



## Sorption of sulfadiazine on Brazilian soils

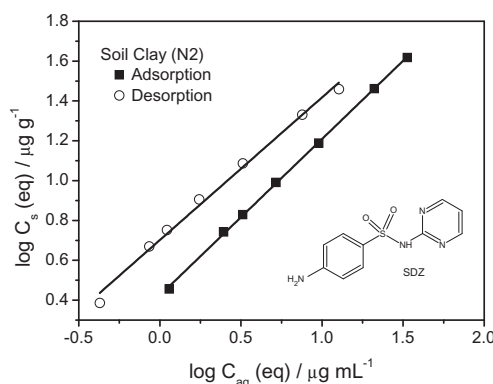
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### HIGHLIGHTS

- ▶ The sorption of sulfadiazine (SDZ) was studied in four tropical soil–water systems.
- ▶ The low values of the  $K_F$  indicate that SDZ is highly mobile in the evaluated soils.
- ▶ The desorption values were higher than those obtained for adsorption of SDZ.
- ▶ A small positive hysteresis was observed with all soils under study.
- ▶ The main mechanism of the sorption of SDZ is partitioning to organic matter.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Antimicrobials, among them sulfonamides are widely used in veterinary medicine and can contaminate the environment. The degree to which antimicrobials adsorb onto soil particles varies widely, as does the mobility of these drugs. Sulfadiazine (SDZ) was used to study the adsorption–desorption in Brazilian soil–water systems, using batch equilibrium experiments. Sorption of SDZ was carried out using four types of soils. Adsorption and desorption data were well fitted with Freundlich isotherms in log form ( $r > 0.999$ ) and ( $0.984 < r < 0.999$ ), respectively. An adsorption–desorption hysteresis phenomenon was apparent in all soils ranging from 0.517 to 0.827. The experimental results indicate that the Freundlich sorption coefficient ( $K_F$ ) values for SDZ ranged from 0.45 to 2.6  $\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$ .

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### 1. Introduction

Sulfonamide antimicrobials comprise a class of synthetic sulfanilamide derivatives which are widely used in human and veterinary medicine. Sulfadiazine (SDZ) belongs to the class of sulfonamides and is – in addition to its use in human medicine – one of the most widely used antibacterial veterinary drugs (Thiele-Bruhn, 2003). Sulfonamides are quickly eliminated from the organism, mainly as the parent compounds or as their acetyl- or hydroxyl-conjugated

metabolites (Boxall et al., 2002; Lamshöft et al., 2007). Therefore, sulfonamides may reach the environment through grazing livestock or spreading of manure on agricultural soils. A further pathway into the environment is the direct use of drugs in aquacultures. Once in the environment, they may sorb onto the soil and sediment, be transported to ground or surface waters, or be degraded. In addition, antimicrobials can provoke the formation of resistant microorganisms (Hirsch et al., 1999; Boxall et al., 2003).

The fate of sulfonamides, including SDZ, in soils, ground waters or surface waters is dependent on the processes of sorption, degradation and leaching. These processes are, in turn, governed by physico-chemical properties, such as structure, size, shape, solubility,

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hydrophobicity, and speciation, and soil properties, such as organic matter content, texture, mineralogy, clay content, pH, ionic strength, and cation exchange capacity, apart from local weather conditions (Sarmah et al., 2006).

For a reliable assessment of sulfonamide mobility and bioavailability, the identification of factors affecting sorption to soils and sediments is essential. Thiele-Bruhn et al. suggested that for sulfonamide sorption to soils, not only is the organic matter content important to be considered, but also the presence of clay minerals and pedogenic oxides (Thiele-Bruhn et al., 2004). In sorption experiments, the addition of manure to soil samples resulted in decreasing sorption of sulfonamides compared to soil without manure. Studies have suggested that sulfachloropyridazine is relatively weakly sorbed in soils and slurry amended soils and is, thus, quite mobile in soil (Boxall et al., 2002). Research indicates that sulfonamides are sorbed on soil particles with distribution constants ( $K_D$ ) ranging from 0.9 to 3.5 L kg<sup>-1</sup> (Boxall et al., 2002; Thiele-Bruhn, 2003). Other results reported by Thiele-Bruhn and Aust suggests lower sorption of sulfanilamide, sulfadimidine, sulfadiazine, sulfadimethoxine and sulfapyridine in pure soil systems than in pig slurry and pig slurry amended soils ( $K_D$  ranging from 0.3 to 2.0 L kg<sup>-1</sup>) (Thiele-Bruhn and Aust, 2004).

Almost all data reported in the literature about antimicrobial sorption in soils were obtained through studies carried out in temperate regions. Different environmental conditions found in the tropics, such as increased rainfall and temperature, predominance of low-activity clays, a lower percentage of organic matter in soils and lower pH will contribute to different behaviors of these antimicrobials in Brazilian soils and need to be evaluated. The aim of this study was to investigate the fate of sulfonamides in four types of Brazilian soils, using sulfadiazine as a model compound. For this purpose batch sorption kinetic experiments were carried out.

## 2. Materials and methods

### 2.1. Soil samples

Sorption studies of sulfadiazine on four different characteristic soils from the state São Paulo, Brazil, named N1 (sandy), N2 (clay), S1 (sandy-clay) and S2 (clay) were carried out.

Soils were collected in 2005 from different locations and transferred to lysimeters (1 × 1 × 2 m) located in the experimental area of the Brazilian Agricultural Research Corporation (Embrapa), Jaguariúna, SP, Brazil.

The origins of the soils were:

N1 – sandy, city of Santa Rita de Passa Quatro, SP (21°42'18,12"S and 47°28'04,82"W, altitude 773 m) (pasture).

N2 – clay, city of Sertãozinho, SP (21°05'20,44"S and 47°48'10,73"W, altitude 538 m) (sugar cane plantation).

S1 – sandy-clay, city of Jagariúna, SP (22°43'14,92"S and 47°01'14,20"W, altitude 617 m) (citrus plantation).

S2 – clay, city of Jagariúna, SP (21°42'59,50"S and 47°01'00,05"W, altitude 609 m) (covered with *Brachiaria*).

The soils were collected from each lysimeter in July 2010, air-dried, sieved to a particle size ≤ 2 mm, and stored in plastic bags at room temperature until use. The physical and chemical characteristics of each soil are presented in Table 1.

### 2.2. Reagents and chemicals

All solvents used were HPLC grade and all reagents were at least analytical grade. Calcium chloride was supplied by Nuclear (Brazil).

**Table 1**

Physical and chemical properties of the selected soils.

Property	Soil			
	N1	N2	S1	S2
pH (in 0.01 mol L <sup>-1</sup> CaCl <sub>2</sub> )	5.0	4.9	4.1	4.4
Depth of soil (cm)	0–20	0–20	0–20	0–20
Organic material (% w/w)	1.53	2.88	2.48	3.23
Organic carbon (% w/w)	0.89	1.67	1.44	1.87
Texture (%): sand	91.1	14.9	52.9	43.5
Silt (0.053–0.002 mm)	1.8	30.2	10.5	7.0
Clay (<0.002 mm)	6.2	54.6	36.2	49.2
Cation exchange capacity (mmol <sub>c</sub> kg <sup>-1</sup> )	19.3	52.7	51.9	66.0

Sulfadiazine (SDZ; benzenesulfonamide, 4-amino-N-2-pyrimidyl; CAS Registry No. 68-35-9; 99%) was purchased from Sigma-Aldrich, Belgium. Molecular structure and some physico-chemical properties of SDZ are shown in Table 2. Throughout the study, water was obtained from a Milli-Q purification system (Millipore, USA). A standard stock solution (750 µg mL<sup>-1</sup>) of SDZ was prepared by dissolving 75 mg of SDZ in 100 mL warm water. Working solutions of SDZ were prepared by appropriate dilution of the standard stock solution with 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>.

### 2.3. HPLC analyses

Chromatographic analysis were carried on an Agilent HPLC Series 1200 system (Agilent, USA) equipped with a G1311A quaternary pump, a G1315D photodiode array detector (PAD), a G1316A column oven and G1329A auto sampler. Chromatographic separation of SDZ was achieved using a XBridge™ reversed-phase column (RP-18, 150 × 4.6 mm, 3.5 µm particle size) from Waters (Ireland) at 40 °C. Methanol with 0.1% (v/v) formic acid added and water with 0.1% (v/v) formic acid added (10:90 v/v) was the mobile phase. Injection volume was 20 µL and the flow rate was 0.7 mL min<sup>-1</sup>. Quantitation of SDZ was performed at 266 nm. The retention time for SDZ was 8.6 min.

### 2.4. HPLC method validation

The method was *in house* validated and the following parameters were evaluated: linear range, linearity, selectivity, matrix effect, intra- and inter-day precision, limit of detection and limit of quantitation. The linearity and linear range were established through calibration obtained, by triplicate analyses, of five concentrations levels (0.05; 0.1; 2.0; 6.0 and 10.0 µg mL<sup>-1</sup>) of SDZ in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>.

The matrix effect was evaluated for all soils under study through fortification (10.0 µg g<sup>-1</sup> SDZ) of the supernatant obtained after soil samples were equilibrated (48 h, at room temperature) with CaCl<sub>2</sub>, centrifuged and filtered with 0.22 µm membrane filters. The fortified extract was analyzed by HPLC-PAD and the area obtained compared with the area of a SDZ solution at the same concentration level in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. All analyzes were carried out in triplicate.

The selectivity of the method was evaluated by the analyses of the chromatograms obtained with equilibrated 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> blank soil sample solutions and with SDZ in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. The purity of SDZ using the spectral data generated by the photodiode array detector was verified by the full spectrum at the upslope-, the apex- and the downslope in order to ensure that no coeluting impurities or compounds of the soil matrix contributed to peak response.

The intra-day precision of the method was evaluated through the analyses of the CaCl<sub>2</sub> extracts obtained of each soil fortified with 10.0 µg g<sup>-1</sup> SDZ, after an apparent equilibrium time of 48 h.

**Table 2**  
Physical and chemical properties of sulfadiazine (SDZ).

Antimicrobial	Physico-chemical properties
Sulfadiazine (SDZ)	Molecular formula: C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> S Molar mass: 250.28 g mol <sup>-1</sup> pK <sub>a</sub> : 1.57/6.50

All analyses were carried out in sextuplicate on the same day, by the same analyst and using the same method and equipment. The inter-day precision was established at the same concentration level as described for the intra-day precision; the analyses were performed on three different days (sextuplicate analysis in the first day, and triplicate analyses in the two other occasions). The intra- and inter-day precisions were expressed as the relative standard deviation (RSD).

The limit of detection (LOD) and quantitation (LOQ) were determined as the signal-to-noise ratio of 3 and 10, respectively. For this purpose, solutions of SDZ in CaCl<sub>2</sub> in decreasing concentrations were prepared and the signal measured at the corresponding retention time of SDZ.

### 2.5. Adsorption/desorption experiments

All experiments were carried out at ambient temperature (between 20 °C and 25 °C) in the dark and were performed according to the OECD Test Guideline 106 (OECD, 2000).

Sorption tests were performed in the presence and absence of sodium azide (0.001 mol L<sup>-1</sup>) to verify the presence of microbial activity. Statistically there was no difference in the results obtained, so further sorption studies with SDZ were carried out only in calcium chloride.

The optimal ratios soil/solution were evaluated in a preliminary study according to the OECD Test Guideline 106 (OECD, 2000) and determined for all four soils to be 1:1 (w/v) soil/solution.

In order to define the time for SDZ to reach sorption equilibrium in each soil presented in Table 1, batch kinetic experiments were conducted at the natural, unaltered pH of the medium. Briefly, an amount of 2 g of soil was mixed with 2 mL 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution containing 10.0 µg mL<sup>-1</sup> SDZ in centrifuge tubes and shaken (150 rpm) from 0 to 60 h. After that, the tubes were centrifuged at 4186g for 15 min. The clear supernatants were removed, filtered through 0.22 µm syringe filters and analyzed by HPLC-PAD as described earlier.

Sorption isotherms were determined using the batch equilibrium method. Briefly, 2.0 g of dried soils (N1, N2, S1 or S2) were added to 1.8 mL of 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> in 50 mL centrifuge tubes and, after an equilibration period (12 h), an appropriate volume of a SDZ solution, prepared in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> (100.0 µg mL<sup>-1</sup>), was added in order to adjust the final volume to 2 mL. For each soil type, sorption isotherms were determined using soil samples fortified at concentrations ranging from 4.0 to 75.0 µg g<sup>-1</sup>. The tubes were agitated in a horizontal shaker (150 rpm) for 48 h for all soils. The samples were centrifuged at 4186g for 15 min and the supernatant separated from the soil. The supernatants were filtered through a 0.22 µm syringe filters and analyzed by HPLC-PAD. The remaining soil (RS) was stored to be used for desorption studies. For that, an aliquot of 2 mL of 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> was added to each remaining soil and the tubes were agitated (150 rpm) for 48 h. The samples were centrifuged at 4186g for 15 min and the

supernatants again separated from the soils. The supernatants were filtered through 0.22 µm syringe filters and analyzed by HPLC-PAD.

Two blank samples per soil without SDZ were run for each initial concentration. Blanks without SDZ revealed that none of the soils was contaminated with SDZ (limit of detection 8.0 ng mL<sup>-1</sup> solution). In addition, a control sample with only SDZ in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> was underwent the same test procedure. All analyses were performed in duplicate.

### 2.6. Determination of adsorption/desorption coefficients

The amount of SDZ adsorbed onto soil (C<sub>s</sub><sup>ads</sup>, µg g<sup>-1</sup> soil) was calculated from the difference between the initial concentration and concentration in batch solution after the respective contact times (C<sub>s</sub><sup>ads</sup>, µg mL<sup>-1</sup>), using:

$$C_s^{\text{ads}} = \frac{V_0}{m_{\text{soil}}} \times (C_0 - C_{\text{aq}}^{\text{ads}}) \quad (1)$$

where V<sub>0</sub> (mL) is the initial volume of solution, m<sub>soil</sub> (g) is the mass of soil, C<sub>0</sub> (µg mL<sup>-1</sup>) is the initial concentration of SDZ and C<sub>s</sub><sup>ads</sup> (µg mL<sup>-1</sup>) is the concentration of SDZ remaining in solution after apparent equilibrium has been reached. To obtain the adsorption and desorption isotherms, seven SDZ concentrations levels were used. Assays were performed as described in Section 2.5. All results were modeled to linear and Freundlich isotherms.

$$\log C_s^{\text{ads}}(\text{eq}) = \log K_F^{\text{ads}} + \frac{1}{n} \times \log C_{\text{aq}}^{\text{ads}}(\text{eq}) \quad (2)$$

where K<sub>F</sub> (µg<sup>1-1/n</sup> (cm<sup>3</sup>)<sup>1/n</sup> g<sup>-1</sup>) is the Freundlich adsorption coefficient and 1/n is the slope (Freundlich exponent) of the linear form. For 1/n = 1, Eq. (2) is converted to the linear distribution:

$$C_s^{\text{ads}} = K_D \times C_{\text{aq}}^{\text{ads}} \quad (3)$$

where K<sub>D</sub> (cm<sup>3</sup> g<sup>-1</sup>) is the distribution coefficient for adsorption. One should note that for cases when the Freundlich 1/n is unity, the Freundlich adsorption coefficient (K<sub>F</sub>) becomes equal to the distribution coefficient for adsorption (K<sub>D</sub>) (OECD, 2000). All results were modeled by both linear and nonlinear Freundlich isotherms.

Since soil organic material is highly variable among soils, an approach for sorption coefficients accounting for the organic carbon (OC) was used. This sorption coefficient normalized to organic carbon (K<sub>OC</sub>, cm<sup>3</sup> g<sup>-1</sup>) reduces the variability in sorption data among soils for a particular compound (Cox et al., 1997). K<sub>OC</sub> values were calculated as a function of the organic carbon content and K<sub>D</sub> of the soil (OECD, 2000) using:

$$K_{\text{OC}} = K_D \times \frac{100}{\% \text{OC}} \quad (4)$$

Hence, from the organic material (OM) content obtained for each soil it is possible to calculate the organic carbon (OC) content using the relationship %OM/%OC = 1.724 (Sabljic, 1989).

The hysteresis coefficient ( $H$ ) was calculated for the adsorption/desorption isotherms according to (Deng et al., 2010):

$$H = \frac{\left(\frac{1}{n} \text{desorption}\right)}{\left(\frac{1}{n} \text{adsorption}\right)} \quad (5)$$

where  $1/n$  desorption and  $1/n$  adsorption are the Freundlich exponent for the desorption and adsorption isotherms, respectively, as previously described.

### 3. Results and discussion

#### 3.1. Preliminary studies

Possible adsorption of SDZ on the surface of test vessels, as well its stability in solution was evaluated. For this purpose, control samples ( $10.0 \mu\text{g mL}^{-1}$  SDZ in  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$ ) were employed and analyzed by HPLC-PAD. The results showed that SDZ is stable in the medium during the required time and no adsorption onto the vessels occurs.

The linear range of the calibration curve for SDZ was  $0.026$ – $10.0 \mu\text{g mL}^{-1}$  with linearity ( $r$ ) of  $0.999$ . The limits of detection and quantitation were  $8.0 \text{ ng mL}^{-1}$  and  $26.0 \text{ ng mL}^{-1}$ , respectively.

No interferences of the four different soil sample matrices in the chromatograms were observed under the established experimental conditions, conferring adequate selectivity to the method. Characteristic chromatograms of  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  of blank soil samples and SDZ in  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  are presented in Fig. 1. Peak purity was confirmed in all soils under study. In addition, it was verified that the slope of the calibration graphs obtained for SDZ in  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  and SDZ in the equilibrated  $\text{CaCl}_2$  soil solution

do not differ significantly ( $P < 0.05$ ), confirming the absence of matrix effect. The intra-day precision for soils N1, N2, S1 and S2 were 2.7%, 2.0%, 1.7% and 2.1%, respectively, and the inter-day precision for N1, N2, S1 and S2 were 3.3%, 9.9%, 8.9% and 10.7%, respectively. It is worth emphasizing that in these studies the fortification level of the soil was  $10 \mu\text{g g}^{-1}$  SDZ and the remaining concentration of SDZ in the extracts of the four types of soils were about  $2.8$ – $7.0 \mu\text{g mL}^{-1}$ .

The initial concentration of the SDZ for adsorption/desorption studies should be at least two orders of magnitude higher than the limit of detection of the method. Therefore, a concentration of  $10.0 \mu\text{g g}^{-1}$  SDZ was employed in the subsequent preliminary studies. All experiments, including controls and blanks, were performed in duplicate.

Selection of appropriate soil to solution ratios for sorption studies depends on the distribution coefficient  $K_D$  and the relative degree of adsorption. Two soil/solution ratios (1:1 and 1:5 w/v) were assessed. The optimal soil/solution ratio, that gives depletion above 20% and preferably higher than 50% at equilibrium for all soils, was achieved with a soil/solution ratio 1:1 w/v for all soils under study.

The apparent equilibration time of SDZ for each soil was established through a plot of adsorption percentage of SDZ versus time (data not shown). The apparent equilibrium was reached for SDZ in 48 h for all soils.

#### 3.2. Adsorption/desorption isotherms

The sorption of SDZ in soil is important for the fate and transport of this antimicrobial in the environment and for the estimation of the risk posed by this compound. Isotherms, for all four soils, represent the amount of adsorbed SDZ per gram of soil as a function of apparent equilibrium concentration ( $C_{\text{aq}}^{\text{ads}}$ ). Data fitted well with Freundlich model in the logarithmic form (Fig. 2). There was no loss in the control samples (without soil). Sulfadiazine adsorbed differently in soils N1, N2, S1, and S2. Values of the Freundlich sorption coefficient ( $K_F$ ) and the slope ( $1/n$ ; site energy heterogeneity factor or linearity factor, which is a constant depicting the sorption intensity) using Eq. (2) were determined by linear regression and are listed in Table 3 for the four soil types. Considering the small concentration range of the sorption isotherm, which is limited by the detection limit of the method and the solubility of sulfadiazine in calcium chloride, the data given provide and indication that the sorption isotherms are non-linear.

The experimental data were fitted quite well by Freundlich isotherms in log form ( $r \geq 0.999$ ) (Table 3, Fig. 2).

The low values of the Freundlich sorption coefficient ( $K_F$ ) indicate that SDZ is probably highly mobile in soil. The adsorption of SDZ was higher in the clay soils (N2 > S2 > S1) than in the sandy soil N1. Over the entire concentration range studied, all Freundlich isotherms were observed to be nonlinear with  $1/n$  coefficients of less than unity. The isotherms obtained suggest that, as the concentration of SDZ in the aqueous phase increased, the sorption sites became increasingly saturated and, hence, less able to sorb additional molecules (Kurwadkar et al., 2007); that is, a strong interaction between soil and SDZ molecules and a decreasing sorption tendency with increasing equilibrium concentration (Calvet, 1989; Singh, 2002).

Often  $\text{pK}_a$  values for antimicrobials are in the range of soil pH values and the charge of the antimicrobials may vary as soil pH changes. Sulfonamides are fairly water soluble and polar compounds and, thus, sorption-desorption of these compounds is influenced by soil pH, which might be related to ionization of the amphoteric sulfonamides (Tolls, 2001; Boxall et al., 2002). Sulfadiazine could exist in the environment as cationic ( $\text{SDZ}^+$ ), neutral ( $\text{SDZ}^0$ ) and/or anionic species ( $\text{SDZ}^-$ ) (Sukul et al., 2008). The soil

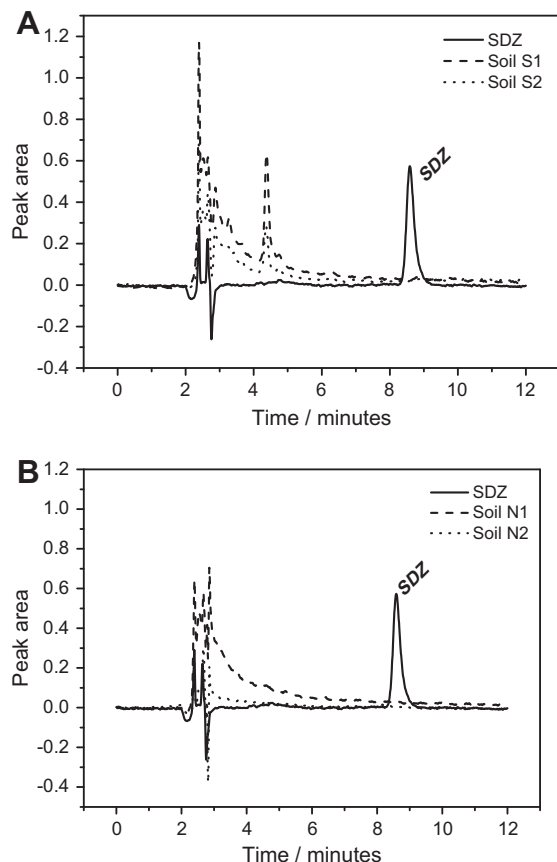


Fig. 1. Chromatograms of sulfadiazine ( $0.1 \mu\text{g mL}^{-1}$ ) in pre-equilibrated soil solutions (A) S1 and S2; (B) N1 and N2.

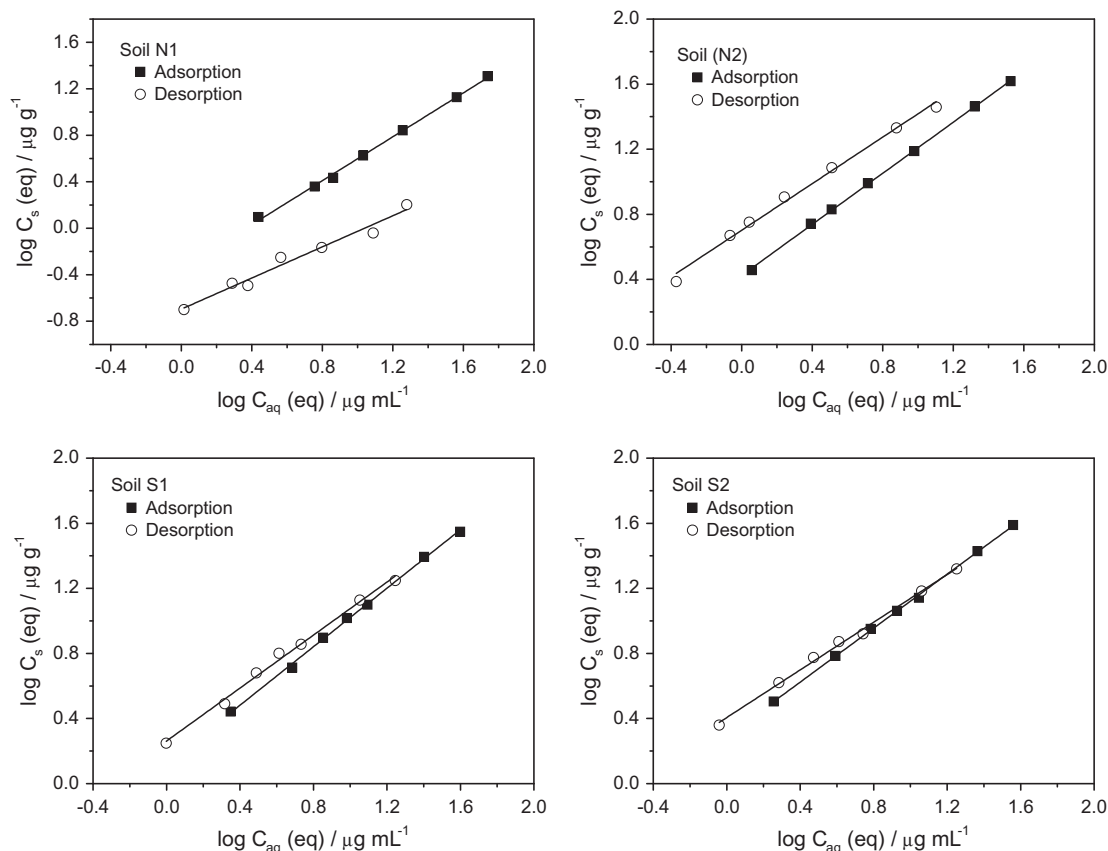


Fig. 2. Adsorption and desorption isotherms for SDZ in soils N1, N2, S1 and S2.

Table 3

Values obtained for the Freundlich sorption coefficients ( $K_F$  and  $1/n$ ), correlation coefficient ( $r$ ), sorption coefficient normalized to organic carbon ( $K_{OC}$ ) and hysteresis ( $H$ ).

Soil	Study	Freundlich			H	$K_{OC}$ ( $\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$ )
		$K_F$ ( $\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$ )	$1/n$	$r$		
N1	Ad <sup>a</sup>	0.45(0.06)	0.94(0.04)	0.999	0.71(0.04)	52(6.0)
	Des <sup>b</sup>	0.20(0.01)	0.67(0.00)	0.984		
N2	Ad	2.6(0.05)	0.78(0.01)	0.999	0.92(0.01)	159(3.0)
	Des	5.0(0.02)	0.73(0.00)	0.996		
S1	Ad	1.3(0.04)	0.89(0.01)	0.999	0.91(0.01)	92(3.0)
	Des	1.8(0.05)	0.81(0.01)	0.997		
S2	Ad	2.0(0.03)	0.83(0.01)	0.999	0.88(0.00)	105(2.0)
	Des	2.5(0.06)	0.73(0.01)	0.999		

<sup>a</sup> Ad: adsorption.

<sup>b</sup> Des: desorption. Values in parentheses refer to the average deviation ( $n = 2$ ).

types evaluated in this study have pH in the range of 4.1–5.0. Considering the  $pK_a$  values of SDZ ( $pK_{a1} = 1.57$  and  $pK_{a2} = 6.50$ ) it is expected that SDZ will be present in its neutral form in all soils.

The Freundlich sorption coefficients were normalized to the OC of the soil resulting in the  $K_{OC}$  coefficient (Eq. (4), Table 3) since the adsorption is in general correlated, among other factors, with the OC of the soil. Thus, expressing sorption as a function of soil organic carbon content reduces variability between soils (Cox et al., 1997) over the entire concentration range.

Sorption capacity is dependent of the physico chemical properties of the soil, as well as the speciation (cation, neutral or anionic) of SDZ, which is pH dependent. The soil pH in this study varied from 4.1 to 5.0, and therefore SDZ is found mostly in its neutral form. Studies by Bialk-Bielińska et al. (2012) showed significant

negative correlation between  $\log K_F$  and pH (pH of the soils vary of 5.27–7.38), indicating that the trend of sulfonamides sorption capacity decreased with increasing pH.

In our studies a positive correlation between  $\log K_F$  and OC ( $R^2 = 0.9131$ ) and  $\log K_F$  and clay fraction ( $R^2 = 0.9966$ ), were observed. These results suggest that the organic matter, as well as the clay fraction contribute to SDZ sorption. In contrary, a negative correlation was found between  $\log K_F$  and sand fraction ( $R^2 = 0.9499$ ), suggesting that SDZ sorption on sand is not favored.

Attributing sorption of polar pharmaceuticals solely to hydrophobic partitioning to soil organic matter is, thus, an inappropriate concept. The results also suggest SDZ sorption by clay fraction which confirms the trend that sulfonamides are preferably retained by particles of fine texture (Thiele-Bruhn et al., 2004).

**Table 4**  
Comparison of the  $K_f$  values reported in the literature for sulfonamides, including sulfadiazine, sorption on soils.

Solute	Sorberent	$t_{eq}^a$ (h)	Soil properties							$K_D$ ( $cm^3 g^{-1}$ )	$K_f$	References
			OC (%)	OM (%)	Particle size (%)			pH	CEC ( $cmol_c kg^{-1}$ )			
					Clay	Silt	Sand					
SDZ <sup>b</sup>	Eutric cambisol	480	3.3	–	23	43	34	6.1	17.4	–	13 $mg^{1-1/n} L^{1/n} kg^{-1}$	Wehrhan et al. (2010)
SDZ <sup>b</sup>	KAL Ap <sup>c</sup>	336	1.07	–	4.9	26.7	68.5	5.7	7.8	–	6.14 $\mu mol^{1-1/n} L^{1/n} kg^{-1}$	Kasteel et al. (2010)
	KAL Bw <sup>c</sup>		0.25	–	2.8	21.6	75.6	6.1	–	–	1.58 $\mu mol^{1-1/n} L^{1/n} kg^{-1}$	
	MRZ Ap <sup>c</sup>		1.24	–	15.4	78.7	5.9	7.0	11.4	–	5.00 $\mu mol^{1-1/n} L^{1/n} kg^{-1}$	
	MRZ Bt <sup>c</sup>		0.37	–	23.4	75.2	1.4	7.4	–	–	1.27 $\mu mol^{1-1/n} L^{1/n} kg^{-1}$	
SDZ <sup>b</sup>	Orthic luvisol	#	1.24	–	15.4	78.7	5.9	6.2	11.4	–	0.17 $\mu g^{1-1/n} (cm^3)^{1/n} kg^{-1}$	Unold et al. (2009)
	Gleyic cambisol		1.07	–	4.9	26.7	68.5	5.9	7.8	–	0.32 $\mu g^{1-1/n} (cm^3)^{1/n} kg^{-1}$	
SDZ	Cambisol <sup>d</sup>	24	0.99	–	3.0	22	75	6.0	6.7	20	–	Förster et al. (2009)
	Luvisol <sup>d</sup>		1.22	–	16	78	6.0	6.3	10.7	30	–	
SDZ	Soil-I <sup>e</sup>	50	0.6	–	42.0	15.5	42.5	6.7	9.2	–	4.1 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	Sukul et al. (2008)
	Soil-II <sup>e</sup>		0.8	–	42.5	34.0	23.5	4.8	11.0	–	1.5 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	
	Soil-III <sup>e</sup>		1.2	–	15.5	12.5	72.0	5.2	10.0	–	2.4 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	
	Soil-IV <sup>e</sup>		0.5	–	19.4	12.4	68.2	4.4	7.4	–	0.1 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	
	Soil-V <sup>e</sup>		2.9	–	16.1	73.2	10.7	4.4	14.8	–	24.3 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	
SDZ	Guangzhou	24 336	–	1.14	30	9	60	4.3	3.37	0.19 0.98	–	Yang et al. (2009)
	Zengcheng		–	0.35	16	22	62	7.2	2.90	0.09 0.06	–	
	Zhongshan		–	2.57	39	60	1	8.5	13.99	0.24 0.35	–	
SMZ	Clarion-1	24	0.1	–	18	26	56	8.2	12.1	0.32	0.13 $cm^3 g^{-1}$	Lertpaitoonpan et al. (2009)
	Clarion-2		1.4	–	10	22	68	7.8	10.7	0.55	0.35 $cm^3 g^{-1}$	
	Clarion-3		2.2	–	20	34	46	5.4	15.7	2.52	4.77 $cm^3 g^{-1}$	
	Nicollet		2.7	–	18	38	44	5.5	20.0	3.77	3.98 $cm^3 g^{-1}$	
	Harps		3.8	–	26	36	38	8.2	23.3	1.70	1.77 $cm^3 g^{-1}$	
SMZ SCP	Waukegan	14	1.8	–	23.6	56.5	19.9	7.5	–	–	6.75 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$ 6.11 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	Accinelli et al. (2007)
SMX	Soil 1	24	0.37	–	43.28	27.2	29.52	6.8	–	0.23	0.28 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	Drillia et al. (2005)
	Soil 7		7.1	–	15.84	26.64	57.52	4.3	–	37.6	36.2 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	
SDM SDG	Sandy-calvey silt	24	24.50	–	94.0	–	–	5.27	27.0	107.53 30.99	24.95 $cm^3 g^{-1}$ 12.60 $m^3 g^{-1}$	Bialk-Bielińska et al. (2012)
	Alluvial soil		19.43	–	16.7	–	–	6.65	85.6	4.83 2.26	1.53 $cm^3 g^{-1}$ 5.07 $cm^3 g^{-1}$	
	Beach sand		0.14	–	0.2	–	–	7.38	3.0	0.31 1.03	0.07 $cm^3 g^{-1}$ 0.72 $cm^3 g^{-1}$	
SMX SMM SDM	Sludge	12	–	75	–	–	–	6.8	–	28.6 55.7 110.0	35.2 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$ 79.2 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$ 133.6 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$	Yang et al. (2011)
SMZ	Bearden	168	1.9	7.5	34	51	15	7.9	–	18.58	–	Fan et al. (2011)
	Gardena		4.3	5.3	27	44	29	8.2	–	16.55	–	
	LaDelle		2.5	9.2	26	62	12	7.8	–	206.18	–	
	Renshaw		2.4	7.5	20	34	46	7.9	–	17.10	–	
	Sand		–	0	0	0	100	7.0	–	7.52	–	
SDM	Ultisol	48	–	1.5	5	13.5	81.5	5.03	3.19	10.4	2.1 $\mu g^{1-1/n} L^{1/n} kg^{-1}$	Sanders et al. (2008)
	Inceptisol		–	2.07	10	38	52	4.66	6.64	25.8	14.5 $\mu g^{1-1/n} L^{1/n} kg^{-1}$	
	Sand		–	0	0	0	100	6.97	0.33	0.4	3.1 $\mu g^{1-1/n} L^{1/n} kg^{-1}$	

SDM: sulfadimethoxine; SDG: sulfaguanidine; SMX: sulfamethoxazole; SMM: sulfamonomethoxine; SMZ: sulfametazine; SDZ: sulfadiazine; SPC: sulfachloropyridazine.

– Not determined or not found.

#: Soil column.

<sup>a</sup>  $t_{eq}$ : equilibrium time.

<sup>b</sup> SDZ: <sup>14</sup>C-SDZ radioactivity. The duration of the leaching experiment was 1200 h for soil gleyic cambisol compared to 500 h for soil orthic luvisol.

<sup>c</sup> Ap and Bw horizon of an inceptisol near kaldenkirchen (KAL) and Ap and Bt horizon of a typic hapludalf near merzenhausen (MRZ).

<sup>d</sup> Soil with application of manure from the pig.

<sup>e</sup> Soil-I: fine mixed hyperthermic typic endoaquents; Soil-II: hyperthermic aeric haplaquepts; Soil-III: typic endoaquents; Soil-IV: lithic rhodustalfs; Soil-V: haplic cambisol.

Values of  $1/n < 1$  are indicative of adsorption by heterogeneous media where high energy sites are occupied first, followed by adsorption at lower energy sites (Sukul et al., 2008).

Desorption isotherms represent the amount of SDZ still adsorbed per gram of soil as a function of equilibrium concentration after one desorption cycle. The data from the desorption experiment were well fitted to the logarithmic Freundlich isotherms for all soils, as indicated by the regression coefficients ( $0.984 \leq r \leq 0.999$ ) obtained (Table 3, Fig. 2). The desorption  $K_F$  values were consistently higher than those obtained for adsorption of SDZ on soils N2, S1 and S2. However, the desorption  $K_F$  value obtained for soil N1 was lower than those for adsorption, suggesting that SDZ desorbs more easily from the sandy soil N1. The highest Freundlich desorption coefficient ( $5.0 \mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$ ) was determined for soil N2, suggesting that this soil which contains large amounts of clay and OC has a lower desorption capacity. The values of  $1/n$  in the desorption process were lower than unity in the tested soils confirming a nonlinear relationship between concentration of SDZ and its sorption to these soils.

Freundlich sorption coefficients calculated for SDZ were similar to those of other antimicrobials, including sulfonamides, reported in the literature (Rabolle and Spliid, 2000; Tolls, 2001; Thiele-Bruhn et al., 2004). Freundlich sorption coefficients,  $K_F$ , for all soils under study ranged from  $0.45$  to  $2.6 \mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$ . Similar sorption data in soils have been found for other antimicrobials, such as olaquinox with sorption coefficients ranging from  $0.69$  to  $1.67 \text{ L kg}^{-1}$  (Rabolle and Spliid, 2000). Research performed on other sulfonamides has also determined low sorption coefficients,  $K_D$ , in the range of  $0.62$ – $10 \text{ L kg}^{-1}$  for these compounds (Tolls, 2001; Boxall et al., 2002; Thiele-Bruhn et al., 2004).

Based on soil column studies without manure application, Wehrhan et al. (2007) described breakthrough curves of  $^{14}\text{C}$ -SDZ applied to soil column surface with a model approach assuming two reversible and one irreversible sorption site. Unold et al. (2009) complemented this model by applying two empirical models assuming high-order irreversible sorption in the first approach and, second, an experimental model to predict irreversible sorption. Kasteel et al. (2010) did not identify irreversible sorption and discussed it as a consequence of their experimental design focusing on short-term processes. Wehrhan et al. (2010) identified irreversible sorption in long-term adsorption–desorption studies. Their final model for SDZ comprised first-stage instantaneous Freundlich sorption and second-stage kinetic Freundlich sorption which was partially irreversible.

Table 4 shows a compilation of  $K_F$  values reported in the literature for sulfonamides, including sulfadiazine, on soils with different properties.

In fact the comparison of results is not a simple task due the fact that soil properties, such as organic matter content, mineral fractions, cation exchange capacity, and pH are different.

Hysteresis ( $H$ ) is a common phenomenon observed and is attributed to different forces involved in sorption and desorption. When the Freundlich sorption coefficient is higher in the desorption step, after reaching apparent equilibrium, than in the adsorption step, it indicates that the compound, once sorbed, is difficult to desorb. Hysteresis has been reported for many organic compounds where either soil or sludge acts as sorbent (Huang et al., 2003; Kim et al., 2005; Conrad et al., 2006). It is known that a number of experimental artifacts may also contribute to the hysteresis (Celis and Koskinen, 1999). The non-reversibility of the adsorption process may be due to the entrapment of the sorbed molecules in the soluble organic matter and inorganic matrices enhanced by artifacts in the experimental procedure (Huang and Weber, 1998; Huang et al., 1998) or entrapment in soils with low TOC and high internal surface area (Huang et al., 2003). In the present study, a small positive hysteresis was observed with all soils, and the

magnitude of the hysteresis was evaluated using the ratio of the Freundlich isotherms coefficients for adsorption and desorption. This suggests that SDZ is retained by strong binding mechanisms on soils, in spite of its lower adsorption capacity. Negative hysteresis is observed when the desorption isotherm slope is greater than the adsorption isotherm slope. The  $1/n_{\text{ads}}$  values are greater than  $1/n_{\text{des}}$ , suggesting that the SDZ sorption by soils was not reversible. Hysteresis values are also listed in Table 3. A value of  $H$  close to 1 means that hysteresis is absent. In all desorption studies it was observed that the amount of desorbed SDZ was smaller than the total amount of sorbed SDZ (Table 3, Fig. 2), indicating a positive hysteresis and suggesting that a significant amount of SDZ was tightly bound to the soil particles and did not readily desorb. The higher hysteresis coefficients determined correspond to soils N2, S1 and S2, indicating that, although these soils have a much higher sorption capacity than soil N1, amounts in the range of 20–40% (in this study) of the total amount of sorbed SDZ can be desorbed.

However, further studies are necessary to clarify the role of different soil components in SDZ sorption on soil.

#### 4. Conclusion

The sorption of sulfadiazine onto soil is important for the fate and transport of this compound in the environment and for the estimation of the risk posed by this compound. Adsorption and desorption of sulfadiazine onto four different acidic soils were studied applying the OECD test guideline 106. The experimental data for adsorption fitted quite satisfactorily to Freundlich isotherms. Sorption of SDZ in this study followed the sorption trend of  $\text{N1} < \text{S1} < \text{S2} < \text{N2}$ . In the present study, we found that SDZ have higher adsorption in soils with high organic carbon content and clay. The soils corresponding to these features are soils S2 and N2, which are the most representative soils of the São Paulo State with a coverage of 41.2% and 30.2%, respectively. The high level of  $K_{\text{Des}}$  as compared to low level of  $K_{\text{Fad}}$  exhibited a positive hysteresis effect and leads to a conclusion that whatever amount of SDZ was sorbed to soil never desorb readily at the soil pH range. A hysteresis phenomenon was higher in the soils N2 and S2, indicating strong irreversible interactions between the compound molecule and the soil particles. The higher hysteresis coefficients correspond to the N2 and S2 soil indicating that although these soils have much higher sorption capacity than the N1 and S1 soil, greater amounts can be desorbed. The relatively low sorption coefficients for SDZ found in this study indicate its weak interaction with the binding sites in soils; this suggests that this antimicrobial has potential to reach surface and ground waters. Further studies are necessary to clarify the role of different soil components in SDZ sorption on soil.

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