

SOIL-WATER- SOLUTE PROCESS CHARACTERIZATION

An Integrated Approach

Edited by

JAVIER ÁLVAREZ-BENEDÍ
RAFAEL MUÑOZ-CARPENA



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3 Modeling as a Tool for the Characterization of Soil Water and Chemical Fate and Transport

Javier Álvarez-Benedí

Instituto Tecnológico Agrario de Castilla y León,
Valladolid, Spain

Rafael Muñoz-Carpena

IFAS/TREC, University of Florida, Homestead,
Florida, USA

Marnik Vanclooster

Catholic University of Louvain, Louvain-la-Neuve, Belgium

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3.1 INTRODUCTION

Modeling is at the core of any experimental characterization, and hence also the characterization of soil water and chemical fate and transport processes. The use of a conceptual model (rather than a numerical model) is necessary before undertaking any process characterization. Thus, from this point of view, modeling can be considered as the starting point of any soil characterization process. It is important to recognize that the end result of most of the characterization efforts is to describe how the processes will evolve in space and time through a mathematical model. Hence, while the characterization process as such is based on modeling, soil process simulation modeling also builds on the results of the soil characterization. Conceptual models, for instance, are often translated into mathematical models as a basis for the interpretation of soil observations, thereby supporting the process characterization. Modeling can further be used to optimize the characterization effort in terms of data collection quantity and quality (frequency of data needed, parameters to monitor, need to assess variability, etc.).

Chapter 2 established the need for field studies and outlined a number of preliminary issues, including the selection of a theoretical methodology that takes into account the purpose of characterization (research, consulting, etc.). This is, in fact, the core of the integrated approach for process characterization, as it requires the coupling of a model with a monitoring methodology, both designed as a trade-off between the desired degree of detail of process description and cost. No general guidelines can be given for shifting from a more generalized to a more detailed degree of process description in modeling processes. But as stated in Chapter 2, this will depend very much on the modeling objective, or, as stated in Chapter 1, it will be dictated by the spatial-temporal scale of process or the process description. Bouma (1997) illustrates this question with three examples:

1. Soil chemical phase transfer and transformation processes are often characterized under equilibrium conditions in the laboratory, which are quite different from the field conditions, where equilibria often do not occur. These experiments could provide a basic understanding of process characterization and approximate independent estimations of certain parameters, but will yield soil parameters that may be ineffective in predictive simulation modeling. Hence, it should be questioned when soil properties determined under equilibrium conditions in the laboratory should no longer be used in predictive modeling and when

- characterization should shift to procedures based on larger *in situ* experiments performed under transient conditions.
2. Most simulation models for solute transport in soil implicitly assume soils to be homogeneous and isotropic, although field soils are rarely homogeneous and isotropic. More general approaches for representing heterogeneous systems include stochastic, stratified, and two-domain or dual-porosity approaches. Therefore, one should also question in which conditions more detailed and complicated solute transport models should be preferred.
 3. Complex, deterministic models are often used to model solute fluxes within landscapes. However, taking into account the lack of data to feed part of these models, simpler modeling approaches could be considered in some conditions in a predictive simulation context.

Hence, the complexity of the modeling-based soil characterization procedure will depend on the modeling objectives and the accuracy required. For the description of nitrate fate and transport in soil, for example, the characterization of the hydrodynamic dispersion process will not be significant, given the low sensitivity of the simulated nitrate concentration profiles and fluxes to this parameter. On the other hand, when dealing with fate and transport at low concentration levels, as is the case when predicting pesticide transport at the ppm level, then the consideration of the hydrodynamic dispersion in the flow and transport model is essential. This illustrates clearly that the complexity of the model to be considered in the soil characterization process depends very much on the characterization and modeling objective.

Taking into account the characterization-modeling tandem as the basis for an integrated approach to process characterization, a previous modeling perspective must be given before introducing characterization strategies and methods of measurement. Thus, the purpose of this chapter is to develop a modeling framework for soil process description that will serve as the basis for characterization methods described in the next sections of this book. This will be done in three steps. First, a general classification of soil processes based on their conceptual and mathematical description will be presented. This classification includes equilibrium, reversible and irreversible rate processes, and transport processes. The starting points will be simple conceptualizations, and the discussion will be directed towards higher description levels, taking into account the constraints imposed by scale and variability. Second, as the transport mechanisms of the solvent and solute are different in nature, driving forces for water flow and solute movement will be described using different conceptual and mathematical models. For this reason, soil-water and soil-solute processes (including biological transformations) will be analyzed separately. Finally, the development of complex models is presented by integrating the description of several individual processes. Inverse modeling is introduced as a characterization tool that will be further developed in Chapter 20.

3.2 GENERAL CONCEPTUALIZATION OF SOIL PROCESSES

Jury and Flühler (1992) proposed five elements in a general soil chemical fate and transport model: (1) division of chemical mass into appropriate phases requiring separate description (e.g., the gaseous, the dissolved, the adsorbed, and the nonaqueous liquid phase); (2) interphase mass transfer; (3) intraphase mass transformation describing the rate of appearance or disappearance of mass per unit volume from the system; (4) mass conservation; and (5) mass transport according to a given flux law for each mobile phase. Considering the corresponding mathematical formulation of the above elements and taking into account the rate (temporal scale) and nature (mass transfer, thermodynamics, etc.), a general classification of individual soil process description for characterization purposes could be:

1. Local phase transfer and transformation process description: (a) *instantaneous equilibrium soil process description*: at a particular time scale, the rate of the process is fast enough to be considered instantaneous and reversible (e.g., instantaneous sorption of a chemical released in the soil solution at the liquid solid inter-phase); (b) *irreversible soil process description*: nonreversible rate-limited processes (e.g., hydrolysis of a chemical); (c) *reversible soil process description*: reversible rate-limited processes (e.g., some sorption-desorption processes).
2. Transport process description: processes where spatial coordinates are required for the description. This group includes the description of several transport mechanisms that are different for solvent (water) and solute. These will be described separately in more detail in Sections 3.3 and 3.4.

It is interesting to note that a particular process can be considered instantaneous, rate limited, or stationary depending on the model time scale, and thus, the temporal scale will dictate the appropriate description for rated processes. Figure 3.1 shows different examples of rate processes simultaneously occurring at different time scales. When modeling the process represented by the central block (e.g., sorption), the process occurring at a lesser time scale can be considered as "instantaneous," while the process taking place at a higher time scale can be considered as "stationary."

Thus, a general chemical transport and transformation model will use these basic process descriptions as "building stones" to construct each of the five elements. For example, the inter-phase mass transfers can be described using equilibrium, kinetic, or mass transfer descriptions, while the reaction term can be described through rate equations (equilibrium, reversible, and irreversible kinetics). Finally, transport processes will combine mass conservation and flux laws for each phase. Each of these building stones will next be described in detail.

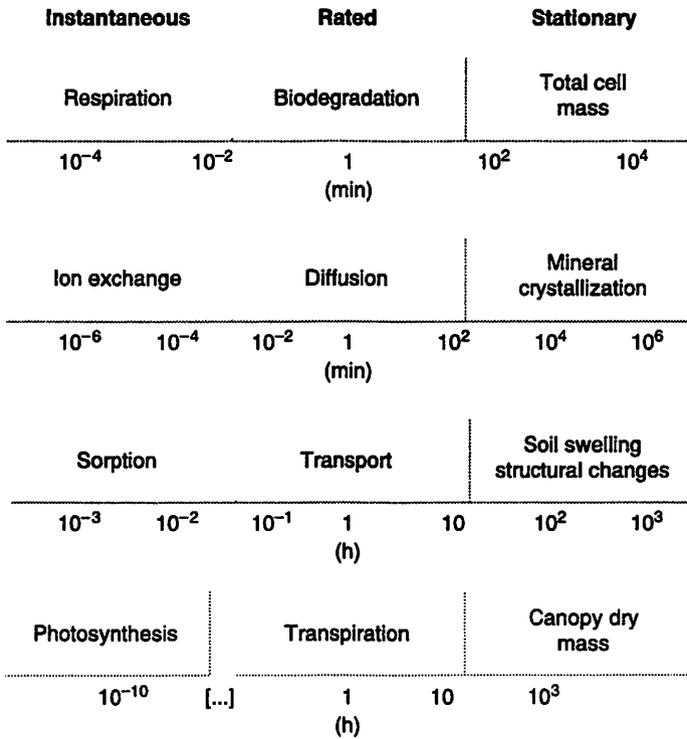


FIGURE 3.1 Time scales of soil reactions. Each row represents an example of three simultaneous processes occurring at different time scales. The central process can be considered as rate limited, the processes at smaller time scales (left) can be considered instantaneous when observed at the “central” time scale, and those occurring at larger time scales (right) can be considered as “stationary.” Time scales are approximated.

3.2.1 INSTANTANEOUS EQUILIBRIUM

Equilibrium is rarely achieved in natural environments. However, this simple conceptualization sometimes gives reasonable approximations when characterizing soil processes. For example, a simple linear equilibrium model describing the partitioning of a solute between two phases is given by:

$$c_i = K_D c_{ii} \tag{3.1}$$

where c_i [e.g., $M M^{-1}$] and c_{ii} [e.g., $M L^{-3}$] are the concentrations in the two phases and K_D [e.g., $L^3 M^{-1}$] is the distribution or partition coefficient. This conceptualization can be used for describing liquid-solid, liquid-liquid, or liquid-gas partitioning. The above linear relationship for describing equilibrium is a simplified conceptualization that is usually valid only for a limited range of concentrations and temperatures. Other soil properties such as the soil

pH or the ionic strength of the solution can limit the validity of the linear equilibrium for a soil chemical process. For example, Henry's law, which is the linear equilibrium model [Eq. (3.1)] for the liquid-gas phase transfer, is only valid for diluted solutions. In addition, the partition of a solute between two immiscible liquids can only be described successfully with a linear equilibrium model for a small range of concentrations. More complex equilibrium models can be obtained by using nonlinear models (such as the Freundlich sorption model described in Sec. 3.4) or the use of conceptual models based on thermodynamic theory, which consider activity coefficients, description of ionic interaction, or computation of the free Gibbs energy.

3.2.2 IRREVERSIBLE KINETICS

Soil processes are often rate limited due to the heterogeneity of the porous medium and the simultaneous occurrence of several coupled mechanisms. The kinetics of slow reactions act together with scale-dependent transport mechanisms (e.g., diffusion processes) that take place simultaneously, and thus the applicability of a particular model is restricted to the scale of use (e.g., batch, column, field, landscape, region, etc.).

This is the general case for batch methods, which can be used for characterizing process kinetics and equilibrium (or pseudo-equilibrium if equilibrium is not fully achieved). Batch methods for obtaining kinetic data present several advantages, including low-cost equipment, the elimination of several mechanisms by mixing such as film diffusion and sometimes particle diffusion, achievement and control of a constant soil-to-solution ratio, and control of reaction conditions (O_2 , pH, etc.). However, these experiments also have a number of limitations: the values of several experimental variables can be far from those found in natural scenarios, the products are not removed and are allowed to accumulate in the closed system, etc. (Amacher, 1991).

In a general process $A \rightarrow B$, rates can be expressed as a decrease in the concentration of the source A as a function of time, or an increase in the product formation as a function of time:

$$\text{Rate} = -\frac{dc_A}{dt} = \frac{dc_B}{dt} \quad (3.2)$$

where c_A and c_B are the concentration of reactant and products [ML^{-3}], and *Rate* is the reaction rate [$ML^{-3}T^{-1}$]. The most frequently used kinetics are, by far, *first-order kinetics*, given by:

$$\frac{dc}{dt} = -k_1c \quad (3.3)$$

where c [M L⁻³] is the concentration and k_1 [T⁻¹] is the first-order kinetics constant. The corresponding integrated form is:

$$c = c_0 e^{-k_1 t} \tag{3.4}$$

where c_0 [M L⁻³] is the initial concentration. The *half-life* ($t_{1/2}$) represents the time corresponding to a concentration $c = c_0/2$. Substituting this concentration in Eq. (3.4), the half-life for first-order kinetics is obtained:

$$t_{1/2} = \frac{\ln(2)}{k_1} \tag{3.5}$$

Also, the *zero-order kinetics* can represent a stationary source or sink of a chemical of concentration c :

$$\frac{dc}{dt} = \pm k_0 \tag{3.6}$$

where k_0 [M L⁻³ T⁻¹] is the zero-order rate parameter.

Table 3.1 summarizes the most frequently used kinetics equations used in soil science. The integrated forms are given for solute sinks (solute

TABLE 3.1
Equations for Extended Kinetics Models

Order	Differential	Integrated sinks, $-k$ (initial condition: $t = 0, C = C_0$)	Half-life (sinks)	Integrated form sources, $+k$ (initial condition: $t = 0, C = 0$)
Zero-order	$\frac{dC}{dt} = \pm k$	$C = C_0 - kt$	$t_{1/2} = \frac{1}{2k}$	$C = kt$
First-order	$\frac{dC}{dt} = \pm kC$	$\frac{C}{C_0} = e^{(-kt)}$	$t_{1/2} = \frac{\ln(2)}{k}$	$\frac{C}{C_0} = 1 - e^{(-kt)}$
n -Order	$\frac{dC}{dt} = \pm kC^n$	$\frac{1}{C^{n-1}} = \frac{1}{C_0^{n-1}} + (n-1)kt$	$t_{1/2} = \frac{(2^{n-1} - 1)}{C_0^{n-1}(n-1)k}$	
Elovich	$\frac{dC}{dt} = \alpha^{-\beta C}$			$C = \frac{1}{\beta} \ln(1 + \alpha\beta t)$
Elovich (simplified)*	$\frac{dC}{dt} = \alpha^{-\beta C}$			$C_t = a + b \ln t$
Power		$C = C_0 - at^b$	$t_{1/2} = \left(\frac{C_0}{2a}\right)^{1/b}$	$C_t = at^b$
Parabolic diffusion law		$C = C_0 - at^{1/2}$	$t_{1/2} = \sqrt{\frac{C_0}{2a}}$	$C = at^{1/2}$

* Assuming $\alpha\beta t \gg 1$. $b = 1/\beta$. $a = b \ln(\alpha\beta)$.

disappearance considering as initial condition $c = c_0$) and sources (considering $c = 0$ as initial condition). In the case of solute sinks, the variation of solute concentration c with time is a negative value ($-k$). On the other hand, solute production from sources is represented mathematically by a positive variation of c with time ($+k$). Power and parabolic diffusion law kinetics are generally enunciated directly in its integrated form. In fact, parabolic diffusion law can be considered as a singular case of the more generalized power kinetics (with $b = 1/2$). In addition, Elovich and simplified Elovich kinetics are reflected in Table 3.1.

In the simplest cases, the kinetics parameters are considered as constants. However, in many soil chemical fate and transport models, rate parameters are considered as variables. Variable rates have been applied to the case when several time scales are characterized simultaneously. For example, Bloom and Nater (1991) described the rate of mineral dissolution as weathering reactions proceed, with rates decreasing several orders of magnitude from the first day to several years. Another example is the reduction of the rate parameters for biologically mediated processes when soil environmental conditions (e.g., soil temperature, soil moisture, soil pH) will limit the rate of certain processes. Soil temperature dependency of biologically mediated rate parameters, for instance, can easily be encoded by multiplying the reference rate constant with a Q_{10} reduction function (e.g., Reduction = $Q_{10}^{(T - T_{ref})/10}$) in Vanclouster et al., 1996). Another popular concept is the use of the trapezoidal soil moisture-dependent reduction function, allowing reaction rate parameters to reduce when soil becomes too dry or too wet.

3.2.3 REVERSIBLE KINETICS

The above equations refer to irreversible processes, although they can be considered as a simplified form of the more generalized model of reversible kinetics. The rate of variation of the concentration for a given compound C will be proportional to the kinetics of solute loss plus the corresponding kinetics of solute increase. For example, in a reversible first-order kinetics sorption process, the rate of variation of the concentration of the dissolved phase (c) is given by:

$$\frac{\partial c}{\partial t} = -k_{ads}c + k_{des} \frac{\rho}{\theta} s \quad (3.7)$$

where c [$M L^{-3}$] is the concentration in the dissolved phase, s is the concentration in the sorbed phase [$M M^{-1}$], ρ is the bulk density of soil [$M L^{-3}$], θ is the soil water content [$L^3 L^{-3}$], and k_{ads} [T^{-1}] and k_{des} [T^{-1}] are the rate parameters for the sorption and desorption reactions, respectively.

Another example is the partitioning processes between two liquids, two regions, or two phases, which can be described by means of a mass transfer coefficient, assuming that the rate of exchange is proportional to the

concentration difference between the two liquid regions:

$$\frac{dc}{dt} = \alpha(c_{II} - c_I) \quad (3.8)$$

where c_I and c_{II} are the concentrations in phases or regions I and II, respectively, and α is the mass transfer coefficient [T^{-1}]. This conceptual description has been used to describe mass transfer between water in different soil domains in physical nonequilibrium models (Sec. 3.4.2) and transfer of gases from soil to atmosphere (Sec. 3.4.5).

3.2.4 TRANSPORT

Mass flow in the liquid phase requires a different treatment for solvent (usually water) and solute, because solvent and solute transport in soil obey different driving forces. This holds also for mass flow in the gaseous phase.

Water flow in soil is mainly governed by capillarity (Ψ), gravity (z), pressure (Ψ_p), and osmotic forces (Ψ_o), which are the dominant components of the total hydraulic head, H [L]. The total hydraulic head is then used for describing the liquid water flux, J_w [LT^{-1}], which for one-dimensional flow yields:

$$J_w = -K \frac{\partial H}{\partial x} \quad (3.9)$$

where K is the unsaturated hydraulic conductivity function [LT^{-1}], which also strongly depends on the water potential and properties of the porous media.

In the case of chemical transport in the soil liquid phase, the two dominant transport mechanisms are advection (transport of dissolved species due to a water flow) and dispersion (a macroscopic effect that accounts for microscopic variability in the flow field). Then, the total mass flow in the liquid phase, J_S [$M L^{-2} T^{-1}$], can be described through the sum of each mass flow component:

$$J_S = J_c + J_D \quad (3.10)$$

with J_c [$M L^{-2} T^{-1}$] the convective mass flux ($J_c = J_w C$), and J_D [$M L^{-2} T^{-1}$] the dispersive mass flux. Note that the total solute (J_S) and dispersive flux (J_D) are expressed in terms of solute mass per cross-sectional area of soil and per unit of time [$M L^{-2} T^{-1}$], whereas the water flux [J_w in Eq. (3.9)] corresponds to the Darcian velocity [LT^{-1}]. The description of the chemical flux term J_S requires accounting for each possible transport mechanism. The dispersive flux per unit area of soil can be written as:

$$J_D = -\theta D \frac{\partial C}{\partial x} \quad (3.11)$$

where D is an effective dispersion coefficient (see Sec. 3.4.3). A description of other possible mechanisms can be found in Scanlon et al. (2002).

Within a continuum approach, the flux laws are further combined with the mass conservation equation to yield the governing soil flow and transport equations. The above descriptions of water and solute transport are the simplest classical conceptualizations, which consider the soil as a continuous homogeneous system. Sections 3.3 and 3.4 will discuss the main constraints of classical approaches and alternatives for description of soil-water and soil-solute.

3.3 SOIL-WATER TRANSPORT PROCESSES

3.3.1 CLASSICAL DESCRIPTION OF WATER MOVEMENT

Water movement in soils is generally described by assuming the soil to be a homogeneous (and rigid) medium. Assuming laminar one-dimensional flow and neglecting the inertial terms of the momentum conservation equation, the macroscopic water flux is given by Darcy's flow equation [Eq. (3.9)], which can be written for one-dimensional vertical flow in terms of the hydraulic head:

$$q = J_w = -K \frac{\partial H}{\partial z} \quad (3.12)$$

where H [L] is the hydraulic head, and z [L] is the depth. In rigid unsaturated soils, the hydraulic head consists of the gravimetric potential or piezometric head z [L] and the pressure or suction head ψ [L], often referred to as the matric potential, which result from capillary forces. Equation (3.12) indicates that the water flow through the soil is in the direction of and proportional to the hydraulic gradient, which is the driving force, and proportional to the hydraulic conductivity, which is an intrinsic property of the medium. Darcy's law is valid only for laminar flow, since the linearity of flux versus hydraulic gradient fails at high flow velocities (where inertial forces are not negligible). In addition, another assumption of this equation is that the osmotic potential is not a significant mass transfer factor, which is generally acceptable at the macroscopic scale when the soil solution is diluted. Water movement in rigid, homogeneous, isotropic, variably saturated soil is described by combining mass conservation with Darcy's flow equation in an equation proposed by Richards (1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\psi) \left(\frac{\partial \psi}{\partial z} + 1 \right) \right] \quad (3.13)$$

where $\theta = \theta(\psi)$ is the volumetric water content [$L^3 L^{-3}$], t is time [T], and $K(\psi)$ the unsaturated hydraulic conductivity [$L T^{-1}$]. Both $\theta(\psi)$ and $K(\psi)$ are functions of the matric potential head ψ . Equation (3.13) is known as the *mixed*

form, as it contains two dependent variables θ and ψ . By defining the *hydraulic diffusivity* function $\zeta(\theta)$ [$L^2 T^{-1}$] as,

$$\zeta(\theta) = K(\theta) \frac{\partial \psi}{\partial \theta} \quad (3.14)$$

the *diffusive* or θ -form of Richards' equation is obtained:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[\zeta(\theta) \frac{\partial \theta}{\partial z} + K(\theta) \right] \quad (3.15)$$

In addition to the simplification of the equation with just one variable, $\zeta(\theta)$ varies less over the range of θ than $K(\theta)$, which improves the stability of the numerical solution of Richards' equation. The drawback of this form is that $\zeta(\theta)$ is only defined for unsaturated conditions, which makes the equation unusable for general conditions where the soil is saturated. An alternative formulation can be obtained by defining the *hydraulic capacity* function, $C(\psi)$ [L^{-1}] as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial \theta}{\partial \psi} \frac{\partial \psi}{\partial t} = C(\psi) \frac{\partial \psi}{\partial t} \quad (3.16)$$

yielding the *capacitive* or ψ -form of Richards' equation:

$$C(\psi) \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left[K(\psi) \left(\frac{\partial \psi}{\partial z} + 1 \right) \right] \quad (3.17)$$

Although this is a simpler formulation in terms of a single variable, it contains two rapidly varying functions in ψ (C and K), which complicates its solution and usually translates to poor numerical mass balance.

Celia et al. (1990) showed that the *mixed form* of the Richards' equation (Eq. 3.13), although somewhat more complex to solve numerically, presents the advantage of being valid for the entire soil moisture range (i.e., saturated and unsaturated conditions) and improves the mass balance of the numerical solution as compared to the other formulations.

Although Richards' equation provides a complete description of water flow in soils, there are important limitations. Although this was originally defined for homogeneous isotropic media, soil heterogeneity can be partially handled through different numerical methods by assigning different properties to the nodes of the numerical grid. The equation in its basic form will not be valid for nonrigid media (i.e., swelling soils). However, by introducing an overburden component in the total hydraulic head, flow in the matrix of nonrigid media can be described with a modified version of the Richards' equation (Kim et al., 1993). The equation will also not be valid when specific forms of preferential flow occur, such as macropore flow in well structured

soils, by-pass flow in hydrophobic soils (highly organic or certain sandy soils), or funneled flow in sloping stratified soils. Another problem or limitation in applying the Richard's equation is the difficulty of correctly describing the intrinsic soil properties such as the $\theta(\psi)$ relationship (soil moisture retention characteristic) and the unsaturated hydraulic conductivity, $K(\psi)$. These two important soil hydraulic functions are presented in the next section.

3.3.2 CHARACTERIZATION OF WATER CONTENT–PRESSURE HEAD AND HYDRAULIC CONDUCTIVITY–PRESSURE HEAD RELATIONSHIPS

Soil volumetric moisture content θ [$L^3 L^{-3}$] and suction head ψ [L] are related by the soil water characteristic (soil moisture retention) curve, $\theta = \theta(\psi)$. Since suction is related to capillarity forces and these to pore diameter, soils with coarse structure (larger pore size in general) release moisture readily even at low suction values, where for the same suction values fine soils (small pores) retain most of the moisture. Thus, the shape of the nonlinear relationship depends largely on the soil pore size distribution and hence on soil texture (Figure 3.2). A similar effect, although more pronounced, can also be seen in the unsaturated conductivity function, $K(\psi)$ (Figure 3.2). However, for this latter relationship, soil structural properties related to the pore water connectivity and tortuosity will additionally determine the shape of the curve.

Several analytical expressions for $\theta(\psi)$ and $K(\psi)$ have been proposed in the literature (Table 3.2). The analytical description of these functions typically exhibits limitations close to saturation and dry soil conditions. Close

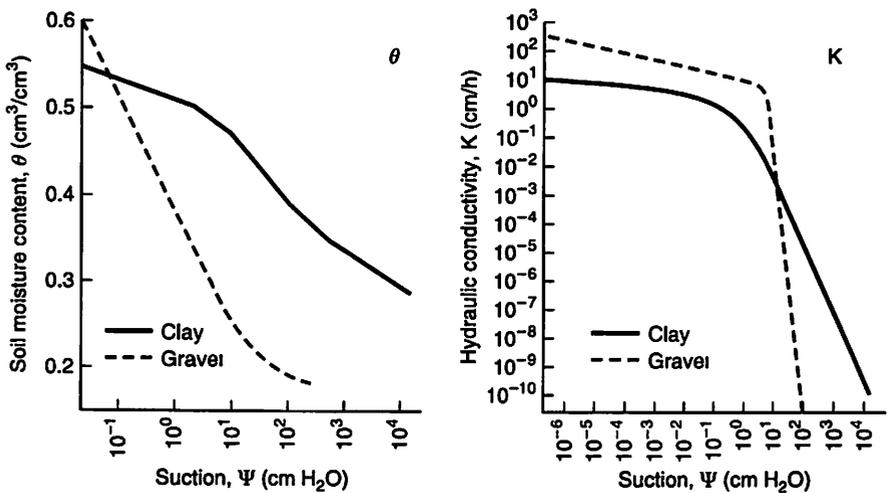


FIGURE 3.2 Effect of soil texture on soil water characteristics and unsaturated hydraulic conductivity functions.

TABLE 3.2
Soil Moisture Characteristic and Hydraulic Conductivity Equations

Type	Equation*	Parameters	Range (frequent)	Comments
Soil water characteristic function				
Hyperbolic	$ \psi = a\theta^b$	a, b	—	General shape but does not fit well values close to saturation.
Brooks and Corey (1964)	$S_r = \left(\frac{\psi_s}{\psi}\right)^\lambda$	ψ_s λ (θ_r, θ_s)	Point at $d\theta/d\psi = 0$ 2-5 — (measured/fitted)	High values of λ indicate uniform pore distribution and low values wide range of pores sizes. Depending on soil type, does not fit well values close to saturation.
van Genuchten (1980)	$S_r = [1 + (\alpha\psi)^n]^{-m}$ for $\psi \geq 0$	α n m (θ_r, θ_s)	0-1 (0.005-0.05 cm^{-1}) > 1 (1.2-4) 0-1 (1 - 1/n) — (measured)	More parameters required but fits values close to saturation well. On the Mualem version ($m = 1 - 1/n$) and if θ_r and θ_s are measured, only 2 parameters.
Hydraulic conductivity function				
Leibenzon (1947)	$K_r = S_r^{n_i}$	n_i (θ_r, θ_s)	1-4 (3) $3 + \frac{2}{\lambda}$ (Brooks Corey) — (measured/fitted)	Derived from Kozeny's principle. Works well for low permeable media (compacted clay). The Brooks and Corey exponent is more general and lends some physical significance to the parameter, although inherits some of its limitations.
Brooks and Corey	$K_r = \left(\frac{\psi_s}{\psi}\right)^m$	ψ_s m	Point at $d\theta/d\psi = 0$ 3-11	Frequently used. Derived from studies of capillarity in sands.
Gardner (1958)	$K_r = e^{\alpha\psi}$	α	0.1-0.01	α relates to soil texture and structure. Simple exponential formulation is easy to integrate and use in inverse problems. Usually only valid in the wet range up to a certain limit value.
Mualem (1976), van Genuchten (1980)	$K_r = S_r^{1/2} [1 - (1 - S_r^{1/m})^m]^2$	m n (θ_r, θ_s)	0-1 (1 - 1/n) > 2 — (measured)	Works well with a wide range of soils. Parameters can be estimated graphically from Brooks and Corey values or by non-linear fitting.

*with $S_r = (\theta - \theta_r)/(\theta_s - \theta_r)$; and $K_r = K(\psi)/K_s$.

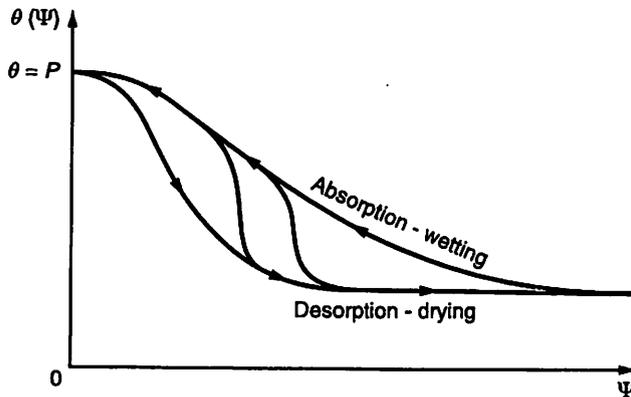


FIGURE 3.3 Hysteresis in the soil water characteristic curve.

to saturation, θ_s , some soils display inflexion points in the $\theta(\psi)$ and $K(\psi)$ relationships that are better described by alternative models (Table 3.2). The main problem in the dry range of the curve is related to the determination of the residual moisture content, θ_r , [$L^3 L^{-3}$]. In some instances, if θ_r is estimated by fitting experimental soil moisture or hydraulic conductivity data, the values cannot be interpreted physically. A simple method for independently estimating θ_r has not been tested on a broad scale (Kutilek et al., 1994).

Another complicating factor is the occurrence of hysteresis in the soil moisture retention characteristic (Figure 3.3). The irregular pore geometry of natural soils and in particular solid-liquid interphase mechanisms on a microscopic scale results in different θ - ψ relationships for the draining and moistening phase of soils. Different conceptual models have been proposed to describe soil water hysteresis. Viaene et al. (1994), for example, reviewed different hysteresis models of the soil hydraulic functions. Among these, Mualem's model (Mualem, 1976) was found to be one of the most accurate. This is a two-branch conceptual model, where the soil hydraulic status is defined as a function of the two principal drying and wetting retention curves, each described by a set of Mualem-van Genuchten parameters (Table 3.2).

Critical comparisons of field methods to measure the $\theta(\psi)$ and $K(\psi)$ relationships are presented in Chapter 5 and Chapter 6, respectively.

3.3.3 DUAL POROSITY MODELS

Soil homogeneity was one of the assumptions made by the Richards' equation in the classical description of water flow. A more realistic representation of soil water flow is given by a dual-porosity model, which accounts for two flow domains. The first domain comprises unsaturated flow, which is

described by Richards' equation. The second flow domain accounts for the flow through macropores. When the soil is (nearly) saturated, vertical water flow in structured soils will be dominated by macropore flow, as these pores drain at low suctions. Although macropores represent a small part of the porosity, they induce preferential flow paths, allowing fast transfer of an important fraction of the flow (Bouma and Wosten, 1979; Luxmoore, 1981; Beven and Germann, 1982). The generation of robust methodologies for the *in situ* direct characterization of the macroporous flow domain of soils remains a challenging task. Indirect methods are often proposed where $K(\psi)$ or $K(\theta)$ is estimated from more easily measured soil properties, such as the retention curve (van Genuchten and Leij, 1992). Additional approaches have been developed for bi-modal porosity models exhibiting macropore flow (Othmer et al., 1991; Ross and Smettem, 1993; Durner, 1994) but remain subject to much uncertainty. Field methods for *in situ* measurement of soil hydraulic properties are discussed in Chapter 6, and preferential flow characterization is described in Chapter 8.

3.4 SOIL-SOLUTE TRANSPORT PROCESSES

The four major processes that control the movement of contaminants in porous media are advection (or convection), dispersion, interphase mass transfer, and reaction or transformation (Brusseau, 1994). Advection refers to the movement of a solute with the flowing water and is described by the water flux and dissolved solute concentration (J_w, C). Dispersion represents the spreading of solute about a mean position, such as the center of mass and is a consequence of several transport mechanisms depending on the water regime. Phase changes include sorption, volatilization, and partitioning (e.g., two immiscible liquids such as octanol-water). Reaction can be conceptualized as a sink or source of the solute, expressed in terms of a rate equation.

3.4.1 CLASSICAL DESCRIPTION OF SOLUTE MOVEMENT

The simplest and classical approach describing "ideal" solute transport assumes that soil is homogeneous and rates of interphase mass transfer are fast enough to be considered as instantaneous (*local equilibrium assumption*). The expression of the one-dimensional advection-dispersion equation (ADE) for solute transport in a homogeneous soil is [from Eqs. (3.9) and (3.10), considering $J_S = J_w C + J_D$, and mass conservation: $\partial\theta c/\partial t = -\nabla J_S \pm \theta\Gamma$]:

$$\frac{\partial\theta c}{\partial t} = -\frac{\partial}{\partial x} \left(J_w c - \theta D \frac{\partial c}{\partial x} \right) + \theta\Gamma \quad (3.18)$$

where θ is the water content [$L^3 L^{-3}$], c is the solute resident concentration [$M L^{-3}$], t is time [T], x is the distance [L], J_w is the water flux [$L T^{-1}$], D is the dispersion coefficient [$L^2 T^{-1}$], and $\theta\Gamma$ is the solute sink/source term

[$\text{M L}^{-3} \text{T}^{-1}$]. Equation (3.18) is also designated as the convective-dispersive equation (CDE).

When the water content is constant with time and space (e.g., under saturated conditions), the equation can be simplified as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + \Gamma \quad (3.19)$$

where $v = J_w/\theta$ [L T^{-1}] is the average linear velocity of the fluid in the pores of the medium (*pore water velocity*). This equation is a second-order partial differential equation (classified as a parabolic equation). Analytical solutions of Eq. (3.19) for specific boundary conditions are described by van Genuchten and Alves (1982) and Leij and van Genuchten (2002). When the solute is sorbed to soil constituents, the mass conservation principle should take into account the total mass of solute $c_T = \theta c + \rho s$. Following the same mathematical derivation, the transport ADE (or CDE) equation for sorbed solutes is given by:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + \Gamma \quad (3.20)$$

where R is the retardation factor ($R = 1 + \rho(ds/dc)/\theta$). Mathematical expressions of the retardation factor for linear and Freundlich isotherms are developed in Chapter 11.

3.4.2 NONEQUILIBRIUM MODELS

The governing transport model for solute transport in porous media (i.e., ADE) was based on assumptions that the porous medium was homogeneous and that the interphase mass transfers were linear and essentially instantaneous. Brusseau (1998) reviewed several nonideal transport analyses of reactive solutes in porous media. Four major factors were identified as responsible for nonideal transport:

1. **Physical nonequilibrium:** Most solute transport models consider that all soil water contributes to solute transport, while this is often not the case in structured or heterogeneous soils. Soil domains with minimal flow and advection originate in soil regions with smaller hydraulic conductivity.
2. **Rate-limited sorption:** Most field-scale solute transport models include the assumption that equilibrium for mass-transfer processes is attained instantaneously, while experimental evidence shows that sorption-desorption of many organic compounds can be significantly rate limited.

3. Nonideal sorption: Most solute transport models include the assumption of a linear equilibrium sorption isotherm. Yet many chemicals, especially in field conditions, do not obey this simplified isotherm relationship.
4. Field-scale heterogeneity: The influence of spatially variable hydraulic conductivity on water flow and solute transport at the field scale generates apparent values of longitudinal dispersivity which are much larger than those observed in soil columns.

The four above-mentioned factors can be described with different modeling approaches. The simplest conceptualization of physical nonequilibrium consists of dividing the soil flow domain into mobile (i.e., advective flow) and immobile soil regions. Thus, the total volumetric water content of the soil is divided into mobile and immobile (stagnant) fractions, and solute concentration is considered different for each region. This mobile-immobile concept was proposed by Deans (1963) and Coats and Smith (1964) and was later developed and applied in soil science by Skop and Warrick (1974), van Genuchten and Wierenga (1976), and Vancloster et al. (1991), among others. Alternatively, the simplest conceptualization of solute nonequilibrium sorption models is the kinetic adsorption (one-site) model introduced by van Genuchten et al. (1974). Cameron and Klute (1977) applied a two-adsorption site model based on the different affinities of soil components to solutes. More sophisticated conceptualisations have been published, which include multi-reaction retention models and nonequilibrium based on maximum adsorption capacity (second-order models). These models were reviewed by Ma and Selim (1998).

The two-site and two-region nonequilibrium models have equivalent dimensionless formulations according to Nkedi-Kizza et al. (1984) and van Genuchten and Wagenet (1989):

$$\begin{aligned} \beta R \frac{\partial C_I}{\partial t} + (1 - \beta) R \frac{\partial C_{II}}{\partial T} &= \frac{1}{P} \frac{\partial^2 C_I}{\partial X^2} - \frac{\partial C_I}{\partial X} - \xi C_I \\ (1 - \beta) R \frac{\partial C_{II}}{\partial T} &= \omega(C_I - C_{II}) - \eta C_{II} \end{aligned} \quad (3.21)$$

where C_I and C_{II} are dimensionless equilibrium and nonequilibrium concentrations; T is dimensionless time, X is dimensionless distance, P is the Peclet number, ω is a dimensionless mass transfer coefficient, and the subscripts I and II refer to the equilibrium and nonequilibrium phases, respectively. R is the retardation factor. For the two-region model:

$$\begin{aligned} X &= x/L, T = vt/L, P = vL/D, R = 1 + \rho_b K_D / \theta \\ \beta &= \frac{\theta_m + f \rho_b K_D}{\theta + \rho_b K_D}, \omega = \frac{\alpha L}{\theta v}, C_I = \frac{c_m}{c_0}, C_{II} = \frac{c_{im}}{c_0} \end{aligned} \quad (3.22)$$

where x is distance [L]; v is the pore water velocity [$L T^{-1}$]; ρ_b and K_D are the soil bulk density [$M L^{-3}$] and distribution coefficient for linear sorption [$L^3 M^{-1}$]; f is the dimensionless fraction of sorption sites in equilibrium with the fluid of the mobile region; θ is the volumetric water content [$L L^{-3}$]; α is a mass transfer coefficient between the two regions [T^{-1}]; c_m , c_{im} are the resident concentration [$M L^{-3}$], respectively, in the mobile and the immobile soil region; L is the characteristic length [L]; and c_0 is the arbitrary characteristic concentration. The subscripts m and im denote mobile and immobile regions, respectively. ξ and η are the dimensionless degradation rate parameters:

$$\xi = \frac{L}{J_w} (\theta_m \mu_{lm} + f \rho K_D \mu_{sm}), \quad \eta = \frac{L}{J_w} (\theta_{im} \mu_{lim} + (1-f) \rho K_D \mu_{sim}) \quad (3.23)$$

where μ is a first-order rate degradation coefficient [T^{-1}], lm and sm denote liquid and solid mobile phases, and lim and sim denote liquid and solid immobile phases, respectively.

3.4.3 SOLUTE DISPERSION

Soil (and heterogeneous porous media in general) is a complex and irregular distribution of voids and solids. Fried and Combarous (1971) described three levels in the study of dispersion phenomena, which could be applied to the characterization of any physical property or process: a *local level*, where the physical quantity is described in an "infinitely small" volume element; a *fluid volume level*, which considers means of the corresponding local parameters over a pore or a set of pores; and a *macroscopic level*. The macroscopic level is only used in porous media, when a solid matrix exists, to define an equivalent continuum. Hence, assumptions of a geometrical structure of the porous media are not required. The parameters at this level are the averages of the corresponding local parameters taken over a finite volume of the medium.

Dispersion is due to a combination of both, a purely mechanical phenomenon and a physico-chemical phenomenon. The first phenomenon is denoted as *mechanical dispersion*, originated by boundary and geometrical effects when a fluid flows through a porous medium. Mechanical dispersion increases with the fluid velocity. The physical-chemical dispersion is referred to as *molecular diffusion*, which results from a chemical potential gradient. This mechanism is not dependent on fluid velocity (and therefore it exists even when there is no flow). However, the diffusion coefficient may depend on concentration if the viscosity of the mixture varies with concentration or if the mixture is not ideal (Harned and Owen, 1963). In addition, a rise in temperature will increase molecular agitation with consequent change of diffusion coefficients. In practice, diffusion in porous media has been described by the general diffusion equation with the introduction of an *effective diffusion coefficient*, which depends on the texture of the medium. This equation, based on Fick's first law of diffusion, is used for convenience to describe

macroscopic solute flux, despite the conceptual differences between diffusion and dispersion.

Since it is impractical, if not impossible, to define flow at the microscopic scale, averaging of the water flow over a representative volume is necessary. This averaging introduces some uncertainty in the velocity, which implies an uncertainty as to the dispersion coefficient. The averaging, or the scale which is chosen to define the flow, can result in a scale and flow rate dependency of the mechanical dispersion coefficient or dispersivity (Pickens and Grisak, 1981; Morel-Seytoux and Nachabe, 1992; Logan, 1996; Vanderborght et al., 1997; Javaux and Vanclooster, 2002). These authors developed expressions for dispersivity as a function of the mean travel depth and flow rate. van Wesenbeeck and Kachanoski (1994) also reported a spatial scale dependence of dispersion measured in terms of variance of solute travel time.

When representing the dispersion coefficient versus mean velocity, several velocity ranges can be recognized:

1. Pure molecular diffusion: This regime occurs when the mean velocity is very small or in a fluid at rest. The porous media slows down the diffusion processes so that the effective dispersion coefficient is always lower than the molecular diffusion ($D/D_0 < 1$):

$$D = \frac{D_0}{T_p} \quad (3.24)$$

2. Superposition: The contribution of mechanical dispersion becomes of the same order as the molecular diffusion.
3. Major mechanical dispersion: The contribution of mechanical dispersion is predominant, but molecular diffusion cannot be neglected and reduces the effects of mechanical dispersion.

$$D = \frac{D_0}{T_p} + \lambda v \quad (3.25)$$

4. Pure mechanical dispersion: The influence of molecular diffusion becomes negligible.
5. Mechanical dispersion: the flow regime is out of the domain of Darcy's law.

For a one-dimensional system, the macroscopic (effective) dispersion coefficient is usually defined by means of Eq. (3.25) (Freeze and Cherry, 1979; Brusseau, 1993). In this equation, T_p is the dimensionless tortuosity factor (> 1), defined as $T_p = (L_{dif}/L)^2$ with L_{dif} [L] and L [L] being the actual and the shortest path lengths for diffusion. And λ is the (longitudinal) dispersivity [L]. It should be noticed that the above equation can be found as:

$$D = \tau D_0 + \lambda v \quad (3.26)$$

where τ is the *apparent tortuosity factor* (< 1) defined as $\tau = (L/L_{dif})^2$, and thus, terms such as *tortuosity* (defined as L_{dif}/L), *tortuosity factor*, and *apparent tortuosity factor* have not been consistently used in the literature (Leij and van Genuchten, 2002).

A second approach for modeling the effect of multiple sources of dispersion to the *lumped* coefficient consists of coupling additional coefficients to Eq. (3.24). Brusseau (1993) presented a modified version of the equation of Horvath and Lin (1976), written in terms of the lumped dispersion coefficient D^* :

$$D^* = \frac{D_0}{T_p} + \frac{\lambda v_m}{1 + [(6(1 - \theta_m)\delta)/(\theta_m d_n)]} + \frac{(d_n v_m)^2 F^2 \varepsilon \theta_i}{36 D_0 (1 - \theta_m) [1 + F(\theta_i)/(\theta_m)]^2} + \frac{(d_n v_m)^2 F \theta_i T_i}{60 D_0 \theta_m [1 + F(\theta_i)/(\theta_m)]^2} \quad (3.27)$$

where the four terms account for axial diffusion, hydrodynamic dispersion, film diffusion, and intra-particle diffusion, respectively, and where δ is the thickness of the stagnant water film surrounding the particles [L], ε is the porosity of the particles, d_n [L] is the nominal particle diameter, T_p is the tortuosity factor (interparticle), T_i is the intraparticle tortuosity factor, θ_m [$L^3 L^{-3}$] is the volumetric water content of the mobile domain, θ_i [$L^3 L^{-3}$] is the volumetric water content of the immobile domain (intraparticle), F is the fraction of the intraparticle porosity accessible by the solute, and v_m is the pore water velocity (J_w/θ_m).

Also, a *lumped* or apparent dispersivity (λ^*) could be defined as:

$$D^* = \lambda^* v_m \quad (3.28)$$

Dependence of the axial diffusion [i.e., the first term of Eq. (3.27)] with soil volumetric water content can be described through a dependence of the tortuosity factors on water contents (Bear, 1972; Šimůnek et al., 1999):

$$T_p = \frac{\theta^{7/3}}{\theta_s^2} \quad (3.29)$$

where θ and θ_s are the actual and the saturated volumetric water contents, respectively. Alternatively, Vanclouster et al. (1996) used an equation previously introduced by Kemper and Van Schaik (1966) to estimate the effective diffusion coefficient from the chemical diffusion coefficient [first term in Eq. (3.27)] and the following tortuosity factor:

$$T_p = \frac{\theta_m}{\alpha e^{b\theta_m}} \quad (3.30)$$

However, Beven et al. (1993) reported differences in dispersivities and effective dispersion coefficients of more than four orders of magnitude, which reveals a tremendous difficulty in characterizing dispersion as a macroscopic (effective) process. It is not surprising, then, that several authors have suggested omitting the modeling of physical dispersion when using numerical methods with numerical dispersion in the solution. Bresler et al. (1982), when discussing the salt dynamics and distribution in fallow soils, observed that salt distribution profiles computed using both physical and numerical dispersion terms were similar to the profiles obtained by the numerical solution from an expression in which the dispersion terms were omitted. Analogous observations were made by García-Delgado et al. (1997). The role of dispersion in stochastic models has also been the focus of much discussion. For example, Isabel and Villeneuve (1991) observed that the dispersion coefficient had little influence on a stochastic convection-dispersion model. They found, through a set of numerical simulations, that the stochastic convection model produced numerically equivalent results under most soil conditions. Thus, the stochastic convection model was proposed to replace the stochastic convection-dispersion conceptualization in the modeling of solute transport at the field scale. Zhang et al. (1996) compared stochastic and deterministic models to simulate solute transport through the vadose zone at the field scale. Comparison of the simulation results with field data showed that the models described the mean concentration reasonably well without considering the pore scale dispersivity. However, the pore scale dispersivity had a significant impact on the estimation of the concentration variance. This will therefore have important consequences when predicting leaching fluxes, especially for trace elements. Indeed, at low concentration levels, fluxes will be extremely sensitive to variance of the resident concentration profile and therefore to the dispersion parameters. This is a serious point of concern when predicting, for instance, pesticide leaching in soils at the ppm level (Boesten, 2004).

3.4.4 SORPTION

The degree of accuracy required in the characterization of the sorption processes is dependent upon its interaction with other soil-solute processes. Among them, the most important processes are solute transformations (e.g., degradation) and volatilization (or other distribution between physical phases). The characterization of sorption is discussed in Chapter 12. Conceptual description of sorption requires accounting for kinetics and equilibrium, although the most simplistic assumption assumes only a conceptual model for equilibrium, e.g., the Freundlich model (Table 3.3).

A useful simplifying assumption of the Freundlich equation is given by isotherm linearity ($N_f = 1$, linear isotherm). The first concern, as stated before, is the role of kinetics in the scenario in which sorption processes take place, as equilibrium rarely, if ever, occurs in soil-solute experiments. A more accurate

TABLE 3.3
Equilibrium Isotherms Used for Characterizing Sorption Processes in Soil and Corresponding Description of Hysteresis for the Desorption Process*

Isotherm	Equation	Parameters	Hysteresis
Linear	$C_s = K_D C_e$	K_D	
Langmuir	$C_s = \frac{c_m K_l C_e}{1 + K_l C_e}$	c_m, K_l	
Freundlich	$C_s = K_f C_e^{N_f}$	K_f, N_f	$\frac{N_{f,ads}}{N_{f,des}} = a + b C_{s,max}^c$ (van Genuchten et al., 1974)
Modified Langmuir model	$C_s = \frac{c_m K_g e^{-2bC_e} C_e}{K_l e^{-2bC_e} C_e + (C_e/C_{me})^h}$ (Gu et al., 1994; Cartón et al., 1997)	K_l, c_m, b, h	C_{me}, h

* C_s : solute concentration in the sorbed phase; C_e : Solute concentration at equilibrium in the dissolved phase; K_D, K_f, K_l, K_g : equilibrium constants (for a given temperature); N_f : nonlinearity parameter of the Freundlich isotherm; $C_{s,max}$: maximum adsorbed concentration; C_{me} : equilibrium adsorbate concentration after adsorption; h : hysteresis coefficient ($h=0$ for complete reversibility). c_m, a, b, c : isotherm parameters. The subscripts *ads* and *des* represent adsorption and desorption, respectively.

description of sorption would include a hysteresis effect, as represented in Figure 3.4.

Rambow and Lennartz (1994) evaluated the effect of different degrees of complexity for describing herbicide sorption in the estimation of leaching. Total atrazine discharge calculated with the linear isotherm was approximately three times larger than for the Freundlich and for the hysteresis version. These results demonstrate that careful consideration of the applied sorption-desorption assumptions must be taken when assessing the transport of chemicals in soils. Koskinen et al. (1979) and Brusseau and Rao (1989) suggested several possible mechanisms responsible for hysteresis: chemical precipitation, variation of the binding mechanism with time, incorporation of the solute into the soil matrix, and physical trapping. Also, several experimental artifacts can generate an "apparent hysteresis effect."

A higher degree of complexity for the description of sorption is given by considering temperature effects on sorption isotherm. Sorption is an exothermic process, and, depending on the magnitude of the sorption enthalpies, a decrease in sorption with temperature occurs. For example, Koskinen and Cheng (1983) and Cartón et al. (1997) found that low-magnitude values of the isosteric heats of adsorption revealed a slight increase in adsorption as temperature decreased. Finally, the effect of competitive solutes (co-solutes) in scenarios where competitive sorption could occur could be included in more complex descriptions of sorption.

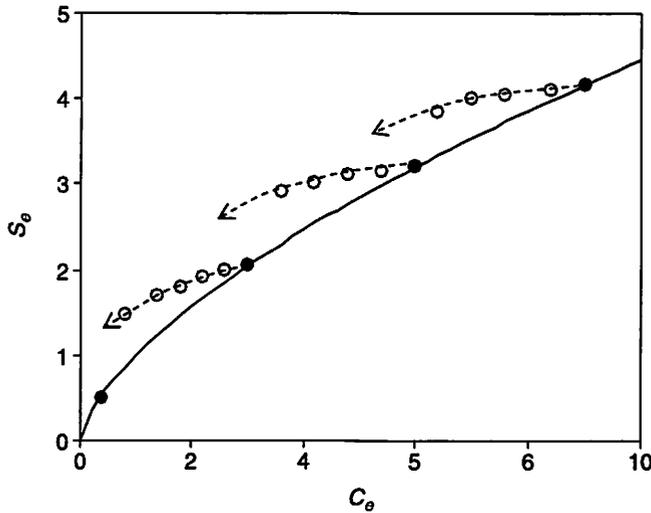


FIGURE 3.4 Sorption-desorption equilibrium for the dissolved (C_e) and sorbed (S_e) solute concentrations in the presence of a hysteresis effect. Solid circles represent the sorption equilibrium points. Empty circles represent the desorption equilibrium starting from different initial concentrations at equilibrium.

3.4.5 VOLATILIZATION AND GAS SOLUBILITY

Volatilization and gas solubility can be conceptualized as solute exchanges from the liquid to the gas phase (volatilization) or vice versa (gas solubility), which take place in the bulk soil. This phenomenon should be taken into account when the process of solute transport in the gaseous phase is considered. Henry's law describes the distribution of a chemical between gaseous and liquid phases at equilibrium:

$$K_H = \frac{c_a}{c_w} \quad (3.31)$$

where K_H is the distribution coefficient (Henry's constant) and c_a and c_w are the concentrations of the solute in air and water, respectively. A similar expression could be used to represent solid and gas. Henry's law can be expressed in terms of partial pressure of the chemical in the gaseous phase (p_a):

$$K_H^p = \frac{p_a}{c_w} \quad (3.32)$$

The equivalence between the two expressions is given by:

$$K_H = \frac{K_H^p}{RT} \quad (3.33)$$

where R is the gas constant [8.3 kJ/mol $^{\circ}$ K] and T [K] is temperature. Care must be taken, because sometimes Henry's law is expressed in terms of gas solubility instead of solute volatility, and thus Eq. (3.33) is inverted (i.e., expressed as a ratio of water concentrations divided by air concentrations or partial pressures). Henry's law assumes equilibrium and is therefore applicable only at small scales under laboratory-controlled conditions. K_H increases with increasing temperature (Bamford et al., 1999). A simple description of temperature dependence is given by Sander (1999):

$$K_H = K_H^{ref} \left[\exp \left(\frac{\Delta H_{soln}}{R} \left(\frac{1}{T} - \frac{1}{T^{ref}} \right) \right) \right]^{-1} \quad (3.34)$$

where ΔH_{soln} is the enthalpy of solution.

Volatilization processes can be studied in chambers at laboratory scale under controlled conditions of temperature, wind speed, and air humidity. In these scenarios, volatilization and sorption processes are two dominating processes that can be described with a conceptual coupled model (Álvarez-Benedí et al., 1999). Although sorption-desorption processes and volatilization can be described with equilibrium equations as given by the sorption isotherm and Henry's law, kinetics or mass transfer equations should be used to account for the limited availability of the desorbed chemical as well as the volatilization rate. Thus, the boundary condition at the soil surface can be described by a mass-transfer equation:

$$J_o = -k_{am}(c_{am} - c_g) \Big|_{z=0} \quad (3.35)$$

where J_o [M L $^{-2}$ T $^{-1}$] is the solute flux to the atmosphere, k_{am} is a mass transfer coefficient analogous to the one used in water evaporation (Brussaert, 1975), and c_{am} is the solute concentration in the atmosphere (which can be assumed negligible in certain experimental conditions, such as wind tunnels with an external input air stream). The mass balance for a sorbed solute in soil under volatilization, considering $c_{am} = 0$, could be written as:

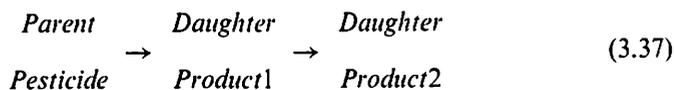
$$\theta \frac{\partial c}{\partial t} + \rho \frac{\partial s}{\partial t} = -k_{am}\theta c \quad (3.36)$$

A major disadvantage of this formulation is the strong dependence of the kinetics constant k_{am} with experimental conditions. The above conceptualization is very useful for characterizing the sorption-volatilization coupled processes at the laboratory scale, as a tool to study the kinetics and reversibility of sorption-desorption processes, and also to quantify the relative importance of volatilization under varying conditions of soil and air humidity and temperature. However, at larger scales and considering field environments, there are several experimental variables with simultaneous influence on volatilization that further complicate the process.

Most techniques for characterizing the gas exchange at the soil surface can be categorized using a soil mass balance, chambers, or micrometeorological methods. Chapter 13 studies the application of an appropriate methodology taking into account the availability of equipment, sample analysis capacity, resolution of sensors over the sampling period, treatment plot size or sampling interval. Micrometeorological techniques employ a combination of atmospheric turbulence theory and measurement to estimate gas flux to or from a surface. These techniques allow near-continuous flux estimates; some techniques also allow temporal averaging through sampling accumulation. Micrometeorological techniques can accommodate a wide range of plot sizes. The aerodynamic technique consists of the measurement of gas concentration and wind speed at two (or more) different heights. Other approaches reviewed in Chapter 13 are the Bowen ratio–energy balance technique (which does not require a wind speed profile) and other available alternatives based on different conceptual models and measurement strategies.

3.4.6 TRANSFORMATION

Despite the enormous variety of different possible solute transformations, the strategy of characterization follows the same methodological objectives, which consist of the estimation of the reaction pathways and rates of transformation (kinetics) for each solute studied. First, reaction pathways must be known. Second, data on solute concentrations for each chemical species must be determined with time in order to finally define a kinetics conceptual model. Concentration-time relationships can be obtained in incubation studies by chemical analysis or using radiolabeled compounds. For example, pesticide transformations can be represented as a simple linear pathway (Wagenet and Hutson, 1987):



Note that each of the above chemical species can be involved in sorption and volatilization processes. Thus, it is important to simplify the transformation scheme as much as possible when working with field scenarios. Again, a trade-off between the degree of the complexity of description and the needs for data must be achieved in order to finally select a reasonable conceptual model and the corresponding sampling strategy.

Most of the chemical and physically mediated transformation processes can be well described by zero- or first-order kinetics. Rate equations for these processes have been summarized in Table 3.1. Microbial mediated processes, however, present a more complex component in which microbial biomass and activity can require a higher degree of description complexity. In this case, the rate constants are a function of microbial biomass and activity, and these in turn are a function of several additional environmental factors such as

soil water content, temperature, aeration, pH, substrate availability, etc. Hence, it is important to have a conceptual model for microbial growth, maintenance, and decay (Starr, 1983). If a population of microorganisms uses a compound as its source of energy (and C), its population will be dependent on substrate concentration. At low concentrations the growth rate of the microorganisms would be slow because it is limited by the availability of substrate. Conversely, the growth rate will increase with concentration until a maximum level of growth is achieved. This conceptualization was formulated by Monod (1949):

$$\mu_g = \frac{\mu_{max}c}{K_C + c} \quad (3.38)$$

where μ_g is the specific growth rate [$M T^{-1}$] of the bacterium, μ_{max} is the maximum growth rate [$M T^{-1}$], c is the substrate concentration [$M L^{-3}$], and K_C [$M L^{-3}$] is a constant representing the substrate concentration at $\mu = \mu_{max}/2$.

In general, the rate that a given substrate c is utilized by microorganisms in soil can be described as (McLaren, 1973):

$$\frac{\partial c}{\partial t} = -A \frac{dm}{dt} - \alpha_b m - \beta_b m \quad (3.39)$$

where m is the biomass of the microbes [M] and A [L^{-3}], α_b [$L^{-3} T^{-1}$], and β_b [$L^{-3} T^{-1}$] are coefficients related to growth, maintenance and waste, respectively. If a steady state is assumed and the biomass m is constant, the expression may reduce to the Michaelis-Menten rate:

$$\frac{\partial c}{\partial t} = -\frac{kmc}{K + c} \quad (3.40)$$

where k and K are the Michaelis-Menten rate constants. Note that $K \gg C$ gives a first-order kinetics and $K \ll c$ is equivalent to a zero-order kinetics. As stated by Starr (1983), a major factor limiting the use of such conceptual models in the field is the lack of input data.

Some examples of the above-mentioned concepts are given below. Estrella et al. (1993) applied a nonlinear regression analysis of the simultaneous solution of the Monod equation for growth of cell mass (X), substrate utilization, and CO_2 production:

$$\begin{aligned} \frac{\partial X}{\partial t} &= \mu_m \cdot \frac{XC}{K_{hs} + C} - k_{dr}X \\ \frac{\partial C}{\partial t} &= -\frac{1}{Y} \cdot \mu_m \cdot \frac{XC}{K_{hs} + C} \\ \frac{\partial CO_2}{\partial t} &= Y_{CO_2\text{substrate}} \left(-\frac{\partial C}{\partial t} \right) + Y_{CO_2\text{endogenous}} k_{dr}X \end{aligned} \quad (3.41)$$

where X is the cell mass concentration, t is time, C is the solution phase concentration of substrate, μ_m is the maximum specific growth rate, K_{hs} is the half-saturation constant, k_{dr} is the cell death rate coefficient, Y is the cell mass yield from substrate degradation, $Y_{CO_2\text{substrate}}$ is the CO_2 mass yield from substrate degradation, and $Y_{CO_2\text{endogenous}}$ is the CO_2 mass yield from endogenous decay of cells.

The complexity level of the selected transformation model will strongly depend on the desired level of explanation. For describing nitrogen turnover in soil for instance, a simple first-order decay model might give a good description of the mineralization processes shortly after the addition of organic matter. However, this model might fail to describe the long-term mineralization process involving decomposition of the organic matter fractions (Vanclooster et al., 1996). On the other hand, a more detailed description reduces the applicability for extrapolation purposes and requires a greater experimental effort for characterization. A long-term approach for nitrogen transformations and resulting mineralization of organic carbon was developed by Johnsson et al. (1987). The conceptualization is based on a three-pool concept, which consists of (1) organic matter/microbial biomass complex (soil litter pool), (2) receiving fresh organic matter, and (3) slow cycling pool of stabilized decomposed products (soil humus pool). This representation was used by Vereecken et al. (1990, 1991) and was further included in the WAVE model (Vanclooster et al. 1996).

In conclusion, each microbiological transformation scenario should be characterized with a particular degree of description complexity. The fundamental aspects related to the characterization of soil microbiological processes are reviewed in Chapter 15, including methods for soil microbial characterization, sampling, soil handling, and choice of methods.

3.5 MODELING SOIL PROCESSES

3.5.1 BUILDING SOIL PROCESS MODELS

The construction of more complete models is generally based on the above equations, which can be considered "pieces" for more sophisticated conceptualization. The simplest case would be an equilibrium description for solute sorption, in which the solute concentrations at equilibrium in the dissolved (C_e) and sorbed (S_e) phases are related through a sorption isotherm. This model can be represented by two boxes for C_e and S_e , respectively, and an equilibrium relationship between them (Figure 3.5). The equilibrium could be given by any of the equations presented in Table 3.3. Similarly, a rate-limited reversible sorption is described by a kinetic model considering the rate of approach towards equilibrium between C_e and S_e (e.g., Hornsby and Davidson, 1973). In this case, a double arrow in Figure 3.5 represents the reversible kinetics process.

The two-region model considers mass transfer between two flow domains (mobile with a solute concentration C_m , and immobile with a solute

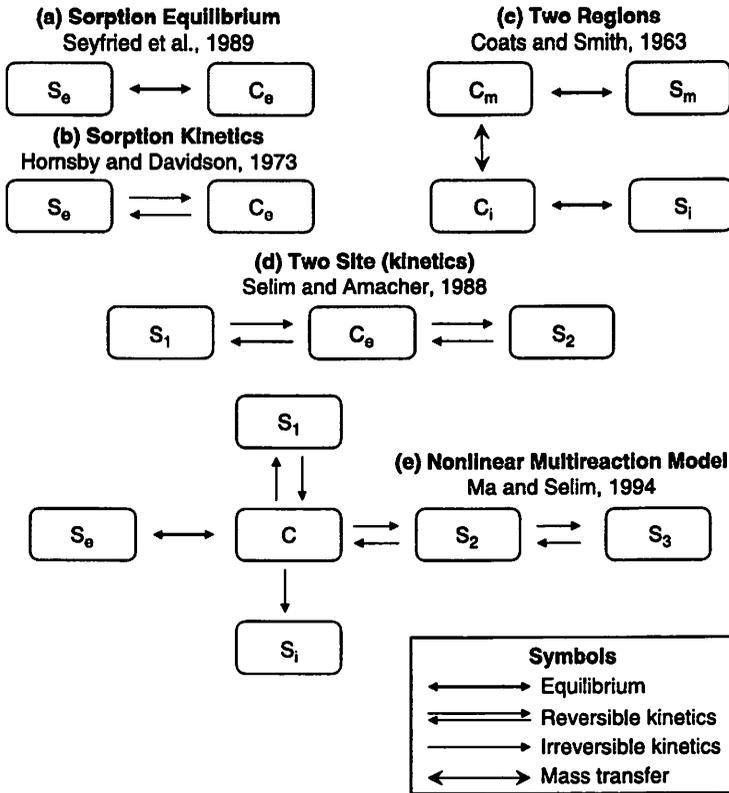


FIGURE 3.5 Schematic of some conceptual models for sorption processes: (a) sorption equilibrium (Seyfried et al., 1989); (b) sorption kinetics (Hornsby and Davidson, 1973); (c) two region (Coats and Smith, 1963); (d) two site (kinetics) (Selim and Amacher, 1988); (e) nonlinear multireaction model (Ma and Selim, 1994).

concentration C_{im}), where both domains are assumed to have the same retention mechanism (e.g., Coats and Smith, 1963). This conceptualization requires four boxes: mobile and immobile concentrations of sorbed and dissolved solutes, a mass transfer relationship between dissolved mobile and immobile solute, and sorption equilibrium for relating sorbed and dissolved solute amounts (Figure 3.5c). A two-site kinetic sorption model considering different rate-limited sorption with soil sites of type I and II (Selim and Amacher, 1988) is also depicted in Figure 3.5d. Brusseu et al. (1989) developed a transport model including two reversible kinetics, two irreversible kinetics, and a mass transfer between six different domains. An alternative generalized multireaction model was also described by Ma and Selim (1998), which considers five possible processes (Figure 3.5e). Depending on the purpose of a specific study and/or the data available, the appropriate process can be selected.

3.5.2 INVERSE CHARACTERIZATION OF SOIL PROCESSES

If a particular soil process can be described by a particular forward simulation model, then inverse methods can be used to characterize the soil process properties. Inverse methods are now becoming popular tools to identify the soil flow and transport properties. For example, Dane and Hruska (1983) used a numerical solution of Richards' equation assuming the equations of van Genuchten (1980) for $\theta(\psi)$ and $K(\psi)$. The solution was optimized to find α and n in these equations. This procedure was also applied in layered soils by Lambot et al. (2002), and Ritter et al. (2003, 2004) comparing several methodological approaches for characterizing hydraulic parameters in a layered soil.

The required premises to apply the inverse estimation are identifiability and uniqueness. Different parameter sets must lead to different solutions. If not, the parameters are unidentifiable. Additionally, nonuniqueness appears when one parameter set results in more than one solution. Care must also be taken with the simultaneous optimization of several model parameters of a physically based model as the curve can be fitted by a set of parameters that do not correspond with the true set (global minimum). In such a case, the model parameters are no longer representing the physics of the soil system. For example, the use of single parameter model to systems affected by at least more than one parameter will yield a lumped empirical single parameter. The single parameter in this case will only be valid for that specific situation. For instance, this is the case when fitting the governing ADE solute transport model with local equilibrium assumption to data from transport experiments affected by nonequilibrium flow. In this case the dispersion parameter will be a lumped parameter encompassing some of the terms of Eq. (3.26). The apparent hydrodynamic dispersivity inferred from such an experiment is not necessarily a measure of the microscopic variability of the flow field in the soil matrix.

Additional problems occur when parameters are correlated. For example, the parameters of the nonequilibrium two-region model are often strongly interdependent. This strong correlation between parameters implies that changes in one parameter can be compensated by corresponding changes in the correlated parameter. Thus, a simultaneous optimization of all of the model parameters will result in "shape parameter values" without a physical plausibility (Koch and Flühler, 1993).

Chapter 20 presents a general discussion on the use of a inverse estimation methodology. The application of inverse techniques to estimate hydraulic properties are discussed in Chapter 5, and Chapter 11 shows the application to estimate solute transport properties.

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NOTATION

c	Concentration (dissolved phase) [M L ⁻³]
c_A, c_B	Concentration of reactant and products [M L ⁻³]
c_i, c_{ii}	Concentration of a partitioning solute in phases I and II [M L ⁻³]
c_a, c_w	Concentration of a volatile solute in air and water [M L ⁻³]
c_I, c_{II}	Concentrations in phases or region I and II, respectively [M L ⁻³]
C_I, C_{II}	Dimensionless concentration in regions I and II ($C_I = c_I/c_0$, $C_{II} = c_{II}/c_0$) [-]
c_m, c_{im}	Resident concentration in the mobile and immobile regions [M L ⁻³]
c_0	Characteristic concentration [M L ⁻³]
c_T	Total mass of solute [ML ⁻³]
$C(\psi)$	Hydraulic capacity function [L ⁻¹]
D	Effective dispersion coefficient [L ² T ⁻¹]
H	Hydraulic head [L]
F	Fraction of the intraparticle porosity accessible by the solute [-]
J_c	Convective mass flux ($J_c = J_w C$) [M L ⁻² T ⁻¹]
J_D	Dispersive mass flux [M L ⁻² T ⁻¹].
J_o	Solute flux of a volatile compound to the atmosphere [M L ⁻² T ⁻¹]
J_w	Water flux [LT ⁻¹]
J_S	Total mass flow in the liquid phase [M L ⁻² T ⁻¹]
k_0	Zero-order rate parameter [M L ⁻³ T ⁻¹]
k_1	First-order kinetics constant [T ⁻¹]
k_{ads}	Rate parameters for the sorption reaction [T ⁻¹]
k_{des}	Rate parameters for the desorption reaction [T ⁻¹]
K	Unsaturated hydraulic conductivity [LT ⁻¹]
K_D	Distribution or partition coefficient
K_H	Henry's distribution coefficient
L	Characteristic length [L]
P	Peclet (vL/D) [-]
R	Retardation factor [-]
s	Concentration in the sorbed phase [M M ⁻¹]
t	Time [T]
T	Number of pore volumes (vt/L)
T_p	Tortuosity factor [-]
$t_{1/2}$	Half-life [T]
x	Distance [L]
X	Dimensionless distance ($X = x/L$) [-]
z	Depth [L]

GREEK

Γ	Solute sink/source term [M L ⁻³ T ⁻¹]
α	Mass transfer coefficient [T ⁻¹]

δ	Thickness of the stagnant water film surrounding (soil) particles [L]
ε	Porosity of the particles [-]
λ	Dispersivity [L]
μ	First-order rate degradation coefficient [T^{-1}]
v_m	Pore water velocity of the mobile region ($v_m = J_w/\theta_m$) [$L T^{-1}$]
v	Average linear velocity ($v = J_w/\theta$) [$L T^{-1}$]
θ	Soil volumetric water content [$L^3 L^{-3}$]
θ_m	Volumetric water content of the mobile domain [$L^3 L^{-3}$]
θ_i	Volumetric water content of the immobile domain [$L^3 L^{-3}$]
ρ	Bulk density of soil [$M L^{-3}$]
τ	Apparent tortuosity factor $\tau = (L/L_{dif})^2$ [-]
ψ	Pressure or suction head [L]
$\zeta(\theta)$	Hydraulic diffusivity function [$L^2 T^{-1}$]
[-]	Dimensionless

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