ANALYTICAL AND NUMERICAL MODELING OF PHYSICAL AND CHEMICAL PROCESSES IN THE VADOSE ZONE

SHORT TITLE: MODELS FOR SOIL POLLUTION RISK ASSESSMENT

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Abstract. A large number of models for simulating water flow and solute transport in the unsaturated zone are now used for a wide range of applications in research, management, and risk assessment of subsurface systems. 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 contaminant transport in the unsaturated zone. Modeling approaches range from relatively simple analytical and semi-analytical solutions, to complex numerical codes. In this paper a brief overview of more widely used analytical and numerical models is given. Some typical problems in which the numerical codes have been applied are also identified.

Keywords: Vadose zone; analytical models; numerical models; STANMOD; HYDRUS

1. Introduction

A large number of models for simulating water flow and solute transport in the unsaturated zone are now used for a wide range of applications in research, management, and risk assessment of subsurface systems. 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 contaminant transport in the unsaturated zone. Modeling approaches range from relatively simple analytical and semi-analytical solutions, to complex numerical codes. While analytical and semi-analytical solutions are still popular for some applications, the ever-increasing

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power of personal computers and the development of more accurate and numerically stable solution techniques have motivated the 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.

2. Analytical Models

While under certain conditions (i. e., for linear sorption, a concentration independent sink term, and a steady-state flow field) solute and heat transport equations are linear equations, water flow equations are generally a highly nonlinear because of the nonlinearity of the soil hydraulic properties. Consequently, many **analytical solutions** have been derived in the past for solute transport equations and these analytical solutions are now widely used for analyzing solute transport under steady-state conditions. Many of these analytical solutions were compiled in STANMOD (STudio of ANalytical MODels, www.hydrus2d.com) (Šimůnek et al., 1999b), a public domain Windows based computer software package for evaluating solute transport in porous media using analytical solutions of the convection-dispersion solute transport equation. It includes at present the following one-dimensional models: CFITM (van Genuchten, 1980), CFITIM (van Genuchten, 1981), CHAIN (van Genuchten, 1985), CXTFIT (Toride et al., 1995), and SCREEN (Jury et al., 1983), and two- and three-dimensional models: 3DADE (Leij and Bradford, 1994) and N3DADE (Leij and Toride, 1997).

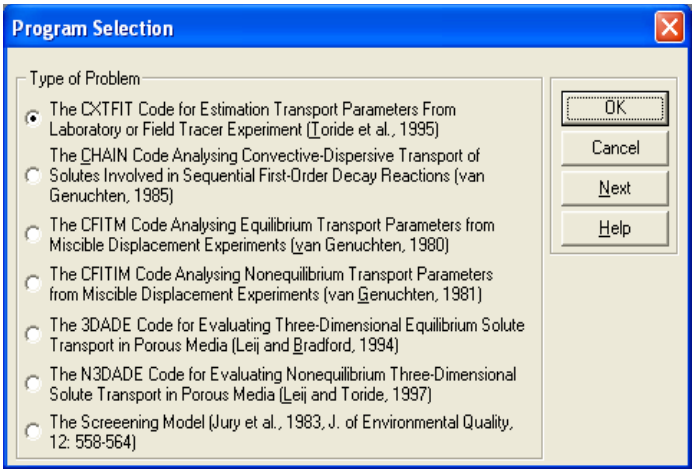

Figure 1. The "Program Selection" dialog window in the STANMOD software package.

2.1. ONE-DIMENSIONAL ANALYTICAL MODELS

An updated version of the **CFITM** code of van Genuchten (1980) that is included into STANMOD is intended for analyzing observed column effluent data using analytical solutions of the one-dimensional **equilibrium** convective-dispersive transport equations. The code considers analytical solutions for both semi-finite and finite columns. The model provides an easy to use, efficient and accurate means of determining various transport parameters by optimizing observed column effluent data.

An updated version of the **CFITIM** code of van Genuchten (1981) can be used for analyzing observed column effluent data using analytical solutions of the one-dimensional equilibrium and **nonequilibrium** convective-dispersive transport equations. The code includes analytical solutions for semi-finite columns. The nonequilibrium solutions consider the two-region dual-porosity (bi-continuum) flow model for physical nonequilibrium and the one-site or two-site sorption models for chemical nonequilibrium. CFITM and CFITIM represent simple alternatives to the much more comprehensive, but also more complex, CXTFIT model.

A modified and updated **CHAIN** code of van Genuchten (1985) analyzes the convective-dispersive transport of 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 species.

A modified and updated version of the **CXTFIT** code of Toride et al. (1995) that is included in STANMOD is intended for estimating solute transport parameters using a nonlinear least-squares parameter optimization method. This code may be used to solve the inverse problem by fitting a variety of mathematical solutions of theoretical transport models, based upon the one-dimensional convection-dispersion (or advection-dispersion) equation (CDE), to experimental results. The program may also be used to solve the direct or forward problem to determine concentrations as a function of time and/or position. Three different one-dimensional transport models are considered: **(i) the conventional CDE**; **(ii) the chemical and physical nonequilibrium CDEs**; and **(iii) a stochastic stream tube model** based upon the local-scale equilibrium or nonequilibrium CDE.

Finally, the screening model of Jury et al. (1983), **SCREEN**, for behavior assessment of trace organics in soils is included. This model is intended to classify and screen organic chemicals for their relative susceptibility to different loss pathways (volatilization, leaching, and degradation in the soil and air). The model considers the following processes: gaseous diffusion, liquid dispersion, liquid convection, volatilization, sorption, and first-order degradation processes.

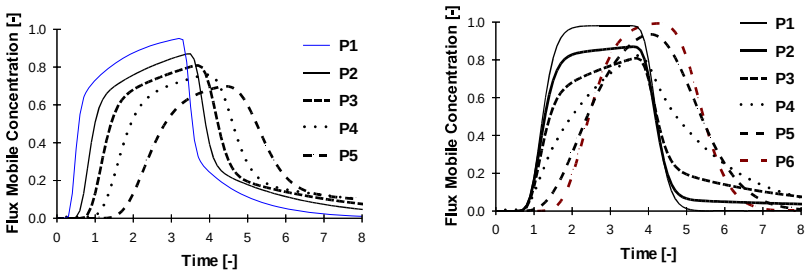

Figure 2. Examples of breakthrough curves at the end of the soil column (40 cm long) demonstrating the effect of the retardation factor (R=1, 1.75, 2.5, 3.5, and 5) and the mass transfer coefficient (ω=0.02, 0.2, 0.5, 1.5, 7.5, and 1000) in the two region model. Calculations were carried out using CXTFIT2 in STANMOD.

2.2. TWO- AND THREE-DIMENSIONAL ANALYTICAL MODELS

STANMOD also includes the **3DADE** code of Leij and Bradford (1994) for evaluating analytical solutions for **three-dimensional equilibrium** solute transport in the subsurface. The analytical solutions pertain to selected cases of three-dimensional solute transport during steady unidirectional water flow in porous media having uniform flow and transport properties. The transport equation contains terms accounting for solute movement by convection and dispersion, as well as for solute retardation, first-order decay, and zero-order production. The 3DADE code can be used to solve the direct problem, i.e., the concentration is calculated as a function of time and space for specified model parameters, and the indirect (inverse) problem in which the program estimates selected parameters by fitting one of the analytical solutions to specified experimental data.

Finally, STANMOD incorporates the **N3DADE** code of Leij and Toride (1997) for evaluating analytical solutions for a **three-dimensional nonequilibrium** solute transport in porous media. The analytical solutions pertain to three-dimensional solute transport during steady unidirectional water flow in porous media in systems of semi-infinite length in the longitudinal direction, and of infinite length in the transverse direction. The solutions can be applied also to one- and two-dimensional problems. The flow and transport properties of the medium are again assumed to be macroscopically uniform. Nonequilibrium solute transfer can occur between two domains in either the liquid or the absorbed phase. The transport equation contains terms accounting for solute movement by advection and dispersion, as well as for solute retardation, first-order decay, and zero-order production.

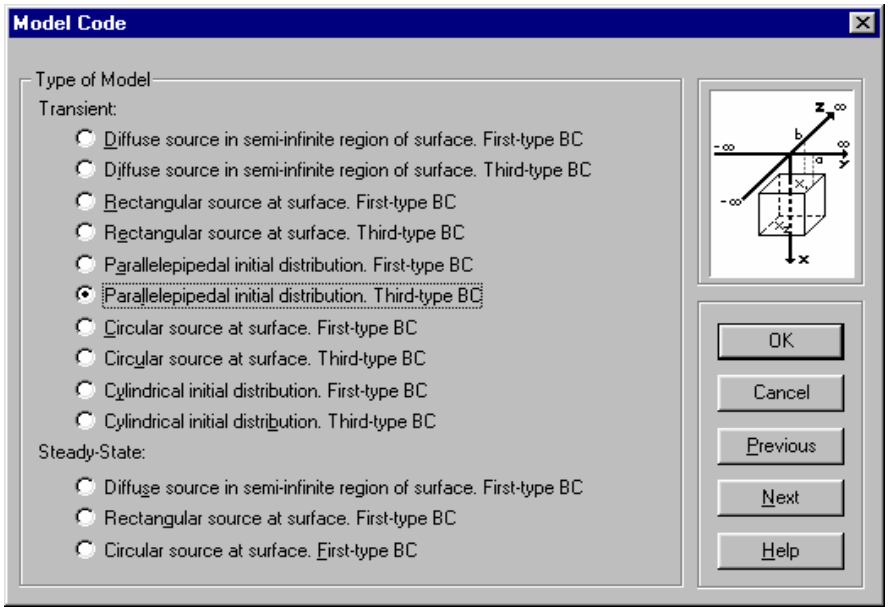

Figure 3. The "Model Code" dialog window for the 3DADE model in the STANMOD software package.

3. Numerical Models

Although a large number of analytical solutions also exist for water flow equation, they can generally be applied only to drastically simplified problems. The majority of applications for water flow in the vadose zone require a numerical solution of the Richards equation.

Numerical methods are in general superior to analytical methods in terms of being able to solve much more 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 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.

There is a large number of **numerical models** that are available for evaluating

variably-saturated water flow and solute transport in the subsurface. Some of these models are in the public domain, such as MACRO (Jarvis, 1994), SWAP (van Dam et al., 1997), UNSATH (Fayer, 2000), VS2DI (Healy, 1990), and HYDRUS-1D (Šimůnek et al., 1998; www.hydrus2d.com), while others are in the commercial domain, such as HYDRUS-2D (Šimůnek et al., 1999a) and MODFLOW-SURFACT (HydroGeoLogic, 1996). 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 (e.g., Šimůnek et al., 1998; 1999a).

Models have recently 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. For example, the general formulation of the transport equations in the HYDRUS codes allows one to simulate not only non-adsorbing or linearly sorbing chemicals, but also a variety of other contaminants, such a viruses (Schijven and Šimůnek, 2001), colloids (Bradford et al., 2002), cadmium (Seuntjens et al., 2001), and hormones (Casey et al., 2003, 2004), or chemicals involved in the sequential biodegradation of chlorinated aliphatic hydrocarbons (Schaerlaekens et al., 1999; Casey and Šimůnek, 2001).

A substantial amount of research has been recently devoted to developing methods for describing **preferential/nonequilibrium flow** in structured media (macroporous soils). A variety of dual-porosity, dual-permeability, multi-porosity, and/or multi-permeability models (e.g., Gerke and van Genuchten, 1993; Jarvis, 1994; Šimůnek et al., 2003) has been developed to describe preferential flow. Dual-porosity and dual-permeability models both assume that the porous medium consists of two interacting regions, one associated with the inter-aggregate, macropore, or fracture system, and the other one comprising micropores (or intra-aggregate pores) inside soil aggregates or the rock matrix. While dual-porosity models assume that water in the matrix is stagnant, dual-permeability models allow for water flow in the matrix as well. For a recent comprehensive review of various modeling approaches used to simulate preferential flow see Šimůnek et al. (2003).

Several of the dual-porosity and dual-permeability features were recently included in the HYDRUS software packages (Šimůnek et al., 2003, 2005). Examples of their application to a range of laboratory and field data involving

transient flow and solute transport are given by Šimůnek et al. (2001), Zhang et al. (2004), Köhne et al. (2004, 2005), Kodešová et al. (2005), Haws et al. (2005), and Pot et al. (2005), among others.

Numerical models are, however, still lacking that would fully describe colloid transport and **colloid-facilitated solute transport** in a complex subsurface environment. This complex process requires knowledge of variably saturated water flow, colloid transport, dissolved contaminant transport, and colloid-facilitated contaminant transport. Colloids are inorganic and/or organic constituents that are generally chemically reactive. Inorganic colloids are primarily fine-sized mineral soil constituents, while organic colloids are organic matter-based. Transport equations must be formulated for both colloids and contaminants, in all its forms. Equations therefore must be written for the total contaminant, for contaminant sorbed kinetically or instantaneously to the solid phase, and for contaminant sorbed to mobile colloids, to colloids attached to the soil solid phase, and to colloids accumulating at the air-water interface. Some of these processes were recently incorporated in the HYDRUS software package (van Genuchten and Šimůnek, 2004). A complete description of the colloid-facilitated transport can be, for example, found in Hornberger et al. (1992) and van Genuchten and Šimůnek (2004).

4. Biogeochemical Models

Significant efforts have recently been carried out 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. Geochemical models can be divided into two major groups: those with specific chemistry and general models (Šimůnek and Valocchi, 2002). Models with specific chemistry are limited in the number of species they can handle and their application is quite restricted to problems having a prescribed chemical system. They are, however, much easier to use and can be more computationally efficient than general models. Typical examples of models with specified chemistry are models simulating the transport of major ions, such as LEACHM (Wagenet and Hutson, 1987) and UNSATCHEM (Šimůnek and Suarez, 1994; Šimůnek et al., 1996), and various reclamation models (Šimůnek and Valocchi, 2002). These models typically consider transport of major ions and their mutual reactions such as complexation, cation exchange, and precipitation/dissolution. Also models simulating carbon and nitrogen cycles are becoming a standard feature of many environmental models, such as COUP (Jansson and Karlberg, 2001) or HYDRUS-2D coupled with CW2D (Langergraber and Šimůnek, 2005). 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 inter-pool transfer of carbon and nitrogen, nitrification (ammonium to nitrate-N), denitrification (leading to the production of N_2 and N_2O), volatilization losses of ammonia (NH_3), and microbial biomass growth and death. HYDRUS-2D coupled with CW2D (Langergraber and Šimůnek, 2005) was specifically developed to describe processes in constructed wetlands.

Models with generalized chemistry provide users with much more freedom in designing their particular chemical systems; possible applications of these models are also much wider. Users can either select species and reactions from large geochemical databases, or are able to define their own species with particular chemical properties and reactions. Most codes with general geochemistry are limited to fully saturated porous media with constant water contents and velocities, and evaluate only solute transport and biogeochemical reactions (e.g., PHREEQC, Parkhurst and Appelo (1999)). Only few models allow the velocity field to be calculated internally. Several codes for transient unsaturated flow have also been coupled to general biogeochemistry models. These include, for example, 3DHYDROGEOCHEM (Yeh and Cheng, 1999) and HP1 (Jacques and Šimůnek, 2005).

4.1. HP1

The HP1 program (Jacques and Šimůnek, 2005) resulted from coupling HYDRUS-1D (Šimůnek et al., 1998) with the PHREEQC geochemical code (Parkhurst and Appelo, 1999). This new, very powerful code contains modules simulating (1) transient water flow in variably-saturated media, (2) the transport of multiple components, (3) mixed equilibrium/kinetic biogeochemical reactions, and (4) heat transport. HP1 is a significant expansion of the individual HYDRUS-1D and PHREEQC programs by preserving and combining most of their original features and capabilities. The code still uses the Richards equation for simulating variably-saturated water flow and advection-dispersion type equations for heat and solute transport. However, the HP1 program can now simulate also a broad range of instantaneous and kinetic low-temperature biogeochemical reactions in water, the vadose zone and in ground water systems, including interactions with minerals, gases, exchangers and sorption surfaces based on thermodynamic equilibrium, kinetic, or mixed equilibrium-kinetic reactions. HP1 uses the operator-splitting approach with no iterations during one time step (non-iterative sequential approach). The accuracy of this operator-splitting approach for (a) a kinetic reaction network (i.e., sequential and parallel kinetic degradation reactions) by comparing HP1

with an analytical solution for TCE-degradation and (b) for mixed equilibrium and kinetic reactions for different flow conditions (steady-state and transient) has been evaluated by Jacques et al. (2005b). HP1 is available on request from www.sckcen.be/hp1.

Jacques et al. (2003, 2005), Jacques and Šimůnek (2005), and Šimůnek et al. (2006) demonstrated the versatility of HP1 on several examples such as a) the transport of heavy metals (Zn^{2+}, Pb^{2+}, and Cd^{2+}) subject to multiple cation exchange reactions, b) transport with mineral dissolution of amorphous SiO_2 and gibbsite ($Al(OH)_3$), c) heavy metal transport in a medium with a pH-dependent cation exchange complex, d) infiltration of a hyperalkaline solution in a clay sample (this example considers kinetic precipitation-dissolution of kaolinite, illite, quartz, calcite, dolomite, gypsum, hydrotalcite, and sepiolite), e) long-term transient flow and transport of major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and heavy metals (Cd^{2+}, Zn^{2+}, and Pb^{2+}) in a soil profile, f) cadmium leaching in acid sandy soils, g) radionuclide transport, h) long term uranium migration in agricultural field soils following mineral P-fertilization, and i) fate and subsurface transport of explosives.

There is an increasing concern about the presence of explosives and energetics in the subsurface environment. Such chemicals are the result of the manufacture, distribution, testing and/or unsafe disposal of ammunition, but can also be released into the environment during a terrorist attack. Šimůnek et al. (2006) showed an application of HP1, in which they simulated the transport of the major explosive (the parent product TNT, 2,4,6-trinitrotoluene), and its various metabolites (the daughter products) 2ADNT, 4ADNT, and TAT, as they are being created sequentionally by degradation of the parent compounds. HP1 further allows the parent and daughter compounds to have different mobilities in the subsurface as dictated by their specific dissolution, sorption and transport properties. In its most general case, the model permits contaminants to reside in all three phases, i.e., the liquid, solid (precipitated and sorbed), and gaseous phases. This example indicated that ground water may be more vulnerable to leaching of TNT daughter products (notably TAT) than of the parent compound itself, and that monitoring for the daughter products may provide an early warning of possible TNT leaching.

These various examples demonstrate that the coupling of HYDRUS-1D and PHREEQC leads to a potentially very powerful tool for simulating a broad range of interacting physical, chemical and biological processes affecting transport of contaminants in soils.

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