**Hydrology and Earth System Sciences Discussions**

# A novel explicit approach to model bromide and pesticide transport in soils containing macropores

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## Abstract

The present study tests whether an explicit treatment of worm burrows is feasible for simulating water flow, bromide and pesticide transport in structured heterogeneous soils. The essence is to represent worm burrows as morphologically connected paths of low flow resistance in the spatially highly resolved model domain. A recent Monte Carlo study (Klaus and Zehe, 2010) revealed that this approach allowed successful reproduction of tile drain event discharge recorded during an irrigation experiment at a tile drained field site. However, several "hillslope architectures" that were all consistent with the available extensive data base allowed a good reproduction of tile drain flow response. Our second objective was thus to find out whether this "equifinality" in spatial model setups may be reduced when including bromide tracer data in the model falsification process. We thus simulated transport of bromide and Isoproturon (IPU) for the 13 spatial model setups, which performed best with respect to reproduce tile drain event discharge, without any further calibration. All model setups allowed a very good prediction of the temporal dynamics of cumulated bromide leaching into the tile drain, while only four of them matched the accumulated water balance and accumulated bromide loss into the tile drain. The number of behavioural model architectures could thus be reduced to four. One of those setups was used for simulating transport of IPU, using different parameter combinations to characterise adsorption according to the Footprint data base. Simulations could, however, only reproduce the observed leaching behaviour, when we allowed for retardation coefficients that were very close to one.

## 1 Introduction

Since the mid-nineties it has become evident that preferential flow is the rule rather than the exception in structured soils (Flury, 1996). Preferential flow processes are highly relevant in runoff generation at the hillslope (Weiler and McDonnell, 2007; Zehe

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and Sivapalan, 2009) and headwater scales (Zehe and Blöschl, 2004; Zehe et al., 2005, 2006) and consequently are a prime cause for the spatial variability in soil water content (de Lannoy et al., 2006; Zehe et al., 2010b). Originally, the term "preferential flow" was coined after realising that water flow and transport in non-capillary soil structures – often worm burrows, root channels or soil cracks – was much faster than could be expected from classical theory of flow and transport in porous media (Beven and Germann 1982; Zehe and Flühler, 2001). Rapid flow in morphologically connected preferential flow paths controls transport and residence times of pesticides (e.g. Flury et al., 1995; Elliot et al., 2000; Šimůnek et al., 2003), anions (Flury et al., 1995; Villholth et al., 1998; Lennartz et al., 1999; Köhne et al., 2006; Stone and Wilson, 2006) and of strongly adsorbing phosphorus (Stamm et al., 1998, 2002). Vertical distances are in most cases too small for the central limit theorem to apply (Blöschl and Zehe, 2005). We cannot assume fully mixed conditions and characterize yet imperfect mixing by a well defined macro dispersion coefficient.

Consequently a variety of approaches has been proposed to effectively represent preferential flow in soil physical or soil hydrological models. Šimůnek et al. (2003), Gerke (2006) and Köhne et al. (2009a) published very nice and helpful reviews of different approaches, like composite hydraulic function models (Zurmühl and Durner, 1996), dual porosity and dual permeability models. Recent studies suggested explicit representation of preferential flow paths as connected structures in the model domain either at the pedon scale (Vogel et al., 2006; Sander and Gerke, 2009) or at hillslope scale (Klaus and Zehe, 2010; Zehe et al., 2010a). The number of studies dealing with modelling preferential transport of solutes at the hillslope and field scale is so large, that an exhaustive overview is beyond the scope of this paper. Hendriks et al. (1999) simulated bromide and nitrate transport in a soil with apparent shrinkage cracks using a modified version of the FLOCR/ANIMO model. Model parameters were estimated by using data of groundwater levels, soil moisture, and concentrations of bromide in both the groundwater body and the soil profile. While the model results for nitrate were poor, bromide concentrations in soil could be adequately reproduced, and

predicted bromide concentrations in groundwater matched the mean observed values. Gerke and Köhne (2004) modelled water flow and bromide transport at a tile drain field site using a dual porosity approach (based on the DUAL model of Gerke and van Genuchten (1993)) and a single domain approach. While the single domain approach failed to reproduce observed transport, the DUAL model was able to reproduce the long term dynamics of water and bromide transport well. Nevertheless, the authors report that the DUAL model failed in exactly reproducing observed bromide concentrations. Köhne et al. (2006) used seasonal discharge and bromide data observed at one plot to calibrate different models and then predicted seasonal transport behaviour at two nearby field plots. They compared a single porosity and a mobile-immobile model where both were set up in one and two dimensions (referred to as 1-D and 2-D hereafter). Calibration and prediction of bromide plateau concentrations were only successful when using the 2-D mobile-immobile model approach. Haws et al. (2005) compared a single-porosity and a dual-porosity approach based on HYDRUS-2-D (Šimůnek et al., 1999) to simulate tile drain discharge and the transport of applied chloride and bromide. Although both model approaches were able to reproduce the shape of measured cumulative outflow well, simulated transport deviated considerably from the observations. The authors stated that no approach was able to reproduce rapid transport of solutes to the subsurface tile drain in an acceptable manner and concluded that a well matched hydrograph does not automatically imply that the corresponding model parameters are physical meaningful (see also McGuire et al., 2007). Köhne and Gerke (2005) compared a model based on 2-D-Richards Equation and 2-D Convection-Dispersion-Equation (CDE) with a model based on the mobile-immobile approach when simulating tile drain discharge and bromide transport observed at an experimental field site in northern Germany. As only the mobile-immobile approach yielded a good match of the observed bromide peak, the authors concluded that this peak was caused by preferential transport. Gerke et al. (2007) achieved a clearly better match of tracer concentrations observed at the same site when using a 2-D-dual-permeability model and injecting the bromide tracer exclusively into the soil matrix domain of the model.

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Pang et al. (2000) studied bromide and pesticide transport at a tile drained field site in New Zealand using HYDRUS-2-D. Simulated soil moisture was in good accordance with observation. The model failed, however, in reproducing observed bromide and pesticide concentrations. Pang et al. (2000) thus concluded that a successful match of preferential transport requires a refinement of the dual-permeability approach.

Leaching and long term fate of non-conservative solutes such as pesticides and pharmaceutics is even far more difficult to predict as sorption behaviour and degradation processes come into play (Köhne et al., 2009b). Gärdenäs et al. (2006) compared four different approaches to simulate long term soil water flows and pesticide transport at a tile drained field site in southern Sweden. Transport behaviour was observed by taking 13 water samples during a period of 6 weeks. One approach was based on a modification of soil hydraulic conductivity near saturation and the remaining were a mobile-immobile, a dual-porosity and a dual-permeability approach, respectively. The dual-permeability approached performed best, followed by the dual-porosity approach, while the other approaches failed both to reproduce water flows and pesticide transport. Boivin et al. (2006) also used HYDRUS-2-D to simulate tile drain discharge and pesticide concentrations observed during a 100-day period for three different soils. Water samples were taken as flow proportional daily mixing samples. Simulated discharge was, after the soil hydraulic functions were modified to account for preferential flow, in good accordance with observations. Boivin et al. (2006) stress that the non-equilibrium mobile-immobile approach allowed acceptable reproduction of the observed pesticide concentrations, while the advection-dispersion approach failed.

The present study suggests a novel approach for simulating soil water flows, tracer and pesticide transport in soils. The essence is to represent preferential flow paths explicitly as morphologically connected paths of low flow resistance in the spatially highly resolved model domain. Klaus and Zehe (2010) gave evidence that this approach allows successful reproduction of tile drain event discharge recorded during an irrigation experiment at a tile drained field site in the Weiherbach catchment (Zehe and Flühler, 2001). The relevant preferential flow paths – in this case anecic worm

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burrows – were generated using an agent based model (compare Sect. 2.3). However, in accordance with studies of Larsbo and Jarvis (2005) and McGuire et al. (2007) they found a considerable equifinality (Beven, 1993) in their spatial model setup. Several "hillslope architectures" that were all consistent with the available extensive data base allowed a good reproduction of tile drain flow response (compare Sect. 3.1). In this follow-up study we use the best 13 best hillslope architectures (NS > 0.9) from Klaus and Zehe (2010) to address the following questions:

- Does the approach proposed by Klaus and Zehe (2010) additionally allow reproduction of the bromide and the Isoproturon (IPU) concentrations that have been observed during the irrigation experiment at this site?

- Can we reduce the set of the best model setups (Klaus and Zehe, 2010) by rejecting those that do not match observed bromide transport behaviour?

- Can we employ those behavioural model setups that allowed a good match of both the discharge and bromide loss at the tile drain for simulating transport behaviour of the pesticide at this site?

In Sect. 2 we present a short characterisation of (a) the study site and the underlying irrigation experiment (Zehe and Flühler, 2001), (b) the corresponding modelling study by Klaus and Zehe (2010) and our model approach. In Sect. 3 we compare simulated and observed breakthroughs of bromide and IPU. The paper closes with discussion and conclusions in Sect. 4.

## 2 Methodology

### 2.1 Study area, irrigation experiment and available data

The Weiherbach valley is a rural catchment of $3.6\,\text{km}^2$ size in south-west Germany. About 95% of the total catchment area is used for growing agricultural crops. The climate is semi-humid with an average annual precipitation of $750–800\,\text{mm yr}^{-1}$, average

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annual runoff of 150 mm yr$^{-1}$, and annual potential evapo-transpiration of 775 mm yr$^{-1}$. The geology consists of Keuper sandstone, marl and mudstone (lower and middle Triassic) covered with a Loess layer up to 15 m thick.

The focus of this study is to simulate solute transport within a tile-drained field close to the stream channel that was performed in an irrigation experiment in April 1997 by Zehe and Flühler (2001). One day before irrigation of the 900 m$^2$ site the herbicide IPU was applied by the farmer with a mounted spray bar and the site was instrumented with 25 TDR-Probes of 30 cm length. Irrigation was performed with twelve evenly distributed sprinklers in three blocks with a sum of $46 \pm 5$ mm. Ten minutes after onset of the first irrigation block a bromide and brilliant blue pulse was added to the sprinkling water. Water samples were taken at the tile drain outlet, which was located approximately 1.2 m below the field level. Tile drain discharge was measured using a calibrated Venturi tube and a pressure sensor. Zehe and Flühler (2001) report a first flush of high bromide and IPU concentrations in the early phase (10 and 30 min after onset) via the tile drains into the brook, while the tile discharge showed only a very small reaction. In contrast, later on during the second and third irrigation blocks, peak concentrations and peaks in tile drain discharge correlated well (Fig. 1). Additional dye tracer experiments showed that connected burrows of anecic worms that linked the surface and the gravel layer above the tile drain likely acted as short-cuts for water and solutes to bypass the soil matrix during the irrigation experiment.

## 2.2 The CATFLOW model

CATFLOW is a physically based model for plot, hillslope and catchment scale modelling of water and solute transport (Maurer, 1997; Zehe et al., 2001; Zehe and Blöschl, 2004; Zehe et al., 2005). A catchment is treated as an ensemble of hillslopes that are interconnected via the drainage network. In CATFLOW a hillslope is represented as a two-dimensional cross section along the steepest descent line that is discretised by two-dimensional curvilinear orthogonal coordinates. The hillslope is thus assumed to

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be uniformly perpendicular to the slope line. Soil water dynamics are described by the Richards equation in the potential form that is numerically solved by an implicit mass conservative Picard iteration (Celia et al., 1990). The simulation time step is dynamically adjusted to achieve optimal convergence of the iteration scheme and reaches from several seconds during rainfall conditions up to one hour, which is the allowed maximum. Soil hydraulic functions are described after van Genuchten (1980) and Mualem (1976). Evapo-transpiration is represented by an advanced Soil Vegetation Atmosphere Transfer (SVAT) approach based on the Penman-Monteith equation. Surface runoff routing down the hillslopes is based on the diffusion wave approximation to the one-dimensional Saint-Venant equations. It is numerically solved by an explicit upstream finite difference scheme.

Solute transport in CATFLOW is calculated by a particle tracking scheme based on a Random Walk approach. The deterministic part of a particle step is determined based on the seepage velocities using a backward two level Runge Kutta scheme as suggested by Roth and Hammel (1996). The random part of the particle step is determined based on the square root of the dispersion/diffusion coefficient multiplied by the time step. Sorption can be described either by linear instantaneous adsorption, the Freundlich or the Langmuir isotherms. Additionally, the model may account for first order decay.

## 2.3 Worm burrows as connected structures in the model domain

Our working paradigm to represent worm burrows as morphologically connected flow paths of low flow resistance in our model domain and the selected grid size has been mainly motivated by the study of Klaus and Zehe (2010) but also by the studies of Zehe and Blöschl (2004) and Vogel et al. (2006). The population of worm burrows is generated by an agent based approach as explained in the following.

### 2.3.1  Agent based generation of worm burrows

For each surface element we simulated the number of apparent worm burrows at the soil surface by assuming they are Poisson distributed (Beven and Clarke, 1986). The Poisson parameter is the average worm burrow density per unit area multiplied by the area of a surface element. Next we simulated the lengths of each macropore located in the surface element (can be more than one) assuming a normal distribution. In the next step we used a stochastic agent, which extended the worm burrow into the domain by an anisotropic random walk. The probability for digging into the vertical was $1-2 \times p_{\text{lat}}$ while $p_{\text{lat}}$ was 0.05. This approach ensures that the burrow is continuous and thus connected and allows accounting for tortuosity. When used with a grid as fine as that outlined above, this procedure yields a worm burrow system that is consistent with our findings (Zehe et al., 2010a) and those reported by Shipitalo and Butt (1999). After the procedure was completed we assigned a flag or characteristic function to any grid cell in the domain that is one if the grid cell contains at least one macropore and zero otherwise (Fig. 2).

Our fundamental assumption is (a) that vertical water flow in the grid elements with worm burrows is dominated by macropore flow and (b) this might be accounted for by assigning an effective medium to these model elements. To this end we multiplied the number of macropores in a grid element by the maximum volumetric water flow in the worm burrow and divided this value by the cross sectional of the grid element to obtain its effective hydraulic conductivity. Klaus and Zehe (2010) compared values for maximum volumetric water flows in worm burrows from different experimental studies of Shipitalo and Butt (1999), Weiler (2001), and Zehe and Flühler (2001) for this purpose. Finally, we assigned an effective porous medium with very low retention properties to the model elements containing macropores to minimise the effect of capillary forces during simulation. The study of Klaus and Zehe (2010) revealed that this approach is feasible at least for simulating soil water flows, as this explicit treatment of macropores as connected structures yielded successful predictions of observed tile drain discharge

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with a Nash-Sutcliffe (NS) of up to 0.95. The big drawback of this approach is the relatively high computational cost.

## 2.3.2 Infiltration into connected structures

Infiltration and runoff generation is treated in CATFLOW by means of a Cauchy boundary condition. The uppermost model layer is usually very fine (1–5 cm). Rainfall is treated as a flow boundary condition, as long as the uppermost grid cell is unsaturated. In the case of saturation, the model switches to a Dirichlet boundary condition using the overland flow depth as a pressure boundary to drive infiltration. The infiltrating water flux is then calculated using Darcy's law. This approach works well to capture the onset of overland flow as shown, for instance, in Zehe et al. (2001) or to simulate infiltration at small scales (Zehe and Blöschl, 2004). Infiltration into the grid cells that contain the effective macropore medium works identically. In the case of overland flow, the effective drainage area of the macropore elements may increase due to runoff from upslope sectors. The boundary conditions at the remaining boundaries were no flow at the left, free flow at the right and gravity flow at the lower boundary.

## 2.4 Spatial model setups used in the present study

Ideally the outlined approach is used at a very fine spatial grid size in downslope/lateral direction (2–3 cm). In this case each surface element of the 2-D domain contains either a single worm burrow or not (Zehe et al., 2010a). Such a fine lateral discretization of the 30 m long hillslope, combined with a vertical grid size of 2 cm, resulted however in computation times of 200 h for a single model run. This was unacceptable as the purpose of the previous model study of Klaus and Zehe (2010) was to investigate whether the inherent uncertainty of key model parameters results in equifinality of the spatial model setup. Klaus and Zehe (2010) used available extensive data on soil hydraulic properties and initial conditions as well as statistical data on the worm burrow system (the density per unit area and average burrow length) to generate 432 setups of the

tile drained field site. Tile drain flow response to the irrigation was simulated for each of these setups using CATFLOW. To keep computation time reasonable, Klaus and Zehe (2010) used a downslope/lateral grid size of 30 cm, which resulted in a computation time of up to 20 h per run.

As outlined above Klaus and Zehe (2010) found that several spatial setups allowed a very good match of the observed hydrograph at the study site. None of these possible setups could be rejected as all key parameters (the worm burrow density, the hydraulic conductivity of the worm burrows, etc.) were within ranges either reported in the literature (Shipitalo and Butt, 1999; Weiler, 2001; Zehe and Flühler, 2001) or of local observations. Also, simulated soil moisture patterns within the model domain appeared to be realistic.

Within the present study we employ the 13 best spatial models setups, simulate in addition transport of bromide and IPU and compare the results with the corresponding concentrations observed during the irrigation test. Table 1 characterises the soil profile at the field site and lists the corresponding soil water characteristics and characterises the macropore medium. Table 2 lists the most important characteristics of the 13 best model runs, the corresponding Nash-Sutcliffe efficiency and the differences between simulated and observed time to peak (denoted as timing error hereafter).

### 2.4.1 Representation of the tile drain and weighting factor for scaling length specific outflow

The tile drain and its gravel embedding is also represented as a connected flow path by assigning a band with the "worm burrow" medium to a depth of 95–120 cm that extended across the entire length of the domain. Klaus and Zehe (2010) compared three different maximum filter velocities in the tile drain. Table 2 lists the corresponding value for each of the most likely model setups. As CATFLOW is a 2-D model the output is length specific and must be scaled by multiplying simulated length specific outflow by the width of cross section that is drained by the tile drain. Consequently, Klaus and Zehe (2010) scaled the output such that simulated peak flows matched the observed

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peak flows. The study revealed that the "drained width" of the cross section was in most cases between 1 and 3 m (compare Table 2). Please note that within the present study these widths were not modified to match bromide concentrations and cumulated bromide loss from the tile drain. This is thus a generic test to find out whether the approach proposed by Klaus and Zehe (2010) allows a consistent prediction of flow and transport. For further details about the limitations of the approach the reader should refer to the sect. "Key assumptions underlying the 2-D approach" and the discussion section in Klaus and Zehe (2010).

### 2.4.2 Transport parameters during simulation

Bromide transport was simulated for the 13 model setups using the initial soil moisture state listed in Table 2. Simulated irrigation occurred during the field experiment in three blocks of uniform intensity with a sum of $46 \pm 5$ mm. At the beginning of simulation 1500 g of bromide was evenly distributed within the upper layer of the model domain. During all simulated cases we used a constant isotropic effective diffusion coefficient of $D = 5 \times 10^{-7}$ m$^2$ s$^{-1}$ for bromide (Zehe and Blöschl, 2004) and IPU.

IPU transport was simulated for the model setup named "run 1" that yielded the best discharge simulation and an acceptable good match of the time series of cumulated bromide mass flow at the tile drain outlet (see Sect. 3.2). 270 g of IPU was spatially homogeneously distributed in the upper 2 cm of the soil corresponding to the amount of IPU that has been applied to the field one day before the experiment. Non-linear adsorption behaviour of IPU was parameterised according to the Freundlich-isotherm:

$$C_a = k_f \times C^n$$

Where $C_a$ is the concentration in the adsorped phase [g g$^{-1}$], $k_f$ is the Freundlich coefficient [g l$^{-1}$], $C$ is solute concentration in the water phase [g l$^{-1}$] and $n$ is the Freundlich exponent [–].

As Zehe and Flühler (2001) did not determine the Freundlich parameters for IPU at their irrigation site, we tested different values reported in the Footprint data base

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(http://www.eu-footprint.org). According to the Footprint data base, $k_f$ may range from 0.26 and 27.1 while $n$ is reported as 0.8. During simulation we varied $k_f$ between 0.5 and 20 within 8 steps and allowed $n$ to vary within 0.2, 0.5, 0.8, 1.5, 2, 2.5, 3, and 5. We are aware that, in the case of behavioural adsorption, $n$ should be smaller or equal to one (please refer to Sect. 3.3 for further explanation).

As a first step we assumed that adsorption was uniform in the entire domain and selected the parameter set that performed best. Next we assigned these parameters exclusively to the macropore medium and characterised adsorption behaviour in the soil matrix with average parameters $n = 0.8$ and $k_f = 10$.

# 3 Results

## 3.1 Simulated and observed hydrographs

Figures 3, 4, and 5 present simulated discharge plotted against observed tile drain discharge (panels in the left column), time series of simulated and observed bromide concentrations (in the middle column) and cumulated bromide loss from the 13 simulations and plotted against the corresponding observation (right column). Simulated discharge is generally in very good accordance with the observations, except that the first discharge increase comes systematically too late during simulations. While Nash-Sutcliffe efficiencies are larger than 0.9 (compare Tables 2 and 3), some of the simulations (runs 7, 8, 11 and 13) have water mass balance errors that exceed 10%. Peak time errors are in general of the order of 7 or 17 min, corresponding to 1 or 2 model output time steps. Please note that discharge measurements during the irrigation experiment stopped 5 h after irrigation, although tile drain discharge was still approximately two times above the pre-event level. For additional details on the entire Monte Carlo study, especially on the sensitivity of predicted discharge on key parameters such as average density of worm burrows or maximum flow rates in macropores, please refer to Klaus and Zehe (2010).

## 3.2 Simulated and observed bromide concentration and mass flows

As can be seen from Fig. 1 or the panels in the middle column of Figs. 3, 4, and 5, observed bromide concentration peaked in the very first sample taken 36 min after irrigation onset. This first flush can be attributed to rapid preferential transport as no significant increase in discharge was detectable. Within the second irrigation block, 145 min after irrigation onset, bromide concentration levelled out at a concentration of 1.9 mg l$^{-1}$ for almost 40 min, then declined to a pretty constant value of around 1.2 mg l$^{-1}$.

Simulated bromide concentrations are calculated from the cumulated bromide loss within a model output time step, which is 10 min, divided by the accumulated water volume that left the model domain within this time. Simulated bromide concentrations are clearly more "noisy" than the observed ones. Although the simulated bromide concentrations are different among model runs, the temporal pattern is similar for all runs. Simulated concentrations show an early peak in the order of 0.5 to 2 mg l$^{-1}$ within the first 30 min, then decrease to zero or near zero values for all runs and re-rise again to values of about 2 mg l$^{-1}$. The observed peak at minute 36 is often reproduced as a double peak by the model. During the second irrigation block some simulations reproduce a concentration peak instead of a plateau concentration, while some runs capture this plateau. Simulated concentrations are in acceptable accordance with the observed ones during the last irrigation block. Overall, we can state that simulated concentrations match the magnitude of the observed ones and also roughly the timing of the peaks. Part of the mismatch might be attributed to the fact that rather small errors in simulated discharge (magnitude and timing) propagate to considerable errors in concentrations (magnitude and timing). However, as the model was not tuned to reproduce the observed concentration we did not expect a really good match in absolute concentrations on a time scale of minutes.

There is however a good accordance between the cumulated bromide losses derived from simulation when compared to the observed cumulated bromide loss (Figs. 3, 4 and 5, right column). Despite the fact that all simulations underestimate the observed

cumulated leaching within the early phase of the irrigation, simulation and observations are in very good linear accordance, as the coefficients of determination, $R^2$, are always larger than 0.95. Within the model runs 1, 4, 9 and 10, the simulation matches the observed accumulated bromide loss to the tile drain with a relative error in the order of 5–12%, which is within the error range of the observed data, 10% for discharge and 15% for bromide (compare Table 3). Table 3 lists furthermore the slope and intersect of a linear regression between observed and simulated cumulative bromide leaching; regression lines of model runs 1, 4, 9 and 10 are close to one. Thus we may state that the spatial model setups of 1, 4, 9 and 10 reproduce the observed time series of cumulated bromide loss in an almost unbiased manner. This is remarkable as the model has not been attuned for this purpose. Klaus and Zehe (2010) showed that the soil moisture dynamics followed a realistic pattern. Figure 6 presents the hillslope scale bromide concentrations at five different time points. The solute transport is driven by the generated macropore system, indicated by the distribution of the solute along lines from the soil surface down.

### 3.3  Simulated and observed cumulative leaching of IPU

We selected the model setup one (run 1) for simulating IPU transport as it performed best with respect to discharge and was ranked fourth with respect to reproducing cumulated bromide loss. Simulated and observed cumulated leaching of IPU is shown in Fig. 7, each panel corresponds to a case were $n$ was fixed at 0.2, 0.5 or 0.8 and $k_f$ was varied between 0.5 and 20. To put it in short, none of the simulations based on these parameterisations came anywhere close to the observed leaching behaviour. Retardation was clearly far too strong. Please note that the simulations are rather insensitive for the $k_f$. This finding is in accordance with observations during the irrigation experiment (Zehe and Flühler, 2001) who pointed out that the effective retardation coefficient of IPU against bromide was almost one. We therefore allowed for the $n$-values that exceeded one, because this ensures that retardation coefficients are decreasing towards one.

Figure 8 presents similar graphs to Fig. 7 for $n$-values 1.5, 2, 2.5, 3 and 5. A value of $n = 5$ allows a good match of the non-linear part of the cumulative leaching curve but leads to a vast overestimation of the total amount that leached into the tile drain. At value $n = 2.5$ the model result becomes rather sensitive for $k_f$. When selecting $k_f = 5$, the simulated curve does not match the dynamics but does match the observed overall loss within an error of 5.8%.

Finally, we allowed for different adsorption behaviour in the soil matrix and in the macropore medium. We selected $n = 0.8$ for the soil matrix and $n = 2.5$ in the macro-pores and varied $k_f$ values according the scheme outlined above. Heterogeneous adsorption caused a slight "damping" of the cumulated leaching curves, while the shape remained unchanged (Fig. 9). We may thus state that without any prior knowledge about the retardation behaviour, simulated leaching is way off the observations. When such information is available, as in the present case, the model can be attuned to reproduce the overall amount that leached to the tile drain, while the dynamics is hardly reproduced.

## 4 Discussion and conclusion

### 4.1 "Preferential structures" for preferential transport

The proposed approach to represent macropores, or more precisely anecic earthworm burrows, as morphologically connected structures in a 2-D model domain (Klaus and Zehe, 2010; Zehe et al., 2010a) is feasible to:

– Setup several spatial hillslope architectures that are consistent with detailed field observations, especially on the density and depth distribution of worm burrows and to reproduce observed tile drain discharge (see also Klaus and Zehe, 2010).

– The 13 best hillslope architectures, which achieved a Nash-Sutcliffe efficiency larger than 0.9 in combination with a small peak time error, predicted dynamics of

accumulated bromide leaching into the tile drain well ($R^2 > 0.95$) without additional calibration.

Four of those hillslope architectures (run 1, 4, 9 and 10) matched the total accumulated water balance (compare Table 3) within the relative error range of 10% according to Zehe and Flühler (2001). It is remarkable that the same hillslope architectures also matched the total amount of bromide that leached into the tile drain within the range of the observation errors (please note that due to Gaussian error propagation, the relative error of the bromide mass flow at the tile drain outlet equals the sum of the relative errors in discharge (10%) and bromide concentrations (5%)). We may thus state that only four of the 432 hillslope architectures tested in the study of Klaus and Zehe (2010) matched both flow dynamics and bromide leaching very well and in an unbiased manner.

However, the proposed model structures are, without additional calibration, unable to reproduce exactly the time series of bromide concentrations, but do capture the order of magnitude of the concentrations. Bromide concentrations and mass flows in the first phase of the irrigation experiment are systematically underestimated. A closer look at model runs 1, 4, 9 and 10 reveals that predicted concentrations match the observations in later stages ($t > 100$ min) in an acceptable manner. Run 4, which performs best with respect to the overall bromide mass balance, and run 1 capture even the magnitude of the maximum observed bromide concentration, although the timing is roughly 50 min too late. This is consistent with the fact that first discharge reactions within the model are also systematically 50 min too late (except for run 9 and 10).

Transport velocities and bromide concentration in the model are obviously both too small to match the first flush of bromide into the tile train. One possible explanation for this is that the proposed approach is too slow to capture the obviously very fast initialisation of macropore flow in the real system. This might be true, but note that simulated first arrivals of bromide are around 10 min (compare Figs. 3, 4 and 5), which is deemed to be rather fast. Another likely explanation is that we simulate a spatially homogeneous irrigation, while Zehe and Flühler (2001) reported that their irrigation

scheme was rather heterogeneous shortly after bromide application: a lot of irrigation water with a large amount of bromide concentrated along the middle axis of the 30 by 30 m$^2$ large irrigation site (compare their Fig. 12). These locally increased irrigation and mass inputs could, according to Weiler and Naef (2003), cause fast preferential flow
5    rates and enhance mass transport into the tile drain and result in the observed first flush. This effect cannot be reproduced by simulating (a) an homogeneous irrigation and (b) neglecting the microtopography that determines local scale lateral redistribution of ponded irrigation water. We have neither information about the exact spatial pattern of irrigation rates nor details on microtopography (which would be rather difficult to
10   include into a 2-D model). We thus omit any trial to reproduce this first flush effect within a simulation, as the underlying assumption would be rather speculative.

As CATFLOW is a 2-D model, predicted discharge is length specific and model output has thus to be scaled to 3-D reality by specifying the width of the irrigated site that feeds tile drain discharge. As elaborated in Klaus and Zehe (2010) we selected this
15   drained width such that the simulated peak discharge matched the observed peak discharge. As these values, which are in the order of 1–3 m (compare Table 2), were kept constant in the present study, we may state that the same scaling factor allows simulation of flow and transport in a consistent manner. This corroborates that this factor is more than a "quick fix" to reproduce water flows, but is related to the real width of the
20   irrigation site that contributed to the tile drain water flow and bromide mass flows.

We thus overall conclude that:

  – A realistic representation of dominating structures and their topology is of key importance for predicting preferential water and mass flows at tile drained hillslopes. This requires detailed knowledge about the topology of preferential flows paths –
25      which is simple in the present case of anecic worm burrows.

  – Those hillslope architectures that perform best with respect to the integral discharge response are also suitable for predicting dynamics of accumulated bromide leaching, partly without a bias. This finding is clearly opposite to what has

been achieved by Haws et al. (2005) but in accordance with the finding of McGuire et al. (2007).

## 4.2 Simulations of pesticides transport as a remaining challenge

Even if the model structure has been shown to reproduce both discharge and bromide transport behaviour, the reproduction of the observed accumulated leaching for IPU was rather challenging. An "orthodox" parameterisation of the Freundlich isotherm based on values reported in the Footprint data base (www.eu-footprint.org) did not reveal any meaningful result. Based on the finding of Zehe and Flühler (2001) at this site, who report an effective retardation coefficient of one at the end to the experiment and similar findings of Kung et al. (2000) who found similar behaviour for bromide and the sorbing tracer rhodamin WT, we allowed for $n$ values larger than one, which reduced retardation coefficients to values close to one. Model runs using a values of $n = 3$ and $n = 5$ were able to reproduce the timing and dynamics of leaching but overestimated the total amount that leached into the brook, while a parameterisation of $n = 2.5$ produced dynamics which were too slow but did capture the overall amount that leached into the brook. With a parameterisation of $n = 2.5$ and $k_f = 5$, a mass balance error of 5.8% could be achieved. A heterogeneous parameterisation of adsorption parameter that differed between the soil matrix and the connected flow paths (e.g. as suggested by Ray et al., 2004) did not lead to a clear improvement. The retardation characteristics of the soil at the study site are probably more heterogeneous, both in the soil matrix and the soil macropores, when considering effects like macropore coating (e.g. Gerke, 2006).

A possible explanation that simulated first breakthroughs are 50 min too late might be the fact that Zehe and Flühler (2001) explained the first flush of pesticide as being facilitated transport by colloids (de Jonge et al., 1998; de Jonge et al., 2004; Villholt et al., 2000). This process cannot be captured with the proposed model. Overall, we may state that a simulation of pesticide transport is, without having detailed local data on the adsorption characteristics in different subsurface compartments (e.g. Mallawatantri

et al., 1996; Larsbo et al., 2009), largely an unsatisfying issue of trial-and-error, even when using data from the Footprint data base.

## 4.3 Equifinality of spatial hillslope structures

Several networks of worm burrows allow us to produce an integrated system response, i.e. dynamics of water flow and of accumulated bromide leaching, although the set of best model structures can be boiled down to four (runs 1, 4, 9, 10) by taking the water and the bromide mass balances into account. Also, McGuire et al. (2007) were able to reduce model uncertainty and increased parameter identifiability by the additional use of tracer data in the hillslope model used, (Hill-vi, Weiler and McDonnell, 2004), compared to a singular calibration on discharge data. Figure 10 shows the relative difference between simulated and observed cumulated bromide leaching plotted against the Nash-Sutcliffe efficiency (left panel) and against the water balance error (right panel). As there is no clear relationship between these quality criteria, all of them have to be evaluated to reject non behavioural model setups.

Prior to this study, we were not sure whether the proposed way of treating macropores and scaling the 2-D model domain is feasible at all. We thus did not selected criteria for model rejection a priori, as it is recommended by Beven (2010) for hypothesis testing. However, based on the now available knowledge, we propose the following two-stage procedure for rejecting model structures:

- Select those hillslope architectures as behavioural that reproduced tile drain discharge with a Nash-Sutcliffe efficiency larger than 0.9 and match the water balance within the error range (10%). Thus runs 7, 8, 11 and 13 would be rejected.

- Select from the behavioural hillslope architectures of the previous stage those that match dynamics of accumulated bromide leaching with a coefficient of determination larger than 0.9 and match the bromide mass balance within the error range (15%). Thus runs 2, 3, 5, 6, 8, 11, 12 and 13 would be rejected.

From this we conclude:

– The number of hillslope architectures that are behavioural with respect to reproducing tile drain discharge dynamics can be reduced by using orthogonal data sources such as tracer data (McGuire et al., 2007; Klaus et al., 2008) and analyzing the mass balances.

– Generic knowledge about the origin of dominating structures is crucial to reproduce these structures in a simplified yet a sufficiently realistic manner and thus reduce equifinality in the spatial model setup to a minimum amount.

Nevertheless, in our case four behavioural hillslope architecture structures remain. Probably we have to accept that a possible cause of equifinality is that part of the indeterminacy may be essentially system inherent, in the sense that several types of architectures of subsurface flow pathways may yield the same integral response in discharge and mass flows.

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**A novel explicit approach to model bromide and pesticide transport**

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**Table 1.** Soil hydraulic parameters determined by Schäfer (1999). $S$: specific storage coefficient of the soil [–], $k_s$: saturated hydraulic conductivity [m s$^{-1}$], $\theta_s$: saturated vol. soil moisture [–], $\theta_r$: residual vol. soil moisture [–], $\alpha$: reciprocal air entry point [m$^{-1}$], $n$: quantity characterising the pore size distribution [–], $\rho$: bulk density [kg m$^{-3}$].

| Parameter | Colluvisol subsoil | Colluvisol plow horizon 0–10 cm | Colluvisol plow horizon 10–35 cm | Macropore medium |
|---|---|---|---|---|
| $S$ | $5 \times 10^{-3}$ | $5 \times 10^{-3}$ | $5 \times 10^{-3}$ | $1.1 \times 10^{-1}$ |
| $k_s$ | $5 \times 10^{-5}$ | $5 \times 10^{-4}$ | $2.7 \times 10^{-5}$ | variable |
| $\theta_s$ | 0.4 | 0.46 | 0.43 | 0.4 |
| $\theta_r$ | 0.04 | 0.1 | 0.11 | 0.057 |
| $\alpha$ | 1.9 | 2.4 | 3.8 | 11.4 |
| $n$ | 1.25 | 1.22 | 1.2 | 2.28 |
| $\rho$ | $1.50 \times 10^{3}$ | $1.3 \times 10^{3}$ | $1.59 \times 10^{3}$ | $1.6 \times 10^{3}$ |

**Table 2.** Parameters and goodness of fit criteria to characterise the 13 model setups. NS: is the Nash-Sutcliffe efficiency, DT: differences between modelled and simulated time to peak, NP: number of macropores per unit area [m$^{-2}$], MWF: maximum volumetric water flow in a macropore [m$^3$ s$^{-1}$], IMC: initial moisture conditions (the wet case corresponds to a suction head of $-50.66$ hPa throughout the profile; the intermediate case had a suction head of $-303.98$ hPa in the upper 40 cm of the profile and $-101.33$ hPa below this layer; the dry setting corresponds to a head of $-405.3$ hPa in the upper 40 cm of the profile and $-151.99$ hPa in the remaining soil profile), $k_D$ tile drain conductivity [cm s$^{-1}$], GW: Groundwater occurrence, C-Sec: drained width of the cross-section in meters adjusted to match the peak.

| run | NS | DT | NP | MWF | IMC | GW | $k_D$ | C-Sec |
|-----|-----|-----|-----|---------|--------------|-----|------|-------|
| 1 | 0.952 | 7 | 30 | 7.90E-06 | wet | yes | 20.3 | 0.832 |
| 2 | 0.948 | 7 | 10 | 1.33E-05 | wet | yes | 2.03 | 2.114 |
| 3 | 0.942 | 7 | 10 | 1.33E-05 | wet | no | 2.03 | 2.146 |
| 4 | 0.941 | 7 | 30 | 7.90E-06 | wet | no | 20.3 | 0.815 |
| 5 | 0.934 | 7 | 30 | 7.90E-06 | wet | no | 2.03 | 1.588 |
| 6 | 0.932 | 7 | 30 | 7.90E-06 | wet | yes | 2.03 | 1.588 |
| 7 | 0.923 | 7 | 10 | 1.33E-05 | intermediate | yes | 20.3 | 1.989 |
| 8 | 0.917 | 17 | 10 | 1.33E-05 | dry | no | 20.3 | 2.243 |
| 9 | 0.914 | 7 | 10 | 1.33E-05 | wet | yes | 20.3 | 1.335 |
| 10 | 0.907 | 7 | 10 | 1.33E-05 | wet | no | 20.3 | 1.330 |
| 11 | 0.904 | 7 | 30 | 1.33E-05 | dry | yes | 20.3 | 0.697 |
| 12 | 0.901 | 17 | 10 | 1.33E-05 | intermediate | yes | 2.03 | 3.079 |
| 13 | 0.9 | 7 | 30 | 1.33E-05 | intermediate | yes | 20.3 | 0.673 |

**Table 3.** Number of model run, Nash-Sutcliffe efficiency (NS) of hydrograph modelling, relative water balance error in % (WB), relative error in bromide mass balance in % (BMB), the slope of the regression line fitted to the compared cumulative transport of measured and modelled values ($m$), the intercept of the regression line ($b$) and the corresponding coefficient of determination ($R^2$).

| run | NS | WB | BMB | $m$ | $b$ | $R^2$ |
|---|---|---|---|---|---|---|
| 1 | 0.952 | −6.5 | −13.47 | 0.876 | −0.946 | 0.972 |
| 2 | 0.948 | 0.31 | 23.63 | 1.37 | −0.743 | 0.981 |
| 3 | 0.942 | −0.77 | 25.74 | 1.375 | −0.745 | 0.983 |
| 4 | 0.941 | −6.86 | −10.97 | 0.902 | −0.998 | 0.972 |
| 5 | 0.934 | 1.6 | 35.39 | 1.394 | −1.245 | 0.983 |
| 6 | 0.932 | 2.04 | 32.69 | 1.365 | −1.112 | 0.983 |
| 7 | 0.923 | −13.06 | 14.55 | 1.241 | −0.983 | 0.977 |
| 8 | 0.917 | −19.03 | 21.28 | 1.306 | −0.773 | 0.98 |
| 9 | 0.914 | −5.05 | −11.34 | 0.957 | −0.644 | 0.984 |
| 10 | 0.907 | −7.5 | −12.64 | 0.956 | −0.672 | 0.983 |
| 11 | 0.904 | −16.3 | −29.36 | 0.724 | −1.046 | 0.95 |
| 12 | 0.901 | −8.19 | 63.06 | 1.804 | −1.117 | 0.974 |
| 13 | 0.9 | −17.87 | −30.93 | 0.711 | −1.039 | 0.95 |
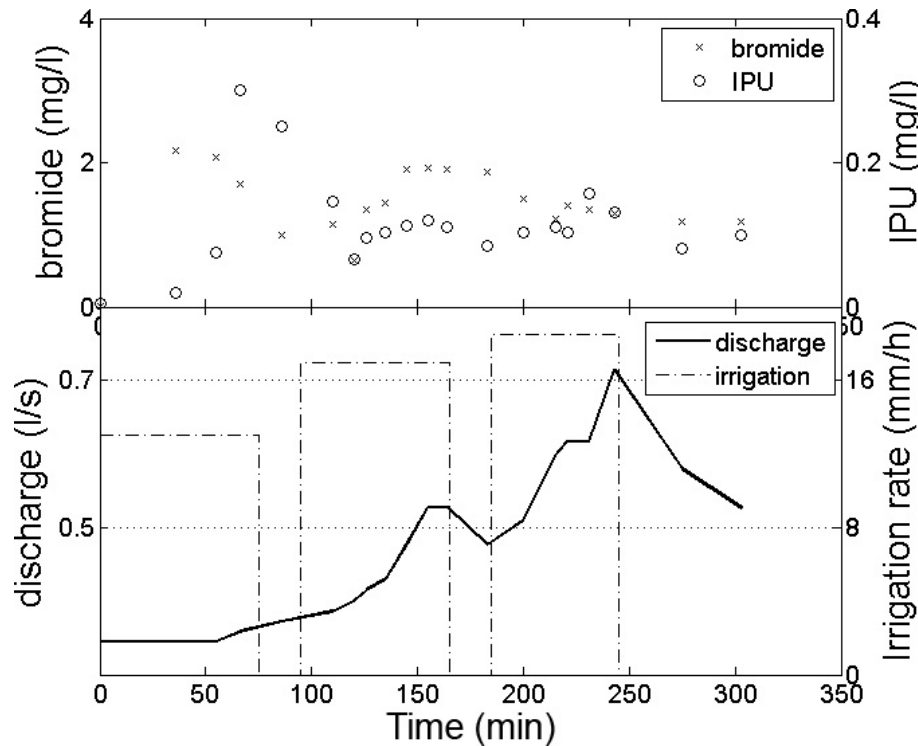
**Fig. 1.** The experimental results from the study of Zehe and Flühler (2001). The upper panel presents the bromide and Isoproturon (IPU) concentrations, while the lower panel presents the tile drain discharge and the irrigation rate.
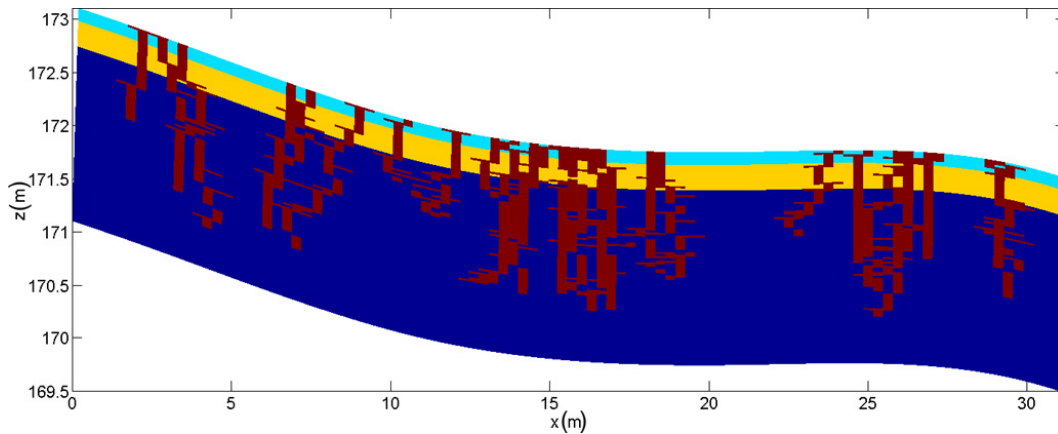
**Fig. 2.** One of the model setups. Hillslope with different soil layers and the macropores as explicit structures (red).
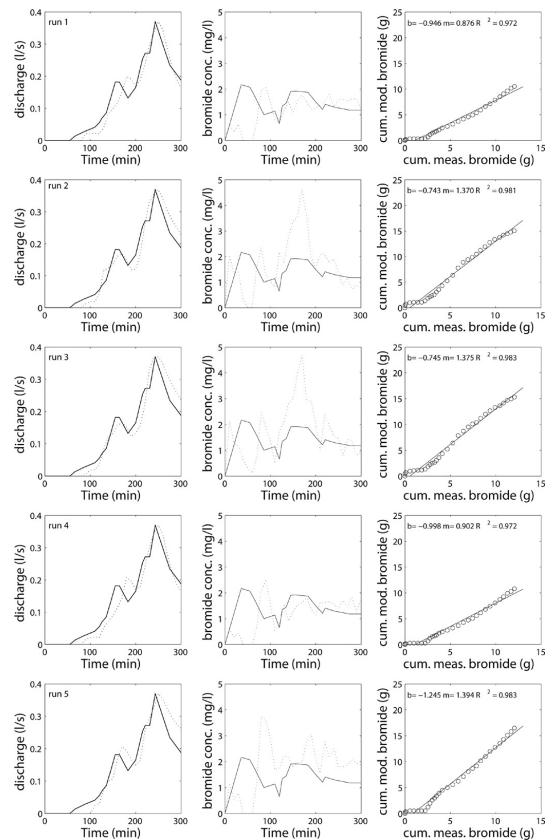
**Fig. 3.** The left column presents the observed discharge (solid line) and the modelled discharge (dotted line), the centre column presents the observed (solid line) and modelled (dotted line) bromide concentrations in the tile drain, while the right column presents the cumulated modelled bromide outflow versus the measured one and a linear regression line between them (*b* denotes the intersect and *m* the slope of the regression). The runs 1 to 5 are shown here.
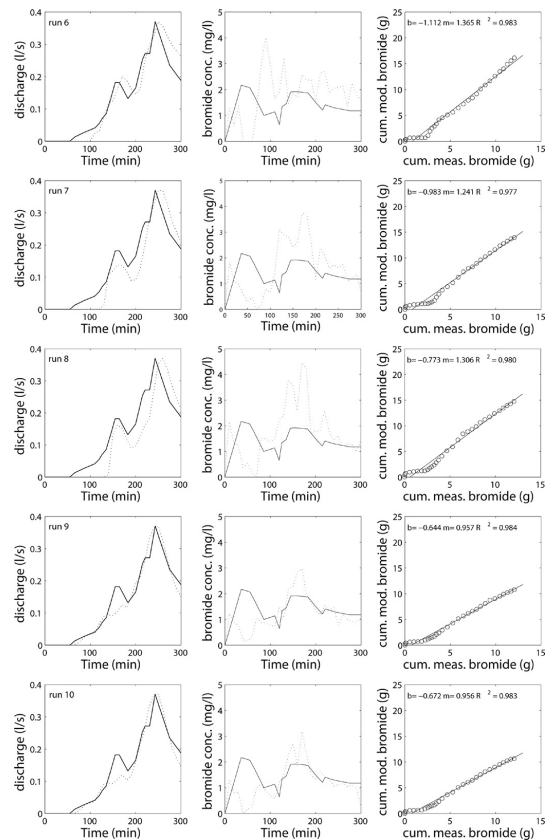
**Fig. 4.** The left column presents the observed discharge (solid line) and the modelled discharge (dotted line), the centre column presents the observed (solid line) and modelled (dotted line) bromide concentrations in the tile drain, while the right column presents the cumulated modelled bromide outflow versus the measured one and a linear regression line between them ($b$ denotes the intersect and $m$ the slope of the regression). The runs 6 to 10 are shown here.

**Fig. 5.** The left column presents the observed discharge (solid line) and the modelled discharge (dotted line), the centre column presents the observed (solid line) and modelled (dotted line) bromide concentrations in the tile drain, while the right column presents the cumulated modelled bromide outflow versus the measured one and a linear regression line between them (*b* denotes the intersect and *m* the slope of the regression). The runs 11 to 13 are shown here.

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Interactive Discussion
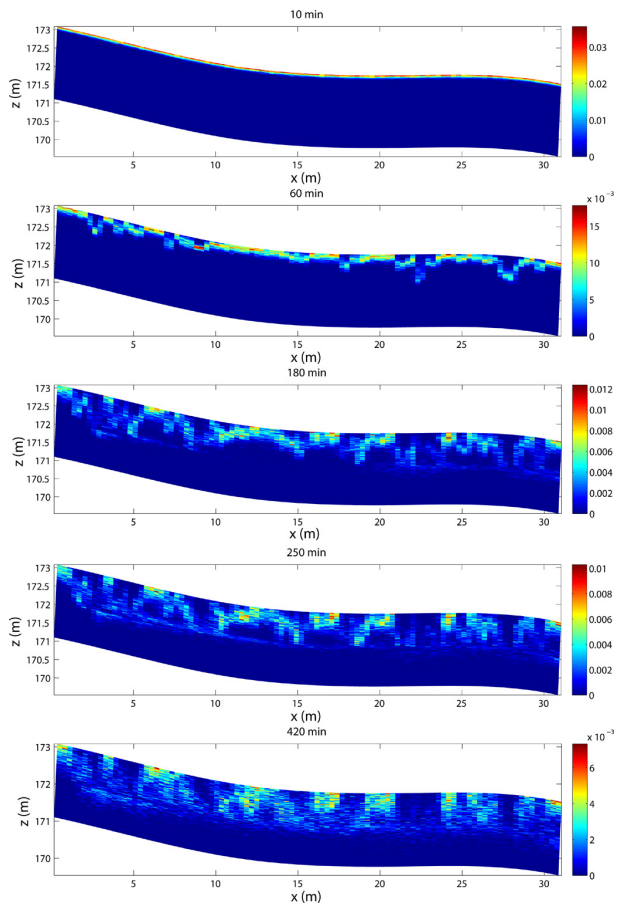
**Fig. 6.** Bromide concentrations ($g\,kg^{-1}$ dry soil) in the model domain, and the development over time. Please note that the concentrations are plotted for a 30 m wide hillslope, and that the colour scale changes over time.

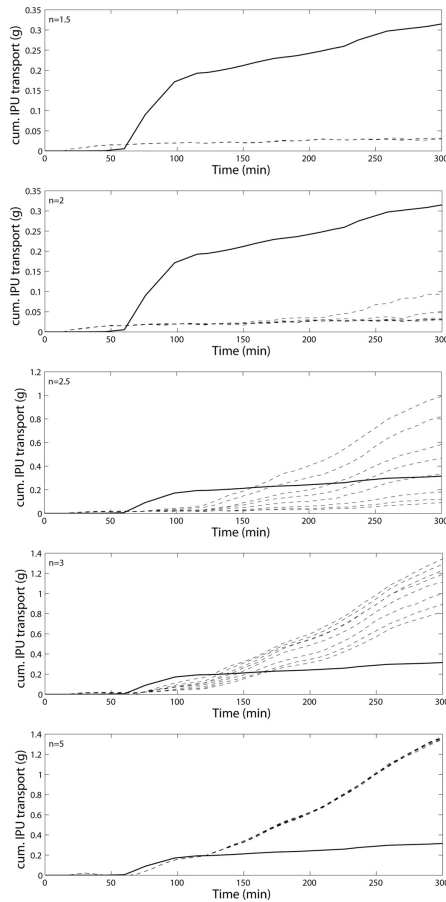Printer-friendly Version

Interactive Discussion
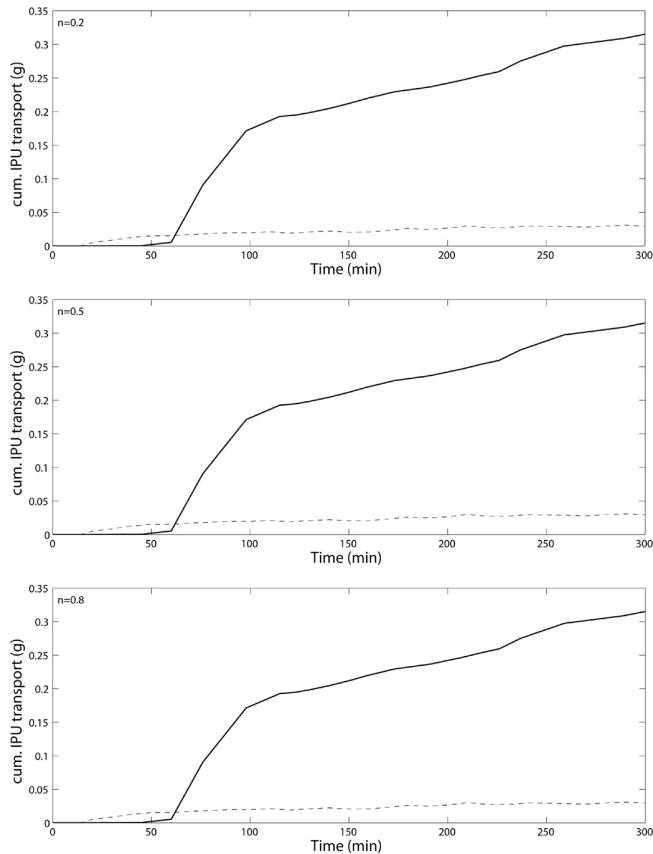
**Fig. 7.** Cumulated IPU loss plotted against simulation time for different parameterisations of the Freundlich isotherm. The solid line presents the observed IPU leaching, the dashed lines model runs with different parameterisation of the Freundlich parameters. Every plot includes eight model realisations with a fixed value for the Freundlich exponent $n$ and varied values for the Freundlich coefficient $k_f$ between 0.5 and 20 within 8 steps.

**Fig. 8.** Cumulated IPU loss plotted against simulation time for different parameterisations of the Freundlich isotherm. The solid line presents the observed IPU leaching, the dashed lines model runs with different parameterisation of the Freundlich parameters.. Every plot includes eight model realisations with a fixed value for the Freundlich exponent $n$ (in this realisation exceeding 1) and varied values for the Freundlich coefficient $k_f$ between 0.5 and 20 within 8 steps.
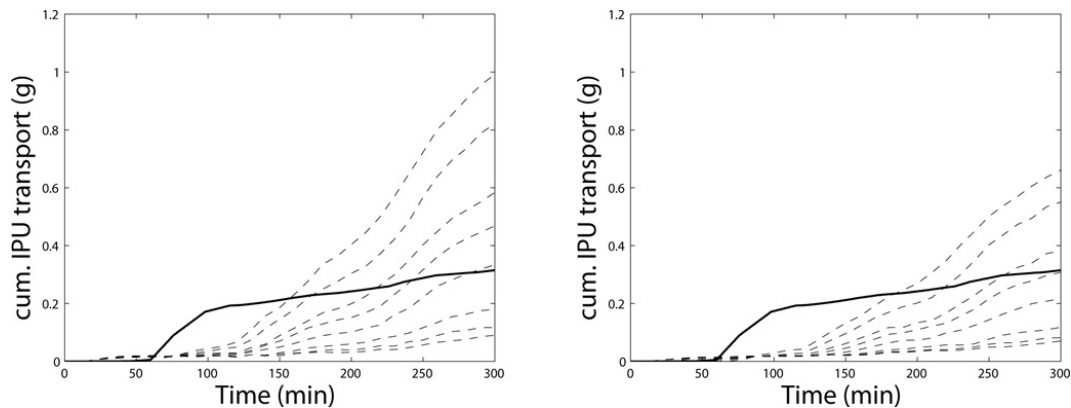
**Fig. 9.** Modelling IPU transport with spatial homogenous (left) and spatial heterogeneous (right) sorption parameter. The solid black line denotes the sampled cumulative breakthrough curve, the dashed lines display the modelled breakthrough curves.
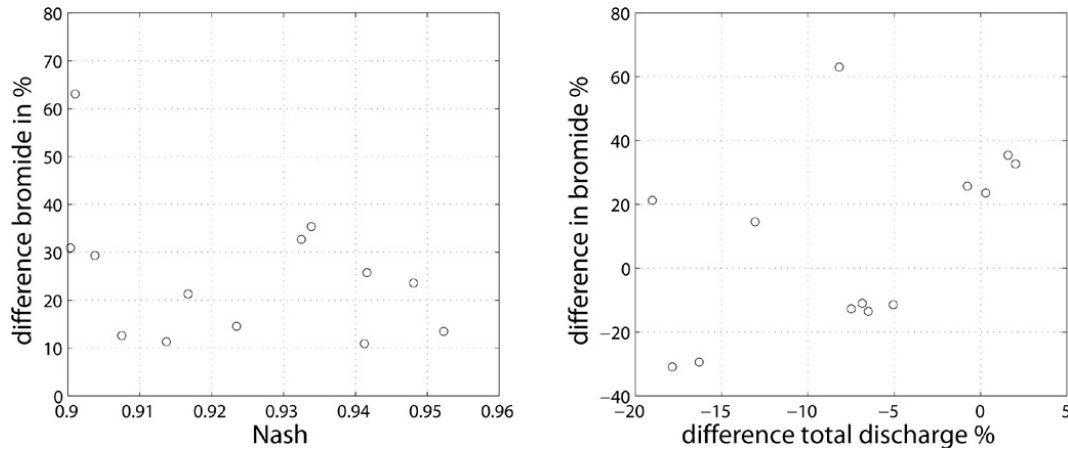
**Fig. 10.** Left panel: Differences in bromide (observed to modelled) versus the Nash-Sutcliffe efficiency of the discharge modelling. Right panel: Differences in total modelled bromide versus total observed bromide concentrations differences in total modelled to total observed discharge.