# MODELING NONEQUILIBRIUM CONTAMINANT TRANSPORT PROCESSES IN SOILS AND GROUNDWATER

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## INTRODUCTION

This paper deals with the problem of nonequilibrium (or preferential) fluid flow and contaminant transport in the subsurface. We focus especially on flow and transport processes in the variably-saturated vadose zone between the soil surface and the groundwater table. Predictions of water and solute movement in the vadose zone are generally made using the classical Richards equation for flow in unsaturated porous media and the advection-dispersion equation for solute movement. For a one-dimensional profile and assuming linear equilibrium sorption, these equations are given by

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial x}\left( K(h)\frac{\partial h}{\partial x} - K(h) \right) \tag{1}$$

$$\frac{\partial (\theta R c)}{\partial t} = \frac{\partial}{\partial x}\left( \theta D \frac{\partial c}{\partial x} - qc \right) - \phi \tag{2}$$

respectively, where $t$ is time, $x$ is distance from the soil surface downward, $\theta$ is the volumetric water content, $h$ is the soil water pressure head, $K$ is the unsaturated hydraulic conductivity, $c$ is the solution concentration, $D$ is the dispersion coefficient, $q$ is the volumetric fluid flux density given by Darcy-Buckingham's law, $\phi$ is a general source-sink term, and $R$ (=1+$\rho k/\theta$) is the retardation factor in which $\rho$ is the bulk density and $k$ the distribution coefficient accounting for linear equilibrium sorption. Similar equations can be formulated for two- and three-dimensional problems.

Equations (1) and 2 are relatively standard in that they have been used for the past 50 years or more in various forms, simplifications or extensions in a large number of research and engineering applications. The equations typically predict uniform flow and transport processes in the subsurface. Unfortunately, the vadose zone can be extremely heterogeneous at a range of scales from the microscopic (e.g., pore) to the macroscopic (field or larger) scale. These heterogeneities often lead to preferential or nonequilibrium flow and transport processes that are very difficult to capture macroscopically using Eqs. (1) and (2). Examples of preferential flow are the rapid movement of water and dissolved solutes through soil macropores or rock fractures, unstable or gravity-dominated flow caused by soil textural changes or water repellency, and funneling of water along inclined textural boundaries [Hendrickx and Flury 2001; Šimůnek et al. 2003].

## DUAL-POROSITY AND DUAL-PERMEABILITY FORMULATIONS

Nonequilibrium and preferential flow processes in macroporous soils and fractured rocks can be described using a variety of dual-porosity or dual-permeability models. A commonality of these models is the assumption that the porous medium consists of two interacting but overlapping pore regions, one associated with the inter-aggregate, macropore, or fracture system, and one comprising the micropores (or intra-aggregate pores) inside soil aggregates or the rock matrix. Dual-porosity models assume that water in the matrix is stagnant, while the more complex dual-permeability models also allow for water flow within the soil or rock matrix. Different formulations arise depending upon how water and/or solute movement in the micropore (matrix) and macropore (fracture) regions are modeled, and how water and solutes in the two regions are allowed to interact [Šimůnek and van Genuchten, 2008].

Applications of dual-permeability flow models typically require two sets of constitutive relationships describing the water retention (capillary pressure-saturation) and unsaturated hydraulic conductivity properties of the medium, one for the matrix and one for the fracture pore system. Additionally, a separate conductivity function may be needed in the exchange term governing the rate of exchange between the fracture and matrix pore systems [e.g., Gerke and van Genuchten, 1993]. Such information, unfortunately, is seldom available.

To avoid over-parameterization of the governing equations, one approach is to assume instantaneous hydraulic equilibration between the fracture and matrix region. In that case it is still possible to use Eq. (1) for variably-saturated flow, but now with composite hydraulic properties that are weighted averages in some manner of the fracture and matrix hydraulic properties. A variety of forms have been proposed for this purpose, including by Vogel and Cislerová [1988], Durner [1994], and Mohanty et al. [1997]. While still leading to uniform flow, models using composite hydraulic properties do allow for faster flow during conditions near saturation, and as such may provide more realistic simulations of field data. In soils, the two parts of the composite hydraulic functions may be associated with soil structure (near saturation) and soil texture (at lower negative pressure heads). Such an approach is consistent with field data indicating that the macropore conductivity of soils may be one to two orders of magnitude larger than the matrix conductivity at saturation [Schaap and van Genuchten, 2006].

If Eq. (1) is used in conjunction with composite hydraulic functions, the transport equations for nonequilibrium transport reduce to a relatively standard dual-porosity formulation which assumes that the liquid phase can be partitioned into mobile, $\theta_m$, and immobile, $\theta_{im}$, regions, with advective-dispersive transport being restricted to the mobile region as follows [van Genuchten and Wierenga, 1976]:

$$\frac{\partial(\theta_m R_m c_m)}{\partial t} = \frac{\partial}{\partial x}\left( \theta_m D_m \frac{\partial c_m}{\partial x} - q c_m \right) - \alpha(c_m - c_{im}) - \phi_m \tag{3}$$

$$\frac{\partial(\theta_{im} R_{im} c_{im})}{\partial t} = \alpha(c_m - c_{im}) - \phi_{im} \tag{4}$$

where the subscripts $m$ and $im$ refer to the mobile and immobile regions, respectively, and $\alpha$ is a mass transfer coefficient. The retardation factors $R_m$ and $R_{im}$ for the mobile and immobile regions are given by

$$R_m = 1 + \frac{f\rho k}{\theta} \qquad R_{im} = 1 + \frac{(1-f)\rho k}{\theta} \tag{5}$$

in which $f$ is the fraction of sorption sites in contact with mobile water.

Equations (3) and (4) for solute transport, in conjunction with Eq.(1) and the use of composite hydraulic functions, provide a very convenient and parsimonious description of nonequilibrium transport processes in the subsurface. The model contains three additional parameters relative to the equilibrium model: $\theta_m$ (or $\theta_{im}$), $f$, and $\alpha$. A good first approximation for $f$ is to assume that this parameter is equal to the relative fraction of mobile water (i.e., $f = \theta_m/\theta$), while for $\alpha$ one could use values recommended by Maraqa [2001] based on an analysis of previously published laboratory and field-scale experiments. Maraqa [2001] found that the mass transfer coefficient $\alpha$ is inversely related to the residence time of the contaminant in the system as follows:

$$\alpha = at_r^{-b} \tag{6}$$

where $t_r$ is the residence time in hours ($t_r=LR/v$ in which $L$ is the scale of the transport process), and $b$ is in the range 0.73 to 0.88. This shows that the mass transfer coefficient $\alpha$ is a scale-dependent variable, roughly inversely proportional (exactly if $b$=1) to the scale of an experiment. Scale dependency has long been known for several transport parameters such as the longitudinal dispersivity, $\lambda = \theta D/q$ , which is generally assumed to increase with the length of the transport domain [e.g., Anderson, 1984]. Scale dependency may well exist also macroscopically for the matrix diffusion coefficient [Liu et al., 2004].

The scale dependency of the mass transfer coefficient makes sense intuitively also if one accepts the notion that some degree of nonequilibrium always will be present during transport in naturally heterogeneous media, with the degree of non-equilibrium being controlled by new heterogeneities continuously being encountered as the transport domain increases (e.g., Pachepsky, 2008). This can be demonstrated also by placing Eqs. (3) and (4) for steady-state flow conditions in dimensionless form [van Genuchten and Wierenga, 1976], and assuming a constant dimensionless mass transfer coefficient, $\omega=\alpha L/q$, independent of scale, in the resulting formulation. Constancy of the dimensionless parameter $\omega$ would imply an inverse relationship between $\alpha$ and $L$.

## APPLICATIONS

In this paper we review a broad range of dual-porosity and dual-permeability formulations, and show their application to several flow and transport problems at different scales. One application concerns pesticide transport in a large-scale tile-drained field from which only limited data were available for model calibration [Boivin et al., 2006]. A second application involves the long-term environmental fate of a radionuclide decay chain released from a conventional mining installation in Amazonia processing ore containing natural occurring radioactive materials (NORMs). The latter analysis was applied to the decay chain $^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra \rightarrow {}^{210}Pb$ [Pontedeiro et al., 2008]. The general reaction terms $\phi$ in Eqs. (1), (3) and (4) were for this problem used to represent first-order source-sink coupling of consecutive radionuclides within the decay chain, with decay occurring in both the solution and adsorbed phases. The system was modeled by assuming that rainfall percolated vertically downward through the disposal site and the unsaturated zone, and then mixed with and moved laterally in groundwater until being intercepted by a well 100 m downgradient of the landfill. For both calculations we used the HYDRUS computer software packages [Šimůnek et al., 2008]. The two examples show that preferential flow can have a major effect on the simulation results.

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