Modeling Soil Solute Release into Runoff and Transport with Runoff on a Loess Slope

Wencai Dong[1] and Quanjiu Wang[2]

Abstract: Rainfall results in the transfer of chemicals from soil to surface runoff. A physically-based solute transport model was developed for estimating the solute concentration in runoff originating from the soil surface. The model accounts for the effects of soil infiltration, raindrops, the water runoff rate, and the return flow, all of which influence the concentration of the solutes in the runoff. It was assumed that the depth of mixing zone changed with the varieties of the raindrop hits, return flow, and overland flow. It was also assumed that runoff and soil in the mixing zone mixed instantaneously and that the solute in the soil beneath the mixing zone was moved to the mixing zone by diffusion. The mixing zone was included in the model and was based on the deposited layer or shield concept. To test the model, laboratory experiments were carried out that used two soil types that were exposed to simulated rainfall. The results simulated by the model were highly correlated with the experimental data. In the first few minutes after rainfall began, the solute concentration in the runoff was mainly controlled by the rainfall rate and solute concentration in the mixing zone; higher solute levels in the mixing zone resulted in higher solute concentrations in runoff. When the solute concentration in the runoff stabilized, the solute concentration in the runoff was mainly controlled by the diffusion of solutes from the soil beneath the mixing zone. The simulated data showed a high level of correlation with the measured data for both runoff volume and solute concentration in the runoff. This demonstrates that the model captured the temporal behavior of the runoff and solute transport in the runoff. **DOI:** [10.1061/(ASCE)HE.1943-5584.0000622](). © 2013 *American Society of Civil Engineers*.

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Introduction

Rainfall increases the transfer of chemicals from soil to surface runoff and may cause nonpoint source pollution in the water body that receives the runoff. The development of a physically-based model to simulate soil solute transport with runoff would provide a better understanding of soil solute transport mechanisms and assist in the development of effective methods to control nutrient loss from soils and the pollution of waterways. Previous models have been developed based on the physical processes of soil solute transfer in runoff. The exchange layer, or mixing zone framework, was the most commonly used approach for models of chemical transport into runoff (Steenhuis and Walter 1980; Ahuja et al. 1981; Ahuja and Lehman 1983; Wallach et al. 1988; Steenhuis et al. 1994; Steenhuis 2001; Zhang et al. 1997, 1999; Gao et al. 2004, 2005; Deng et al. 2005; Walter et al. 2007). In the development of early models,

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it was assumed that rainwater mixes completely and uniformly with a thin zone of surface soil and soil water (Donigian et al. 1977; Steenhuis and Walter 1980). Ahuja et al. (1981) used ^{32}P as a tracer, placing sources of this radioisotope on the soil surface and at 5-mm-depth intervals in different soil samples, to show that the interaction between the droplet-liquid-solid was greatest at the soil surface and decreased very rapidly with soil depth. On the basis of their results, Ahuja and Lehman (1983) proposed the concept of an effective average depth of interaction (EDI), but noted that the EDI model was inappropriate for conditions under which water infiltration was very low or inhibited. Under such conditions, some authors suggested that the overall transfer process should be regarded as an accelerated diffusion process, and that a conventional convective-dispersion equation could be used to describe solute transport, with the transfer coefficients varying as a function of the depth. This accelerated diffusion process has been supported by numerous experimental studies (Green and Houke 1979; Ingram and Woolhiser 1980; Ahuja et al. 1982; Havis 1986; Sharpley et al. 1981). The other popular types of chemical transfer models assumed that diffusionlike processes control chemical transfer between soil and runoff, whereas rain impact was considered to be negligible (Wallach et al. 1988, 1989; Wallach 1991; Wallach and van Genuchten 1990). The effective depth of transfer (EDT) model assumed that the solute concentration in the EDT was equal to the soil surface concentration in the absence of infiltration (Wallach et al. 1989). Wang et al. (1998, 2002a) carried out laboratory experiments to evaluate the different methods for calculating the raindrop and soil surface interaction depth and developed the equivalent interacting depth (EID) and equivalent transfer depth (ETD) models. These experiments showed that the EID and ETD models were suitable for loess soils. Furthermore, based on the effective mixing depth concept, Wang and Wang (2010) developed a mathematical model describing the soil solute transport with

JOURNAL OF HYDROLOGIC ENGINEERING © ASCE / MAY 2013 / **527**

J. Hydrol. Eng., 2013, 18(5): 527-535

surface runoff on a loess slope and demonstrated that the incomplete mixing model was more appropriate than the complete mixing model. The results of Zhang et al. (1997) were consistent with the predictions of the completely mixed model; these authors reported that the effective mixing depth appeared to be less than 3–4 mm. Tong et al. (2009) used a two-layer system model to describe the transfer of chemicals to surface runoff; in this model, the mixing zone and surface runoff were combined into a single layer. The transfer coefficient or exchange rate was used to describe the solute that was exchanged between the active surface layer and the overlying flow (Wallach et al. 1988, 2001; Wang et al. 1999; Deng et al. 2005).

Both raindrop-driven processes and diffusion played important roles in the transfer of chemicals from soil to surface runoff. Gao et al. (2004, 2005) and Walter et al. (2007) developed physically-based solute transport models that assumed that chemicals near the surface of the soil were most likely to run off as a result of raindrop impact. Chemicals in the deeper soil then diffused into a surface layer, or exchange layer, through diffusion. Raindrop-driven processes occurred in both the drop-solid and the drop-liquid-solid domains. The hydrodynamics of the drop-liquid impact process were important in the drop-liquid-solid domain.

Fluid movements can be characterized by two well-known hydrodynamic phenomena: impinging and Rayleigh jets (Wang 1970). Impinging jets are formed by the outward motion of water from an impact site and often give rise to craters, as described by Mutchler (1967). The crater decays when the surface tension of the water and the energy gradient cause water to move into the impact site, producing what is known as the Rayleigh jet phenomenon. These nearly instantaneous outward and inward movements of water generate shear stress, which reaches its peak around the edge of the crater and is directed radially outwards. Impingement and Rayleigh jets may contribute to the mixing processes, especially when runoff occurs and water and soil are mixed. The laboratory experiments performed by Zhang et al. (1997) and Ahuja et al. (1982) showed that return flow may occur under some conditions, and the depth of the exchange layer was very thin. Hairsine and Rose (1991) developed a soil erosion model that described the erosion transport of the multiparticle sizes in sediment for rain-impacted flows in the absence of entrainment in overland flow. Heilig et al. (2001) used a simple experiment to test the model developed by Hairsine and Rose (1991). Such research has shown that the mixing zone could instead be described as the deposited layer or in terms of the shield concept. The shield was included in this model, which was further developed to simulate solute loss with runoff by Gao et al. (2004, 2005); subsequently, Walter et al. (2007) tested this model.

In this study, a physically-based solute transport model was developed for soil that underwent water infiltration on the Loess Plateau in China. There was no model calibration or fitting for this model, which differed from a variety of other similar models published in the 1990s. The mixing zone was included in this model and was based on the deposited layer or shield concept described by Hairsine and Rose (1991). However, this model differed from the model developed by Gao et al. (2004, 2005), which was also based on the deposited layer and shield concept. There was not the detachability of the bare soil a (Gao et al. 2004, 2005; Walter et al. 2007), which was difficult to determine for different kinds of soil in the model. Specifically, this model did not attempt to directly assess how the raindrops, runoff flow, and return flow impacted the transport of solutes from the soil surface to the runoff. Instead, these terms were replaced by the variable: the change in the depth of the mixing zone. Laboratory experiments were performed to assess the accuracy of the new model's predictions.

Theory

The focus was on the transport of dissolved chemicals during soil infiltration on the Loess Plateau in China and when infiltration excess was the main contributor to runoff. Soils covering the Loess Plateau are derived from deep loess deposits. Intense summer rainstorms are typical of the regional arid to semiarid climate.

The model included mass balance equations for both the water flow and chemical transport in the soil profile and surface runoff. In the conceptual model, which was similar to that described by Gao et al. (2004, 2005), the soil-water system was divided into three vertically-distributed horizontal layers (Fig. 1): the runoff or surface ponding water, an exchange-zone or mixing zone, and the underlying soil. The concept of a deposited layer or shield proposed by Hairsine and Rose (1991) was extended as mixing zone and it was assumed that runoff and water from the mixing zone mixed completely and instantaneously when hit by raindrops. It was also assumed that the depth of the mixing zone changed with raindrop splash, water flow, and return flow. Therefore, it was not necessary to consider how the raindrop splash, water flow, and return flow influenced the solute transport into surface runoff from the soil profile, because the solute concentrations in the runoff and the mixing zone were assumed to be identical. The chemical fluxed into the mixing zone from beneath the mixing zone can be described by a diffusion process, and the underlying soil solute transport can be described by convection-diffusion equations.

Flow Equations

Water movement included infiltration and overland flow. For simplicity, water movement in the soil profile was considered to be a vertical one-dimensional movement during rainfall. One-dimensional vertical soil water movement can be described by the Richards' equation, as follows:

$$\frac{\partial \theta(z,t)}{\partial t} = \frac{\partial}{\partial z}\left[D(\theta)\frac{\partial \theta(z,t)}{\partial z} - k(\theta)\right] \tag{1}$$

where t = time (min); θ = water content (%); $D(\theta)$ = soil water diffusivity (cm²/min); $k(\theta)$ = unsaturated hydraulic conductivity (cm/min); $\theta(z,t)$ = water content at depth z(%); and z = vertical
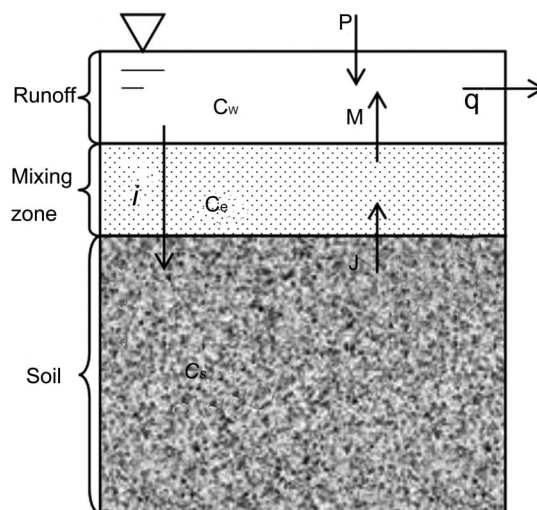

Fig. 1. Conceptual schematic of the physical and chemical transport processes of the model; M = total raindrop splash, overland flow, and return flow function

soil depth (cm). The initial and boundary conditions imposed on Eq. (1) are

$$
\begin{aligned}
\theta &= \theta_i & t &= 0 & z &\geq 0 \\
D(\theta)\frac{\partial \theta(z,t)}{\partial z} - k(\theta) &= -R & t &> 0 & z &= 0 \\
D(\theta)\frac{\partial \theta(z,t)}{\partial z} - k(\theta) &= -i & 0 &< t < tp & z &= 0 \\
\theta &= \theta_i & t &> 0 & z &\to \infty
\end{aligned}
\tag{2}
$$

where R = infiltration capacity (cm/min); θ_i = initial soil water content (%); tp = time period over which runoff takes place (min); and i = rainfall intensity (cm/min).

Overland flow was generally described by the kinematic wave equation—an approximation of the Saint-Venant equations, which were one-dimensional laws of conservation of mass and momentum for shallow longitudinal water flow, allowing for some vertical infiltration (Woolhiser 1975; Singh 1996; Liu and Singh 2004). The kinematic wave equation (Woolhiser and Ligget 1967) can be expressed as

$$
\frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} = p\cos\phi - i \qquad q = \frac{1}{n}h^{5/3}s_0^{1/2}
\tag{3}
$$

where h = depth of overland flow (cm); t = time (min); q = flux of the flow (l); x = distance along the flow direction (cm); p = rainfall intensity (cm/min); ϕ = slope inclination (°); i = infiltration capacity of the soil (cm/min); n = Manning roughness coefficient; and s_0 = slope gradient, $s_0 = \sin(\theta)$.

The initial and boundary conditions imposed on Eq. (3) are

$$
h(x,0) = 0 \quad \text{for } 0 \leq x \leq L \qquad h(0,t) = 0 \quad \text{for } 0 \leq t \leq \infty
\tag{4}
$$

where L = length of the overland flow along a uniform slope for homogeneous soil (cm). The simulation of soil water movement and overland flow then reduces to the solution of Eqs. (1) and (3), subject to Eqs. (2) and (4).

Solute Transport Equations

The solute transport into runoff at the mixing zone was a result of raindrops, overland flow, and return flow being completely mixed instantaneously. Solute transported from the soil profile into the mixing zone occurred by diffusion.

Solute transport was generally described by the advection-dispersion equation (ADE) (Kiely 1997; Martin and McCutcheon 1999; Deng 2002; Deng et al. 2005). The conceptual model for overland solute transport was shown in Fig. 1. Based on the mass equation, the ADE can be expressed as

$$
\frac{\partial hC}{\partial t} + \frac{\partial QC}{\partial x} = J\frac{h}{h + de\theta_e} + PC_r - iC
\tag{5}
$$

where Q = volumetric runoff flux per unit width (l); C = chemical solute concentration in the runoff (mg/l); ∂x = length per unit (cm); P = rainfall intensity (cm/min); h = depth of runoff (cm); de = depth of the exchange layer (cm); θ_e = water content in the mixing zone (cm^3/cm^{-3}); C_r = chemical solute concentration in the rainwater (mg/l); t = time (min); and J = diffusion rate of the solute from the soil below the mixing zone, which is described by Fick's law: $J = -D_S\frac{\partial C_S}{\partial z}$, where D_S = dispersivity of the chemical in the soil; C_S = solute concentration in the soil water below the mixing zone (mg/l); and z = vertical dimension (cm).

The initial and boundary conditions for Eq. (5) are

$$
C(x,t) = C_O \quad t = t_p \qquad C(0,t) = C_{ss} \quad t > t_p
\tag{6}
$$

where C_O = solute concentration in the mixing zone (mg/min) when the runoff takes place; C_{ss} = solute concentration at the mixing zone (mg/l); and t_p = time from when the rainfall started to when runoff took place (min).

Solute transport within the soil profile below the mixing zone was controlled by both infiltration and diffusion and can be described by the following advection-diffusion equation:

$$
\frac{\partial \alpha C_s}{\partial t} = \frac{\partial}{\partial z}\left(D_s\frac{\partial C_s}{\partial z} - iC_s\right)
\tag{7}
$$

where C_s = chemical concentration in the soil water below the mixing zone (mg/l); $\alpha = \rho_b k_p + \theta$, ρ_b is the dry soil bulk density; and k_p = constant partition coefficient. For nonadsorbed chemicals, α = soil moisture θ; t = time (min); z = vertical dimension (cm); i = infiltration rate in the soil (cm/min); and D_s = dispersivity of the chemical in the soil and is taken as the sum of the molecular diffusivity and the mechanical diffusion coefficient (cm^2/s) (Bresler 1973; Bear and Bachmat 1990; Ahuja 1990).

The boundary condition at the underlying soil surface for Eq. (7) was related to two stages during rainfall-runoff.

$$
\begin{aligned}
d[\theta(0,t)C(0,t)]/dt &= J(0,t) - iC_s(0,t) & 0 &\leq t \leq t_p \\
d[\theta(0,t)C(0,t)]/dt &= J(0,t) - iC_s(0,t) + iC(0,t) & t_p &\leq t
\end{aligned}
\tag{8}
$$

The initial condition was

$$
C(z,0) = C_{so}
\tag{9}
$$

where C_{so} = chemical concentration in the soil (mg/l) when rainfall begins.

Experimental Methods

The experiment was established in the artificial rainfall simulation laboratory at the Institute of Soil and Water Conservation, Chinese Academy of Sciences, in Shaanxi province, China, from April–September 2010. The basic components of the rainfall simulator were computerized rain intensity and rain simulator, and the nozzles had a height of 15 m from the soil surface. Six soil flumes (made of steel) with the following dimensions were used: 1.00 m length × 0.40 m width × 0.50 m height. The depth of soil in the flumes was 0.35 m, which was enough for infiltration to occur, and meant that the soil at the base of the flumes remained dry. The remaining 0.15 m of the flume was used to hold back the raindrop splash. The flume gradient could be changed from 0–30° (Fig. 2).
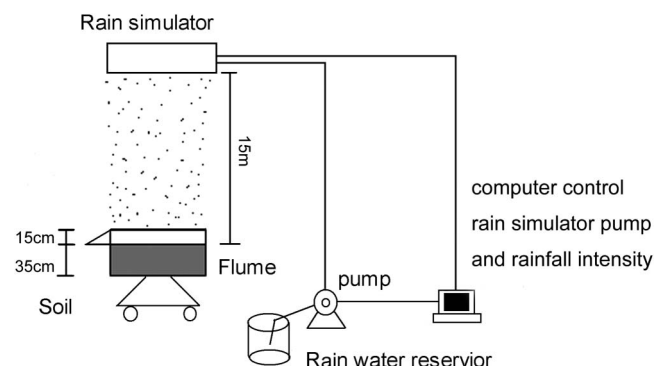

Fig. 2. Schematic of the experimental apparatus and setup

JOURNAL OF HYDROLOGIC ENGINEERING © ASCE / MAY 2013 / **529**

J. Hydrol. Eng., 2013, 18(5): 527-535

Two soil types (loam and sandy loam) were air dried (approximately 2%, gravimetrically) prior to the start of the experiment and then exposed to simulated rainfall. The simulated rainfall intensity was 0.15 ± 0.004 and 0.16 ± 0.004 mm/min for the loam and sandy loam, respectively. In this experiment, the initial soil moisture content was 13.56% for loam and 12.48% for sandy loam. The slope of the soil surface had a gradient of 5°. In a further experiment, both soil types were exposed to a rainfall intensity of 0.10 ± 0.004 mm/min, and vertical and horizontal measurements were taken to estimate the soils' basic hydraulic parameters.

The loam soil samples were collected from unfarmed land in Yangling, in the Shaanxi province of China; sandy loam samples were collected from Ansai, which is also in Shaanxi province. The physical and chemical properties of the soils are shown in Table 1.

The soil samples were sieved (0.004 m aperture) to remove coarse rock and debris, and then air dried. Bromide was used as a tracer. It was dissolved in water and added to the test soils based on their designed soil water content and bromide concentration; the soil was then thoroughly mixed. The soil flume was filled layer by layer to achieve a dry bulk density of 1.35 g · cm⁻³. To obtain a flat surface, a sharp-edged straight knife was used to remove excess soil, and then the soil was gently tapped with an iron block until it reached the required density. The surface of the soil was then covered with plastic. The rainfall experiment was conducted after the soil surface had been covered with plastic for 24 h. During the experiment, the water outflow was systematically collected in plastic containers from a hole in the flumes every min to analyze the amount of runoff and the concentrations of sediment and solutes within it. During the period of simulated rainfall, dry tracing with potassium permanganate was used to measure the overland flow velocity. When the rainfall stopped, soil samples were immediately taken along a vertical section at 10-mm intervals to analyze their water contents and solute concentrations; the depth of the mixing zone was also measured. The bromide content in the runoff and soil sample were measured with an ion meter, and the soil water content was measured by drying the sample to constant weight. The sediment was collected on a filter paper and measured by drying the sample to constant weight.

The agreement between the model simulations and the measured data was quantified using the root mean square error (RMSE) method (Willmott 1982). The RMSE can be expressed as

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (p_i - o_i)^2}{N}} \tag{10}$$

where N = total number of data points; p_i = simulated data point; and o_i = measured data point.

Parameter Determination and Finalization of the Model

Soil Hydraulic Parameters

The soil water diffusivity $D(\theta)$ and the unsaturated hydraulic conductivity $k(\theta)$ were determined using the Brooks-Corey model for the hydraulic properties of porous media (Brooks and Corey 1964), as follows:

$$k(\Theta) = k_s \Theta^M \tag{11}$$

$$D(\Theta) = \frac{K_S h_d \Theta^{l+1/N}}{N(\theta_s - \theta_r)} \tag{12}$$

$$\Theta = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{13}$$

Where N and M = shape parameters, $M = 3 + 2/N$; h_d = air entry suction; l = pore tortuosity, which takes a value of 2 in the Brooks-Corey model; θ_s = saturated water content (%); and θ_r = water content (%). The values of θ_s and θ_r are measured directly. Vertical and horizontal soil column infiltration experiments were carried out following the method described by Wang et al. (2002b) to determine the parameters N, h_d, and k_s (Table 2). These parameters were then used to determine the soil water diffusivity $D(\theta)$ and the unsaturated hydraulic conductivity $k(\theta)$.

The Manning roughness coefficient n was calculated from Eq. (14) (Liang and Levent Kavvas 2008)

$$n = V_1^{-1} s_o^{1/2} R_1^{2/3} \tag{14}$$

where V_1 = flow velocity (m/min); s_o = average slope (sine of the slope angle); and R_1 = hydraulic radius (cm). The average flow velocity for loam was 18.8 m/min, which corresponds to a Manning roughness coefficient of 0.045 m⁻¹ s. The average flow velocity of sandy loam was 22.9 m/min, which corresponds to a Manning roughness coefficient of 0.036 m⁻¹ s. The values of the other parameters listed in Table 2 were determined by direct measurement.

According to Parlange (1971, 1972), the boundary conditions from the start of rainfall to soil saturation can be expressed as

$$\theta_0'(t) = -\frac{R}{\theta_0(t) - \theta_i} \frac{k[\theta_0(t)] - R}{D[\theta_0(t)]} \tag{15}$$

where $\theta_0(t)$ = water content of the soil surface (%). By combining $D(\theta)$ and $k(\theta)$ with Eq. (15), the differential algorithm was used

Table 1. Selected Soil Properties of the Two Soils

Soil	Particle size distribution (%)			Organic matter g kg⁻¹	CaCO₃ g kg⁻¹	Total phosphorus g kg⁻¹	Total potassium g kg⁻¹	Total nitrogen g kg⁻¹	pH	Bulk density g cm⁻³	Saturated water content cm³ cm⁻³
	Clay <0.002	Silt 0.002–0.05	Sand >0.05								
Loam	31.65	64.03	4.32	9.3	26.8	1.1	18.6	0.71	8.35	1.35	0.38
Sandy loam	15.18	60.11	24.71	6.5	93.5	1.2	1.5	0.62	8.5	1.35	0.346

Table 2. Soil Parameters for Loam and Sandy Loam

Soil	θ_i (%)	θ_r (%)	P (mm min⁻¹)	C_r (mg cm⁻³)	C_o (mg cm⁻³)	N	L	h_d (cm)	K_s (cm min⁻¹)
Loam	0.1356	0.027	0.15 ± 0.004	0	2.88	0.215	2	11.15	0.0171
Sandy loam	0.1248	0.041	0.16 ± 0.004	0	2.697	0.32	2	14.66	0.0432

Note: The water content was determined gravimetrically.

with time steps of 1 min; the boundary conditions, including the soil surface water content, were determined. One min was selected as the time step duration, and multiple layers of 1-cm depth in the soil profile below the mixing zone were considered; 24 layers were examined for loam, and 32 layers were examined for sandy loam. It was then possible to determine the water movement in the soil [Eqs. (1) and (2)] by using the differential algorithm approach.

The infiltration rate can be expressed as

$$i = \left[\sum_{j=1}^{n_1} z(\theta_j, t+1) - \sum_{j=1}^{n_1} z(\theta_j, t) \right] \cdot V/A \qquad (16)$$

where n_1 = number of soil sections along the defined depth; $z(\theta_j, t)$ = water content of section j at time t; V = total soil volume (cm^3); and A = area of infiltration (cm^2). When Eq. (16) was substituted into Eq. (3), 10 cm was taken as the length step along the slope, and 1 min as the time step; the depth of the overland flow and the runoff volume were determined using a differential algorithm.

Solute Transport Parameter

For the nonadsorbed chemicals, α = soil moisture (θ) in Eq. (7). Therefore, bromide was used as a tracer; assuming α = soil moisture (θ), Eq. (7) can be expressed as

$$\left| \frac{\partial \theta C_s}{\partial t} = \frac{\partial}{\partial z} \left(D_s \frac{\partial C_s}{\partial z} - iC_s \right) \right. \qquad (17)$$

$$D_s = \alpha'|v|^\gamma + D_s' \qquad (18)$$

$$D_s' = D_0 a e^{b\theta} \qquad (19)$$

where a and b = empirical coefficients with values of $a = 0.005$ and $b = 10$ (Olsen and Kemper 1968); D_0 = dispersivity of chemicals in free water (cm^2/s) for Br$^-$; $D_0 = 1.2 \times 10^{-5}$ cm^2/s (Bennett and Myers 1982; Wallach et al. 1988; Ahuja 1990); e = constant (2.7183); γ = constant (1); v = velocity of flow in soil pores (cm/min); and α' = dispersion rate (cm^2/min). Based on the water transport determined from Eqs. (1) and (2) and the solute movement in the soil profile from Eqs. (7), (8), and (9), the α values for loam and sandy loam were 0.35 and 0.38 cm^2, respectively. These values were the best fit to the experiment data when using a rainfall rate of 0.10 ± 0.004 mm/min.

The different soil particle colors allowed direct measurement of the depth of the mixing zone (Gao et al. 2004). In this experiment, the shield depths were 2.7 and 1.8 mm for loam and sandy loam, respectively (these values represent the average from three separate experiments).

Ahuja and Lehman (1983) and Snyder and Woolhiser (1985) showed that the concentration of chemicals in the soil solution was much higher than in the runoff, which was consistent with the results. Accordingly, it was assumed that no significant error would be introduced by regarding the runoff concentration in Eq. (8) as being negligible (Wallach et al. 1988). The soil surface boundary condition would then reduce to

$$c(0, t) = 0 \quad t > 0 \qquad (20)$$

Data from dissection of the soil profile below the mixing zone and the slope surface allowed simulation of the water flow through the soil profile and overland flow with 1-min time steps. When the temporal change in solute concentration in the soil surface was calculated, the temporal change in the solute concentration in the runoff (Cs) could be calculated by solving Eqs. (5) and (6).

Results and Discussion

The model was used to simulate the instantaneous changes in water content and solute concentration in the soil profile and the subsequent change in volume and solute concentration of surface runoff. Two soil types were used to test the model.

Soil Water Content and Solute Concentration in the Soil Profile

The predicted water content and solute concentration in the soil profile 90 min after runoff began are shown in Figs. 3 and 4. The measured and simulated times from when rainfall began until the point when runoff started (tp) are shown in Table 3.

The time step in the simulations was 1 min, so the simulated data agreed very well with the experimental observations, as shown in Table 3. It was found that cumulative infiltration quantity before the generation of runoff had a considerable impact on the solute concentration in the runoff: the greater the cumulative infiltration, the less solute was found in the runoff, which corresponded to a lower solute concentration in the soil surface; similar results were found by Wallach et al. (2001). According to the model, the solute concentration in the soil beneath the mixing zone when runoff was occurring was 556 mg/L for sandy loam and 647 mg/L for loam.

Fig. 3 showed a comparison between the model results and the experimental soil water content for the two different soil types after runoff had been occurring for 90 min. There was a boundary interaction in the sandy loam experiment: the soil samples that were taken to measure soil moisture content and solute concentration in the soil profile were insufficient if they were 1-cm-deep layers that were the width of the flume in sandy loam. This was because too much of the sample was adjacent to the flume, resulting in a boundary interaction. The results indicated that the Richards' equation and the Brooks-Corey model can accurately predict the water movement in the two soils that were used in the experiment.

The solute concentration in the soil profile changed immediately following the onset of rainfall. Fig. 4 shows the simulated and measured solute concentration in the soil when rainfall stopped. The coefficient of determination [Eq. (19), R^2] for the data simulated by the model and experimental data were 0.97 and 0.89 for loam and sandy loam, respectively.

Runoff Volume and Solute Concentration in the Runoff

The overland flow collected from the flumes and the concentration of Br$^-$ in the soil and runoff 90 min after runoff began were compared with the measured data (Figs. 5 and 6). The simulated data showed a high level of correlation with the measured data for both runoff volume and solute concentration in the runoff. This demonstrated that the model captured the temporal behavior of the runoff and solute transport in the runoff.

A difference was found in runoff volume (Fig. 5) between the two soils. This was because the loam structure was less uniform and stable than the sandy loam. The loam, therefore, broke into smaller pieces much more readily when hit by raindrops, and these smaller pieces were more easily carried away in runoff or infiltrate; in the latter case, this could lead to pore blockage. The loam soil particles expanded more readily than the sandy loam particles when infiltration took place. The hydraulic conductivity of the loam decreased faster than that of the sandy loam, resulting in decreased water infiltration and increased runoff from the loam. Therefore, the runoff volume associated with the loam increased more sharply than that of the sandy loam, as shown in Fig. 5. From Fig. 5, it can be seen that the simulated data showed a high level of correlation with the temporal change in runoff volume for the two soils.
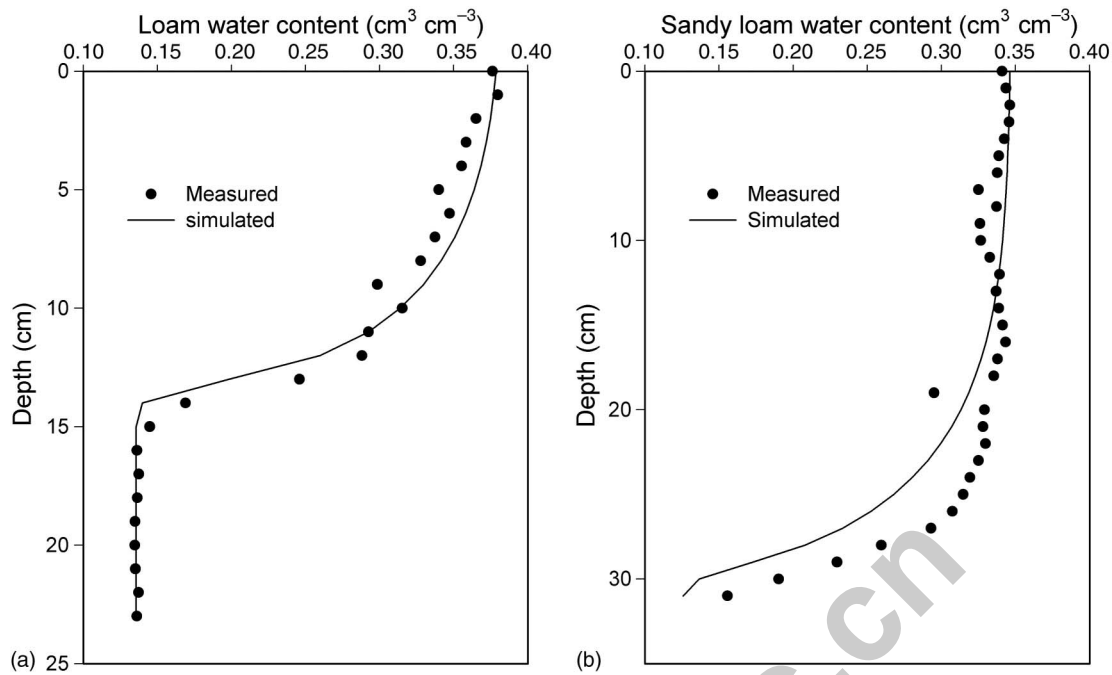
JOURNAL OF HYDROLOGIC ENGINEERING © ASCE / MAY 2013 / 531

J. Hydrol. Eng., 2013, 18(5): 527-535

Fig. 3. Comparison between model results and those determined using experimental soil water content data for two soil types: (a) loam; (b) sandy loam; diamonds represent the measured data and the solid line shows the simulated data
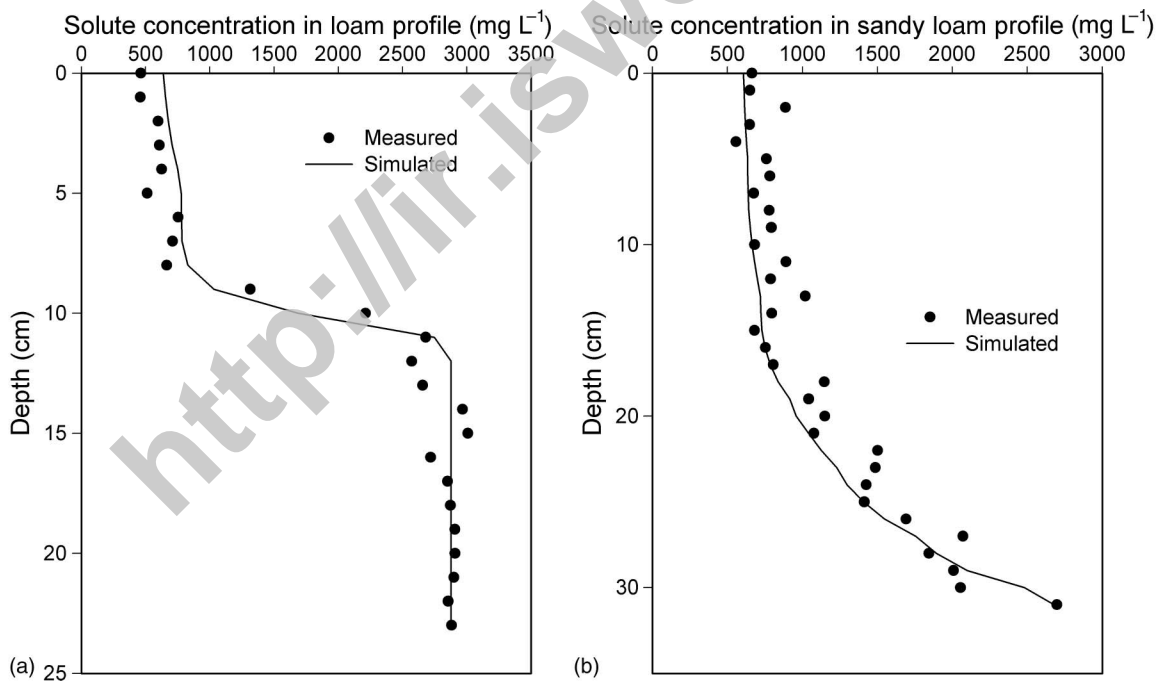

Fig. 4. Comparison of model results with the experimental soil solute concentration for two soil types: (a) loam; (b) sandy loam; squares represent the measured data and the solid line the simulated data

Table 3. Measured and Simulated Times (tp) between the Start of the Rainfall and the First Observation of Runoff for Two Soil Types

Soil	Measured tp	Simulated tp
Loam	2.38	3
Sandy loam	5.6	6

The measured and simulated solute concentration in the runoff was shown in Fig. 6. The coefficient of determination (R^2) for the simulated and measured solute concentration in runoff was 0.95 for loam and 0.93 for sandy loam. During the initial few minutes after runoff began, the solute concentration in the runoff was mainly controlled by the raindrops and solute concentration in the mixing
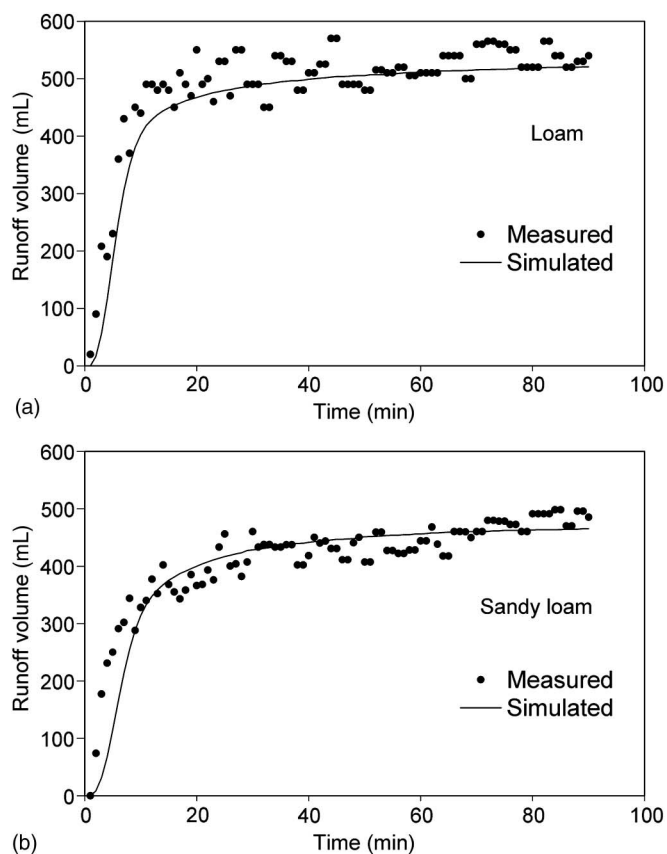
Fig. 5. Comparison of model results with experimental flux data for two different soil types: (a) loam; (b) sandy loam; squares represent the measured data and the solid line the simulated data

Fig. 6. Comparison of model results with experimental solute concentration in the runoff data for two soil types: (a) loam; (b) sandy loam; squares represent the measured data and the solid line the simulated data

zone; the more solute in the mixing zone, the more solute in the runoff. When the solute concentration in the runoff stabilized, the solute concentration in the runoff was mainly controlled by diffusion from the soil beneath the mixing zone. The higher the solute concentration in the soil below the mixing zone, the more solute diffused into the mixing zone, and consequently the more solute was lost with runoff.

The model was mainly designed to examine infiltration excess. Saturation excess was another contributor to runoff. Solute release from saturation runoff exhibits a very different mechanism. When the soil was saturated, there was no infiltration, but there was interflow. If the slope gradient was gentle, there was little interflow, which could be ignored; the solute transported within the soil profile that entered the runoff and moved away could be simulated within the model by deleting the infiltration term.

The RMSE for the different models is shown in Table 4. Table 4 and Figs. 3–6 show that the model correctly captured the temporal behavior of the water and Br^- concentration in the soil profile and runoff for both soil types.

Sensitivity Analysis

The mixing zone depth was correlated with initial soil moisture content, rainfall intensity, and slope gradient. However, from Fig. 7(a), it was determined that the mixing zone depth had little influence on the solute concentration in the runoff. Although the water content in the mixing zone was much lower than the amount in runoff, and therefore the depth of mixing zone changed considerably, it still had very little influence on the solute concentration in runoff. To account for this, the other parameters were analyzed
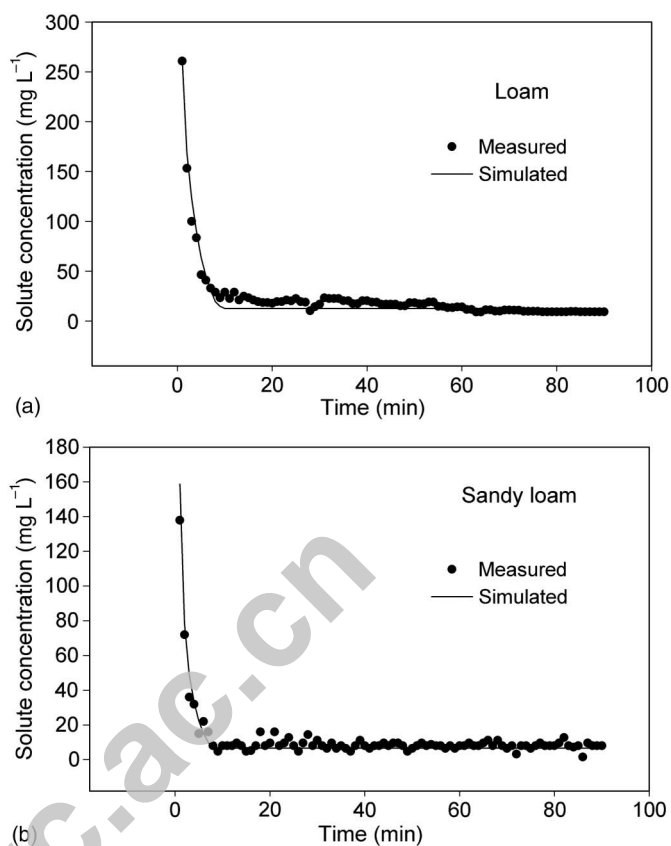
Table 4. RMSE to Compare the Simulated Results from the Model and the Experimental Data

Soil	Variable	RMSE
Loam	Soil water content	0.016 ($cm^3\ cm^{-3}$)
	Runoff volume	41.586 (mL)
	Solute concentration in soil profile	178.05 ($mg\ L^{-1}$)
	Solute concentration in runoff	6.892 ($mg\ L^{-1}$)
Sandy loam	Soil water content	0.028 ($cm^3\ cm^{-3}$)
	Runoff volume	40.472 (mL)
	Solute concentration in soil profile	176.268 ($mg\ L^{-1}$)
	Solute concentration in runoff	12.638 ($mg\ L^{-1}$)

without considering the change in the mixing zone depth. Fig. 7 shows how the model responded when various parameters were changed independently. The time until runoff took place is shown in Table 5.

The initial soil moisture content, rainfall intensity, and slope gradient had a considerable influence on the solute concentration in the runoff [Figs. 7(b–d)]. From Table 5, it was found that initial soil moisture content had an important influence on the surface runoff solute concentration because of its effect on the time before runoff commences. Lower initial soil moisture content increases the time period during which solutes are displaced downward by the infiltrating water prior to the initiation of runoff; this reduces the subsequent solute flux to the surface runoff, supporting previous results presented by Wallach et al. (2001).
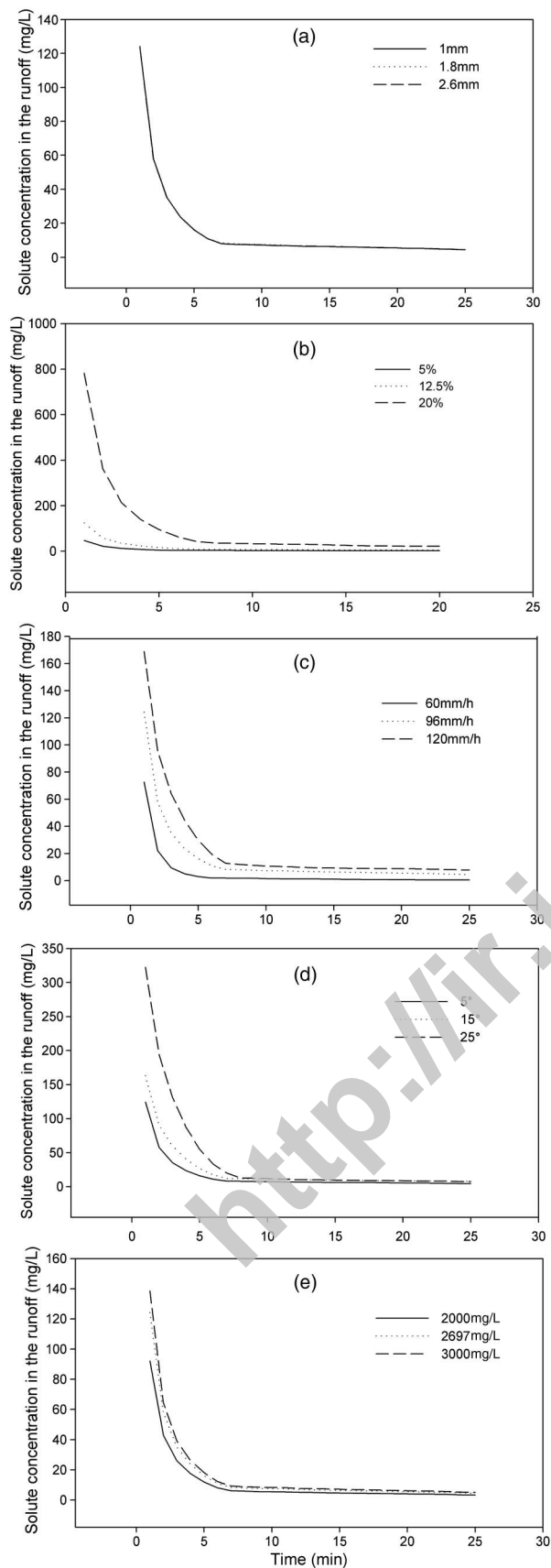
Fig. 7. Model results for changes in chemical transport in surface runoff in response to different soil parameters (a) depth of the exchange layer de; (b) initial soil water content θ_i; (c) rainfall intensity p; (d) slope gradient s_0; (e) chemical concentration in the soil (mg/L) when rainfall begins C_{S0}

Table 5. Time Until Runoff Takes Place Simulated by the Model

Variable	Treatment	Time until runoff takes place (min)
Initial soil moisture content (%)	5	8
	12	6
	20	5
Rainfall intensity (mm h^{-1})	60	10
	96	6
	120	5
Slope gradient (°)	5	6
	15	5
	25	4

The same effect was seen for soil moisture content; the rainfall intensity effected the solute concentration in the runoff by controlling the time until runoff occurred. It took longer for runoff to occur at lower rainfall intensities for a given initial soil moisture content. Higher solute concentrations were found in the runoff for higher slope gradients.

The slope gradient influenced the solute concentration in the runoff by controlling water infiltration and the depth of the mixing zone in the model. The rainfall and runoff erosion ability increased with slope gradient, resulting in more soil erosion to runoff, and therefore more solute in the runoff. The mixing zone depth can express the rainfall and runoff erosion ability, but the mixing zone depth counts for little when the soil erosion is serious. Fig. 7(e) shows the relationship between solute concentration in runoff and the initial solute concentration in the soil. This relationship differed from the other model relationships because unlike for the other factors, the solute concentration in the runoff became stable over the same time.

Conclusions

Water transport in the soil profile can be accurately described by the Richards' equation and the kinematic wave approximation when provided with realistic simulations for overland flow. A physically-based transfer model was developed that showed strong correlation with the experimental data. The results showed that rainfall-driven processes thoroughly mix the runoff and water in the mixing zone, and that the solute in the deeper soil was transported into the mixing zone by molecular and flow mechanical dispersion. The chemical transported into the soil from beneath the mixing zone can be described by convection-diffusion equations. It was important to note that the model cannot simulate the solute transport in the runoff under high levels of soil erosion. The infiltration had the greatest impact on solute concentration in the runoff, both before the runoff starts and during the period that runoff occurs. If infiltration is increased, then the solute concentration in the runoff will decline, resulting in a reduced nutrient loss.

Acknowledgments

References

Ahuja, L. R. (1990). "Modeling soluble chemical transfer to runoff with rainfall impact as a diffusion process." *Soil Sci. Soc. Am. J.*, 54(2), 312–321.

Ahuja, L. R., and Lehman, O. R. (1983). "The extent and nature of rainfall-soil interaction in the release of soluble chemicals to runoff." *J. Environ. Qual.*, 12(1), 34–40.

Ahuja, L. R., Sharpley, A. N., and Lehman, O. R. (1982). "Effect of soil slope and rainfall characteristics on phosphorus in runoff." *J. Environ. Qual.*, 11(1), 9–13.

Ahuja, L. R., Sharpley, A. N., Yamamoto, M., and Menzel, R. G. (1981). "The depth of rainfall-runoff-soil interaction as determined by ^{32}P." *Water Resour. Res.*, 17(4), 969–974.

Bear, J., and Bachmat, Y. (1990). *Introduction to modelling phenomena of transport in porous media*, Kluwer Academic, Dordrecht, Netherlands.

Bennett, C. O., and Myers, J. E. (1982). *Momentum, heat, and mass transfer*, 3rd Ed., McGraw-Hill, New York.

Bresler, E. (1973). "Simultaneous transport of solutes and water under transient unsaturated flow conditions." *Water Resour. Res.*, 9(4), 975–986.

Brooks, R. H., and Corey, A. J. (1964). *Hydraulic properties of porous media*, Colorado State Univ., Fort Collins, CO.

Deng, Z. Q. (2002). "Theoretical investigation into longitudinal dispersion in natural rivers." Ph.D. dissertation, Lund Univ., Lund, Sweden.

Deng, Z. Q., de Lima, J. L. M. P., and Singh, V. P. (2005). "Transport rate-based model for overland flow and solution transport: Parameter estimation and process simulation." *J. Hydrol.*, 315(1–4), 220–235.

Donigian, A. S., Beyerlein, D. C. Jr., Davis, H. H., and Crawford, N. H. (1997). "Agricultural runoff management (ARM) model, version II, Refinement and Testing, USEPA." *Rep. 600/3–77–098*, U.S. Environmental Protection Agency and Environmental Research Laboratory, Athens, GA.

Gao, B., et al. (2005). "Investigating raindrop effects on transport of sediment and non-sorbed chemicals from soil to surface runoff." *J. Hydrol.*, 308(1–4), 313–320.

Gao, B., Walter, M. T., Steenhuis, T. S., Hogarth, W. L., and Parlange, J. Y. (2004). "Rain induced chemical transport from soil to runoff: Theory and experiments." *J. Hydrol.*, 295(1–4), 291–304.

Green, T., and Houke, D. F. (1979). "The mixing of rain with near surface water." *J. Fluid Mech.*, 90(3), 569–588.

Hairsine, P. B., and Rose, C. W. (1991). "Rainfall detachment and deposition: Sediment transport in the absence of flow-driven processes." *Soil Sci. Soc. Am. J.*, 55(2), 320–324.

Havis, R. N. (1986). "Transport from overland flow." Ph.D. dissertation, Colorado State Univ., Fort Collins, CO.

Heilig, A., et al. (2001). "Testing of a mechanistic soil erosion model with a simple experiment." *J. Hydrol.*, 244(1–2), 9–16.

Ingram, J. J., and Woolhiser, D. A. (1980). "Chemical transfer into overland flow." *Proc., Symp. Watershed Management*, ASCE, New York, 40–53.

Kiely, G. (1997). *Environmental engineering*, McGraw-Hill International (UK) Limited, Singapore.

Liang, L., and Levent Kavvas, M. (2008). "Modeling of solute transport and macrodispersion by unsteady stream flow under uncertain conditions." *J. Hydrol. Eng.*, 13(6), 510–520.

Liu, Q. Q., and Singh, V. P. (2004). "Effect of microtopography, slope length and gradient, and vegetative cover on overland flow through simulation." *J. Hydrol. Eng.*, 9(5), 375–382.

Martin, J. L., and McCutcheon, S. C. (1999). "Hydrodynamics and transport for water quality modeling." CRC, Boca Raton, FL, 7–220.

Mutchler, C. K. (1967). "Parameters for describing raindrop splash." *J. Soil Water Conserv.*, 22, 91–94.

Olsen, S. R., and Kemper, W. D. (1968). "Movement of nutrients to plant roots." *Adv. Agron.*, 30, 91–151.

Parlange, J. Y. (1971). "Theory of water-movement in soils: I. One-dimensional absorption." *Soil Sci.*, 111(2), 134–137.

Parlange, J. Y. (1972). "Theory of water movement in soils: I. One-dimensional infiltration with constant flux at the surface." *Soil Sci.*, 114, 1–4.

Sharpley, A. N., Ahuja, L. R., Yamamoto, M., and Menzel, R. G. (1981). "The release of soil phosphorus to runoff in relation to the kinetics of desorption." *J. Environ. Qual.*, 10(3), 386–391.

Singh, V. P. (1996). *Kinematic wave modeling in water resources: Surface-water hydrology*, Wiley, New York, 897–940.

Snyder, I. K., and Woolhiser, D. A. (1985). "Effect of infiltration on chemical transport into overland flow." *Trans. ASAE*, 28, 1450–1457.

Steenhuis, T. S. (2001). "Testing of a mechanistic soil erosion model with a simple experiment." *J. Hydrol.*, 244(1–2), 9–16.

Steenhuis, T. S., Boll, J., Shalit, G., Selker, J. S., and Merwin, I. A. (1994). "A simple equation for predicting preferential flow solute concentrations." *J. Environ. Qual.*, 23(5), 1058–1064.

Steenhuis, T. S., and Walter, M. F. (1980). "Closed form solution for pesticide loss in runoff water." *Trans. ASAE*, 23(3), 615–628.

Tong, J. X., Yang, J. Z., and Bao, R. C. (2009). "Model for chemicals transfer to surface runoff in unsaturated soil and its analytical modeling." *J. Adv. Water Sci.*, 20(1), 10–17 (in Chinese).

Wallach, R. (1991). "Runoff contamination by soil chemicals-time scales approach." *Water Resour. Res.*, 27(2), 215–223.

Wallach, R., Grigorin, G., and Rivlin, J. (2001). "A comprehensive mathematical model for transport of soil-dissolved chemicals by overland flow." *J. Hydrol.*, 247(1–2), 85–99.

Wallach, R., and van Genuchten, M. T. (1990). "A physically based model for predicting solute transfer from soil solution to rainfall-induced runoff water." *Water Resour. Res.*, 26(9), 2119–2126.

Wallach, R., van Genuchten, M. T., and Spencer, W. F. (1989). "Modeling solute transfer from soil to surface runoff: The concept of effective depth of transfer." *J. Hydrol.*, 109(3–4), 307–317.

Wallach, R., William, A. J., and William, F. S. (1988). "Transfer of chemical from soil solution to surface runoff: A diffusion-based soil model." *Soil Sci. Soc. Am. J.*, 52(3), 612–617.

Walter, M. T., Gao, B., and Parlange, J. Y. (2007). "Modeling soil solute release into runoff with infiltration." *J. Hydrol.*, 347(3–4), 430–437.

Wang, Q. J., Horton, R., and Shao, M. A. (2002a). "Effective raindrop kinetic energy influence on soil potassium transport into runoff." *Soil Sci.*, 167(6), 369–376.

Wang, Q. J., Horton, R., and Shao, M. A. (2002b). "Horizontal infiltration method for determining Brooks-Corey model parameters." *Soil Sci. Soc. Am. J.*, 66(6), 1733–1739.

Wang, Q. J., Shao, M. A., Li, Z. B., and Lei, T. W. (1999). "Analysis of simulating methods for soil solute transport with runoff in Loess Plateau." *Research of Soil and Water Conservation*, 2, 67–71 (in Chinese).

Wang, Q. J., and Wang, H. (2010). "Analysis on the feature of effective mixing depth model forsoil solute transporting with surface runoff on loess slope." *Hydrol. Proc.*, 41(6), 671–676 (in Chinese).

Wang, Q. J., Wang, W. Y., Shen, B., and Shao, M. A. (1998). "Interacting depth of rainfall-runoff-soil solute." *J. Soil Eros. Water Conserv.*, 2(4), 41–46 (in Chinese).

Wang, R. C. (1970). "The mechanics of a drop after striking a stagnant water layer." Ph.D. thesis, Dept. of Civil Engineering, Univ. of Illinois.

Willmott, C. J. (1982). "Some comments on the evaluation ofmodel performance." *Bull. Am. Meteorol. Soc.*, 63(11), 1309–1313.

Woolhiser, D. A. (1975). "Simulation of unsteady overland flow." *Unsteady flow in open channels*, Vol. 2, K. Mahmood and Y. Yevjevich, eds., Water Resources, Fort Collins, CO, 485–508.

Woolhiser, D. A., and Ligget, J. A. (1967). "Unsteady, one dimensional flow over a plane—The rising hydrograph." *Water Resour. Res.*, 3(3), 753–771.

Zhang, X. C., Norton, D., Lei, T., and Nearing, M. A. (1999). "Coupling mixing zone concept with convection–diffusion equation to predict chemical transfer to surface runoff." *Trans. ASAE*, 42(4), 987–994.

Zhang, X. C., Norton, D., and Nearing, M. A. (1997). "Chemical transfer from soil solution to surface runoff." *Water Resour. Res.*, 33(4), 809–815.

JOURNAL OF HYDROLOGIC ENGINEERING © ASCE / MAY 2013 / **535**

J. Hydrol. Eng., 2013, 18(5): 527-535