Estimating transport of chemicals from soil to ponding water

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Abstract

We simulate the accumulation of a chemical transported from soil to ponding water. We consider one-dimensional convective–diffusive solute transport in water and soil. The results are compared with those of models which simulate an instantaneous mixing in the surface water layer and the surface solute flux dependent on the difference in solute concentrations between soil and water. Numerical inversion of Laplace transforms is used to obtain the simulation results for all models. Results of this work show that the relative effect of diffusion on the accumulation of a solute in ponding water may be significant at infiltration rates that are not uncommon in agriculture practice. The results also imply that locations with low infiltration rates within fields may have a large effect on the overland accumulation of chemicals. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemicals can move from ponded soil to water standing on the soil surface. The chemicals may then be transported in runoff to drains, rivers, lakes or ponds, and may affect water quality. A quantitative description of chemical transport from soil to the surface water is needed.

Most models developed to date deal with runoff induced by a rainfall. The earliest works assumed instantaneous equating of concentrations between a thin mixing zone of soil and the surface water layer (Bruce et al., 1975; Donigian et al., 1977; Haith, 1980; Steenhuis and Walter, 1980). The thickness of the mixing zone was a lumped parameter that varied from 0.2 cm (Ahuja, 1982) to 2.1 cm (Snyder and Woolhiser, 1985). Ahuja (1982), Ahuja and Lehman (1983), and Snyder and Woolhiser (1985) presented experimental data that indicated that a more detailed description of chemical transport in soil and water was needed.

Ahuja (1982) suggested that a depth-dependent mixing in soil was a more feasible physical model. The corresponding mathematical model was developed by Ahuja and Lehman (1983). Parr et al. (1987) and Wallach et al. (1988; 1989) applied a diffusive transport model to predict the solute transport in soil in the absence of infiltration. Snyder and Woolhiser (1985) conjectured that using a convective–dispersive model of solute transport in soils would be most appropriate when infiltration occurred. This model was used by Wallach and Van Genuchten (1990) and Wallach and Shabtai (1992) to describe the downward solute movement in soil in the presence of surface water.
The transport of solutes from soil to surface water was initially simulated as a result of mixing surface water and soil. As the diffusive or convective-dispersive transport models were applied to the solute transport in soil, it was assumed that the flux of the solute to the surface water was proportional to the difference in concentration between the soil solution and the surface water (Parr et al., 1987; Wallach et al., 1988; Wallach and Van Genuchten, 1990). Instantaneous mixing was assumed to take place in the surface water layer, and vertical solute transport in surface water was not simulated.

Ignoring vertical transport of the chemical in surface water is obviously a viable approach for a thin water layer in rainfall-induced runoff. However, a relatively thick layer of water can remain for a significant time over soil containing chemicals. Flood irrigation and rice production give examples of such ponding water–soil interfaces. A chemical may have time to move from the soil to the ponding water and then to be transported with this water to surface drains or to waterways. In such cases, transport of the chemicals near a soil surface is controlled by the interplay of (a) diffusion from soil to the surface water and diffusion within the surface water and (b) convective-diffusive transport within the soil. When the infiltration is slow, there may exist a potential for the accumulation of the chemical in water prior to returning back into the soil with infiltration water or removal of the excess water from the soil surface.

Our objective was twofold: (a) to estimate the extent to which diffusive solute transport in a thick ponding water layer may cause an accumulation of a chemical in this layer, and (b) to analyze how models with instantaneous mixing in the surface water layer can approximate the chemical accumulation in the surface water caused by the diffusive chemical transport.

2. Model of convective-dispersive solute transport in soil and in ponding water

2.1. Governing equations

The flow domain is shown in Fig. 1. Solute transport is described explicitly both in soil and in ponding water. The one-dimensional convective-

\[
R \theta \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} \tag{1}
\]

is assumed to be valid both in soil and in water. In this equation, \(D\) is the dispersion coefficient, \(R\) is the retardation factor, \(q\) is the steady flow flux or the infiltration rate, and \(\theta\) is the volumetric water content. Coefficients \(R\), \(D\), and \(\theta\) are piecewise functions of the coordinate \(x\) directed downwards:

\[
R = \begin{cases} 
R_1 & x \geq 0 \\
R_2 = 1 & x < 0
\end{cases} \quad \theta = \begin{cases} 
\theta_1 & x \geq 0 \\
\theta_2 = 1 & x < 0
\end{cases}
\]

\[
D = \begin{cases} 
D_1 & x \geq 0 \\
D_2 = 1 & x < 0
\end{cases}
\tag{2}
\]

Here and below subscripts "1" and "2" denote values in soil and water respectively. The dispersion coefficient in the water, \(D_2\), is assumed to be equal to the molecular diffusion coefficient of the solute, \(D_m\). The dispersion coefficient in soil is
defined as:

\[ D_1 = \theta_1 \beta D_m + \lambda |q| \]  

where \( \beta \) is the tortuosity factor, and \( \lambda \) is the dispersivity. The retardation factor in soil is given by

\[ R_1 = 1 + \frac{\rho K_d}{\theta_1} \]  

where \( \rho \) is the soil bulk density, and \( K_d \) is the distribution coefficient for the partitioning of the solute between liquid and solid phases of the soil.

The following boundary conditions are imposed on the soil surface to account for the concentration continuity and the solute flux continuity on the surface:

\[ c(x = +0, t) = c(x = -0, t) \quad D_1 \frac{\partial c}{\partial x} \bigg|_{x = +0} = D_2 \frac{\partial c}{\partial x} \bigg|_{x = -0} \]  

Zero gradients are assumed at infinity:

\[ \frac{\partial c}{\partial x} \bigg|_{x = +\infty} = \frac{\partial c}{\partial x} \bigg|_{x = -\infty} = 0 \]  

and initial conditions simulate the incorporation of the chemical within the depth interval from 0 to \( L \):

\[ c(x, 0) = \begin{cases} c_0 = \text{const} & \text{for } x < L \\ 0 & \text{for } 0 \leq x \leq L \end{cases} \]  

2.2. Solution technique

We use the Laplace transformation and its numerical inversion to obtain a solution of the boundary problem given by Eqs. (1), (2), (5)–(7). The Laplace transformation taken in Eq. (1) with respect to \( t \) yields the ordinary differential equation:

\[ D_k c^\prime - q c^\prime - R_k \theta_k s c = -R_k \theta_k c_0 \]  

where \( c \) is the Laplace transform of \( c(x, t) \):

\[ \hat{c}(x, s) = \int_0^\infty c(x, t) \exp(-st) \, dt \]  

and subscript \( k \) is equal to 1 or 2 for \( x < 0 \) and \( x \geq 0 \), respectively.

The total overland mass of the solute

\[ M_2 = \int_0^\infty c(x, t) \, dx \]  

has a Laplace transform

\[ \hat{M}_2(s) = \frac{2D_2 c_0}{qs} \frac{z_1 - 1}{(z_2 + z_1)(z_1 + 1)} \times \left\{ 1 - \exp \left[ -\frac{qL}{2D_1}(1 + z_1) \right] \right\} \]  

where \( z_k, k = 1,2, \) are defined as

\[ z_k = \sqrt{1 + \frac{4sR_k \theta_k D_k}{q^2}} \quad k = 1, 2 \]  

2.3. Numerical inversion of the Laplace transforms

We used the subroutine DINLAP from the IMSL library (Microsoft IMSL Library) to invert the Laplace transforms. This subroutine has two user-supplied parameters: (a) the relative accuracy desired (RELLERR), and (b) the number of function evaluations allowed (KMAX). To select the parameters and to test the performance of this subroutine, we used the fact that the Laplace transform (11) could be inverted analytically when transport parameters are the same above and below the surface. When \( D_1 = D_2 = D, R_1 = R_2 = R, \) and \( \theta_1 = \theta_2 = \theta, \) Eq. (11) yields

\[ \hat{M}(s) = \frac{2Dc_0 \sqrt{s+a} - \sqrt{a} \sqrt{a} - 1}{qs \sqrt{s+a} + \sqrt{a} \sqrt{a} \left[ \frac{1 - \exp \left( -\frac{Pe}{2} \left( 1 + \sqrt{\frac{s+a}{a}} \right) \right)}{2} \right]} \times \left\{ 1 - \exp \left[ -\frac{Pe}{2} \left( 1 + \sqrt{\frac{s+a}{a}} \right) \right] \right\} \]  

Here and below \( a = q^2/(4R\theta D), \) and \( Pe = (qL)/D. \) Inversion of this transform yields:

\[ M(t) = \frac{2Dc_0}{q} \sqrt{at} \left[ \text{erfc}(\sqrt{at}) - \text{erfc} \left( \sqrt{at} + \frac{Pe}{\sqrt{at}} \right) \right] \]  

We selected a desired relative accuracy RELERR equal to \( 10^{-6}, \) and found that this accuracy can be reached for the transform (13) with KMAX equal to 100 for the values of Pe in the range between 0.1 and 200. The same value for KMAX was used in numerical inversion of the transform (11). The subroutine DINLAP produces an error message to indicate when the algorithm is not able to achieve the accuracy requested within KMAX function evaluations. The selection of KMAX = 100 was determined to be...
satisfactory since all the inversions of the Laplace transform (11) have been performed without this error message occurring.

3. Models of convective–dispersive solute transport in soil with kinetic release of the solute to the ponding water

Two models are described in this section. Both models account for solute transport from soil to the ponding water assuming the flux of the solute to the surface water is proportional to the difference in concentration between the soil solution and the surface water. Instantaneous mixing is assumed in the ponding water. The first model uses an infinite depth of the mixing zone in the surface water, whereas the second employs a finite depth. Since the flux is proportional to the concentration difference, we call these models kinetic for the sake of brevity.

3.1. Governing equations

The first model we consider is the one of Wallach and Van Genuchten (1990). The flow domain is shown in Fig. 1. The one-dimensional convective–dispersion Eq. (1) with coefficients from Eqs. (3) and (4) is used to describe the solute transport in soil. The boundary condition on the soil surface reflects the assumption that solute flux across the soil surface interface is proportional to the difference in concentrations between the soil solution and surface water:

\[
\frac{-D}{x} \frac{\partial c}{\partial x} + qc \bigg|_{x=0} = -\theta k[c(0, t) - c_r]
\]  

(14)

Here \(c_r\) is the solute concentration in the ponding water, and \(k\) is the mass transfer coefficient. Wallach and Van Genuchten (1990) have assumed that \(c_r = 0\). A semi-infinite soil profile is considered. Zero concentration gradient at infinity and constant initial concentration in the soil profile are assumed.

In this model, the mass of the solute in the surface water has the Laplace transform:

\[
\hat{M}(s) = \frac{k\theta c_0}{s^2} \frac{\sqrt{1 + \frac{s}{a} - 1}}{\sqrt{1 + \frac{s}{a} + 1 + \frac{2k\theta}{q} s + N}}
\]

(15)

The assumption \(c_r = 0\) can be interpreted as the result of assuming instantaneous mixing in the infinitely thick layer of ponding water.

We construct the second model assuming instantaneous mixing in a layer of ponding water having finite thickness \(d\). The solute transport in soil will be simulated using Eqs. (1), (3) and (4) as above. The boundary condition on the surface will be given by Eq. (14) where \(c_r\) will not be a constant but will depend on the total accumulated overland mass of the solute in the ponding water:

\[
c_r = \frac{M(t)}{d}
\]

(16)

The Laplace transform of the overland solute mass in this model is

\[
\hat{M}(s) = \frac{k\theta c_0}{s(s+N)} \frac{\sqrt{1 + \frac{s}{a} - 1}}{\sqrt{1 + \frac{s}{a} + 1 + \frac{2k\theta}{q} s + N}}
\]

(17)

where \(N = k\theta/d\).

The last fraction in the denominator approaches unity as \(N\) approaches zero, i.e. \(d\) approaches infinity. Thus Eq. (17) reduces to Eq. (15) as the mixing depth increases infinitely.

Laplace transforms (15) and (17) were inverted numerically using subroutine DINLAP from the IMSL library (Microsoft IMSL Library). Although the Laplace transform (17) can be inverted analytically (details available upon request), we preferred the numerical inversion to the use of the analytical solution because the latter required the use of complex numbers, and this annulled the advantages of the use of the analytical solution. We found that subroutine DINLAP provided a desirable precision of \(10^{-6}\) and the value of the parameter \(KMAX = 100\) was sufficient.

Since one of the objectives was to analyze how the models with instantaneous mixing in the surface water layer can approximate the accumulation of the chemical in the surface water caused by the diffusive chemical transport, the function \(M(t)\) found from Eq. 17 was fit to the function \(M_2(t)\) found from Eq. (10). Both dependencies were tabulated in points \(t = t_i, i = 1,\ldots,80\), and \(t_i = 10^{k_{11}}\). The values of parameters \(d\) and \(k\) were searched to minimize the mean square
relative difference

\[ \Phi = \sqrt{\frac{1}{80} \sum_{i=1}^{80} \left( 1 - \frac{M_{\text{kin}}(t_i)}{M_{\text{cdm}}(t_i)} \right)^2} \]

between the two functions in these points. We used a version of the Marquardt-Levenberg algorithm published by Van Genuchten (1981) since this version proved to be very efficient in multiparametric nonlinear optimization.

4. Numerical results

4.1. Dependencies of the overland solute mass on time

Graphs in Fig. 2 illustrate the effect of soil parameters \( \lambda \) (cm) and \( R \) on dependencies of the total overland solute mass on dimensionless time \( \tau = q^2 t / D_m \). An infinite incorporation depth has been assumed for these simulations. The vertical axis shows the ratio of the total overland flow to the initial concentration. This ratio represents the thickness of an imaginary layer that, with the solute concentration \( c_0 \) in it, would contain the same mass as that of the actual ponding water layer.

An increase in either the dispersivity \( \lambda \) or the retardation factor \( R \) results in the growth of the maximum value of the solute overland mass. As \( \lambda \) or \( R \) increases, we find an increase in time when the solute overland mass reaches a maximum.

Fig. 3 shows the effects of the infiltration rate \( q \) and the dispersivity \( \lambda \) on the dependencies of the solute overland mass \( M \) on time with an infinite incorporation depth. The diffusion-driven accumulation of the solute in the overland water is a two-stage process. The overland solute mass increases relatively rapidly during the first stage and decreases relatively slowly during the second stage. An increase in the infiltration rate shortens the first stage and also decreases the maximum overland solute mass. An increase in the dispersivity value prolongs the first stage of the overland mass increase and has little effect on the relative rate of the overland mass decrease after the maximum has been reached.

The effect of the incorporation depth on the overland accumulation of the solute is shown in Fig. 4. The solute accumulation in the overland water has the same two-stage accumulation pattern for the finite incorporation depth as for the infinite one. The larger the incorporation depth, \( L \), the smaller the maximum fraction of the solute mass to appear in the overland water. The increase in the incorporation depth leads to the increase in time needed to reach the maximum of the accumulated overland solute mass. The increase in the retardation factor value, \( R \), slightly decreases the maximum of the overland solute mass and delays the reverse movement of the chemical back to the soil.

\[ R_1 = 1 \quad \text{or} \quad R_1 = 5 \]

Fig. 2. Dependencies of the total overland solute mass \( M \) on dimensionless time \( \tau = q^2 t / D_m \) as affected by the soil dispersivity \( \lambda \) and the retardation factor \( R_1 \). Calculations have been made with \( q = 10^{-5} \text{cm s}^{-1} \), \( D_m = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \), the dispersion coefficient in soil \( D_1 = \theta \beta D_m + \lambda q, \beta = 0.7 \).
Fig. 3. Dependencies of the total overland solute mass $M$ on dimensionless time $\tau = q^2t/D_m$ as affected by the soil dispersivity $\lambda$ and the infiltration rate $q$. Calculations made with the retardation factor $R_1 = 1$, $D_m$ and $D_1$ are the same as in Fig. 2.

Fig. 5 shows the effects of the infiltration rate $q$ and the incorporation depth on the dependencies of the solute overland mass $M$ on time. The smaller the incorporation depth, the faster the first stage of the solute overland accumulation. Both the accumulation of the solute in the overland water and the release of the solute back to the soil is very sensitive to the infiltration rates in the range between $10^{-6}$ and $10^{-5}$ cm s$^{-1}$. About 50% and 5% of the total solute mass are in the overland water at the end of the first day of infiltration with rates $10^{-6}$ and $10^{-5}$ cm s$^{-1}$, respectively.

4.2. Kinetic approximations for the solute flux to the overland water

For the model of Wallach and Van Genuchten (1990), dependencies of the overland mass on time are shown in Fig. 6. Graphs of $M(t)$ are $S$-shaped. There is an asymptotic value $M_\infty$ that is approached as time grows. It can be shown that this asymptotic value is

$$M_\infty = \frac{R\theta_2 Dc_0k}{q(k\theta + q)}$$

Fig. 4. Fraction $f$ of the total solute mass transported to the overland water: effect of the incorporation depth $L$ and the retardation factor $R_1$. In the fraction $f = M/(c_0LR_1)$, $M$ is the total overland mass (g cm$^{-2}$), $c_0$ is the initial solute concentration (g cm$^{-2}$). Calculations have been made with the dispersivity $\lambda = 1$, the infiltration rate $q = 10^{-5}$ cm s$^{-1}$, values of $D_m$ and $D_1$ are the same as in Fig. 2.
For this model, the shape of the $M$-on-$t$ curves differs qualitatively from that of the model with convective–dispersive transport in water and soil. Some correspondence between shapes can be found only at early stages of the process for times up to $10^3$ s. The assumption of the infinitely thick mixing layer is not a good approximation when the ponding water does not move along the soil surface.

The kinetic model with finite mixing depth could provide dependencies of $M$ on $t$, $M_{\text{mix}}(t)$, that are more like those from the convective–dispersive model $M_{\text{cdm}}(t)$ described in Section 2.2. Both models produced $M$-on-$t$ dependencies that have a maximum and approach zero as time grows. The increase and the decrease in $M_{\text{kin}}(t)$ values with time were steeper than that in $M_{\text{cdm}}(t)$. The maximum of $M_{\text{kin}}(t)$ was higher than that in $M_{\text{cdm}}(t)$. The larger the infiltration rate, the closer the fitted function $M_{\text{kin}}(t)$ to $M_{\text{cdm}}(t)$. Mean square relative differences between $M_{\text{kin}}(t)$ and $M_{\text{cdm}}(t)$ in this example were $0.56 \times 10^{-5}$, $0.081 \times 10^{-5}$, $0.014 \times 10^{-5}$, and $2.1 \times 10^{-5}$ for $q = 1 \times 10^{-6}$, $3.16 \times 10^{-6}$, $1 \times 10^{-5}$, and $3.16 \times 10^{-5}$ cm s$^{-1}$ respectively, when we carried out calculations with the dispersivity $\lambda = 1$, $D_m = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$, the dispersion coefficient in soil $D_1 = \frac{1}{2} D_m + \lambda q$, $\zeta = 0.35$, and the retardation factor $R_1 = 1$.

We tabulated the dependence of the mean square relative difference between $M_{\text{kin}}(t)$ and $M_{\text{cdm}}(t)$ on values of parameters $d$ and $k$. The largest errors arose when either $k$ or $d$ were very small. There existed a vast region of parameter values in which the error was very small and did not change significantly as the parameter values varied.

The formal fitting of $M_{\text{kin}}(t)$ to $M_{\text{cdm}}(t)$ resulted in dependencies of the parameter estimates on the infiltration rate shown in Fig. 7. As the infiltration rate increased, the estimate of $d$ first decreases rapidly and then remains almost constant over a wide range of infiltration rates. The estimate of $k$ grows exponentially with the infiltration rate. An increase in the retardation coefficient of the solute in the soil...
markedly decreased values of $k$, and affected values of $d$ to a minor extent.

5. Discussion

The liquid–liquid diffusion of the dissolved chemicals from soil water to overland water is recognized as a primary mechanism of the transport of pollutants to surface water (Bailey et al., 1974; Ingram and Woolhiser, 1980). Results of this work show that the relative effect of diffusion on the accumulation of a solute in ponding water may be significant at infiltration rates that are not uncommon in agriculture practice (Hubbard et al., 1989). The results also imply that locations with low infiltration rates within fields may have a large effect on the overland accumulation of chemicals. These locations usually dominate the area, and lognormally distributed hydraulic conductivity is often found. Results of this work show that factors that slow down the solute transport in soils, i.e. adsorption and dispersion, enhance the accumulation of chemicals in the overland water and delay the return of chemicals back to the soil as the infiltration progresses.

The results of this study have many features in common with the results of experiments on the chemical accumulation in rain-induced runoff. A fast accumulation of the chemical in the surface water followed by a slow decrease has been observed, for example, by Ahuja et al. (1981) and Snyder and Woolhiser (1985). The effect of the incorporation depth on chemical accumulation in the runoff (Feagley et al., 1992) is similar to the effect shown in Fig. 5. The decrease of the solute overland mass with an increasing infiltration rate (Figs. 3, and 5) is analogous to that observed in experiments of Snyder and Woolhiser (1985). We conjecture that these parallels imply a potential applicability of the model of this study in rainfall-induced runoff studies. A development of the model may be needed to replace the infinite overland water layer with the finite layer of variable depth.

The kinetic model with the finite mixing depth seems to have a redundancy that makes its parameters correlated when the mass accumulation predicted by this model is fitted to that predicted by the convective–dispersive model. However, this kinetic model can be of use if the mixing occurs in reality, for example, due to heat-induced convection or gas production in the soil. The kinetic model with the infinite mixing depth can describe the solute transport from soil to the fresh overland water only during very early stages. This appears to be sufficient when the thin layer of the surface water is continuously replenished with fresh water, and the contaminated water is removed as in the experiments of Ahuja (1982).

The convective–dispersive model of this paper may need development to account for processes affecting the solute in water, such as degradation of a chemical or its adsorption on thin particles. Therefore, this needs to be checked with experimentally obtained values, and we plan to do this in the near future.
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