A Physically Based Model for Predicting Solute Transfer From Soil Solution to Rainfall-Induced Runoff Water

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A model was developed to predict the field outlet concentration hydrograph for chemicals released into overland runoff induced by continuous rainfall on a sloping soil. The model accounts for convective-dispersive solute transport in the soil and also considers rate-limited mass transfer through a laminar boundary layer at the soil surface/runoff water interface. Solute transfers are assumed to be subject to linear equilibrium sorption onto the solid phase of the soil. Concentration hydrographs for rainfall-induced runoff were derived by treating the runoff zone as a well-stirred reactor characterized by an appropriate residence time distribution. The model was used to predict experimental data obtained by Ahuja and Lehman (1983) for runoff from soil boxes with permeable basins. Good agreement was obtained between predicted and measured outflow concentrations for relatively low infiltration rates, provided relatively large dispersion coefficients were used in the calculations. Solute concentrations in the soil were also well predicted. Results for relatively high infiltration rates were less accurate, perhaps in part because of an incorrect assumption in the model that the infiltration rate remained constant in time and space during the runoff experiment.

INTRODUCTION

Surface-applied or soil-incorporated pesticides, nutrients and other agricultural chemicals are often transferred from soil to surface runoff water during periods of heavy rainfall or surface irrigation. This transfer into runoff water decreases the efficiency of the applied chemicals and also poses a potential threat to the quality of the environment. Once released to runoff water, chemicals may reach nearby surface water bodies and thus lead to their exposure to aquatic organisms. Dissolved chemicals in ponds and lakes may indirectly also reach groundwater, often faster than if they were carried by infiltrating water through the vadose zone. Models describing the release of chemicals from soil to runoff water are needed as a predictive tool in the management of agricultural soils, such as for establishing optimum nutrient or pesticide applications, for irrigation scheduling purposes, and for the design of improved soil tillage systems.

Chemical runoff from soil is affected by a large number of processes [Bolger et al., 1974; Ahuja, 1986]. Modeling these processes, and their interactions, requires the solution of relatively complicated coupled linear and nonlinear partial differential equations subject to time-dependent boundary conditions. To reduce the mathematical complexity, many investigators in the past have considered the entire field as consisting of only one unit in which various transport mechanisms are conveniently lumped together. The approach generally leads to single mixing-cell type models based on instantaneous equilibration between soil solution and runoff water over the entire field (e.g., see Ahuja [1986] for a review). Most of these models assume that a thin soil surface horizon of fixed thickness participates in the mixing process and that concentrations in the runoff water are the same as, or a given fraction of, those in the soil solution.

Field runoff concentrations predicted with these models typically decrease exponentially with time, as has been shown by Ahuja [1986] and Wallach et al. [1986a], among others. Unfortunately, limited field tests have revealed the inadequacy of these models in predicting soil and runoff concentrations, especially for individual runoff events [Ahuja, 1986]. Nearly all models thus far have failed to predict outflow concentrations from laboratory experiments in which most of the parameters could be measured or carefully controlled [Ahuja, 1982; Ahuja and Lehman, 1983]. Also, chemicals in the soil are usually not distributed uniformly with depth, as is characteristic of mixing-cell type models [Ahuja and Lehman, 1983; Snyder and Woodhead, 1985]. These results indicate that lumped parameter models cannot accurately predict chemical runoff hydrographs and that more sophisticated models are needed to better quantify relevant solute transport processes.

Any realistic, physically based approach toward modeling the release of chemicals from soil to overland flow must include most relevant processes, including those that are not immediately obvious. Wallach et al. [1986a] attempted to predict the chemical runoff hydrograph from basic soil properties and the type of runoff regime involved. Overland flow was described by means of a resident time distribution characterizing runoff induced by spatially uniform rainfall or by excess surface irrigation entering a field from the side. The analysis was carried out using the popular assumption that chemicals in the runoff water equilibrate instantaneously with those in the soil solution at the soil surface. Wallach et al. [1986b] modified this approach by coupling solute diffusion in the bulk soil with a rate-limited chemical transfer process across a laminar boundary layer at the soil surface/runoff water interface. Solute exchange through this boundary layer was modeled by means of a first-order rate equation involving the mass transfer coefficient k. By using film model theory the mass transfer coefficient was found to be proportional to: the diffusion coefficient and inversely proportional to the thickness of the laminar boundary layer at the soil surface. The value of k was also shown to increase with increasing soil
surface roughness, runoff hydraulic gradient, and hydraulic radius [Walling et al., 1989].

While the model of Wallach et al. [1988] considers liquid diffusion and equilibrium sorption/exchange with the solid phase, convective (advection) mass transport in the soil due to infiltrating water was assumed to be negligible. Good agreement was obtained when the model was used to predict measured runoff water and soil concentration data observed by Abajis and Lehman [1983] for soil boxes with impermeable bottoms. However, a major limitation of the model of Wallach et al. [1988] was its neglect of convective transport with infiltrating water. In this paper we develop a more comprehensive model that also considers the effects of infiltration on the runoff concentration hydrograph.

THEORY

Governing Equations

The equation of continuity for a single chemical species in soil is

$$\frac{\partial c}{\partial t} + \rho \frac{\partial J}{\partial x} = 0$$  \hspace{1cm} (1)

where $c$ and $s$ are the solute concentrations associated with the liquid and solid phases of the soil; respectively, $\theta$ is the volumetric water content, $\rho$ is the soil bulk density, $z$ is distance, $t$ is time, and $J$ is the solute mass flux density given by

$$J = qc - \theta D \frac{\partial c}{\partial z}$$  \hspace{1cm} (2)

in which $q$ is the soil water flux density, and $D$ is the dispersion coefficient (assumed to be independent of the concentration $c$). We assume that diffusion and hydrodynamic dispersion both contribute to $D$ as follows:

$$D = D_0 \alpha + c \beta$$  \hspace{1cm} (3)

where $D_0$ is the ionic or molecular diffusion coefficient in pure water, $\alpha$ is a tortuosity factor, $\beta$ is the dispersivity, and $c$ is the average pore water velocity, approximated by the relation $\alpha \beta$.

The tortuosity factor $\alpha$ in (3) accounts for a tortuous flow path of the solute during diffusion in soils. Its value is often estimated using the Millington and Queck [1961] tortuosity model as $\alpha = \theta^{0.5}/n$, where $n$ is the soil porosity. The dispersivity $\beta$ in (3) typically ranges from about 0.5 cm or less for laboratory-scale displacement experiments involving disturbed soils, to about 10 cm or more for field-scale experiments [Nielson et al., 1986]. The dependency of $D$ on $c$ has usually been measured for cases where the convective transport direction coincides with the diffusion direction. Convective mass transport in our study is directed downward, while diffusive transport occurs upward toward the soil surface. The consequence of having opposite directions for diffusion and mechanical dispersion will be discussed later.

Partitioning of the solute between the liquid and solid phases of the soil is accomplished by means of a linear isotherm of the form

$$s = K_c c$$  \hspace{1cm} (4)

where $K_c$ is the distribution coefficient. Substituting (2) and (4) into (1) gives the one-dimensional convection-dispersion solute transport equation

$$\frac{\partial c}{\partial t} + \frac{\partial (qc)}{\partial z} = \frac{\partial}{\partial z} \left( \frac{\partial c}{\partial z} \right)$$

in which the retardation factor $R$ is given by

$$R = 1 + \frac{K_c}{\beta}$$  \hspace{1cm} (5)

The following third-type boundary condition is imposed at the soil surface to account for the convective and dispersive modes of transfer between soil and runoff water:

$$J_0(t), z = 0 = -D \frac{\partial c}{\partial z}(z = 0) = -\theta D \frac{\partial c}{\partial z}(z = 0)$$  \hspace{1cm} (6)

where $k$ is a mass transfer coefficient that relates the solute flux across the soil surface interface to the difference in concentration between the soil solution ($c$) and the runoff water ($c_r$). Using film model theory, an expression for $k$ was derived by Wallach et al. [1988] for laminar surface runoff.

Although controlled mainly by the diffusion coefficient, the mass transfer coefficient is also affected by such flow characteristics as soil surface lateral slope, surface roughness, runoff water depth, and rainfall intensity and duration. Experimental measurements with films [Ivagon and Woolhiser, 1980; Abajis and Lehman, 1983] showed that concentrations in the surface runoff are much lower than those in the near-surface zone of the porous medium. Therefore (7) may be simplified by assuming that the runoff concentration $c_r$ is small as compared to the soil solution concentration $c$. This assumption may cause some overestimation in runoff water concentrations at early stages of the runoff process, especially for relatively long fields with small slopes (i.e., situations with large runoff residence times) and hence may need to be examined more closely in the future. Assuming that $c_r$ in (7) can be neglected leads to

$$\frac{\partial c}{\partial t} + (v + k_c) \frac{\partial c}{\partial z} = 0$$

for $k < \infty$  \hspace{1cm} (8)

Equations (7) and (8a) assume finite values for $k$. The limiting case when $k \rightarrow \infty$ characterizes instantaneous equilibration between soil and surface runoff water (no film water resistance). Dividing (8a) by $k$ and then letting $k$ go to infinity shows that the boundary condition for no film resistance reduces to

$$c(0, t) = 0$$

for $k \rightarrow \infty$  \hspace{1cm} (9)

We emphasize that the assumption of zero $c_r$ in (7) is used here only for estimating the solute flux $J_0$ from soil to surface runoff water and indirectly later for calculating the field runoff concentration hydrograph based on $J_0(t)$. We shall show below that the assumption, both for finite and infinite $k$, does not imply that the runoff concentration is actually zero, nor that a zero runoff concentration will be calculated with the final model.

Equation (3) will be solved for a semi-infinite soil profile characterized by the condition

$$\frac{\partial c}{\partial z} = 0$$

and a constant initial concentration $C_0$ in the soil profile:
\[ c(z, t) = C_0 \]  
\[ c(z, t) = C_0 \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{Rz - vt}{2(DR)^{1/2}} \right) \right) \]  
\[ c(z, t) = C_0 \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{Rz}{2(DR)^{1/2}} \right) \right) \]  
\[ c(z, t) = C_0 \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{Rz + vt}{2(DR)^{1/2}} \right) \right) \]  
\[ c(z, t) = C_0 \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{Rz + vt}{2(DR)^{1/2}} \right) \right) \]  
\[ c(z, t) = C_0 \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{Rz + vt}{2(DR)^{1/2}} \right) \right) \]  

**Analytical Solution**

The analytical solution of (5) subject to conditions (8), (9), and (10) can be easily derived using standard Laplace transform techniques (e.g., using Appendix A of van Genuchten and Alves [1982]). We obtained the following result:

**Concentration profiles based on (11) for various values of t are shown in Figure 1. The curves were calculated using experimental data obtained by Abujia and Lehman [1983] for rainfall-induced runoff from water-saturated soil boxes filled with a Ruston fine sandy loam. The soil was first equilibrated with a bromide solution and subsequently subjected to spatially uniform simulated rainfall. Relevant parameters for the experiment are listed in Table 1. Several of the parameters not available from the original study of Abujia and Lehman [1983] were estimated independently, as discussed by Wallach et al. [1988]). The rainfall intensity \( P \) was 6.8 cm/hr, and the infiltration rate \( I \) was 0.28 cm/hr. Note that the assumption of steady state water flow implies that at all times and depths the fluid flux density \( q \) in the soil profile is equal to the infiltration rate. Abujia and Lehman [1983], in their experiments, observed a significant effect of the infiltration rate \( I \) on the measured concentration hydrographs at the runoff outlet. Concentration distributions near the soil surface should be similarly affected by the magnitude of \( I \). Figure 2 illustrates this effect on calculated concentration profiles after 50 min of continuous rainfall. The dispersion coefficient used in this case did not include the effects of mechanical dispersion and hence only reflected diffusion in soil water. As expected, the figure shows a significant downward translation of the relatively steep concentration front with increasing infiltration rate. The relatively low or zero concentration near the soil surface suggest little or no transfer of chemicals from soil to runoff water for infiltration rates greater than about 0.3 cm/hr. This**

**Table 1. Data for the Ruston Fine Sandy Loam Runoff Experiment of Abujia and Lehman [1983]**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainfall intensity</td>
<td>( P )</td>
<td>6.8</td>
<td>cm/hr</td>
</tr>
<tr>
<td>Runoff surface length</td>
<td>( L )</td>
<td>100</td>
<td>cm</td>
</tr>
<tr>
<td>Surface slope</td>
<td>( s )</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Runoff water height</td>
<td>( H )</td>
<td>0.075</td>
<td>cm</td>
</tr>
<tr>
<td>Volumetric water content</td>
<td>( \theta )</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Initial soil solution conc.</td>
<td>( C_0 )</td>
<td>4000</td>
<td>ppm</td>
</tr>
<tr>
<td>Distribution coefficient</td>
<td>( K )</td>
<td>0.0</td>
<td>cm^3/hr</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>( D )</td>
<td>0.004</td>
<td>cm^3/hr</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>( x )</td>
<td>0.85</td>
<td>cm/hr</td>
</tr>
</tbody>
</table>
observation is in marked contrast to the measured results of
Abuja and Lehnman [1981] for infiltration rates which are
very similar to those used for Figure 2. Thus we tentatively
conclude that mechanical dispersion, in addition to diffusion,
must be a significant factor contributing to the transport of
solute at or near the soil surface and their concomitant
release to surface runoff water.

Chemical Hydrograph for Rainfall-Induced Runoff

Two transport processes are responsible for the appear-
ance of chemicals in runoff water at the field effluent. One
process is the diffusive-dispersive transport of solutes to-
ward the soil surface as described by (5). Another process is
the lateral transport of these chemicals by surface runoff
water toward the downstream outlet of the field. If the fluid
flow dynamics of the surface runoff system (notably the
deterministic flow velocity distribution in time and space)
were known exactly, then one should be able to also predict
the behavior of the overland transport runoff subsystem. It
is unlikely that this type of information ever will be avail-
able. Fortunately, complete knowledge of the flow dynamics
is not conditional for formulating chemical surficial distri-
butions with time. Information on how long an individual solute
remains in the system, or equivalently on the distribution of
the residence times [Hinman and Bischoff, 1980] in the
runoff fluid, may be sufficient to quantify the overland runoff
process. If the response, $E(t)$, of the runoff system to an
instantaneously applied tracer pulse is known, then the
concentration hydrograph $c_r$ may be expressed by means of a
convolution of the impulse response and the solute transfer
rate from the soil solution to the runoff water, that is,

$$ c_r(t) = \left[ \frac{1}{Q} \int J_d(r') E(t - r') dr' \right] $$ (12)

where $J_d(t) = -D J_x(t)$ is the solute mass flux from soil to
runoff water, and $Q$ is the runoff water flux. During steady
state flow, $Q$ is equal to the difference between the rainfall
rate $P$ and the infiltration rate $I$. When the rainfall and infiltration rates are constant in time and space, the residence time distribution $E(t)$ for runoff water can be taken as [Wallach et al., 1986a]

$$ E(t) = \exp \left( -\frac{t}{\tau} \right) $$ (13)

in which $\tau$ is the mean residence time of a runoff water
element in the field, approximated by the ratio of the average
surface water depth $H$ and the excess rainfall rate $P - I$. We
note that (13) also describes the solute residence time
distribution $E(t)$ of a well-mixed reactor, even though the
physical processes during runoff are completely different
than those of a well-mixed reactor [Wallach et al., 1986a].
Hence (13) does not imply that the field is a perfect mixture
since the residence time distribution is exponential. We also
note that $E(t)$ as used here is applicable only after a steady
runoff flow regime has been established. In actuality, the
water height on the soil surface will likely build up slowly
during the rainfall event and probably also will be greater at
the downstream side of the field. These complications are
neglected here as being only higher-order effects. We refer to

the paper by Wallach et al. [1986a] for a more detailed
discussion of (13).

Equation (12) assumes that initially no solutes are present
in the runoff water and that the solute flux $J_x$ from soil to
runoff water is not affected by the runoff water concentra-
tion. In a dynamic rainfall-runoff system the runoff water
flow generally builds up gradually over the surface, and a
steady runoff flow regime will be reached only after an initial
stage when chemicals are already exchanged between the
soil and the runoff water. Hence at the time when the runoff
flow becomes steady there is already an initial concentration
$c_{0r}$ in the runoff water. By using superposition, (12) becomes
den then

$$ c_r(t) = C_{0r} \exp \left( -\frac{t}{\tau} \right) + \left[ \frac{1}{Q} \int J_d(r') E(t - r') dr' \right] $$ (14)

The solute flux $J_x$ across the soil surface into the runoff
water is given by (7) (assuming, as explained above, that $c_r
in (3) can be set equal to zero):

$$ J_d(t) = \theta E^\infty \left[ k + \frac{v}{4\pi DR} \right] \exp \left[ -\frac{k + \frac{v}{4\pi DR}}{2DR} \right] $$ (11a)

$$ J_d(t) = \theta E^\infty \left[ k + \frac{v}{4\pi DR} \right] \exp \left[ -\frac{k + \frac{v}{4\pi DR}}{2DR} \right] $$ (11b)

For the limiting case of no film resistance ($k \rightarrow 0$), (11a)
reduces to

$$ J_d(t) = \theta E^\infty \left[ \frac{DR}{\tau} \right] \exp \left[ -\frac{\tau}{4DR} \right] $$ (11c)

Equation (16b) can also be derived by evaluating the second
term of (7) in conjunction with (11b). Because of the assump-
tion that the solute flux from soil to surface runoff is
independent of the runoff water concentration ($c_r$ in (7) was
set to zero), (16a) and (16b) are independent of the spatial
location in the field. Hence vertical concentration profiles in
the field are assumed to be the same everywhere.

Substituting (13) and (16) into (14), and integrating, yields
the concentration runoff hydrograph at the field's outlet
details of the derivation are given in the Appendix)

$$ c_r(t) = C_{0r} \exp \left( -\frac{t}{\tau} \right) + \frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] + \frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] $$

$$ -\frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] $$

$$ -\frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] $$

$$ -\frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] $$

$$ -\frac{\theta C_0}{2\pi \sqrt{\pi} \tau} \exp \left[ -\frac{v}{4\pi \tau} \right] $$
Fig. 3. Comparison of calculated bromide runoff concentration hydrographs for different values of the infiltration rate $I$ with experimental data of Ahuja and Lehman [1983] for Roston fine sandy loam ($I = 0.83$ cm/hr).

\[ \exp(-\theta r) \text{ erf} \left( \frac{at}{2(DR)^{1/2}} \right) \]

\[ \frac{\exp(-\theta r)}{(v + k) + DR} \text{ erf} \left( \frac{at}{2(DR)^{1/2}} \right) \]

(17a)

\[ \chi(t) = C_0 \exp \left(-\theta^* r \right) + \frac{\theta^*_0 v}{2D_0} \text{ erf} \left( \frac{at}{2(DR)^{1/2}} \right) \]

(17b)

where

\[ \theta = \sqrt{\frac{2D_0}{I} + \frac{1}{\sqrt{\pi}} \text{ erf}^{-1} \left( \frac{2(DR)^{1/2}}{\sqrt{2}} \right)} \]

MODEL APPLICATION

Concentration runoff hydrographs predicted with (17a), and concentration distributions versus soil depth predicted with (11a), will be compared with the measured data of Ahuja and Lehman [1983]. Runoff in that study was induced by applying spatially uniform rainfall to 10-cm deep water-saturated soil boxes which were initially equilibrated with a 4000 ppm bromide solution. Figure 3 shows a semilogarithmic plot comparing measured data with calculated concentration hydrographs for the Roston fine sandy loam experiment at infiltration rates $I$ of 0.0, 0.28, and 2.75 cm/hr. Figure 4 shows a similar plot comparing measured data with predicted soil solution concentrations versus soil depth after 60 min of rainfall. The diffusion coefficient for the zero-infiltration case ($I = 0$), as well as additional data for the experiment as estimated by Wallach et al. [1986], are listed in Table 1. The average water height $H$ and the mass transfer coefficient $k$ were calculated from channel flow hydraulic and other equations using procedures as explained by Wallach et al. [1988b]. The dispersion coefficients for cases with $I > 0$ were obtained by best fit between calculated and measured data, while the mass transfer coefficient was kept constant for all runs. Keeping $k$ constant is justified by the fact that this parameter depends primarily on the diffusion coefficient of the chemical in water rather than on the dispersivity which depends mainly on the pore water velocity and other soil properties. We also ignored the dependence of $k$ on surface runoff water depth because of a lack of information in the paper by Ahuja and Lehman on such parameters as soil surface roughness and surface water depth along the flume for each run. For infiltration rates $I$ of 0.28 and 2.75 cm/hr the dispersion coefficients were estimated to be 0.09 and 1.08 cm$^2$/hr, which translates to dispersivity values ($\alpha$ in (1)) of 0.11 and 0.20 cm, respectively. A good agreement is obtained between predicted and measured concentrations in both surface runoff water and soil solution for the zero and the lower infiltration rate. Observed runoff concentration could not be well predicted at large times for the higher infiltration rate. However, notice that the concentrations in this case are very low and as such do not significantly contribute to the pollution of surface runoff water. A relatively poor description was also obtained for the concentration distribution in the soil after 60 min of rainfall (Figure 4).

Figures 5 and 6 show semilogarithmic plots of calculated and measured concentration hydrographs for the Roston loam and Parsons clay experiments, while Figures 7 and 8 show plots of the soil solution concentration versus soil depth after 60 minutes of rainfall for the same two soils. The measured data were taken from the experiments of Ahuja and Lehman [1983]. The dispersion coefficients were again estimated; their values appear in Table 2. As for the Roston fine sandy loam experiments, the mass transfer coefficient $k$ was kept constant for all runs; values were only corrected for different porosities of the soils (Table 2). The calculated curves for the Roston fine sandy loam agree fairly well with the observed data in the runoff water as well as with those in the soil solution for the zero and lower infiltration rates. Less accurate predictions were again obtained at relatively long times for the highest infiltration rate. The calculated disper-
Fig. 5. Comparison of calculated bromide runoff concentration hydrographs for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Ruston loam (k = 0.9 cm/hr).

Fig. 6. Comparison of calculated bromide runoff concentration hydrographs for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Parsons clay (k = 0.79 cm/hr).

Fig. 7. Comparison of calculated bromide concentrations versus depth for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Ruston loam (k = 0.9 cm/hr).

Fig. 8. Comparison of calculated bromide concentrations versus depth for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Parsons clay (k = 0.79 cm/hr).

Conclusions

We conclude that the physically based model proposed in this study describes the chemical transfer from soil solution to runoff water reasonably well, except for large times at relatively high infiltration rates. The model correctly describes most experimental runoff concentration hydrographs obtained by Ahuja and Lehman [1983] using model parameters which were either measured directly, calculated independently using standard hydrodynamic theory [Wallach et al., 1986], or estimated in order to fit measured to calculated data. The dispersivity values obtained from the estimated dispersion coefficients are within the range of values that were measured elsewhere for similar soils. The model appears to predict the measured data better than the lumped models introduced previously by Ahuja and Lehman [1983]. Results of this study indicate that direct mixing between runoff water and the soil solution is responsible for chemical transfer only at very early stages of the runoff process when surface water begins to build up on top of the soil surface. Later, when a given runoff water height has been established with an initial concentration $C_0$, convective mass transfer by
TABLE 2. Data for the Three Soil Runoff Experiments of Abrah and Lehman [1983]

<table>
<thead>
<tr>
<th>Runoff</th>
<th>Fine Sandey</th>
<th>Runoff</th>
<th>Loom</th>
<th>Parson's Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta )</td>
<td>0.55</td>
<td>0.55</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>L, cm/hr</td>
<td>0.86</td>
<td>0.86</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>D, cm/hr</td>
<td>0.056</td>
<td>0.056</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>C, cm/hr</td>
<td>0.056</td>
<td>0.056</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>C, ppm</td>
<td>4000</td>
<td>4000</td>
<td>4000</td>
<td></td>
</tr>
<tr>
<td>s, cm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>s, cm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\[ \hat{E}(s) = \frac{1}{1 + \tau s} \]  
(A4)

Substituting (A3) and (A4) in (A1) gives

\[ \frac{\tau}{\theta} = \frac{1}{\frac{1}{\tau} + \frac{1}{\theta}} \]  
(A5)

which may be expanded to yield

\[ \hat{E}(s) = \frac{\theta}{\tau} \]  
(A6)

The inverse Laplace transform of (A6) is

\[ c_i(t) = \frac{\theta}{\tau} \left[ 1 - \exp\left(-\frac{\theta}{\tau}t\right) \right] \]  
(A7)

where \( L^{-1}[f(s)] \) indicates inverse Laplace transforms, and where

\[ f(s) = \frac{2(\nu + k)}{\nu + 2k + (\nu^2 + 4\nu \sigma \gamma)^{1/2}} \]  
(A8)

\[ g(s) = \frac{2(\nu + k)}{\nu + 2k + (\nu^2 + 4\nu \sigma \gamma)^{1/2}} \]  
(A9)

The inverse Laplace transform of (A9) is

\[ L^{-1}[g(s)] = \frac{\nu}{2k} \exp\left(-\frac{\theta}{\tau}t\right) + \frac{1}{2(\nu + k)} \left[ 2(\nu + k) \exp\left(-\frac{\theta}{\tau}t\right) - \nu \exp\left(-\frac{\theta}{\tau}t\right) \right] \]  
(A10)

and of (A9)

\[ L^{-1}[\hat{E}(s)] = \frac{\nu}{2k} \exp\left(-\frac{\theta}{\tau}t\right) + \frac{1}{2(\nu + k)} \left[ 2(\nu + k) \exp\left(-\frac{\theta}{\tau}t\right) - \nu \exp\left(-\frac{\theta}{\tau}t\right) \right] \]  
(A11)

where

\[ \phi = \left(\frac{4\nu \sigma \gamma}{\nu^2 \tau^2}\right)^{1/2} \]  
(A12)

overland water flow becomes the main transport mechanism. The infiltration rate then controls the transfer rate of chemicals near the soil surface by mechanical dispersion, a process which is strongly influenced by the pore water velocity.

The analytical model proposed in this study assumes that the infiltration rate and the soil water content remain constant during the infiltration-runoff event. These simplifying assumptions undoubtedly are not appropriate for most field situations where transient changes in the water content and the soil water flux are the norm. Hence we view the present model as a useful first step toward the development of a more comprehensive numerical model which must also consider the time-dependent nature of the runoff flow process.

**Appendix**

Using Laplace transforms, the convolution integral of (12) can be written in the following form

\[ c_i(t) = \frac{\theta}{\tau} \int_0^t \exp(-s\tau) c_i(t) dt \]  
(A1)

where the overbars denote Laplace transforms \( L \) with respect to \( t \).

\[ c_i(s) = L[c_i(t)] = \int_0^\infty \exp(-s\tau) c_i(t) dt \]  
(A2)

and where \( s \) is the Laplace transform variable, \( \hat{E}(s) \) is obtained from (16) as

\[ \hat{E}(s) = \theta \frac{1}{s} \left[ \frac{2(\nu + k)}{\nu + 2k + (\nu^2 + 4\nu \sigma \gamma)^{1/2}} \right] \]  
(A3)

while \( E(s) \) follows from (14):
The concentration hydrograph, without adjustment for $C_{lp}$, is hence

\[
c(t) = \frac{6C_0}{2Q_t} \left[ \frac{(v + 24)DR}{(v + k)k + DR} \right] - \frac{\exp \left[ \frac{-(v + k)k}{2DR} \right]}{2(DR)^{1/2}} - \frac{\exp \left[ \frac{(v + k)k - 24DR}{(v + k)k + DR} \right]}{2(DR)^{1/2}} \exp \left[ \frac{-v}{(v + k)k + DR} \right]
\]  

(A13)

Note that $\omega$, and hence also $erfc(\omega)$, become complex variances when $v^2 < 4DR$. We used a subroutine listed by van Genuchten [1985] to evaluate the complex complementary error function.

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