78: Models of Water Flow and Solute Transport in the Unsaturated Zone

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A large number of models for simulating water flow and solute transport in the unsaturated zone are now increasingly being used for a wide range of applications in both research and management. Modeling approaches range from relatively simple analytical and semianalytical solutions, to complex numerical codes. While analytical and semianalytical solutions are still popular for some applications, the ever-increasing power of personal computers and the development of more accurate and numerically stable solution techniques have motivated much wider use of numerical codes in recent decades. The wide use of numerical models is also significantly enhanced by their availability in both the public and commercial domains, and by the development of sophisticated graphics-based interfaces that can tremendously simplify their use.

In this paper I focus mainly on numerical models, give a brief history of their development, and discuss some of the more often used numerical techniques including relatively efficient matrix solvers that now are available for multidimensional models. Names and web addresses of some of the more popularly used numerical codes simulating vadose zone processes are also provided. Finally, some typical problems in which the numerical codes have been applied are identified.

INTRODUCTION

Many models of varying degree of complexity and dimensionality have been developed during the past several decades to quantify the basic physical and chemical processes affecting water flow and pollutant transport in the unsaturated zone. Computer models based on analytical and numerical solutions of the flow and solute transport equations are now increasingly being used for a wide range of applications in research and management of natural subsurface systems. Modeling approaches range from relatively simple analytical and semianalytical models to more complex numerical codes that permit consideration of a large number of simultaneous nonlinear processes. Whereas analytical and semianalytical solutions are still more popular for most relatively simple applications, the ever-increasing power of personal computers and the development of more accurate and numerically stable solution techniques have given rise to the much wider use of numerical models in recent decades. The wide use of numerical models has also been significantly enhanced by their availability in both public and commercial domains, and by the development of sophisticated graphics-based interfaces that tremendously simplify their use.

Analytical, semianalytical, and numerical models are usually based on the following three governing equations for water flow, solute transport, and heat movement, respectively:

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] - S \qquad (1)$$

$$\frac{\partial \theta Rc}{\partial t} = \frac{\partial}{\partial z}\left[\theta D\left(\frac{\partial c}{\partial z}\right) - qc\right] - \phi \qquad (2)$$

$$\frac{\partial C(\theta)T}{\partial t} = \frac{\partial}{\partial z}\left[\lambda(\theta)\left(\frac{\partial T}{\partial z}\right) - C_{\mathrm{w}}qT\right] \qquad (3)$$

Suitable simplifications (mostly for analytical approaches) or extensions thereof (e.g. for two- and three-dimensional systems) are also employed. In equation (1), often referred to as the Richards equation, z is the vertical coordinate positive upwards, t is time, h is the pressure head, θ is

Encyclopedia of Hydrological Sciences. Edited by M G Anderson.

the water content, S is a sink term representing root water uptake or some other sources or sinks, and $K(h)$ is the unsaturated hydraulic conductivity function, often given as the product of the relative hydraulic conductivity, K_r, and the saturated hydraulic conductivity, K_s. In equation (2), known as the *convection-dispersion equation* (CDE), c is the solution concentration, R is the retardation factor that accounts for adsorption, D is the dispersion coefficient accounting for both molecular diffusion and hydrodynamic dispersion, q is the volumetric fluid flux density, and ϕ is a sink/source term that accounts for various zero- and first-order or other reactions. In equation (3), T is temperature, λ is the apparent thermal conductivity, and C and C_w are the volumetric heat capacities of the soil and the liquid phase, respectively. Solutions of the Richards equation (1) require knowledge of the unsaturated soil hydraulic functions, that is, the soil water retention curve, $\theta(h)$, describing the relationship between the water content θ and the pressure head h, and the unsaturated hydraulic conductivity function, $K(h)$, defining the hydraulic conductivity K as a function of h or θ. While under certain conditions (i.e. for linear sorption, a concentration-independent sink term ϕ, and a steady flow field) equations (2) and (3) are linear equations, equation (1) is generally highly nonlinear because of the nonlinearity of the soil hydraulic properties. Consequently, many analytical solutions have been derived in the past for equations (2) and (3) and these analytical solutions are now widely used for analyzing solute and heat transport under steady-state conditions. Although a large number of analytical solutions of (1) exist, they can generally be applied only to drastically simplified problems. The majority of applications for water flow in the vadose zone requires a numerical solution of the Richards equation.

ANALYTICAL MODELS

Analytical methods represent a classical mathematical approach to solve differential equations, leading to an exact solution for a particular problem. Analytical solutions are usually obtained by applying various transformations (e.g. Laplace or Fourier transformations) to the governing equations, invoking a separation of variables, or the Green's function approach (e.g. Leij *et al.*, 2000). Analytical models usually result in an explicit equation that, for example, states that concentration (or the pressure head, water content, or temperature) is equal to a certain value at particular time and location. One can therefore evaluate a particular variable directly without time-stepping, typical of numerical methods. Many analytical solutions lead to relatively complicated formulations that include infinite series and/or integrals that need to be evaluated numerically, which suggests some ambiguity in the often-claimed advantage of exactness of analytical methods over numerical techniques. On the other hand, using analytical solutions one can often more easily evaluate interrelationships among parameters, and get better insight into how various processes control the basic flow and transport processes (e.g. using dimensionless variables and parameters). Analytical solutions are often also used to check the correctness and accuracy of numerical models, although numerical models can equally well be used to check the correctness of the complex analytical solutions.

Analytical solutions can usually be derived only for simplified transport systems involving linearized governing equations, homogeneous soils, simplified geometries of the transport domain, and constant or highly simplified initial and boundary conditions. Unfortunately, analytical solutions for more complex situations, such as for transient water flow or nonequilibrium solute transport with nonlinear reactions, are generally not available and/or cannot be derived, in which case numerical models must be employed.

Solute Transport

Numerous analytical solutions of equations (2) and (3), or their two- and three-dimensional equivalents, have been developed in the last 40 years and are now widely used for predictive purposes and/or analyzing laboratory and/or field observed concentration distributions. The majority of these solutions pertains to equations (2) and (3) assuming constant water content, θ, and flux, q, values (i.e. for steady-state water flow conditions). Since equation (2) and (3) have the same form, analytical solutions derived for solute transport can often also be used immediately for many heat transport problems, and *vice versa*.

Some of the more popular one- and multidimensional analytical transport models have been CXTFIT (Parker and van Genuchten, 1984), AT123D (Yeh, 1981), and 3DADE (Leij and Bradford, 1994). A large number of analytical models for one-, two-, and three-dimensional solute transport problems were recently incorporated into the comprehensive software package STANMOD (STudio of ANalytical MODels) (Šimůnek *et al.*, 1999b) (**http://www.ussl.ars.usda.gov/models/stanmod/stanmod.HTM**). This Windows-based computer software package includes not only programs for evaluating analytical solutions for equilibrium convective-dispersive solute transport (i.e. the CFITM of van Genuchten (1980) for one-dimensional transport and 3DADE for three-dimensional problems), but also additional programs that solve more complex problems. For example, it also incorporates the CFITIM (van Genuchten, 1981) and N3DADE (Leij and Toride, 1997) programs for nonequilibrium convective-dispersive transport (i.e. the two-region mobile-immobile model for physical nonequilibrium and the two-site sorption model for chemical nonequilibrium) for one- and multidimensional formulations, respectively. STANMOD also includes CXTFIT2 (Toride *et al.*, 1995), an updated

version of CXTFIT to solve both direct and inverse problems for three different one-dimensional transport models: (i) the conventional CDE (1); (ii) the chemical and physical nonequilibrium CDEs; and (iii) a stochastic stream tube model based upon the local scale equilibrium or nonequilibrium CDE. All three models consider linear adsorption, as well as the zero- and first-order decay/source terms. In addition, STANMOD includes the CHAIN code of van Genuchten (1985) for analyzing the convective-dispersive transport of up to four solutes involved in sequential first-order decay reactions. Examples are the migration of radionuclides, in which the chain members form first-order decay reactions, and the simultaneous movement of various interacting nitrogen or organic chemicals. The latest version of STANMOD also includes the screening model of Jury *et al.* (1983) for describing transport and volatilization of soil-applied volatile organic chemicals.

Water Flow

The highly nonlinear Richards equation can be solved analytically only for a very limited number of cases involving homogeneous soils, simplified initial and boundary conditions, and relatively simple constitutive relationships describing the unsaturated soil hydraulic properties. The Richards equation for this purpose needs to be first linearized. This can be accomplished using several mathematical transformations, with the most common transformation being the Kirchhoff integral transformation:

$$\Phi = \int_{-\infty}^{h} K(h)\,\mathrm{d}h \tag{4}$$

Linearization of the Richards equation often also involves using an exponential law relating hydraulic conductivity and the pressure head (Gardner, 1958):

$$K(h) = K_s \exp(\alpha h) \tag{5}$$

where α is an empirical coefficient.

Development of analytical and semianalytical solutions of the unsaturated flow equations has been geared mostly towards infiltration problems (Wooding, 1968; Philip, 1969, 1992). While some analytical solutions are widely used, for example, for evaluating tension disc experiments (Wooding, 1968), designing irrigation systems (Philip, 1992), or studying flow around buried objects (Warrick and Knight, 2002), many others appear to be only of academic interest.

NUMERICAL METHODS

Numerical methods are superior to analytical methods in terms of being able to solve practical problems. They allow users to design complicated geometries that reflect complex natural geologic and hydrologic conditions, control parameters in space and time, prescribe realistic initial and boundary conditions, and to implement nonlinear constitutive relationships. Numerical methods usually subdivide the time and spatial coordinates into smaller pieces, such as finite differences, finite elements, and/or finite volumes, and reformulate the continuous form of governing partial differential equations in terms of a system of algebraic equations. In order to obtain solutions at certain times, numerical methods generally require intermediate simulations (time-stepping) between the initial condition and the points in time for which the solution is needed. The following two sections review the history of development of various numerical techniques used in vadose zone flow and transport models. The review is based in part on an earlier review by van Genuchten and Šimůnek (1996). After reviewing various numerical techniques I will also discuss the need for efficient matrix solvers for 2D and 3D models, and provide a list of some of the most often used flow/transport models.

Numerical Solution of Richards Equation

A variety of numerical methods may be used to solve the variably saturated flow equation. The popularity of numerical methods stems from the fact that the Richards equation can be solved analytically only for a very limited number of cases. Even so, the highly nonlinear nature of the Richards equation also hampered the development of computationally efficient numerical methods that are stable under all conditions, particularly for infiltration in very dry soils. Stable numerical solutions still require relatively fine discretizations of both the time and space domains, often resulting in excessive CPU and simulation times, especially for two- and three-dimensional problems and/or problems involving highly transient boundary conditions.

Early applications of numerical methods for solving variably saturated flow problems generally used classical finite differences. Integrated finite difference, finite volumes, and especially, finite element methods (Neuman, 1973; Huyakorn *et al.*, 1986; Šimůnek *et al.*, 1999a) became increasingly popular in the seventies and thereafter. While finite difference methods today are used in a majority of one-dimensional models, finite volume methods and/or finite element methods coupled with mass lumping of the mass balance term are usually used in two- and three-dimensional models. Finite element methods used with unstructured triangular and tetrahedral elements allow for a more precise description of complex transport domains compared to finite differences.

The Richards equation can be formulated in three different ways. A mixed formulation arises when both the water content and the pressure head variables appear simultaneously in the governing equation, such as in equation (1). The h-based formulation is obtained when the time derivative of the water content ($\partial\theta/\partial t$) on the left side of

(1) is rewritten using the soil water capacity C as follows: $C\partial h/\partial t$, where C is defined as the slope of the retention curve, that is, $\mathrm{d}\theta/\mathrm{d}h$. The θ-based formulation is obtained when the product of the hydraulic conductivity $K(h)$ and the pressure head gradient ($\partial h/\partial z$) on the right side of (1) is replaced with the product of the water diffusivity $D_{\mathrm{w}}(\theta)$ and the water content gradient, $\partial\theta/\partial z$. The θ-formulation allows for very efficient numerical solutions, even for infiltration into initially dry soils. The use of this formulation is, however, straightforward only for homogeneous and unsaturated soils. This is because, the driving force for water movement is not the water content gradient, but the pressure head gradient; water in heterogeneous soils hence does not necessarily flow from locations with a higher water content to locations with a lower water content. Special provisions must be taken for such heterogeneous systems (Hills *et al.*, 1989), a likely reason why θ-formulations are rarely used in numerical models.

Celia *et al.* (1990) suggested that numerical solutions based on the standard h-based formulation of the Richards equation often yield poor results, characterized by relatively large mass balance errors and incorrect predictions of the pressure head distributions in the soil profile. They solved the mixed formulation of the Richards equation using a modified Picard iteration scheme that possesses mass-conserving properties for both finite element and finite difference spatial approximations. Milly (1985) earlier presented two mass-conservative schemes for computing nodal values of the water capacity in the h-based formulation to force global mass balance. Several highly efficient numerical schemes based on different types of pressure head transformations were presented recently by Hills *et al.* (1989), Ross (1990), and Kirkland *et al.* (1992). Hills *et al.* (1989) showed that the θ-based form of the Richards equation can yield fast and accurate solutions for infiltration into very dry heterogeneous soil profiles. However, the θ-based numerical scheme cannot be used for soils having saturated regions. Kirkland *et al.* (1992) expanded the work of Hills by combining the θ-based and h-based models to yield a transformation method applicable also to variably saturated systems. Their approach involved a new dependent variable, being a linear function of the pressure head and the water content in the saturated and unsaturated zones, respectively. Additional transformations of the Richards equation, with the common goal of decreasing its nonlinearity and increasing the efficiency of the numerical solution, were reviewed by Williams *et al.* (2000). Many of these transformations were, however, used mostly by the authors themselves and have not reached wide acceptance. Most popularly used vadose zone flow models presently utilize the mixed formulation of Celia *et al.* (1990); these models include SWAP (van Dam *et al.*, 1997) and HYDRUS (Šimůnek *et al.*, 1998, 1999a).

Time and space discretization of the Richards equation generally leads to a nonlinear system of algebraic equations. These equations are most often linearized and solved using the Newton–Raphson or Picard iteration methods. Picard iteration is widely used in unsaturated zone models because of its ease of implementation, and because this method preserves symmetry of the final system of equations. The Newton–Raphson iteration procedure is more complex and results in nonsymmetric matrices, but often achieves a faster rate of convergence and can be more robust than Picard iteration for certain types of problems (Paniconi and Putti, 1994).

Numerical Solution of the Transport Equation

A large number of methods are also available to numerically solve the convection-dispersion solute transport equation. These methods may be broadly classified into three groups: (i) Eulerian, (ii) Lagrangian, and (iii) mixed Lagrangian–Eulerian methods. In the Eulerian approach, the transport equation is discretized by means of a usual finite difference or finite element method using a fixed grid system. For the Lagrangian approach, the mesh moves along with the flow or remains fixed in a deforming coordinate system. A two-step procedure is followed for a mixed Lagrangian-Eulerian approach. First, convective transport is considered using a Lagrangian approach in which Lagrangian concentrations are estimated from particle trajectories. Subsequently, all other processes including sinks and sources are modeled with an Eulerian approach using any finite element or finite differences method, leading to the final concentrations.

Standard finite difference and Galerkin-type finite element methods belong to the first group of Eulerian methods. Finite differences and finite elements methods provided the early tools for solving solute transport problems and still are the most popular methods being used. Numerical experiments have shown that both methods give good results for transport in which dispersion is a relatively dominant process (e.g. as indicated by the grid Peclet number, $v\Delta x/D$, where v is pore-water velocity and Δx the grid size). However, both methods can lead to significant numerical oscillations and/or artificial dispersion for convection-dominated transport problems. Still, a relatively simple method may be used to prevent or limit numerical oscillations. By selecting an appropriate combination of relatively small space and time steps, it is possible to virtually eliminate all oscillations. Perrochet and Berod (1993) developed criteria for minimizing or eliminating numerical oscillations based on a "performance index". They concluded that all oscillations should be eliminated when the performance index, defined as the product of the local Peclet and Courant ($v\Delta t/\Delta x$) numbers, is less than 2. When small oscillations in the solution can be tolerated, the performance index can be easily increased to about 5 or 10 (Perrochet and Berod, 1993).

One alternative is the use of upwind finite difference methods. This method virtually eliminates numerical oscillations, even for purely convective transport. The disadvantage of this method is that it may create significant and often unacceptable numerical dispersion. Similarly, upstream weighting has been proposed for finite elements. The method consists of using different weighting functions for terms having spatial derivatives than for other terms in the transport equation. This approach places greater weight on the upstream nodes within a particular element.

While Lagrangian methods (or method of characteristics) virtually eliminate problems with numerical oscillations, they may introduce other problems, notably artificial dispersion and nonconservative solutions. Lagrangian methods are also relatively difficult to implement in two and three dimensions. Instabilities resulting from inappropriate spatial discretizations may occur during longer simulations because of deformation of the stream function. Furthermore, nonrealistic distortions of the results may occur when modeling the transport of solutes that are subjected to different sorption/exchange or precipitation reactions.

The Eulerian and Lagrangian approaches can also be combined to the mixed Eulerian–Lagrangian method. Because of the different mathematical nature of the diffusive (parabolic) and convective (hyperbolic) terms in the convection-dispersion equation, the transport equation is best decomposed into a mixed problem consisting of a purely convective problem, followed by a pure diffusion-only problem. Methods based on this approach are called *operator-splitting* or *splitting-up methods*. Convective transport is then solved with the Lagrangian approach, while all other terms of the transport equation are solved using Eulerian methods.

Still other solutions exist, such as the use of a so-called "random walk" process or a combination of analytical and numerical techniques. In a random walk approach, solute transport is modeled using a large number of particles. Displacement of each particle during each time step is given by a certain distance, this being the sum of two velocity contributions – a deterministic and stochastic contribution. Studies with this type of method indicate that it may be necessary to use many thousands of particles in order to obtain relatively precise results. An example of a combination of analytical and numerical techniques is given by Sudicky (1989) who modeled solute transport using Laplace transforms with respect to time, and Galerkin finite elements for the spatial domain. The use of Laplace transforms avoids the need for intermediate simulations (time-stepping) between the initial condition and the points in time for which solutions are needed, while also less stringent requirements are needed for the spatial discretization. This combination of analytical and numerical techniques, unfortunately, has however, one important limitation. Since Laplace transforms eliminate time as an independent variable in the governing transport equation, all coefficients such as water content, flow velocity, and retardation factors, must be independent of time. This means that combination methods can only solve solute transport problems during steady-state water flow, and hence are inappropriate for transient variably saturated flow situations typical of most field problems.

Many of the above methods for numerically solving transport equation were developed primarily for saturated conditions, for which coarse spatial discretizations and large flow velocities often produce large Peclet numbers, which may lead to significant numerical oscillations. Flow velocities in the vadose zone are usually much smaller. Also, the nonlinearity of the Richards equation generally requires numerical solutions on much finer spatial grids than in groundwater studies. Consequently, the Peclet numbers are significantly smaller for vadose zone applications than in groundwater flow studies, thereby allowing the adoption of more oscillation-prone methods. The majority of vadose zone models therefore can use relatively standard finite element or finite difference methods, which, if combined with upwind or upstream weighting or proper self-adjusting or other time step scheme, should eliminate most or all numerical oscillations.

Matrix Solvers

Discretization and subsequent linearization (as needed) of the governing partial differential equations for water flow and solute transport leads to a system of linear equations

$$[\mathbf{A}]\{\mathbf{x}\} = \{\mathbf{b}\} \tag{6}$$

in which $\{\boldsymbol{x}\}$ is an unknown solution vector, $\{\boldsymbol{b}\}$ is the known right-hand-side vector of the matrix equation, and $[\boldsymbol{A}]$ is a sparse banded matrix, which is symmetric for water flow if the modified Picard procedure is used, but asymmetric for water flow if the Newton–Raphson method is used. Matrix $[\boldsymbol{A}]$ is generally asymmetric for solute transport, unless convection is not considered in the formulation. Matrix $[\boldsymbol{A}]$ is tridiagonal for one-dimensional applications and thus can be solved very quickly and efficiently using simple Gaussian elimination. For higher-dimensional application, matrix $[\boldsymbol{A}]$ is a sparse matrix with a number of lines equal to the number of nodes in the spatial discretization scheme. The number of nodes is on the order of tens of thousands for a typical two-dimensional application, and on the order of millions for a three-dimensional application. Since this matrix needs to be inverted many times during a typical numerical run (at each time step for solute transport, and additionally also at each iteration for unsaturated water flow), the need for very efficient solvers cannot be underestimated.

Traditionally, the matrix equations have been solved using direct methods, such as Gaussian elimination or LU decomposition. These methods usually take advantage of the banded nature of the coefficient matrices and, in the case of water flow, of the symmetric properties of the matrix. Direct solution methods have several disadvantages as compared to iterative methods. For example, they require a fixed number of operations (depending upon the size of the matrix), which increases approximately by the square of the number of nodes. Iterative methods, on the other hand, require a variable number of repeated steps, with the number increasing at a much smaller rate (about 1.5) with the size of a problem (Mendoza *et al.*, 1991). A similar reduction also holds for the memory requirement since iterative methods do not require one to store nonzero matrix elements. Memory requirements, therefore, increase at a much smaller rate with the size of the problem when iterative solvers are used. This memory requirement is associated with the need to minimize the size of the band (i.e. the largest distance between two neighboring nodal numbers) of matrix [$\boldsymbol{A}$] for direct methods. While minimization of the matrix band is trivial for finite difference methods, it can be rather complex when unstructured triangular finite element meshes are used. Round-off errors also represent less of a problem for iterative methods as compared with direct methods. This is because round-off errors in iterative methods are self-correcting. Finally, for time-dependent problems, a reasonable approximation of the solution (i.e. the solution at the previous time step) exists for iterative methods, but not for direct methods. In general, direct methods are more appropriate for relatively small problems and for finite difference codes, while iterative methods are more suitable for larger problems and codes using unstructured finite element grids.

While many iterative methods have been used in the past for handling large sparse matrix equations, a variety of increasingly powerful preconditioned accelerated iterative methods, such as the preconditioned conjugate gradient method (PCG), are now becoming available also. Since the system of linear equations resulting from discretization of the solute transport equation is nonsymmetrical, it is necessary to either formulate the transport problem in such a way that it leads to a symmetric matrix, or to use an extension of PCG for nonsymmetrical matrices, such as ORTHOMIN (generalized conjugate residual method) (Mendoza *et al.*, 1991), GMRES (generalized minimal residual method), biconjugate gradients, TFQMR (transpose-free quasi-minimal residual algorithm), CGSTAB (conjugate gradient stabilized method), and conjugate gradient squared procedures. Both the preconditioned conjugate gradient and ORTHOMIN methods consist of two essential parts: initial preconditioning, and iterative solution with either conjugate gradient, CGSTAB, or ORTHOMIN acceleration (Mendoza *et al.*, 1991). Incomplete lower-upper (ILU) factorization can be used as preconditioning of matrix [$\boldsymbol{A}$], which is then factorized into lower and upper triangular matrices by partial Gaussian elimination. The preconditioned matrix is subsequently inverted repeatedly using updated estimates to provide a new approximation of the solution.

Available Model for Unsaturated Zone

Most of the early models developed for studying processes in the near-surface environment focused mainly on variably saturated water flow. They were used primarily in agricultural research for the purpose of optimizing moisture conditions to increase crop production. This focus has increasingly shifted to environmental research, with the primary concern now being the subsurface fate and transport of various agricultural and other contaminants, such as pesticides, nutrients, pathogens, pharmaceuticals, viruses, bacteria, colloids, toxic trace elements, and/or fumigants, and also the evaluation of water recharge through the vadose zone. While the earlier models solved the governing equations (1) through (3) for relatively simplified system-independent boundary conditions (i.e. specified pressure heads or fluxes, and free drainage), models developed recently can cope with much more complex system-dependent boundary conditions evaluating surface flow and energy balances and accounting for the simultaneous movement of water, vapor, and heat. Examples are DAISY (Hansen *et al.*, 1990), TOUGH2 (Pruess, 1991), SHAW (Flerchinger *et al.*, 1996), SWAP (van Dam *et al.*, 1997), HYDRUS-1D (Šimůnek *et al.*, 1998), UNSATH (Fayer, 2000), and COUP (Jansson and Karlberg, 2001). Several models now account also for the extremely nonlinear processes associated with the freezing and thawing cycle (e.g. DAISY, SHAW, and COUP).

Models have recently also become increasingly sophisticated in terms of the type and complexity of solute transport processes that can be simulated. Transport models are no longer being limited to solutes undergoing relatively simple chemical reactions such as linear sorption and first-order decay, but now consider also a variety of nonlinear sorption and exchange processes, physical and chemical nonequilibrium transport, volatilization, gas diffusion, colloid attachment/detachment, decay chain reactions, and many other processes (e.g. the HYDRUS-1D and -2D codes of Šimůnek *et al.*, 1998, 1999a). For example, the general formulation of the transport equations in the HYDRUS codes allows one to simulate not only nonadsorbing or linearly sorbing chemicals but also a variety of other contaminants, such as viruses (Schijven and Šimůnek, 2002), colloids (Bradford *et al.*, 2002), cadmium (Seuntjens *et al.*, 2001), and hormones (Casey *et al.*, 2003), or chemicals involved in the sequential biodegradation of chlorinated

aliphatic hydrocarbons (Schaerlaekens *et al.*, 1999; Casey and Šimůnek, 2001).

Options to simulate carbon and nitrogen cycles are also becoming a standard feature of many environmental models, such as DAISY, LEACHN (Hutson and Wagenet, 1992), RZWQM (Ahuja and Hebson, 1992), and COUP. These models typically distribute organic matter, carbon, and organic and mineral nitrogen over multiple computational pools, while allowing organic matter to be decomposed by multiple microbial biomass populations. They can account for most of the major reaction pathways, such as mineralization-immobilization of crop residues, manure and other organic wastes, mineralization of the soil humus fractions, interpool transfer of carbon and nitrogen, nitrification (ammonium to nitrate-N), denitrification (leading to the production of N_2 and N_2O), volatilization loss of ammonia (NH_3), production and consumption of methane (CH_4) and carbon dioxide (CO_2), changes in the carbon nitrogen ratio of organic matter, and microbial biomass growth and death (Ahuja and Hebson, 1992).

Efforts are also on to couple physical flow and transport models with geochemical models to simulate even more complex reactions, such as surface complexation, precipitation/dissolution, cation exchange, and/or biological reactions (e.g. Ahuja and Hebson, 1992; Šimůnek and Suarez, 1994; Šimůnek and Valocchi, 2002; Jacques *et al.*, 2002). Models considering these chemical reactions, including the ability to simulate the transport of multiple chemical species and carbon dioxide, are required for studying water management practices and irrigation techniques under arid and semiarid conditions, evaluation of water suitability for irrigation, and reclamation of sodic soils (Šimůnek and Suarez, 1997).

Another active area of research involves attempts to extend existing models that simulate uniform flow to situations where nonequilibrium and/or preferential flow occurs. Examples of this are the MACRO (Jarvis, 1994) and HYDRUS-1D (Šimůnek *et al.*, 2003) models. Possible approaches for simulating preferential flow differ in terms of their underlying assumptions and complexity. They range from relatively simplistic models to more complex, physically based, dual-porosity, dual-permeability, and multiregion-type models. A relatively simple dual-porosity flow model results when the Richards equation is combined with composite (double-hump type) equations for the hydraulic properties to account for both soil textural (matrix) and soil structural (fractures, macropores, peds) effects on flow. A more complex dual-porosity, mobile-immobile water flow model results when the Richards or kinematic wave equations are used for flow in the fractures, and immobile water is assumed to exist in the matrix. Even more complex are various dual-permeability models such as the formulations of Gerke and van Genuchten (1993) and Pruess (1991), or the kinematic wave approach as used in the MACRO model of Jarvis (1994). These formulations all assume that water is mobile in both the matrix and fracture domains, while invoking terms that account for the exchange of water and solutes between the matrix and the fractures.

A large number of models are now available for simulating processes in the vadose zone. Some of these models are in the public domain, such as MACRO, SWAP, UNSATH (Fayer, 2000), VS2DI (Healy, 1990), and HYDRUS-1D (Šimůnek *et al.*, 1998), while others are in the commercial domain, such as HYDRUS-2D (Šimůnek *et al.*, 1999a). These models vary widely in terms of their complexity, sophistication, and ease of use. Although some models are still being run under the DOS operating system, with associated difficulties of preparing input files and interpreting tabulated outputs, many others, especially those in the commercial domain, are supported by sophisticated graphics-based interfaces that tremendously simplify their use (Šimůnek *et al.*, 1998, 1999a).

Table 1 gives a summary of some of the more widely used numerical models for simulating variably saturated water flow and solute transport in soils. This table also provides Internet addresses and references where additional information about each model can be found. With the exception of HYDRUS-2D, TOUGH2, and VS2DTI, all models given in Table 1 are one-dimensional models, perhaps reflecting the fact that the majority of applications for unsaturated zone models is still only one dimensional.

CONCLUSIONS

Much of the research in the field of soil science has focused in recent decades upon understanding the fundamentals of variably saturated water flow and pollutant fate and transport processes. As society continues its rapid technological development, the types of pollution problems and chemicals posing significant environmental threats, have become increasingly complex. Problems such as the transport of pesticides, colloids, bacteria, viruses, pharmaceuticals, reproductive hormones, nutrients, and toxic trace elements, carbon sequestration, and bioremediation of organic contaminants, all require a thorough understanding and coupling of multiple hydrogeological, geochemical, and microbiological processes. It is the continually increasing speed and power of modern computers that will enable such models to become convenient tools for analysis of complex geochemical systems. Although more and more complex models are being constantly developed, currently available models are still relatively specialized and no single model is presently available that can describe the multiple problems and chemicals mentioned above. Development of numerical models capable of describing unstable and/or preferential flow, as well as models coupled with sophisticated geochemical models capable of describing both instantaneous

Table 1 Some of the widely used numerical models for simulating variably saturated water flow and solute transport in soils

Model name	Internet address, reference, interesting/special features
COUP	**http://www.lwr.kth.se/Vara**%20 Datorprogram/CoupModel/ (Jansson and Karlberg, 2001) Carbon/nitrogen cycle, thawing/freezing cycle, coupled water, vapor, and heat transport, crop growth
DAISY	**http://www.dina.dk/~daisy/** (Hansen *et al.*, 1990) Carbon/nitrogen cycle, crop growth, management practices, pesticide processes
HYDRUS-1D	**http://www.hydrus2d.com** (Šimůnek *et al.*, 1998) Multiple soil hydraulic functions, neural network-based pedotransfer functions, nonlinear nonequilibrium solute transport, mobile-immobile and two-site sorption concepts, chain reactions, volatilization, inverse option, intuitive sophisticated graphical interface
HYDRUS-2D	**http://www.hydrus2d.com** (Šimůnek *et al.*, 1999a) Two-dimensional, multiple soil hydraulic functions, neural network-based pedotransfer functions, nonlinear nonequilibrium solute transport, mobile-immobile and two-site sorption concepts, chain reactions, inverse option, unstructured triangular finite element meshes, intuitive sophisticated graphical interface
MACRO	**http://www.mv.slu.se/BGF/Macrohtm/macro.htm** (Jarvis, 1994) Preferential flow using kinematic wave equation, snow accumulation, pesticide transport
RZWQM	**http://gpsr.ars.usda.gov/products/rzwqm.htm** (Ahuja and Hebson, 1992) Complex modular program, crop growth, chemical equilibrium module, management practices, pesticide processes
SHAW	**http://www.nwrc.ars.usda.gov/models/shaw** (Flerchinger *et al.*, 1996) Thawing/freezing cycle, coupled water, vapor, and heat transport, multispecies plant canopy
SWAP	**http://www.swap.alterra.nl/** (van Dam *et al.*, 1997) A three-level drainage system at regional scale, crop growth
SWIM	**http://www.clw.csiro.au/products/swim** (Verburg *et al.*, 1996) Bypass flow, flexible description of hydraulic properties, hyperbolic sine transformation of the pressure head
TOUGH2	**http://www-esd.lbl.gov/TOUGH2/** (Pruess, 1991) Multidimensional multiphase fluid and heat flow, dual permeability
UNSATH	**http://hydrology.pnl.gov/resources/unsath/unsath_download.asp** (Fayer, 2000) Coupled water, vapor, and heat transport, no solute transport
VS2DTI	**http://water.usgs.gov/software/vs2di.html** (Healy, 1990) Two-dimensional, finite differences

and kinetic chemical and biological reactions will undoubtedly remain a focus of research in the near future.

The accuracy of the obtained predictions depend to a large extent upon the accuracy of available model input parameters and upon proper conceptualization of soil heterogeneity and other system complexities, such as the possible presence of nonequilibrium flow and transport, including preferential flow. Processes are often described and their parameters measured on a much smaller scale than those for which the model predictions are being sought. Consequently, many model parameters often need to be calibrated so that they reflect the bulk behavior of the heterogeneous system, in which case they can be used for larger scale predictions. New measuring techniques that provide model parameters on the scale at which predictions are made are badly needed for successful applications of unsaturated flow and transport models in a predictive mode at the larger scale.

One may expect that unsaturated zone flow and transport models will be used increasingly for integrating fundamental knowledge about the vadose zone to yield tools for developing cost-effective, yet technically sound strategies for resource management and pollution remediation and prevention. Unsaturated zone transport models are indispensable tools for analyzing complex environmental pollution problems, and for developing practical management strategies. Models can help guide field observations by identifying which parameters and processes control system behavior. Following Steefel and Van Cappellen (1998) and Šimůnek and Valocchi (2002), several specific key ways in which unsaturated flow and transport models can be used are identified below:

1. Physical, chemical, and biological processes are often studied in isolation either in the laboratory or in the field under controlled conditions. Mathematical models can be used to investigate the impacts of multiple coupled biogeochemical reactions and other interactions in the presence of complex flow fields and spatial heterogeneity. These models also enable extrapolation to environmentally relevant temporal and spatial scales.
2. Numerical transport models provide a useful tool for interpreting experimental results. Models can help understand qualitative and quantitative trends and relationships present in the data. Properly applied modeling to interpret results of field experiments can lead to more effective quantitative understanding of underlying biogeochemical processes.
3. One of the most powerful applications of numerical flow and transport models is conducting sensitivity

analyses. Such analyses permit a systematic evaluation of the impact of model parameters (physical, chemical, and/or biological), initial conditions, and boundary conditions upon the model output. The results of a sensitivity analysis provide insight into the relative importance of individual processes and reactions within a complex biogeochemical system. Results can help one identify the most important parameters and processes, and thereby provide guidance in allocation of resources for laboratory and field investigations.

4. Numerical flow and transport models are tools for integrating all of our knowledge obtained from simulations, sensitivity analyses, and laboratory and field experimentation. This integration will often lead to more coherent and rigorous conceptual models for the underlying coupled flow, transport, and reactions processes.

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