A composite numerical model for assessing subsurface transport of oily wastes and chemical constituents

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Abstract

Subsurface fate and transport models are utilized to predict concentrations of chemicals leaching from wastes into downgradient receptor wells. The contaminant concentrations in groundwater provide a measure of the risk to human health and the environment. The level of potential risk is currently used by the U.S. Environmental Protection Agency to determine whether management of the wastes should conform to hazardous waste management standards. It is important that the transport and fate of contaminants is simulated realistically. Most models in common use are inappropriate for simulating the migration of wastes containing significant fractions of nonaqueous-phase liquids (NAPLs). The migration of NAPL and its dissolved constituents may not be reliably predicted using conventional aqueous-phase transport simulations. To overcome this deficiency, an efficient and robust regulatory assessment model incorporating multiphase flow and transport in the unsaturated and saturated zones of the subsurface environment has been developed. The proposed composite model takes into account all of the major transport processes including infiltration and ambient flow of NAPL, entrapment of residual NAPL, adsorption, volatilization, degradation, dissolution of chemical constituents, and transport by advection and hydrodynamic dispersion. Conceptually, the subsurface is treated as a composite unsaturated zone–saturated zone system. The composite simulator consists of three major interconnected computational modules representing the following components of the migration pathway: (1) vertical multiphase flow and transport in the unsaturated zone; (2) areal movement of the free-product lens in the saturated zone with vertical equilibrium; and (3) three-dimensional aqueous-phase transport of dissolved chemicals in ambient groundwater. Such a composite model

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configuration promotes computational efficiency and robustness (desirable for regulatory assessment applications). Two examples are presented to demonstrate the model verification and a site application. Simulation results obtained using the composite modeling approach are compared with a rigorous numerical solution and field observations of crude oil saturations and plume concentrations of total dissolved organic carbon at a spill site in Minnesota, U.S.A. These comparisons demonstrate the ability of the present model to provide realistic depiction of field-scale situations. © 1997 Elsevier Science B.V.

1. Introduction

Under Section 3001 of the Resource Conservation and Recovery Act (RCRA) of 1976, the U.S. Environmental Protection Agency (EPA) has been charged with identifying wastes that pose a hazard to human health and the environment if improperly managed. As a part of this effort, the Agency needs to evaluate alternatives for the identification and quantification of subsurface releases of oily wastes so as to protect the human health and the environment. Oily wastes are defined as contaminants that are only slightly soluble in water and exist principally in a separate nonaqueous-phase liquid (NAPL); many of these contaminants also volatilize. Existing in a separate liquid phase, transport of such contaminants cannot be simulated adequately using the conventional aqueous-phase flow and transport models. In order to assess the potential human and environmental impacts of oily wastes at a large number of sites nationwide, a reliable, robust, and efficient modeling approach is needed for simulating their subsurface migration and fate.

Numerous physical and chemical processes control the migration of NAPLs in the subsurface. The processes of oily waste movement in the unsaturated zone have been described in several references including Freeze and Cherry (1979), and Schwille (1981). Typically, an oily waste released at or near the soil surface will move primarily downward under the influence of gravitational forces. Capillary forces may produce some lateral spreading in the unsaturated zone. Upon reaching the water table, a NAPL that is lighter than water (LNAPL) will then migrate laterally, forming a lens or pancake on top of the water table. A NAPL that is denser than water (DNAPL) will sink to the base of the aquifer, where it will spread laterally due to gravity and ambient flow forces. In addition, a small fraction of each NAPL contaminant will dissolve in groundwater (in the saturated and unsaturated zones), forming a soluble contaminant plume migrating with the ambient groundwater flow. A NAPL contaminant may also become adsorbed to soil or sediment particles, volatilize into pore spaces, or undergo biological or chemical degradation.

Several models have been developed to simulate the flow of multiple fluid phases in the subsurface. Complex three-phase and compositional models have been presented by Corapcioglu and Baehr (1987), Forsyth and Shao (1991), Falta et al. (1992), Sleep and Sykes (1993), Huyakorn et al. (1994a) and Panday et al. (1995). A decoupled flow and transport model that includes dissolution of NAPL is discussed in Reeves and Abriola (1988). Unsaturated–saturated zone three-phase models with a passive air phase can be

found in Faust (1985), Faust et al. (1989), Kaluarachi and Parker (1989), and Forsyth (1991). Saturated-zone, two-phase (NAPL and water) models are detailed in Schwille (1981) and Hochmuth and Sunada (1985). Several models have reduced dimensionality to analyze a radial or vertical cross-section within the domain of an unsaturated–saturated system, while one-dimensional (1-D) (vertical) models were developed to quantify the migration of NAPLs from the release source to the water table, assuming that the unsaturated-zone migration is vertically downward (Ryan and Cohen, 1991; Weaver et al., 1994). Vertical equilibrium (areal two-dimensional, 2-D) models with history-dependent pseudo functions have also been developed by Wu et al. (1994), and Huyakorn et al. (1994b). All these models include a NAPL contaminant mass balance, water and air in the subsurface, and simplifying assumptions with respect to phase presence or dimensionality.

Rigorous models that simulate three-dimensional (3-D) flow and transport of NAPL contaminants in the saturated and unsaturated zones have extremely complex data requirements and are computationally intensive. On the other hand, oversimplified models may not provide the required level of detail for the analysis. To support nationwide environmental assessments, an effective modeling approach is required that can assess contaminant behavior in both saturated and unsaturated zones and evaluate the most common waste disposal scenarios and site conditions. Quantifying regulatory limits and standards for oily waste disposal nationwide requires many simulation scenarios with a model that is robust and computationally efficient. The model should also be economical with respect to data requirements and make use of hydrogeological data already compiled by the U.S. EPA for use in contaminant fate and transport modeling, together with oily waste specific data. In this paper, a composite modeling approach is presented for regulatory application, to provide the required level of detail in analysis with an efficient simulation scheme and commensurate data requirements.

2. Model formulation

The proposed model, named *EPA*'s *C*omposite *M*odel for *O*ily *W*aste (EPACMOW), is designed to handle typical scenarios shown in Fig. 1. Conceptually, the subsurface is treated as a composite unsaturated zone–saturated zone system. The model comprises three sets of computational modules: (1) 1-D modules for simulating multiphase fluid flow and soluble contaminant transport in the unsaturated zone; (2) 2-D (areal) modules for simulating simultaneous flow of groundwater and NAPL in the saturated zone assuming vertical equilibrium; and (3) 3-D modules for simulating soluble contaminant transport in the saturated zone. A preliminary version was presented at the Annual Hydrocarbon Conference in Houston, Texas, U.S.A. (Saleem et al., 1994).

A rigorous multiphase analysis is used in the unsaturated zone to represent the three-phase (water–NAPL–air) system above the water table where capillary effects and air-phase transport (volatilization) are likely to be important. The present modeling approach includes the assumption of 1-D (vertically downward) flow and transport in the unsaturated zone, which is reasonable for the scenarios of interest (Fig. 1) and consistent with EPA's previous composite aqueous-phase models (U.S. EPA, 1990,
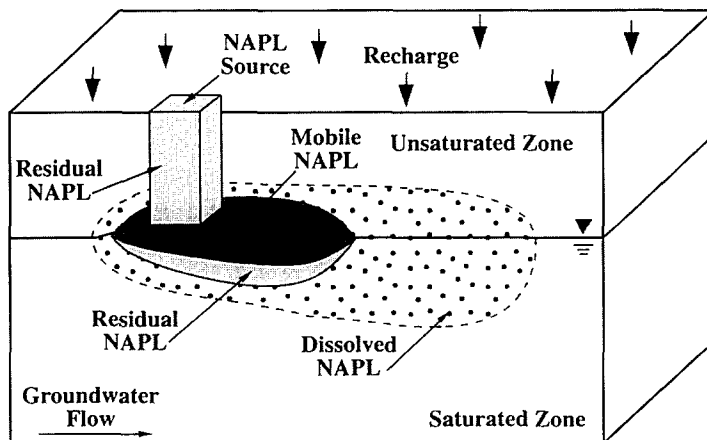
LNAPL SCENARIO
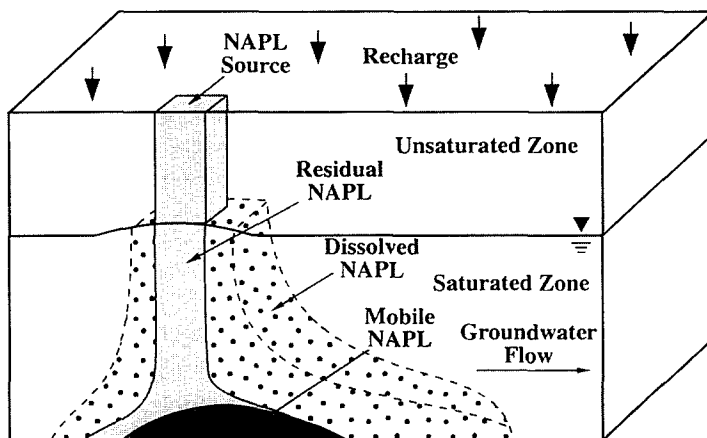
DNAPL SCENARIO

Fig. 1. A schematic view of modeling scenarios simulated by the composite modeling approach.

1995; Kool et al., 1994) for assessing the migration and fate of miscible contaminants from land disposal facilities. Because unsaturated-zone flow and transport simulation problems are one-dimensional, their computational requirements are minimal. In addition, data pertaining to multiphase constitutive relations are likely to be more readily available for near-surface unsaturated soils than for the deeper and less easily accessible

saturated zone. The unsaturated-zone modules are linked to the saturated-zone flow modules, by assuming that all fluids and contaminants leaving the bottom boundary of the unsaturated zone are injected into the saturated zone. A vertical equilibrium approximation is used to describe the two-phase flow of NAPL and groundwater in the saturated zone of the aquifer. The vertical equilibrium formulation is based on the approach originally developed for petroleum reservoirs (e.g., Coats et al., 1971). The main benefits of using the areal flow formulation instead of the rigorous 3-D two-phase formulation are computational efficiency and much reduced input data requirements. The model formulation can handle both LNAPL and DNAPL scenarios and takes into account the residual NAPL left behind as NAPL moves through pristine portions of the aquifer. The flow modules are in turn linked to the fully 3-D saturated-zone transport modules which simulate soluble contaminant transport and predict contaminant concentrations at receptor well locations. The composite model also has the capability of simulating chain decay reactions and the generation of transformation products. This decoupled approach to flow and transport assumes that dissolution of contaminant does not affect the saturation or flow characteristics of the phases, and can greatly enhance simulation speeds. A brief description of the governing equations and numerical schemes implemented in the model is given below.

2.1. Unsaturated-zone flow and transport

The 1-D mass-balance equations for flow of three active fluid phases (water, NAPL, and gas) are used to describe the NAPL movement in the unsaturated zone. These equations may be expressed as:

$$\frac{\partial}{\partial z}\left[k_z \tau_l \frac{\partial \Phi_l}{\partial z}\right] + \rho_l q_l = \frac{\partial}{\partial t}(\phi \rho_l S_l), \quad l = \text{w, n, g} \tag{1}$$

where z is a vertical coordinate; t is time; l is the fluid-phase index (w = water, n = NAPL, and g = gas); k_z is the vertical intrinsic permeability; τ_l is the phase mobility; Φ_l is the fluid potential; ρ_l is the fluid density; ϕ is porosity; S_l is phase saturation; and q_l is the volumetric source/sink term for phase l. The above mass-balance equations are complemented by constitutive relations describing fluid retention characteristics in the porous medium.

The van Genuchten and Brooks–Corey functions (van Genuchten, 1980; Brooks and Corey, 1966) are used to describe capillary pressure and relative permeability characteristics. The retention functions for the two-phase (water, air) system are extended to three-phase relations using the procedure developed by Lenhard and Parker (1987). Hysteresis in these constitutive relations are neglected. Equation system (1) is discretized using a linear 1-D finite-element technique with upstream weighting of relative permeabilities and a lumped mass matrix. A Newton–Raphson linearization is performed on the discretized equations, and the block-tridiagonal system of equations is solved using a direct Thomas algorithm. Surficial boundary conditions include volumetric injection rates for NAPL and/or water, or prescribed pressure conditions for any or all of the three phases. The bottom boundary corresponds to water-table atmospheric

pressure conditions. Liquid fluxes calculated at the bottom boundary then become the fluid flux boundary conditions for the saturated-zone flow module.

A 1-D phase-summed transport equations used to describe transport of a dissolved chemical species c in the unsaturated zone. This equation may be expressed as:

$$\frac{\partial}{\partial z}\left[D_{\mathrm{T}zz}\frac{\partial \omega_{\mathrm{w}}^c}{\partial z}\right] - \frac{\partial}{\partial z}\left(V_{\mathrm{T}z}\,\omega_{\mathrm{w}}^c\right) = \frac{\partial}{\partial t}\left(\phi R_{\mathrm{T}}^c\,\omega_{\mathrm{w}}^c\right) + \lambda^c\phi R_{\mathrm{T}}^c\,\omega_{\mathrm{w}}^c - \phi\sum_{m=1}^{M}\lambda^m\xi_m^c R_{\mathrm{T}}^m\omega_{\mathrm{w}}^m \tag{2}$$

where $D_{\mathrm{T}zz}$ is phase-summed (with respect to water, NAPL, and air) and density multiplied values of vertical hydrodynamic dispersion; $V_{\mathrm{T}z}$ and R_{T}^c are vertical Darcy velocity and retardation, respectively; ω_{w}^c is the mass fraction of species c in the aqueous phase; λ^c is the component degradation constant; M is the total number of parents of species c; and ξ_m^c is the mass fraction of the parent component m that transforms to species c. Equilibrium partitioning provides the concentration values in the other phases present. A detailed derivation of the phase-summed transport Eq. (2) is provided by Huyakorn et al. (1992).

The surface boundary condition for the transport equation may be the prescribed water-phase concentration or the prescribed solute mass flux for each species being analyzed. For the case of a decaying source, the source boundary conditions may be obtained from the Bateman (1910) equations. The bottom boundary conditions correspond to zero concentration gradient for chemical components, and the efflux of each component is input as a mass flux boundary condition into the saturated-zone transport module. Equation system (2) is approximated using an upstream weighted finite-element technique. The resulting tridiagonal system of equations is solved using a direct Thomas algorithm.

2.2. Saturated-zone flow of groundwater and NAPL

In the liquid-saturated zone the gas phase vanishes, and the flow system reduces to two phases (water and NAPL). The two-phase flow system is considered to be in vertical equilibrium (VE) whenever the pressure in each liquid phase is approximately hydrostatic. Conditions of VE are satisfied in aquifers having one or more of the following properties (Thomas, 1982): (a) high vertical permeabilities; (b) high gravity and/or capillary zones; (c) high fluid mobilities; (d) low rates of areal fluid movement; and (e) low vertical potential gradients.

When the VE approximation is applicable, the dimension of the two-phase flow system can be reduced by one by integrating equations along the vertical direction over the liquid-saturated thickness to give (Wu et al., 1994):

$$\frac{\partial}{\partial x}\left[\frac{\rho_l b}{\mu_l}k_x\bar{k}_{rlx}\frac{\partial \Phi_l}{\partial x}\right] + \frac{\partial}{\partial y}\left[\frac{\rho_l b}{\mu_l}k_y\bar{k}_{rly}\frac{\partial \Phi_l}{\partial y}\right] = \frac{\partial}{\partial t}\left(\rho_l b\phi\bar{S}_l\right), \quad l = \mathrm{w, n} \tag{3}$$

where k_x and k_y are intrinsic permeability along the x- and y-directions, respectively;

ρ_l and μ_l are density and dynamic viscosity of fluid phase l, respectively; b is the thickness of liquid-saturated zone; and the vertically averaged variables are defined as

$$\bar{k}_{rl} = \frac{1}{b} \int_{Z_B}^{Z_T} k_{rl}(z) \, dz \tag{4}$$

and

$$\bar{S}_l = \frac{1}{b} \int_{Z_B}^{Z_T} S_l(z) \, dz \tag{5}$$

where Z_B is the aquifer base elevation; and Z_T is the top elevation of the liquid-saturated zone, which, in general, is a function of both space and time. In addition to the average relative permeability, a pseudo capillary pressure relation is needed to relate the different phase pressures.

In general, the dependence of the average relative permeability and the pseudo capillary pressure on the average saturation can be determined using real capillary pressure and relative permeability curves at the reference plane and the VE condition (Coats et al., 1967, 1971; Martin, 1968). The resulting formulation is referred to as gravity-capillary vertical equilibrium formulation. A further simplification is to ignore the capillary transition zone by assuming that a sharp interface separates the zones of NAPL and fresh water in gravity-segregated vertical equilibrium (GSVE). The GSVE formulation is provided in the composite model. The formulation is applicable for both LNAPL and DNAPL scenarios. Equation system (3) is discretized using a modified Galerkin technique with influence coefficient algorithms that produce 9-point (finite-element) or 5-point (finite-difference) nodal lattices for a rectangular grid. A residual-based, Newton–Raphson iterative technique is used to handle the non-linearity. Specific details pertinent to the GSVE formulation can be found in Huyakorn et al. (1994a). The formulation contains history-dependent schemes for tracking the NAPL movement taking into account residual saturations. Being based on the sharp-interface assumption, the GSVE formulation would simulate a NAPL lens with separate immobile and mobile zones (Fig. 1) within which the NAPL and water saturations are, respectively, at their residual values.

2.3. Saturated-zone transport of dissolved chemicals

A 3-D phase-summed transport equation is used to describe transport of a dissolved chemical species c in the saturated zone. This equation may be expressed as:

$$\frac{\partial}{\partial x_i}\left[D_{Tij} \frac{\partial \omega_w^c}{\partial x_j} \right] - \frac{\partial}{\partial x_i}\left(V_{Ti}\, \omega_w^c \right) = \frac{\partial}{\partial t}\left(\phi R_T^c\, \omega_w^c \right) + \lambda^c \phi R_T^c\, \omega_w^c - \phi \sum_{m=1}^{M} \lambda^m \xi_m^c R_T^m\, \omega_w^m \tag{6}$$

where x_i ($i = 1, 2, 3$) are spatial coordinates; D_{Tij} is the phase-summed (with respect to water and NAPL) and density-multiplied values of hydrodynamic dispersion; and V_{Ti} and R_T^c are Darcy velocity and retardation, respectively.

For each fluid phase, the hydrodynamic dispersion is determined as the sum of the

contributions from mechanical dispersion and molecular diffusion. If an isotropic porous medium is assumed, the mechanical dispersion tensor is computed via the standard formula (Bear, 1972) based on the longitudinal and transverse dispersivities. Otherwise the model employs a more general procedure (Burnett and Frind, 1987) by which the dispersion tensor for a stratified porous medium is determined in terms of three dispersivities including the horizontal longitudinal, horizontal transverse, and vertical transverse dispersivities.

Three saturated-zone transport simulation scenarios are accommodated by the model. The first is the most general fully transient case in which contaminant source boundary conditions, fluid velocities, and saturation distributions are wholly time-dependent. This case is handled using a time-stepping upstream weighted residual technique with influence coefficient algorithms that produce 27-point (finite-element) or 7-point (finite-difference) nodal lattices for a 3-D rectangular grid. Matrix solution is performed using an Orthomin iterative method (Behie and Forsyth, 1984). The second scenario is referred to as the quasi or pseudo transient case. It is assumed that the infiltration and redistribution of NAPL has occurred before the transient transport analysis is performed. The groundwater flow field is at a steady state and a limited quantity of NAPL redistributes within the domain at residual saturation. The pseudo transient transport case is efficiently handled for a finite NAPL source using a Laplace transform Galerkin (LTG) technique (Sudicky, 1988). The immobile NAPL zone below the water table is regarded as a volume source from which leaching of contaminants occurs. In time, the NAPL phase is stripped of all soluble contaminants which migrate downstream in the water phase due to ambient flow gradients and steady-state recharge. The analysis necessarily invokes the assumption that the NAPL infiltration and redistribution occur in a relatively short time as compared to the solute transport times of interest. The third scenario is referred to as the pseudo steady-state case, representing a worst case scenario. Steady-state flow conditions and a residual NAPL distribution are again assumed. However, the attenuation of the NAPL zone due to dissolution of the chemical constituents is neglected, and the NAPL zone acts as a continuous source to the dissolved-phase transport module. For this case, the model conservatively predicts steady-state concentration values in the groundwater system.

2.4. Module linkage and overall simulation scheme

The three simulation modules presented in the foregoing sections are integrated into the composite model. In a comprehensive simulation run, the 1-D unsaturated-zone module is first used to generate the flux boundary conditions at the water table directly beneath the surface source. The unsaturated-zone flow module is linked to the 2-D, areal saturated-zone flow module via the fluid flux boundary conditions at the water table. The simulation of NAPL migration in the saturated zone is performed using the GSVE formulation.

A inter-module-precessing coupler is utilized to link the unsaturated-zone transport module and the saturated-zone flow module to the fully 3-D saturated-zone transport module. Source flux boundary conditions are derived for dissolved contaminants with the conservation of mass. For transient transport simulations, the source boundary

conditions and velocity fields are appropriately updated with time. For each chemical of concern, the concentration in the aqueous phase is computed by solving the phase-summed solute transport equation. The concentrations in the remaining phases are determined via their partitioning coefficients.

One key advantage of the composite modeling approach is that it is designed to recognize specific scenarios that do not require calculations within each module. For example, a case may arise where the quantity of subsurface release or spill is so small that the NAPL mass is totally captured at residual saturation within the vadose zone. In such a case, there is no need to invoke the saturated-zone flow module because the NAPL flux at the water table is always zero. The dissolved chemicals, however, may reach the water table, and there is a need to conduct a single-phase saturated-zone transport analysis to determine concentrations at receptor wells.

3. Model verification

During the development of the composite model, the unsaturated-zone and saturated-zone simulation modules were individually tested using a series of carefully designed benchmark problems that exercise the various flow and transport formulations presented. Some of these problems have been documented by Huyakorn et al. (1992, Huyakorn et al., 1994a,b) and Wu et al. (1994). Presented below is a verification case that invokes all of the computational modules in an integral manner.

The selected scenario (Fig. 2) involves a 20-day release of LNAPL form a surface
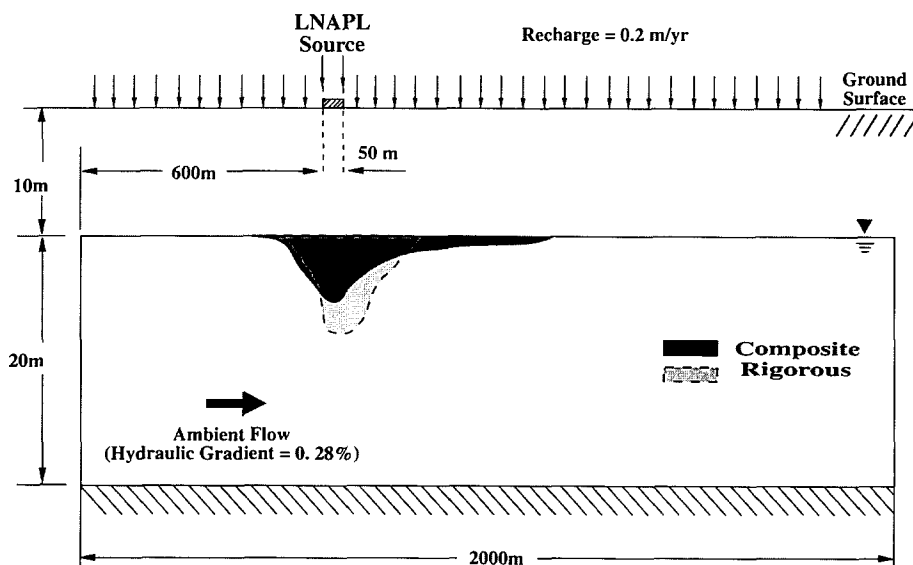

Fig. 2. Model verification example showing a comparison of oil lenses simulated by the composite and rigorous models.

Table 1

Parameters values used in the model verification

Parameter	Value	Unit
Source parameters:		
Source length (area per unit width)	50	m
Water infiltration rate	0.20	m/yr
NAPL leakage rate	9863	kg/day
NAPL release time duration	20	days
NAPL chemical concentration	0.01	kg/kg
NAPL properties:		
NAPL density	900	kg/m^3
NAPL dynamic viscosity	0.64×10^{-3}	Pa s
Chemical transport parameters:		
Partition coefficient between water and NAPL	100	
Partition coefficient between water and air (Henry's constant)	0.05	
Distribution coefficient	1.5×10^{-4}	m^3/kg
Water diffusion coefficient	2×10^{-9}	m^2/s
NAPL diffusion coefficient	2×10^{-10}	m^2/s
Air diffusion coefficient	1×10^{-5}	m^2/s
Degradation constant	0	
Unsaturated zone parameters:		
Unsaturated zone thickness	10	m
Intrinsic permeability	1.5×10^{-10}	m^2
Porosity	0.30	
Bulk density	1650	kg/m^3
Vertical (longitudinal) dispersivity	0.10	m
van Genuchten parameter, α, for air–water system	3.0	m^{-1}
van Genuchten parameter, β, for air–water system	1.6	
Brooks–Corey pore size distribution index, n	2	
Interfacial tension between NAPL and air	0.0378	N/m
Interfacial tension between NAPL and water	0.035	N/m
Interfacial tension between air and water	0.0728	N/m
Residual water saturation	0.30	
Residual NAPL saturation	0.30	
Saturated zone parameters:		
Saturated zone thickness	20	m
Hydraulic gradient	0.0028	
Groundwater recharge rate	0.20	m/yr
Intrinsic permeability	1.5×10^{-10}	m^2
Effective porosity	0.30	
Bulk density	1650	kg/m^3
Horizontal longitudinal dispersivity	10	m
Vertical transverse dispersivity	0.1	m
Residual water saturation	0.30	
Residual NAPL saturation	0.30	

Table 1 (continued)

Discretization parameters:

Temporal discretization: Rigorous model:

First time step	10.0	s
Minimum allowable time step	0.001	s
Maximum allowable time step	1,728,000	s
Maximum allowable time step multiplier	4.0	–

Temporal discretization: Composite model (unsaturated zone):

First time step	3.0	s
Minimum allowable time step	0.3	s
Maximum allowable time step	864,000	s

Temporal discretization: Composite model (saturated zone):

Automatic time stepping

Spatial discretization: Rigorous model:

Vertical (Δz)	1.0	m
Horizontal (Δx)	see Table 2 for horizontal gridline coordinates	

Spatial discretization: Composite model:

Vertical (Δz) unsaturated zone	1.0	m
Vertical (Δz) saturated zone	see Table 2 for vertical gridline coordinates	
Horizontal (Δx)	see Table 2 for horizontal gridline coordinates	

source to an unconfined aquifer with ambient groundwater flow and recharge. We elected to perform the analysis for a vertical cross-section of unit width. The composite modeling approach was verified against a rigorous 3-D multiphase flow/transport modeling approach (Huyakorn et al., 1992; Panday et al., 1994) that does not require the assumptions of vertical flow and transport in the unsaturated zone and areal flow (i.e. vertical equilibrium) in the saturated zone.

The composite model was run in a fully transient mode using a 1-D vertical grid to represent the unsaturated soil column beneath the source and an areal grid to represent the saturated zone of the subsurface system. The parameter values used in the simulation are summarized in Tables 1 and 2. The properties of water and air are not included in the table because these are well known at standard temperature and pressure.

The parameter values listed in Table 1 were also used in the rigorous multiphase flow and transport analysis performed with a fully 3-D grid of unit width representing the entire subsurface system. Note that the fluid retention parameters of the saturated zone were regarded as being the same as those for the unsaturated zone.

Model runs were executed on a SUN Sparc station 20. The composite model took only 2.5 min whereas the rigorous model took over 5 h of CPU time. Simulation results obtained from both modeling approaches are compared in Figs. 2 and 3. In Fig. 2, a comparison of predicted boundaries of immobile LNAPL lenses is presented. The

Table 2
Gridline coordinates

Rigorous model: Horizontal:				
0.00	52.72	244.80	382.00	480.00
550.00	600.00	618.75	637.50	650.00
656.25	675.00	693.75	712.50	731.25
750.00	800.00	865.00	949.50	1059.35
1202.16	1387.80	1587.80	1787.80	2000.00
Composite model: Saturated zone — vertical:				
0.000	0.529	2.529	4.529	6.529
8.529	10.529	12.529	14.529	16.156
17.458	18.500	18.917	19.333	19.667
20.000				
Composite model: Saturated zone — horizontal:				
(same as rigorous model)				

overall agreement between the two modeling approaches is reasonable when taken into consideration the assumptions used in the simpler composite model. Note that the rigorous model produces a deeper lens, which is as expected because vertical flow components are taken into account. On the other hand, the composite model produces a
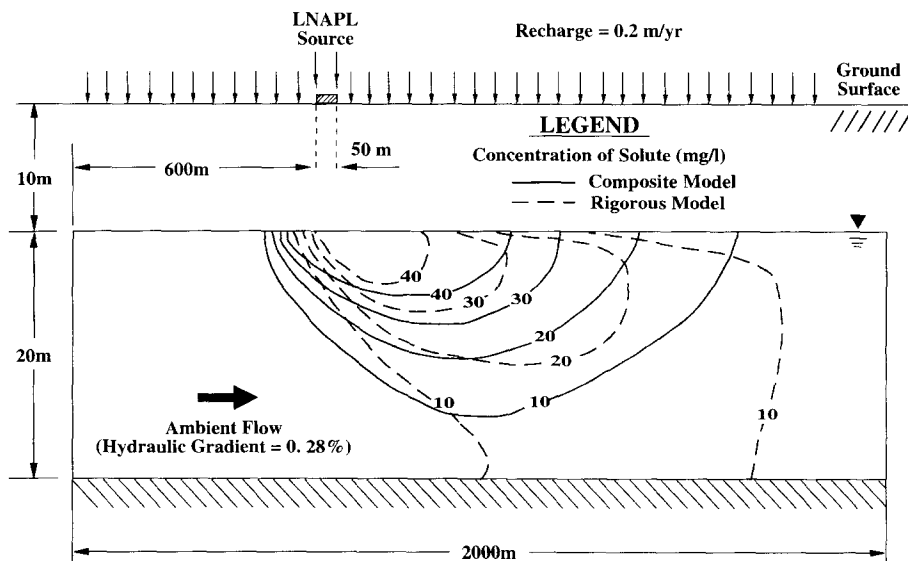

Fig. 3. Comparison of constituent plume concentrations obtained using the composite and rigorous models for $t = 800$ days.

lens that shows greater spreading in the horizontal ambient flow direction. This is because of the sharp-interface, GSVE assumptions used in simulating NAPL flow in the saturated zone.

The constituent plume concentrations simulated by both models are presented in Fig. 3. Note that the higher-concentration contours (40 and 30 mg/l) produced by the composite model exhibit greater horizontal and vertical spreading. On the other hand, the lower-concentration contours (20 and 10 mg/l) produced by the rigorous model exhibit greater vertical depression downstream from the source. The discrepancy between the two simulated concentration distributions may be attributed to two factors: (1) differences in the configuration of LNAPL lens which acts as the source; and (2) vertical
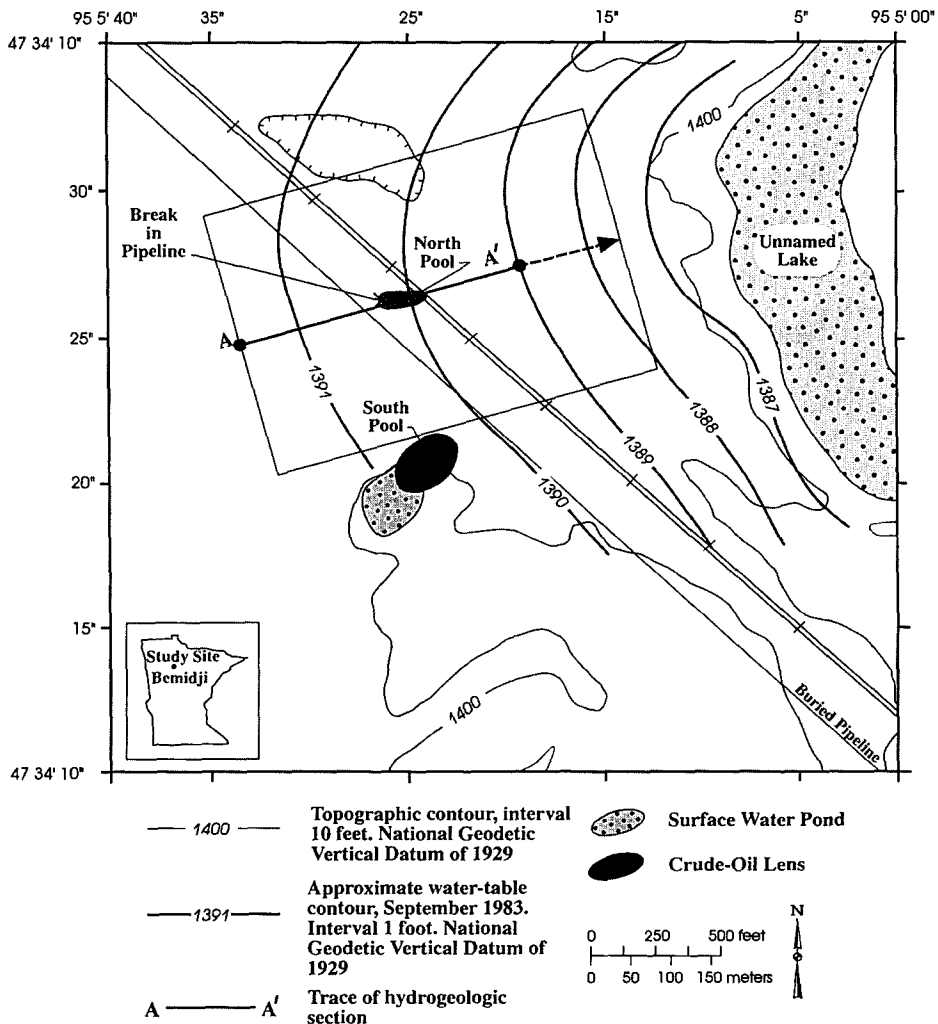

Fig. 4. Field example: Crude oil contamination at Bemidji site, Minnesota, U.S.A.

flow components which were neglected in the composite modeling approach. These factors apparently offset each other and upon combination with the effect of vertical dispersion lead to the behavior of concentration contours depicted in Fig. 3.
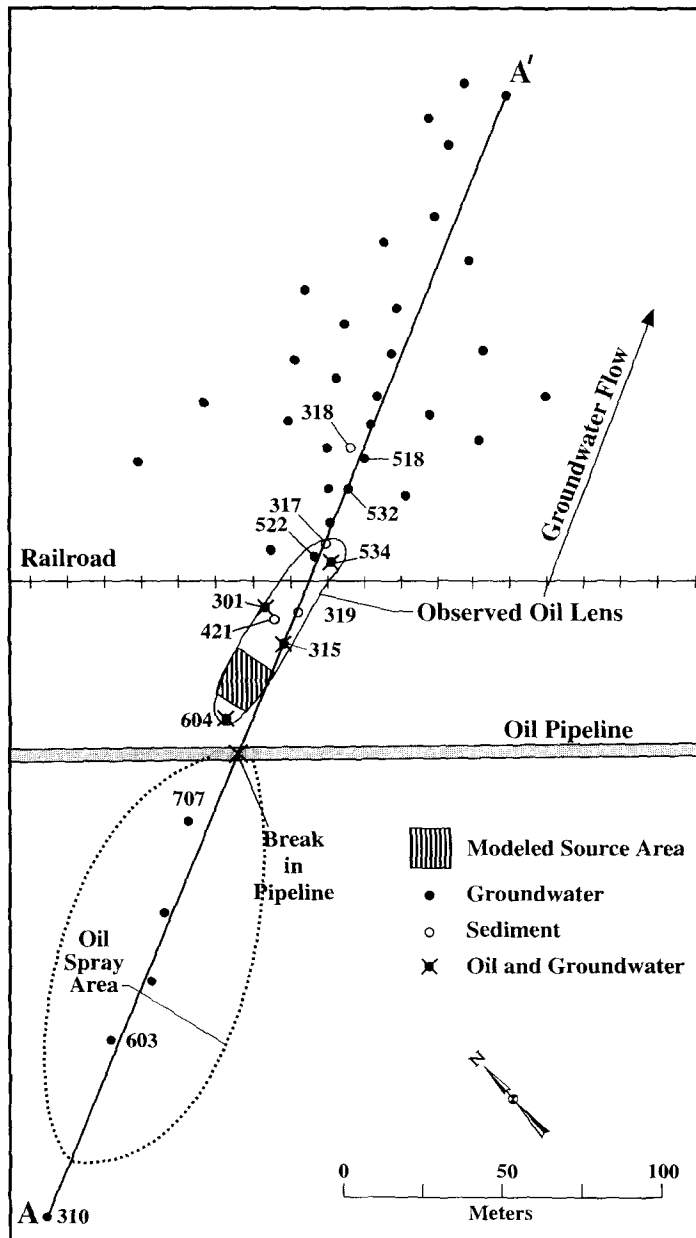

Fig. 5. Main sampling transect showing locations of water-table wells, oil body, and oil pipeline.

4. Site application

A site near Bemidji, Minnesota, U.S.A., with subsurface crude oil contamination was selected for demonstration of the composite model application. An accidental spill of 10,500 barrels (1.62×10^6 l) of crude oil occurred at the site when a buried pipeline broke on August 20, 1970 (Baedecker et al., 1984; Hult, 1984). The oil in the pipeline was under pressure causing it to be sprayed over ~ 6500 m^2 at the site. Despite cleanup efforts, an estimated 2700 barrels (0.42×10^6 l) of crude oil infiltrated the unsaturated zone and remains in the subsurface.

4.1. Site description

The site is located in a sparsely populated area in north-central Minnesota ~ 18 km northwest of Bemidji (Fig. 4). The contaminated area is in the recharge region of a local groundwater flow system that discharges to a small, unnamed lake. The oil collected in topographic depressions and two major pools of oil developed: one near the point of pipeline rupture (north pool), and the second in the vicinity of a small pond (south pool).

Geologically the site belongs to a pitted and dissected outwash plain. The predominant geologic unit is a brown to buff, variably sorted, medium-grained, calcareous, quartz-rich sand. Detailed geologic data are available on particle size analyses, permeability and percent organic carbon for shallow samples in the immediate vicinity of the pipeline break (Hult, 1984). Approximately 24.5 m below ground surface, the outwash is underlain by a gray, calcareous, clay-rich till with a very low vertical hydraulic conductivity.

The local hydrogeology at the site is relatively simple. Groundwater flow is largely horizontal and controlled by the water table surrounding the lake (Fig. 4). The main flow
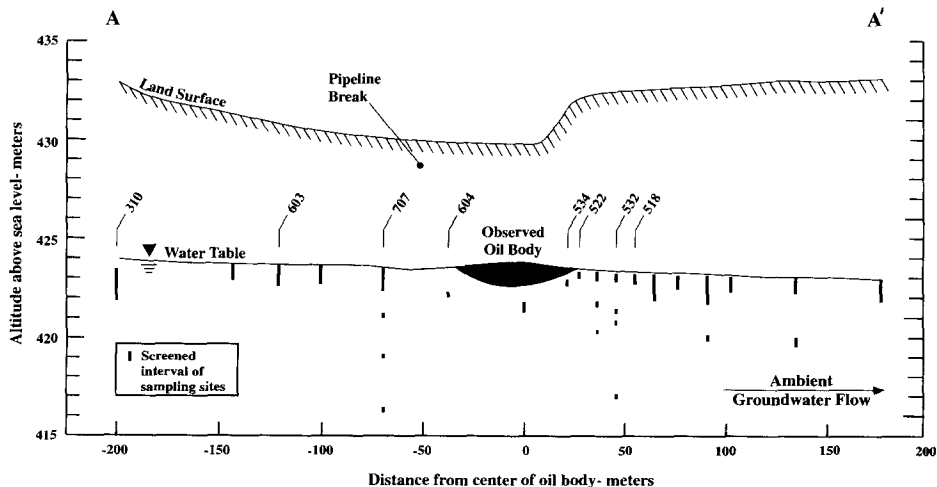

Fig. 6. Cross-section along the main sampling transect.

Table 3
Parameters used in the site application example

Parameter	Value	Unit
Source parameters:		
Source area	169	m^2
Water infiltration rate	0.13	m/yr
NAPL leakage rate	12890	kg/day
NAPL release time duration	7	days
Mass fraction of organic carbon in NAPL	0.02	kg/kg
NAPL properties:		
Density	857	kg/m^3
Dynamic viscosity	1.02×10^{-2}	Pa s
Chemical transport properties:		
Partition coefficient between water and NAPL	100	
Partition coefficient between water and air (Henry's Constant)	0.1	
Distribution coefficient	1×10^{-5}	m^3/kg
Water diffusion coefficient	2×10^{-9}	m^2/s
NAPL diffusion coefficient	2×10^{-10}	m^2/s
Air diffusion coefficient	1×10^{-5}	m^2/s
Degradation constant	0	
Unsaturated zone parameters:		
Unsaturated zone thickness	4.5	m
Intrinsic permeability	1×10^{-11}	m^2
Porosity	0.35	
Bulk density	1650	kg/m^3
Vertical longitudinal dispersivity	0.05	m
van Genuchten parameter, α, for air–water system	3.41	1/m
van Genuchten parameter, β, for air–water system	2.57	
Brooks–Corey pore size distribution index, n	2	
Interfacial tension between NAPL and air	0.0263	N/m
Interfacial tension between NAPL and water	0.0266	N/m
Interfacial tension between air and water	0.0728	N/m
Residual water saturation	0.05	
Residual oil saturation	0.20	
Saturated zone parameters:		
Saturated zone thickness	18	m
Hydraulic gradient	0.0026	
Groundwater recharge rate	0.13	m/yr
Intrinsic permeability	5.0×10^{-12}	m^2
Effective porosity	0.25	
Bulk density	1650	kg/m^3
Horizontal longitudinal dispersivity	25	m
Horizontal transverse dispersivity	5	m
Vertical transverse dispersivity	0.10	m
Residual water saturation	0.05	
Residual oil saturation	0.20	

Table 3 (continued)

Discretization parameters:

Temporal discretization: Unsaturated zone:

First time step	10	d
Minimum allowable time step	0.1	d
Maximum allowable time step	1000	d

Temporal discretization: Saturated zone:

Automatic time stepping

Spatial discretization:

Vertical (Δz) unsaturated zone	0.5	m
Vertical (Δz) saturated zone	see Table 4 for gridline coordinates	
Horizontal (Δx, Δy) saturated zone	see Table 4 for gridline coordinates	

direction is to the east-northeast. The water table contours are approximately parallel to the edges of the lake. Estimates of the groundwater velocities range from 0.15 to 0.5 m/day. The groundwater hydrology is dominated by a fine-grained silty layer at the water table. The major part of the saturated zone of the aquifer is, however, coarse-grained (Bennett et al., 1993). Shown in Fig. 5 is a sampling transect, $A–A'$, along the groundwater flow direction and passing through the north pool of oil. Also included are locations of monitoring wells, oil body, and oil pipeline. The oil body is on the order of 1 m thick, and by 1990 it had spread to a length of 80 m in the direction of groundwater flow (Essaid et al., 1991). The cross-section of the aquifer along the main sampling transect is presented in Fig. 6. The oil lens is located at ~ 5.5 m below the ground surface. The ruptured pipeline is at a depth of 1 m, and just upstream of the oil lens. The average hydraulic gradient for the cross-section is 0.0026. The water table, however, fluctuates 0.15–0.25 m about the mean annual value.

Petroleum hydrocarbons from crude oil have been major sources of groundwater contamination at the site since the spill. The transport of spilled petroleum hydrocarbons in the shallow subsurface is the result of a complex combination of fluid flow, gaseous diffusion, and advective and dispersive transport in groundwater. The soil volume is variably saturated with petroleum hydrocarbons, and continues to act as a source of contamination to the groundwater system. Only heavier fractions of crude oil have been left in the unsaturated zone, and almost all the lighter fractions have reached the water table, and formed an oil lens. Plumes containing dissolved petroleum hydrocarbons and by-products from biochemical reactions have developed downgradient from the oils lens in the saturated zone, 5–7 m below ground surface. Since the spill, the oil has moved more than 30 m downgradient, as a separate phase. Dissolved petroleum hydrocarbons have moved at least 200 m, and vapors in the unsaturated zone have moved horizontally ~ 100 m (Essaid et al., 1991). In the vicinity of the oil body, total dissolved organic carbon (TDOC) concentrations are 48 mg/l, 58% of the TDOC being composed of

Table 4
Gridline coordinates — Saturated zone

Horizontal (parallel to plume axis):				
0.000	52.707	102.648	138.320	163.800
182.000	195.000	199.875	204.750	208.000
209.625	214.500	219.375	224.250	229.125
234.000	247.000	263.900	285.870	314.431
351.560	399.828	462.577	525.000	
Horizontal (perpendicular to plume axis):				
0.000	2.167	3.250	6.500	9.750
13.975	19.468	26.608	35.890	47.957
63.644	84.037	110.549	145.013	175.000
Vertical:				
0.000	0.476	2.276	4.076	5.876
7.676	9.476	11.276	13.076	14.541
15.712	16.650	17.025	17.400	17.700
18.000				
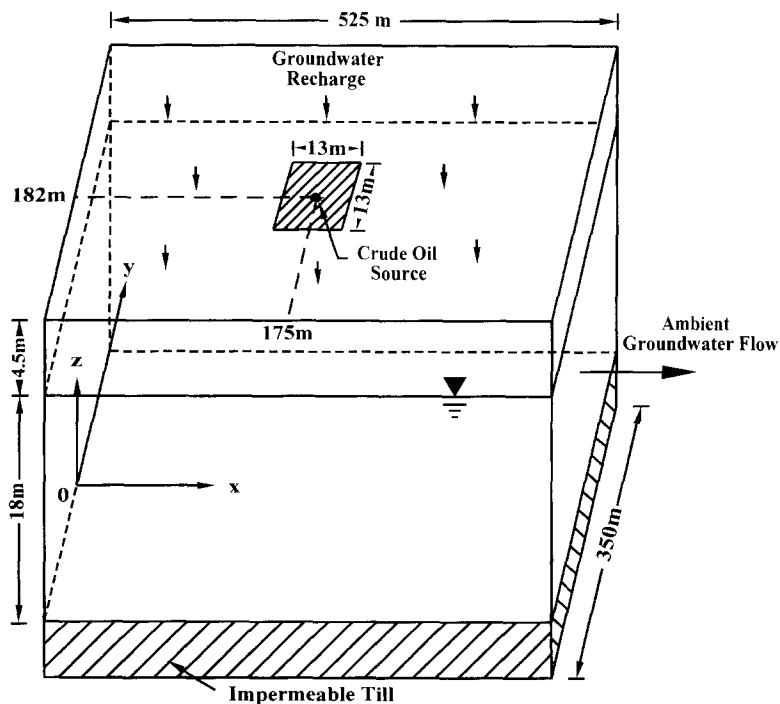
Fig. 7. Idealization of the modeled domain and boundary conditions for the field simulation example.

non-volatile organic carbon. The majority of the volatile DOC (63%) is a mixture of low-molecular-weight saturated, aromatic and alicyclic hydrocarbons derived from the oil (Eganhouse et al., 1993).
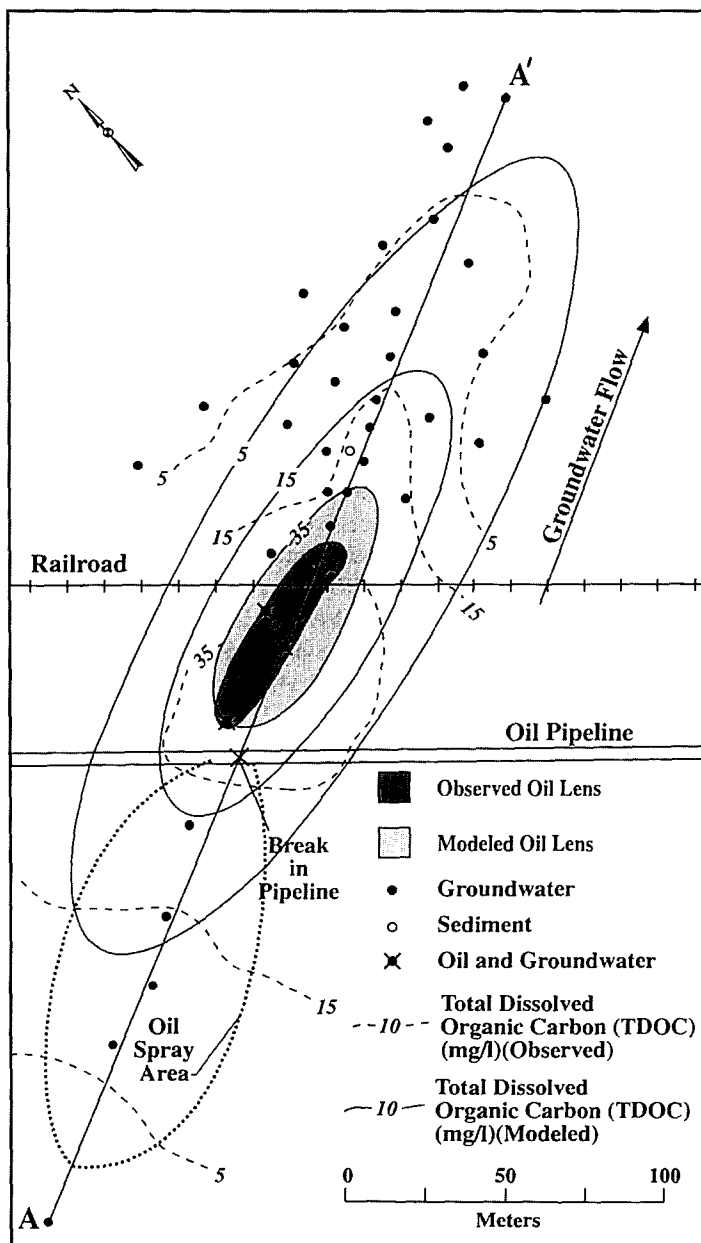

Fig. 8. Plan view of oil lenses and TDOC plumes for 1987.

4.2. Simulations and results

Crude oil is a complex mixture of petroleum hydrocarbons with a wide range of physical and chemical properties, and diversity in their geochemical and transport behavior in the saturated zone with respect to decay rates, partition coefficients, and dispersion coefficients. In view of the lack of detailed information on the petroleum hydrocarbons at the site, we selected representative parameter values for the model, and provide these in Tables 3 and 4. Note that mass fraction of organic carbon in NAPL and dispersivities were determined via model calibration.

Our multiphase flow and transport simulations focus on the north pool for which TDOC plume concentration data are available (i.e. the south pool is not considered). The south pool was previously modeled by Essaid et al. (1993). However, their work does not include constituent transport simulations (M.J. Baedecker, U.S. Geological Survey, Reston, VA, pers. commun., 1995).

The present model domain is oriented along the groundwater flow direction, and encompasses an area of 183,750 m^2 (Fig. 4). A 3-D view of the domain is shown in Fig. 7. The top of the domain corresponds to the elevation of the buried pipeline (i.e. 1 m from the land surface). The underlying unsaturated zone is 4.5 m thick, and is subjected to a steady recharge of 0.13 m/yr. Oil is infiltrated through the source area of 169 m^2 at a rate of 0.089 m/day (12,890 kg/day) for a duration of 7 days. This leads to a total volume of 105.29 m^3 (675 barrels) estimated for the north pool.

The bottom boundary, sitting on the low-permeability till, is treated as a no-flow boundary, as are the sides parallel to the flow direction (x-axis). Constant hydraulic heads are imposed along the upstream and downstream boundaries such that ambient hydraulic gradient is equal to 0.0026. Taking advantage of the symmetry about the centerline of the contaminant source, the model grid was set up to represent only one
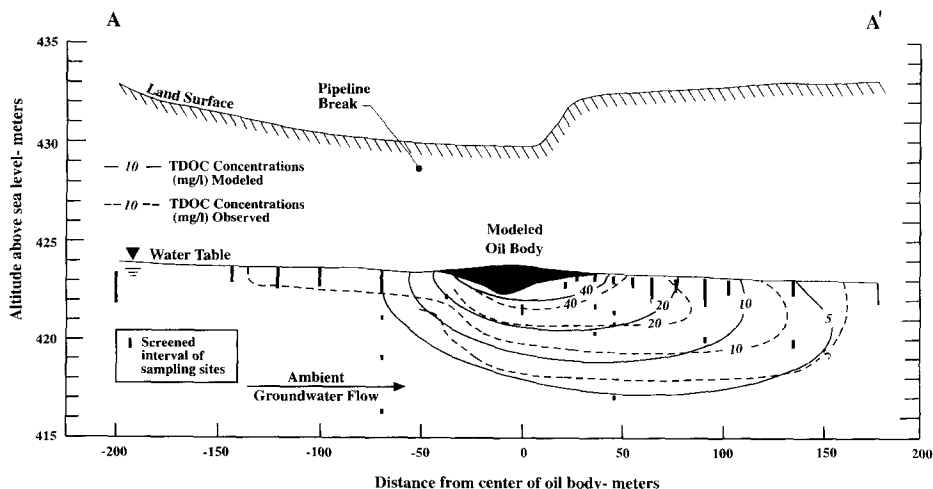

Fig. 9. Cross-section of simulated and observed oil lenses, and TDOC plume for 1987.

half of the region depicted in Fig. 7. Soil parameter values used in the present study are based on the data available from the literature (Bennett et al., 1993; Essaid et al., 1993). To simulate the 1987 condition, the composite model was run for a simulation period of 8 years (i.e. 1979–1987). To complete this simulation of a field problem, the composite model took only 3 min on the SUN Sparc work station.

Shown in Figs. 8 and 9 are comparisons of simulated and observed lenses and TDOC plumes in plan and cross-section views, respectively. Note that the model prediction agrees reasonably well with the observed data. Owing mainly to the GSVE assumptions, the model predicts an areally more extensive (considerably longer and wider) lens than that observed oil body. In plan view, the shape of the observed lens is slightly distorted, probably as a result of aquifer heterogeneity. Note, however, that the extent of the simulated lens is fairly similar to that observed along cross-section $A-A'$ (see Figs. 9 and 7).

In an overall sense, the model provides reasonably good predictions of areal and vertical distributions of TDOC plume concentration. Irregularities in the shape of observed concentration contours may be attributed to aquifer heterogeneity which is unknown and unaccounted for in the modeling. Note that the field observation shows TDOC concentration that exists well beyond the upstream edge of the simulated plume (see Fig. 8). This is mainly due to the contribution of the oil spray area.

5. Conclusions

A composite numerical model has been developed for assessing the multiphase migration of oily wastes and dissolved chemical constituents in the subsurface. The model was constructed by integrating various simulation modules for the unsaturated and saturated zones. The model was made efficient and robust by taking full advantage of certain key assumptions including: one-dimensional downward flow and transport in the unsaturated zone, gravity segregated vertical equilibrium (GSVE) or sharp-interface conditions for the NAPL movement in the saturated zone, and vertically averaged aquifer properties. Invoking these assumptions also led to substantial reduction in data requirements which would make the model appealing for nationwide regulatory applications.

The composite model was verified against a rigorous 3-D three-phase model. Agreement between simulation results obtained from both models was favorable. The CPU time requirement of the composite model run was noted to be at least 2 orders of magnitude less than the rigorous model run (e.g., 2.5 min vs. 5 h on a SUN Sparc workstation to complete a practical field simulation). Simulations of subsurface crude oil contamination at a site near Bemidji, Minnesota, were attempted. The composite model produced predictions of the LNAPL lens and dissolved plume concentrations that are in reasonable agreement with field observations.

The simulation examples presented have demonstrated the ability of the composite model to provide realistic depiction of field-scale situations involving LNAPL contamination. These sites adhered well to the simplifying assumptions invoked for the composite model (i.e. a non-layered fairly homogeneous unsaturated zone allowing

vertical migration of fluids, and low capillary saturated zone soils). The composite model will be further tested on several other sites with LNAPL and DNAPL contamination problems to provide possible insight on the validity of the assumptions of the composite model, for a wide variety of soil conditions. The practicality of incorporating the Monte Carlo procedure into the modeling approach will also be assessed.

Acknowledgements

References

Baedecker, M.J., Eganhouse, R.P. and Lindsay, S.S., 1984. Organic geochemistry of crude-oil contaminants in the subsurface: Preliminary results and project plan. In: M.F. Hult (Editor), Ground Water Contamination by Crude Oil at the Bemidji, Minnesota, Research Site. U.S. Geol. Surv., Water-Resour. Invest. Rep., 84-4188: 65–79.

Bateman, H., 1910. The solution of a system of differential equations occurring in the theory of radio-active transformations. Proc. Cambridge Philos. Soc., 15(5): 423–427.

Bear, J., 1972. Dynamics of Fluids in Porous Media. American Elsevier, New York, NY, 764 pp.

Behie, G. and Forsyth, P.A., 1984. Incomplete factorization methods for fully implicit simulation of enhanced oil recovery. Soc. Ind. Appl. Math. J. Sci. Stat. Comput., 543–561.

Bennett, P.C., Siegel, D.E. and Baedecker, M.J., 1993. Crude oil in a shallow sand and gravel aquifer, I. Hydrogeology and inorganic geochemistry. Appl. Geochem., 8: 529–549.

Brooks, R.H. and Corey, A.T., 1966. Properties of porous media affecting fluid flow. Proc. Am. Soc. Civ. Eng., J. Irrig. Drain. Div., 92(IR2): 61–68.

Burnett, R.D. and Frind, E.O., 1987. Simulation of contaminant transport in three dimensions: 1. The alternating direction Galerkin technique. Water Resour. Res., 23(4): 683–694.

Coats, K.H., Nielson, R.L., Terhune, M.H. and Weber, A.G., 1967. Simulation of three-dimensional, two-phase flow in oil and gas reservoirs. Soc. Pet. Eng. J., 12: 377–388.

Coats, K.H., Demsey, J.R. and Henderson, J.H., 1971. The use of vertical equilibrium in two-dimensional simulation of three-dimensional reservoir performance. Soc. Pet. Eng. J., 11: 63–71.

Corapcioglu, M.Y. and Baehr, A., 1987. A compositional multiphase model for groundwater contamination by petroleum products: Theoretical considerations. Water Resour. Res., 23(1): 191–200.

Eganhouse, R.P., Baedecker, M.J., Cozzarelli, I.M., Aiken, G.R., Thorn, K.A. and Dorsey, T.F., 1993. Crude oil in a shallow and gravel aquifer, II. Organic geochemistry. Appl. Geochem., 8: 551–567.

Essaid, H.I., Herkelrath, W.N. and Hess, K.M., 1991. Air, oil, and water distributions at a crude-oil spill site, Bemidji, Minnesota. U.S. Geol. Surv., Open-File Rep. 91-88.

Essaid, H.I., Herkelrath, W.N. and Hess, K.M., 1993. Simulation of fluid distribution observed at a crude oil

spill site incorporating hysteresis, oil entrapment, and spatial variability of hydraulic properties. Water Resour. Res., 29(6): 1753–1770.

Falta, R.W., Pruess, K., Javandel, I. and Witherspoon, P.A., 1992. Numerical modeling of steam injection for the removal of non-aqueous phase liquids from the subsurface, 1, numerical formulation. Water Resour. Res., 28(2): 443–449.

Faust, C.R., 1985. Transport of immiscible fluids within and below the unsaturated zone: A numerical model. Water Resour. Res., 21(4): 587–596.

Faust, C.R., Guswa, J.H. and Mercer, J.W., 1989. Simulation of three-dimensional flow of immiscible fluids within and below the unsaturated zone. Water Resour. Res., 25(12): 2449–2464.

Forsyth, P.A., 1991. A control volume finite element approach to NAPL groundwater contamination. SIAM J. Sci. Stat. Comput., 12(5): 1029–1057.

Forsyth, P.A. and Shao, B.Y., 1991. Numerical simulation of gas venting for NAPL site remediation. Univ. of Waterloo, Waterloo, Ont., Res. Rep. CS-91-06.

Freeze, R.A. and Cherry, J.A., 1979. Groundwater. Prentice-Hall, Englewood Cliffs, NJ, 604 pp.

Hochmuth, D.P. and Sunada, D.K., 1985. Groundwater model for two phase immiscible flow in coarse material. Ground Water, 23(5): 617–626.

Hult, M.F., 1984. Groundwater contamination by crude oil at the Bedmidji, Minnesota, research site. U.S. Geol. Surv., Water-Resour. Invest. Rep. 84-4188, 107 pp.

Huyakorn, P.S., Wu, Y.S. and Panday, S., 1992. A comprehensive three-dimensional numerical model for predicting the transport and fate of petroleum hydrocarbons in the subsurface. Proc. Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston, TX, Nov. 4–6, 1992.

Huyakorn, P.S., Panday, S. and Wu, Y.S., 1994a. A three-dimensional multiphase flow model for assessing NAPL contamination in porous and fractured media, 1. Formulation. J. Contam. Hydrol., 16(2): 109–130.

Huyakorn, P.S., Wu, Y.S. and Park, N.S., 1994b. An improved sharp-interface model for assessing NAPL contamination and remediation of groundwater systems. J. Contam. Hydrol., 16(3): 203–234.

Kaluarachi, K. and Parker, J., 1989. An efficient finite-element method for modeling multiphase flow. Water Resour. Res., 25(1): 43–54.

Kool, J.B., Huyakorn, P.S., Sudicky, E.A. and Saleem, Z.A., 1994. A composite modeling approach for subsurface transport of degrading contaminants from land-disposal sites. J. Contam. Hydrol., 17: 69–90.

Lenhard, R.J. and Parker, J.C., 1987. Measurement and prediction of saturation–pressure relationships in three-phase porous media systems. J. Contam. Hydrol., 1: 407–424.

Martin, J.C., 1968. Partial integration of equations in multiphase flow. Pet. Eng. J., 8: 370–380.

Panday, S., Wu., Y.S., Huyakorn, P.S. and Springer, E.P., 1994. A three-dimensional multiphase flow model for assessing NAPL contamination in porous and fractured media, 2. Porous medium simulation examples. J. Contam. Hydrol., 16: 131–156.

Panday, S., Forsyth, P.A., Falta, R.W., Wu, Y.S. and Huyakorn, P.S., 1995. Considerations for robust compositional simulations of subsurface nonaqueous liquid contamination and remediation. Water Resour. Res., 31(5): 1273–1289.

Reeves, H.W. and Abriola, L.M., 1988. A decoupled approach to the simulation of flow and transport on non-aqueous organic phase contaminants through porous media. In: Proceedings of the Seventh International Conference on Computational Methods in Water Resources: Volume 1. Modeling Surface and Subsurface Flows. Developments in Water Science, Vol. 35. Elsevier, Amsterdam, pp. 147–152.

Ryan, P.A. and Cohen, Y., 1991. One-dimensional subsurface transport of a non-aqueous phase liquid containing sparingly water soluble organics: A front tracking model, Water Resour. Res., 27(7): 1487–1500.

Saleem, Z.A., Panday, S., Wu, Y.S. and Kool, J.B., 1994. A regulatory subsurface fate and transport assessment model for oily wastes. Proc. 1994 Conf. on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, pp. 383–397.

Schwille, F., 1981. Groundwater pollution in porous media by fluids immiscible with water. In: Quality of Groundwater. Elsevier, Amsterdam, pp. 451–463.

Sleep, B.E. and Sykes, J.F., 1993. Compositional simulation of groundwater contamination by organic compounds, 1. Model development and verification. Water Resour. Res., 29(6): 1697–1708.

Sudicky, E.A., 1988. The Laplace transform Galerkin technique: A time-continuous finite element theory and application to mass transport in groundwater. Water Resour. Res., 25: 1833–1847.

Thomas, G.W., 1982. Principles of Hydrocarbon Reservoir Simulation. International Human Resources Development Corp., Boston, MA.

U.S. EPA (Environmental Protection Agency), 1990. Background document for EPA's composite model for landfills (EPACML). U.S. Environ. Prot. Agency, Off. Solid Waste, Washington, DC.

U.S. EPA (Environmental Protection Agency), 1995. Background document for EPA's composite model for leachate migration with transformation products (EPACMTP). U.S. Environ. Prot. Agency, Off. Solid Waste, Washington, DC.

van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. Am. J., 44: 892–898.

Weaver, J.W., Charbeneau, R.J. and Lien, B.K., 1994. A screening model for non-aqueous phase liquid transport in the vadose zone using Green–Ampt and kinematic wave theory. Water Resour. Res., 30(1): 93–105.

Wu, Y.S., Huyakorn, P.S. and Park, N.S., 1994. A vertical equilibrium model for assessing nonaqueous phase liquid contamination and remediation of groundwater systems. Water Resour. Res., 30(4): 903–912.