



Project Summary

Identification and Compilation of Unsaturated/Vadose Zone Models

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Many ground-water contamination problems are derived from sources at or near the soil surface. Consequently, the physical and (bio-)chemical behavior of contaminants in the shallow subsurface is of critical importance to the development of protection and remediation strategies. Mathematical models, representing our understanding of such behavior, provide tools useful in assessing the extent of pollution problems and evaluating means to prevent and remediate them.

In classifying models generally applied to soil- and ground-water pollution problems, a distinction can be made between the transport of the contaminants from the point of their introduction into the subsurface (*i.e.*, contaminant source) to the location of concern (*i.e.*, point of exposure), and the (bio-)chemical transformations that may occur in the subsurface. Models specifically simulating fluid flow are referred to as *flow models*. Models describing the movement of dissolved chemicals and their interaction with the soil or rock matrix in terms of concentrations and mass fluxes are often referred to as *contaminant transport models* or *solute transport models*. Furthermore, some vadose models focus on the resulting fate of contaminants, in particular, simulating the (bio-)chemical changes and transformations that occur in the subsurface. Increasingly, combinations of these three model types are employed to adequately simulate site-specific pollution problems and their remediation.

To identify existing models for simulation of flow and contaminant transport in the unsaturated subsurface, a database search and literature review were conducted. From the review a catalogue was developed consisting of approximately 100 flow and

transport models that may be used for the simulation of flow and transport processes in the unsaturated zone to determine the effectiveness of soil remediation schemes among other uses. The models considered range from simple mass balance calculations to sophisticated, multi-dimensional numerical simulators. There are six categories of models listed, including models for single-fluid flow, coupled and uncoupled flow and solute and/or heat transport, and solute transport for given pressure head distribution. Finally, models are listed that provide soil parameters from column experiments on soil samples.

In the full report each model is described in an uniform way by a set of annotations describing its purpose, major hydrological, mathematical and operational characteristics, input requirements, simulative capabilities, level of documentation, availability, and applicability. In some cases, the model description includes comments made by the model author and the investigator concerning development, testing, quality assurance and use, as well as references of studies using the model and references that are part of the documentation or considered pertinent to the model.

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

Many contamination problems find their cause at or near the soil surface. Consequently, the physical and (bio-)chemical behavior of



these contaminants in the shallow subsurface is of critical importance to the development of protection and remediation strategies. Mathematical models, representing our understanding of such behavior, provide tools useful in assessing the extent of pollution problems and evaluating means to prevent and remediate them.

Increasingly, detailed understanding and subsequent modeling of the near-surface zone are crucial in designing effective remediation approaches. At many sites, this near-surface zone is only partially saturated with water, requiring specially designed mathematical models. The full report focuses on models that might prove useful in simulating contaminant levels in such partially saturated systems.

Modeling contaminant behavior in the unsaturated zone is generally aimed to address such issues as [NRC, 1990]:

- Determining the arrival time of a contaminant at a certain depth; this requires a prediction of the travel time for the contaminant. Examples of depths of interest are the bottom of the root zone, the bottom of the treatment zone of a hazardous waste land treatment system facility, or the water table.
- Predicting the amount of the surface-applied (or spilled) contaminant that might arrive at the depth of interest within a certain time (or mass flux passing this depth); this requires assessment of the transport, (temporary) retention, transformation and degradation (fate) of the contaminant.
- Predicting the concentration distribution and/or the contaminant mass flux in the unsaturated zone (in both the aqueous and solid phases) at a particular time or their changes over time.

The latter purpose is of specific interest to this study as it relates to predicting the amount of hazardous constituents remaining in the soil following a soil remediation or due to natural processes.

Contaminating chemicals may leave the soil zone by leaching downwards to the water table, by volatilization and escape to the atmosphere, by (bio-)chemical transformation or degradation, and by plant uptake [Jury and Valentine, 1986]. Leaching constitutes mass flow of a chemical constituent and is the product of water flux and dissolved chemical concentration. Mass flow is dependent on the amount of applied water, the water application intensity, the saturated hydraulic conductivity of the soil, the chemical concentration, the adsorption site density, and, indirectly, temperature [Jury and Valentine, 1986]. Soils provide a strong capacity for adsorbing chemicals and thus a factor in determining the amount of chemical

available for mass flux. This is due to the presence of electrically charged clay minerals and organic matter and the large surface areas of minerals and humus. Volatilization of chemical to the atmosphere takes place in the vapor phase of the soil and is controlled by chemical, soil, and atmospheric conditions. Volatilization is dependent on Henry's constant, chemical concentration, adsorption site density, temperature, water content, wind speed, and water evaporation. Other potentially important transport processes include vapor and liquid diffusion. Transformation and degradation processes determine the "fate" of the chemical of concern in the soil. The most important processes include chemical hydrolysis, (bio-)chemical transformations, and oxidation-reduction.

In classifying models generally applied to soil- and ground-water pollution problems, a distinction can be made between the transport of the contaminants from the point of their introduction into the subsurface (*i.e.*, contaminant source) to the location of concern (*i.e.*, point of exposure), and the (bio-)chemical transformations that may occur in the subsurface. A major transport mechanism results from the hydrodynamic behavior of contaminant carrying fluids or fluid phases in porous or fractured media. Models specifically simulating fluid flow are referred to as *flow* models. Models describing the movement of dissolved chemicals and their interaction with the soil or rock matrix in terms of concentrations and mass fluxes are often referred to as *contaminant transport models* or *solute transport models*. Furthermore, some vadose models focus on the resulting fate of contaminants, in particular, simulating the (bio-)chemical changes and transformations that occur in the subsurface. The latter type of models may be based on a simple mass balance approach for the chemical of concern, lumping spatial variations in a single value for the parameters of interest (*e.g.*, SUMMERS model; U.S. EPA, 1989, pp. 28-29), or it may constitute a set of complex equations describing the (bio-)chemical reactions of interest including a reaction constant database. Increasingly, combinations of these three model types are employed to adequately simulate site-specific pollution problems and their remediation (*e.g.*, Yeh *et al.*, 1993).

The success of a given model depends on the accuracy and efficiency with which the physical and (bio-)chemical processes controlling the behavior of water and introduced nonaqueous liquids and the chemical and biological species they transport are simulated. The accuracy and efficiency of the simulation, in turn, depend heavily on the applicability of the assumptions and simplifications adopted

in the model, the availability and accuracy of process information and site characterization data, and subjective judgments made by the modeler and management.

As stated, flow models simulate the movement of one or more fluids in porous or fractured rock. One such fluid is water; the others, if present, can be air or vapors such as methane (in soil) or immiscible nonaqueous phase liquids (NAPLs), in both fully and partially saturated systems) such as certain solvents, which may have a density distinct from water (LNAPLs, DNAPLs). In the context of the full report, only the flow of water (under unsaturated conditions) is considered. Most flow models are based on a mathematical formulation that considers the hydraulic system parameters as independent field information and hydraulic head, fluid pressure or water content and fluid flux as dependent variables. They are used to calculate the steady-state spatial distribution, the changes in time in the spatial distribution, or the temporal distribution at a particular location of such variables as:

- hydraulic head, pressure head (or matric head), and suction head;
- saturation or moisture content;
- magnitude and direction of flow in terms of flow velocities or water mass fluxes;
- flowlines and travel times; and
- position of infiltration fronts.

Inverse flow models simulate the flow field to calculate the spatial distribution of unknown system parameters using field or experimental observations on the state variables such as hydraulic head, fluid pressure, water content and fluid flux. Due to the complexity of the relationships between pressure head, saturation and hydraulic conductivity, there are no truly inverse models available for flow in partially saturated porous media.

The dominant parameter affecting flow and contaminant transport in the unsaturated zone is hydraulic conductivity. Since hydraulic conductivity varies with water content, accurate measurements of this parameter are difficult to make and very time-consuming. Therefore, theoretical methods have been developed to calculate the hydraulic conductivity from more easily measured soil water retention data based on statistical pore-size distribution models [van Genuchten *et al.*, 1991]. The resulting functional relationship between pressure head and volumetric water content (*i.e.*, soil-water retention function) is presented in tabular form or as closed-form analytical solutions that contain functional parameters that are fitted to observed data. With the soil water retention function known, the unsaturated hydraulic conductivity can be calculated using the model of Mualem [1976].

Models have been developed to fit mathematical functions to water retention with known hydraulic conductivity or to water retention and hydraulic conductivity simultaneously [van Genuchten *et al.*, 1991]. These models may also be used to predict hydraulic conductivity for given soil retention data.

Solute transport models are used to predict movement or displacement, concentrations, and mass balance components of water-soluble constituents and to calculate concentrations or radiological doses of soluble radionuclides [van der Heijde *et al.*, 1988]. To do so, solute transport models incorporate various relevant physical and chemical processes. Flow is represented in the governing convective(-dispersive) equation by the flow velocity in the advective transport term. The velocities are also used for the calculation of the spreading by dispersion. If the velocity field is stationary, it may be either calculated once using an external flow program or read into the program as observed or interpreted data. If the velocity field (*i.e.*, spatial distribution of velocities in terms of direction and magnitude) is dependent on time and/or concentration, then calculation of velocities at each time step is required, either through an internal flow simulation module or an external flow model linked by means of input and output files. If a dissolved contaminant is present in relative high concentrations, changes in its distribution during the simulations might affect the flow behavior through changes in the fluid density. In that case, coupling of the flow and solute transport equations occurs through an equation of state, resulting in a system of equations that needs to be solved simultaneously (*i.e.*, iteratively-sequentially [Huyakorn and Pinder, 1983]).

Generally, modeling the transformation and fate of chemical constituents is conducted in one of three possible ways [van der Heijde *et al.*, 1988]: (1) incorporating simplified transformation or fate formulations in the equation describing solute transport; (2) formulating a mass-balance approach to (bio-)chemical transformation and fate; and (3) by coupling separate equations describing the (bio-)chemical processes with the advective-dispersive transport equation. Including transformation processes in solute transport models results in so-called nonconservative (*i.e.*, with respect to mass in solution) transport and fate models. The more complex of these nonconservative transport models may include advective and dispersive transport, molecular

diffusion, adsorption (equilibrium and kinetics based), ion-exchange, radioactive decay, and (bio-)chemical decay.

Mathematical Solutions in Unsaturated/Vadose Models

Most mathematical models for the simulation of flow and solute transport in the unsaturated zone are distributed-parameter models, either deterministic or stochastic [van der Heijde *et al.*, 1988]. Their mathematical framework consists of one or more partial differential equations describing the flow and/or transport and fate processes, as well as initial and boundary conditions and solution algorithms. Some of these models assume that the processes active in the system are stochastic in nature or, at least, that the process variables may be described by probability distributions. In such stochastic models, system responses are characterized by statistical distributions estimated by solving a deterministic governing equation.

The governing equations for flow and transport in the unsaturated zone are usually solved either analytically or numerically. Analytical models contain a closed-form or analytical solution of the field equations subject to specified initial and boundary conditions. To obtain these analytical solutions, simplifying assumptions have to be made regarding the nature of the soil-water-solute system, geometry, and external stresses, often limiting their application potential. Because of the complex nature of single- and multi-phase flow in the unsaturated zone and the resulting nonlinearity of the governing equation(s), very few analytical flow solutions have been published [Bear, 1979]. With respect to transport and fate the situation is somewhat different. Many one-, two-, and three-dimensional analytical solutions for the classical convection-dispersion equation exist, often requiring a uniform flow field. Some of these solutions, specifically one-dimensional solutions, can be used in the unsaturated zone assuming a uniform vertical soil water flux.

In semi-analytical models, complex analytical solutions are approximated, often using numerical techniques. In the case of unsaturated flow, semi-analytical solutions may be derived by using analytical expressions for the relationships between the dependent variables and the hydraulic parameters and involving numerical integration [Bear, 1979]. Models based on a closed-form solution for either the space or time domain, and which contain additional

numerical approximations for the other domain, are also considered semi-analytical models. Various quasi-analytical techniques and approximate (analytical) equations have been developed for simulating infiltration of water in soils [El-Kadi, 1983]. These techniques are also used for the one-dimensional transport of solutes [van Genuchten and Alves, 1982].

In numerical models, a discrete solution is obtained in both the space and time domains by using numerical approximations of the governing partial differential equation. As a result of these approximations, the conservation of mass and accuracy in the prediction variable are not always assured (because of truncation and round-off errors), and thus, these need to be verified for each application. Spatial and temporal resolution in applying such models is user-defined. If the governing equations are nonlinear, as is the case in simulating flow in the unsaturated zone, linearization often precedes the matrix solution [Remson *et al.*, 1971; Huyakorn and Pinder, 1983]. Usually, solution of nonlinear equations is achieved employing nonlinear matrix methods such as the Picard, Newton-Raphson, and Chord-Slope methods [Huyakorn and Pinder, 1983].

The numerical solution techniques used for approximating the spatial components of the governing flow equations in the unsaturated zone are primarily the finite-difference methods (FD), the integral finite-difference methods (IFDM), and the Galerkin finite-element method (FE). In most cases, time is approximated by finite-difference techniques resulting in an explicit, (weighted) implicit or fully implicit solution scheme. A finite-difference solution is obtained by approximating the derivatives of the governing equation. In the finite-element approach an integral equation is formulated first, followed by the numerical evaluation of the integrals over the discretized flow or transport domain. The formulation of the solution in each approach results in a set of algebraic equations that are then solved using direct or iterative matrix methods. Specific schemes may be required for the constitutive relationships, specifically in the presence of hysteresis.

There are many numerical considerations in selecting a model for simulation of a particular soil-water-solute system. Simulating flow in relatively wet soils (*e.g.*, nearly saturated conditions and ponding) requires expression of the Richard's equation in terms of hydraulic head, matric head or suction head, especially when parts of the modeled soil system become fully saturated.

However, application of this form of the Richard's equation causes significant convergence problems when simulating an infiltration front in extremely dry soil conditions; in the latter case, formulation of Richard's equation should be based on saturation or mixed pressure-saturation [Huyakorn and Pinder, 1983; Celia et al., 1990]. An advantage of the mixed form is that it allows the transition from unsaturated to saturated conditions while maintaining numerical mass conservation [Celia et al., 1990]. Also, significant mass balance problems might occur when site-specific conditions result in highly nonlinear model relationships [Celia et al., 1990].

Other issues that should be addressed in selecting a model for simulating flow in the unsaturated zone are the possible needs for double precision versus single precision variables, the time-stepping approach incorporated, the definition used for intercell conductance (e.g., harmonic mean versus geometric mean), and, if present, the way steady-state simulation is achieved (most models do not provide steady-state flow solutions). Some problems encountered with specific models (or modeling techniques) include code limitations on gridding flexibility, numerical problems in zones with high-contrast soil or rock properties, and inaccuracy and instability in areas where the flow field changes significantly in magnitude and direction. In some cases, avoiding inaccuracy and instability problems require very small spatial and temporal increments, making multi-dimensional simulations expensive or even unfeasible. Sometimes, an adaptive time-stepping scheme is implemented in the computer program to optimize time-step requirements.

Typical numerical techniques encountered in solving the convective-dispersive solute transport equation in the unsaturated zone are comparable to those employed in simulating solute transport in the saturated zone and include various finite-difference methods, the integral finite-difference method, various Galerkin finite-element formulations, and variants of the method of characteristics [Yeh et al., 1993]. As with flow, time is generally approximated by finite-difference techniques resulting in an explicit, (weighted) implicit or fully implicit solution scheme.

Typical problems found in applying traditional finite-difference and finite-element techniques to simulate contaminant transport in both the saturated and unsaturated zones include numerical dispersion and oscillations. Numerical dispersion is referred to when the actual physical dispersion mechanism of the contaminant transport cannot be distinguished from the front-smearing effects of the computational

scheme [Huyakorn and Pinder, 1983]. For the finite-difference method, this problem can be reduced by using the central difference approximation. Spatial concentration oscillations (and related overshoot and undershoot) may occur near a sharp concentration front in an advection-dominated transport system. Remedies for these problems are found to some extent in the reduction of grid increments or time-step size, or by using upstream weighting for spatial derivatives. The use of weighted differences (combined upstream and central differences) or the selection of other methods (e.g., the method of characteristics, and the Laplace transform Galerkin method) significantly reduces the occurrence of these numerical problems.

Unsaturated/Vadose Model Data Requirements

The number and type of parameters required for modeling flow and transport processes in soils depend on the type of

model chosen. These parameters can be categorized as control parameters (controlling the operation of the computer code), discretization data (grid and time stepping), and material parameters. The material parameters can be grouped in six sets [Jury and Valentine, 1986]: static soil properties, water transport and retention functions, basic chemical properties, time-dependent parameters, soil adsorption parameters, and tortuosity functions. Table 1 lists many of the relevant material model parameters.

Selection of Models

To identify existing models for simulation of flow and contaminant transport in the unsaturated subsurface, a database search and literature review have been conducted. The database search was focused on the MARS model annotation database of the IGWMC, which contains about 650 descriptions of soil- and ground-water simulation models. Information for the

Table 1. Selected Material Parameters for Flow and Transport Parameters in Soils (After Jury and Valentine, 1986)

<p><i>Static Soil Properties</i></p> <ul style="list-style-type: none"> porosity bulk density particle size specific surface area organic carbon content cation exchange capacity pH soil temperature 	<p><i>Time Dependent Parameters</i></p> <ul style="list-style-type: none"> water content water flux infiltration rate evaporation rate solute concentration solute flux solute velocity air entry pressure head volatilization flux
<p><i>Flow and Transport Variables and Properties</i></p> <ul style="list-style-type: none"> saturated hydraulic conductivity saturated water content matric head-water content function hydraulic conductivity function dispersion coefficient or dispersivity 	<p><i>Soil Adsorption Parameters</i></p> <ul style="list-style-type: none"> distribution coefficient isotherm parameters organic carbon partition coefficient
<p><i>Basic Chemical Properties</i></p> <ul style="list-style-type: none"> molecular weight vapor pressure water solubility Henry's constant vapor diffusion coefficient in air liquid diffusion coefficient in water octanol-water or oil-water partition coefficient half-life or decay rate of compound hydrolysis rate(s) 	<p><i>Tortuosity Functions</i></p> <ul style="list-style-type: none"> vapor diffusion tortuosity liquid diffusion tortuosity
<p><i>Contaminant Source Characteristics</i></p> <ul style="list-style-type: none"> solute concentration of source solute flux of source source decay rate 	

literature review has been obtained from various sources, including the IGWMC literature collection of more than 3000 titles and about 20 serials, and through interlibrary loan. Additional information was received from the U.S. EPA Center for Subsurface Modeling Support (CSMoS) located at RSKERL, Ada, Oklahoma. After reviewing the model's documentation and other pertinent literature, additional information was obtained from model authors and code custodians when necessary.

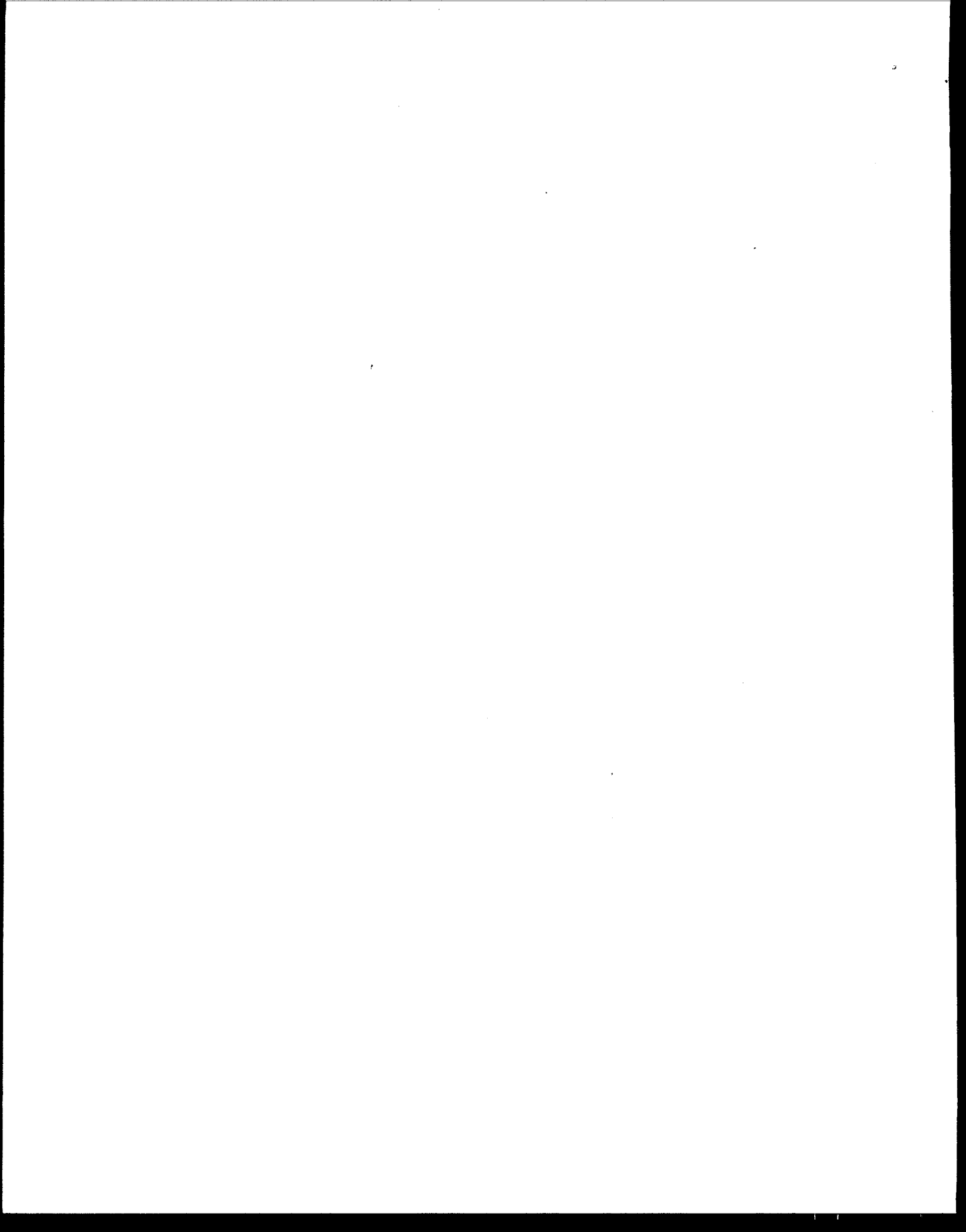
From the review a catalogue was developed consisting of approximately 100 flow and transport models that may be used for the simulation of flow and transport processes in the unsaturated zone to determine the effectiveness of soil remediation schemes among other uses. The models considered range from simple mass balance calculations to sophisticated, multi-dimensional numerical simulators. There are six categories of models listed, including models for single-fluid flow, coupled and uncoupled flow and solute and/or heat transport, and solute transport for given pressure head distribution. Finally, models are listed that provide soil parameters from column experiments on soil samples.

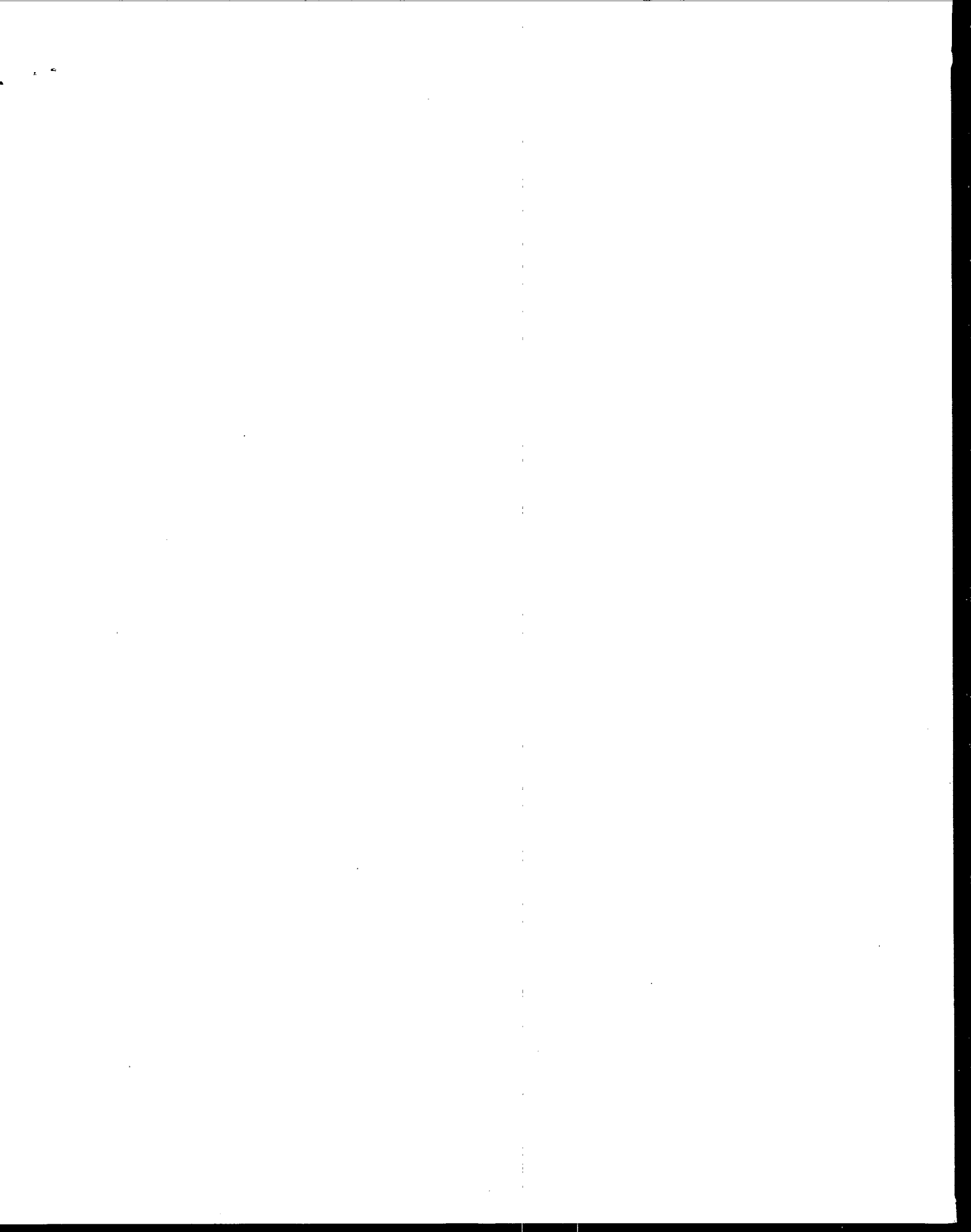
In the full report each model is described in a uniform way by a set of annotations defining the purpose and major hydrologic, mathematical and operational characteristics, input requirements, simulative capabilities, level of documentation, availability, and applicability. In some cases, the model description includes comments made by the model author and IGWMC staff concerning development, testing, quality assurance and use, as well as references of studies using the model and references that are part of the documentation or considered pertinent to the model.

It should be noted that the full report does not pretend to be complete in its listing of appropriate models. Moreover, many codes have been developed primarily for research purposes and are not readily available. Also, there are many simple models based on mass balance evaluation or analytical solution of highly simplified systems not presented in this catalogue. An effort has been made to select those 'simple' models that either are known for their use in a regulatory or enforcement mode or that are considered representative for a certain type of model. The report does not discuss multi-fluid flow and associated transport of contaminants since a considerable amount of research is currently focussed on understanding and mathematically describing the physics and chemistry of these systems.

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The complete report, entitled, "Identification and Compilation of Unsaturated/Vadose Zone Models," (Order No. PB 94-157773; Cost: \$27.00, subject to change) will be available only from

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