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Modeling soil solute release into runoff with infiltration

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Summary Despite empirical evidence that infiltration plays an important role in controlling the transfer of chemicals from soil to surface runoff, few mechanistic models have been tested under both infiltrating and non-infiltrating conditions. We used previously published experimental data to test a physically-based, solute transport model. The model's underlying conceptual basis is that near-surface soil chemicals are ejected into runoff by raindrop impact and chemicals deeper in the soil diffuse into this near-surface raindrop "exchange-layer." The experiments consisted of three soil types (clay, loam, and fine sandy loam) subjected to three infiltration conditions (none, full drainage, and reduced infiltration). Model parameters that could not be directly determined from the descriptions of the experiments were determined from previously published information or otherwise internally constrained. The model's governing equations were solved numerically and the results agreed well with measured solute concentrations in both runoff and soil-water for all the experiments. The results emphasize the potentially important role of saturated, poorly draining parts of the landscape in contributing solutes to streams and lakes via overland flow.

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Introduction

Accurate, physically-based modeling of soil chemical transfer into runoff is essential for developing predictive non-

point source pollution models. Gao et al. (2004) demonstrated that solute release from soil during storms depends on both the ejection of soil-water by raindrop impacts and the diffusion of deeper solutes into the near-surface raindrop driven "exchange" layer. This finding was in strong contrast to many previously published models that either assumed a single process dominated the system or that multiple, interacting processes could be represented by using "effective" parameters (e.g. Frere et al., 1980; Ingram and Woolhiser, 1980; Steenhuis and Walter, 1980;

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Ahuja et al., 1981; Wallach et al., 1988; Wallach and van Genuchten, 1990; Wallach, 1991; Ahuja, 1990; Steenhuis et al., 1994).

However, despite good empirical evidence to the contrary (e.g., Ahuja and Lehman, 1983; Snyder and Woolhiser, 1985; Parr et al., 1998), the role of infiltration is often overlooked in soil-solute release models (e.g., Wallach et al., 1988). The most robust exceptions are various works by Wallach and collaborators (e.g., Wallach and van Genuchten, 1990; Wallach et al., 2001), which generally include a full, physically-based porous media transport model, but simplify the solute exchange between the soil and overland flow to a mixing-layer concept, which does not explicitly account for solute diffusion from deeper soil. Although Gao et al. (2004) included infiltration in the theoretical development of their model, they did not test their model against any experiments that included infiltration. Interestingly, Zhang et al. (1999) coupled the mixing-layer, diffusion, and infiltration concepts in a way that is somewhat similar to Gao et al. (2004), but to fit experimental data they sometimes omitted diffusion and/or dispersion. In this short paper we will apply the Gao model (Gao et al., 2004) to data from previously published experiments that included both infiltrating and non-infiltrating conditions.

Theory

The model, which is described and justified fully in Gao et al. (2004), is briefly outlined here. The conceptual model considers a soil-water system divided into three vertically distributed, horizontal layers: runoff or surface ponding water, an exchange-layer, and the underlying soil (Fig. 1).

The exchange-layer transport processes are controlled by the interactions between raindrops and the soil surface and it is from this layer that chemicals leave the soil and enter

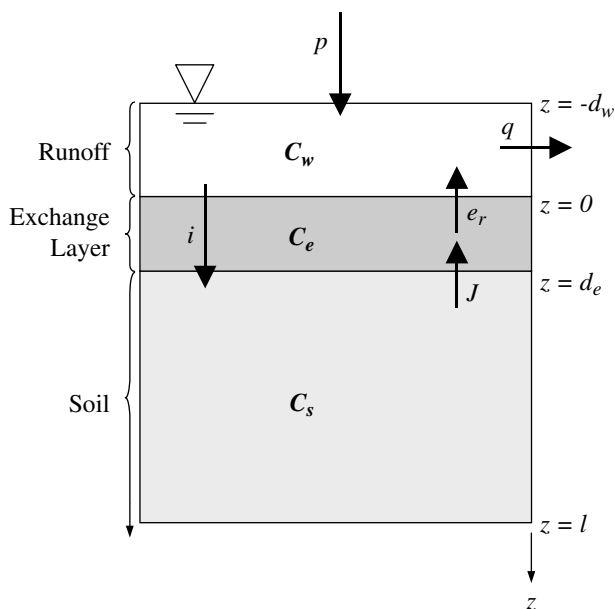


Figure 1 Conceptual schematic of the model's physical chemical transport processes and nomenclature (from Gao et al., 2004).

surface runoff. We assumed the exchange-layer is well mixed and can be characterized by a single concentration throughout the layer, $C_e(t)$. Expanding the expression widely used to describe soil erosion by raindrop impact (Rose, 1985; Rose et al., 1994; Sharma et al., 1993, 1995; Jayawardena and Bhuiyan, 1999), Gao et al. (2003, 2004, 2005) developed a synonymous term for soil-water ejected from the soil during rainfall

$$e_r = \frac{ap}{\rho_b} \theta \quad (1)$$

where e_r is the raindrop induced water transfer rate [LT^{-1}], a is the soil detachability [ML^{-3}], p is the rainfall rate [LT^{-1}], ρ_b is the soil dry bulk density [ML^{-3}], and θ is the soil-water content [-]. Although not directly relevant to this study, for completion we should note that θ can be replaced by $(\rho_b K_p + \theta)$ to account for chemical sorption to soils; where K_p is a soil sorption partition coefficient (e.g., Steenhuis et al., 1994).

Chemical transport within the soil profile, below the exchange-layer, is controlled by both infiltration and diffusion and can be described by the advection-diffusion equation

$$\frac{\partial \theta C_s}{\partial t} = \frac{\partial}{\partial z} \left[D \frac{\partial C_s}{\partial z} - i C_s \right] \quad (2)$$

where C_s is the chemical concentration in the soil-water below the exchange-layer [ML^{-3}], t is time, z is the vertical dimension (+ downwards), i is the infiltration rate in the soil [LT^{-1}], D is the dispersivity of chemicals in the soil [L^2T^{-1}] and is taken as the sum of the molecular diffusivity and the mechanical dispersivity (e.g., Bresler, 1973; Bear and Bachmat, 1990; Ahuja, 1990).

Chemical transport in the exchange-layer involves diffusion into the layer from deeper soil, raindrop driven exchange with the runoff water, and infiltration mediated fluxes into the soil below

$$\frac{d(\theta d_e C_e)}{dt} = J + e_r(\lambda C_w - C_e) + i(C_w - C_e) \quad (3)$$

where d_e is the depth of the exchange-layer [L], C_e is the solute concentration in the exchange-layer [ML^{-3}], C_w is the solute concentration in the runoff water [ML^{-3}], e_r is the rate soil-water is ejected into the runoff, i.e., Eq. (1), λC_w is the concentration of the water entering the exchange-layer [ML^{-3}], ($0 \leq \lambda \leq 1$, however, the model is insensitive to this parameter (Gao et al., 2004) so we will assume $\lambda = 1$), and J is the diffusion rate of solute from the soil below the exchange-layer, which is described by Fick's law

$$J = D_s \frac{\partial C_s}{\partial z} \quad (4)$$

Raindrop driven processes, in the exchange-layer, and infiltration most directly control the chemical transport into the runoff or ponding water layer. Diffusion between the exchange-layer and ponding is neglected in this model since the diffusivity, D_s , is much smaller than the raindrop induced mass transfer rate, e_r . The mass conservation of chemical solute in the runoff is expressed as

$$\frac{\partial (d_w C_w)}{\partial t} + \frac{\partial (q C_w)}{\partial x} = e_r(C_e - \lambda C_w) - i C_w \quad (5)$$

where d_w is the ponding water depth [L], C_w is the chemical solute concentration in the runoff [ML^{-3}], and q is the volumetric runoff flux per unit width [L^2T^{-1}]. In the case of shallow, kinematic overland flow, d_w and q are related by

$$\frac{\partial d_w}{\partial t} + \frac{\partial q}{\partial x} = (p - i) \quad (6)$$

Eqs. (5) and (6) can be combined to give

$$d_w \frac{\partial C_w}{\partial t} + q \frac{\partial C_w}{\partial x} = e_r(C_e - \lambda C_w) - p C_w \quad (7)$$

The chemical concentration throughout the system and the interactions between the different layers are described by Eqs. (3) and (7), which can be used as the boundary condition of the advection–diffusion equation for the underlying soil layer, Eq. (2).

Experiments

The experimental data used were from Ahuja and Lehman (1983). Because the original data have been misplaced (Ahuja, personal communication), we digitized the relevant graphs from original publication to capture the measured solute concentrations in runoff and the soil-water. The original Ahuja and Lehman (1983) paper describes the experimental methods in full; we will briefly summarize the experiments here.

Experiments used three different soil types, clay, loam, and fine sandy loam, and three infiltration conditions, no infiltration, full drainage, and reduced infiltration. Soils were sieved (4-mm) and packed into Plexiglas boxes, 100-cm long, 15-cm wide, and 10-cm deep. “No-infiltration” was imposed by attaching a solid bottom to the

boxes and full drainage was achieved by attaching a perforated bottom to the boxes. Reduced infiltration was invoked by covering the perforated bottom with a layer of “slurry” made from topsoil. Soil properties are summarized in Table 1. The packed soil boxes were saturated with a solution of KBr (4000 mg L^{-1}) prior to commencing rainfall. After setting for a day, the boxes were subjected to 61-min of rainfall at 6.8 cm h^{-1} and falling from 2.5-m. Runoff was collected at one end of the boxes, which were slightly sloped; the first sample was collected as soon as possible after runoff was initiated ($\sim 1.5 \text{ min}$) and then at 5, 10, 20, 30, 40, 50, and 60 min after rain began. After each experiment the boxes were sampled at 5 depths between 0 and 3 cm to assess the distribution of solute in the soil-water after the experiments. This sampling took $\sim 30\text{-min}$ for the loam and fine sandy loam and $\sim 2\text{-h}$ for the clay. All runoff and soil-water samples were analyzed for Br using an electrode (minimum detection limit was not noted).

Model application

Eqs. 7, 3, and 2 were solved using the Crank–Nicholson central difference scheme to model solute concentrations in the runoff, exchange-layer, and deep soil, respectively using the following boundary and initial conditions

$$\text{at } z = l: \quad D_s \frac{\partial C_s}{\partial z} = 0 \quad (8a)$$

$$\text{at } z = d_e: \quad C_s = C_e \quad (8b)$$

$$\text{at } t = 0, z \geq 0: \quad C_s = C_e = C_o \quad (8c)$$

$$\text{at } t = 0, -d_w \leq z < 0: \quad C_w(t = 0) = \frac{e_r C_o}{(\lambda e_r + p)} \quad (8d)$$

where $C_o = 4000 \text{ mg L}^{-1}$. The spatial mesh used in the numerical modeling was 0.02 cm and the time step was 1.0 s for the soil underlying the exchange-layer. Note that Eq. (8d) is different from Gao et al. (2004), because these experiments begin with $d_w = 0$ and, thus, Eq. (7) must be satisfied.

The raindrop induced mass transfer coefficient, e_r , was calculated from Eq. (1) using the bulk density, ρ_b , and saturated moisture content, θ_s , reported by Ahuja and Lehman (1983) (Table 1) and by finding a best fit soil detachability, a , for the no-infiltration situation similar to previous studies (Heilig et al., 2001; Gao et al., 2004). Based on Walker et al. (2007), we assumed that a could be considered constant regardless of infiltration. The exchange depth, d_e , was also

Table 1 Soil characteristics (from Ahuja and Lehman, 1983)

	Fine sandy loam	Loam	Clay loam
Bulk density, ρ_b (g cm^{-3})	1.35	1.42	1.21
Soil moisture, $\theta \approx$ porosity	0.53	0.49	0.55
Sat. hydraulic conductivity ^a (cm h^{-1})	2.75	1.39	1.58
Reduced infiltration rate (cm h^{-1})	0.28	0.21	0.35

^a Infiltration rate under full drainage.

Table 2 Model parameters

	Fine sandy loam	Loam	Clay
Soil erodibility, a^a (g cm^{-3})	0.5	0.8	2
Exchange-layer depth, d_e^b (cm)	0.20/0.15/0.10	0.15/0.09/0.08	0.50/0.20/0.10
Diffusivity, D_s^c ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	8.6	7.7	9.0
Dispersivity, α_L^d (cm)	0.88	0.70	0.23

^a Based on best fit to the no infiltration experiments.

^b Exchange-layers assumed for no infiltration/reduced infiltration/full drainage conditions, respectively.

^c Eq. (9).

^d Calibrated to best fit the soil solute data.

best fit for all the experiments with but was constrained for the no-infiltration conditions to depths of 2–3 mm for the fine sandy loam and loam based on Ahuja et al. (1981) and to depths <7 mm for the clay based on Heilig et al. (2001) and Gao et al. (2004, 2005). One unique addition to this study is the explicit recognition that the exchange depth decreases with increasing infiltration (Walker et al., 2007), which we imposed on the reduced-infiltration and full drainage conditions.

The diffusion constant, D_s , was based on a general value for an aqueous solute diffusion coefficient ($D_a = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and Millington and Quik (1961) tortuosity model

$$D_s = D_a (\theta^{10/3} / \theta_s^2) \quad (9)$$

where θ_s is the saturated water content for these experiments (Table 1); and $\theta \approx \theta_s$.

Hydrodynamic dispersion, D , (Eq. (2)) for a given soil is usually assumed to follow the form (e.g., Bear, 1972; Maidment, 1993).

$$D = \alpha_L v + D_s \quad (10)$$

where α_L is the dispersivity and v is the average pore water velocity (i/θ). There is a wide range of values for dispersivity, even among similar soils (e.g., Evenson and Dettinger, 1980), which makes it difficult to approximate *a priori*. Therefore, we allowed α_L to be a fitted parameter for each soil but assumed it must be constant for all infiltration rates.

The soil model parameters that were not explicitly known from Ahuja and Lehman (1983) are summarized in Table 2. Although a , d_e , and α_L were not necessarily tightly constrained by our understanding of the experiments or previously published information, they were somewhat internally constrained. Specifically, single values of a and α_L had to be chosen to represent all the infiltration conditions and, based on Walker et al. (2007) d_e had to decrease with increasing infiltration rates.

Unlike the (Gao et al., 2004, 2005) experiments, ponding, although small (Ahuja and Lehman, 1983), was not constant for these experiments. Wallach et al. (1988) determined the ponding, $d_w \approx 0.1$ cm. Based on the St. Venant equation, the time required to reach full ponding was short (~ 30 s) (see appendix in Walter et al., 2001) for all the experiments so we used a simple a linear function of ponding [$d_w = f(p-i)$ for $d_w < 0.1$ cm] and once $d_w = 0.1$ cm runoff was equal to the difference between precipitation and infiltration. Infiltration was assumed constant throughout each experiment and f was 0.003 s^{-1} .

Results and discussion

The model correctly captured the temporal behavior of the Br concentration in runoff for all the experiments (Fig. 2a–c). Especially noteworthy are the model's ability to predict the elevated long-time solute concentrations for the no-infiltration condition, which persisted due to the inclusion of upward solute diffusion from deeper soil (Zhang et al., 1997, 1999; Gao et al., 2005). The slight under prediction of the long-time solute concentration is directly linked to the estimate of D_s , which we chose not calibrate. The model also correctly captured the increasingly rapid drop in short-

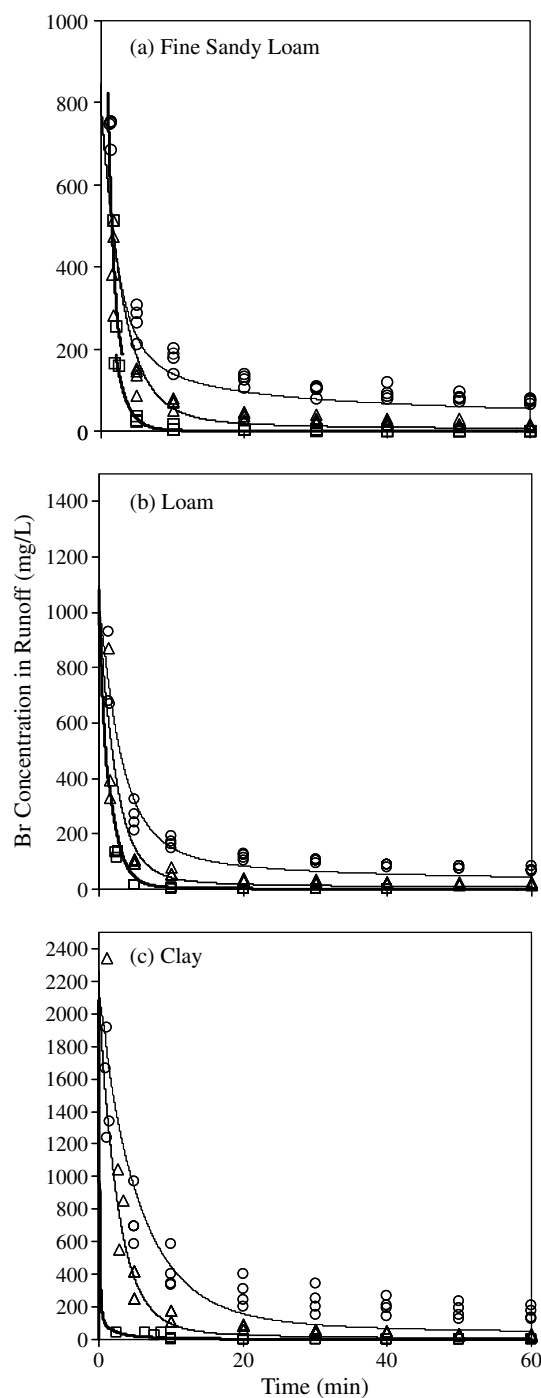


Figure 2 Modeled and measured Br concentrations in runoff over time for three different soils, (a) fine sandy loam, (b) loam, (c) clay, and three infiltration conditions, circles = no infiltration, triangles = reduced infiltration, squares = free drainage. Lines = model results, increasing line weight corresponds to increasing infiltration rate.

time solute concentration with increasing infiltration rates for all the soils.

The clay soil's exchange-layer depth, d_e , under non-infiltrating conditions (Table 2) was similar order of magnitude as that used by Gao et al. (2004), $d_e \approx 0.5$ cm, although the

detachability, a , was substantially higher than Gao et al. (2004), $a = 0.4 \text{ g cm}^{-3}$. As mentioned earlier, the exchange-layer depths for the fine sandy loam and loam soils were constrained to 2–3 mm by previously published experimental observations (Ahuja et al., 1981). This agreement between curve-fit and previously published d_e values perhaps provides added justification to these largely curve-fit parameters. The soil detachabilities for the loam and fine sandy loam were substantially lower than for the clay (Table 2), suggesting that the loams were more resistant to rain-drop impacts.

Following our internal constraints on the exchange-layer depth, d_e decreased for all soils with increasing infiltration rate. We found that a small amount of infiltration had a disproportionately large impact on d_e . For example, all the soils had reduced infiltration rates that were less than ~20% of the free drainage rates and yet the exchange-layer depths decreased from 40–60% of the no-infiltration exchange depths (Table 2). Increasing the infiltration to the free drainage rate only decreased the fine sand loam's and loam's exchange-layer depths by another ~10%. The clay soil's exchange-layer depth increased by another 40% at full drainage relative to reduced infiltration. This relationship in which small amounts of infiltration had large effects on reducing the exchange-layer depth and subsequent increases in infiltration had diminishing effects on reducing the exchange-layer depth agree with the results found by Walker et al. (2007). This agreement adds credence the relationship among our calibrated exchange-layer depths even though we have no good way, without additional experimentation, of independently estimating exchange-layer depths under infiltrating conditions.

The modeled runoff Br concentrations correlated well with all measured data (Fig. 3, $R^2 = 0.90$). The correlation for each individual experiment was generally in the range of 0.91–0.99; the exceptions were loam under reduced infiltration ($R^2 = 0.88$) and clay under free drainage ($R^2 = 0.64$). One reason for the relatively low correlation for the clay with free drainage is that the range of experimental data (squares in Fig. 2c) was an order of magnitude or more lower than any of the other experiments (Fig. 2). Interesting, the most seemingly obvious and systematic discrepancy between modeled and measured runoff Br concentrations was for loam under free drainage (open squares in Fig. 3), although the absolute discrepancies were only on the order of 1 mg L^{-1} .

Although there was substantial scatter in the soil solute data (Ahuja and Lehman, 1983), our model reproduced the general spatial solute distribution relatively well, especially for the fine sandy loam and loam soils (Fig. 4). Like previous researchers (e.g., Wallach and van Genuchten, 1990; Zhang et al., 1999), we calibrated our hydrodynamic dispersion to fit the soil solute data. Using a single parameter for each soil (α_L in Table 2), we achieved generally good agreement for the fine sandy loam and loam soils under all infiltration conditions. As suggested by Ahuja (1990), the sampling errors in the soil solute concentrations preclude more stringent quantitative comparisons. Interestingly, unlike the seemingly similar model presented by Zhang et al. (1999), the model presented here reproduced the concentrations under full drainage for the fine sandy loam and loam soils reasonably well. Although the model agreement with the clay soil solute concentrations was substantially poorer than for the other two soils (Fig. 4c compared to Fig. 4a and b), the sampling

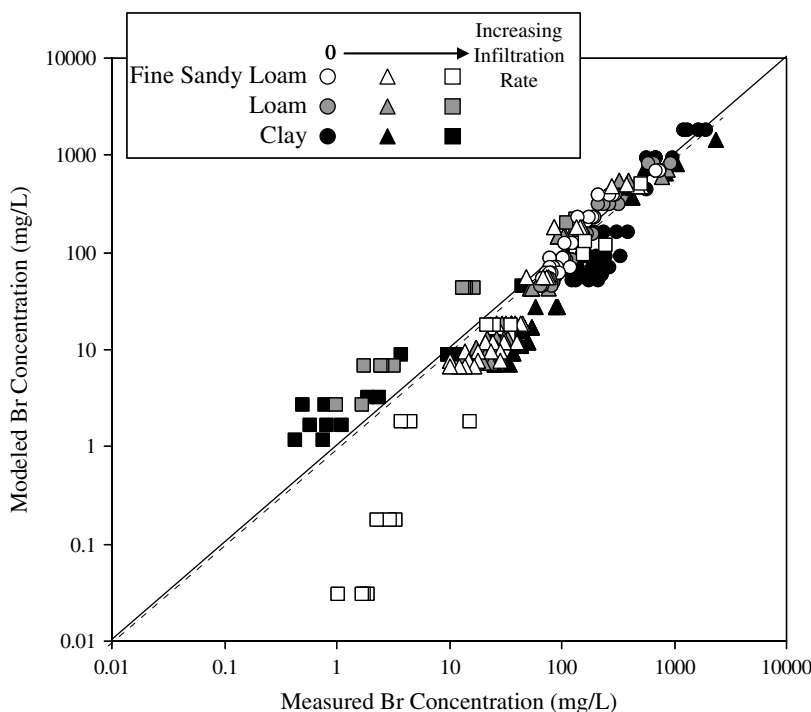


Figure 3 Comparison of model results with experimental Br concentration in runoff ($R^2 = 0.90$), the dashed line is the linear regression (slope 0.99) and the solid line is 1:1 (they may not be uniquely distinguishable). Open, grey, and black symbols represent fine sandy loam, loam, and clay soils, respectively. Circles, triangles, and squares represent no-infiltrations, reduced infiltrations, and free drainage conditions, respectively.

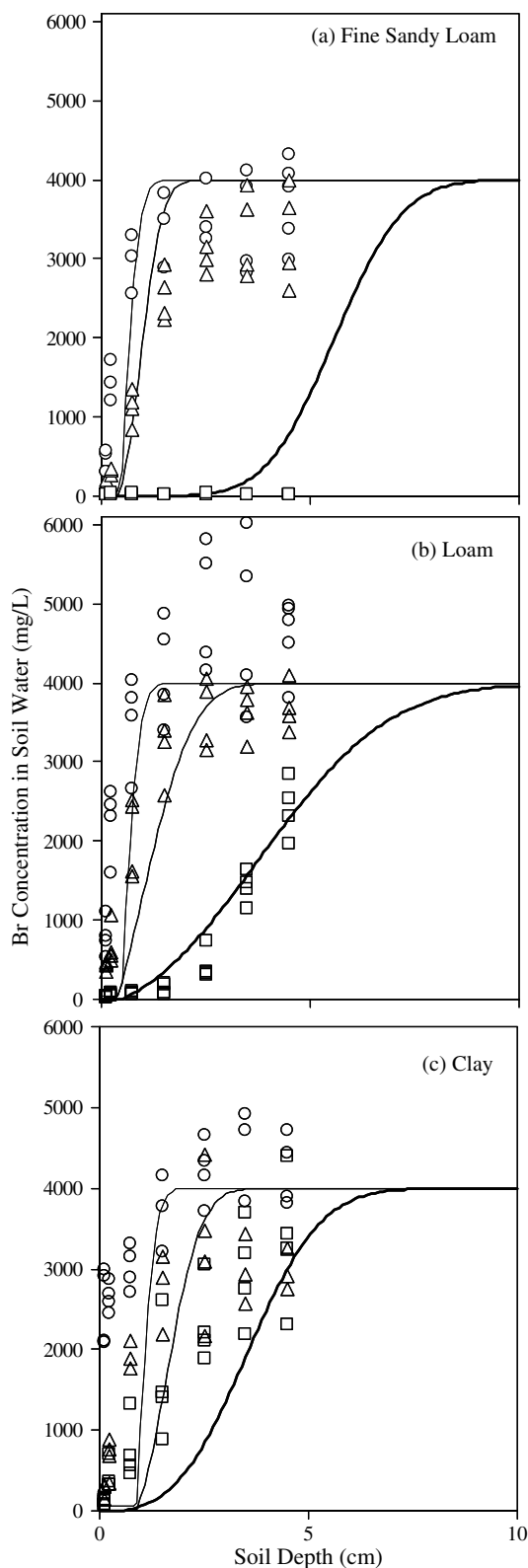


Figure 4 Modeled and observed Br concentrations in soil-water for (a) fine sandy loam, (b) loam, and (c) clay for three different infiltration conditions, circles = no infiltration, triangles = reduced infiltration, and squares = full drainage. Increasing line weight corresponds to model results for increasing infiltration rates.

occurred over several hours (Ahuja and Lehman, 1983), during which time we would expect substantial upward solute diffusion and, thus, it is encouraging that our model predicted deeper than observed solute flushing. It may be worthwhile to note, that although this data set has been widely used to test soil solute release models, few (if any) modelers have shown their results with respect to the obviously difficult-to-model clay situation. Although α_L was fitted for each soil, we generally expect this parameter to scale with soil particle size (e.g., Bear, 1972) and, indeed, our values are smallest for the clay and largest for the fine sandy loam. This adds another level of internal consistency to our parameterization, which was not imposed *a priori*.

Like the model of Zhang et al. (1999), our model generally under-predicted near-surface solute concentrations (Fig. 4). Two of the previously suggested explanations for this are chemical entrapment in aggregates and lateral flow bringing solutes back to the surface in the down-slope portions of the soil boxes (Zhang et al., 1999). Upward diffusion prior to or during soil sampling could also have contributed to this discrepancy.

Our findings suggest that saturated, poorly drained soils are especially prone to enriching runoff with soil solutes, because it is these soils that produce the highest peak solute concentrations in runoff and, due to upward solute diffusion, have relatively elevated concentrations even after the surface soil has been flushed by raindrop impacts (Fig. 2). Additionally, the saturated, non-infiltrating soils retained high solute concentrations in the near-surface after the rain event (Fig. 4). Thus, the results emphasize the importance of focusing management practices for controlling non-point source pollution on parts of the landscape that are especially prone to saturation (e.g., Gburek and Sharpley, 1998; Walter et al., 2000; Gburek et al., 2002; Agnew et al., 2006). These results also re-emphasize the need for spatially distributed non-point source pollution models (e.g., Emmerich et al., 1989; Garen and Moore, 2005; Easton et al., 2007). These results also demonstrate the need for critical interpretation of stream water chemical measurements used to attribute quantities of runoff to so-called "old" and "new" water (e.g., Waddington et al., 1993; Burns, 2002; Walter et al., 2005), i.e., some old-water may simply be due to near-surface exchange between rain and soil-water rather than mobilization of subsurface water (e.g., McDonnell, 1990; Eshleman et al., 1993).

Conclusions

Chemical transport from the soil into runoff is complicated, involving a combination of transport mechanisms including raindrop driven processes, diffusion, and advection by infiltrating water. We demonstrated that the Gao-model (Gao et al., 2004) correctly, for the most part, captures the solute concentrations in runoff and soil-water under a range of infiltration conditions using consistent, physically-realistic and largely uncalibrated parameters. One important factor that was uniquely included in this study was the recent discovery that infiltration dramatically reduces the depth of raindrop penetration into the soil or, in terms of previously published models, infiltration reduces the depth of the so-called "mixing-zone." Our results reinforce previous

research suggesting that non-point source pollution control practices should be targeted towards parts of the landscape that are especially prone to soil saturation.

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