Fate of the antibiotic sulfadiazine in natural soils: Experimental and numerical investigations

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ABSTRACT

Based on small-scale laboratory and field-scale lysimeter experiments, the sorption and biodegradation of sulfonamide sulfadiazine (SDZ) were investigated in unsaturated sandy and silty-clay soils. Sorption and biodegradation were low in the laboratory, while the highest leaching rates were observed when SDZ was mixed with manure. The leaching rate decreased when SDZ was mixed with pure water, and was smallest with the highest SDZ concentrations. In the laboratory, three transformation products (TPs) developed after an initial lag phase. However, the amount of TPs was different for different mixing-scenarios. The TP 2-aminopyrimidine was not observed in the laboratory, but was the most prevalent TP at the field scale. Sorption was within the same range at the laboratory and field scales. However, distinctive differences occurred with respect to biodegradation, which was higher in the field lysimeters than at the laboratory scale. While the silty-clay soil favored sorption of SDZ, the sandy, and thus highly permeable, soil was characterized by short half-lives and thus a quick biodegradation of SDZ. For 2-aminopyrimidine, half-lives of only a few days were observed. Increased field-scale biodegradation in the sandy soil resulted from a higher water and air permeability that enhanced oxygen transport and limited oxygen depletion. Furthermore, low pH was more important than the organic matter and clay content for increasing the biodegradation of SDZ. A numerical analysis of breakthrough curves of bromide, SDZ, and its TPs showed that preferential flow pathways strongly affected the solute transport within shallow parts of the soil profile at the field scale. However, this effect was reduced in deeper parts of the soil profile. Due to high field-scale biodegradation in several layers of both soils, neither SDZ nor 2-aminopyrimidine was detected in the discharge of the lysimeter at a depth of 1 m. Synthetic 50 year long simulations, which considered the application of manure with SDZ for general agricultural practices in Germany and humid climate conditions, showed that the concentration of SDZ decreased below 0.1 μg/L in both soils below the depth of 50 cm.

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1. Introduction

Veterinary antibiotics are used all over the world for preventive and therapeutic treatments and growth promotion in industrial livestock farming, as well as in aquaculture (Boxall et al., 2003; Chee-Sanford et al., 2009; Du and Liu, 2011; Halling-Sørensen et al., 1998; Sarmah et al., 2006). The German Pharmaceutical Law follows EU legislation and restricts the usage of pharmaceuticals for therapeutic use only (EAEM, 1997), while the application as a growth promoter has been prohibited in the EU since 2006 (Council of the European Union, 2001). The use of pharmaceuticals in livestock results in residues reaching the environment via human fertilization

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practices with their manure, or directly via animal grazing (Sukul and Spiteller, 2006). During passage through the animal body parent compounds are partly transformed into products (transformation products) that may have even higher water solubility, lower sorption, or limited degradation properties than the parent substance.

As a result of wide applications of manure to the environment, sulfonamides were detected in Germany in surface waters at concentration levels between 7 and 100 ng/L (Christian et al., 2003). Under specific circumstances, such as highly permeable soils, high infiltration rates, or high temperatures, sulfonamides may be able to migrate through the soil and reach the groundwater (Boxall, 2008). This hypothesis is underpinned by a screening conducted in Germany, where sulfonamides were found in 2012 in 12% of groundwater wells above the limit of quantification (LOQ) and in 2013 in 15% of groundwater wells above LOQ, with concentrations of 11 ng/L to 950 ng/L for sulfadiazine (SDZ) and sulfamethoxazole, respectively (Hannappel et al., 2014).

The effects of veterinary antibiotics range from acute toxicity to *Daphnia magna* (Halling-Sørensen, 2000), development of resistant genes (Chee-Sanford et al., 2009; Gullberg et al., 2011), inhibition of soil bacteria growth, and changes in the composition of the soil microbial population. Veterinary antibiotics can thus also reduce the soil degradation properties for other organic substances (Thiele-Bruhn, 2003). Gullberg et al. (2011) showed that resistant bacteria develop even in conditions with concentrations below the minimum inhibitory concentrations for tetracyclines and other antibiotics. Heuer and Smalla (2007) investigated the persistent effects of SDZ on soil bacterial communities, and showed that the numbers of culturable resistant bacteria and sulfonamide resistance genes increased. However, the investigations of Halling-Sørensen (2000) indicated that the transformation products of SDZ showed no significant impact on the bacterial population in sewage and sludge habitats.

In this research, we focus on one of the widely used veterinary antibiotics: SDZ (IUPAC: 4-amino-N-(2-pyrimidinyl)benzene sulfonamide; SDZ). SDZ is a slightly hydrophilic compound with a low sorption affinity that forms non-extractable residues in soils (e.g., Müller et al., 2013; Rosendahl et al., 2011; Sittig et al., 2012). SDZ undergoes several transformation processes, in which the parent compound can be inactivated (acetylation), transformed into a less toxic state (hydroxylation), or to a more polar metabolite with a lower molecular mass (Sittig et al., 2014). Concentrations of SDZ measured in pig manure range between 0.3 and 198 mg of SDZ per kg dry matter, depending on medication, dilution, and age of the manure (Grote et al., 2004; Hamscher et al., 2005; Höper et al., 2002). When SDZ is fed to pigs, a mixture of the parent compound and two main metabolites is excreted (Lamshöft et al., 2007). When SDZ is applied together with manure to soils, current investigations by Hammesfahr et al. (2011) and Fang et al. (2014) indicate that manure can affect the microbial biomass by changing the biomass' structural composition and thus its functional processes.

Distinctive differences exist in the observed leaching potential of sulfonamides. In laboratory column experiments, Kwon (2011) observed increased leaching of three sulfonamides when they were applied together with manure. This was the consequence of elevated pH that resulted from the manure application. Kreuzig and Höltge (2005) detected not only higher leaching, but also increased degradation rates when SDZ was applied together with manure. In contrast, Unold et al. (2009) observed a low mobility and accumulation of SDZ in the presence of manure in laboratory column experiments on disturbed soil samples. Different leaching, sorption, and degradation may have been due to different types of manure that were used in the three experimental set-ups.

Wehrhan et al. (2007) observed that kinetic sorption was the most relevant process for the removal of SDZ at the laboratory scale. Within a larger scale of lysimeter studies, Aust et al. (2010) observed an increased leaching potential of sulfonamides after their application with manure. However, Aust et al. (2010) did not investigate the transformation processes of SDZ, nor did they use numerical models to analyze or predict the long-term and large-scale fate of sulfonamides. Currently, long-term and large-scale field studies that investigate the leaching potential and biodegradation of sulfonamides, such as SDZ, using undisturbed natural soils and under variable hydrological conditions, are still not available. Currently, research results are usually based on small-scale laboratory experiments, while research is still needed with respect to i) transformation pathways in native soils, and the impact of ii) manure, and iii) natural climate conditions on the leaching potential of the sulfonamides (Sukul and Spiteller, 2006).

Therefore, the objective of this study was to investigate the migration, retardation, and biodegradation of SDZ and its transformation products (TPs) over three years and at the field scale. Lysimeter experiments were employed to analyze the migration of ^{14}C-labeled SDZ and manure using i) a highly permeable homogeneous sandy soil and ii) a heterogeneous clayey silt soil containing a less permeable soil matrix and preferential flow pathways. Results of the lysimeter experiments were compared with small-scale laboratory experiments. The lysimeter experiments were analyzed using a joint inversion of measured saturation, discharge, and breakthrough curves of the tracer bromide, the parent SDZ, and its transformation products. The experimental and numerical investigations accounted for the natural heterogeneity of soils, variable hydrological conditions, and reactive transport processes under variably-saturated conditions. The calibrated numerical model was then used to carry out predictive scenario simulations to estimate the long-term leaching risk of SDZ and its accumulation in soil.

2. Materials and methods

2.1. Soil types and climate

Laboratory small-scale soil column and field-scale lysimeter experiments were conducted with two types of soil: an orthic luvisol and a cambisol. The luvisol was located near Merzenhausen (MER) and the cambisol near Kaldenkirchen (KAL), both in a region of North Rhine-Westphalia, Germany, that is intensively used for agricultural production. The luvisol (MER) is dominated by silt (83%) and clay (13%). It contains 0.97% (mass-based) of organic carbon and has a CEC of 11.4 cmol kg^{-1}. The cambisol (KAL) is a loamy sand (70% sand and 26% silt) with 0.88% of organic carbon and a CEC of

7.8 cmol kg^{-1}. A detailed description of the soil properties is given in Sittig et al. (2012) and Unold et al. (2009).

Undisturbed soil profiles at a depth of 1.20 m were excavated for the lysimeter experiments (Steffens et al., 1992). The cambisol lysimeter contained four layers: Ap (0–0.33 m depth), Bv1 (0.33–0.55 m depth), Bv2 (0.55–0.70 m depth), and Bv3 (0.70–1.20 m depth). The luvisol lysimeter contained five layers: Ap (0–0.39 m depth), Al (0.39–0.55 m depth), Bt1 (0.55–0.77 m depth), Bt2 (0.77–0.98 m depth), and Bt3 (0.98–1.20 m depth). The laboratory soil column experiments were conducted with the plow layer (Ap horizon) of the two soils. Undisturbed soil cores (8 cm diameter, 10 cm length) were collected approximately 5 cm under the soil surface. The columns were stored in the dark at 4 °C before usage.

The field-scale lysimeter experiments were conducted over three years at the outdoor facilities of the Forschungszentrum Jülich, Germany, under natural humid climate conditions (Steffens et al., 1992). The climate conditions (precipitation, temperature, relative humidity, wind speed, global radiation) were hourly recorded at the meteorological station of the Forschungszentrum Jülich. Annual precipitation ranged between 720 mm (2006) and 882 mm (2007), with a maximum precipitation event of 56 mm in the summer of 2007. The mean temperature was about 13 °C in both years, with a maximum air temperature of 33 °C in the summer of 2006.

2.2. Experimental investigations

2.2.1. Chemicals and analytical methods

The investigated veterinary antibiotic SDZ (IUPAC: 4-amino-N-(2-pyrimidinyl)benzene sulfonamide; SDZ) was radioactively labeled at the C-2-atom of the pyrimidine ring (purity: 99%), resulting in a specific radioactivity of 8.88 MBq mg^{-1} (Bayer HealthCare AG, Wuppertal, Germany). In the facilities of Bayer AG, Monheim pigs were fed with the radio-labeled SDZ, and the manure with a total SDZ concentration of 0.63 mmol kg^{-1} was collected. As observed earlier by Lamshöft et al. (2007), manure used in the experiments initially contained the hydroxylated transformation products 4-OH-SDZ and Acetyl-SDZ in fractions of 26% and 21%, respectively. However, this composition changed during the storage of manure to 40% of 4-OH-SDZ, while Acetyl-SDZ was completely transformed to 4-OH-SDZ and thus reduced to zero.

Total radioactivity in water was measured by liquid scintillation counting (LSC; 2500 TR, Packard Bioscience, Dreieich, Germany). Radioactivity in soil was measured using 0.01 M CaCl$_2$/methanol for an easily accessible fraction (EAS) and for a residual fraction (RES) by (multiple) extracts with acetonitrile using the microwave. The concentrations of SDZ and its transformation products (TPs) were measured using the Radio-HPLC (LB 509 detector, Berthold Technologies, Bad Wildbad, Germany), as described in Sittig et al. (2012).

2.2.2. Small-scale laboratory soil column experiments

The small-scale laboratory soil columns (length of 10 cm and diameter of 8 cm) (Fig. 1) were irrigated with a peristaltic pump (REGLO Digital MS-2/12, ISMATEC Laboratoriumstechnik GmbH, Wertheim-Mondfeld, Germany) that applied 0.01 M CaCl$_2$ to the top of the columns using 12 needles. The irrigation rate was controlled gravimetrically (Kern DS 8K0 1, Gottl. Kern & Sohn

GmbH, Balingen-Frommern, Germany). At the bottom of the columns, suction was applied to establish unit-gradient conditions. Due to zero differences in the matric potential over the entire length of the columns, the water content in the columns was constant and water flow was solely driven by gravity. Identical pressure heads along the columns were established by adjusting the pressure at the suction plates and were controlled by two tensiometers (UMS GmbH, München, Germany) at depths of 2.5 and 7.5 cm (approximately −40 mbar). During the experiment, volumes of 15 mL of the percolation solution were drained to a fraction collector by closing an electrical circuit with two water-level sensors. The system was software-controlled with a LabView based system.

In the laboratory experiments, the soil columns were carefully water-saturated from bottom to top, to avoid air entrapment and the formation of preferential flow pathways due to possible water-repellence. Unit-gradient conditions were obtained by balancing the irrigation rate with the applied suction of −40 mbar. Subsequent irrigation was applied at the top of the column at a rate of 0.2 cm h^{-1}. To investigate the soil hydrodynamic properties, a pulse of a 0.05 M CaCl$_2$ solution was applied for 1 h and the specific electrical conductivity in the outflow was measured. Then, 15 g of manure that contained 10 μmol SDZ was applied to the first centimeter of the column. The manure was adjusted with NaOH to a pH value of 8.3. By measuring the specific electrical conductivity in the outflow, the breakthrough of SDZ and its TPs was controlled by the conservative tracer Cl$^-$. ^{14}C-SDZ equivalent concentrations, as well as the transformation products, were measured in the outflow. Finally, a profile of radioactivity in the soil was measured at the end of the experiments.

SDZ was applied four times during the experimental period of one-month: during the initial application at the very beginning of the experiment, and then after one, two, and three weeks. The initial application of SDZ was incorporated into the first centimeter of the soil column together with manure obtained from pig-feeding experiments. The second, third, and fourth applications were spiked into a liquid solution that contained SDZ in low (1.5 μmol L^{-1}) and high (14 μmol L^{-1}) concentrations. This procedure was meant to simulate how veterinary pharmaceuticals are inadvertently applied as fertilizers to agricultural fields. In summary, these different scenarios accounted for the effects of (i) multiple SDZ applications and (ii) the mixing of SDZ with manure on the SDZ leaching potential in natural soils. Furthermore, transformation products that developed during the experiments with and without manure could be identified.

2.2.3. Large-scale and long-term lysimeter experiments

The large-scale experiments were conducted with two lysimeters with two different undisturbed soils from the Merzenhausen and Kaldenkirchen field sites for three years, from November 14th, 2005 until September 18th, 2008. The lysimeters had a surface area of 1 m^2 and a depth of 1.10 m. At 30 and 60 cm depths, they were equipped with time-domain reflectometry (TDR) probes and temperature sensors to observe the water contents and soil temperatures during the experiments. Suction cups were installed at 30 and 60 cm depths to collect soil solutions. The lysimeter surface was kept free of any vegetation.
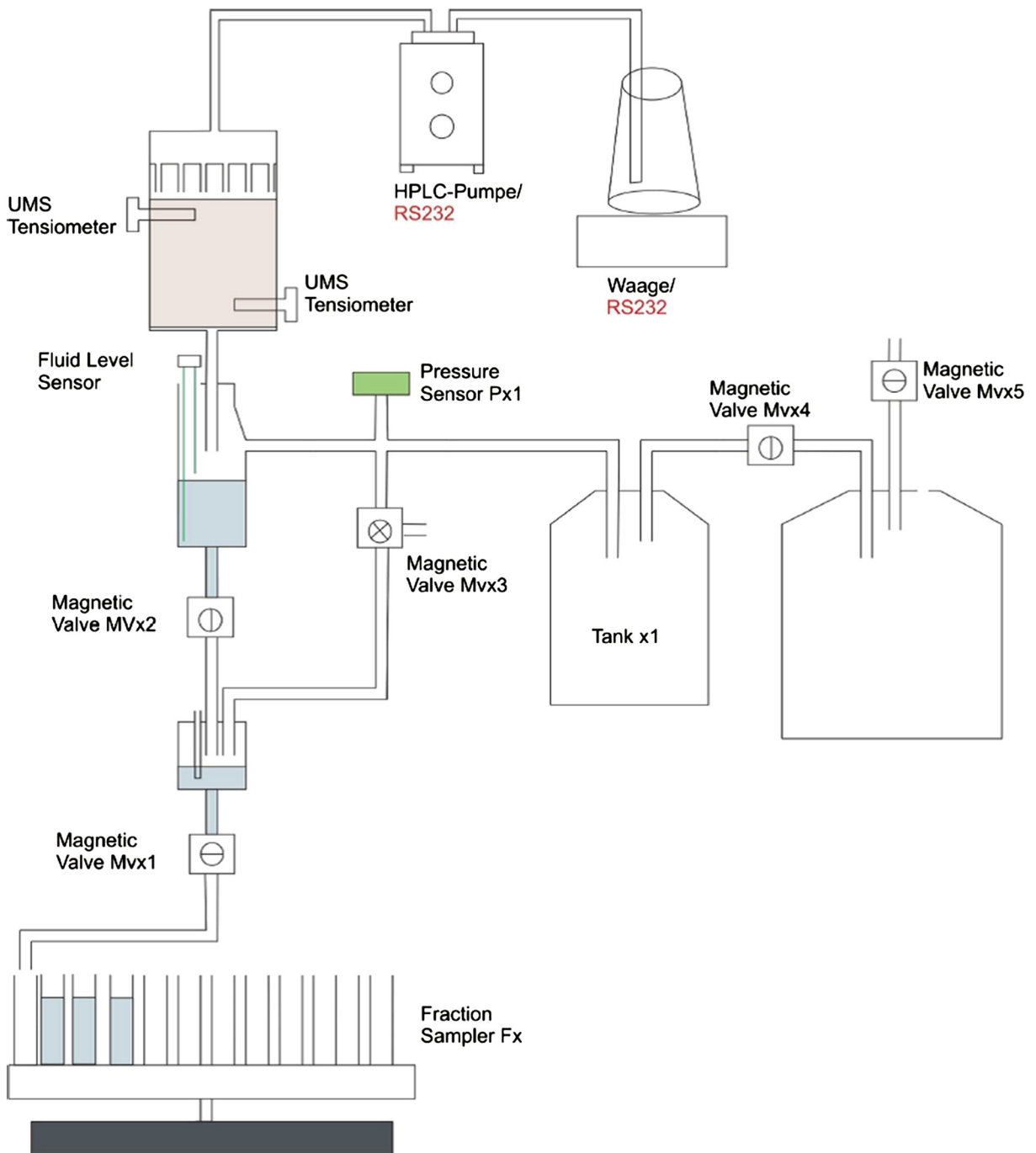
Fig. 1. Experimental set-up of the small-scale laboratory experiments.

When the lysimeter experiments were started, 2.875 kg of manure with the radio-labeled SDZ was applied to the top of the lysimeters. Manure contained a total radioactivity of 100 MBq (or 11.4 mg SDZ) per lysimeter, together with 31.29 g of the conservative tracer bromide, which was dissolved within the manure. The SDZ–bromide–manure mixture was manually incorporated into the first 3–5 cm of the lysimeter. Lysimeters were initially irrigated two times with 2.85 L of water. Discharge volumes and soil water contents at 30 and 60 cm depths were measured daily. Water samples were collected daily at 30 and 60 cm depths, from the lysimeter discharge, and were stored cooled. Water samples were analyzed for total radioactivity and concentrations of bromide, SDZ, and its transformation products every 30 days. Soil samples were taken after 4, 29, 120, 218, and 1022 days and radioactivity within the soil was measured at 0–5 cm, 5–10 cm, 10–20 cm and 20–30 cm depths.

2.3. Numerical modeling

2.3.1. Governing flow and transport equations

The lysimeter experiments were analyzed using the numerical code Hydrus-1D (Šimůnek et al., 2008). The lysimeter was discretized into 121 nodes with a constant thickness of 1 cm. The four (KAL) and five (MER) horizons of the two soil types were defined by assigning different material groups to the respective layers. The simulations were run for 1094 days with daily values of boundary conditions. This allowed for the consideration of daily variability of precipitation, temperature, and evaporation.

2.3.1.1. Water flow and heat transport. The Richards equation was used to simulate one-dimensional water flow in variably-saturated uniform porous media. The unsaturated soil hydraulic properties, i.e. $\theta(h)$ and $K(h)$, are highly nonlinear functions of the pressure head, h. Different analytical models are available to describe these soil hydraulic functions. The soil hydraulic functions of van Genuchten (1980) were used in this study for the single domain model of the Kaldenkirchen soil:

$$\theta(h) = \begin{cases} \theta + \dfrac{\theta_S - \theta_r}{(1 + |\alpha h|^n)^m} \\ \theta_S \end{cases} \qquad (1)$$

$$K(h) = K_S S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \qquad (2)$$

with $S_e = \dfrac{\theta - \theta_r}{\theta_s - \theta_r}$ and $m = 1 - \dfrac{1}{n}$ where h is the soil water pressure head (m), K is the unsaturated hydraulic conductivity (m s^{-1}), K_S is the saturated hydraulic conductivity (m s^{-1}), S_e is the effective saturation (–), θ_r is the residual volumetric water content (–), θ_s is the saturated water content (–), α (m^{-1}) is a fitting parameter that can be physically related to the air-entry pressure, and m (–) and l (–) are fitting parameters that can be physically related to pore size distribution and pore connectivity, respectively.

The governing equation for heat transport considers the conduction of sensible heat and the convection of sensible heat by liquid water (Šimůnek et al., 2009). The water flow and heat transport equations are solved in a fully coupled way. The equation of Chung and Horton (1987) was used to describe the thermal conductivity k (W/m/K) as a function of the volumetric water content:

$$k(\theta) = b1 + b2 * \theta + b3 * \theta^{0.5} \qquad (3)$$

where b1, b2, and b3 are empirical parameters (W/m/K).

Preferential flow pathways were expected in the Merzenhausen soil due to the existence of small root channels and fractures and fissures in the clayey soil layers below the plow layer. Therefore, a dual-permeability non-equilibrium model of Gerke and van Genuchten (1993) was used to simulate water flow in both the macropore or fracture domains, as well as in the soil matrix. The subscript f is used for the macropore domain and the subscript m for the soil matrix.

$$\frac{\partial \theta_f (h_f)}{\partial t} = \frac{\partial}{\partial z} \left[K_f(h_f) \left(\frac{\partial h_f}{\partial z} + \cos \alpha \right) \right] - S_f (h_f) - \frac{\Gamma_w}{w} \qquad (4a)$$

$$\frac{\partial \theta_m (h_m)}{\partial t} = \frac{\partial}{\partial z} \left[K_m(h_m) \left(\frac{\partial h_m}{\partial z} + \cos \alpha \right) \right] - S_m (h_m) - \frac{\Gamma_w}{1-w} \qquad (4b)$$

with $\theta = w\theta_f + (1 - w)\theta_m$ where w (–) is the ratio of the volume of the macropore domain to the total soil system volume, θ_f and θ_m (–) are the water contents of the two pore domains, S_f and S_m (s^{-1}) are sink terms for both regions, Γ_w is the transfer rate (s^{-1}) from the macropore domain into the matrix domain, K_f and K_m (m s^{-1}) are the unsaturated hydraulic conductivities of the two domains, α is the angle between the flow direction and the vertical axis (equal to zero for vertical flow), z (m) is the depth, and t (s) is time.

2.3.1.2. Solute transport and reaction network. Conservative solute transport is described using the Fickian-based convection–dispersion equation:

$$\frac{\partial \theta C}{\delta t} = -\frac{\partial v \theta C}{\partial z} + \theta D \frac{\partial^2 C}{\partial z^2} \qquad (5)$$

where v is the average pore velocity (m s^{-1}), C is the solute concentration (mol L^{-1}), and D is the dispersion coefficient [m^2 s^{-1}].

In the dual-permeability model used for the Merzenhausen soil, the advective–dispersive transport is accounted for in both flow domains: in the highly permeable macropores/fractures and in the low conductive soil matrix.

SDZ is a slightly hydrophilic compound with a K_{OW} value of −0.09 (Sukul and Spiteller, 2006). Sorption of SDZ to the soil matrix is not mainly due to hydrophobic partitioning (Tolls, 2001), as it is common for several other organic xenobiotics, but results from other processes such as ion exchange, surface complexation, and hydrogen bonding (Sukul and Spiteller, 2006). Factors other than the soil organic carbon content and hydrophobicity, such as pH and clay content, thus play an important role (Anskjær et al., 2014; Boxall, 2008). According to the results of Doretto and Rath (2013), the Freundlich isotherm was used to describe the non-linear sorption of SDZ and its transformation products.

The first-order degradation was used to represent biotransformation of SDZ and its TPs (Tappe et al., 2013). However, since only one TP, 2-aminopyridine, was detected in the field-scale experiments, a set of simultaneously occurring biotransformation pathways was reduced to: i) SDZ into 2-aminopyridine, ii) 2-aminopyridine into an "unknown" end product, and iii) SDZ into other TPs such as M1, M2, M3, 4-OH-SDZ and N-acetyl-SDZ (Sittig et al., 2012). The third pathway was lumped into one step as these five TPs were below the limit of detection in the soil solution in the lysimeter (Fig. 2).

The resulting transport equations accounting for sorption and degradation of SDZ and 2-aminopyridine can be written as:

$$\frac{\partial \theta C_{SDZ}}{\partial t} + \frac{\rho \, \partial S_{k,SDZ}}{\partial t} = -\frac{\partial v \theta C_{SDZ}}{\partial z} + \theta D \frac{\partial^2 C_{SDZ}}{\partial z^2} - \mu_1 \theta C_{SDZ} - \mu_2 \theta C_{SDZ} \qquad (6a)$$

$$\frac{\partial \theta C_{TP}}{\partial t} + \frac{\rho \, \partial S_{k,TP}}{\partial t} = -\frac{\partial v \theta C_{TP}}{\partial z} + \theta D \frac{\partial^2 C_{TP}}{\partial z^2} - \mu_1' \theta C_{TP} + \mu_1 \theta C_{SDZ} \qquad (6b)$$
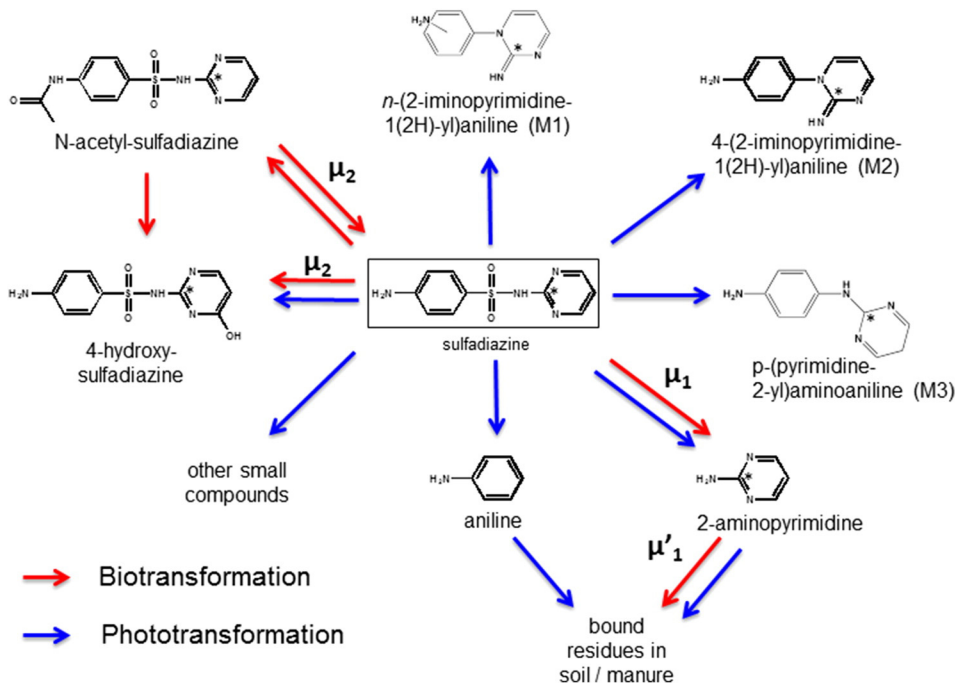
Fig. 2. Reaction network employed in the numerical investigations of the lysimeter experiment. Modified after Sukul et al. (2008a).

where C_{SDZ} and C_{TP} are the concentrations of SDZ and its TPs [mol L^{-3}], respectively, $S_{k,SDZ,TP}$ [mol kg^{-1}] are the sorbed concentrations of SDZ and TPs, $\mu_{1,2}$ [s^{-1}] is the first-order transformation rate for the degradation of SDZ, the suffix 1 is for the TP 2-aminopyrimidine and the suffix 2 for the sum of other TPs, and μ_1' [s^{-1}] is the first-order transformation rate for the degradation of 2-aminopyrimidine.

Microbial activity depends on temperature and thus degradation rates are related to temperature according to the Arrhenius equation (Šimůnek et al., 2009):

$$a_T = a_r \exp\left[\frac{E_a\left(T^A - T^A_r\right)}{R_u T^A T^A_r}\right] \qquad (7)$$

where a_r and a_T are reaction rates at reference T^A_r and actual T^A temperatures, respectively, R_u is the universal gas constant (8.314 J·K^{-1}·mol^{-1}), and E_a [J mol^{-1}] is the activation energy of a particular reaction or process.

Numerical investigations also account for, in the single domain model, the impact of the water content on degradation rates. Therefore, a saturation dependency of biodegradation according to Walker (1974) is included. It assumes that the maximum degradation occurs under water saturated conditions:

$$\mu(\theta) = \mu_{ref}(\theta_{ref}) \min\left[1, \left(\frac{\theta}{\theta_{ref}}\right)^B\right] \qquad (8)$$

where μ_{ref} is the biodegradation coefficient at a reference water content θ_{ref} and μ is the biodegradation coefficient at the actual water content θ. Reference water content, θ_{ref}, may be different for different soil layers, and is usually equal to the water content

at field capacity. B is an empirical parameter, which was set to 0.7 according to Walker (1974).

2.3.2. Initial and boundary conditions

For the simulations of the lysimeter experiments, the initial water content was set similar to values measured using TDR at the beginning of the experiment on November 14th, 2005, at 30 cm ($\theta = 0.1$) and 60 cm ($\theta = 0.2$) depths. The resulting gradient was used to interpolate the initial water content between the top and bottom of the lysimeter. At the top of the lysimeter, the initial concentrations of bromide and SDZ were set to the concentrations and radioactivity that prevailed in the manure. However, since 40% of SDZ was immediately transformed into 4-OH-SDZ, initial SDZ radioactivity was reduced to 60 MBq. In the remaining part of the lysimeter the initial concentrations of bromide, SDZ, and its TPs were zero.

In water flow simulations, the upper boundary condition was defined as an atmospheric boundary condition with specified values of precipitation and potential evaporation. Potential evaporation was calculated with an external routine based on the FAO method (Scharnagl et al., 2011). The FAO method consists of two steps. First, potential evapotranspiration for a land surface covered with reference grass (ET$_{ref}$) is calculated using a modified Penman–Monteith equation (Allen et al., 1998). This equation requires hourly values of air temperature, relative humidity, wind speed, incoming short-wave radiation, and atmospheric pressure as input variables. Second, potential evapotranspiration is scaled using an empirical coefficient to account for an increased evaporation potential of bare soils compared to a wet grassland surface as follows: $E_{pot} = 1.15 * ET_{ref}$ (Allen et al., 1998). A zero-gradient boundary condition was assigned at the bottom of the

lysimeter to simulate free drainage. A zero-gradient pressure head boundary condition was most appropriate, because it does not require explicit information about soil water state variables or fluxes at the lower boundary.

A concentration flux boundary condition was assigned to the top of the soil profile, and a zero concentration gradient was used at the bottom of the soil profile in simulations of the transport of SDZ and bromide.

2.3.3. Model calibration

The Marquardt–Levenberg parameter estimation technique (Marquardt, 1963) is used in Hydrus-1D for an inverse estimation of soil hydraulic and/or solute transport and reaction parameters from measured transient or steady-state flow and/or transport data. This method combines the Newton and steepest descent methods, and generates confidence intervals for optimized parameters.

The calibration of the water flow and conservative transport model was based on a joint inversion of water contents continuously measured at depths of 30 and 60 cm, discharge volumes, and bromide concentrations measured in the discharge every two weeks. This resulted in a total number of 1783 data points used in the inversion. The parameters of the soil-hydraulic functions (Eqs. (1) and (2)) of the single-domain model (KAL), the additional soil hydraulic parameters of the dual-domain model (MRZ) (Eqs. (4a) and (4b)), and the dispersivity were all calibrated.

The Freundlich equation parameters and the degradation coefficients of SDZ and 2-aminopyrimidine were estimated by a joint inversion of SDZ and 2-aminopyrimidine concentrations measured every 14 to 30 days at depths of 30 and 60 cm and in the discharge, which resulted in 84 data points.

Parameters of the empirical function that describes the thermal conductivity as a function of the volumetric water content were calculated using the Chung and Horton (1987) equation based on the two dominant grain sizes of the soils. All thermal conductivity parameters were fixed during the calibration. The empirical parameter describing the dependency of the degradation process on saturation was set to 0.7 according to Walker (1974) and kept constant during the calibration.

Initial parameter values of the soil hydraulic functions were based on values calculated by Kasteel et al. (2007) for the Merzenhausen soil and laboratory measurements of the pF curve for the Kaldenkirchen soil. Parameters of the soil hydraulic functions and dispersivity were kept constant during the model calibration against the measured SDZ and 2-aminopyrimidine concentrations. Initial values of the Freundlich parameters for SDZ were obtained from Sittig et al. (2012). No information was available about the sorption parameters of 2-aminopyrimidine, and thus their initial values were set equal to those for SDZ.

In the last step, the Freundlich parameters were fixed in order to limit the correlation with other adjustable parameters during the inversion. However, note that the Freundlich parameters depend on each other and thus their calibrated values may not be unique and represent only one possible combination. Initial values of the degradation rates of SDZ into 2-aminopyrimidine and other TPs were based on the laboratory column experiments. Similarly as for sorption, no experimental data have been published on the degradation of 2-aminopyrimidine in natural soils. Therefore, initial values for the degradation rates of 2-aminopyrimidine were set equal to values obtained in the laboratory for SDZ.

2.3.4. Scenario simulations: the long-term SDZ/manure field application

Hypothetical long-term SDZ field simulations were carried out for both soils using the calibrated model. Hypothetical scenarios started in the year 2000 and continued until 2050. Precipitation, temperature, wind speed, and evaporation were defined using daily values measured in 2000. Climate change was neglected in these scenarios and thus precipitation and evaporation values from 2000 were applied throughout the 50-year simulation period.

Manure that contained SDZ was applied 5 times per year: on March 19th; April 30th; June 21st; July 30th; and September 6th as recommended in the German livestock waste regulations. Following the German recommendations for the best practice for manure applications to low and moderately fertile soils, it was assumed that a maximum of 10 m^3 of manure was applied per hectare. SDZ concentrations can be related to the dry matter content of manure with 51 mg SDZ per kg dry matter (Guo et al., 2012; Massé et al., 2014). Since manure may contain 10 to 20% of dry matter, a dry matter content of 20% was selected as the worst case scenario, resulting in a total SDZ concentration of 10.2 mg/m^2 per manure application. Note that this value is similar to the SDZ concentration used in our lysimeter experiments. Profiles of mobile SDZ and 2-aminopyrimidine concentrations were plotted after 50 years of manure applications for both soils and down to a depth of 1 m below the soil surface.

3. Results and discussion

3.1. Small-scale and short-term sorption and degradation of SDZ

The small-scale column experiments showed unimodal breakthrough curves (BTCs) for chloride, SDZ, and its TPs in both soils, indicating that preferential flow pathways were absent at a laboratory scale. In the Merzenhausen soil (MER), the first arrival of the tracer and SDZ was similar, whereas the tracer arrived considerably earlier than SDZ in the discharge of the Kaldenkirchen (KAL) soil. In addition, the maximum concentration of SDZ in the discharge was higher for the MER soil than for the KAL soil (Fig. 3).

Different scenarios, with and without manure and with variable SDZ concentrations in water, were investigated at the laboratory scale for both soils. The results show that in the MER soil, the maximum concentration of SDZ arrived earlier when SDZ was mixed with manure compared to the scenarios when SDZ was dissolved in pure water. In the two scenarios when SDZ was mixed with water, the first arrival time increased with a decrease in the SDZ concentration in the solution.

Sorption (Freundlich) and degradation (half-life) parameters (Table 1) were estimated from BTC obtained from the small-scale column experiments. Retardation and degradation were slightly higher in the KAL soil than in the MRZ soil. Sorption of SDZ strongly depends on pH as the chemical structure of SDZ changes in response to soil pH: the cationic form dominates for low pH values (<2), the neutral SDZ form prevails for pH values between 2 and 6.5, and the anionic SDZ form dominates for pH values larger than 6.5 (Sukul et al.,
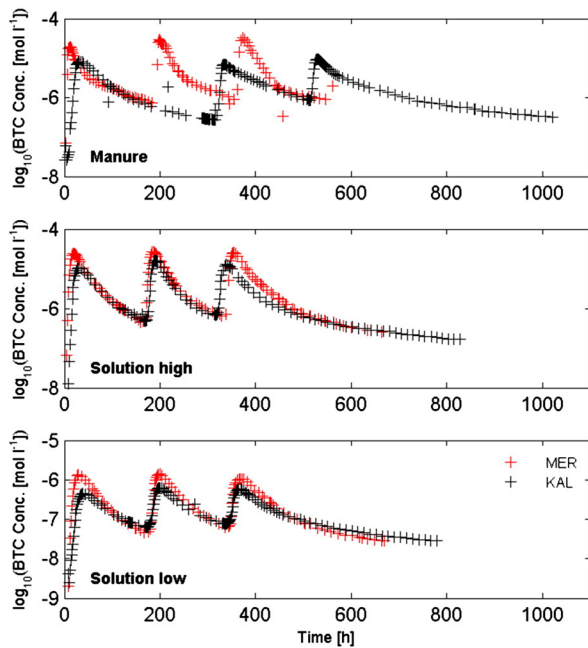
Fig. 3. Breakthrough curves of ^{14}C SDZ for laboratory experiments with soils from Merzenhausen (MER, red cross) and Kaldenkirchen (KAL, black cross). Three (0, 200 and 400 h) applications of SDZ mixed with manure (top figure), SDZ dissolved at a high concentration in water (middle figure), and SDZ dissolved at a low concentration in water (bottom figure). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2008a). Under humid climate conditions, sorption occurs mainly on negatively charged surfaces (clay surfaces, organic matter). Thus, the low pH value of 5.7 in the KAL soil enabled sorption as the neutral and cationic SDZ species developed, while in the MRZ soil with a pH of 7, sorption was distinctively lower as the anionic SDZ form dominated. The strong impact of pH on sorption of sulfonamides was also pointed out by Yang et al. (2009), who observed that sorption of SDZ decreased to zero even in soils with a high organic matter content of up to 3% at pH values of 7.2. In summary, and according to Kahle and Stamm (2007), sorption of SDZ depends strongly on i) the soil type (a content of organic material) and ii) the prevailing pH value. Anskjær et al. (2014) observed a general trend of increasing sorption at low pH and decreasing sorption at high pH for clayey sand and silty clay and a wide range of pH values between 4.3 and 7.6.

Yang et al. (2009) also detected that SDZ degradation did not occur in anoxic or sterile soils, and thus that a higher microbial activity plays a key role in the SDZ degradation since it was observed to be highest in the sandy MRZ soil.

Table 1
Sorption and degradation parameters of SDZ for the Ap horizon and for the SDZ application with manure. Parameters were derived from the small-scale laboratory experiments.

	K_f [cm^3 mg^{-1}]	n [−]	μ_1 [day^{-1}]
Kaldenkirchen soil	5×10^{-4}	0.38	0.0032
Merzenhausen soil	4×10^{-5}	0.28	0.0026

Degradation rates are small at the laboratory scale for both soils compared to the field scale. The shortest SDZ half-life was obtained in the scenario without manure and ranged between 216 (KAL) and 266 (MRZ) days (Fig. 3). The half-life increased with higher SDZ concentrations in the solution and was highest when SDZ was mixed with manure. However, manure does not only influence degradation and half-life of SDZ, it also affects the migration of SDZ through the soil. There are several properties of manure that control the fate of SDZ in the soil. First, manure can change the soil pH and thus the SDZ sorption. Second, the organic matter content (DOM) in manure may also be able i) to increase the SDZ sorption or ii) to enhance the SDZ migration due to facilitated transport of SDZ with the mobile DOM fraction.

Concentrations of SDZ and TPs that resulted from transformation of ^{14}C-labeled SDZ were analyzed in the outflow (Fig. 4). The overall mass balances were 101% for the Merzenhausen soil and 105% for the Kaldenkirchen soil. After 30 days, 62% (MRZ) and 58% (KAL) of SDZ remained unchanged, while 42% (MRZ) and 38% (KAL) of the initially applied SDZ mass were transformed into TPs, respectively.

The composition of discharge changed for different scenarios and the two soils. 4-OH-SDZ was the most relevant TP of SDZ in all scenarios. The other TP of phase I (M1) was present in high concentrations only when manure was absent.

The amount of TPs of phase II (Ac-SDZ, M2, M3, 2-aminopyrimidine) was different in different scenarios. Ac-SDZ developed when SDZ was mixed with manure, but then transformed quickly back into SDZ (Fig. 2). Ac-SDZ was not found when manure was not added. In the scenario without manure, the TP M3 occurred at high concentrations that were only slightly below the concentration of 4-OH-SDZ in the scenario with the high SDZ concentration. However, in no scenario was the TP 2-aminopyrimidine detected in the outflow of the one-month experiment.

### 3.2. Large-scale and long-term fate of SDZ

3.2.1. Unsaturated flow and advective–dispersive transport characteristics

Large-scale hydraulic and conservative transport parameters were estimated from the lysimeter experiments using a joint inversion of water contents measured at depths of 30 and 60 cm, discharge volumes, and bromide concentrations (Table 2). The calibrated model had the root mean square errors (RMSEs) of 0.009 and 0.044 for water contents and 0.051 and 0.048 for discharge for the KAL and MRZ soils, respectively.

The initial water content of 0.1 was measured at the 30-cm depth at the beginning of the field experiment in the KAL soil (in November 2005). Due to precipitation events, the water content fluctuated between 0.09 and 0.2, and thus even during the dry summer periods the water content did not significantly decrease below the initial value. The water content was less affected by precipitation events and remained between 0.17 and 0.2 at a depth of 60 cm (not shown). Simulated soil water contents responded to precipitation events more than the measured data, which led to a small overestimation of the maximum water content during the simulations (Fig. 5).

The initial water content of 0.2 was measured at a depth of 30 cm in the MRZ soil and was thus distinctively higher than in the KAL soil. During the three investigated years, the measured
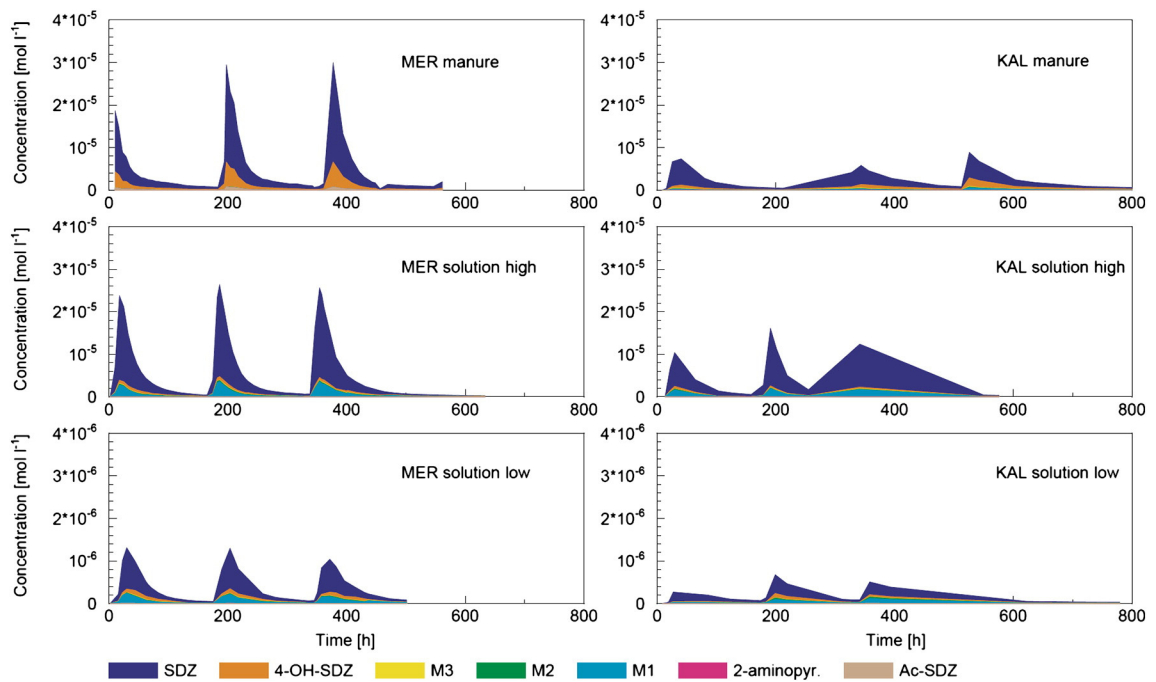
Fig. 4. Concentrations of SDZ and its TPs measured over 30 days in the discharge resulting from three applications of SDZ with manure (top figure), SDZ dissolved at a high concentration in water (middle figure), and SDZ dissolved at a low concentration in water (bottom figure) obtained from the short-term and small-scale column experiments using the Merzenhausen (left figures) and Kaldenkirchen (right figures) soils.

water content increased quickly at the 30 cm depth to 0.4 and then oscillated around this value. This increase may have resulted from TDR measurement errors and could not thus be reproduced by the model. At the 60 cm depth (not shown), the water content remained at its initial value of 0.3 and did not reflect precipitation events.

Estimated soil hydraulic parameters (Table 2) showed a higher permeability of the KAL soil compared to the MRZ soil, which was expected due to the higher sand and lower silt contents of the KAL soil. The residual water content, θ_r, the saturated water content, θ_s, and pore size distribution index, n, were relatively similar for both soils. However, some differences were obtained for the air-entry parameter α, which was

estimated to be up to 2 times higher for the matrix of the silty MRZ soil than for the sandy KAL soil.

The calibration of the bromide BTCs resulted in the RMSE of 0.027 and 0.003 for the KAL and MRZ soils, respectively. For the MRZ soil, the dual-permeability model was the only modeling concept that was able to reproduce the measured pattern of the bromide BTC. The dual-permeability model could simulate preferential flow through the highly permeable fissures or fractures of the clay soil that were responsible for the early arrival of bromide in the discharge at 156 days. After 206 days, 50 days later, the first arrival of bromide occurred in the discharge of the sandy KAL soil. Flow through the less permeable matrix of the MRZ soil produced the second

Table 2
Calibrated soil hydraulic parameters of the Kaldenkirchen soil using the soil hydraulic functions of van Genuchten (1980) and of the Merzenhausen soil using the dual-permeability model of Gerke and van Genuchten (1993).

Layer	Matrix flow						Preferential flow pathways				
	θ_r	θ_s	α	n	K_S	α_L	θ_r	θ_s	α	n	K_S
	[–]	[–]	[cm^{-1}]	[–]	[cm day^{-1}]	[cm]	[–]	[–]	[cm^{-1}]	[–]	[cm day^{-1}]
Merzenhausen											
Ap	0.09	0.47	4.1×10^{-4}	2.38	0.47	10	0[a]	0.35[a]	0.001[a]	2.9[a]	280[a]
A1	0.09	0.39	3.9×10^{-5}	1.54	0.49	10					
Bt1	0.1	0.48	2.5×10^{-3}	1.99	0.53	10					
Bt2	0.05	0.49	4.0×10^{-3}	3.0	0.54	10					
Bt3	0.1	0.55	6.0×10^{-4}	2.37	0.56	10					
Kaldenkirchen											
Ap	0.03	0.30	0.044	1.6	44	7.5	–	–	–	–	–
Bv1	0.07	0.39	0.051	1.4	141	7.5	–	–	–	–	–
Bv2	0.10	0.30	0.047	1.4	442	7.5	–	–	–	–	–
Bv3	0.10	0.34	0.038	.19	266	7.5	–	–	–	–	–

[a] Fixed, not optimized.
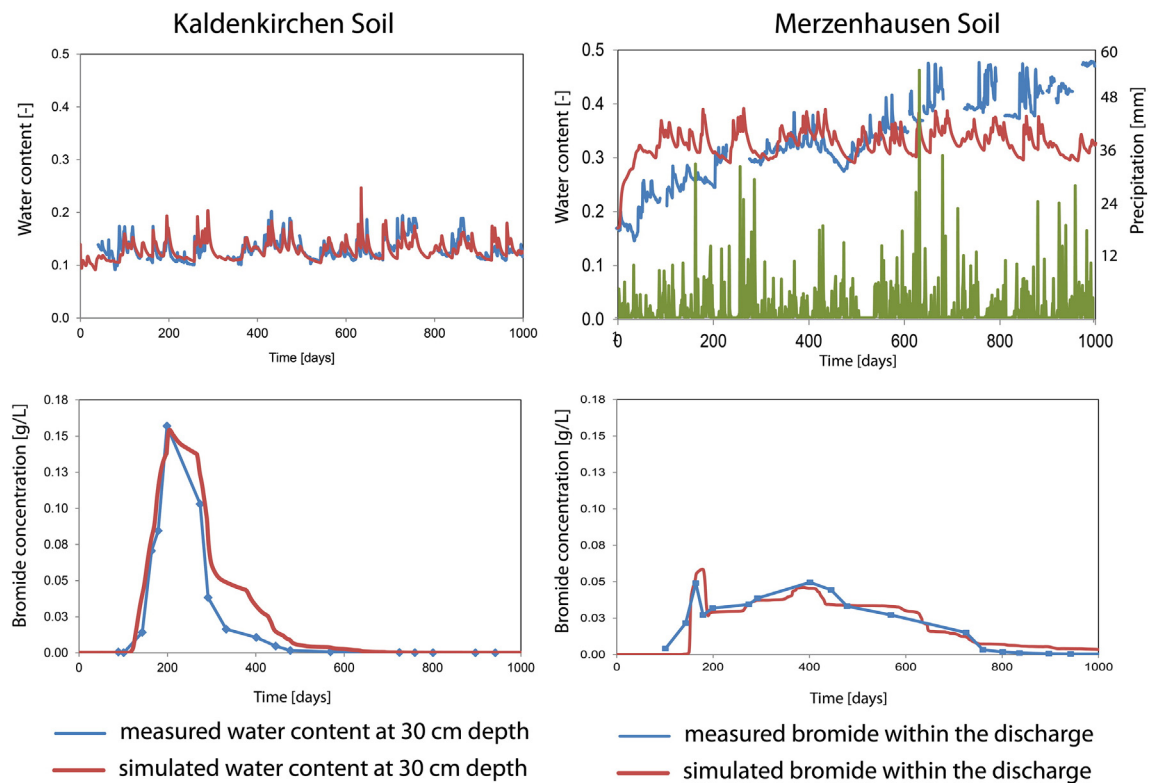
Fig. 5. Precipitation (green line), measured (blue symbols and blue line) versus simulated (red line) water contents at the 30 cm depth and bromide breakthrough curve at the bottom of the lysimeter for the Kaldenkirchen soil (left) and the Merzenhausen soil (right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

overlapping BTC, with the second "first arrival" of bromide at 400 days. The bromide breakthrough continued in the MRZ soil during the next 600 days and finally stopped 800 days after the start of the lysimeter experiment. The BTC in the KAL soil occurred over a period of 250 days and had already stopped 450 days after the beginning of the experiment.

3.2.2. SDZ and 2-aminopyrimidine sorption and degradation characteristics

Simulated SDZ and 2-aminopyrimidine concentrations reproduced the measured pattern of SDZ and 2-aminopyrimidine concentrations in both soils, resulting in the RMSE of 0.95 Bq/mL for the Kaldenkirchen soil and 0.88 Bq/mL for the Merzenhausen soil. The good correspondence between measured and simulated data could be achieved using the dual-permeability model that was employed for the Merzenhausen soil. However, a mismatch in the tailing occurred for the Merzenhausen soil, which may have resulted from the impact of the low permeable clayey matrix on the solute transport that was not captured by the dual-permeability concept. Diffusion from the matrix into the highly permeable pathways may have increased the BTC concentrations and thus created the observed tailing pattern. This effect is most pronounced for solutes with high diffusion coefficients, e.g., for large organic molecules such as sulfonamides.

Transport and retardation parameters of SDZ, derived from the Kaldenkirchen soil lysimeter experiment, for the Bv1 to Bv3

($K_{f,SDZ}$: 7×10^{-4}–1×10^{-3} cm^3 mg^{-1}) horizons, resulted in similar values as estimated from the small-scale laboratory experiments for the Ap horizon. However, the field-scale retardation was distinctively higher for the Ap horizon ($K_{f,SDZ}$: 3×10^{-2} cm^3 mg^{-1}) than measured at the laboratory scale (Tables 1 and 3). The Merzenhausen soil displays a scale-dependency of the Freundlich coefficient $K_{f,SDZ}$, which was in all layers several orders of magnitude higher at the field scale than determined in the laboratory, where maximum values reached 2 to 7×10^{-2} cm^3 mg^{-1} for Bt2 and A1, respectively, and minimum values decreased to 3×10^{-3} cm^3 mg^{-1} for Bt3.

At depths between zero and 30 cm, the transport of SDZ and 2-aminopyrimidine was strongly affected by the more permeable fractures and fissures within the clayey Merzenhausen soil that resulted in higher concentrations of SDZ and 2-aminopyrimidine than in the Kaldenkirchen soil. Adsorption to the clayey matrix of the Merzenhausen soil reduced SDZ and 2-aminopyrimidine concentrations to very small values at a depth of 60 cm and below the detection limit at the bottom of the lysimeter. Due to a smaller sorption capacity of the sandy Kaldenkirchen soil, a limited amount of SDZ (2 Bq/mL) and 2-aminopyrimidine (0.1 Bq/mL) was found in the outflow of the lysimeter (Figs. 6 and 7). However, note that radioactivity of 1 Bq/mL equals a SDZ concentration of only 1×10^{-4} μg/L. The long-term, field-scale lysimeter experiments indicated that the leaching potential of SDZ and 2-aminopyrimidine was limited to 2 Bq/mL (2×10^{-4} μg SDZ L^{-1}) and less than

Table 3
Calibrated sorption and degradation parameters for SDZ and 2-aminopyrimidine for the Kaldenkirchen and Merzenhausen soils.

| Layer	$K_{f,SDZ}$	$K_{f,2AP}$	n_{SDZ} n_{2AP}	μ_1	μ_2	μ_1'
	[cm³ mg⁻¹]		[–]	[day⁻¹]		
Merzenhausen						
Ap	7×10^{-3}	4×10^{-3}	0.28	2×10^{-2}	6×10^{-3}	8×10^{-2}
A1	2×10^{-2}	1×10^{-2}	0.28	1×10^{-4}	1×10^{-4}	1×10^{-1}
Bt1	6×10^{-3}	1×10^{-1}	0.28	1×10^{-4}	1×10^{-3}	5×10^{-3}
Bt2	7×10^{-2}	3×10^{-3}	0.28	1×10^{-3}	1×10^{-3}	3×10^{-3}
Bt3	3×10^{-3}	3×10^{-3}	0.28	7×10^{-1}	7×10^{-1}	3×10^{-3}
Kaldenkirchen						
Ap	3×10^{-2}	3×10^{-3}	0.38	8×10^{-2}	1×10^{-1}	5.9
Bv1	8×10^{-4}	4×10^{-4}	0.38	2×10^{-2}	2×10^{-3}	1.2
Bv2	7×10^{-4}	3×10^{-4}	0.38	1×10^{-5}	4×10^{-3}	1×10^{-1}
Bv3	1×10^{-3}	6×10^{-4}	0.38	2×10^{-2}	3×10^{-3}	3×10^{-2}

0.1 Bq/mL (1×10^{-5} SDZ µg L⁻¹) in the KAL soil, respectively, and below the limit of detection (4×10^{-4} Bq/mL or 4×10^{-8} µg SDZ L⁻¹ for SDZ and 2-aminopyrimidine, respectively) in the MRZ soil.

The biodegradation of SDZ was slow at both laboratory and field scales in many soil horizons, resulting in large SDZ half-lives of more than 700 days in the lysimeter and between 216 (KAL) and 266 (MRZ) days in the laboratory. However, at the field scale, a SDZ half-life decreased between 1 to 34 days in several soil horizons. The observed variability of half-lives indicates the impact of different soil layers and decreased oxygen access into deeper parts of the soil profile. SDZ biodegradation thus becomes an important and limiting factor for the migration of SDZ in shallow parts of the soil profile. The short half-life that occurred in the lysimeter experiments corresponds well with the SDZ half-lives of 11 to 28 days obtained by Halling-Sørensen (2000) and Tappe et al. (2013).

2-Aminopyrimide was below the detection limit (0.2 µg mL⁻¹) during the one-month laboratory experiments. At the field scale, the 2-aminopyrimidine concentration was less than 1% of the SDZ concentration (Figs. 6 and 7). In both soils, sorption of 2-aminopyrimidine was slightly smaller than that of SDZ. However, 2-aminopyrimidine was characterized by fast biodegradation with small half-lives of only a few hours and it was degraded in all layers of both soils at high rates. The sandy Kaldenkirchen soil especially favors the microbial activity. The high degradation rate may result from i) a higher hydraulic conductivity that increases the oxygen migration through the soil and ii) lower pH values in the KAL soil as SDZ becomes persistent in anoxic soils and at pH values larger than 6.5 (Sukul et al., 2008b).

3.2.3. Long-term leaching potential and accumulation of SDZ in natural soils

The long-term leaching potential of SDZ and 2-aminopyrimidine was evaluated for both soils (Fig. 8) using hypothetical field-scale scenarios and single- and dual-domain modeling concepts. The sensitivity of simulation results was studied using the parameters calibrated against the lysimeter experiments. The results showed the highest sensitivity to the saturated hydraulic conductivity of all layers of the soil profile, and only moderate sensitivity to the pore size distribution
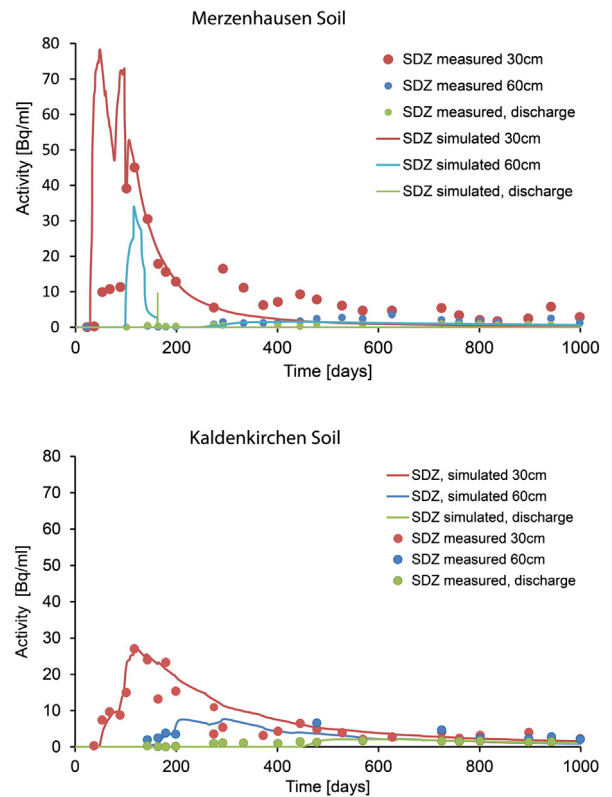
Fig. 6. Measured (symbols) versus simulated (lines) concentrations of SDZ at depths of 30 (red) and 60 cm (blue), and within the discharge (green) of the lysimeter for the sandy soil of Kaldenkirchen (bottom) and the clayey silt soil from Merzenhausen (top). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

index and the residual water content of the top soil layer. Dispersivity and the half-life of 2-aminopyrimidine have the highest impact on the transport, retardation, and degradation of SDZ and 2-aminopyrimidine, respectively. The 2-aminopyrimidine concentrations are moderately sensitive to the value of the Freundlich coefficient. However, the retardation and degradation characteristics of SDZ displayed only a limited impact on the transport of SDZ and 2-aminopyrimidine. For the parameters with the highest impact on the results, the confidence interval for the hydraulic conductivity ranged between 0.1 m day⁻¹ and 27 m day⁻¹ (for the KAL soil), and the degradation rate of 2-aminopyrimidine varied over several orders of magnitude. These two parameters can thus introduce the highest uncertainty into the hypothetical simulations.

The SDZ concentrations did not exceed the threshold value of 0.1 µg/L in both soils below the depth of 30 cm after 50 years of five SDZ applications per year, as defined by the EU Water Framework Directive (EU-WFD) for pharmaceuticals such as diclofenac. In the silty-clay MRZ soil, due to its higher retardation, the SDZ concentrations decreased to zero at a depth of 50 cm. In the sandy KAL soil, SDZ was able to migrate into deeper parts of the soil and reached 0.05 µg/L at a depth of 50 cm. However, at the 80 cm depth, the SDZ concentration decreased below 0.02 µg/L. Due to 2-aminopyrimidine's high biodegradation rates, its concentrations were predicted to be very low even in shallow depths of the soil profile. In summary,
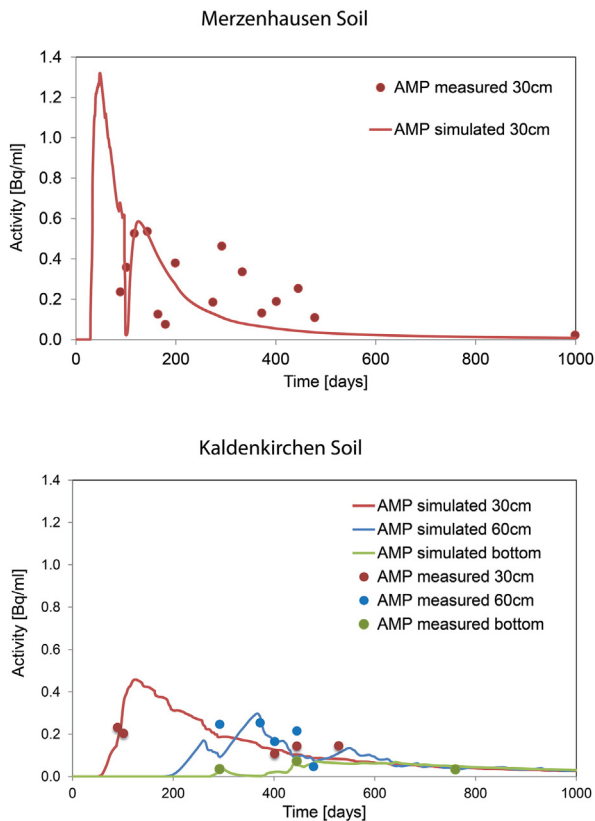
Fig. 7. Measured (symbols) versus simulated (lines) concentrations of the transformation product 2-aminopyrimidine at depths of 30 (red) and 60 cm (blue), and within the discharge (green) of the lysimeter for the sandy soil of Kaldenkirchen (bottom) and the clayey silt soil from Merzenhausen (top). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the long-term leaching potential of SDZ and 2-aminopyrimidine can be assessed as very small for sandy and clayey soils if the current agricultural practices used in Germany are taken into account.
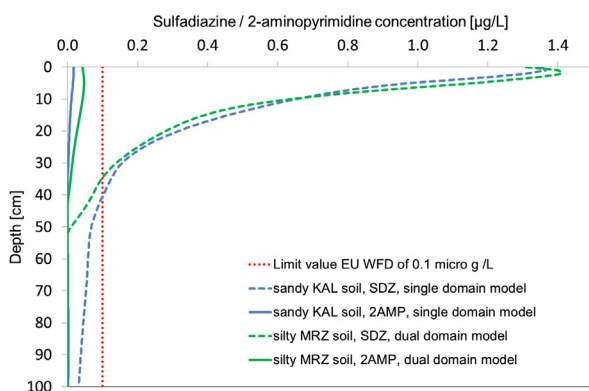
Fig. 8. Simulated profiles of SDZ (dashed line) and 2-aminopyrimidine (2AMP, solid line) concentrations for the sandy Kaldenkirchen soil (blue line) using a single-domain model and for the clayey-silty Merzenhausen soil (green line) using a dual-domain model after 50 years of manure/SDZ applications. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

A comparison between small-scale, short-term laboratory experiments and field-scale, long-term lysimeter experiments showed that the number of TPs was limited in the lysimeter and it was high in the laboratory. In addition, biodegradation strongly increased at the field scale, resulting in a reduced leaching risk into groundwater. The occurrence of SDZ transformation products was different in experiments with and without manure. While the TP 2-aminopyrimidine did not develop in the one-month long laboratory experiments, it was the most prevalent TP during the three-year lysimeter study. Moreover, manure contains DOM colloids that can enhance the mobility of SDZ and 2-aminopyrimidine due to their co-transport with a mobile DOM fraction. Thus, in the presence of manure even hydrophobic substances may show an increased leaching potential.

Laboratory experiments strongly underestimated (by 2 orders of magnitude) the Freundlich coefficient in both soils. At the field scale in deeper parts of the soil profile, sorption of sulfonamides increased, while hydraulic properties, e.g., preferential flow pathways, became less important for the migration of SDZ.

The laboratory experiments were not affected by the impact of soil heterogeneity, such as preferential flow pathways that controlled the transport of SDZ in the lysimeter with the clayey soil. At the field scale, the degradation rate was one order of magnitude higher than that derived from the laboratory experiments. In contrast to the results obtained at the laboratory scale, the lysimeter experiments showed higher biodegradation in the sandy soil than in the clayey soil.

Over longer time periods, e.g., after 50 years of multiple SDZ and manure applications, the higher leaching risk of SDZ in the sandy soil due to a higher permeability and decreased retardation is reduced. Below a depth of 30 cm, the SDZ concentrations in both soils were below 0.1 μg/L. Due to high retardation of SDZ and high biodegradation of 2-aminopyrimidine, neither sulfonamide could migrate into deeper parts of the soil profile.

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