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V.3

Computer modeling of organic pollutant transport to groundwater – exemplified by SNAPS

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V.3.1. Introduction

Considerable efforts have been d one to evaluate pesticides with respect to their adverse effects on the environment. The spectrum of efforts spans a wide range of approaches. The simplest one begins with a comparison by substance data only, for example the GUS-index (Halfon et al., 1996). Even a simple consideration of different substance data can be extended to rather sophisticated methods (e.g. Lerche et al., 2002). The next step might be characterized by the PEC/PNEC-concept, e.g. presented by Beinat and van den Berg (1996), which is of high interest currently due to the "White Paper" of the EU (see e.g. discussion by Friege, 2002). Sophisticated approaches aim to combine exposure and effect models (Behrendt and Brüggemann, 1993); whereas effect models are still hardly ready to work routinely, exposure models are more or less ready to forecast the distribution behavior of organic pollutants in the environment. Here we focus on distribution processes within the unsaturated soil zone, i.e. on processes determining the concentrations of pollutants affecting the groundwater.

V.3.2. Exposure soil models

V.3.2.1. Preliminaries

Deterministic exposure models quantify the chemical mass flows and concentrations in environmental media such as soil, water or plants by more or less physically based mathematical equations (Hern and Melancon, 1986; Matthies and Klein, 1994; Van Leeuwen and Hermens, 1995; Trapp and Matthies, 1998). These models may be further classified into evaluative models and simulation models, although there is no sharp borderline between these two groups of models. In the following we will focus on soil exposure models as an example.

The starting point to develop models is the differential mass balance of a chemical, which can simply be formulated as:

Changes of the total concentration in a small soil volume
element =
+ transport into the soil volume by a carrier (for example flow of water)
− dispersive/diffusive loss
− degradation processes
− volatilization, run-off, and uptake into plants
(only at or near the soil surface)
− run-off (only at the soil surface)
+ sorption
− desorption

This (over)simplified scheme poses several questions that will be answered step by step. (Note that some chemicals may form their own phases, for example as micro-droplets, see Fauser and Thomsen (2002). Such kind of advanced studies is not considered here). Before going into details some classification principles should be discussed.

V.3.2.2. Classification principles

Mathematical models can be classified by the time and space scale they are appropriate, and also after the degree of "black box-character" they have. Furthermore, they can be classified according to more mathematical point of views, e.g. whether or not the models bear some stochastic fluctuations explicitly. Further classifications are possible referring to the numerical techniques to solve the equations. However, the last two aspects will be omitted within this text (Richter, 1987; Richter and Söndgerath, 1990; Richter et al., 1996).

V.3.2.3. Classification by the degree of sophistication

V.3.2.3.1. Evaluative models

The evaluative models tend to use a limited set of key transport processes. They often use empirical (regression) equations and/or restrictive boundary conditions to achieve a simplified model description. There are two reasons that may lead to a simplified model description. Firstly, the limited knowledge of the evolved processes and the limited data availability for non-key processes. Secondly, the purpose of the model, i.e. if the model is used as a screening model or a management model, it is not necessary that the model describes all evolved processes in detail. Often evaluative models are the basis for a comparative evaluation or a ranking of pesticides, as is described by Jury et al. (1983, 1984a–c) and Behrendt et al. (1997). Later, as one of the examples of evaluative models, the Jury model (Jury et al., 1983) will be discussed more deeply. Other examples of evaluative soil transport models are the EXSOL model (EXposure in SOiL) (Matthies and Behrendt, 1991; Brüggemann et al., 1996; Brüggemann and Drescher-Kaden, 2003) and a derived version on a rather modern platform: SOIL (Trapp and Matthies, 1998).

V.3.2.3.2. Simulation models

Simulation models try to avoid the shortcomings of the evaluative models and tend to have a sounder physically based concept and less restrictive boundary/initial conditions. Hence, the simulation models are applicable to a wider range of scenarios. Although, in practice one may have difficulties to supply the huge amount of input data required for the simulation runs. Examples of soil exposure simulation models for organic compounds are the PRZM model (Dean et al., 1989), the LEACHP model (Wagenet and Hutson, 1997), the Boesten model (Boesten and van der Linden, 1991) and the SNAPS (Simulation model Network Atmosphere–Plant–Soil) model (Behrendt and Brüggemann, 1993; Behrendt, 1999). All four models have in common a deterministic description of the coupled chemical temperature and water transport processes in a 1D soil column. The simulation models are often used to answer a "what-if-scenario" in a high-dimensional parameter space (Boesten, 1991; Behrendt et al., 1995).

V.3.2.4. Classification by the characteristic scales

Evaluative and simulation models have to refer to the scale, for which they can be used. Thus it makes no sense to use a local model and to extend the results up to a regional scale. The reason is that the processes and the parameters needed to describe the processes depend on the spatial resolution. Typically for unsaturated soil zones are pores. If exclusively the transport within pores is to be described, processes and parameters differ from those which characterize the transport within the bulk system consisting of soil matrix and pores. (Dagan, 1989). Transport processes in pores may be one extreme; another extreme is the consideration of regional transport phenomena in catchment areas of rivers that can be exemplified in the MONERIS model (Behrendt et al., 2000). The consideration of scales is extremely important, when the water flow itself is to be modeled. Spatial and temporal averaging has to be in agreement with the spatial and temporal dimensions of the model. Newer approaches to derive model parameters use the fractal theory to transform distribution functions between different scales (Braun et al., 1996).

Even the use of empirical parameters, derived from soil properties, depends on the scale. Nevertheless here, local models on the scale, where the Darcy law of flow is valid, are introduced and discussed.

V.3.3. Examples of model architecture

V.3.3.1. Jury model

The Jury "screening" model (Jury et al., 1983) calculates the transport of a chemical (e.g. pesticide) in a 1D (vertical) semi-infinite homogeneous soil column. Transport processes such as convection in soil water and diffusion in soil water and in soil air are included in the model. Existing applications of the Jury model are for example, the comparative evaluation of the transport of pesticides in the unsaturated upper soil zone (Jury et al., 1983; 1984a–c; Jury et al., 1987) and the evaluation of the volatilization sub-model in a field study (Jury et al., 1984a).

V.3.3.1.1. Equilibrium partitioning in soil

The chemicals concentration in soil is assumed to be low, e.g. the concentration in soil water is small compared to the water solubility of the chemical. Therefore, the chemicals (total) concentration in a soil volume C_T may be expressed by the quantities adsorbed to the soil matrix C_S, dissolved in soil water C_L and as a gaseous phase in soil air C_G:

$$C_T = \rho_b C_S + \theta C_L + a C_G \qquad \text{(V.3.1)}$$

where ρ_b is the soil bulk density (g/m^3), θ is the soil water content (m^{3}water/m^{3}soil) and a is the soil air content (m^{3}air/m^{3}soil). Additionally, an equilibrium partitioning of the chemical in soil water, soil air and adsorbed on the soil matrix is assumed. Thus, the concentration in soil water and adsorbed on the soil matrix may be related by the linear equilibrium partition coefficient K_d (Thibodeaux, 1996):

$$C_S = K_d C_L \qquad \text{(V.3.2)}$$

Analogously, the Henry's law coefficient K_{aw} may be used to relate the concentration in soil air and in soil water (Thibodeaux, 1996):

$$C_G = K_{aw} C_L \qquad \text{(V.3.3)}$$

As the experimental determination of K_{aw} is difficult, it may be helpful to know how K_{aw} may be estimated from other substance properties. This can be found in an overview by Altschuh et al. (1999).

Using Equations (V.3.2) and (V.3.3), the concentration of the chemical in soil water, soil air, sorbed on the soil matrix and the total concentration in soil may be related by linear "capacity coefficients":

$$C_T = R_L C_L = R_S C_S = R_G C_G \qquad \text{(V.3.4)}$$

where

$$\begin{aligned} R_L &= \rho_b K_d + \theta + a K_{aw} \\ R_G &= R_L / K_{aw} \\ R_S &= R_G / K_d \end{aligned} \qquad \text{(V.3.5)}$$

V.3.3.1.2. Darcy water flow in soil

A time and depth constant vertical downward (or upward in the case of evaporation) water flux J_W is assumed, which obeys Darcy's law. Darcy's law states (Darcy, 1856) that the water flux J_W through a porous soil column is proportional to the gradient of the total water potential H_T in soil, where K is the soil specific hydraulic conductivity (m/d):

$$J_W = -K\frac{\partial H_T}{\partial z} \tag{V.3.6}$$

Darcy's law applies to cases in which the Reynolds number of the fluid flow in soil is less than one (Marshall et al., 1996). Under these conditions the water flow is laminar and accelerations are unimportant. J_W is a macroscopic flow parameter, defined as the volume of water flowing through a cross-sectional area per time unit. Equation (V.3.6) was derived for saturated soil water conditions, but it may also be used for unsaturated conditions (Jury et al., 1991). The hydraulic conductivity K strongly depends on the pore size and the tortuosity and in the case of unsaturated conditions, also on the soil water content or the soil water matrix potential.

V.3.3.1.3. Convective transport in soil

The percolating water flux in soil may carry along dissolved chemicals (solutes) by a passive transport process "convection" (also called advection). One may observe a sharp boundary or interface zone of the concentration in the resident soil water and the concentration in the displacing soil water (Jury et al., 1991). In the latter case the transport process is also called a "piston flow" process. In mathematical terms we may write the convective mass flux in the vertical direction J_{LC} as:

$$J_{LC} = J_W C_L \tag{V.3.7}$$

V.3.3.1.4. Diffusion/dispersive transport in soil water and soil air

The "diffusive" flux of solutes in soil water results from the greater tendency to move from points of high concentrations to points of low concentration. Using Fick's first law, the diffusive flux J_{LD} is proportional to the concentration gradient (Equation (V.3.8)), where D_L is the diffusion coefficient of the solute in soil water (Jury et al., 1991):

$$J_{LD} = -D_L\frac{\partial C_L}{\partial z} \tag{V.3.8}$$

The diffusion coefficient of chemicals depends on the geometry of the water-filled pores of the soil. D_L is less than the molecular diffusion coefficient in free water $D_{L,bin}$. Using the empirical model of Millington (Millington and Quirk, 1961), we may calculate D_L from $D_{L,bin}$ the soil water content and the porosity of the soil:

$$D_L = \xi(\theta)D_{L,bin} = \frac{\theta^{3/2}}{\varepsilon^2}D_{L,bin} \tag{V.3.9}$$

In analogy of the diffusion in soil water, we write for the diffusive flux in soil air J_G (Jury et al., 1991):

$$J_G = -D_G\frac{\partial C_G}{\partial z} = -\xi(a)D_{G,bin}\frac{\partial C_G}{\partial z} \tag{V.3.10}$$

where $D_{G,bin}$ is the molecular diffusion coefficient in free air. The molecular coefficients $D_{L,bin}$ and $D_{G,bin}$ depend on the temperature, molar volume, and viscosity of the fluid media. There exist empirical relationships that enable the calculation of the molecular diffusion coefficients from the molar mass, and from parameters of the structure of the molecule (for property estimation methods, see Baum, 1998). The molecular diffusion coefficients of organic pesticides are very similar, $D_{G,bin}$ is in the order of 0.1 m^2/d and $D_{L,bin}$ is in the order of 10^{-5} m^2/d (Jury et al., 1983). Thus, the diffusive transport in soil air is usually more effective than that in soil water. Convective transport in soil air is neglected here, as it is especially important for high-temperature gradients in soil and for chemicals with high vapor pressure (Cohen et al., 1988).

In soil column leaching experiments one often recognizes spreading of the transition zone between the displacing water and the resident water. This phenomenon is known as "hydrodynamic dispersion", which can be attributed to three mechanisms: the velocity distribution within a pore, the pore size distribution of the pores, and the fluctuating water flow path within the mean direction (Thibodeaux and Scott, 1985). The approximation of the convective mass flux on pore scale by a volume-averaged macroscopic flux in the 1D model results in the dispersive flux J_{LH} (Bear, 1972), where D_{LH} is the hydrodynamic dispersion coefficient.

$$J_{LH} = -D_{LH}\frac{\partial C_L}{\partial z} \tag{V.3.11}$$

In empirical models D_{LH} is often described as linear function of the pore water velocity v (see Equation (V.3.12)) (Klotz, 1980), where λ_{disp} is the dispersivity $[L]$:

$$D_{LH} = \lambda_{disp}|v| = \lambda_{disp}\left|\frac{J_W}{\theta}\right| \tag{V.3.12}$$

In soil column leaching experiments, the dispersivity is in the order of 1 cm (Beese, 1982), while in field studies D_{LH} is in the range of 10–100 cm and even higher values are found (Behrendt et al., 1994). In general, the diffusive flux J_{LD} is significantly lower than the dispersive flux J_{LH}, which is true except for low pore water velocities.

Within the Jury model, the dispersive contributions to the mass flux in the soil water phase is neglected, so that the total mass flux J_C is:

$$J_C = J_{LC} + J_{LD} + J_G = J_W C_L - D_L\frac{\partial C_L}{\partial z} - D_G\frac{\partial C_G}{\partial z} \tag{V.3.13}$$

V.3.3.1.5. Derivation of the transport equation

The law of conservation of mass states that any changes in the amount of solute in a given volume of soil must be due to convergence toward or divergence away from the soil volume (Thibodeaux and Scott, 1985). In mathematical terms this may be written as the solute conservation equation (V.3.14), where S_C is an additional source/sink term:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial J_C(z,t)}{\partial z} + S_C(z,t) \tag{V.3.14}$$

Using Equation (V.3.13) we arrive at:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial (J_W C_L(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_L \frac{\partial C_L(z,t)}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_G \frac{\partial C_G(z,t)}{\partial z}\right) + S_C(z,t) \tag{V.3.15}$$

Furthermore, we may use Equations (V.3.4) and (V.3.5) to derive the "convection–dispersion" equation:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial (V_E C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E \frac{\partial C_T(z,t)}{\partial z}\right) + S_C(z,t) \tag{V.3.16}$$

$$V_E = \frac{J_W}{R_L} \tag{V.3.17}$$

$$D_E = (K_{aw} D_G + D_L)/R_L \tag{V.3.18}$$

Using the assumption that J_W, D_G, D_L and R_L do not depend on the soil depth, we arrive at:

$$\frac{\partial C_T(z,t)}{\partial t} = -V_E \frac{\partial C_T(z,t)}{\partial z} + D_E \frac{\partial^2 C_T(z,t)}{\partial z^2} + S_C(z,t) \tag{V.3.19}$$

V.3.3.1.6. Degradation in soil

The degradation rate of organic chemicals in soil depends on soil-specific parameters as pH, organic C content, clay content, temperature, soil water content, and nutrient supply, and on biotic parameters as amount and type of microorganisms (see for example in Valentine and Schnoor (1986) and Domsch (1992)). Here it is assumed, that we may specify a bulk first-order degradation rate μ ($1/T$), which is not dependent on the concentration of the chemical:

$$S_C(z,t) = -\mu C_T(z,t) \tag{V.3.20}$$

V.3.3.1.7. Boundary conditions

The upper boundary condition is determined by the transport of volatile chemicals from soil surface to free atmosphere, which often uses the concept of a mass transfer coefficient (Thibodeaux and Scott, 1985). The mass transfer coefficient k_A is defined by Equation (V.3.21), where J_A is the mass flux of the chemical perpendicular to the soil surface, C_A is the concentration in the air layer adjacent to the soil surface, and C_{A0} is the concentration in air far removed from the soil surface:

$$J_A = k_A (C_A - C_{A0}) \tag{V.3.21}$$

As it is discussed in detail by Thibodeaux and Scott (1985), the transfer coefficient k_A depends on the flow as related by the Reynolds number, the transport properties as related by the Schmitt number and on the geometry of the system as related to some length. Jury et al. (1983) made the assumption that J_A may be modeled by a diffusive transport through a stagnant air layer of depth d. Thus, a diffusive type boundary condition may be specified as:

$$J_C(0,t) = \left(V_E C_T - D_E \frac{\partial C_T}{\partial z}\right)_{t,z=0} = J_A = \frac{-D_G^A (C_G(0,t) - C_{A0})}{d} \tag{V.3.22}$$

In Equation (V.3.22) D_G^A is the diffusion coefficient in free air, and C_{A0} is the concentration in free atmosphere, which is assumed as zero. Jury et al. (1983, 1984a) estimated d from measured soil water evaporation rates and they recommend $d = 0.5$ cm.

The lower boundary condition uses the assumption that the concentration gradient is zero at the lower boundary of the semi-infinite soil column:

$$J_C(\infty, t) = V_E C_T(\infty, t) \tag{V.3.23}$$

As initial conditions, a constant concentration from soil depth $z = 0$ to $z = L$ is assumed. Using the boundary and initial condition an analytical solution may be derived for the transport equation (V.3.19) (Jury et al., 1983).

V.3.3.2. EXSOL model

The EXSOL model (EXposure in SOiL) (Matthies and Behrendt, 1991; Brüggemann et al., 1996; Brüggemann and Drescher-Kaden, 2003) calculates the transport of organic chemicals in soil by solving a convection–dispersion equation. The transport equation of the EXSOL model includes the dispersive flux J_{LH} (see Equation (V.3.11)) and additionally the model enables the definition of multiple soil horizons. Thus the transport equation of the EXSOL model is specific for each horizon of the soil profile, and the parameters D_E^i, V_E^i and μ^i depend on the soil horizon number i of the soil profile:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial(V_E^i C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E^i \frac{\partial C_T(z,t)}{\partial z}\right) + \mu^i C_T(z,t) \tag{V.3.24}$$

The effective dispersion–diffusion coefficient D_E^i and the effective convection coefficient V_E^i are defined as:

$$D_E^i = (K_{aw} D_G^i + D_{LH}^i + D_L^i)/R_L^i \tag{V.3.25}$$

$$V_E^i = \frac{J_W}{R_L^i} \tag{V.3.26}$$

Furthermore, the upper boundary conditions may be specified as time-dependent. Time series of the precipitation rate P, the evapotranspiration rate E, and the surface run off R may be used to calculate the Darcy water flux rate J_W for each day of the simulation period:

$$J_W = P - E - R \tag{V.3.27}$$

A convective transport out of the soil column is assumed at the bottom of the soil column. The flux type boundary condition is defined as:

$$t \geq 0 \qquad z = Z_L \qquad J_C = \max(J_W C_L, 0) \tag{V.3.28}$$

Concentration gradients are assumed to be negligible at the depth Z_L of the soil column.

The transport equation (V.3.24) is solved by a numerical procedure. Applications of the EXSOL model include the analysis of soil column and field leaching studies (Behrendt et al., 1990; Schernewski et al., 1990), and assessment studies of groundwater contamination (Matthies and Behrendt, 1991; Altschuh et al., 1996).

V.3.3.3. SNAPS model

The SNAPS soil model "Simulation model Network Atmosphere–Plant–Soil" (Behrendt and Brüggemann, 1993; Behrendt, 1999) calculates the transport of organic chemicals in soil by solving a convection–dispersion equation, similar to the EXSOL model. Additionally, this model includes an explicit calculation of the water and heat transport in soil by solving the corresponding transport equations. The boundary condition at the soil surface, i.e. evaporation, transpiration and infiltration rates are determined from time series of climatic and plant specific parameters. The uptake of dissolved organic chemicals in soil water into plants is also included in the model. Furthermore, there exists an interface of the SNAPS soil model to the PLANTX model, which describes the transport and the partitioning of organic chemicals within plants (Trapp and Matthies, 1997). The SNAPS model was used for the interpretation of pesticide leaching studies (Behrendt et al., 1994), and in assessment studies of uptake of solutes in plant shoots (Behrendt and Brüggemann, 1993; Behrendt et al., 1995).

V.3.3.3.1. Water flow in soil

The water flow in soil is based on Darcy's law (Equation (V.3.6)), which we may write for unsaturated soil water conditions as:

$$J_{\mathrm{W}} = -K(\psi_{\mathrm{m}})\frac{\partial H_{\mathrm{T}}}{\partial z} = -K(\psi_{\mathrm{m}})\frac{\partial(\psi_{\mathrm{m}} + z)}{\partial z} \qquad \text{(V.3.29)}$$

In Equation (V.3.29) the total soil water potential H_{T} is defined as the sum of the soil matrix potential ψ_{m} and the gravitational potential. Contribution to the total soil water potential, as for example the osmotic potential, is neglected in Equation (V.3.29). Furthermore, the unsaturated hydraulic conductivity $K(\psi_{\mathrm{m}})$ is assumed to be a function of the soil matrix potential only. In the case of non-stationary water flow the transport equation may be derived by the combined use of the conservation equation for water in soil and of the Darcy equation (V.3.29):

$$\frac{\partial \theta(z,t)}{\partial t} = \frac{\partial}{\partial z}\left(-K(\psi_{\mathrm{m}})\frac{\partial(\psi_{\mathrm{m}} + z)}{\partial z}\right) - S_{\mathrm{w}}(z,t) \qquad \text{(V.3.30)}$$

The sink term $S_{\mathrm{w}}(z,t)$ accounts for the root water uptake by plants. Equation (V.3.30) may not be solved in the form it is, because it contains two unknowns $\psi_{\mathrm{m}}(z,t)$ and $\theta(z,t)$. This difficulty may be overcome by using the water content matrix potential function $\theta(\psi_{\mathrm{m}})$:

$$\begin{aligned} c(\psi_{\mathrm{m}})\frac{\partial \psi_{\mathrm{m}}}{\partial t} &= \frac{\partial}{\partial z}\left(-K(\psi_{\mathrm{m}})\frac{\partial(\psi_{\mathrm{m}} + z)}{\partial z}\right) - S_{\mathrm{w}}(z,t) \\ c(\psi_{\mathrm{m}}) &:= \frac{\partial \theta}{\partial \psi_{\mathrm{m}}} \end{aligned} \qquad \text{(V.3.31)}$$

Equation (V.3.31) is the matrix potential form of the one-dimensional Richards equation, where $c(\psi_{\mathrm{m}})$ is the water capacity function. In Equation (V.3.31) it is assumed that there exists a continuous and differentiable function $\theta(\psi_{\mathrm{m}})$, which implies that hysteresis, as it is observed in measured water content matrix potential relationships, is negligible (Jury et al., 1991). The SNAPS model uses the parameter functions of the Van Genuchten–Mualem model (Mualem, 1976; Van Genuchten, 1980) to describe the soil water content matrix potential function $\theta(\psi_m)$ and the hydraulic conductivity matrix potential function $K(\psi_m)$. The Van Genuchten–Mualem model has been found to be very useful in describing measured soil hydraulic properties for many soils (Van Genuchten and Nielsen, 1985; Woesten and Van Genuchten, 1988).

Initial values and boundary conditions have to be specified to derive a solution of the transport equation (V.3.31). As initial conditions, measured or estimated values of the soil matrix potential may be used. In the case of unsaturated soil water profile the equation (V.3.31) is a parabolic partial differential equation, this type of equations may be solved numerically by implicit finite differential methods (Knabner and Angermann, 2000).

V.3.3.3.2. Boundary conditions of the water flow in soil

At the lower boundary of the soil column it is assumed that the gradient of the matrix potential is zero, i.e. there is a free drainage of the soil water driven by the gravitational potential only. Using Equation (V.3.29) and the above assumption we arrive at:

$$|J_{Wn}| = K(\psi_m) \tag{V.3.32}$$

In mathematical terms we have a third-order type boundary condition, where $|J_{Wn}|$ is the normal flux at the lower boundary.

The boundary conditions for the atmosphere are determined by time series of climatic and crop-specific parameters on a daily basis. For each day of the simulation period the potential infiltration rate is calculated from the precipitation rate, the interception storage of the crop, and the potential evapotranspiration rate. The (positive) difference between potential and actual amount of water infiltrating the soil is accounted for the surface run-off. A reduced potential evaporation E_R is calculated according to the procedures of Ritchie (1972) and Feddes et al. (1978). The potential water flux at the soil surface q_{pot} is determined from a mass balance equation of the reduced potential evaporation E_R, the precipitation P and the crop interception storage E_i:

$$q_{pot} = E_R - (P - E_i) \tag{V.3.33}$$

By a set of inequalities the boundary conditions at the soil surface of the flux q_s and of the matrix potential ψ_s are defined: The Darcy flux q_s is limited by q_{pot} in the case of infiltration as well as in the case of evaporation.

In case of infiltration:

$$\begin{aligned} &\psi_s \leq \psi_{pot} = 0, \qquad |q_s| \leq |q_{pot}| \\ &\text{and} \quad (\psi_s - \psi_{pot})(q_s - q_{pot}) = 0 \end{aligned} \tag{V.3.34}$$

If $|q_s|$ is less than $|q_{pot}|$, the difference between $|q_{pot}|$ and $|q_s|$ is accounted for the surface run-off.

In case of evaporation:

$$\psi_s \geq \psi_{pot} = \psi_{ad}, \qquad |q_s| \leq |q_{pot}|$$

and $\quad (\psi_s - \psi_{pot})(q_s - q_{pot}) = 0 \qquad$ (V.3.35)

where ψ_{ad} is the soil matrix potential for dry air. If the soil matrix potential is in equilibrium with the atmosphere, we may calculate ψ_{ad} from the relative humidity of the atmosphere (Campbell, 1985).

$$\psi_{ad} = \frac{RT}{Mg} \ln(rh_{ad}) \qquad \text{(V.3.36)}$$

where R is the universal gas constant, T is the absolute temperature, M is the molar weight of water, g is the gravitational acceleration, and rh_{ad} is the relative humidity for dry air.

V.3.3.3.3. Water uptake by plants

The potential transpiration of the plants is determined by an energy balance equation according to Monteith and Ritjema (Feddes et al., 1978). Furthermore, the root length distribution is used to distribute the (potential) root water uptake along the soil profile. Root length distributions may be estimated from empirical relationships to soil texture and crop development stages (Wessolek and Gaeth, 1989). In the case of water stress of the plants, the potential root water uptake rate is reduced by an empirical function of the soil matrix potential $\alpha(\psi_m)$ (Feddes et al., 1978). Using the above assumptions, we may specify the sink term for root water uptake as:

$$S_W(z,t) = \alpha(\psi_m(z,t))S_p(z,t) \qquad \text{(V.3.37)}$$

$$S_p(z,t) = T_p(t)\frac{w(z,t)}{\int_0^{zmax} w(z,t)\mathrm{d}z} \qquad \text{(V.3.38)}$$

where $S_P(z,t)$ is the potential root water uptake rate, and $w(z,t)$ is the root length distribution.

V.3.3.3.4. Heat transport in soil

Physical, chemical, and biological processes are influenced by soil temperature. Biological processes influencing the fats of organic chemicals in soil are strongly affected by soil temperature (Domsch, 1992). The soil temperature may significantly determine the (biotic) degradation rate in soil. Furthermore, it may also affect the transport of water and solutes in soil (Feddes et al., 1988), which is neglected here.

The following assumptions are used for the heat transport equations:

- the water transport affects the heat transport,
- the heat transport does not affect the water or solute transport in soil,
- there are no sinks or sources for heat transport in soil,
- the thermal conductivity is a function of the soil water content.

The assumptions above may be used to derive the following heat transport equation (Campbell, 1985):

$$\frac{\partial (C_V T)}{\partial t} = \frac{\partial}{\partial z}\left(\lambda(\theta)\frac{\partial T}{\partial z}\right) - C_{VW}\frac{\partial (qT)}{\partial z} \tag{V.3.39}$$

where T is the temperature in the soil, $\lambda(\theta)$ is the thermal conductivity in soil, and C_V and C_{VW} are the volumetric heat capacities for soil and water.

The transport parameter volumetric heat capacity C_V and thermal conductivity $\lambda(\theta)$ may be estimated by regression equation to soil texture and soil water content (Campbell, 1985).

As boundary conditions given temperatures at soil surface and at the bottom of the soil column in soil are used. The temperature at the bottom of the soil column is assumed to be time constant. The temperature at the boundary to atmosphere is estimated from the minimum and the maximum of the daily air temperatures. The estimation procedure assumes that the temperature is a quasi-period function of time with the maximum at 4.5 h before sunset and the minimum at 1.5 h before sunrise (Ca'Zorzi and Dalla Fontana, 1986). As in the case of the water transport equation, the numerical solution of the parabolic equation (V.3.39) is derived by an implicit finite differential method (Knabner and Angermann, 2000).

V.3.3.3.5. Solute transport in soil

As in the case of the Jury model, the linear partition coefficients (Equations (V.3.2) and (V.3.3)) are used to described the chemical mass balance in soil. Similar to the EXSOL model the processes convection in soil water, dispersion–diffusion in soil water, and diffusion in soil air are included within the transport equation of the chemical:

$$\begin{aligned}\frac{\partial C_T(z,t)}{\partial t} &= -\frac{\partial (V_E(z,t)C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E(z,t)\frac{\partial C_T(z,t)}{\partial z}\right)\\ &\quad - S_{\deg}(z,t) - S_{\mathrm{root}}(z,t)\end{aligned} \tag{V.3.40}$$

The effective convection coefficient V_E and the dispersion–diffusion coefficients D_E are both dependent on the time variable t and depth variable z as result of the time and depth-depended water flux $q(z,t)$ and the soil water content $\theta(z,t)$. The sink term $S_{\deg}$ accounts for the assumed biotic degradation in soil and the sink term S_{root} accounts for the uptake of solutes into the shoots of the plants.

V.3.3.3.6. Degradation in soil

Similar to the model of Boesten (Boesten and van der Linden, 1991), the biotic degradation of chemicals in soil is described by a first-order degradation rate for reference conditions μ_{ref} and additionally coefficients that account for the soil depth $f(z)$, and temperature in soil $g(T)$:

$$S_{\deg}(z,t) = -g(T)f(z)\mu_{\mathrm{ref}}C_T(z,t) \tag{V.3.41}$$

where μ_{ref} is the degradation rate at 20°C in the plow layer of the soil. The temperature correction $g(T)$ is defined as a numerically approximated Arrhenius equation:

$$g(T) = \exp[\gamma(T - T_{20^\circ})] \qquad T \in [5°C, 30°C] \tag{V.3.42}$$

Boesten et al. (Boesten, 1986; Boesten and van der Linden, 1991) used data from 50 degradation studies with varying soils types, to specify $\gamma = 0.08 \pm 0.02\ K^{-1}$. The value of γ corresponds to mean activation energy of 55 kJ/mol. The depth-dependence of the degradation rate $f(z)$ is defined as 1 for the plow layer of the soil profile and decreases to zero for lower soil horizons. It is assumed, that $f(z)$ is correlated to the soil organic C-content of the soil horizons.

The sink term S_{root} describes the uptake of dissolved organic chemicals in soil water into the shoots of the plant. It is assumed that the uptake may be described as passive mass flux with the transpiration stream of the plant:

$$S_{root}(z, t) = \mathrm{TSCF}(K_{OW})S_W(z, t)C_L(z, t) \tag{V.3.43}$$

The transpiration-stream-concentration-factor (TSCF) is a chemical specific transmission coefficient, which accounts for the passage of the bio-membranes of the plant. For non-dissociating and non-polar organic chemicals, the empirical model of Briggs et al. (1982) may be used to correlate the TSCF to the octanol–water partition coefficient K_{OW}:

$$\mathrm{TSCF}(K_{OW}) = 0.784 \exp\left(-\frac{(\log(K_{OW}) - 1.78)^2}{2.44}\right) \tag{V.3.44}$$

V.3.3.3.7. Boundary conditions

At the soil surface the diffusive–dispersive flux is neglected. In the case of infiltration, the input flux of the chemical is defined as the convective input flux with the infiltrating water:

$$t \geq 0 \qquad z = 0 \qquad J_C(t, z) = q_{inf}C_{inf} \tag{V.3.45}$$

where q_{inf} is the water infiltration rate and C_{inf} is the concentration in the infiltrating water. In the case of evaporation chemicals may be also transported from soil to atmosphere by diffusion through a stagnant air layer at the soil surface. This process is known as volatilization from soil to atmosphere (Korte et al., 1992), and may be modeled as in the case of the Jury model by a flux type boundary conditions (V.3.22). The SNAPS model neglects the volatilization transport process, which may be an acceptable approximation for low Henry's law coefficients ($<< 10^{-5}$) (Jury et al., 1984a). The boundary condition at the soil surface in the case of evaporation is defined as:

$$t \geq 0 \qquad z = 0 \qquad J_C(t, z) = 0 \tag{V.3.46}$$

As in the case of the EXSOL model a convective transport out of the soil column is assumed at the bottom of the soil column (see Equation (V.3.23)).

V.3.4. Inverse modeling

The fate of pesticides in the subsurface is based on the water movement in the unsaturated zone and in the aquifer and above all it depends on sorption and degradation processes.

Considering only the soil water flow non-linear functions describing the unsaturated hydraulic properties and, for the groundwater zone aquifer parameters as transmissivity and storability must be determined.

Traditionally, direct steady-state methods for the estimation of these parameters exist, but recently, transient experimental methods coupled with inverse modeling techniques have become more attractive (Kool et al., 1987; Nützmann et al., 1997). Less work has been done for simultaneous estimation of flow and solute transport parameters, i.e. sorption coefficients K_d and transformation rates μ.

Inverse modeling of the transport equation with respect to these parameters requires formulation of an objective function $O(v_A)$ as in the case of least-square optimization:

$$O(v_A) = \sum_{i=1}^{N} [c_i^* - c_i(v_A)]^T [c_i^* - c_i(v_A)] \qquad \text{(V.3.47)}$$

where v_A is the vector of parameters, (K_d, μ), and c_i^* are the measured and $c_i(v_A)$ are the simulated concentrations. Other techniques are also used, like the maximum likelihood method, which allows inclusion of prior information about parameters quite easily (Medina and Carrera, 1996), or Bayesian statistics (e.g. Omlin and Reichert, 1999). This allows one to obtain not only the values of estimated parameters but also information about their certainty and facilitates the use of model selection criteria.

Solving the parameter estimation problem as formulated above the Levenberg–Marquardt algorithm could also be used to minimize the objective function. This was done to estimate coefficients of a non-linear sorption kinetic function for phosphorus migration in sandy soils (Pudenz and Nützmann, 1999). Without additional effort sensitivities with respect to the parameters are obtained from the first derivatives of $O(v_A)$ and therefore conditions of identification can be examined. This is advantageous to overcome the problem of ill-posed parameters in the estimation procedure. As reported by Marsili-Libelli (1992), the sensitivity functions can be related to parameter calibration accuracy and a numerical method for estimating the parameter error covariance matrix is to be used.

In a case study, Kluge et al. (1994) demonstrated that parameters depend on the site and the way of averaging the input data with respect to time. They concluded that the sensitivity and the number of required parameters decrease with increasing spatial and temporal averaging level. In general, it is more difficult to simulate single events or extreme values than averaged dynamics or trends.

V.3.5. Ranking as an example of model application

As an example, model calculations are performed to assess the accumulation potential in soil of several triazine herbicides and their metabolites. As a model the Jury approach is used. A dynamical calculation of the water and heat balance as done in SNAPS is not needed, because the environmental conditions can be held constant in order to perform comparisons of the chemicals under a given environmental scenario. The degradation of the chemicals was estimated with help of the program EROS, "elaboration of reactions for organic synthesis" (Gasteiger et al., 1995, 1997). Details of the calculation of the fate descriptors by the combined use of the Jury model and of the program EROS are shown elsewhere (Behrendt et al., 1997, 1999).

It is known that the water flux boundary conditions may significantly determine the dominating transport process of a chemical in soil (Jury et al., 1984a). Therefore three descriptors D_E, D_T, and D_{Lea} were defined from the results of the Jury model calculations to quantify the accumulation potential in soil for the boundary conditions, such as: downward water flux, transpiration or evaporation. Each of the descriptors D_E, D_T, and D_{Lea} gives the time in days until the chemical's concentration in soil is reduced to 50% of the initial concentration. The descriptor D_E accounts for boundary conditions with evaporation and without transpiration, the descriptor D_T accounts for boundary conditions with transpiration and no evaporation, and the descriptor D_{Lea} accounts for boundary conditions with downward water flux and transpiration. The definition implies that chemicals resting in soil and degrading slowly have a high accumulation potential and vice versa. In addition to the descriptors defined from the Jury model results, the natural log of the chemical's concentration time integral of the EROS model run (the persistence) is defined as an accumulation potential descriptor D_P. The descriptor D_P is intended to account for the parent–daughter relationships of the chemicals.

Each descriptor aggregates deterministically a large amount of information, valuable for priority setting procedures and for sustainable development of new chemicals on the market ("ecodesign"). To come up to a ranking without an arbitrary aggregation of these four descriptors to get a ranking index, the theory of partially ordered sets is applied. The main idea is, how to compare objects (here: chemicals), if they are characterized by a list of properties. Here is no space to explain the rather extensive theory (see for e.g. Brüggemann and Halfon, 1997; Brüggemann et al., 2001); the results in a graphical form of a Hasse Diagram are given in Figure V.3.1.

Note that classified data, not the original numerical values, were used to construct this diagram. The numerical range of each descriptor was divided into three classes: 0 not relevant, 1, relevant, 2 very relevant. The diagram shows that there are long sequences of triazines that are mutually comparable. The least hazardous chemical with respect to the fate, given by the four descriptors is AO10 and the most hazardous chemical is TB4, which is a metabolite of terbutylazine (TBA) and which is in all four aspects more hazardous than TBA. The diagram shows also two groups of chemicals separated, on the right-hand-side chemicals with high descriptor D_P and on the left-hand-side chemicals with intermediate or low descriptor D_P. Furthermore, there are metabolites of TBA, which are not comparable to each other. For example AO6 and AZ2 and AO9 and AZ2 are non-comparable to each other due to contradictions between the descriptors D_T and D_P.

A full Hasse diagram is shown in another publication (Behrendt et al., 1997). Here the example shows, how a model calculation can help to combine pure substance properties with that of a specific scenario and to derive a hazard assessment, specified by the chosen descriptors.

Similarly waste disposals should be evaluated by model calculations, descriptors should be defined and a ranking developed, based on the techniques briefly outlined here. In any case, a decision should be based on validated models, accommodated to the specific questions, scales and data availability. The manifoldness of model results should not be masked in an aggregation just to perform a ranking, but should also apply rather modern mathematical tools, as shown here by the Hasse diagram technique. As regulators often do not feel comfortable by this use of graph theory, the recent development aims at a

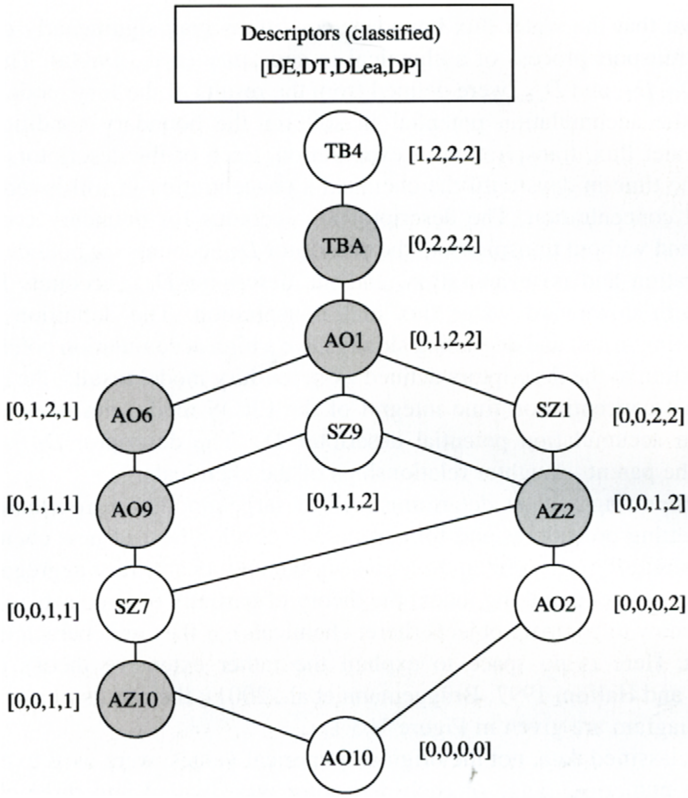

Figure V.3.1. Hasse diagram of those triazines (and their metabolites) that are comparable with terbutylazine (TBA). Shaded circles: TBA and metabolites of TBA. Further explanation: see text.

probabilistic extension: a linear rank is derived, however, a probability distribution of the ranks is added (e.g. Sørensen and Lerche, 2002, and references cited therein).

Nomenclature

C_A	concentration in atmosphere (μg/m^3)
C_G	concentration in soil air (μg/m^3 air)
C_{inf}	concentration in infiltrating water at the soil surface (μg/m^3)
C_L	concentration dissolved in soil water (μg/m^3 water)
C_S	concentration adsorbed on the soil matrix (μg/g soil)
C_T	total concentration soil (μg/m^3 soil)
C_V	volumetric heat capacity of soil (J/m^3/K)
C_{VW}	volumetric heat capacity of water (J/m^3/K)
D_E	effective diffusion coefficient in soil (m^2/d)
D_G	diffusion coefficient in soil air (m^2/d)
$D_{G,bin}$	molecular diffusion coefficient in free air (m^2/d)

D_{LE}	effective dispersion–diffusion coefficient (m^2/d)
D_{LH}	hydrodynamic dispersion coefficient (m^2/d)
D_L	diffusion coefficient in soil water (m^2/d)
$D_{L,bin}$	molecular diffusion coefficient in free water (m^2/d)
E	evaporation rate (m/d)
E_i	crop interception storage (m/d)
E_R	reduced evaporation rate (m/d)
H_T	total water potential in soil (m)
J_G	diffusive flux in soil air ($\mu g/m^2/d$)
J_A	mass flux of the chemical from soil air to atmosphere ($\mu g/m^2/d$)
J_L	total mass flux in soil water ($\mu g/m^2/d$)
J_{LC}	vertical convective mass flux ($\mu g/m^2$ soil/d)
J_{LD}	diffusive flux in soil water ($\mu g/m^2/d$)
J_{LH}	dispersive flux in soil water ($\mu g/m^2/d$)
J_W	Darcy water flux in soil ($m^3/m^2/d$)
K	hydraulic conductivity (m/d)
K_{aw}	air–water partition coefficient (–)
K_d	linear equilibrium partition coefficient soil matrix/soil water (cm^3/g)
K_{ow}	octanol–water partition coefficient (–)
M	molar weight of water (kg/mol)
P	precipitation rate (m/d)
R	universal gas constant (J/mol/K)
R	surface run-off (m/d)
R_L	capacity coefficient soil water (–)
R_S	capacity coefficient soil matrix (g/m^3)
R_G	capacity coefficient soil air (–)
S_{deg}	sink term for biotic degradation in soil ($\mu g/m^3$ soil/d)
$S_P(z,t)$	potential root water uptake rate (m/d)
S_{root}	sink term for uptake of solutes into plants ($\mu g/m^3$ soil/d)
S_w	root water uptake rate (m^3 water/m^3/d)
T	absolute temperature (K)
$TSCF$	transpiration stream concentration factor (–)
V_E	effective pore water velocity (m/d)
Z_L	depth in soil of the bottom boundary of the soil column (m)
a	soil air content (m^3/m^3)
c	soil water capacity (m^{-1})
$f(z)$	empirical function of soil depth (–)
g	gravitational acceleration (m/s^2)
$g(T)$	temperature dependence of the degradation rate in soil (–)
k_a	mass transfer coefficient for volatilization (m/d)
q_{inf}	water infiltration rate at the soil surface (m/d)
rh_{ad}	relative humidity for dry air (–)
t	time (d)
v	pore water velocity (m/d)
$w(z,t)$	root length distribution (m/m^3)
z	depth in soil (m)

α empirical function (−)
μ first-order degradation rate (d^{-1})
μ_{ref} first-order degradation rate at reference conditions 20 °C and 70–100 kPa soil water matrix potential in the plow layer (d^{-1})
ε soil porosity (m^3/m^3)
ψ soil matrix potential (m)
θ soil water content (m^3water/m^3)
$\xi(\cdot)$ tortuosity factor (−)
$\lambda(\theta)$ thermal conductivity in soil (W/°K/m)
ρ_b soil bulk density (g/m^3)

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