

# Miscible displacement in Porous Media: Theoretical Evaluation

M. K. Shukla, S. Klepsch and W. Loiskandl

## Theorie des Transports gelöster Substanzen im porösen Medium

### 1. Introduction

Miscible displacement is a process that occurs when one fluid mixes with and displaces another fluid. The complex pore geometry of soils makes the mathematical conceptualization of solute transport phenomenon at the microscopic or at an individual pore level difficult (JURY and FLÜHLER, 1992). Hence most mathematical models have been developed for a macroscopic description of solute transport. The convective-dispersive transport equation remains the foundation upon which several analysis of solute transport in porous media

have been based. At the same time questions have also been raised on the suitability of this equation to porous media exhibiting large variations in pore water velocities due to the presence of continuous macropores or by field scale variability of soil hydrological properties (VAN GENUCHTEN and WIERENGA, 1976). Under certain limiting conditions (i. e., for low apparent dispersivities) all solutions of the classical convection dispersion equation yield symmetrical concentration distributions in time and space. However several experiments conducted with aggregated or fractured porous media have yielded asymmetrical spatial and temporal concentra-

### Zusammenfassung

Die mathematische Formulierung von Stofftransportprozessen auf mikroskopischer Ebene, d. h. innerhalb einer Pore, ist wegen der komplexen Porengeometrie von Böden äußerst schwierig. Deswegen werden die meisten Modelle auf makroskopischer Ebene unter Einführung einer mittleren Porenwassergeschwindigkeit für konvektive Strömung und eines Diffusions-Dispersionskoeffizienten entwickelt. Die Unterscheidung der Dispersion eines gelösten Stoffes innerhalb einer Kapillare konstanten Durchmessers durch molekulare Diffusion von der Dispersion durch Geschwindigkeitsvariationen wurde erstmals von TAYLOR (1953) vollzogen. SCHEIDEGGER (1954) u. a. verwendeten eine stochastische „random walk“ Methode, um den Transport im gesättigten homogenen, isotropen porösen Medium zu beschreiben. Die Kapillarmodelle konnten durch das Konzept des repräsentativen Elementarvolumens physikalisch realistischer erklärt werden. RIFAI et al. (1956) und EINSTEIN (1937) entwickelten unter der Annahme, daß Flüssigkeit ein kontinuierliches Medium ist und jeder Punkt einer Bahnlinie zugeordnet werden kann, ein stochastisches Modell, welches den Transport sowohl in einer Phase mit konvektiver Bewegung als auch in einer Phase im Ruhezustand beschreibt. Die klassische Konvektions-Dispersionsgleichung wurde von LAPIDUS und AMUNDSON (1952) vorgeschlagen, welche später mit einigen komplizierteren Gleichgewichts- und Nichtgleichgewichtsprozessen erweitert wurde (NIELSEN et al., 1986; VAN GENUCHTEN and WIERENGA, 1976; SELIM et al., 1976; CAMERON and KLUTE; 1977, KRUPP et al., 1972 etc.). Im vorliegenden Artikel sind einige mathematische Gleichgewichts- sowie Nichtgleichgewichtsmodelle zusammen mit den analytischen Lösungen bei verschiedenen Anfangs- und Randbedingungen sowohl für kontinuierliche als auch „pulse type“ Tracerapplikationen beschrieben. Ebenfalls aufgelistet sind dimensionslose Parameter. Die „two site“, „one site“, „two region“ und Anionenausschluß-Modelle wurden unter Berücksichtigung der Nichtgleichgewichtsprozesse in einer dimensionslosen Gleichung zusammengefaßt. Weiters sind einige Softwareprodukte für ein-, zwei- und dreidimensionalen Stofftransport angeführt. Verschiedene Adsorptionstheorien, die in diesen Modellen implementiert sind, werden ebenfalls erklärt. Zuletzt wird eine iterative Lösung präsentiert, die zur Verifikation der in diversen Modellen inkludierten Adsorptionisothermen dienen kann, wenn der source code nicht zur Verfügung steht.

**Schlagnworte:** Stofftransport, Durchbruchskurven, poröses Medium, Porenwassergeschwindigkeit, Gleichgewichts-, Nichtgleichgewichtsprozesse, Adsorption.

### Summary

Mathematical conceptualization of the solute transport phenomenon at the microscopic level i. e. at an individual pore, is difficult because of the complex pore geometry of soils. Hence most models are developed at macroscopic level using an average pore water velocity for convective flow and a diffusion-dispersion coefficient. The insights into separate dispersion of a solute within a capillary of constant diameter caused by molecular diffusion from that by velocity distribution was first provided by TAYLOR (1953). Using statistical concepts, SCHEIDEGGER (1954) and others have assumed a simple random walk stochastic process to describe transport in a fluid saturated homogeneous, isotropic porous medium. Using the representative elementary volume concept, the random capillary models were made physically more realistic. Assuming fluid is a continuous medium and each point has a flow path RIFAI et al. (1956) and EINSTEIN (1937) developed a stochastic model which accounts for displacement for motion and rest phases. The classical convective dispersion equation was proposed by LAPIDUS and AMUNDSON (1952) which was later extended to include several complicated equilibrium and nonequilibrium processes (NIELSEN et al., 1986; VAN GENUCHTEN and WIERENGA, 1976; SELIM et al., 1976; CAMERON and KLUTE; 1977, KRUPP et al., 1972 etc.). In this paper several equilibrium and nonequilibrium mathematical models are described along with their analytical solutions for various initial and boundary conditions for both continuous and pulse type tracer application. The nondimensional parameters are also given in this paper. The nonequilibrium two site, one site, two region and anion exclusion models have also been combined into one nondimensional equation taking into account all the nonequilibrium processes. The paper further describes some of the commercially available software describing solute transport. The software described in the paper include one, two and three dimensional solute transport through porous media using either analytical or numerical solution of the problem. The various adsorption isotherms which could be employed in these models are also included in the paper. At the end an iterative solution is presented which is helpful to verify some of the models in case source code is not available.

**Key Words:** Miscible displacement, breakthrough curves, porous media, pore water velocity, equilibrium, nonequilibrium, adsorption.

tion distributions with first moments significantly different compared with those anticipated for symmetrical distributions. A rapid breakthrough in laboratory soil columns is observed with such media, apparently because a large portion of pore space is by passed, which results in the discrepancy between effluent concentration and volume averaged resident pore fluid concentration in the vicinity of exit boundary (PARKER and VAN GENUCHTEN, 1984).

As solute transport in soil and groundwater systems is governed by a large number of complicated and often interactive physical, chemical, and microbiological processes several transport models have been developed which consider simultaneous effects of diffusion, dispersion, convection, sorption, production and decay (JURY et al., 1991). Miscible transport in the soil system does not always remain in equilibrium, the presence of different types of sorption sites or flow regions results in nonequilibrium. The nonequilibrium models are grouped into physical nonequilibrium models which presume that nonequilibrium results from a heterogeneous flow regime and chemical nonequilibrium

models which presume that it is due to chemical-kinetic processes. Physical nonequilibrium is often modeled by a two-region (dual-porosity) type formation which partitions the medium into mobile and immobile liquid regions (VAN GENUCHTEN and WIERENGA, 1976). The solute exchange between the two regions is considered to be a first order mass transfer process. In this case transfer between the two liquid regions presumably a diffusion process is proportional to the concentration gradient between mobile and immobile regions. Chemical nonequilibrium models include the one site and two site sorption models which consider sorption on some sites to be an instantaneous equilibrium process, while sorption on the remaining sites is considered to be governed by first order kinetics (SELIM et al., 1976; CAMERON and KLUTE, 1977). Transport in soils with bimodel and/or dual porosity which describes the preferential flow in this pore size distribution was described by GERKE and VAN GENUCHTEN (1993).

Currently numerous analytical solutions for one dimensional equilibrium and nonequilibrium transport are exist-

ing. Most of them are for unique initial and boundary conditions. A comprehensive set of analytical solutions for the one dimensional convective dispersive solute transport equation is presented by VAN GENUCHTEN and ALVES (1982). Analytical solutions for one dimensional nonequilibrium transport were first derived by LINDSTROM and NARASIMHAN (1973) and LINDSTROM and STONE (1974) for one site formation without considering first order degradation and zero order production. LINDSTROM (1976) later extended these solutions to first order decay for pulse type of input assuming an initially solute free profile. VAN GENUCHTEN and WIERENGA (1976) derived the analytical solutions for two region nonequilibrium transport for pulse type of input. DE SMEDT and WIERENGA (1979) later generalized these solutions. Several other analytical solutions were derived considering two region or two site formations with and without the consideration for first order decay and zero order production terms (VAN GENUCHTEN et al., 1974; SELIM et al., 1976; CAMERON and KLUTE, 1977; TORIDE et al., 1993; etc.). In this paper several analytical and numerical mathematical concepts and software for describing solute transport through porous media are compiled to provide the reader with a comprehensive overview of modelling approaches. Dimensional and nondimensional parameters of these solute transport models along with several boundary and initially conditions are also included. Various adsorption isotherms which could be incorporated in these models are described as well. A simple zero-dimensional approach to explain an iterative solution strategy or to verify some of the presented models when the source code is not available is also included in this paper.

## 2. Dimensional Deterministic Solute Transport Models

### 2.1 Equilibrium Transport Models

TAYLOR (1953) presented a model for solute movement through a single capillary tube of constant radius  $a$ , using the parabolic formula for laminar flow, when the invading fluid moves at constant average velocity,  $v_0$

$$v = 2v_0\left(1 - \frac{r^2}{a^2}\right) \quad (1)$$

In the above equation  $v$  is the velocity at the radial distance  $r$  from the center of the capillary tube and the velocity at the axis is  $2v_0$ . Following equation combines dispersion due to

velocity distribution and to molecular diffusion when diffusion coefficient  $D$  is assumed constant

$$D\left(\frac{\partial^2 C}{\partial x^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2}\right) = \frac{\partial C}{\partial t} + 2v_0\left(1 - \frac{r^2}{a^2}\right) \frac{\partial C}{\partial x} \quad (2)$$

where  $C$  is the concentration of invading fluid and  $x$  is the distance along the capillary tube. TAYLOR (1953) has given the solution of this equation assuming that longitudinal molecular diffusion is negligible compared to the radial diffusion. According to NIELSEN and BIGGAR (1962), capillary models fail to describe the miscible displacement because soil pore sequences are neither cylindrical nor constant in diameter. At the same time a mathematical solution exactly describing the solute dispersion through an exactly known complex pore geometry will not be possible. A statistical description of solute transport through porous medium disregarding the actual flow path and physical properties of fluid was proposed by SCHEIDEGGER (1954), BERAN (1955) and DAY (1956). This model assumed that the solute transfer is taking place as a result of hydrodynamic mechanism not involving molecular diffusion. Displacement was treated as random walk process and using central limit theorem the probability function of displacement was found to be normal with variance proportional to time. Upon integration the following solute transport equation was obtained

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc}\left(\frac{x - vt}{\sqrt{4Dt}}\right) \quad (3)$$

where  $C_0$  is concentration of displacing solution,  $x$  is the distance,  $v$  is average pore water velocity,  $t$  is time and  $D$  is factor of dispersion. The drawback with this equation is that at  $x = vt$ ,  $C/C_0$  always comes out to be half, which is practically not correct (NIELSEN and BIGGAR, 1962). A stochastic model which does not have this drawback was proposed by RIFAI et al. (1956) and EINSTEIN (1937). This model assumes that fluid is a continuous medium and each point has a flow path. The fluid moves as piston flow and displacement is divided into two phases, motion and rest phase. Time in motion phase is assumed small compared to rest phase and probability of occurrence of rest phase is considered independent of time and position. The concentration distribution for this model is given by

$$\frac{C}{C_0} = \frac{v^2}{D} \int_0^t \exp\left(-\frac{x + vt}{D/v}\right) I_0\left(\frac{2v}{D} \sqrt{xvt}\right) dt \quad (4)$$

Owing to the assumption that rest phase times are much greater than motion phase times, this equation fails to describe miscible displacement for  $vx/D < 10$ .

Following differential equation describing the solute transport for a constant molecular diffusivity  $D$  for a given porosity and average flow velocity was given by LAPIDUS and AMUNDSON (1952)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (5)$$

This equation does not consider adsorption or solute interaction with solid phase as well as chemical or biological reactions. The comprehensive miscible displacement equation for those solutes whose vapor phase is negligible was given by BIGGAR and NIELSEN (1967)

$$\frac{\partial}{\partial t}(\rho_b C_a + \theta C_l) = \frac{\partial}{\partial z}(D_e \frac{\partial C_l}{\partial z}) - \frac{\partial}{\partial z}(J_w C_l) - r_s \quad (6)$$

where  $\rho_b$  is the bulk density of soil,  $\theta$  is the volumetric water content,  $C_l$  and  $C_a$  are dissolved and adsorbed solute concentrations,  $D_e$  is the effective diffusion-dispersion coefficient,  $J_w$  is the water flux,  $r_s$  is the reaction term,  $t$  is time and  $z$  is depth.

One additional term is added to equation (5) when chemical adsorption which accounts for the interaction between the chemical and solid phase is also considered. Following is the one dimensional solute transport equation describing transport through a homogeneous medium during steady state flow with adsorption

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (7)$$

where  $S$  is the adsorbed concentration ( $MM^{-1}$ ). The solution of above equation depends upon the knowledge of the relationship between adsorbed concentrations,  $S$ , and the solution concentration,  $C$ . Adsorption or exchange reactions perceived as instantaneous are described by equilibrium isotherms  $S(C)$ , which can be of the mass action, linear, Freundlich, Langmuir or any other functional form (NIELSEN et al., 1986). Besides adsorption, the reactive process such as first-order degradation or zero-order production can also be taken into account during miscible displacement processes. Therefore, the comprehensive convection-dispersion equation (CDE) for one dimensional transport of reactive solutes, subject to adsorption, first-order degradation, and zero order production, in a homogeneous soil, is written as

$$\frac{\partial}{\partial t}(aC_g + \theta C_r + \rho_b S) = \frac{\partial}{\partial x} \left( \theta D_g \frac{\partial C_g}{\partial x} + \theta D \frac{\partial C_r}{\partial x} - J_w C \right) \quad (8)$$

$$- \theta \mu_l C_r - \rho_b \mu_s S + \theta \gamma_l(x) + \rho_b \gamma_s(x)$$

where  $C_r$  is the volume-averaged or resident concentration of liquid phase ( $ML^{-3}$ ),  $S$  is the concentration of the adsorbed phase ( $MM^{-1}$ ),  $C_g$  is the gaseous solute concentration ( $ML^{-3}$ ),  $a$  is the volumetric air content,  $D_g$  is the soil gas diffusion coefficient,  $J_w$  is the volumetric water flux density ( $LT^{-1}$ ),  $\mu_l$  and  $\mu_s$  are first-order decay coefficients for degradation of the solute in the liquid and adsorbed phases respectively ( $T^{-1}$ ),  $\gamma_l$  ( $ML^{-3}T^{-1}$ ) and  $\gamma_s$  ( $MM^{-1}T^{-1}$ ) are zero-order production terms for the liquid and adsorbed phases,  $D$ ,  $\theta$ ,  $\rho_b$ ,  $x$  and  $t$  are same as defined above. The one dimensional form of equation (8) is also valid for a multidimensional flow process, provided that the lateral boundaries normal to the mean flow direction do not have mass entering or leaving through them (JURY and FLÜHLER, 1992).

## 2.2 Nonequilibrium Transport Models

The application of equation (7) or (8) to transport through laboratory soil columns and in fields having relatively uniform soils involving nonreacting or weakly reactive solutes was found to be fairly successful. However, for strongly adsorbed chemicals and aggregated soils this equation has not performed very well. One of the various reasons is that the chemical transport through soil does not take place in equilibrium. It is affected by a variety of physical and chemical nonequilibrium processes. This paved the way for the examination of diffusion controlled or chemically controlled kinetic rate reactions, or both of the form  $\partial S/\partial t = f(S, C)$ .

### 2.2.1 Two Site Model

SELIM et al. (1976), and CAMERON and KLUTE (1977) have proposed a two site chemical nonequilibrium model where the adsorption term consists of two components, one is governed by equilibrium adsorption and the other by first order kinetics. The sorption or exchange sites in this model are assumed to account for instantaneous adsorption (type-1 sites) and time dependent kinetic adsorption (type-2 sites). At equilibrium, adsorption on both types of sorption sites is described by following linear equations

$$S_1 = K_1 C = FK_D C \quad (9)$$

$$S_2 = K_2 C = (1-F)K_D C \quad (10)$$

where subscript 1 refers to type 1 or equilibrium site and subscript 2 refers to type 2 or kinetic sites respectively and  $F$  is the fraction of all sites occupied by type 1 sorption sites.

Total adsorption at equilibrium is

$$S = S_1 + S_2 \quad (11)$$

Because type 1 sites are always at equilibrium therefore

$$\frac{\partial S_1}{\partial t} = FK_D \frac{\partial C}{\partial t} \quad (12)$$

The adsorption rate for type 2 kinetic nonequilibrium sites is given by a linear and reversible first order equation of following form

$$\frac{\partial S_2}{\partial t} = \alpha[(1-F)K_D C - S_2] \quad (13)$$

where  $\alpha$  is the first order rate coefficient. Combining above equations with (7) lead to following formulation (NKEDI-KIZZA et al., 1984)

$$\left(1 + \frac{F\rho K_D}{\theta}\right) \frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (14)$$

### 2.2.2 One Site Model

The one-site kinetic nonequilibrium adsorption model is a special case of the two-site adsorption model where parameter  $F$  is assumed to be zero. This leads to the assumption that all the adsorption sites present are only type 2 or kinetic or time dependent sites. This simplification leads to the following set of equations

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (15)$$

$$\frac{\partial S_2}{\partial t} = \alpha[K_D C - S_2] \quad (16)$$

### 2.2.3 Two Region Model

Physical nonequilibrium is modeled using a two region (dual porosity) type formulation. In this formation the medium is assumed to contain two distinct mobile (flowing) and immobile (stagnant) liquid regions, and mass transfer between the two regions is modeled as a first order process. Convective diffusion transport is assumed to take place in the mobile region while transfer of solutes into and out of mobile region is assumed to be diffusion controlled. The one dimensional solute transport for an exchanging solute during steady state flow through a homogeneous porous medium, where the liquid phase is presumed to consist of a mobile and immobile

region and includes a Freundlich type equilibrium adsorption-desorption process (VAN GENUCHTEN and WIERENGA, 1976) can be described by a two region model as below

$$\theta_m \frac{\partial C_m}{\partial t} + f\rho \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} = \quad (17)$$

$$\theta_m D_m \frac{\partial^2 C}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (18)$$

where  $t$  is time (T);  $C_m$  and  $C_{im}$  are the solute concentrations in the mobile and immobile liquid phases ( $ML^{-3}$ ) with corresponding volumetric water contents  $\theta_m$  and  $\theta_{im}$  ( $L^3/L^3$ ) respectively;  $S_m$  and  $S_{im}$  are concentrations of adsorbed phase in mobile and immobile phase respectively ( $MM^{-1}$ );  $R_m$  and  $R_{im}$  are retardation factors accounting for equilibrium type adsorption processes in mobile and immobile regions respectively;  $D_m$  is apparent diffusion coefficient of mobile liquid phase ( $L^2T^{-1}$ ),  $x$  is the distance from the inflow boundary in the direction of flow (L),  $v_m$  is the average mobile pore water velocity ( $LT^{-1}$ );  $\alpha$  is the first order rate coefficient ( $T^{-1}$ ) and parameter  $f$  represents the mass fraction of solid phase that is in direct contact with the mobile liquid phase. If the exchange process in both the dynamic ( $S_m$ ) and stagnant ( $S_{im}$ ) region is assumed to be instantaneous, linear and reversible process,  $S_m = K_D C_m$ ; and  $S_{im} = K_D C_{im}$ ; and the total adsorption can be represented by

$$S = fS_m + (1-f)S_{im} \quad (19)$$

For equilibrium adsorption, transferring these into equation (17) and (18) results in the following set of equations

$$(\theta_m + \rho f K_D) \frac{\partial C_m}{\partial t} + [\theta_{im} + (1-f)\rho K_D] \frac{\partial C_{im}}{\partial t} = \quad (20)$$

$$= \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x}$$

$$[\theta_{im} + (1-f)\rho K_D] \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (21)$$

### 2.2.4 Anion Exclusion Model

Certain anions interact with the solid phase of the soil and are excluded from liquid zones adjacent to negatively charged soil particle surfaces. The soil water phase is divided into mobile and immobile zones and anion exclusion is assumed to be restricted to immobile water phase only. The

immobile water phase is synonymous to either the smaller sized pores inside dense aggregates, or to immobile water along pore walls analogous to situation described by KRUPP et al. (1972). For a freely extended diffuse double layer (BOLT and DE HAAN, 1979), anion concentration within an individual pore increases roughly exponentially with distance from the pore wall. In the model described here, it is assumed that such a nonlinear concentration distribution can be replaced by an equivalent step function which has a value of zero in the anion excluded part of the liquid phase adjacent to the pore walls, and a value equal to that of bulk solution near the center of pore. This assumption leads to an equivalent exclusion distance,  $d_{ex}$ , near the pore walls where concentration remains zero (KRUPP et al., 1972; BOLT and DE HAAN, 1979; VAN GENUCHTEN, 1981). The specific exclusion volume,  $V_{ex}$  ( $cm^3$  water/g soil) is given by

$$V_{ex} = d_{ex} A_0 \quad (22)$$

Where  $A_0$  is the specific surface area ( $cm^2/g$ ). Anion exclusion volume can also be expressed in terms of an equivalent volumetric soil-water content,  $\theta_{ex}$

$$\theta_{ex} = V_{ex} \rho \quad (23)$$

Assuming that anion exclusion takes place only in the immobile zone and  $\theta_{ex}$  is less than  $\theta_{im}$ , following transport equations can be used to describe anion exclusion process

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_a \frac{\partial C_a}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (24)$$

$$\theta_a \frac{\partial C_a}{\partial t} = \alpha (C_m - C_{im}) \quad (25)$$

where,  $a$  refers to that part of the immobile liquid phase which is unaffected from anion exclusion process  $\theta_a = \theta_{im} - \theta_{ex}$

Equations (24) and (25) are similar to the equations (20) and (21) when adsorption is neglected and the immobile sink is reduced from  $\theta_{im}$  to  $\theta_a$ .

### 3. Nondimensional Solute Transport Equations

In table 1 nondimensional parameters transferred in each of the above models are presented. Substitution of these parameters into equation (7) results in following nondimensional equilibrium adsorption equation

$$R \frac{\partial C_1}{\partial t} = \frac{1}{P} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} \quad (26)$$

Substitution of dimensionless variables listed in table 1 in the equations (13), (14); or (15), (16); or (20), (21); or (24), (25) results in the following nondimensional nonequilibrium equation

$$\beta R \frac{\partial C_1}{\partial T} + (1 - \beta) R \frac{\partial C_2}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} \quad (27)$$

$$(1 - \beta) R \frac{\partial C_2}{\partial T} = \omega (C_1 - C_2) \quad (28)$$

nondimensional initial and boundary conditions for above equations are described in the next section by (36) to (40) for continuous tracer application and (43) to (45) for pulse application. It can be understood from the above sections that all the nonequilibrium phenomena discussed in this paper i. e. presence of mobile immobile regions or presence of kinetic and equilibrium sites, and anion exclusion can be represented mathematically by equation (27) and (28). Including the nondimensional first order coefficient for degradation and nondimensional zero order production coefficient, the equations (27) and (28) are modified to obtain following set of equations (VAN GENUCHTEN, 1981; TORIDE et al., 1993)

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega (C_1 - C_2) - \mu_1 C_1 + \gamma_1 (Z) \quad (29)$$

$$(1 - \beta) R \frac{\partial C_2}{\partial T} = \omega (C_1 - C_2) - \mu_2 C_2 + \gamma_2 (Z) \quad (30)$$

The solutions of (29) and (30) have been derived by various researchers for a variety of initial and boundary conditions (LINDSTROM and BOERSMA, 1973; CAMERON and KLUTE, 1976; LINDSTROM, 1976; VAN GENUCHTEN and ALVES, 1982).

### 4. Initial and Boundary Conditions for Experiments

Analytical solutions of one dimensional convective dispersion equation (5) or (7); nonequilibrium two site equation (13), (14); nonequilibrium one site equation (15), (16); nonequilibrium two region equation (20), (21); and nonequilibrium anion exchange equation (24), (25) can be obtained for a large number of initial and boundary conditions for both finite and semi-infinite systems (VAN GENUCHTEN, 1981; VAN GENUCHTEN and ALVES, 1982). Field experiments or laboratory experiments can be carried

Table 1: Nondimensional variables introduced in the solute transport equations

Tabelle 1: Dimensionslose Variable in den Stofftransportgleichungen

<b>With all the Equations</b>				
$T = \frac{vt}{L}$	$Z = \frac{x}{L}$	$P = \frac{vL}{D}$	$R = 1 + \frac{\rho K_D}{\theta}$	$C_1 = \frac{C - C_i}{C_0 - C_i}$
<b>With Two Site Equation</b>				
$R_m = 1 + \frac{F\rho K_D}{\theta_m}$	$\beta = \frac{\theta + F\rho K_D}{\theta + \rho K_D} = \frac{R_m}{R}$	$\omega = \frac{\alpha_2(1-\beta)RL}{v}$	$C_2 = \frac{S_2 - (1-F)K_D C_i}{(1-F)K_D(C_0 - C_i)}$	
<b>With One Site Equation</b>				
$\beta = 1/R$	$\omega = \alpha(R-1)L/v$	$C_2 = \frac{S_2 - K_D C_i}{K_D(C_0 - C_i)}$		
<b>With Two Region Equation</b>				
$C_1 = C_m/C_0$	$C_2 = C_m/C_0$	$P = \frac{v_m L}{D_m}$	$\phi_m = \frac{\theta_m}{\theta}$	$\omega = \frac{\alpha L}{q}$
$R_m = 1 + \frac{f\rho K_D}{\theta_m}$	$R_{im} = 1 + \frac{(1-f)\rho K_D}{\theta_m}$	$\beta = \frac{\theta_m + f\rho K_D}{\theta + \rho K_D} = \frac{\phi_m R_m}{R}$		
$C_1 = \frac{C_m - C_i}{C_0 - C_i}$	$C_2 = \frac{C_m - C_i}{C_0 - C_i}$	$T = \frac{v_m \phi_m t}{L}$	$q = \theta_m v_m$	
<b>Anion Exclusion Equation</b>				
$P = \frac{v_m L}{D}$	$R = 1 - \phi_{ex}$	$T = \frac{v_m t \phi_m}{L}$	$\phi_m = \frac{\theta_m}{\theta}$	
$c_1 = \frac{C_m - C_i}{C_0 - C_i}$	$c_2 = \frac{C_a - C_i}{C_0 - C_i}$	$\omega = \frac{\alpha L}{q}$		

out either for a continuous tracer application or the tracer can be applied as a pulse. Dimensional and nondimensional initial and boundary conditions for both types of tracer applications employed in the present study are discussed in this section.

#### 4.1 Dimensional Initial and Boundary Conditions for Continuous Tracer Application

Analytical solutions of the above mentioned equations exist for several sets of dimensional initial and boundary conditions for CDE, two site and two region equation

$$\begin{aligned}
 C(x,0) &= C_i \text{ or } 0 \\
 C(x,0) &= S_2(x,0) = C_i \text{ or } 0 \\
 C_m(x,0) &= C_{im}(x,0) = C_i \text{ or } 0
 \end{aligned}
 \tag{31}$$

At the inflow boundary of the column ( $x = 0$ ), two different conditions can be considered. One of them is a first type or constant concentration boundary condition

$$\begin{aligned}
 C(0,t) &= C_0 \\
 C_m(0,t) &= C_0
 \end{aligned}
 \tag{32}$$

and the other is a third type or constant flux boundary condition

$$-D \frac{\partial C}{\partial x} + vC \Big|_{x=0} = vC_0
 \tag{33}$$

$$-D_m \frac{\partial C_m}{\partial x} + v_m C_m \Big|_{x=0} = v_m C_0$$

All the variables remain the same as discussed earlier. It has been reported that for column displacement experiments where a chemical is applied at a constant rate, use of boundary condition specified by equation (32) leads to mass balance errors. For large values of  $(D/v)$ , the mass balance errors could become quite significant (VAN GENUCHTEN, 1981; PARKER and VAN GENUCHTEN, 1984). However, equation (33) conserves mass inside the soil column, if dispersion outside the soil is ignored. Therefore, a third type inlet condition is preferred over first type inlet condition (VAN GENUCHTEN and PARKER, 1984; TORIDE et al., 1993).

In order to describe the outlet conditions it is assumed that the concentration is macroscopically continuous at the outlet and no dispersion occurs outside the soil. PARKER and VAN GENUCHTEN (1984) have suggested that by assuming that the upstream solute concentrations are not affected by the outlet boundary, solutions for an infinite outlet condition can be applied to the finite region. The outlet condition for a semi infinite profile ( $0 \leq x < \infty$ ) and a finite system of length  $L$  can be specified in terms of a zero concentration gradient as below

$$\frac{\partial C}{\partial x}(\infty, t) = 0
 \tag{34}$$

$$\frac{\partial C_m}{\partial x}(\infty, t) = \frac{\partial C_{im}}{\partial x}(\infty, t) = 0$$

$$\frac{\partial C}{\partial x}(L, t) = 0
 \tag{35}$$

The boundary condition (34) assumes the presence of a semi-infinite soil column. When effluent curves from finite columns are calculated using analytical solutions based on boundary condition (34), some errors may be introduced. Therefore, zero concentration gradient specified by equation (35) at the outflow is frequently used for column displacement studies. However, there is no clear evidence available to prove that the boundary condition (35) leads to a better description of physical processes at and around  $x = L$ . On the other hand, the inflow boundary condition at  $x = 0$ , specified by (33), leads to a discontinuous distribution at the inlet position and thus seems to contradict the requirements of continuous distribution at  $x = L$  (VAN GENUCHTEN, 1981).

**4.2 Nondimensional Initial and Boundary Conditions for Continuous Tracer Application**

The substitution of nondimensional parameters (table 1) into dimensional initial and boundary conditions presented by equations (31) to (35) results in the following nondimensional initial and boundary conditions for both concentration type or first type and flux type or third type boundary conditions

$$C(Z,0) = C_i(Z) \text{ or } 0$$

$$C_1(Z,0) = C_2(Z,0) = C_i(Z) \text{ or } 0 \tag{36}$$

where  $C_i$  is the initial concentration given as a function of  $Z$ . The first type (concentration type) or a third type (flux type) nondimensional boundary condition at inflow boundary are described as

$$C_1(0,T) = 1 \tag{37}$$

$$C_1(0,T) - \frac{1}{P} \frac{\partial C_1(0,T)}{\partial Z} = 1 \tag{38}$$

Similarly, the nondimensional outflow boundary conditions for a semi-infinite and finite column can be described as below

$$\frac{\partial C_1}{\partial Z}(\infty, T) = 0$$

$$\frac{\partial C_1}{\partial Z}(\infty, T) = \frac{\partial C_2}{\partial Z}(\infty, T) = 0 \tag{39}$$

$$\left(\frac{\partial C_1}{\partial Z}\right)(1, T) = 0 \tag{40}$$

**4.3 Dimensional Initial and Boundary Conditions for Pulse Application**

Assuming that the concentrations are continuous across the inflow boundary and input solution is well mixed, a first type boundary condition across the inflow boundary for a pulse type injection can be specified as

$$C(0,t) \begin{cases} = C_0 & 0 < t \leq t_0 \\ = 0 & t > t_0 \end{cases} \tag{41}$$

A third type boundary condition for the pulse input for a well mixed input solution can be specified as

$$-D \frac{\partial C}{\partial x} + vC \Big|_{x=0} = vC_0 \quad 0 < t \leq t_0$$

$$= 0 \quad t > t_0$$

$$-D_m \frac{\partial C_m}{\partial x} + v_m C_m \Big|_{x=0} = v_m C_0 \quad \text{for } 0 < t \leq t_0$$

$$= 0 \quad \text{for } t > t_0 \tag{42}$$

The initial condition and the boundary condition at outflow remain the same as described by (31) and (34) or (35) respectively. The boundary condition at inlet described by (41) becomes inappropriate when the input solution is not well mixed. Other arguments against the applicability of (41) can be that the plane we consider as macroscopic boundary has no physical relevance at the microscopic level as irregularity in pore structure and morphology become manifest at this level. Also the medium properties vary continuously over a finite transition zone of  $l/2$ , where  $l$  is the representative elementary volume (REV) of the porous medium (PARKER and VAN GENUCHTEN, 1984).

**4.4 Nondimensional Initial and Boundary Conditions for Pulse Application**

The nondimensional initial and boundary conditions for pulse type of tracer applications are obtained by substituting the nondimensional variables given in table 1 into the initial and boundary conditions presented at (41) and (42)

$$C(0,t) \begin{cases} = 1 & 0 < T \leq T_0 \\ = 0 & T > T_0 \end{cases} \tag{43}$$

$$-\frac{1}{P} \frac{\partial C_1}{\partial Z} + C_1 \Big|_{z=0} = 1 \quad 0 < T \leq T_0$$

$$= 0 \quad T > T_0 \tag{44}$$

$$\frac{\partial C_1}{\partial Z}(\infty, T) = \frac{\partial C_2}{\partial Z}(\infty, T) = 0 \tag{45}$$

**4.5 Analytical Solutions**

Analytical solutions of equilibrium and nonequilibrium transport equations for given boundary conditions are presented in table 2. Concentrations and boundary conditions are given in their dimensionless form.

Table 2: Analytical solutions of equilibrium and nonequilibrium transport equations  
 Tabelle 2: Analytische Lösungen von Gleich- und Nichtgleichgewichtstransportgleichungen

		Concentration-type boundary conditions:		Flux-type boundary conditions:	
		$C_i(0, T) = 1$	$\frac{\partial C_i(\infty, T)}{\partial Z} = 0$	$\left(-\frac{1}{P} \frac{\partial C_i(Z, T)}{\partial Z} + C_i(Z, T)\right)_{z=0} = 1$	$\frac{\partial C_i(\infty, T)}{\partial Z} = 0$
DIMENSIONLESS EXIT CONCENTRATION	<b>CDE</b> $C_e$	$C_e = \frac{1}{2} \operatorname{erfc}\left[\left(\frac{P}{4RT}\right)^{1/2} \cdot (R - T)\right] + \frac{1}{2} \exp(P) \cdot \operatorname{erfc}\left[\left(\frac{P}{4RT}\right)^{1/2} \cdot (R + T)\right]$		$C_e = \frac{1}{2} \operatorname{erfc}\left[\left(\frac{P}{4RT}\right)^{1/2} \cdot (R - T)\right] + \left(\frac{PT}{\pi R}\right)^{1/2} \cdot \exp\left[-\frac{P}{4RT} \cdot (R - T)^2\right] - \frac{1}{2} \cdot \left(1 + P + \frac{PT}{R}\right) \cdot \exp(P) \cdot \operatorname{erfc}\left[\left(\frac{P}{4RT}\right)^{1/2} \cdot (R + T)\right]$	
	<b>NE-models</b> $G(\tau)$	$G(\tau) = \frac{1}{2} \operatorname{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} \cdot (\beta R - \tau)\right] + \frac{1}{2} \exp(P) \cdot \operatorname{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} \cdot (\beta R + \tau)\right]$		$G(\tau) = \frac{1}{2} \operatorname{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} \cdot (\beta R - \tau)\right] + \left(\frac{P\tau}{\pi\beta R}\right)^{1/2} \cdot \exp\left[-\frac{P}{4\beta R\tau} \cdot (\beta R + \tau)^2\right] - \frac{1}{2} \cdot \left(1 + P + \frac{P\tau}{\beta R}\right) \cdot \exp(P) \cdot \operatorname{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} \cdot (\beta R + \tau)\right]$	
	$F(\tau)$	$F(\tau) = \frac{\beta}{\tau} \left(\frac{PR}{4\pi\beta\tau}\right)^{1/2} \cdot \exp\left[-\frac{P}{4\beta R\tau} \cdot (\beta R - \tau)^2\right]$		$F(\tau) = \left(\frac{P}{\pi\beta R\tau}\right)^{1/2} \cdot \exp\left[-\frac{P}{4\beta R\tau} \cdot (\beta R - \tau)^2\right] - \frac{P}{2\beta R} \cdot \exp(P) \cdot \operatorname{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} \cdot (\beta R + \tau)\right]$	

### 5. Numerical Methods

The four numerical methods used frequently are finite difference method (FDM), finite element method (FEM), method of characteristics (MOC) and method of random walk (MORW). When flow processes are simulated along with migration, numerical stability, consistency criteria and convergence criteria need to be considered carefully. As stated before every numerical model needs to be validated and compared with analytical solutions. The parabolic (diffusion equation) and hyperbolic (wave equation) properties of transport equations require often more than just plain methods and sometimes have proven quite complicated (KINZELBACH, 1987; LUCKNER and SCHESTAKOW, 1991). The spatial and independent variables such as dispersivity are discretized to develop a simulation model. The dependent variables like concentration and temperature are approximated at a limited number of points in space (x, y, z) and time (t). Discretization results in a set of algebraic equations. The step lengths  $\Delta x$ ,  $\Delta y$ ,  $\Delta z$  and  $\Delta t$  are selected to obtain high accuracy for given conditions and available data. The resulting systems of equations can be either solved with direct, or iterative methods. Usually the former requires more storage and the later more simulation time. An example for direct methods with constant  $\Delta t$  is the Crout method, for iterative methods the ADI- (block iteration) or the GAUSS-SEIDEL-method

(point iteration) combined with overrelaxation. Iterative methods are recommendable for nonlinear models.

#### 5.1 Numerical Models

Simulation models for migration processes in saturated and unsaturated zones fundamentally differ with regard to kinetics, dimensionality, geometry and applied algorithm. Some of the available programs are briefly described in the following sections.

##### 5.1.1 One Dimensional Models

The Pesticide Assessment Tool for Rating Investigations of Transport (PATRIOT) (IMHOFF et al., 1993) is composed of a pesticide fate and transport model (PRZM2) (MULLINS et al., 1993), a comprehensive database, an interface facilitating data exploration, interaction tools and user-selected methods of summarizing and visualizing model results. PRZM2 simulates the fate of agricultural pesticides both in the crop root zone and the underlying unsaturated zone and links together the two models PRZM and VADOFT (Vadose Zone Flow and Transport Model using a finite element code). PRZM is a one-dimensional, dynamic model



which also includes soil temperature simulation, volatilization, vapor phase transport, irrigation simulation and microbial transformation. This model employs two options for solving the transport equations. One is a backward difference implicit scheme that may be affected by excessive numerical dispersion at high Peclet numbers. And second is MOC which eliminates numerical dispersion while increasing model execution time. Further developed from PRZM, additionally accounting for an improved calculation of evapotranspiration and volatility was PELMO (Version 2.01). Freundlich constants can be defined for each layer, pKA values are used to correct the sorption coefficient through pH, and an increase in sorption with time is also included.

The 1D-FDM Vadose Zone Leaching Model (VLEACH) (RAVI and JOHNSON, 1997) employs linear isotherms describing the partitioning of the pollutant between the soil, liquid and vapor phases assuming local or instantaneous equilibrium. Dispersion and in situ degradation or production are neglected in this model. Leaching is simulated in a number of polygons each with different soil properties, recharge rate, depth to water or initial conditions. Likewise CHEMFLO utilizes the 1D FDM to simulate advection, dispersion, first order decay in liquid and solid phase, zero order production or decay and linear equilibrium adsorption (NOFZIGER et al., 1989). HYD1D (INTERNATIONAL GROUND WATER MODELING CENTER, 1998) calculates 1D transient water flow, solute transport and heat movement in variably saturated porous media employing the Galerkin linear FEM. The flow equation includes liquid-phase water flow, hysteresis in soil hydraulic functions, scaled unsaturated soil hydraulic properties and water uptake by roots. The solute transport equation accounts for ionic or molecular diffusion, dispersion, linear or nonlinear equilibrium adsorption, first order decay, zero order production and solute uptake by plants. Both equations are assumed not to be influenced by temperature variations.

TRANSOL (KROES, 1991) is a dynamic model for transport, degradation and adsorption of a single solute in the soil. The programs WATBAL or SWATRE deliver the water-quantity input to the program TRANSOL. The solution method is partly analytical since the transport equation is solved analytically at every time step for every freely chosen layer. For the calculation of the adsorbed concentration either linear adsorption or nonlinear Freundlich-adsorption is assumed. An iterative method for the solution of nonlinear sorption is employed, using the transport and conservation equation to calculate the Freundlich coefficient.

The seasonal soil compartment model (SESOIL) utilizes a FDM developed for long-term hydrologic, sediment and pollutant fate simulations. A soil column extending from ground surface through the unsaturated zone represents one compartment. Beside advection and diffusion the included processes for pollutant transport and fate component are volatilization, adsorption or desorption and chemical degradation or decay (BONAZOUNTAS and WAGNER, 1984).

### 5.1.2 Two and Three Dimensional Models

SWMS\_2D (SIMUNEK et al., 1994) is a computer program for simulating two-dimensional water flow and solute transport in variably saturated media. The flow equation incorporates a sink term to account for water uptake by plant roots. The transport equation describes linear equilibrium adsorption, zero-order production, and first-order degradation. The flow region may have an arbitrary degree of local anisotropy and may be delineated by irregular boundaries. Galerkin-type linear finite element schemes are used to solve the equations numerically. For the solution of the matrix equations resulting from discretization either Gaussian elimination for banded matrices, a conjugate gradient method for symmetric matrices or the ORTHOMIN method for asymmetric matrices is used with respect to the size of the problem.

The FEM Seepage Analysis Model (SEEP/W, 1991) is a software-tool to model transport and pore water-density-distributions in porous materials. It contains saturated and unsaturated stream flow analysis, equilibrium and transient conditions, two-dimensional and axial-symmetric problems, different types of soil and anisotropic hydraulic conductivity coefficients. For computing the FEM is used. The flow velocities calculated by SEEP/W are utilized by a model for finite element contaminant transport analysis (CTRAN/W, 1993) to simulate the migration of dissolved solutes through porous materials, including diffusion, dispersion, linear adsorption and radioactive decay. For problems where advective mass transport is the dominating process CTRAN/W offers the method of particle tracking. The transport of solutes is computed as the movement of particles proportional to flow velocity and magnitude of the time step, the density of particles in a certain area representing the specific concentration. VS2D is a 2D finite difference program for flow and solute transport in variably saturated, single phase flow in porous media including first-order decay, equilibrium adsorption (FREUNDLICH or LANGMUIR) isotherms and ion exchange.

VS2D simulates cross-sectional or cylindrical variably saturated flow including non-linear storage, conductance, sink terms and boundary conditions, implementing ponding, infiltration, evaporation, plant root uptake and seepage faces (LAPPALA et al., 1987; HEALY, 1990). The Saturated-Unsaturated Ground Water Transport Model (SUTRA) (VOSS, 1984), a 2D hybrid finite element and integrated finite difference model, computes fluid movement and transport of either energy or dissolved substances in saturated ground water flow systems for areal and cross-sectional flow, and in the unsaturated zone for cross-sectional flow. The transport equation for single reacting solutes includes sorption, zero and first order decay, zero order production, hydrodynamic dispersion and molecular diffusion. The moisture-characteristic curve can be calculated by three options during simulation of unsaturated flow.

TARGET (INTERNATIONAL GROUND WATER MODELING CENTER, 1998) employs an integrated FDM and includes independent programs for transient ground-water flow and solute transport. One is a 2D vertically integrated, confined/unconfined, second a 2D vertically oriented, variably saturated, density coupled, third a multi-layer confined/unconfined, and fourth a 3D saturated, density coupled computer code. Some of the incorporated processes and mechanisms are heterogeneity, anisotropy, hysteresis in the unsaturated zone, advection, dispersion, molecular diffusion, density effects from contamination or salt water intrusion, viscosity effects, linear equilibrium adsorption and first-order decay. The 3D FE model of WATER flow (FEMWATER) (YEH and WARD, 1980), is a density driven flow and transport model for the saturated-unsaturated zone. It is a combination of the original FEMWATER (just for flow) and the LEWASTE program calculating the transport process.

### 5.1.3 Models Accounting for Nonequilibrium

Leaching Estimation and Chemistry Model (LEACHM) was produced by WAGENET and HUTSON (1989). The water regime and chemistry together with the transport of solutes in partially saturated soils can be simulated to a depth of about two meters. The program consists of four sub-models describing nitrogen transport and transformation, pesticide displacement and degradation, transient movement of eight inorganic ions and the water regime. Pesticides and nitrogen are assumed to obey a linear sorption isotherm. Additional to the local equilibrium assumption, or a linear isotherm of

pesticide sorption (Version 2), sorption kinetics i.e. two-site sorption using linear sorption isotherms for both sides, and nonlinear isotherms (Freundlich equation) can be chosen in Version 3. The transformation and degradation rate constants of the respective pathways are of first order. All four sub-models include estimates of plant growth and adsorption of water and solutes by plant roots beneath a flexible means of describing precipitation and surface evaporation of water. In order to adjust rate constants according to temperature, a heat flow simulation is incorporated in the first two models. The Crank-Nicolson implicit method and the Gaussian elimination (Thomas algorithm) are applied.

CHAIN\_2D (SIMUNEK and VAN GENUCHTEN, 1994) calculates two dimensional movement of solutes in sequential first order decay reactions, variably saturated water flow and heat transport. Nonequilibrium interactions between the liquid and adsorbed concentrations, besides equilibrium interactions between the solution and gaseous concentrations can also be simulated. For each of the solid, liquid and gaseous phases first and zero order rate constants, and additionally first order rate constants providing connections between chain reactions are included in the solute transport equations. The nonequilibrium two site adsorption model accounts for instantaneous and kinetic sorption. Nonequilibrium is realized with a generalized nonlinear empirical equation while a linear dependency is assumed for the liquid-gas-interaction. Galerkin type linear finite element schemes are employed to solve the governing flow and transport equations. The matrix equations are again solved with either Gaussian elimination for banded matrices or the conjugate gradient method for symmetric matrices, or the ORTHOMIN method for asymmetric matrices.

SWACRO is a 1D dynamic, deterministic FD model and was originally developed for water flow in the saturated and unsaturated zone (BELMANS et al., 1983; FEDDES et al., 1978). The extended version implements the model concept of PESTLA as a subroutine to simulate pesticide transport in the soil, accounting for nonlinear sorption (Freundlich isotherm), temperature dependent first order transformation and passive plant uptake. Microbial transformation, transport in the gas phase crop water use, crop yield and lateral transport of solutes and pesticides are also included in SWACRO. The process of preferential flow according for mobile and immobile concept is incorporated as an option. Preferential flow through cracks in clay soils can be described with imaginary drains, depending on the infiltration capacity.

## 6. Practical Considerations

### 6.1 Methods of solution for transport problems

The physical and chemical transport models can be solved analytically assuming that pore water velocity, soil water content, dispersion coefficient, and soil bulk density are constant in time and space. This situation is in contrast to most of the field conditions where the flow and transport regimes may be highly variable because of transient flow induced by time-dependent boundary conditions, or because of spatial and temporal variability in the hydraulic and solute transport properties (TORIDE et al., 1993). Hence, the applicability of analytical solutions for solute transport problems is limited as compared to the more versatile and flexible numerical solutions. Still, the analytical solutions when applied over large spatial and temporal scales provide rapid and initial estimates of scenarios. They are also used to validate the numerical models. It has been reported that analytical solutions also provide more insight into the underlying physical and chemical processes than the numerical solutions and are helpful for sensitivity analyses to investigate the effects of various transport parameters. Apart from this analytical solutions can be incorporated more easily in stochastic approaches for describing solute transport in heterogeneous soils (DAGEN and BRESLER, 1979).

### 6.2 Local Equilibrium Assumption

In order to model sorbent/sorbate interactions it has to be discussed whether an equilibrium assumption describes sorption sufficiently well, or if a kinetic sorption reaction must be incorporated into the transport equation. When velocities are slow compared to the rate of reactions the local equilibrium assumption (LEA) may be justified, thus reducing the complexity of transport models. However, sometimes the LEA does not seem to be adequate for describing reversible chemical reactions. Thus, it is very important to investigate how fast reversible chemical reactions must be before instantaneous equilibrium can be assumed. VALOCCHI (1985) investigated transport equations including linear adsorption isotherms with some non-equilibrium models, two implementing diffusion limited reactions and one accounting for first-order chemical reactions. He found that parameters such as the average linear velocity, the dispersion and equilibrium distribution coefficient

or the source function determine the justification of local equilibrium.

### 6.3 Adsorption Isotherms

Adsorption isotherms are used to describe the steady state between the adsorbent and solute concentration. An adsorption isotherm is valid only for a certain temperature, pressure and soil composition. Impact of temperature on adsorption from liquid solutions is smaller than on gas adsorption. In view of a thermodynamically exact definition state of adsorption equilibrium cannot be termed real equilibrium, since the way of the process and changes in the sorbent structure may sometimes influence the final state (SONTHEIMER, 1985). The numerous isotherm equations are based on chemical, physical or thermodynamic model assumptions or are solely empirical. Three adsorption isotherms most frequently used in soil physics are (linear) Henry, Freundlich, and Langmuir isotherm. Together with several different dynamic models they are listed in the table 3, also presented is a model for competing species, occupying the adsorber places according to the ratio of their concentrations or activities, respectively.

Table 3: Isotherms  
Tabelle 3: Isothermen

	Equilibrium processes	Non-equilibrium processes	Processes near Equilibrium
Henry	$s = k_1 \cdot c$	$ds/dt = k_1 \cdot c$	$ds/dt = k_1 \cdot c - k_2 \cdot s$
Freundlich } equation	$s = k_3 \cdot c^{k_4}$	$ds/dt = k_3 \cdot c^{k_4}$	$ds/dt = k_3 \cdot c^{k_4} - k_5 \cdot s$
Langmuir	$s = s_m \cdot c / (b + c)$	$ds/dt = k_6 \cdot c \cdot a \cdot (n - s)$	$ds/dt = k_6 \cdot c \cdot a \cdot (n - s) - k_7 \cdot a \cdot s$
Competition reaction	$s_1/s_2 = k' \cdot c_1/c_2$	$ds_1/dt = k' \cdot c_1 \cdot s_2$	$ds_1/dt = k' \cdot c_1 \cdot s_2 - k' \cdot c_2 \cdot s_1$

In table 3  $s$  is the adsorbed concentration,  $c$  the solute concentration;  $s_m$  the maximum of sorbed concentration,  $a$  the concentration of adsorbent,  $n$  the adsorption capacity [e. g. in  $g/cm^3$ ],  $b = k_7/k_6$ ,  $k' = k'_1/k'_2$ , and  $k_{1-7}$ ,  $k'$ ,  $k'_{1,2}$  are constants (RICHTER, 1986).

The Henry isotherm is valid for small concentrations,  $k_1$  is called distribution coefficient. Freundlich postulated the nonlinear equilibrium-isotherm with constant coefficients  $k_3$  (*Freundlich-coefficient*) and  $k_4$  (*Freundlich-exponent*). The Freundlich-exponent is usually lower than 1 and larger than 0 and is enhanced with decreasing  $c$ . Thus it should reach the value 1 in highly diluted solutions. This isotherm is only valid for a certain range of concentration. Neither a maximal adsorbed concentration nor the linear isotherm

can be found as limit values. Another nonlinear equilibrium-isotherm was derived by Langmuir. Originally developed to describe gas-adsorption on solids the Langmuir isotherm can be derived from a quite simple kinetic point of view or with statistical thermodynamics. The kinetic reaction of sorption is assumed to be formed by adsorption and desorption with the reaction rate of adsorption,  $r_{ads} = k_6 (s_m - s) \cdot c$ , and the reaction rate of desorption,  $r_{des} = k_7 \cdot s (k_6$  is the constant of adsorption rate,  $k_7$  the constant of desorption rate). The first reaction depends on the solute concentration and the free adsorber places on the surface of the adsorbent, whereas desorption velocity is solely determined by the number of occupied places. If all adsorber places are occupied a monomolecular covering of the surface is obtained.  $s_m$  usually is, in contrast to the factor  $b$ , also dependent on the type of sorbate and sorbent, and independent of temperature. For large concentrations the isotherm becomes independent of  $c$ , and  $s$  approximates its maximum value  $s_m$ . When  $c$  is small the Henry isotherm is attained, that is,  $s_m/b$  equals the Henry constant  $k_1$ . The Langmuir isotherm with constant  $b$  should only be used for that part of the isotherm where the curve of the integral adsorption enthalpy over  $s$  can be approximated by a straight line.

Three examples for the often reversible, rapid equilibrium sorption mechanisms of pesticides are presented in Table 4 (SPARKS, 1989).

Table 4: Sorption processes of pesticides  
Tabelle 4: Pestizidsorption

(a) Van Genuchten et al. (1974)		$\frac{\partial s}{\partial t} = k_1 \cdot \left[ \left( \frac{k_1 \cdot \theta}{k_1 \cdot \rho_b} \right) \cdot c^N - s \right]$
(b) Lindstrom et al. (1970)	equilibrium: $s = \left( \frac{K \cdot \theta}{K_1 \cdot \rho_b} \right) \cdot c \exp(-2\beta s)$	$\frac{\partial s}{\partial t} = K_1 \exp(\beta s) \cdot \left[ \left( \frac{K \cdot \theta}{K_1 \cdot \rho_b} \right) \cdot c \exp(-2\beta s) - s \right]$
(c) McCall, Agin (1985)	$C_{B1} \xrightleftharpoons[k_2]{k_1} C_{B2} \xrightleftharpoons[k_F]{k_2} C_F$	$\frac{dC_{B1}}{dt} = -k_1 \cdot C_{B1}$ $\frac{dC_F}{dt} = k_1 \cdot C_{B1} + k_2 \cdot C_{B2} - k_2 \cdot C_F$ $\frac{dC_{B2}}{dt} = k_2 \cdot C_{B2} - k_2 \cdot C_F$

In table 4  $K_{1,2}$  are the forward and backward rate coefficients [ $h^{-1}$ ];  $\beta$  is the surface stress coefficient;  $c_{B1}$  the picloram bound at fast desorbing sites,  $c_{B2}$  the picloram retained at slow desorbing sites,  $c_F$  the free form of picloram,  $k_1$  the fast desorption rate coefficient,  $k_2$  the slow desorption rate coefficient, and  $k_2$  is the reversible slope sorption rate coefficient

In table 4a reversible nonlinear kinetics is assumed, and for equilibrium the Freundlich-equation  $s = k_F \cdot c^N$  with the

Freundlich coefficient  $k_F = k_1 \cdot \theta k_2 \cdot \rho_B$  is obtained. In table 4b a sticking probability for the sorbate on the sorbent surface, permitted to change with the degree of surface coverage, is introduced. Adsorption and desorption energies can vary with coverage. In table 4c a two site model for pesticide desorption kinetics using a reversible first-order equation for picloram desorption from soil was used by MCCALL and AGIN (1985). The pesticide could be desorbed slowly and reversible from B2-sites, but rapidly, and perhaps also reversible, from B1-sites.

### 6.4 Iterative solution of an equation accounting for storage and kinetic processes

In the above sections several equilibrium and nonequilibrium solute transport models along with their analytical solutions for different boundary conditions are given. Several commercially available software for modeling solute transport through porous media employing numerical or analytical solutions of transport equations are also described above. In case the source code of a software is not available, the storage and kinetic processes existing in these equations can be separately simulated and verified. In this paper as an example an iterative solution strategy for equation (7) additionally including storage and kinetic processes, sources and sinks is presented. Divergence and all spatial dependencies of the parameters are neglected and thus an ordinary nonlinear differential equation is obtained as given by (46).

$$\frac{d(n_w \cdot R(t) \cdot c(t))}{dt} = \lambda(t) \cdot n_w \cdot R(t) \cdot c(t) + q(t) \tag{46}$$

$$R(t) = \frac{s(t)n_f + c(t)n_w}{c(t)n_w} = 1 + \frac{s(t)n_f}{c(t)n_w} \tag{47}$$

$$s(t) = \frac{k_{1d}c(t)^\nu}{1 + k_{2d}c(t)} \tag{48}$$

$$\lambda(t) = \frac{\lambda_1}{1 + \lambda_2 c(t)} \tag{49}$$

where  $c$  is the partial density of the liquid phase [ $g/m_w^3$ ],  $s$  the density of the solid phase [ $g/m_f^3$ ],  $k_{1d}$ ,  $k_{2d}$  are adsorption coefficients [ $m_w^3/g$ ],  $\lambda_1$  is a reaction rate [ $1/s$ ],  $\lambda_2$  a reaction coefficient [ $m_w^3/g$ ],  $n_w$  the volumetric content of liquid phase [ $m_w^3/m_R^3$ ],  $n_f$  the volumetric content of the solid phase [ $m_f^3/m_R^3$ ],  $\nu$  an exponent [-],  $R$  the retardation factor [-], and  $q$  a source/sink [ $g/m_R^3s$ ].

By selecting the parameters  $k_{1d}$ ,  $k_{2d}$  and  $v$  in (48) three different adsorption isotherms can be computed through one equation. A kinetic reaction of first order results when  $\lambda_1 < 0$  and  $\lambda_2 = 0$  in (49), a Michaelis-Menten kinetic for  $\lambda_1 < 0$  and  $\lambda_2 > 0$ . Because of the restrictions in equation (46) the only discretization has to be carried out in time. A centralized scheme is used to approximate (46) and all terms without time derivations are weighted by a factor 1/2. For constant  $R$  and dividing (46) by  $(n_w \cdot R)$  the following equation is obtained:

$$\frac{c(t) - c(t - \Delta t)}{\Delta t} = \frac{1}{2} \left[ \lambda(t - \Delta t) \cdot c(t - \Delta t) + \frac{q(t - \Delta t)}{n_w \cdot R} \right] + \frac{1}{2} \left[ \lambda(t) \cdot c(t) + \frac{q(t)}{n_w \cdot R} \right] \quad (50)$$

and for this case the iteration (time-dependency is not explicitly written but as an index,  $p$  is the iteration index)

$$c^{p,t} = c^{t - \Delta t} + \frac{1}{2} \cdot \Delta t \cdot \left[ \lambda \cdot c + \frac{q}{n_w \cdot R} \right]^{t - \Delta t} + \frac{1}{2} \cdot \Delta t \cdot \left[ \lambda \cdot c + \frac{q}{n_w \cdot R} \right]^{p-1,t} \quad (51)$$

can be used to calculate the concentration. For  $R$  being not constant, the next equation is employed:

$$c^{p,t} = c^{t - \Delta t} - \frac{(c^{p-1,t} + c^{t - \Delta t})}{(R^{p-1,t} + R^{t - \Delta t})} \cdot (R^{p-1,t} - R^{t - \Delta t}) + \frac{1}{2} \cdot \Delta t \cdot \left[ \lambda \cdot c + \frac{q}{n_w \cdot R} \right]^{t - \Delta t} + \frac{1}{2} \cdot \Delta t \cdot \left[ \lambda \cdot c + \frac{q}{n_w \cdot R} \right]^{p-1,t} \quad (52)$$

A computer code can now be developed for equation (52) and the variables  $c$ ,  $s$ ,  $R$  and  $\lambda$  can be calculated for given parameters  $k_{1d}$ ,  $k_{2d}$ ,  $\lambda_1$ ,  $\lambda_2$ ,  $v$ ,  $n_p$ ,  $n_w$ ,  $q$  and initial values for  $c$ . In order to test a software the boundary conditions should be set so that they represent the above discussed zero dimensional problem.

**Appendix: List of Notations**

- C Solution concentration (M)
- C<sub>0</sub> Input concentration (M)
- C<sub>1</sub> Dimensionless solution concentration of mobile liquid phase for TRM and of total liquid phase for TSM
- C<sub>2</sub> dimensionless solution concentration of immobile liquid phase for TRM and adsorbed concentration for type 2 kinetic sites in TSM

- C<sub>im</sub> Average concentration of immobile liquid phase
- C<sub>m</sub> Average concentration of mobile liquid phase
- D Apparent diffusion coefficient of total liquid phase (cm<sup>2</sup>/h) for EM and TSM
- D<sub>m</sub> Apparent diffusion coefficient of mobile liquid phase (cm<sup>2</sup>/h) for TRM
- f Mass fraction of adsorbed sites in dynamic region for TRM
- F Fraction of adsorption sites in equilibrium with solution concentration for TSM
- K<sub>D</sub> Distribution coefficient for linear adsorption (cm<sup>3</sup>/g)
- L Length of column (cm)
- P Peclet Number
- Q Volumetric flux density (cm/h)
- R Retardation factor
- R<sub>m</sub> Retardation factor for dynamic region for TRM
- R<sub>im</sub> Retardation factor for immobile region for TRM
- S Adsorbed concentrations (MM<sup>-1</sup>)
- S<sub>1</sub> Adsorbed concentrations associated with type 1 (equilibrium sites) in TSM
- S<sub>2</sub> Adsorbed concentrations associated with type 2 (kinetic sites) in TSM
- S<sub>m</sub> Adsorbed concentrations in the dynamic regions of soil in TRM
- S<sub>im</sub> Adsorbed concentrations in the stagnant regions of soil in TRM
- t Time in hours
- t<sub>1</sub> Time of applied concentration pulse, hours
- T pore volume or dimensionless time
- T<sub>0</sub> dimensionless pulse time
- v Average pore water velocity (cm/h)
- v<sub>m</sub> Average pore water velocity in mobile liquid region in TRM (cm/h)
- x Dimensionless distance
- z Distance (cm)
- α Rate coefficients: first order mass transfer coefficient in TRM and first order kinetic rate coefficient in TSM
- β Dimensionless partition coefficient
- θ Volumetric water content
- θ<sub>m</sub> Volumetric water content in mobile liquid region
- ρ Bulk density (g/cm<sup>3</sup>)
- φ<sub>m</sub> Fraction of liquid phase considered to be mobile in TSM
- ω Dimensionless mass transfer coefficient

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### Addresses of authors

- M. Tech. Dr. Manoj K. Shukla, Ao. Univ.-Prof. Dipl.-Ing. Dr. Willibald Loiskandl, Institute of Hydraulics and Rural Water Management, University of Agricultural Sciences, Vienna, Muthgasse 18, A-1190 Wien. e-mail: H522T26@edv2.boku.ac.at
- Dipl.-Ing. Sabine Klepsch, Austrian Research Centers Seibersdorf, Division of Life Sciences, A-2444 Seibersdorf.

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