

Transport of Manure-Based Applied Sulfadiazine and Its Main Transformation Products in Soil Columns

M. Unold,* J. Šimůnek, R. Kasteel, J. Groeneweg, and H. Vereecken

Solute displacement experiments with the antibiotic sulfadiazine (SDZ) and its main transformation products in pig manure were performed to investigate the influence of manure on SDZ transport. Either pig manure containing ^{14}C -sulfadiazine (4-amino-*N*-2-pyrimidinyl-benzenesulfonamide), and its main transformation products ^{14}C -4-OH-SDZ and ^{14}C -*N*-Ac-SDZ, or a ^{14}C -SDZ solution was incorporated in the first centimeter of undisturbed and repacked soil columns, which were then irrigated. Breakthrough curves (BTCs) of ^{14}C , SDZ, 4-OH-SDZ, *N*-Ac-SDZ and 4-[2-iminopyrimidine-1(2*H*)-yl]-anilin were measured. The ^{14}C distributions vs. depths were determined after the conclusion of the leaching experiments. An application of SDZ together with manure resulted in lower peak values of the ^{14}C BTCs and a slightly lower amount of eluted mass. In the experiments with manure, the ^{14}C concentrations in the uppermost layers of the soil columns were higher, probably due to the filtration of manure particles onto which SDZ or its transformation products were sorbed. The transformation products showed a relatively high leaching potential similar to SDZ. Cotransport with organic particles seemed to be of minor relevance for the eluted amounts of solutes. All BTCs were modeled using a numerical model that considered degradation chains from *N*-Ac-SDZ into SDZ and from SDZ into 4-OH-SDZ, as well as one reversible and one irreversible kinetic sorption site for each solute. The applied model fitted the BTCs of SDZ and its transformation products reasonably well. The fitting process revealed a high mobility of both SDZ and its transformation products. While *N*-Ac-SDZ degradation into SDZ was fast and no extended tailing of *N*-Ac-SDZ was observed, the transport behavior of 4-OH-SDZ was similar to that of SDZ.

ABBREVIATIONS: BTC, breakthrough curve; CDE, convection–dispersion equation; HPLC, high performance liquid chromatography; SDZ, sulfadiazine; TOC, total organic carbon.

IN RECENT YEARS, several studies have shown the widespread occurrence of sulfonamide antibiotics in surface waters (Christian et al., 2003; Managaki et al., 2007), groundwaters (Sacher et al., 2001; Hamscher et al., 2005; Focazio et al., 2008) and soils (Höper et al., 2002; Boxall, 2004; Hamscher et al., 2005). The major risk of introducing these substances into the environment is the development and spread of resistant pathogens (Kemper, 2008), especially since the probability of these chemicals reaching the food chain via drinking water (Batt et al., 2006; Ye et al., 2007) or root uptake by plants (Dolliver et al., 2007) is high.

The main difference in how antibiotics and other organic contaminants, such as pesticides, are introduced into the environment is the way of their application. While pesticides are intentionally spread over the field, antibiotics are mostly

introduced unintentionally with the application of manure (Jørgensen and Halling-Sørensen, 2000). The application of the sulfonamide antibiotic SDZ with manure into the root zone, which is a common practice in Germany, may influence soil structure and other conditions affecting solute transport in the soil profile. The effects of manure application on soil aggregation have been studied by many, including Wortmann and Shapiro (2008). These researchers found that manure application resulted in the formation of macroaggregates. They concluded that the risk of surface runoff may be greatest shortly after application because macroaggregates have had no time to develop.

Suspended colloidal material, as found in manure, can facilitate the transport of pollutants in soils. Molecules of organic substances can sorb to small particles (McGechan and Lewis, 2002) and travel along with them at usually rapid, unretarded velocities. Colloid-facilitated transport has been shown, for example, to accelerate the transport of pesticides, phosphates, and heavy metals (Hesketh et al., 2001; de Jonge et al., 2004; Pang and Šimůnek, 2006). McGechan and Lewis (2002) indicated in their review that macropores are the main pathways for colloidal transport since such larger particles are otherwise effectively retained by physical filtration processes (Jarvis et al., 1999; Kretzschmar, 1994).

Due to speciation, sorption of sulfonamide antibiotics to soils (Kurwadkar et al., 2007) and organic material (Kahle and Stamm, 2007) is strongly dependent on pH. Due to high amounts of NH_4 present in manure, the soil water pH can increase by 1.5 units after the application of manure (Kay et al., 2005a), which may lead to a significantly lower sorption of SDZ.

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Vadose Zone J. 8:677–689
doi:10.2136/vzj2008.0122

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Several studies focused on the sorption and transport of antibiotics in the presence of manure (Boxall et al., 2002; Kay et al., 2004, 2005a; Kreuzig and Hölte, 2005; Blackwell et al., 2007; Stooß et al., 2007). Antibiotics of the sulfonamide group seem to have a stronger tendency for leaching and overland flow than other antibiotics, such as tetracyclines and tylosin. Blackwell et al. (2007) and Kay et al. (2005b) demonstrated this tendency for sulfachloropyridazine in field and lysimeter studies. Kay et al. (2005a) found no influence of manure on the transport of the tetracycline antibiotic oxytetracycline. In batch studies, Kreuzig and Hölte (2005) observed a tendency of SDZ to form a nonextractable fraction, which remained in the manure matrix. Additionally, the extractable fraction of SDZ in a soil was much lower when SDZ was applied together with manure. In contrast, Thiele-Bruhn and Aust (2004) and Boxall et al. (2002) found decreased sorption of SDZ and other sulfonamide antibiotics in the presence of manure, probably due to the use of different soils and manures in their experiments.

Kreuzig et al. (2005) and Heise et al. (2006) reported that sulfonamides quickly form nonextractable residues in soils. Bialk and Pedersen (2008) showed that the sulfonamide antibiotic sulfapyridine can be covalently bound to the model humic substance protocatechuic acid, which is one explanation for the observed irreversible sorption behavior of sulfonamides. While degradation of sulfonamides has often been observed (Sukul et al., 2008b; Wang, 2006), their mineralization has been found to be relatively low (Loftin et al., 2008; Schmidt et al., 2008).

Various studies have shown that manure from SDZ-administered animals contains the parent compound SDZ as well as several transformation products. Lamshöft et al. (2007) studied excretion patterns from pigs that were administered with ^{14}C -SDZ. They detected about 96% of the applied ^{14}C excreted in manure and identified five transformation products in addition to SDZ. While 4-*N*-acetyl-SDZ (*N*-Ac-SDZ) and 4-hydroxy-SDZ (4-OH-SDZ) were found in relatively large concentrations, formyl-SDZ and acetyl-hydroxyl-SDZ were present only in trace amounts.

The occurrence of these transformation products cannot be regarded as the result of a degradation process that makes the parent compound harmless, since it is known, for example, that the metabolite 4-OH-SDZ can still be microbially active (Nouws et al., 1989) and that *N*-Ac-SDZ can retransform into the active parent compound SDZ (Berger et al., 1986). There are indications that transformations not only occur during metabolization in animals, but also in soils (Burkhardt et al., 2005; Wehrhan, 2006; Wehrhan et al., 2007) and aqueous solutions (Sukul et al., 2008b).

Up to now, little has been known about the occurrence and fate of transformation products in the environment. This may be due to a lack of reference substances (Díaz-Cruz and Barceló, 2006). Their relevance in environmental assessments was shown by Hilton and Thomas (2003), who detected relatively high concentrations of the acetyl form of the antibiotic sulfamethoxazole in effluent and surface waters, whereas the concentration of the parent compound was lower than the detection limit.

Various types of models are available to simulate the transport of antibiotics. These models need to consider various physical processes involved in the transport of antibiotics, as well as chemical processes, including kinetic and equilibrium sorption

and degradation. The process of degradation is usually simulated in transport models as a first-order process. Examples of model applications that considered first-order degradation are, for example, Casey and Šimůnek (2001) and Schaerlaekens et al. (1999) for the transport of trichloroethylene, Casey et al. (2003, 2004, 2005), Das et al. (2004), and Fan et al. (2007) for the transport of hormones, and Papiernik et al. (2007) for the transport of an herbicide. Das et al. (2004), for example, used a bicontinuum model with first-order degradation to describe the transport of estradiol and testosterone, as well as their daughter products. Similarly, Casey et al. (2003, 2004, 2005) included first-order degradation to describe the transport of estradiol and testosterone and their daughter products. Similar first-order reaction pathways are also often used to describe the simultaneous transport of N species (Hanson et al., 2006), radionuclides (van Genuchten, 1985), or organic explosives (Šimůnek et al., 2006).

The main objectives of this study were to investigate (i) the effects of pig manure on the fate and transport of SDZ in soil columns and (ii) the transport in soil columns of two SDZ transformation products present in applied manure. To achieve these objectives, solute displacement experiments were performed using both repacked and undisturbed soil columns involving two soils. Pig manure containing ^{14}C -SDZ, ^{14}C -4-OH-SDZ, and ^{14}C -*N*-Ac-SDZ was incorporated into the top of the soil columns. A ^{14}C -SDZ solution was additionally incorporated into one repacked column of each soil. Breakthrough curves and ^{14}C distributions vs. depth were analyzed using a transport model that considered convective–dispersive transport with one kinetic reversible and one kinetic irreversible sorption site. Transformation and sorption rates for the different solutes were determined using an inverse parameter optimization procedure based on the Levenberg–Marquardt algorithm.

Materials and Methods

Experimental Setup

To study the effects of manure on the transport of SDZ and its transformation products, we conducted experiments on undisturbed and repacked columns of two soils. Soil samples for both the repacked and undisturbed soil columns were collected from the upper 30 cm of two fields with soil types that are typical for agricultural land use in Northrhine-Westphalia, Germany. A silt loam soil (an Alfisol or Orthic Luvisol) was collected from a field near Jülich-Merzenhausen (denoted below as Soil M), while a loamy sand soil (an Inceptisol or Gleyic Cambisol) was sampled from a field near Kaldenkirchen (denoted below as Soil K). Selected soil properties are shown in Table 1.

For the repacked soil columns, the soils were sieved (2 mm) and air dried. During the packing procedure, layers of about 0.5-cm thickness were added to the columns and compacted by weakly pressing with a pestle. Columns constructed of polyvinyl chloride (PVC) with an inner diameter of 8 cm and heights of 10 cm were used for all experiments. The excellent solute mass recoveries in most experiments suggested that we could neglect SDZ sorption onto the PVC material.

Undisturbed soil columns were collected using PVC columns and a metal adaptor with a sharp front attached at one end to facilitate entry into the soil. No roots were visible in the soil, so only fine roots may have existed in the soil columns. The

TABLE 1. Selected physical and chemical properties of the Kaldenkirchen soil (K) and the Merzenhausen soil (M).

Property	Soil K	Soil M
Clay (<0.002 mm), mass %†	4.9	15.4
Silt (0.002–0.064 mm), mass %†	26.7	78.7
Sand (0.064–2.0 mm), mass %†	68.5	5.9
pH (0.01 mol L ⁻¹ CaCl ₂)‡	6.8	7.4
Total organic C, mass %†	1.07	1.24
Cation exchange capacity, cmol _c kg ⁻¹ §	7.8	11.4

† Data were measured at the Institut für Nutzpflanzenwissenschaften und Ressourcenschutz of the University of Bonn.

‡ Average pH values in soil column effluents for the columns with manure.

§ Data taken from Förster et al. (2009).

repacked and undisturbed soil columns were mounted on porous glass plates having a high conductivity and an air-entry value >100 mbar. Overall, seven experiments were performed. The experimental conditions for each setup are shown in Table 2.

While either manure or the SDZ solution was applied to the repacked soil columns, only manure was incorporated into the undisturbed soil columns. The soil columns were slowly saturated from the bottom with 0.01 mol L⁻¹ CaCl₂ for approximately 2 d before displacement experiments started. The same solution was also used as a background solution. A thin layer of coarse quartz sand was placed on top of the columns to protect the bare soil surface from the impact of the irrigation water. Six soil columns were irrigated at a constant flow rate of about 0.19 cm h⁻¹. An additional experiment was performed using a second undisturbed column containing Soil K to which manure was applied. In this case, the same amount of irrigated water per hour was applied at a higher flow rate for 5 min, followed by 55 min of redistribution.

All soil column experiments were run with software-controlled equipment. Irrigation of the soil columns started a few days before the leaching experiments. The irrigation rate was recorded by weighing the storage bottle of the irrigation solution. Suction was applied at the bottom of the soil columns. Suctions within the range of 4 to 41 mbar were chosen separately for each soil column to establish a constant pressure head (water content) in the soil columns for a given flow rate. This meant that gravity was the primary factor driving water flow. The suction inside of the columns were followed using two tensiometers installed 2.5 and 7.5 cm below the soil columns' surfaces. Fifteen milliliters of the outflow was collected in test tubes for each sample. Water lost due to evaporation, which was approximately 2.19 × 10⁻⁶ L h⁻¹, was included in calculations of the solute concentrations to correct the measured concentrations for evaporation losses.

TABLE 2. Experimental conditions for different soil column experiments.

Soil column†	Soil	Packing	Sulfadiazine application	Irrigation	Bulk density g cm ⁻³	Flow velocity cm h ⁻¹	Applied suction mbar
KrepMAN	K	repacked	manure	constant	1.42	0.18	23
KrepSOL	K	repacked	solution	constant	1.37	0.19	41
KundMAN	K	undisturbed	manure	constant	1.49	0.20	10
KundMAN _i	K	undisturbed	manure	intermittent	1.40	0.18	10
MrepMAN	M	repacked	manure	constant	1.34	0.19	30
MrepSOL	M	repacked	solution	constant	1.27	0.19	29
MundMAN	M	undisturbed	manure	constant	1.88	0.19	4

† The first letter represents soil type (either K or M), columns were either repacked (rep) or undisturbed (und), and either manure (MAN) or a stock solution (SOL) was incorporated into the column; subscript i denotes intermittent infiltration.

Evaporation losses were determined by weighing two water-filled tubes at regular time steps.

Before and after the SDZ-transport experiments, we used Cl⁻ as a non-reactive tracer to characterize the physical transport mechanisms in the soil columns. For this purpose, pulses of 0.05 mol L⁻¹ CaCl₂ solution were applied to the columns for 1 h (corresponding pore volumes are listed in Table 3). The Cl⁻ concentration in the outflow samples was measured using an electrical conductivity sensor included in the experimental setup. The correlation between electrical conductivity and Cl⁻ concentration was determined by establishing a calibration curve using samples of known Cl⁻ concentration.

For determining the BTCs of SDZ and its transformation products, either 15.07 g of pig manure containing ¹⁴C-SDZ or 15.07 g of a 0.01 mol L⁻¹ CaCl₂ solution with the same amount of SDZ was incorporated into the top 1 cm of the soil columns. Manure or the SDZ solution was first mixed with the air-dried soil of the particular soil type and then added to the top of the soil columns from which the original soil had been removed.

When the leaching experiments were finished, the soil columns were cut into slices of 0.5- or 1-cm thickness to measure ¹⁴C concentrations in the column profiles by combusting aliquots of each slice in an oxidizer (Robox 192, Zinsser Analytik GmbH, Frankfurt, Germany), following the approach described in Unold et al. (2009). This method allows ¹⁴C concentrations in soils to be measured without applying any extraction procedures, which were reported to have low efficiencies and variations between fresh (<71%) and aged (<46%) SDZ residues (Förster et al., 2009). Thus only the total amount of radioactivity was measured in the soil. For each slice, three 0.5-g replicates of oven-dried (105°C), ground, and homogenized soil were combusted in an oxidizer. After combustion, the evolving gas was washed into a scintillation cocktail (Oxysolve C-400, Zinsser Analytik, Frankfurt, Germany), in which the labeled CO₂ was trapped and then analyzed by liquid scintillation counting (LSC). Blanks were run before and after the samples to check for background and cross-contamination. The efficiency of the combustion process (>95%) was ascertained by combusting samples spiked with a known amount of the model compound ¹⁴C-anilazine prior to and after analyzing the samples.

All experiments were performed in a laboratory without sunlight to prevent photodegradation. Samples were exposed only briefly to artificial light during sample collection and preparation. Biodegradation was not impeded. Samples were stored in a refrigerator until measurements were conducted within approximately 2 or 3 wk. We assumed that concentrations of

TABLE 3. Transport parameters for the conservative tracer Cl^- : V is the pore-water velocity, D is the dispersion coefficient, R^2 is a measure of the relative magnitude of the total sum of squares associated with the fitted equation, λ is dispersivity, and θ is water content.

Soil column†	V cm h ⁻¹	D cm ² h ⁻¹	Pore volumes	R^2	λ cm	θ cm ³ cm ⁻³
KrepMAN	0.56 (± 0.02)‡	0.41 (± 0.04)	17.9	0.97	0.74	0.32
KrepSOL	0.78 (± 0.03)	0.42 (± 0.10)	12.7	0.94	0.54	0.25
KundMAN	0.54 (± 0.01)	0.85 (± 0.04)	16.4	0.99	1.57	0.37
KundMAN _i	0.53 (± 0.01)	0.45 (± 0.02)	18.7	0.99	0.84	0.34
MrepMAN	0.44 (± 0.01)	0.25 (± 0.02)	22.7	0.99	0.57	0.43
MrepSOL	0.54 (± 0.01)	0.29 (± 0.02)	18.5	0.99	0.54	0.36
MundMAN	0.46 (± 0.01)	0.71 (± 0.02)	21.7	0.99	1.54	0.42

† The first letter represents soil type (either K or M), columns were either repacked (rep) or undisturbed (und), and either manure (MAN) or a stock solution (SOL) was incorporated into the column; subscript *i* denotes intermittent infiltration.

‡ Values in parentheses indicate 95% confidence intervals.

the transformation products did not change during this time due to the low-temperature environment.

The content of total organic C (TOC) in selected samples was measured using a TOC 5050A analyzer (Shimadzu, Duisburg, Germany). Samples for this purpose were frozen before TOC measurements.

Analysis of Sulfadiazine and Transformation Products

The pig manure containing ¹⁴C-labeled sulfonamides used in our studies was obtained from a feeding experiment conducted at Bayer AG Monheim where ¹⁴C-SDZ with single labeling of the pyrimidine ring and ¹²C-SDZ were administered to pigs in a ratio of 1:19. The specific radioactivity of SDZ in manure was 0.44 MBq mg⁻¹. After dosing, manure was collected, mixed, and stored at 4°C in darkness. The total ¹⁴C concentration of the manure was 270 mg L⁻¹ in mass equivalents of SDZ.

Carbon-14-SDZ was provided by Bayer HealthCare AG (Wuppertal, Germany) as a powder with a purity of 99% and a specific radioactivity of 8.88 MBq mg⁻¹. The application solution for the experiments without manure was prepared by adding appropriate amounts of ¹⁴C- and ¹²C-SDZ (Sigma Aldrich, Germany) to a 0.01 mol L⁻¹ CaCl₂ solution. Since the pH value of the manure was approximately 8, the SDZ application solutions were buffered to this pH value by adding low amounts of 0.01 mol L⁻¹ NaOH. Since the added amounts of Na were very low, its presence should not have substantially affected the results.

The method of Lamshöft et al. (2007) was used to determine the transformation products in the manure. Briefly, 4 cm³ of McIlvaine buffer (1 mol L⁻¹ citric acid/1 mol L⁻¹ Na₂HPO₄, 18.15 cm³/81.85 cm³; adjusted to pH 7) was added to centrifuging vials containing 1 g of homogenized manure. The extracts were shaken for 30 s with a vortex mixer, treated for 15 min in an ultrasonic bath, and centrifuged for 0.5 h (514 × *g*) in an Allegra 6 KR centrifuge (Beckmann Coulter, Palo Alto, CA). This procedure produced clear supernatants, which were transferred into high performance liquid chromatography (HPLC) vials and analyzed with radio HPLC (LB 509 detector, Berthold Technologies, Bad Wildbad, Germany). Our HPLC system included a reversed-phase column (Phenomenex Synergi Fusion RP 80, 250 by 4.6 mm), which was eluted with a mixture of water (490 cm³) and methanol (10 cm³), buffered with 0.5 cm³ of a 25% H₃PO₄ solution. The

injection volume was 0.25 cm³ for each sample. A gradient with an increased amount of methanol was used for peak separation, starting with 100% water for 6 min. The methanol fraction increased linearly to 27% during the first 23 min, then to 37% within the next 3 min, and to 47% during the following 2 min. The methanol part reached its maximum of 57% after 30 min. Sulfadiazine, *N*-Ac-SDZ, and 4-OH-SDZ could be detected using this HPLC method. The substances were identified according to their retention times compared with standards of SDZ and *N*-Ac-SDZ. The retention time of 4-OH-SDZ was known from previous experiments. Retention times of SDZ, *N*-Ac-SDZ, and 4-OH-SDZ were approximately 16.70, 20.18, and 15.60 min. The detection limit of the radio HPLC was about 3 µg L⁻¹ mass equivalents of SDZ. For two manure extractions that we conducted, 7.6 and 8.3% of the radioactivity could not be assigned to a peak, probably due to sorption onto organic material.

Sulfadiazine and its main transformation products in the outflow samples were also separated using radio HPLC. Using the measurement protocol described above, four peaks could be distinguished in the chromatograms. In addition to SDZ and the two main transformation products, we also detected 4-[2-iminopyrimidine-1(2*H*)-yl]-anilin with a known retention time from previous experiments of approximately 6.2 min.

The same measurement technique applied in previous experiments (Unold et al., 2009) was also used here to detect SDZ and its transformation products in samples with concentrations below the detection limit of the HPLC radio detector. Outflow from the HPLC was collected during the retention times of SDZ and its transformation products, as well as within these time frames, for background correction. Solutes in three replicate samples were quantified with LSC using a counting time of 15 min, for which the samples were mixed with 10 cm³ of the scintillation cocktail (Insta-Gel Plus, Canberra Packard GmbH, Dreieich, Germany). The detection limit of the LSC detector was 0.4 Bq, which corresponds to 0.045 ng mass equivalents of SDZ dissolved in an aliquot of the outflow sample. Non-zero concentrations were assigned to a solute when the measured radioactivity was >1.2 Bq, which was three times the detection limit of LSC. Otherwise its contribution was set to zero. Using this method, the transformation products could be quantified with the help of the specific radioactivity of ¹⁴C down to a concentration of 0.5 µg L⁻¹ mass equivalents of SDZ in the outflow samples. A background correction of the HPLC measurements was done and the method was validated by measuring a calibration curve. Triplicate measurements of total radioactivity in the samples were performed with LSC after mixing an aliquot of 0.5 cm³ with 10 cm³ of the scintillation cocktail.

Selected samples were filtered (Centricon 10, Millipore, Billerica, MA) and total ¹⁴C was measured before and after filtration. Since there was no difference in the measurements, we concluded that solutes in the outflow samples were not attached to colloidal particles.

Theory of Solute Transport

The steady-state transport experiments on unsaturated repacked and undisturbed soil columns were analyzed as one-

dimensional transport problems, assuming constant water contents and fluxes throughout the soil columns. Solute transport is commonly described using the convection–dispersion equation (CDE), which for conservative, nonreacting tracers during steady-state flow conditions can be expressed as

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial z} + D \frac{\partial^2 C}{\partial z^2} \quad [1]$$

where t is time [T], V is the average pore-water velocity [$L T^{-1}$], C is the solute concentration in the liquid phase [$M L^{-3}$], D is the dispersion coefficient [$L^2 T^{-1}$], and z is depth [L]. The parameters V and D for the Cl^- BTCs were estimated using a nonlinear parameter estimation procedure based on the Levenberg–Marquardt algorithm. We used the CXTFIT code (Toride et al., 1999), which analytically solves the CDE for appropriate boundary conditions. The estimated transport parameters (i.e., V and D) and the experimentally determined Darcian flux, q [$L T^{-1}$], were then used to evaluate the volumetric water content, $\theta = q/V$ [$L^3 L^{-3}$], and the longitudinal dispersivity, $\lambda = D/V$. These parameters were assumed to fully characterize the physical transport process and were fixed in subsequent transport simulations of reactive SDZ and its transformation products using a modified version 4.03 of HYDRUS-1D (Šimůnek et al., 2008).

Based on a previous study with SDZ BTCs (Unold et al., 2009), a model concept with one reversible and one irreversible kinetic sorption site was used to analyze the BTCs of SDZ and its transformation products. The model concept (Fig. 1) for the experiments was developed to account for all known processes. We included the transformation of *N*-Ac-SDZ into SDZ according to information from the literature (Berger et al., 1986). The irreversible sorption site was omitted for *N*-Ac-SDZ according to Förster et al. (2009), who found no significant sequestration of the *N*-Ac-SDZ metabolite in soils. Covalent coupling to organic material as described by Bialk and Pedersen (2008) is also unlikely for *N*-Ac-SDZ since the free aniline moiety is not available. A transformation from SDZ into 4-OH-SDZ was included in the model according to our experimental results using SDZ solutions.

Using the above model concept, the transport equation for each solute with the transformation chain can now be written as

$$\begin{aligned} \frac{\partial C_k}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_{k,k}}{\partial t} = \\ -V \frac{\partial C_k}{\partial z} + D \frac{\partial^2 C_k}{\partial z^2} - \mu_{irr,k} C_k - \mu_{deg,k} C_k + \mu_{deg,k-1} C_{k-1} \end{aligned} \quad [2]$$

$k = 1, 2, 3$

where ρ is the soil bulk density [$M L^{-3}$], $S_{k,k}$ is the sorbed solute concentration at the kinetic sorption site [$M M^{-1}$], the subscript k indicates the k th solute, μ_{irr} [T^{-1}] is a first-order coefficient that is used to mimic irreversible sorption (Baek et al., 2003), and $\mu_{deg,k}$ [T^{-1}] is a first-order rate constant that accounts for the degradation of the k th solute into the solute $k + 1$.

The sorbed concentration at the kinetic sorption sites of the fully kinetic model was calculated as

$$\frac{\partial S_{k,k}}{\partial t} = \alpha_k (K_{f,k} C_k^{\beta_k} - S_{k,k}) \quad [3]$$

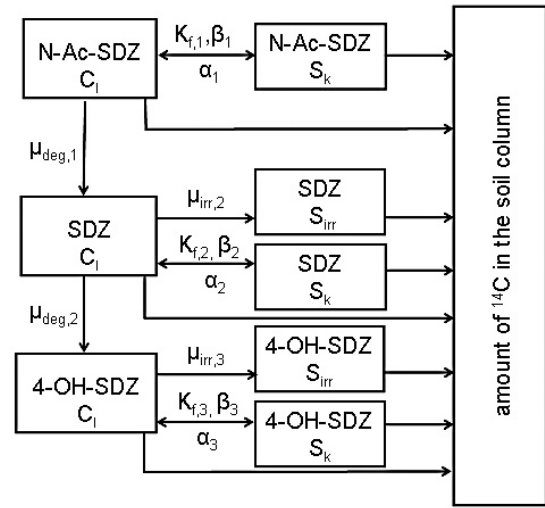


FIG. 1. Conceptual model for the transport of sulfadiazine (SDZ) and its transformation products in the experiments with manure.

where $K_{f,k}$ [$M^{1-\beta}$ solute $L^{3\beta} M^{-1}$ soil] is the Freundlich coefficient, β_k (dimensionless) is the Freundlich exponent, and α_k [T^{-1}] is a first-order sorption rate coefficient.

While a flux-type boundary condition with zero concentration for all compounds was used as the upper boundary condition, the lower boundary condition was a zero-concentration gradient in the numerical solutions. Liquid-phase initial concentrations of SDZ and its transformation products in the uppermost centimeter of the soil profile were calculated using the initial total mass of solutes (Table 4) and water contents of the particular soil columns. In the experiments with the SDZ solution, all of the mass was initially contributed to SDZ since no transformation products were present in the input solution. For the fully kinetic model, all solid-phase concentrations were initially set to zero.

While BTCs were available for each particular solute, only total ^{14}C measurements (i.e., the sum of all three solutes in both the liquid and the solid phases) were available for the various solutes in the soil columns at the end of the experiments. The HYDRUS-1D code was therefore modified to add the sorbed (both reversible and irreversible) and liquid concentrations of all three solutes in a particular degradation chain.

Concentrations of the transformation products were lower than those of SDZ. To obtain adequate fits for all BTCs during the simultaneous fitting process, the data points of *N*-Ac-SDZ, 4-OH-SDZ, and the total concentration profile were weighed relative to SDZ according to

$$w = \frac{n_{BTC_{deg}, Profile} \sum_{i=1}^{n_{SDZ}} C_{i,SDZ}}{n_{SDZ} \sum_{i=1}^{n_{BTC_{deg}, Profile}} C_{i,BTC_{deg}, Profile}} \quad [4]$$

where n accounts for the number of data points of the BTCs or concentration profiles of SDZ and its transformation products (BTC_{deg}), and C_i are measured concentrations at the i th time for a particular BTC expressed in mass equivalents of SDZ per volume of solution (or per volume of soil for the concentration profile).

The goodness of fit for particular solutes and BTCs was expressed using the mean absolute error:

TABLE 4. Mass fractions of ^{14}C in the breakthrough curves (BTCs) and the soil profile and mass fractions (in %) of the parent compound sulfadiazine (SDZ) and its transformation products in the BTCs.

Column†	Radioactivity in BTC	Radioactivity in soil profile	Total mass recovery	SDZ				4-[2-iminopyrimidine-1(2H)-yl]-anilin
				%				
Manure1				67.7‡	14.9‡	17.4‡	ND§	
Manure2¶				82.4‡	8.7‡	8.8‡	ND	
KrepMAN	70.3	32.3	102.6	76.0	9.7	17.3	ND	
KrepSOL	76.0	19.0	95.0	75.9	ND	7.8	16.1	
KundMAN	70.9	30.5	101.4	78.0	9.9	15.2	ND	
KundMAN _i	74.2	28.3	102.5	80.7	8.9	12.5	ND	
MrepMAN	75.3	29.0	104.3	74.0	7.7	18.5	ND	
MrepSOL	86.0	6.4	92.4	90.0	ND	1	12.0	
MundMAN	62.0	37.8	99.8	91.0	7.4	4.8	0.9	

† The first letter represents soil type (either K or M), columns were either repacked (rep) or undisturbed (und), and either manure (MAN) or a stock solution (SOL) was incorporated into the column; subscript i denotes intermittent infiltration.

‡ The amount of ^{14}C which could not be associated with a peak was distributed among SDZ and the transformation products.

§ ND indicates that the transformation product could not be detected.

¶ Manure 2 was applied to soil columns MundMAN.

$$\text{MAE} = \frac{1}{n} \sum |f_i - y_i| \quad [5]$$

where n is the number of data points on a particular BTC, and f_i and y_i are predicted and measured values, respectively.

Except for several BTCs of *N*-Ac-SDZ and 4-OH-SDZ, most BTCs showed extensive tailing on a logarithmic scale, a phenomenon that was also observed in two previous studies (Wehrhan et al., 2007; Unold et al., 2009). In these two studies, the numerical models were fitted to logarithmically transformed outflow ^{14}C concentrations to better capture the long tailing. Fitting of logarithmically transformed data had the advantage of adding additional weight to, and thus properly describing, low concentration values, while at the same time decreasing the weight on, and hence probably describing less well, the concentration of the peaks. A disadvantage of fitting log-transformed data is that the model may also capture less well the overall leached mass. Therefore in this study the observed data were fitted without the logarithmic transformation.

Results and Discussion

Chloride Breakthrough Curves

Chloride BTCs (Fig. 2) were measured on soil columns before and after the incorporation of pig manure or the SDZ stock solution (except for the repacked column of Soil K treated with the SDZ solution, KrepSOL, for which only the “before” BTC was measured). Time is expressed in Fig. 2 as dimensionless pore volumes, i.e., the time needed to replace all the water in the soil column. Although most measured Cl^- BTCs were very similar before and after the SDZ experiments, some BTCs differed slightly. There was no visible trend in Cl^- BTCs that would indicate that incorporation of manure or the stock solution affected the soil structure. Transport parameters obtained by fitting the Cl^- BTCs after the incorporation of manure were used to model the BTCs of SDZ and its transformation products, except for soil column KrepSOL, for which the “after” BTC was not available. Fitted transport parameters for the Cl^- BTCs are summarized in Table 3. The dispersivity of two of the three undisturbed soil columns was higher than those of the

repacked soil columns, indicating more heterogeneity in the original soil material.

Since Cl^- BTCs from both repacked and undisturbed soil columns could be described well using the CDE for conservative tracers, we concluded that physical nonequilibrium processes, such as preferential flow, did not influence solute transport in our columns. The Cl^- BTC for the soil column subject to transient water flow (i.e., intermittent irrigation) could also be described well using the CDE. Intermittent irrigation was used to generate higher water contents and higher fluxes to induce macropore flow, which apparently did not happen.

Carbon-14 Breakthrough Curves and Concentration Profiles

Figure 3 presents ^{14}C BTCs and profiles in the soil columns for all column experiments. The amounts of ^{14}C that were eluted or that remained in the soil columns, as well as the sums of both, are summarized in Table 4. Solute mass recoveries were, in most cases, between 95 and 105%. Although the manure was stirred before its application, the applied radioactivity in the experiments with manure may differ due to inhomogeneities in the substrate. This explains why some mass recoveries are >100%. Recovery rates for the experiments with the SDZ solution were

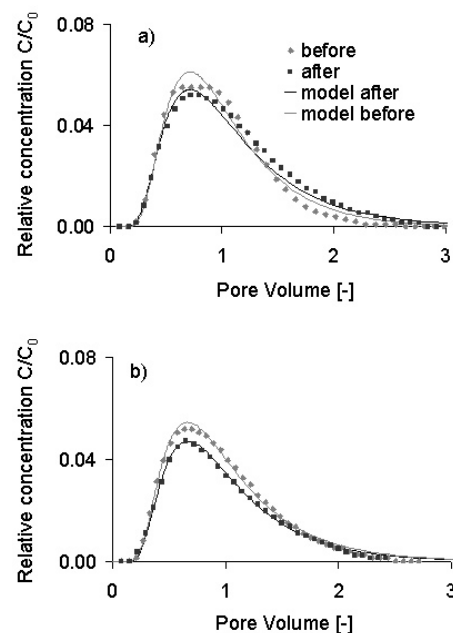


FIG. 2. Selected Cl^- breakthrough curves for soil columns (a) KundMAN and (b) MundMAN measured before and after incorporating pig manure.

<100%. The missing amount can be assigned to the profile data, since mass errors in BTCs are less likely because more data points were available and more precise experimental techniques had been used.

Peaks in the ^{14}C BTCs for the loamy sand (Soil K) appeared after approximately 1.3 pore volumes, which was about 0.6 pore volume later than in the silt loam (Soil M). There are several factors indicating more extensive sorption in Soil M. Due to the larger clay content of Soil M, a larger specific surface area of the mineral phase can be expected, which is also reflected in the cation exchange capacity. Additionally, the fraction of TOC was higher in this soil. One possible explanation for the faster observed transport is the amphoteric character of SDZ, which causes a pH-dependent sorption of sulfonamides (Kurwadkar et al., 2007; Gao and Pedersen, 2005). The average pH value in the outflow samples from Soil M was higher than from Soil K, as was shown for the repacked soil columns with manure (Table 1). This leads to the presence of relatively more of the less sorbing anionic SDZ species in Soil M (89%) than in Soil K (68%). Calculations of the species distribution were done according to Schwarzenbach et al. (2003). Another factor that may cause the difference in apparent transport velocities between the soils is the kinetic component of SDZ sorption.

All BTCs were characterized by a fast initial increase in concentration at the beginning and extended tailing after the peak concentration was reached. In general, the peak height was influenced by the dispersivity of the soil columns. Undisturbed soil columns of both soils with manure added (KundMAN and MundMAN) with dispersivities of around 1.5 cm had about $2 \mu\text{g cm}^{-3}$ lower peak concentrations than the repacked soil columns ($7.75 \mu\text{g cm}^{-3}$), with dispersivities ranging from 0.54 to 0.84 cm. Similar ^{14}C peak concentrations were observed for the undisturbed soil column with intermittent irrigation and the repacked soil column with constant irrigation (Soil K), indicating that a similar dispersivity was more important than the modality of irrigation. Of the two columns receiving the SDZ solution, the ^{14}C peak in Soil K ($13.8 \mu\text{g cm}^{-3}$) was lower than the corresponding ^{14}C peak of Soil M ($17.4 \mu\text{g cm}^{-3}$), although both had similar dispersivities. While Soil K showed similar amounts of ^{14}C (71%) eluted from both the undisturbed and repacked columns with manure, the amounts were different for the repacked (75%) and undisturbed (62%) soil columns of the silt loam (Table 4).

Compared with the experiments with the SDZ solution, lower ^{14}C peaks and slightly lower eluted amounts of ^{14}C were observed for the soil columns spiked with manure. These lower eluted amounts in the experiments with manure can be explained using the ^{14}C -concentration profiles. Although the highest ^{14}C concentrations were found in the first centimeter of all soil columns, these surface layer concentrations were much higher for the columns with manure. We hypothesize that this accumulation of ^{14}C in the uppermost centimeter of the soil columns with manure was caused by the sorption of SDZ and its transformation products to colloidal particles in the manure. These particles then may have been unable to move through the soil because of straining in small pores. This assumption was supported by the fact that, during the HPLC measurements of the manure extracts, approximately 8% of the radioactivity could not be related to a peak, probably due to adsorption to organic material. Filtration of manure particles dependent

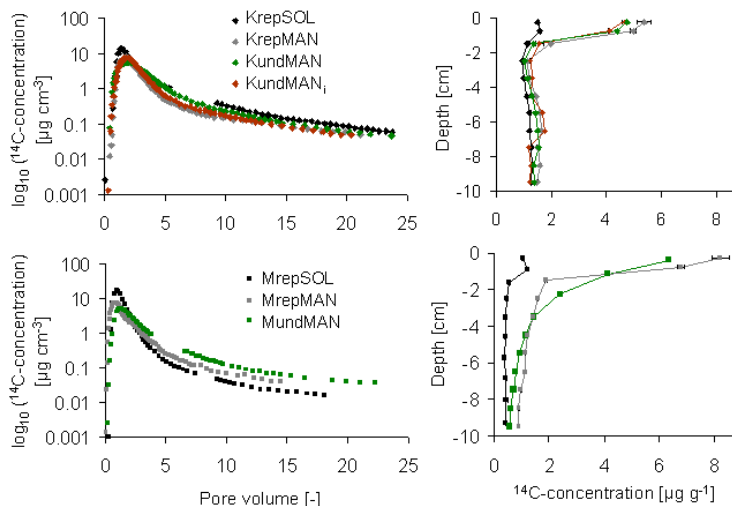


FIG. 3. Carbon-14 breakthrough curves for (a) Soil K and (c) Soil M, as well as distributions of ^{14}C in the soil column profiles for (b) Soil K and (d) Soil M. The ^{14}C concentrations are given in mass equivalents of sulfadiazine.

on the pore size distribution of the porous medium was shown by Bradford et al. (2006). They determined concentration profiles of manure particles in sandy soil columns and similarly found that most manure particles were retained in the uppermost layer.

The presence of manure may also influence sorption behavior in other ways. Sukul et al. (2008a) found in batch experiments an increased sorption of SDZ onto soils of different origins when manure was present. Kreuzig and Höltege (2005) also found in batch experiments a higher tendency of SDZ to form nonextractable residues in the presence of manure with 7-d-old SDZ. In their lysimeter studies in which an SDZ test slurry was incorporated into undisturbed profiles, Kreuzig and Höltege (2005) observed similar concentration profiles as in our soil columns.

Distinct differences were observed in the ^{14}C concentration profiles between the sand and loam columns. The observed amount of ^{14}C in the first centimeter of the loam soil (Soil M) was higher than in the sand soil (Soil K). There are two explanations for this phenomenon. On the one hand, this finding corresponds with the results of Schmidt et al. (2008), who studied the formation of nonextractable residues of manure-based ^{14}C -SDZ to the same two soils. For short contact times, the nonextractable part was higher in a silt loam (Soil M) (69%) than in a loamy sand (Soil K) (54%). On the other hand, smaller pore sizes could have led to enhanced filtration in this soil.

The ^{14}C concentrations gradually decreased with depth in the experiments with manure on Soil M. The ^{14}C concentrations in the soil profiles were more or less constant below the first centimeter in the experiments with Soil K and in the repacked column of Soil M treated with the SDZ solution (MrepSOL), although in the Soil K columns with manure a slight increase in concentrations was observed below a depth of about 4 cm.

Breakthrough Curves of Sulfadiazine and Its Transformation Products

Both experimental and simulated BTCs of SDZ and its transformation products 4-OH-SDZ, *N*-Ac-SDZ, and 4-[2-iminopyrimidine-1(2*H*)-yl]-anilin are presented in Fig. 4 and 5. Although no transformation products were present in the input

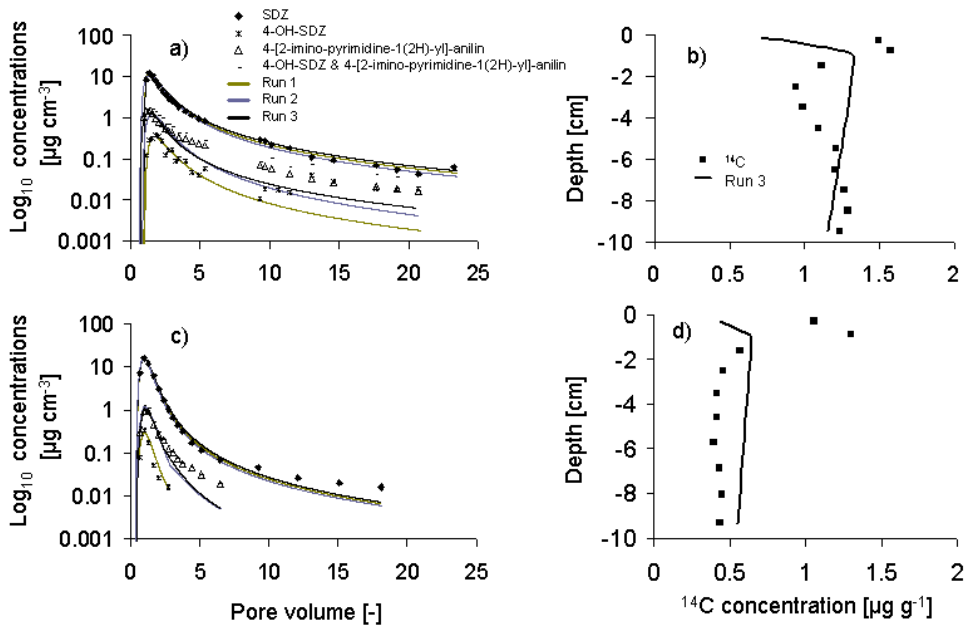


FIG. 4. Breakthrough curves of sulfadiazine (SDZ) and its transformation products 4-OH-SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin, as well as ^{14}C -concentration profiles for the experiments with the SDZ solution for the (a) and (b) KrepSOL experiments and (c) and (d) MrepSOL experiments. Simulations using a model with one reversible kinetic and one irreversible sorption site are also presented. Concentrations are given in mass equivalents of SDZ. Run 1: models were fitted to breakthrough curves (BTCs) of SDZ and 4-OH-SDZ; Run 2: models were fitted to BTCs of SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin; Run 3: models were fitted to BTCs of SDZ and the sum of both transformation products as well as to the ^{14}C data in the profile.

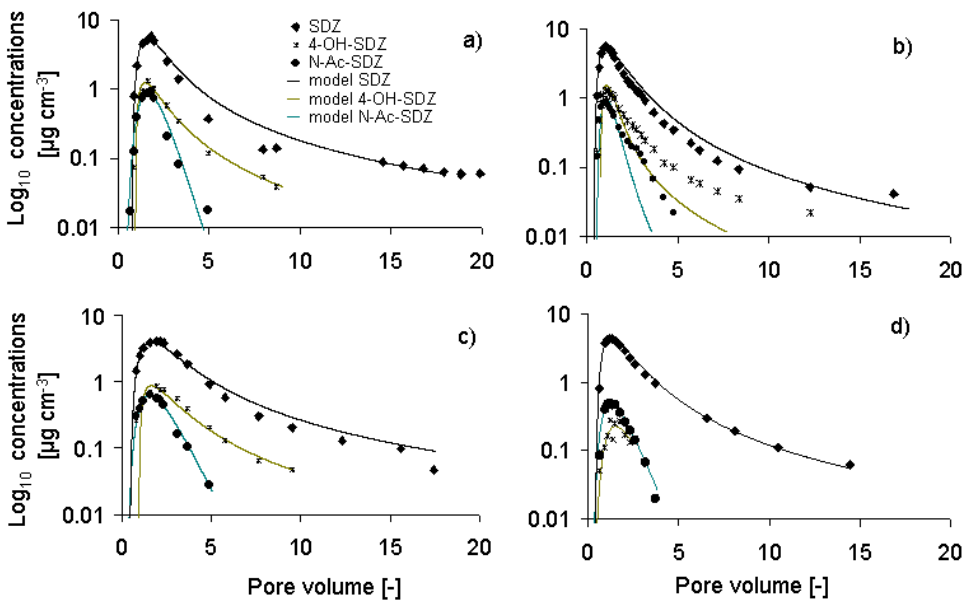


FIG. 5. Breakthrough curves of sulfadiazine (SDZ), 4-OH-SDZ, and *N*-Ac-SDZ in repacked and undisturbed soil columns of Soils K and M for the experiments with manure, as well as simulations using a model with one reversible kinetic and one irreversible sorption site: (a) KrepMAN, (b) MrepMAN, (c) KundMAN, and (d) MundMAN experiments. Concentrations are given in mass equivalents of SDZ.

solution of the experiments with the SDZ solution (KrepSOL and MrepSOL), both 4-OH-SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin were detected in the outflow from these columns (Fig. 4).

Mass fractions of particular transformation products for all soil columns are listed in Table 4. For the experiments with

the SDZ solution, the mass fraction of SDZ was largest compared with its transformation products in all soil columns. The 4-[2-iminopyrimidine-1(2H)-yl]-anilin was the main transformation product, followed by 4-OH-SDZ, which provided only a minor contribution. The transformation from SDZ into 4-[2-iminopyrimidine-1(2H)-yl]-anilin and 4-OH-SDZ was higher in Soil K than in Soil M.

The 4-[2-iminopyrimidine-1(2H)-yl]-anilin was detected in the outflow of the columns with the SDZ solution and also in the manure experiment on the undisturbed Soil M (MundMAN), but at very low concentrations. Sukul et al. (2008b) identified this compound to be the major photoproduct of SDZ, but they observed it also as a product of biodegradation. We can assume that 4-[2-iminopyrimidine-1(2H)-yl]-anilin was formed in the soil column, since our experiments were conducted in the dark. So far we have no explanation why we detected this transformation product in the experiments with the SDZ solution and not in the experiments with manure.

In the soil columns with manure (Fig. 5), SDZ, 4-OH-SDZ, and *N*-Ac-SDZ were detected in the outflow as well as in the manure at the time of application. Mass fractions of the two transformation products in the outflow samples differed with time. While *N*-Ac-SDZ was characterized by a fast dissipation, the mass fraction of 4-OH-SDZ was stable or increased. According to these results, we can expect a constant release of low 4-OH-SDZ concentrations from soils in the long term, similarly as for SDZ. Note that manure incorporated in the undisturbed Soil M column (MundMAN) had lower mass fractions of 4-OH-SDZ and *N*-Ac-SDZ, probably due to advanced aging. The lower fraction of applied transformation products was also reflected in their lower fractions in the column effluents (Table 4).

Breakthrough Curve of the Organic Material

Figure 6 shows BTCs of ^{14}C concentrations, the electrical conductivity, pH, and the TOC for soil column KundMAN. The TOC reflects the amount of organic substances in the outflow samples. Changes in pH were relatively small, ranging from 6.6

to 7.0. This indicates fast dilution of the slurry, which had a higher pH of 8. The peak of the electrical conductivity appeared a short time before the peak in ^{14}C , probably reflecting the breakthrough of the main anion in the manure (i.e., Cl^-). The peak in TOC also appeared shortly before the peak in ^{14}C , at the same time as the peak in the electrical conductivity. This indicates that the main part of SDZ was not transported together with the dissolved organic material (i.e., facilitated transport). We could not observe any differences in ^{14}C concentrations between filtered and unfiltered outflow samples. These findings are consistent with observations by Thiele-Bruhn and Aust (2004), who did not find any sulfonamide losses in their batch experiments during solid-phase extraction with the supernatants. Solid-phase extraction is supposed to remove the dissolved organic material (pig slurry and soil organic matter) together with the adsorbed substances. We therefore conclude that although transport facilitated by dissolved organic C may not be completely ruled out, this process does not seem to be a major transport mechanism involved in the leaching of SDZ and its transformation products. The outflow TOC concentrations, however, did not reach zero during the experiments (Fig. 6), thus suggesting a continuous release of organic material. While this supports the hypothesis that the ^{14}C accumulation in the first centimeter of the soil columns is caused by the filtration of organic material, in the long term the release of organic material, possibly together with bound SDZ residues, may still be possible.

Modeling Results

Similarly to Unold et al. (2009), we selected a transport model with one kinetic reversible and one kinetic irreversible sorption site. Sorption on the reversible site was described assuming a first-order process and Freundlich-type sorption. The conceptual model could describe most curves quite well (see Fig. 4 and 5). The long tailing is characteristic for chemical nonequilibrium processes and nonlinear sorption. The tailing could not be described solely by assuming a fully kinetic process, however. It was also necessary to consider nonlinearity of the sorption process by using low values of the Freundlich exponent, β . Initial estimates of the Freundlich parameters were selected in a way so that the tailing was described well. This was accomplished by choosing a Freundlich exponent <0.44 , similar to the findings of the previous studies of Wehrhan et al. (2007) and Unold et al. (2009). In the experiments of Kurwadkar et al. (2007), a linear sorption isotherm was able to describe the sorption data of sulfonamides for concentrations up to approximately 0.5 mg L^{-1} . Concentrations of both the applied solution and the manure were much higher (272 mg L^{-1}) in our study. Because of the much wider concentration range in our study, we can assume strong nonlinear sorption behavior.

Experiments with the Sulfadiazine Solution

The modeling process for each experiment with the SDZ solution was split into three parts, since it was not possible with HYDRUS-1D to simultaneously fit degradation from SDZ into 4-OH-SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin. In the first run, the BTCs of SDZ and 4-OH-SDZ were fitted without considering the profile data. In the second model run, the same was done for 4-[2-iminopyrimidine-1(2H)-yl]-anilin. The profile data were not included in these optimization runs since

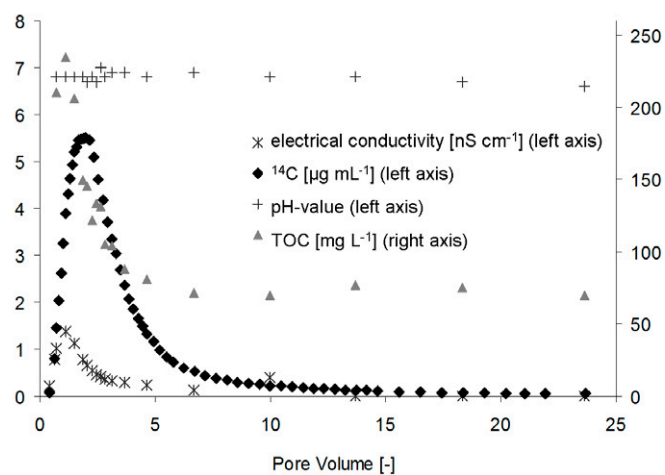


FIG. 6. Breakthrough curves of ^{14}C , electrical conductivity, and total organic C (TOC) measured in the soil column KundMAN after the manure application.

degradation into a particular transformation product was compensated by an increase in irreversible SDZ sorption. Irreversible sorption of the transformation products was fixed to zero since the rate of their formation (degradation of SDZ) would have otherwise been influenced by this process. In the third run, concentrations of the two transformation products were summed up and the resulting BTC was fitted together with the BTC of SDZ and the ^{14}C concentration profile data. The degradation coefficient in this case refers to the sum of 4-OH-SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin degradation. For all transformation products that showed very low concentrations in the SDZ-solution experiments, we fixed the kinetic sorption rate coefficient, α , at the very high value of 10 h^{-1} , thus assuming that sorption was basically an equilibrium process. This was done to reduce the number of optimized parameters and to increase the reliability of the optimized sorption parameters, which had in some cases large confidence intervals. Values of the Freundlich exponents for SDZ and its transformation products were closely correlated with the K_f values and therefore were fixed in optimization model runs to values that were needed to describe the tailing of the BTCs.

The model could describe the BTCs of SDZ and 4-OH-SDZ reasonably well, except for the observed increase in the 4-OH-SDZ concentration after 10 pore volumes. There is a clear difference between the two soils in terms of the Freundlich sorption coefficients for SDZ (Table 5). While the Freundlich sorption coefficients for the silt loam are lower than for the loamy sand, the Freundlich exponents are in a similar range. This indicates a lower sorption capacity for the silt loam and reflects the earlier breakthrough in this soil. On the other hand, the lower kinetic sorption rate reflects the slightly faster transport in Soil M.

Optimized Freundlich parameters for 4-OH-SDZ in the loamy sand produced an isotherm with a much lower sorption capacity than for SDZ. No sorption parameters were fitted for this transformation product for the silt loam because of very low observed concentrations. Sorption capacities for 4-[2-iminopyrimidine-1(2H)-yl]-anilin were in a similar range in both soils and for Soil K the sorption capacity for 4-[2-iminopyrimidine-1(2H)-yl]-anilin was lower than for 4-OH-SDZ. Breakthrough curve tailing of 4-[2-iminopyrimidine-1(2H)-yl]-anilin in both soils

TABLE 5. Fitting parameters for the breakthrough curves (BTCs) of sulfadiazine (SDZ), 4-OH-SDZ, and 4-[2-imino-pyrimidine-1(2H)-yl]-anilin for the experiments with the SDZ solution (SOL) in repacked columns (rep) of Soils K and M. Run 1: parameters were fitted to the BTC data of SDZ and 4-OH-SDZ; Run 2: parameters were fitted to the BTC data of SDZ and 4-[2-imino-pyrimidine-1(2H)-yl]-anilin; Run 3: parameters were fitted to the BTC data of SDZ, the ¹⁴C-profile data, and the sum of the BTCs of both transformation products.

Parameter†	KrepSOL			MrepSOL		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
SDZ						
$K_{f1}, \mu\text{g}^{1-\beta} \text{cm}^3\beta \text{g}^{-1}$	1.18 (± 0.03)	1.20 (± 0.04)	1.29 (± 0.07)	0.52 (± 0.03)	0.55 (± 0.04)	0.50 (± 0.1)
β_1	0.38§	0.38‡	0.38‡	0.44§	0.44‡	0.44‡
$\mu_{irr1}, \text{h}^{-1}$	0.035 (± 0.004)	0.026 (± 0.002)	0.018 (± 0.003)	0.010 (± 0.002)	0.0044 (± 0.002)	0.006 (± 0.001)
$\mu_{deg1}, \text{h}^{-1}$	0.0036 (± 0.0002)	0.012 (± 0.0006)	0.011 (± 0.001)	0.0016 (± 0.0001)	0.0061 (± 0.0002)	0.0076 (± 0.002)
α_1, h^{-1}	10‡	10‡	0.74 (± 0.3)	0.50 (± 0.09)	0.43 (± 0.07)	0.55 (± 0.4)
MAE	0.13	0.16	0.23	0.028	0.086	0.078
Transformation products						
	4-OH-SDZ	4-[2-imino-pyrimidine-1(2H)-yl]-anilin	Sum of both transformation products	4-OH-SDZ	4-[2-imino-pyrimidine-1(2H)-yl]-anilin	Sum of both transformation products
$K_{f2}, \mu\text{g}^{1-\beta} \text{cm}^3\beta \text{g}^{-1}$	0.098 (± 0.008)	0.044 (± 0.03)	0.12 (± 0.003)	0‡	0.052 (± 0.009)	0.36 (± 0.05)
β_2	0.53§	0.27§	0.50§	0‡	0.72§	0.72§
$\mu_{irr2}, \text{h}^{-1}$	0‡	0‡	0‡	0‡	0‡	0‡
α_2, h^{-1}	10‡	10‡	10‡	0‡	10‡	10‡
MAE	0.023	0.09	0.12	0.035	0.036	0.032
MAE _{profile}	0.79	0.35	0.21	0.51	0.19	0.25
Eluted, %	59.4	65.0	72.3	75.4	80.9	0.77
R^2	1	0.99	0.98	0.99	1	0.98

† K_{fj} , Freundlich coefficient for solute j ; β_j , Freundlich exponent for solute j ; μ_{irrj} , irreversible sorption rate for solute j ; μ_{degj} , transformation rate of solute j ; α_j , kinetic sorption rate of solute j ; MAE, mean absolute error; Eluted, mass eluted out of the soil column.

‡ Parameter was fixed.

§ Parameter was fixed at a value determined in a previous model run.

could not be described with the model, although the Freundlich exponent was in a range low enough to describe the tailing of SDZ and 4-OH-SDZ in the experiments with manure.

In the first model run to optimize the BTC parameters of 4-OH-SDZ and SDZ, the profile data were considerably overestimated for both soils since the amount of SDZ that degraded to form 4-[2-iminopyrimidine-1(2H)-yl]-anilin was added to irreversible sorption. While the same tendency was observed for Soil K for the model run that optimized the BTC parameters of SDZ and 4-[2-iminopyrimidine-1(2H)-yl]-anilin, this run described the profile data best for Soil M. The reason is that the effect of 4-OH-SDZ formation on irreversible sorption was negligible. Since the third model run included the profile data (Fig. 4), this run was expected to provide the best fits. While this was true for Soil K, we overestimated data points in deeper layers of Soil M. Increased irreversible sorption to reduce the misfits between observed and simulated values in the top layer was the reason for this overestimation. This effect was smaller for Soil K, where the difference between concentrations in the top and deeper soil layers was smaller. Average concentrations in the soil profiles were captured reasonably well by the model, although the sorption process was probably not correctly understood. This became obvious from the opposite trends between the data and the model in the uppermost layers.

Compared with previous experiments with SDZ solutions (Unold et al., 2009), optimized values of the kinetic sorption rate coefficient, α , were higher, indicating that kinetic sorption was faster when SDZ was incorporated directly into the soil. In several cases, sorption was even close to equilibrium. Therefore, some BTCs could be fitted reasonably well by assuming equilibrium

reversible sorption, but in such cases the initial increase in the BTCs was predicted less well.

Experiments with Manure

For each experiment with manure, the BTCs of SDZ and its transformation products were fitted simultaneously together with the concentration profile data below the uppermost 1 cm. Concentrations in the top 1 cm were significantly higher than in the rest of the soil profile. We hypothesized that the high sorbed concentrations in the uppermost soil column layers were the result of interactions between the organic material of the slurry and the soil structure. We did not attempt to model these processes. Therefore, the two uppermost data points in the profiles were not included in the objective function and hence we did not expect that the high sorbed concentrations in the top of the soil columns would be reproduced by the model.

The Freundlich exponents for SDZ were fixed to values optimized to experimental data with the SDZ solution to avoid large parameter correlations with the Freundlich distribution coefficients. The kinetic sorption rate coefficients for the transformation products were again fixed to 10 h^{-1} to decrease the number of parameters and to increase parameter reliability. Since most BTCs of *N*-Ac-SDZ did not show much tailing, its Freundlich exponent was fixed to one, thus assuming linear sorption in all soil columns except for the repacked Soil M column treated with manure (MrepMAN). In preliminary model runs, the tailing of 4-OH-SDZ concentrations was not captured well since it was described by only a few data points. Therefore, we increased the weights on the tailing concentrations compared with the data points in the peak according to Eq. [4]. For Soil K, the Freundlich exponent was fitted for the repacked soil column with the manure

application and fixed for the undisturbed soil columns. For Soil M, this parameter was fitted for each soil column separately, since no extended tailing for the 4-OH-SDZ BTC was observed for the undisturbed column treated with manure (MundMAN).

The relatively low transformation rates from SDZ into 4-OH-SDZ as estimated from the experimental data with the SDZ solution were used to model the experiments with manure. A possible transformation reaction from 4-OH-SDZ into another product was not included in the model, since no additional product was detected in the outflow samples. The model with optimized parameters produced reasonable descriptions of the transport of SDZ and its two transformation products for the experiments with manure. Four examples are presented in Fig. 5.

Similarly as for the experiments with the SDZ solution, the SDZ sorption capacity for the experiments with manure was lower for Soil M than for Soil K, but the difference was smaller. The same tendency in K_f values as for SDZ was found for *N*-Ac-SDZ, and partly also for 4-OH-SDZ, for which the soil column MrepMAN had a similar Freundlich coefficient as the soil column KrepMAN. For 4-OH-SDZ, fitted Freundlich exponents were similar as for SDZ but the Freundlich coefficients were lower, indicating a lower sorption capacity for 4-OH-SDZ. On the other hand, the irreversible sorption rate was higher for 4-OH-SDZ and thus the overall sorption may be similar. Since linear sorption was found for *N*-Ac-SDZ in most soil columns, the sorption capacity was lower than for SDZ only when the concentration was $<8 \mu\text{g cm}^{-3}$. In our experiments, both higher and lower concentrations were present.

Fitted Freundlich coefficients for SDZ in the experiments with manure were higher than for the experiments with the

SDZ solution for both soils, reflecting the slightly higher sorbed amounts in the experiments with manure. For Soil K, the kinetic effect was more distinct for the experiments with manure than for the experiments with the SDZ solution (Table 6). There was no clear difference in the kinetic sorption rates α in the experiments with manure between the two soils.

The ^{14}C -concentration profiles were described quite well in the deeper soil layers below the depth of application, where they reached more or less constant values (Fig. 7). Simulations for cases where no profile data were included in the objective function led to similar results (data not shown).

Eluted solute masses were described quite well with the numerical model, which over- or underestimated the maxima by only about 5%. Since the mass in the uppermost layer of the soil columns of the experiments with manure was not included in the optimization, the model compensated for this missing mass by slightly overestimating concentrations below the 1-cm depth or by predicting higher eluted masses (KundMAN and KundMAN_i). Because of the complex nature of the invoked transport model, it was difficult to find unique solutions; however, the BTCs could not be described with parameter combinations out of the range of the fitted ones.

Optimized parameters for the Freundlich isotherm characterize the sorption equilibrium state and thus can only be compared with sorption parameters from batch experiments determined when equilibrium is reached. This was the case for the batch experiments of Kurwadkar et al. (2007) and Sukul et al. (2008a). In both studies, the Freundlich exponents for sulfonamides were higher than in our study. In the study of Sukul et al. (2008a), they were even >1 . An explanation for

TABLE 6. Fitting parameters for the breakthrough curves (BTCs) of sulfadiazine (SDZ), 4-OH-SDZ, and *N*-Ac-SDZ for the experiments with manure (MAN) on columns of Soil K or M that were either repacked (rep) or undisturbed (und); subscript i denotes intermittent infiltration.

Parameter†	KrepMAN	KundMAN	KundMAN _i	MrepMAN	MundMAN
<i>N</i> -Ac-SDZ					
K_{f1} , $\mu\text{g}^{1-\beta} \text{cm}^3 \text{g}^{-1}$	0.30 (± 0.02)	0.37 (± 0.03)	0.35 (± 0.05)	0.16 (± 0.02)	0.25 (± 0.02)
β_1	1‡	1‡	1‡	0.70§	1‡
μ_{deg1} , h^{-1}	0.063 (± 0.006)	0.067 (± 0.007)	0.053 (± 0.008)	0.054 (± 0.008)	0.040 (± 0.005)
α_1 , h^{-1}	10‡	10‡	10†	10‡	10‡
MAE	0.05	0.03	0.05	0.09	0.02
SDZ					
K_{f2} , $\mu\text{g}^{1-\beta} \text{cm}^3 \text{g}^{-1}$	1.49 (± 0.05)	1.58 (± 0.1)	1.53 (± 0.1)	1.18 (± 0.1)	1.03 (± 0.06)
β_1	0.38‡	0.38‡	0.38‡	0.44‡	0.44‡
μ_{irr1} , h^{-1}	0.012 (± 0.002)	0.0054 (± 0.002)	0.0061 (± 0.002)	0.0078 (± 0.003)	0.017 (± 0.004)
μ_{deg1} , h^{-1}	0.0036‡	0.0036‡	0.0036‡	0.0016‡	0.0016‡
α_2 , h^{-1}	0.57 (± 0.07)	0.36 (± 0.1)	0.68 (± 0.2)	0.13 (± 0.02)	0.51 (± 0.2)
MAE	0.19	0.15	0.31	0.33	0.13
4-OH-SDZ					
K_{f1} , $\mu\text{g}^{1-\beta} \text{cm}^3 \text{g}^{-1}$	0.39 (± 0.04)	0.52 (± 0.06)	0.50 (± 0.007)	0.19 (± 0.04)	0.41 (± 0.04)
β_1	0.44§ (± 0.03)	0.44‡	0.44‡	0.41§	1§
μ_{irr1} , h^{-1}	0.040 (± 0.005)	0.035 (± 0.007)	0.033 (± 0.007)	0.036 (± 0.006)	0.090 (± 0.009)
α_3 , h^{-1}	10‡	10‡	10‡	10‡	10‡
MAE	0.07	0.09	0.09	0.13	0.03
Profile MAE	0.84	0.73	0.78	1.43	1.30
R^2	0.98	0.97	0.97	0.95	0.99
Eluted, %	72.3	75.1	74.2	75.3	63.7

† K_{fj} , Freundlich coefficient for solute j ; β_j , Freundlich exponent for solute j ; μ_{irrj} , irreversible sorption rate for solute j ; μ_{degj} , transformation rate of solute j ; α_j , kinetic sorption rate of solute j ; MAE, mean absolute error; Eluted, mass eluted out of the soil column.

‡ Parameter was fixed.

§ Parameter was fixed at a value determined in a previous model run.

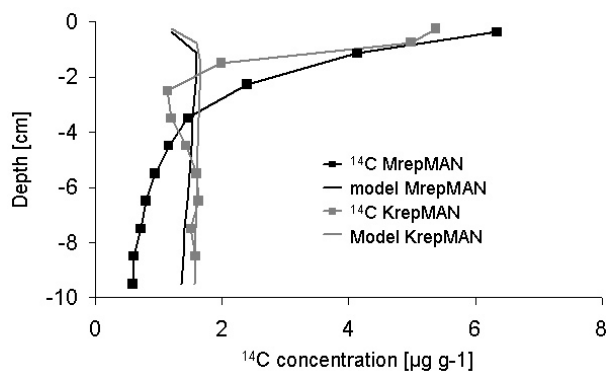


FIG. 7. Carbon-14 distributions in soil columns KrepMAN and MrepMAN and simulations using a model with one reversible and one irreversible kinetic sorption site. The ^{14}C concentrations are given in mass equivalents of sulfadiazine.

the lower exponents fitted to our transport experiments is that a kinetic process leading to extended tailing may partly mask strong sorption nonlinearity. To compare our results with the results reported in these two studies, we calculated the sorption capacity for a liquid concentration of $1 \mu\text{g cm}^{-3}$ and compared it with the highest and lowest reported values. The Freundlich sorption capacities in the batch studies were higher than in our study, probably because in batch sorption experiments the process of irreversible sorption is not considered separately.

Conclusions

The application of pig manure containing SDZ and its transformation products to soil columns led to an accumulation of total ^{14}C in the uppermost soil layers and resulted in lower peak values of the ^{14}C BTCs compared with experiments with a pure SDZ solution. For the assumed experimental conditions, SDZ as well as its transformation products showed a high potential for leaching. Co-transport with dissolved organic matter did not seem to be a major transport mechanism for the solutes.

The conceptual model with degradation and one kinetic and one irreversible sorption site provided a good description for most BTCs of SDZ and its transformation products 4-[2-iminopyrimidine-1(2*H*)-yl]-anilin, *N*-Ac-SDZ, and 4-OH-SDZ. The ^{14}C concentrations remaining in the soil columns could not be predicted correctly for the experiments with the SDZ solution, which suggests a sorption process that is not well understood. Transport parameters fitted to BTCs of individual species (SDZ and its transformation products) revealed a lower sorption capacity for the transformation products than for SDZ in the low concentration ranges. The *N*-Ac-SDZ was rapidly transformed and did not show any patterns useful for characterizing SDZ transport, such as an extended tailing of the BTCs or irreversible sorption. The transport behavior of 4-OH-SDZ seemed to be similar to that of SDZ. The model also revealed a higher sorption capacity for SDZ in the presence of manure.

ACKNOWLEDGMENTS

We acknowledge the German Research Foundation (DFG) for their financial support (FOR566), Bayer HealthCare (Wuppertal, Germany) for providing the ^{14}C -labeled sulfadiazine, BayerCropScience AG for the performance of the SDZ feeding experiment, and the Division of Soil Science of INRES at the University of Bonn for the measurements of soil texture. We thank Stephan Köppchen for the HPLC measure-

ments; Thorsten Büttner, Stefan Masjosthusman, Kavita Mayekar and Maja Stiefelhagen for their assistance in the laboratory; and Jürgen Höltkemeier and Ansgar Weuthen for building the experimental setup.

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