Sulfadimethoxine and sulfaguanidine: Their sorption potential on natural soils

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ABSTRACT

Sulfonamides (SAs) are one of the oldest groups of veterinary chemotherapeutic agents. As these compounds are not completely metabolized in animals, a high proportion of the native form is excreted in feces and urine. They are therefore released either directly to the environment in aquacultures and by grazing animals, or indirectly during the application of manure or slurry. Once released into the environment, SAs become distributed among various environmental compartments and may be transported to surface or ground waters. The physicochemical properties of SAs, dosage and nature of the matrix are the factors mainly responsible for their distribution in the natural environment. Although these rather polar compounds have been in use for over half a century, knowledge of their fate and behavior in soil ecosystems is still limited. Therefore, in this work we have determined the sorption potential of sulfadimethoxine and sulfaguanidine on various natural soils. The influence on sorption of external factors, such as ionic strength and pH, were also determined. The sorption coefficients (K_d) obtained for the sulfonamides investigated were quite low (from 0.20 to 381.17 mL g^{-1} for sulfadimethoxine and from 0.39 to 35.09 mL g^{-1} for sulfaguanidine), which indicated that these substances are highly mobile and have the potential to run off into surface waters and/or infiltrate ground water. Moreover, the sorption of these pharmaceuticals was found to be influenced by OC, soil solution pH and ionic strength, with higher K_d values for soils of higher OC and lower K_d values with increasing pH and ionic strength.

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1. Introduction

Sulfonamides are among the most commonly consumed veterinary antibiotics in the EU (García-Galán et al., 2009): they are used in agriculture to prevent disease and to treat illness in livestock. Following their administration, substantial quantities may be excreted as the parent compounds and/or metabolites and leak into the environment while animals are grazing or during the spreading of manure. Moreover, during the storage of manure, the excreted acetyl conjugates can be cleaved back to the parent compound (Sukul and Spiteller, 2006). Therefore, once released into the environment, SAs are distributed among different environmental compartments and can be transported to surface and ground waters. They can also enter the food chain and impact on natural environment and human health. The physicochemical properties, applied dosage and the nature of the environmental components with which they interact govern the whole process. However, knowledge of the behavior and fate of these rather polar pollutants in soil ecosystems is still limited.

Previous studies revealed that these compounds are present in soils and manure in concentrations of up to 15 µg kg^{-1} of soil and 20 mg kg^{-1} of liquid manure (Sukul and Spiteller, 2006). As soil is the most exposed to pollution by these substances, the degree to which they disperse in this matrix needs to be assessed. It is also important to determine the mobility of these substances in soils with different physicochemical properties in order to gain a better understanding of the general risk accompanying the entry of sulfonamides into surface and ground waters, and thus to assess the scale of threats to the environment and human health. Such studies are necessary as far as the ecotoxicological potential of sulfonamides is concerned. Our recent studies have shown that these compounds can pose a real risk to aquatic organisms, especially to higher plants like duckweed Lemna minor and algae (Białk-Bielińska et al., 2011). It is therefore of the utmost importance to evaluate their sorption potential and to determine their behavior and fate in the soil environment.

Although SAs have been the subject of many investigations, to date only a few studies have focused on the behavior and fate in soils of these rather polar pharmaceuticals. Moreover, most studies have dealt with sulfadiazine (Thiele-Bruhn et al., 2004; Burkhardt et al., 2005; Stoob et al., 2007; Sukul et al., 2008; Schauss et al.,

2009; Unold et al., 2009), sulfamethazine (Thiele-Bruhn et al., 2004; Burkhardt et al., 2005; Gao and Pedersen, 2005; Kurwadkar et al., 2007; Stoob et al., 2007; Lertpaitoonpan et al., 2009; Figueroa-Diva et al., 2010), sulfathiazole (Burkhardt et al., 2005; Kahle and Stamm, 2007a,b; Kurwadkar et al., 2007; Stoob et al., 2007) and sulfachloropyridazine (Boxall et al., 2002; ter Laak et al., 2006). Sorption studies have shown that all of the investigated sulfanamides are characterized by a low sorption potential and are adsorbed less in soil containing manure. Even so, the environmental fate of SAs is still difficult to predict since field and plot studies have yielded an inconsistent picture of SA mobility, which depends on soil and experimental conditions (Boxall et al., 2002; Burkhardt et al., 2005; Kahle and Stamm, 2007a,b; Stoob et al., 2007). Therefore, identification of the factors affecting sorption is essential for a reliable assessment of SA mobility, and hence, their bioavailability. Knowledge of SA sorption remains limited, but existing data suggest that these compounds behave in a complex manner.

Widely used in veterinary medicine, sulfonamides, sulfadimethoxine (SDM) and sulfaguanidine (SGD) were selected for the present work. SDM was chosen mainly because it was recently shown to have the strongest phytotoxic potential of all sulfonamides ever investigated (Białk-Bielińska et al., 2011) and because the sparse data regarding its sorption potential (Thiele-Bruhn et al., 2004; Stoob et al., 2007; Sanders et al., 2008; Figueroa-Diva et al., 2010). It is thus a matter of urgency to determine its mobility in the environment, as it can pose a real threat to the whole ecosystem once it reaches the aquatic environment. On the other hand, sulfaguanidine was selected mainly because, according to the 'Analysis of Antimicrobial Agents' Treatment of Swine in Poland in 2010', it is the most frequently used sulfonamide in medicated feeds (Krasucka et al., 2010), and because there are no studies describing its behavior in soils. Furthermore, even though these two compounds belong to the same group of pharmaceuticals, they differ in their physico-chemical properties (Table 1). SGD has an extremely high second dissociation constant compared with SDM and other sulfonamides (Carda-Broch and Berthod, 2004), so it may behave differently in the soil from other sulfonamides.

In the present study, the mechanism of sulfonamide (SDM and SGD) sorption onto three natural soil types differing in their organic content (OC), cation exchange capacity (CEC) and particle size distribution was investigated in detail (Table 2). Isotherms were employed to describe sorption phenomena. The influence of external factors such as ionic strength and pH on sorption was also determined.

2. Materials and methods

2.1. Chemicals

Standards of sulfaguanidine and sulfadimethoxine sodium salt as well as trifluoroacetic acid 99% (TFA) were purchased from Sigma–Aldrich (Steinheim, Germany). Deionized water was produced by the HYDROLAB System (Gdańsk, Poland). Acetonitrile (ACN), hydrochloric acid (HCl), potassium chloride (KCl), calcium chloride ($CaCl_2$) and potassium hydroxide (KOH) were purchased from POCH (Gliwice, Poland).

Standard stock solutions of sulfaguanidine and sulfadimethoxine (800 μg mL^{-1}) were prepared by dissolving the pure compounds in 0.01 M $CaCl_2$ with the optional addition of HCl or KOH (1 M solutions) to achieve the appropriate pH (pH-dependent sorption experiments). $CaCl_2$ in concentrations of 0.001 M or 0.1 M was used in the ionic strength sorption experiments. The solutions were sonicated for 15 min to ensure complete dissolution. The spiked solutions (8 points) were prepared from stock solutions in accordance with the serial dilution method in the appropriate $CaCl_2$ solution.
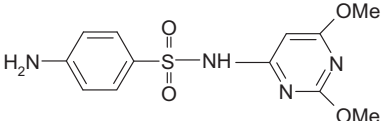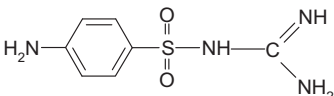
2.2. Soils

The experiments were carried out using three soils with different physicochemical properties (Table 2). The soils were sampled from the region of Pomerania in northern Poland. Afterwards they were air-dried, ground in a mortar and passed through a 2 mm sieve, then re-ground in a mortar with a small rubber pestle. The soil pH was determined with a glass electrode in a 1:2.5 soil/water suspension using deionized water and a 1 M KCl solution. Soil OC was determined by loss-on-ignition. CEC was determined using the $BaCl_2$ Compulsive Exchange Method.

2.3. Sorption studies

Batch sorption experiments were performed according to the OECD Technical Guideline 106 (OECD, 2000). All samples were pre-

Table 1
Structures and properties of the sulfonamides investigated.

Substance [CAS]	Structure	M.w.[a] (g mol^{-1})	pK_{a1}	pK_{a2}	log$P$[a]
Sulfadimethoxine (SDM) [122-11-2]		310.3	2.5[c]	5.9[c]	1.63
Sulfaguanidine (SGD) [57-67-0]		214.3	2.8[b]	12.1[b]	−1.22

[a] Data obtained from http://www.vcclab.org/lab/alogps/start.html (ALOGPS 2.1).
[b] http://web.squ.edu.om/med-Lib/MED_CD/E_CDs/A%20Practical%20Guide%20to%20Contemporary%20Pharmacy%20Practice/pdf/pKa-table.pdf.
[c] Lo and Heyton, 1981; Sukul and Spiteller, 2006.

Table 2
Physico-chemical properties of soils.

Soil	pH (H$_2$O)	pH (KCl)	OC (%)	CEC (cmol(+) kg^{-1})	Clay fraction (<0.01 mm) (%)
Sandy–clayey silt (CA1)	5.80	5.27	24.50	27.0	94.0
Alluvial soil (R13)	7.21	6.65	19.43	85.6	16.7
Beach sand (CA3)	7.38	7.38	0.14	3.0	0.2

pared in triplicate. Tests were performed using a laboratory shaker (RS 10 Control, IKA, Germany), ensuring constant contact with the soil sample solution containing the compound to be tested. To avoid photodegradation of sulfonamides, the experiments were performed in the dark by covering the tubes with aluminum foil.

Selection of optimum soil/solution ratios was based on the calculated percentage of chemical adsorbed to the soil, which should be > 20%, and preferably > 50%. The ratios for SDM and SGD were 1:2 for soil CA3, 1:5 for soil R13 and 1:25 for soil CA1. Finally, although equilibrium was reached for both SDM and SGD in all three media after 18 h, 24 h was chosen as the equilibrium time for both drugs.

Each sorption experiment involved the following steps: (1) 1 g of air-dried soil sample was equilibrated by shaking with an appropriate volume – calculated from the ratio of the soil/water solution (1.8, 4.5 and 22.5 mL for soils CA3, R13 and CA1 respectively) – of $CaCl_2$ at a concentration of 0.01 M overnight (12 h) before the day of the experiment; (2) a certain volume (0.2, 0.5 and 2.5 mL for soils CA3, R13 and CA1, respectively) of the spiked solutions of the test substance was added to adjust the final volume. Eight concentrations for determining the sorption isotherms were anticipated (0.625, 1.25, 2.5, 5, 10, 20, 40, 80 $\mu g\,mL^{-1}$ of SDM or SGD); (3) the mixture was shaken for 24 h until adsorption equilibrium was reached; (4) subsequently, samples were centrifuged at 4000 rpm for 10 min (MPW-250 Centrifuge, Warsaw, Poland), passed through 0.45 μm syringe filters (Chromafil® PET 15/25, Marchery-Nagel, Düren, Germany) and placed in HPLC vials. At this step the soil samples were also subjected to a desorption experiment. To attain desorption equilibrium, the desorption experiment was carried out by adding an extra amount of freshly prepared 0.01 M $CaCl_2$ solution to the soil in the centrifuge tubes and maintaining the total amount of the solution at exactly 2, 5 or 25 mL depending on the type of soil. Afterwards the samples were again shaken for 24 h, centrifuged and filtered; (5) the concentration of test substance in the supernatant was analyzed by reverse-phase HPLC with UV detection.

The strength and the extent of sorption phenomena were determined by the sorption coefficient, isotherms and sorption kinetics. The influence of external factors on the sorption of the pharmaceuticals, like solution pH and ionic strength, was also investigated. For this purpose, the three soils were equilibrated with different concentrations of HCl and KOH in addition to 0.01 M $CaCl_2$ (for pH – dependent sorption experiments) and with different salt concentrations – 0.001 M, 0.01 M and 0.1 M of $CaCl_2$ (for ionic strength – dependent sorption experiments). The sorption coefficients for the analyzed sulfonamides at different pH values (SGD 3, 6, 12 and for SDM 3, 6 and 8) and ionic strength were then determined using the approach described above.

2.4. Chemical analysis

Filtrate samples from the sorption studies were analyzed by isocratic reversed phase HPLC using a Phenomenex Gemini C18-110A column, 150 mm × 4.6 mm i.d., 5 μm (Torrance, USA). The analytical system (Perkin Elmer Series 200) consisted of a chromatographic interface (Link 600), a binary pump, a UV/VIS detector, a vacuum degasser and a Rheodyne injection valve.

Both compounds were detected at a wavelength of 270 nm. The mobile phase for the determination of SGD was $ACN:H_2O$ (6.94, v:v) at a 0.5 mL min^{-1} flow rate and $ACN:H_2O$ (with 0.00025% of TFA) (45:55, v:v) at a 0.7 mL min^{-1} flow rate for SDM. The injection volume was 30 μl for SGD and 50 μl for SDM. Detection limits for
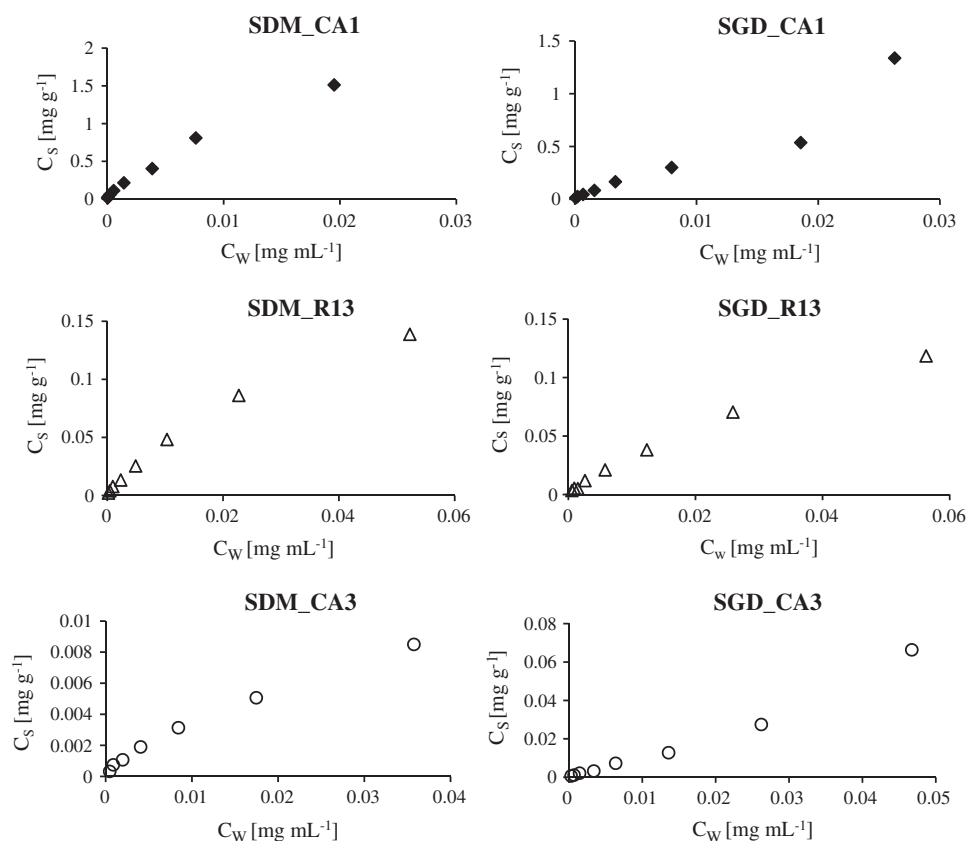

Fig. 1. Sorption isotherms of SDM and SGD in three investigated soils (CA1, CA3, R13); Cs – the content of test substance adsorbed on the soil at adsorption equilibrium (mg g^{-1}), Cw – the mass concentration of test substance in the aqueous phase at adsorption equilibrium (mg mL^{-1}).

SGD and SDM in soil extracts were 16.7 and 3.3 μg L^{-1}. All the chromatographic analyzes were carried out on two replicates.

2.5. Calculations

The amount of sulfonamide remaining in solution after equilibrium was determined. The concentrations of sorbed sulfonamides were calculated from the difference between the control and the final sulfonamide concentration. All the results were modeled by linear, Freundlich and Langmuir sorption isotherms according to Schwarzenbach et al. (2003) and are presented in Appendix A.

Prediction of soil influence on the sorption of sulfonamides was performed by analyzing the correlations between soil variables and sorption coefficient, K_d. Statistical significance was considered at $P < 0.05$.

3. Results and discussion

3.1. Sorption isotherms

Sorption isotherms of the sulfonamides tested are presented in Fig. 1, and Freundlich and Langmuir isotherms calculated for SGD and SDM in the three soils are illustrated in Fig. 2. Table 3 summarizes the equilibrium sorption coefficients (K_d) and the Freundlich and Langmuir model parameters estimated in this study. It was observed that all three models were suitable to describe sorption behavior of these compounds in the investigated soils, as indicated by the high regression coefficient ($R^2 > 0.97$ for linear and Freundlich isotherms; $R^2 > 0.92$ for Langmuir isotherm). However, previous studies focused only on fitting such data to linear and Freundlich isotherms. In this matter, our results are in agreement with these studies investigating SA (including SDM) sorption behavior (Boxall et al., 2002; Thiele-Bruhn et al., 2004; Gao and Pedersen, 2005; Kurwadkar et al., 2007; Sukul et al., 2008; Sanders et al., 2008; Lertpaitoonpan et al., 2009). All $1/n$ values were below 1 (in the range 0.67–0.89), which suggests a decreasing sorption tendency with increasing initial concentration. This may be due to the fact that the high energy sites of the soil are first occupied, followed by adsorption at lower energy sites, an observation characteristic of heterogeneous media. This non-linearity of sorption indicates specific interactions with functional groups in the soil organic matter, an observation also made by Thiele-Bruhn et al. (2004). However, the suitability of using a Langmuir isotherm to describe the sorption behavior of the investigated sulfonamides can be explained either by the low concentrations used in the experiments or probably by the homogeneity of the interaction sites.

The estimated K_d values ranged from 0.31 to 107.53 mL g^{-1} for SDM and from 1.03 to 30.99 mL g^{-1} for SGD, depending on the soil characteristics. The K_d values for SDM and SGD obtained in this study decreased in the sequence CA1 > R13 > CA3 and were generally higher for SDM, suggesting that not only the soil's
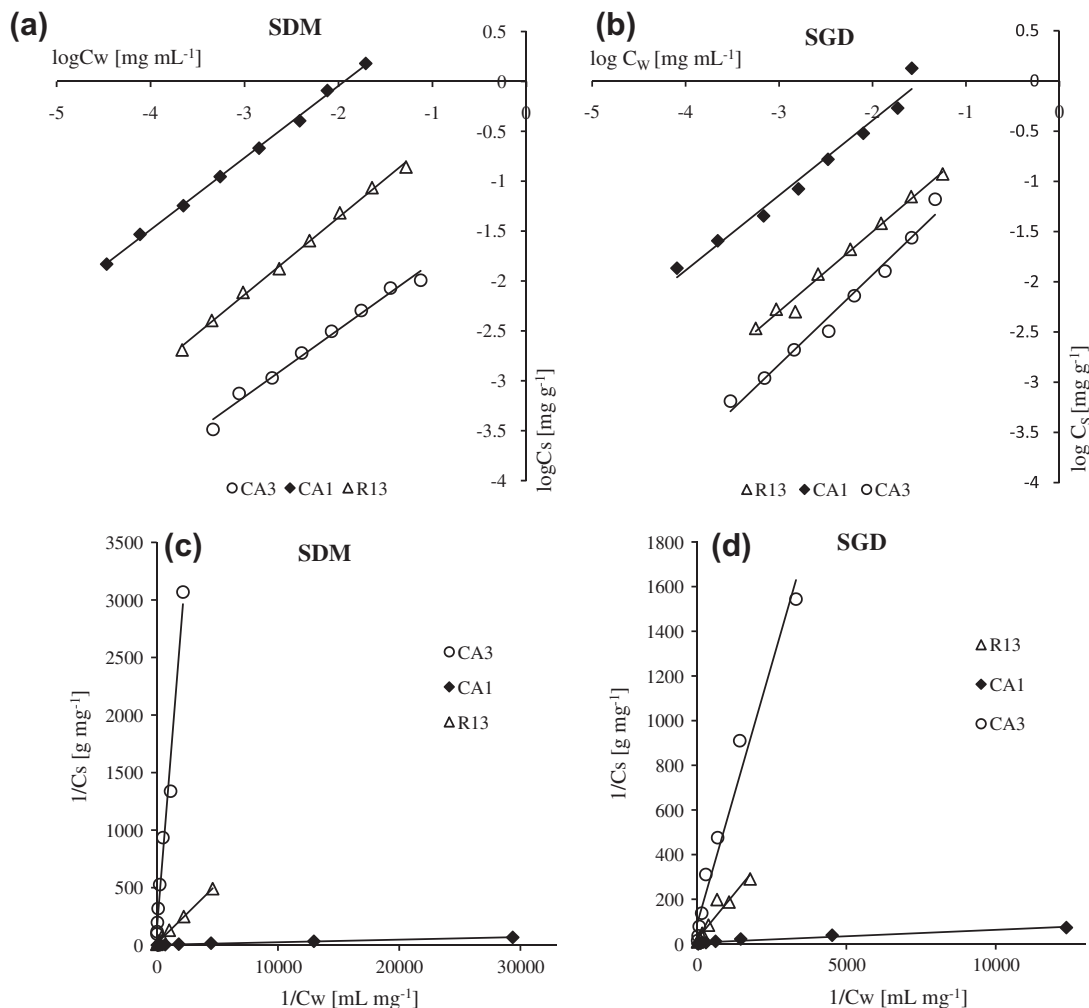

Fig. 2. Freundlich (a and b) and Langmuir (c and d) adsorption isotherms for SDM and SGD in three investigated soils (CA1, CA3, R13).

Table 3
Sorption coefficients (K_d); Freundlich and Langmuir adsorption isotherm parameters.

Substance	Soil	OC (%)	Linear sorption		Desorption (%)	Langmuir sorption			Freundlich sorption		
			R^2	K_d (mL g^{-1})		R^2	C_{max}	K_L	R^2	$1/n$	K_F
SDM	CA1	24.50	0.992	107.53 ± 5.42	13.4 ± 0.8	0.989	0.314	1449.91	0.998	0.72	24.95
	R13	19.43	0.993	4.83 ± 0.20	74.6 ± 1.2	0.997	0.065	148.37	0.997	0.77	1.53
	CA3	0.14	0.975	0.31 ± 0.03	96.8 ± 7.6	0.983	0.008	93.84	0.985	0.67	0.07
SGD	CA1	24.50	0.976	30.99 ± 2.44	14.3 ± 0.4	0.957	0.173	1012.21	0.976	0.75	12.60
	R13	19.43	0.980	2.26 ± 0.16	54.5 ± 1.3	0.928	46.512	0.13	0.989	0.79	5.07
	CA3	0.14	0.997	1.03 ± 0.03	71.6 ± 12.1	0.972	0.011	190.75	0.982	0.89	0.72
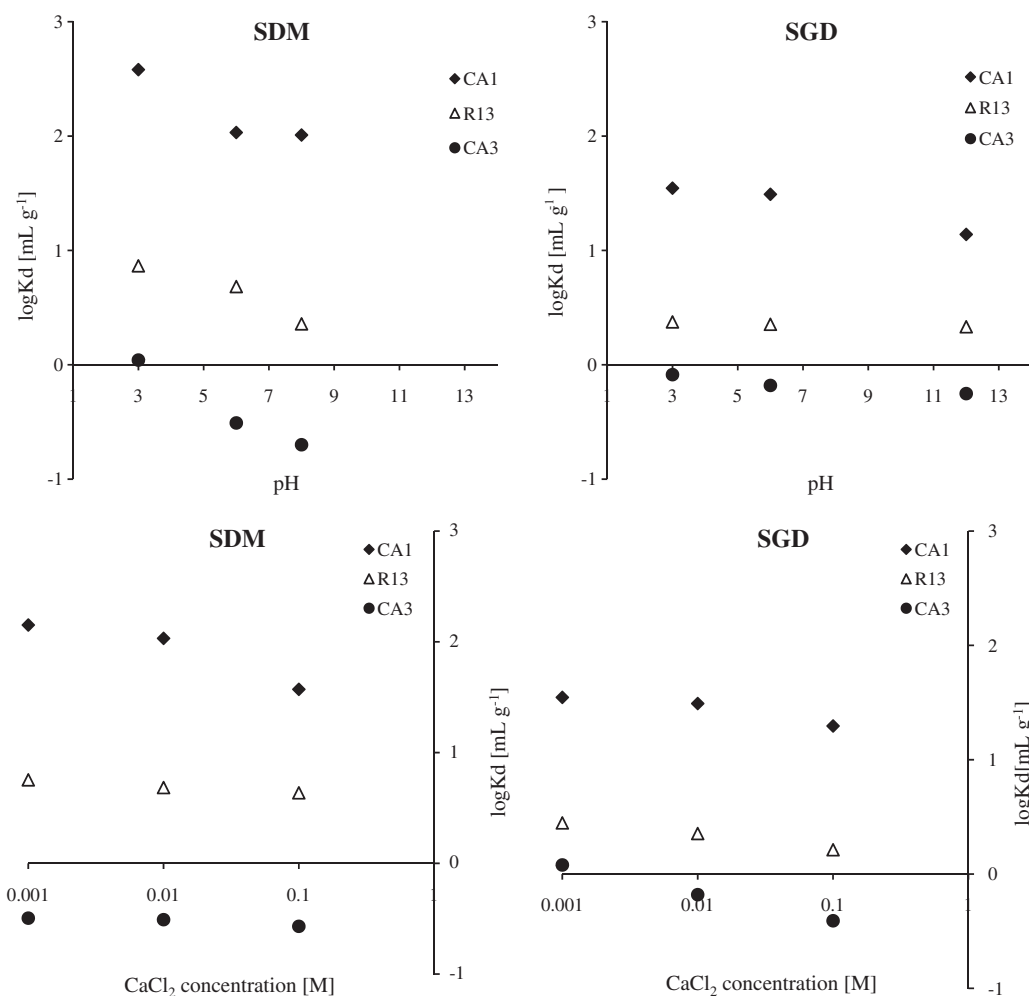
Fig. 3. The influence of pH and ionic strength on $\log K_d$ of SDM and SGD in three investigated soils (CA1, CA3, R13).

physico-chemical properties but also the R-side-chain play a crucial role in the fate of sulfonamides in soil ecosystems. Nevertheless, K_d values for calculated soils CA3 and R13 were in the same range as the values reported previously (Thiele-Bruhn et al., 2004; Sanders et al., 2008; Figueroa-Diva et al., 2010). However, K_d values in soil CA1 are higher than those for other sulfonamides in soils reported by Tolls (2001), Boxall et al. (2002), Thiele-Bruhn et al. (2004), ter Laak et al. (2006), Kahle and Stamm (2007a,b), Kurwadkar et al. (2007), Sanders et al. (2008), Lertpaitoonpan et al. (2009) and Figueroa-Diva et al. (2010). This can be attributed to differences in soil properties such as pH, OC and clay fraction. A strong dependency of sorption and weak desorption (Table 3) was observed with increase in organic carbon. Generally, lower OC enhances the desorption, which was indeed observed for soils CA3 and R13. This is in agreement with the

research of Thiele-Bruhn et al. (2004), who concluded that the sorption of sulfonamides is influenced by many factors such as the molecular structure and physicochemical properties of sulfonamides, pH, accessible functional groups at organic-mineral surfaces and the accessibility of voids and cavities in the 3D structure of soil organic matter (SOM). He also observed that in soils, binding moieties of high polarity interact preferably with the polar functional groups of sulfonamides. The investigated antibiotic-SOM complexes were predominantly formed by nonbonding van der Waals and hydrogen bonding. Such weak bonding forces are susceptible to desorption processes; unaltered sulfonamides molecules are therefore released following prior surface adsorption.

Nevertheless, our experiments demonstrated that the sulfonamides investigated here (sulfaguanidine and sulfadimethoxine)

Table 4
Multiple linear regression of obtained data, $P < 0.05$.

	pH	Organic content [OC]	Cation exchange capacity [CEC]	Clay fraction [CF]	Sorption coefficient [K_d]
pH		0.139	0.139	−0.998	−0.998
OC	−0.731		0.574	0.776	0.668
CEC	0.139	0.574		−0.072	−0.199
CF	−0.998	0.776	−0.072		0.992
K_d	−0.998	0.668	−0.199	0.992	

are less strongly sorbed to soils than antibiotics of other classes (like tetracyclines and fluoroquinolones with K_d values higher than 400 mL g^{-1} (Tolls, 2001)).

3.2. Influence of pH and ionic strength

SAs are characterized by two dissociation constants. The first one (pK_{a1}) describes the equilibrium between the positively charged, protonated amino group of the compound and its electrically neutral conjugate base; pK_{a2}, in turn, signifies the deprotonation of the SO$_2$NH moiety (Sukul and Spiteller, 2006; Babić et al., 2007) (Table 1). Hence, the neutral species dominates between the pK_{a1} and pK_{a2} values, the cationic species prevails at pH values below pK_{a1}, and the anionic species at pH > pK_{a2}. Cationic, neutral, zwitterionic and anionic species have different chemical properties and are thus differently sorbed onto soil. Sorption was therefore studied in ambient 0.01 M CaCl$_2$ at adjusted pH. The influence of ionic strength was also investigated, as solution ionic strength influences the double layer thickness of a sorbent surface and the aqueous activity of sulfonamide species.

Linear, Freundlich and Langmuir sorption isotherms were used to describe the process. The logarithmized K_d values were plotted against pH or salt concentration, respectively, as shown in Fig. 3. Detailed information of the linear sorption coefficients (K_d), and of the Freundlich and Langmuir model parameters are summarized in Tables A1 and A2 in Appendix A. It was found that both the linear and the Freundlich isotherms fitted the SGD and SDM sorption data best. Moreover, most soils showed increasing n values with increasing pH and ionic strength.

As predicted on the basis of the pH-dependency investigations, the apparent value of K_d decreased with increasing pH (Fig. 3). This is presumably due to electrostatic repulsion between anionic SGD and SDM and the negatively charged soil surface. However, at lower pH, sorption of SAs is enhanced primarily due to the exchange of predominantly cationic forms of the adsorbate. The proportion of ionic species of SGD and SDM in the investigated pH is presented in Fig. A1 in Appendix A. These results are in agreement with previous studies of SDM (Figueroa-Diva et al., 2010) and other SAs (Boxall et al., 2002; Gao and Pedersen, 2005; Kahle and Stamm, 2007a,b; Kurwadkar et al., 2007; Lertpaitoonpan et al., 2009).

Furthermore, it was observed that the sorption coefficients of the investigated SAs decrease with increasing ionic strength (Fig. 3). The influence of ionic strength on adsorption is related mostly to the decreased thickness of the "electrical double layer" of the charged surface, resulting in a decreasing surface charge and, finally, in a smaller number of interactions between the protonated form of the compound and the soil surface. However, as sulfaguanidine hardly ever occurs in ionized form, the "salting-out" effect of the soil surface is also possible. Only Gao and Pedersen (2005) determined the influence of ionic strength and type of exchangeable cation on the adsorption of uncharged sulfamethazine to clay minerals like montmorillonite and kaolinite. A large decrease in the cationic form of sulfamethazine was observed with increasing ionic strength, which suggests that the sulfamethazine cation interacts with the mineral surface by a cation exchange mechanism. Although our results for SDM are in agreement with

this trend, the lower K_d values we obtained can be explained by the various quality and smaller quantities of the clay minerals in the soils studied.

For both studied sulfonamides the obtained correlation coefficients were the same, and are presented in Table 4. The highest correlation was observed for pH with K_d. The negative value indicated on decrease in sorption potential with the rise in pH, which is in agreement with experimental results. Second major factor was the content of clay fraction, which is probably due to extent in available surface area of interactions. Surprisingly, lower correlation was observed for the OC, what may be probably explained by quality of organic matter (not fully humificated). The CEC was not playing important role in correlation, what was also in agreement with batch study. However, we must indicate that to obtain the full spectrum of correlations, the larger data set (number of soils) is needed.

4. Conclusions

To prevent further environmental contamination and adverse effects of antimicrobial substances, an understanding of the environmental fate of these compounds is necessary. To assess the mobility of pollutants in the environment, knowledge of their persistence and sorption behavior is crucial. Our experiments demonstrated that the sulfonamides investigated (sulfaguanidine and sulfadimethoxine) sorb to soils less strongly than other antibiotics (like tetracyclines and fluoroquinolones). However, their sorption potential and mobility is strongly influenced by the soil's physico-chemical properties (pH, OC, CEC), the ionic strength of the soil solution, and the physico-chemical properties of sulfonamides. Adsorption coefficients increased with OC content and decreased at higher values of pH and ionic strength. A high content of sorptive organic matter and low pH can immobilize sulfonamides, consequently reducing the risk of direct impact on microorganisms or of ground water contamination. However, cationic species, present in an acidic environment, are more likely to sorb onto soil particles, and will exist at pH values <4.5, which is on the borderline of pH conditions typical of the natural environment, whereas pK_a values for the deprotonation of the amide group lie within the typical soil pH range. As sorption to the soil matrix governs the transport, persistence and (bio) availability of pharmaceuticals in the environment, it can be assumed that obtained results (low K_d) altogether with physico-chemical properties of these compounds (water solubility, hydrophilicity) indicate that investigated sulfonamides can be characterized as very mobile and highly bioavailable with low bioaccumulation potential due to their low log P values. They can therefore be easily transported from soil surfaces to the aquifer causing surface and groundwater contamination. Moreover, being very bioavailable to organisms, plants and other species, they can have a direct effect of them. Research on bioaccumulation of these compounds is needed since the information on this topic is very limited. However, the enhanced mobility of sulfonamides and their strong phytotoxic properties (especially of SDM) are of great environmental concern. The multiple linear regression indicated on pH and clay fraction content as the major factor responsible for sorption of studied sulfonamides. Therefore, more detailed research

should be performed with the aim of reaching a full understanding of the environmental fate of sulfonamides.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.11.058.

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