

COUPLING MIXING ZONE CONCEPT WITH CONVECTION-DIFFUSION EQUATION TO PREDICT CHEMICAL TRANSFER TO SURFACE RUNOFF

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ABSTRACT. Modeling chemical transfer from soil solution to surface runoff is essential for developing a surface water quality model that can be used to assess pollution potentials of agricultural chemicals. Chemical transfer to runoff can be modeled as a two-rate process. A fast rate subprocess, which prevails at early stages of rainfall, causes an exponential depletion of chemicals from the mixing zone. A slow rate subprocess, which becomes significant under poor drainage conditions, transports chemicals into the mixing zone from the soil below. The two-rate process can be described by coupling the mixing zone concept with the convection-diffusion equation (CDE). We evaluated this coupling approach by comparing predicted results with measured bromide concentration data. A finite element scheme was developed to solve the CDE in conjunction with a near-surface boundary condition derived from a complete and uniform mixing theory. Overall results showed that without a calibration the coupling approach satisfactorily predicted bromide concentrations in both surface runoff and soil solution under the zero infiltration conditions. The proposed model adequately reproduced measured data for restricted infiltration conditions by introducing a mechanical dispersion coefficient (D_h). The fitted D_h is within the range reported in the literature for the repacked soil conditions. The coupling approach, while allowing for direct use of the mixing theory under free infiltration conditions, refines the theory for use under poorly drained conditions.

Keywords. Runoff, Water quality, Nonpoint source pollution, Solute transport.

Agricultural chemicals such as mobile fertilizers and pesticides are major nonpoint source pollutants that deteriorate surface and subsurface water quality. Polluted surface runoff or water bodies such as lakes and ponds can contaminate groundwater either through direct contact with groundwater table or macropore flow (Steenhuis et al., 1994; Ahuja et al., 1993). Thus, a thorough understanding of mechanisms involved in chemical transfer from soil solution to surface runoff can further the development of mathematical models that can be used to predict pollution potentials of nonpoint source pollutants and to develop the best management plans for controlling surface and subsurface water contamination.

The conventional mixing zone theory assumes that there exists a region below the soil surface in which surface water, soil solution, and infiltrating water mix completely and instantaneously and that there is no chemical transfer into that region from the soil below (fig. 1). The mixing zone depth (z) or effective depth of rainfall-soil interaction is the most critical parameter in this approach because it determines chemical availability to runoff extraction. The mixing concept has been widely accepted and used to predict chemical loss in surface runoff (Donigian et al.,

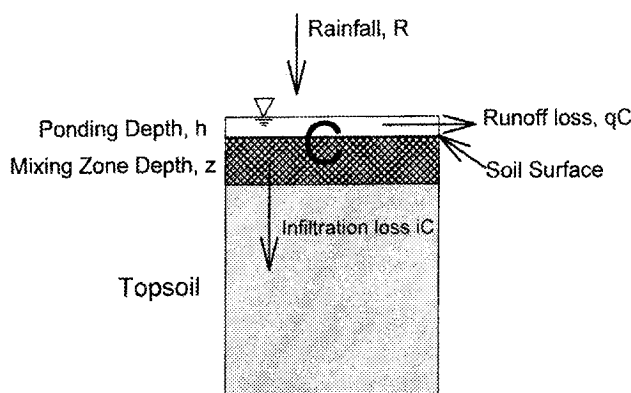


Figure 1—Schematic representation of the complete and uniform mixing concept.

1977; Frere et al., 1980; Ahuja et al., 1981; Steenhuis et al., 1994). However, a wide range of mixing depths has been used in various models. A depth of 10 mm was used in many models such as CREAMS (Frere et al., 1980), while a shallower depth of <3 mm was reported and used by other researchers in their models (Donigian et al., 1977; Ahuja et al., 1981; Zhang et al., 1997a,b).

Based on the mixing theory and the assumption that mixing depth (z) and the saturated volumetric water content (θ_s) do not change with time, a mass balance equation for a mobile chemical with a transient ponding depth (h) can be written as:

$$z\theta_s \frac{\partial C}{\partial t} + \frac{\partial(hC)}{\partial t} = -(q+i)C \quad (1a)$$

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where C is the chemical concentration in the mixing zone, runoff, and infiltrating water; t represents time; q is the rainfall access rate; and i is the infiltration rate. Under steady ponding conditions, equation 1a reduces to:

$$(z\theta_s + h_c) \frac{dC}{dt} = -RC \quad (1b)$$

where h_c is a constant ponding depth; and R is the rainfall rate and is equal to $(q + i)$. It should be pointed out that an upward chemical transport by molecular diffusion and mechanical dispersion was not considered in the derivation of equation 1. A solution to equation 1 shows that chemical concentration in the mixing zone decreases exponentially with time. Ahuja and Lehman (1983) and Snyder and Woolhiser (1985) reported that equation 1 was approximately valid under free infiltration conditions, but was invalid under poorly drained conditions. This is likely because the assumption that no chemical transfer takes place to the mixing zone from the soil below is invalid under poor drainage conditions (Zhang et al., 1997a). Therefore, the conventional mixing concept should be modified and a chemical flux into the mixing zone from the soil below should be considered under poorly drained conditions or during a prolonged rain. The chemical transfer between the mixing zone and the soil below can be simulated by the conventional convection-diffusion equation (CDE).

Ahuja (1990) hypothesized that rainfall impacts could enhance the diffusion process in the top 2-cm layer of soil and this increased transfer could be modeled as an accelerated diffusion process with the convection-diffusion type of equations. By adjusting the diffusion coefficient in the top 2-cm layer to constant or exponentially diminishing values with depth, he successfully reproduced measured Br concentration in surface runoff. Wallach and van Genuchten (1990) took a different approach. They hypothesized that chemical transfer from soil solution to surface runoff was a rate-limited process, which was controlled by molecular diffusion rates across a stagnant water film located at the interface between soil surface and surface runoff water. In their model, the chemical transport in the soil profile was modeled by a normal CDE.

Zhang et al. (1997a) identified two transfer subprocesses in their experimental study. A fast rate subprocess, which is confined to the mixing zone and operates on a shorter time scale, causes an exponential depletion of chemicals in that zone. A slow subprocess, which becomes significant on a longer time scale (normally in order of hours) and is dominated by molecular diffusion and mechanical dispersion, simulates chemical transfer from the underlying soil to the mixing zone. The fast rate subprocess predominates under free infiltration conditions, while the slow rate subprocess becomes significant under poorly drained conditions. In their article, they hypothesized that this two-rate process could be modeled by coupling the mixing theory with a normal CDE, which simulates a chemical transfer between the mixing zone and the soil below.

The objective of this study was to develop a surface water quality submodel by coupling the mixing zone theory with CDE to describe nonreactive chemical transfer from

soil solution to surface runoff, and to test the model by comparing calculated results with measured bromide data of Ahuja and Lehman (1983) under a constant rainfall intensity and pre-saturated soil conditions. The CDE was solved numerically for a near-soil surface boundary condition derived from the uniform and complete mixing zone concept using a finite element scheme.

QUANTITATIVE DESCRIPTION

Transport of a nonreactive chemical in a soil profile, which doesn't have a sink or source term, can be described by the CDE as:

$$\theta_s \frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} \left[iC - D \frac{\partial C}{\partial x} \right] \quad (2)$$

where C is the dissolved chemical concentration in soil solution; x is the depth from the soil surface; and D is the summation of the molecular diffusion coefficient D_s and mechanical dispersion coefficient D_h as defined below:

$$D = D_s + D_h \quad (3a)$$

$$D_h = \varepsilon(R - q) \quad (3b)$$

in which ε is the dispersivity. The D_s in soil may be estimated by Millington and Quirk (1961) as:

$$D_s = D_w \frac{\theta^{10/3}}{\theta_s^2} \quad (4)$$

where D_w is the molecular diffusion coefficient in pure water; and θ is the soil water content. Zhang et al. (1997a) have shown that the assumption of no chemical transfer into the mixing zone from the underlying soil (fig. 1), which was used in deriving equation 1, was invalid under poorly drained conditions. Therefore, equation 1 must be modified to allow a chemical input into the mixing zone from the underlying soil. If we define a net transfer flux between the mixing zone and the underlying soil as J_n (i.e., J_n equals iC minus an upward chemical flux due to molecular diffusion and mechanical dispersion), equation 1a can be modified as:

$$-(z\theta_s) \frac{\partial C}{\partial t} - \frac{\partial(hC)}{\partial t} - qC = J_n \quad (5a)$$

For a constant rainfall intensity and a pre-saturated soil condition as was used in this application study, equation 5a can be simplified for two distinct surface ponding conditions. Prior to the establishment of a constant ponding depth (h_c), we could assume that runoff was zero and h was equal to $q \times t$, because rainfall excess was used to build-up surface storage during this stage. This assumption implies that chemical loss in runoff (qC term in eq. 5a) was zero. By the substitution, equation 5a reduces to:

$$-(z\theta_s + h) \frac{\partial C}{\partial t} - \frac{\partial h}{\partial t} C = J_n \quad (h < h_c) \quad (5b)$$

where $\partial h/\partial t$ was actually equal to the rainfall access rate (q). After a steady h_c was established, $\partial h/\partial t$ reduced to zero and chemical loss in runoff was equal to qC . Thus under steady conditions, equation 5a becomes:

$$-(z\theta_s + h_c) \frac{\partial C}{\partial t} - qC = J_n \quad (h \geq h_c) \quad (5c)$$

Note that equations 5b and 5c are virtually the same except for that different values of h were used in numeric computation.

Based on equations 2 and 5, a flux boundary condition at the interface between the mixing zone and the underlying soil (at $x = z$) can be written as:

$$D \frac{\partial C}{\partial x} - (q + i) C = (h + z\theta_s) \frac{\partial C}{\partial t} \quad (6)$$

where $h = qt$ when $h < h_c$ and $h = h_c$ when $h \geq h_c$. This boundary condition assumes that the chemical concentration in the mixing zone is equal to that in the underlying soil at the interface (at $x = z$). In this study, a zero-concentration gradient for the lower boundary condition at the bottom of a soil box ($x = L_b$) was assumed as:

$$\frac{\partial C}{\partial x} = 0 \quad t > 0, x = L_b \quad (7)$$

This condition implies that chemical concentration did not vary with x at and beyond the soil box outlets. A constant initial concentration of C_0 throughout the soil profile or soil column was used:

$$C = C_0 \quad t = 0, 0 \leq x \leq L_b \quad (8)$$

Equations 2 through 8 were solved with a finite element scheme. Assuming that the runoff area is small enough to be treated as a uniform point source, solutions at $x \leq z$ represent the chemical concentrations in surface runoff. To mathematically simplify the scheme, the mixing zone was treated as a super diffusion layer in which a unit fictitious diffusion coefficient was used to simulate complete mixing within the mixing zone when solving the governing equation of equation 2. In this approach, the storage change within the mixing zone is governed by equation 2. Therefore, the flux boundary condition at the soil surface ($x = 0$) can be used instead.

The new boundary condition at $x = 0$ can be developed by eliminating the storage term of the mixing zone in equation 6 as:

$$D \frac{\partial C}{\partial x} - (q + i) C = h \frac{\partial C}{\partial t} \quad (9)$$

This boundary condition allows for a gradual accumulation of a well stirred water layer at the soil surface before a constant ponding depth (h_c) is established. A constant h_c is used afterwards.

FINITE ELEMENT FORMULATIONS

Since an approximation of equation 2 does not satisfy the equation, a non-zero residual results. To minimize the residual, a weighted residual method, which requires that the integral of the product of a weighting function and the residual at each node to be zero, is used to generate the final system of equations or global matrices. The global matrices can be easily obtained by incorporating element matrices using the direct stiffness method (Seegerlind, 1984). The element matrices are derived after evaluating the residual integral for each element by using a continuous piecewise smooth linear equation. Given an arbitrary linear element e with nodes i and j , the residual integral can be written as:

$$\{R^{(e)}\} = - \int_{x_i}^{x_j} \begin{bmatrix} N_i \\ N_j \end{bmatrix} \left(D \frac{\partial^2 C}{\partial x^2} - (R - q) \frac{\partial C}{\partial x} - \theta_s \frac{\partial C}{\partial t} \right) dx \quad (10)$$

where X_i and X_j are coordinates at nodes i and j ; N_i and N_j are the shape functions for nodes i and j of element e . If the Galerkin formulation is used, the shape functions take the form of:

$$N_i = \frac{X_j - x}{L} \quad \text{and} \quad N_j = \frac{x - X_i}{L} \quad (11)$$

where L is the distance between nodes i and j . Equation 10 can be easily integrated with the linear shape functions given in equation 11. Integrating the first part of equation 10 yields:

$$I_1 = D \begin{bmatrix} 1 \\ 0 \end{bmatrix} \frac{\partial C}{\partial x} \Big|_{x=X_i} - D \begin{bmatrix} 0 \\ 1 \end{bmatrix} \frac{\partial C}{\partial x} \Big|_{x=X_j} + \frac{D}{L} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} C_i \\ C_j \end{Bmatrix} \quad (12)$$

where C_i and C_j are node values at i and j . After incorporating the upper boundary condition of equation 9 to the first term and the lower boundary condition of equation 7 to the second term, equation 12 becomes:

$$I_1 = \begin{bmatrix} R & 0 \\ 0 & 0 \end{bmatrix} \begin{Bmatrix} C_i \\ C_j \end{Bmatrix} + \begin{bmatrix} h(t) & 0 \\ 0 & 0 \end{bmatrix} \begin{Bmatrix} \bar{C}_i \\ \bar{C}_j \end{Bmatrix} + \frac{D}{L} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} C_i \\ C_j \end{Bmatrix} \quad (13)$$

where \bar{C}_i and \bar{C}_j are time derivatives ($\partial C/\partial t$) at nodes i and j . The integration of the second part of equation 10 yields:

$$I_2 = \frac{(R - q)}{2} \begin{bmatrix} -1 & 1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} C_i \\ C_j \end{Bmatrix} \quad (14)$$

The integration of $\partial C/\partial t$ with respect to x , the third part of equation 10, is evaluated with the lumped formulation. The lumped formulation assumes that $\partial C/\partial t$ is constant between the midpoints of adjacent elements, and uses step functions as shape functions for interpolating $\partial C/\partial t$ between nodes. Evaluation of the integration with the step functions given by Segerlind (1984) results in:

$$I_3 = \frac{\theta_s L}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{Bmatrix} \bar{C}_i \\ \bar{C}_j \end{Bmatrix} \quad (15)$$

Summing up equations 13, 14, and 15, we have the general form of element matrices as:

$$\{R^{(e)}\} = [K^{(e)}] \{C^{(e)}\} + [\lambda^{(e)}] \{\bar{C}^{(e)}\} \quad (16)$$

where (K) and (λ) are usually called the elemental stiffness and capacitance matrices; $\{C\}$ and $\{\bar{C}\}$ are column vectors and vary with time. To solve this for different time steps, a finite difference method is used to approximate $\{C\}$ and $\{\bar{C}\}$. The central difference method gives:

$$\{C^{(e)}\} = \frac{1}{2} \{C^{(e)}\}_a + \frac{1}{2} \{C^{(e)}\}_b \quad (17)$$

where $\{C\}_a$ and $\{C\}_b$ are values of C at $t = a$ and b . The $\{\bar{C}\}$ can be approximated as:

$$\frac{d\{C^{(e)}\}}{dt} = \frac{\{C^{(e)}\}_b - \{C^{(e)}\}_a}{\Delta t} \quad (18)$$

where Δt is the time step and is equal to $(b - a)$. By substituting equation 17 and 18 into equation 16 and further using the direct stiffness method (Segerlind, 1984), the final system of equations becomes:

$$\{R\} = [A] \{C\}_b - [P] \{C\}_a = \{0\} \quad (19)$$

where (A) and (P) are $(n + 1) \times (n + 1)$ global matrices (n is the total number of nodes). The final $(n + 1)$ linear

equations are solved for the solution for the next time step with known values from the previous time step. A computer program written in C++ was used to solve equation 19 for time and positions.

MODEL APPLICATION AND DISCUSSION

Experimental data of Ahuja and Lehman (1983) from two soils (Ruston fine sandy loam and Ruston loam soils; fine-loamy, siliceous *Typic Paleudult*) under three infiltration conditions (zero, restricted, and free infiltration) were used to evaluate this model. In their experiments, a 61-min rain with a mean rainfall intensity of 68 mm/h was delivered to a pre-saturated soil box ($100 \times 15 \times 10$ cm), where the soils were initially equilibrated with 4000 mg/L Br solution and the soil box was set at 4% slope. The three infiltration treatments were obtained by using impervious, slurry-covered, and perforated bases in the soil boxes. During each rain, surface runoff was collected for flow rate and Br concentration determination at the time of runoff initiation and periodically thereafter. At the end of each rain, the soil in the box was sampled from depth intervals of 0 to 2.5, 0 to 5, 5 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 50 mm below the soil surface. Samples from each interval were composited and analyzed for Br concentration.

The finite element scheme, which couples the mixing zone concept with the CDE, was used to predict chemical concentrations in both runoff and soil solution for the zero and restricted infiltration conditions. Analytical solutions to equations 1a and 1b, which are solely based on the conventional mixing zone concept, were used under free infiltration conditions. To simulate a transient build-up of a surface water layer, equation 1a was solved for chemical concentrations in the mixing zone before a steady state ponding depth (h_c) was established under an assumption that there was no surface runoff generated during this stage. Equation 1b was then solved for chemical concentrations in surface runoff afterwards. A constant effective mixing zone depth of 2 mm and an average maximum ponding depth of 0.5 mm were used in the calculation for both soils. The former was based on the previous work of Ahuja et al. (1981), who used ^{32}P as a tracer and found the effective mixing depths for Ruston fine sandy loam and other two soils were between 2 and 3 mm. We chose 2 mm based on our experience and experimental observations (Zhang et al., 1997a). The average maximum ponding depth at steady state was computed as a mean flow depth weighted by flow length. The steady state flow depth was estimated using relationships developed by Julien and Simons (1985) for raindrop-impacted sheet flow in conjunction with friction vs. rainfall intensity relationship derived by Li (table 1 of Julien and Simons, 1985). A fictitious unit value of D was used within the mixing zone to ensure complete mixing in that zone. The other parameter values used in the model prediction are given in table 1. Except for D_h , which was set to zero for the zero infiltration conditions and was estimated by comparing measured with calculated data for the restricted infiltration conditions, the rest of the data were either directly measured by Ahuja (1990) or independently estimated with equation 4.

Table 1. Measured and estimated parameter values* used in the numerical solutions

Infiltration Treatment	θ_s (cm ³ /cm ³)	C_0 (mg/L)	R (cm/s)	q (cm/s)	D_s (cm ² /s)	D_b (cm ² /s)
Ruston Fine Sandy Loam						
Zero	0.53	4000	1.98×10^{-3}	1.98×10^{-3}	5.15×10^{-6}	0
Restricted			1.97×10^{-3}	1.89×10^{-3}	5.15×10^{-6}	9.85×10^{-6}
Free			1.79×10^{-3}	1.03×10^{-3}	NA	NA
Ruston Loam						
Zero	0.49	4000	2.00×10^{-3}	2.00×10^{-3}	4.64×10^{-6}	0
Restricted			1.96×10^{-3}	1.91×10^{-3}	4.65×10^{-6}	5.36×10^{-6}
Free			2.02×10^{-3}	1.63×10^{-3}	NA	NA

* θ_s , saturated water content; C_0 , initial chemical concentration; R, rainfall rate; q, runoff rate; D_s , molecular diffusion coefficient in soil (eq. 4); D_b , mechanical dispersion coefficient; NA, not appropriate.

A numerical solution of equation 2 in conjunction with the boundary and initial conditions of equations 7 to 9 for chemical concentrations in surface runoff under the zero infiltration conditions for the Ruston fine sandy loam soil is shown in figure 2. Zero ponding and mixing depths ($z = h = 0$) were imposed on the solution, and the other parameter values were from table 1. A corresponding analytical solution of Crank (1956) under the same conditions is also presented. A spatial increment of 0.1 mm and a time step of 0.2 s were used in the numerical solution. Results showed that both solutions agreed well. Relative difference was shown to decrease with time, being 1.6% at 30 s and 0.08% at 10 min. The close agreement to some degree verified our finite element scheme. Although the solution was not sensitive to time and spatial increments, an increment of 0.1 mm and a time step of 0.2 s were used throughout this study.

Predicted chemical concentrations in surface runoff under three infiltration conditions for Ruston fine sandy loam using the proposed coupling model and the mixing model of equation 1 were compared with those of measured in figure 3. In general, the predictability of the simple mixing model increased progressively as infiltration rates increased from impervious to free drainage conditions. A close agreement between predicted and measured data under free infiltration conditions (fig. 3c)

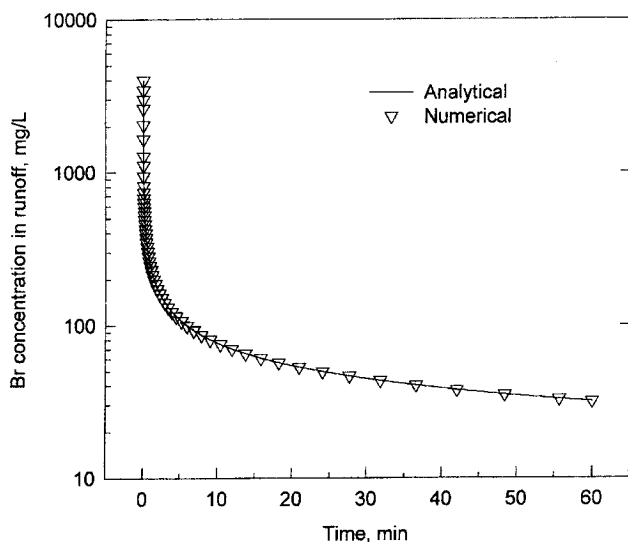
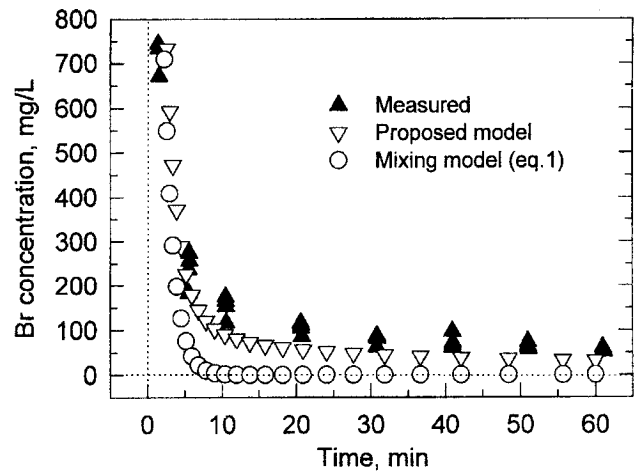
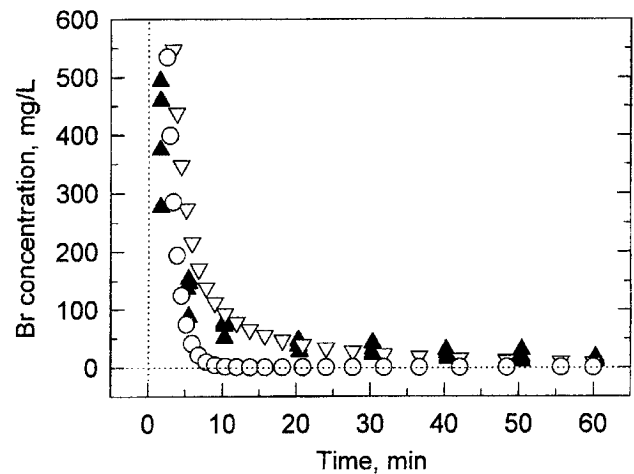


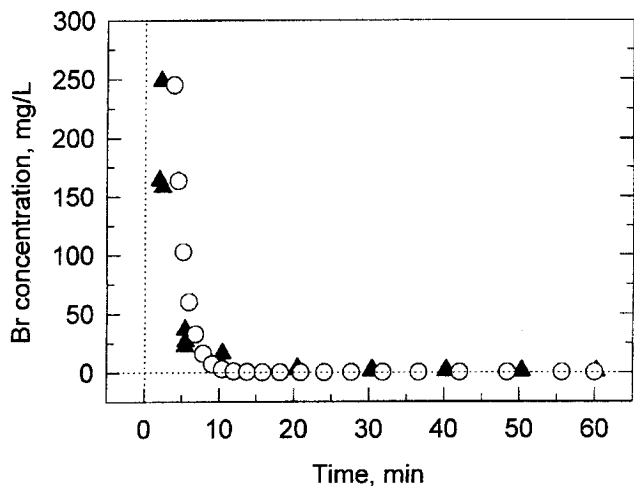
Figure 2—Comparison of numerical and analytical solutions for the chemical concentration in surface runoff under zero infiltration conditions with no ponding and zero mixing zone depth for the Ruston fine sandy loam.



(a) Zero infiltration



(b) Restricted infiltration



(c) Free infiltration

Figure 3—Measured and predicted Br concentrations in surface runoff during 60-min rains under three infiltration conditions for the Ruston fine sandy loam soil. Measured data were from Ahuja and Lehman (1983).

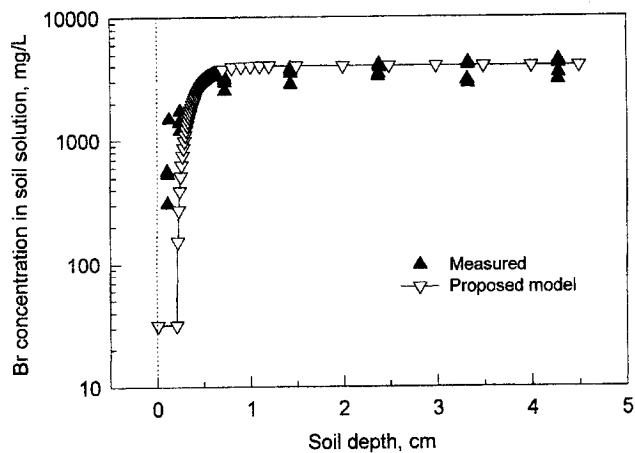
indicated that equation 1, which assumes there is no chemical transfer into the mixing zone from the underlying

soil layer, was valid under these conditions, and it further indicated that there was no need to use complicated models to predict chemical concentrations in surface runoff under these conditions. Similar conclusions have been drawn by Ahuja and Lehman (1983) and Ahuja et al. (1981). Zhang et al. (1997b) also reported that equation 1 produced satisfactory predictions for moderately adsorbed herbicides if a desorption/adsorption isotherm was included. However, the mixing model considerably underpredicted Br concentrations under zero and restricted infiltration conditions (figs. 3a and 3b). This is because the upward chemical transfer into the mixing zone by molecular diffusion and mechanical dispersion cannot be ignored under poorly drained conditions.

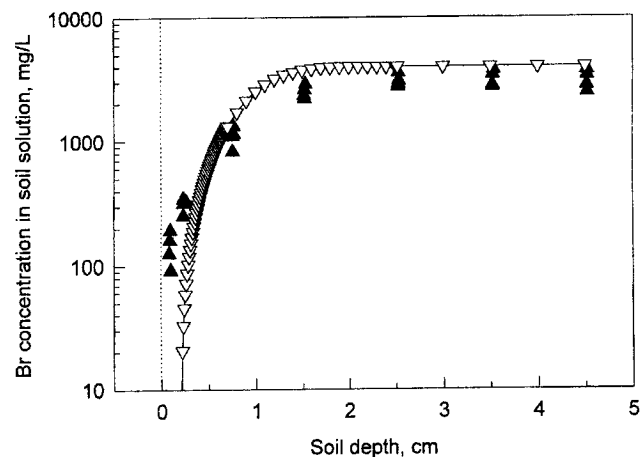
Coupling the CDE with the mixing model provided a better solution under zero and restricted infiltration conditions. Under zero infiltration conditions where the molecular diffusion coefficient (D_s) was used, numerical solution predicted well at early stages of runoff. However, it underpredicted chemical concentrations at large time scales. There could be several reasons for the underprediction. First, chemicals retained inside the soil aggregates could not mix completely and instantaneously with soil solution as assumed in the mixing zone, and might be slowly released into soil solution by the soil aggregates through molecular diffusion. Secondly, it was possible that chemicals could be transported to the soil surface by subsurface lateral flow at 4% slope under zero infiltration conditions (Zhang et al., 1997a). Finally, an accelerated diffusion due to mechanical raindrop impact could have occurred below the mixing zone (2 mm) as suggested by Ahuja (1990).

We did not calibrate the proposed coupling model by adjusting the diffusion coefficient D of equation 2 to match measured data for zero infiltration conditions. The input parameter values used in the prediction were either directly measured or independently computed using equation 4 (table 1). Therefore, the better prediction over the mixing model indicated the improved model predictability, rather than the feasibility of fitting the data with this model. Another reason for not adjusting D was that the contributions from subsurface lateral flow or release by soil aggregates were unknown. Under restricted infiltration conditions, since the mechanical dispersion caused by downward movement of infiltrating water could be significant as suggested by Wallach and van Genuchten (1990), the D_h of equation 2 was calibrated to match the experimental data at large time scales (fig. 3b). The measured data were satisfactorily reproduced by the proposed model using the calibrated D_h (table 1). The dispersivity (ϵ), estimated by dividing D_h by infiltration flux in our notations, was about 1.6 cm, which was within ranges for disturbed or repacked soil columns (van Genuchten and Wierenga, 1986).

Measured and predicted chemical concentrations in the soil solution at the end of 60 min rainfall are plotted with soil depth in figure 4. For both zero and restricted infiltration conditions, the predicted concentrations agreed qualitatively well with measured values. As suggested by Ahuja (1990), more stringent quantitative comparison was not suitable due to considerable sampling errors expected due to the nature of the sampling procedures. No plots are presented for free infiltration conditions, since the



(a) Zero infiltration

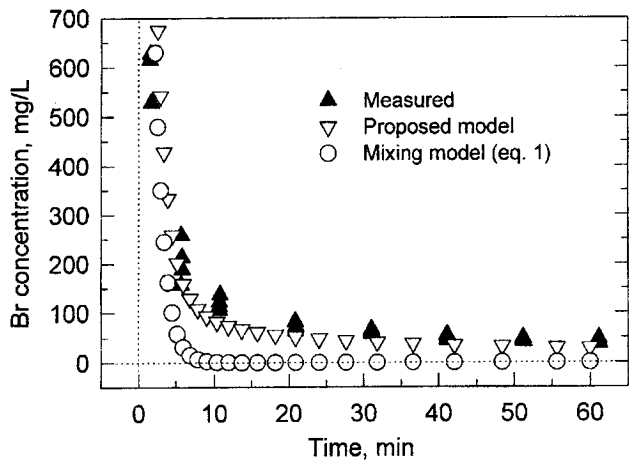


(b) Restricted infiltration

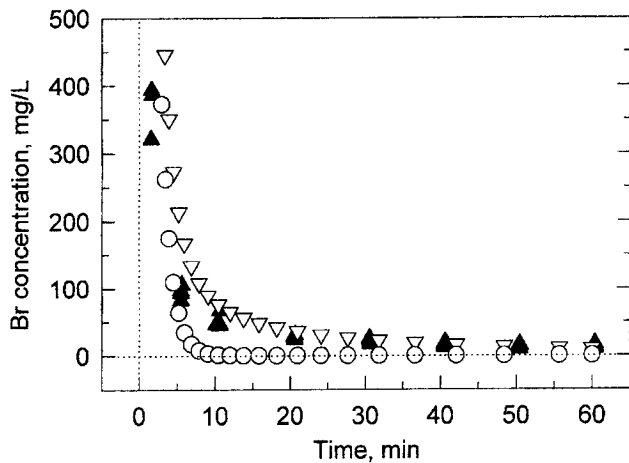
Figure 4—Comparison of predicted Br concentration profile in soil water at the end of 60-min rains with those measured by Ahuja and Lehman (1983) for the Ruston fine sandy loam soil.

simplified mixing zone approach of equation 1 is unable to predict concentration distribution with soil depth.

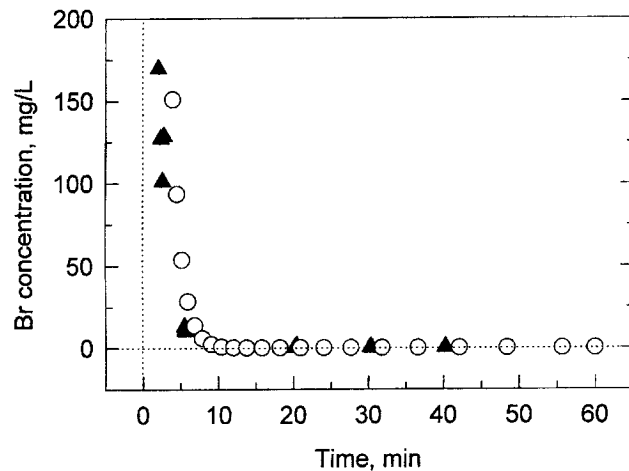
Measured and predicted chemical concentrations for Ruston loam soil are shown in figure 5. The general trends of model predictability were similar to those of Ruston fine sandy loam under all three infiltration conditions. Comparatively, a better agreement was obtained at large time scales for zero infiltration conditions with only the molecular diffusion coefficient (D_s) without any calibration. Again, the addition of a calibrated D_h under the restricted infiltration conditions improved the goodness of fit at large time scales. Inclusion of a D_h term also caused a slight rightward shift in the early prediction curve. This suggests that in addition to the mechanical dispersion transport, other chemical sources might also contribute to the soil solution of the mixing zone. The possible sources could be the release of chemicals by soil aggregates and/or transport of chemicals to the mixing zone by lateral flow. A close agreement was exhibited in figure 5c, which once again showed the simplified mixing zone approach worked well under free drainage conditions. This result not only suggests that there is no need to use complicated models under free drainage conditions if the primary goal is to



(a) Zero infiltration



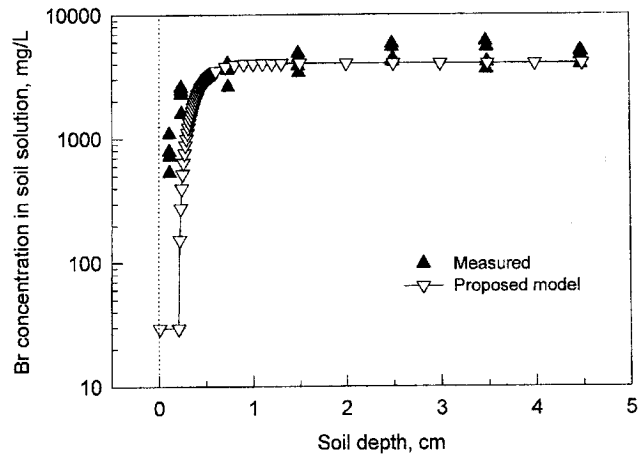
(b) Restricted infiltration



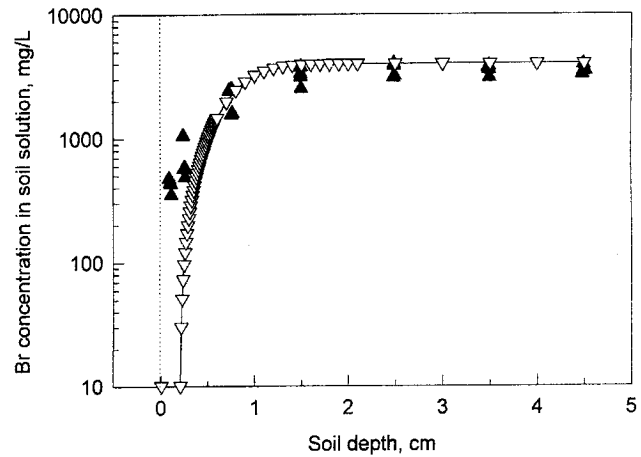
(c) Free infiltration

Figure 5—Comparison of predicted Br concentration in surface runoff with measured data of Ahuja and Lehman (1983) during 60-min rains under three infiltration conditions for the Ruston loam soil.

predict chemical loss in surface runoff during single rainfall event, but also indicates that the mixing depth is less than 2-3 mm as was reported by Zhang et al. (1991a,b) rather than 10 mm or even greater as was used in other



(a) Zero infiltration



(b) Restricted infiltration

Figure 6—Comparison of predicted Br concentration profile in soil water at the end of 60-min rains with those measured by Ahuja and Lehman (1983) for the Ruston loam soil.

models. The spatial distributions of chemical concentrations in soil solution with depth at the end of rainfall for Ruston loam are shown in figure 6. Similar agreements between measured and predicted data as compared to Ruston fine sandy loam were exhibited, showing that the model predicted concentration profiles reasonably well for both soils.

CONCLUSIONS

This study demonstrates that nonreactive chemical transfer from soil solution to surface runoff can be described as a two-rate process. A fast rate subprocess, which is limited to the mixing zone (< 2-3 mm), is responsible for an exponential depletion of chemicals in the zone. A slow rate subprocess, which can be simulated by the conventional CDE, describes chemical transfer into the mixing zone from the soil below. The fast rate subprocess prevails at earlier stages of rainfall, while the slow subprocess becomes predominant at later stages, especially for the cases when a perched water table is close to the soil surface (Zhang et al., 1997a). Successful applications of the coupling approach, which combines the mixing zone

concept with the CDE, indicate that the identification of the fast and slow rate subprocesses is useful. The separation of the two rate subprocesses not only allows for refinement of the mixing zone concept for use under poorly drained conditions, but also allows for direct application of the mixing concept under free drainage conditions.

The overall results showed that the coupling approach satisfactorily predicted chemical concentrations in both surface runoff and soil solution for nonreactive chemicals under poorly drained conditions. However, further tests on reactive chemicals such as herbicides are needed. The finite element scheme used in this study can be easily modified for this purpose by incorporating an adsorption/desorption isotherm into the formulation.

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