

## Transfer of Chemicals from Soil Solution to Surface Runoff: A Diffusion-based Soil Model

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### ABSTRACT

A physically-based diffusion and transport model is developed to describe chemical outflow concentrations during chemical removal from soil to overlying runoff water induced by continuous rainfall over the soil surface. In contrast to earlier models, movement from the soil to the runoff water is described as a liquid diffusion process to the surface, coupled to the runoff zone through a laminar boundary layer at the runoff interface with the soil surface. Within the soil, diffusion is moderated by equilibrium adsorption to solid surfaces characterized by a partition coefficient. The runoff concentration at the outlet is derived by treating the runoff zone as a well-mixed reactor, characterized by a residence time. The model was used to predict the results obtained in the experimental study of L.R. Ahuja and O.R. Lehman (1983) where infiltration was suppressed, with good agreement obtained between predicted and measured outflow concentrations when the model parameters were estimated independently using standard engineering equations from channel flow hydraulics. The model also predicted the final soil concentrations satisfactorily after runoff ceased.

*Additional Index Words:* Flood irrigation, Chemical transport, Concentration, Hydrograph.

**S**URFACE RUNOFF WATER from agricultural fields may be contaminated by chemicals which either have been applied to the field surface or have been added to the irrigation water. In either case, some chemicals are lost from the field, which lowers the quality of the return flow at the downstream end of the field. The mechanisms governing release of chemicals from soil to surface water and their subsequent transport to the downstream end of the field are not well understood. From early experiments and calculations it has been determined that only a certain thin zone at the soil surface interacts with the rainfall and overland flow (Bailey, et al., 1974; Frere et al., 1975, 1980; Donigian et al., 1977; Ahuja et al., 1981; Ahuja, 1982; Ahuja and Lehman, 1983; Snyder and Wool-

hiser, 1985). The extent of mixing between soil and runoff water has been assumed to be influenced chiefly by the impact of raindrops on the soil surface.

Various simplified lumped parameter models have been proposed to describe the chemical concentration in runoff water. In the majority of these models, the release of dissolved chemicals from soil solution to runoff water was represented as an instantaneous equilibration with the runoff water caused by a rapid and complete mixing process (Donigian et al., 1977; Steenhuis and Walter, 1980; Frere et al., 1980; Ahuja and Lehman, 1983). To model chemical transport, the runoff water zone and the soil water zone were treated as well-stirred chemical tank reactors through which water was flowing in steady state. The soil zone was coupled to the runoff zone by the mixing assumption.

The thickness of soil mixing layer required for model validation is unknown a priori. In the solution to the well-stirred chemical reactor model, the predicted outflow concentration decreases exponentially as a function of time (Ahuja and Lehman, 1983). The thickness of the soil layer in this model appears as a parameter which is part of the exponential rate coefficient and thus affects the shape of the chemical concentration outflow. Hence, when outflow concentration data is available, one may fit the exponential function in the model solution to the data and indirectly determine the thickness of the soil layer by parameter adjustment. However, even though such a model may describe outflow concentrations for similar flow events in the same soil adequately after calibration, this does not imply that the physical mixing mechanism employed in the model is correct. In fact, Wallach et al., (1988) showed that both the well-stirred reactor and the piston-flow reactor model formulations of rainfall-induced runoff have the same residence time distribution function, even though the physical mechanisms implied by these two models are totally different.

Although lumped parameter approaches have the advantages of simplicity and few parameters to calibrate, their ability to predict outflow concentrations for complex coupled processes such as the soil-runoff system may be doubtful because for the most part they

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do not use a physically-based description of the processes they represent. As a result, parameters calibrated in model flow experiments may be given unrealistic values which are only able to represent the data with which they were calibrated. For example, the thickness of the apparent soil mixing layer obtained by Donigian et al. (1977) from model calibration to experimental data was found to be in the range of 0.2 to 0.6 cm. Similarly, Frere et al. (1980) assumed that the quantity of dissolved chemical released to surface runoff water was proportional to the concentration present in the top 1 cm of soil. The proportionality constant in their experiment was termed the extraction coefficient.

In contrast, Ahuja et al. (1981) conducted runoff studies using soil boxes with permeable bottoms and concluded from this experiment that there did not exist a zone of uniform and complete mixing within the soil layer. The degree of mixing they observed was greatest at the soil surface and decreased exponentially with depth. To take this into account, they proposed using an effective depth of interaction (EDI) within which the degree of mixing was uniform and equal to that at the soil surface. Although they found that the EDI increased with time during a rainstorm, they used a time-averaged value. They attributed the increase in EDI with time to the tracer and not to the chemical transfer process. In later work, Ahuja (1982) concluded that a constant EDI concept was not valid for bromide transfer from soil to runoff water. To understand this transfer process better, Ahuja and Lehman (1983) conducted experiments with simulated rainfall to boxes containing three different soils pretreated with a bromide solution. The bottom of the boxes were either impervious, allowing no downward infiltration, or pervious, allowing a controlled infiltration rate to percolate through the soil.

A plot of their measured outflow concentrations on semilogarithmic paper showed that there were two characteristic decay rates. The first decay rate was rapid, occurring at the very beginning of the rainfall event. It was followed by a second, relatively slow decay rate which had a significant cumulative effect on the mass release to runoff over long periods of time. Although it is reasoned that the early decay rate should be associated with the residence time of the fluid in the runoff, attempts by these authors to predict the decay coefficient from the well-mixed reactor model succeeded only when runoff volumes were used in the model which were greater than those actually present in the experiments. The slower decay rate, which is characteristic of a persistent slow supply of chemical from the soil to the runoff water, could not be explained by any of the equilibrium mixing models.

At the end of the rainfall event the authors determined the chemical concentration distribution as a function of soil depth. Depletion of bromide occurred principally in the top 1.5 cm and decreased rapidly with depth.

The experimental results presented by Ahuja and Lehman cast serious doubts on the validity of direct mixing models for rainwater and soil water which assume a constant zone of interaction within the soil. The alternative approach used by the authors, which

employed an exponentially decreasing degree of mixing as a function of soil depth, was more successful in describing the outlet concentrations. However, this approach uses additional parameters, requires that the model be calibrated at each site, and does not address the mechanisms involved in the mixing process.

This study will present a different model based on convective mass transfer from soil surface to surface runoff. The results obtained by coupling this model to a residence time distribution representation of surface runoff flow will be compared to observations in the laboratory study of Ahuja and Lehman (1983) where infiltration was suppressed.

## THEORETICAL ANALYSIS

Transport of chemical within the soil profile ( $z \leq 0$ ) below the runoff water, for the case when infiltration is suppressed, is assumed to occur by molecular diffusion as described by the flux equation

$$J_s = -D_s(\partial C_L/\partial z) \quad [1]$$

where  $J_s$  is the mass flux,  $C_L$  is the soil solution concentration, and  $D_s$  is the soil water diffusion coefficient.  $D_s$  is related to the molecular diffusion coefficient,  $D_w$ , of the chemical in water by

$$D_s = \Omega(\theta)D_w \quad [2]$$

where  $\theta$  is the volumetric water content.  $\Omega(\theta)$  is the tortuosity factor, which accounts for the decreased cross-sectional area and increased pathlength of the chemical in soil. The model used for the tortuosity is that given in Jury et al. (1983)

$$\Omega(\theta) = \theta^{10/3}/\phi^2 \quad [3]$$

where  $\phi$  is soil porosity. This is the Millington and Quirk (1961) tortuosity model applied to the liquid phase.

Within the soil the solute is assumed to obey the mass conservation equation

$$(\partial C_T/\partial t) + (\partial J_s/\partial z) = 0 \quad [4]$$

where  $C_T$  is total concentration. For an adsorbed solute, the total concentration is equal to

$$C_T = \rho_b C_a + \theta C_L \quad [5]$$

where  $\rho_b$  is soil bulk density and  $C_a$  is adsorbed solute concentration. The adsorbed and dissolved concentrations are assumed to be related by the linear equilibrium model

$$C_a = K_d C_L \quad [6]$$

where  $K_d$  is the distribution coefficient. Combining Eq. [5] and [6] gives

$$C_T = R_L C_L \quad [7]$$

where  $R_L$

$$R_L = \rho_b K_d + \theta \quad [8]$$

is the liquid partition coefficient or retardation factor defining the ratio between the total and dissolved solute concentrations (Jury et al., 1983). By combining Eq. [1], [4], [7], and [8] one obtains

$$\partial C_T/\partial t = D_E(\partial^2 C_T/\partial z^2) \quad [9]$$

where  $D_E$  is the effective diffusion coefficient given by

$$D_E = D_s/R_L \quad [10]$$

This assumes that the water content of the soil is not a function of position or time.

### Boundary and Initial Conditions

The boundary condition at the soil surface forming the soil runoff interface must be constructed so as to provide a description of the mass transfer rate from the soil to the runoff water. In this model, the process is represented by a transfer coefficient describing diffusion-controlled transport through a thin laminar boundary layer. Thus, the flux at the soil surface  $z = 0$  is given by

$$J_s(0,t) = -D_s(\partial C_L/\partial z)_0 = k_L[C_L(0,t) - C_w(t)] \quad [11]$$

where  $C_w$  is the average concentration of the chemical in the runoff water above the soil surface and  $k_L$  is the mass transfer coefficient whose value for laminar overland flow is calculated in Appendix C. It is assumed that  $C_w$  is uniform over the thickness of the runoff water zone due to rapid mixing caused by turbulent eddies and raindrop impact. The value of the transfer coefficient generally depends upon the specific chemical involved in the process, the soil surface physical characteristics such as surface roughness, lateral slope and soil type, and runoff discharge, rainfall intensity and duration.

Ahuja and Lehman (1983) and Snyder and Woolhiser (1985) showed in laboratory studies that the chemical concentration in soil solution is much higher than in runoff water. Accordingly, we will assume that the runoff concentration can be neglected in Eq. [11] without creating too great an error. Thus, Eq. [11] for the upper boundary condition may be expressed as

$$J_s(0,t) = -D_E(\partial C_T/\partial z) \cong k_E C_T(0,t) \quad [12]$$

where  $k_E = k_L/R_L$  is the effective mass transfer coefficient. In the analysis to follow it will be assumed that the chemical is initially incorporated within a thick soil layer infinite in extent. Accordingly, the lower boundary condition at  $z = -\infty$  is given as

$$C_T(-\infty,t) = C_o \quad [13]$$

and the initial condition is given as

$$C_T(z,0) = C_o \quad [14]$$

where  $C_o$  is the uniform initial soil concentration.

When the runoff water concentration is neglected, the soil concentration profile is effectively decoupled from the runoff water. Therefore Eq. [9], [12], [13], and [14] may be solved directly, producing (Carslaw and Jaeger, 1959)

$$C_T(z,t)/C_o = \exp(h^2 D_E t) \left[ -hz \operatorname{erfc}(h\sqrt{D_E t} - z/2\sqrt{D_E t}) - \operatorname{erf}(z/2\sqrt{D_E t}) \right] \quad (z \leq 0) \quad [15]$$

where  $h = k_E/D_E$ . Equation [15] describes a concentration profile which increases with soil depth at any given time and has an increasing depletion depth with time in a manner similar to the experimental results observed by Ahuja and Lehman (1983) and Snyder and Woolhiser (1985) for simulated rainfall over soil boxes. Plots of dimensionless concentration  $C_T/C_o$  as a function of dimensionless distance  $y = -hz$  for various values of dimensionless time  $T = h^2 D_E t$  are given in Fig. 1. As shown in this figure, the depth of the so-called mixing zone increases with time during the soil depletion process, in contrast to the models which only allow depletion to occur within a layer of constant thickness during the time of exchange.

### Transfer of the Chemical to Runoff Water

The concentration of the dissolved chemical at the soil surface is given by Eq. [15] with  $z = 0$ , or

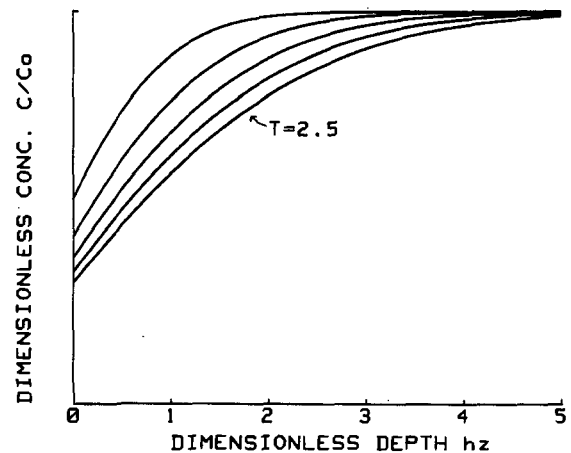


Fig. 1. Dimensionless soil chemical concentration  $C_T(Z,t)/C_o$  as a function of dimensionless depth  $hz$  for  $T = h^2 D_E t = 0.5, 1.0, 1.5, 2.0$ , and  $2.5$  during runoff induced by continuous rainfall.

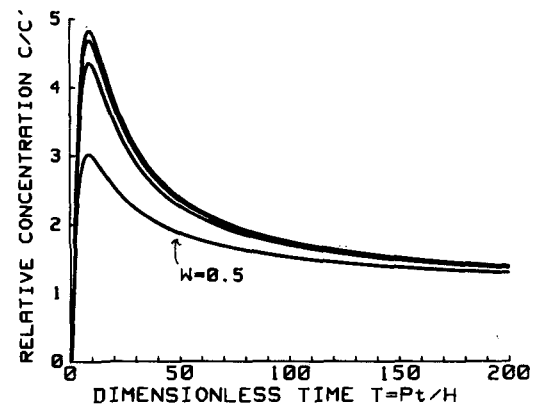


Fig. 2. Relative outflow concentration  $C_{out}(T)/C_o$  as a function of dimensionless time  $T = h^2 D_E t$  where  $W = k_E^2 H / (P D_E) = 0.5, 1.0, 1.5, 2.0$  and  $C' = C_o k_E / P$  during runoff induced by continuous ponding.

$$C_T(0,t) = C_o \exp[h^2 D_E t] \operatorname{erfc}[h\sqrt{D_E t}]. \quad [16]$$

By Eq. [11], the flux from the soil water to the runoff is given by

$$J_s(0,t) = k_E C_o \exp[h^2 D_E t] \operatorname{erfc}[h\sqrt{D_E t}]. \quad [17]$$

The outlet concentration of the runoff water as a function of dimensionless time  $T = Pt/H$  is equal to

$$C_{out}(T) = \frac{C_o \xi}{(1+w)} \left[ \exp(wT) \operatorname{erfc}(\sqrt{wT}) - \exp(-T) + 2 \sqrt{\frac{w}{\pi}} E(\sqrt{T}) \right] \quad [18]$$

where  $\xi = k_E/P$ ,  $w = k_E^2 H / (P D_E)$  are dimensionless groups,  $P$  is rainfall rate,  $H$  is runoff water height, and

$$E(x) = \exp(-x^2) \int_0^x \exp(y^2) dy \quad [19]$$

is Dawson's integral (Abramowitz and Stegun, (1970). Equation [18] is derived in Appendix A. Plots of relative concentration  $C_{out}(t)/C_o \xi$  versus dimensionless time  $T$  for various  $w$  are shown in Fig. 2.

Equation [18] was derived using the assumption that the runoff flow at any point across the surface in response to uniformly distributed, time-invariant rainfall is steady over time and that the initial chemical concentration in the fully

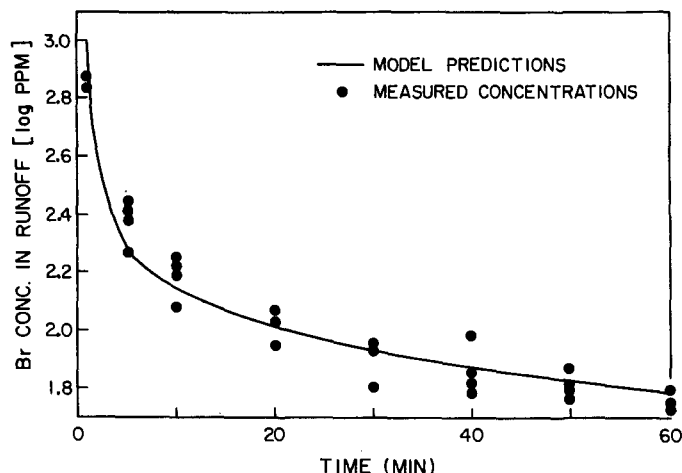


Fig. 3. Comparison between model prediction of outflow concentration using Eq. [18] and the experimental results of Ahuja and Lehman (1983).

flowing runoff water was zero. In a dynamic rainfall-runoff system, however, the runoff water flow builds up gradually over the surface and a steady runoff flow is reached only after an initial stage when chemical may be exchanged between the soil and the water. Hence, at the time when the runoff flow becomes steady there is already a small initial concentration  $C_{Ro}$  in the runoff water. By superposition, the approximate solution for this case is obtained by adding  $C_{Ro} \exp(-T)$  to the solution in Eq. [18] (Wallach and Jury, 1988).

### Comparison to Experimental Results

In order to check the validity of this enhanced diffusion model, a comparison will be made with data taken from the study of Ahuja and Lehman (1983). In their laboratory study, simulated rainfall was applied to boxes containing three different soils prewetted with bromide. The dimensions of the soil boxes were 1.0 m by 0.15 m in area and 0.1 m deep. Although their experiments included cases both with and without infiltration, we will restrict our comparison to the study in which infiltration was suppressed. The soil boxes were placed on a supporting stand to create a slope for runoff generation. During the rainstorm, surface runoff effluent concentration was measured at 0, 5, 10, 20, 30, 40, and 60 min after rainfall initiation. The measured bromide concentration was plotted versus time on a semilogarithmic graph. As reported earlier, those semilog plots of the concentration-time curves were nonlinear, in contrast to the linear relationship predicted by using an equilibrium partition model to represent the mixing of the soil solution and runoff water. In order to predict those results, Ahuja and Lehman (1983) modified the model by assuming an exponential decrease in the degree of mixing between rainfall and soil water with depth. The coefficient which they used to represent the exponential decrease was obtained from the data by curve fit-

Table 1. Experimental data from runoff experiment of Ahuja and Lehman (1983).

Parameter	Symbol	Value	Units
Rainfall intensity	$P$	$1.89 \times 10^{-5}$	$\text{m s}^{-1}$
Slope length	$L$	1	m
Slope	$S$	0.04	-
Runoff water height	$H$	0.0007m†	m
Volumetric water content	$\theta$	0.49	-
Initial solution concentration	$C_{Lo}$	4000	$\text{g m}^{-3}$
Distribution coefficient	$K_d$	0	$\text{m}^3 \text{kg}^{-1}$

† Calculated in Appendix B.

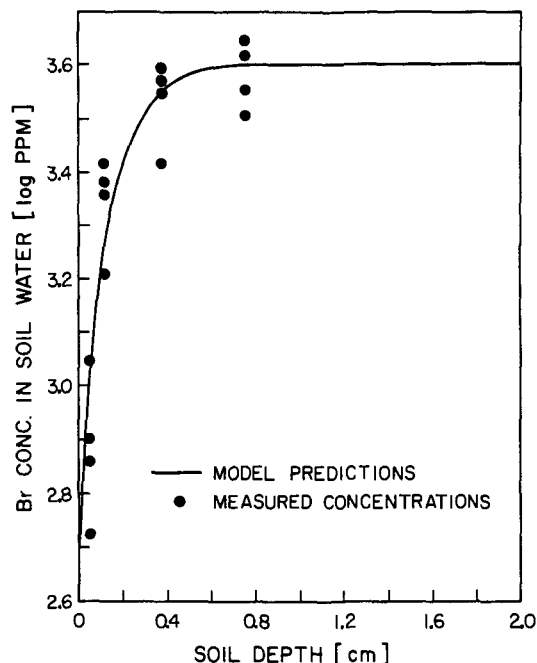


Fig. 4. Comparison between model prediction of final soil concentration using Eq. [15] and the experimental results of Ahuja and Lehman (1983).

ting. This modified mixing model is independent of the chemical characteristics, the soil type, and the hydraulic features of the runoff system.

To contrast this approach we will use the rate-limited soil diffusion model to predict the chemical outflow concentrations in the experiment Ahuja and Lehman conducted in Ruston loam soil. The experimental conditions for this study are summarized in Table 1. Values for parameters required for our model, which are not available, will be calculated from the available data in Table 1 using channel flow hydraulic formulas, as presented in Appendices B and C. The average flow height (Appendix B) is  $\bar{h} = 0.0007$  m, and the average mass transfer coefficient (Appendix C) is  $\bar{k}_L = 1.22 \times 10^{-6}$  m/s. A literature value was selected for the diffusion coefficient of bromide in water [ $D_w = 1.2 \times 10^{-9}$  m<sup>2</sup>/s (Bennet and Myers, 1982)]. Combining this value with the Millington-Quirk model, Eq. [2] and the measured volumetric water content of 0.49, produces a soil diffusion coefficient  $D_s = 4.64 \times 10^{-10}$  m<sup>2</sup>/s. From Eq. [9] and Table 1, the liquid partition coefficient  $R_L = 0.49$ . Therefore, the effective soil solution diffusion coefficient and the effective mass transfer coefficient are, respectively,  $D_E = 9.47 \times 10^{-10}$  m<sup>2</sup>/s and  $k_E = 2.49 \times 10^{-6}$  m/s. Using those calculated values in the model, Eq. [18] produces the predicted bromide outflow concentration, which is compared to the measured data in Fig. 3. Also shown in Fig. 4 is the comparison between predicted Eq. [15] and measured final soil concentration.

## DISCUSSION

The soil-runoff model developed above, which couples the soil to the runoff by molecular diffusion through the soil and through a stagnant boundary layer above the surface, did a good job of reproducing the data of Ahuja and Lehman (1983), without local calibration. In contrast, none of the other models which used a mixing cell concept for the soil and instantaneous partitioning between soil and runoff water could

explain the data. These earlier models used a penetration depth into the soil of the order of 0.02 m. Although raindrop kinetic energy can cause runoff water to penetrate to a certain depth in the soil, it is unlikely to be as large as the order of centimeters for several reasons. First, if the overland flow height is not shallow, the surface water covering the soil will cause the raindrop kinetic energy to dissipate before reaching the soil surface, which will increase the degree of mixing in the runoff water but not in the soil. Second, the profile of chemical concentration with soil depth observed in various experiments discussed above is not consistent with the assumption of uniform mixing in a thin soil surface layer. Rather than showing uniform depletion, these profiles show a decrease with soil depth and a penetration which increases with time. As shown above, (Fig. 1) this time-dependent concentration profile is predicted by our soil-runoff diffusion model.

To explain the observed depth profiles, Ahuja and Lehman (1983) proposed a modified equilibrium model which modified the mixing zone concept by assuming an exponentially-declining degree of mixing between rainfall and soil water. In their model, the decay constant describing the exponential decrease must be obtained for each soil by fitting the model parameters to the observed concentration. Further, the decay constant depends not only on the soil but on the experimental conditions. Thus, it can only be used to predict phenomena similar to those used in the calibration.

In contrast, in our model the mass transfer coefficient  $k_L$  depends in a known way on rainfall intensity, soil surface slope, length and roughness, runoff flow regime, and chemical characteristics, and can be calculated without calibration (see Appendix C and Wallach et al., 1988). The soil diffusion coefficient is based on the Millington-Quirk (1961) model which has received widespread validation (Jury et al., 1983). Thus, the parameters in our proposed model may be modified for different conditions without calibration to data. Consequently, this physically based model can be used for prediction as well as for monitoring and management.

## CONCLUSIONS

The diffusion model proposed in this paper differs from other models of the soil-runoff system in several respects. First, other models assume that soil and runoff compartments are well mixed and instantaneously partition to equilibrium, whereas this model uses a transfer rate coefficient to couple soil to runoff. Second, the models employ a mixing zone concept to model the soil water zone, assuming either a uniform or an exponentially decreasing depth of depletion. This model uses a diffusion transfer process for chemicals in soil, which produces a time-dependent depth of interaction in the soil profile.

A major limitation of our approach is that infiltration is suppressed. Although it increases the mathematical complexity of the solution, a simple infiltration model can easily be added to the approach we use above. This will be the subject of a future paper.

## APPENDIX A

### Derivation of the Runoff Outflow Concentration

#### A. Direct Integration

If the runoff water is modeled as a well-mixed reactor, the mass balance equation for the runoff volume may be written as

$$H(dC_R/dt) = J_s(o,t) - PC_R \quad [A.1]$$

where  $C_R$  is runoff concentration,  $H$  is average runoff height,  $P$  is average rainfall rate, and  $J_s(o,t)$  is the flux of chemical from the soil to the runoff water. As shown in the text,

$$J_s(o,t) \cong k_E C_T(o,t) = k_E C_o \exp[h^2 D_E t] \operatorname{erfc} [h(D_E t)^{1/2}] \quad [A.2]$$

where the symbols are defined in the text.

Equation [A.1] is to be solved for the initial condition

$$C_R(o) = C_{R_o} \quad [A.3]$$

which represents the concentration in the runoff water at the time the runoff reaches steady state.

It is useful to define a dimensionless time in Eq. [A.1-A.2], as

$$T = Pt/H. \quad [A.4]$$

With this substitution, Eq. [A.1-A.2] become

$$(dC_R^*/dT) = J_s^*(o,T) - C_R^* \quad [A.5]$$

$$J_s^*(o,T) = \xi \exp[wT] \operatorname{erfc} [(wT)^{1/2}] \quad [A.6]$$

where  $\xi = k_E/P$  and  $w = h^2 D_E H/P$  are dimensionless constants,  $C_R^* = C_R/C_o$ , and  $J_s^* = J_s/PC_o$ .

Equation [A.5] may be written as

$$e^{-T} \frac{d}{dT} (e^T C_R^*) = J_s^*(o,T) \quad [A.7]$$

which integrates to, using Eq. [A.3]

$$C_R^*(T) = f e^{-T} + \xi e^{-T} \int_0^T \exp$$

$$[(1+w)T'] \times \operatorname{erfc}[(wT')^{1/2}] dT' \quad [A.8]$$

where  $f = C_{R_o}/C_o$ . Substituting  $y = (wT')^{1/2}$  in the integral in Eq. [A.8] gives

$$C_R^*(T) = f e^{-T} + \frac{\xi e^{-T}}{w} \int_0^{\sqrt{wT}} \exp [(1+w)y^2 \times 2y \operatorname{erfc} y dy] \quad [A.9]$$

Equation [A.9] may be integrated by parts, producing (with  $dv = 2(1+1/w)y \exp(1+1/w)y^2 dy$  and  $u = \operatorname{erfc} y$ )

$$C_R^*(T) = f e^{-T} + \frac{\xi}{(1+w)} [e^{wT} \operatorname{erfc} [(wT)^{1/2}] - e^{-T}] + \frac{2\xi}{(1+w)} (w/\pi)^{1/2} E[T^{1/2}] \quad [A.10]$$

where

$$E(x) = e^{-x^2} \int_0^x e^{y^2} dy \quad [A.11]$$

is Dawson's integral [Abramowitz and Stegun, 1970].

#### B. LaPlace Transform Inversion

Since Dawson's integral is not widely used, an alternative evaluation of  $C_R(t)$  will be provided using Laplace transforms.

The Laplace transform of Eq. [A.5] is

$$S\tilde{C}_R^* - f = \tilde{J}_s^*(o) - \tilde{C}_R^* \quad [\text{A.12}]$$

where

$$\tilde{C}_R^* = \int_0^\infty \exp(-sT) \tilde{C}_R^*(T) dT \quad [\text{A.13}]$$

and

$$\tilde{J}_s^*(o) = \int_0^\infty \exp(-sT) \tilde{J}_s^*(o, T) dT. \quad [\text{A.14}]$$

The Laplace transform of  $J_s^*(o, T)$  in Eq. [A.6] is given in Carslaw and Jaeger (1959) as

$$\tilde{J}_s^*(o) = \xi/s^{1/2}(s^{1/2} + w^{1/2}) \quad [\text{A.15}]$$

Thus, combining [A.12] and [A.15]

$$\tilde{C}_R^* = \frac{f}{(s+1)} + \frac{\xi}{s^{1/2}(s^{1/2} + w^{1/2})(1+s)}. \quad [\text{A.16}]$$

The inverse Laplace transform may be obtained numerically by the method given in Sposito et al. (1986), using the inversion procedure of Talbot (1979).

## APPENDIX B

### Calculation of Average Water Height in the Experiment of Ahuja and Lehman (1983)

When the dimensions of the box and the flow conditions of the experiment given in Table 1 are plugged into the formula for the Reynolds number  $Re$ , one obtains

$$Re = VH/\nu = q/\nu = PL/\nu = 18.52 \quad [\text{B.1}]$$

where  $q$  is the volume flow rate or discharge per unit width,  $H$  is the height of overland flow,  $\nu$  is the kinematic viscosity ( $1.02 \times 10^{-6} \text{ m}^2/\text{s}$ ),  $L$  is the length of the flow field, and  $P$  is the rainfall intensity. Thus, the flow regime is laminar (i.e.  $Re \ll 1000$ ). Using the standard approach in channel flow hydraulics, one may write  $q$  as (Linsley et al., 1982)

$$q = KH^m S^\mu \quad [\text{B.2}]$$

where  $m$  and  $\mu$  are coefficients and  $S$  is the slope. The parameter  $K$  is called Izzard's  $K$ .

Thus, the height of water due to a given discharge per unit width  $q$  is

$$H = (q/KS^\mu)^{1/m}. \quad [\text{B.3}]$$

The discharge per unit width at point  $x$  along the field caused by rainfall is simply equal to

$$q = P \cdot x \quad [\text{B.4}]$$

provided that there is no infiltration.

The values for  $m$  and  $\mu$  in Eq. [B.2] for laminar flow are equal to 3 and 1, respectively, and Izzard's  $K$  is (Linsley et al. 1982)

$$K = (2.76 \times 10^{-5} P + C)^{-3} \quad [\text{B.5}]$$

where  $C$  is a friction factor comparable, but not equal to the Manning roughness coefficient for overland turbulent flow.

The average water height for the entire stream may be calculated from

$$\bar{H} = \int_0^L H(x) dx. \quad [\text{B.6}]$$

After substitution of Eq. [B.3] and [B.4] in [B.6], one obtains

$$\bar{H} = (P/KS)^{1/3} L^{1/3} = \frac{3}{4} H(L) \quad [\text{B.7}]$$

where  $H(L)$  (see Eq. [B.3]) is the water depth at the field outlet, at a distance  $L$  from the upstream boundary where runoff begins.

Using a value of 0.02 for the friction factor  $C$  (Table 7.2 of Linsley et al., 1982), one obtains from Eq. (B.3-B.5)  $\bar{H}(L) = 0.00093 \text{ m}$  from which the value  $H = 0.0007 \text{ m}$  is obtained with Eq. [B.7]. This value was used in calculating Fig. 3.

## APPENDIX C

### Calculation of the Mass Transfer Coefficient

The overland flow regime in Ahuja and Lehman (1983) is laminar as shown in Eq. [B.1] of Appendix B. Therefore, the equation for the mass transfer coefficient in turbulent flow, developed in Wallach et al. (1988) cannot be used. Instead, the coefficient must be calculated from a molecular diffusion model.

The diffusion coefficient for bromide in water is  $D_w = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$  (Bennett and Myers, 1982). The Schmidt number  $Sc$ , which is the ratio between the kinematic viscosity and the mass diffusion coefficient is equal to

$$Sc = \nu/D_w = 840 \quad [\text{C.1}]$$

which indicates that the water is a much better conductor of momentum than mass. Thus, the velocity distribution spreads out more rapidly than the concentration profile in the boundary layer.

The average mass transfer coefficient  $\bar{K}_L$  for a plate of finite length  $L$  cm, is (Bennet and Myers, 1982)

$$\bar{K}_L = 0.664 (D_w/L) Re_L^{1/2} Sc^{1/3} \quad [\text{C.2}]$$

where the overall Reynolds number is defined as:

$$Re_L = (VL/\nu) (PL/\bar{H}\nu) \quad [\text{C.3}]$$

with  $V = P/\bar{H}$  the average runoff velocity and  $\bar{H}$  the average runoff height.

Using  $\bar{H} = 0.0007 \text{ m}$  (Appendix B),  $\nu = 1.02 \times 10^{-6} \text{ m}^2/\text{s}$ , and the values from Table 1, one obtains

$$K_L = 1.22 \times 10^{-6} \text{ m/s}. \quad [\text{C.4}]$$

This value was used to calculate Fig. 3.

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