Integrated Dynamic Modeling of Contaminant Fate and Transport within a Soil–Plant System

Contaminants found in the soil and in the atmosphere frequently find their way into plants. Because plants are at the bottom of the food chain, analysis of this pathway contributes to health risk assessment studies. On the other hand, plants that exist at a contaminated site have a potential effect on contaminant transformation and migration within the soil or the atmosphere. In this study, a modeling framework was developed to integrate the plant pathway into soil contaminant transport models. A soil–plant system model was developed by coupling soil moisture distribution, contaminant transport, plant life cycle, and plant pathway models. The outcome unifies single-medium continuous models with multimedia compartmental models in a flexible framework. The framework recognizes that plants are dynamic biologic systems that regulate their life cycle in interaction with existing conditions in the ambient environment, which significantly influence the dynamics of the overall complex system. The model developed was applied to a hypothetical contamination scenario where the effect of plants on contaminant migration within the system was investigated. Also, the outcome of the plant pathway as it responds to water flow and contaminant transport dynamics was analyzed. A mass balance analysis found that the processes of volatilization and root water uptake are very critical in determining the contaminant fate within the system. A sensitivity analysis showed that the contaminant concentration within the plant is significantly affected by the variation in the values of the retardation factor, transpiration stream concentration factor, and contaminant half-life within the plant. The outcome of these applications reflects the effect of multiple levels of complexity associated with plant growth and root water uptake representations within the soil.

Plants have the potential to be used as field biomonitors (Powell, 1997) because they may become a depository for contaminants in the soil and atmosphere due to their continuous interaction with these two media. Additionally, plant contaminant uptake has critical implications from a human health perspective because plants are at the bottom of the food chain and thus are at the beginning of an exposure route via food intake by animals and humans (Currado and Harrad, 2001). The other factor that needs to be understood is the effect of plant contaminant uptake on the overall contaminant migration pattern at a site. There is a need to develop reliable models of plant root uptake and plant contamination to improve soil and atmospheric contamination models as well as to better understand and predict the exposure of humans to contaminants through food intake. Plant contaminant uptake modeling is impeded, however, by the extreme complexity of this process and its dependence on the life cycle of the plant.

In this study, soil transport and plant pathway models were developed for organic contaminants. The integrated modeling framework that was developed can be applied to other contaminants, however, after introducing the necessary modifications for the process associated with the contaminant studied.

The modeling of plants as environmental media and a pathway for contaminant transport has been the focus of multimedia environmental modeling research for several decades. Trapp and McFarlane (1995) provided an overview of plant physiology and plant pathway modeling principles and presented several modeling applications. Cousins and Mackay (2001) discussed the inclusion of plant models into multimedia models after assessing the importance of the plant pathway. More recently, Trapp (2004) reviewed the theory of plant pathway models while differentiating between the models for neutral chemicals and ionic chemicals.
The models for plant contaminant uptake have different levels of complexity, which stems mainly from the number of compartments used to represent the plant. Simpler ones model the plant as a single compartment that represents the aboveground plant parts (e.g., Cousins and Mackay, 2001; Severinsen and Jager, 1998; Trapp and Matthies, 1995), while more complex models represent different plant organs (e.g., roots, leaves, and fruit) as separate compartments interacting with each other (e.g., Batiha et al., 2009; Trapp, 1995, 2007; Undeman et al., 2009). When multiple plant organs are modeled, the transport of contaminants from the leaves to the other plant compartments via phloem flow has to be considered as well as transport through the transpiration stream (Undeman et al., 2009). On the other hand, in most multimedia models that have incorporated plants, the soil interacting with the plant is modeled as a single compartment (e.g., Batiha et al., 2009; Cousins and Mackay, 2000; Hung and Mackay, 1997). Although the model of Trapp (2007) includes two separate soil compartments, each of these compartments only interacts with its corresponding root compartment, and contaminant migration and the spatial variability of contaminant concentrations within the soil are not considered. Matthies and Behrendt (1995) presented one of the rare modeling studies where a plant pathway model (Trapp, 1995) was integrated with a soil water flow and contaminant transport model.

A schematic representation of the mass transfer processes between the plant and the soil and between the plant and the atmosphere considered in typical multimedia compartmental models is shown in Fig. 1. In this conceptualization, soil and plants are described as single compartments that interact with each other and with the atmosphere, which is treated as a part of the external environment. When the soil is modeled as a single compartment, the spatial distribution of moisture and the contaminant within the soil have to be neglected. This simplification has important consequences when determining contaminant transfer between the soil and the plant and between the soil and the atmosphere. Contaminant uptake by plants is dependent on the root water uptake rate and the soil contaminant concentration, both of which may be highly variable throughout the soil depth.

Contaminant transfer processes between the atmosphere and the soil are highly dependent on the near-surface characteristics of the soil. These issues can be addressed by integrating a plant root uptake model with a contaminant transport model that tracks the spatial and temporal distribution of contaminants within the soil.

Plant growth is a critical process in assessing the level of contamination within the plant (Undeman et al., 2009). Plant models use information on the plant biomass and volume in determining the contaminant concentration within the plant. Also, atmospheric deposition rates, diffusive transfer processes between the plant and the atmosphere, and root uptake rates are dependent on the plant’s growth stage. Plant growth is usually neglected (e.g., Cousins and Mackay, 2001), however, or represented using growth rate coefficients (e.g., Hung and Mackay, 1997; Trapp, 2007) when developing the plant models. The plant growth rate is variable with time and depends on the environmental conditions. Therefore, to obtain an accurate description of contaminant concentration evolution within the plant, the plant’s life cycle as it interacts with its environment should be taken into account.

The soil domain that is interacting with the plants is the vadose zone, where soil grains and water and air phases coexist. This region has traditionally been studied by soil and agricultural scientists. More recently, it has also become an important subject of environmental research because the introduction of contaminants to the subsurface often occurs through this region (Fetter, 1999; Šimůnek and Bradford, 2008). In the recent literature, contaminant transport modeling within the vadose zone has been well developed, although the plant-related processes have not been satisfactorily incorporated into these models. The HYDRUS software series (HYDRUS-1D, -2D, and -3D) is a widely used simulation tool that models vadose zone flow and contaminant transport in great detail together with the processes of water and nutrient uptake by roots (Šimůnek et al., 2008, 2006). Plants are treated as external entities, however, and thus plant growth and plant pathway models are not considered. The SWAP model has much in common with HYDRUS but its more recent versions also include a generic crop growth model (Kroes et al., 2008; van Dam et al., 2008), although the plant pathway is again not a part of the modeling domain. Agriculture-oriented detailed crop models such as CropSyst (Stöckle et al., 2003) and DAISY (Abrahamsen and Hansen, 2000) perform water flow and nutrient transport modeling as well. They are aimed at determining the crop yield response to different environmental conditions and management scenarios, however, and were not designed to perform pollution analysis.

The hypothesis of the study presented here was that a modeling framework that would integrate vadose zone contaminant transport models with dynamic plant root uptake models would significantly improve the comprehensive understanding of the vadose zone plant–soil system under study. Thus, our objective here was to develop this conceptualization and the analytical framework and analyze several example applications.
Unsaturated Zone Soil Water Flow Model

The governing equation for water flow in the unsaturated zone is the Richards equation (Richards, 1931). The one-dimensional pressure head based form of the Richards equation, with root water uptake represented as a sink term, is

\[
\frac{C A \partial h}{\partial t} = \frac{\partial}{\partial z} \left( K \frac{\partial h}{\partial z} - U \right)
\]

where \( C = C(h) = (\partial h/\partial b) \) is the moisture capacity [L\(^{-1}\)], \( h \) is the volumetric water content [L\(^3\) L\(^{-3}\)], \( b \) is the soil water pressure head [L], \( t \) is time [T], \( z \) is the soil depth (directed positive downward) [L], \( K \) is the hydraulic conductivity [L T\(^{-1}\)], and \( U \) is the root water uptake rate [T\(^{-1}\)].

Solving the Richards equation requires knowledge of the constitutive relationships between \( \theta, K, \) and \( b \). A widely used method to estimate the soil water retention and hydraulic conductivity relationships is the van Genuchten (1980) equations:

\[
S_r(h) = \left( \frac{h - \theta_r}{1 - \theta_r} \right) \left( 1 + \left( \alpha_r \right)^n \right) - m_c
\]

\[
K(h) = \left[ S_r(h) \left( 1 - \left[ S_r(h) \right]^{1/m_c} \right) \right]^{-2/m_c}
\]

where \( S_r \) is the effective saturation [L\(^3\) L\(^{-3}\)], \( \theta_r \) is the residual water content [L\(^3\) L\(^{-3}\)], \( \theta_s \) is the saturated water content [L\(^3\) L\(^{-3}\)], \( K_r \) is the saturated hydraulic conductivity [L T\(^{-1}\)], and \( n_r, m_c \) (dimensionless) are constants depending on the soil type, where \( m_c = (1 - 1/n_r) \).

In this study, the control volume method was used to solve Eq. [1] (Berg, 1999). An implicit time integration method together with Picard iteration was used to obtain the spatial and temporal distribution of the soil water pressure head within the soil column. The water flow component of the model is standard practice in the vadose zone literature (Berg, 1999; Celia et al., 1990; van Dam and Feddes, 2000).

Vadose Zone Organic Contaminant Transport Model

To model contaminant transport in the vadose zone, the advection–dispersion–reaction equation was used. The transport equation for an organic contaminant assuming linear equilibrium partitioning between three phases (i.e., soil solids, soil water, and soil air), similar to the form used by Chu and Mariño (2006, 2004), is given by

\[
\frac{\partial}{\partial t} (G_w C_w) = \frac{\partial}{\partial z} \left( G_v \frac{\partial C_w}{\partial z} - G_r C_w \right) + G_s (C_w - G_v C_u)
\]

where \( G_i \) is the bulk coefficient for the partitioning processes [L\(^3\) L\(^{-3}\)], \( C_w \) is the contaminant concentration in the soil water [M L\(^{-3}\)], \( G_v \) is the bulk coefficient for the dispersion process [L\(^2\) T\(^{-1}\)], \( G_r \) is the bulk coefficient for the advection process [L T\(^{-1}\)], \( G_s \) is the bulk source term [M T\(^{-1}\)]. \( \lambda_{fg} \) is soil gas saturation [L\(^3\) L\(^{-3}\)], \( \lambda_{sw} \) is soil water saturation [L\(^3\) L\(^{-3}\)], \( \lambda_p \) is the partition coefficient between soil solids and soil water [L\(^3\) M\(^{-1}\)], \( \phi \) is porosity [L\(^3\) L\(^{-3}\)], \( \theta_s \) is soil water mass [M L\(^{-3}\)], \( \theta_r \) is residual water content [L\(^3\) L\(^{-3}\)], \( \theta_s \) is soil water saturation [L\(^3\) L\(^{-3}\)], \( \lambda_{fg} \) is the diffusion coefficient in the soil air [L\(^2\) T\(^{-1}\)], \( \lambda_{sw} \) is the dimensionless Henry’s law constant, \( \lambda_{fg} \) is soil gas saturation [L\(^3\) L\(^{-3}\)], \( \lambda_{sw} \) is soil water saturation [L\(^3\) L\(^{-3}\)], \( D_{fg} \) is the diffusion coefficient in the soil air [L\(^2\) T\(^{-1}\)], \( \lambda_{fg} \) is the diffusion coefficient in the soil air [L\(^2\) T\(^{-1}\)], \( \lambda_{sw} \) is the diffusion coefficient in the soil air [L\(^2\) T\(^{-1}\)], and \( \lambda_{sw} \) is the diffusion coefficient in the soil water [L\(^2\) T\(^{-1}\)]. The numerical solution procedure used for the contaminant transport equation (Eq. [4]) is given in the Appendix.

The Plant Pathway Model

In this study, the plant pathway for contaminant transport was modeled by representing the aboveground parts of the plant as a single compartment. Using this approach, the parameterization of the transport via phloem flow and the modeling of fruit growth could be ignored. On the other hand, the plant roots are represented by root growth and root density distribution functions (see below), which are critical in determining the root water uptake (see below) and thus in determining plant contaminant uptake by the roots. A mass balance equation for the plant compartment was developed by considering the processes given in Table 1.

Diffusive Transfers between Plant and Atmosphere

The diffusive flux between the plant and the atmosphere can be expressed as

\[
J_{fa} = k_{fa} (C_A - C_f K_{AP})
\]
where $f_{p,a}$ is the diffusive flux between the plant and the atmosphere [M L^{-2} T^{-1}], $k_{a,p}$ is the air-to-plant diffusive mass transfer rate coefficient [L T^{-1}], $C_A$ is the concentration in the atmosphere [M L^{-3}], $C_p$ is the concentration in the plant [M L^{-3}], and $K_{AP}$ is the contaminant-specific air–plant partition coefficient [L^3 L^{-3}].

To calculate the air-to-plant diffusive mass transfer rate coefficient, a two-resistance model was adopted as proposed by Cousins and Mackay (2000). This model assumes that the exchange of chemicals between the atmosphere and the plant is occurring in series by diffusion through the leaf and the air boundary layer. Note that more detailed models do exist in the literature (e.g., see Riederer, 1995). The two-resistance in-series model for calculating $k_{a,p}$ can be written as

$$
\frac{1}{k_{a-p}} = \frac{1}{k_{ab-p} LAI} + \frac{1}{k_c LAI} \quad [6]
$$

where $k_{ab-p}$ is the mass transfer rate coefficient for diffusive transport across the plant's air boundary layer [L T^{-1}], LAI is the leaf area index [L^2 L^{-2}], and $k_c$ is the mass transfer rate coefficient for diffusive transport through the leaf cuticle [L T^{-1}]. The parameter $k_{ab-p}$ can be estimated as (Cousins and Mackay 2000)

$$
k_{ab-p} = \frac{D_p^a}{d_{ap}^a} \quad [7]
$$

where $D_p^a$ is the diffusion coefficient in free air [L^2 T^{-1}] and $d_{ap}^a$ is the air–plant boundary layer thickness [L]. The coefficient $d_{ap}^a$ is an unknown quantity, but Cousins and Mackay (2000) suggested that it should be on the same order as the soil–air boundary thickness (2–6 mm) or less. The coefficient $k_c$ can be estimated using (Cousins and Mackay, 2001)

$$
k_c = P_c \left( \frac{1}{K_{aw}} \right) \quad [8]
$$

where $P_c$ is the cuticle permeability [L T^{-1}] and $K_{aw}$ is the air–water partition coefficient [L^3 L^{-3}]. To estimate $P_c$, Cousins and Mackay (2000) proposed using the following equation, which takes the average of two relationships derived through experiments:

$$
\log P_c = \frac{0.704 \log K_{aw} - 11.2}{2} + \frac{-3.47 - 2.79 \log MW + 0.970 \log K_{aw}}{2} \quad [9]
$$

where $K_{aw}$ is the contaminant-specific octanol–water partition coefficient [L^3 L^{-3}] and MW is the molecular weight of the contaminant (g mol^{-1}).

**Transformation within the Plant**

Assuming that a first-order decay rate coefficient can explain the contaminant transformations within the plant, the following equation can be written:

$$
R_p = \lambda_p C_p V_p \quad [10]
$$

where $R_p$ is the contaminant decay rate within the plant [M L^{-2} T^{-1}], $\lambda_p$ is the first-order decay rate coefficient of the contaminant within the plant [T^{-1}], and $V_p$ is the plant volume per unit land area [L^3 L^{-2}]. The mass transfer rate coefficient that describes the contaminant transformation within the plant, $k_{p}$ [L T^{-1}], is then

$$
k_p = \lambda_p V_p \quad [11]
$$

**Root Uptake**

If we neglect diffusive uptake by the roots (as in Cousins and Mackay, 2000) and only consider contaminant uptake by mass flow, organic chemical uptake by the roots can be expressed as

$$
R_U = \int_0^L \left( k_{p,a} C_a \right) dz \quad [12]
$$

$$
k_{p,a}(z) = S(z) \text{TSCF} \quad [13]
$$

where $R_U$ is the mass flow rate into the plant via root uptake [M L^{-2} T^{-1}], $L$ is the root depth [L], $k_{p,a}$ is the mass transfer rate coefficient from the soil to the plant via root uptake [L T^{-1}], $z$ is the soil depth (directed positive downward) [L], TSCF is the transpiration stream concentration factor [L^3 L^{-3}], and $S(z)$ is the root water uptake rate [T^{-1}]. The parameter TSCF is commonly used in modeling the passive uptake of neutral organic chemicals into plants through the transpiration stream (Dettenmaier et al., 2009). Chemicals that are actively taken up by plants would have TSCF values >1.0. Nutrients (N, P, and K) are among such chemicals and to be able to simulate their uptake from the soil, this module could be expanded to include an active uptake process such as the nutrient uptake module in HYDRUS (Šimůnek et al., 2008). On the other hand, to be able to simulate the uptake of ionized compounds, a more complex uptake module is required (Trapp, 2004).

To estimate the TSCF for nonionized compounds, Dettenmaier et al. (2009) recommended the following empirical relationship based on the octanol–water partition coefficient ($K_{ow}$) of the specific chemical being studied:

$$
\text{TSCF} = \frac{1}{1 + 11.6 \log K_{ow}} \quad [14]
$$

**Mass Balance for the Plant Compartment**

The resulting mass balance equation for the plant compartment is

$$
\frac{d(V_p C_p)}{dt} = k_{a-p} C_A - \left( k_{p,a} + k_p \right) C_p + \int_{root zone} \left( k_{a-p} C_a \right) dz \quad [15]
$$

where $V_p$ is the plant volume [L^3 L^{-2}] and $C_p$ is the contaminant concentration in the plant [M L^{-3}].

[Note: The original text contained several equations and mathematical expressions that were not fully transcribed or formatted correctly in the text provided.]
The Plant Life Cycle Model

The plant life cycle model is a critical component of this analysis because it provides the time-dependent values for the LAI, the root depth, the root density distribution, and the plant volume, all of which are used by the other models described above. In this study, a crop growth model that has been successfully applied to agricultural water management by Mailhol et al. (1997), Wöhling and Schmitz (2007), and Mailhol and Merot (2008) was used.

The LAI simulation model calculates the daily average values of LAI based on a thermal time concept following the approach of the PILOTE 1.3 model of Mailhol et al. (1997) and generalization of the same model by Wöhling and Schmitz (2007) to crop growth. In this model, thermal time is the basic driving force for LAI development. The plant response to water stress is modeled through the inclusion of a water stress index (WSI) term:

\[
LAI(i) = \text{LAI}_{\text{max}} \left[ \left( 1 - WSI(i) \right)^\lambda \right] - \left[ 1 - \left( 1 - \exp \left( -\beta \frac{TT(i)}{T_f} \right) \right) \right] \quad \text{(16a)}
\]

\[
TT(i) = \sum_{k=1}^{i} \left( T(i) - T_b \right) \quad \text{(16b)}
\]

where \( i \) is the number of days since sowing, \( \text{LAI}_{\text{max}} \) is the maximum LAI value \([L^2 L^{-2}]\), \( TT(i) \) is the thermal time on the \( i \)th day (°C), \( T_s \) is the thermal time of emergence (°C), \( T_f \) is the threshold thermal time corresponding to \( \text{LAI}_{\text{max}} \) (°C), \( \beta \) and \( \delta \) are parameters related to the shape of the LAI curve, WSI(\( i \)) is the water stress index on the \( i \)th day, \( \lambda \) is a dimensionless parameter governing the plant sensitivity to water stress, \( T(i) \) is the daily mean air temperature on the \( i \)th day (°C), \( T_b \) is the base temperature of the crop (°C), \( T_A(i) \) is the actual daily transpiration rate on the \( i \)th day \([L T^{-1}]\), and \( T_p(i) \) is the potential transpiration rate on the \( i \)th day \([L T^{-1}]\).

The terms \( T_f \) and \( \text{LAI}_{\text{max}} \) are plant specific and are obtained by measurement. The information on how the LAI curve changes with time for a crop under certain conditions may be used to determine the parameters \( \beta \), \( \delta \), and \( \lambda \). Mailhol et al. (1997) proposed changing \( \delta \) to a lower value after \( \text{LAI}_{\text{max}} \) or \( TT(i) = T_f + 40°C \) are reached to simulate slow senescence for crops such as corn (Zea mays L.). The details of the calculations to obtain the potential and the actual transpiration rates are given below, where the root water uptake module is described.

The plant biomass is calculated as in Mailhol and Merot (2008). In their study, they modified the crop yield model of Mailhol et al. (1997) and calculated the dry matter accumulation of hay at daily time steps. They introduced a new dimensionless parameter, \( R_p \), to simulate plant growth hindered by decreased LAI values:

\[
m_p(i) = m_p(i-1) + R_p(i) \left[ \text{RUE}(i) \text{ISR}^*(i) \right] \quad \text{(17)}
\]

\[
R_p(i) = \frac{\text{CLAI}(i-3)}{\text{CLAI}^*(i-3)} \quad \text{(17a)}
\]

\[
\text{ISR}^*(i) = 1 - \exp \left\{ -\left[ \frac{\epsilon_{\text{ext}}(i) \text{LAI}^*(i)}{10.0.1.43(LAI^*(i))^{-0.5}} \right] \right\} \quad \text{(17b)}
\]

\[
\epsilon_{\text{ext}}(i) = \min \left\{ 1, 0.1, 4.3(LAI^*(i))^{-0.5} \right\} \quad \text{(17c)}
\]

where \( m_p(i) \) is the total aboveground dry biomass on the \( i \)th day \([M L^{-2}]\), RUE is the intercepted radiation use efficiency (i.e., the amount of aboveground biomass produced per solar energy received) \([T^2 L^{-2}]\), SR is the daily incident solar radiation per area \([M T^{-2}]\), \( \text{ISR}^*(i) \) is the fraction of solar radiation intercepted by the crop on the \( i \)th day, CLAI(\( i - 3 \)) is the cumulative LAI value on the last 3 d \([L^2 L^{-2}]\), CLAI*(\( i - 3 \)) is the cumulative LAI value calculated assuming no water stress on the last 3 d \([L^2 L^{-2}]\), \( \epsilon_{\text{ext}}(i) \) is a dimensionless extinction coefficient, and LAI*(\( i \)) is the LAI value on the \( i \)th day calculated assuming no water stress \([L^2 L^{-2}]\). The dry biomass calculated using Eq. (17) is converted to fresh volume by using average values for the plant’s water content and dry density.

The time-dependent values of root depth and root distribution are required for dynamic representation of the root water uptake rate distribution within the soil column as plants go through different growth stages. In this study, the root depth was estimated using a linear root growth function as used by Wöhling and Schmitz (2007). Sigmoidal (Yadav et al., 2009b) and sinusoidal (Yadav et al., 2009a) growth functions were also considered as alternative root growth models; however, no significant difference in the overall model output was observed and the linear growth function was selected because it required fewer input parameters. The daily root depth values were calculated using

\[
L_R(t_R) = \begin{cases} 
L_R(0) + \frac{L_{R,max} - L_R(0)}{t_{R,max}} t_R & t_R \leq t_{R,max} \\
L_{R,max} & t_R \geq t_{R,max}
\end{cases} \quad \text{(18)}
\]

where \( L_R(t_R) \) is the root depth at time \( t_R \) \([L]\), \( L_R(0) \) is the initial root depth \([L]\), \( L_{R,max} \) is the maximum root depth \([L]\), and \( t_{R,max} \) is the time required to reach \( L_{R,max} \) \([T]\).

The root distribution was calculated by using the exponential root distribution function of Novak (1987):

\[
b(z) = \frac{\delta_R \exp \left( -\delta_R \frac{z}{L_R} \right)}{L_R [1 - \exp(-\delta_R)]} \quad \text{(19)}
\]

where \( b(z) \) is the normalized root distribution \([L^{-1}]\), \( z \) is the soil depth (directed positive downward) \([L]\), and \( \delta_R \) is a dimensionless empirical constant (3.64 for corn). The term normalized root distribution indicates that the value returned by Eq. (19) is not the actual root density at the given depth but is the fraction of the total root...
density residing at that depth. The integration of Eq. [19] across the root depth ($L_R$) results in a value of 1, so it can be used in a macroscopic root water uptake model without any modifications. The root water uptake model used in this study is described below when the coupling of the soil water flow and plant life cycle models is discussed.

**Coupling the Models**

To build the integrated model, the submodels described above had to be coupled. This coupling was established at multiple interfaces and at different levels of solution steps (i.e., the model development phase vs. the numerical solution phase). The overall coupling scheme can be divided into two main categories: (i) coupling the unsaturated zone soil water flow and plant life cycle models; and (ii) coupling the vadose zone contaminant transport and plant pathway models.

**Coupling the Unsaturated Zone Soil Water Flow and Plant Life Cycle Models**

The coupling of the unsaturated zone soil water flow and plant life cycle models is achieved by special handling of two modules: (i) the ground surface boundary (the upper boundary of the soil column); and (ii) root water uptake. In both of these modules, LAI is the key parameter that defines the interaction between the two models.

**Ground Surface Boundary**

In the treatment of the ground surface boundary when solving for soil water flow, the algorithm used in the SWAP model formed the foundation (van Dam and Feddes, 2000). At each time step of the numerical solution, the algorithm determines whether evaporation or infiltration conditions prevail at the soil surface. The head or flux that defines the boundary condition is then specified according to the weather conditions and soil moisture availability near the ground surface. Interaction with the plant growth model occurs when determining the potential water flux at the ground surface. The potential flux at the ground surface is dependent on precipitation that is not intercepted by the plants covering the soil surface and on the potential soil evaporation rate:

$$q_{\text{top}} = (1 - f_{\text{int}})q_{\text{rain}} - E_p$$

where $q_{\text{top}}$ is the potential flux at the ground surface [L T$^{-1}$], $f_{\text{int}}$ is the fraction of the precipitation that is intercepted by the vegetation [L L$^{-1}$], $q_{\text{rain}}$ is the precipitation rate [L T$^{-1}$], and $E_p$ is the potential soil evaporation rate [L T$^{-1}$].

The intercepted fraction of the precipitation during a certain time period is determined by comparing the volume of precipitation during that time period with the available volume for interception storage for the same time period. To estimate the available volume for interception storage, a water budget is calculated, taking into account the maximum interception storage capacity, precipitation, and the evaporation from interception. The maximum interception storage capacity is assumed to be dependent on the LAI and a specific storage capacity for the plant. The interception water budget calculations were performed following the method of Panday and Huyakorn (2004).

The potential soil evaporation rate is also dependent on the plant’s growth stage and determined using

$$E_p = (1 - f_c)E_{p,0}$$

where $f_c$ is the vegetation cover fraction and $E_{p,0}$ is the potential evaporation rate for bare, wet soil according to the site conditions [L T$^{-1}$]. Equation [21] is the same relationship used in the SWAP model (Kroes et al., 2008) for determining the potential evaporation rate from partially covered soil when $f_c$ is calculated based on the Beer–Lambert equation that describes the radiation attenuation as a function of LAI (van Dijk and Bruijnzeel 2001a):

$$f_c = 1 - \exp(-\kappa \text{LAI})$$

where $\kappa$ is the plant-specific dimensionless extinction coefficient, which most commonly varies in the range 0.5 to 0.7.

The actual flux occurring at the ground surface may be less than the potential flux that is calculated in Eq. [20] due to physical limits to soil water flow near the surface. The maximum flux allowed at the soil surface ($q_{\text{top, max}}$) is calculated using Darcy’s law:

$$q_{\text{top, max}} = -K_{1/2} \left( \frac{h - h_{\text{top}}}{0.5 \Delta z_t} - 1 \right)$$

where $K_{1/2}$ is the hydraulic conductivity between the ground surface and the center of the uppermost soil cell [L T$^{-1}$], $h$ is the soil water pressure head in the uppermost soil cell [L], $h_{\text{top}}$ is the soil water pressure head at the ground surface [L], and $\Delta z_t$ is the thickness of the uppermost soil cell [L]. The value of $h_{\text{top}}$ depends on the environmental conditions at the specific time step in which it is being calculated. If $q_{\text{top}} > 0$, which indicates that infiltration prevails, $h_{\text{top}}$ is assigned the water depth value at the ground surface ($h_{\text{top}} = h_{\text{surf}}$). If $q_{\text{top}} < 0$, $h_{\text{top}}$ becomes the soil water pressure head in equilibrium with the prevailing relative humidity in the atmosphere ($h_{\text{top}} = h_{\text{atm}}$). The $h_{\text{top}}$ value also identifies the limit of the soil water pressure head at the soil surface because it becomes the boundary condition when the potential flux exceeds the maximum flux (i.e., when $|q_{\text{top}}| > |q_{\text{top, max}}|$). In that case, the top boundary condition switches to a specified head boundary condition equal to $h_{\text{surf}}$ or $h_{\text{atm}}$ as infiltration or evaporation, respectively, dominates.

**Root Water Uptake**

In this study, a macroscopic root water uptake model was adopted. The macroscopic root water uptake models assume a soil plant–atmosphere continuum and conceptualize plant roots as channels that convey soil water into the atmosphere. This conceptualization
The soil column may not be able to satisfy this potential root water uptake rate due to water scarcity, and the actual root water uptake may be less than the potential value, creating water stress on the plant. In this case, the macroscopic root water uptake models use various functions to model the reduction in the water uptake rate at depths where the soil water content is relatively lower.

The potential transpiration rate is calculated by multiplying the potential evapotranspiration rate by the vegetation cover fraction:

\[ T_p = f_c ET_p - E_{int} \]  \[24\]

where \( ET_p \) is the potential evapotranspiration rate [L T\(^{-1}\)] representing the combined effect of the evaporation and transpiration processes occurring at the site and \( E_{int} \) is the evaporation rate from interception [L T\(^{-1}\)]. When Eq. [24] gives a negative potential transpiration rate, potential transpiration is set to zero. Thus, it is assumed that there is no transpiration while there is evaporation from interception.

The crop coefficient approach detailed by Allen et al. (1998) was used to determine the potential evapotranspiration. The crop coefficient approach is based on modifying a reference evapotranspiration value using a crop-specific coefficient:

\[ ET_p = K_c ET_0 \]  \[25\]

where \( K_c \) is a dimensionless crop coefficient and \( ET_0 \) is the reference evapotranspiration rate [L T\(^{-1}\)]. The value of \( K_c \) is related to the growth stage of the crop and can be calculated as (Mailhol et al., 1997)

\[ K_c = K_{c,max} [1 - \exp(-x_h LAI)] \]  \[26\]

where \( K_{c,max} \) is the maximum value of \( K_c \) for the crop depending on the local site conditions and \( x_h \) is a dimensionless parameter that reflects the crop’s water consumption characteristics.

The potential root water uptake rate, \( S_p \) [T\(^{-1}\)], is obtained by distributing the potential transpiration throughout the root zone using the root distribution function (Eq. [19]) discussed above:

\[ S_p = b(z) T_p \]  \[27\]

The soil column may not be able to satisfy this potential root water uptake demand due to water scarcity, and the actual root water uptake may be less than the potential value, creating water stress on the plant. In this case, the macroscopic root water uptake models use various functions to model the reduction in the water uptake rate at depths where the soil water content is relatively lower.

The actual root water uptake rate, \( S \), is calculated from the potential uptake rate by using the water stress reduction and water stress compensation functions:

\[ S = \alpha \beta_c S_p \]  \[28\]

where \( \alpha \) is the function that accounts for the reduced water uptake by the roots and \( \beta_c \) is the water stress compensation function. Both of these functions return dimensionless values. In the current model, the value of \( \alpha \) is calculated using the water stress response function of Feddes et al. (1978).

To model the water stress compensation, Li et al. (2001) proposed a function that is basically a weighted stress index calculated based on water availability and root distribution, which was later tested by Braud et al. (2005) and found robust. Li et al. (2006) successfully applied a generalized version of this function:

\[ \beta_c (h,z) = \frac{\alpha(h)}{\int_{L_h} \alpha(h) b(z) dz} \]  \[29\]

Combining Eq. [27–29], the root water uptake rate distribution can be obtained by

\[ S(h,z) = \alpha(h) \beta_c (h,z) b(z) T_p \]  \[30\]

After the root water uptake distribution throughout the soil column is determined, it is included in the soil water flow model as a sink term. The coupling between the unsaturated zone soil water flow model and the plant life cycle model occurs at this sink term. The potential transpiration is estimated based on the environmental conditions and the plant’s growth stage. Thus, the plant life cycle model is critical in calculating the spatially distributed root water uptake sink term in the flow equation because it provides the potential transpiration rate and the root distribution. On the other hand, the solution of the soil water flow model provides the water distribution throughout the soil depth, which in turn determines if the plant will experience water stress. When the plant experiences water stress, its growth is impeded. The actual transpiration rate is given by the integration of the root water uptake rates over the root zone:

\[ T_A = \int_{L_h} S(h,z) dz \]

\[ = \int_{L_h} \alpha(h) \beta_c (h,z) b(z) T_p dz \]  \[31\]

As given in Eq. [16b], the ratio of the actual transpiration rate to the potential transpiration rate gives the WSI used in the LAI simulation. Thus, throughout the root water uptake calculations, there is a two-way interaction between the unsaturated zone soil water flow model and the plant life cycle model, and the coupled solution of the two requires an iterative approach (Wöhling and Schmitz, 2007).

### Coupling the Vadose Zone Contaminant Transport and Plant Pathway Models

The coupling of the soil contaminant transport and plant pathway models occurs at the numerical solution phase, more specifically, at....
The solution of the matrix equation that represents the whole soil–plant system. The complete system can now be compactly represented in a matrix–vector format, which has been used to obtain the solution.

In all applications, we used a hypothetical heterogeneous soil column of 2-m length. The soil media information was adopted from Wöhling and Mailhol (2007) as determined at a site in Montpellier, France. The soil profile was divided into three layers of different types of soil. The soil characteristics within each layer are given in Table 2.

To facilitate interpretation of the results, a simplified weather data set was used. Constant values were assigned to the air temperature \( T \approx 20°C \), reference evapotranspiration \( ET_0 = 2.5 \text{ mm d}^{-1} \), the potential evaporation rate for bare soil according to the site conditions \( (E_{p,0} = 2.0 \text{ mm d}^{-1}) \), the potential evaporation rate from free water surfaces \( (E_{p,w} = 3.0 \text{ mm d}^{-1}) \), soil surface pressure head in equilibrium with atmospheric water vapor \( (h_{\text{atm}} = −160 \text{ m}) \), and daily solar radiation \( (SR = 20 \text{ MJ m}^{-2}) \) throughout the simulation.

The simulation time was set as 120 d in order to cover a sufficiently long period of time to include the full crop growth and subsequent senescence. A cycle of 30 d of no rainfall followed by 30 d of constant rainfall \( (6 \text{ mm d}^{-1}) \) was repeated until the end of the simulation. This simple rainfall pattern created distinct dry and wet periods. The crop-related model parameters were adopted from Mailhol et al. (1997) and Wöhling and Mailhol (2007) for corn (Table 3). The specific interception storage capacity was taken as 0.075 mm (van Dijk and Bruijnzeel, 2001b).

The top 20 cm of the soil column was divided into cells with a thickness \( (\Delta z) \) of 0.01 m, while a \( \Delta z \) value of 0.05 m was used throughout the rest of the soil column. The initial time step was set as 1 h. During the simulation, the time step was allowed to change between 1 s and 1 d according to the convergence properties of the water flow model. The variable time step algorithm works similarly to that of van Dam and Feddes (2000).

### Applications

Several applications were used to test the integrated modeling methodology developed above. These examples were structured around analyzing the effects of plant life cycle modeling on the water and contaminant distribution within the soil, and in turn, on the evolution of the plant’s contaminant content. Simple weather data and irrigation schedules were used to facilitate the interpretation of the results. The crop data were obtained from the literature (Mailhol et al., 1997; Wöhling and Mailhol, 2007). Mass balance analysis was performed to identify the fate of the contaminant once it was introduced to the system. Finally, a sensitivity analysis investigated the importance of model input parameters on the plant pathway outcome.

### Modeling Domain and the Model Parameters

An initial soil water pressure head of −10 m throughout the column was assumed. In the flow simulations, the top boundary condition was variable, dependent on weather conditions, and a free drainage boundary condition was applied at the bottom of the soil column.

To facilitate interpretation of the results, a simplified weather data set was used. Constant values were assigned to the air temperature \( T = 20°C \), reference evapotranspiration \( ET_0 = 2.5 \text{ mm d}^{-1} \), the potential evaporation rate for bare soil according to the site conditions \( (E_{p,0} = 2.0 \text{ mm d}^{-1}) \), the potential evaporation rate from free water surfaces \( (E_{p,w} = 3.0 \text{ mm d}^{-1}) \), soil surface pressure head in equilibrium with atmospheric water vapor \( (h_{\text{atm}} = −160 \text{ m}) \), and daily solar radiation \( (SR = 20 \text{ MJ m}^{-2}) \) throughout the simulation.

The simulation time was set as 120 d in order to cover a sufficiently long period of time to include the full crop growth and subsequent senescence. A cycle of 30 d of no rainfall followed by 30 d of constant rainfall \( (6 \text{ mm d}^{-1}) \) was repeated until the end of the simulation. This simple rainfall pattern created distinct dry and wet periods. The crop-related model parameters were adopted from Mailhol et al. (1997) and Wöhling and Mailhol (2007) for corn (Table 3). The specific interception storage capacity was taken as 0.075 mm (van Dijk and Bruijnzeel, 2001b).

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### Table 2. Soil types used in the applications and their values for saturated volumetric water content, \( \theta_s \), residual volumetric water content, \( \theta_r \), fitting constants \( \alpha \) and \( m \), saturated hydraulic conductivity, \( K_s \), and bulk density, \( \rho_b \) (Wöhling and Mailhol, 2007).

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Layer</th>
<th>( \theta_s )</th>
<th>( \theta_r )</th>
<th>( \alpha )</th>
<th>( m )</th>
<th>( K_s )</th>
<th>( \rho_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m</td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
<td></td>
<td></td>
<td>Mg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.0–0.55</td>
<td>0.35</td>
<td>0.05</td>
<td>1.5</td>
<td>1.46</td>
<td>7.5 $\times$ 10$^{-6}$</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>0.55–0.95</td>
<td>0.38</td>
<td>0.05</td>
<td>1.3</td>
<td>1.45</td>
<td>1.85 $\times$ 10$^{-6}$</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>0.95–2.0</td>
<td>0.41</td>
<td>0.05</td>
<td>1.9</td>
<td>1.31</td>
<td>5.2 $\times$ 10$^{-7}$</td>
<td>1.40</td>
</tr>
</tbody>
</table>

† Assumed.
The model parameters used to run the multimedia contaminant fate and transport model are given in Table 4. The pesticide diazinon (O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) was selected to be the contaminant of concern for the example runs. Its physicochemical properties were compiled from the literature and typical values were used for the transport parameters.

The contamination scenario included the surface application of diazinon once on the 45th d of the simulation. The application quantity was set at 0.15 g m\(^{-2}\), which seemed to be compatible with the actual areal diazinon application rates given in Chu and Marino (2004). The atmospheric concentration was assumed to be zero throughout the simulation so there would be no contaminant input to the system via atmospheric deposition processes. An initially uncontaminated soil column and plant was assumed. A zero-gradient boundary condition was applied at the bottom of the soil column.

**Description of Simulations**

A set of simulations was designed to analyze the effect of vegetation on the water and contaminant distribution within the soil with time, to investigate how the plant growth modeling complexity affects the overall model outcome, and to observe the plant pathway response to different modeling assumptions. The simulation set details are given in Table 5, in which the simulations are ranked by the level of detail they incorporate in handling the presence of plants. In the first simulation (No Plant), the model was run without a plant compartment. All the subsequent simulations contained the plant compartment but differed in the way they modeled plant LAI, plant biomass (\(m_p\)), root growth, and root water uptake. In the second simulation (Const. Plant), the plant life cycle was not modeled but constant values were assigned to the related parameters. The third simulation (No Stress) assigned to the related parameters. The third simulation (No Stress) to investigate how the plant growth modeling complexity affects the overall model outcome, and to observe the plant pathway response to different modeling assumptions. The simulation set details are given in Table 5, in which the simulations are ranked by the level of detail they incorporate in handling the presence of plants. In the first simulation (No Plant), the model was run without a plant compartment. All the subsequent simulations contained the plant compartment but differed in the way they modeled plant LAI, plant biomass (\(m_p\)), root growth, and root water uptake. In the second simulation (Const. Plant), the plant life cycle was not modeled but constant values were assigned to the related parameters. The third simulation (No Stress) was set at 0.15 g m\(^{-2}\), which seemed to be compatible with the actual areal diazinon application rates given in Chu and Marino (2004). The atmospheric concentration was assumed to be zero throughout the simulation so there would be no contaminant input to the system via atmospheric deposition processes. An initially uncontaminated soil column and plant was assumed. A zero-gradient boundary condition was applied at the bottom of the soil column.

**Table 4. Multimedia contaminant fate and transport model parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, g mol(^{-1})</td>
<td>304.36</td>
<td>Mackay (2003)</td>
</tr>
<tr>
<td>Soil–water partition coefficient ((K_{ow})), cm(^3) g(^{-1})</td>
<td>2.0</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Air–water partition coefficient or dimensionless Henry’s law constant ((K_{aw}) or (K_H))</td>
<td>(5.0 \times 10^{-5})</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Logarithm of octanol–water partitioning coefficient (log(K_{ow}))</td>
<td>3.3</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Water solubility ((S_w)), mg L(^{-1})</td>
<td>60.0</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Vapor pressure ((P_v)), Pa</td>
<td>0.008</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Diffusion coefficient in free air ((D_a)), m(^2) d(^{-1})</td>
<td>0.43</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Diffusion coefficient in water ((D_w)), m(^2) d(^{-1})</td>
<td>(0.000043)</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Degradation half-life in air, h</td>
<td>550</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Degradation half-life in water, h</td>
<td>1700</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Degradation half-life in soil, h</td>
<td>1700</td>
<td>Mackay (2001)</td>
</tr>
<tr>
<td>Degradation half-life in plant, h</td>
<td>283</td>
<td>assumed 1/16 of the degradation half-life in soil (Jurasko et al. 2008)</td>
</tr>
<tr>
<td>Soil-related transport parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal dispersivity ((\nu_L)), m</td>
<td>0.05</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Air boundary layer thickness ((\delta_{ab})), m</td>
<td>0.005</td>
<td>Chu and Mariño (2004)</td>
</tr>
<tr>
<td>Plant-related transport parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air–plant boundary layer thickness, m</td>
<td>0.002</td>
<td>Cousins and Mackay (2000)</td>
</tr>
<tr>
<td>Water content ((W_p)), m(^3) water m(^{-3}) total plant</td>
<td>0.75</td>
<td>assumed</td>
</tr>
<tr>
<td>Density of the dry plant, g m(^{-3})</td>
<td>(9 \times 10^5)</td>
<td>assumed</td>
</tr>
</tbody>
</table>
The results of the different simulations deviated after about Day 70 (about 10 d after the end of the first wet period) (Fig. 2a). After this date, the available moisture in the soil column began to be inadequate to sustain the plants, which were now in their early senescence period with high LAI and biomass. This situation was ignored in the No Stress simulation, and its LAI stayed at its potential value. The decreasing LAI curve was much steeper for the No Compensation simulation than for the Full simulation because the compensation mechanism in the Full simulation enabled the plant to make more efficient use of the water available in the root zone. This second period of water stress ended after Day 90 as the precipitation input resumed. Note that the thermal time corresponding to LAI_{max} (T_f = 1005°C) was reached on Day 79. This was the start of the natural senescence period and LAI values started to decrease even with no water stress. The decrease in the LAI values, however, was at a slower rate because a smaller \( \delta \) value was used during this period (\( \delta_2 = 0.2 \) vs. \( \delta_1 = 1.4 \)) to simulate the slow senescence observed in the corn plant (Mailhol et al., 1997).

The response of the plant biomass growth model to water stress is also obvious when the results from different simulations are compared (Fig. 2b). The No Stress simulation ignored the effect of water stress, and the biomass continued to increase at the same rate throughout the simulation. The No Compensation and Full simulations responded to water stress by decreasing the rate of biomass growth during the initial dry period (to Day 30) and at the end of the second dry period (Day 90). As expected, the growth rate was the lowest for the No Compensation simulation. Due to the decreased growth rate in the initial dry period and late emergence, the biomass values from the No Compensation simulation were lower than that of the Full simulation throughout the whole period. Note that a constant daily solar radiation value was used to simulate plant growth and hence the potential biomass growth from the No Stress simulation follows a straight line. Also, the plant biomass values continued to increase even after LAI senescence had begun because a different and later maturation point (\( T_{mat} = 1925°C \)) was adopted for stopping the biomass growth. As the plants started to experience increased water stress toward the end of the second dry period, only a subtle decrease in the biomass growth rate was observed in the No Compensation and Full simulations because this was a brief period and ended on Day 90.

**Soil Water Distribution**

Because the plant life cycle model and soil water flow models are in close interaction, the results from both models should be analyzed together. The soil water pressure head profiles given in Fig. 3 show the effect of plant growth on the soil water distribution. The profile snapshots in Fig. 3 are plotted at the times corresponding to the start

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Plant life cycle</th>
<th>Root water uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Plant</td>
<td>no plant; LAI = 0, ( m_p = 0 )</td>
<td>no root water uptake.</td>
</tr>
<tr>
<td>Const. Plant</td>
<td>no plant life cycle modeling (constant LAI, plant biomass, and plant volume throughout the simulation); LAI = 3.0 m^2 m^{-2}, ( m_p = 1000 ) g m^{-2}, ( L_R = 1.2 ) m</td>
<td>root water uptake modeling ignoring water stress compensation; ( \overline{\beta}_c = 1 )</td>
</tr>
<tr>
<td>No Stress</td>
<td>plant life cycle modeling ignoring the effect of water stress on LAI variation; WSI = 1, LAI = LAI(t), ( m_p = m_p(t) ), ( L_R = L_R(t) )</td>
<td>root water uptake modeling ignoring water stress compensation; ( \overline{\beta}_c = 1 )</td>
</tr>
<tr>
<td>No Compensation</td>
<td>plant life cycle modeling considering the effect of water stress on LAI variation; WSI = WSI(t), LAI = LAI(t), ( m_p = m_p(t) ), ( L_R = L_R(t) )</td>
<td>root water uptake modeling ignoring water stress compensation; ( \overline{\beta}_c = 1 )</td>
</tr>
<tr>
<td>Full</td>
<td>plant life cycle modeling considering the effect of water stress on LAI variation; WSI = WSI(t), LAI = LAI(t), ( m_p = m_p(t) ), ( L_R = L_R(t) )</td>
<td>root water uptake modeling considering water stress compensation; ( \overline{\beta}_c = \beta_c(h, z) )</td>
</tr>
</tbody>
</table>

| \( \overline{\beta}_c \) | water stress compensation function; \( h \), pressure head; \( z \), depth. |\( \beta_c \) | water stress compensation function; \( h \), pressure head; \( z \), depth. | \( \beta_c \) | water stress compensation function; \( h \), pressure head; \( z \), depth. |
and end of the wet periods. The root water uptake rate distributions at the start and end of the wet periods are shown in Fig. 4.

The highest soil water pressure heads were observed in the No Plant simulations because the only means of water depletion was evaporation from the soil surface (Fig. 3). On the other hand, the lowest soil water pressure head values were observed in the Const. Plant simulation results due to the fact that a high and constant transpiration demand was imposed throughout the simulation. When the root water uptake rate profiles (Fig. 4) are compared with the soil water pressure head profiles (Fig. 3), it can be consistently observed that there was reduced water uptake within the zones of low soil water pressure head for the corresponding simulations.

For the simulations that modeled plant growth (No Stress, No Compensation, and Full), very similar soil water pressure head profiles are obtained at the end of the wet periods (Days 60 and 120), whereas the soil water pressure head profiles for these simulations are slightly different at the end of the dry periods (Days 30 and 90) (Fig. 3). Analyzing the corresponding root water uptake rate profiles (Fig. 4) and also comparing the corresponding LAI values (Fig. 2a) are helpful for a better interpretation of these discrepancies. On Day 30, the No Stress simulation had the highest LAI among the simulations that modeled plant growth, so it simulated higher root water uptake and thus higher water depletion in the root zone. The same is true for Day 90. As a result of root growth, however, the effect of the compensated root water uptake model was more pronounced in the Full simulation results as the active water uptake region moved to deeper soil than in the other simulations. Of course, this more efficient water uptake is reflected in the simulated LAI value, which was higher for the Full simulation than for the No Compensation simulation on Day 90.

**Contaminant Distribution in Soil**

The bulk soil concentration profiles obtained by the different simulations are given in Fig. 5. The concentration profiles for the simulations that included plants are similar, while the profile for the No Plant simulation is easily distinguished from the others. This discrepancy can be explained by the combined effect of volatilization and root contaminant uptake. As discussed below, the volatilization loss was higher in the No Plant simulation, resulting in a decrease in the contaminant mass available to migrate within the soil. On the other hand, for the other simulations, the soil contaminant concentration was decreased by the root contaminant uptake processes. The combined effect is the concentration profile in Fig. 5a, with deeper contaminant migration and a lower peak value for the simulations that considered the presence of plants compared with the concentration profile given by the No Plant simulation.

A better picture of the contaminant concentration change with respect to time in the soil is provided by Fig. 6. A sharp increase in the contaminant concentration can be observed at the soil surface on the day of contaminant input, which is immediately followed by a sharp decrease (Fig. 6a). Volatilization and infiltration, acting together, rapidly decreased the contaminant concentration at the soil surface. The peaks get less sharp in the lower soil layers. (Note the scale difference in the y axis of the figures belonging to different depths.) Among the simulations with plants, in the deeper soil layers (Fig. 6c–6d) the contaminant concentrations are always higher for the Const. Plant simulation than the simulations that modeled plant growth (No Stress, No Compensation, and Full). This can be explained by the lower root water uptake as a result of lower LAI in the Const. Plant simulation than the simulations that modeled plant growth (No Stress, No Compensation, and Full).
change with time were similar for the simulations that modeled plant growth. The effect of increased contaminant migration to deeper soil due to increased infiltration is visible in Fig. 6d, where the contaminant concentrations start to increase with the start of the second wet period after Day 90.

Plant Pathway

The contaminant concentration evolution within the plant throughout the simulation period is shown for the different simulations in Fig. 7. In the contamination scenario applied in this example, the only route for a plant’s contamination is root uptake. Because the atmospheric concentration was assumed to be zero all throughout the simulations, no atmospheric deposition occurred; however, volatilization to the atmosphere as well as decay acted as routes of contaminant loss from the plant. The concentrations estimated by the simulations that modeled plant growth (No Stress, No Compensation, and Full) were similar to each other. Although there were slight differences in the peak concentrations obtained by these simulations, they agreed on the timing of the peak. These slight differences in the peak concentrations can be explained by the differences in the plant volumes in corresponding simulations. On the other hand, the peak concentration for the Const. Plant was much lower than those of the rest of the simulations. This was due to the lower root contaminant uptake in the Const. Plant simulation as a result of lower root water uptake after the day of contaminant input. Toward the second half of the dry period (Days 75–90), the
contaminant concentration values converged in all of the simulations as they decreased due to the loss processes together with a decrease in root uptake. This decreasing trend of concentration with time was disturbed in all the simulations by the start of the second wet period. After Day 90, the increase in concentration for the Const. Plant was higher than that of the other simulations, and the Const. Plant simulation ended up with a higher in-plant concentration than any of the others.

Because the contaminant did not penetrate into deep soil, root uptake occurred near the soil surface. The differences between the simulations regarding the in-plant concentrations can therefore be explained by the differences in root water uptake patterns and the available soil concentrations in this region. The higher concentration increase after the start of the second wet period for the Const. Plant simulation can be explained by the combined effect of two factors. First is the increased root water uptake due to new soil water that became available because of the precipitation. The second is the generally higher contaminant soil concentrations for this simulation, especially for relatively deeper soil layers. It should also be noted, however, that the contaminant concentration within the plant is dependent on the plant volume. The plant volume is calculated from the plant biomass, which was assigned a constant value for the Const. Plant simulation but which was calculated using the plant growth model (Eq. [17]) for the other simulations (Fig. 2b).

Mass Balance Analysis
At any time during the simulation, the equation for the whole system must hold:

![Fig. 4. Root water uptake rate distributions at the beginning and end of the wet periods obtained by different model simulations: Const. Plant, plant life cycle not modeled and constant values assigned to related parameters; No Stress, daily variation in plant-life-cycle-related parameters but no effect of water stress; No Compensation, effect of water stress on plant life cycle considered but compensation via modified root water uptake distribution neglected; Full, water compensated root water uptake modeling.](image-url)
The change in contaminant mass within the soil and the plant is shown in Fig. 8, and the daily cumulative values of the amount of mass transferred via the relevant processes given in Eq. [33] are plotted in Fig. 9 and 10. In the contamination scenario applied in this study, the only inflow to the system was through contaminant input onto the soil surface. The outflows from the system were volatilization and decay, which occurred both in the soil and in the plant (Fig. 9). On the other hand, root uptake transferred the contaminant from the soil to the plant, so it was an intermedia mass transfer process within the system (Fig. 10).

The mass balance error was calculated for the whole system and also for the plant compartment and the soil column using the following generic equation:

\[
MBE_\text{t} = 100 \left( \frac{(\text{cumulative mass inflow to the system})_t - (\text{mass in the system})_t}{(\text{mass in the system})_t} - (\text{cumulative mass outflow from the system})_t \right)
\]

where MBE_t is the percentage mass balance error at time \( t \). The cumulative mass balance error for the plant compartment, the soil column, and the whole system at the end of the simulation did not exceed 5.6 × 10^{-4}, 2.4 × 10^{-6}, and 2.3 × 10^{-11}\%, respectively, for any of the simulations.

The mass balance analysis results reveal the importance of volatilization as a contaminant loss process from the soil (Fig. 9a). The highest contaminant loss occurred through volatilization in all of the simulations, and the No Plant simulation had the highest amount of volatilization loss. As a result, the total contaminant mass within the soil for the No Plant simulation decreased more rapidly than in the other simulations (Fig. 8a). Further analysis of the simulation results revealed that there was a greater accumulation of contaminant at the soil surface for the
No Plant simulation due to lower infiltration rates in this simulation causing higher volatilization. The reason for the lower infiltration rate is attributed to the lower pressure head gradient at the soil surface due to the relatively more moist conditions in the No Plant simulation. The pressure gradient near the soil surface was higher for the simulations that considered the presence of plants because root water uptake consumed soil water in the root zone. These results indicate a complex interaction among volatilization, infiltration, and root water uptake processes. A detailed analysis of these interactions can be conducted by the integrated model developed in this study. Because such a detailed analysis requires multiple new model simulations, this important application will be the subject of future studies.

The contaminant mass within the plant was similar for the simulations that modeled the plant life cycle (No Stress, No Compensation, and Full), whereas it was lower for the Const. Plant simulation (Fig. 8b). This can be explained by the lower root uptake due to lower LAI for the Const. Plant simulation than the other simulations after the day of contaminant application (Fig. 10 and 2).

**Sensitivity Analysis**

The sensitivity of the contaminant concentration within the plant to a selected set of contaminant fate and transport parameters was analyzed. In the analysis, different values were assigned to the parameter of interest while keeping all the other model parameters constant. The sensitivity to a 20% variation in the parameter of...
interest was investigated for all the selected parameters; however, greater variation was also included in the analysis if the literature indicated a greater uncertainty in the parameter value.

The sensitivity of the contaminant concentration within the plant to the longitudinal dispersivity, retardation factor, bulk decay rate in the soil, TSCF, contaminant half-life within the plant, and the air-to-plant diffusive mass transfer rate coefficient were analyzed. Among these parameters, it was found that the longitudinal dispersivity, bulk decay rate in the soil, and the air-to-plant diffusive mass transfer rate coefficient did not affect the in-plant concentrations significantly for the application problem investigated in this study. The sensitivity of the contaminant concentration within the plant to variation of the retardation factor, TSCF, and contaminant half-life within the plant is shown in Fig. 11. The Full simulation was used as the base case in this analysis.

The retardation factor ($R$) in unsaturated soil can be defined as

$$R = 1 + \frac{\phi w K_d + \phi s K_H}{\phi s_w}$$

Values of $R$ vary both spatially and temporally. The main uncertainty in the $R$ value comes from the uncertainty in the value of the partition coefficient, $K_d$. A $K_d$ value of 2.0 cm$^3$ g$^{-1}$ was used in the original simulation. In Fig. 11a, the plant contaminant concentration variation with time is compared for model simulations that increased and decreased the original $R$ value by 20%. It is seen that the plant contaminant concentration is higher for the low $R$ value. This was expected because lower $R$ values increase the water availability of the contaminant, facilitating its uptake through plant roots. The effect of the $R$ value was significant for the periods with wet soil conditions because there was increased root water uptake.
In the example application, the relationship of Dettenmaier et al. (2009) was used to estimate the TSCF value (Eq. [14]) from the log $K_{ow}$ value of the contaminant. This is not the only relationship that can be used to estimate the TSCF. Another popular but older equation to estimate the TSCF is that developed by Briggs et al. (1982):

$$\text{TSCF} = 0.784 \exp \left( -\frac{(\log K_{ow} - 1.78)^2}{2.44} \right)$$  \[36\]

This equation produces a bell-shaped relationship between TSCF and log $K_{ow}$, which estimates a reduced TSCF for highly polar (low log $K_{ow}$) and highly lipophilic (high log $K_{ow}$) substances. Trapp (2007) discussed the accuracy of the Briggs et al. (1982) relationship in the case of polar compounds because there are studies that contradict the reduced uptake predicted by Eq. [36]. Dettenmaier et al. (2009) also observed a high uptake of polar compounds in their extended study of TSCF measurements to reevaluate the relationship and produced a new empirical relationship that is nearly sigmoidal (Eq. [14]).

The compound that was used in the application simulations, diazinon, with its log $K_{ow}$ value of 3.3, is slightly lipophilic and both of the relationships estimated similar values for the TSCF for diazinon (0.30 using the relationship of Briggs et al. [1982], 0.32 using the relationship of Dettenmaier et al. [2009]). It is common to measure a range of TSCF values for a specific compound due to variations in the experimental setup (Dettenmaier et al. [2009]).

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**Fig. 9.** Cumulative mass removed from the system via volatilization and decay obtained by different model simulations: No Plant, model run without a plant compartment; Const. Plant, plant life cycle not modeled and constant values assigned to related parameters; No Stress, daily variation in plant-life-cycle-related parameters but no effect of water stress; No Compensation, effect of water stress on plant life cycle considered but compensation via modified root water uptake distribution neglected; Full, water compensated root water uptake modeling.
et al., 2009). There is also evidence that supports the concept that the TSCF is, in fact, not a constant but a variable that is affected by environmental conditions (Trapp, 2007). In Fig. 11b, the effect of TSCF variation on the plant pathway outcome is shown. It can be seen that variation in the TSCF is immediately reflected in the contaminant concentration values within the plant because increased TSCF allows more contaminant uptake. This effect is also dependent on the water and contaminant availability in the soil, however, and it is more pronounced in the earlier stages of contamination, which were also governed by wet conditions in this example.

The contaminant half-life within the plant is one of the parameters with the greatest uncertainty. In the absence of data, extrapolation from degradation half-lives in soil is a commonly used method to estimate in-plant half-lives. There is a lot of uncertainty in the results of these extrapolations, however, and there is no consensus in the literature on the conversion factors to be used (Juraske et al., 2008). Juraske et al. (2008) reported studies that assumed in-plant half-lives that were half that of the soil half-life (a conversion factor of 2) as well as studies that assumed a conversion factor of 10. They determined a conversion factor of 16 for in-plant half-lives through their own field experiments. Following their suggestion, a conversion factor of 16 was used as the basis in determining the in-plant degradation rate in this example. In Fig. 11c, the outcome of using the lower conversion factors is shown.
Conclusions

In this study, a methodology that unifies single-medium continuous models with multimedia compartmental models in a flexible framework was developed for analyzing contaminant transport in a soil–plant system. Multiple models, each describing a different set of processes that belong to the system, were integrated within this framework. Together with the contaminant fate and transport models, water flow and plant life cycle models were also included in the integrated model. The resultant model was applied to a hypothetical contamination scenario where the effect of the presence of plants on the contaminant distribution within the system was investigated. The model outcomes obtained by using multiple levels of complexity in the plant growth and root water uptake models were compared.

The results obtained from the applications showed the close interaction between plants and the soil water flow. The presence of plants considerably modified the spatial and temporal water distribution within the root zone. When the fact that plants are dynamic biological systems with a capability of growing and regulating their interaction with the soil (regarding root water uptake) was taken into account, the results were further modified and they became dependent on the way the plant’s response to environmental conditions were modeled. When the model of contaminant transport within the soil was integrated with the plant life cycle and soil water flow models, the results became difficult to interpret by intuition as a result of the complexity involved. The comparison of different model simulations with and without plants showed the effects of plants and plant life cycle modeling on the contaminant distribution within the soil. The results indicated a complex interaction among the volatilization, infiltration, and root water uptake processes, with important consequences for contaminant fate in the soil. The root water uptake rate distribution within the soil, which is determined by the coupled models of soil water flow and LAI, was very important in describing the contaminant distribution within the soil and its transfer to the plant. The plant’s contamination modeling as coupled with the plant life cycle, soil water flow, and soil contaminant transport models showed that contaminant concentrations within the plant were highly variable with time, indicating potentially important consequences when assessing the risk associated with this exposure pathway. The integrated model developed in this study can be a very useful risk management tool because it can describe the effects of the date of crop sowing, irrigation scheduling, and the timing of contaminant application on the plant’s contamination.

This study should serve as a basis for integrating physically based models that describe the various processes related to contaminant fate and transport in the soil–plant system. The individual modules (e.g., LAI simulation) used in this study may be easily replaced with others. The mathematical definitions of the processes can be changed. Even adding new expressions for processes that are absent in this study would be straightforward. New compartments can be added to increase the detail if the proper expressions to define mass transfer among the other compartments being modeled can be developed. For example, adding a litter compartment residing at the soil surface would be trivial if the litterfall rate to model mass transfer between the plant and the litter compartments, and the litter decomposition rate to model mass transfer between the litter compartment and the uppermost soil cell can be defined. On the other hand, the model itself can be used as a tool in developing the definitions for these processes. Various hypotheses that describe different processes related to the soil–plant system can be tested using the model. These tests can be performed on field data as well as on laboratory data because the model is capable of describing soil heterogeneity together with soil hydraulics.

Appendix

Spatial Discretization of the Vadose Zone Contaminant Transport Model

The contaminant transport equation (Eq. [4]) is spatially discretized using the finite volume methods after dividing the soil column into N cells. As a result, the following set of equations are obtained for \( j = 1, \ldots, N \):

\[
\frac{d(G_j C_w)}{dt} = M_j + S'_j(C_w)_{j-1} + S_j(C_w)_j + S''_j(C_w)_{j+1} = F_j \tag{A1}
\]

\[
M_j = \Delta z_j \tag{A1a}
\]

\[
S'_j = -A_j \left(1 - \alpha_j \right) + D_j \tag{A1b}
\]

\[
S_j = -A_j \left(1 + \alpha_j \right) + A_j \left(1 - \alpha_j \right) - D_j \tag{A1c}
\]

\[
S''_j = -A_j \left(1 + \alpha_j \right) + D_j \tag{A1d}
\]

\[
F_j = (G_j) \Delta z_j \tag{A1e}
\]

\[
A_{j-1/2} = (G_j)_{j-1/2} \tag{A1f}
\]

\[
A_{j+1/2} = -(G_j)_{j+1/2} \tag{A1g}
\]

\[
D_{j-1/2} = \frac{(G_j)_{j-1/2}}{\left((\Delta z)_j + (\Delta z)_{j-1}\right)^{1/2}} \tag{A1h}
\]

\[
D_{j+1/2} = \frac{(G_j)_{j+1/2}}{\left((\Delta z)_{j+1} + (\Delta z)_j\right)^{1/2}} \tag{A1i}
\]

where \( \Delta z_j \) is the thickness of the \( j \)th cell, the terms \( A_{j\pm1/2} \) represent the “advective strength” between the \( j \)th cell and its neighboring cells [L T\(^{-1}\)], the \( \alpha \) terms are the weighting factors used in the discretization of the advection term, and the terms \( D_{j\pm1/2} \) represent...
the “diffusive conductance” between the jth cell and its neighboring cells \(\text{[L}^{-1}\text{T}^{-1}\text{]}\) (Wheeler et al., 2007). Using the value \(\sigma_{1/2} = \sigma_{1+1/2} = 1/2\) yields the central differencing scheme used in this study.

A separate equation was developed to handle the soil surface boundary in a way similar to the “zero thickness” cell approach applied in Berg et al. (2007). The soil surface boundary equation is written in the same format as the spatially discretized transport equation (Eq. [A1]), and it is added to the equation set with the index \(j = 0\) referring to the soil surface boundary located just above Cell 1:

\[
\frac{d(G C_w)}{dt}\bigg|_0 - M_0 + S^0_0 (C_w)_0 + S^1_1 (C_w)_1 = F_0
\]

\[M_0 = \Delta q_0 = 0\]

\[S_0^0 = -(A_{1/2}1/2 - D_{1/2} - D_{\text{soil–atm}})\]

\[S_1^1 = -\left[\frac{A_{1/2}}{1 - \alpha_{1/2}} + D_{1/2}\right]\]

\[F_0 = (D_{\text{atm–soil}})C_A + F_{\text{atm–soil}} + F_0\]

where \(D_{\text{soil–atm}}\) is the diffusive mass transfer rate coefficient from the soil to the atmosphere (volatilization rate coefficient) \([\text{L}^{-1}\text{T}^{-1}]\), \(D_{\text{atm–soil}}\) is the diffusive mass transfer rate coefficient from the atmosphere to the soil \([\text{L}^{-1}\text{T}^{-1}]\), \(C_A\) is the contaminant concentration in the atmosphere \([\text{M}^{-1}\text{L}^{-2}\text{T}^{-1}]\), \(F_{\text{atm–soil}}\) is the atmospheric deposition rate onto the soil \([\text{M}^{-1}\text{L}^{-2}\text{T}^{-1}]\), and \(E_0\) is the source input rate \([\text{M}^{-1}\text{L}^{-2}\text{T}^{-1}]\).

The diffusive flux between the soil and the atmosphere can be expressed using a boundary layer model (Chu and Marino 2004) as

\[J_{\text{s,a}} = \frac{D_k^b C_A - K_{\text{aw}} C_w(0)}{d}\]

where \(J_{\text{s,a}}\) is the diffusive flux between the soil surface and the atmosphere \([\text{M}^{-1}\text{L}^{-2}\text{T}^{-1}]\), \(D_k^b\) is the diffusion coefficient in free air \([\text{L}^2\text{T}^{-1}]\), \(K_{\text{aw}}\) is the air–water partition coefficient \([\text{L}^{-1}\text{M}^{-3}\text{T}^{-1}]\), \(C_w(0)\) is the water-phase contaminant concentration at the soil surface \([\text{M}^{-1}\text{L}^{-2}\text{T}^{-1}]\), and \(d\) is the soil–boundary layer thickness \([\text{L}]\). The diffusive flux between the soil and the atmosphere are then determined by rewriting Eq. [A3] as

\[J_{\text{s,a}} = D_{\text{atm–soil}}C_A - D_{\text{soil–atm}}C_w(0)\]

\[D_{\text{atm–soil}} = \frac{D_k^b}{d}\]

\[D_{\text{soil–atm}} = \frac{D_k^b}{d} K_{\text{aw}}\]

References


