Predicting the Fate of Preferentially Moving Herbicides
Bahareh Hassanpour, Brian K. Richards,* Larry D. Goehring, Jean-Yves Parlange, and Tammo S. Steenhuis

Simulation of preferential flow remains a challenge despite being a recognized phenomenon. With short-interval data, we adapted and tested the preferential flow model (PFM) to simulate the vertical transport of herbicides to lower soil layers. The PFM divides the soil profile into a top distribution zone and a conveyance zone below. The distribution zone acts as a reservoir, with an exponential loss of solutes to the conveyance zone. In the conveyance zone, water and solutes move as convective-dispersive flow through multiple flow paths—preferential and matrix—to shallow groundwater. Our field experiment was performed on a structured Hudson silt loam soil (a fine, illitic, mesic Glossaquic Hapludalf) that exhibits preferential flow. The site was instrumented with a variety of soil water samplers placed at depths of 60 cm to monitor the volume and quality of the leachate. Agronomic application of atrazine [6-chloro-N-ethyl-N’-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and 2,4-D [2-(2,4-dichlorophenoxy)acetic acid] was used, followed by 75 cm of controlled and natural rainfall over 100 d. In addition, Cl− was applied as a conservative tracer. All samplers monitored during this period showed a fast breakthrough of solutes consistent with the occurrence of preferential flow, with two groups of breakthrough curves observed. By fitting the Cl− breakthrough curve for each group, PFM input parameters were estimated including water velocity in preferential flow paths and the fraction of water moving through each flow path. With two additional parameters for herbicide adsorption and degradation rates, the model successfully simulated the extent of preferential flow of herbicides.

Abbreviations: PFM, preferential flow model; BTC, breakthrough curve; MCE, mean cumulative error; CD, coefficient of determination.

Susceptibility of groundwater to contamination with pesticides has long been documented (Hallberg, 1989; Leistra and Boesten, 1989; Ghodrati and Jury, 1992; Flury, 1996; Guzzella et al., 2006; Vryzas et al., 2012; Toccalino et al., 2014; Vryzas, 2018). In structured soils, this is largely because of preferential flow through macropores, such as cracks, worm holes, and root channels (Lawes et al., 1882; Beven and Germann, 1982; Gerke, 2006; Beven and Germann, 2013), and in coarse unstructured or water repellent soils, it is through unstable wetting fronts leading to rapid “fingered flow” (Hill and Parlange, 1972; Bauters et al., 1998; Li et al., 2018). Preferential flow allows a fast transport of water and solute to lower soil horizons by bypassing the soil matrix (Kung et al., 2000a, 2000b). Preferential flow influences the transport of both absorbent and non-absorbent tracers under field conditions.

It is now generally accepted that preferential flow at the field scale is rather the rule than the exception (Vanclooster et al., 2000; Beven, 2018; Guo and Lin, 2018), especially in structured soils (Gerke, 2006; Köhne et al., 2009a, 2009b). Preferential flow occurs in both tilled and untilled soils (Andreini and Steenhuis, 1990; Gish et al., 1995; Shalit and Steenhuis, 1996; Elliott et al., 2000). The breakthrough curves (BTCs) were right skewed in no-tilth soils, which was attributed to the greater infiltration rate in such soils (Boll et al., 1997; Siczek et al., 2008). Sanders et al. (2012) found that in an untilled agricultural silty clay loam soil, preferential flow comprised 34 to 99% of the infiltrated water. Most of the classical pesticide transport and fate models fall short because they are based on mass...
transfer (Queyrel et al., 2016) or the convective–dispersive equation and do not allow for different velocities of water in the porous media (Richard and Steenhuis, 1988; Gärdenäs et al., 2006).

Given the importance of preferential flow, numerous water and solute transport models have emerged that consider preferential flow in the vadose zone (Köhne et al., 2009a, 2009b; Jarvis et al., 2016), which include RZWQM (Kumar et al., 1998), MACRO (Larsbo et al., 2005; Jarvis and Larsbo, 2012), STICS-MACRO (Lammoglia et al., 2018), and HYDRUS (Šimůnek et al., 2005, 2009). Although these models have different complexities, they all assume that water and solute move faster in preferential pathways than in the matrix (Hutson and Wagenet, 1995; Köhne et al., 2009b; Jarvis et al., 2016). Among these models, dual-region models are most common (Šimůnek et al., 2003). These models assign two flow pathways, preferential and matrix, for water and solute transport and usually rely on numerical solutions with multiple inputs to model the transport of water and chemicals (Gerke, 2006; Wu et al., 2014; Jarvis et al., 2016). Gärdenäs et al. (2006) compared four conceptually different models and concluded that dual-porosity and -permeability models successfully predicted drainage discharge and pesticide concentrations. Multiregion models that are conceptually similar to dual-region models and better represent the porous media are used less often. The increased flexibility of multiregion models is generally offset by additional input parameters that are often poorly defined or difficult to determine (Wu et al., 2004; Gerke, 2006; Zhang et al., 2018).

Kim et al. (2005) overcame the difficulty of applying multiregion models by providing the preferential flow model (PFM) with input parameters that are easily defined. The PFM divides the soil profile into two layers, a distribution zone near the surface layer and a conveyance zone below. These two distinct soil layers were observed previously in the profile of soils with preferential pathways (Steenhuis et al., 1994; Ritsema and Dekker, 1995; de Rooij and de Vries, 1996; Barry et al., 2013; Liu et al., 2018). The distribution zone behaves like a first-order reservoir, with an exponential loss of solutes to the conveyance zone (Steenhuis et al., 1994, 2001). Water and solute in the conveyance zone flow through multiple preferential pathways, obeying the convective–dispersion equation in each flow path. It is noteworthy that the PFM relies on an analytical solution for the transport of preferentially moving chemicals.

The PFM was used for simulating the transport of non-adsorbed solutes in undisturbed laboratory columns (Darnault et al., 2004; Kim et al., 2005). It was also used but not tested for locating landscape areas with high risk of agrochemical leaching (Sinkевич et al., 2005). Although the PFM has been used sparsely, it remains attractive because of its simplicity of modeling preferential flow of pesticides in natural soils. Thus, its validation under field conditions is of interest. With the application of a multitude of field samplers including wick pan, gravity pan, pipe, and suction cup samplers, BTCs of Cl−, atrazine, and 2,4-D were measured in a structured soil. These samplers allowed investigation of the transport of chemicals in great detail because leached water was collected in entirety (Jarvis et al., 1995; Vanclooster et al., 2000; Köhne et al., 2009b).

Evaluation of the potential of pesticide contamination of groundwater requires a systematic approach through mathematical modeling coupled with field validation. The objective of this study was, therefore, to adapt and test a multiregion model for predicting pesticide movement and validating it with the Cl− and pesticide BTCs determined by Peranginangin et al. (2009).

### Material and Methods

#### Mathematical Modeling

The PFM developed by Kim et al. (2005) was adapted to describe herbicide transport and degradation. It assumes that all percolating water and solutes mix uniformly in the upper distribution zone (Fig. 1). Preferential flow occurs when water entering the soil exceeds the amount needed to saturate the distribution zone. Therefore, this zone acts as a linear reservoir, resulting in an exponential loss of solutes to the lower conveyance zone, described as (Steenhuis et al., 1994)

\[
C = C_0 \exp \left( \int \frac{R \, dt}{W} \right) + \beta t
\]

where \(C\) is the solute concentration [M L\(^{-3}\)], \(R\) is the rainfall rate [LT\(^{-1}\)], \(\beta\) is the first-order degradation rate of the chemical in the soil [T\(^{-1}\)], \(t\) is time [T], and \(W\) is the apparent water content of the distribution zone [L]; \(C_0\) is the initial solute concentration [M L\(^{-3}\)], which equals \(C_0 = M_0 / W\), where \(M_0\) is the mass of solute applied per unit of surface area [M L\(^{-2}\)]. For non-adsorbed chemicals, \(W\) is simply the water content of the distribution zone per unit area. For adsorbed (desorbed) chemicals, \(W\) is calculated as

\[
W = d (\rho k_d + \theta_d)
\]
where $d$ is the depth of the distribution zone [L], $\rho$ is the bulk density of the soil [M L$^{-3}$], $k_d$ is the desorption partition coefficient [L$^3$ M$^{-1}$], and $\theta_d$ is the moisture content of the distribution zone [L$^3$ L$^{-3}$].

Under steady-state conditions, Eq. [1a] reduces to

$$C = C_0 \exp \left[ -\left( \frac{q}{W} + \beta \right) t \right]$$

where $q$ is the average steady-state rainfall rate [L T$^{-1}$].

When the distribution zone is near saturation, water and solutes are released to the subsoil via the conveyance zone as preferential and matrix flow. The transport in the conveyance zone can be described with a convective–dispersive equation for each flow path, with a sink term to describe the irreversible degradation or decay of pesticides. The governing equation for one-dimensional transport in the conveyance zone under steady-state flow is

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - v_i \frac{\partial C_i}{\partial x} - \beta_i C_i$$

where $v_i$ is the velocity of water and solutes [L T$^{-1}$], $x$ is vertical distance from the source of input to the point of sampling [L], $\beta$ is the first-order decay rate [T$^{-1}$], and $D$ is the dispersion coefficient [L$^2$ T$^{-1}$]. It is worth mentioning that in the current study, $\beta$ was assumed to be the same for both distribution and conveyance zones because of the shallow depth of the samplers. Equation [2] can be solved for boundary condition Eq. [1] using Laplace transforms for $4D(q/W)/v^2 < 1$ as (van Genuchten and Alves, 1984)

$$C_i = \frac{1}{2d} \frac{M_0}{(\rho k_d + \theta_d)} \exp \left[ -\left( \frac{q}{W} + \beta \right) t \right]$$

$$\times \left[ \exp \left( \frac{v_i x}{2D} \right) (1 - \alpha_i) \right] \text{erfc} \left( \frac{x - v_i f \alpha}{2\sqrt{Dt}} \right)$$

$$+ \left[ \exp \left( \frac{v_i x}{2D} \right) (1 + \alpha_i) \right] \text{erfc} \left( \frac{x + v_i f \alpha}{2\sqrt{Dt}} \right)$$

where

$$\alpha_i = \sqrt{1 - \frac{4D(q/W) + \beta}{v_i^2}}$$

Assuming that water and solutes in the flow paths do not mix, the average solute concentration at any point $x$ can simply be expressed by summing the contributions of the various flow paths, e.g.,

$$C = \sum_{i=1}^{n} A_i C_i$$

where $A_i$ is the fraction of water moving through the $i$th flow path at a velocity of $v_i$.

**Site Description**

Experiments were performed in Ithaca, NY, at a field site instrumented with a range of soil water samplers. A worst-case scenario was created by applying cumulative rain and irrigation of 75 cm following herbicide application at typical agronomic rates. Two commonly used herbicides, atrazine and 2,4-D, were chosen as model compounds with different adsorption and degradation characteristics in the soil. A conservative tracer, Cl$^-$ (KCl), was used to determine the transport properties of the soil above each sampler.

The site was located on long-term, regularly mowed grass sod comprised of a 70:30 mixture of perennial ryegrass (*Lolium perenne* L.) and creeping red fescue (*Festuca rubra* L.) within the Cornell University Orchards (Merwin and Stiles, 1994; Merwin et al., 1997). The site was formed in clayey and silty lacustrine sediments and is fine grained with a subangular blocky structure and hexagonal-shaped peds of 0.2 to 0.3 m in diameter (Boll et al., 1997). It is mapped as Hudson silty clay loam, with 7% sand, 71% silt, and 22% clay. The organic matter content of this soil was 53 g kg$^{-1}$ (Merwin et al., 1994).

Field observation made while digging the observation pit for the current experiment showed that the depth of the A horizon was 10 cm. The top 10 cm was brown with a weak, subangular blocky structure parting to granular—was broken down easily by hand—and had fine roots and small worm holes. The bottom layer was pale brown with a firm, subangular blocky structure and peds and contained vertical worm holes and few roots.

According to Neeley et al. (1965), the upper 25-cm permeability ranges from 40 to 120 cm d$^{-1}$, and for depths from 25 to 110 cm, the permeability is between 1 and 40 cm d$^{-1}$. Earlier experiments on this site included blue dye tracers to visualize preferential flow paths showing well-defined macropore networks and preferential flow between the peds (Steenhuis et al., 1994; Ogawa et al., 2000; Richards et al., 2000; Akhtar et al., 2003) (Fig. 1).

**Field Experiment**

In conducting the leaching experiment, two wick pan samplers, one gravity pan sampler, two pipe samplers, and five suction cups, made of non-reactive material, were installed in a plot area of 2.4 by 6.6 m. The two wick pan samplers and one gravity pan sampler, each with a surface area of 1090 cm$^2$, were installed 1 m apart, 0.6 m below the soil surface in 0.7-m horizontal tunnels excavated laterally under the test plot. The samplers were pressed upward against the exposed face of the undisturbed subsoil using wedges and blocks. Two pipe samplers with a diameter of 28 cm were excavated by inserting a pipe, hand excavating undisturbed wedges and blocks. Two pipe samplers with a diameter of 28 cm were excavated by inserting a pipe, hand excavating undisturbed soil columns, and placing sample collectors below them. The soil columns were secured by being placed on a plastic screen and using expanding polyurethane foam around them. In addition, five suction cup samplers were installed at the 60-cm depth. Below all samplers, at a depth of 0.9 to 1.05 m, backup tile drains were installed to prevent overflow into the wick pan samplers. The details of each sampler and their installation were described by Peranginangin et al. (2009).

After approximate steady-state soil moisture conditions were established by applying irrigation at 2.6 cm d$^{-1}$ for four consecutive days, a Cl$^-$ tracer solution was sprayed using a sprinkler at a
rate of 441 kg Cl\(^{-}\) ha\(^{-1}\). Atrazine and 2,4-D were then applied on the same day, each at typical agronomic rates of 2 kg ha\(^{-1}\). Following herbicide application, irrigation was again applied with two sprinklers. During the first 4 d, an average of 2.6 cm of rain was applied daily at a mean rate of 1.6 cm h\(^{-1}\). After the fourth day (10.4 cm of cumulative rain), the rain was applied every 2 to 4 d at similar intensity and duration. When natural rainfall occurred, the irrigation amount was reduced accordingly to achieve approximately 2.6 cm of total rain per day. Percolating water was collected immediately after rainfall simulation ceased and in the morning following rain application. The leachate volume from each sampler was also recorded. Final samples were collected when cumulative rain and irrigation totaled 75 cm over the course of 100 d, composed of 31 cm of natural rainfall and 44 cm of irrigated water. Two days after an accumulative rain of 63 cm, three duplicate soil cores were extracted to a depth of 90 cm, with samples taken at depths of 15, 30, 45, 60, and 90 cm below the ground surface.

Leachate samples were analyzed for Cl\(^{-}\) content using a Buchler Instruments Model 442-5000 digital chloridometer. Enzyme-Linked Immunosorbent Assays (ELISA) from Strategic Diagnostics were used for the analysis of the herbicides in the samples. The detection limit for atrazine and 2,4-D were 0.04 and 0.7 \(\mu\)g L\(^{-1}\), respectively. The corresponding quantification limits for these two herbicides were 0.1 and 0.7 \(\mu\)g L\(^{-1}\). More details are provided elsewhere (Peranginangin et al., 2009).

**Model Evaluation**

To evaluate how well the model fits the observed data, both graphical displays and statistical criteria were used. Four numerical assessment criteria were used to evaluate model performance: (i) standard \(R^2\) correlation method, (ii) mean cumulative error (MCE; Perrin et al., 2001), (iii) Nash–Sutcliffe model efficiency (E\(_n\); Nash and Sutcliffe, 1970), and (iv) coefficient of determination (CD; Loague and Green, 1991). The value of \(R^2\) ranges from 0 to 1, MCE and E\(_n\) range from \(-\infty\) to 1, and CD ranges from 0 to \(\infty\); in all cases, 1 represents a perfect fit. These statistical quality measures are sensitive to a few large errors, especially in small data sets.

The MCE evaluates how well a model correctly reproduces the concentrations during the entire experimental period, given as (Perrin et al., 2001)

\[
\text{MCE} = 1 - \frac{\sum_{i=1}^{n} (C_{\text{obs},i} - C_{\text{sim},i})^2}{\sum_{i=1}^{n} (C_{\text{obs},i})^2}
\]  

where \(C_{\text{obs},i}\) is the observed concentration at the \(i\)th time, and \(C_{\text{sim},i}\) is the model simulated concentration at the \(i\)th time.

The third criterion, \(E_n\), is another indicator of model performance. If \(E_n\) is less than zero, the simulated values are worse than simply using the observed mean (Loague and Green, 1991). The \(E_n\) is given as (Nash and Sutcliffe, 1970)

\[
E_n = 1 - \frac{\sum_{i=1}^{n} (C_{\text{obs},i} - C_{\text{sim},i})^2}{\sum_{i=1}^{n} (C_{\text{obs},i} - C_{\text{obs}})^2}
\]

where \(C_{\text{obs}}\) is the mean observed concentration throughout the experiment and was calculated separately for each sampler.

The fourth criterion, CD, is a measure of the proportion of the total variance of observed data explained by the model simulated data and is given as (Loague and Green, 1991)

\[
\text{CD} = \frac{\sum_{i=1}^{n} (C_{\text{obs},i} - C_{\text{obs}})^2}{\sum_{i=1}^{n} (C_{\text{sim},i} - C_{\text{obs}})^2}
\]

All the above statistical criteria were applied to the modeled data for the entire solute leaching experiment.

**Results**

Chloride BTCs for various samplers are shown in Fig. 2a to 6a. All samplers had a breakthrough of Cl\(^{-}\) during the application of the first 2.6 cm of rain. The peak concentration of Cl\(^{-}\) for the wick pan sampler A (Wick A) was substantially greater than for the other samplers, with a maximum concentration of \(C = 502\) mg L\(^{-1}\) in the first sample taken after the application of Cl\(^{-}\) on the soil surface (Fig. 2a). Early peak concentrations were also observed with the pipe samplers but at a slightly lower value of \(C = 418\) mg L\(^{-1}\) (Fig. 3a). The peak concentration of Cl\(^{-}\), \(C = 190\) mg L\(^{-1}\) of the wick pan sampler B (Wick B) was relatively delayed and arrived at 10 cm cumulative rain, 4 d after pulse application (Fig. 4a). Similarly, early peak concentrations of \(C = 157\) mg L\(^{-1}\) and \(C = 180\) mg L\(^{-1}\) were observed for the gravity pan sampler and suction cup samplers, respectively (Fig. 5a and 6a). At the end of the experiment (75 cm cumulative rain), 95.7, 109, 115, and 75% of the applied Cl\(^{-}\) leached through Wick B, Wick A, gravity pan, and pipe samplers, respectively. Therefore, pipe samplers under-collected Cl\(^{-}\). For all samplers, it was observed that secondary and tertiary peaks occurred at a cumulative rain application of 15 and 33 cm, respectively, suggesting that the tracer traveled through different preferential flow paths. Pronounced secondary peaks were observed in Wick B and in the gravity pan sampler. Overall, two groups of BTCs were observed. Group 1 consisted of Wick A and the pipe samplers (Fig. 2a and 3a), with sharp peaks observed that ceased quickly; Group 2 consisted of Wick B, the gravity pan sampler, and suction cup samplers (Fig. 4a–6a), with rounded peaks and a gradual decline.

The BTCs of atrazine, despite its possible adsorption to soil organic matter, closely followed those observed for Cl\(^{-}\), especially in Wick A and the pipe samplers (Fig. 2b and 3b), indicating rapid preferential transport that prevented solutes from being in full contact with the soil matrix. The observed peak concentration of atrazine in all the samplers varied from 195 \(\mu\)g L\(^{-1}\) in Wick B to 1214 \(\mu\)g L\(^{-1}\) in the pipe samplers. Despite similarities in the location of the peaks between the atrazine BTC of the gravity pan sampler and Wick B, the concentrations of atrazine in the gravity pan sampler were two times greater than those of Wick B (Fig. 4b and 5b). The peak concentration of atrazine in the gravity pan sampler was 300 \(\mu\)g L\(^{-1}\), whereas it was 195 \(\mu\)g L\(^{-1}\) for Wick B, despite the fact that these samplers observed relatively
similar concentrations of Cl$^-$, (161 and 190 mg L$^{-1}$ in the gravity pan sampler and Wick B sampler, respectively). Similar values and trends to those of the gravity pan were observed in the suction cup samplers (Fig. 6b).

The BTCs for 2,4-D were generally similar to those of atrazine (Fig. 2c–6c). Breakthroughs for all samplers were in the same order as atrazine and occurred either on the day of or the day following application, except for suction cup samplers where the 2,4-D peak concentration was 1391 mg L$^{-1}$ (Fig. 6c), whereas the atrazine concentration was lower at 275 mg L$^{-1}$ (Fig. 6b). In addition, the peak concentration of 2,4-D in the pipe sampler occurred later than the atrazine peak (Fig. 3b and 3c).

As expected, observed 2,4-D concentrations declined more rapidly after the initial breakthroughs because of the rapid degradation in macropores, as shown by Pivetz and Steenhuis (1995). After 10 cm of cumulative rain, 2,4-D ceased to be detected in Wick A and the pipe samplers (Fig. 2c and 3c), and it was not detected in the rest of the samplers after 30 cm of cumulative rain (Fig. 4c, 5c, and 6c). The soil moisture profile taken 24 h after rain application (after a cumulative rain application of 63 cm) showed volumetric soil moisture contents of 0.37 in the top 15 cm of soil and about 0.26 in the subsoil. At these moisture contents, the rainfall intensity of 2.6 cm d$^{-1}$ would conventionally be expected to result in pore water velocities of 7 to 10 cm d$^{-1}$. Accordingly, if all water and non-adsorbed tracer moved with this average velocity, we would expect the peak concentration to be observed at the 60-cm soil depth 6 to 9 d after pulse application. For pesticides with an adsorption partition coefficient of about 0.45 cm$^3$ g$^{-1}$, we would expect delayed peaks to appear at intervals 2.5 to 3 times longer than that (i.e., about 20 d or more). Clearly, this did not occur in the Hudson soil, where solute was observed at 2.6 cm of cumulative applied rain, thus confirming the dominant influence of preferential flow.

**Modeling**

The model requires the fitting of parameters related to preferential flow through porous media. It is unfortunate that in soil physics, in situ methods do not yet exist for determining parameters for preferential flow models, and thus fitting is required. Malone et al. (2004) used 39 intact soil columns to estimate the number of percolate-producing macropores for the RZWQM model. The input parameters for the PFM are the depth and moisture of the distribution zone, $d$ and $q_d$, the proportion $a_i$ of water flowing with velocities $v_i$ through the flow paths in the conveyance zone, and those specific to the solutes, consisting of the dispersion coefficient, $D$, the adsorption partition coefficient of the pesticides, $k_a$, and first-order decay rate of the pesticides, $\beta$.

The porous media related parameters, $d$, $a_i$, and $v_i$, and the dispersion coefficient $D$ ($k_a$ and $\beta$ equal zero) were determined first by fitting the Cl$^-$ BTCs of Wick A for Group 1 and Wick
Because two groups of BTCs were observed in this study, we used the same values of $a_i$, $l_i$, $v_i$, and $d$ with each group.

Our field observations showed that the depth of the A horizon was 10 cm, with a weak, subangular blocky structure parting to granular. Assuming that mixing happened in this layer, the depth of the distribution zone was 10 cm, which agreed with prior blue dye field infiltration tests at the site. The volumetric moisture content of the top layer measured during the experiment was 0.37, which was used as the water content of the distribution zone. Because three Cl$^-$ peaks were observed in the BTCs in the samplers (Fig. 2a–6a), we used three flow paths. The fitted velocity of water and Cl$^-$ moving through preferential flow paths ($v_1$) ranged from 35 cm d$^{-1}$ for Group 2 to 120 cm d$^{-1}$ for Group 1 (Table 1). The other fitted velocities, $v_2$ and $v_3$, were 6.8 and 3 cm d$^{-1}$ for both groups (Table 1).

After determining the values for the velocities using the nonreactive tracer, the values for adsorption and decay rates for atrazine and 2,4-D were determined by fitting with the BTCs (Table 1; Fig. 2b, 2c, 6b, and 6c). The sorption and degradation parameters for each chemical were the same for all samplers because they were located in close proximity.

We first found the adsorption partition coefficients ($k_a$) for atrazine and 2,4-D for the Wick A sampler and used them to model solute transport in the other samplers. The calibrated $k_a$ was 0.45 for both atrazine and 2,4-D. The value of $\beta$ for atrazine of 0.05 d$^{-1}$ corresponds with a half-life ($t_{1/2} = \ln2/\beta$) of 14 d. The value used for $\beta$ for 2,4-D was 0.35 d$^{-1}$, equal to a half-life of 2 d (Table 1).

Figures 2 to 6 show that the model fit well with the observed data. The model, however, did not predict the maximum concentrations of 2,4-D in the pipe and suction cup samplers (Fig. 3c and 6c).

Overall, the four evaluation criteria indicated that the model was in reasonable agreement with the observed data, with $R^2$ values of 0.59 to 0.99, positive $E_f$ values, and MCE values between 0.16 and 0.99, with the exception of the 2,4-D in the suction cup samplers (Table 2). Note that these values exclude the maximum concentration of 2,4-D in the pipe samplers (Fig. 3c; open circle). The model was able to match the data for most initial peaks (Fig. 2–6), with few under predictions—CD values >1—or over predictions—CD values <1—as indicated by CD values of 0.49 to 1.66, with the exception of 2,4-D in the suction cup (Table 2). Furthermore, the model adequately fit the significant asymmetry and tailing of the pesticide’s BTCs obtained from field experiments.

It is of note that the greater the degree of preferential flow (i.e., the more progressive shifting of the BTC to the left), the better the model fit the observed BTCs, as can be seen from the statistical results and fitting illustration of Wick A and the pipe samplers (Table 2; Fig. 2 and 3).

**Discussion**

Atrazine and 2,4-D were applied at agronomic rates on grass sod followed by 75 cm of rain, of which 10.4 cm was applied

<table>
<thead>
<tr>
<th>Group</th>
<th>Sampler</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$l_1\uparrow$</th>
<th>$l_2$</th>
<th>$l_3$</th>
<th>$V_1$</th>
<th>$V_2$</th>
<th>$V_3$</th>
<th>$d$</th>
<th>$\beta$</th>
<th>$k_a$</th>
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<tr>
<td>1 Wick A and pipe samplers</td>
<td>70</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>120</td>
<td>6.8</td>
<td>3</td>
<td>10</td>
<td>0.05</td>
<td>0.45</td>
<td>0.35</td>
<td>0.45</td>
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<tr>
<td>2 Wick B, gravity pan, and suction cup samplers</td>
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<td>35</td>
<td>30</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>35</td>
<td>6.8</td>
<td>3</td>
<td>10</td>
<td>0.05</td>
<td>0.45</td>
<td>0.35</td>
<td>0.45</td>
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† Dispersivity (D/v, where D is the dispersion coefficient and v is the velocity of water).
on each of four consecutive days. The pesticide concentrations observed after the first 4 d were used in testing the model but are not likely to be found in the field under natural rainfall conditions.

Two groups of BTCs were observed. It is less likely that the type of sampling device impacted the observation of the two groups because the groups were observed across the samplers. In other words, the concentrations of tracer and herbicides observed in Wick A were similar to those of the pipe sampler, and the BTC of Wick B was similar to that of the gravity pan sampler. Peranginangin et al. (2009) discussed the performance of each sampler in comparison to others. They suggested that the pan samplers collected water at greater rates than other samplers. In addition, wick pan samplers behave better under decreased soil moisture and matrix flow (Boll et al., 1997). However, both Wick B and the gravity pan sampler captured the long receding tail of the tracer concentrations as both had the same concentration of Cl−.

The BTCs produced from the suction cup lysimeters were variable (Fig. 6). Such erratic BTCs had been observed previously (Boll et al., 1997) and were attributed to the proximity of the local flow paths to their location. Therefore, individual cups were not able to capture the extent of the preferential flow or conversely exaggerated it. In the wick pan samplers, the variation in preferential flow pathways within a sampler was offset by variation between the different wicks because pan samplers can capture soil solution from a larger area of soil. Indeed, the pan samplers that are constructed in field settings can best represent the local field conditions and, although expensive, have great utility investigating groundwater pollution risks (Boesten, 2007; Köhne et al., 2009b).

<table>
<thead>
<tr>
<th>Sampler</th>
<th>Chloride</th>
<th>Atrazine</th>
<th>2,4-D</th>
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<td></td>
<td>$R^2$</td>
<td>MCE</td>
<td>$E_f$</td>
</tr>
<tr>
<td>Wick A</td>
<td>0.94</td>
<td>0.82</td>
<td>0.94</td>
</tr>
<tr>
<td>Pipe samplers</td>
<td>0.96</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Wick B</td>
<td>0.63</td>
<td>0.72</td>
<td>0.42</td>
</tr>
<tr>
<td>Gravity pan</td>
<td>0.62</td>
<td>0.69</td>
<td>0.20</td>
</tr>
<tr>
<td>Suction cup samplers</td>
<td>0.61</td>
<td>0.75</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Fig. 5. Gravity pan sampler breakthrough curves for (a) Cl−, (b) atrazine, and (c) 2,4-D. The observed data points are shown with filled circles and model-simulated values are shown with black lines. Input parameters are given in Table 1. The initial solute concentration $C_0$ is calculated with Eq. [1b] and [1c].

Fig. 6. Suction cup sampler breakthrough curves for (a) Cl−, (b) atrazine, and (c) 2,4-D. The observed data points are shown with filled circles and model-simulated values are shown with black lines. Input parameters are given in Table 1. The error bars show standard deviation. The initial solute concentration $C_0$ is calculated with Eq. [1b] and [1c].
1% of the applied atrazine leached through the preferential flow (Kladivko et al., 1991; Flury, 1996; Kung et al., 2000b; Torrentó et al., 2018). Thus, the similarity of travel time independent of the sorption properties is largely due to the fast flow of water and, consequently, the short time that is available for adsorption to occur. This response does not allow equilibrium to be reached in the soil until the water stops flowing (Steenhuis et al., 1997; Kim et al., 2008; Liu et al., 2018). This preferential flow breakthrough pattern is distinctly different than that based on the convective–dispersive equation, where adsorbed solutes move more slowly than non-adsorbed solutes (Smith et al., 1990; Kladivko et al., 1991; Ghodrati and Jury, 1992; Gerke, 2006; Jarvis, 2007; Köhne et al., 2009a).

While the velocities of the tracer and herbicides were comparable, the relative concentration ($C/C_0$) of the two herbicides collected by the samplers was generally less than the $C/C_0$ of the non-adsorbed Cl$^-$ tracer (Table 2; Fig. 2–6). This was probably due to adsorption of the herbicides to the soil in the distribution and degradation of the herbicides in both distribution and conveyance zones. The 2,4-D concentrations ceased after application of 20 cm cumulative rain, whereas atrazine was still detected due to its slower degradation rate. Mass balance shows that only 1% of the applied atrazine leached through the preferential flow paths, although this amount would be sufficient to exceed the drinking water standard concentration of 3 μg L$^{-1}$ for atrazine and 70 μg L$^{-1}$ for 2,4-D (according to the USEPA) by two orders of magnitude (Fig. 2–6).

The PFM assumes a distribution zone that funnels water and dissolved pesticides in preferential flow paths to the conveyance zone below. Because field soils are heterogeneous, some input parameters cannot be determined a priori. To obtain the measured breakthrough curves, we therefore used a tracer to characterize and set the parameters for the number of flow paths, including the velocity and proportion of water and the dispersion coefficient for each. A non-reactive tracer test is essential in identifying preferential flow parameters (Jarvis and Larsbo, 2012).

For predicting pesticide movement when BTCs are not available, half a century after the first preferential flow experiments were done by Quisenberry and Phillips (1976) and Beven and Germann (1981), it may be feasible to develop a pedotransfer function for generalized preferential from the data available in the literature. A start was made by Selker et al. (1992), who described the wetted area occupied by fingered flow as a ratio of maximum rainfall intensity and the soil saturation in sandy and water-repellent soils. The advantage of the PFM is that the number of parameters needed are manageable and physically based.

The depth of the topsoil horizon was used to determine the depth of the distribution zone. A depth of 10 cm was within the range of earlier experiments (Steenhuis et al., 1994). The adsorption partition coefficient of 0.45 cm$^3$ g$^{-1}$ for both herbicides in the distribution zone, although within the range of published values (FAO, 1998; Moorman et al., 2001), is lower than that generally found in the literature for atrazine (Ahmad and Rahman, 2009). Given that the Hudson soil is rich in organic matter, the likely reason for a low $k_a$ is that an adsorption equilibrium did not occur because the topsoil was kept wet so that there was no intimate contact between the soil and the pesticides. In addition, due to the rapid water transport, chemical equilibrium may not have happened. Nonequilibrium adsorption was used previously in transport models and depends on the kinetics of the adsorption reaction (Leij et al., 1993; Köhne et al., 2009b; Celestino Ladu and Zhang, 2011).

In the conveyance zone, three different flow paths with different velocities were utilized to represent the initial breakthrough and the tailing. In a shorter duration experiment by Kim et al. (2005), two flow paths adequately predicted Cl$^-$ BTCs through undisturbed soil cores. Darnault et al. (2004), in an experiment in coarse sandy soil with fingered flow, showed that one flow path was sufficient to predict Cryptosporidium parvum oocyst transport. At this field site, water and solute travel times were 5 to 35 times faster through the macropores than through the slowest flow path. The portion of the water flowing through preferential flow paths ($a_j$) for the Wick A pan sampler was 70%, whereas it was only 40% for Wick B and the gravity pan samplers (Table 1). This was expected because the soil above each sampler was undisturbed and, consequently, the soil structure was heterogeneous, causing various degrees of preferential flow that cannot be predicted very well beforehand; however, the information was essential to model the herbicide loss well. Despite this variation, the estimated velocities were within the range of permeability previously characterized for the region (Neeley et al., 1965). The highest fitted velocity of 120 cm d$^{-1}$ is the value of the highest infiltration rate found for the Hudson soil. Saturated hydraulic conductivity was previously used to describe preferential flow in the MACRO model (Jarvis and Larsbo, 2012).

Fitted dispersivity values, λ (the quotient of dispersion coefficient and solute velocity), in the preferential pathways varied from 1 cm in the matrix to 10 cm in preferential pathways, values that are within observed dispersivity values under field conditions according to Lal and Shukla (2005).

The decay rates ($\beta$) of 0.05 d$^{-1}$ for atrazine and 0.35 d$^{-1}$ for 2,4-D (Table 2) agree with those previously observed in the literature. These decay rates correspond to half-lives of 14 d for atrazine and 2 d for 2,4-D. A similar half-life for atrazine has been observed previously in multiple studies (Jones et al., 1982; Vanderheyden et al., 1997; World Health Organization, 2010), although Seybold et al. (2001) indicated longer half-lives of atrazine. Taking into account that our experiment took place in an organic-rich topsoil with macropores, observing values at the low end of the range reported in the literature is expected. A half-life of 2 d for 2,4-D is within the observed values by Wilson et al. (1997). Decay rates of 2,4-D that are 10 times faster than those of atrazine agree with the finding that 2,4-D disappearance time may be up to 10 times earlier than that of atrazine (Hamaker, 1972).

The model predicted early sharp peaks better than rounded peaks with extended tails (Table 2). This is attributed to the
utilization of the exponential loss of chemicals from the distribution layer, projecting a sharp decline in the solute leachate from the top layer. Therefore, in the case of rounded peaks with extended tails, the model assumption of simple conceptualization did not comport with field observations. Despite this, the locations of the peaks and the overall pattern of the BTCs are well identified, as shown in Fig. 2 to 6.

Conclusion

The observed herbicide leaching mobility for an experiment on a well-structured Hudson silt loam soil in Ithaca, NY, was much faster than would be predicted by convective–dispersive flow. This was attributed to preferential flow. The PFM used seven input parameters (dispersivity, depth and moisture of the distribution zone, the velocity of water, the portion of water transported at each velocity, adsorption coefficient, and degradation rate) to model the preferential flow. With realistic input values, the PFM described the early breakthroughs and the extensive tailings of experimental breakthrough curves of non-adsorbed (Cl–) and adsorbed (atrazine and 2,4-D) solutes under field conditions in soil at or above field capacity.

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