COLUMN AND BATCH TESTS OF SULFONAMIDES LEACHING FROM DIFFERENT TYPES OF SOIL

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EXTENDED ABSTRACT

Sulfonamides (SAs) and their metabolites represent 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 leaching tests such as batch and column tests are important tools for determining the release potential of contaminants from soil or waste materials. Batch and column tests with different types of soil (particle size distribution, organic matter content, pH) were therefore carried out, each spiked with sulfonamides (sulfadimethoxine (SDM), sulfaguanidine (SGD), sulfisoxazole (SX)), 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: it was fastest for coarse-grained soil with the smallest organic matter content (100% decrease of concentration up to a liquid-to-solid ratio (L/S) of 0.9 L kg⁻¹) and slowest for sulfadimethoxine (24.5 % decrease to L/S 1.22 L kg⁻¹). The results of the batch and column tests were roughly comparable, with slightly higher concentrations being obtained in the column test experiments of fine-grained soils with a high organic matter content.

Keywords: sulfonamides, leaching, column test, batch test, soil

1. INTRODUCTION

The relatively low cost of sulfonamides and their broad spectrum of antimicrobial activity has made them the usual choice of antibiotics in animal breeding (i.e., feedstuff additives). Generally, medicines are excreted as the parent compounds or their metabolites. Only small amounts of sulfonamides are metabolized immediately after administration [1], but up to 90% are excreted into the environment within 2 days of administration [2]. Their large-scale use poses a real danger to different environmental compartments and human health, mainly because of antibiotic resistance phenomena. 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. Therefore, the use of antibiotics in farm animals
contributes to the development of resistant bacterial infections in humans [3]. It is therefore a matter of urgency 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 [4,5]. Sorption experiments can provide much valuable insight into the mobility of various classes of contaminants in the environment.

The possible impact of contaminated materials on the soil-groundwater pathway can be determined by laboratory leaching tests such as column and batch tests. 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 at a defined 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 [6-8].

In the present study we focused on sulfonamides, which are usually described by two dissociation constants ($pK_a$) [9]. To date, there are only a few reports on the transport of sulfonamides in lysimeters or lysimeter-like soil columns, and these focus solely on sulfadiazine, its conversion products [10,11] and sulphachloropyridazine [12]. Leaching tests, on the other hand, have so far concentrated on inorganic contaminants and non-polar organic contaminants like PAHs and TPHs. 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. It results in varying eluate turbidities 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 BAM Federal Institute for Materials Research and Testing, Berlin, Germany. 6 kg of the respective soil were mixed with 60 mg of sulfonamide. 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. 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. The $F$-values of all the SAs were < 3.50 (the reference value for a 2x8 matrix and 95 % confidence level), which indicates that the soil samples spiked with SAs were homogenous.

2.2. Equipment and chemicals

The batch tests were performed in duplicate with a liquid to solid ($L/S$) ratio of 2 L/kg according to E DIN 19527 with representative subsamples of 250 g. After agitation of the sample in an end-over-end tumbler for 24 h at 7 rpm, the eluate was separated from the soil by pressure filtration through a 0.45 µm glass fiber filter after centrifugation for 30 min at 20,000 g in stainless steel containers.
Column tests were carried out in triplicate as a basic characterization on the basis of DIN 1952 with a L/S ratio up to 3.5 L/kg using glass columns of internal diameter 6.45 cm and typical weighed samples of 1.3 kg. The column tests of each soil without sulfonamides were performed as single experiments. We analyzed the samples without further preparation.

The L/S ratios specified in the following text are always given in L/kg.

2.3. Equipment and chemicals

Automated percolation equipment from ecoTech Umwelt-Meßsysteme GmbH, Germany, was used for the column tests, and a Beckmann Coulter Avanti J-E with JA-14 fixed angle rotor for centrifugation. The pH values were measured with a Schott CG 841 pH-meter equipped with a WTW SenTix 41 pH electrode, the electrical conductivity with a WTW LF 437 microprocessor conductivity meter, the turbidity with a Hach 2100 IS turbidity meter, and the TOC/TN content with a Shimadzu TOC-VCPH analyzer, equipped with a TNM-1 total nitrogen measuring unit.

Standards of sulfaguanidine (SGD), sulfadimethoxine sodium salt (SDM), sulfisoxazole (SX) and trifluoroacetic acid 99% (TFA) were purchased from Sigma-Aldrich (Steinheim, Germany). Deionized water was produced by the HYDROLAB System (Gdańsk, Poland), and acetonitrile (ACN) was obtained from POCH (Gliwice, Poland).

The filtrates from the leaching and batch studies were analyzed by isocratic reversed phase HPLC on a Phenomenex Gemini C\textsubscript{18} – 110A column, 150 mm x 4.6 mm i.d., 5 μm (Torrance, USA). The Perkin Elmer Series 200 analytical system consisted of a chromatographic interface (Link 600), a vacuum degasser, a binary pump, a UV/VIS detector and a Rheodyne injection valve.

All the compounds were detected at a wavelength of 270 nm. The mobile phase for determining SGD was ACN:H\textsubscript{2}O (94:6, v:v) at a flow rate of 0.5 mL min\textsuperscript{-1}; for SDM and SX it was ACN:H\textsubscript{2}O (with 0.0025% of TFA) (45:55, v:v) at 0.7 mL min\textsuperscript{-1}. Injection volumes were 30 µl for SGD and 50 µl for SDM and SX. All the chromatographic analyses were carried out in triplicate.

3. RESULTS AND DISCUSSION

The concentrations of sulfonamides in the eluates collected during the column test were plotted against the L/S ratio. The curves for SGD and SX dropped abruptly at the beginning of the process, which was indicative of rapid leaching from the soil. Both SGD and SX were leached equally rapidly from US soil. The SX concentration in the eluates fell by about 99.8 % from L/S 0.28 to 3.52, and the SGD concentrations decreased by 99.7 % within the same L/S ratio range. In the LS soil, SX was leached faster than SGD, SX dropped by about 98.2 % from L/S 0.31 to 2.35, whereas SGD decreased by about 89.7 % (L/S from 0.12 to 1.22). This indicates that the sorption phenomena relating to SGD could be more strongly dependent on the organic matter content than SX, since the organic matter content of LS is considerably higher. SDM leaches slowly from LS soils, indicating strong sorption: in such soil the SDM concentration in the eluate dropped by about 24.5 % from L/S 0.12 to 1.22. This is presumably due to the large amount of fine particles as well as the organic matter content of LS soils. SDM leaches much faster from US soil than from LS soil. The SDM concentration in the eluate dropped by about 93.8 % for US soil but only by about 24.5 % in the case of LS soil. This confirms that the strength of bonding between SAs and soil particles is closely related to the organic matter content and the presence of fine particles. SDM exhibits a similar leaching behavior from the LS
soil if tested alone or in a mixture with SGD. In the experiment where only SDM was tested, its concentration fell from 1.7 mg L\(^{-1}\) for LS 0.3 to 1.05 mg L\(^{-1}\) for L/S 2.2. During the test where we mixed SDM with SGD, its concentration dropped from 2 mg L\(^{-1}\) to 1.51 mg L\(^{-1}\) (L/S from 0.12 to 1.22). We therefore conclude that the mixture of different sulfonamides in the current work had a negligible effect on their leaching behavior. Column tests of the MS soil material indicate rapid leaching of all three sulfonamides: concentrations of all SAs in the eluates dropped by almost 100 % from L/S 0.26 to 0.9. This is probably due to the small amount of fine particles in the MS soil and its low organic matter content. Thus, poorer sorption of sulfonamides to soil particles is possible, leading to rapid leaching.

4. CONCLUSIONS

It has been demonstrated that both batch and column tests are suitable for assessing the leaching behavior of polar and ionizable compounds like the three sulfonamides examined in this study. The results show that these compounds are highly mobile, rapidly capable of reaching water compartments once they have entered soils, and that their bioavailability in soils is considerable. These results will therefore contribute to a better understanding of the environmental fate of these pharmaceuticals.

REFERENCES