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Numerical simulations in a heterogeneous media were used to estimate the uncertainty of pesticide sampling by suction cups under transient boundary conditions. The results indicate that the variability of the derived concentrations and leached mass fractions highly depend on the physico-chemical characteristics of the pesticides.

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Uncertainty in Pesticide Monitoring Using Suction Cups: Evidence from Numerical Simulations

Knowledge of the spatial and temporal distribution of pesticide concentrations is essential for pesticide registration. In field experiments performed during the registration procedure, suctions cups are widely used to monitor the evolution of pesticide leaching over time and to calculate the mean concentration for a given drainage period. Until now, there has been no detailed information regarding whether soil water sampling by suction cups is suitable for accurately predicting the field-scale leaching of pesticides in heterogeneous soils. To address this, we performed a numerical study to evaluate the uncertainties associated with suction cup sampling in heterogeneous soils under atmospheric boundary conditions using two pesticides with contrasting sorption and degradation properties. To address the two main operation modes of suction cup sampling, continuous and weekly sampling were analyzed. First, the variability of pesticide breakthrough concentrations was analyzed for a single pesticide application in a physically heterogeneous soil profile. Second, a 10-yr time series was used to analyze repeated pesticide applications, and estimate variability in the leached mass fraction (LMF) and mean concentrations. In both cases, pesticide breakthrough was compared to the breakthrough of an inert tracer. The results indicate that for a single pesticide application, pore water velocities varied only slightly for all operation sampling modes and compounds. On the other hand, the total extracted mass and LMF varied greatly, suggesting that the acceleration of the breakthrough sampled by suction cups plays an important role in terms of LMF and the mean concentration, especially for degradable substances.

Abbreviations: BTC, breakthrough curves; CDE, convection–dispersion equation; LMF, leached mass fraction; PPP, plant protection product.

Risk assessments of pesticide leaching into the groundwater have become required to a greater and greater extent in the recent past. In the European registration procedure for plant protection products (PPP), a tiered approach, with respect to the estimation of groundwater contamination, has been established. In the third tier, evidence relevant to authorization must be provided (in particular evidence using lysimeter studies or field experiments) regarding the possibility and extent of groundwater contamination by a PPP after its application while using good agricultural practice (Winkler et al., 1999).

Various methods are available to monitor the transport and leaching of PPPs in the vadose zone. The most common is the lysimeter concept (Führ et al., 1998). For experiments at the field scale, soil coring or in situ sampling using capillary wicks, porous plates, and suction cups is used. The advantage of in situ sampling systems is the high temporal resolution of solute extraction at different depths or horizons (Weihermüller et al., 2007). In particular, suction cups play an important role in PPP monitoring due to their easy installation and low cost and have therefore been used and studied widely. In general, most scientists have focused on the alteration of the soil solution sampled by suction cups by chemical processes, such as sorption and desorption of PPPs, as well as filtering effects (e.g., Grossmann and Udluft, 1991; Wessel-Bothe et al., 2000; Weihermüller et al., 2007). However, Dorrance et al. (1991) have already stated that the chemical alteration of the sampled soil solution may be less significant than variability in extracted soil water concentrations due to soil physical heterogeneities, changes in the natural water flow field, and/or preferential flow.

During the last few years, various numerical approaches for characterizing and interpreting measured data from various sampling devices, including lysimeters, suction cups, porous plates, and wick samplers, have been published (e.g., Tseng et al., 1995; Wu et al., 1995; Flury et al., 1999; Abdou and Flury, 2004; Köhne, 2005; Mertens et al., 2005, 2007; Weihermüller et al., 2005, 2006; Boesten, 2007; Kasteel et al., 2007). All of these

approaches have clearly shown that numerical modeling is a powerful tool for designing efficient experimental setups and for obtaining better understanding of the effects of the sampling procedure on collected results in natural soils.

Vanderborght and Vereecken (2007) showed that the use of different sampling systems may greatly influence the apparent spreading of reactive substances estimated from breakthrough curves (BTC), compared to the theoretical dispersivities calculated from the flow rate and the actual water content. They also stated that spreading can be related to the soil volume sampled by the method. Weihermüller et al. (2005) presented the results of numerical experiments by analyzing water extraction using a suction cup and found that these samplers only extract water locally, so that only a small fraction of the total cross-sectional area is sampled, even when a large number of samplers is used. As a consequence, BTCs determined using local measurements may deviate from the averaged BTC or average solute fluxes at the same depth (Weihermüller et al., 2005, 2006). On the other hand, since suction cups also influence the natural flow field (Warrick and Amoozegar-Fard, 1977), natural pore water velocities and dispersivities may deviate from those calculated from suction-cup-derived BTCs (Weihermüller et al., 2005, 2006).

One major disadvantage of the published work analyzing suction cup samplers thus far (e.g., Tseng et al., 1995; Weihermüller et al., 2005, 2006), is that only steady-state flow conditions and nonreactive solutes have been considered. Therefore, we expanded these simulations to compounds with different physicochemical properties and more realistic transient upper boundary conditions to examine the effect of soil heterogeneity on the BTCs measured by suction cups. To be comparable to already published work (e.g., Boesten, 2007) and with already existing scenarios that are used to assess pesticide leaching for registration of PPP in the EU, soil parameters and meteorological data were taken from the FOCUS Hamburg Scenario (FOCUS, 2000). This scenario is one of eight test scenarios developed within the FOCUS working group to harmonize pesticide registration within the European Community. So far, numerical studies have only focused on the effects that soil solution sampling by suction cups, which were run in a continuous suction mode, had on the measured breakthrough curves and estimated solute fluxes (Tseng et al., 1995; Weihermüller et al., 2005, 2006). Therefore, a second objective of our study was to investigate the effects of the sampling mode. Results obtained using a continuous operation mode were compared with those obtained using a discontinuous mode, whereby temporary suction is only applied to the cup during the extraction of the soil solution. In practice, a discontinuous sampling scheme is easier to accomplish. However, the effects of a discontinuous sampling scheme on the transport process cannot be compared directly with those using continuous extraction. Finally, we analyzed how annually repeated applications of a chemical affect the variability of mass recovered, mean concentration, and leached mass fraction.

For comparison, we used calculated effective transport variables, such as mean pore water velocity, as well as peak concentration, and mass recovery. Additionally, calculated mean solute concentrations and leached mass fractions were used for an uncertainty assessment. Note that preferential flow due to cracks, worm holes, and root channels, which may be also important in naturally structured soils, especially in fine clay soils, was neglected in our numerical experiments. On the other hand, preferential or heterogeneous flow processes were already accounted for by considering the heterogeneous distribution of the hydraulic properties, which are typical for a coarse structured soil like that analyzed in this study.

Materials and Methods

For the simulation of water flow, the two-dimensional Richards equation (Eq. [1]) was solved using the finite element code HYDRUS-2D (Šimůnek et al., 1999, 2008; Šimůnek and van Genuchten, 2008):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(\psi)\frac{\partial \psi}{\partial x}\right] + \frac{\partial}{\partial z}\left[K(\psi)\left(\frac{\partial \psi}{\partial z} - 1\right)\right] \qquad [1]$$

where θ is the volumetric water content [cm^3 cm^{-3}], ψ is the pressure head expressed in head units [cm], x and z are horizontal and vertical coordinates [cm] with z positive in the downward direction, and $K(\psi)$ is the unsaturated hydraulic conductivity function [cm d^{-1}]. The van Genuchten–Mualem functions were used to describe the relations between K, ψ, and θ (van Genuchten, 1980), where θ_r [cm^3 cm^{-3}] and θ_s [cm^3 cm^{-3}] are the residual and saturated volumetric water contents, respectively; α [cm^{-1}], n [-], and m [-] ($m = 1 - 1/n$) are shape parameters; and K_s [cm d^{-1}] is the saturated hydraulic conductivity.

Solute transport for conservative (bromide) and reactive (pesticides) substances is described by a convection–dispersion equation (CDE) that includes degradation and sorption (Eq. [2]):

$$\frac{\partial \theta R c}{\partial t} = -\frac{\partial (v_i \theta c)}{\partial x_i} + \frac{\partial}{\partial x_i}\left(D_{ij}\theta\frac{\partial c}{\partial x_j}\right) - \mu c\theta - \mu\rho s \qquad [2]$$

where D_{ij} are the components of the dispersion coefficient tensor [cm^2 d^{-1}], v is the mean pore water velocity [cm d^{-1}], c and s are the solute concentrations in the liquid phase [μg cm^{-3}] and on the solid phase [g g^{-1}], μ [d^{-1}] is the first-order rate coefficient for degradation in the liquid phase and the solid phase, and R [-] is the retardation factor. The components of the dispersion tensor D_{ij} describing the subscale dispersion are given by

$$\theta D_{ij} = \alpha_l |q|\delta_{ij} + (\alpha_l - \alpha_t)\frac{q_i\,q_j}{|q|} + \theta D_d\tau\delta_{ij} \qquad [3]$$

where α_l and α_t are the longitudinal and transversal dispersivities [cm], respectively; q_i and q_j are the water flux densities in the

x and z directions [cm d^{-1}], $|q|$ is the absolute value of the water flux density [cm d^{-1}]; D_d is the molecular diffusion coefficient of the substance in free water [cm^2 d^{-1}]; $\tau = \theta^{7/3}/\theta_s^2$ is the Millington and Quirk (1961) tortuosity factor; and δ_{ij} is the Kronecker delta, taking values of 1 for $i = j$ and 0 otherwise. The retardation factor R is defined by

$$R = 1 + \frac{\rho}{\theta}\frac{ds}{dc} \qquad [4]$$

where ds/dc is the first derivative of the relationship between concentrations in the solid (s) and liquid (c) phases, expressed by any sorption isotherm. Finally, the first-order degradation coefficient μ equals $\ln(2)/D_{eg}T_{50}$, where $D_{eg}T_{50}$ is the half-life of a substance at reference conditions. For both pesticides studied (denoted A and D) linear sorption was assumed. Additionally, degradation of the pesticides was assumed to be independent of temperature; therefore, heat transfer was not simulated.

For the simulations, a two-dimensional 100-cm-wide and 150-cm-deep flow domain was defined, which was discretized nonequidistantly using smaller nodal distances in the vicinity of the suction cup and at the upper boundary where larger gradients are to be expected (the total number of nodes was 23,351). A suction cup with an outer radius of 2.0 cm was located 100 cm below the soil surface in the horizontal center of the flow domain. A sketch of the simulation domain is shown in Fig. 1. The boundary condition at the upper surface was set to atmospheric conditions, using meteorological data from the Hamburg scenario of FOCUS (2000) to quantify the atmospheric inputs (rainfall and potential evaporation, calculated using the Penman equation). This data set consists of 20 yr of weather data (1975–1994), of which only the first 10 yr were chosen for simulations (a total of 3652 d). The initial conditions for the pressure heads were set to −150 cm at the bottom and −100 cm at the top of the domain, with linear interpolation in between. The first 820 d, up until 31 March (in the third year), were used as a "warming-up" period before the application of the test compounds was begun (both for single and repeated applications) to ensure that the initial conditions did not influence the modeling results. An overview of the meteorological data is plotted in Fig. 2. Note that since a bare soil system was considered (i.e., no plants), transpiration was assumed to be zero. The lower boundary of the flow domain was defined as free drainage, which may be used when the groundwater table is far below the soil surface. No-flow boundary conditions were imposed along the remaining boundaries.

The boundary condition at the surface of the suction cup was specified as a prescribed time-variable pressure head for the continuous mode or as a constant pressure head during sampling and zero flux otherwise for the discontinuous mode. A modification of the HYDRUS-2D code was necessary to ensure that water and solute could leave across this boundary, but not enter the simulation domain at times when the prescribed pressure head was higher than the soil pressure head in the direct vicinity of the suction cup. In all simulations, either a prescribed pressure head of −600 cm was applied at the suction cup
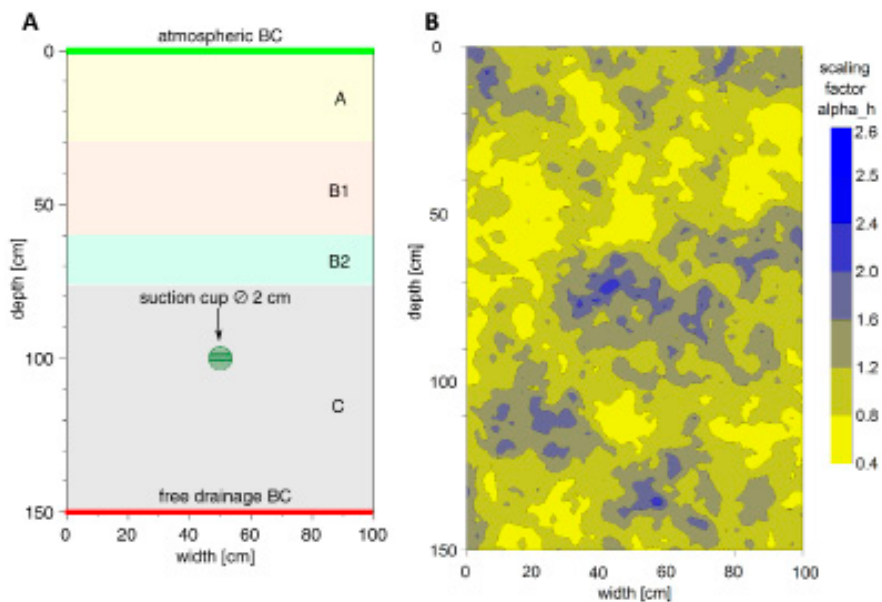

Fig. 1. (a) Schematic overview of the simulation domain with boundary conditions, soil horizons, and a location of the suction cup and (b) dimensionless scaling factor for α_h [-] associated with the pressure head for realization run 1.
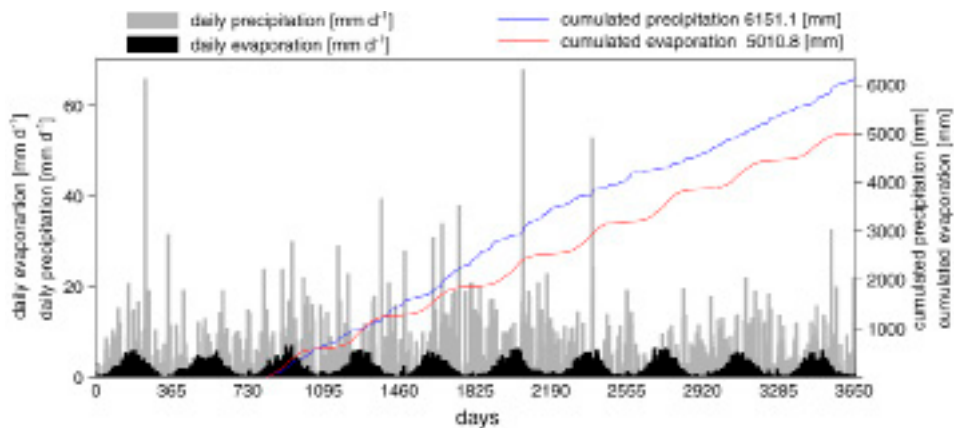

Fig. 2. Climate data (rainfall and potential evaporation) for the *Hamburg scenario* (FOCUS, 2000). Cumulative values start at a time of compound application.

for 1 d a week starting from Day 820 (for a discontinuous mode), or a time-variable pressure head was continuously applied at the suction cup (for a continuous mode). The value of this time-variable pressure head (Fig. 3) was calculated on a daily basis as the horizontally averaged pressure head at the installation depth (100 cm), using a reference simulation for a 150- by 1000-cm flow domain without any suction cups. An additional offset of −30 cm was added to these pressure heads. The technical limitations of the suction cup method (a bubble point of most porous materials is smaller than −1000 cm, and the limit of pressure pumps is approximately −1000 cm) were also taken into account in the simulation exercise by fixing all calculated pressure heads smaller than −1000 at a threshold value of −1000 cm.

A sandy soil was chosen for the simulations. The hydraulic properties and the bulk density of the soil were taken from the Hamburg scenario of FOCUS (2000) (Table 1). The hydraulic properties of the suction cup were taken from Weihermüller et al. (2006), whereby its saturated hydraulic conductivity was modified to ensure that the conductance of the suction cup would not limit the quantity of extracted water and solute.
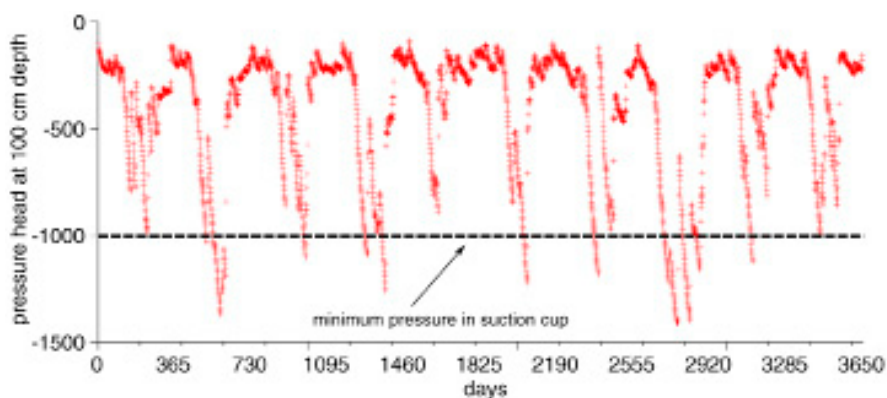

Fig. 3. Simulated mean pressure heads at a depth of 100 cm for the 10-yr climate data of the Hamburg scenario (FOCUS, 2000).

Table 1. Hydraulic properties and the bulk density for soils of the soil profile used in the simulations (taken from the Hamburg scenario of FOCUS 2000). Suction cup parameters were taken from Weihermüller et al. (2006) with adapted K_s.

Material	Depth	θ_s	θ_r	α	n	K_s	Bulk density	C_{org}
	cm	——— cm^3 cm^{-3} ———		cm^{-1}	-	cm d^{-1}	g cm^{-3}	%
Horizon A	0–30	0.391	0.036	0.01491	1.468	201.57	1.50	1.5
Horizon B1	30–60	0.370	0.030	0.01255	1.565	273.63	1.60	1.0
Horizon B2	60–75	0.351	0.029	0.01808	1.598	244.77	1.56	0.2
Horizon C	75–150	0.310	0.015	0.02812	1.606	244.77	1.61	0.0
Suction cup	–	0.500	0.001	0.00050	2.800	280.00	1.50	0.0

Local-scale heterogeneity in hydraulic properties was generated using the Miller–Miller scaling theory (Miller and Miller, 1956). The geostatistical parameters were chosen to be the same as those used by Weihermüller et al. (2006), with a variance, σ^2_β of 0.25 and a correlation length, λ_β of 10 cm. The dimensionless scaling factor for α_h [-] associated with the pressure head is given exemplarily for the geostatistical realization of run 1 in Fig. 1b. Note that the underlying heterogeneous structure, which was generated using the geostatistical parameters listed above, will increase the effective dispersivity, λ_{eff}. Even when the longitudinal and transversal dispersivities were set to 3 and 1.5 cm, respectively, the resulting effective longitudinal dispersivity, λ_{eff}, is about 7.6 cm at the lower boundary for the conservative tracer with the given heterogeneity of the underlying flow field and a simulation depth of 1 m. This value is still within the range of dispersivities that can be expected for field-scale transport in natural soils (Vanderborght and Vereecken 2007).

Ten realizations of the heterogeneous flow field of 150 by 100 cm were simulated. Simulating flow fields of this size, rather than the entire ensemble of all realizations in a 150- by 1000-cm flow field, greatly facilitated our numerical study. In general, 10 simulations represented an ensemble 150 cm deep and 1000 cm wide, containing a total of 10 suction cups installed at a

depth of 100 cm with a horizontal spacing of 100 cm. Since no-flow boundary conditions were imposed at both sides of the flow domain, it was assumed that there was no lateral flow between domains.

The two different pesticides, denoted A and D, with contrasting sorption and degradation properties were chosen from FOCUS (2000). Parameter values chosen for substances A and D are used to evaluate the pesticide leaching scenarios developed for pesticide registration procedures in Europe, but are not intended to represent any specific compounds. For both pesticides, no further reactions of the pesticide metabolites were assumed. For comparison, the nonreactive tracer (e.g., bromide) was simultaneously applied with the pesticides. The transport and fate parameters, D_d, K_{oc}, and $D_{eg}T_{50}$, are listed in Table 2 for all three chemicals. Note that $D_{eq}T_{50}$ had to be recalculated to match the input of the degradation rate μ coefficient. Additionally, the degradation rate μ was kept constant over the entire simulation depth and was assumed to be independent of temperature and water content. In correspondence with the FOCUS recommendations, 1 kg ha^{-1} of the substances A, D, and bromide were applied once per year on 31 March, beginning on Day 820. For the single application this was only done once, on Day 820. In general, global water and solute numerical mass balance errors were always less than 1 and 2.5% for all time steps, respectively.

Table 2. Properties of pesticides A and D (taken from the Hamburg scenario of FOCUS, 2000) and of conservative tracer bromide.

Substance	D_d†	K_{OC}	$D_{eg}T_{50}$
	$cm^2\, d^{-1}$	$cm^3\, g^{-1}$	d
Bromide	1.728	–	–
Pesticide A	0.430	103	60
Pesticide D	0.430	60	20

† Diffusion coefficient in water.

To compare with the one-dimensional simulations that are usually performed in the FOCUS scenarios (FOCUS 2000), the results of the two-dimensional simulations in the heterogeneous flow fields with suction cups were compared with one-dimensional simulations using the HYDRUS-1D code (Šimůnek et al., 2008). These one-dimensional simulations were performed using the same setup described above. These one-dimensional simulations were also used as a reference case, whereby the one-dimensional simulations give information about the complete mass recovery since no water and solute can bypass the depth of measurement without being sampled. Reference parameters used for scaling stochastic heterogeneity were used as the hydraulic parameters in one-dimensional simulations (Table 1). The dispersivity was adjusted to match an effective dispersivity, λ_{eff}, of 7.6 cm, calculated from the bromide breakthrough curve at a depth of 100 cm, obtained by the two-dimensional simulation of a 150- by 1000-cm large heterogeneous flow domain discussed above.

The BTCs of solute concentrations in water extracted by the suction cup were used to evaluate the transport behavior of different compounds utilizing the moment analysis. This is a purely statistical characterization of BTCs without any assumptions regarding underlying processes. Because of the transient nature of the flow regime and for a better comparison with the one-dimensional simulations, we used a transformed time coordinate, that is, a normalized cumulative amount of extracted water depth, I [cm], in our analysis. However, suction cups extract a volume of water. To convert this volume of water to a water depth, the extracted volume needs to be divided by the area. In general, the definition of this area is not trivial for suction cup samplers. It could be either the area of the suction cup surface, through which water is extracted from the soil, or the area of the suction cup capture zone at the soil surface. To compare the extracted water depth directly with a cumulative infiltration depth or a cumulative depth of drainage for a flow field that is not disturbed by a suction sampler, the surface area of the capture zone is more appropriate. The fraction of total infiltration surface corresponding to the suction cup sampling area (SCSA) can be approximated by the ratio of the extracted water volume to the total infiltrated water volume when differences in water storage in the soil are neglected. Therefore, we first calculated the SCSA [cm²] as defined by Weihermüller et al. (2005):

$$SCSA = \frac{total\_vol_{sampled}}{total\_vol_{infiltrated}} Infiltration\ surface \qquad [5]$$

where $total\_vol_{sampled}$ [cm³] is the cumulative amount of water extracted by the suction cup during a certain time interval, $total\_vol_{infiltrated}$ [cm³] is the cumulative amount of net infiltration during a time interval, and the Infiltration surface is the length of the upper boundary multiplied by a unit length in a perpendicular direction (i.e., 100 cm²). SCSA, as defined above, can be modified to provide information about the sampled mass fraction by substituting water volume (sampled and infiltrated) with mass (sampled and applied), resulting in SCSA_solute. To calculate $total\_vol_{sampled}$ and $total\_vol_{infiltrated}$, we used the cumulative quantity of water between the time of application (Day 820) and a chosen point in time (i.e., detection time), when only minimal concentrations (below an assumed detection limit) appeared in water captured by the suction cup. The detection time for bromide was set to 1933 d, and to 2157 d for pesticides A and D. Note that $total\_vol_{infiltrated}$ was calculated for the 150- by 1000-cm flow domain and was equal for all 10 realizations of smaller flow domains, irrespective of any small variations that may occur between realizations.

In the second step, the normalized cumulative amount of extracted water depth, I [cm], was calculated as

$$I = \frac{vol_{sampled}(t)}{SCSA} \qquad [6]$$

where $vol_{sampled}(t)$ [cm³] is the sampled water volume captured by the suction cup at time t (day). Note that in the HYDRUS-2D program, water volumes and surface areas are expressed per a unit length in the direction perpendicular to the simulation domain.

For the moment analysis, we used the Nth normalized and transformed time moment, T_N (cm^N), as defined by Jury et al. (1991):

$$T_N = \frac{\tau_N}{\tau_0} = \frac{\int_0^\infty I^N C_w^f \mathrm{d}I}{\tau_0} \qquad [7]$$

where the zeroth time moment, $\tau_0 = \int_0^\infty C_w^f \mathrm{d}I$ [µg cm^{-2}], is equal to the total mass of the substance recovered by the suction cup, or for one-dimensional simulations to the total mass leaving the bottom boundary of the simulation domain. C_w^f is the flux concentration [µg cm^{-3}].

The first normalized time moment, T_1 (i.e., μ_t), yields the quantity of water required for the center of mass to arrive at the observation depth. The second central moment (variance $\sigma_t^2 = T_2 - T_1^2$) describes the spreading of the solute pulse relative to the quantity of water required for the center of mass to arrive at the observation depth.

Finally, travel time moments (Eq. [7]) can be used to derive transport parameters, such as pore water velocity, v_s [cm cm^{-1}], and effective dispersivity, λ_{eff} [cm]. As a consequence of the transformation of time into the cumulative extracted water depth, pore water velocity, v_s, is expressed as the transport distance of solute per a unit length of extracted water [cm cm^{-1}]. The first and second moments are related to effective CDE parameters by the following equations (Jury and Roth, 1990) with

$$v_s = \frac{z}{\mu_t} \qquad [8]$$

and

$$\lambda_{eff} = \frac{v_s^2 \sigma_t^2}{2z} \qquad [9]$$

where z [cm] is the observation depth.

For a better comparison of the results from the two operation modes of the suction sampler and to compare these findings with one-dimensional simulations, we define a leached mass fraction (LMF) by

$$LMF = \frac{mass\_sampled}{mass\_applied} \frac{infiltration\ surface}{SCSA} \qquad [10]$$

where mass_applied [μg] is the total applied mass at the upper boundary and mass_sampled [μg] is the mass extracted by the suction cup.

From Eq. [10] it becomes clear that for steady-state flow conditions, the LMF of an inert tracer is equal to 1. Note that SCSA depends on the hydraulic conductivity of the soil, the hydraulic conductivity of the suction cup, the applied pressure head at the cup, and the water pressure and flow rate in the soil (Weihermüller et al., 2006). Under transient flow conditions and for an operation mode of the suction sampler with a time-variable pressure head, these variables change so that SCSA varies over time as well. Since we define SCSA as a ratio of sampled and infiltrated waters, which are collected over a certain period of time, the SCSA represents an averaged value of the SCSA for that time period. The time-averaged SCSA obtained may therefore differ from the SCSA at each single time period between the solute application and the full breakthrough of the solute plume. To evaluate the effect of transient flow on the LMF as defined in Eq. [10], LMFs for the inert tracer and different realizations of the heterogeneous flow field were calculated. Therefore, the deviation of LMF from that calculated for the inert tracer is a measure of the uncertainty of the mass flux derived from suction cup measurements.

Results and Discussion

The BTCs calculated for a scenario when the suction cup was sampled at a continuous variable pressure (an ambient pressure head plus −30-cm offset, Fig. 3) and the three substances were applied on Day 820 are plotted in Fig. 4, whereby the run labels indicate the different geostatistical realizations of the underlying flow field. Cumulative water was set to zero at the day of application (820 d). As expected, the highest concentrations were calculated for bromide (Fig. 4a) and the lowest for pesticide D, which degrades the most quickly. Figure 4 clearly demonstrates the influence of the underlying heterogeneous structure of the soil and the actual location of the suction cup within the flow field. As a result, BTCs vary between different realizations in terms of peak concentrations and the time (here expressed in units of the
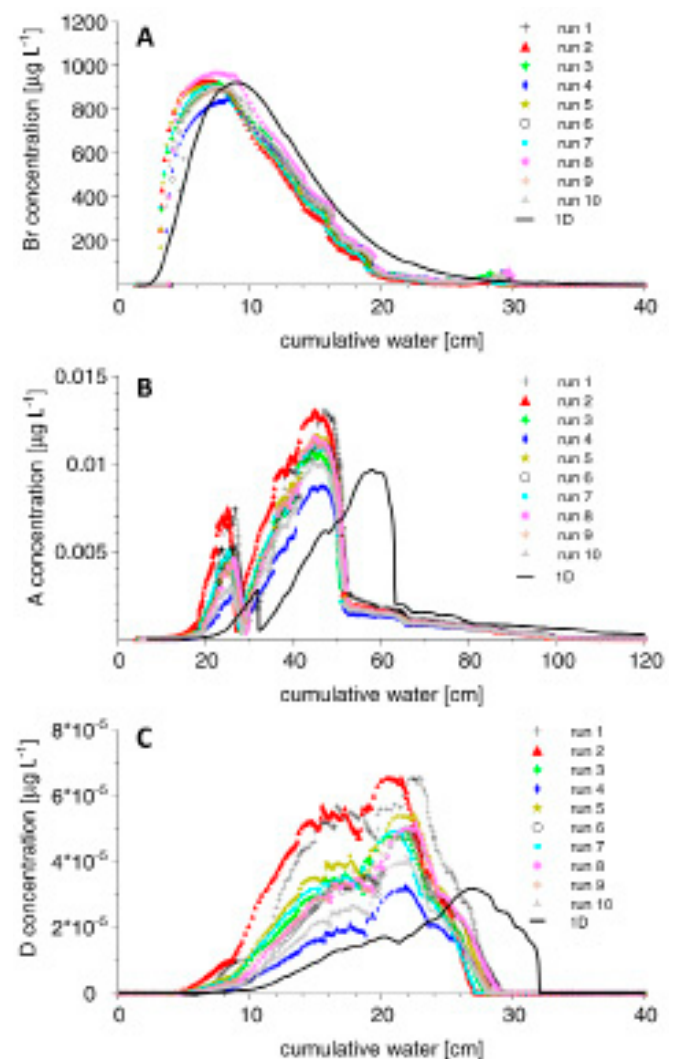

Fig. 4. Breakthrough curves for (a) bromide, (b) pesticide A, and (c) pesticide D for 10 realizations of a heterogeneous flow field and a continuously applied pressure head with a −30-cm offset. A reference one-dimensional simulation with free drainage bottom breakthrough curve. Note that axes do not have the same scale. Run 1 to 10 indicate the different geostatistical realizations.

normalized cumulative amount of extracted water according to Eq. [6]) when breakthrough starts. Additionally, temporal variability greatly increased for reactive substances, compared to the inert tracer. Contrary to bromide, which leached primarily during the first winter, pesticide A showed double-peak BTCs, which were a result of the annual water cycle, with high net infiltration fluxes during winter and low fluxes during summer. The first peak is associated with downward flow during the first winter after the application. During the following summer, the drainage flux ceases, and due to evaporation, the substance plume moves upward in the soil profile. As this occurs, water from below the suction cup with lower pesticide concentrations is extracted. The subsequent rise in concentrations corresponds with leaching during the second winter period. Compared with pesticide A, the first arrival of pesticide D is much earlier due to weaker sorption of pesticide D, and is therefore not directly influenced by changes in flow direction as discussed above. On the other hand, pesticide D also exhibited a double-peak breakthrough, but to a much smaller degree, and at earlier times.

Moment analysis was performed to quantitatively interpret particular BTCs. The results of the moment analysis, as well as the calculated minimum (min) concentrations, maximum (max) concentrations, arithmetic means, percentages of variability [100(max/min)], and coefficients of variation calculated from the 10 realizations are listed in Table 3. In general, the mean dispersivity for bromide BTCs is slightly higher (mean = 10.2 cm, min. = 9.6 and max. = 10.8 cm, with a standard deviation of 0.4 cm) than that for the flow field undisturbed by the suction cup at the same depth (7.6 cm). As was already shown by Weihermüller et al. (2005), sampling by a suction cup deforms streamlines toward the sampler, leading to longer travel paths and a pronounced tailing of the breakthrough. The calculated mean pore water velocity for the bromide BTC is 10.10 cm cm^{-1} (CV = 0.044), while the

minimum and maximum velocities are 9.56 and 10.81 cm cm^{-1}, respectively. Due to sorption, mean transport velocities decrease to 5.26 cm cm^{-1} (CV = 0.037) for pesticide D and 2.25 cm cm^{-1} (CV = 0.025) for pesticide A. In all cases, the variability between minimum and maximum pore water velocities ranges between 110 and 113% (Table 3).

Looking at the total extracted solute mass calculated from the zero moment, the largest quantities can be recovered for bromide (mean = 463.3 µg, CV = 0.081), followed by pesticide A (mean = 0.0132 µg, CV = 0.167), and pesticide D (mean = 2.96 10^{-5} µg, CV = 0.266). Note that these relatively low values correspond with low quantities of water extracted by the suction cups from the two-dimensional plane. Nevertheless, this pattern clearly reflects the degradation characteristics of individual substances, with the $D_{eg}T_{50}$ value for pesticide D (20 d) one-third of that for pesticide A (60 d). Irrespective of the total sampled mass, variability between the minimum and maximum total extracted mass (Table 3) increased with decreasing $D_{eg}T_{50}$ from 133% for bromide to 180 and 260% for pesticides A and D, respectively.

The BTCs for all three substances and a scenario with weekly sampling using a pressure head of −600 cm during 1 d per week are depicted in Fig. 5. Comparable results of water depths [cm] for weekly and continuous sampling scenarios were obtained due to normalization based on Eq. [6], even though only one-half the quantity of water was sampled during the weekly operation. In comparison to the scenario with the continuous time-variable pressure head (Fig. 4), fewer data points are available, due to less frequent sampling. Nevertheless, the same BTC patterns are observed as for the continuous sampling scenario, except that the observed peak concentrations are always lower for both pesticides (on average by 6 and 10% for pesticide A and D, respectively) for the weekly sampling strategy. On the other hand, weekly sampling

Table 3. Calculated minimum, maximum, arithmetic mean, percentage of variability [100(max/min)], and coefficient of variation (CV) of the mean pore water velocity and the total mass of three substances for 10 realizations of heterogeneous flow fields. Continuous (continuous pressure head offset by −30 cm), weekly (a pressure head of −600 cm applied for 1 d a week), and one-dimensional refer to operational modes.

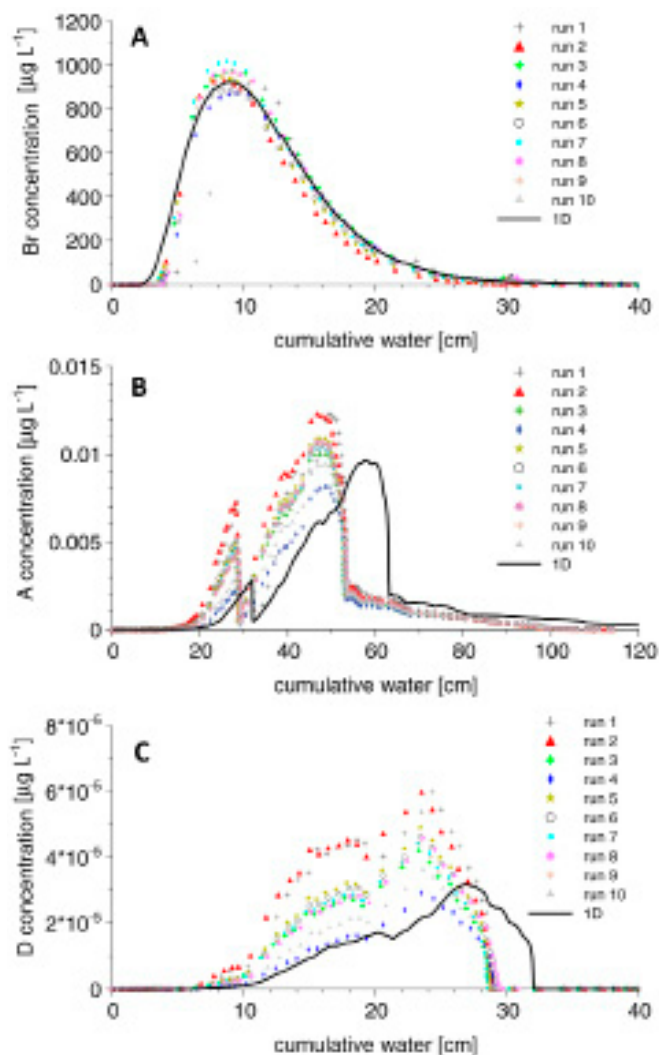| Substance		Velocity					Total mass				
		Min	Max	Mean	%	CV	Min	Max	Mean	%	CV
		cm cm^{-1}					µg				
Continuous	Bromide	9.56	10.81	10.10	113.1	0.044	406.9	539.7	463.3	132.6	0.081
	Pesticide A	2.15	2.37	2.25	110.2	0.025	0.00995	0.01784	0.01321	179.3	0.167
	Pesticide D	5.06	5.68	5.26	112.3	0.037	1.81E-5	4.71E-5	2.96E-5	260.2	0.266
Weekly	Bromide	8.36	9.12	8.73	109.1	0.031	203.9	275.9	229.9	135.3	0.099
	Pesticide A	2.07	2.25	2.16	108.7	0.024	0.00449	0.00762	0.00587	125.4	0.105
	Pesticide D	4.70	5.05	4.86	107.4	0.022	0.82E-6	0.19E-5	1.31E-5	231.7	0.246
One-dimensional	Bromide	–	–	7.55	–	–	–	–	1000	–	–
	Pesticide A	–	–	1.71	–	–	–	–	0.0238	–	–
	Pesticide D	–	–	3.96	–	–	–	–	3.67E-5	–	–

Fig. 5. Breakthrough curves for (a) bromide, (b) pesticide A, and (c) pesticide D for 10 realizations of a heterogeneous flow field and a weekly applied pressure head of −600 cm applied for 1 d. Note that axes do not have the same scale. Run 1 to 10 indicate the different geostatistical realizations.

produces slightly higher peak concentrations for bromide (on average by 3%).

In general, the calculated mean pore water velocities (Table 3) are only slightly higher for the continuous sampling scenario, compared to the weekly extraction scenario for all substances. On the other hand, weekly sampling produced slightly lower coefficients of variation (Table 3). At the same time, the total sampled mass was roughly only one-half of the reference mass for continuous sampling (Table 3), which corresponds to a smaller amount of extracted water (also about two times lower). Nevertheless, these findings are at first sight rather surprising, considering that water was extracted only during one-seventh of the total time. On the other hand, there is a simple explanation for this. Due to larger pressure head gradients between the soil and the suction cup during weekly sampling, considerably larger quantities of water

are extracted, especially during wetter periods (main drainage events). Even if the total mass recovery is not the best comparative indicator for the two operation modes, because the total amount of cumulative water will also be lower for weekly sampling, variability between individual realizations remains nearly unchanged (Table 3). Variability only decreased significantly for pesticide A.

If we look at the SCSA as defined in Eq. [5] for water (SCSA_water), we can use it analogically for solutes after substituting vol_sampled and vol_infiltrated with mass_sampled and mass_applied to get the SCSA_solute. For the bromide application (Table 4), we can clearly see that while roughly 50% of the surface was sampled in terms of SCSA_water (mean = 50.1 cm^2) when the continuous sampling strategy was used, the SCSA_solute (mean = 46.3 cm^2) was only slightly smaller. In the weekly sampling mode, the mean SCSA_water and the SCSA_solute were only about one-half that (24.1 and 23.0 cm^2, respectively). For both cases, the ratio of SCSA_water to SCSA_solute is close to 1, with ratios of 1.08 and 1.05 for the continuous and weekly sampling modes, respectively. Small differences between SCSA_water and SCSA_solute can be attributed to small changes in soil water storage between the final time selected for total_vol$_{sampled}$ and total_vol$_{infiltrated}$, and the time during which the breakthrough occurred. These differences can also be attributed to mixing processes between those flow channels bypassing the suction cup and those that are sampled.

As a somewhat longer simulation time was used for pesticides A and D, the SCSA_water is 55.8 cm^2 and for the continuous sampling mode and 28.0 cm^2 for the weekly sampling mode, resulting in a ratio between continuous and weekly SCSA_solute of 2.0. The corresponding SCSA_solute for pesticide A are 1.32×10^{-3} and 5.87×10^{-4} and for pesticide D 2.96×10^{-6} and 1.31×10^{-6}, for the continuous and weekly sampling modes, respectively. The relatively low SCSA_solute for both pesticides and operation modes is a direct consequence of the degradation process, whereby the ratio of continuous to weekly SCSA_solute was also close to 2, with 2.26 for pesticide A and 2.27 for pesticide D.

Finally, the LMF was calculated according to Eq. [10]. For bromide, the mean LMF was 0.92 for the continuous sampling mode and 0.95 for the weekly sampling strategy. For pesticides A and D, the LMF was 2.36×10^{-5} and 5.29×10^{-8} for continuous and 2×10^{-5} and 4.68×10^{-8} for weekly sampling modes, respectively (Table 4).

To better understand the importance of these findings, we used the results of a homogeneous one-dimensional simulation for comparison. As was already shown, the LMF was 1 for bromide for the one-dimensional simulation. As a consequence of degradation, the LMF dropped to 2.4×10^{-5} for pesticide A and 3.7×10^{-8} for pesticide D. It is somewhat surprising that the LMF for pesticide A for the one-dimensional simulation was similar to the LMF in a heterogeneous flow field with continuous sampling by the suction

Table 4. Calculated arithmetic mean (mean), standard deviation (STD), and coefficient of variation (CV) for the SCSA_water, SCSA_solute, leached mass fraction (LMF), and mean concentration [µg L^{-1}] for one substance application, for 10 realizations of heterogeneous flow fields and for a one-dimensional simulation.

Substance		SCSA_water			SCSA_solute			LMF			Mean concentration		
		Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
				cm^2								µg L^{-1}	
Continuous	bromide	50.1	3.3	0.065	46.3	3.7	0.081	0.92	0.04	0.042	90.1	3.8	0.042
	pesticide A	55.8	3.7	0.066	1.3E-3	2.0E-4	0.168	2.4E-5	3.2E-6	0.136	2.17E-3	2.94E-5	0.136
	pesticide D	55.8	3.7	0.066	3.0E-6	7.9E-7	0.266	5.3E-8	1.2E-8	0.234	4.86E-6	1.14E-6	0.234
Weekly	bromide	24.1	2.6	0.106	23.0	2.3	0.099	0.95	0.06	0.060	93.1	5.7	0.060
	pesticide A	28.0	3.0	0.108	5.9E-4	9.9E-5	0.169	2.1E-5	2.9E-6	0.136	2.06E-3	2.81E-5	0.136
	pesticide D	28.0	3.0	0.108	1.4E-6	3.2E-7	0.246	4.7E-8	1.1E-8	0.229	4.59E-6	1.05E-6	0.239
One-dimensional	bromide	-	-	-	-	-	-	1.0	-	-	87.0	-	-
	pesticide A	-	-	-	-	-	-	2.4E-5	-	-	1.81E-3	-	-
	pesticide D	-	-	-	-	-	-	3.7E-8	-	-	2.78E-6	-	-

cup. However, the LFM for pesticide D was somewhat lower in the one-dimensional simulation (Table 4). As was shown by Weihermüller et al. (2005), suction cup sampling increases water flow toward the cup and therefore reduces breakthrough times. This accelerated breakthrough is detectable for all substances shown in Fig. 4. While bromide shows only a small delay in the one-dimensional simulation, both pesticides produce much later arrivals. Especially for substances with a small $D_{eg}T_{50}$, the reduced residence time in the soil can have important consequences for the LMF by decreasing degradation.

Finally, the mean concentration was calculated (Table 4) using the total quantity of extracted water and solute mass since application. In general, there is no clear trend in systematically over- or underestimating the mean concentration by one of the sampling modes (continuous or weekly sampling) in the heterogeneous flow field. For bromide, the mean concentration for each single realization and the weekly sampling mode varied between 97.4 and 112.3% compared to the results for scenarios with continuous pressure head. Variations between 93.8 and 96.8% were obtained for pesticide A, and between 93.6 and 104.3% for pesticide D. The overall differences between the weekly and continuous sampling modes calculated by summing up all mass loads and extracted water for all 10 realizations were 103 for bromide, 95.0 for pesticide A, and 94.5% pesticide D. This indicates that weekly sampling may slightly underestimate the mean concentrations for reactive substances. Compared to the mean concentration (87.0 µg L^{-1}) calculated by the one-dimensional simulation for homogeneous undisturbed flow conditions, two-dimensional simulations for weekly and continuous sampling modes produced only slightly higher mean bromide concentrations of 93.1 and 90.1 µg L^{-1}, respectively. For pesticide A, a slightly lower mean concentration was observed for the one-dimensional simulation (1.81 × 10^{-3} µg L^{-1}) in comparison to the two-dimensional simulations with the suction cup sampling (continuous = 2.17 × 10^{-3} and weekly =

2.06 × 10^{-3} µg L^{-1}). For pesticide D on the other hand, the mean concentration calculated from the one-dimensional breakthrough is only about one-half of values obtained by the two-dimensional simulations with the suction cup sampling (Table 4). The explanation for these differences is the same as for the differences in LMF.

Additionally, we plotted breakthrough curves versus time for 10 two-dimensional realizations with continuous sampling with an applied pressure head of −600 cm and three substances in Fig. 6. For comparison, the BTC obtained from the reference one-dimensional simulation is also shown. In all cases, the timing (the first arrival and tailing) of the one-dimensional breakthrough is nearly the same as that for the heterogeneous flow field with suction cups. On the other hand, as already discussed, pesticide concentrations are much lower for the one-dimensional free drainage case.

To evaluate differences in leaching and sampling behavior over a longer observation time, a third set of simulations was performed. As already stated, the solute application was repeated eight times, with 1 yr between each application (all applications were done on March 31). To reduce the computational effort, only the weekly sampling for heterogeneous flow fields was analyzed. Solute concentration versus normalized cumulative flow captured by the suction cups over the entire simulation period of 10 yr (eight repeated annual applications) is plotted in Fig. 7. While the annual peaks in bromide concentrations are clearly visible, the frequency between peaks differs slightly between individual years as a result of changing atmospheric boundary conditions. Additionally, peak concentrations within each leaching period vary only slightly between the model runs. Unlike the conservative tracer, pesticides A and D show a totally different breakthrough pattern with high concentrations over a certain period of time (∼60–100 cm cumulative water), and low concentrations during all other years (Fig. 7b and 7c). Three major peaks are detectable for pesticide D at 48, 80, and 115 cm cumulative water. This pattern of unequal
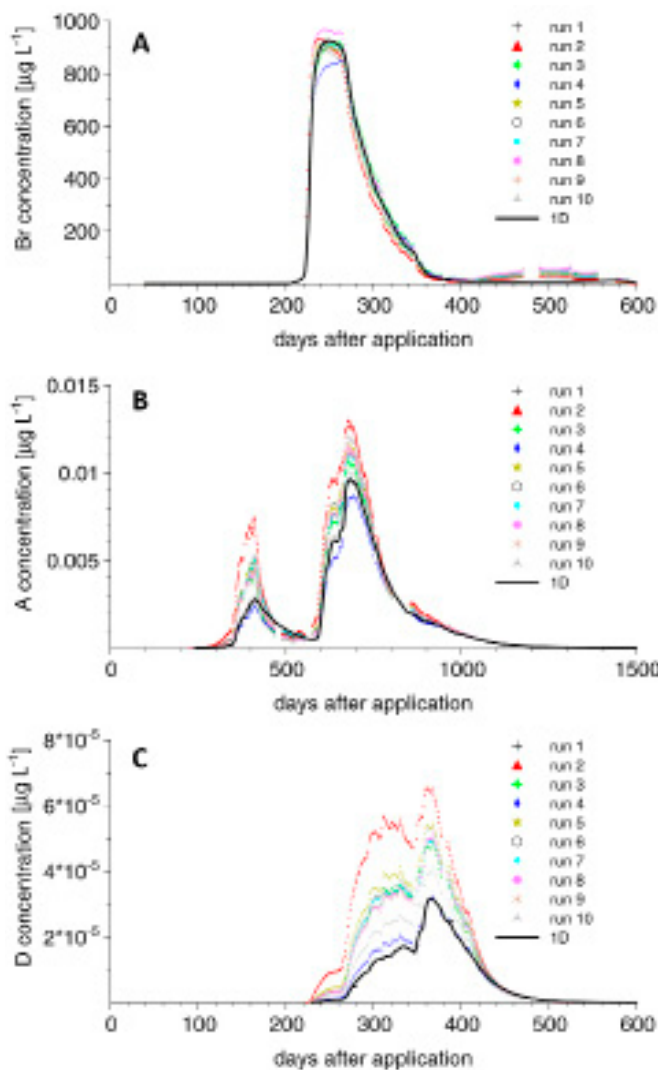
Fig. 6. Breakthrough curves versus time for (a) bromide, (b) pesticide A, and (c) pesticide D for 10 realizations of a heterogeneous flow field and a continuously applied pressure head with a −30-cm offset. A reference breakthrough curve for a one-dimensional simulation with free drainage breakthrough curve. Note that axes do not have the same scale. Run 1 to 10 indicate the different geostatistical realizations.
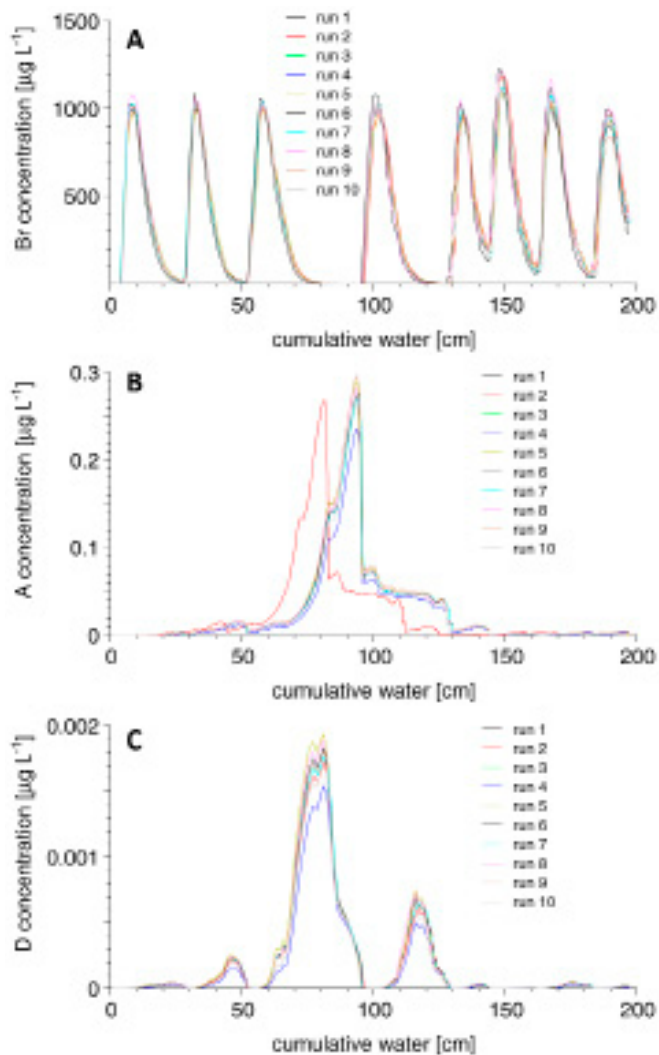
Fig. 7. Breakthrough curves for (a) bromide, (b) pesticide A, and (c) pesticide D for a weekly applied pressure head of −600 cm applied for 1 d and eight annually repeated application on 31 March. Note that axes do not have the same scale. Run 1 to 10 indicate the different geostatistical realizations.

concentrations during different years reflects actual water contents at the time of solute application and subsequent atmospheric conditions during dry and wet seasons.

The total mass of bromide sampled in different years varied between 1740 and 2383 μg, with a mean of 1977 μg (Table 5). At the same time, the quantity of extracted water varied between 4.64 and 6.31 L, with a mean of 5.14 L. Mean bromide concentrations reflected differences in the extracted quantity of water and total mass between the model runs, and varied between 368 and 401 μg L^{-1}, with the mean value of 384.4 μg L^{-1}. For pesticide A, the total extracted mass varied between 0.130 and 0.189 μg (mean = 0.152 μg) and the mean concentrations varied between 2.40×10^{-2} and 3.74×10^{-2} μg L^{-1} (mean = 2.96×10^{-2} μg L^{-1}). For pesticide D, the total sampled mass varied between 8.94×10^{-4} and 1.40×10^{-3} μg with the mean

value of 1.10×10^{-3} μg, and the mean concentration varied between 1.88×10^{-4} and 2.61×10^{-4} μg L^{-1}, with the mean value of 2.12×10^{-4} μμg L^{-1}. The CV increased from bromide with a value of 0.097, to pesticide A with a value of 0.144, and 0.154 for pesticide D. This pattern indicates increasing variability in the captured mass for reactive substances compared to the conservative tracer. As stated before, the quantity of sampled water varied between 4.64 and 6.31 L, resulting in a difference of 36%. Nevertheless, the mean concentration varied only by 9% for bromide. Much higher variations were detected for pesticides A and D, with differences as high as 56 and 39% (see Table 5). Again, the mean LMF of 0.93 for bromide was close to 1, reflecting the conservative behavior of the substance. Reflecting the degradation of pesticides and the low sampled mass, the LMF dropped to a mean of 7.17×10^{-5} and 5.15×10^{-7} for pesticides A and D, respectively.

Table 5. Minimum (min), maximum (max), arithmetic mean (mean), SCSA_water, SCSA_solute, leached mass fraction (LMF), and mean concentration for three substances, a simulation period of 10 yr with eight annually repeated substance applications as plotted in Fig. 7.

Substance	Parameter	Cumulative water	Total mass	SCSA Water	Solute	LMF	Mean concentration
		L	µg	—— cm^2 ——			µg L^{-1}
Bromide	Min	4.64	1740	23.74	21.75	0.89	367.9
	Max	6.31	2383	32.64	29.79	0.97	401.2
	Mean	5.14	1977	26.59	24.71	0.93	384.4
	SD	0.51	192.6	2.64	2.41	0.024	9.75
	CV	0.099	0.097	0.099	0.100	0.025	0.025
Pesticide A	Min	4.64	0.1299	23.74	1.62e-3	5.80e-5	2.40e-2
	Max	6.31	0.1889	32.64	2.36e-3	9.04e-5	3.74e-2
	Mean	5.14	0.1515	26.59	1.89e-3	7.17e-5	2.96e-2
	SD	0.51	0.0214	2.64	2.67e-4	8.27e-6	3.42e-3
	CV	0.099	0.144	0.099	0.141	0.115	0.115
Pesticide D	Min	4.64	8.94e-4	23.74	1.21e-5	4.54e-7	1.88e-4
	Max	6.31	1.40e-3	32.64	1.75e-5	6.30e-7	2.61e-4
	Mean	5.14	1.10e-3	26.59	1.38e-5	5.15e-7	2.12e-4
	SD	0.51	1.70e-4	2.64	2.01e-6	4.96e-6	2.05e-5
	CV	0.099	0.154	0.099	0.146	0.096	0.096

The calculated LMF of the inert tracer, which should theoretically equal 1, was slightly underestimated (0.93) due to the fact that we had to approximate the SCSA. In general, SCSA varies over time for transient flow conditions. To convert the recovered solute mass to a fraction of the solute mass that leaches below the sampling depth for flow conditions that are not disturbed by the suction sampler, an averaged value of the SCSA must be used. One way to obtain such an average value is to compare the sampled water volume with the infiltrated water volume. Unfortunately, this averaging procedure may not represent the average SCSA relevant for the solute transport process. However, our simulations demonstrated that using an average SCSA based on water volume measurements may lead to an error in the estimated total solute leaching of less than 13%.

Calculated mean concentrations were used for direct comparisons of two operation modes. In general, the maximum differences in the mean concentration for the same flow field were 12% for bromide, 7% for pesticide A, and 11% for pesticide D. Averaging over all flow fields led to a small overestimation in the mean concentration for bromide (+3%), and a systematic underestimation for pesticides A (−5.0%) and D (−5.5%). Additionally, the normalized and time-dependent BTCs do not indicate large differences between the two operation modes. This suggests that the effect of the sampling strategy on mean concentrations, times of breakthrough, and peak concentrations is negligible.

In the final step, solute applications were repeated eight times during a 10-yr simulation period, and water was extracted by suction cups on a weekly basis. Again, the results indicate that the total amount of extracted water is less variable between different realizations of the flow field compared to the total mass of sampled pesticides. As a consequence, variability of calculated mean concentrations is greater for pesticides than for bromide. Finally, the results in terms of absolute numbers are only representative for the particular heterogeneous structure and soil type used in this study. Nevertheless, the overall findings of variable breakthrough and mean concentrations will also be valid, to some degree, for other heterogeneous soils. Additionally, pesticide leaching, and therefore, pesticide concentrations captured by the suction cups highly depend on the weather conditions during application and the percolation period.

In comparison to the standard FOCUS scenarios (e.g., Boesten, 2007), root water uptake was neglected, and a constant $D_{eg}T_{50}$ value was assumed over the entire simulated soil depth. The consequence of the first assumption is faster drainage, resulting in

◆ Summary and Conclusion

The uncertainty in solute monitoring using suction cups induced by the soil's heterogeneity was assessed using numerical simulations in a layered soil profile with atmospheric boundary conditions. To account for reactive processes, two different pesticides were applied together with an inert tracer. Additionally, two different operation modes (sampling with a continuous pressure head and weekly sampling) were used to evaluate the impact of the mode of applied pressure head at the cup.

Flow and transport were simulated in 10 realizations of a heterogeneous flow field generated using the Miller–Miller scaling theory. First, all substances were applied a single time after a two year "conditioning" phase. The results indicated variability in pore water velocities, sampled quantities, suction cup sampling areas for water (SCSA_water) and solute (SCSA_solute), leached mass fractions (LMF), and mean concentrations.

In general, the variability in calculated pore water velocities ranged between 110.0 and 113.0% for the continuous tensiometer-controlled sampling and 107.6 and 109.1% for the weekly sampling with a constant pressure head of −600 cm. The total sampled mass showed larger variability for both pesticides in comparison to bromide. Overall, largest variability was found for pesticide D, with 260 and 230% for the continuous and weekly sampling, respectively, while bromide varied only between 133 and 135%.

reduced decomposition of the reactive substances. The second assumption, on the other hand, will lead to greater decomposition at greater depths, reducing the total sampled mass, and consequently the LMF and mean concentrations. However, the aim of this study was not an environmental risk assessment of the studied substances, but an assessment of how suction cups can bias the description of pesticide leaching. On the other hand, root water uptake would likely increase differences in the captured solute mass and, consequently, in mean concentrations.

In conclusion, soil heterogeneity can produce large variations in the concentrations and leached mass fractions measured by suction cups. The coefficient of variation of the leached mass fraction estimated from suction cup measurements in our study was found to be up to 35%, and was the largest for the pesticide with the smallest leached mass fraction. Second, suction cup samplers influence the flow regime and generally lead to a faster breakthrough than would be otherwise observed under natural, undisturbed flow conditions. This may lead to an overestimation of the leached solute mass by a factor 2 for the pesticide with the lowest LMF. Compared to the two previously mentioned effects, the impact of the suction sampler operation mode (a continuous tensiometer-controlled pressure head versus a periodical sampling) on LMFs and mean concentration of the pesticides is negligible. Therefore, the additional effort required to control the continuous pressure head by reference tensiometers does not seem to be justified. Finally, uncertainty in the leached mass fraction due to transient flow conditions and the time-variable suction cup sampling area is negligible compared with the effects of soil heterogeneity and the bias caused by the disturbance of the flow field.

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