter models have accounted for the presence of a NAPL phase. Roberts and Wilson [17] developed a model that included the dissolution of a NAPL droplet in stagnant water and subsequent aqueous diffusion of the dissolved contaminant to flowing water, followed by advective transport to a cylindrically shaped sparging zone. The difficulty associated with use of the model is estimation of an effective NAPL-drop radius. Practically, this term would be a fitting parameter. Wilson et al. [18] improved on the model by incorporating kinetic NAPL dissolution and contaminant diffusion from low-permeability layers. A follow up to this work was conducted by Gomez-Lahoz et al. [19], who incorporated diffusion-induced concentration rebound after shutdown of an air-sparging system. Wilson et al. [16] incorporated theories from previous works [17,18] to develop air-sparging models that accounted for dissolution of NAPL droplets and subsequent diffusion to multiple air channels.

Rabideau and Blayden [20] developed an analytical model to simulate the removal of dissolved VOCs by air sparging. The simplified approach treats the air-sparging zone as a completely mixed region wherein mass removal of contaminants from the air zone occurs by advection and the mass-transfer processes of volatilization and first-order kinetic mass transfer. The mathematical formulation is similar to the popular mobile–immobile model, or two-domain model, traditionally used for solute-transport applications [21]. Thus, the non-dimensional form of this model can be used to simulate many different two-compartment processes and is quite useful. For example, the authors demonstrate that tailing in the extracted vapor concentrations may be interpreted in terms of either kinetic desorption of contaminants or by diffusion of contaminants into discrete air channels [22]. In addition, as will be discussed, mixing of clean and contaminated vapors in the vacuum-extraction zones may cause similar tailing.

3.4. Applicability of lumped-parameter models

Compartmentalized or lumped-parameter models cannot fundamentally describe the spatial distribution of injected air and the associated spatial behaviors of air-sparging physics and chemistry. However, these models may account for many complex processes in a bulk volume of porous media. The principle limitation of these models is the assumption of complete mixing within compartments. However, based on the discussion regarding air-channel flow provided earlier, formation of numerous air channels in homogeneous media may form a near continuum and may provide sufficient air–water contact to allow the complete mixing assumption to be feasible for practical applications. Under conditions of severe heterogeneity, the well-mixed aquifer assumption may not hold. However, this limitation exists for any model. It is certainly possible to develop a series of lumped-parameter models to represent various porous media types, although no such model description was found during the literature search.

Another potential drawback to these models is that several processes may influence what is assumed to be a specific mass-transfer behavior, such as the example described in Section 3.3. This problem is a direct consequence of using ''lumped'' parameters to simulate mass-transfer phenomena. Nonetheless, these models are useful for laboratory research, as well as for field applications if they are calibrated to specific site data. Unfortunately, there are few published results documenting the successful testing of these models. Summaries of published results are offered below.

3.5. Testing of lumped-parameter models

Calibrated lumped-parameter models have been used to simulate laboratory column experiments. Chao et al. [13] used their air-channel model to simulate effluent vapor concentrations in one-dimensional air-sparging column experiments. The model considered air advection and kinetic mass transfer between contaminated water and air. Braida and Ong [15] used a lumped-parameter model to simulate diffusion of contaminants from water to an air channel and subsequent mass transfer across the air–water interface. The model was designed specifically to analyze data obtained from an idealized laboratory experiment wherein a single compartment containing advecting air (i.e. an air channel) was allowed to contact a stagnant aqueous phase that contained dissolved organic chemicals.

In a field application, Rabideau et al. [22] simulated an air-sparging field experiment. Three fitting parameters were required for the model. These parameters were calibrated using data collected during an early 7-month shutdown period. The fitted parameters where then used in the model for the purpose of simulating 3 years of air sparging. The compartmentalized model was used to simulate air injection from up to 36 wells located within a 2500 m^2 source zone, whereby the multiple wells were treated as a single injection source into a well-mixed, two-compartment aquifer. The model reasonably predicted measured aqueous contaminant concentrations for the 3-year operating period.

3.6. State-of-the-art contributions from lumped-parameter modeling

Wilson et al. [23] proposed that the radius-of-influence (ROI) of a single vertical air-sparging well could be determined from measurements of vadose-zone soil–gas pressures near the water table. This method for ROI determination has successfully been used in the field (see Ref. [24]). Wilson [12] found that low-permeability lenses resulted in significant increases in cleanup times that were dependent on the average thickness of the low-permeability layers. This study also suggested that extracted vapor concentrations might exhibit significant tailing due to relatively slow diffusion of contaminant to the air-stripping zone, and that the spatial distribution of VOC had little impact on mass removal effectiveness provided air is delivered to the entire contaminated zone. These authors also found that cleanup rates increased drastically as the Henry's constant increased. Additionally, this work proposed that contaminants with a dimensionless Henry's constant (K_H) of greater than 0.05 were amenable to air-sparging.

Useful information related to contaminant-mass transfer between the air and water phases during sparging has been gained by model simulation of laboratory-experiment data. Based on results obtained from air-sparging experiments using three different sands, Chao et al. [13] determined that air–water mass transfer coefficients were larger in the coarser-grained sands for several VOCs. Based on this evidence, the authors hypothesized that air channels were less numerous and more widely spaced in fine sands than in course sands. Reddy and Adams [9] reached the same conclusion based on qualitative assessments of laboratory-column experiments. Braida and Ong [15] numerically analyzed VOC removal in a single-air-channel laboratory experiment, and determined that contaminant mass transfer across the air–water interface was proportional to the gas-phase diffusivity and inversely proportional to K_H. In addition, mass transport to the air channel was determined to be proportional to the aqueous diffusivity of the VOC, a result also achieved in the hypothetical studies conducted by Wilson et al. [12,23].

Rabideau et al. [22] simulated ground-water concentrations during field-sparging operations. The two limiting mass-transfer processes thought a priori to be most important were kinetic desorption and diffusion of contaminant to air channels. Their lumped-parameter approach combined these two processes, as well as other potential mass-transfer processes into a single set of parameters. Sorption parameters obtained from results of laboratory sorption would not, on their own, allow the model to predict the field data. Thus, the authors concluded that diffusion of contaminant to air channels was the predominant mass-transfer process. By giving physical meaning to model parameters consistent with an air-channel model, the authors were able to calculate that about 18% of the porosity in the subsurface was influenced by the air channel (''clean zone'') and the remainder was not influenced by sparging (''dirty zone'').

Lumped-parameters models have also been used without calibration to experimental data to theoretically assess NAPL remediation by air sparging. Roberts and Wilson [17] determined that cleanup of NAPL droplets by air sparging is likely to be limited by aqueous-phase contaminant diffusion; and thus increases in airflow rates beyond a limiting value would not reduce cleanup times. In a follow-up effort, Wilson et al. [18] proposed that cleanup times would be directly proportional to the average size of NAPL droplets. A follow-up work by Gomez-Lahoz et al. [19] determined that the aqueous-phase diffusion and dissolution kinetics result in a rebound in the aqueous-phase VOC concentrations after a sparging well is shut down. The authors contend that the magnitude of the rebound depends on such factors as sample location and the extent to which overall cleanup has progressed.

Mathematical models have also been used to study the theoretical influence of pulsed air injection on cleanup times. Based on numerical experiments conducted using their random-air-channel model, Wilson et al. [16] found pulsed air injection should improve sparging efficiency because of enhanced aqueous-phase dispersion. This conclusion is inherently based on the assumption that air-channel locations are random and likely to differ between successive startups of an air-sparging system. These authors also concluded that the distribution and spacing of air channels exerted a great impact on sparging efficiency, and that low-solubility compounds, such as alkanes, would experience decreased removal efficiency (regardless of volatility) due to dissolution limitations. This latter result was observed in the field by Gierke et al. [25]. The results of Rabideau et al. [22] also indicate that shutdown periods would improve remediation efficiency because aqueous concentrations rebound, presumably due to the previously discussed mass-transfer limitations.

Wilson and colleagues have published many articles associated with mathematical modeling of various engineered air-sparging applications. Wilson et al. [23] developed a model to simulate removal of organic contaminants flowing into a trench filled with saturated crushed rock wherein air was injected via a horizontal slotted pipe. The model developed by Wilson et al. [18] is similar, except that it incorporates NAPL dissolution and subsequent transport to the zone of injected air. Gomez-Lahoz et al. [19] suggested that, for NAPL remediation, vertical sparging wells were more efficient than horizontal wells because tailing of the extracted vapor concentrations was reduced. Wilson and Norris [26] developed models to simulate bioremediation with aeration curtains (essentially migration barrier trenches). The models included the processes of contaminant removal by air stripping and biodegradation, and also included mass transport kinetics of oxygen and organic contaminant at the air bubble–water interface. Wilson et al. [27] developed a model to simulate biosparging, whereby air injection is accomplished with a horizontal slotted pipe. Johnson [28] offers a conceptual sparging model for biodegradation and volatilization and discusses the relative importance of these two mechanisms.

4. Multiphase fluid-flow models

Simultaneous flow of water and air, which occurs during air sparging, is a multiphase fluid-flow process. Thus, the effects of capillary pressures between the air and water phases, and the mutual flow impedance between the two phases (relative permeability), should be considered in a rigorous theoretical assessment of airflow in the saturated zone (e.g. Refs. [29,30]). For remediation scenarios, partitioning of contaminant mass between the phases, and subsequent transport of contaminant within each phase, should also be incorporated in the model (e.g. Refs. [30–34]).

4.1. General mathematical formulation for multiphase fluid flow

A general mathematical formulation for a multiphase flow model is presented below. This formulation is based on the T2VOC simulator [35], and is provided as an example because the author is familiar with it. The formulations of other models will be different, but are based on the same physical principles. While most of the models to be discussed in this review are two-phase flow models, this formulation assumes three phases: gas, aqueous and NAPL. However, the fluid flow relationships provided also generally apply for two-phases. For T2VOC, there are also three components: air, water and chemical. In general, any component may reside in any phase, although NAPL is often assumed to contain no water or air. A mass balance may be written in integral form for some volume of the flow region, V_{I}, having a surface area of Γ_{I} as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_1} M^{\mathrm{K}}\mathrm{d}V_1 = \int_{\Gamma_1}\mathbf{F}^{\mathrm{K}}\mathbf{n}\,\mathrm{d}\Gamma_1 + \int_{V_1} q^{\mathrm{K}}\mathrm{d}V_1 \tag{4}$$

where K denotes the component, M^{K} is the amount of component K per unit porous media volume, $\mathbf{F}^{\mathrm{K}}$ is the total flux of component K into the flow region volume, $\mathbf{n}$ is the outward unit vector normal to the volume surface, and q^{K} is the rate of generation of component K within the volume.

The mass accumulation term for air, water and chemical includes a sum over the gas, aqueous and NAPL phases (β = g, w, N):

$$M^{\mathrm{K}} = \phi\sum_{\beta} S_\beta\,\rho_\beta\,\omega_\beta^{\mathrm{K}} \tag{5}$$

where ϕ is the porosity, S_β is the β phase saturation, ρ_β is the β phase density, and ω_β is the mass fraction of component K in phase β. S_β is defined as the volume percent of the phase in the pore space; thus, $S_{\mathrm{g}} + S_{\mathrm{w}} + S_{\mathrm{N}} = 1$. The organic chemical accumulation term may also include the effect of linear equilibrium adsorption to the solid phase by the use of a soil–water distribution coefficient:

$$M^{\mathrm{c}}\rho_{\mathrm{b}}\,\rho_{\mathrm{w}}\,\omega_{\mathrm{w}}^{\mathrm{c}}\,K_{\mathrm{D}} + \phi\sum_{\beta} S_\beta\,\rho_\beta\,\omega_\beta^{\mathrm{c}}. \tag{6}$$

The three mass flux terms (air, water, chemical) sum over the three phases (g, w, n)

$$\mathbf{F}^{K}\sum_{\beta}\mathbf{F}_\beta^{K}. \tag{7}$$

Advective fluid flows for each phase (β) occur due to the driving forces of pressure and gravity according to a multiphase extension of Darcy's law.

$$\mathbf{F}_\beta^{\mathrm{K}} = \frac{-kk_{\mathrm{r}\beta}\,\rho_\beta}{\mu_\beta}\,\omega_\beta\left(\nabla P_\beta - \rho_\beta\,\mathbf{g}\right) \tag{8}$$

where k is the intrinsic permeability, $k_{\mathrm{r}\beta}$ is the β-phase relative permeability, μ_β is the β phase dynamic viscosity, P_β is the β phase pressure, and $\mathbf{g}$ is the gravitational acceleration vector. Several relations are available for relative permeability in the literature. Models may also include diffusion in the aqueous phase or gas phases (T2VOC incorporates both), but these topics are not discussed in this paper.

Generally, relative permeability for a given phase is a nonlinear (typically cubic) function of the phase saturation [36]. The fluid-flow equations for each phase are linked by the capillary pressures (P_C) between each phase:

$$P_{Cgw} = P_g - P_w \qquad P_{Cnw} = P_n - P_w \qquad P_{Cgn} = P_g - P_n. \tag{9}$$

Where the capillary pressure is equal to the pressure in the non-wetting phase minus the pressure in the wetting phase. For water wet aquifers, the highest wettability is typically associated with the aqueous phase, while the lowest wettability is associated with the gas phase. Many capillary pressure relationships are available for two-phase and three-phase flow (e.g. see Falta et al. [35]; McCray and Falta [32]). The capillary pressure is generally a nonlinear function of porous medium properties and the phase saturations.

In general, low-permeability media also have high capillary pressures. Clays, for example, will tend to retard the advective flow of any phase (relative to a more permeable media such as sand) due to the reduced permeability. The high capillarity of clay, however, will influence the capillary-related flow for each phase differently. For example, a relatively dry clay will exert capillary suction on an imbibing wetting phase (e.g. water during infiltration) and allow capillary transport of the wetting phase into the clay. A water-wet clay, on the other hand, will tend to act as a capillary barrier to a non-wetting phase (NAPL or air), causing the non-wetting fluid to be directed around the capillary barrier. If the pressure in the non-wetting phase is great enough to overcome the capillary-barrier force, however, the non-wetting fluid may then enter the clay. These phenomena greatly influence the airflow behavior in the subsurface during sparging (e.g. Ref. [32]). A literature review of current multiphase flow models is provided below.

4.2. Numerical models

The nonlinearity of the partial differential equations governing multiphase flow, and the associated complexities of incorporating capillary pressure and relative permeability relationships into these equations, generally precludes solution by analytical methods. Thus, the earliest and the most frequent multiphase modeling attempts have utilized numerical solution techniques [29–35,37–39] [40–46]. The numerical models proposed by van Dijke et al. [43,46] and Mohtar et al. [39,40] are valid only for steady-state flow conditions. Chen et al. [47] developed a quasi-multiphase one-dimensional model using fractional flow theory combined with the Buckley–Leverett equation.

With the advent of high-performance personal computers, numerical models are advantageous in that only the extent and accuracy of site characterization limit the level of complexity that may be incorporated into the model. While site characterization is by no means a trivial problem, it will always limit the modeling process, and thus cannot be considered a problem specific to multiphase-flow modeling. Other difficulties exist when invoking a multiphase formulation, however, and these issues will be discussed.

4.3. Analytical models

A few investigators have developed multiphase analytical models for air sparging [43,46,48]. Analytical solution of the governing equations for multiphase flow is a very challenging task, and these efforts have contributed greatly to a mechanistic understanding of air sparging. Unfortunately, because of the strong non-linearity of the equations governing multiphase flow, restrictive simplifying assumptions are generally required to obtain analytical solutions. For example, assumptions that may be required include steady-state air flow, simplified forms of the relative-permeability or capillary-pressure relationships, incompressible air flow, constant gas-phase velocities, neglect of water-phase velocities, and linearization of some of the governing equations [43,46,48].

The assumption of a homogeneous and isotropic medium is often required [43,48]. After comparing their analytical solution with a more rigorous multiphase numerical model, van Dijke et al. [43] proposed that the conditions imposed on gas-phase velocities and compressibility are realistic at steady state. The model proposed by van Dijke and van der Zee [46] allowed simulation of airflow in the presence of a single heterogeneity of infinite extent. The analytical solution for this case is quasi-analytical in that it contains an integral that requires numerical integration to solve. The models of van Dijke et al. [43,46] also require that vertical capillary gradients be neglected, and that the airflow domain does not extend below the air-injection screen. Thus, while analytical models solve the differential equations exactly, the physical processes are often approximated to obtain the equations.

Nonetheless, models developed from analytical solutions are generally much easier to use than numerical simulators. That is, analytical solutions can often be programmed into spreadsheets or within simple computer programs, require less user training, and may be used on even archaic desktop computers. Thus, good multiphase analytical models may provide considerable insight to air sparging flow physics, and should prove to be excellent screening tools for practitioners. For these reasons, development of analytical solutions for multiphase flow should be encouraged, and testing and benchmarking of these solutions is a worthwhile research endeavor.

4.4. Applicability of multiphase-flow models

A difficulty associated with using multiphase-flow models for air sparging is meeting the requirement that a ‘‘continuum’’ model can represent the flow physics of sparging, particularly with regard to the constitutive relationships of capillary pressure and relative permeability. These relationships are traditionally derived from column-scale laboratory experiments conducted using homogeneous porous media. It is generally assumed that, for these relationships to hold, the multiple phases within a volume of porous medium must maintain efficient contact. A common-sense requirement is that these relationships should hold at a scale the size of a numerical model gridblock. In the case of an analytical model, the assumption must hold over the entire solution domain. The process of interphase mass transfer of chemicals between phases is generally consistent with the continuum assumption. However, as discussed previously, the geometry of the gas and aqueous phases may require that the mass-transfer limitations be taken into account in some manner. Recall that this problem also exists for the lumped-parameter models described earlier.

An additional complication associated with the continuum issue is that, based on traditional fluid-stability analysis, air–water interfaces are not inherently stable. That is, during sparging, water is displaced in the upward direction by air, which is a less viscous, less dense immiscible fluid. For these conditions, the gravitational and viscous forces act in such a manner to cause the interface between the air and the water to be unstable (e.g. Refs. [36,49]). Unstable interfaces may result in formation of air ‘‘fingers’’. This type of air channeling is not explicitly accounted for in current multiphase-flow formulations.

The traditional stability theory is based primarily on work from the oil industry (e.g. Ref. [36]). This theory does not generally account for the impact of capillarity on stability, because capillarity can often be ignored for reservoir-scale problems important in petroleum recovery. However, it has long been known that the capillary force may be a stabilizing factor [50], as well as a destabilizing force due to the entry-pressure effect [49]. Keuper and Frind [49] argue that, even in media with small pore-size heterogeneities, channel formation is dominated by differences in entry pressure that cause the displacing fluid to preferentially flow in the lower capillary-pressure medium. As will be discussed, multiphase flow models have been used to successfully simulate the general airflow patterns in homogeneous soils, even though microscale air channeling was prevalent in the soil (e.g. Ref. [32]). In this case, the air channel density was sufficiently high to allow the continuum assumption to hold within the model REV.

After conducting laboratory air-sparging experiments and analyzing additional data compiled from various field and laboratory studies, Clayton [6] questioned the growing belief that airflow during sparging universally occurs in widely spaced air channels. Clayton’s discussion will not be repeated here; the reader is referred to his paper for details. However, it is useful to summarize his conclusions. First, he observed that homogeneous fine-grained soils (such as silts and fine sands) exhibited little airflow fingering beyond the pore scale. Rather, airflow in these media can be described by microscopic fingering that effectively results in spatially uniform air saturations that decrease from the air-injection point. For unconfined systems, Clayton [6] found that widely spaced air channels were more likely to develop in coarse media, while continuous, relatively large, air saturations were prevalent in fine-grained soils. Ahlfeld et al. [2] and Clayton [6] concluded that dominant air channels observed in the field probably resulted from stratigraphic heterogeneities (i.e. permeability and capillarity heterogeneities). The experimental results of Chen et al. [47] obtained using X-ray tomography imaging of air flow in 7-in. diameter cylindrical soil columns, offer strong support for this theory.

After consideration of the state-of-the-art research on this topic, it is reasonable to assume that ‘‘channeling’’ at the field scale is likely to be dominated by channels formed as a result of heterogeneities. As will be discussed in the next section, multiphase-flow models are capable of simulating formation of air channels due to this phenomenon, provided the necessary discretization of capillary-pressure and permeability heterogeneities is provided in the model [30–33,38].

Fig. 2 illustrates the ability of the multiphase flow model T2VOC to simulate complex airflow in a two-dimensional sparging simulation. The simulated sparging regime consists of a sandy soil with six small, high-capillary, low-permeability clay zones. The high water-saturation regions (i.e. low gas-saturation regions) in the sparge zone distinguish the locations of the clay zones because the clays inhibit air entry,

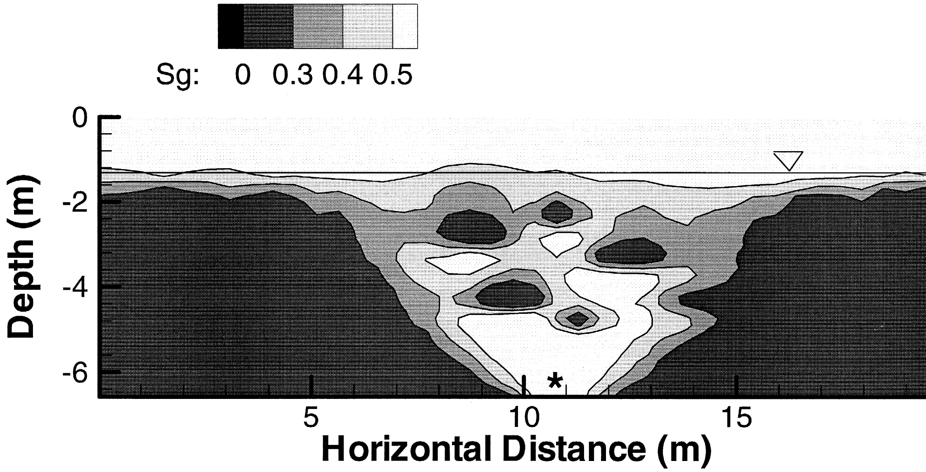

Fig. 2. Complex distribution of gas-phase saturations (S_g) during air sparging in a two dimensional soil profile (simulated using T2VOC). Model element size is 0.5×0.5 m, except for the column of elements containing the air-sparging point, which are 10 cm wide. The soil is sandy except for six small clay lenses that are 0.5 m thick and 0.5 to 1.0 m wide. Air is injected at point (*) at a rate 5.0×10^{-3} kg/s. Porous media characteristics for the sand and clay are the same as those used in McCray and Falta [32].

creating air ''fingers''. Nonuniform zones of gas-saturation occur even though the degree of heterogeneity is relatively mild. By incorporating a more complex heterogeneity distribution and a finer numerical mesh, sharper channels may be simulated.

4.5. Testing of multiphase-flow models

The success of multiphase flow models to simulate air sparging in homogenous and heterogeneous porous media has been confirmed by simulation of data obtained from laboratory and field experiments. McCray [38] and McCray and Falta [32] used numerical simulations to successfully mimic the airflow patterns in the well known homogeneous and heterogeneous (layered) media experiments of Ji et al. [4]. In the laboratory experiments, the dominant air channels were formed because low-permeability, high-capillarity layers prevented air entry. The air collected below these layers, and eventually moved laterally to the edge of the layers where upward flow resumed. The model simulations, conducted using estimated input parameters with no calibration, mimicked the photographed airflow patterns in the experiments (spatial pressures and air saturations were not measured). The multiphase flow model adequately represented the average behavior of the air plume (which actually consisted of small air fingers) in the homogeneous media, as well as the larger heterogeneity-dependent air channels formed in the heterogeneous media. This modeling study demonstrated that airflow in heterogeneous porous media could be simulated accurately if the locations of heterogeneities are known.

Mohtar et al. [40] developed a two-dimensional steady-state multiphase simulator called SPARG to model experimental results obtained from a two-dimensional sparging experiment. Air was injected into the center of a tank filled with water-saturated homogeneous porous media. The model was able to mimic the shape of the injected air plume. In addition, the simulated air-flux rates compared favorably with measured flow rates above 9 l/min (generally within 5%–30%). Larger discrepancies at small flow rates were attributed to difficulties in measuring small flows. The model was also reasonably successful at simulating the volume of the air zone based on comparison with a measured desaturated-water volume. As was the case for air flux, the measurements were most accurate at higher flow rates. At low flow rates microscale air channeling is more prevalent (e.g. Ref. [4]), possibly due to increased pore-scale fluid instabilities. Thus, the continuum assumption required for multiphase flow models may not be valid under low-flow conditions. This topic is in need of additional research.

Hein et al. [45] used T2VOC to simulate air sparging in a ''bath tub'' of homogeneous, saturated sand. Soil parameters, capillary pressure, and a two-point relative permeability curve were measured for the soil. For an injection rate of 283 lpm, vertical airflow measurements at 24 surface locations were generally within a factor of 1.5 of simulated values. The model accurately predicted the radius constraining 75% of the measured airflow. These levels of model representation were deemed acceptable for design purposes.

Chen et al. [47] imaged airflow in a relatively large cylindrical column using X-ray tomography imaging, and successfully used a one-dimensional numerical model to simulate air distributions in the presence of low-permeable layers. While the locations of low-permeability lenses in the field are difficult to ascertain, these studies demonstrate the applicability of multiphase-flow models.

Larson and Falta [41] used T2VOC to simulate subsurface air pressures measured during an air-sparging field operation at a site comprised primarily of sand and silty-sand. Measurements were read from pressure gages mounted atop small-diameter probes that were screened below the water. The probes were installed between 0.5 and 4.4 m radially from the injection source. Model input was manually calibrated with field data to produce acceptable results assuming two homogeneous layers of soil. Simulated values were within about 20% of measured values. In addition, based on comparison with air-pressure measurements obtained from monitoring probes installed along a cross-section of the air plume, numerical simulations of transient air-plume development accurately matched the actual development of the plume. Discrepancies between measured and simulated results for one probe were attributed to the presence of a small silt lens in the vicinity of the probe that had not been accounted for in model simulations. Subsequent simulations that incorporated this heterogeneity would be expected to improve the modeling results. Once calibrated, such a technique might provide insight into additional design or the long-term performance of the sparging system, particularly if chemical mass transfer is incorporated into the model.

These examples support the claim that, while there are difficulties associated with using multiphase flow models, these models may be useful for design and assessment of air-sparging operations. As with any modeling effort, however, subsurface heterogeneities must be characterized to a satisfactory level of detail appropriate for the site and for the model application.

Several multiphase flow simulations of air sparging have included dissolved chemicals or NAPLs with the aim of investigating remediation effectiveness under various scenarios [30–33,38]. These model studies assumed equilibrium interphase mass transfer of contaminants. A numerical formulation proposed by Reddy and Zhou [34] included nonequilibrium mass transfer, although application examples for this model could not be located in the current literature. While these authors [30–34,38] have conducted theoretical studies related to NAPL cleanup, no published research is available to date to confirm the validity of the chemical-mass removal results in these simulations with laboratory or field data. It is reasonable to assume that the impacts of rate-limited mass transfer of chemicals from water to air channels, or across the air–water interface, will be incorporated into multiphase flow models. For example, rate-limited mass transfer is currently being incorporated into the T2VOC model (Ron Falta, 1999, personal communication).

4.6. State-of-the-art contributions from multiphase-flow modeling

Multiphase flow models have made significant contributions toward understanding the theoretical aspects of air sparging, and have been responsible for several improvements in the design of air-sparging systems. Many of these contributions are described in the following paragraphs.

Lundegard and Andersen [29,37] performed two-phase (gas–water) numerical simulations of air sparging in a homogeneous, anisotropic aquifer using a simulator called TETRAD. Their results provided theoretical explanations for transient water table mounding, which is observed in the field, and described that the duration of this transient period (and thus the time to achieve a steady-state air plume) generally increases with decreasing aquifer permeability, increasing injection depth, and increasing injection rate. This result was also confirmed experimentally by Chen et al. [47]. The authors found that air-plume width does not vary significantly with injection depth once steady-state flow conditions are reached. Lundegard and Andersen [29] also clarified the relationship between injection pressure and injection flowrate. In particular, the authors found that the flowrate increases as the injection pressure increases. For a given injection pressure, the permeability of the soil controls the maximum flow rate. The results of Mohtar et al. [40] and McCray and Falta [30] are consistent with these results.

Multiphase modeling experiments [29,30] also indicated that because water-table mounding is transient, it is not a good indicator of the sparging radius of influence (ROI). These authors have also found that the ROI, as defined by a selected gas-phase saturation, was strongly dependent on anisotropy and vertical permeability. In particular, the ROI increases with the degree of anisotropy, and with increasing vertical permeability. McCray and Falta [30] proposed a thumbrule for estimating the ROI for two different soils of varying anisotropy:

$$\mathrm{ROI}_1 = \mathrm{ROI}_2 \left(\frac{\delta_1}{\delta_2} \right)^{1/2} \tag{10}$$

where δ is the ratio of horizontal to vertical permeability, and the ROI is defined by an arbitrary gas-phase saturation within the gas plume (McCray and Falta [30] used a value of 0.1). This thumbrule was found to apply for a large range of vertical permeabilities (i.e., representing sands through clays), but required a constant horizontal permeability. Lundegard and Andersen [29] found that horizontal permeabilities had little impact on the steady-state plume width. Thus, the an improved thumbrule is offered:

$$\mathrm{ROI}_1 = \mathrm{ROI}_2 \left(\frac{k_{v2}}{k_{v1}} \right)^{1/2} \tag{11}$$

where k_v is the vertical permeability. Based on the results of Lundegard and Andersen [29] and McCray [38], we might expect this relation to reasonably hold for horizontal permeabilities in the range of 10^{-8}–10^{-11} cm^2 (i.e. silts and sands). Similar numerical studies have not been conducted for coarser or finer soils. Lundegard and Andersen [29] concluded that anisotropy and vertical permeability might be the most important factor controlling the width of the steady-state air plume. These numerical results have yet to be verified experimentally.

McCray and Falta [30] proposed that accurate measurements of the sparging ROI, as defined by arbitrary gas-phase saturation, could be easily obtained from gas-phase pressure measurements. These measurements are easily obtained in the field using pressure monitoring probes provided that the probes are capped and screened over a very small length in the sparging zone [41]. In a two-phase air–water system, the wetting fluid (water) prefers to exist in the small pores due to capillarity, and the non-wetting fluid (air) tends to remain in the larger pores. Thus, the gas-phase will enter the monitoring well. A detailed explanation of this behavior follows.

After an initial transient phase, the gas plume is steady and the water phase returns to essentially hydrostatic conditions similar to those present before air injection. Hydrostatic water conditions at steady state have been observed in mathematical-modeling experiments [29,30,43], as well as in the field [2]. McCray and Falta [30] found this to be true except very near the sparge well, where small water circulation currents were present. In a steady-state two-phase system, the non-wetting phase exhibits the greater pressure, and the pressure difference between the two phases is the capillary pressure. Thus, the steady-state positive air-phase pressure at any given monitoring location equals the magnitude of the capillary pressure for the soil–air–water system in that location. In a monitoring well, the capillary pressure is negligible due to the relatively large radius of the well (compared to soil pores). Thus, there is a capillary-force gradient that drives the gas phase from the porous media into the monitoring probe cavity.

This monitoring system for a two-phase air–water sparging system is analogous to that used for collecting water samples in the two-phase vadose zone. Due to capillarity, the water will not enter a vadose-zone monitoring well, although vapors enter easily. To collect water samples in the vadose zone, the capillary forces must be overcome by using a porous cup. Similarly, in a two-phase sparging zone, the water will remain in the soil, while the air will preferentially enter the monitoring well. However, water (as a single phase) is not held in the soil by tension below the water table. Thus, if the monitoring well is screened over an area that does not experience two-phase conditions, or where air saturations are very small, then water will enter the well. Thus, the monitoring well screen should be very small to maximize the potential to positively detect the presence of air. Morton et al. [51] and Larson and Falta [41] have verified this method in the field. Details regarding construction and use of a sparge-pressure-monitoring probe may be found in Morton et al. [51].

McCray and Falta [30] also found that capillary pressure has an important effect on the ROI in a homogeneous media. Based on numerical-model results, these authors found that the lateral extent of air flow, as well as the air saturation at a given location, were larger under the influence of capillary pressure than when capillary pressure was neglected. This occurs because capillary forces can counter buoyancy forces and allow a wider horizontal distribution of the air plume. This phenomenon has recently been verified experimentally by Clayton [6]. In addition, Clayton [6] also demonstrated that air saturations are likely to be larger and more uniform in media of lower permeability and higher capillary pressure. Larger air saturations could lead to more efficient mass-transfer in lower-permeability soils, which may mitigate the adverse impact of the reduced conductivity to airflow in these zones.

The implications of capillarity on airflow in homogeneous media are startling. For example, it has long been proposed that sparging is efficient only in soils with high hydraulic conductivities (and thus low capillarity). For example, a conductivity value of about 10^{-3} cm/s has been proposed as a lower limit for sparging operations (e.g. Ref. [8]). However, the results discussed in the previous paragraph would suggest that sparging in lower-permeability media might be effective due to an increased ROI and more efficient air–water mass transfer.

It is important to realize, however, that additional constraints are associated with air sparging in low-permeability, high capillarity soil. For example, low-permeability soils will require a greater injection pressure to achieve the same net airflow, and thus energy costs are higher. In addition, some soils may have such a low permeability that the air injection necessary to overcome air-entry pressure may exceed the overburden force of the soil and cause fracturing, which is generally undesirable [29]. Finally, when air is injected into a high-permeability zone, the air tends to be excluded from low-permeability zones because of their high capillary pressure, as described previously. Fig. 2 illustrates this effect. Additional research is recommended to test the viability of air sparging in high-capillarity, low-permeability soils.

Hein et al. [45] recommend the following procedure for modeling air-sparging in soils that are relatively homogeneous, isotropic, and permeable. First obtain measurements for porosity, capillary-pressure saturation data, and intrinsic permeability. Next, choose an appropriate relative-permeability function and measure at least one gas-phase relative-permeability data point to verify the relationship is appropriate. Finally, select a system configuration consistent with conventional design practices for the particular site.

Several multiphase-modeling studies have investigated the impact of sparging on contaminant mass removal [30–33]. The study by Unger et al. [33] indicated that solubility was far more important than volatility as an indicative property to predict sparging effectiveness for various contaminants. Results of a field experiment by Gierke et al. [25] support this finding. McCray and Falta [30] found that, for equilibrium chemical partitioning of TCE and *o*-Xylene, relatively high mass removal ($< 90\%$) occurred at relatively low gas-phase saturations (about 0.1).

McCray and Falta [32] used a numerical model to simulate the tailing of contaminant concentrations in extracted vapors during air sparging (see Fig. 3). This behavior is

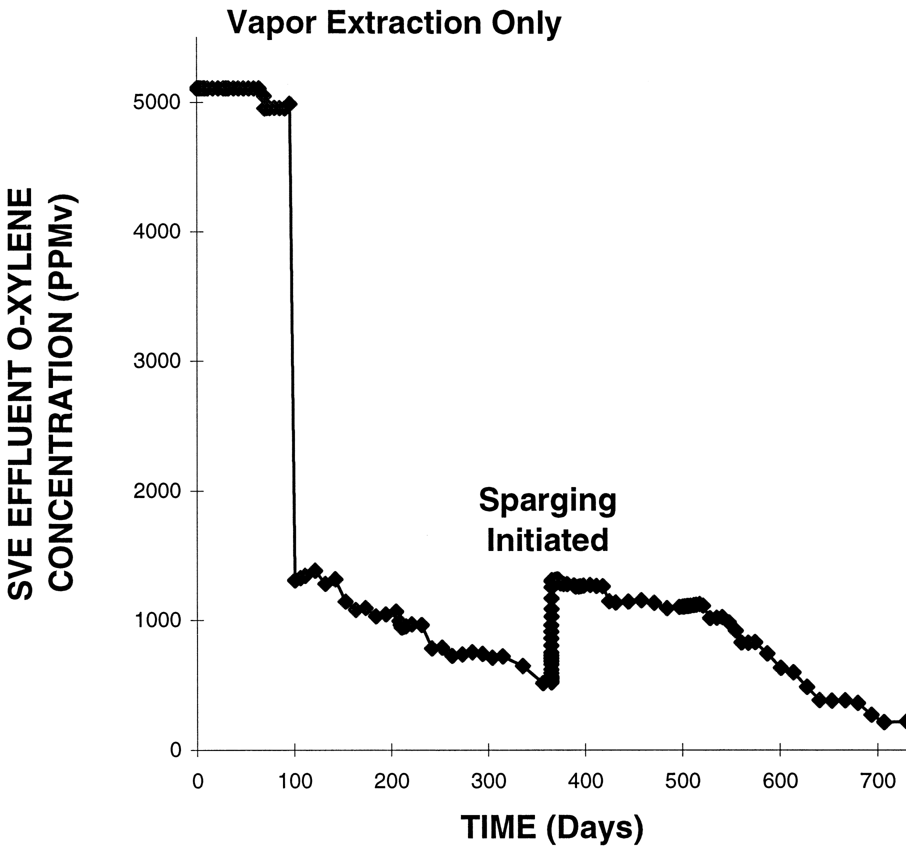

Fig. 3. Tailing of vapor concentrations in the vapor extraction effluent during air sparging due to mixing of relatively clean and contaminated air. The data shown above was obtained using numerical simulations of *o*-Xylene NAPL remediation in homogeneous media. Simulation parameters are the same as those in McCray and Falta [32].

commonly observed in the field. Tailing is generally attributed to kinetic mass-transfer processes such as kinetic desorption and diffusion of aqueous-phase contaminants to air channels (e.g. Ref. [22]). However, in this modeling study, tailing was simulated in homogeneous porous media even though no kinetic mass-transfer relationships were used in the model. Simulated tailing occurred due to mixing of contaminant vapors with different concentrations. Spatially and temporally varying vapor concentrations can result from spatial and temporal changes in NAPL saturation. An explanation for this type of mixing follows.

Some of the advecting air in the vadose zone and below the water table is relatively clean because it does not contact NAPL, while air that experiences direct contact with the NAPL is relatively ‘‘dirty’’. Clean and dirty air mix within the vacuum-extraction zone, and the effluent air concentrations represent an average. As the NAPL disappears, a smaller volume percentage of the extracted air is dirty, and thus vapor-phase concentrations decline. The presence of heterogeneities is likely to exacerbate this effect by creating zones of inefficient mixing. This behavior would also occur to a lesser extent if NAPL was not present (i.e. if only dissolved contamination was present). Thus, tailing may be due, in part, to mixing phenomena in addition to kinetic mass transfer processes.

Multiphase flow modeling has been successfully used to gain a better understanding of the impact of heterogeneities on remediation. Several studies have verified that the presence of saturated clay layers inhibit air flow, cause formation of large air channels, and may significantly extend the distance to which air propagates [29–32,37,38,46]. van Dijke and van der Zee, [46] demonstrated that airflow above a clay later was minimal and primarily driven by buoyancy. By comparison to experimental results (discussed previously), the simulations of McCray and Falta [32] verified that multiphase modeling of air sparging in heterogeneous porous media is possible if the locations of the heterogeneities are known. More importantly, from a practical view, these studies indicated that airflow in the presence of low-permeable layers could be simulated if reliable estimates of air-entry pressures for the layers are known, and that accurate representation of the entire capillary vs. saturation curve for a lowly permeable lens may not be required. Chen et al. [47] were also able to model airflow in a heterogeneous laboratory column using a fractional-flow model that is based on multiphase-flow theory.

McCray and Falta [32] showed that a single low-permeability clay disk could seriously impact the amount of NAPL removed compared to the same spill and air-injection locations in a homogeneous media. Unger et al. [33] determined that, after a short period of effective NAPL volatilization occurring in the vadose zone and in high-air-saturation zones below the water table, aqueous dispersion and groundwater advection of contaminant to the heterogeneity-induced air channels limited contaminant mass removal.

Unger et al. [33] also used two possible realizations of random permeability fields to assess the sensitivity of two TCE-remediation schemes to the degree of permeability variance. A design that is not impacted by the degree of heterogeneity is desirable, even though it may be inherently less efficient, because inadequate subsurface characterization would exert a less-adverse impact on remediation. Both remediation schemes involved two horizontal sparging wells and one vapor-extraction well. One scheme simulated an impermeable fully enclosed wall that was keyed into a bottom impermeable layer. For this case, the sparging operations were fully contained and no groundwater flow was permitted to enter the treatment zone. For the second scheme, the walls were partially penetrating (i.e. did not reach the bottom boundary) and thus groundwater flow into and out of the treatment zone was permitted. The authors found that partially penetrating impermeable walls resulted in more effective clean up than fully penetrating walls because advection and dispersion of aqueous-phase contamination to the air-phase zones were enhanced in the former design. This design was also less sensitive to the initial permeability distribution, and was thus determined to be a more robust technique. This study is an excellent example of how mathematical modeling may be used to improve remediation design efforts.

5. Issues to address in future modeling efforts

5.1. Rate-limited mass-transfer

It is clear that sparging efficiency may be greatly influenced by rate-limited mass transfer processes [13,22]. However, the specific mass-transfer processes that are important for a given site are rarely known, and are thus frequently lumped into a single parameter. Mass transfer limitations may be due to physical processes (e.g. diffusion of contaminant mass to air channels) or chemical/biological processes (such as those described earlier).

Air channeling may be indirectly accounted for in the lumped-parameter approach, with the noted drawbacks. As described previously, multiphase-flow models can accurately account for air channeling provided an accurate representation of the subsurface heterogeneities is incorporated in the model conceptualization. An acceptable modeling approach might proceed as follows. First, one should attempt to identify the major heterogeneities likely to cause macroscale air channels to form using data from well logs or geophysical techniques. This information should be incorporated into the conceptual model to allow simulation of the dominant airflow patterns. The kinetic mass-transfer effects due to pore-scale channeling and interphase mass transfer could be handled using a dual-domain approach (similar to the approach used for lumped-parameter models). Multiphase flow models inherently include advection of contaminant to air channels, and are often formulated to include aqueous-phase diffusion and dispersion.

Nonequilibrium effects associated with diffusion- or dispersion-limited mass transfer of VOC from the bulk water to air channels, and subsequent mass transfer across the air–water interface, are important topics for continued research. Currently, there are few published laboratory studies that address these issues. Additional experimentally based data is necessary if investigators are to develop accurate air-sparging models.

Kinetic sorption/desorption of contaminant to/from soil and kinetic NAPL dissolution may also be very important at many sites. Biodegradation also plays an important role in air sparging efficiency (e.g. Ref. [25]), even though this process is rarely accounted for in air-sparging models. Currently, most model applications assume a priori that specific mass-transfer processes are relevant, even though other mass-transfer phenomena could cause the contaminant behavior demonstrated by the observed concentrations. Indeed, air channels alone are associated with two mass-transfer processes: contaminant diffusion to the air channels and nonequilibrium air–water mass transfer.

Thus, two models that include different mass-transfer processes could hypothetically be used ‘‘successfully’’ to simulate the same experimental data. Because the long-term effects of different mass-transfer processes on sparging efficiency are likely to vary, more research should be conducted to better understand the relative importance of various mass-transfer processes under various conditions. Research efforts to improve incorporation of mass transfer processes into models are also encouraged.

5.2. Pulsed sparging operations

Pulsed operation of air injection wells (i.e. shutdown periods included in air sparging operations) often substantially improves cleanup efforts (e.g. Refs. [22,52]). The increased contaminant-removal efficiency after a shutdown period may be due to increases in the local groundwater velocity and dispersivity [16]. It may also be due, in part, to mixing between dirty and clean zones as water refills pores previously filled by air (e.g. Ref. [38]). For these cases, subsequent startup allows more efficient contact between dirty water or NAPL and injected air. Thus, models should include the capability to simulate rebound of contaminant concentrations during air-sparging shutdown. The following processes may also be important and therefore should be incorporated into a model for both shutdown and startup fluid-flow conditions: rate-limited mass transfer from NAPL to water, diffusion from fine-grained soils, kinetic desorption, and subsequent mixing after shutdown of sparging operations. Most current multiphase flow models inherently account for mixing, which is due simply to a sudden redistribution of pressures (driving forces) in the aquifer. These models can and should also be formulated to account for the kinetic mass-transfer processes. Lumped-parameter models do not explicitly account for mixing that occurs during shutdown.

5.3. Characterization of subsurface heterogeneity

Given the strong impact of permeability and capillarity on sparging airflow, an ideal goal would be to extensively characterize the subsurface and use a three-dimensional, multiphase-flow model to simulate airflow and chemical mass transfer during sparging. Unfortunately, one rarely has sufficient data on in situ permeability or capillary pressure (or even air-entry values) to develop an accurate model. Use of a multi-dimensional model based on information obtained from sparse data sets may often provide misleading results. Of course, this potential problem exists for any subsurface modeling effort.

Even when locations of subsurface heterogeneities are unknown, however, results from three-dimensional models may be useful provided the results are evaluated within the appropriate framework. The studies of Larson and Falta [41] discussed previously are an example of such an application. In addition, recent developments in subsurface characterization using geophysical techniques are making three-dimensional modeling more feasible [53]. Some novel characterization techniques that are related directly to air sparging might also be useful for improving air-sparging models. For example, Lundegard and LeBrecque [54], Schima et al. [55], and Daily and Ramirez [56] used cross-hole electrical resistance tomography to develop three-dimensional images of airflow. McKay and Acomb [57] used a neutron probe to measure water saturations (and thus air saturations) at several vertical locations near a sparging well. Chen et al. [47] used computerized X-ray tomography to visualize centimeter-scale airflow in a large laboratory column. Airflow during sparging has also been ‘‘observed’’ in large tanks using ground penetrating radar (Gary Olhoeft, 1999, Colorado School of Mines, personal communication). Larson and Falta [41] used air-pressure measurements, as proposed by McCray and Falta [30] (described previously), to determine the presence or absence of air channels.

Geophysical methods such as those described above for measuring airflow may provide a relatively detailed characterization of the subsurface heterogeneities that impact airflow. For example, regions with no significant airflow may be assumed to contain low permeability, high capillarity layers that preclude airflow. Thus, air-sparging models may incorporate this information after initiation of air sparging operations. If appropriate provisions are included in the model to simulate rate-limited mass transfer of dissolved contaminant to macro-scale air channels, the models may be subsequently used to estimate clean-up times and to analyze the long-term performance of existing air-sparging systems.

5.4. Determination of model-input parameters

No model can produce successful results without careful attention to determining input parameters. Physical factors such as porosity, permeability, relative permeability functions, and capillary pressure relationships should be measured for the major media types at a site even if it is not feasible to obtain a complete data set for the site. For example, Hein et al. [45] showed that even a few measured relative permeability data points could significantly improve performance of a multiphase flow model. Certainly, as discussed previously, locating the major heterogeneities in the subsurface can greatly improve a model's ability to predict airflow patterns. In addition, determination of the average air-channel widths and spacing would be useful for optimizing performance of lumped-parameter models, which often require a gas phase volume as input. This characterization is very difficult to perform in the field, although some of the geophysical techniques described earlier show promise for this task.

Mass-transfer parameters such as sorption rates, biodegradation rates, and NAPL dissolution rates are likely to be very important. Currently, it is only feasible to determine these parameter for small batches of porous media in a laboratory. However, the spatial variation in mass transfer domains may be important. When possible, soil samples should be collected from each sparge zone for laboratory measurement of mass-transfer parameters. Unfortunately, we do not currently understand the impact of scale on mass-transfer behavior. That is, it has not been rigorously demonstrated that laboratory measurements are truly representative of field-scale conditions. Thus, future research addressing the impact of scale on mass transfer is encouraged.

Finally, it will not be possible to determine the values for many model-input parameters. In these cases, model calibration to experimental data may prove useful for inverse estimation of these parameters. This topic is discussed below.

5.5. Model calibration and testing using experimental data

The recent development and use of inverse modeling techniques may aid in the application of all air sparging models, particularly three-dimensional and multiphase-flow models [58,59]. Inverse methods may be used in conjunction with existing models to calculate model-input parameters by automatically calibrating simulated parameters against observed data.

Inverse models can be formulated to perform extensive error analyses that provide statistical information about the differences between actual and predicted values, and estimation uncertainties of the best-estimate parameter set [58,59]. These statistics are useful for evaluating the validity of a certain model, for assessing the robustness of a model, for discriminating among various model alternatives, and for evaluating the quality of model calibration.

Once a model is calibrated to field data (or laboratory data), it is important to test the model's applicability to expected conditions outside the spatial and temporal domains of the calibration. For example, it should not be assumed that calibration of a model using 3 months of field data in a selected area is sufficient justification to use the model over a period of years, or at another sparge location. While it may be appropriate to make interim predictions of sparging performance based on a short period of calibration, the calibration should be frequently updated and evaluated if the long-term predictive capability of the model is to be preserved. In addition, models should be calibrated for a range of sparging flow rates and pressures.

6. Conclusions

Compartmentalized lumped-parameter models and multiphase flow models have dominated air-sparging modeling efforts. Each approach has significant benefits as well as some inherent disadvantages. Both approaches are very useful for gaining a mechanistic understanding of the air-sparging process. However, the literature suggests that for any air-sparging model to be useful for field applications, detailed model calibration is necessary.

Lumped-parameter models have the advantage of being relatively simple to use. These models are also attractive in that they do not tend to cause overconfidence in the modeling results, because it is clear that these models represent the average behavior of the system. A disadvantage is that these models generally do not yield useful information regarding subsurface air pressures or gas-phase saturations, which are beneficial in determination of the sparging ROI. Nonetheless, as shown by Rabideau et al. [22], these models may be useful for predicting the long-term performance of an air-sparging system given an initial period of operation for model calibration. In addition, it is logical that these models are more appropriate for initial site screening than are the more complex models.

An advantage provided by multiphase-flow models is that they have the potential to provide more accurate representations of the actual flow physics of an air-sparging system. For example, air pressures and air saturations can be estimated in addition to vapor-phase and aqueous-phase contaminant concentrations. Knowledge of these parameters is useful for determination of the sparging ROI, and thus is important in design and cost-benefit analysis. However, for a multiphase flow model to produce accurate results, the subsurface heterogeneities must be characterized to a level appropriate for the modeling effort and expectations. This conclusion also applies generally to three-dimensional models.

As discussed previously, because of the recent development of new techniques for inverse modeling and subsurface characterization, it may be possible to characterize the important flow-controlling heterogeneities based on measured airflow patterns. This may be accomplished using sparging pilot tests, or even using operating air-sparging systems. In this manner, the sparging model for a certain site can be refined after the start of operation, and different operation modes may be tested numerically for effectiveness prior to implementation. Inverse modeling, when used in conjunction with air-sparging pilot tests and measurement of traditional hydrogeologic parameters (e.g. porosity, intrinsic permeability, sorption capacity), is likely to improve the feasibility of three-dimensional modeling efforts. In addition, inverse modeling may be used to estimate mass-transfer parameters that are difficult to measure.

For any modeling effort, it is important to consider the constraints imposed by inadequate data sets. The cost of developing an adequate data set may be prohibitive. As such, it is very important that engineers, regulators and policy makers understand, before commencement of a modeling effort, that the results are of limited accuracy, even if sophisticated models are used. That is, it is important to maintain consistency between monitoring, modeling and assessment.

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References

[1] R.L. Johnson, P. Johnson, R. McWhorter, R. Hinchee, I. Goodman, Ground Water Monit. Rem. 13 (4) (1993) 127–135.
[2] D.P. Ahlfeld, A. Dahmani, W. Ji, Ground Water Monit. Rem. 14 (3) (1994) 132–139.
[3] K.R. Reddy, S. Kosgi, J. Zhou, J. Hazard. Waste Hazard. Mater. 12 (2) (1995) 97–118.
[4] W. Ji, A. Dahmani, D.P. Ahlfeld, J.D. Lin, E. Hill, Ground Water Monit. Rem. 13 (4) (1993) 115–127.
[5] S.E. Roosevelt, M.Y. Corapcioglu, Water Resour. Res. 34 (5) (1998) 1131–1142.
[6] W.S. Clayton, Ground Water Monit. Rem. 18 (3) (1998) 134–145.
[7] R. Semer, J.A. Adams, K.R. Reddy, Geotech. Geol. Eng. 16 (1998) 59–75.
[8] M.E. Loden, A Technology Assessment of Soil Vapor Extraction and Air Sparging, US EPA/600/R-92/173, US EPA Office of Research and Development, Washington, DC, 1992.
[9] K.R. Reddy, J.A. Adams, J. Environ. Eng. 124 (3) (1998) 288–299.
[10] K. Sellers R. Schreiber, in: Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston, TX, 1992, National Ground Water Association, Dublin, OH, 1992, pp. 365–376.
[11] D.J. Wilson, C. Gomez-Lahoz, J.M. Rodriguez-Maroto, Sep. Sci. Technol. 29 (18) (1994) 2387–2418.
[12] D.J. Wilson, Sep. Sci. Technol. 27 (13) (1992) 1675–1690.
[13] K.P. Chao, S.K. Ong, A. Protopapas, J. Environ. Eng. 124 (11) (1998) 1054–1060.
[14] G.L. Hein, N.J. Hutzler, J.S. Gierke, in: J.N. Ryan, M. Edwards (Eds.), Proceedings of the 1994 National Conference on Environ. Engineering, Am. Soc. Civ. Eng., NY, 1994, pp. 556–563.
[15] W.J. Braida, S.K. Ong, Water Resour. Res. 34 (12) (1998) 3245–3254.
[16] D.J. Wilson, A. Clarke, K. Kaminski, E. Chang, Sep. Sci. Technol. 32 (18) (1997) 2969–2992.
[17] L. A Roberts, D.J. Wilson, Groundwater cleanup by in situ sparging: III. Modeling of dense nonaqueous phase liquid droplet removal, Sep. Sci. Technol. 28 (5) (1993) 1127–1143.

[18] D.J. Wilson, J.M. Rodriguez-Maroto, C. Gomez-Lahoz, Sep. Sci. Technol. 29 (11) (1994) 1401–1432.
[19] C. Gomez-Lahoz, D.J. Wilson, J.M. Rodriguez-Maroto, Sep. Sci. Technol. 29 (12) (1994) 1509–1528.
[20] A.J. Rabideau, J.M. Blayden, Ground Water Monit. Rem. 18 (4) (1998) 120–130.
[21] M.T. van Genuchten, Non-equilibrium transport parameters from miscible displacement experiments, Res. Rep. 119, US Salinity Lab, US Dept. Agriculture, Riverside, CA, 1981.
[22] A.J. Rabideau, J.M. Blayden, C. Ganguly, Environ. Sci. Technol. 33 (1) (1999) 157–162.
[23] D.J. Wilson, S. Kayano, R.D. Mutch, A.N. Clarke, Sep. Sci. Technol. 27 (8) (1992) 1023–1041.
[24] D.W. Felten, M.C. Leahy, L.J. Bealer, B.A. Kline, in: Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston TX, 1992, National Ground Water Association, Dublin, OH, 1992, pp. 365–376.
[25] J.S. Gierke, C.L. Wojick, N.J. Hutzler, in: M.L. Brusseu, D. Sabatini, J. Gierke, M. Annable (Eds.), Innovative Subsurface Remediation: Physical, Chemical, and Characterization Technologies, Am. Chem. Soc., Washington, DC, 1999.
[26] D.J. Wilson, R.D. Norris, Sep. Sci. Technol. 32 (16) (1997) 2569–2589.
[27] D.J. Wilson, A.N. Clarke, K.M. Kaminski, E.Y. Chang, Sep. Sci. Technol. 33 (1) (1998) 97–118.
[28] P.C. Johnson, Environ. Sci. Technol. 32 (2) (1998) 276–281.
[29] P.D. Lundegard, G. Andersen, Ground Water 34 (3) (1996) 451–460.
[30] J.E. McCray, R.W. Falta, J. Contam. Hydrol. 24 (1) (1996) 25–52.
[31] J.E. McCray, R.W. Falta, in: E.L. Gaden (Ed.), AICHE Symposium Series, 91 (306), American Institute of Chemical Engineers, Washington, DC, 1995, pp. 50–57.
[32] J.E. McCray, R.W. Falta, Ground Water 35 (1) (1997) 99–110.
[33] A.J. Unger, E.A. Sudicky, P.A. Forsyth, Water Resour. Res. 31 (8) (1995) 1913–1926.
[34] K.R. Reddy, J. Zhou, in: M. Kamon (Ed.), Proceedings of the 2nd International Congress on Environmental Geotechnics, Osaka, Japan, 1996, Balkema, Rotterdam, 1996, pp. 299–304.
[35] R.W. Falta, K. Pruess, S. Finsterle, A. Battistelli, T2VOC User's Guide, Rep. LBL-36400 UC-400, Berkeley, CA, 1995, 154 pp.
[36] L.W. Lake, Enhanced Oil Recovery, Prentice Hall, Englewood Cliffs, NJ, 1989, 550 pp.
[37] P.D. Lundegard, G. Andersen, in: Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston TX, 1993, National Ground Water Association, Dublin, OH, 1993, pp. 461–476.
[38] McCray, J.E., Numerical analysis of air sparging for subsurface remediation, MS Thesis, Dept. of Environmental Systems Engineering, Clemson University, Clemson, SC, 1994.
[39] R.H. Mohtar, R.B. Wallace, L.J. Segerlind, in: A. Peters (Ed.), Computational Methods in Water Resources X (2), Kluwer Aademic Publ., Dordrecht, 1994, pp. 967–974.
[40] R.H. Mohtar, R.B. Wallace, L.J. Segerlind, Fluid Part. Sep. J. 9 (3) (1996) 239–255.
[41] A.G. Larson, R.W. Falta, in; L.N. Reddi (Ed.), Non-aqueous phase liquids (NAPLs) in subsurface environment: assessment and remediation, Proceedings, ASCE National Convention, Washington, DC, 1996, Environ. Eng. Div., Am. Soc. Civ. Eng., 1996, pp. 551–562.
[42] M.C. Marley, F. Li, in: R.E. Hinchee (Ed.), Air Sparging for Site Remediation, Lewis Publishers, Boca Raton, FL, 1994, pp. 23–27.
[43] M.I.J. van Dijke, S.E.A.T.M. van der Zee, C.J. van Duijn, Adv. Water. Resour. 18 (1995) 319–333.
[44] J.R. Lang, K.M. Rathfelder, L.M. Abriola, in: R.E. Hinchee, R.N. Miller, P.C. Johnson (Eds.), In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes, Battelle Press, Columbus, OH, 1995, pp. 447–453.
[45] G.L. Hein, J.S. Gierke, N.J. Hutzler, R.W. Falta, Ground Water Monit. Rem. 17 (3) (1997) 222–230.
[46] M.I. van Dijke, E.A. van der Zee, Water Resour. Res. 34 (3) (1998) 341–354.
[47] M. Chen, R.E. Hinkley, J.E. Kilough, Water Resour. Res. 32 (10) (1996) 3013–3024.
[48] J.R. Philip, J. Contam. Hydrol. 33 (1998) 337–345.
[49] B.H. Kueper, E.O. Frind, J. Contam. Hydrol. 2 (1988) 95–110.
[50] R. Chouke, P. Van Meurs, C. Van der Poel, AIME Petrol. Trans. 216 (1959) 188–194.
[51] L.D. Morton R.W. Falta, D.S. Henderson, C.A. Kern, in; L.N. Reddi (Ed.), Non-aqueous Phase Liquids (NAPLs) in Subsurface Environment: Assessment and Remediation, Proceedings, ASCE National Convention, Washington, DC, 1996, Environ. Eng. Div., Am. Soc. Civ. Eng., 1996, pp. 127–138.
[52] P.C. Johnson, A. Das, C. Bruce, Environ. Sci. Technol. 33 (10) (1999) 1726–1731.

[53] E.P. Poeter, S.A. McKenna, W.L. Wingle, Improving Ground-Water Project Analysis with Geophysical Data, The Leading Edge, November 1997, 1675–1681.
[54] P.D. Lundegard, D. LeBreque, J. Contam. Hydrol. 19 (1) (1995) 1–27.
[55] S. Schima, D.J. LaBrecque, P.D. Lundegard, Ground Water Monit. Rem. 16 (2) (1996) 131–138.
[56] W. Daily, A. Ramirez, J. Appl. Geophys. 33 (1995) 239–249.
[57] D.J. McKay, L.J. Acomb, Ground Water Monit. Rem. 16 (4) (1996) 86–94.
[58] S. Finsterle, K. Pruess, Water Resour. Res. 31 (4) (1995) 913–924.
[59] E.P. Poeter, M.C. Hill, Ground Water 35 (2) (1997) 250–260.