MODELING OF OVERLAND FLOW CONTAMINATION DUE TO HEAVY METALS IN SHALLOW SOIL HORIZONS

R.S. Govindaraju and L.E. Erickson, Departments of Civil and Chemical Engineering, Kansas State University, Manhattan, KS 66506

ABSTRACT

Heavy metals in southeast Kansas are frequently found in the shallow soil layers. Rainfall events in this region often generate overland flows which cause the release and migration of these chemicals into surface waters. The chemicals are then transported in surface waters to downstream locations and, as such, pose a threat to the quality of both fields along streams and surface and ground waters. In many instances, overland flow does not develop immediately as a sheet over the land surface, but gradually increases in extent in accordance with the variable source area (VSA) concept. The overland flow regions diminish once the surface water application rate ceases. This paper deals with the modeling of surface contamination under such circumstances. Results were obtained for a single hypothetical plot. These simulation results indicate that source area for heavy metal removal varies in a similar manner to source area of water. Some comparisons were made regarding the relative amounts of solute lost to overland flow and to those leached into the soil as a function of time. The subsurface response was found to be slower than surface response to the rainfall event.

KEY WORDS

overland flow, contamination, transport, variable source areas

INTRODUCTION

Extensive mining activities in portions of southeast Kansas have resulted in significant heavy metal concentrations in soils. For example, heavy metals have been transported, both by surface and subsurface waters, to the flood plains of Spring river watershed, leading to reduced plant growth and agricultural productivity [1-2]. The magnitude and frequency of water application, antecedent soil moisture conditions, vegetation and soil characteristics are some of the factors which govern what portion of applied water infiltrates into the soil. Ponded conditions occur frequently, leading to overland flow which provides a rapid means of transport for the chemicals at the soil surface. The transport of heavy metals may be separated into three different phases (i) via overland flows, which is the topic of study in this paper, (ii) via subsurface flows, and (iii) via streams. This paper presents some preliminary efforts at linking surface flows, subsurface flows, and a solute transport component to describe solute movement via overland flow. The solute transport component describes the movement of a conservative tracer. A condensed version of this paper has been tentatively accepted for publication in Water Resources Research.

There have been several modeling efforts in the past to describe chemical transport over land surfaces. Ahuja [3] states that the commonly used models (such as ARM — Agricultural Runoff Management model [4], and CREAMS model [5]) are not satisfactory for predicting chemical transfer from agricultural plots for individual rainfall-runoff events. These models assumed that a zone of effective depth of interaction exists at the soil surface, within which soil solution concentrations remain constant and are equal to that in the surface water [4, 6]. The studies of Ingram and Woolhiser [7], Ahuja and Lehman [8], and Snyder and Woolhiser [9] indicated that solute concentrations in runoff water are usually lower than those in soil solution, thus invalidating the assumption of perfect mixing between surface and soil water. Based on experimental results [8, 10], it was concluded that the degree of interaction or mixing between the surface and soil water was not uniform and decreased exponentially with depth below the soil surface. Ahuja [3] provides a review of experimental and mathematical modeling practices for chemical transfer into overland flow.

More recently, Wallach et al. [11, 12], Wallach and van Genuchten [13] and Wallach and Shabtai [14-16] have utilized physics-based approaches to address the problem of transfer of chemicals from land surfaces to overland flows. Wallach et al. [11] used a convective-dispersive model for solute transport in soil and considered rate limited transfer at the interface of soil surface and water surface. They treated the runoff zone as a well-mixed unit characterized by a residence time. Sorption-desorption kinetics were included by Wallach and Shabtai [15] in their analysis. These studies have not simulated surface water flow in a detailed manner. Spatial variation of overland flow initiation and development was not addressed. Peyton and Sanders [17] have emphasized the importance of mixing due to raindrop impact action on solute travel times and distances in overland flows. However, their studies were restricted to impervious surfaces.

This study focuses on solute transport in overland flow over infiltrating surfaces which are neighboring streams. The presence of such streams leads to interesting hydrologic situations because regions immediately bordering streams saturate rapidly and develop surface flow even if water application rate (rainfall/irrigation) is less than soil hydraulic conductivity. These regions of surface flow expand under prolonged rainfall, as does the region over which the soil surface is losing chemicals to surface flow. When rainfall/irrigation stops, these surface-contributing regions diminish. These regions, contributing to overland flow (and corresponding chemical loss), which expand and contract in response to water application onto the soil surface and the subsurface soil-moisture status, are called variable source areas (VSAs). Water travels 100 to 500 times faster as overland flow than it does as subsurface flow. In investigating the stream hydrograph, the response time of any water in the system is therefore controlled by how far it has to travel to get to the stream (slope length) and the mechanics of its transfer (pathway). Methods of predicting VSA expansion and shrinkage during rainfall/irrigation events are useful since overland flow routes from the near-channel contributing areas have practically zero time lag (as compared to subsurface flow contributions of water and solutes) in reaching the streams. The purpose of this paper is to develop a preliminary physics-based model for analyzing surface flow and heavy metal transport in such situations.

The problem of mathematical modeling of water movement alone under VSA hydrology has received considerable attention in the literature. Freeze [18] was the first to address the effect of hillslope parameters on the stream hydrograph at the outlet of a hillslope section. He found that on concave slopes with low soil permeabilities and on most convex slopes, the dominating contribution to the stream hydrograph comes from overland flows on transient variable source areas neighboring the streams. Beven [19] used a finite element model for a two-dimensional subsurface flow coupled to a one-dimensional stream flow. He demonstrated that the initial conditions, particularly in the unsaturated zone, are of primary importance in determining the time and magnitude of the hillslope hydrograph peaks. Smith and Hebbert [20] studied the surface-subsurface flow interaction using the kinematic wave approximation for surface flows in conjunction with a simplified but analytical infiltration model which is applicable to cases when rainfall exceeds infiltration capacity of the soil. Binley [21, 22] and others have studied the problem of stochastic runoff generation by using a physically based heterogeneous hillslope model where surface flow routing is based on a linearized approach instead of the solution of the partial differential equations governing unsteady flows. Govindaraju and Kavvas [23] developed a physics-based model for VSA hydrology based on numerical solution of overland flows, stream flows and the subsurface saturated-unsaturated flows with dynamic interaction at common boundaries. Their model is used to generate the flow field in this study. Many physics-based modeling studies have emphasized the nonlinear nature of the rainfall-runoff relationship at small scales (agricultural plot scale). This work presents an extension to that of Govindaraju and Kavvas [23] by including a solute transport component for the surface flow section. The responses of the surface and subsurface to flow and solute transport for an individual storm event were investigated.

MATHEMATICAL FORMULATION OF THE HYDROLOGIC SYSTEM

The mathematical representation of the flow and transport processes over an agricultural plot leads to a set of nonlinear partial differential equations. Analytical solutions of such systems are not available, and numerical techniques are used to solve them. The equations used in this study for describing the flow processes are presented in this section. The flow equations are presented in detail in other studies (see [23]) and are presented here for completeness.

Stream flow equations

The equations of continuity and momentum in a channel are

$$V\frac{\partial A}{\partial x} + A\frac{\partial V}{\partial x} + \frac{\partial A}{\partial t} = Q \qquad (1)$$

$$S_f = S_0 - \frac{\partial y}{\partial x} - \frac{V}{g}\frac{\partial V}{\partial x} - \frac{1}{g}\frac{\partial V}{\partial t} - \frac{QV}{gA} \qquad (2)$$

These are the Saint-Venant equations describing the propagation of flood waves in a channel. In the above equations, x is the distance along the horizontal direction, V is the mean velocity of water in the channel cross-section, A is the area of flow cross-section normal to the horizontal direction, t is the time, Q is the lateral inflow entering the channel per unit length, S_0 is the channel bed slope, y is the flow depth normal to the flow direction, g is acceleration due to gravity and S_f is the friction slope or the slope of the total energy line along the channel.

Numerical solutions to the above equations suffer from problems of convergence and stability due to their highly nonlinear nature. Hence investigators have used simplified versions of these equations whenever justified. Common simplification techniques have been discussed elsewhere [24]. Gonwa and Kavvas [25] have demonstrated that the diffusion wave approximation to the full Saint Venant equations is adequate for many cases of practical interest. The diffusion wave approximation was used in analyzing the stream flow component in this study. Substituting the diffusion approximation of the momentum equation into the continuity equation (1) leads to the following equation describing the flood propagation in trapezoidal channels:

$$\frac{\partial y}{\partial t} + C_w\frac{\partial y}{\partial x} + \delta = \alpha\left(\frac{\partial^2 y}{\partial x^2} - \frac{\partial S_0}{\partial x}\right) \qquad (3)$$

For trapezoidal channels, the cross sectional area, A, is

$$A = by + zy^2 \quad (4)$$

where b is the bottom width and z is the inverse of the side slope. The generalized friction law is represented as

$$V = DR^m \left(S_0 - \frac{\partial y}{\partial x} \right)^j \quad (5)$$

where R is the hydraulic radius of the flow section. With appropriate choice of D, m and j, the familiar Manning's law, Chezy's law or the Darcy-Weisbach friction relationship can be obtained from Equation 5. In Equation 3 the wave celerity C_w is

$$C_w = V(1 + m\Omega) \quad (6)$$

where Ω is given by the expression

$$\Omega = 1 - \frac{2R}{T}\left(1 + z^2\right)^{1/2} \quad (7)$$

in which T is the top width of the flow section. In Equation 3,

$$\delta = \frac{Vy}{T}\frac{\partial b}{\partial x} + \frac{Vy^2}{T}\frac{\partial z}{\partial x} + \frac{VAm}{TR}\xi - \frac{Q}{T} \quad (8)$$

where ξ is defined as

$$\xi = \frac{1}{P}\left(y\frac{\partial b}{\partial x} + y^2\frac{\partial z}{\partial x} \right) - \frac{A}{P^2}\left\{ \frac{\partial b}{\partial x} + 2zy\left(1 + z^2\right)^{-1/2}\frac{\partial z}{\partial x} \right\} \quad (9)$$

Here P is the wetted perimeter, which for trapezoidal sections is

$$P = b + 2y\left(1 + z^2\right)^{1/2} \quad (10)$$

The diffusion coefficient α in Equation 3 is defined as

$$\alpha = \frac{VAj}{T\left(S_0 - \frac{\partial y}{\partial x} \right)} \quad (11)$$

Equations 3 to 11 constitute the nonlinear diffusion wave approximation for the description of flood propagation in trapezoidal channels.

Overland flow equations

The diffusion wave approximation for overland flows leads to the following equation [23]

$$\frac{\partial h}{\partial t} + C_{wo}\frac{\partial h}{\partial x} + \delta_o = \alpha_o\left(\frac{\partial^2 h}{\partial x^2} - \frac{\partial S_{0_o}}{\partial x} \right) \quad (12)$$

with the generalized friction law for overland flows becoming

$$V_o = D_o h^{mo}\left(S_{0_o} - \frac{\partial h}{\partial x} \right)^{jo} \quad (13)$$

where h is the depth of flow, V_o is the depth averaged overland flow velocity, S_{0_o} is the slope of the overland flow bed, x is the coordinate along the horizontal direction and t is time. In Equation 13, D_o, mo and jo are constants. The value assigned to these constants depends on whether the flow is laminar or turbulent, the effect of vegetation which may be present, and an appropriate friction relationship for the conditions on the plot. For overland flow applications, the definitions of terms appearing in Equation 12 are

$$C_{wo} = V_o(1 + mo) \quad (14)$$

$$\delta_o = -Q_o \quad (15)$$

$$\alpha_o = \frac{V_o hjo}{s_{0_o} - \partial h / \partial x} \quad (16)$$

where Q_o is the net lateral inflow to the overland flow section per unit length of flow.

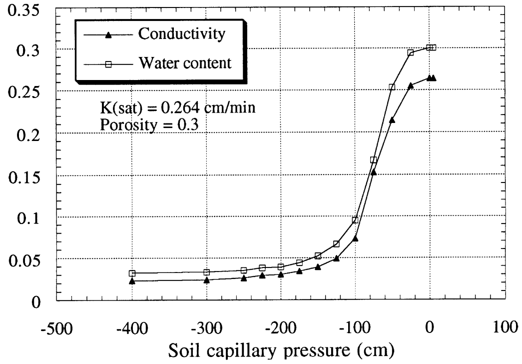

Figure 1. Hydraulic conductivity $K(\psi)$ and water content $\theta(\psi)$ versus capillary pressure (ψ). The saturated soil hydraulic conductivity is 0.264 cm/min and porosity is 0.3 (adapted from [18]).

Saturated-unsaturated ground water flow equations

The subsurface region is comprised of saturated (capillary pressure $\psi > 0$) and unsaturated regions ($\psi < 0$) which are separated by the water table (surface at which $\psi = 0$). Some of the basic assumptions made in modeling subsurface flows are: (a) only liquid flow is considered even though the flow may occur both in liquid and vapor form, (b) the porous medium is incompressible, and (c) Darcy's law is valid. Within these limitations, subsurface flow may be described by a continuity equation expressed as

$$\frac{\partial}{\partial t}[\rho\theta] + \operatorname{div}(\rho q) = s \tag{17}$$

where q is the specific discharge of water, ρ is the density of water, θ is the moisture content by volume of the soil, s is a source/sink term (incorporating the effects of evapotranspiration, rain infiltration, etc.). The continuity Equation 17 is combined with Darcy's law which may be stated as

$$q = -K(\theta)\,\mathrm{grad}\,\phi \tag{18}$$

where $K(\theta)$ is the hydraulic conductivity of the soil and ϕ is the piezometric head which may be expressed as

$$\phi = \psi + z \tag{19}$$

where ψ is the capillary potential or suction head of the soil and z is the elevation above some fixed datum. Combining Equations 17, 18 and 19 leads to a single equation for a two-dimensional slice in the vertical (x,z) plane in terms of ψ as [23]

$$\left[\frac{\theta}{\eta}S_s + C(\psi)\right]\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial x}\left\{K_x(\psi)\frac{\partial\psi}{\partial x}\right\} + \frac{\partial}{\partial z}\left\{K_z(\psi)\left(\frac{\partial\psi}{\partial z}+1\right)\right\} + s \tag{20}$$

where $C(\psi)$ is called as the specific moisture capacity of the soil medium and is expressed as

$$C(\psi) = \frac{d\theta}{d\psi} \tag{21}$$

In Equation 20, η denotes the soil effective porosity and S_s is the specific storage of the soil defined as

$$S_s = \rho g\eta(C_w + C_f) \tag{22}$$

where g is the acceleration due to gravity, C_w is the compressibility of water and C_f is the compressibility of the soil medium. The soil porosity was taken as 0.3 and the specific storage for the soil matrix was assumed to be 0.0001 m in all examples presented in this paper. Thus, under isotropic conditions, only two functional relationships are required to solve for Equation 20: $\theta(\psi)$ and $K(\psi)$. These functions are shown for a typical sandy soil in Figure 1. The hydraulic conductivity of the soil is usually expressed as

$$K(\psi) = K(sat).K_r(\psi) \tag{23}$$

Flow boundary conditions:

ABC:	Region in contact with stream	$\psi = y(l,t)$
CD:	Overland flow region (VSA)	$\psi = h(x,t)$
DE:	Flux boundary. Net flux = I(x,t)	$I(x,t) = K(x,t)[\frac{\partial \psi(x,t)}{\partial z} + 1]$
EG:	Impermeable boundary	$\frac{\partial \psi}{\partial x} = 0$
HG:	Impermeable base	$\frac{\partial (\psi + z)}{\partial z} = 0$
AH:	Impermeable boundary	$\frac{\partial \psi}{\partial x} = 0$

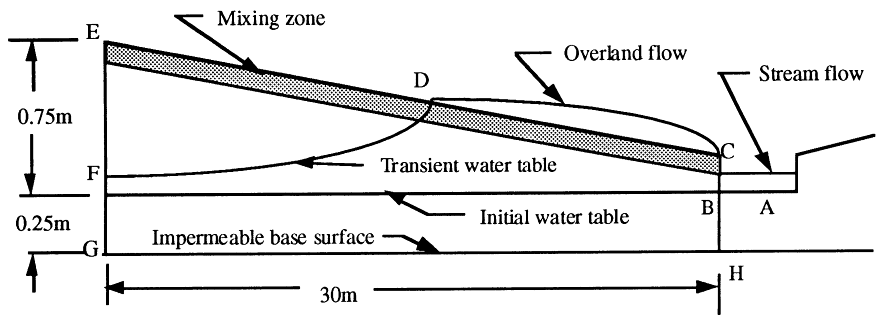

Figure 2. Description sketch of the agricultural plot showing the flow boundary conditions (adapted from [23, 27]) and the mixing zone.

where K(sat) is the saturated hydraulic conductivity of the soil and is a constant for a given soil type and $K_r(\psi)$ is the relative hydraulic conductivity of the soil. Figure 1 shows single valued relationships for the characteristic curves of a soil but, in general, these functions are hysteretic and, hence, non-unique specification for $K(\theta)$ and $\psi(\theta)$ may result for a given θ depending on the wetting and drying history of the soil.

Solute transport equations

Figure 2 is a description of the flow and surface solute transport problem. It was assumed that the soil surface has a uniform initial concentration of solute (Cm) to a depth ε. This region is the mixing zone. This is a different concept from effective depth of interaction used in previous studies. The mixing zone distributes solute to overland flow or to subsurface flow. These distribution rates are proportional to (i) infiltration rates, and (ii) solute concentration gradients. A simple model was utilized at this stage because exact relationships are not known. A convective-dispersive transport equation was used to describe the movement of a conservative solute in the overland flow region (similar to the one adopted by Peyton and Sanders [17])

$$\frac{\partial (ch)}{\partial t} + \frac{\partial (qc)}{\partial t} - \frac{\partial}{\partial x}\left(Eh \frac{\partial c}{\partial x} \right) = -k_1 (c - C_m) \quad (24)$$

$$\frac{\partial}{\partial t}(\varepsilon Cm) = k_1 (c - C_m) + k_2 (C_s - C_m) \quad (25)$$

where c(x,t) denotes the time-space dependent concentration of solute in the overland flow section, $C_m(x,t)$ is the concentration in the mixing zone, C_s is concentration in the soil beneath the mixing zone, h(x,t) is the overland flow depth, q(x,t) denotes the one-dimensional flow discharge, E indicates dispersion due to raindrop impact, flow and molecular diffusion, k_1 and k_2 are rate constants which are proportional to r1(x,t) (the infiltration rate at the soil surface) and r2(x,t) (the infiltration rate from the mixing zone into the soil below). The above representation treats the mixing zone as a single lumped unit in the vertical direction.

Initial and boundary conditions

Figure 2 shows the hypothetical section of two similar agricultural plots separated by a central stream. The subsurface section is 30 meters long. The overland and subsurface flow phenomena occur on the two side slopes and drain into the stream. Freeze [18] and Govindaraju and Kavvas [23] have discussed the end conditions applicable to such sections. These are presented in Figure 2. Note that the location of the point D determines the extent of the ponded domain at any time, and the region CD is the variable source area (Figure 2). The upstream boundary condition for the channel was taken as the zero inflow condition. It is usually assumed that the channel achieves uniform flow at the downstream. The downstream boundary condition of zero-depth-gradient was adopted for overland flow regions. However, one could also utilize a critical flow condition at the overland flow downstream section. The upstream moving boundary condition for overland flow was taken as the zero depth condition at the transient point D (see Figure 2). The lateral inflow into the stream at any section is the sum of the rainfall and the contribution from the overland flow section at the outlet point C (note that a symmetric section exists on both sides of the stream) minus/plus the quantity infiltrating/exfiltrating from/onto the base of the stream surface. Thus the lateral inflow into the channel at any channel node is

$$Q = R(t) + Q(over) \pm Qs(t) \tag{26}$$

where R(t) is the time varying rain falling over the width of the stream section (positive for rainfall and negative for evaporation), Q(over) is the overland flow contribution and Qs(t) is the quantity infiltrating into (or exfiltrating from) the soil over the width of the channel section.

Similarly the lateral inflow into the overland flow nodes are determined by the algebraic sum of precipitation and infiltration into the soil. Mathematically this is represented as

$$\begin{aligned} Q_o(x,t) &= I(x,t) - K(\psi)\left[\frac{\partial \psi(x,t)}{\partial z} + 1\right], \qquad && Q_o > 0 \\ &= 0, && Q_o \le 0 \end{aligned} \tag{27}$$

where I(x,t) represents the rainfall intensity contribution to the lateral inflow and $\psi(x,t)$ represents the capillary pressure on the subsurface boundary nodes along CE in Figure 1. If $Q_o(x,t)$ as determined from Equation 27 is negative, then there is no net lateral inflow contribution to that particular overland flow node for that time instant. The situation of partially ponded areas, CD, in Figure 3 occurs when the rain intensity does not exceed the saturated soil hydraulic conductivity.

Note that Equation 27 essentially dictates what portion of the rainfall enters the soil through infiltration and what portion of the rainfall contributes to overland flow. Overland flows are also governed by a continuity equation similar to Equation 1 as

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}(hV_o) = Q_o(x,t) \tag{28}$$

where the variables are defined as in Equation 12 except that the net lateral inflow to overland flow $Q_o(x,t)$ is obtained from Equation 27. The second term on the right hand side of Equation 27 (call it $I_2(x,t)$ for convenience) represents the rate of water infiltrating into the soil medium. Equation 27 holds even for ponded conditions when the quantity of water infiltrating into the soil depends on the rainfall, the overland flow depth on the soil surface, and the status of soil moisture at the surface of the soil. At initial times, the soil surface is dry and $I_2(x,t)$ is greater than I(x,t) and thus

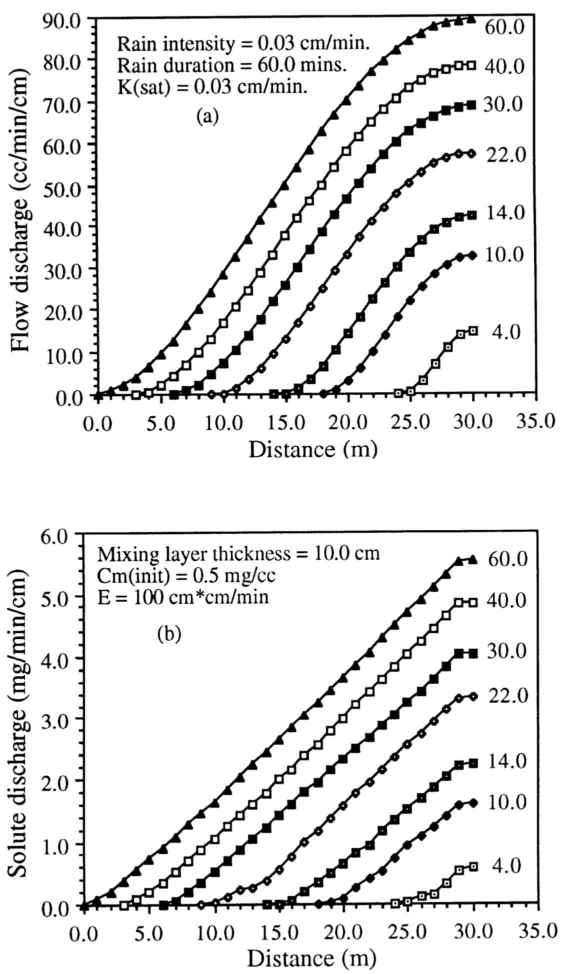

Figure 3. Flow discharge (3a) and solute discharge (3b) over the agricultural slope during the rising phase for several different values of elapsed time since rainfall began. The 30 m location is adjacent to the stream.

$Q_o(x,t)$ is zero for this point in time and space. As the water table rises and the initial moisture deficit is satisfied, $I_2(x,t)$ gradually becomes smaller, but there will still be no contribution to overland flow if the rain intensity does not exceed the saturated hydraulic conductivity of the soil. In such instances, overland flow will have positive contributions when the ground water table practically reaches the soil surface.

Static initial conditions were chosen for the subsurface domain in the simulation efforts of this study. The initial condition for overland and stream flow components, dictated by static initial conditions for the subsurface, is that of a dry section. The solute was assumed to be uniformly distributed in the mixing zone at the beginning of the simulation. The outflow boundary condition for solute was chosen as one of zero gradient (i.e., $\partial c(L,t)/\partial x = 0$). At the transient point D on the soil surface where overland flow begins, the concentration was chosen as $c = 0$ in keeping with the zero flow depth boundary condition. The initial distribution of solute in the overland flow domain and in the subsurface region below the mixing zone was zero.

Solution methodology for conjunctive modeling

Implicit centered finite difference techniques were used for solving the equations governing water flow and solute transport. Details of this scheme can be obtained elsewhere [23] and are not repeated here. Small time steps (in the order of seconds) were used in the beginning of each simulation because of the highly nonlinear nature of the equations.

The equations used in the subsurface are two-dimensional with a one-dimensional overland flow description on the surface. Such a unit of overland and subsurface flow is called a 'slice' (see [23]). The channel flow is perpendicular to the orientation of these slices (see Figure 2). The time space varying channel flow depth serves as a boundary condition for the subsurface nodes attached to the channel bottom (region ABC in Figure 2). To simulate this situation, many slices are chosen along the channel reach and each slice interacts with the channel depending on its location along the channel reach. This approximates the three-dimensional nature of flow and leads to considerable savings in computer effort.

The problem now reduces to the simultaneous solution of a one-dimensional stream section and various slices. These compo-

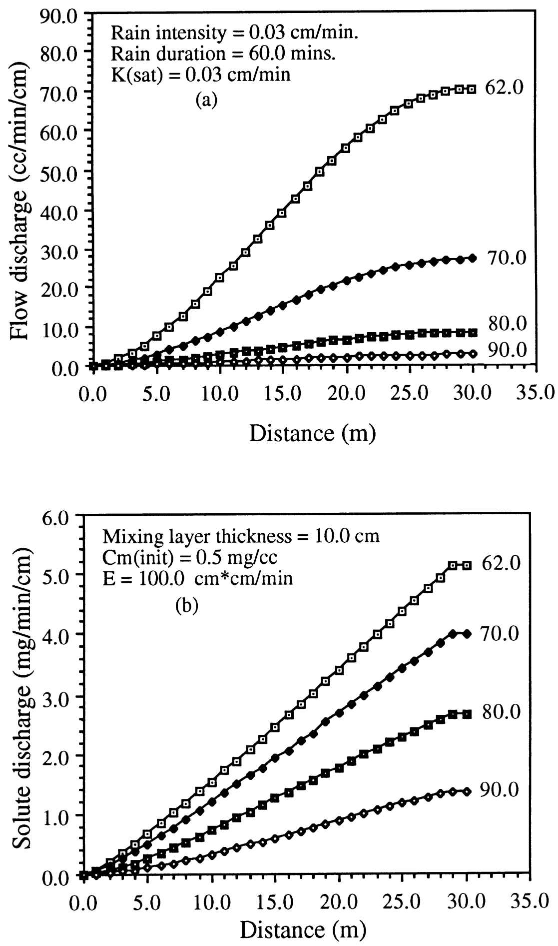

Figure 4. Flow discharge (4a) and solute discharge (4b) over the agricultural slope during the recession phase for several different values of elapsed time. The 30 m location is adjacent to the stream.

nents are coupled internally since solving one component modifies the boundary conditions or the lateral inflow/outflow conditions for the other components. The stream depths and the overland flow depths at each surface node and the capillary potentials at each subsurface node are used as the convergence criterion quantities during the iteration procedure. Convergence is achieved when the maximum difference for any nodal value of these quantities between two successive iterations is less than some preset tolerance. Each sweep starts with the numerical solution of the stream flow section using the net lateral inflow from rainfall and baseflow and overland flow discharge from each slice (estimated from solution at the previous time step). The new stream solution thus obtained prescribes a new head condition at each slice along region ABC for the subsurface (see Figure 2). Using this new boundary condition, obtained from the time-space varying stream depth, the subsurface flow components are solved for all slices. The new subsurface solutions prescribe new values of net lateral inflows to overland flows along CD or change the capillary potentials along DE for each slice. The overland flow component is now solved for each slice. The new overland flow solutions for each slice determine new boundary conditions along CDE for the subsurface flow and provide new lateral outflow for each slice to a particular stream location. This starts off a new sweep cycle with the stream flow being solved for new lateral inflows from the subsurface and new overland flow inputs. These cycles continue until all the nodes for each component in the system converge within preset tolerances.

Once the flow field was obtained at each time step, the infiltration rates r1(x,t) and r2(x,t) were determined. Using these infiltration rates, the solute transport Equations 24 and 25 were solved numerically.

DISCUSSION OF RESULTS

The results pertaining to surface and subsurface flow dynamics were discussed by Govindaraju and Kavvas [23]. In this study, results from one of those simulations was augmented with a solute transport component to study surface transport phenomena. This paper deals with surface contamination and only surface results are presented here. Figures 3 and 4 show the results for the slope under a rainfall event of 0.03 cm/min intensity and a duration of 1.0 hours. The soil saturated hydraulic conductivity is 0.03 cm/min in this example.

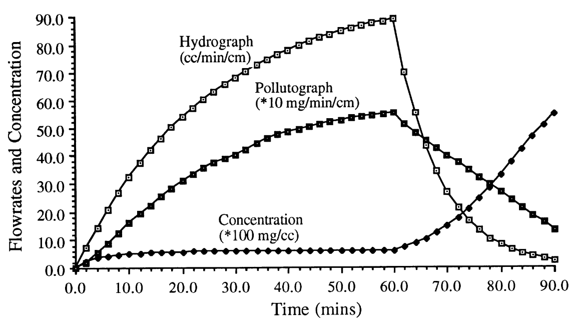

Figure 5. Flow discharge (hydrograph), solute discharge (pollutograph) and solute concentration as functions of time at the outflow section of overland flow before joining the stream.

Figure 3a shows rising profiles of overland flow discharge over one of the side slopes and their spatial extent at different times. The distance x = 30.0 m is adjacent to the stream. A short time after rainfall commencement (say 4.0 mins), about 5.0 m of the slope immediately neighboring the stream has developed overland flow. As time increases, the flow discharge rises and the region over which overland flow occurs also increases. Figure 3a is a typical response that is observed in hydrologic events exhibiting VSAs. By the time the rainfall stops (i.e., 1 hour), almost the whole 30 m of the agricultural plot has developed overland flow.

Figure 3b shows the corresponding solute discharge hydrographs over the soil surface at various times. The solute discharge is a product of the flow discharge and the flow concentration. The solute discharge over the slope also exhibits a time-space dependent variable source area along with the flow field. The area contributing to surface contamination increases with time. The solute discharge hydrographs (Figure 3b) do not exhibit as much curvature as the flow discharge hydrographs (in Figure 3a).

In this example rainfall stops after 1 hour. Figures 4a and 4b show the water and solute discharge profiles respectively during the recession phase. Recession of flow is very rapid, and contributions from surface flow to the stream hydrograph diminish rapidly. The solute discharge also diminishes after rainfall stops (Figure 4b), but at a slower rate than water discharge (Figure 4a). This indicates that the concentrations in surface flow do not behave in the same manner as the flow discharge once the rainfall stops.

This conclusion is stated more explicitly in Figure 5, which shows the outflow section flowrates, solute discharges and concentrations. The flow hydrograph measures the total flow discharge to the stream from one agricultural side slope as a function of time. This quantity increases until 60.0 min., at which time the rain stops, and then the outflow hydrograph recedes rapidly. The corresponding outflow pollutograph shows a similar behavior. This curve represents the product of the flow discharge and the solute concentration at the outflow section adjacent to the stream and determines the time dependent pollutant load that reaches the stream from the overland flow section. The outflow concentration is also shown in Figure 5. The concentration reaches a steady state value in about 10.0 mins and remains practically unchanged until rain stops. At this time, there is a dramatic increase in concentration at the outflow section. Once the rain stops, the dilution effect of rainfall and the lateral inflow contribution to overland flow stops. Meanwhile solute is being transported to the outflow section from upstream flow regions, all of which leads to a concentration build up at the outflow section. Nevertheless, the pollutograph to the stream recedes after rain stops, because the recession in the flow discharge hydrograph is faster than the increase in concentration.

Figure 6 compares the relative amounts of solute that are washed off by overland flow and the amounts that are leached to the subsurface below the mixing zone. Initially the contribution rate to subsurface flow is very high because the infiltration rates are very high and practically all the rainwater

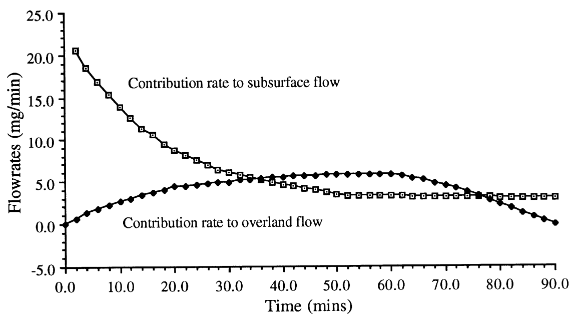

Figure 6. Solute transfer rates over the whole flow section into the subsurface region beneath the mixing zone and into the overland flow region above the mixing zone.

enters the soil. As time increases, this infiltration rate goes down. Simultaneously, increasing portions of the surface develop overland flow, and the solute contribution rate to overland flow increases. After about 35 mins, the amount of solute being washed off by surface flow is comparable to the amount that is being leached into the soil. After rain ceases at 60.0 mins, the amount of solute washed off by overland flow decreases rapidly. The subsurface contribution shows little change at the end of the rainfall. This indicates that the subsurface response to change in rainfall is slower than surface flow response.

Vegetation impacts the movement of both surface and subsurface water. Evapotranspiration reduces subsurface moisture, thus increasing infiltration capacity. The parameters of Equation 5 will be different if the surface flow occurs through grasses or other plants which reduce the flow velocity. Leaves often act to reduce the velocity of falling rain drops, thus reducing erosion and sediment movement. The beneficial effects of vegetation on water, sediment and solute management will be considered in future work.

SUMMARY AND CONCLUDING REMARKS

The problem of surface contamination over heavy metal contaminated sites was addressed in this paper. Physics-based models were developed for both the flow and surface solute transport components. Numerical simulations over a hypothetical agricultural plot adjacent to a stream were performed to study the behavior of solute movement over the soil surface. The dynamic response of variable source areas for both water and solute movement were discussed using the concept of moving boundaries for the overland flow domain. The upstream overland flow boundary moves back and forth in response to infiltration-exfiltration processes. A physics-based distributed model was used to study this phenomena by internally coupling the nonlinear partial differential equations for the flow components and then augmenting the flow model with a surface solute transport model. The solute was assumed to be uniformly mixed in the subsurface in the mixing zone at the beginning of simulations. The purpose of the mixing zone in this modeling effort was to distribute the solute to overland flow above or to subsurface flow underneath, depending on respective concentration gradients. The concentration in the mixing zone changes with space (distance away from stream) and time.

The subsurface response to rainfall in terms of water and solute movement was very slow compared to the response of overland flow. Surface flow transmits water and solute 100-500 times faster than subsurface water. During the simulations, the subsurface concentrations did not change appreciably, and remained constant for all practical purposes. The response of surface and subsurface components occurs over different time scales and makes the modeling of such processes over long periods of time difficult.

Previous studies (e.g., [18, 26]) have described the conditions which favor the development of variable source areas. Modeling studies, which deal with prediction of contaminants in surface waters, need to be cognizant of the role of VSA hydrology. The portion of applied chemicals that is transported by surface flow may show spatial variation as indicated by model results. The timing of rainfall/irrigation after fertilizer and pesticide application on agricultural areas also has a great influence on the fate and transport of agrichemicals. In watershed scale studies, variable source areas need to be identified for an estimate of the fraction of the area that contributes to surface water contamination.

Many chemicals adsorb on to the soil particles, and are subsequently entrained into surface flow as these particles are eroded by the moving water. This study neglects the transport of chemicals which are brought into solution by this action. This would require the inclusion of a surface erosion model coupled with solute adsorption and transport model. Inclusion of these physical processes would result in prediction of greater solute loss through overland flow. These aspects are beyond the scope of this study and are topics of further research.

ACKNOWLEDGMENTS

This research was partially supported by the U.S. EPA under assistance agreement R-819653 to the Great Plains-Rocky Mountain Hazardous Substance Research Center for Regions 7 and 8. It has not been submitted to the EPA for peer review and, therefore, may not necessarily reflect the views of the agency. No official endorsement should be inferred. The Center for Hazardous Substance Research and the EPA EPSCoR program also provided partial support.

REFERENCES

1. G.M. Pierzynski and A.P. Schwab, Reducing Heavy Metal Availability to Soybeans Grown on a Metal Contaminated Soil, In: L.E. Erickson, S.C. Grant and J.P. McDonald (Eds.), Proc. Conf. on Hazardous Waste Research, University of Colorado, Boulder, CO, 1992, pp. 543-553.

2. G.M. Pierzynski, J.L. Schnoor, M.K. Banks, J.C. Tracy, L. Licht and L.E. Erickson, Vegetative Remediation at Superfund Sites, In: R.E. Hester and R.M. Harrison (Eds.), Mining and Its Environmental Impact-Issues in Environmental Science and Technology, Royal Society of Chemistry, vol. 1, 1994, pp. 46-69.

3. L.R. Ahuja, Characterization and Modeling of Chemical Transfer to Runoff, In: B.A. Stewart (Ed.), Advances in Soil Science, vol. 4, Springer-Verlag, New York, 1986, pp. 149-188.

4. A.S. Doonigan, Jr., D.C. Beyerlein, H.H. Davis and N.H. Crawford, Agricultural Runoff Management (ARM) Model Version II: Refinement and Testing, EPA 600/3-77-098, Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA, 1977, 293 pp.

5. W.G. Knisel (Ed.), CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems, U.S. Dept. Agr. Conservation Res. Rept., 26, 1980, 640 pp.

6. N.H. Crawford and A.S. Doonigan, Jr., Pesticide Transport and Runoff Model for Agricultural Lands, EPA 600/2-73-013, Southeast Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA, 1973, 211 pp.

7. J.J. Ingram and D.A. Woolhiser, Chemical Transfer into Overland Flow, Proc. ASCE Symp. Watershed Management, July 1980, Boise, ID, Am. Soc. Civil Eng., New York, 1980, pp. 40-53.

8. L.R. Ahuja and O.R. Lehman, The Extent and Nature of Rainfall-Soil Interaction in the Release of Soluble Chemicals to Runoff, J. Environ. Qual., 12 (1983) 34-40.

9. I.K. Snyder and D.A. Woolhiser, Effects of Infiltration on Chemical Transport onto Overland Flow, Trans. Am. Soc. Agric. Eng., 28 (1985) 1450-1457.

10. L.R. Ahuja, A.N. Sharpley, M. Yamamoto and R.G. Menzel, The Depth of Rainfall-Runoff-Soil Interactions as Determined by ^{32}P, Water Resour. Res., 17 (1981) 969-974.

11. R. Wallach, M.Th. van Genuchten and W.F. Spencer, Modeling Solute Transfer from Soil to Surface Runoff: The Concept of Effective Depth of Transfer, J. Hydrol., 109 (1989) 307-317.

12. R. Wallach, W.A. Jury and W.F. Spencer, Transfer of Chemicals from Soil Solutions to Surface Runoff: A Diffusion Based Soil Model, Soil Sci. Soc. Am. J., 52(3) (1988) 612-618.

13. R. Wallach and M.Th. van Genuchten, A Physically Based Model for Predicting Solute Transfer from Soil Solution to Rainfall-Induced Runoff Water, Water Resour. Res., 26(9) (1990) 2119-2126.

14. R. Wallach and R. Shabtai, Modeling Surface Contamination by Soil-Applied Chemicals Under Transient Infiltration, J. Hydrol., 132 (1992a) 263-281.

15. R. Wallach and R. Shabtai, Surface Runoff Contamination by Soil Chemicals: Simulations for Equilibrium and First-Order Kinetics, Water Resour. Res., 28(1) (1992b) 167-173.

16. R. Wallach and R. Shabtai, Surface Runoff Contamination by Chemicals Initially Incorporated Below the Soil Surface, Water Resour. Res., 29(3) (1993) 697-704.

17. R.L. Peyton and G. Sanders, Mixing in Overland Flow During Rainfall, Am. Soc. Civil Eng. J. Environ. Eng, 116(4) (1990) 764-784.

18. R.A. Freeze, Role of Subsurface Flow in Generating Surface Runoff, 1, Base Flow Contribution to Channel Flow, Water Resour. Res., 8(3) (1972) 609-623.

19. K. Beven, Hillslope Hydrographs by the Finite Element Method, Earth Surf. Processes, 2 (1977) 13-28.

20. R.E. Smith and R.H.B. Hebbert, Mathematical Simulation of Interdependent Surface and Subsurface Hydrologic Processes, Water Resour. Res., 19(4) (1983) 987-1001.

21. A. Binley, J. Elgy and K. Beven, A Physically Based Model of Heterogeneous Hillslopes, 1, Runoff Production, Water Resour. Res., 25(6) (1989a) 1219-1226.

22. A. Binley, J. Elgy and K. Beven, A Physically Based Model of Heterogeneous Hillslopes, 2, Effective Hydraulic Conductivities, Water Resour. Res., 25(6) (1989b) 1227-1233.

23. R.S. Govindaraju and M.L. Kavvas, Dynamics of Moving Boundary Overland Flows over Infiltrating Surfaces at Hillslopes, Water Resour. Res., 27(8) (1991) 1885-1898.

24. R.S. Govindaraju, S.E. Jones and M.L. Kavvas, On the Diffusion Wave Model for Overland Flow, 1, Solution for Steep Slopes, Water Resour Res., 24(5) (1988) 734-744.

25. W.S. Gonwa and M.L. Kavvas, A Modified Diffusion Wave Equation for Flood

Propagation in Trapezoidal Channels, J. Hydrol., 9 (1986) 237-258.

26. T. Dunne, Field Studies of Hillslope Flow Processes, In: M.J. Kirkby (Ed.), Hillslope Hydrology, John-Wiley, New York, 1978, pp. 227-293.

27. R.A. Freeze, Mathematical Models of Hillslope Hydrology, In: M.J. Kirkby (Ed.), Hillslope Hydrology, Wiley Interscience, New York, 1978, pp. 177-225.

28. R. Brown, Selenium Threatens Irrigators, Wildlife, Civil Engineering, 57(2) (1987) 40-43.