

Chemical transfer from soil solution to surface runoff

X. C. Zhang, D. Norton, and M. A. Nearing

USDA-ARS National Soil Erosion Research Laboratory, Purdue University, West Lafayette, Indiana

Abstract. Three soils were exposed to three consecutive simulated rains under dry, wet, and water table conditions with gypsum as a tracer placed at a 5-mm depth to evaluate the extent and nature of chemical transfer from soil solution to runoff and to determine the effective depth of the mixing zone. No electrolyte release was detected in runoff during the dry run for any of the soils. Electrical conductivity decreased exponentially with time during the initial stages of the wet and water table runs. Results were consistent with the complete mixing concept, but they also suggest that the assumption of no chemical transfer into the mixing zone from below should be modified. The effective mixing depth appears to be less than 3–4 mm. Two timescale processes were identified. The fast rate process, driven by raindrop impact and confined to the mixing zone, causes an exponential depletion of chemicals from that zone. The slow rate process, dominated by molecular diffusion and mechanical dispersion, describes chemical transfer to the mixing zone from below. The identification of the two processes indicates that the fast rate process is adequate for approximating chemical loss under free drainage conditions, while otherwise the slow rate process must be considered.

Introduction

Surface water and groundwater quality have been of great concern in the past 30 years. The potential for surface and groundwater contamination is shown to increase because of increasing use of pesticides in modern agricultural systems. No-till systems, which are growing in use, require increased pesticide use and surface-application practices. No-till systems preserve macropores such as worm and decayed root holes, which may exacerbate the potential for groundwater contamination [Steenhuis *et al.*, 1994; Ahuja *et al.*, 1993]. Amounts of chemicals entering macropores at the soil surface are dependent on their concentrations in surface runoff. Thus modeling the chemical release from soil to runoff is of great importance in determining both surface water and groundwater contamination potentials.

Chemical transfer to surface runoff involves adsorption and desorption of reactive chemicals by soil constituents, transport of dissolved chemicals to the soil surface by convection and ordinary or enhanced diffusion [Ahuja, 1990; Wallach *et al.*, 1989], transfer from soil water at or near the soil surface to runoff using film theory [Wallach *et al.*, 1988] or the chemical mixing concept, chemical dissolution into runoff [Bailey *et al.*, 1974], and release by return flow [Ahuja *et al.*, 1982]. Two distinct approaches have been taken in modeling chemical transfer from soil solution at or near the soil surface into surface runoff. One uses the film theory as proposed and developed by R. Wallach and his coworkers [Wallach *et al.*, 1988; Wallach and van Genuchten, 1990; Wallach, 1991]. This approach assumes that there exists a stagnant water film at the soil-runoff interface and that chemical transfer through the stagnant film is an ordinary molecular diffusion process. In contrast to the film theory, the other is a simplified and lumped parameter approach developed under a mixing zone concept. The mixing concept assumes there exists a mixing zone below

the soil surface in which rain water, soil solution water, and infiltrating water mix instantaneously and that there is no chemical transfer to the mixing zone from below. The mixing process was assumed to be either uniform and complete [Donigan *et al.*, 1977; Steenhuis *et al.*, 1994], uniform but incomplete [Frere *et al.*, 1980; Ingram and Woolhiser, 1980], or nonuniform and incomplete [Ahuja *et al.*, 1981].

Mixing zone depth or effective depth of rainfall-soil interaction is a critical parameter in the mixing approach because it determines how much of a chemical is available for extraction. A depth of 10 mm has been used in many models, such as CREAMS (chemicals, runoff, and erosion from agricultural management systems) [Frere *et al.*, 1980]. Several experimental studies have indicated that the mixing depth might be less than 10 mm. Through model calibration, Donigan *et al.* [1977] found the mixing zone depth ranged from 2 to 6 mm. Ahuja *et al.* [1981] applied ^{32}P at several soil depths and found effective average depth of interaction was between 2 to 3 mm. They also observed that the degree of mixing decreased exponentially with depth to as deep as 20 mm. Snyder and Woolhiser [1985] conducted a flume study with sand and tracer dye and reported that the effective mixing zone depths under infiltration conditions were mostly less than 10 mm.

The objectives of this study were (1) to evaluate the extent and nature of different processes involved in chemical transfer into surface runoff, (2) to test the uniform and complete mixing concept under various environmental conditions and to refine it if necessary, and (3) to estimate the mixing depth, if appropriate.

Background

For the complete, uniform, and instantaneous mixing model [Donigan *et al.*, 1977], a mass balance equation for nonreactive chemicals with negligible surface water ponding can be written as

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

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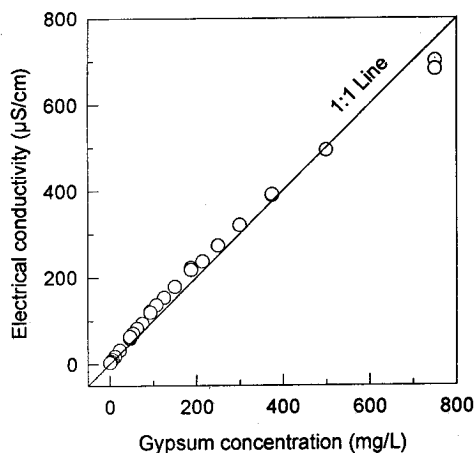


Figure 1. Relationship between gypsum concentrations and electrical conductivities of gypsum solutions.

where θ_s is the saturated volumetric water content in the mixing zone; z is the average mixing zone depth; C is the chemical concentration in surface runoff, soil water of the mixing zone, and infiltration water leaving the mixing zone; t is time; and R is a constant rainfall rate.

The mixing zone concept used in deriving (1) assumes that there exists a complete and uniform mixing zone where dissolved chemicals are apportioned between runoff, soil water in the mixing zone, and infiltrating water in proportion to the amounts of water in each phase; and there is no chemical transfer from the underlying layer to the mixing zone. These assumptions are usually invalid for cases when infiltration is restricted or significant amounts of chemicals are retained inside soil aggregates. The solution to (1) is

$$C(t) = C_0 \exp\left(-\frac{Rt}{z\theta_s}\right) \quad (2)$$

where C_0 is the initial concentration. This solution indicates that chemical concentration in runoff is a function of rainfall rate but is independent of water infiltration rate. The advantages of (2) are its simplicity and ease of use.

Diffusion is cited as another important process relative to the release of agrichemicals to surface water runoff. The steady state rate of one-dimensional diffusion through soils can be described by Fick's first law:

$$J = -D_s \frac{dC}{dx} \quad (3)$$

where J is the mass flux, C is the dissolved chemical concentration, x is the distance, and D_s is the diffusion coefficient through the soil medium. This coefficient can be estimated by Millington and Quirk [1961] as

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

in which D_w is the diffusion coefficient in water, θ is the soil water content, and ϕ is the soil porosity. The transient state of one-dimensional diffusion can be described by Fick's second law:

$$\theta_s \frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} \quad (5)$$

Materials and Methods

Analytical grade gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was used as a tracer in this study. Equilibrium solubility of gypsum is $1820 \mu\text{S/cm}$ ($\approx 1820 \text{ mg/L}$) at 25°C , and diffusivity in water at 25°C is $0.91 \times 10^{-5} \text{ cm}^2/\text{s}$. Electrical conductivity (EC) of a gypsum solution is linearly related to its concentration (Figure 1). Dissolution rate in water follows an inverse exponential decay function (Figure 2). Gypsum concentration increases rapidly within 2 min following the start of dissolution (reaches $>75\%$ of its solubility) and then "levels off" gradually.

Cecil sandy loam (clayey, kaolinitic, thermic Typic Kanhapludult), Miami silt loam (fine loamy, mixed, mesic Typic Hapludalf), and Heiden clay (fine, montmorillonitic, thermic Udic Chromustert) soils were studied. Selected soil properties are presented in Table 1. Particle size distribution was measured with the pipette method. Organic carbon was determined with dry combustion (model CHN-600, Leco Corporation, St. Joseph, Missouri). The pH values in water and 0.01 M CaCl_2 solution were measured in 1:1 solid to water mix. Cation-exchange capacity was determined by the NH_4OAc method [Thomas, 1982]. Soil samples from the tilled layer (Ap horizon) were air-dried and passed through a 4-mm sieve.

An oscillating type of rainfall simulator was used to deliver a constant rainfall intensity of 63 mm/h with the raindrop impact energy around 28 J/m^2 per millimeter of rain [Meyer and Harmon, 1979]. Runoff pans (450 by 320 mm) with three drainage holes in the bottom were packed with a 170-mm washed sand layer. A 25-mm layer of air-dried soil was packed over the sand layer in $<10\text{-mm}$ increments. Gypsum powder was uniformly applied on the soil surface at a 5-Mg/ha rate. A previous test showed that this rate was sufficient to provide a constant gypsum source throughout the course of the experiment. The pan side walls were carefully wiped to minimize gypsum contamination. A 5-mm soil layer was then packed over the gypsum layer. The packed average bulk densities and calculated porosities for three soils are given in Table 1. For the expansible Heiden clay soil, the final soil surface was packed 5 mm below the pan surface to allow for swelling. A Plexiglas splash guard projecting 200 mm above the pan surface on all sides was used to prevent soil and water loss from splash.

Two gypsum-treated pans and two control pans were run at the 0.05- and 0.005-m/m slopes for each soil. Three consecutive

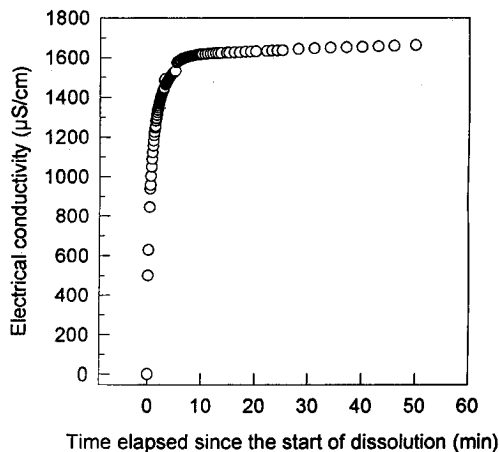


Figure 2. Kinetics of gypsum dissolution at 24°C .

Table 1. Selected Soil Properties for the Three Soils

Soil	Sand, g/kg	Clay, g/kg	Organic Matter, g/kg	Cation Exchange Capacity, cmol _e /kg	1:1 pH		Bulk Density, g/cm ³	Saturated Water Content, cm ³ /cm ³
					H ₂ O	CaCl ₂		
Cecil	729.0	88.5	1.1	3.35	5.88	5.44	1.46	0.448
Heiden	93.2	439.5	55.5	48.54	7.14	6.42	1.18	0.562
Miami	128.4	180.0	12.9	14.27	5.70	5.24	1.04	0.609

rains were made on each pan, and each rain lasted 50 min. Deionized water with EC < 10 $\mu\text{S}/\text{cm}$ was used for all the runs. The first rain (dry run) was delivered onto the dry soil to eliminate molecular diffusion prior to rainfall initiation. After the first rain, pans were covered with plastic sheets to prevent water evaporation. The second rain (wet run) was made on the wet soil 48 h following the first rain. Following the wet run, pans were again covered and allowed to stand for 34 hours; then a constant water table was applied from the drainage holes for 14 hours with the Tygon tubes. The water table was maintained at the same level as the downslope edge of the pan. Prior to rain, the tubes were clamped to prevent water infiltration.

Runoff was collected from a covered outlet flume in 1-L plastic bottles in 1- to 2-min intervals during the first 5–6 min after runoff initiation and in 3-min intervals afterwards. The

EC of runoff samples was taken immediately after each collection. Runoff volume was determined with the gravimetric method. After each run, sediment in all runoff samples from each pan and sediment deposited in the flume during the rain were combined for a total soil loss determination.

Background EC in rainwater measured from a rain gauge was subtracted from the measured EC of each runoff sample for both treatments. Then the EC of each runoff sample from the control treatment was further subtracted from the EC of the gypsum treatment for each corresponding time interval to correct for electrolyte release from the soil. This adjustment assumed there exists a complete and instantaneous mixing zone at or near the soil surface; therefore a difference in runoff volumes is not expected to considerably affect EC values. Nevertheless, the runoff rates of the control and the gypsum treatments were similar.

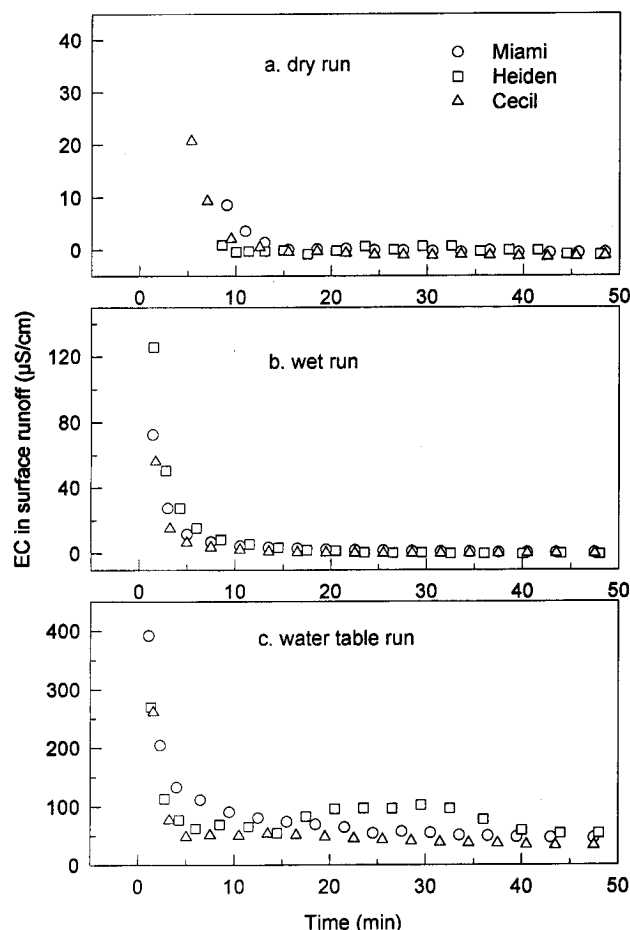


Figure 3. Changes of volume-averaged electrical conductivities of surface runoff with time during (a) dry run, (b) wet run, and (c) water table run for the three soils at the 5% slope.

Results and Discussion

Volume-averaged ECs in surface runoff for the three soils are plotted versus time in Figure 3 for three initial water content conditions. Because some ion exchange may have occurred on the exchange sites, measured EC could not be solely attributed to the gypsum electrolyte. However, assuming electrical neutrality, the EC values should closely estimate gypsum electrolyte in the surface runoff. Similar trends were exhibited for the three soils under each initial condition. During the first rain (dry run), no gypsum was detected in runoff for the Heiden soil, and only very little at the early stage of runoff for the Cecil and Miami soils (Figure 3a). The initial concentration was probably attributable to gypsum contamination, since gypsum dust could drift to the side walls of the pan during application. The results from the dry runs, where molecular diffusion before the initiation of rainfall was eliminated, clearly showed that the mixing zone depth was less than 5 mm under these experimental conditions. Runoff started between 6 to 10 min (≈ 6 to 10 mm rainfall depth) after the runoff initiation for all three soils. If piston-type infiltration is assumed, the 5-mm soil layer near the soil surface would have been saturated at the time when runoff began. This means molecular diffusion could become effective a few minutes after the initiation of rainfall.

The solute transport by molecular diffusion in this experiment can be estimated by solving (5) for a constant source boundary condition ($C_0(t) = 1820 \mu\text{S}/\text{cm}$ at the gypsum layer) and for a zero initial concentration ($C = 0$ at $t = 0$). The solution of Crank [1956] to (5) for a semi-infinite medium and under the above initial and boundary conditions is shown in Figure 4 for three selected times. A D_s of $0.41 \times 10^{-5} \text{ cm}^2/\text{s}$, which was estimated with (4) for the condition of $\theta_s = \phi = 0.55$, was used in the calculation. The result showed it took more than 50 min for gypsum to diffuse about 5 mm. This indicated that solute transport to the soil surface by direct

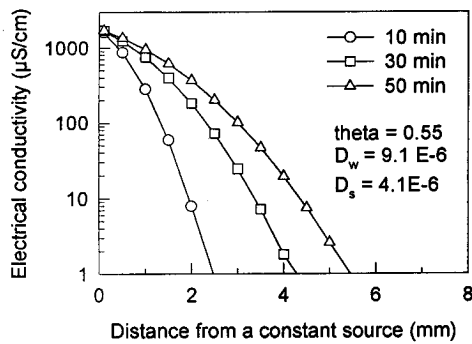


Figure 4. Solutions to (5) for a zero initial concentration and a constant concentration boundary condition in a semi-infinite medium for the selected parameter values.

molecular diffusion was unlikely under the dry run conditions. Although existence of a thin mixing layer at or near the soil surface could have enhanced the diffusion process by shortening the diffusion distance, high infiltration rates under dry soil conditions would have suppressed the upward diffusion process considerably through the downward convective transport by infiltrating water. Therefore it is reasonable that no gypsum was detected in surface runoff for the dry runs.

During the second rain (wet run), runoff began in less than 1 min after the initiation of rainfall, and considerable EC, ranging from 60 to 120 $\mu\text{S}/\text{cm}$, was measured in runoff (Figure 3b). This was because the gypsum was transferred to or near the soil surface by molecular diffusion during the 48-hour standing under the wet soil conditions. The gypsum concentration decreased rapidly to near zero within 5 min after the runoff initiation. This implies that there may exist a very thin mixing layer where gypsum electrolyte was completely mixed and rapidly depleted by both runoff and infiltrating water. The lack of rapid gypsum transfer from the underlying soil to the mixing zone led to a quick decline in the concentration during depletion and a near zero concentration after the depletion. Obviously, the downward displacement of gypsum by infiltrating water outweighed the upward molecular diffusion and mechanical dispersion. Small infiltration depths and very low infiltration rates, ranging from 3 to 8 mm/h (Table 2), were sufficient to eliminate or suppress gypsum transfer into the mixing zone by diffusion and mechanical dispersion. This can be supported by the following calculation. Under the steady state conditions, the gypsum flux to the soil surface per unit surface area can be calculated by (3), assuming $D_s = 0.41 \times 10^{-5}$ (for $\theta_s = 0.55$), $C_0 = 1820$, and $dx = 5$ mm. The flux leaving the soil surface per unit area can be estimated by $R \times C$. Equating the two fluxes resulted in an 8.5 $\mu\text{S}/\text{cm}$ concentration. If a mixing depth of 2.5 mm is assumed, the runoff concentration would then be doubled. This demonstrates that the complete and uniform mixing model, assuming negligible chemical transfer from the underlying layer to the mixing zone, as presented in (2), is valid for the free drainage or under the infiltration conditions. This observation agrees with the findings by Ahuja and Lehman [1983] and Snyder and Woolhiser [1985].

Runoff started immediately following the onset of rainfall during the third rain (water table run) since water infiltration was eliminated. The initial ECs were much greater than those from the previous runs. The gypsum concentrations declined rapidly within the first 5 min and then leveled off to relatively

high levels for all three soils (Figure 3c). Longer tails of the concentration curves as compared to the two previous runs were because the downward movement of the gypsum electrolytes by infiltrating water (which counteracts the upward molecular diffusion) was eliminated under the zero infiltration conditions. The overall results indicate a fast depletion of gypsum in the mixing zone and a constant supply of gypsum to the mixing zone by molecular diffusion. The convex curvature of the gypsum concentration curve for the Heiden soil might be caused by a return flow. The Heiden clay soil, which is less susceptible to surface sealing because of higher organic matter content and more stable aggregates, would have had higher near surface return flow rates.

Figures 3b and 3c are plotted with time in a semilogarithmic scale in Figure 5. These plots should be straight lines if (2) is valid. Despite the lack of linearity on each plot in Figure 5a, a straight line can be reasonably fitted to the data points for the wet runs under free drainage conditions. The coefficients of determination (r^2) for the transformed data are 0.90 for Miami, 0.96 for Cecil, and 0.95 for Heiden. If the concentrations in the lower range (<1 for the Cecil and Heiden, <5 $\mu\text{S}/\text{cm}$ for the Miami) are excluded, the linearity is improved. The overall fitted straight lines might underestimate the gypsum loss in runoff in the lower concentration range, but the underestimation was negligible for most cases. This trend was also reported by Ahuja and Lehman [1983]. The nonlinearity in the low concentration range was possibly caused by the slow release of gypsum electrolyte that was detained inside soil aggregates and did not mix completely and instantaneously with soil water in the mixing zone, as assumed in the mixing model. However, (2) is expected to predict total chemical loss reasonably well under free drainage conditions since most of chemical loss is from the early stage of runoff.

For the third rain (Figure 5b), two straight lines must be fitted to the data points for each soil because the assumption used in deriving (2), that no chemical transfer took place to the mixing zone from the lower soil, was invalid under the zero infiltration conditions. Obviously, significant amounts of gypsum were transported into the mixing zone by diffusion. This

Table 2. Replicate Means of Selected Variables for Three Soils and Three Rainfall Events

Run	Final Infiltration Rate,* mm/h	Total Infiltration Depth, mm	Chemical Loss by Fast Rate Process,† %	Total Soil Loss per Event, g
<i>Cecil</i>				
Dry	6.0	15.6	NA	27.2
Wet	3.5	5.4	81.8	XX
Water table	0	T	25.9	37.2
<i>Heiden</i>				
Dry	10.1	20.0	NA	28.3
Wet	7.3	7.9	80.1	43.9
Water table	0	T	20.1	64.8
<i>Miami</i>				
Dry	14.5	22.8	NA	43.8
Wet	5.7	6.9	61.3	52.7
Water table	0	T	27.8	72.6

NA, not appropriate; XX, missing data; T, trace amount.

*Averaged during the last 20 min of rain.

†Percent gypsum loss in runoff during the first 6, 7, and 8 min of rainfall for Cecil, Heiden, and Miami, respectively.

observation does not necessarily mean the mixing zone concept is invalid; however, the conditions under which (2) was developed must be modified, and a chemical flux to the mixing zone from the underlying soil must be included.

The need to fit two straight lines in Figure 5b reveals that two distinct processes, which operate on different rates or timescales, can be identified. The fast rate process, which operates on a shorter timescale, is responsible for the depletion of existing chemicals in the soil solution within the mixing zone. This process is driven mainly by the mixing action imparted by mechanical raindrop impact and prevails during a short period of time following the initiation of runoff. The fast rate process is presumably confined to the mixing zone, and therefore, the mixing zone depth is somewhat dependent on raindrop impact energy and surface conditions. The slow rate process, which operates on a longer timescale, is a rate-limiting process which controls the chemical transfer from the underlying soil into the mixing zone. This process is attributed to molecular diffusion and mechanical dispersion and is influenced by soil water content, pore size distribution, and water infiltration rate. The effective depth or distance in which chemicals are transported into the mixing zone is time dependent. The fast rate process prevails over the slow rate process under free drainage conditions and accounts for most of the chemical loss in runoff, whereas the slow process becomes significant when a perched water table is close to the soil surface or when infiltration rate is severely restricted. This is supported by the data in Table 2. The fast rate process contributed about 82, 80, and 61% of the total loss of dissolved gypsum in runoff during the first 6–8 min in the second rain (free drainage) for the Cecil, Heiden, and Miami soils, respectively; while it only accounted for 26, 20, and 28% during the third rain (zero infiltration).

Since the fast rate process, which is consistent with the mixing zone concept, prevails in early runoff stage, (2) is

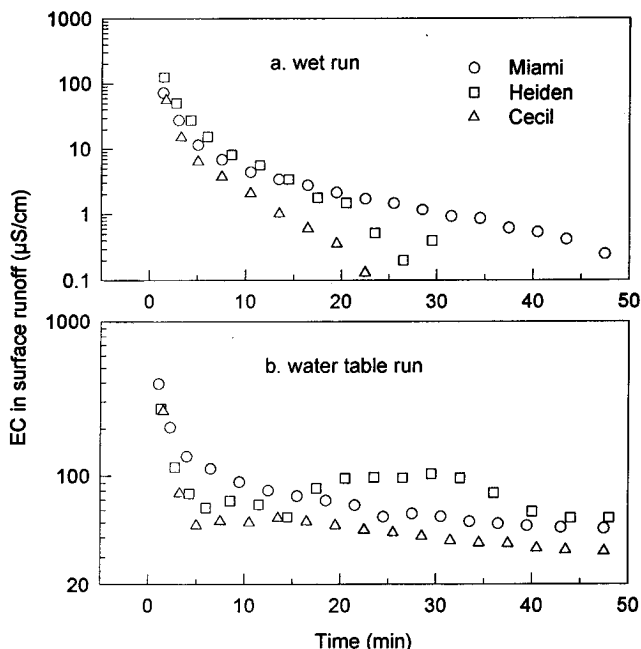


Figure 5. Common-log transformed electrical conductivities are plotted with time during (a) wet run and (b) water table run at the 5% slope for the three soils.

Table 3. Estimated Mixing Zone Depth for the Fast Rate Process With the Model: $\ln C = \ln C_0 - Rt/(z\theta_s)$

Run	Mixing Depth, mm	r^2
<i>Cecil</i>		
Wet	4.6	0.94
Water table	3.5	0.98
<i>Heiden</i>		
Wet	4.3	0.95
Water table	3.4	0.97
<i>Miami</i>		
Wet	4.6	0.95
Water table	3.2	0.99

pertinent to simulate gypsum concentration in runoff during this stage. The log transformed form of (2), that is, $\ln C = \ln C_0 - Rt/(z\theta_s)$, was fitted to the data points from the early runoff stage, and the results are tabulated in Table 3. The predicted mixing zone depths for the second and third runs were less than 5 mm (probably less than 3–4 mm). These values are in agreement with the direct measurement during the first run and the results reported in earlier studies [Donigan *et al.*, 1977; Ahuja *et al.*, 1981]. The existence of a thin complete mixing layer at the soil surface, as evidenced by the formation of large-sized raindrop craters on the unsealed soil surfaces, can be explained by vigorous dislodgment of surface water and soil materials. Bradford and Foster [1995] reported that the steady state splash rate of soil materials was 2 to 5 kg/m² per hour for the Miami and Heiden soils. Indirect mixing due to pumping action of raindrop impact by fluctuating near-surface pressure gradients as proposed by Ahuja [1990] may also contribute to the mixing processes, especially for cases when soil surface is sealed. Erosion depths calculated using the total soil losses of Table 2 and the bulk densities of Table 1 for the dry runs under the dominant sheet erosion conditions, were 0.1, 0.3, and 0.2 mm for the Cecil, Miami, and Heiden soils, respectively. These erosion depths would change the initial gypsum depth only slightly. The cumulative erosion depths during the subsequent rains would not affect the results because the gypsum depth was not a primary concern. Interestingly, the perched water table increased soil loss for all the three soils. This indicates that the return flow or seepage caused by an impermeable layer will increase soil and chemical losses in both the dissolved and adsorbed phases for adsorbed chemicals.

The curves of Figure 5b are nonlinear because the assumption that there was no chemical transfer into mixing zone from the underlying soil was not true. The separation of the two-rate processes allows the modification of (2) by defining an input flux term that simulates the slow rate process. For simplicity, the zero infiltration case of the third run is discussed here. Based on mass balance, (1) can be modified as

$$(h + z\theta_s) \frac{dC}{dt} + RC - J_d = 0 \quad (6)$$

where J_d is the input flux from the underlying soil layer to the mixing zone and h is the average ponding or flow depth and is negligible in this study (the estimated average h with Manning's equation for a smooth surface is about 0.13 mm). Since there is no mechanical dispersion for the zero infiltration case,

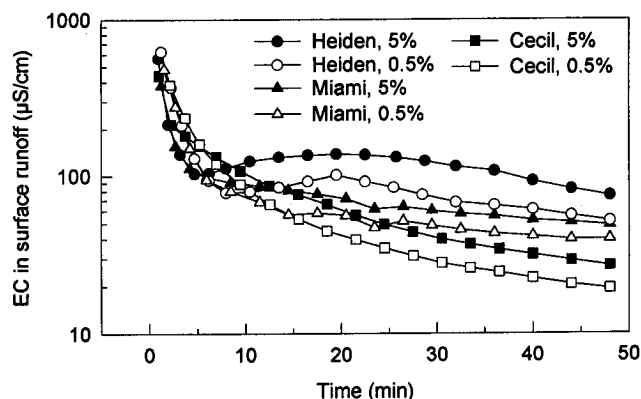


Figure 6. Volume-averaged electrical conductivities are plotted in a semicommon-logarithmic scale with time during water table run at the two slopes for the three soils.

the J_d can then be modeled as a molecular diffusion process by (3) as

$$J_d = D_s \frac{C_0 - C}{\lambda} \quad (7)$$

in which λ is the diffusion distance (equals to 5 mm minus the mixing zone depth z). The solution to (6) and (7) is given as

$$C = \frac{D_s C_0}{\lambda R + D_s} + \left(C_0 - \frac{D_s C_0}{\lambda R + D_s} \right) \exp \left(- \frac{\lambda R + D_s}{\lambda z \theta_s} t \right) \quad (8)$$

where the variables are as defined earlier. This solution is composed of two terms that separately represent the fast and slow rate processes as discussed above. The fast rate process (second part) decreases exponentially with time, while the slow rate process remains constant with time. If the averaged mixing depth of 3.4 mm is taken from Table 3 for the water table runs, the steady state transport of gypsum to the mixing zone by the slow process, calculated with the first part in (8), would be 20, 27, and 30 $\mu\text{S}/\text{cm}$ for Cecil, Miami, and Heiden soils, respectively. Values of D_s used in the calculation were estimated from (4) using the porosities given in Table 1. After adjusting gypsum fluxes for return flow contributions, which can be roughly estimated from Figure 6, the gypsum fluxes at steady state agreed reasonably well with the observed values near the end of each run for the three soils (Figure 5b). This result indicates that transport by molecular diffusion can be significant under high concentration gradients and zero infiltration rates.

Similar to the above case study, a more general process-based model can be proposed. The transport of nonreactive chemicals below the mixing zone under the influence of infiltration water can be modeled with the conventional convection-diffusion equation:

$$\theta_s \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} - (R - q)C \right] \quad (9)$$

where x is the depth, D is the sum of diffusion and mechanical dispersion coefficients, and q is the runoff rate. Based on (9) and the mass balance equation in the mixing zone for the complete and uniform mixing case, the flux boundary condition at the interface (at $x = 0$, $t > 0$) between the mixing zone and the underlying soil can be derived as

$$-D \frac{\partial C}{\partial x} + RC = -(h + z\theta_s) \frac{\partial C}{\partial t} \quad (10)$$

The solution to (9) and (10) can be obtained easily with numerical methods. Runoff concentration will be equal to C at $x = 0$.

The overall results of this study showed that the experimental data were consistent with the mixing concept. A mixing layer, though very thin, does exist and can be explained by the vigorous splash dislodgment of surface water and soil materials due to raindrop impact. *Sharma et al.* [1995] predicted that dislodgment or the detachment rate of soil materials from the unsealed soil surface ranged from 5 to 25 $\text{kg m}^{-2} \text{h}^{-1}$ for most soils with less than 40% clay fractions. This result supports the thin mixing layer approach. In contrast to the mixing concept, the film theory approach, which assumes that there exists a stagnant water film at the soil surface, describes the chemical transfer to surface runoff as an ordinary molecular diffusion process [*Wallach et al.*, 1988]. This approach tended to underestimate gypsum loss in surface runoff as compared to the mixing approach. This was because the absence of the mixing layer would have increased the diffusion distance between the gypsum layer and the soil surface. The inadequacy of the film theory in describing chemical transfer to surface runoff at the early stage of runoff was also shown in the paper of *Wallach et al.* [1988], as pointed out by *Ahuja* [1990]. *Wallach et al.* [1988] had to superimpose an arbitrary exponential decay term in order to match measured data. This exponential decay term was later termed as the fast timescale process that describes the lateral and convective transport of chemicals in runoff or by overland flow [*Wallach*, 1991] and was further justified by assuming that initial chemical concentration in surface water at the time of runoff initiation was equal to the concentration in soil solution at the soil surface by *Wallach and Shabtai* [1993]. The assumption of this initial condition is consistent with the mixing concept rather than the film theory. Also, *Ahuja* [1990] has demonstrated that chemical transfer to the soil surface by ordinary molecular diffusion and mechanic dispersion was not rapid enough to provide a good match with measured data. An additional diffusion term known as accelerated diffusion due to raindrop impact was required. The calibrated values of the accelerated diffusion were equal to 2.5 to 19 times the ordinary molecular diffusion coefficient. Furthermore, with an infiltration water flux penetrating the soil surface, it is unlikely that a stagnant water film at the soil-water interface could exist.

An additional experiment was conducted during this study at 0.005- and 0.05-m/m slopes in a parallel manner to examine the contribution of chemical runoff from return flow. The results from the water table runs are shown in Figure 6 for the three soils. No appreciable differences in runoff concentrations were observed under free drainage conditions compared to water table runs at the two slopes. The runoff concentrations from the 0.05-m/m slope were consistently greater than those from the 0.005-m/m slope for all the three soils, indicating that the gypsum transport by return flow under the experimental settings was significant. This finding agreed with those reported by *Ahuja et al.* [1982].

Conclusions

There exists an effective mixing depth where complete and uniform mixing of runoff, soil water, and infiltration water takes place. This mixing depth appeared to be less than 3–4

mm, rather than 10 mm as often used in literature. The model of (2), which is based upon the complete and uniform mixing concept, is valid only under free drainage conditions and must be modified under restricted infiltration conditions by introducing a chemical flux to describe chemical transfer from the underlying soil into the mixing zone. This refinement, which allows chemical transfer from below into the mixing zone, enables this approach to be used for predicting chemical concentrations under zero infiltration or poorly drained conditions. The chemical flux into the mixing zone from below can be described by conventional convection-diffusion equations such as (9).

Two rate processes were proposed to describe chemical transfer from the soil solution to surface runoff. A fast rate process, which operates on a shorter timescale and is driven by raindrop impact, causes an exponential depletion of dissolved chemicals in the mixing zone. A slow rate process, which operates on a longer timescale and is dominated by molecular diffusion and flow mechanical dispersion, simulates chemical transfer from the underlying soil to the mixing zone. This process becomes significant during a prolonged rainfall event or for cases when a water table is close to the soil surface. The identification of the two processes allows the simplification of loss prediction by using the mixing concept of (2) for free drainage conditions. This has practical significance because most parameters needed by physically based models are usually unavailable; however, a sophisticated model including the two processes is needed for poorly drained conditions or prolonged rainfall events. This also implies that updating chemical concentration between rains based on the slow rate process is necessary in continuous simulation models.

Although the gypsum was artificially applied at the 5-mm depth, the results drawn from this study have direct indications for predicting chemical runoff of nonreactive agrichemicals such as nitrate-N. The concept and findings can also be easily modified to predict reactive chemical loss in runoff such as pesticides by including an adsorption/desorption isotherm. The study indicates updating or predicting the initial chemical concentration in the mixing zone prior to a storm is critical for chemical loss prediction, and small time steps during the storm must be used in order to predict chemical runoff more accurately because of the rapid change of chemical concentrations during the storm. It should also be pointed out that the proposed models are point models and do not simulate the chemical transport over the land surfaces or interactions with sediment.

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M. A. Nearing, D. Norton, and X. C. Zhang, USDA-ARS National Soil Erosion Research Laboratory, Purdue University, 1196 Soil Building, West Lafayette, IN 47907-1196. (e-mail: zhangxun@ecn.purdue.edu)

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