

8 Solute transport

J.C. van Dam, J.J.T.I. Boesten

8.1 Introduction

Many solutes enter the natural system at the soil surface. The solute residence time in the unsaturated zone is important for soil- and groundwater pollution management. For instance organic compounds are mainly decomposed in the unsaturated zone, where the biological activity is concentrated. Most plants are able to extract water and nutrients from the soil only in the unsaturated zone. In irrigated areas, the long term salinity in the root zone will depend on the amount of percolation from the unsaturated zone. Whereas in the unsaturated zone the transport of solutes is predominantly vertical, once being in the groundwater solutes may diverge in any direction, threatening surface waters, nature reserves and drinking wells. Using an analytical model, Beltman et al. (1995) show the importance of the transport processes in the unsaturated zone as compared to the transport processes in the saturated zone. It is clear that a thorough understanding is needed of the processes that govern the transport, adsorption, root uptake and decomposition of the solutes in the unsaturated zone, in order to analyse and manage soil and water related environmental problems.

SWAP is designed to simulate transport processes at field scale level. Although for management purposes most farmers try to have more or less the same soil and drainage condition per field, still the existing soil spatial heterogeneity within a field may cause a large variation of solute fluxes (Biggar and Nielsen, 1976; Van de Pol et al., 1977; Van der Zee and Van Riemsdijk, 1987). Most of this variation is caused by spatial variation of the soil hydraulic functions (Par. 6.3), preferential flow due to macropores in structured soils (Par. 6.5) or unstable wetting fronts in unstructured soils (Par. 6.4). In many cases it will not be possible to determine the variation (including the correlations) of all the physical parameters. One approach is to measure for a period of time the solute concentrations in the soil profile and drainage water and apply calibration or inverse modelling to determine 'effective' transport parameters (Groen, 1997). Another approach is the use of Monte Carlo simulations, where the variation of the transport parameters is derived from comparable fields (Boesten and Van der Linden, 1991). Jury (1982) proposed to use transfer functions, which don't explicitly describe the transport processes within the soil, but just describe the relation between solutes that enter and that leave a soil profile. Some limitations of the transfer function approach are that it requires a field experiment for calibration and that extrapolation to other circumstances is risky because of its stochastic rather than physical basis. SWAP confines to the physical processes in order to be flexible in parameter input and allow the simulation of all kind of design and management scenario's. The spatial variability can be taken into account by calibration, inverse modelling or Monte Carlo simulation.

SWAP is focused on the transport of salts, pesticides and other solutes that can be described with relatively simple kinetics. Processes that are not considered in SWAP are:

- volatilization and gas transport
- transport of non-mixing or immiscible fluids (e.g. oil and water)
- chemical equilibria of various solutes (e.g. between Na^+ , Ca^{2+} and Mg^{2+})

- chemical and biological chain reactions (e.g. mineralization, nitrification)

In case of advanced pesticide transport, including volatilization and kinetic adsorption, SWAP can be used in combination with the model PESTLA (Van den Berg and Boesten, 1998) and PEARL (Leistra et al., 2000; Tiktak et al., 2000). For nutrient transport (nitrogen and phosphorus), SWAP can be used in combination with the model ANIMO (Rijtema et al., 1997; Kroes and Roelsma, 1998).

First we describe the transport processes that are considered in SWAP. Next we discuss the applied boundary conditions. Finally we consider how SWAP deals with solute transport in water repellent soils and in cracked clay soils.

8.2 Basic equations

8.2.1 Transport processes

The three main solute transport mechanisms in soil water are diffusion, convection and dispersion. *Diffusion* is solute transport which is caused by the solute gradient. Thermal motion of the solute molecules within the soil solution cause a net transport of molecules from high to low concentrations. The solute flux J_{dif} ($\text{g cm}^{-2} \text{d}^{-1}$) is generally described by Fick's first law:

$$J_{\text{dif}} = -\theta D_{\text{dif}} \frac{\partial c}{\partial z} \quad (8.1)$$

with D_{dif} the diffusion coefficient ($\text{cm}^2 \text{d}^{-1}$) and c the solute concentration in soil water (g cm^{-3}). D_{dif} is very sensitive to the actual water content, as it strongly affects the solute transport path and the effective cross-sectional transport area. In SWAP we employ the relation proposed by Millington and Quirk (1961):

$$D_{\text{dif}} = D_w \frac{\theta^{7/3}}{\phi_{\text{por}}^2} \quad (8.2)$$

with D_w the solute diffusion coefficient in free water ($\text{cm}^2 \text{d}^{-1}$) and ϕ_{por} the soil porosity ($\text{cm}^3 \text{cm}^{-3}$).

The bulk transport of solutes occurs when solutes are carried along with the moving soil water. The mean flux of this transport is called the *convective* flux, J_{con} ($\text{g cm}^{-2} \text{d}^{-1}$), and can be calculated from the average soil water flux:

$$J_{\text{con}} = qc \quad (8.3)$$

When describing water flow, we usually consider the Darcy flux q (cm d^{-1}), which is averaged over a certain cross section. In case of solute transport, we need to consider the water velocity variation between pores of different size and geometry and also the water velocity variation inside a pore itself. The variety of water velocities cause some solutes to advance faster than the average solute front, and other solutes to advance slower. The overall effect will be that steep solute fronts tends to smoothen or to disperse. Solutes seem to flow from high to low concentrations. If the time required for solutes to mix in the transverse direction is small, compared to the time required for solutes to move in the flow

direction by mean convection, the *dispersion* flux J_{dis} ($\text{g cm}^{-2} \text{d}^{-1}$) is proportional to the solute gradient (Bear, 1972):

$$J_{\text{dis}} = -\theta D_{\text{dis}} \frac{\partial \theta}{\partial z} \quad (8.4)$$

with D_{dis} the dispersion coefficient ($\text{cm}^2 \text{d}^{-1}$). Under laminar flow conditions D_{dis} itself is proportional to the pore water velocity $v = q/\theta$ (Bolt, 1979):

$$D_{\text{dis}} = L_{\text{dis}} |v| \quad (8.5)$$

with L_{dis} the dispersion length (cm). Dispersion length depends on the scale over which the water flux and solute convection are averaged. Typical values of L_{dis} are 0.5 - 2.0 cm in packed laboratory columns and 5-20 cm in the field, although they can be considerably larger in regional groundwater transport (Jury et al., 1991). Unless water is flowing very slowly through repacked soil, the dispersion flux is usually much larger than the diffusion flux.

The total solute flux J ($\text{g cm}^{-2} \text{d}^{-1}$) is therefore described by:

$$J = J_{\text{dif}} + J_{\text{con}} + J_{\text{dis}} = qc - \theta (D_{\text{dif}} + D_{\text{dis}}) \frac{\partial c}{\partial z} \quad (8.6)$$

<i>Model input</i>			
<i>Variable</i>	<i>Code</i>	<i>Description</i>	<i>Default</i>
D_w	DDIF	solute diffusion coefficient in free water ($\text{cm}^2 \text{d}^{-1}$)	0.0
	LDIS	solute dispersion length (cm)	5.0

8.2.2 Continuity and transport equation

By considering conservation of mass in an elementary volume, we may derive the continuity equation for solute transport:

$$\frac{\partial X}{\partial t} = -\frac{\partial J}{\partial z} - S_s \quad (8.7)$$

with X being the total solute concentration in the soil system (g cm^{-3}) and S_s the solute sink term ($\text{g cm}^{-3} \text{d}^{-1}$) accounting for decomposition and uptake by roots.

The solutes may be dissolved in the soil water and/or may be adsorbed to organic matter or to clay minerals:

$$X = \theta c + \rho_b Q \quad (8.8)$$

with ρ_b being the dry soil bulk density (g cm^{-3}) and Q the amount adsorbed (g g^{-1}). The adsorption isotherm describes the amount of solutes adsorbed in equilibrium with the dissolved concentration. At this stage we will assume instantaneous equilibrium between c and Q and use the non-linear Freundlich equation, which is a flexible function for many organic and inorganic solutes. However the mobile-immobile concept as implemented in SWAP, allows the transfer of solutes from the dissolved state to the adsorbed state and vice versa at a certain rate (Par. 6.4 and 8.3). Freundlich adsorption can be written as:

$$Q = K_f c_{\text{ref}} \left(\frac{c}{c_{\text{ref}}} \right)^{N_f} \quad (8.9)$$

with K_f the Freundlich coefficient ($\text{cm}^3 \text{g}^{-1}$), N_f is the Freundlich exponent (-) and c_{ref} is a reference value of the solute concentration (g cm^{-3}) which is used to make N_f dimensionless.

The solute sink term S_s can be written as:

$$S_s = \mu(\theta c + \rho_b Q) + K_r S c \quad (8.10)$$

where μ is the first order rate coefficient of transformation (d^{-1}), K_r is the root uptake preference factor (-) and S the root water extraction rate (d^{-1}). At the right hand side of Eq. (8.10), the first term accounts for linear decomposition and the second term for root uptake proportional to water uptake. K_r accounts for positive or negative selection of solute ions relative to the amount of soil water that is extracted.

The coefficient μ is affected by soil temperature, water content and depth. Analogous to Boesten and Van der Linden (1991), SWAP calculates μ from:

$$\mu = f_T f_\theta f_z \mu_{\text{ref}} \quad (8.11)$$

in which f_T is a soil temperature factor (-), f_θ and f_z are reduction factors (-) accounting for the effect of soil water content and soil depth, and μ_{ref} (d^{-1}) is μ at reference conditions (e.g. soil from the plough layer at 20 °C and at suction $h = -100$ cm).

The factor f_T is described according to Boesten (1986) as:

$$f_T = e^{\gamma_T (T-20)} \quad (8.12)$$

where γ_T is a parameter ($^{\circ}\text{C}^{-1}$), and T is the soil temperature in °C.

Wolfe et al. (1990) describe the importance of the water content in transformation processes. Realizing that it is a large simplification, in SWAP we adopt the relation as proposed by Walker (1974) :

$$f_\theta = \left(\frac{\theta}{\theta_{\text{ref}}} \right)^B \quad \text{with } f_\theta \leq 1.0 \quad (8.13)$$

where θ_{ref} is θ at $h = -100$ cm and B is a constant (-).

The transformation reduction factor for soil depth, f_z , should be derived from in situ measurements. The user may specify f_z as function of soil depth in the input file.

Combination of Eq. (8.6), (8.7), (8.8), and (8.10), yields the transport equation applied in SWAP which is valid for dynamic, one-dimensional, convective-dispersive mass transport, including non-linear adsorption, linear decay and proportional root uptake in unsaturated/saturated soil (Van Genuchten and Cleary, 1979; Nielsen et al., 1986; Boesten and Van der Linden, 1991):

$$\frac{\partial(\theta c + \rho_b Q)}{\partial t} = -\frac{\partial(qc)}{\partial z} + \frac{\partial\left[\theta(D_{\text{dif}} + D_{\text{dis}})\frac{\partial c}{\partial z}\right]}{\partial z} - \mu(\theta c + \rho_b Q) - K_r S c \quad (8.14)$$

An explicit, central finite difference scheme is used to solve Eq. (8.14):

$$\frac{\theta_i^{j+1} c_i^{j+1} + \rho_b Q_i^{j+1} - \theta_i^j c_i^j - \rho_b Q_i^j}{\Delta t^j} = \frac{q_{i-1/2}^j c_{i-1/2}^j - q_{i+1/2}^j c_{i+1/2}^j}{\Delta z_i} + \frac{1}{\Delta z_i} \left[\frac{\theta_{i-1/2}^j D_{i-1/2}^j (c_{i-1}^j - c_i^j)}{\Delta z_u} - \frac{\theta_{i+1/2}^j D_{i+1/2}^j (c_i^j - c_{i+1}^j)}{\Delta z_\ell} \right] - \mu_i^j (\theta_i^j c_i^j + \rho_b Q_i^j) - K_r S_i^j c_i^j \quad (8.15)$$

where D ($= D_{\text{dif}} + D_{\text{dis}}$) is the overall dispersion coefficient ($\text{cm}^2 \text{d}^{-1}$); the superscript j denotes the time level, subscript i the node number and subscripts $i-1/2$ and $i+1/2$ refer to linearly interpolated values at the upper and lower compartment boundary, respectively. Compared to an implicit, iterative scheme, above explicit scheme has the advantage that incorporation of non-linear adsorption, mobile/immobile concepts, and other non-linear processes is relatively easy. In order to ensure stability of the explicit scheme, the time step Δt^j should meet the criterium (Van Genuchten and Wierenga, 1974):

$$\Delta t^j \leq \frac{\Delta z_i^2 \theta_i^j}{2D_i^j} \quad (8.16)$$

This stability criterium applies to non-sorbing substances and is therefore also safe for sorbing substances.

<i>Model input</i>			<i>Default</i>
<i>Variable</i>	<i>Code</i>	<i>Description</i>	
K_f	KF	Freundlich adsorption coefficient ($\text{cm}^3 \text{mg}^{-1}$)	
N_f	FREXP	Freundlich exponent (-)	
c_{ref}	CREF	reference solute concentration for adsorption (mg cm^{-3})	
K_r	TSCF	relative uptake of solutes by roots	0.0
μ_{ref}	DEC POT	decomposition rate at reference conditions (d^{-1})	
γ_T	GAMPAR	factor for reduction of decomposition due to temperature ($^{\circ}\text{C}^{-1}$)	
θ_{ref}	RTHETA	minimum water content for maximum decomposition ($\text{cm}^3 \text{cm}^{-3}$)	
B	BEXP	exponent for reduction of decomposition due to dryness (-)	
f_z	FDEPTH	reduction of ref. decomposition in each soil layer	

8.3 Boundary conditions

As *initial condition*, the user needs to specify the solute concentrations, c_i (g cm^{-3}), in the soil water and the average solute concentration, c_{gr} (g cm^{-3}), in the groundwater.

For the *top boundary condition*, the solute concentrations in irrigation and rain water, c_{irr} and c_{prec} (g cm^{-3}), need to be specified. During evaporation no solutes enter the soil profile

at the surface. During infiltration, the solute concentration of water that enters the soil profile at the top, c_{pond} (g cm^{-3}), is affected by the ponding layer and its concentration at the former time step, the solute amounts coming in by rain and irrigation, and the solute amounts transported laterally to cracks:

$$c_{\text{pond}}^j = \frac{(P_{\text{net}}^j c_{\text{prec}} + I_{\text{net}}^j c_{\text{irr}}) \Delta t^j + h_{\text{pond}}^{j-1} c_{\text{pond}}^{j-1}}{h_{\text{pond}}^j - (q_{\text{top}} + q_{\text{lat}}) \Delta t^j} \quad (8.17)$$

where P_{net} is the net precipitation rate (cm d^{-1} , see Par. 3.3), I_{net} is the net irrigation rate (cm d^{-1}), h_{pond} is the height of water ponding on the soil surface, q_{top} is the water flux at the soil surface (cm d^{-1} , positive upward) and q_{lat} is the water flux flowing to cracks (cm d^{-1} , see Par. 8.5). The solute flux J_{top} (g cm^{-2}) entering the soil at the surface, equals:

$$J_{\text{top}} = q_{\text{top}} c_{\text{pond}} (1.0 - A_c) \quad (8.18)$$

where A_c is the relative crack area ($\text{cm}^2 \text{cm}^{-2}$). The solute flux that enters the cracks is described in Par. 6.5.3.5.

For the *drainage boundary condition*, SWAP assumes that the lateral drainage flux leaves the soil profile laterally at the lowest compartment. During drainage ($q_{\text{drain}} > 0$), the solute flux J_{drain} (g cm^{-2}) that leaves the one-dimensional soil profile is calculated as:

$$J_{\text{drain}} = q_{\text{drain}} c_n \quad (8.19)$$

where c_n is the solute concentration in the lowest compartment. During infiltration ($q_{\text{drain}} < 0$), J_{drain} follows from:

$$J_{\text{drain}} = q_{\text{drain}} c_{\text{gr}} \quad (8.20)$$

where c_{gr} is the average solute concentration in the groundwater (g cm^{-3}).

For the *bottom boundary condition*, SWAP uses the flux through the bottom of the soil profile q_{bot} (cm d^{-1} , see Chapter 5). In case of upward flow ($q_{\text{bot}} > 0$), the solute flux J_{bot} (g cm^{-2} , positive is upwards) equals:

$$J_{\text{bot}} = q_{\text{bot}} c_{\text{gr}} \quad (8.21)$$

If q_{bot} is directed downwards ($q_{\text{bot}} < 0$), the solute flux J_{bot} (g cm^{-2}) equals:

$$J_{\text{bot}} = q_{\text{bot}} c_n \quad (8.22)$$

<i>Model input</i>			
<i>Variable</i>	<i>Code</i>	<i>Description</i>	<i>Default</i>
c_i	CML	initial solute concentrations (mg cm^{-3})	
c_{prec}	CPRE	solute concentration in precipitation (mg cm^{-3})	0.0
c_{irr}	IRCONC	solute concentration in irrigation water (mg cm^{-3})	
c_{gr}	CDRAIN	solute concentration in groundwater (mg cm^{-3})	

8.4 Mobile/immobile solute transport

The water flow in soils with mobile/immobile flow has been described in Par. 6.4. In the mobile region the transport of solutes is affected by convection, dispersion, adsorption, decomposition and root water uptake (Figure 30). These processes are included in the solute transport equation, but corrections are needed as only the soil volume fraction F_{mob} is mobile:

$$\frac{\partial \left(\theta c + F_{\text{mob}} \rho_b K_f c_{\text{ref}} \left(\frac{c}{c_{\text{ref}}} \right)^{N_f} \right)}{\partial t} = -\frac{\partial qc}{\partial z} + \frac{\partial \left(\theta D \frac{\partial c}{\partial z} \right)}{\partial z} - \mu \left(\theta c + F_{\text{mob}} \rho_b K_f c_{\text{ref}} \left(\frac{c}{c_{\text{ref}}} \right)^{N_f} \right) - K_r S_a c - G_c \quad (8.23)$$

with c the solute concentration in the mobile soil water (g cm^{-3}), ρ_b the soil dry bulk density (g cm^{-3}), K_f the Freundlich coefficient ($\text{cm}^3 \text{g}^{-1}$), c_{ref} the reference concentration for adsorption (g cm^{-3}), N_f the Freundlich exponent (-), t the time (d), D the overall dispersion coefficient ($\text{cm}^2 \text{d}^{-1}$), μ the first order rate coefficient for decomposition (d^{-1}), K_r the root uptake preference factor (-), and G_c the transfer rate of solutes from the mobile to the immobile region ($\text{g cm}^{-3} \text{d}^{-1}$). G_c contains a diffusion term and a term that accounts for solute transfer due to variation of F :

$$G_c = K_{\text{dif}} (c - c_{\text{im}}) + G_w c_x \quad (8.24)$$

with K_{dif} a solute transfer coefficient (d^{-1}) between the mobile and immobile region, c_{im} is the solute concentration in the immobile region and c_x equals c if G_w is positive (mobile region decreases) and equals c_{im} if G_w is negative (mobile region increases).

In the immobile region, water flow is absent and transport of solutes will occur by diffusion only. The roots are assumed to avoid largely the immobile regions. Hence rootwater uptake in the immobile region is small and can be neglected. The change of solute amounts in the immobile region is therefore governed by solute transfer between mobile and immobile regions and by solute decomposition:

$$\frac{\partial (1 - F_{\text{mob}}) \left(\theta_{\text{im}} c_{\text{im}} + \rho_b K_f c_{\text{ref}} \left(\frac{c_{\text{im}}}{c_{\text{ref}}} \right)^{N_f} \right)}{\partial t} = -\mu (1 - F_{\text{mob}}) \left(\theta_{\text{im}} c_{\text{im}} + \rho_b K_f c_{\text{ref}} \left(\frac{c_{\text{im}}}{c_{\text{ref}}} \right)^{N_f} \right) + G_c \quad (8.25)$$

Equations (8.23) and (8.24) are solved with the previously described explicit central finite difference scheme.

<i>Model input</i>			
<i>Variable Code</i>		<i>Description</i>	<i>Default</i>
K_{dif}	KMOBIL	solute transfer between mobile and immobile parts (d^{-1})	

8.5 Crack solute transport

In current SWAP version solute transport in cracked clay soils can only be calculated in combination with the simple macro pore flow model (Par. 6.5.2). The transport processes incorporated are described hereafter. If you want to calculate solute transport in combination with the advanced macro pore flow model, SWAP may generate soil water fluxes which are input to the pesticide model PEARL or the nutrient model ANIMO.

The solutes that enter the cracks may originate from the precipitation directly falling into the cracks, or from runoff water when the infiltration capacity at the soil surface is exceeded ($P > I_{\max}$). The solute concentration of the water entering the cracks, c_{in} (g cm^{-3}), equals:

$$c_{\text{in}} = \frac{A_{\text{m}} (P - I_{\max}) c_{\text{pond}} + A_{\text{c}} P c_{\text{prec}}}{I_{\text{c}}} \quad (8.26)$$

with c_{pond} and c_{prec} solute concentrations (g cm^{-3}) of water ponding on the soil surface and of the precipitation, respectively.

When water flows down the cracks during intensive rain showers, solutes are leached out of the crack walls and transported quickly to the subsoil (e.g. Bronswijk et al., 1995). Therefore, lateral solute transfer between the soil matrix and water flowing down the cracks should be taken into account. The lateral solute transfer, $s_{\text{lat},i}$ ($\text{g cm}^{-2} \text{d}^{-1}$), for the nodes $GW_c < z < 0$ is calculated by:

$$s_{\text{lat},i} = D_{\text{lat}} I_{\text{c}} (c_i - c_{\text{in}}) \Delta z_i \quad (8.27)$$

where D_{lat} is the lateral transfer coefficient (cm^{-1}) and c_i the solute concentration in the soil matrix (g cm^{-3}). D_{lat} is a function of crack morphology and transmitting properties of the crack wall and has to be derived from field or laboratory measurements. The amount of solutes that enter the water reservoir in the cracks, $s_{\text{c,in}}$ ($\text{g cm}^{-2} \text{d}^{-1}$), equals:

$$s_{\text{c,in}} = I_{\text{c}} c_{\text{in}} + \sum_{z=GW_c}^{z=0} s_{\text{lat},i} \quad (8.28)$$

In the crack water reservoir the solutes are mixed. Part of the solutes will enter the soil matrix along the crack wall in contact with the water. Another part is transported with the bypass flow directly to the drains and/or ditches (Figure 33):

$$s_{\text{c,out}} = c_{\text{c}} (q_{\text{c,m}} + q_{\text{c,d}}) \quad (8.29)$$

with $s_{\text{c,out}}$ the total flux of solutes leaving the crack reservoir ($\text{g cm}^{-2} \text{d}^{-1}$) and c_{c} the solute concentration in the crack reservoir (g cm^{-3}).

Change of solute storage in the cracks S_{c} (g cm^{-2}) is straightforwardly calculated as:

$$\Delta S_{\text{c}} = (s_{\text{c,in}} - s_{\text{c,out}}) \Delta t \quad (8.30)$$

In the soil matrix the convection-dispersion equation is applied, as described in Par. 8.2.2. The lateral diffused solute amounts due to water flowing down the cracks, $c_{\text{lat},i}$, and the

adsorbed solutes from the water reservoir in the cracks, $q_{c,i}c_c$, are added as a source term to Eq. (8.14).

Model input			
Variable	Code	Description	Default
D_{lat}	DIFDES	effective lateral transfer coefficient (cm^{-1})	

8.6 Residence time in the saturated zone

In case of heterogeneous groundwater flow or multi-level drainage, the residence time approach described in chapter 4 can be used. This paragraph describes a concept assuming a homogeneous aquifer and field drainage at one level.

In the saturated zone, prevailing soil water pressure gradients will induce a three-dimensional flow and transport pattern. A strict deterministic approach would require a coupling of the one-dimensional agrohydrological model with a two- or three-dimensional model for the saturated zone. In many situations this is not feasible due to limitations of data, time, computer resources or experience. Also the required accuracy of the analysis might not justify such a detailed approach. Therefore in SWAP a simplified approach is followed to calculate the transport of solutes to drains or ditches.

Ernst (1973) and Van Ommen (1985) showed that the breakthrough curve of a field with fully penetrating drainage canals, is identical to the breakthrough curve of a reservoir with complete mixing. This is also valid if linear adsorption and transformation at first order rate take place (Van Ommen, 1985). Linear adsorption might be described by:

$$Q = k_{ads} c_{gr} \quad (8.31)$$

where k_{ads} is the linear adsorption coefficient in the saturated zone ($\text{cm}^3 \text{g}^{-1}$) and c_{gr} is the average solute concentration in the groundwater (g cm^{-3}). Numerical analysis by Duffy and Lee (1992) showed that dispersion in the saturated zone has only a minor effect for $L_{drain}/d_{aquif} \geq 10$, where L_{drain} is the distance between the drainage canals (cm) and d_{aquif} the thickness of the aquifer (cm). Generally L_{drain}/d_{aquif} will be around 10 or larger, therefore dispersion might be ignored.

In order to derive the breakthrough curve, we will use the similarity between breakthrough curves of drained fields and mixed reservoirs. Starting point is the solute transport equation of the unsaturated zone, Eq. (8.14). Replacement of non-linear adsorption by linear adsorption, and omission of dispersion and root water uptake, results in the mass balance equation of the saturated zone:

$$\frac{\partial(\theta_s c_{gr} + \rho_b k_{ads} c_{gr})}{\partial t} = \frac{q_{drain}}{d_{aquif}} (c_{in} - c_{gr}) - \mu_{gr} (\theta_s c_{gr} + \rho_b k_{ads} c_{gr}) \quad (8.32)$$

where θ_s is the saturated water content ($\text{cm}^3 \text{cm}^{-3}$), q_{drain} is the drainage flux (cm d^{-1}), c_{in} is the solute concentration of water percolating from the unsaturated zone (g cm^{-3}) and μ_{gr} is the first order rate coefficient for transformation in the saturated zone (d^{-1}). Eq. (8.32) applies to a drainage situation ($q_{drain} > 0$). In case of infiltration ($q_{drain} < 0$), SWAP assumes the infiltrating water from the drainage system to be solute free, and Eq. (8.32) transforms to:

$$\frac{\partial(\theta_s c_{gr} + \rho_b k_{ads} c_{gr})}{\partial t} = \frac{q_{drain}}{d_{aquif}} c_{gr} - \mu_{gr} (\theta_s c_{gr} + \rho_b k_{ads} c_{gr}) \quad (8.33)$$

Eq. (8.32) and (8.33) are discretized as an explicit, forward difference scheme. For instance, SWAP discretizes Eq. (8.32) as follows:

$$\frac{c_{gr}^{j+1} - c_{gr}^j}{\Delta t^j} (\theta_s + \rho_b k_{ads}) = \frac{q_{drain}^j}{d_{aquif}} (c_{in}^j - c_{gr}^j) - \mu_{gr} (\theta_s c_{gr}^j + \rho_b k_{ads} c_{gr}^j) \quad (8.34)$$

The stability of Eq. (8.34) depends on the size of the time step. In SWAP, the time step will be limited by the soil water dynamics and solute transport near the soil surface, and no stability problems are expected. The boundary conditions that apply to the saturated zone, are included in (8.32) and (8.33).