

TECHNICAL REPORT

Environmental Models, Modules, and Datasets

Long-term sulfamethazine leaching simulation in two different soils using the MACRO model

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Abstract

Physically based models have been part of many risk assessment studies concerning pesticide or nutrient transport within (sub)catchments or at plot scale, but they are only poorly validated for simulating the transport of veterinary medicinal products. Veterinary medicinal products not only pose a risk to the quality of our waters but also tend to accumulate in soils, where they are associated with the appearance of resistant bacteria and long-term leaching. In this study, the physically based leaching model MACRO 5.2 was applied for simulating sulfamethazine (SMZ) transport over a period of more than 10 yr. The model was set up using reversible kinetic adsorption and equilibrium adsorption forming non-extractable residues. Two different calibration periods were used to estimate uncertainties in predicted SMZ leaching associated with calibration based on short-term data. Using the whole period for model calibration, SMZ leaching could be simulated adequately, but parameter ranges were wide due to correlation between the parameters. When using only the first period for calibration, the quality of the prediction strongly depended on the information content of the data set. The calculation of temporal sensitivity indices revealed that the effect of complex sorption parameters on the model output increased with time. Thus, parameters that appeared insensitive in a short-term calibration were required for reliable long-term simulations. In conclusion, a temporal sensitivity analysis beyond the calibration period might identify parameters that were not constrained enough by the calibration procedure. This could help to confirm leaching predictions even for periods without sampling data.

Abbreviations: KGE', modified Kling–Gupta efficiency; LOD, limit of detection; LOQ, limit of quantification; NER, non-extractable residue; OC, organic carbon; PCC, partial correlation coefficient; PRCC, partial rank correlation coefficient; SMZ, sulfamethazine.

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1 | INTRODUCTION

The use of antibiotics-containing veterinary drugs in intensive livestock and the spreading of manure from such facilities for fertilizing purposes lead to the distribution of pharmacologically active substances within the aquatic environment (Halling-Sørensen et al., 1998; Hamscher & Mohring, 2012; Spielmeyer, 2018). In addition to the transport of dissolved substances via runoff to surface water bodies (Burkhardt et al., 2005; Kay et al., 2005; Knäbel et al., 2016) or via leaching to groundwater (Boxall et al., 2002; Hamscher et al., 2005) being of concern, the accumulation of adsorbed substances on soil particles and a slow leaching over several years are considered highly relevant (Kay et al., 2004; Spielmeyer et al., 2017, 2020).

A commonly administered antibiotic substance is the sulfonamide sulfamethazine (SMZ). Sulfamethazine is regularly detected in manure and slurry (Haller et al., 2002; Martínez-Carballo et al., 2007; Spielmeyer, 2018), soils (Hamscher & Mohring, 2012; Hamscher et al., 2002; Martínez-Carballo et al., 2007; Thiele-Bruhn, 2003), surface waters (Christian et al., 2003), and groundwater samples (Hamscher et al., 2005; Hirsch et al., 1999).

Sulfamethazine ionizes depending on the soil pH at pKa and pKb values of 2.65 and 7.65, respectively (Tolls, 2001). Whereas the neutral form of SMZ shows an affinity to sorb onto soil organic material via hydrophobic partitioning (Lertpaitoonpan et al., 2009), the cationic SMZ is more likely to be bound to negatively charged clay particles via cation exchange (Gao & Pedersen, 2005; Srinivasan et al., 2014). Higher pH values, on the other hand, lead to more negatively charged, less sorptive SMZ (Gao & Pedersen, 2005; Park & Huwe, 2016).

The complex long-term transport and transformation processes of SMZ are not yet fully understood, leading to different hypotheses about its retention in soils. Sulfamethazine has been found to be one of the most leachable veterinary antibiotics (Leal et al., 2013; Park & Huwe, 2016; Spielmeyer et al., 2017, 2020; Srinivasan et al., 2014). At the same time, its environmental behavior is associated with a fast dissipation and low recovery rates from soils (Bailey et al., 2016). This can be attributed to biodegradation (Accinelli et al., 2007; Fan et al., 2011) or abiotic processes, such as hydrolysis or photolysis (Białk-Bielińska et al., 2012; Biošić et al., 2017), but also to the analytical methods, which might not be harsh enough to extract the adsorbed SMZ from the soil matrix (Bailey et al., 2016; Kreuzig & Höltge, 2005; Nurk et al., 2019; Rosendahl et al., 2011). Existing long-term experiments under field conditions, however, showed evidence for an accumulation in soils and a later leaching (Aust et al., 2008; Hamscher et al., 2005; Spielmeyer et al., 2017, 2020; Stoob et al., 2007).

Core Ideas

- The MACRO model was successfully used to simulate long-term SMZ leaching.
- A high information content of short-term SMZ leaching data was key to successful long-term simulations.
- The effect of environmental fate parameters (sorption, degradation) on the model outcome may change over time.
- Implementing complex sorption processes was mandatory for SMZ long-term simulation.
- Temporal sensitivity analysis beyond the calibration span may detect parameters required for long-term simulation.

This supports the assumption that both reversible sorption and the formation of non-extractable residues (NERs), rather than mineralization, might be the main contributors to the dissipation of SMZ. A long-term behavior like this, however, cannot be captured by short-term laboratory experiments.

Leaching models are mainly used for simulating pesticide fate in soil and are applied in risk assessment (Fait et al., 2010; Giannouli & Antonopoulos, 2015; Jarvis, 1995; Lindahl et al., 2005; Scorza Júnior & Boesten, 2005; Scorza Júnior et al., 2007). Until now, only a few studies applied such models to simulate the transport and transfer of pharmaceuticals (García-Santiago et al., 2017; Larsbo et al., 2009) or veterinary antibiotics (Conde-Cid et al., 2019; Larsbo et al., 2008; Wehrhan et al., 2007; Zarfl et al., 2009), even though this can be a method to assess long-term leaching potential. Some studies already simulated SMZ within different contexts, including transport in surface runoff (Knäbel et al., 2016; Larsbo et al., 2008) or leaching through soil columns (Fan et al., 2011; Park & Huwe, 2016). A long-term leaching simulation over several years, providing environmental fate information beyond short-term experiments, has not been performed.

In this study, the observations of a long-term lysimeter study over 10 yr, performed on two different soils, were used for model setup, calibration, and validation of the physically based MACRO 5.2 model (Jarvis & Larsbo, 2012). The MACRO model was chosen because complex sorption behavior can be taken into account (Larsbo & Jarvis, 2003; Larsbo et al., 2005).

This study sought to answer two major questions: (a) Can the long-term behavior of SMZ be represented by the MACRO model? and (b) Are short measurement campaigns sufficient for forecasts of future leaching?

2 | MATERIALS AND METHODS

2.1 | Experimental data

The data used in this study originated from a lysimeter study performed between 2009 and 2019 on two different soils, both located in agricultural fields in Lower Saxony, Germany (Hamscher et al., 2013; Spielmeyer et al., 2017, 2020). During an initial period of 2 yr, SMZ-containing manure was applied five times in total (Supplemental Table S1).

Due to their soil structures (Supplemental Table S2), both locations have a high risk of fast substance leaching to the groundwater. At Site A (Jühnde), the 1-m-deep, clayey soil with a percentage of rock fragments up to 52% supports the formation of macropores. The sandy soil at Site B (Hohenzethen) shows generally less macroporosity but tends to have a lower water retention capacity and thus a high leaching potential for solved substances. The pH value and the amount of organic carbon (OC) are both lower on Site B (pH, 4.6–5.5; C_{org} , 0.04–1.01%) compared with Site A (pH, 7.4–7.6; C_{org} , 0.91–2.59%).

Sulfamethazine concentrations were determined in the lysimeter outflow once every week directly after the application. Later, the sampling frequency was decreased to 2 wk. Between January 2013 and spring 2015, percolation rates were measured, but no SMZ concentrations were measured. For SMZ, the limit of detection (LOD) was 2 ng L⁻¹, and the limit of quantification (LOQ) was 10 ng L⁻¹. The majority of samples are in this range, leading to high uncertainties concerning the load transported through the soil.

2.2 | Model description

MACRO is a one-dimensional solute transport model with a focus on macropore flow. By considering and coupling two flow domains in the vadose zone, it can be classified as a dual-permeability model (Jarvis & Larsbo, 2012; Larsbo & Jarvis, 2003; Larsbo et al., 2005).

Water transport through the soil matrix is calculated with the Richards equation, considering a source-sink term for root water uptake or water exchange between matrix and macropores. The Mualem–van Genuchten model is used to describe the soil hydraulic properties (Larsbo & Jarvis, 2003; Larsbo et al., 2005). Transport through macropores is based on gravity, using the kinematic wave equation (Larsbo & Jarvis, 2003). When the water content in the matrix reaches a defined saturation, any excess water is diverted instantaneously to the macropores. If the water content in the matrix decreases, water is transferred back to the matrix from the macropores. This process takes place depending on the diffusivity of soil water D_w (m² s⁻¹), the matrix water deficit ($\theta_{\text{sat}} - \theta_{\text{mi}}$) (–), a scaling factor γ_w (–), and the effective diffusion path length

d (mm), which is a factor summarizing macropore-specific aspects like geometry, size, and surface characteristics (Šimůnek et al., 2003).

Pollutant transport through the soil matrix is described by the convection–dispersion equation, considering a source-sink term U . This term includes all processes that lead to a loss or gain of substance (e.g., kinetic adsorption and desorption, degradation, or plant uptake). Mass exchange between both flow domains is calculated analogue to the water diffusion equation with an additional term for convective flow (Larsbo & Jarvis, 2003).

The Freundlich isotherm is used for describing equilibrium sorption.

$$s = K_f \cdot c_{\text{soil}}^n \quad (1)$$

By including kinetic sorption, a chemical non-equilibrium can be considered. The amount of kinetically adsorbed solute A_k (g m⁻³) is dependent on a defined fraction of kinetic sorption sites f_{kin} (–); a first-order transfer coefficient $\alpha_{\text{kin}} = [\ln(2)/DT_{50\alpha_{\text{kin}}}]$ (d⁻¹), describing the transfer velocity between the two sorption sites; and the current amount of substance adsorbed to equilibrium sorption sites at every time step.

$$U_k = \frac{\partial A_k}{\partial t} = \alpha_{\text{kin}} \left(\gamma s - \frac{A_k}{f_{\text{kin}}} \right) \quad (2)$$

where γ is the soil bulk density (kg m⁻³), and s is the solute concentration in the solid phase (kg kg⁻¹).

First-order degradation rates can be defined separately for each soil layer. MACRO also distinguishes between degradation in the liquid and solid phase and in matrix and macropores, respectively. Kinetic sorption sites can be excluded from degradation. A more detailed description can be found in the technical manual by Larsbo and Jarvis (2003).

2.3 | Model setup, calibration strategy, and parametrization

A model warm-up period of 6 mo was chosen. The lower boundary condition was defined as a lysimeter with free drainage. The soil solute concentration for SMZ was set to zero prior to the first application (Hamscher et al., 2013).

Forcing input data were obtained from meteorological stations installed on both sites. These data included wind speed at 4 m height above the ground, precipitation, solar radiation, air temperature, and vapor pressure. To account for measurement errors, the Richter correction factor was applied to the precipitation data (Richter, 1995). An annual crop rotation was included. Crop parameters were taken from the FOCUS groundwater scenarios (FOCUS, 2014) and were adjusted

TABLE 1 Prior ranges of substance parameters

Parameter	Description	Site A	Site B
n	Freundlich exponent (–)		0.61–1.1 ^{a,b,c,d}
K_{fOC}	organic C-normalized sorption coefficient, L kg ⁻¹	36–476 ^{a,b,c,d}	149–579 ^{a,b,c,d}
f_{kin}	fraction of kinetic sorption sites (–)		0.05 – 0.95 ^e
$DT_{50,kin}$	half-life transfer to/from kinetic sorption sites, d		1 – 720 ^e
$DT_{50,NER}$	half-life soil, d		1 – 365 ^e
$DT_{50,bio}$	half-life soil water, d		1 – 365 ^e
DV	dispersivity, cm		2 – 12 ^f

^aKurwadkar et al. (2007).

^bLeal et al. (2013).

^cLertpaitoonpan et al. (2009).

^dPark and Huwe (2016).

^eEstimated.

^fPerfect et al. (2002).

according to the management practice on the field site, such as additional irrigation at Site B.

Hydrological calibration included saturated micropore hydraulic conductivity, the boundary pressure between micro- and macropores, the site albedo, and the minimal stomatal resistance of all plants. All other plant and site parameters, as well as the soil parameters that were calculated by the pedo-transfer functions implemented in MACRO, were fixed. The complete MACRO setup and all values included in the calibration process for percolation can be found in Supplemental Tables S3–S7.

Table 1 summarizes all parameter ranges included in the calibration process for SMZ transport. Because soil pH values vary only slightly within each of the soils, whereas OC is more variable, we chose the Freundlich isotherm, which was calculated from the OC-normalized sorption coefficient K_{fOC} , to represent equilibrium sorption. Sorption coefficients were chosen based on values measured on soils with similar characteristics as the ones of this study (Table 1). Due to the lower soil pH at Site B, sorption coefficients are slightly higher on this site.

Temperature- and moisture-independent degradation rates in micro- and macropores were included in the liquid phase ($DT_{50,bio}$) as well as equilibrium sorption sites ($DT_{50,NER}$). The term $DT_{50,bio}$ represents biological degradation (Bailey et al., 2016), which was assumed to take place in the liquid phase (Fan et al., 2011; Harms & Bosma, 1997). It decreases with depth, according to Boesten and Linden (1991). The term $DT_{50,NER}$ represents all processes that lead to the observed dissipation of the substance, such as the formation of NERs. A similar approach was used by Larsbo et al. (2008) and Gassmann et al. (2021). Regarding the complex sorption characteristics, a kinetic sorption was included as well. Degradation on kinetic sorption sites was switched off. With this approach, a non-equilibrium sorption with hysteresis of desorption could be simulated.

Calibration was performed based on Monte Carlo simulations, sampling from a uniform parameter distribution in the ranges given in Table 1. The likelihood of a certain parameter set was assessed by a modified Kling–Gupta efficiency (KGE') (Gupta et al., 2009; Kling et al., 2012):

$$KGE' = 1 - \sqrt{(r - 1)^2 + (\beta - 1)^2 + (\gamma - 1)^2} \quad (3)$$

r = correlation coefficient

$$\beta = \frac{\mu_{sim}}{\mu_{obs}} = \text{bias ratio}$$

$$\gamma = \frac{\sigma_{sim}/\mu_{sim}}{\sigma_{obs}/\mu_{obs}} = \text{variability ratio}$$

where μ is the mean output, and σ is the standard deviation of the output. The KGE' varies from $-\infty$ to 1, whereby 1 indicates optimum model performance. In a first step, the hydrology was calibrated, performing 35,000 Monte Carlo runs. The parameter set that led to the highest KGE' (Supplemental Table S7) was taken as basis for the calibration of substance parameters performing another 70,000 Monte Carlo simulations.

Sulfamethazine leaching was calibrated with the data of the first period until the end of 2012 (short-term scenario), but the simulation was performed until 2019. To evaluate differences in parameter estimations using long-term data compared with short-term data, a calibration considering the whole sampling data until 2019 (long-term scenario) was carried out as well. Uncertainty bounds were calculated by using the highest and lowest value of each time step of all behavioral models. The threshold to estimate acceptable model runs and parameter values was calculated by the maximum KGE' for each scenario on each site minus 0.2 (Gassmann et al., 2014). To determine whether median values of the parameter distributions of the different scenarios were significantly different, t tests were

performed. A correlation matrix with all significant correlations ($p < .05$) revealed internal dependencies of the model parameters.

2.4 | Handling of uncertainties and sensitivity analysis (SA)

The majority of the observed SMZ values were between LOD and LOQ ($2\text{--}10\text{ ng L}^{-1}$). Model outputs were therefore categorized according to these limit values before calculating the goodness-of-fit measurement (i.e., every concentration $<2\text{ ng L}^{-1}$ was handled as 0 ng L^{-1} , every concentration between 2 and 10 ng L^{-1} as 6 ng L^{-1} , and every value $>10\text{ ng L}^{-1}$ as the actual simulated value).

To obtain further insight into parameter behavior, a global sensitivity analysis based on the partial correlation coefficient (PCC) (Iman & Helton, 1988) was performed. The PCC estimates the linear relationship between an input parameter x_i and the model output y . Linear effects of other parameters are removed before determining the correlation. Calculation of the PCC requires no model fitting, so the subjective nature of goodness-of-fit measurements is avoided. By performing a rank-transformation before calculating the PCC, monotonic, nonlinear relationships, which are commonly found in leaching models, can be turned into linear ones (Iman & Conover, 1979; Iman & Helton, 1988). It has been shown that the partial rank correlation coefficient (PRCC) is a robust way to handle complex, nonlinear models (Iman & Helton, 1988; Manache & Melching, 2008) and to identify time-dependent relationships (Helton et al., 2006). We calculated the sensitivity for monthly SMZ concentrations in leachate (y) to identify the influence of the substance parameters at different time steps. The Mann–Kendall test (Kendall, 1975; Mann, 1945) was performed to confirm the observed trends. The PRCC was calculated using the R-Package sensitivity (Iooss et al., 2020).

3 | RESULTS

3.1 | Model performance

Percolation was simulated adequately with a maximum KGE' of 0.8 at Site A and a maximum KGE' of 0.79 at Site B. At both sites, some percolation peaks were underestimated, whereas smaller percolation rates were mostly within the uncertainty bounds (Figure 1, top and Figure 2, top). One reason for the underestimation could be the daily resolution of rainfall input. This led to a damping of high rainfall intensities within the model, which resulted in macropores not being activated. Even though soil and evapotranspiration parameters were adjusted during calibration, the number of calibrated parameters might not have been enough to adequately adjust

for all processes. The overestimated percolation peak at Site A resulted from some heavy rainstorms in August 2010. Even though the formation of runoff from lysimeters is not common, the high precipitation rates of $\sim 170\text{ mm}$ in 1 d may have resulted in surface runoff. Yet, the model structure of MACRO only allows runoff when the infiltration capacity of the soil is exceeded by the precipitation intensity. Thus, the damping of rainfall intensity might be the reason for a higher proportion of rainfall infiltration instead of an immediate transfer into surface runoff.

At Site A, nearly all measured values for SMZ concentration were 6 or 0 ng L^{-1} (i.e., below LOQ or LOD), except for some single peak values (Figure 1, bottom). This led to a few data points having a high influence on the correlation coefficient as well as on the standard deviation, which both influence the KGE', leading to comparatively low goodness-of-fit values. The maximum KGE' for the long-term scenario at Site A is 0.42, but a visual evaluation confirms that the simulations captured the characteristic dynamics: the simulations remained between the LOD and the LOQ, with characteristic peaks during short time periods. Further, both simulated and observed concentration peaks could only be found in the first period, whereas later, SMZ concentrations were less variable. During the second calibration period (2015–2019), the uncertainty bounds of the simulation mostly covered the “uncertainty range” of the analytical SMZ concentration.

Some concentration peaks could not be simulated by MACRO. Shortly after the beginning of the experiment, a measured peak concentration of 25 ng L^{-1} indicated fast transport of SMZ via macropores in the lysimeter. At the same time, the simulation underestimated percolation, which may have been a result of missing preferential flow in the model and thus no rapid SMZ transport. For late winter/early spring in 2011, a similar situation occurred. The first percolation was underestimated from January until March 2011, leading to less SMZ being transported into deeper soil layers. In the following dry period, no SMZ was available to be leached via micropores. During the overestimated percolation peak in August 2010, the reverse case occurred. Overestimated infiltration rates resulted from an activation of macropores and thus led to leaching of SMZ during a period, where no SMZ was measured in the percolation of the lysimeters. This shows that macropore flow is an important factor for fast transfer into deeper soil layers and a cause for peak concentrations.

The short-term simulations using sampling data up to 2012 led to a similar course for SMZ leaching compared with the long-term scenario, with a maximum KGE' of 0.48. The peaks were simulated similarly well with similar problems as described for the long-term scenario. However, the uncertainty bounds of the short-term simulations were wider and include values lower than LOD during the second period (Figure 1, middle).

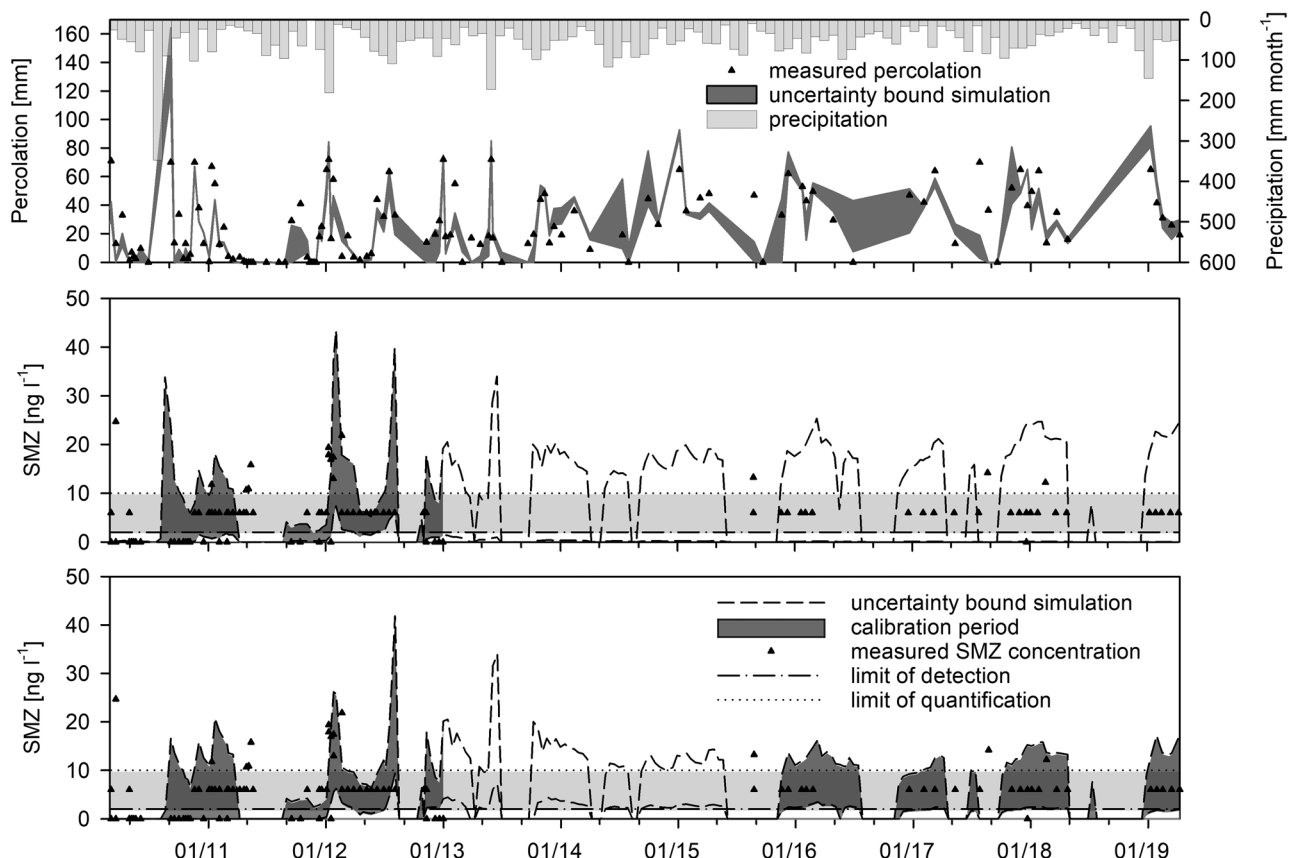


FIGURE 1 Long-term simulation of percolation (top), the short-term sulfamethazine (SMZ) leaching scenario (93 behavioral runs) (middle), and the long-term SMZ leaching scenario (79 behavioural runs) (bottom) for Site A

Although the long-term rising concentrations of SMZ in leachate on Site B could be simulated by the long-term simulations with a maximum KGE' of 0.84, the early leaching (up until 2012), which is characterized by constant concentrations within LOD and LOQ, was not captured well (Figure 2, bottom). Compared with the lysimeter experiment, the leaching generally started too late. The uncertainty bounds of the simulations were initially narrow but were getting larger than the range between LOD and LOQ very quickly, varying from 0 to 25 $ng L^{-1}$ in 2012. During the period without measurements, the range of the uncertainty bounds was getting wider before it converged to the measured values again during the second measurement campaign. Despite the underestimation of SMZ leaching at the beginning of the period, the uncertainty bounds of the long-term scenario still comprised most of the measurements and thus could be evaluated as an acceptable simulation of SMZ transport.

When only considering the first measurement campaign for calibration, the early slow, uniform leaching of SMZ at Site B could be simulated better compared with the long-term scenario (Figure 2, middle), but the maximum KGE' was much smaller (0.33). The lower uncertainty boundary did not exceed LOD until February 2011. This is in accordance with the observed concentrations that varied continuously between 0

and $>2 ng L^{-1}$. Concentrations also did not increase as fast as observed in the long-term simulation. Instead, the plume seemed to move slightly slower down the soil profile, as is also suggested by the lysimeter experiment. The uncertainty bounds after the calibration period, however, failed to enclose the measured concentrations. In 2014, the lower boundary reached 0 $ng L^{-1}$, whereas the upper boundary was below most of the measurements.

3.2 | Sensitivity

The temporal evolution of parameter sensitivity provides information about the importance of different processes at specific time points (Figure 3). The lack of percolation during some time spans explains the leaps of the PRCC. At Site A (Figure 3, top), the Freundlich exponent n and $DT_{50,NER}$ were positively correlated with the SMZ concentration during the whole period, meaning a rise in the parameter value resulted in a rise in SMZ concentration. However, K_{fOC} was strongly negatively correlated with the output SMZ concentration, but after the first period, the sensitivity slowly decreased. Although f_{kin} was not a sensitive parameter during the first period, the PRCC value increased with time.

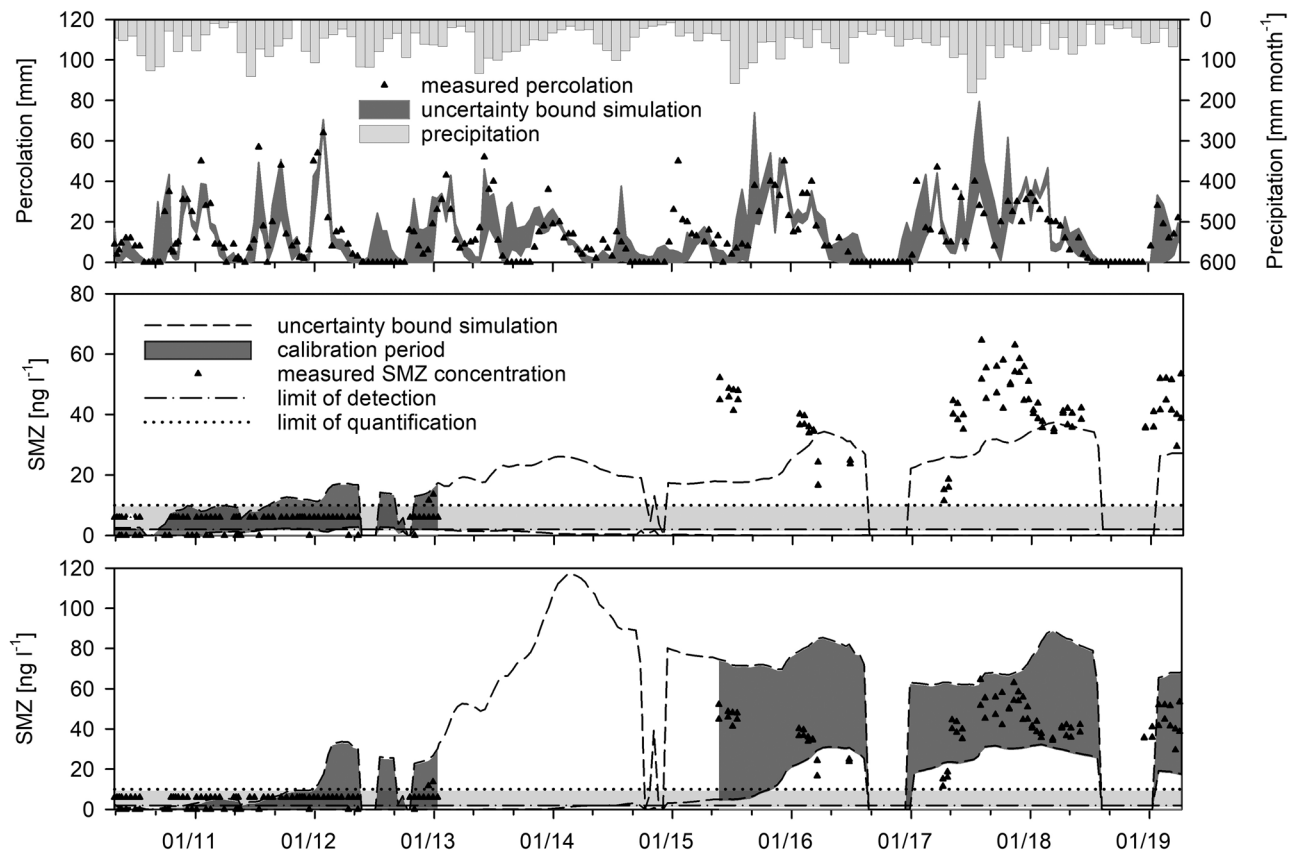


FIGURE 2 Long-term simulation of percolation (top), the short-term sulfamethazine (SMZ) leaching scenario (220 behavioral runs) (middle), and the long-term SMZ leaching scenario (459 behavioral runs) (bottom) for Site B

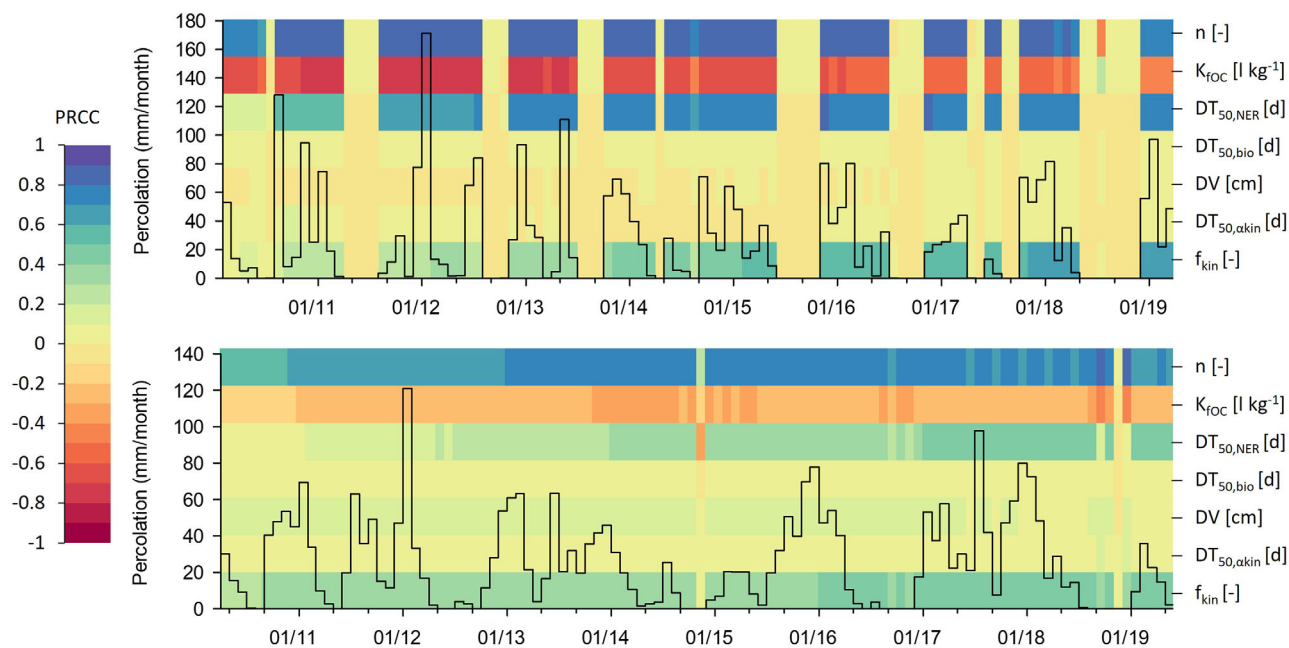


FIGURE 3 Temporal evolution of parameter sensitivity, using partial rank correlation coefficient (PRCC) (colored) on sulfamethazine output concentrations in the leachate and simulated percolation (black line) of Site A (top) and Site B (bottom). $DT_{50,akin}$, half-life transfer to/from kinetic sorption sites; $DT_{50,bio}$, biological degradation; $DT_{50,NER}$, processes that lead to the observed dissipation of the substance, such as the formation of non-extractable residues; f_{kin} , fraction of kinetic sorption sites; K_{foc} , organic C-normalized sorption coefficient; DV, dispersivity; n , Freundlich exponent

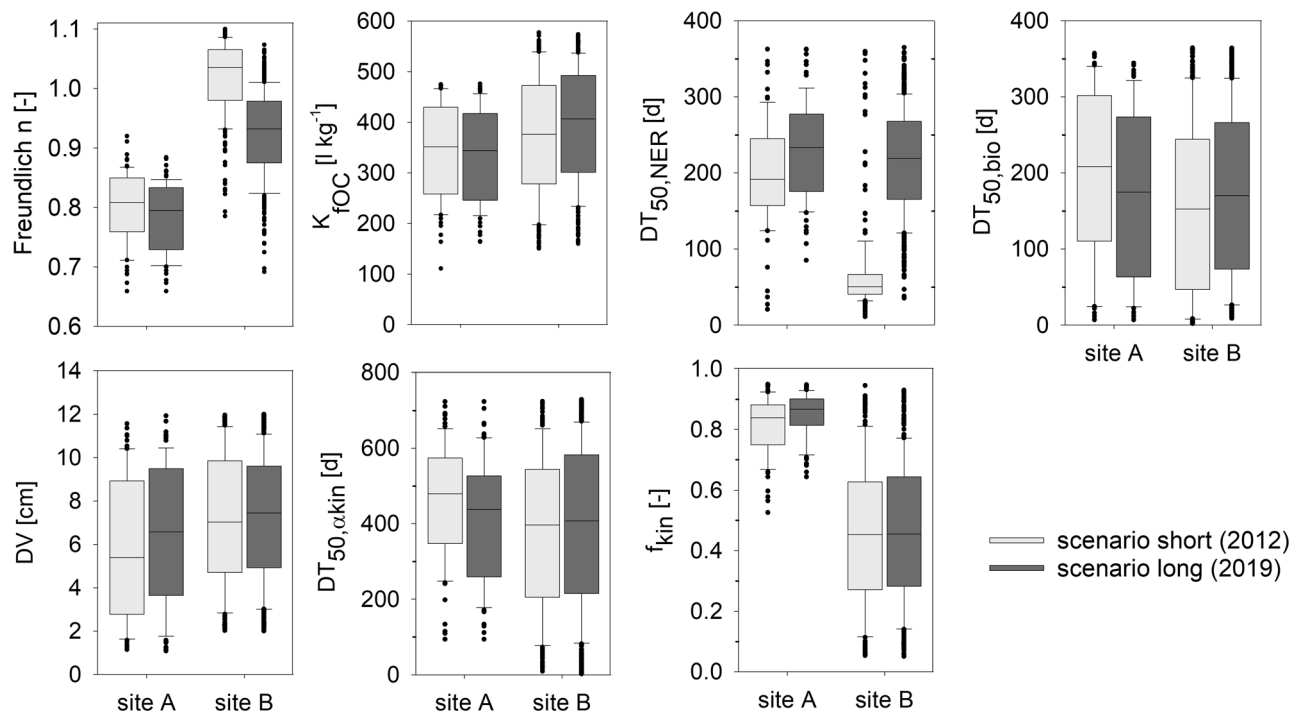


FIGURE 4 Posterior parameter distribution of behavioral models at both sites and for both calibration scenarios. $DT_{50,\alpha_{kin}}$, half-life transfer to/from kinetic sorption sites; $DT_{50,bio}$, biological degradation; $DT_{50,NER}$, processes that lead to the observed dissipation of the substance, such as the formation of non-extractable residues; f_{kin} , fraction of kinetic sorption sites; K_{fOC} , organic C-normalized sorption coefficient; DV, dispersivity; n , Freundlich exponent

Partial rank correlation coefficients were generally smaller at Site B. They showed the same tendencies as Site A, with K_{fOC} being negatively correlated with SMZ concentration, whereas n , $DT_{50,NER}$, and f_{kin} were positively correlated, and $DT_{50,NER}$ showed an even increase of sensitivity until the end of the simulation period. At both sites, $DT_{50,bio}$, DV, and $DT_{50,\alpha_{kin}}$ only showed a low effect, with PRCC values close to 0. This supports the assumption that the formation of NERs was more relevant for SMZ dissipation than the degradation within the liquid phase. The Mann–Kendall test, which can be found in the Supplemental material (S8), confirmed the observed trends.

3.3 | Posterior parameter distribution

Parameter ranges of the acceptable model runs were generally wide (Figure 4). This applies especially for $DT_{50,bio}$, $DT_{50,\alpha_{kin}}$, and DV. Some parameters showed significant differences between the two sites, such as the Freundlich exponent n , which was higher for Site B. The K_{fOC} values could only be limited at the lower boundary at Site A, where the minimum K_{fOC} values were 163 (long-term scenario) and 111 L kg⁻¹ (short-term scenario). At Site B, the whole range of the prior K_{fOC} distribution could also be found in the posterior distribution. Freundlich n and K_{fOC} were strongly corre-

lated (Table 2), which explains the wide parameter ranges. For Site B, the parameter distribution of n also varies between the two scenarios. For the short-term scenario, the median Freundlich exponent is 1.03. This is significantly ($p < .05$) higher than the long-term n with a median Freundlich exponent of 0.93.

Mean values for the formation dynamics of non-extractable residues $DT_{50,NER}$ were significantly different between scenarios, but the parameter ranges were still wide. On both sites, median values were smaller for the short-term scenarios. At Site A, the difference was less concise (short-term scenario: 192 d; long-term scenario: 234 d), whereas at Site B the median values were 50 d for the short-term scenario and 219 d for the long-term scenario. The short-term scenario at Site B was the only one where $DT_{50,NER}$ had much smaller correlation coefficients with other parameters, whereas at Site A, $DT_{50,NER}$ was strongly negative correlated ($r < -.60$) with n (long- and short-term scenarios) and K_{fOC} (long-term scenario). At Site A the 0.25 and 0.75 quantiles for kinetic sorption sites f_{kin} ranged from 0.75 to 0.88 for the short-term scenario and from 0.82 to 0.90 for the long-term scenario. Other studies found similar values (Fan et al., 2011; Wehrhan et al., 2007). However, f_{kin} could not be limited efficiently at Site B. The reason could be again highly negative correlation coefficients with n (short- and long-term scenarios) and $DT_{50,NER}$ (long-term scenario).

TABLE 2 Correlation coefficients (only significant ones are shown) between different parameters for all behavioural model runs for Site A (lower left part) and Site B (upper right part) and for long-term scenario/short-term scenario

	n	K_{fOC}	$\text{DT}_{50,\text{NER}}$	$\text{DT}_{50,\text{bio}}$	DV	$\text{DT}_{50,\alpha\text{kin}}$	f_{kin}
n		.73 .31	.12 -.17		-.36	-.17 -.24	-.60 -.64
K_{fOC}	.97 .80				1.26		-.19 .15
$\text{DT}_{50,\text{NER}}$	-.68 -.71	-.60 -.32		-.26 -.40	.22	.26 .21	-.63
$\text{DT}_{50,\text{bio}}$.22		1.17		-.11 -.15
DV	.26 .24		-.27 -.30				1.12
$\text{DT}_{50,\alpha\text{kin}}$.23		
f_{kin}	-.28 -.43	-.26 -.52	-.28				

Note. $\text{DT}_{50,\alpha\text{kin}}$, half-life transfer to/from kinetic sorption sites; $\text{DT}_{50,\text{bio}}$, biological degradation; $\text{DT}_{50,\text{NER}}$, processes that lead to the observed dissipation of the substance, such as the formation of non-extractable residues; f_{kin} , fraction of kinetic sorption sites; K_{fOC} , organic C-normalized sorption coefficient; DV, dispersivity; n , Freundlich exponent. All correlations are significant at the .05 probability level.

4 | DISCUSSION

The quality of simulations and forecasts strongly depended on the information content of the available data. At Site A, the information content of the data of the first measurement campaign seemed to be high enough to approximate the behavior of the second period, whereas at Site B, the data of the first period, showing a constant leaching of low concentrations, did not contain enough information to adequately calibrate the model to predict the observed leaching from 2015 on forward. In addition, the PRCC of $\text{DT}_{50,\text{NER}}$ at Site B only became influential at the end of the first period. Thus, calibration based on the short-term data did not constrain the parameters in the period with significantly higher PRCC values and therefore probably had a low predictive power.

A way to limit uncertainties could be to calibrate the model based on additional measurements, such as the substance concentration in the soil. This might also reduce parameter correlation and thus result in better parameter conditioning (Larsbo & Jarvis, 2005). Still, for lysimeters containing undisturbed soil, such as the ones in this study, this is a challenging point because the extraction of soil samples would lead to a disturbance of the original soil structure.

With longer simulation time, sensitivities of complex sorption parameters (f_{kin} , $\text{DT}_{50,\text{NER}}$) increased. For our model, this means that a slow transfer to NER ($\text{DT}_{50,\text{NER}}$) gained importance and that f_{kin} was required to store SMZ over several years in the mobile sorption pool, simulating the sorption-desorption hysteresis. This confirms the importance of complex sorption models in environmental fate assessment of sulfonamides (Wehrhan et al., 2007), especially for long-term simulations and forecasts.

Taking all the analyses into account, some conclusions concerning sorption processes in the soil can be drawn. At Site A, a higher share of potential sorption sites on clay and OC

is available in the soil. At the same time, the pH of the soil is close to the pK_b value (7.6) of SMZ. As a consequence, SMZ is mostly present in its neutral and anionic form. Neutral SMZ can be electrostatically bound to soil mineral surfaces and adsorbs to soil organic material via hydrophobic partitioning (Gao & Pedersen, 2005; Leal et al., 2013; Lertpaitoonpan et al., 2009; Park & Huwe, 2016), but it also showed a pronounced sorption-desorption hysteresis from the clay and OC fractions (Bialk et al., 2005; Gao & Pedersen, 2010). This might explain the high share of kinetic sorption sites (70–90%), which might be a reference value for future studies performed on soils with similar characteristics.

At Site B, the median half-life for the formation of NER changed from 50 (short-term scenario) to 219 d (long-term scenario). A fast transfer of SMZ to NER seemed to be necessary to approximate the uniform leaching of the first period until 2012. At the same time, too much SMZ was eliminated from mobile sorption sites, leaving no SMZ in the mobile pool for leaching during the second period. This indicates a change of sorption dynamics either with time and/or with depth, which could not be captured by the MACRO model or by our model setup. Despite lower pH values close to the pK_a value of SMZ at Site B, leading to SMZ being mostly present in its more sorptive, neutral, and cationic form, low amounts of OC and clay in the lowest soil layer may lead to less formation of NER in the lysimeter (Bialk et al., 2005; Gao & Pedersen, 2010), whereas $\text{DT}_{50,\text{NER}}$ was kept constant with soil depth during the simulation. Furthermore, some studies suggest that sorption strength increases after application (Bailey et al., 2016; Srinivasan et al., 2014). Even though including kinetic sorption sites leads to an increase in sorption strength with time in the model, this effect might not be strong enough. This is supported by the fact that the influence of $\text{DT}_{50,\alpha\text{kin}}$ on the output was low at all times. This might not only explain the different parameter distributions for both scenarios at Site B but might also be the reason why

the first leaching from May to July 2010 (short-term scenario) is underestimated. A variation of $DT_{50,NER}$ or a calculation of sorption parameters depending on additional factors such as the share of clay or the pH value might help to improve the simulations and could also lead to an improvement of the short-term scenario despite the poor information content of the data.

5 | CONCLUSION

The performed analyses demonstrate that MACRO is capable of simulating the transport behavior of SMZ in different soils. Our analysis led to the following three conclusions:

1. Depending on the information content of the data, the simulations are linked with high uncertainties. A model calibration based on a few characteristic measurements might lead to an acceptable prediction, with uncertainty bounds only slightly wider than those parameterized with longer data sets (Site A). Such data are suitable to estimate the leaching over several years. An example of sampling data with a low information content was the short-term scenario at Site B, where even wide simulation uncertainty bounds could not capture sampled long-term leaching concentrations.
2. Internal dependencies between some of the parameters hampered the identification of posterior parameter ranges.
3. Complex sorption parameters were getting more sensitive the longer the simulation period lasted. Thus, sensitivity analyses based on shorter time periods may lead to the false assumption that these parameters are not relevant for the simulation.

The first two aspects could be addressed by restricting the model using additional measurements, such as substance concentrations in soils. On the other hand, performing a sensitivity analysis exceeding the calibration period might indicate whether parameters become influential after the calibration period and thus could help to evaluate the predictive power of leaching models, even with poor calibration data.

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AUTHOR CONTRIBUTIONS

Caroline Spill: Conceptualization; Formal analysis; Investigation; Methodology; Validation; Visualization; Writing –


original draft. Matthias Gassmann: Conceptualization; Methodology; Supervision; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

- Accinelli, C., Koskinen, W. C., Becker, J. M., & Sadowsky, M. J. (2007). Environmental fate of two sulfonamide antimicrobial agents in soil. *Journal of Agricultural and Food Chemistry*, 55(7), 2677–2682. <https://doi.org/10.1021/jf063709j>
- Aust, M.-O., Godlinski, F., Travis, G. R., Hao, X., McAllister, T. A., Leinweber, P., & Thiele-Bruhn, S. (2008). Distribution of sulfamethazine, chlortetracycline and tylosin in manure and soil of Canadian feedlots after subtherapeutic use in cattle. *Environmental Pollution*, 156(3), 1243–1251. <https://doi.org/10.1016/j.envpol.2008.03.011>
- Bailey, C., Spielmeyer, A., Hamscher, G., Schüttrumpf, H., & Frings, R. M. (2016). The veterinary antibiotic journey: Comparing the behaviour of sulfadiazine, sulfamethazine, sulfamethoxazole and tetracycline in cow excrement and two soils. *Journal of Soils and Sediments*, 16(6), 1690–1704. <https://doi.org/10.1007/s11368-016-1370-0>
- Bialk, H. M., Simpson, A. J., & Pedersen, J. A. (2005). Cross-coupling of sulfonamide antimicrobial agents with model humic constituents. *Environmental Science & Technology*, 39(12), 4463–4473. <https://doi.org/10.1021/es0500916>
- Białk-Bielińska, A., Stolte, S., Matzke, M., Fabiańska, A., Maszkowska, J., & Kołodziejewska, M. (2012). Hydrolysis of sulphonamides in aqueous solutions. *Journal of Hazardous Materials*, 221–222, 264–274. <https://doi.org/10.1016/j.jhazmat.2012.04.044>
- Biošić, M., Mitrevski, M., & Babić, S. (2017). Environmental behavior of sulfadiazine, sulfamethazine, and their metabolites. *Environmental Science and Pollution Research International*, 24(10), 9802–9812. <https://doi.org/10.1007/s11356-017-8639-8>
- Boesten, J. J. T. I., & Linden, A. M. A. (1991). Modeling the influence of sorption and transformation on pesticide leaching and persistence. *Journal of Environmental Quality*, 20(2), 425–435. <https://doi.org/10.2134/jeq1991.00472425002000020015x>
- Boxall, A. B. A., Blackwell, P., Cavallo, R., Kay, P., & Tolls, J. (2002). The sorption and transport of a sulphonamide antibiotic in soil systems. *Toxicology Letters*, 131(1-2), 19–28. [https://doi.org/10.1016/S0378-4274\(02\)00063-2](https://doi.org/10.1016/S0378-4274(02)00063-2)
- Burkhardt, M., Stamm, C., Waul, C., Singer, H., & Müller, S. (2005). Surface runoff and transport of sulfonamide antibiotics and tracers on manured grassland. *Journal of Environmental Quality*, 34(4), 1363–1371. <https://doi.org/10.2134/jeq2004.0261>
- Christian, T., Schneider, R. J., Färber, H. A., Skutlarek, D., Meyer, M. T., & Goldbach, H. E. (2003). Determination of antibiotic residues in manure, soil, and surface waters. *Acta Hydrochimica et Hydrobiologica*, 31(1), 36–44. <https://doi.org/10.1002/ahch.200390014>
- Conde-Cid, M., Nóvoa-Muñoz, J. C., Núñez-Delgado, A., Fernández-Sanjurjo, M. J., Arias-Estévez, M., & Álvarez-Rodríguez, E. (2019). Experimental data and modeling for sulfachloropyridazine and

- sulfamethazine adsorption/desorption on agricultural acid soils. *Microporous and Mesoporous Materials*, 288, 109601. <https://doi.org/10.1016/j.micromeso.2019.109601>
- Fait, G., Balderacchi, M., Ferrari, F., Ungaro, F., Capri, E., & Trevisan, M. (2010). A field study of the impact of different irrigation practices on herbicide leaching. *European Journal of Agronomy*, 32(4), 280–287. <https://doi.org/10.1016/j.eja.2010.02.001>
- Fan, Z., Casey, F. X. M., Hakk, H., Larsen, G. L., & Khan, E. (2011). Sorption, fate, and mobility of sulfonamides in soils. *Water, Air, & Soil Pollution*, 218(1-4), 49–61. <https://doi.org/10.1007/s11270-010-0623-6>
- FOCUS. (2014). *Generic guidance for tier 1 FOCUS ground water assessments, Version 2.2*. https://esdac.jrc.ec.europa.eu/public_path/projects_data/focus/gw/NewDocs/GenericGuidance2_2.pdf
- Gao, J., & Pedersen, J. A. (2005). Adsorption of sulfonamide antimicrobial agents to clay minerals. *Environmental Science & Technology*, 39(24), 9509–9516. <https://doi.org/10.1021/es050644c>
- Gao, J., & Pedersen, J. A. (2010). Sorption of sulfonamide antimicrobial agents to humic acid-clay complexes. *Journal of Environmental Quality*, 39(1), 228–235. <https://doi.org/10.2134/jeq2008.0274>
- García-Santiago, X., Garrido, J. M., Lema, J. M., & Franco-Uría, A. (2017). Fate of pharmaceuticals in soil after application of STPs products: Influence of physicochemical properties and modelling approach. *Chemosphere*, 182, 406–415. <https://doi.org/10.1016/j.chemosphere.2017.05.049>
- Gassmann, M., Khodorkovsky, M., Friedler, E., Dubowski, Y., & Olsson, O. (2014). Uncertainty in the river export modelling of pesticides and transformation products. *Environmental Modelling & Software*, 51, 35–44. <https://doi.org/10.1016/j.envsoft.2013.09.021>
- Gassmann, M., Weidemann, E., & Stahl, T. (2021). Combined leaching and plant uptake simulations of PFOA and PFOS under field conditions. *Environmental Science and Pollution Research International*, 28(2), 2097–2107. <https://doi.org/10.1007/s11356-020-10594-6>
- Giannouli, D. D., & Antonopoulos, V. Z. (2015). Evaluation of two pesticide leaching models in an irrigated field cropped with corn. *Journal of Environmental Management*, 150, 508–515. <https://doi.org/10.1016/j.jenvman.2014.12.044>
- Gupta, H. V., Kling, H., Yilmaz, K. K., & Martinez, G. F. (2009). Decomposition of the mean squared error and NSE performance criteria: Implications for improving hydrological modelling. *Journal of Hydrology*, 377(1-2), 80–91. <https://doi.org/10.1016/j.jhydrol.2009.08.003>
- Haller, M. Y., Müller, S. R., McArdell, C. S., Alder, A. C., & Suter, M. J.-F. (2002). Quantification of veterinary antibiotics (sulfonamides and trimethoprim) in animal manure by liquid chromatography–mass spectrometry. *Journal of Chromatography A*, 952(1-2), 111–120. [https://doi.org/10.1016/S0021-9673\(02\)00083-3](https://doi.org/10.1016/S0021-9673(02)00083-3)
- Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P. F., Ingerslev, F., Holten Litzhøft, H. C., & Jørgensen, S. E. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment: A review. *Chemosphere*, 36(2), 357–393. [https://doi.org/10.1016/S0045-6535\(97\)00354-8](https://doi.org/10.1016/S0045-6535(97)00354-8)
- Hamscher, G., Mohring, S., Höper, H., Stahl, J., Kietzmann, M., Haiß, A., & Kümmerer, K. (2013). *Identification and characterization of environmental friendly veterinary drugs using the example of sulfonamides*. (In German.) Abschlussbericht, TihoTox/JLU GIE, LBEG, TihoPHarm/WDT, Leuphana. www.dbu.de/OPAC/ab/DBU-Abschlussbericht-AZ-26852.pdf
- Hamscher, G., & Mohring, S. A. I. (2012). Veterinary medicinal products in soils and in the aquatic environment. (In German.) *Chemie Ingenieur Technik*, 84(7), 1052–1061. <https://doi.org/10.1002/cite.201100255>
- Hamscher, G., Pawelzick, H. T., Höper, H., & Nau, H. (2005). Different behavior of tetracyclines and sulfonamides in sandy soils after repeated fertilization with liquid manure. *Environmental Toxicology and Chemistry*, 24(4), 861–868. <https://doi.org/10.1897/04-182R.1>
- Hamscher, G., Sczesny, S., Höper, H., & Nau, H. (2002). Determination of persistent tetracycline residues in soil fertilized with liquid manure by high-performance liquid chromatography with electrospray ionization tandem mass spectrometry. *Analytical Chemistry*, 74(7), 1509–1518. <https://doi.org/10.1021/ac015588m>
- Harms, H., & Bosma, T. N. P. (1997). Mass transfer limitation of microbial growth and pollutant degradation. *Journal of Industrial Microbiology and Biotechnology*, 18(2-3), 97–105. <https://doi.org/10.1038/sj.jim.2900259>
- Helton, J. C., Johnson, J. D., Sallaberry, C. J., & Storlie, C. B. (2006). Survey of sampling-based methods for uncertainty and sensitivity analysis. *Reliability Engineering & System Safety*, 91(10-11), 1175–1209. <https://doi.org/10.1016/j.res.2005.11.017>
- Hirsch, R., Ternes, T., Haberer, K., & Kratz, K.-L. (1999). Occurrence of antibiotics in the aquatic environment. *Science of the Total Environment*, 225(1-2), 109–118. [https://doi.org/10.1016/S0048-9697\(98\)00337-4](https://doi.org/10.1016/S0048-9697(98)00337-4)
- Iman, R. L., & Conover, W. J. (1979). The use of the rank transform in regression. *Technometrics*, 21(4), 499–509. <https://doi.org/10.1080/00401706.1979.10489820>
- Iman, R. L., & Helton, J. C. (1988). An Investigation of uncertainty and sensitivity analysis techniques for computer models. *Risk Analysis*, 8(1), 71–90. <https://doi.org/10.1111/j.1539-6924.1988.tb01155.x>
- Iooss, B., Janon, A., & Pujol, G. (2020). *Package 'sensitivity', Version 1.2.7*. <https://cran.r-project.org/web/packages/sensitivity/sensitivity.pdf>
- Jarvis, N., & Larsbo, M. (2012). MACRO (v5.2): Model use, calibration, and validation. *Transactions of the ASABE*, 55(4), 1413–1423. <https://doi.org/10.13031/2013.42251>
- Jarvis, N. J. (1995). Simulation of soil water dynamics and herbicide persistence in a silt loam soil using the MACRO model. *Ecological Modelling*, 81(1-3), 97–109. [https://doi.org/10.1016/0304-3800\(94\)00163-C](https://doi.org/10.1016/0304-3800(94)00163-C)
- Kay, P., Blackwell, P. A., & Boxall, A. B. A. (2004). Fate of veterinary antibiotics in a macroporous tile drained clay soil. *Environmental Toxicology and Chemistry*, 23(5), 1136–1144. <https://doi.org/10.1897/03-374>
- Kay, P., Blackwell, P. A., & Boxall, A. B. A. (2005). Transport of veterinary antibiotics in overland flow following the application of slurry to arable land. *Chemosphere*, 59(7), 951–959. <https://doi.org/10.1016/j.chemosphere.2004.11.055>
- Kendall, M. G. (1975). *Rank correlation methods* (4th ed.). Charles Griffin.
- Kling, H., Fuchs, M., & Paulin, M. (2012). Runoff conditions in the upper Danube basin under an ensemble of climate change scenarios. *Journal of Hydrology*, 424–425, 264–277. <https://doi.org/10.1016/j.jhydrol.2012.01.011>
- Knäbel, A., Bundschuh, M., Kreuzig, R., & Schulz, R. (2016). Runoff of veterinary pharmaceuticals from arable and grassland: A

- comparison between predictions from model simulations and experimental studies. *Agriculture, Ecosystems & Environment*, 218, 33–39. <https://doi.org/10.1016/j.agee.2015.10.022>
- Kreuzig, R., & Hölte, S. (2005). Investigations on the fate of sulfadiazine in manured soil: Laboratory experiments and test plot studies. *Environmental Toxicology and Chemistry*, 24(4), 771–776. <https://doi.org/10.1897/03-582R.1>
- Kurwadkar, S. T., Adams, C. D., Meyer, M. T., & Kolpin, D. W. (2007). Effects of sorbate speciation on sorption of selected sulfonamides in three loamy soils. *Journal of Agricultural and Food Chemistry*, 55(4), 1370–1376. <https://doi.org/10.1021/jf060612o>
- Larsbo, M., Fenner, K., Stoob, K., Burkhardt, M., Abbaspour, K., & Stamm, C. (2008). Simulating sulfadimidine transport in surface runoff and soil at the microplot and field scale. *Journal of Environmental Quality*, 37(3), 788–797. <https://doi.org/10.2134/jeq2007.0432>
- Larsbo, M., & Jarvis, N. (2003). MACRO 5.0. SLU Centre for Pesticides in the Environment. <https://www.slu.se/en/Collaborative-Centres-and-Projects/SLU-centre-for-pesticides-in-the-environment/models/macro-52/>
- Larsbo, M., & Jarvis, N. (2005). Simulating solute transport in a structured field soil: Uncertainty in parameter identification and predictions. *Journal of Environmental Quality*, 34, 621–634. <https://doi.org/10.2134/jeq2005.0621>
- Larsbo, M., Lapen, D. R., Topp, E., Metcalfe, C., Abbaspour, K. C., & Fenner, K. (2009). Simulation of pharmaceutical and personal care product transport to tile drains after biosolids application. *Journal of Environmental Quality*, 38(3), 1274–1285. <https://doi.org/10.2134/jeq2008.0301>
- Larsbo, M., Roulier, S., Stenemo, F., Kasteel, R., & Jarvis, N. (2005). An improved dual-permeability model of water flow and solute transport in the vadose zone. *Vadose Zone Journal*, 4(2), 398–406. <https://doi.org/10.2136/vzj2004.0137>
- Leal, R. M. P., Alleoni, L. R. F., Tornisielo, V. L., & Regitano, J. B. (2013). Sorption of fluoroquinolones and sulfonamides in 13 Brazilian soils. *Chemosphere*, 92(8), 979–985. <https://doi.org/10.1016/j.chemosphere.2013.03.018>
- Lertpaitoonpan, W., Ong, S. K., & Moorman, T. B. (2009). Effect of organic carbon and pH on soil sorption of sulfamethazine. *Chemosphere*, 76(4), 558–564. <https://doi.org/10.1016/j.chemosphere.2009.02.066>
- Lindahl, A. M. L., Kreuger, J., Stenström, J., Gärdenäs, A. I., Alavi, G., Roulier, S., & Jarvis, N. J. (2005). Stochastic modeling of diffuse pesticide losses from a small agricultural catchment. *Journal of Environmental Quality*, 34(4), 1174–1185. <https://doi.org/10.2134/jeq2004.0044>
- Manache, G., & Melching, C. S. (2008). Identification of reliable regression- and correlation-based sensitivity measures for importance ranking of water-quality model parameters. *Environmental Modelling & Software*, 23(5), 549–562. <https://doi.org/10.1016/j.envsoft.2007.08.001>
- Mann, H. B. (1945). Nonparametric tests against trend. *Econometrica*, 13, 245–259. <https://doi.org/10.2307/1907187>
- Martínez-Carballo, E., González-Barreiro, C., Scharf, S., & Gans, O. (2007). Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria. *Environmental Pollution*, 148(2), 570–579. <https://doi.org/10.1016/j.envpol.2006.11.035>
- Nurk, L., Knörzer, S., Jacobi, H. F., & Spielmeier, A. (2019). Elimination of sulfonamides and tetracyclines during anaerobic fermentation: A “Cheshire Cat” phenomenon. *Sustainable Chemistry and Pharmacy*, 13, 100157. <https://doi.org/10.1016/j.scp.2019.100157>
- Park, J. Y., & Huwe, B. (2016). Effect of pH and soil structure on transport of sulfonamide antibiotics in agricultural soils. *Environmental Pollution*, 213, 561–570. <https://doi.org/10.1016/j.envpol.2016.01.089>
- Perfect, E., Sukop, M. C., & Haszler, G. R. (2002). Prediction of dispersivity for undisturbed soil columns from water retention parameters. *Soil Science Society of America Journal*, 66(3), 696–701. <https://doi.org/10.2136/sssaj2002.6960>
- Richter, D. (1995). Results of methodical investigations to correct the systematic measurement error of the Hellmann precipitation meter. (In German.) In D. Richter (Ed.), *Reports of the German weather services* (Vol. 194). Deutscher Wetterdienst.
- Rosendahl, I., Siemens, J., Groeneweg, J., Linzbach, E., Laabs, V., & Herrmann, C. (2011). Dissipation and sequestration of the veterinary antibiotic sulfadiazine and its metabolites under field conditions. *Environmental Science & Technology*, 45(12), 5216–5222. <https://doi.org/10.1021/es200326t>
- Scorza Júnior, R. P., & Boesten, J. J. T. I. (2005). Simulation of pesticide leaching in a cracking clay soil with the PEARL model. *Pest Management Science*, 61(5), 432–448. <https://doi.org/10.1002/ps.1004>
- Scorza Júnior, R. P., Jarvis, N. J., Boesten, J. J., van der Zee, S. E., & Roulier, S. (2007). Testing MACRO (version 5.1) for pesticide leaching in a Dutch clay soil. *Pest Management Science*, 63(10), 1011–1025. <https://doi.org/10.1002/ps.1434>
- Šimůnek, J., Jarvis, N., van Genuchten, M., & Gärdenäs, A. (2003). Review and comparison of models for describing nonequilibrium and preferential flow and transport in the vadose zone. *Journal of Hydrology*, 272, 14–35. [https://doi.org/10.1016/S0022-1694\(02\)00252-4](https://doi.org/10.1016/S0022-1694(02)00252-4)
- Spielmeier, A. (2018). Occurrence and fate of antibiotics in manure during manure treatments: A short review. *Sustainable Chemistry and Pharmacy*, 9, 76–86. <https://doi.org/10.1016/j.scp.2018.06.004>
- Spielmeier, A., Höper, H., & Hamscher, G. (2017). Long-term monitoring of sulfonamide leaching from manure amended soil into groundwater. *Chemosphere*, 177, 232–238. <https://doi.org/10.1016/j.chemosphere.2017.03.020>
- Spielmeier, A., Petri, M. S., Höper, H., & Hamscher, G. (2020). Long-term monitoring of sulfonamides and tetracyclines in manure amended soils and leachate samples: A follow-up study. *Heliyon*, 6(8), e04656. <https://doi.org/10.1016/j.heliyon.2020.e04656>
- Srinivasan, P., Sarmah, A. K., & Manley-Harris, M. (2014). Sorption of selected veterinary antibiotics onto dairy farming soils of contrasting nature. *Science of the Total Environment*, 472, 695–703. <https://doi.org/10.1016/j.scitotenv.2013.11.104>
- Stoob, K., Singer, H. P., Mueller, S. R., Schwarzenbach, R. P., & Stamm, C. H. (2007). Dissipation and transport of veterinary sulfonamide antibiotics after manure application to grassland in a small catchment. *Environmental Science & Technology*, 41(21), 7349–7355. <https://doi.org/10.1021/es070840e>
- Thiele-Bruhn, S. (2003). Pharmaceutical antibiotic compounds in soils: A review. *Journal of Plant Nutrition and Soil Science*, 166, 145–167.

- Tolls, J. (2001). Sorption of veterinary pharmaceuticals in soils: A review. *Environmental Science & Technology*, 35(17), 3397–3406. <https://doi.org/10.1021/es0003021>
- Wehrhan, A., Kasteel, R., Simunek, J., Groeneweg, J., & Vereecken, H. (2007). Transport of sulfadiazine in soil columns: Experiments and modelling approaches. *Journal of Contaminant Hydrology*, 89(1-2), 107–135. <https://doi.org/10.1016/j.jconhyd.2006.08.002>
- Zarfl, C. Klasmeier, J., & Matthies, M. (2009). A conceptual model describing the fate of sulfadiazine and its metabolites observed in manure-amended soils. *Chemosphere*, 77(6), 720–726. <https://doi.org/10.1016/j.chemosphere.2009.08.035>

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