

# A comprehensive mathematical model for transport of soil-dissolved chemicals by overland flow

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Received 23 June 1999; revised 25 January 2001; accepted 26 February 2001

## Abstract

The model developed in this study simulates the contamination of overland flow by soil chemicals that reside near its surface during a surface runoff event. The model includes mass-balance equations for both water flow and chemical transport in the soil profile and surface runoff. A rate-limited mass transfer through an overland-flow boundary layer at the soil overland flow interface controls the dissolved chemical transfer from soil solution to overland flow, once formed. The model predicts water flow and chemical transport in the soil profile prior to the rainfall ponding (when overland flow starts) and during the surface runoff event. The predictions of these variables, together with the total load to the surface runoff, were successfully compared with the measured data of Hubbard et al. [Trans. ASAE, 32(4) (1989) 1239]. Being physically based, the model was used to investigate the dependence of surface runoff pollution and its extent on the system hydrological parameters. A key factor on the availability of soil chemicals to pollute the overland flow is their displacement by infiltrating water prior to runoff initiation. Being dependent on soil moisture prior to rainfall initiation and on rainfall intensity, a lower chemical concentration and a lower load in surface runoff are obtained for longer ponding times, ones that are associated with lower rainfall rates and initially drier soil profiles. During the surface runoff flow, the chemical concentration in overland flow at the slope outlet is affected by the contact time of an overland flow parcel with the soil surface. Thus, it increases for higher values of equilibrium time —  $t_E$ , lower rainfall rates, slope gradients, and higher soil-surface roughness coefficients. These parameters have an inverse effect on the surface runoff concentration by affecting the transfer coefficient of soil chemical to overland flow. A different insight into the relationship between the relevant dynamic processes throughout the storm event is achieved by studying the transient variation of soil chemical flux to overland flow, the chemical flux at the slope outlet, and the change of chemical mass in the overland flow. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Overland flow; Mass transfer; Rainfall ponding; Infiltration; Water pollution

## 1. Introduction

Surface applied or soil-incorporated pesticides, nutrients, and other agricultural chemical are often

transferred from soil to surface runoff water during periods of heavy rainfall or surface irrigation. The transfer into runoff water decreases the efficiency of the applied chemical and poses a potential threat to the quality of the environment. Once released to runoff water, the chemical may reach nearby surface water bodies and thus lead to their exposure to aquatic

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organisms. Dissolved chemical in ponds and lakes also may indirectly reach groundwater, often faster than if they were carried by infiltrating water through the vadose zone. Of the many factors that influence the extent of pesticides and other agrochemical runoff from agricultural lands, several may be controlled to minimize pollution. If the role of different hydrological factors (e.g. rain intensity and duration, infiltration rate, soil slope length, degree of slope, soil cover, and chemical solubility and adsorption characteristics) on the surface water pollution by the soil-dissolved agrochemical were clearly known, usage guidelines could be developed. This knowledge would aid in preventing or reducing runoff and subsequent pollution.

The process of soil-dissolved chemical transfer to runoff and its transport to the field outlet is complex. Modeling the large number of processes involved and their interactions requires the solution of relatively complicated, coupled linear and nonlinear partial differential equations subject to time-dependent boundary conditions. To reduce mathematical complexity, many investigators have lumped various transport mechanisms together. The simplest approach states that solute concentrations in runoff water, both within a soil surface layer and in infiltrating water, are equal due to an instantaneous equilibration by mixing. In a very simplified version, the transient-runoff and infiltration-water concentrations exhibit the same dilution curve as obtained when a solution of a certain concentration is poured into an overflowing container initially at a higher concentration. The result of this lumped description of the system is an exponential decay of runoff concentration with time (Steenhuis and Walter, 1980; Ahuja, 1982; Ahuja and Lehman, 1983). Measurements of non-uniform chemical distribution below the soil surface after a rainfall–runoff event (Ahuja and Lehman, 1983; Snyder and Woolhiser, 1985) and contamination of overland flow by a tracer that was located 2 cm below the soil surface prior to rainfall initiation (Ahuja et al., 1981) call for revision of the mixing concept within the soil surface layer. Parr et al. (1987), Wallach et al. (1988), Wallach and Shabtai (1992a,b), Havis et al. (1992) used the rate-limited film model to describe the chemical transfer process across the soil-surface/runoff-water interface. In Havis et al. (1992), the film transport coefficient was independent of the overland-flow parameters (depth, velocity, length) and was assumed to be constant

throughout the storm. Its value was determined at the ponding time,  $t_p$ , based on the rainfall rate and the chemical concentrations in the soil and runoff at  $t = 0$  and  $t = t_p$ . Moreover, Wallach et al. (1988), Wallach and Shabtai (1992a,b) described the transfer of soil chemicals, both upward and downward, by using a solute-diffusion model in the soil bulk with a rate-limited chemical transfer across a laminar boundary layer at the interface between the soil-surface and runoff-water. Also, Wallach and Shabtai (1993) demonstrated that the concept used in their previous work is capable of predicting fluxes of soil-dissolved chemicals that were initially incorporated at a certain depth below the soil surface into the overland-flow. The commonly used mixing models can not predict such fluxes.

Simplified and lumped models have been used to describe the dissolved chemical transport in overland flow, mainly in those using the mixing concept. Wallach et al. (1988), Wallach and Genuchten (1990) used the residence-time distribution theory, which indicates how long an individual solute parcel has remained along the slope since being transferred from the soil. This approach enabled to solve the mass balance equations analytically. In a further step to model explicitly the lateral transport in overland flow, Wallach and Shabtai (1992a,b) assumed that the overland flow depth is momentarily uniform along the slope but ignored the spatial variation of chemical concentration along the slope. In the current study, we incorporate a detailed model for overland flow dynamics and lateral transport of dissolved chemicals toward the slope outlet is incorporated with a model for water flow and chemical transport in soil. The comprehensive model will be used to study the effect of different hydrological parameters on overland flow concentration and load.

## 2. The mathematical model

The entire system has been divided into two subsystems: the soil profile and overland flow. The soil surface is the interface between the two systems. The mass balance equations for the water and dissolved chemicals are written for each unit with water infiltration and rate-limited chemical exchange through the interface as the continuity conditions.

### 2.1. Overland water flow and lateral chemical transport

The mass balance equation for the surface runoff along a uniform slope is

$$\frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} = f(t) - i(x, t), \quad (1)$$

where  $x$  is the axis along the slope,  $h(x, t)$  the overland flow depth,  $q(x, t)$  the unit discharge in the slope direction,  $f(t)$  the rainfall rate, and  $i(x, t)$  is the infiltration rate. The water mass balance equation is combined with a momentum balance equation that gives, after neglecting the acceleration and pressure terms, the kinematic-wave equation

$$q = \alpha h^m. \quad (2)$$

Overland flow can be laminar or turbulent. The coefficients in Eq. (2) for laminar flow ( $Re = u/\nu < 500$ ) are  $m = 3$  and  $\alpha = 8gs/K_r\nu$  and for turbulent flow, the coefficients are ( $Re > 500$  and  $n^6(hs)^{1/2} > 1.1 \times 10^{-13}$  in SI units)  $m = 5/3$  and  $\alpha = s^{1/2}/n$ . Further,  $s$  is the soil surface gradient,  $g$  the acceleration due to gravity,  $\nu$  the kinematic viscosity of water,  $K_r$  a parameter related to soil surface roughness in laminar flow, and  $n$  is Manning's coefficient for turbulent flow.

The boundary and initial conditions to Eq. (1) are

$$h(0, t) = 0 \quad \text{for } t \geq t_p; \quad h(x, t_p) = 0, \quad (3)$$

where  $t_p$  is the ponding time, i.e. the time at which the water-pressure potential at the soil surface becomes zero and the soil surface turns out to be saturated (Rubin, 1966).

Conservation of dissolved-chemical mass in the overland flow is

$$\frac{\partial(c_r h)}{\partial t} + \frac{\partial(c_r q)}{\partial x} = k[c(x, 0, t) - c_r], \quad (4)$$

where  $c_r(x, t)$  is the dissolved chemical concentration in overland flow,  $c(x, z, t)$  is the dissolved chemical concentration in soil, and  $c(x, 0, t)$  is its value at the soil surface. Note that the soil surface concentration varies along the slope. The right hand side of Eq. (4) expresses the rate-limited dissolved chemical transfer from the soil solution to overland flow. It is driven by the concentration gradient across the hydrodynamic boundary layer that separates the stagnant soil

solution and the moving overland flow (Wallach et al., 1988; Wallach et al., 1989).

The boundary and initial conditions for Eq. (4) are

$$c_r(0, t) = 0 \quad \text{for } t \geq t_p; \quad c_r(x, t_p) = c(x, 0, t_p). \quad (5)$$

The second part of Eq. (5) is written under the assumption that  $k(x, t_p) \rightarrow \infty$  as  $h \rightarrow 0$ . The overland-flow depth and velocity in Eq. (4) are known from the solution of Eq. (1). These equations were solved by the nonlinear implicit scheme of Li et al. (1975) using Newton's iterative method for Eq. (1) and the four-point implicit method second-order scheme for Eq. (4).

### 2.2. Soil water flow and chemical transport

Water flow and chemical transport in soil takes place both vertically and laterally. The slope and soil profile is assumed to be uniform and the rainfall-runoff event is assumed to be single. For such conditions, changes in moisture content in the lateral direction due to lateral moisture flow are small and slow relative to moisture variation due to externally induced spatially variable infiltration (Wallach et al., 1989). Therefore, the equations for infiltration and solute transport are solved in the vertical direction in parallel soil columns all across the slope, without horizontal interactions between them. The boundary condition at the soil surface will be the local overland flow,  $h(x, t)$ . The dependence on variations in the lateral direction is only parametric through the spatial and temporal variation in the overland flow depth (Wallach et al., 1997).

The vertical infiltration rate at any point  $x$  along the slope is determined by the solution of Richard's equation

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ K(\psi) \frac{\partial \psi}{\partial z} \right] - \frac{\partial K(\psi)}{\partial z}, \quad (6)$$

where  $z$  is the vertical space coordinate positively downward,  $\theta$  is the volumetric water content,  $\psi(x, z, t)$  is the soil-water matric potential, and  $K(\psi)$  is the soil's hydraulic conductivity.

The boundary condition to Eq. (7) at the soil surface is composed of three stages. During the first stage, prior to the overland flow initiation, the rainfall

entirely infiltrates into the soil profile

$$i = K(\psi) \left[ \frac{\partial \psi}{\partial z} - 1 \right] = f \quad \text{for } z = 0, 0 < t < t_p, \quad (7)$$

where  $i$  is the infiltration rate that is spatially uniform for a uniform rainfall distribution. The second stage starts when surface runoff initiates, and the infiltration rate is controlled by the local overland flow depth

$$\psi(x, 0, t) = -h(x, t) \quad \text{for } z = 0, \quad t_p < t < T. \quad (8)$$

$T(x)$  is the time when overland flow ceases at point  $x$  along the slope. The parametric dependence of Eq. (8) on the coordinate along the slope is by  $h(x, t)$  and  $T(x)$ . Eqs. (1) and (6) are dependent since the infiltration rate,  $i(x, t)$ , in Eq. (1) is determined by the solution of Eq. (6) whose boundary condition (8) is the solution of Eq. (1). This nonlinear system is solved by iterations at each time step in the numerical scheme. The third stage is the redistribution of soil water after overland flow cessation

$$i = K(\psi) \left[ \frac{\partial \psi}{\partial z} - 1 \right] = 0 \quad \text{for } z = 0, t > T. \quad (9)$$

Eq. (9) depends parametrically on  $T(x)$ . The soil is assumed to be homogeneous and deep. The lower boundary condition is

$$\frac{\partial \psi(\infty, t)}{\partial z} = 0 \quad \text{for } t > 0. \quad (10)$$

The initial matric potential (moisture) in the soil profile is assumed to be uniform

$$\psi(x, z, 0) = \psi_0. \quad (11)$$

Solute transport in soil is described by the convective-dispersive equation

$$\frac{\partial}{\partial t} [R(\theta)c] = \frac{\partial}{\partial z} \left[ D(\theta, v) \frac{\partial c}{\partial z} \right] - \frac{\partial}{\partial z} [vc], \quad (12)$$

$$R(\theta) = 1 + \frac{\rho K_d}{\theta},$$

where  $c$  denotes the solute concentration in the soil,  $K_d$  the soil-chemical distribution coefficient for chemicals adsorbed to the solid phase,  $\rho$  the soil bulk density, and  $D$  is the dispersion coefficient that

depends on the soil structure and solute flow,

$$D(\theta, v) = D_0 \lambda + \epsilon v. \quad (13)$$

$\lambda$  is the tortuosity factor that depends exponentially on the moisture content (Kemper and Schaik, 1966),  $D_0$  is the diffusion coefficient,  $\epsilon$  the dispersivity, and  $v$  is the average pore-water velocity.

The boundary condition at the soil surface for Eq. (12) is related to the three stages of the rainfall-runoff problem (Eqs. (7)–(9))

$$vc - D \frac{\partial c}{\partial z} = 0 \quad \text{for } z = 0, 0 < t < t_p, \quad (14)$$

$$vc - D \frac{\partial c}{\partial z} = -k[c(0, t) - c_r(t)] \quad (15)$$

for  $z = 0, t_p < t < T,$

$$vc - D \frac{\partial c}{\partial z} = 0 \quad \text{for } z = 0, t < T. \quad (16)$$

The initial condition is

$$c(z, 0) = c_0. \quad (17)$$

A finite difference scheme (Wallach and Shabtai, 1992a) was used to solve the equations for water flow and chemical transport in soil.

### 3. Model verification

The adequacy of the numerical solution for Eqs. (1) and (4) is tested by its comparison with an analytic solution obtained by Rivlin (Byk) and Wallach (1995) for constant rainfall and infiltration rates in Eq. (1) and constant mass-transfer coefficient and soil-surface concentration,  $c(0, t)$ , in (4). The calculated hydrograph and concentration at the outlet of a 100 m long uniform slope are shown in Figs. 1 and 2, respectively. These hydrographs are calculated for a rainfall rate of 1.6 cm/h and a duration of 15 min, and an infiltration rate of 0.3 cm/h,  $\alpha = 5.8 \times 10^6$  and  $k = 0.9$  cm/h. An excellent agreement is obtained between the numerical and analytic solutions for both overland flow depth and chemical concentration at the slope outlet.

The model's output is further compared with the experimental study of Hubbard et al. (1989), which was performed under controlled conditions. Hubbard

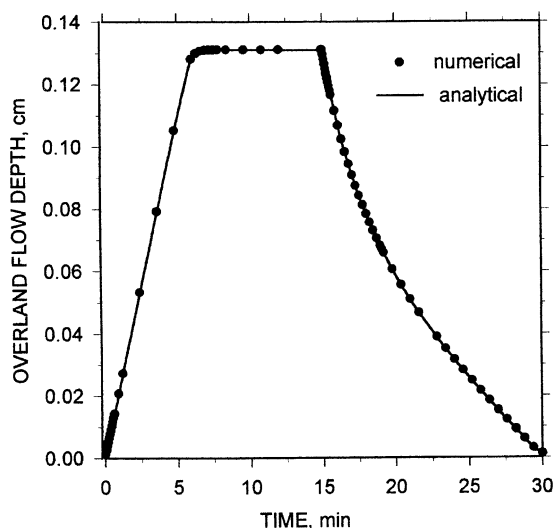


Fig. 1. Comparison between analytic (Rivlin (Byk) and Wallach, 1995) and the current solutions for the overland flow hydrograph at the outlet of a 100-m long slope calculated for  $f = 1.6$  cm/h,  $T = 15$  min,  $i = 0.3$  cm/h and  $K_r = 24$ .

et al. experiment data was compared elsewhere with the output of two other models: GLEAMS, developed by Leonard et al. (1987), and RUNOFF3 (Ashraf and Borah, 1992). Both, GLEAMS and RUNOFF3, differ from the current model in the way the dissolved chemicals' transport in soil and their transfer to overland flow.

Hubbard et al. (1989) used rectangular stainless steel boxes ( $100 \times 50 \times 80$  cm<sup>3</sup>) with surface runoff and percolate collection funnels for three soil types. Individual boxes were used for each combination of soil type and rainfall intensity. The soil depth in each box was 10 cm. The boxes were placed underneath a rainfall simulator and adjusted to a 2% slope. The soil was saturated from below until surface ponding occurred, and it was then allowed to drain for 24 h prior to chemical application and rainfall simulation. Nitrate was applied in 0.5 l volume in as uniform a manner as possible, using a hand-held, squeeze spray bottle of KNO<sub>3</sub> at rate equivalent to 250 kg/ha. After nutrient application, an additional 0.5 l of water was applied for complete quantitative transfer of the nutrients in the spray bottle. The boxes were allowed to equilibrate for 1 h prior to rainfall application. The simulated rainfall was applied for 2 h at high (12.5 cm/

h), medium (7.5 cm/h), and low (4.3 cm/h) intensities. Water samples were collected from surface runoff and percolation at 6 min time intervals, starting when surface runoff or percolation began.

In order to run the model, the soil characteristic curves and dispersivity, soil surface roughness, and the initial distributions of moisture content and chemical concentration in the soil profile, are needed. Since these data are not given in Hubbard et al. (1989) they were estimated from the description of the experiment setup.

By neglecting the overland flow depth and assuming a unit hydraulic gradient in the vertical direction along the soil profile, the saturated hydraulic conductivity,  $K_s$ , is equal to the steady percolation rate reached some time after runoff initiation. The current model does not include the effect of soil surface sealing on the infiltration rate and overland flow and  $K_s$  were determined only for boxes in which a constant percolation rate was measured during a certain period. Since no chemical outflow was measured for the low rainfall intensity on Red Bay soil, the low and high rainfall intensities on Bonifay sand boxes are used (denoted as BS and shown in Fig. 6 in Hubbard et al., 1989). The estimated  $K_s$  for the low-rainfall

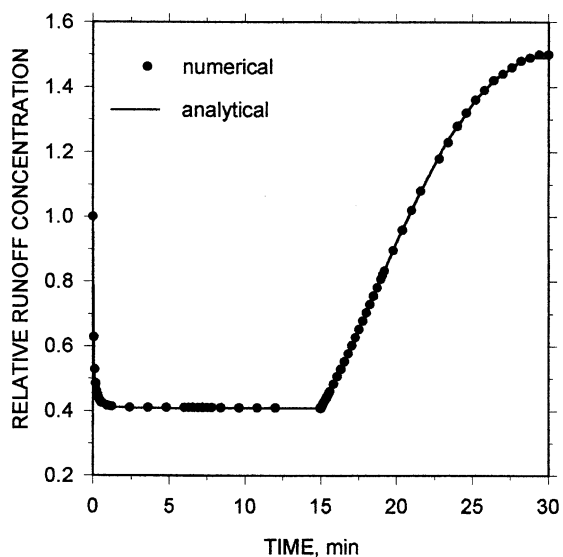


Fig. 2. Comparison between analytic (Rivlin (Byk) and Wallach, 1995) and the current solutions for the dissolved chemical distribution at the outlet of a 100 m long slope calculated for  $f = 1.6$  cm/h,  $T = 15$  min,  $i = 0.3$  cm/h and  $K_r = 24$ .

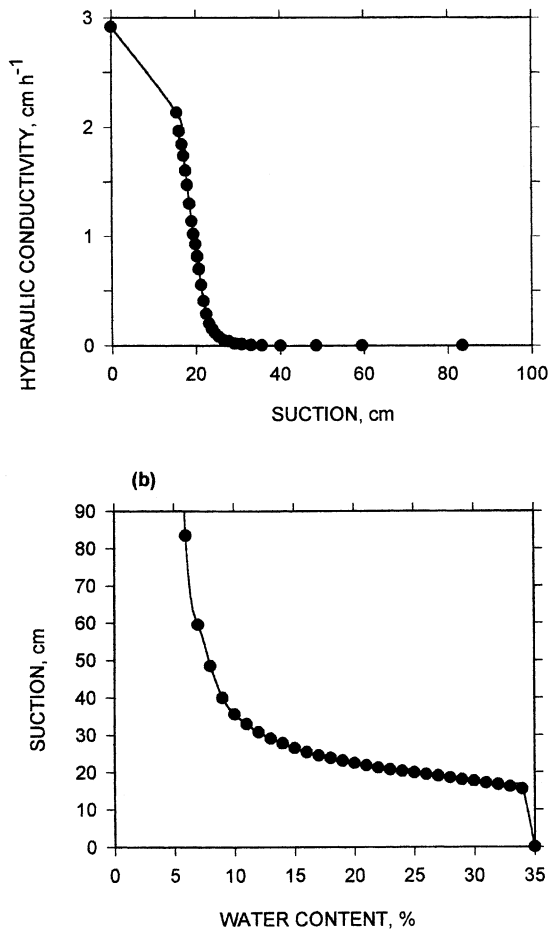


Fig. 3. The characteristic curves for the volcanic sand (Mualem, 1976) used to simulate the Bonifay sand.

intensity is 3.6 cm/h. For the high rainfall intensity, we assume that  $K_s$  is a step function, and from Fig. 6 of Hubbard et al. (1989),  $K_s = 3.6$  for  $0 < t < 18$  min and 2.2 cm/h for  $t > 18$  min.

The characteristic curves  $\theta(\psi)$  and  $K(\theta)$  of volcanic sand Mualem, 1976 were used for the BS since both are sandy soils and have similar  $K_s$  values. These characteristic curves are shown in Fig. 3. During the simulations to follow, the  $K(\theta)$  curves in Fig. 3 are used for BS by using the  $K_s$  values evaluated above.

The soil moisture distribution prior to rainfall initiation was estimated by assuming that hydrostatic

pressure head distribution along the soil profile was reached at the end of the 24 h of free drainage (Hubbard et al., 1989). Thus, the matric potential at the soil bottom prior to rainfall application was  $\psi = 16.2$  cm (the air entry value in Fig. 3), and at the soil surface,  $\psi = 26.2$  cm. During rainfall application, the boundary condition at the soil bottom is  $\partial\psi/\partial z = 0$ , and it becomes  $\psi = 0$  when the soil profile is saturated. Ponding at the soil surface is obtained by the model for the lower rainfall intensity 4.4 min after rainfall initiation, compared to 4.3 min that was measured by Hubbard et al. (1989). Immediate ponding was measured and predicted for the high rainfall intensity. The excellent agreement between the calculated and measured ponding times provides credibility that the characteristic curves and initial conditions were appropriately evaluated.

The soil-chemical distribution with depth prior to rainfall initiation (the model's initial condition) has a substantial effect on the chemical concentration both at the soil surface and in overland flow (Wallach and Shabtai, 1993). Since this distribution was not measured directly by Hubbard et al. (1989) it will be estimated from their description how nitrate was applied to the soil surface. For a soil with field capacity of about 0.17 (Fig. 3a) it can be assumed that a 0.5 l of the nitrate solution resides in a layer of 0.6 cm with an initial uniform concentration of 11.9  $\text{mg/cm}^3$ . The solution is displaced downward by the water added afterward. Based on the evaluated value of  $K_s$ , the solution is estimated to have moved about 2 cm downward during the 1 h period prior to rainfall initiation. Consequently, the estimated initial distribution is that the nitrate was confined within a 0.6 cm layer located 2.0 cm below the soil surface.

The measured (taken from Fig. 6 in Hubbard et al., 1989) and simulated surface runoff hydrographs and transient percolation rates are shown in Fig. 4 for the low and high rainfall intensities. The very good agreement between the measured and simulated distributions indicates that the soil type, initial soil water distribution, and boundary conditions were properly chosen and estimated. For comparison, GLEAMS predictions of the percent of overland flow and percolation losses for the low rainfall intensity are very close to the measured data. However, for the high rainfall intensity, GLEAMS predicts equal losses by surface runoff and percolation water, while 69.8 and

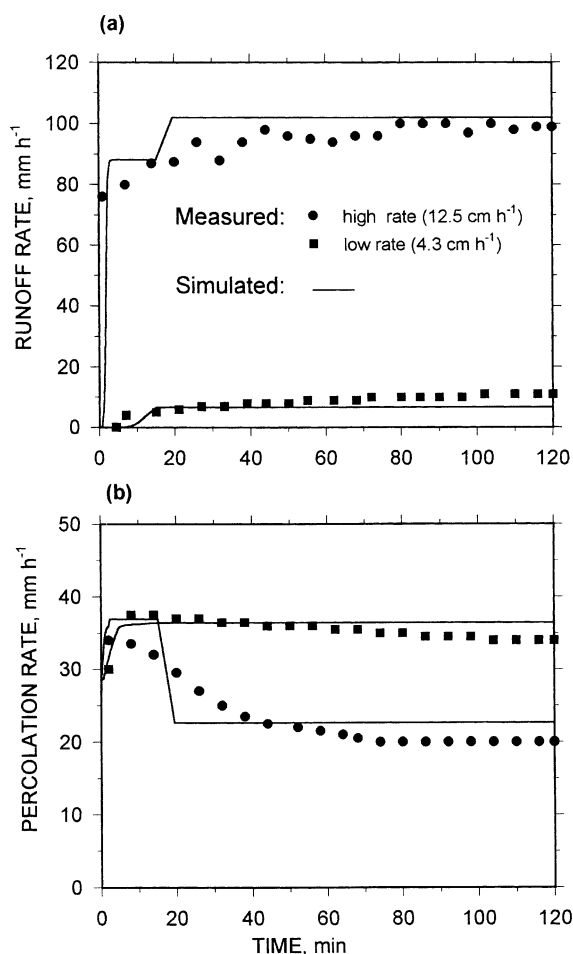


Fig. 4. Measured and predicted surface runoff hydrographs: (a) and percolation-rate distributions with time, (b) for rainfall rates of 4.3 and 12.5 cm/h.

Table 1

Measured (Hubbard et al., 1989) and predicted chemical mass load in surface runoff and deep percolation by the current model (for different initial distributions in the soil), GLEAMS and RUNOFF3 models for rainfall rate of 4.3 cm/h

	Nitrate in surface runoff		Nitrate in percolation water	
	Mg	%	Mg	%
Experiment	< 12.5	< 0.1	12488	99.9
Current model with $2.0 < z < 2.6$ cm	14.5	0.11	12150	97.2
Current model with $2.5 < z < 3.1$ cm	6.15	0.05	12150	97.2
Current model with $2.7 - z < 3.3$ cm	4.33	0.034	12150	97.2
GLEAMS	< 1.25	< 0.01	11050	88.4
RUNOFF3	–	–	–	–

17% were measured, respectively (Table 2 in Hubbard et al., 1989). For RUNOFF3 model losses by surface runoff and percolation water are not given (Ashraf and Borah, 1992). Note that the current model provides both distribution with time and total water losses by surface runoff and percolation water for a given rainfall intensity and duration.

The measured (taken from Fig. 7 in Hubbard et al., 1989) and predicted concentrations in overland flow at the boxes' outlet for the two rainfall intensities and various initial soil chemical distributions are shown in Fig. 5. For the high rainfall intensity, the model successfully predicts the measured data for the estimated initial nitrate distribution (uniform at  $2.0 < z < 2.6$  cm below soil surface). For the low rainfall intensity, the best prediction of the measured overland flow concentration is obtained for an initial nitrate depth of  $2.5 < z < 3.1$  cm below the soil surface, which is slightly larger than what was originally estimated.

The measured (taken from Table 2 in Hubbard et al., 1989) and predicted chemical loads in surface runoff and percolation water (by GLEAMS, RUNOFF3, and the current model) are given in Tables 1 and 2 for the low and high rainfall intensities, respectively. There, the measured chemical load for the lower rainfall rate (4.3 cm/h) is less than 12.5 mg. The current model predicts 6 mg (for initial soil-chemical distribution of  $2.5 < z < 3.1$  cm), and GLEAMS predicts a load smaller than 1.25 g. The chemical load in percolating water predicted by the current model is very close to the measured values (Table 1). GLEAMS predicts 10% less than the measured load. Ashraf and Borah (1992) have not provided predictions of chemical loads in surface and percolation water for the low rainfall intensity.

Table 2

Measured (Hubbard et al., 1989) and predicted chemical mass load in surface runoff and deep percolation by the current model (for different initial distributions in the soil), GLEAMS and RUNOFF3 models for rainfall rate of 12.5 cm/h

	Nitrate in surface runoff		Nitrate in percolation water	
	Mg	%	Mg	%
Experiment	225	1.8	8975	71.8
Current model with $1.0 < z < 1.6$ cm	685	5.48	10800	86.4
Current model with $1.6 < z < 2.2$ cm	221	1.8	11400	91.2
Current model with $2.0 - z < 2.6$ cm	101	0.8	11650	93.2
GLEAMS	–	–	11650	93.2
RUNOFF3	587.9	4.7	–	–

For the higher rainfall intensity (Table 2), the current model successfully predicts the measured chemical loads in surface runoff and percolation water, while GLEAMS predicts no load in surface runoff and a higher load than measured in percolation water. RUNOFF3 predicts a much higher load in surface runoff and does not provide the chemical load in percolation water.

#### 4. Sensitivity analysis

In the following we use the mathematical model to study the effect of the hydrological variables and parameters on the dynamics of surface runoff contamination by the soil dissolved chemicals. The effect of soil and hydrological parameters on chemical concentration in surface runoff is studied in two periods: prior to surface runoff initiation, when these parameters determine the distribution of chemical concentration with soil depth, and following the surface runoff initiation,  $t > t_p$ , when the hydrological parameters directly control the surface runoff flow and chemical transport.

##### 4.1. The effect of the initial soil moisture distribution

The prominent effect of the initial chemical distribution below the soil surface on surface runoff contamination is demonstrated above (Fig. 5 and Tables 1 and 2). For example, if the nitrate is initially located at  $1.0 < z < 1.6$  cm (only 0.6 cm higher than was previously estimated from the description in Hubbard et al., 1989), the chemical load will be three times larger than the predicted load in Table 2. In the sequel we study the effect of initial soil-water

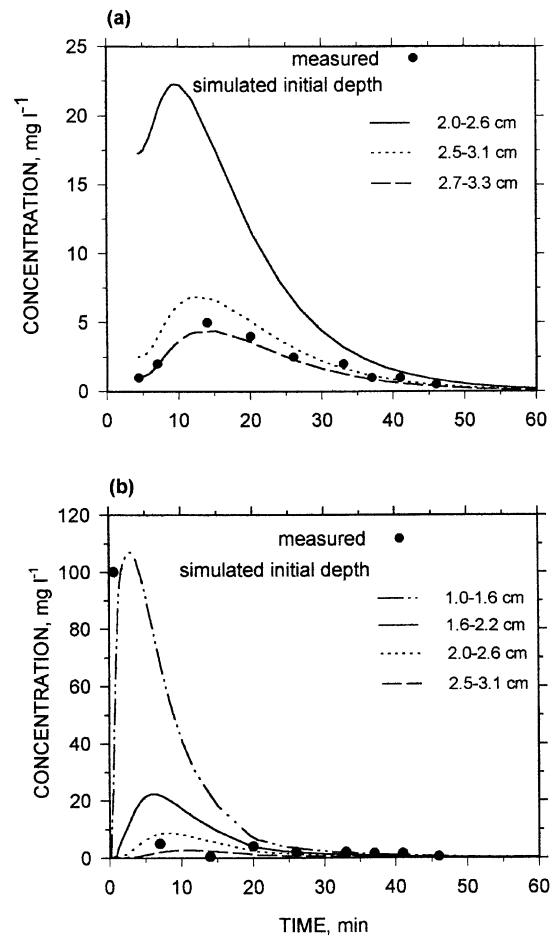


Fig. 5. Measured and predicted overland flow concentrations at the slope outlet for: (a) 4.3 and (b) 12.5 cm/h. The simulations included different depths where soil chemicals are located prior to the rainfall initiation.



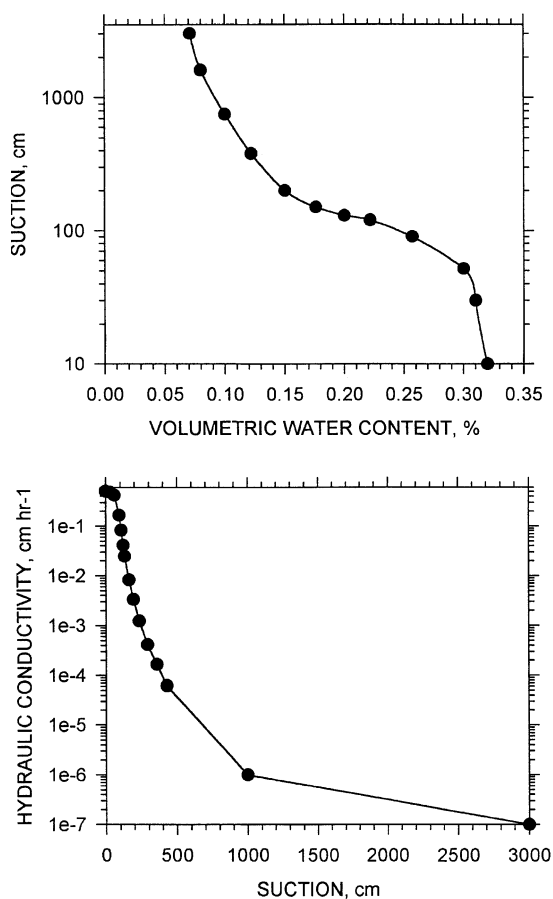


Fig. 6. The characteristic curves (retention curve and hydraulic conductivity versus moisture suction) for Pachappa fine sandy clay.

suction (which is equivalent to the volumetric moisture content through the soil's retention curve,  $\theta(\psi)$ ) on the overland flow hydrograph. The soil used for these simulations is Pachappa fine sandy clay Mualem, 1976, the values of porosity is  $\theta_s = 0.334$ , hydraulic conductivity of the saturated soil  $K_s = 0.504$  cm/h, and  $\rho = 1.42$  g/cm. Its characteristic curves,  $K(\psi)$  and  $\theta(\psi)$ , are shown in Fig. 6. The simulated slope is 100 m long and has a 5% gradient with a roughness coefficient of  $K_r = 500$ . The three hydrographs shown in Fig. 7a were calculated for uniformly distributed initial soil matric potentials ( $\psi = 20, 61.5$  and  $100$  cm) and a rainfall intensity of  $2.7$  cm/h that stops  $60$  min after runoff initiation. The calculated ponding times,  $t_p$ , for these input data are

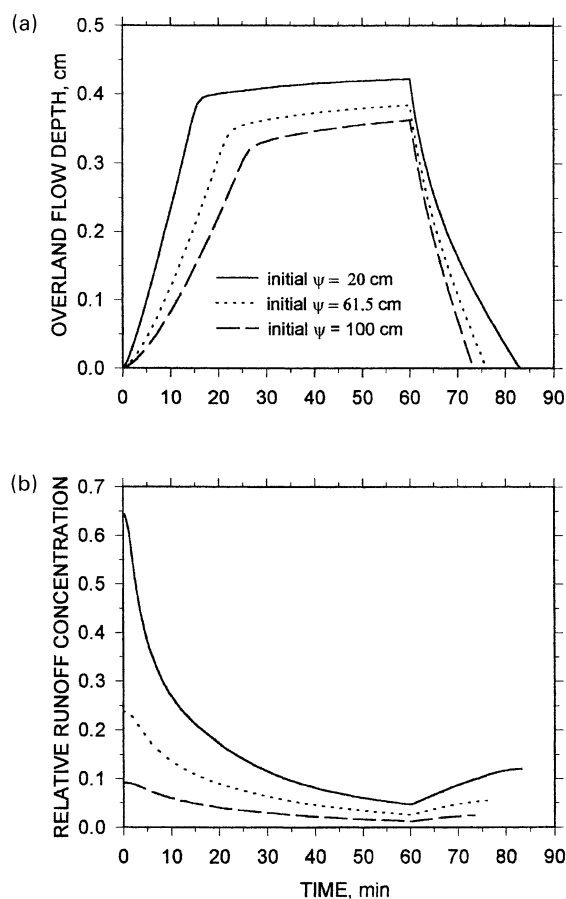


Fig. 7. Variation with time after runoff initiation of: (a) overland-flow depth, and (b) runoff concentration at the outlet ( $L = 100$  m), for different initial soil suction calculated for  $f = 2.7$  cm/h and  $K_r = 500$ .

1.3, 13.5, and 31.1 min, for  $\psi = 20, 61.5$  and  $100$  cm, respectively (Table 3). Also,  $t_p$  is strongly influenced by the initial soil moisture content, since higher rainfall volumes infiltrate before the soil surface becomes saturated, and surface runoff initiates when  $\psi$  is initially higher (initially drier soil).

The effect of the initial matric potential on the distribution of dissolved chemical concentration at the slope outlet,  $c_r(t)$ , is shown in Fig. 7b. The uniformly distributed initial soil chemical concentration,  $c_0$ , is used to normalize the runoff concentration. Higher concentrations are obtained for lower initial matric potentials (initially wet soils). The initial soil

Table 3

Total soil-chemical mass at the field outlet, times of ponding and equilibrium for different rainfall rates and  $\psi_0 = 61.5$  cm

$f$ (cm/h)	$t_p$ (min)	$t_e$ (min)	M	
			At rainfall end	At runoff end
1.6	52.2	40	75.3	83.7
2.7	13.5	23	505	529
6.0	2	12	1510	1540

moisture content plays a major role on surface runoff concentration due to its effect on ponding time. Lower initial moisture contents (higher matric potentials) increase the time during which the dissolved soil chemicals are displaced downward with the infiltrating water prior to runoff initiation. This lowers the soil chemical flux to the overland flow afterward. This lowers the soil chemical flux to the overland flow afterward.

The soil chemical mass (load) leaving the slope outlet during a single storm is calculated by

$$M = \sum_{j=1}^T \sum_{i=1}^L \frac{(c_r)_{ij}}{c_0} \alpha h_{ij}^{m-1}, \quad (19)$$

where  $h_{ij}$  and  $(c_r)_{ij}$  are the overland-flow depth and concentration, respectively, at point  $i$  along the slope and time  $j$  during the runoff event, and  $\alpha$  and  $m$  are overland flow parameters (Eq. (2)). The total chemical loads in overland flow for the three initial matric potentials are given in Table 3 for: (1) when rainfall stops (60 min after runoff initiation) and (2) when overland flow stops. These results, together with Fig. 7, agree with field studies by Baldwin et al. (1975), Wauchope et al. (1990), and Walton et al. (2000) when simulated rainfall is applied to the soil surface. They found that runoff from antecedently dry plots contains lower concentrations in overland flow. Their qualitative explanation of these findings is similar to what has been demonstrated by the current mathematical model.

#### 4.2. The effect of rainfall rate

The effect of rainfall rate on overland flow hydrographs is shown in Fig. 8a where the hydrographs were calculated for three rainfall rates (1.6, 2.7, 6.0 cm/h) that stop 60 min after runoff initiation. The uniformly distributed initial soil matric potential

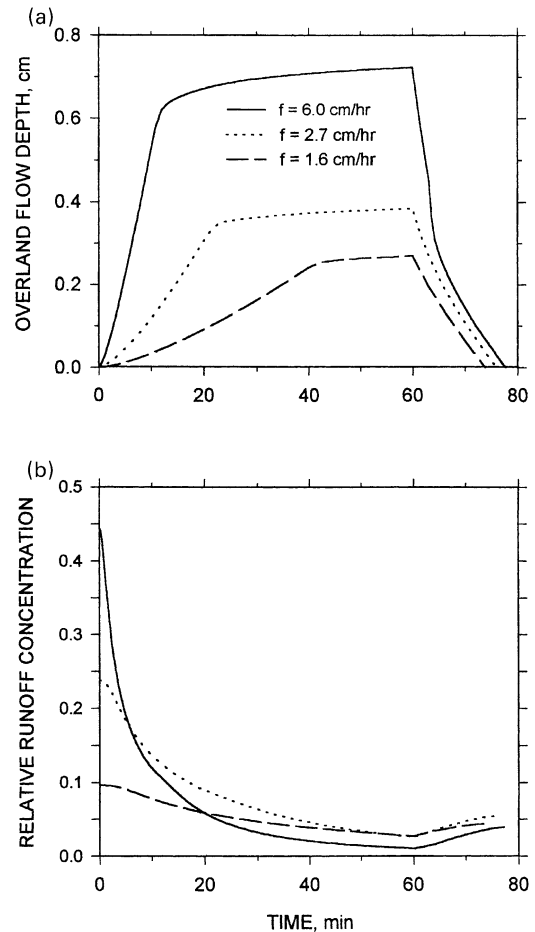


Fig. 8. Variation with time after runoff initiation of: (a) overland-flow depth and (b) runoff concentration at the outlet ( $L = 100$  m), for different rainfall rates calculated for  $\psi_0 = 61.5$  cm and  $K_r = 500$ .

is  $\psi = 61.5$  cm, and the other slope parameters are as in Fig. 7. The calculated ponding times,  $t_p$ , are 52.2, 13.5, and 2.0 min for rainfall rates of 1.6, 2.7, and 6.0 cm/h, respectively (Table 4). Thus, longer ponding times are associated with the lower rainfall rates for a given initial soil moisture content.

The variation of runoff concentration with time at the slope outlet for these three rainfall rates and a uniformly distributed initial soil chemical concentration,  $c_0$ , is shown in Fig. 8b. The positive correlation between the initial chemical concentration in overland flow and rainfall rate (Fig. 8) is explained by the negative correlation between the rainfall rate and

Table 4

Total soil-chemical mass at the field outlet, times of ponding and equilibrium for different initial soil water potentials and  $f = 2.7$  cm/h

$\psi_0$ (cm)	$t_p$ (min)	$t_e$ (min)	M	
			At rainfall end	At runoff end
20	1.3	17	1650	1730
61.5	13.5	23	505	529
100	31.1	29	165	174

ponding time (Table 4). Since ponding time is also negatively related to the initial soil moisture content, it obviously represents the effect of both rainfall rate and initial soil moisture content on surface runoff concentration by the single parameter,  $t_p$ .

After runoff initiation,  $t > t_p$ , the concentration distribution at the slope outlet is affected mainly by the travel time along the slope. The travel time expresses the opportunity time of an overland flow parcel to absorb the rate-limited transfer of soil chemicals. As such, it depends on the overland flow regime and can be related to the equilibrium time,  $t_E$ . This hydrological parameter integrates the role of the following parameters on overland flow: rainfall rate (Table 4), antecedent soil moisture content (Table 3), soil surface roughness, and slope gradient.  $t_E$  is shorter for higher rainfall rates, slope gradients, and  $\alpha$  (Eq. (2)) values and is associated with a steeper increase in overland flow depth toward its ultimate value (Fig. 8a). Regarding chemical transport, shorter  $t_{ES}$  induce quicker washout of the dissolved chemical by overland flow soon after runoff initiation. Therefore, overland flow concentration decreases sharply soon after runoff initiation for shorter  $t_{ES}$  (Figs. 6b and 8b).

The total chemical mass that leaves the 100 m long slope is given in Table 3 for the three rainfall rates. The rainfall rate has a significant impact on the chemical load into surface runoff, and the ratio between any two mass loads is greater than the ratio between the respective rainfall rates.

The effect of rainfall rate on overland flow concentration and load extends throughout the rainfall and runoff duration since it controls ponding and equilibrium times. This is contrary to the initial moisture content, the indirect effect of which is by displacing the soil chemicals downward prior to runoff initiation,  $t < t_p$ .

### 4.3. The momentary chemical balance along the slope

The transfer of dissolved soil chemicals to overland flow and their transport toward the slope outlet are two rate-limited processes in which other rate-limited processes are involved. Thus, their relative concentration distribution at the slope outlet varies with time. Their changing role during the different stages of a rainfall–runoff event is discussed by defining three auxiliary variables: the rate of chemical mass outflow, the rate of chemical mass inflow, and the change in storage of the dissolved-chemical mass in overland flow. The terms ‘inflow’ and ‘outflow’ are related to the overland-flow. The rate of outflow mass at each time step is a multiplication of the momentary overland-water flux by its chemical concentration, both at  $x = L$ . The rate of mass inflow at each time step is a sum of the momentary local values of  $k(c_s - c)$  along the slope. The change in mass-storage is the difference between the momentary chemical mass in surface runoff along the entire slope at any two consecutive time steps. The variation of these three auxiliary variables with time are shown in Fig. 9 for the three previously used rainfall rates ( $f = 1.6, 2.7,$  and  $6.0$  cm/h).

All curves in Fig. 9 start at the origin since the local overland flow and soil surface concentrations are initially equal, ( $c_r(x, t_p) = c(x, 0, t_p)$ ). Soon after runoff initiation, the increase of the mass-inflow rate is much faster than the increase of the mass-outflow rate (Fig. 9), whereas the curves for the mass inflow rate and mass storage change are very close. This indicates that soil chemicals that have been transferred to overland flow during this period reside mainly in the surface runoff. The gap between the curves for mass inflow and mass outflow rates is larger for lower rainfall rates. Note that the chemical concentration at the slope outlet ( $x = L$ ) is highest soon after runoff initiation (Fig. 8b), while the mass outflow rate is small (Fig. 9). This point is discussed further later in this paper. During the next stage of runoff flow, the mass outflow rate becomes larger than the mass inflow rate, which decreases moderately, whereas the change in mass storage decreases sharply down to a minimum value (Fig. 9). Thus, the main source of chemicals leaving the slope outlet during this stage is the depletion of overland flow storage (the negative storage change in Fig. 9). During

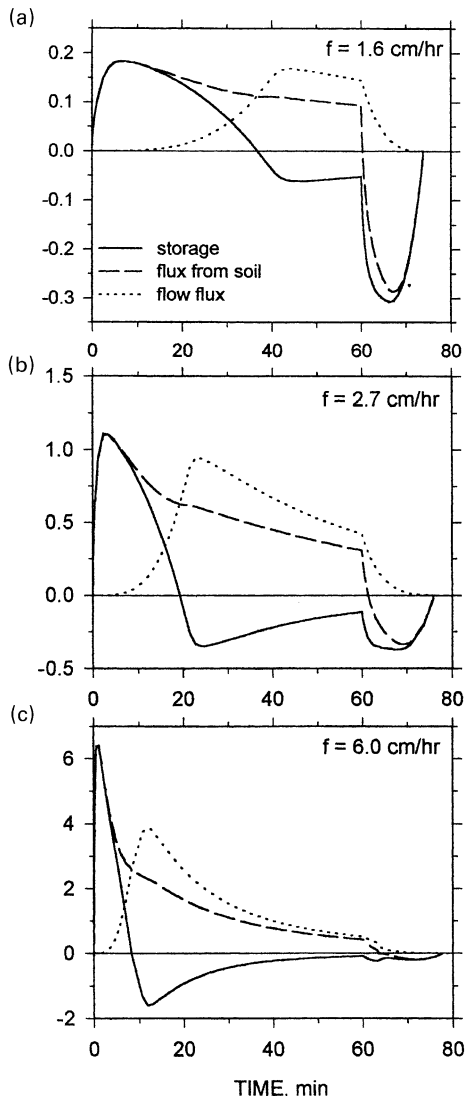


Fig. 9. Variation with time after runoff initiation of the rate of chemical-mass outflow, rate of chemical mass inflow, and change of storage of dissolved chemicals in the overland flow for different rainfall intensities,  $\psi_0 = 61.5$  cm, and  $K_r = 500$ .

its decrease, the change in overland flow storage becomes zero at the time when the rates of mass input and output are equal. Beyond that time, the main source for the momentary mass outflow is the momentary soil chemical inflow. The gap between these two curves diminishes, causing an increase in the change of mass storage in overland flow (Fig. 9).

In spite of the positive values of the chemical outflow rate throughout the overland flow event, the chemical inflow rate is positive only during the rainfall event and becomes negative when rainfall stops and the slope drains (Fig. 9). These negative values indicate that, during the drainage period, the net dissolved chemical flux is from the overland flow to the soil with infiltrating water.

The variation with time of runoff concentration (Fig. 8b) is opposite the mass outflow rate for all rainfall rates that have been studied in Fig. 9a,b,c. While the first is initially high and decreases monotonously, the second increases slowly to a maximum value and decreases afterwards. The opposite pattern of these two curves is because of the dependence of the mass outflow rate on both overland-flow discharge and concentration. Being a multiplication of overland-flow depth (increases with time, Fig. 8a, and is independent of soil chemical transfer and transport) and runoff concentration (decreases with time, Fig. 8b), the mass outflow rate is low soon after runoff initiation in spite of the high overland flow concentration. Afterward, the surface-water concentration decreases, but the mass outflow rate increases with the increasing water discharge. Finally, when overland flow discharge becomes constant ( $t > t_E$ ), the mass outflow rate decreases owing to the diminishing soil chemical flux to surface runoff. Note that the chemical outflow rate and the surface runoff concentration express the actual pollution load in surface water.

The above analysis confirms the findings, shown in Fig. 8b, that higher rainfall rates and shorter ponding times yield higher dissolved chemical fluxes at the slope outlet. This provides additional information on the relationship between chemical fluxes and storage and surface runoff flow.

## 5. Discussion and conclusions

The current model, which contains explicit equations for flow and transport in the soil and overland flow was used to study the dependence of surface runoff pollution on different hydrological parameters. This investigation is achieved owing to the detailed formulation of the different rate-limiting processes. The simulations indicate that the initial dissolved chemical distribution within the soil profile has the most

prominent effect on the load to overland flow and its estimation prior to the model runs is crucial to the model's predictability. Rainfall rate and initial soil moisture content indirectly affect the chemical output at the slope outlet by their role on soil chemical distribution prior to surface runoff initiation. During the rainfall event and before rain-water ponding on the soil surface,  $0 < t < t_p$ , soil dissolved chemicals are being displaced downward by the infiltrating water. This displacement decreases the availability of soil chemicals to pollute the overland flow for  $t \geq t_p$ . As the displacement time (and depth) increases, the potential of overland flow pollution decreases. The effect of rainfall rate and soil moisture prior to rainfall initiation on overland flow pollution could be conveniently represented by a single variable: ponding time,  $t_p$ . Longer ponding times are associated with lower rainfall rates and an antecedently drier soil profile; moreover, longer ponding times induce lower chemical concentration and load in surface runoff. The simulation results indicate that the effect of rainfall intensity and antecedent soil moisture on the soil chemical load to surface runoff is significant. Such a conclusion can not be derived by models in which the flow and transport processes prior to surface runoff generation are not included.

After runoff initiation, the hydrological parameters associated with overland flow have the main role on the concentration distribution at the slope outlet. The effect of rainfall rate, slope gradient, and soil roughness at this stage are represented by a single parameter: the equilibrium time,  $t_E$ , which increases for lower rainfall rates, slope gradients, and higher soil surface roughness coefficients. Being the opportunity time of an overland flow parcel to absorb the soil chemical flux while moving along the slope, a higher equilibrium time increases the chemical concentration in overland flow at the slope outlet for a constant soil-chemical flux. However, the soil-chemical transfer coefficient is positively correlated to the overland flow velocity. Therefore, the soil chemical flux is not constant with time and location along the slope, its value depends on other parameters, and the effect of  $t_E$  on the outflow concentration is not always straightforward and easily predictable.

The study of transient variation of soil chemical flux to overland flow and chemical flux at the slope outlet, and the change of chemical storage in overland

flow, provide new insight into the relationship between the different dynamic processes throughout the storm. It shows that a transition time, soon after runoff initiation, exists during which the sharp decrease in outflow concentration is controlled by the dissolved chemical transport in overland flow rather than by the momentary soil chemical flux. The transition time starts at runoff initiation ( $t = t_p$ ) and ends when the rate of chemical mass inflow is equal to the rate of chemical mass outflow (Fig. 9). It is longer for lower rainfall intensities (Fig. 9) and slopes with lower gradients and higher roughness coefficients. During this time, overland flow depth is shallow, the coefficient for soil-chemical transfer,  $k$ , is very large, and an instantaneous equilibration between soil surface and overland flow concentrations can replace the rate-limited transfer of soil chemicals to overland flow.

The existence of such a transition time and the major effect of some hydrological parameters on the outflow concentration during this period, while the other parameters have a significant effect during other periods, was utilized in Wallach (1991, 1993). There, a time-scale analysis was carried out to normalize the mass balance equations, and this provides a dimensionless ratio of two time scales,  $\delta$ . For the current problem,  $\delta$  is generally small since the time scale of chemical transport in overland flow is much faster than the time scale of soil chemical transfer to the overland flow. The use of the small perturbations method provided inner and outer problems where the inner problem is valid during a transition time at  $t = t_p$ , and the outer problem is valid during the rest of the runoff duration. That transition time coincides with the current one, obtained by calculating the variation of chemical fluxes and storage during the storm. The inner problem that expresses the significant role of surface runoff flow during the transition time includes the equations for surface runoff flow and chemical transport, together with an instantaneous equilibrium between soil surface and overland flow concentrations. The existence of an instantaneous equilibrium in these equations simplifies their solution.

Following the transition time, the rates of inflow and outflow mass vary similarly with time (Fig. 9). This indicates that the source of chemical outflow at this stage is the soil chemicals' transfer to overland

flow, rather than the intensive depletion of chemical storage in the overland flow. Since the rate-limited soil chemical transfer to overland flow has the leading effect on outflow concentration at this stage, the equations for overland flow and transport can be simplified without a major effect on the overall solution. This quantitative analysis agrees well with the outer approximation that was mathematically obtained in Wallach (1991, 1993) by time-scale analysis.

According to the discussion above, runoff concentration prediction by models in which simplified equations are used for flow and transport in surface runoff (e.g. Wallach and Genuchten, 1990; Wallach and Shabtai, 1993) is less accurate soon after runoff initiation. Following the transition period, the concentration distribution at the slope outlet is mainly affected by processes of slower time scales. Therefore, lumped models that are based on mixing between chemicals in the soil-surface mixing layer and overland flow fail to predict the chemical distribution at the slope outlet for these periods. However, if such lumped models combine rate-limited processes of slow time scales (e.g. adsorption–desorption kinetics), substantial predictions could be obtained. The sharp decrease immediately after runoff initiation is due to the depletion of dissolved chemicals that exist in the mixing layer at ponding time. The moderate decrease afterward is due to the rate limited transfer of chemicals to the mixing layer. An example of a model that includes fast and slow time scales which are related to different processes than in the case of the current study has been presented by Zhang et al. (1997). The model includes a soil-surface mixing layer and a rate-limited dissolved chemical diffusion into the mixing layer from a deeper layer, which account for the fast and slow time scales, respectively. In spite of the significant differences between that model and the current model, the existence of fast and slow time scales in both models provides similar concentration distributions at the outlet of short slopes. However, for longer slopes, where runoff flow affects the concentration distributions at the slope outlet, the physically based models have an advantageous over models in which surface runoff flow and transport are lumped into a mixing layer.

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