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Rainfall induced chemical transport from soil to runoff: theory and experiments

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Abstract

Although both raindrop driven processes and diffusion play important roles in the transfer of chemicals from soil to surface runoff, current transport models either do not consider the two processes together, or use 'effective' parameters with uncertain physical definitions. We developed a physically based, solute transport model that couples both mechanisms and tested it with laboratory experiments. One unique aspect of this study is that all the parameters were either directly measured or previously published, that is, there was no model 'calibration' or 'fitting.' Our model assumes that chemicals near the surface of the soil are ejected into runoff by raindrop impact and chemicals deeper in the soil diffuse into a surface layer, or 'exchange layer,' via diffusion. The exchange layer depth and transfer processes are derived from the 'shield' concept in the Rose soil erosion model (e.g. Rose, 1985). The model's governing equations were solved numerically and the results agreed well with experimental data ($R^2 > 0.90$). The model's sensitivity to various physical and chemical parameters illuminated the importance of both raindrop controlled processes and diffusion on chemical transport from soil to surface runoff.

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1. Introduction

Accurate, physically based modeling of soil chemical transfer into runoff is essential for developing predictive non-point source pollution models. Several dynamic, inter-related processes control chemical transport from soil to runoff during rainfall

including ejection of soil water by raindrop impacts, diffusion of chemicals out of soil water, infiltration, and soil water-runoff mixing (Ahuja and Lehman, 1983; Ahuja, 1990; Zhang et al., 1997; Gao et al., 2004). Although many models have been developed to predict chemical transport from soil to surface runoff, they generally assume one process dominates the chemical transport or that multiple mechanisms can be characterized as a single effective process, like diffusion (Ahuja, 1990). These models can generally be fitted to experimental data by calibrating one or

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more unknown parameters so it remains unclear how multiple processes interact to facilitate chemical transport between soil and runoff.

The two distinct approaches that have traditionally been considered in modeling chemical transport from soil to surface runoff are the lumped, mixing-layer approach and the diffusion approach. The mixing-layer, or distribution layer, concept is probably the most commonly used in models for chemical transport in soil (Steenhuis and Walter, 1980; Ahuja et al., 1981; Ahuja and Lehman, 1983; Steenhuis et al., 1994, 2001; Zhang et al., 1997, 1999). This theory assumes that the transport is controlled by a mixing-layer, just below the soil surface, in which rainwater, soil solution, and runoff water mix instantaneously and that there is no substantial chemical transfer to the mixing layer from below, i.e. that diffusion is negligible. Many studies have shown that the observed mixing-layer depth is much shallower than the depth required to fit mixing-layer models to experimental data (Ahuja and Lehman, 1983; Zhang et al., 1997, 1999; Gao et al., 2004). Most likely, the unreasonably large 'effective' mixing-layer depth incorporates diffusion effects that allow the model to be fitted to data. This simple approach continues to be successfully applied to modeling the transport of chemicals via preferential flow (Steenhuis et al., 1994, 2001; Kim, 2003). There have been several suggested modifications to the mixing-layer theory such as uniform, incomplete mixing (Frere et al., 1980; Ingram and Woolhiser, 1980) and non-uniform, incomplete mixing (Ahuja et al., 1981), which add complexity and more fitting parameters without changing the conceptual basis of the mixing-layer approach. In contrast to the mixing-layer theory, the other popular type of chemical transfer model assumes diffusion-like processes control chemical transfer between soil and runoff. Processes controlled by rain-impact are either considered negligible (e.g. Wallach et al., 1988, 1990, 1991) or characterized by diffusion-like equations (Ahuja, 1990). Like the mixing-layer models, diffusion-based models have been well fitted to experimental data. However, to achieve good results for diffusion models, the calibrated diffusion coefficients are used as calibration parameters with uncertain mathematical/physical definitions (Ahuja, 1990) or additional terms are added to enhance effective transport that do not have

clearly defined physical interpretations (Wallach et al., 1988).

Gao et al. (2004) reinterpreted the commonly used expression for the rain induced soil detachment rate, $e = ap$, where a is the soil detachability [M L^{-3}] and p is the rainfall rate [L T^{-1}] (Rose et al., 1985, 1988, 1994; Sharma et al., 1993, 1995; Jayawardena and Bhuiyan, 1999; Gao et al., 2003), in terms of the rate of 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, ρ_b is the soil dry bulk density, and θ is the soil water content. Gao et al. (2004) then developed a model that combined the chemical transfer associated with the raindrop impacts and associated with diffusion by assuming raindrop and diffusion processes could be coupled by simply adding the two processes together, i.e. as though the two processes operated in parallel. The Gao et al. (2004) model captured soil-runoff chemical transfer behavior more realistically than either mixing-layer models or diffusion-based models, assuming that all parameters were physically realistic (Gao et al., 2004). However, this model, like the others, did not fully capture the rapid chemical transfer that occurs immediately after rainfall is initiated. We believe this is because the two processes, rain-impact and diffusion transfer, interact in ways that are not fully represented by simple superposition.

Using a mixed black sand–white clay experimental soil, Gao et al. (2004) showed that the depth of the mixing-layer, in which raindrop impact drives soil water-runoff mixing, is the same depth as the soil-erosional 'shield' layer conceptualized by Rose (1985). When different weight soil particles are ejected from the soil surface by raindrops, light particles are carried away in runoff while heavy particles immediately settle and accumulate on the surface as a shield layer. As the shield layer develops, it increasingly protects the underlying soil from the raindrop impacts until raindrops only eject the shield particles, which rapidly resettle on the surface. This concept is unique to the Rose soil erosion model (Rose, 1985, 1994, 1998; Hairsine and Rose, 1991; Sander et al., 1996; Parlange et al., 1999; Heilig et al., 2001; Gao et al., 2003). Gao et al. (2004) noted that in addition to soil particles, soil water is also ejected into

the runoff and the dark colored ‘shield’ that developed in the experiments indicated the depth of raindrop penetration into the soil. Unlike in erosion, with respect to solute transfer, this layer is not just a ‘shield’ as much as it is an ‘exchange layer’, where raindrops drive the solute exchanged between runoff and surface soil. The thickness of the shield of deposited particles indicates how deeply the raindrops penetrate the soil; the raindrops drive chemical exchange by ‘digging-in’ to the soil during and after shield development. In this investigation the depth of the exchange layer is considered constant, i.e. erosion does not substantially effect how deeply raindrops will penetrate the soil surface.

In this study, we hypothesized a physical model that, rather than superimposing raindrop-impact and diffusion like Gao et al. (2004), assumes the processes act in series. In this new conceptualization, raindrop-impact controls the transfer between the exchange layer at the soil surface and runoff and diffusion controls chemical transfer between the underlying soil and exchange layer (Fig. 1). We also show how soil water advection processes, like infiltration, can be included (Fig. 1). The resulting set of differential equations was solved using the finite difference method and model results were tested against experimental data. An appendix has been included deriving accurate analytical approximate solutions to the model.

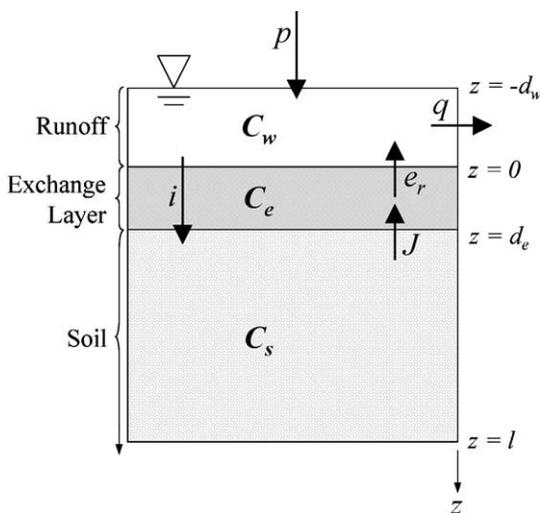


Fig. 1. Conceptual schematic of the model's physical chemical transport processes.

2. Model description

Fig. 1 shows the conceptual arrangement of processes used to develop our model of chemical transport between soil and runoff. We considered a soil water system divided into three different vertically distributed, horizontal layers: runoff or surface ponding water, an exchange layer which is identical to the ‘shield’ in the Rose erosion model, and the underlying soil. 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 surface runoff. We assumed the exchange layer is well mixed and can be characterized by a single concentration throughout the layer, $C_e(t)$.

In this study we focused on dissolved chemical transport. For soil-adsorbed chemicals, the following expression is used to describe the relationship between dissolved and adsorbed chemical concentrations:

$$C_T = \rho_b C_a + \theta C_s \quad (2)$$

where C_T is the total chemical concentration in the soil [$M L^{-3}$], C_s is the dissolved chemical concentration in the soil water [$M L^{-3}$], C_a is the adsorbed chemical concentration in the soil [$M M^{-1}$], θ is the soil water content, and ρ_b is the dry soil bulk density [$M L^{-3}$]. Following the simplifying assumption of Steenhuis et al. (1994), the adsorbed and dissolved concentrations are related by a simple linear relationship via a constant partition coefficient, K_p . Eq. (2) can be rewritten as:

$$C_T = \alpha C_s \quad (3)$$

where $\alpha = \rho_b K_p + \theta$. For the non-adsorbed chemicals, α is equal to the soil moisture, θ .

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:

$$\frac{\partial \alpha C_s}{\partial t} = \frac{\partial}{\partial z} \left[D_s \frac{\partial C_s}{\partial z} - i C_s \right] \quad (4)$$

where C_s is the chemical concentration in the soil water below the exchange layer, t is time, z is the vertical dimension, i is the infiltration rate in the soil, D_s is the dispersivity of chemicals in the soil and is

taken as the sum of the molecular diffusivity and the mechanical diffusion coefficient (Bresler, 1973; Bear and Bachmat, 1990; Ahuja, 1990). For the case when infiltration is suppressed, D_s is equal to the molecular diffusivity of solute in soil.

Chemical transport in the exchange layer involves diffusion into the layer from the soil below, raindrop driven exchange with the runoff water, and infiltration mediated fluxes into the soil below. These processes are included in following equation:

$$\frac{d(\alpha d_e C_e)}{dt} = J + e_r(\lambda C_w - C_e) + i(C_w - C_e) \quad (5)$$

where d_e is the depth of the exchange layer, C_e is the solute concentration in the exchange layer, C_w is the solute concentration in the runoff water, 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, i.e. $\lambda = 0$ if only rainwater (assumed to be solute free) enters the exchange layer and $\lambda = 1$ if the exchange water is only runoff, thus $0 \leq \lambda \leq 1$, and J is the diffusion rate of solute from the soil below the exchange layer, which is described by Fick's law:

$$J = -D_s \frac{\partial C_s}{\partial z} \quad (6)$$

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:

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

where d_w is the ponding water depth, C_w is the chemical solute concentration in the runoff, and q is the volumetric runoff flux per unit width. In the case of shallow, kinematic overland flow, d_w and q are related by:

$$\frac{\partial d_w}{\partial t} + \frac{\partial q}{\partial x} = (p - i) \quad (8)$$

Eqs. (7) and (8) can be combined to give:

$$d_w \frac{\partial C_w}{\partial t} + q \frac{\partial C_w}{\partial x} = e_r(C_e - \lambda C_w) - p C_w \quad (9)$$

The chemical concentration throughout the system and the interactions between the different layers are described by Eqs. (5) and (9), which can be used as the boundary condition of the advection-diffusion equation for the underlying soil layer, Eq. (4).

3. Experimental methods

In order to meaningfully test our model, we designed an experiment for which all parameters could be directly measured, i.e. none are curve-fitted to the experimental results. Some of the data used in this study were previously published by Gao et al. (2004) and the experimental design is discussed fully therein. Fig. 2 shows a schematic of the experimental set-up. The experimental soil, which was made of black sand and white clay in a mass ratio of 9:1, was pre-saturated with a solution of chloride (29.82 g L^{-1}) and phosphorus (2.98 g L^{-1}). Chloride (Cl^-) was used to test the modeling of a non-adsorbed solute and phosphorus (P) to test an adsorbed solute. This soil mixture has been used in previous soil erosion experiments in which the soil erodibility, $a = 0.40 \text{ g cm}^{-3}$, and saturated moisture content, $\theta_s = 0.37$, were determined (Heilig et al., 2001; Gao et al., 2004). The contrasting colors of soil particles allow direct measurement of the exchange layer depth, d_e (Gao et al., 2004). A 0.7 cm ponding water depth was established prior to commencing rainfall and was held constant via overflow holes in the chamber throughout the experiment (Fig. 2). Replicated experiments were run at three different rainfall intensities: 2.1×10^{-3} , 1.4×10^{-3} , and $0.8 \times 10^{-3} \text{ cm s}^{-1}$, 312 (7.4, 5.2, and 3.0 cm h^{-1} , respectively). Samples of outflow were systematically collected and tested for Cl^- and P concentrations using a Digital Chloridimeter (Buchler Instruments, M442-5000) and an OI Analytical FS-3000 Flow Analyzer (O.I. Analytical) with an orthophosphate cartridge (A001558), respectively. Each experiment continued until the ponded water was completely clear of sediment, 1.5–3 h depending on the rainfall rate. Table 1 presents the experimental parameters.

The P partition coefficient (K_p) was determined from adsorption isotherms developed through batch experiments (Syers et al., 1973; Castro and Rolston, 1977). Samples, 5 g each, of the experimental soil

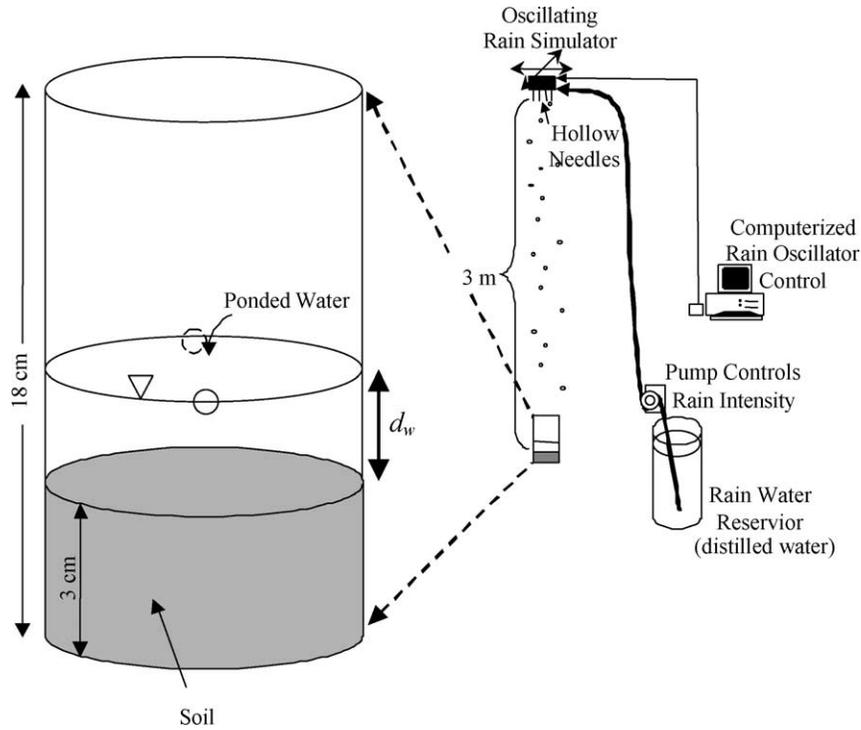


Fig. 2. Schematic of the experimental apparatus and set-up of Gao et al. (2004).

Table 1
Experimental parameters used in the numerical model

	$p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$ (7.4 cm h ⁻¹)	$p = 1.4 \times 10^{-3} \text{ cm s}^{-1}$ (5.2 cm h ⁻¹)	$p = 0.8 \times 10^{-3} \text{ cm s}^{-1}$ (3.0 cm h ⁻¹)
Initial concentration, C_0 (g l ⁻¹) fro Cl ⁻ /P ^a	29.82/2.98	29.82/2.98	29.82/2.98
Ponding depth, d_w (cm) ^b	0.7	0.7	0.7
Exchange layer depth, d_e (cm) ^c	0.76	0.55	0.42
Bulk density, ρ_b (g cm ⁻³) ^d	1.5	1.5	1.5
Soil moisture, θ^d	0.37	0.37	0.37
Soil erodibility, a (g cm ⁻³) ^e	0.40	0.40	0.40
Diffusivity, D_s (10 ⁻⁶ cm ² s ⁻¹) ^f	4.2	4.2	4.2
P Adsorption coefficient, K_p (ml g ⁻¹) ^g	0.16	0.16	0.16
$\alpha = \rho_b K_p + \theta$ for Cl ⁻ /P	0.37/0.61	0.37/0.61	0.37/0.61
'Exchange water' fraction that is runoff, λ^h	1	1	1
Raindrop Chemical Transfer Rate, e_r , (10 ⁻⁴ cm s ⁻¹) ⁱ	2.1	1.5	0.9

^a Initial chemical solutions were prepared in the lab at these concentrations.

^b Measured manually throughout experiments.

^c Directly measured; see Heilig et al. (2001) and Gao et al. (2004) for examples and details. Values shown are the average three runs.

^d Measured using standard methods.

^e Determined by independent soil erosion experiments by Heilig et al. (2001) and Gao et al. (2003).

^f Eq. (11).

^g Determined for P via independent experiments (Fig. 3); The adsorption coefficient for Cl⁻ was zero.

^h $\lambda = 1$ indicates that all the water entering the exchange layer is runoff or ponded water.

ⁱ Eq. (1).

were used for the P sorption isotherm analysis by equilibrating each sample with 10 ml aqueous solutions containing 0, 0.12, 0.24, 0.42, 60, 0.72, 0.96, 0.12, 0.24, 0.60, 1.20, and 2.10 g l⁻¹ KH₂PO₄. Each sample was replicated. The soil solution mixtures were gently mixed and incubated for 24 h to attain sorption equilibrium at room temperature (Chen et al., 1996; Kim, 2003). The supernatant was subsequently extracted and filtered through a 0.45 μm filter. The P not recovered in solution was assumed to be adsorbed. The amount of P adsorbed was calculated on the dry soil basis from the concentration change in the solution phase.

3.1. Model application

For simplicity, the experiments used here did not include infiltration and the experimental design is such that many of the parameters can be assumed constant. The model's governing equations simplify to:

$$\alpha \frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial z^2} \quad (10a)$$

$$\text{at } z = l: \quad D_s \frac{\partial C_s}{\partial z} = 0 \quad (10b)$$

$$\text{at } z = d_e: \quad C_s = C_e \quad (10c)$$

at $0 < z \leq d_e$:

$$\alpha d_e \frac{dC_e}{dt} = D_s \frac{\partial C_s}{\partial z} \Big|_{z=d_e} + e_r(\lambda C_w - C_e) \quad (10d)$$

at $-d_w < z \leq 0$:

$$d_w \frac{dC_w}{dt} = e_r(C_e - \lambda C_w) - pC_w \quad (10e)$$

Using the initial condition, at $t = 0$, $C_s = C_0$, $C_e = C_0$, and $C_w = 0$, we solved Eqs. (10a–e) by the finite-difference method using the Crank-Nicholson central differences scheme. The spatial mesh used in this study was 0.02 cm and the time step was 1.0 s for

the soil underlying the exchange layer (these values were established after trials with different intervals). Note also, we derived approximate analytical solutions to Eqs. (10a–e) and have presented these in the Appendix A.

The raindrop induced mass transfer coefficient, e_r , was calculated from Eq. (1) using the same soil detachability, a , bulk density, ρ_b , and saturated moisture content, θ_s , used by Gao et al. (2004) and Heilig et al. (2001), as discussed earlier (Table 1).

The diffusion constant, D_s , was based on the published Cl⁻ aqueous diffusion coefficient ($D_a = 1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and Millington and Quik's (1961) tortuosity model as also used by Wallach et al. (1988), Ahuja (1990), Zhang et al. (1997), and Gao et al. (2004):

$$D_s = D_a(\theta^{10/3}/\theta_s^2) \quad (11)$$

where θ_s is the saturated water content, 0.37 for these experiments. The diffusion constant for P was determined in the same way and, because values of D_a were not readily available for P, we assumed the same value as for Cl⁻, $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and investigated the sensitivity of the model to this assumption afterward. The Cl⁻ and P diffusion constant calculated using Eq. (11) was $4.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The traditional way to attain P sorption parameters is to fit P sorption isotherm data to the Langmuir equation (Castro and Rolston, 1977):

$$C_a = \frac{bKC_a}{1 + KC_a} \quad (12)$$

where K is the constant related to the binding strength (when $C_a = 1/K$, then half of the adsorption sites on the soil are filled with P), and b is the maximum amount of P that can be adsorbed. Our experimental P adsorption isotherm data were well described by the Langmuir equation, $R^2 = 0.96$ (Fig. 3). Since the early part of the Langmuir isotherm is very close to the linear partition relationship, many researchers have estimated the adsorption partition coefficient, K_p , as the tangent to the Langmuir isotherm at a specific concentration (e.g. Akhtar et al., 2003; Kim, 2003). Because our experiments used high concentrations of P, we employed a simple linear regression of the P adsorption isotherm to approximate our P adsorption partition coefficient. Fig. 3

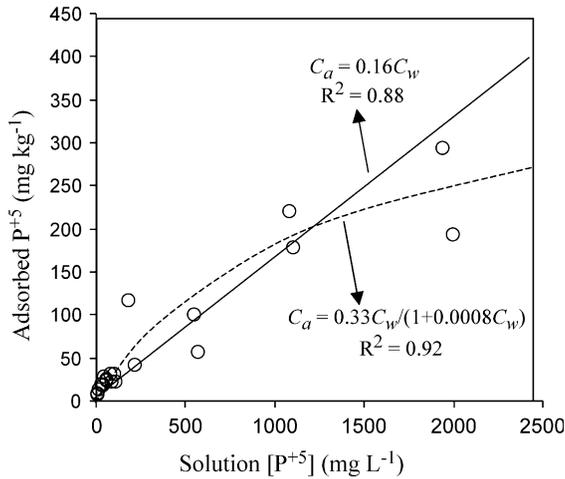


Fig. 3. P adsorption isotherm. Symbols = data; lines = fitted regressions.

shows how a linear regression of the isotherm fits the experimental data, $R^2 = 0.88$, with a partition coefficient of 0.16 ml g^{-1} . This P partition coefficient is much smaller than that of previous studies using natural soils, e.g. $1.4\text{--}26.1 \text{ ml g}^{-1}$ (Akhtar et al., 2003; Kim, 2003). This difference is expected because our experimental soil, pure sand (90%) and clay (10%), contained no organic matter, which is where most P is adsorbed in natural soils (Dion et al., 2001; McGechan and Lewis, 2002). Using experimentally derived K_p , the parameter α for P was 0.61. Chloride was treated as a non-adsorbed chemical in the soil; thus, the parameter α was equal to the experimentally determined soil moisture, 0.37.

Note that essentially all parameters were either determined from independent measurements or theoretical calculations; except for the aqueous diffusion coefficient, D_a , for P and λ which are discussed later. All parameters are shown in Table 1.

4. Results and discussion

The numerically predicted Cl^- concentrations in the runoff water were compared with the measured data for the three different rain intensities (Fig. 4). Fig. 4a shows that the choice λ had little effect on the predicted chemical concentration in the runoff. Although the peak for $\lambda = 0$ (thin line in Fig. 4a) was slightly higher than for $\lambda = 1$ (heavy line in Fig. 4a),

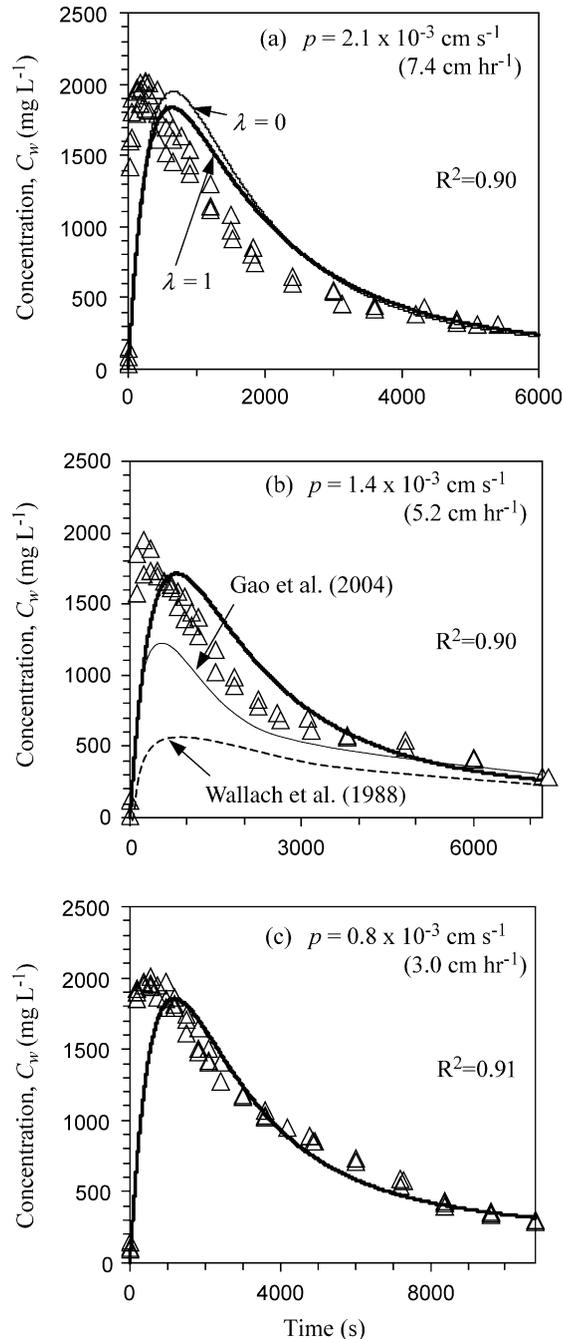


Fig. 4. Comparison of model results with experimental Cl^- data for three different rain intensities. Symbols = data; lines = model results. (a) $p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$, heavy line: $\lambda = 1$, thin line: $\lambda = 0$; (b) $p = 1.4 \times 10^{-3} \text{ cm s}^{-1}$, heavy line: $\lambda = 1$, thin line: model by Gao et al. (2004), dashed line: model by Wallach et al. (1988); (c) $p = 0.8 \times 10^{-3} \text{ cm s}^{-1}$, heavy line: $\lambda = 1$.

their statistical agreements with the data was the same, $R^2 = 0.9$. Unless otherwise noted, we have arbitrarily used $\lambda = 1$ throughout the rest of our results; we found no experiment for which the choice of λ significantly impacted our results. The model predicted the experimental data well for all experiments, with $R^2 > 0.90$ (Fig. 4a–c). In Fig. 4b we shows the improved performance of the model developed in this paper relative to previously published models, Gao et al. (2004) is the thin line and Wallach et al. (1988) is the dashed line. In this example we used our measured parameters in the model by Wallach et al. (1988) and did not include their ‘small initial concentration’ term because it was not well defined and appeared act as a calibration constant. Although the model developed in this paper captures the early, raindrop driven chemical transport better than Gao et al. (2004) or Wallach et al. (1988), the observed early concentration increased more rapidly than any of the models (Fig. 4a–c). Our model’s systematic under-prediction of the early ($t \sim 500$ s) chemical concentration led, subsequently, to slight over-predictions later in the experiment (Fig. 4). We hypothesize that our systematic deviations arises from our assumption of a ‘well mixed’ exchange layer, which is probably not a good assumption for the early part of rainfall. The first several raindrops, presumably hitting different parts of the soil surface, probably eject the soil water with a solute concentration very near the initial concentration. Our model assumes the concentration falls rapidly throughout the exchange layer the moment rainfall begins, as will be discussed in the next paragraph. Other possible processes not included in our model that may explain the observed discrepancies include diffusion from the exchange layer or soil water pumping due to raindrop impacts or the uneven overburden water surface. At this time we do not know how to explicitly include these processes without adding unknown, i.e. calibration, parameters. Interestingly, despite the additional complexity of adsorption, the model predictions of the P experimental data were slightly better than for Cl^- , $R^2 > 0.92$ (Fig. 5). Even with the potentially missing processes, Figs. 4 and 5 suggest that this model captures most of the chemical transport behavior with no curve-fitting.

Although we did not measure the solute concentrations in the soil during the experiments,

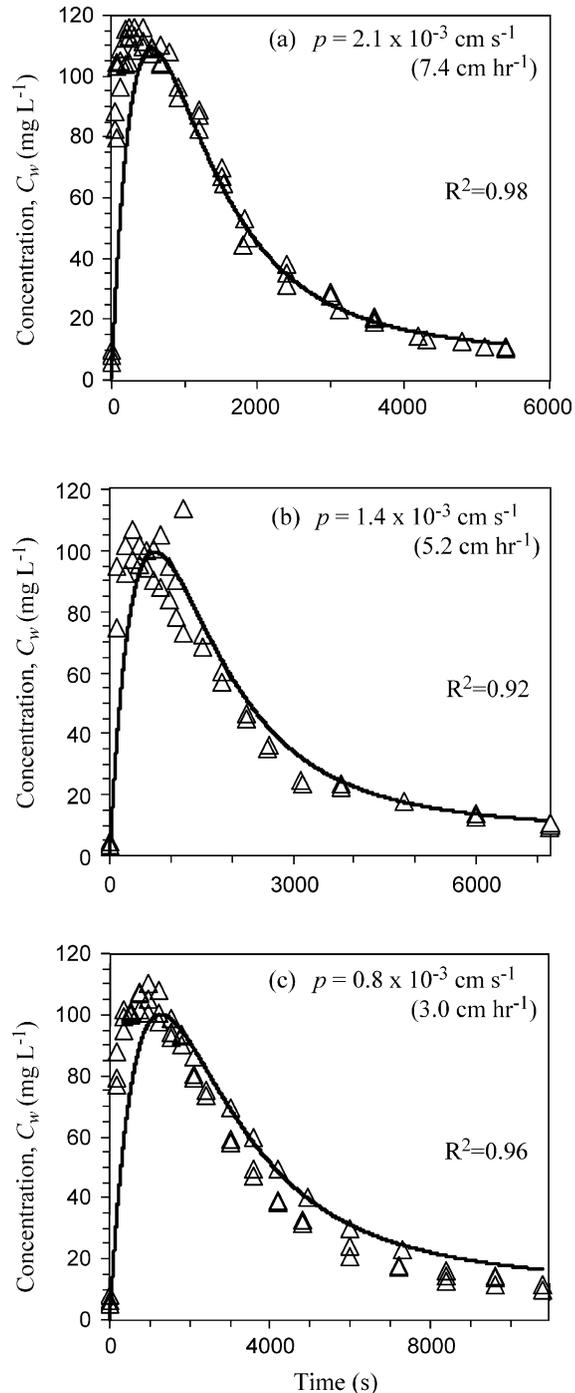


Fig. 5. Comparison of model results with experimental P data for three different rain intensities. Symbols = data; lines = model results ($\lambda = 1$). (a) $p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$; (b) $p = 1.4 \times 10^{-3} \text{ cm s}^{-1}$; (c) $p = 0.8 \times 10^{-3} \text{ cm s}^{-1}$.

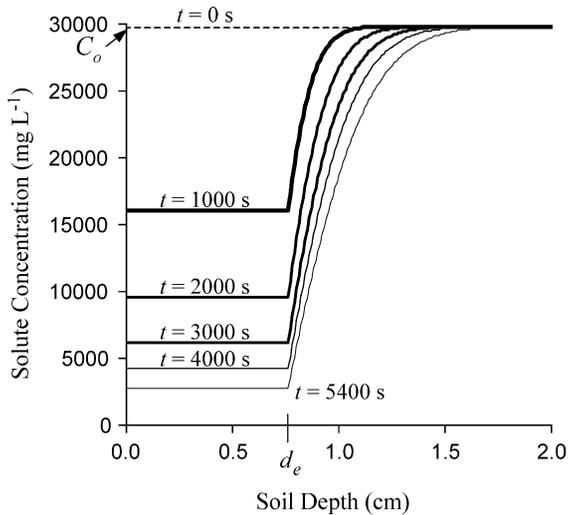


Fig. 6. Example of simulated chemical solute (e.g. Cl^-) distribution in soil at different times. $p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$ (7.4 cm h^{-1}).

the numerical model simulated temporal concentrations throughout the soil–water system. Fig. 6 shows the modeled Cl^- concentrations in the soil. Although the Cl^- concentration in the soil changed slowly and only influenced about 1 cm of the soil below the exchange over two hours, there was still a substantial amount of chemical that diffused out from this layer by the end of the experiment ($t = 7200 \text{ s} = 2 \text{ h}$). After the initial rain impacts ‘flushed’ the exchange layer, the solute concentrations in the runoff were largely controlled by diffusion and both Figs. 4 and 5 show substantially elevated, i.e. non-zero, concentrations at the end of the experiments. These results highlight the problem with the mixing-layer theory’s basic assumption that there is negligible chemical transport into the mixing-layer from below. Note, also, that unlike previous diffusion-based transport models, here diffusion transfers chemicals into the exchange layer, not into the runoff, and the exchange layer’s concentration is different from the runoff’s concentration. This demonstrates that both raindrop impact and diffusion processes control long-time chemical transport.

Fig. 7 shows the simulated Cl^- concentration in the exchange layer and surface runoff. Notice that early in the experiment the difference in the solute concentration between the exchange layer and runoff water decreased dramatically and the concentrations

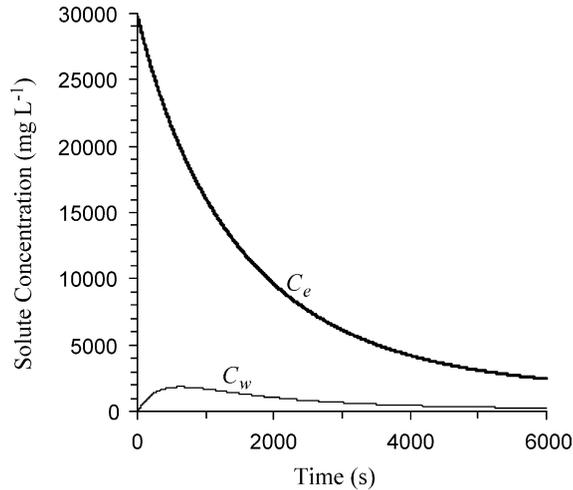


Fig. 7. Example comparison of solute concentration (e.g. Cl^-) in the exchange layer, C_e , and surface runoff, C_w , with respect to time. $p = 1.4 \times 10^{-3} \text{ cm s}^{-1}$ (5.2 cm h^{-1}).

gradually got closer to each other (Fig. 7). The shape of the exchange layer solute curve is similar to an exponential or power function, which explains why mixing-layer models can be fitted to these types of data. But, it is obvious that the runoff water and soil water do not ‘instantaneously mix’ as assumed by the mixing-layer theory. In fact, the large solute concentration differences between exchange layer and runoff persist after $\sim 2 \text{ h}$ (Fig. 7). These results are corroborated by laboratory studies that have also demonstrated similar prolonged, large solute concentration difference between the runoff and soil water near the soil surface (Ahuja and Lehman, 1983; Snyder and Woolhiser, 1985). Qualitatively, these results suggest that there may be substantial diffusion out of the exchange layer early in the rain event and that diffusion would decrease over time; this process was not included in our model and may partially account for the slight, systematic discrepancies in the timing of our modeled peak concentrations.

Fig. 8 shows how the model responds when various parameters are independently varied. Recall that the aqueous diffusivity, D_a , for P was not well quantified and that a value of $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was used assuming similarity with Cl^- . Fig. 8a shows that order-of-magnitude changes in D_a are required before this parameter has a substantial impact on model

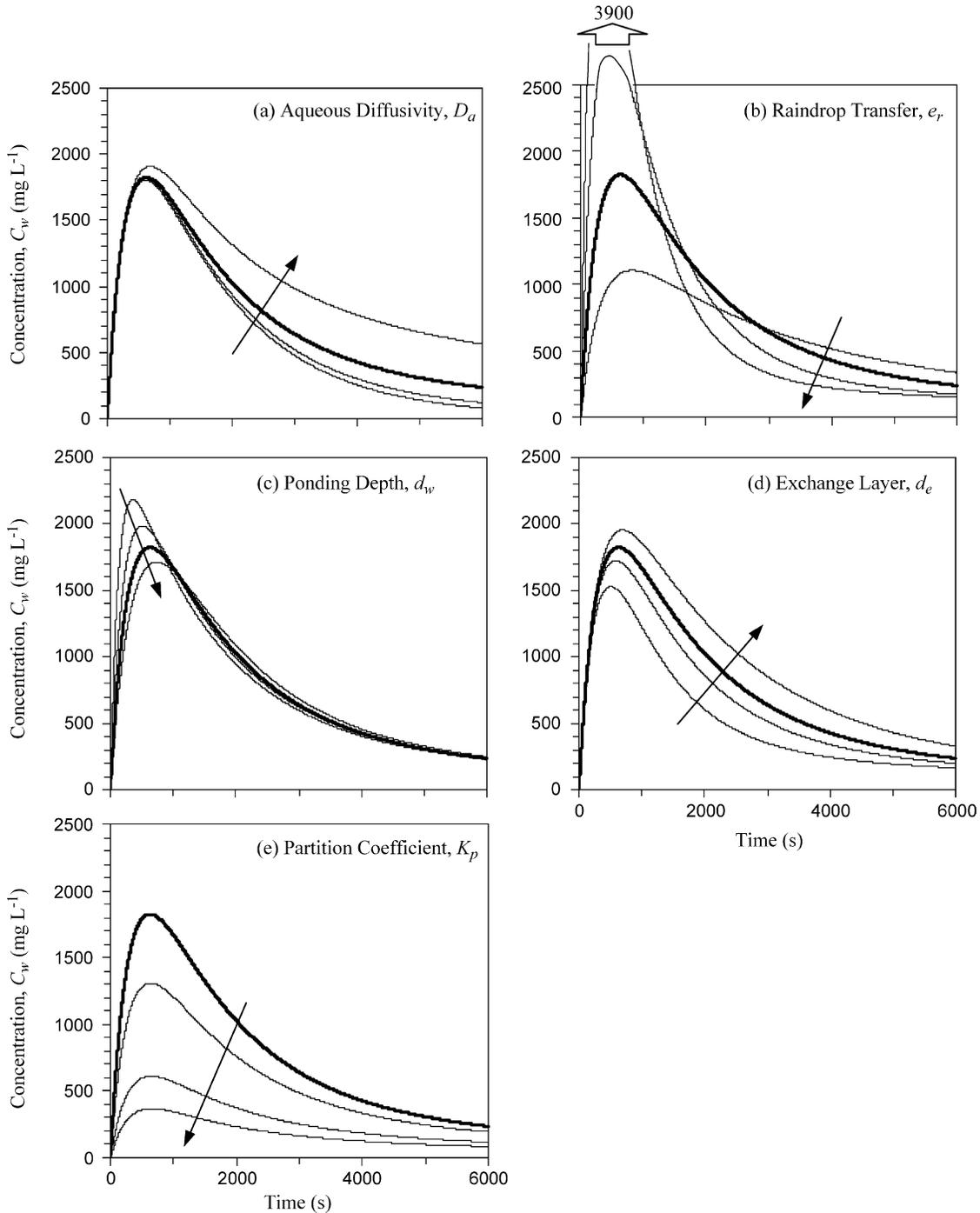


Fig. 8. Variations in model results of chemical transport in surface runoff due to changing individual parameters: (a) $D_a = 0.016, 0.16, \mathbf{1.6}, 16$ ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$); (b) $e_r = 1.05, \mathbf{2.1}, 4.2, 8.4$ ($10^{-4} \text{ cm s}^{-1}$); (c) $d_w = 0.3, 0.5, \mathbf{0.7}, 0.9$ (cm); (d) $d_e = 0.4, 0.6, \mathbf{0.76}, 1$ (cm); (e) $K_p = \mathbf{0}, 0.1, 0.5, 1$ (ml g^{-1}); all the other parameters are as shown for Cl^- in Table 1, $p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$ (7.4 cm h^{-1}). The bold curves are the same as Fig. 4a and correspond to the bolded parameter values in this caption. Arrows indicate trends resulting from increasing parameter values.

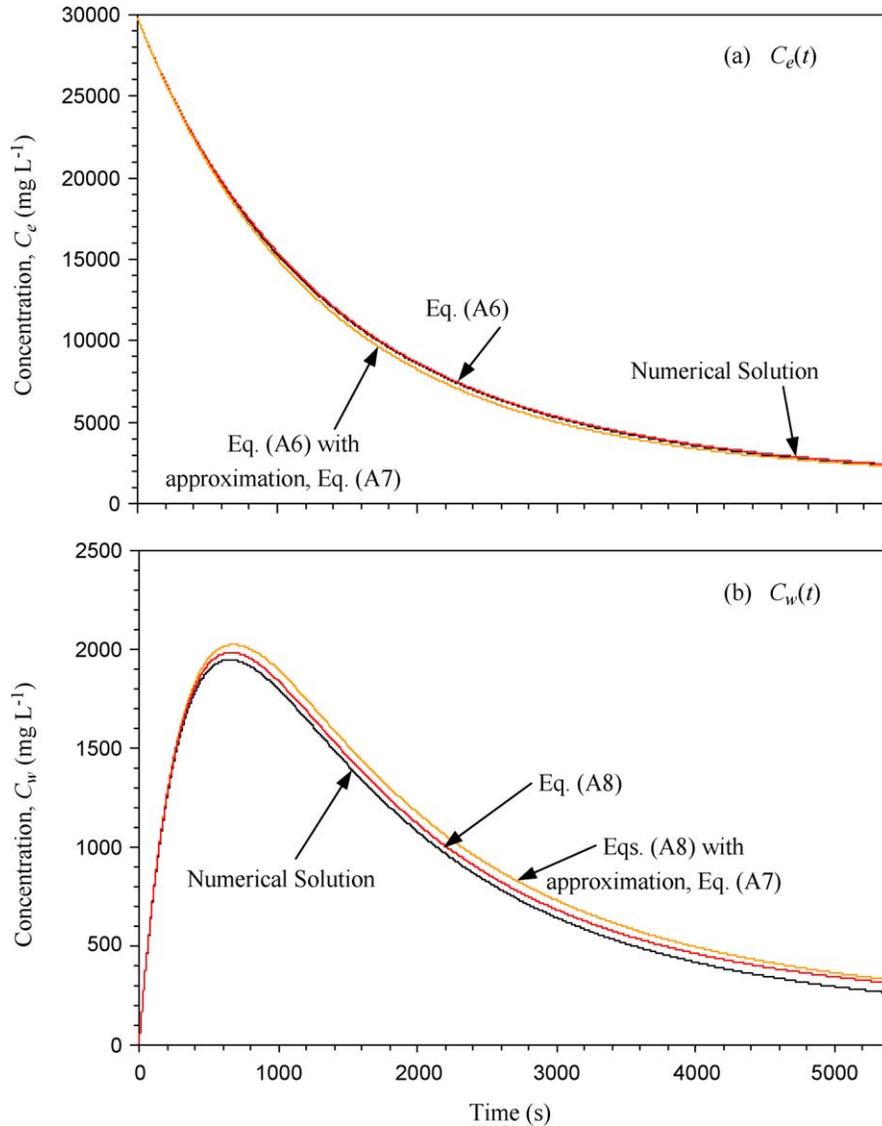


Fig. 9. Comparisons between numerical (black lines) and analytical (colored lines (shown in web version)) solutions of (a) chemical concentration in the exchange layer, C_e , and (b) the chemical concentration in the ponded water, C_w , to the model equations. The cases shown are for Cl^- and $p = 2.1 \times 10^{-3} \text{ cm s}^{-1}$ (7.4 cm h^{-1}) and $\lambda = 0$. The red line is the analytical solution, Eqs. (A6) and (A8); and the orange line is the analytical solution using the approximation, Eq. (A7), for the integral in Eq. (A6).

results. We found that the model results for P were nearly identical using diffusivity values in the range of 1×10^{-5} to $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. As expected, the diffusivity primarily impacts the long-time concentrations and has only a small impact on the peak concentration and the timing of the peak concentration. This is consistent with our conceptual

understanding of the chemical transport processes, i.e. rain impact dominates the early transport and diffusion controls the long-time transport.

In contrast to how the model responds to D_a , the water exchange rate, e_r , strongly influences the peak concentration but has little effect on the solute concentration in runoff beyond the first several

minutes (Fig. 8b). Again, this is consistent with our conceptual understanding of the transport processes. Interestingly, a much smaller range of e_r values, $1.05 \times 10^{-4} - 8.4 \times 10^{-4} \text{ cm s}^{-1}$, than shown for D_a caused more dramatic changes in the concentration curves, but primarily limited to the early part of the figure. These results show that although both raindrop detachment and diffusion have important effects on solute transport from soil to surface runoff, raindrop driven transport controls short time and peak solute concentrations and diffusion controls the long time results. However, for a substantial duration of these experiments, both processes interacted in non-trivial ways to affect chemical transport from soil into runoff.

Fig. 8c–e shows the impacts of runoff depth, d_w , exchange layer depth, d_e , and soil-water partition coefficient, K_p , on the model results. Changing the runoff water depth over a factor of three, i.e. $d_w = 0.3 - 0.9 \text{ cm}$, did not substantially change the overall shape of the curves but it did change the peak concentration; larger water depths diluted the peak concentration (Fig. 8c). The model appears to be most sensitive to the exchange layer depth, d_e (Fig. 8d) and soil-water partition coefficient, K_p (Fig. 8e). These two parameters, d_e and K_p , determine the availability of chemicals for raindrop transport processes. Not explicitly represented in this model is the fact that the exchange layer and runoff depths are interdependent and their relationship is not yet understood well enough to predict with a model; that is why we measured these parameters explicitly. Qualitatively, these two parameters interact in ways that enhance their independent impacts on chemical transfer; for example a deeper runoff depth decreases the exchange layer depth, both of which reduce the peak solute concentration in the runoff.

An analytical solution, derived in Appendix A can be found by taking $\lambda = 0$ so the concentration in the exchange layer, C_e , is expressed by Eq. (A6). The integral in Eq. (A6) is obtained numerically but can be approximated by Eq. (A7). Once C_e is known, the solution for concentration in the runoff can be expressed by Eq. (A8). Fig. 9 shows the strong agreement between the numerical and analytical solutions with $\lambda = 0$. See Appendix A for the derivation of the analytical solution.

5. Conclusions

Chemical transport from the soil into runoff is a complicated process in which both the raindrop driven processes and diffusion are important transfer mechanisms. Using the "shield layer" concept employed in the Rose (1985) model, we developed a new model to improve our understanding of how diffusion and raindrop impact interact to control chemical transport. With no calibration, that is, all parameters were measured or previously published, the model correctly simulated Cl^- and P concentrations in runoff for several laboratory experiments. The model results showed that the raindrop driven processes controlled the solute transport at the beginning of the rainfall event and both raindrop impact and diffusion determined the long-time transport process when infiltration was suppressed. This study demonstrates that the interactions between raindrop driven and diffusion driven processes must be considered to meaningfully model soil transport between soil and runoff.

Appendix A. Analytical solution to the model

Analytical solutions to Eqs. (10a–e) can be found simply by assuming that $\lambda = 0$, i.e. that the water replacing the solution ejected from the exchange layer has a chemical concentration similar to rain (no chemicals). Recall that the numerical solution used in the preceding paper assumed that $\lambda = 1$. Using this assumption of $\lambda = 0$, Eqs. (10d) and (10e) simplify to:

$$\text{at } 0 < z \leq d_e : \quad \alpha d_e \frac{dC_e}{dt} = D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=d_e} - e_r C_e \quad (\text{A1})$$

$$\text{at } -d_w < z \leq 0 : \quad d_w \frac{dC_w}{dt} = e_r C_e - p C_w \quad (\text{A2})$$

Considering a duration short enough that l in condition (10b) is effectively infinite, which is our case in practice, the solution to Eq. (10a) with

condition (10c) can be taken from Carslaw and Jaeger (1986, p. 63)

$$C_e = C_o - 2\pi \int_{x/\sqrt{4kt}}^{\infty} \left[C_o - C_e \left(t - \frac{x^2}{4k\mu^2} \right) \right] \times \exp(-\mu^2) d\mu \quad (\text{A3})$$

where $k = D_s/\alpha$ and x and z differ by d_e . We need the flux $D_s(\partial C_s)/(\partial x)|_{x=0}$ to solve Eq. (A1). To do so simply, we assume that C_e in the integral of Eq. (A3) can be approximated by:

$$C_e \approx C_o \exp(-\beta t) \quad (\text{A4})$$

where $\beta = e_r/(\alpha d_e)$. Eq. (A4) is the solution to Eq. (A1) if we ignore the diffusion term. As a result, C_e in Eq. (A4) must be too small and the flux calculated with Eq. (A3) with this value of C_e will be too large. Hence, the value of C_e calculated from Eq. (A1) will also be too large. Thus, Eqs. (A3) and (A4) give at once:

$$D_s \frac{\partial C_s}{\partial x} \Big|_{x=0} = C_o \exp(-\beta t) \left(\frac{\beta}{\sqrt{\pi k}} \right) \int_0^t \frac{\exp(\beta y)}{\sqrt{y}} dy \quad (\text{A5})$$

Substituting Eq. (A5) into Eq. (A1) yields:

$$C_e = C_o \exp(-\beta t) + \frac{\beta^2}{e_r} \sqrt{\frac{\alpha D_s}{\pi}} \exp(-\beta t) \times \int_0^t \exp(\beta y) \left(\frac{t}{\sqrt{y}} - \sqrt{y} \right) dy \quad (\text{A6})$$

where the integral in Eq. (A6) is obtained numerically. The following simple, but not very accurate, approximation of the integral Eq. (A6) can also be used:

$$\int_0^t \exp(\beta y) \left(\frac{t}{\sqrt{y}} - \sqrt{y} \right) dy = \frac{\exp(\beta t) - 1}{\beta^2 \sqrt{t}} - 2 \frac{\sqrt{t}}{\beta} - \frac{2}{\beta^2 \sqrt{t}} + 2 \frac{\exp(\beta t) - 1}{\beta^3 t^{3/2}} \quad (\text{A7})$$

The solution for Eq. (A2) can be expressed as:

$$C_w = AC_e - C_o A \exp\left(-\frac{pt}{d_w}\right) \quad (\text{A8})$$

where $A = e_r/(p - d_w\beta)$.

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