

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. Solutes 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-mixed 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 bottoms. 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 predicted well. 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 experiments.

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 groundwaters, 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 [Bailey *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.* [1988b], 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 Woolhiser, 1985]. These results indicate that lumped parameter models cannot accurately predict chemical runoff hydrographs and hence that more sophisticated models are needed to better quantify relevant solute transport processes during runoff.

Any realistic, physically based approach toward modeling the release of chemicals from soil to overland flow must include the most relevant processes controlling that release. Wallach *et al.* [1988a] 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.* [1988b] 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

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surface roughness, runoff hydraulic gradient, and hydraulic radius [Wallach *et al.*, 1989].

While the model of Wallach *et al.* [1988b] considers liquid diffusion and equilibrium sorption/exchange with the solid phase, convective (advective) 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 Ahuja and Lehman [1983] for soil boxes with impermeable bottoms. However, a major limitation of the model of Wallach *et al.* [1988b] 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

$$\theta \frac{\partial c}{\partial t} + \rho \frac{\partial s}{\partial t} + \frac{\partial J}{\partial z} = 0 \quad (1)$$

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

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

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:

$$D = D_0\lambda + \varepsilon |v| \quad (3)$$

where D_0 is the ionic or molecular diffusion coefficient in pure water, λ is a tortuosity factor, ε is the dispersivity, and v is the average pore water velocity, approximated by the relation q/θ .

The tortuosity factor λ in (3) accounts for a tortuous flow path of the solute during diffusion in soils. Its value is often estimated using the Millington and Quirk [1961] tortuosity model as $\lambda = \theta^{7/3}/n^2$, where n is the soil porosity. The dispersivity ε 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 [Nielsen *et al.*, 1986]. The dependency of D on v 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

$$s = K_d c \quad (4)$$

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

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} \quad (5)$$

in which the retardation factor R is given by

$$R = 1 + \rho_d K_d / \theta \quad (6)$$

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:

$$J(0, t) = (-\theta D \partial c / \partial z + qc)|_{z=0} = -\theta k [c(0, t) - c_r] \quad (7)$$

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.* [1988b] 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 flumes [Ingram and Woolhiser, 1980; Ahuja 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

$$\left[-D \frac{\partial c}{\partial z} + (v + k)c \right]_{z=0} = 0 \quad (k < \infty) \quad (8a)$$

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

$$c(0, t) = 0 \quad (k \rightarrow \infty) \quad (8b)$$

We emphasize that the assumption of zero c_r in (7) is used here only for estimating the solute flux $J(0, t)$ 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 (5) will be solved for a semi-infinite soil profile characterized by the condition

$$\partial c / \partial z(\infty, t) = 0 \quad (9)$$

and a constant initial concentration C_0 in the soil profile:

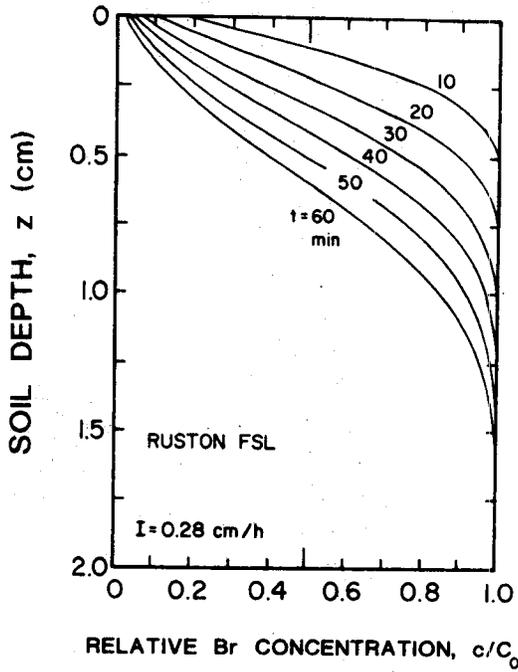


Fig. 1. Calculated solute concentration distributions versus depth during rainfall-induced runoff at an infiltration rate I of 0.28 cm/hr ($D = 0.09$ cm²/hr, $k = 0.83$ cm/hr).

$$c(z, 0) = C_0 \quad (10)$$

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:

$$c(z, t) = C_0 \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{Rz - vt}{2(DRt)^{1/2}} \right] - \frac{v+k}{2k} \exp \left(\frac{vz}{D} \right) \operatorname{erfc} \left[\frac{Rz + vt}{2(DRt)^{1/2}} \right] + \left(1 + \frac{v}{2k} \right) \exp \left[\frac{(k+v)(Rz + kt)}{DR} \right] \cdot \operatorname{erfc} \left[\frac{Rz + (2k+v)t}{2(DRt)^{1/2}} \right] \right\} \quad (k < \infty) \quad (11a)$$

$$c(z, t) = C_0 \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{Rz - vt}{2(DRt)^{1/2}} \right] - \frac{1}{2} \exp \left(\frac{vz}{D} \right) \operatorname{erfc} \left[\frac{Rz + vt}{2(DRt)^{1/2}} \right] \right\} \quad (k < \infty) \quad (11b)$$

Concentration profiles based on (11) for various values of t are shown in Figure 1. The curves were calculated using experimental data obtained by *Ahuja 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 param-

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

Parameter	Symbol	Value	Units
Rainfall intensity	P	6.8	cm/hr
Runoff surface length	L	100.	cm
Surface slope	S	0.04	...
Runoff water height	H	0.07	cm
Volumetric water content	θ	0.53	...
Initial soil solution concentration	C_0	4000.	g/cm ³ (ppm)
Distribution coefficient	K	0.0	cm ³ /g
Diffusion coefficient	D_0	0.034	cm ² /hr
Mass transfer coefficient	k	0.83	cm/hr

ters not available from the original study of *Ahuja and Lehman* [1983] were estimated independently, as discussed by *Wallach et al.* [1988b]. 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.

Ahuja 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

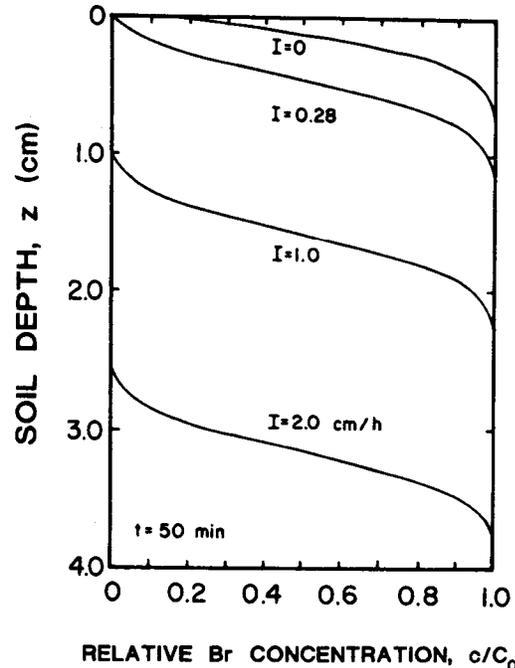


Fig. 2. Calculated bromide concentrations versus depth after 50 minutes of rainfall and for different infiltration rates, I ($D = 0.034$ cm²/hr, $k = 0.83$ cm/hr).

observation is in marked contrast to the measured results of *Ahuja and Lehman* [1983] 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 solutes 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 appearance of chemicals in runoff water at the field effluent. One process is the diffusive-dispersive transport of solutes toward 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 available. Fortunately, complete knowledge of the flow dynamics is not conditional for formulating chemical outflow distributions with time. Information on how long an individual solute remains in the system, or equivalently on the distribution of the residence times [*Himmelblau 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,

$$c_r(t) = \frac{1}{Q_r} \int_0^t J_0(t') E(t-t') dt' \quad (12)$$

where $J_0(t) = -J(0, t)$ is the solute mass flux from soil to runoff water, and Q_r is the runoff water flux. During steady state flow, Q_r 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.*, 1988a]

$$E(t) = \frac{1}{\tau} \exp(-t/\tau) \quad (13)$$

in which τ 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 from those of a well-mixed reactor [*Wallach et al.*, 1988a]. Hence (13) does not imply that the field is a perfect mixer nor that 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 H 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.* [1988a] 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_0 from soil to runoff water is not affected by the runoff water concentration. 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_{r0} in the runoff water. By using superposition, (12) becomes then

$$c_r(t) = C_{r0} \exp(-t/\tau) + \frac{1}{Q_r} \int_0^t J_0(t') E(t-t') dt' \quad (14)$$

The solute flux J_0 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):

$$J_0(t) = \theta k c(0, t) \quad (k < \infty) \quad (15)$$

or with (11a)

$$J_0(t) = \theta C_0 \left\{ \left(k + \frac{v}{2} \right) \exp \left[\frac{(k+v)kt}{DR} \right] \cdot \operatorname{erfc} \left[\frac{(2k+v)t}{2(DRt)^{1/2}} \right] - \frac{v}{2} \operatorname{erfc} \left[\frac{vt}{2(DRt)^{1/2}} \right] \right\} \quad (16a)$$

For the limiting case of no film resistance ($k \rightarrow \infty$), (16a) reduces to

$$J_0(t) = \theta C_0 \left\{ \left(\frac{DR}{\pi t} \right)^{1/2} \exp \left(-\frac{v^2 t}{4DR} \right) - \frac{v}{2} \operatorname{erfc} \left[\frac{vt}{2(DRt)^{1/2}} \right] \right\} \quad (16b)$$

Equation (16b) can also be derived by evaluating the second term of (7) in conjunction with (11b). Because of the assumption 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):

$$c_r(t) = C_{r0} \exp(-t/\tau) + \frac{\theta C_0}{2Q_r} \left\{ \frac{(v+2k)DR}{(v+k)k\tau + DR} \cdot \exp \left[\frac{(v+k)kt}{DR} \right] \operatorname{erfc} \left[\frac{(v+2k)t}{2(DRt)^{1/2}} \right] - v \operatorname{erfc} \left[\frac{vt}{2(DRt)^{1/2}} \right] - \frac{(v+k)\omega\tau}{(v+k)k\tau + DR} \right\}$$

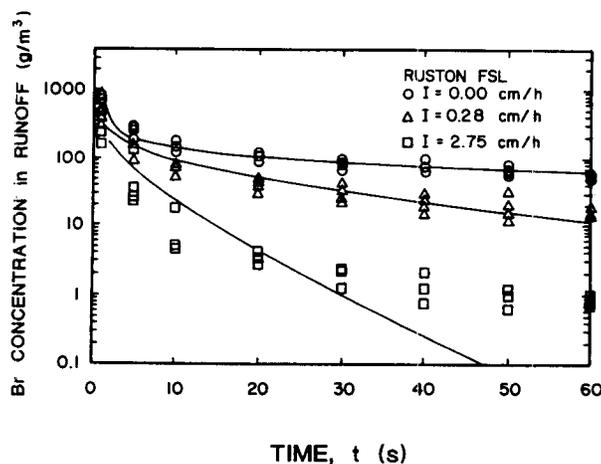


Fig. 3. Comparisons of calculated bromide runoff concentration hydrographs for different values of the infiltration rate I with experimental data of *Ahuja and Lehman* [1983] for Ruston fine sandy loam ($k = 0.83$ cm/hr).

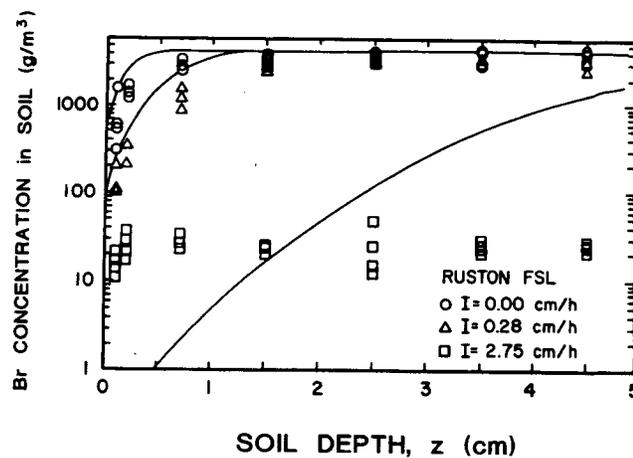


Fig. 4. Comparison of calculated bromide concentrations versus depth for different values of the infiltration rate I with experimental data of *Ahuja and Lehman* [1983] for Ruston fine sandy loam ($k = 0.83$ cm/hr).

$$\begin{aligned} & \cdot \exp(-t/\tau) \operatorname{erf} \left[\frac{\omega t}{2(DRt)^{1/2}} \right] \\ & + \frac{v(v+k)k\tau - 2kDR}{(v+k)k\tau + DR} \exp(-t/\tau) \} \quad (k < \infty) \end{aligned} \quad (17a)$$

$$\begin{aligned} c_r(t) = C_{r0} \exp(-t/\tau) + \frac{\theta C_0}{2Q_r} \left\{ v \exp(-t/\tau) \right. \\ \left. - v \operatorname{erfc} \left[\frac{vt}{2(DRt)^{1/2}} \right] \right. \\ \left. - \omega \exp(-t/\tau) \operatorname{erf} \left[\frac{\omega t}{2(DRt)^{1/2}} \right] \right\} \\ (k \rightarrow \infty) \end{aligned} \quad (17b)$$

where

$$\omega = v \left(1 - \frac{4DR}{v^2\tau} \right)^{1/2}$$

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 Ruston 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.* [1988b], 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 cm²/hr, which translates to dispersivity values (ϵ in (3)) 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 Ruston 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 Ruston 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 Ruston 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-

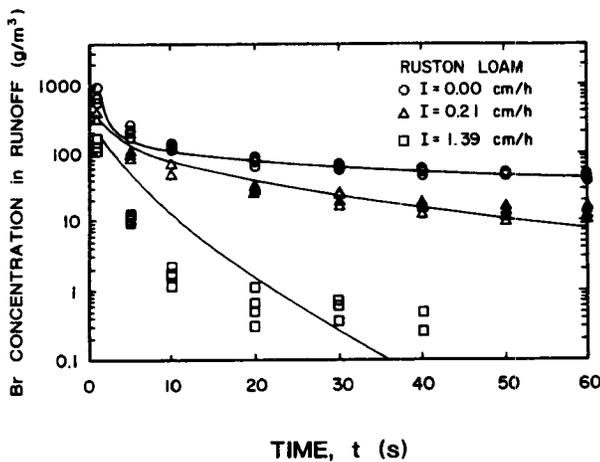


Fig. 5. Comparison of calculated bromide runoff concentration hydrographs for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Ruston loam ($k = 0.9$ cm/hr).

sivities ε for Ruston loam and Parsons clay are 0.084 cm and 0.05 cm, respectively. For each soil type, ε is independent of pore water velocity and within the range of 0.05 to 0.15 cm, evaluated from field measurements for a clay loam by Gvirtzman and Magaritz [1986]. This may further indicate that the current model is physically based, rather than being a lumped model in which the parameters are obtained by matching calculated and measured data.

Although the diffusion coefficient for Parsons clay was expected to be the lowest, its value turned out to be the highest of the three soils (Table 2). This may be explained by the fact that this soil exhibited swelling upon wetting to a height of about 0.5 to 1.0 cm above the level of packing [Ahuja and Lehman, 1983]. This swelling may have caused the topsoil, which contributes most of the chemicals to the surface runoff water, to have a relatively high diffusion coefficient, a relatively high dispersion coefficient, and a high hydraulic conductivity value, as was also observed by Ahuja and Lehman [1983].

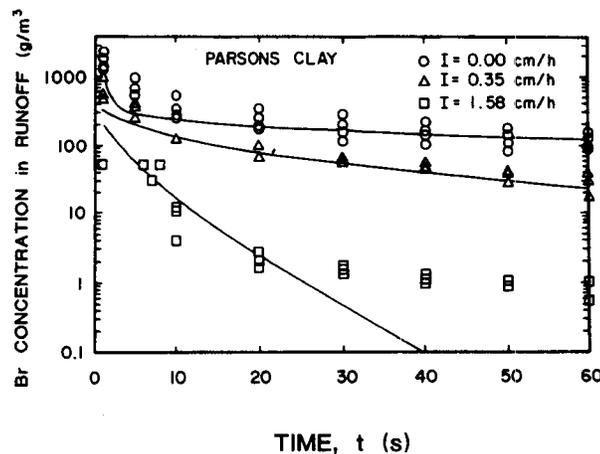


Fig. 6. Comparison of calculated bromide runoff concentration hydrographs for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Parsons clay ($k = 0.79$ cm/hr).

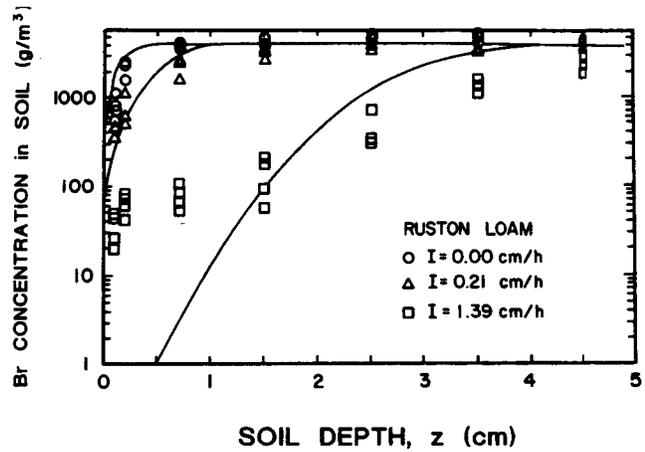


Fig. 7. Comparison of calculated bromide concentrations versus depth for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Ruston loam ($k = 0.9$ cm/hr).

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 described 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.*, 1988b], 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_{r0} convective mass transfer by

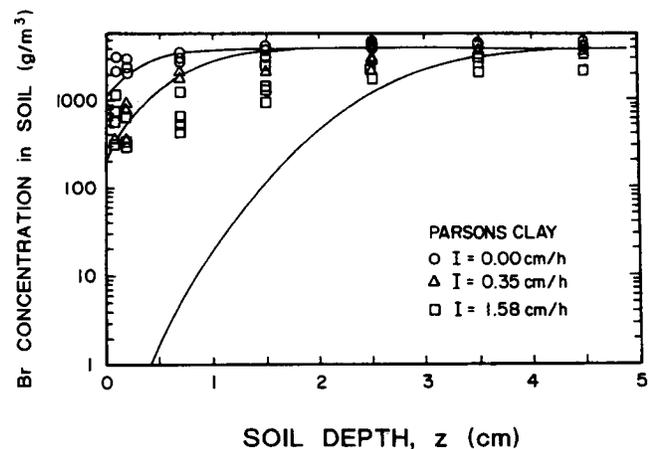


Fig. 8. Comparison of calculated bromide concentrations versus depth for different values of the infiltration rate I with experimental data of Ahuja and Lehman [1983] for Parsons clay ($k = 0.79$ cm/hr).

TABLE 2. Data for the Three Soil Runoff Experiments of Ahuja and Lehman [1983]

	Ruston Fine Sandy Loam	Ruston Loam	Parson's Clay
θ	0.53	0.49	0.55
<i>Experiment 1</i>			
I , cm/hr	0.0	0.0	0.0
D , cm ² /hr	0.034	0.018	0.144
K , cm/hr	0.83	0.90	0.79
C_{r0} , ppm	4000.	4000.	4000.
ϵ , cm	—	—	—
<i>Experiment 2</i>			
I , cm/hr	0.28	0.21	0.35
D , cm ² /hr	0.09	0.054	0.180
K , cm/hr	0.83	0.90	0.79
C_{r0} , ppm	400.	400.	400.
ϵ , cm	0.11	0.084	0.056
<i>Experiment 3</i>			
I , cm/hr	2.75	1.39	1.58
D , cm ² /hr	1.08	0.252	0.288
K , cm/hr	0.83	0.90	0.79
C_{r0} , ppm	0	0	0
ϵ , cm	0.20	0.082	0.050

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

$$\bar{c}_r(s) = \frac{1}{Q_r} \bar{J}_0(s) \bar{E}(s) \quad (A1)$$

where the overbars denote Laplace transforms L with respect to t :

$$\bar{c}_r(s) = L[c_r(t)] = \int_0^\infty \exp(-sT) c_r(t) dt \quad (A2)$$

and where s is the Laplace transform variable. $\bar{J}_0(s)$ is obtained from (16) as

$$\bar{J}_0(s) = \theta k C_0 \left\{ \frac{1}{s} - \frac{2(v+k)}{s[v+2k+(v^2+4DRs)^{1/2}]} \right\} \quad (A3)$$

while $\bar{E}(s)$ follows from (14):

$$\bar{E}(s) = \frac{1}{1+\tau s} \quad (A4)$$

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

$$\bar{c}_r(s) = \frac{AkC_0}{Q_r} \frac{1}{s} \cdot \left[1 - \frac{2(v+k)}{v+2k+(v^2+4DRs)^{1/2}} \right] \left(\frac{1}{1+\tau s} \right) \quad (A5)$$

which may be expanded to yield

$$\bar{c}_r(s) = \frac{AkC_0}{Q_r} \cdot \left\{ \frac{1}{s} - \frac{\tau}{1+\tau s} - \frac{2(v+k) \left(\frac{1}{s} - \frac{\tau}{1+\tau s} \right)}{v+2k+(v^2+4DRs)^{1/2}} \right\} \quad (A6)$$

The inverse Laplace transform of (A6) is

$$c_r(t) = \frac{AkC_0}{Q_r} \{ 1 - \exp(-t/\tau) - L^{-1}[f(s)] - L^{-1}[g(s)] \} \quad (A7)$$

where L^{-1} indicates inverse Laplace transforms, and where

$$f(s) = \frac{2(v+k)}{s[v+2k+(v^2+4DRs)^{1/2}]} \quad (A8)$$

$$g(s) = \frac{2(v+k)}{\left(s + \frac{1}{\tau}\right)[v+2k+(v^2+4DRs)^{1/2}]} \quad (A9)$$

The inverse Laplace transform of (A8) is

$$L^{-1}[f(s)] = 1 + \frac{v}{2k} \operatorname{erfc} \left[\frac{vt}{2(DRt)^{1/2}} \right] - \frac{v+2k}{2k} \exp \left[\frac{k(v+k)t}{DR} \right] \operatorname{erfc} \left[\frac{(v+2k)t}{2(DRt)^{1/2}} \right] \quad (A10)$$

and of (A9)

$$L^{-1}[g(s)] = \frac{(v+k)\tau}{2(v+k)k\tau + 2DR} \left\{ (v+2k) \exp(-t/\tau) - \omega \exp(-t/\tau) \operatorname{erf} \left[\frac{\omega t}{2(DRt)^{1/2}} \right] - (v+2k) \exp \left[\frac{k(v+k)t}{DR} \right] \cdot \operatorname{erfc} \left[\frac{(v+2k)t}{2(DRt)^{1/2}} \right] \right\} \quad (A11)$$

where

$$\omega = v \left(1 - \frac{4DR}{v^2\tau} \right)^{1/2} \quad (A12)$$

The concentration hydrograph, without adjustment for C_{r0} , is hence

$$c_r(t) = \frac{\theta C_0}{2Q_r} \left\{ \frac{(v+2k)DR}{(v+k)k\tau + DR} \cdot \exp\left[\frac{(v+k)kt}{DR}\right] \operatorname{erfc}\left[\frac{(v+2k)t}{2(DRt)^{1/2}}\right] - v \operatorname{erfc}\left[\frac{vt}{2(DRt)^{1/2}}\right] - \frac{(v+k)k\omega\tau}{(v+k)k\tau + DR} \cdot \exp(-t/\tau) \operatorname{erf}\left[\frac{\omega t}{2(DRt)^{1/2}}\right] + \frac{v(v+k)k\tau - 2kDR}{(v+k)k\tau + DR} \exp(-t/\tau) \right\} \quad (\text{A13})$$

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

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