CHAPTER II
REVIEW OF LITTERATURE

II.1. Water flow in soil

Fundamental to our knowledge of water resources is the role of the soil system as a natural reservoir having the capacity to store and supply water for stream flow and biota. This knowledge is essential for understanding ecosystem dynamics and biogeochemical cycles of both terrestrial and downstream aquatic ecosystems. An emerging issue in hydrology and critical zone research is to describe and explain the spatial and internal variability of soil moisture storage and its effects on the soil water balance and stream flow generation. Soil moisture change during hourly to seasonal time periods is necessary to document to fully understand the hydrologic behavior in headwater catchments of these systems **(Swarowsky *et al.*, 2011)**.

The vadose zone is that portion of the earth's surface that encompasses the soil and unsaturated sediments that lie above the water table. The vadose zone affects the movement of water, nutrients, chemicals, pathogens and contaminants to and from the water table. In most cases, the dominant mechanism for movement is the liquid water flux and to some extent in drier region, the vapor flux. Thus, the successful assessment of the quantity and quality of groundwater resources depends, in part, on the ability to predict the flux of water that moves into and through the vadose zone **(Fayer, 2000).**

Direction and rate of water flow depend on differences in hydraulic head between different given soil segment is equal to the hydraulic conductivity of that soil multiplied by the hydraulic gradient that exists in that soil. In order for water actually to move from one point to another, however, two conditions must be met. First, there must be a difference in hydraulic head between the two points (that is, delta H must be greater or less than zero). Second, the soil between these two points must be permeable enough to allow the movement of water **(Bouma *et al.*, 2003)**.

Movement of water within soils controls the rate of infiltration and the flow to springs, streams, and underground aquifers The bulk soil solution moves downward under the influence of gravity through the non-capillary pore space, and more slowly through capillary pore space and in films on surfaces of soil particles mostly under the influence of surface or matric forces . Sometimes both gravitational and matric forces are involved as in water movement down slopes. Downward movement is largely by gravity and depends on the rate at which water is supplied to the wetting front rather than to the difference in –flow between wet and dry soil. Upward movement of water (capillary rise) toward the soil surface is caused chiefly by evaporation from the surface and removal of water by roots of transpiring plants. Two forces primarily affect water movement through soils, gravity and capillary action. Capillary action refers to the attraction of water into soil pores Capillary action involves two types of attraction- adhesion and cohesion forces. The other force governing water movement through soils is gravity, which pulls water downward. Capillary forces can move water in any direction. On the left, lateral and vertical movement occurs at nearly the same rate. Also, downward movement of the wetting front is approximately the same for the single drip source as for the multi-drip source. The two forces that make water move through soil are gravitational forces and capillary forces. Capillary forces are greater in small pores than in large pores **(Gardner, 1962; Watson *et al.*, 1995)**.

Soil-water characteristic curves and hydraulic conductivity curves are needed to describe flow of water in soils. The direction (upward, downward, or lateral) and magnitude of water flow in soils therefore depends upon the direction and magnitude of hydraulic head gradient and the degree of water saturation of the soil. Hydraulic head gradient and the degree of water saturation calculated by Darcy's Law, Darcy's Law is written mathematically as follows:

$$q = - (\Delta H/L)K \qquad\qquad (1)$$

Where: q = flux, or flow rate in centimeters per hour or day, K = hydraulic conductivity (LT^{-1}), ΔH = hydraulic head difference between two points (L) and L = distance between the two points (L).

The larger the K of a soil, the greater will be the movement of water through it for any given hydraulic gradient. A soil has a maximum K value when saturated, lower, K value for each lower water content and corresponding negative pressure head. Such values are characteristically different for different soils, depending upon soil structure and pore-size distribution at saturation; all pores are filled with water **(Bouma et al., 2003)**.

The ground water flow is considered to be under steady state if it flows toward a natural drainage system at a constant rate with no change in the total hydraulic head or volume of saturation. Near a well pumped intermittently, on the other hand, the flow is under transient conditions. Another example is the transient condition in the unsaturated zone around the trenches of a septic system with no ponding, or around the emitters of a drip system receiving wastewater intermittently (with each dosing cycle). The rate of water movement through a volume of a soil under a steady state condition is constant (i.e., does not change with time) **(Gustafson et al., 2005).** Steady state flow: the flow rate of water will reach a stationary value henceforth termed q(h) for greater time values **(Kazemi, 2012).** Under steady-state water flow, distinct flow patterns developed, with regions of high flux and regions of low flux. The flow patterns observed depended on the magnitude of the steady water flux, and consequently on the water content of the porous medium **(Hendrickx** and **Flury, 2001).**

II.2. Types of water flow
There are two types of water flow as follows:

II.2.1. Uniform Water Flow
Uniform flow leads to stable wetting fronts that are parallel to the soil surface **(Hendrickx** and **Flury, 2001)**. One-dimensional uniform (equilibrium) water movement in a partially saturated rigid porous medium is described by a modified form of the Richards equation using the assumptions that the air phase plays an insignificant role in the liquid flow process and that water flow due to thermal gradients can be neglected **(Šimůnek et al., 2013).**

II.2.2. Preferential water flow (non-uniform water flow)

We can begin to assess perceptively the impact of land management on the provision of ecosystem services by macropores and paths of preferential flow. The scientific study of preferential flows and transport in soil is in good heart **(Clothier et al., 2008).**

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Preferential flow happens when there are heterogeneities within the soil profile and when flow instabilities occur. The last 20 years have seen a spectacular growth in our scientific understanding of preferential flow and transport processes. Classification of mechanisms and behaviors has enabled us to understand the influences of capillarity, viscosity and gravity at the pore-and-core scale. It has been possible, using classical physics, to separate fluid controls from medium characteristics in the initiation of instabilities **(Clothier** *et al.,* **2008)**

Preferential flow is a generic term used to describe a range of physical non-equilibrium flow processes occurring under a variety of circumstances **(Kamra** *et al.,* **2001)** Preferential flow is a generic term used for describing the process whereby water movement through a porous medium follows favored routes bypassing other parts of the medium **(Bruggeman, 1997)** non-uniform flow results in irregular wetting. As a direct consequence of these irregular flow patterns, water moves faster and with increased quantity at certain locations in the vadose zone than at others. This non-uniform movement of water and dissolved solutes is commonly denoted *preferential flow.* **(Hendrickx** and **Flury, 2001).** Field and laboratory experiments with conservative tracers and reactive solutes in soils have shown that preferential and heterogeneous flow and non-equilibrium transport conditions often exist **(Jellali** *et al.,* **2010).**

Soil heterogeneity is responsible for the difficulty in predicting the movement of mass (solids, liquids and gases) in field situations at most scales. For example, it often results in faster movement of gas, water, solutes and particles than would be expected from the soil matrix properties. This more rapid mass transport is associated with processes such as flow through earthworm burrows, cracks in soil, or flow associated with soil layering and hydrophobicity. These processes, together, are called preferential flow (PF). Preferential flow (PF): Refers to flow mechanisms where transport of water together with dissolved or suspended matter is primarily associated with a smaller fraction of the total pore network, at any scale much larger than the microscopic (lm) scale. PF is now routinely included in models that predict water, solute, and particle transport in soils. Four types of preferential flow are considered: **crack flow** (CF), **burrow flow** (BF), **finger flow** (FF), and **lateral flow** (LF). **Crack flow**: Refers to PF along continuous cracks through an unsaturated soil profile. **Burrow flow**: Refers to flow through channels created by soil fauna when runoff occurs. **Finger flow**: Occurs when infiltrating water accumulates at the interface between two soil layers, usually in sandy soils, with a coarser layer underlying a finer layer. **Lateral flow**: Occurs when infiltrating water moves laterally and locally along an inclined hydraulically restrictive layer such as along bedrock or along lateral roots **(Allaire** *et al.,* **2009).** *Funnel flow* refers to the lateral redirection and funneling of water caused by textural boundaries **(Hendrickx** and **Flury, 2001)**. Macropores: refer to opening features larger than the microscopic scale in the soil that may cause non-equilibrium of mass movement. There is no accepted definition that characterizes a given soil pore as a macropore. Various authors have given diameter limits to define what they consider macropores and non-macropores. Common to all definitions of macropores is that their diameter is orders of magnitude larger than that of soil matrix textural pores Macropore flow (MF): Refers to the mass movement through macropores, leading to non-equilibrium with the soil matrix. CF and BF together form macropore flow (MF) **(Allaire** *et al.,* **2009).**

Each type of preferential flow is caused by different physical mechanisms. Often, several mechanisms act simultaneously, which leads to a broad variety of flow patterns. In unsaturated porous media, macropores do not necessarily conduct large amounts of water. Flow through the porous matrix, thus slowing down vertical migration considerably. The

interplay of precipitation or irrigation rates with dynamics of the infiltration rate over time adds to the macropore flow mechanism complexity **(Hendrickx** and **Flury, 2001)**.

The local scale (also known as mesoscopic or Darcy scale corresponds to the characteristic dimension of heterogeneities (e.g. aggregate diameter or fracture spacing). **(Szymkiewicz, 2004)**. Different experimental methods for measuring water content and solute concentrations in the field have been used to identify and characterize preferential flow. **Skopp (1981)** presented a qualitative approach defining macroporosity as the pore space that provides preferential flow paths **(Bruggeman, 1997)**.

One of the least understood preferential pathway flow mechanisms is that of *unstable flow.* A stable wetting front is a horizontal front that moves downwards without breaking into fingers. The behavior of such a front can be simulated by one-dimensional computer models. The infiltration theories of Green and Ampt and Philip predict sharp, stable wetting fronts during infiltration in dry, homogeneous wettable soils. These theories were mostly verified in laboratory columns with diameters of a few centimeters, but also in field soils after periods with precipitation. However, many observers noted field phenomena that appear to contradict the universal validity of these infiltration theories **(Hendrickx** and **Flury, 2001)**.

II.3. Type of porous medium

Pores are generally classified based on their equivalent pore size. use of three different soil porosity classes corresponding with three dominant regimes of soil water behavior and associated with some "convenient" equivalent pore diameter ranges. The suggested classification distinguishes: micropores as pores that retain water at field capacity (often referred to as old water), with an equivalent diameter of less than 0.01 mm; mesopores as pores that are generally drained at field capacity, with an equivalent diameter of 0.01 to 1 mm; and macropores as pores that channel flow through the profile from surface ponding or a perched water table, with an equivalent diameter larger than 1 mm. mixing and transfer between macropores and other pores are limited; and matrix porosity as the pore space that transmits water and solute at a rate slow enough to result in extensive mixing and relatively rapid transfer of molecules between different pores. Summarized definitions of minimum equivalent diameters for macropores specified in the literature ranging from 0.03 to 3 mm **(Bruggeman, 1997).**

II.3.1. Homogeneous soils

Homogeneous soils are ideal for pure studies, but one does not expect to find such behavior in a farmland or a forest. The transport process in heterogeneous soils differs from that in homogeneous soils in many ways. The wetting front may show instability in heterogeneous soils **(Zhou, 2002).**

II.3.2. Heterogeneous soils

Infiltration of water in unsaturated soils has long been an interest of study in many branches of science and engineering such as soil science, hydrology, and geotechnical engineering. Because the appearance of layered soil is more common than uniform soil in nature with the latter being the exception, vertical infiltration in layered soils has drawn much attention and been studied by many writers **(Yang** *et al***, 2006).**

II.3.2.1. Dual-Porosity System

Dual-porosity media consist of two interacting sub-domains with contrasted hydraulic properties. One sub-domain corresponds to the porous matrix or soil aggregates, and the other includes inter-aggregate space filled with coarser material, macropores, fractures or fissures which are highly conductive compared to the matrix **(Lewandowska et al., 2004)**. Natural porous geomaterials are very often heterogeneous multiphase materials of complex structure. They are named "double-porosity" materials, when presenting a strong contrast in local hydrodynamic characteristics (aggregated soils, fractured porous rocks), **Tran Ngoc et al. (2010).**

A large class of heterogeneous porous formations can be described as double-porosity media. They are composed of two sub-domains characterized by contrasting hydraulic properties. Typical examples are aggregated soils or fractured rocks. The heterogeneous structure of double-porosity media may result from different physical, chemical and biological processes, which are the origin of fractures, fissures, vugs, shales, aggregates, macropores or cracks. One class of double-porosity structure is represented by media with the two porous sub-domains occupying similar fraction of space, where the water flow in both regions can be described by the Richards equation. Other types of dual-porosity structures are fractured rocks or soils with large fissures or macropores, which appear due to the shrinkage, growth of plants (root channels) or biological activity (wormholes). Due to their particular structure double-porosity media often show non-standard behavior at the macroscopic scale. Another important aspect of the double-porosity models is the representation of the water transfer between the two sub-domains. The most widespread formulation, proposed by **Warren and Root (1963),** relates the water transfer directly to the difference in pressures between the sub-domains. Alternatively, the transfer rate may be related to the difference in saturations of the two regions. One should note that the transfer term approximations have been initially developed for linear problems: diffusion or saturated flow. However, their extension to the nonlinear problems of unsaturated flow is not necessarily straightforward. Instead of using averaged macroscopic variables, the exchange term can be obtained from the direct solution of local flow in weakly conductive aggregates / blocks. In this approach matrix blocks are divided into nested sub-grids to accommodate slow changes in local variables, which vary in function of the distance from fracture **(Szymkiewicz, 2004)**.

Dual-porosity models assume that water flow is restricted to the fractures (or inter-aggregate pores and macropores), and that water in the matrix (the intra-aggregate pores or the rock matrix) does not move at all. These models assume that the matrix, consisting of immobile water pockets, can exchange, retain, and store water, but does not permit convective flow. This conceptualization leads to two-region, dual-porosity type flow and transport models that partition the liquid phase into mobile (flowing, inter-aggregate), θ_{mo}, and immobile (stagnant, intra-aggregate), θ_{im}, regions: $\theta = \theta_{mo} + \theta_{im}$

We will use here the subscript m to represent fractures inter-aggregate pores, or macropores, and the subscript im to represent the soil matrix, intra-aggregate pores, or the rock matrix used a kinematic wave equation to describe gravitational movement of water in macropores. Although dual-porosity models have been popularly used for solute transport studies, they have thus far not been used extensively for water flow problems **(Šimůnek et al., 2013)**.

In this type of medium three distinct observation scales can be considered: the microscopic scale (or pore scale), associated with single grains and pores of the medium, the mesoscopic scale (or Darcy scale), which is the scale of a single soil aggregate or

porous block and the macroscopic scale, which is of major interest from the point of view of soil hydrology and groundwater modeling (**Lewandowska et al., 2004**).
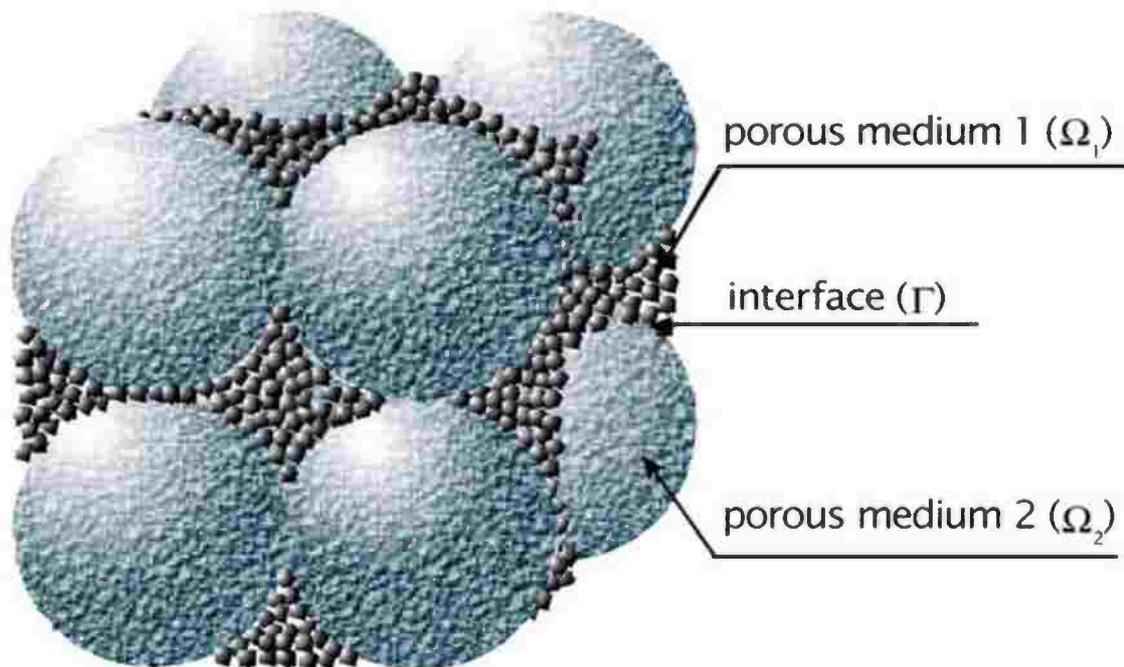

Fig. (1). Structure of double-porosity medium (**Lewandowska et al., 2004**)

II.3.2.2. Dual-Permeability System

While dual-porosity models assume that water in the matrix is stagnant, dual-permeability models allow for water flow in the matrix as well. The approach of **Gerke and van Genuchten (1993a and b)** who applied Richards equations to each of two pore regions, **Vogel et al. (1991)** who modified the equations of **van Genuchten(1980)** to add flexibility in the description of the hydraulic properties near saturation (**Šimůnek et al., 2013**).

Two types of soil heterogeneity which require different modelling approaches are distinguished: micro- and macro-heterogeneity. Micro-heterogeneity refers to the heterogeneity at the pore scale due to the presence of macropores which form a separate pore network and macro-heterogeneity refers to the spatial variability of macroscopic soil properties which define flow and transport at a macroscopic scale. Water flow and solute transport in natural soils are significantly influenced by the occurrence of (1) macropores and structured elements (micro-heterogeneity), (2) spatial variability of soil properties (macro-heterogeneity) or (3) a combination of (1) and (2). The classical water flow theory based on the Buckingham and Darcy law, However, when macropores are present this theory may not adequately describe the infiltration and redistribution of water as shown by **Mallants et al.(1996)** the initial moisture content of the soil matrix and the micro relief of the surface. This behavior is described several times in literature as "channeling flow", "preferential flow", "short-circuiting" or "bypass flow" unequivocal definition of macroporosity does not exist, in part because there are several forming processes resulting in macropores of different size, shape and continuity, and in part because the soil material (texture) has an impact (what can be seen as macropores in a fine textured clay soil, can just be a part of the bulk soil volume in a coarse textured sandy soil (**Feyen et al., 1998**).

II.4. Solute transport

Throughout the top 60 cm of the soil profile the maximum solute concentrations occurred within ten minutes from the end of the one-hour rainstorm. The solute concentrations then decreased, but remained at a relatively constant level throughout the 24 hour drainage period **(Bruggeman, 1997).** Widely different solution techniques have been proposed to deal with the resulting multi-component transport problem. The assumption of instantaneous (equilibrium) sorption is also being questioned. A number of chemical-kinetic and diffusion-controlled "physical" models have been used to describe non-equilibrium transport **(van Genuchten, 1991)**.

Numerical modeling is one of the methods used to estimate the flux of water moving through the vadose zone. Field measurements of recharge rate are ideal but often expensive and of limited spatial and temporal scope. The differential equation for liquid water flow a modified form of Richards' equation **(Richards, 1931).** This equation describes the change in water storage, redistribution, and plant water uptake at every point within the soil profile **(Fayer, 2000).**

II.4.1.Specific Models for Water Flow

We will briefly review the governing equations for both equilibrium (uniform) water flow and for non-equilibrium flow in dual-porosity and dual-permeability systems. Subsequently we will describe various solute transport models that consider either physical or chemical non-equilibrium and models that consider simultaneously both physical and chemical non-equilibrium.

II.4.1.1. Uniform Flow Model (Equilibrium)

Numerical models for water flow in soils (Fig. 2a and 3a) are usually based on the following equation:

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

or its extensions (e.g., for two- and three-dimensional systems). In Eq. (1), often referred to as the Richards equation, z is the vertical coordinate positive upward [L], t is time [T], h is the pressure head [L], θ is the water content [$L^3 L^{-3}$], S is a sink term representing root water uptake or some other source or sink [T^{-1}], and $K(h)$ is the unsaturated hydraulic conductivity function, often given as the product of the relative hydraulic conductivity, K_r (dimensionless), and the saturated hydraulic conductivity, K_s [$L T^{-1}$]. Solutions of the Richards Eq. (1) require knowledge of the unsaturated soil hydraulic functions made up of the soil water retention curve, $\theta(h)$, which describes the relationship between the water content θ and the pressure head h, and the unsaturated hydraulic conductivity function, $K(h)$, which defines the hydraulic conductivity K as a function of h or θ. HYDRUS-1D considers both relatively traditional models **(Brooks and Corey, 1964; van Genuchten, 1980)** for the hydraulic functions, as well as more recent alternative single **(Kosugi, 1996)** and dual-porosity **(Durner, 1994)** models.

The soil water retention, $\theta(h)$, and hydraulic conductivity, $K(h)$, functions according to **Brooks and Corey (1964)** are given by:

$$S_e = |\alpha h|^{-n} \qquad\qquad h < -1/\alpha$$

$$S_e = 1 \qquad\qquad h \geq -1/\alpha \qquad\qquad (2)$$

$$K = K_s S_e^{2/n + t + 2}$$

Where: S_e is effective saturation:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta r} \qquad\qquad (3)$$

in which θ_r and θ_s denote the residual and saturated water contents, respectively; Ks is the saturated hydraulic conductivity, α is the inverse of the air-entry value (or bubbling pressure), n is a pore-size distribution index, and t is a pore-connectivity parameter assumed to be 2.0 in the original study of **Brooks and Corey (1964)**. The parameters α, n and t in HYDRUS are considered to be empirical coefficients affecting the shape of the hydraulic functions.

HYDRUS also implements the soil-hydraulic functions of **van Genuchten (1980)** who used the statistical pore-size distribution model of **Mualem (1976)** to obtain a predictive equation for the unsaturated hydraulic conductivity function in terms of soil water retention parameters. The expressions of **van Genuchten (1980)** are given by:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left[1 + |\alpha h|^n\right]^m} \qquad h < 0$$

$$\theta(h) = \theta_s \qquad\qquad h \geq 0 \qquad\qquad (4)$$

$$K(h) = K_s S_e^t \left[1 - \left(S_e^{1/m}\right)^m\right]^2$$

Where   m=1-1/n, n>1

The above equations contain five independent parameters: θ_r, θ_s, α, n, and K_s. The pore-connectivity parameter t in the hydraulic conductivity function was estimated (**Mualem, 1976**) to be about 0.5 as an average for many soils.

Version 4.0 of HYDRUS allows the soil hydraulic properties to be defined also according to **Kosugi (1996),** who suggested the following lognormal distribution model for $S_e(h)$:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{2} erfc\left[\frac{\ln(h/\alpha)}{\sqrt{2}n}\right] \qquad h < 0$$

$$S_e = 1 \qquad\qquad h \geq 0 \qquad\qquad (5)$$

Application of Mualem's pore-size distribution model (**Mualem, 1976**) now leads to the following hydraulic conductivity function:

$$K = K_s S_e^t \left[\frac{1}{2} erfc\left[\frac{\ln(h/\alpha)}{\sqrt{2}n} + \frac{n}{\sqrt{2}}\right]\right]^2 \qquad h < 0$$

$$K = K_s \qquad\qquad h \geq 0 \qquad\qquad (6)$$

Note that in this manual we use the symbol α instead of h_0 and n instead of σ as used in **Kosugi (1996). Durner (1994)** divided the porous medium into two (or more) overlapping regions and suggested to use for each of these regions a van Genuchten-Mualem type function (**van Genuchten, 1980**) of the soil hydraulic properties. Linear superposition of the functions for each particular region gives then the functions for the composite multimodal pore system (**Durner et al., 1999**):

$$S_e = w_1 \left[1 + \left(\alpha_1 h \right)^{n1} \right]^{-m1} + w_2 \left[1 + \left(\alpha_2 h \right)^{n2} \right]^{-m2} \tag{7}$$

Combining this retention model with Mualem (1976) pore-size distribution model leads now to:

$$K(S_e) = K_s \frac{\left(w_1 S_{e1} + w_2 S_{e2} \right) \left(w_1 \alpha_1 \left[1 - \left(1 - S_{e1}^{1/m1} \right)^{m1} \right] + w_2 \alpha_2 \left[1 - \left(1 - S_{e2}^{1/m2} \right)^{m2} \right] \right)^2}{\left(w_1 \alpha_1 + w_2 \alpha_2 \right)^2} \tag{8}$$

Where: wi are the weighting factors for the two overlapping regions, and αi, ni, mi (=1-1/ni), and i are empirical parameters of the separate hydraulic functions (i=1,2).
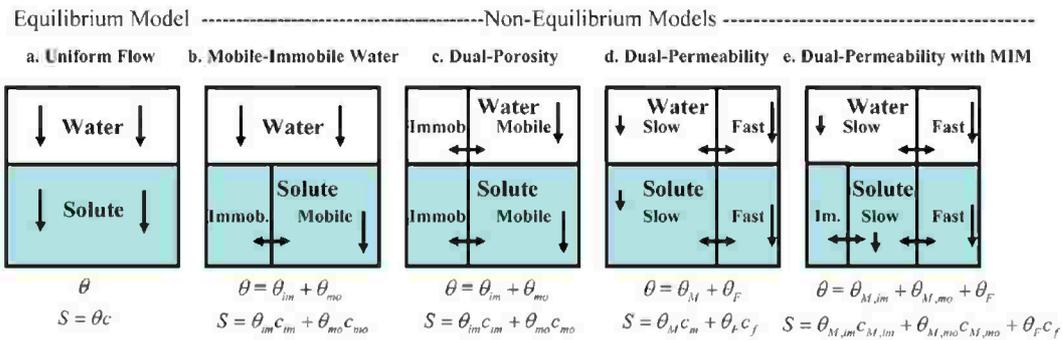

Fig. (2). Conceptual physical non-equilibrium models for water flow and solute transport. In the plots, θ is the water content, θ_{mo} and θ_{im} in (b) and (c) are water contents of the mobile and immobile flow regions, respectively; θ_M and θ_F in (d) are water contents of the matrix and macropore (fracture) regions, respectively, and $\theta_{M,mo}$, $\theta_{M,im}$, and θ_F in (e) are water contents of the mobile and immobile flow regions of the matrix domain, and in the macropore (fracture) domain, respectively; c are concentrations of corresponding regions, with subscripts having the same meaning as for water contents, while S is the total solute content of the liquid phase (**Šimůnek and van Genuchten, 2008**)
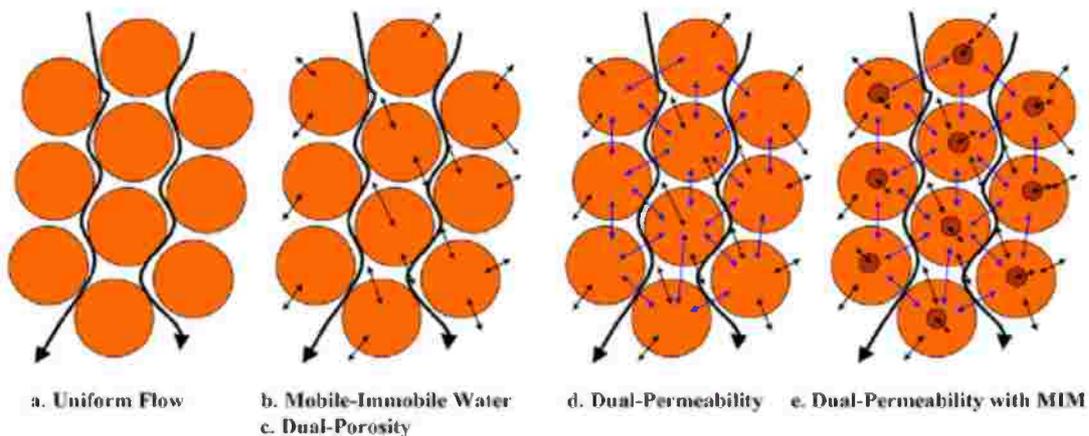

Fig. (3). Conceptual physical non-equilibrium models for water flow and solute transport (**Šimůnek and van Genuchten, 2008**)

II.4.1.2. Dual-Porosity Model

Dual-porosity models assume that water flow is restricted to the macropores (or interaggregate pores and fractures), and that water in the matrix (intraaggregate pores or the rock matrix) does not move at all. This conceptualization leads to two-region type flow and transport models (**van Genuchten and Wierenga, 1976**) that partition the liquid phase into mobile (flowing, interaggregate), θ_{mo}, and immobile (stagnant, intraaggregate), θ_{im}, regions [$L^3 L^{-3}$]:

$$\theta = \theta_{mo} + \theta_{im} \tag{9}$$

The dual-porosity formulation for water flow can be based on a mixed formulation of the Richards Eq. (1) to describe water flow in the macropores (the preferential flow pathways) and a mass balance equation to describe moisture dynamics in the matrix as follows (**Šimůnek et al., 2003**):

$$\frac{\partial \theta_{mo}\left(h_{mo}\right)}{\partial t} = \frac{\partial}{\partial z}\left[K\left(h_{mo}\right)\left(\frac{\partial h_{mo}}{\partial z}+1\right)\right] - S_{mo}\left(h_{mo}\right) - \Gamma_w$$

$$\frac{\partial \theta_{im}\left(h_{im}\right)}{\partial t} = -S_{im}\left(h_{im}\right) + \Gamma_w \tag{10}$$

Where: S_{mo} and S_{im} are sinking terms for the mobile and immobile regions, respectively [T^{-1}], and Γ_w is the transfer rates for water between inter- and intraaggregate pore domains [T^{-1}]. **Šimůnek et al. (2003)** and **Köhne et al. (2004)** discussed different formulations that can be used to evaluate the mass transfer rate Γ_w.

II.4.1.3. Dual-Permeability Model

Different dual-permeability approaches (Fig. 2d, 2e, 3d, and 3e) may be used to describe flow and transport in structured media. While some models invoke similar equations for flow in the fracture and matrix regions, others use different formulations for the two regions. A typical example of the first approach, implemented in HYDRUS-1D, is the work of **Gerke and van Genuchten (1993a,b and 1996)**, who applied the Richards equation to each of the two pore regions. The flow equations for the macropore (fracture) (subscript f) and matrix (subscript m) pore systems in their approach are given by:

$$\frac{\partial \theta_f\left(h_f\right)}{\partial t} = \frac{\partial}{\partial z}\left[K_f\left(h_f\right)\left(\frac{\partial h_f}{\partial z}+1\right)\right] - S_f\left(h_f\right) - \frac{\Gamma_w}{w}$$

$$\frac{\partial \theta_m\left(h_m\right)}{\partial t} = \frac{\partial}{\partial z}\left[K_m\left(h_m\right)\left(\frac{\partial h_m}{\partial z}+1\right)\right] - S_m\left(h_f\right) - \frac{\Gamma_w}{1-w} \tag{11}$$

Where: w is the ratio of the volumes of the macropore or fracture domain and the total soil system (dimensionless). This approach is relatively complicated in that the model requires characterization of water retention and hydraulic conductivity functions (potentially of different form) for both pore regions, as well as a hydraulic conductivity function of the fracture–matrix interface. Note that the water contents, θ_f and θ_m in Eq. (11), have different meanings than in Eq. (10), where they represented water contents of the total pore space (i.e., $\theta = \theta_{mo} + \theta_{im}$), while here they refer to water contents of the two separate (fracture or matrix) pore domains such that:

$$\theta = \theta_F + \theta_M = w\,\theta_f + \left(1-w\right)\theta_m \tag{12}$$

Hence, lowercase subscripts in the dual-permeability model refer to the local (pore-region) scale, while uppercase subscripts refer to the global (total soil medium) scale.

II.4.2. Specific Models for Solute Transport
II.4.2.1.Uniform Transport (Equilibrium)

Solute transport in numerical models is usually described using the relatively standard advection–dispersion equation (Fig.2a and 3a) of the form

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial q c}{\partial z} - \phi \qquad (13)$$

or various extensions thereof (e.g., for two- and three-dimensional systems, or for multiple phases or components). In Eq. (13), c is the solution concentration [M L^{-3}], s is the sorbed concentration [M M^{-1}], D is the dispersion coefficient accounting for both molecular diffusion and hydrodynamic dispersion [L^2 T^{-1}], q is the volumetric fluid flux density [L T^{-1}] evaluated using the Darcy–Buckingham law, and φ is a sink–source term that accounts for various zero- and first-order or other reactions [M L^{-3} T^{-1}]. While HYDRUS-1D considers a general nonlinear sorption equation that can be simplified into a Langmuir or Freundlich isotherm (**Šimůnek et al., 2005**), for simplicity we assume here only linear adsorption of the form:

$$s = K_d c \qquad (14)$$

Where: K_d is the distribution coefficient [L^3 M^{-1}]. Linear sorption leads to the following definition of the retardation factor R (dimensionless):

$$R = 1 + \frac{\rho K_d}{\theta} \qquad (15)$$

In the examples used in **Šimůnek et al. (2008)**, they using Eq. (14) for linear sorption and applying the resulting definition of R to all of the liquid domains involved (e.g., the total liquid phase, the mobile and immobile regions, or the matrix and macropore domains) with their appropriate parameters. Although considered in HYDRUS-1D, the effect of molecular diffusion will be neglected in the various examples. The dispersion coefficient D accounting only for hydrodynamic dispersion [L^2 T^{-1}] is thus defined as:

$$D = \lambda v = \lambda \frac{q}{\theta} \qquad (16)$$

Where: λ is the dispersivity [L] and v the average pore velocity [LT^{-1}]. The same definition of the dispersion coefficient will be used for all mobile phases. HYDRUS-1D additionally considers molecular diffusion for transport in the gaseous phase, which will not be discussed here either. Finally, in the examples we can use the time T needed to reach one pore volume of effluent. This time is given by:

$$T = \frac{\theta L}{q} \qquad (17)$$

Where: L is some distance (e.g., column length) within the transport domain being considered. For the physical nonequilibrium models discussed below, the pore volume for different domains is defined using corresponding water contents and fluxes.

II.4.3. Physical Non-equilibrium Transport Models
II.4.3.1. Mobile–Immobile Water and Dual-Porosity Models

The concept of two-region, dual-porosity type solute transport (Fig. 2b, 2c, 3b, and 3c) was implemented already in earlier versions (1.0 and 2.0) of HYDRUS-1D to permit consideration of physical non-equilibrium transport. While the physical non-equilibrium transport model in the earlier versions was combined only with uniform water flow Eq. (1), Version 3.0 of HYDRUS-1D was expanded to also consider the dual-porosity water flow model Eq. (10) with transient immobile water content. In both implementations, the governing solute transport equations are as follows:

$$\frac{\partial \theta_{mo} c_{mo}}{\partial t} + f_{mo} \rho \frac{\partial s_{mo}}{\partial t} = \frac{\partial}{\partial z}\left(\theta_{mo} D_{mo} \frac{\partial c_{mo}}{\partial z}\right) - \frac{\partial q_{mo} c_{mo}}{\partial z} - \phi_{mo} - \Gamma_s$$

$$\frac{\partial \theta_{im} c_{im}}{\partial t} + (1 - f_{mo}) \rho \frac{\partial s_{im}}{\partial t} = \Gamma_s - \phi_{im} \tag{18}$$

$$\Gamma_s = \omega_{mim}(c_{mo} - c_{im}) + \Gamma_w c^*$$

in which solute exchange between the two liquid regions is modeled as the sum of an apparent first-order diffusion process and advective transport (where applicable). In Eq. (18), c_{mo} and c_{im} are concentrations of the mobile and immobile regions [M L^{-3}], respectively; s_{mo} and s_{im} are sorbed concentrations of the mobile and immobile regions [M M^{-1}], respectively; D_{mo} is the dispersion coefficient in the mobile region [L^2 T^{-1}], q_{mo} is the volumetric fluid flux density in the mobile region [L T^{-1}], φ_{mo} and φ_{im} are sink–source terms that account for various zero- and first-order or other reactions in both regions [M L^{-3} T^{-1}]; f_{mo} is the fraction of sorption sites in contact with the mobile water content (dimensionless), ω_{mim} is the mass transfer coefficient [T^{-1}], and Γ_s is the mass transfer term for solutes between the mobile and immobile regions [M L^{-3} T^{-1}]. Equation (18) describes solute transport in the mobile (macropore) zone, Eq. (18) is a mass balance for the immobile (micropore) domain, while Eq. (18) (Γ_s) describes the rate of mass transfer between the mobile and immobile domains. The second (advective) term of Γ_s in Eq. (18) is equal to zero for the Mobile–Immobile Model since that model does not consider water flow between the two regions. In the Dual-Porosity Model, c^* is equal to c_{mo} for $\Gamma_w > 0$ and c_{im} for $\Gamma_w < 0$.

II.4.3.2. Dual-Permeability Model

Analogous to Eq. [4], the dual-permeability formulation for solute transport is based on advection–dispersion type equations for transport in both the fracture and matrix regions as follows **(Gerke and van Genuchten, 1993a,b)** (Fig. 2d and 3d):

$$\frac{\partial \theta_f c_f}{\partial t} + \rho \frac{\partial s_f}{\partial t} = \frac{\partial}{\partial z}\left(\theta_f D_f \frac{\partial c_f}{\partial z}\right) - \frac{\partial q_f c_f}{\partial z} - \phi_f - \frac{\Gamma_s}{w}$$

$$\frac{\partial \theta_m c_m}{\partial t} + \rho \frac{\partial s_m}{\partial t} = \frac{\partial}{\partial z}\left(\theta_m D_m \frac{\partial c_m}{\partial z}\right) - \frac{\partial q_m c_m}{\partial z} - \phi_m - \frac{\Gamma_s}{1 - w} \tag{19}$$

$$\Gamma_s = \omega_{dp}(1 - w)\theta_m(c_f - c_m) + \Gamma_w c^*$$

The variables in Eq. (19) have similar meanings as in Eq. (18), except that they refer now to two overlapping domains, i.e., the matrix (subscript m) and fracture (subscript f) domains. Equation (19) describes solute transport in the fracture domain, Eq. (19)

transport in the matrix domain, and Eq. (19) advective–dispersive mass transfer between the fracture and matrix domains. Equation (19) assumes complete advective–dispersive transport descriptions for both the fractures and the matrix. **Van Genuchten and Dalton (1986)** and **Gerke and van Genuchten (1996)**, among others, discussed possible expressions for the first-order solute mass transfer coefficient, ω_{dp} [T^{-1}].

II.4.3.3. Dual-Permeability Model with Immobile Water

The Dual-Permeability Model with Immobile Water (Fig. 2e and 3e) assumes that the liquid phase of the matrix can be further partitioned into mobile (flowing), $\theta_{m,m}$ [L3 L^{-3}], and immobile (stagnant), $\theta_{im,m}$ [L^3 L^{-3}], regions as follows:

$$\theta_m = \theta_{m,m} + \theta_{im,m}$$ (20)

Where: θ_m is the volumetric water content of the matrix pore system [L^3 L^{-3}]. The governing advection–dispersion equation for transport in the matrix region (Eq. 19) is then replaced with the modified equations (Eq. 18), **Pot et al. (2005)** to yield:

$$\frac{\partial \theta_f c_f}{\partial t} + \rho \frac{\partial s_f}{\partial t} = \frac{\partial}{\partial z}\left(\theta_f D_f \frac{\partial c_f}{\partial z}\right) - \frac{\partial q_f c_f}{\partial z} - \phi_f - \frac{\Gamma_s}{w}$$

$$\frac{\partial \theta_{im,m} c_{im,m}}{\partial t} + \rho_m \left(1 - f_m\right)\frac{\partial s_{im,m}}{\partial t} = \Gamma_s {}^* - \phi_{im,m}$$ (21)

$$\Gamma_s = \omega_{dp}\left(1 - w\right)\theta_m\left(c_f - c_{m,m}\right) + \Gamma_w c^*$$

$$\Gamma_s {}^* = \omega_{dpm}\left(c_{m,m} - c_{im,m}\right)$$

Where: $c_{im,m}$ and $c_{m,m}$ are solute concentrations in the immobile and mobile zones of the matrix region [M L^{-3}], respectively; $\varphi_{m,m}$ and $\varphi_{im,m}$ represent various reactions in the mobile and immobile parts of the matrix [M L^{-3} T^{-1}], respectively; f_m is again the fraction of sorption sites in contact with the mobile region of the matrix (dimensionless), ω_{dpm} is the mass transfer coefficient between mobile and immobile zones of the matrix region [T^{-1}], and $\Gamma_s *$ is the mass transfer term for solutes between the mobile and immobile regions of the matrix domain [M L^{-3} T^{-1}]. Equation (21) now describes solute transport in the fracture domain, Eq. (21) transport in the mobile zone of the matrix domain, Eq. (21) is a mass balance for the immobile zone of the matrix domain, Eq. (21) describes mass transfer between the fracture and matrix domains, while Eq. (21) describes mass transfer between the mobile and immobile zones within the matrix domain.

II.4.4. Chemical Non-equilibrium Transport Models
II.4.4.1. One Kinetic Site Model

When sorption in the Uniform Transport Model is considered (Fig. 3a) to be kinetic, Eq. (13) needs to be supplemented with an equation describing the kinetics of the sorption process. This is usually done by assuming a first-order process as follows:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s^k}{\partial t} = \frac{\partial}{\partial t}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial q c}{\partial z} - \phi$$

$$\rho \frac{\partial s^k}{\partial t} = \alpha_k \rho\left(s_e^k - s^k\right) - \phi_k$$ (22)

$$s_e^k = K_d c$$

where s_e^k is the sorbed concentration that would be reached at equilibrium with the liquid-phase concentration [M M^{-1}], s^k is the sorbed concentration of the kinetic sorption sites [M M^{-1}], α_k is a first-order rate constant describing the kinetics of the sorption process [T^{-1}], and φ_k represents a sink–source term that accounts for various zero- and first-order or other reactions at the kinetic sorption sites [M L^{-3} T^{-1}].
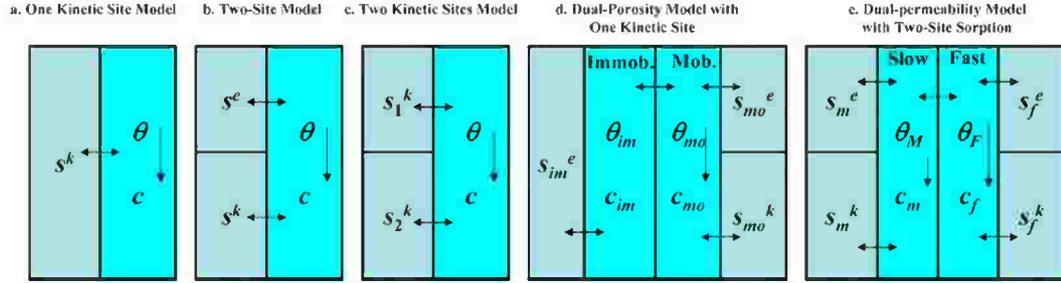

Fig. (4). Conceptual chemical non-equilibrium models for reactive solute transport. In the plots, θ is the water content, θ_{mo} and θ_{im} in (d) are water contents of the mobile and immobile flow regions, respectively; θ_M and θ_F in (e) are water contents of the matrix and macropore (fracture) regions, respectively; c are concentrations of the corresponding regions, s^e are sorbed concentrations in equilibrium with the liquid concentrations of the corresponding regions, and s^k are kinetically sorbed solute concentrations of the corresponding regions (**Šimůnek and van Genuchten, 2008**)

II.4.4.2. Two-Site Model

Similarly to the mobile–immobile water concept, the concept of two-site sorption (**Selim et al., 1976; van Genuchten and Wagenet, 1989**) (Fig. 3b) was implemented already in Versions 1.0 and 2.0 of HYDRUS-1D to permit consideration of non-equilibrium adsorption–desorption reactions. The two-site sorption concept assumes that the sorption sites can be divided into two fractions:

$$s = s^e + s^k \tag{23}$$

Sorption s^e [M M^{-1}], on one fraction of the sites (Type 1 sites) is assumed to be instantaneous, while sorption s^k [M M^{-1}], on the remaining (Type 2) sites is considered to be a first-order kinetic rate process. The system of equations describing the Two-Site Model is given by:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s^e}{\partial t} + \rho \frac{\partial s^k}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} - \phi$$

$$s^e = f_e K_d c \tag{24}$$

$$\rho \frac{\partial s^k}{\partial t} = \alpha_k \rho \left(s^e - s^k\right) - \phi_k$$

$$s_e^k = \left(1 - f_e\right) K_d c$$

Where: f_e is the fraction of exchange sites assumed to be in equilibrium with the liquid phase (dimensionless), and α_k is a first-order rate constant [T^{-1}]. Equation (24) describes solute transport in the total system, Eq. (24) equilibrium sorption onto the instantaneous sorption sites, Eq. (24) is a mass balance of the kinetic sorption sites (**van Genuchten and**

Wagenet, 1989), while Eq. (24) represents the sorbed concentration of the kinetic sites when equilibrium would be reached with the liquid-phase concentration.

II.4.4.3. Two Kinetic Sites Model

To facilitate simulations of the transport of colloids or microorganisms (such as viruses and bacteria), Version 3.0 of HYDRUS-1D also implemented a Two Kinetic Sites Model (Fig. 3c) using the attachment–detachment approach:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s_1^k}{\partial t} + \rho \frac{\partial s_2^k}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} - \phi$$

$$\rho \frac{\partial s_1^k}{\partial t} = k_{a1}\theta c - k_{d1}\rho s_1^k - \phi_{k1} \tag{25}$$

$$\rho \frac{\partial s_2^k}{\partial t} = k_{a2}\theta c - k_{d2}\rho s_2^k - \phi_{k2}$$

Where: s_1^k and s_2^k are sorbed concentrations of the first and second fractions of kinetic sorption sites [M M^{-1}], respectively; k_{a1} and k_{a2} are attachment coefficients for the first and second fractions of kinetic sorption sites [T^{-1}], respectively; k_{d1} and k_{d2} are detachment coefficients for the first and second fractions of kinetic sorption sites [T^{-1}], respectively; and φ_{k1} and φ_{k2} represent sink–source terms for the first and second fractions of kinetic sorption sites [M L^{-3} T^{-1}], respectively. Note that the Two Kinetic Sites Model can be used (and often is used) to describe different processes. While the first kinetic process could be chemical attachment, the second kinetic process could represent physical straining **(Bradford et al., 2004; Gargiulo et al., 2007, 2008)**. Note that in Eq. (25) we do not give the nonlinear blocking coefficients accounting for, for example, Langmuirian blocking to attachment sites or depth-dependent straining that are considered in HYDRUS-1D **(Bradford et al., 2004)**. It is easily shown that the formulation based on attachment–detachment coefficients is mathematically identical to the formulation using first-order mass transfer coefficients. For example, by comparing Eq. (22) with (25) we have:

$$\frac{\partial s^k}{\partial t} = \theta k_a c - k_d \rho s^k = \rho \alpha_k \left(K_d c - s^k\right)$$

$$k_a = \alpha_k \frac{\rho}{\theta} K_d$$

$$K_d = \alpha_k \tag{26}$$

$$K_d = \frac{\theta k_a}{\rho \alpha_k}$$

II.5. Physical and Chemical Non-equilibrium Transport Models

II.5.1. Dual-Porosity Model with One Kinetic Site

This model (Fig. 3d) is similar to the Dual-Porosity Model (Eq. 11) in that the porous medium is divided into mobile and immobile domains such that $\theta = \theta_{mo} + \theta_{im}$. The current model, however, additionally divides the sorption sites in contact with the mobile zone, similarly to the Two-Site Model (Eq. 23), into two fractions involving instantaneous and kinetic sorption such that the total sorption concentration at equilibrium is given by:

$$s = \left(1 - f_{mo}\right) s_{im} + f_{mo} s_{mo}$$

$$= \left(1 - f_{mo}\right) s_{im} + f_{mo}\left(s_{mo}^e + s_{mo,e}^k\right)$$

$$= \left(1 - f_{mo}\right) K_d c_{mo} + f_{mo} f_{em} K_d c_{mo} + f_{mo}\left(1 - f_{em}\right) K_d c_{mo} \qquad (27)$$

$$= K_d c_{mo}$$

Where: s_{mo}^e is the sorbed concentration in equilibrium with the liquid-phase concentration of the mobile region of the Dual-Porosity Model [M M^{-1}], $s_{mo,e}^k$ is the sorbed concentration of the kinetic sites in contact with the mobile region of the Dual- Porosity Model when at equilibrium [M M^{-1}], f_{mo} is the fraction of sorption sites in contact with mobile water (the remainder is in contact with immobile water), and f_{em} is the fraction of sorption sites in equilibrium with the mobile liquid phase (the remaining kinetic sites are also in contact with the mobile liquid phase). The complete Dual-Porosity Model with One Kinetic Site is described using the following equations:

$$\frac{\partial \theta_{mo} c_{mo}}{\partial t} + f_{mo}\rho\frac{\partial s_{mo}^e}{\partial t} = \frac{\partial}{\partial t}\left(\theta_{mo} D_{mo}\frac{\partial c_{mo}}{\partial z}\right) - \frac{\partial q_{mo} c_{mo}}{\partial z} - \phi_{mo} - \Gamma_{s1} - \Gamma_{s2}$$

$$\frac{\partial \theta_{im} c_{im}}{\partial t} + \left(1 - f_{mo}\right)\rho\frac{\partial s_{im}}{\partial t} = \Gamma_{s1} - \phi_{im}$$

$$f_{mo}\rho\frac{\partial s_{mo}^k}{\partial t} = \Gamma_{s2} - \phi_{mo,k}$$

$$\Gamma s_1 = \omega_{ph}\left(c_{mo} - c_{im}\right) \qquad (28)$$

$$\Gamma_{s2} = \alpha_{ch}\rho\left(s_{mo,e}^k - s_{mo}^k\right)$$

$$s_{mo}^e = f_{em} K_d c_{mo}$$

$$s_{mo}^k = \left(1 - f_{em}\right) K_d c_{mo}$$

Where: ω_{ph} and α_{ch} are first-order rate constants [T^{-1}] accounting for physical and chemical rate processes, respectively; Γ_{s1} is the mass transfer term for solute exchange between the mobile and immobile regions [M L^{-3} T^{-1}]; Γ_{s2} represents mass transfer to the kinetic sorption sites in the mobile region [M L^{-3} T^{-1}]; and φ_{mo}, φ_{im}, and $\varphi_{mo,k}$ represent sink–source terms for the equilibrium phases in the mobile zone, the immobile zone, and the kinetic sorption sites [M L^{-3} T^{-1}], respectively. Equation (28) describes transport in the mobile phase; Eq. (28) is a mass balance for the immobile phase, and Eq. (28) a mass balance for the kinetic sorption sites in contact with the mobile zone. Equation (28) describe mass transfer rates between the mobile and immobile zones and to the kinetic sorption sites, respectively, while Eq. (28) represent sorption onto the equilibrium and kinetic sorption sites in contact with the mobile zone, respectively.

II.5.2. Dual-Permeability Model with Two-Site Sorption

Finally, simultaneous physical and chemical non-equilibrium processes are implemented in HYDRUS-1D by assuming applicability of the Dual-Permeability Model (**Gerke and van Genuchten, 1993a; Šimůnek et al., 2003**) and dividing the sorption sites of both the fracture and matrix domains into equilibrium and kinetic sites (Fig. 3e). This model leads to the following set of equations (**Pot et al., 2005**):

$$\frac{\partial \theta_f c_f}{\partial t} + \rho_f \frac{\partial s_f^e}{\partial t} = \frac{\partial}{\partial t}\left(\theta_f D_f \frac{\partial c_{mo}}{\partial z}\right) - \frac{\partial q_f c_f}{\partial z} - \phi_f - \frac{\Gamma_s}{w} - \Gamma_f$$

$$\frac{\partial \theta_m c_m}{\partial t} + \rho_m \frac{\partial s_m^e}{\partial t} = \frac{\partial}{\partial t}\left(\theta_m D_m \frac{\partial c_m}{\partial z}\right) - \frac{\partial q_m c_m}{\partial z} - \phi_m - \frac{\Gamma_s}{1-w} - \Gamma_m$$

$$\rho \frac{\partial s_f^k}{\partial t} = \Gamma_f - \phi_{f,k}$$

$$\rho \frac{\partial s_m^k}{\partial t} = \Gamma_m - \phi_{m,k} \tag{29}$$

$$\Gamma_s = \omega_{dp}(1-w)\theta_m(c_f - c_m) + \Gamma_w c*$$

$$\Gamma_f = \rho_f \alpha_{ch,f}\left[(1-f_f)K_{df}c_f - s_f^k\right]$$

$$\Gamma_m = \rho_m \alpha_{ch,m}\left[(1-f_m)K_{dm}c_m - s_m^k\right]$$

Where: s_m^k and s_f^k are sorbed concentrations of Type 2 (kinetic) sites in the matrix and fracture domains [M M^{-1}], respectively; f_m and f_f are fractions of the exchange sites assumed to be in equilibrium with the solution phases (dimensionless) of the matrix and fracture domains, respectively; φ_f, φ_m, $\varphi_{f,k}$, and $\varphi_{m,k}$ represent reactions in the equilibrium phases of the fracture and matrix domains and at the kinetic sites of the fracture and matrix domains [M L^{-3} T^{-1}], respectively; and $\alpha_{ch,m}$ and $\alpha_{ch,f}$ are again first-order rate constants for the matrix and fracture domains [T^{-1}], respectively. Note that the distribution coefficients can be different in the different regions (i.e., $K_{df} \neq K_{dm}$).