



Project Summary

Modeling Multiphase Organic Chemical Transport in Soils and Ground Water

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Ground-water contamination due to surface spills or subsurface leakage of hydrocarbon fuels, organic solvents and other immiscible organic liquids is a widespread problem which poses a serious threat to ground-water resources. In order to model the movement of such materials in the subsurface, it is necessary, in general, to consider flow of water, nonaqueous phase liquid (NAPL) and air, and transport of individual chemical components, which may move by convection and dispersion in each phase. A mathematical model was developed for multiphase flow and multicomponent transport in porous media with water, NAPL and air or any subset of these phases. Numerical procedures for solving the system of coupled flow equations, based on various formulations of the governing equations, were compared. Accurate representation of three-phase permeability-saturation-capillary pressure (k - S - P) relations is crucial to model multiphase fluid movement and accurate models for interphase mass partitioning are critical to describe species transport. A detailed physically-based model for hysteresis in three-phase k - S - P relations was described. Simplified models, which consider effects of nonwetting fluid entrapment, were shown to provide a reasonable compromise between accuracy, on the one hand, and efficiency and robustness, on the other. Laboratory studies of light and dense NAPLs in a 1 x 1.5 meter sand tank, involving measurements of water and NAPL pressures and satura-

tions and component concentrations, are described. These studies were used to validate the mathematical model for multiphase flow and transport.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Spills and subsurface leaks of immiscible organic liquids are a frequent cause of ground-water contamination. This project was undertaken to improve our understanding of contaminant migration arising from such events and to develop improved quantitative tools for their description. Attention was focused on three fronts involving: (1) the development of efficient and robust numerical methods for simulating simultaneous multiphase flow and transport, (2) developing and numerically implementing theoretical and empirical constitutive models governing multiphase flow and transport processes, and (3) performing laboratory-scale experimental studies to validate the mathematical models developed in conjunction with the first two objectives.

Various formulations of the governing equations for multiphase flow are derived and implemented numerically and compared. The most efficient, accurate and robust formulation employed fluid pressures as the primary variables with saturation time derivatives treated as implicit



functions of pressures, rather than by chaining to obtain pressure time derivatives. A new algorithm is presented and discussed which enables substantial reductions in computational effort by automatic elimination and inclusion of elements in the global solution, based on the degree of transience in the local phase equations.

The theoretical foundation for modeling coupled multiphase flow and multispecies transport with equilibrium interphase mass transfer is described which leads to a system of flow equations for each bulk phase and phase-summed species transport equations for each species. A numerical formulation for solving the system of equations is presented based on partial decoupling of flow and transport equations. Results of several hypothetical numerical simulations are presented to verify the model and to demonstrate its applicability to specific problems. The assumption of local equilibrium-controlled mass transfer is subsequently relaxed; and a formulation is derived which enables the form of the phase-summed equilibrium model to be retained by introducing apparent partition coefficients that depend on the mass transfer rates and first-order mass transfer coefficients, as well as the true equilibrium partition coefficients. Numerical simulations are presented to verify the formulation and to demonstrate effects of nonequilibrium mass transfer. Results of laboratory experiments are presented that indicate interphase mass transfer can be described accurately at the laboratory scale by a first-order mass transfer relation and that mass transfer coefficients may be estimated from empirical relations previously reported in the literature.

Numerical and experimental studies were undertaken to develop and test constitutive models for permeability-saturation-capillary pressure (k - S - P) relations governing three-phase flow. A rigorous, physically-based hysteretic k - S - P relation is described, as well as various simplified models. Numerical comparisons of the models are presented, and results of static and dynamic laboratory column experiments are compared with the models to evaluate their accuracy. Two-dimensional laboratory experiments involving simulated spills of light and dense organic liquids were also conducted. The design of the experimental tanks and procedures for measuring fluid saturations and pressures and component concentrations are described. Experimental results are compared with numerical simulations to provide valida-

tion of the coupled flow and transport model.

Methodology and Results

Formulation of Multiphase Flow Model

The flow of water, air and a nonaqueous phase liquid (NAPL) in soils is described by a system of highly nonlinear and strongly coupled partial differential equations, which in general must be solved numerically. Various solution methods may be derived, based on different forms of the governing equations and using various numerical techniques. Five different equation formulation methods are investigated for solution of the oil (i.e., NAPL) and water flow equations with gas at constant pressure via an upstream-weighted finite element method with Newton-Raphson iteration for nonlinear terms. Method 1: Primary variables are oil and water pressure with saturation time derivatives treated as implicit functions of pressure. Method 2: Primary variables are oil and water pressure with saturation time derivatives chained to yield split oil and water pressure time derivatives. Method 3: Primary variables are oil-water and air-oil capillary pressures. Method 4: Primary variables are oil pressure and water saturation which is a "semi-diffusive" form of the governing equations obtained by expanding pressure derivative terms into saturation gradients and pressure-saturation derivative terms. Method 5: Semi-diffusive formulation in terms of water pressure and total liquid saturation.

The semi-diffusive forms (Methods 4 and 5) were found to be very efficient and accurate under conditions in which all three fluid phases are present (i.e., air, oil, water). However, instability was encountered in circumstances involving oil infiltration in the presence of a water table, especially when oil reached the water table. Method 3 exhibited moderate problems with mass balance and nonconvergence for some problems. A drawback to the capillary pressure formulation is that stipulation of boundary conditions is often difficult since individual phase pressures cannot be controlled independently on boundaries. The pressure-pressure formulations are most convenient in this regard. Method 2 exhibited moderate convergence difficulties and moderate to severe mass balance errors. Method 1 exhibited consistently superior mass balance and convergence behavior and good efficiency relative to the other methods.

Adaptive Solution Domain Method

In most practical multiphase flow problems, large changes in fluid pressures and saturations do not occur throughout the spatial domain at a given time step. Computational effort is thereby inefficiently spent solving equations in areas where little activity occurs, rather than concentrating effort in the more active zones. However, since the location of active zones changes with time (e.g., during oil infiltration or as phases reach a "field capacity" following redistribution), schemes designed to take advantage of these variations must be capable of automatically adapting to the current conditions. One method for doing so involves adaptive grid refinement in which the numerical mesh is automatically refined in active zones and expanded in inactive zones. Another general approach, which employs a fixed grid, varies the solution approach within the domain to gain efficiency. A new Adaptive Solution Domain (ASD) finite element method is described in which elements are categorized as either "active" or "inactive" at a given iteration. If the element is classified as active, then it is included in the global matrix assembly, otherwise it is excluded. The criteria for changing a node from inactive to active is based on the changes in water and oil pressure and saturation at connected nodes from the last converged time step to the current iteration. The criteria for switching an active element to an inactive status is based on differences in the variables at the connected nodes between the converged values at the previous and the current time step.

Example problems involving multiphase flow are presented to illustrate the ASD method and to compare its performance with a conventional full domain finite element approach. The first example involves infiltration and redistribution of oil in a one-dimensional soil column, and the second example involves a two-dimensional domain. Substantial reductions in computational effort are obtained, which can range from small improvements to orders of magnitude, depending on the initial and boundary conditions for the particular problem and the duration of the simulation. For analyses of short-term infiltration behavior from small area sources, the improvements are generally greatest. Major reductions can also be obtained for long-term simulations for cases with steady or near steady boundary conditions for the oil phase.

Constitutive Relations for Three-Phase Flow

In order to model three-phase flow, functional relationships between permeabilities, saturations and capillary pressures (k - S - P) must be known. A model for three-phase saturation-capillary pressure relations is derived assuming wettability in the order: water, NAPL, air. To model hysteresis in three-phase saturation-capillary pressure relations, the concept of apparent saturation may be used. Apparent water saturation is defined as the sum of water and of air and oil trapped in the water phase. Apparent liquid saturation is defined as the sum of water and oil saturations and of trapped air. Apparent water saturation is assumed to be a function of oil-water capillary pressure, and apparent liquid saturation is assumed to be a function of air-oil capillary pressure. Three-phase apparent saturation functions are related to two-phase air-water capillary pressure functions via a scaling procedure that assumes interface curvatures are related to the interfacial tension of the fluid pairs. Hysteresis in apparent saturation functions is described using an empirical method based on a variant of van Genuchten's parametric model. Trapped fluid saturations are computed as a function of saturation history using an empirical relation reported in the petroleum engineering literature. Relative permeability relations are derived from the saturation-pressure relations using the semi-theoretical pore structure model of Mualem.

Due to the computational complexity of the complete hysteretic three-phase relations, various simplifications were investigated. A simplified model was derived which considers hysteresis in saturation-capillary pressure relations and in relative permeability-saturation relations due to nonwetting fluid entrapment, but which disregards hysteresis in apparent saturation-capillary pressure relations. Numerical simulations involving infiltration and redistribution of hydrocarbons in unsaturated soils with fluctuating water tables were performed which indicated that the simplified model closely approximates the more complex model.

Measurements of fluid saturations and pressures as a function of saturation path history were taken in two different porous media to evaluate the hysteretic phenomena. An experimental apparatus consisting of alternating plexiglass sleeves containing treated and untreated porous ceramic rings was designed and constructed to perform two- and three-phase measurements. Model parameters were obtained by best-fitting the model to experimental

water and total liquid saturation path histories or by fitting to two-phase air-water data only and estimating scaling coefficients from interfacial tension data. Consistent model parameters were obtained using both calibration methods, and close agreement was observed between predicted and experimental water and total liquid saturation path histories using the model.

Column experiments were performed to verify the hysteretic k - S - P relation under dynamic flow conditions involving measurements of fluid pressures and saturations during transient flow events. Experiments were performed in two-phase air-water systems involving water infiltration, redistribution and fluctuating water table conditions, and for three-phase flow involving water and oil infiltration and redistribution with a fluctuating water table. A dual gamma attenuation device was used to measure fluid saturations, and hydrophobic and hydrophilic tensiometers were used to measure phase pressures. Using independent calibrations of the hysteretic k - S - P relation, numerical simulations of the experiments were performed and compared to the observed data. The detailed hysteretic model was found to describe the transient flow quite accurately. The simplified model exhibited deviations from the data near the infiltration boundary but provided good predictions at the distances further from the source.

Multiphase Transport with Equilibrium Interphase Mass Transfer

A model for coupled multiphase flow and multicomponent transport is derived. Flow and transport equations are computationally decoupled by time-lagging interphase mass transfer terms and composition-dependent phase densities in the flow equations. Phase-summed component transport equations are derived for transport by convection, diffusion and hydrodynamic dispersion in water, NAPL and air phases, assuming local equilibrium interphase mass transfer. Mass transfer rates are computed by back-substitution in the individual phase transport equations after solving the phase-summed equation at each time step. Components are assumed to exhibit linear equilibrium partitioning among air, water and NAPL phases and between water and solid phases. First-order decay is also considered for each component. Reactions between components are not considered.

A numerical model is developed for three-phase flow of air, water and NAPL (with options for variable or constant air

pressure) and for transport of up to five partitionable components in a vertical two-dimensional domain. The solution procedure involves: 1) solving flow equations using current mass transfer rates and phase densities, 2) solving phase-summed component transport equations serially for each component, 3) back-substitution in phase transport equations to compute interphase mass transfer rates, and 4) updating phase densities based on current phase composition. An upstream-weighted finite element method is used to solve the flow and transport equations. Several example problems are performed to verify the numerical model and to investigate the behavior of light and dense NAPLs.

Transport with Nonequilibrium Interphase Mass Transport

The phase-summed formulation of the transport equations is generalized to account for nonequilibrium phase partitioning by introducing the concept of apparent partition coefficients. Under transient field conditions, at a given location in time and space, actual phase concentration ratios may differ from the true equilibrium ratios due to nonequilibrium interphase mass transfer. Mass transfer rates are assumed to be described by first-order mass transfer relations driven by the difference between the actual and equilibrium concentrations in a given phase relative to an adjacent phase. Apparent partition coefficients, defined as ratios of actual (nonequilibrium) phase concentrations are shown to be a function of the equilibrium partition coefficient as well as the current concentrations and mass transfer rates. The phase-summed transport equation, which invokes apparent partition coefficients, thus becomes nonlinear due to the dependence of apparent partition coefficients on concentrations and mass transfer rates.

A numerical solution for multiphase flow and multicomponent transport was developed for the case of nonequilibrium interphase mass transfer. The solution procedure is identical to that followed for the equilibrium case, except that apparent partition coefficients are employed in the phase-summed transport equations, which are solved iteratively with mass transfer rates updated at each Picard iteration. A numerical verification problem was run to verify the nonequilibrium model's consistency with the equilibrium model, with which it became asymptotically identical as the mass transfer coefficients were increased.

A series of laboratory column experiments was conducted to investigate the nonequilibrium interface mass transfer of soluble constituents from a multicomponent NAPL at residual saturation during steady state water flow. Experiments were performed for different aqueous phase pore velocities, NAPL saturations, and NAPL compositions. Breakthrough curves obtained from the experiments were numerically inverted using a nonlinear optimization program to determine the oil-water mass transfer rate coefficients. An empirical correlation between mass transfer coefficient, pore water velocity, and mean grain size was evaluated. When the d_{10} grain diameter was used in the correlation, the mean estimated rate coefficient was very close to the mean of the measured values, with a standard deviation of about 30%.

Intermediate Scale Laboratory Investigations

Experiments were conducted to simulate flow and transport of a light nonaqueous phase liquid (LNAPL) and a dense nonaqueous phase liquid (DNAPL) in an unconfined aquifer with two-dimensional planar symmetry. A steel reinforced tank, 1.01 m tall x 1.5 m long x 0.085 m thick with amber transparent plastic sides resistant to the organic chemicals was used to perform these experiments. The flume was instrumented with a dual gamma attenuation device enabling readings from 66 locations through the narrow dimension of the cell. At 16 locations, water and oil pressures were measured using hydrophilic and hydrophobic ceramic cups, respectively, instrumented with pressure transducers and tied to a data acquisition system. Twenty-four Teflon tube inserts served as aqueous phase sampling ports in the lower sections of the cell. Aqueous phase samples were analyzed on a gas chromatograph using a packed column.

The LNAPL experiment involved five stages: (1) water drainage by lowering the water table from an initially saturated condition, (2) oil infiltration on a line source at the soil surface, (3) fluid redistribution with a water table gradient, (4) water infiltration along the entire upper surface, and (5) NAPL entrapment due to raising the water table. The experiment was simulated numerically. Soil properties were estimated from the water drainage stage of the experiment, and fluid and component properties were independently determined.

Good correspondence was evident between observed and simulated water saturations at the end of Stage 1 and for water and oil saturations at the end of

Stage 2. Predicted oil drainage from the unsaturated zone, vertical oil penetration at the water table and lateral spreading during Stages 3 and 4 were somewhat greater than observed, possibly reflecting the simplified treatment of hysteresis. Predicted aqueous concentrations of benzene and toluene at the end of Stage 3 also showed greater vertical penetration than observed due to the greater predicted oil phase penetration. At the end of Stage 5, observed and simulated oil saturations exhibited small upward displacements, reflecting the fact that oil had already distributed to close a residual state at which its permeability was very low so that movement was impeded. Aqueous sampling ports at higher elevations exhibited high concentrations which were corroborated by the model.

An experiment involving DNAPL, composed of a mixture of tetrachloroethylene, soltrol, toluene and iodoheptane, was performed in the same apparatus. The experiment involved three stages: (1) water drainage from an initially saturated state, (2) NAPL infiltration on a strip source at the soil surface, and (3) NAPL redistribution with a water table gradient. Water saturations above the water table were generally slightly underestimated by the model. The model predicted an oil phase plume largely confined to a deformed spheroidal region above the water table, although some oil is predicted to have sunk through the aquifer and spread over the tank bottom. Between the water table and the bottom pool, oil saturations after drainage were predicted to be less than 1%. Measurements could not be made near the tank bottom, so confirmation of oil spreading along the tank bottom could not be confirmed. However, nonzero oil saturations at measurement locations 15 cm from the tank bottom suggest oil penetration below the water table. The predicted and measured oil distributions in the unsaturated zone agree with one interesting exception. The observed data show a small amount of oil apparently spread laterally downgradient along the top of the capillary fringe at oil saturations in the vicinity of 1%. The simulation does not predict such lateral migration along the water table. Whether this is due to physical effects disregarded by the model (e.g., nonzero spreading pressures at oil-water interfaces) or to subtle heterogeneities due to packing anomalies is uncertain.

Substantial concentrations along the capillary fringe downgradient of the source confirm the lateral migration phenomena noted based on oil saturation measurements. Sampling locations under the wa-

ter table and immediately beneath the source indicate no dissolved phase contaminants, although gamma measurements indicate DNAPL at or below these depths. This suggests downward migration of DNAPL through the saturated zone occurs through isolated fingers rather than as a uniform front.

Conclusions and Recommendations

Solution of the nonlinear coupled differential equations governing multiphase flow and multicomponent transport is a computationally arduous task. Numerical results of this study have indicated that the accuracy and robustness of multiphase flow problems is quite sensitive to the method of formulating the governing equations. In particular, it has been shown that chaining of saturation time derivative terms can lead to mass balance errors and other difficulties that are greatly reduced by means of an alternative formulation with saturation time derivatives treated as implicit functions of pressure. Marked reductions in computational effort were achieved by an adaptive solution procedure that takes advantage of the fact that flow may be near steady state in large parts of the physical domain. Implementation of schemes to selectively eliminate individual phase equations should prove even more effective in reducing computational effort as well as improving solution robustness. Other facets affecting numerical solution efficiency, accuracy and robustness, such as matrix solution methodology, should be pursued particularly to facilitate practical extensions to three-dimensional problems.

Solution of coupled multiphase flow and transport problems introduces additional numerical difficulties. The semi-decoupled phase-summed approach employed in this study is an efficient formulation, although the efficiency undoubtedly comes at the cost of accuracy and robustness to some degree. The most critical aspect of the decoupled approach is the back-calculation of interphase mass transfer rates, since accumulated small errors can eventually destabilize the solution. Such problems are greatly diminished by suppressing mass transfer calculations during periods of highly transient oil flow. Since compositional changes are generally small over short time periods, mass balance errors incurred by this approach are very small. Future studies to investigate alternative solution formulations and to develop algorithms for automatic component mass balance controls on the solution should be pursued (e.g., "re-injection" of mass bal-

ance errors or iteration of transport and flow with corrected phase transfer terms).

Accurate representation of k -S-P relations is crucial in order to predict multiphase fluid movement in the subsurface, and accurate models for mass interphase partitioning are critical to describe species transport. A detailed model for hysteresis in k -S-P relations has been developed and has proven to accurately describe static laboratory S-P data and transient flow response. Simplified models which consider effects of nonwetting fluid entrapment provide a reasonable compromise between accuracy, on the one hand,

and efficiency and robustness, on the other. Direct measurements of three-phase relative permeabilities for non-monotonic saturation histories is a formidable task, but one that would be highly desirable to undertake in the future.

Existing empirical relations for estimating column scale mass transfer rate constants from basic physical properties of the system yielded surprising accuracy. However, under common field conditions, it may be shown that mass transfer limitations should be of minor importance. Field scale heterogeneity, however, may lead to preferred flow paths that produce ap-

parent nonequilibrium effects controlled by diffusive mass transfer between "fast" and "slow" zones.

Since explicit treatment of heterogeneity is generally impractical, future studies should address the feasibility of describing field-scale behavior using effective large-scale mass transfer relations. Likewise, effective k -S-P relations at the field scale that implicitly consider effects of heterogeneity may well differ from laboratory-scale relations. Substantial future efforts will be needed to more fully understand and model the behavior of large scale heterogeneous systems.

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J.S. Cho and L.G. Swaby are the EPA Project Officers (see below).

The complete report, entitled "Modeling Multiphase Organic Chemical Transport in Soils and Ground Water," (Order No. PB91- 231-514/AS; Cost: \$31.00, subject to change) will be available only from:

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