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Column and batch tests of sulfonamide leaching from different types of soil

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HIGHLIGHTS

- Determination of leaching behavior of 3 sulfonamides (SAs) in soil column tests.
- Discussion of mobility evaluation of investigated SAs in different types of soil.
- Assessment of possible permeation of SAs to groundwater and surface water.
- Discussion the applicability of leaching tests to polar contaminants.
- Comparing results obtained during column and batch tests.

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ABSTRACT

Sulfonamides (SAs) and their metabolites present severe hazards to human health and the environment, mainly because of antibiotic resistance. Knowledge of their bioavailability, including their sorption to soils and their impact on the soil-groundwater pathway, is crucial to their risk assessment. Laboratory batch and column leaching tests are important tools for determining the release potential of contaminants from soil or waste materials. Batch and column tests were carried out with soils differing in particle size distribution, organic matter content and pH, each spiked with sulfonamides (sulfadimethoxine (SDM), sulfaguanidine (SGD), sulfisoxazole (SX)). In order to test the applicability of leaching tests to polar contaminants batch and column tests were also compared. In the column tests, release was found to depend on the properties of both soil and sulfonamides. The fastest release was observed for coarse-grained soil with the smallest organic matter content (MS soil; 100% decrease in concentration until liquid-to-solid ratio (L/S) of 0.9 L kg^{-1} for all SAs). The slowest release was established for sulfadimethoxine (24.5% decrease in concentration until L/S 1.22 L kg^{-1}). The results of the batch and column tests were comparable to a large extent, with slightly higher concentrations being obtained in the column test experiments of fine-grained soils with a high organic matter content.

1. Introduction

The relatively low cost of sulfonamides (SAs) and their broad spectrum of antimicrobial activity has made them the usual choice of antibiotics in animal breeding (*i.e.*, feedstuff additives). Their large-scale use poses a real hazard to different environmental compartments and human health, mainly because of antibiotic resistance phenomena. The genes responsible for such resistance may be transferred from non-pathogenic bacteria to those that do cause disease, leading to clinically significant antibiotic resistance [1,2]. Many of the antibiotics used in animal husbandry are identical or closely related to those used to prevent infections among humans; they include tetracyclines, macrolides, bacitracin, penicillins and sulfonamides. Thus, the increasing prevalence of antibiotic-resistant bacterial infections observed in clinical practice stems from antibiotic use in both human and veterinary medicine.

Generally, medicines are excreted as the parent compounds or their metabolites. Only small amounts of sulfonamides are metabolized immediately after administration [3], but up to 90% are

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excreted into the environment within 2 days of administration [4]. The residues enter the environment together with metabolites in the urine and feces. It is therefore important to assess the mobility and bioavailability of these compounds in soils with different physicochemical properties.

Sorption, a phenomenon during which chemicals become associated with solid phases, is immensely important in this regard as it affects the fate of chemicals in the environment [5,6]. Sorption experiments can provide much valuable insight into the mobility of various classes of contaminants in the environment [5,6].

The possible leaching/release potential of contaminated materials on the soil-groundwater pathway can be determined by laboratory leaching tests such as column and batch tests [7–9]. The release potential of water-soluble contaminants can be assessed as an expression of the source term, which thus gives an indication of their bioavailability. Batch tests provide a snapshot of a particular liquid-to-solid ratio. Column tests, on the other hand, enable time-dependent monitoring of contaminant leaching from soil and waste materials; in addition, the flow-through pattern of such tests resembles actual environmental conditions. Some studies have reported equivalence of batch and column test results [9,10], but discrepancies, due to different release mechanisms, have also been reported for some contaminants like PAHs and some heavy metals [11]. Furthermore, the reproducibility of column tests is reported to be better [8].

Pharmaceuticals can exist as neutral or charged species (*e.g.*, cations, anions, zwitterions), depending on the pH [12]. Therefore, various adsorptive forces can occur. Whereas neutral molecules partition to solid matrices via relatively weak van der Waals and electron donor–acceptor interactions, charged species can interact through stronger electrostatic mechanisms, such as cation-exchange, cation-bridging and complexation. The sorption strength may also be influenced by physicochemical properties such as pH, organic matter content, metal oxide content, ionic strength and cation exchange capacity [13].

In the present study we focused on sulfonamides. So far, only few sulfonamides, mainly sulfachloropyridazine (SCPY) and sulfadiazine (SDZ), have been studied, mostly by means of batch leaching tests [14–17]. Nevertheless, we still know little about the mobility of these compounds in the soil environment as assessed during experiments replicating more realistic environmental conditions. To date, there are only few reports on the transport of sulfonamides in lysimeters or lysimeter-like soil columns, and these focus solely on sulfadiazine, its conversion products [18,19] and sulfachloropyridazine [20]. Leaching tests, on the other hand, have so far concentrated on the investigation of inorganic contaminants and non-polar organic contaminants like PAHs and TPHs. Three sulfonamides (sulfadimetoxine (SDM), sulfaguanidine (SGD) and sulfisoxazole (SX)), the behavior of which in the soil column has not yet been investigated, were therefore chosen. Furthermore it has been reported that these SAs can pose a toxicological risk to non-target organisms [21]. Therefore, the main objectives of the present work were: (i) to assess the leaching behavior of three sulfonamides in soil column tests, and (ii) to compare this behavior in batch and column tests.

2. Materials and methods

2.1. Preparation of test materials

Soils varying in particle size distribution and organic matter content were used in order to cover different soil matrices. Reference soils, characterized as loamy sand (LS) and silty sand (US), were obtained from the Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany, and medium sand (MS) from a construction site at the BAM Federal Institute for Materials Research and Testing, Berlin, Germany. Selected properties of the test materials are given in Table 1. A Schott CG 841 pH-meter equipped with a WTW SenTix 41 pH electrode was used to measure pH values. C_{org} was determined as loss of ignition at 550 °C. The particle size distribution was measured with a combination of sieve analysis (above 125 μm) and X-ray sedigraph analysis (micromeritics 5100 sedigraph; below 125 μm). The effective cation exchange capacity (CEC_{eff}) was determined according to DIN ISO 11 260. 6 kg of the respective air-dried soil were mixed with 60 mg of sulfonamide. Mixing was done in dry form for better miscibility and to avoid biodegradation. After tumbling for 2 h in a gyrowheel mixer and allowing for equilibrium adjustment overnight, the material was divided into representative subsamples of approximately 250 g each with a rotating sample divider. For homogeneity tests (*F*-tests [22]), 16 samples of 10 g each (from eight randomly selected 250 g samples and in each case two subsamples) were taken. Sulfonamides were extracted from these samples in accordance with a procedure developed by the research group at the Department of Environmental Analysis, Faculty of Chemistry, University of Gdańsk, consisting of the following steps: (1) addition of 5 mL NH_4Cl:MeOH [50:50, v/v] and 0.5 mL 0.1 M Na_2EDTA to each soil sample; (2) vortex mixing (1 min), (3) sonication (20 min); (4) centrifugation (10 min, 4000 rpm); (5) filtration; (6) HPLC assay. The respective percentages recoveries of SGD, SDM and SX, depending on the soil type, were in the ranges: 43.2–81.1%; 43.2–75.2%; 52.0–64.7%. Table 2 shows the coding and composition of the tested materials and the results of the homogeneity tests; these were performed to check whether the sulfonamide distribution in the samples was even (ANOVA *F*-tests, one-way analysis of variance). The *F*-values of all the SAs were < 3.50 (the reference value for a 2×8 matrix and 95% confidence level), which indicates that the soil samples spiked with SAs were homogenous.

Table 1
Physicochemical properties of the soils used in the experiments.

	LS	US	MS
pH	5.41	6.00	8.66
C_{org} [%]	2.84	0.96	0.64
CEC_{eff} [$cmol_c\ kg^{-1}$]	7.20	2.75	0.83
Particle size distribution			
>2 mm [%]	–	–	7
2–0.063 mm [%]	78	67	92
0.063–0.002 mm [%]	14	29	1
<0.002 mm [%]	8	4	–

Table 2
Coding and homogenization of the test materials.

Material	Soil	Sulfonamide	*F* value[a]
S1	LS	SGD	0.86
		SDM	1.03
S2	US	SDM	1.00
		SGD	1.01
		SX	0.26
S3	MS	SDM	0.81
		SGD	0.50
		SX	0.64
S4	LS	SDM	0.31
S5	LS	SX	0.64

[a] Values below 3.50 (for a 2×8 matrix and 95% confidence level) indicate homogeneity of the test material.