Single and simultaneous adsorption of three sulfonamides in agricultural soils: effects of pH and organic matter content

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Declarations of interest: none

Abstract

Veterinary antibiotics reaching the environment have become a matter of global concern, since they can cause serious negative impacts on human and ecological health. Therefore, a deep understanding of their behavior and fate once they reach the soil environment is of utmost importance to design and implement appropriate measures that could reduce their potential risks. With this aim, batch-type experiments were carried out to study competitive adsorption and desorption for three sulfonamide antibiotics (sulfadiazine –SDZ-, sulfamethazine –SMT-, and sulfachloropyridazine –SCP-) in six crop soils presenting different characteristics. The results obtained showed that sulfonamides have a low retention in soils, with average adsorption percentages of 40% for SDZ, 44% for SMT and 54% for SCP, and with desorption percentages up to 36% for SDZ and SCP and up to 29% for SMT. The retention of sulfonamides was strongly influenced by the soil organic carbon content (SOC), with higher adsorption and less desorption associated to higher SOC contents. In addition, the hydrophobicity of sulfonamides also had an influence, as higher hydrophobicity resulted in higher affinity for soils, showing the affinity sequences: SDZ ~ SMT <SCP in acid soils, and SDZ ~ SCP <SMT in neutral soils. The results obtained in the ternary systems were very similar to those found in simple systems, indicating the absence of substantial competition for adsorption sites among the three sulfonamides. Despite the low competition among them, these antibiotics have high mobility in soils and, therefore, they imply a significant risk of contamination of water bodies, as well as of entering the food chain, generating serious hazards for human and environmental health. Therefore, fertilization of soils with sulfonamide polluted manures should be controlled, implementing new measurements for the pretreatment of manures before their application, thus contributing to a reduction of potential risks.

Keywords: antibiotics; competitive adsorption/desorption; soil pollution; sulfonamides; water pollution

1. Introduction

In recent years, livestock production has suffered marked changes to increase intensive systems (Van Boeckel et al., 2015). However, these systems require a higher use of antibiotics to treat and prevent diseases (and to promote growth and improve feeding efficiency, in countries where this use is allowed), thus resulting in more consumption of these compounds (Spielmeyer, 2018). In fact, Van Boeckel et al. (2015) estimated that the global use of antibiotics in veterinary medicine was 63,151 tons in 2010, while the World Organization for Animal Health (OIE, 2018) indicated that, in 2015, the consumption of antibiotics in veterinary reached 107,479 tons, which means an increase of 66% in just 5 years. These antibiotics are poorly absorbed in the animal gut, causing that a significant proportion (up to 90%) is excreted as the original compound, reaching the environment mainly by spreading of manure, slurry and sludge in crop soils, used to supplement other fertilizers (Kuppusamy et al., 2018; Sarmah et al., 2006). This constitutes a very widespread practice throughout the world, due to its low cost, as well as the high content of nutrients and organic matter of these waste and by-products, thus improving crop performance (Ghirardini et al., 2020; Tasho and Cho, 2016). However, the application of these materials causes the dispersion of antibiotics in the environment, which can imply different negative impacts, such as: a) generation and proliferation of resistant bacteria (Ezzariai et al., 2018; Pikkemaat et al., 2016); b) toxicity to non-target organisms (Bártíková et al., 2016; Du and Liu, 2012; Kümmerer, 2009); and c) entry of these molecules into the food chain through crops (Pan and Chu, 2017; Tasho and Cho, 2016) and waters (Charuaud et al., 2019), causing serious risks to human and ecological health.

Within antibiotics, sulfonamides are widely used in veterinary medicine. Specifically, they were placed third among the most consumed in Europe during 2017, accounting for 9.2% of total sales of antibiotics for veterinary use, situated after tetracyclines and penicillins (EMA, 2019). Also, sulfonamide residues are frequently detected in soils (Conde-Cid et al., 2018a; Hou et al., 2015; Wei et al., 2019; Zeng et al., 2019). It is relevant that sulfonamides are difficult to degrade, both chemically (Białk-Bielinska et al., 2012b; Conde-Cid et al., 2018b) and biologically (Biošić et al., 2017; Conde-Cid et al., 2018b), which indirectly causes that adsorption is one of the main processes determining its environmental fate once they reach soils. Therefore, the retention capacity of soils will determine both its bioavailability, and its transfer to other environmental compartments, such as water bodies, as well as plant uptake, and, consequently, to the food chain (Kuppusamy et al., 2018; Pikkemaat et al., 2016).

Although studies on the adsorption of different antibiotics, including sulfonamides, onto soils are abundant for systems where just one antibiotic is added (simple systems) (Álvarez-Esmorís et al., 2020; Conde-Cid et al., 2019a, b, c; Figueroa-Diva et al., 2010; Leal et al., 2013; Palović et al., 2014; Rath et al., 2019; Srinivasan and Sarmah, 2014; Vieira et al., 2017), this is not the case for investigations where competitive adsorption is studied for various antibiotics. In this sense, it is well known that in "real world" different antibiotics simultaneously reach the soil, and could compete for the adsorption sites, resulting in a certain saturation, leading to lower retention and greater mobility for the affected antibiotics (Conkle et al., 2010). Therefore, competitive adsorption and desorption of antibiotics can play an important role in their behavior and transport in the soil. Previous works investigated the competitive adsorption of fluoroquinolone (Conkle et al., 2010) or tetracycline antibiotics (Fernández-Calviño et al., 2015), as well as between antibiotics of different groups (Jiang et al., 2020; Wu et al., 2019). In addition, the simultaneous adsorption of antibiotics and heavy metals (Bao et al., 2013; Xu et al., 2015; Zhao et al., 2013) or herbicides (Munira and Farenhorst, 2017; Zhang et al., 2013a) was also investigated. However, in the particular case of sulfonamides, even though the simultaneous detection of these pollutants is frequent in animal waste (Hou et al., 2015; Hu et al., 2010; Spielmeyer, 2018; Wang et al., 2017; Zhang et al., 2013b), to the best of our knowledge no previous works focused on the competitive adsorption/desorption process for different sulfonamide antibiotics present simultaneously in soils. Therefore, the main objective of this work is to shed light on competitive adsorption process (and subsequent desorption) of the sulfonamides sulfadiazine (SDZ), sulfamethazine (SMT) and sulfachlorpyridazine (SCP) in agricultural soils with different characteristics. The results of this study could contribute to a better understanding the environmental fate of these pollutants when they reach soils simultaneously. In addition, increasing the knowledge on adsorption mechanisms affecting these compounds in different circumstances would facilitate the development of palliative measures and/or management strategies to reduce their risks to human and environmental health.

2. Material and methods

2.1. Chemicals and soil samples

2.1.1. Chemicals

The antibiotics sulfadiazine (SDZ, 99.7% purity), sulfamethazine (SMT, 99.6% purity) and sulfachloropyridazine (SCP, 99.7% purity) were supplied by Sigma-Aldrich (Barcelona, Spain). Table 1 shows the main characteristics of these three antibiotics. Especially relevant is the fact that sulfonamides are amphoteric molecules, with two pk_a values (Table 1), which causes that depending on the pH of the medium they can be in cationic, neutral or anionic form, although they are predominantly in neutral form at dominant environmental pH values (between 2.5 and 5 ~ 6) (Pikkemaat et al., 2016). Acetonitrile was of HPLC grade, supplied by Fisher Scientific (Madrid, Spain). All other chemicals were of high purity analytical grade, provided by Panreac (Barcelona, Spain). All solutions were prepared using milliQ water, from a Millipore instrument (Millipore, Madrid, Spain).

2.1.2. Soil samples

Six soils previously characterized by Conde-Cid et al. (2019b) were used to carry out the study. Three of the samples were from agricultural plots located in A Limia (AL), while the other 3 were from Sarria (S), both zones situated in Galicia (NW Spain), and subjected to intense farming activity. In each of the six plots, 10-20 sub-samples were taken from the surface layer of the soil (0-20 cm depth), following a zig-zag pattern and using an Edelman probe. The samples from each plot were pooled, then obtaining a composite sample (~ 2 kg) for each of the plots. Once in the laboratory, these samples were air dried, sieved by 2 mm mesh and stored in polyethylene bottles until analysis. Standard methods where used to determine soil characteristics (Tan, 1996). Complementary details regarding the methods used for soil analyses are shown in Supplementary Material.

Table 2 shows the main physicochemical characteristics of the six soils, indicating that those from A Limia (S1, S2 and S3) have a clearly acidic pH in water (pH_{H2O}), ranging between 4.5 and 4.8, while the three soils from Sarria (S4, S5 and S6) have a pH_{H2O} close to neutrality, varying between 6.2 and 7.1. The pH in KCl (pH_{KCl}) was lower in all soils, ranging between 4.0 and 6.4, indicating a predominance of negative charges on soil reactive surfaces. The studied soils present a wide range of organic carbon contents (SOC), ranging between 1.1 and 10.9%, whereas total soil nitrogen content (TSN) ranges between 0.1 and 0.8% (Table 2). Similarly, the effective cation exchange capacity (eCEC) was also highly variable (between 4.08 and 17.38 $cmol_c\ kg^{-1}$), with Ca as dominant cation. Regarding particle size, sand dominated in A Limia soils, while silt was the dominant fraction in Sarria soils, and clay showed values between 16 and 32 % (Table 2). The contents of Fe and Al compounds were much higher in the soils from Sarria (S4, S5 and S6) than in the soils from A Limia (S1, S2 and S3) (Table 2). Finally, the clay fraction was very similar for the six soils studied, and it was mainly composed by clays of low activity (mainly kaolinite), with much smaller content in mica and vermiculite.

2.2. Adsorption and desorption experiments

Adsorption and desorption were studied using batch-type experiments. Specifically, 2 g of soil were weighed in 15-mL capacity polypropylene centrifuge tubes, then adding 5 mL of the corresponding antibiotic solution (soil:solution ratio 1:2.5). All solutions were made using 0.005 M $CaCl_2$ as background electrolyte. For the ternary competitive tests, the total concentrations used (the sum of the three sulfonamides) were 15, 30, 60, 90 and 120 µmol L^{-1}, with each of the three sulfonamides constituting 1/3 of these total concentrations. For the individual adsorption test of each of the sulfonamides (simple systems), 9 different concentrations were used: 5, 10, 15, 20, 30, 40, 60, 90, and 120 µmol L^{-1}. These tests were performed to obtain details on the affinity of the adsorption surfaces for each antibiotic, and on their eventual degree of competition when present at different concentrations.

The different soil+antibiotic-solution suspensions were shaken for 24 hours in the dark, on a rotary shaker, at 50 rpm and at room temperature (25 ± 2 °C). Previously, kinetic tests were performed, obtaining that 24 hours were sufficient to reach equilibrium (data not shown). After 24 hours of contact, the suspensions were centrifuged for 10 minutes at 2665 *x g* and the resulting supernatant was passed through 0.45 µm nylon syringe filters (Fisher Scientific, Madrid, Spain). Afterwards, the concentration of antibiotic in the equilibrium solution was determined by HPLC-UV (see section 2.3 below), as well as the pH (by means of a combined glass electrode -Crison, Barcelona, Spain). The amount of antibiotic adsorbed onto the soil was calculated by the difference between the amount initially added and that determined in the equilibrium solution.

For the subsequent study of desorption, the centrifuged residues were weighted to calculate the amount of occluded solution and re-suspended in 5 mL of 0.005 M $CaCl_2$. These samples were shaken, centrifuged and analyzed in the same way as in the adsorption process.

All determinations were performed in triplicate. At the same time, control samples (without soil) were made to rule out the possible loss of antibiotic due to degradation or adsorption to tubes and filters, confirming that the loss of antibiotic during the experiments was <3%.

2.3. Quantification of the three sulfonamide antibiotics

The quantification of the three sulfonamides was carried out using the method previously described in Conde-Cid et al. (2018b). For the analyses, a HPLC equipment (Dionex Corporation, Sunnyvale, USA) was used, including a P680 quaternary pump, an ASI-100 auto-sampler, a thermosstated compartment for a TCC-100 column, and a UVD170U ultraviolet-visible detector. In addition, a Luna C18 column (150 mm long; 4.6 mm internal diameter; 5 µm particle size) from Phenomenenex (Madrid, Spain), and a pre-column (4 mm long; 2 mm internal diameter; 5 µm particle size) packed with the same material as that of the column, were used. As further details, the injection volume was 50 µL and the flow rate was 1.5 mL min^{-1}. The mobile phase consisted of acetonitrile (phase A) and 0.01 M phosphoric acid (phase B). A linear gradient that ranged from 5% to 32% phase A, and 95% to 68% phase B, over 10.5 min, was used. Subsequently, the initial conditions were reestablished in 2 min and were maintained for 2.5 min. The total time for analysis was 15 min, with a retention time of 5.3 min for SDZ, 7.6 min for SMT, and 10.3 min for SCP. The detection limits (LOD) were 0.10, 0.07 and 0.06 µM for SDZ, SMT and SCP, respectively, while the quantification limits (LOQ) were 0.33 µM for SDZ, 0.24 µM for SMT and 0.20 µM for SCP. The wavelength used for detection was 270 nm.

2.4. Infrared (FTIR) spectroscopy

Infrared (FTIR) spectroscopy analyses were performed in all six soil samples by means of a FTIR-Bomen MB102 instrument (ABB, Switzerland). For that, infrared spectra were obtained before and after the adsorption process. These analyses were carried out for those samples receiving the highest initial antibiotic concentration used in the competitive adsorption experiments (40 µmol L^{-1} of each of the three sulfonamides). The IR spectra were obtained by transmittance using KBr pellets, performing determinations in the region between 400 and 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

2.5. Data analysis and statistical treatment

All data obtained in the adsorption and desorption experiments were described by means of the Linear (Equation 1) and Freundlich (Equation 2) models:

$$q_a = K_d C_{eq} \qquad \text{(Eq. 1)}$$

$$q_a = K_F C_{eq}^n \qquad \text{(Eq. 2)}$$

where q_a (µmol kg^{-1}) and C_{eq} (µmol L^{-1}) are the concentrations of the antibiotic present in the soil and in the solution at equilibrium, respectively; K_d (L kg^{-1}) is the coefficient of distribution; K_F (L^n µmol^{1-n} kg^{-1}) is the Freundlich affinity coefficient; n (dimensionless) is the Freundlich linearity index.

Furthermore, considering the situations affected by competition for adsorption sites, an initial approach to modify adsorption models can be made by taken into account the total amount of antibiotics adsorbed (Eq. 3 and 4, Arias et al., 2006).

$$(q_a^{SDZ} + q_a^{SMT} + q_a^{SCP}) = K_d\left(C_{eq}^{SDZ} + C_{eq}^{SMT} + C_{eq}^{SCP}\right) \qquad \text{(Eq. 3)}$$

$$(q_a^{SDZ} + q_a^{SMT} + q_a^{SCP}) = K_F\left(C_{eq}^{SDZ} + C_{eq}^{SMT} + C_{eq}^{SCP}\right)^n \qquad \text{(Eq. 4)}$$

where q_a^{SDZ}, q_a^{SMT} and q_a^{SCP} (µmol kg^{-1}), and C_{eq}^{SDZ}, C_{eq}^{SMT} and C_{eq}^{SCP} (µmol L^{-1}) are the concentrations of the antibiotics SDZ, SMT and SCP in the soil and in the solution at equilibrium, respectively; K_d (L kg^{-1}) is the coefficient of distribution, and K_F (L^n µmol^{1-n} kg^{-1}) and n (dimensionless) are the Freundlich parameters.

All these equations (from Eq. 1 to Eq. 4) were used for evaluating the fitting to both adsorption and desorption data. The SPSS 15.0 software was used to fit the adsorption and desorption models to the experimental data, as well as to perform all additional statistical treatments.

3. Results

3.1. Competitive adsorption of the three sulfonamide antibiotics onto soils

Figure 1 shows adsorption curves for the three sulfonamides in the six soils studied, which were derived from competitive tests carried out using ternary systems (with all three sulfonamides added simultaneously). These curves are almost linear, and also show that the maximum adsorption capacity was not reached for any of the soils under the experimental conditions used, where the highest C_0 added was 40 µM for each sulfonamide, which means 100 µmol kg^{-1}.

Figure 2 shows the amount adsorbed and the percentage of adsorption for each of the three sulfonamides and for each of the soils, taking into account the different initial concentrations used. The adsorption of the three sulfonamides onto the different soils was highly variable, with soil S3 being the one with the highest adsorption capacity for the three sulfonamides (82.7, 83.6 and 90.0 µmol kg^{-1} for SDZ, SMT and SCP, respectively, for the highest initial antibiotics concentration added), and this one was also the soil with the highest SOC and TSN contents (10.9% and 0.8%, respectively -Table 2). Conversely, soil S5 had the lowest adsorption capacity for SDZ and SCP (being 14.8 µmol kg^{-1} for SDZ and 17.6 µmol kg^{-1} for SCP, when the highest initial concentration was added), while, in the case of SMT, soil S1 was the one showing the lowest adsorption capacity (20.1 µmol kg^{-1}). In addition, these both soils (S5 and S1) were those that had the lowest organic matter contents (Table 2). In the case of soils S2 and S3, adsorption percentages did not vary when antibiotics concentrations added were increased, for any of the three sulfonamides. However, in the case of soils S4 and S5, adsorption percentages slightly decreased for the three sulfonamides as a function of increasing initial antibiotics concentrations, suggesting a slightly and progressive saturation of adsorption sites. This behavior was also observed for soils S1 and S6, but just for SDZ and SMT, while percentage adsorption remained constant in the case of SCP. Taking into account all soils and all the initial concentrations used, adsorption percentages ranged between 14 and 83% (average 40%) for SDZ, between 20 and 84% (average 44%) for SMT and between 18 and 96% (average 54%) for SCP. In addition, both the slope of the adsorption curves (Figure 1), and the percentages of adsorption (Figure 2), show that SCP was the sulfonamide with the highest affinity for adsorption sites in soils S1, S2, S3 and S6, while SMT was the sulfonamide with the highest affinity in soil S5, and all three sulfonamides had similar affinity in the case of soil S4.

Table 3 shows the parameters resulting from the adjustments of the experimental data to the Linear and Freundlich adsorption models, with good fitting to adsorption curves (R^2 values higher than 0.961 in all cases). The values of the coefficient of distribution (K_d) ranged between 0.40 and 9.43 L kg^{-1} for SDZ, between 0.62 and 11.05 L kg^{-1} for SMT, and between 0.54 and 24.40 L kg^{-1} for SCP. The values of the Freundlich linearity index (n) were close to 1 in most cases, ranging between 0.78 and 0.94 for SDZ, 0.74-0.92 for SMT, and 0.79-1.00 for SCP, which explains that both models satisfactorily describe adsorption curves, due to the fact that the Freundlich equation is equivalent to the Linear equation when $n = 1$. In line with this, the values of the Freundlich affinity coefficient (K_F) are of the same order as those obtained for K_d, and ranged 0.92-11.31, 1.31-12.97, and 0.67-32.00 L^n µmol^{1-n} kg^{-1} for SDZ, SMT and SCP, respectively (Table 3). Depending on the values of the adsorption parameters K_d and K_F (Table 3), the following affinity sequence can be established for soils S1, S2, S3 and S6: SCP >> SMT ~ SDZ. However, the sequence was SMT > SDZ ~ SCP for soil S5, and in the case of soil S4 it was SMT ~ SCP > SDZ (even if the three sulfonamides exhibited a similar behavior), as observed from the adsorption curves.

Table 3 also shows the values of the adsorption parameters for ternary systems, where all three sulfonamides were in competition for adsorption sites. These values were obtained from Equations 3 and 4, and varied between 0.56 and 12.76 L kg^{-1} for K_d, while ranging from 1.25 to 17.30 L^n µmol^{1-n} kg^{-1} for K_F. Based on these K_d values (obtained from Equation 3), the following sequence can be established for adsorption of the three sulfonamides onto the studied soils: S3 > S6 > S2 > S4 ~ S1 ~ S5, while the sequence would change to S3 > S6 > S2 ~ S4 ~ S1 ~ S5 when taking into account the K_F values (obtained from Equation 4). To note that soils S5 and S1 are the ones with the lowest organic matter contents, while soils S6 and S3 have the highest levels, indicating that this soil characteristic has relevant influence on the adsorption process.

3.2. Competitive desorption of the three sulfonamide antibiotics from soils

Figure 3 shows desorption curves for the three sulfonamides in the six soils studied, which were derived from competitive tests carried out using ternary systems, while Figure 4 shows the desorbed amounts of each of the three sulfonamides (SDZ, SMT and SCP) for each of the initial concentrations used, as well as the percentages of desorption with respect to the amount previously adsorbed. In all cases, the amount of antibiotic desorbed increased with the amount of antibiotic initially added. Considering absolute values, and taking into account the highest initial antibiotic concentration added (40 µmol L^{-1} of each antibiotic), soil S5 was the one that desorbed the least amount of the three sulfonamides (2.08, 3.96 and 3.44 µmol kg^{-1}, for SDZ, SMT and SCP, respectively). In the opposite side, soil S6 was the one that desorbed the highest amount of SDZ and SMT (12.40 µmol kg^{-1}), and soil S2 desorbed the highest amount of SCP (15.26 µmol kg^{-1}). However, when expressed as percentages (also taking into account the highest initial antibiotics concentration added), soil S1 (the one with the lowest organic matter content) showed the highest desorption for SDZ (41.75%) and SMT (34.11%), while the highest desorption corresponded to soil S4 in the case of SCP (40.20%). Soil S3 (the one with the highest organic matter content), showed the lowest desorption percentages for the three sulfonamides, with values of 11.87, 8.42 and 5.18% for SDZ, SMT and SCP, respectively. In general, taking into account all the soils studied and all initial concentrations of antibiotics added, desorption percentages were similar for the three sulfonamides in the ternary systems, ranging from 7 to 36% (average 20%) for SDZ, 6-29 (average 17%) for SMT, and 3-36% (average 18%) for SCP.

Both the Linear and Freundlich models satisfactorily described experimental data for desorption, although with lower R^2 values than those obtained for adsorption (Table 4). K_d values ranged between 4.62 and 26.02

L kg^{-1} for SDZ, 5.68-36.86 L kg^{-1} for SMT, and 4.59-64.59 L kg^{-1} for SCP, while K_F values varied between 5.20 and 27.56, 7.09-36.71, and 4.74-60.56 L^n µmol^{1-n} kg^{-1} for SDZ, SMT and SCP, respectively. Table 4 also shows the values of the desorption parameters corresponding to the ternary systems (obtained from Equations 3 and 4), which varied between 5.35 and 37.98 L kg^{-1} for K_d and between 6.63 and 37.00 L^n µmol^{1-n} kg^{-1} for K_F. It should be noted that, for desorption, the higher the values of these parameters, the lower the magnitude of desorption. Taking into account the values of K_d (obtained from Equation 3), the following sequence of desorption can be established for the studied soils: S3 <S6 ~S5 <S2 ~S1 ~S4, while the sequence would change to S3 ~S6 ~S5 <S4 ~S2 ~S1 when taking into account the values of K_F (obtained from Equation 4), both parameters indicating that soil S3 (the one with the highest organic matter content) is that experiencing least desorption.

3.3. Adsorption of the three sulfonamides in simple and ternary systems

Adsorption results obtained in simple systems (just one sulfonamide added) were compared with those from ternary systems (all three sulfonamides added simultaneously). Figure 5 shows adsorption percentages for each of the sulfonamides obtained from the simple tests (using an initial concentration added of 40 µmol L^{-1}) with those from the ternary systems (with an initial concentration added of 40 µmol L^{-1} from each of the three antibiotics, which means that a total concentration of 120 µmol L^{-1} was added).

Taking into account that the total concentration of the system is three times higher in the ternary than in the simple system (thus resulting in clearly different ionic strengths), additional comparisons were performed. Specifically, the percentages of adsorption for each of the sulfonamides, obtained in simple systems using an initial concentration of antibiotic of 120 µmol L^{-1} (instead of just 40 µmol L^{-1}) were compared with those obtained in the competitive systems using an initial concentration of 40 µmol L^{-1} of each of the sulfonamides, totalizing 120 µmol L^{-1} (which is the same concentration, and equivalent ionic strength, as in these additional simple systems). As shown in Figure 5, no differences were observed between the results from simple and ternary systems, for any of the three sulfonamides in any of the soils.

Furthermore, Table 5 shows the adsorption parameters of the Linear and Freundlich models corresponding to the experimental data obtained for the adsorption of the three sulfonamides in simple systems. As in the case of the ternary systems, both models satisfactorily described all the experimental data, with $R^2 > 0.981$ in all cases. Comparing the values of the adsorption parameters from ternary systems (Table 3) with those from simple systems (Table 5), it is clear that both are similar, with sulfonamides showing similar behavior in both simple and ternary systems. In fact, a paired t-test was carried out to compare the values of the adsorption parameters K_d and K_F, finding that they were not significantly different for simple and ternary systems ($t = 1.131$; $p = 0.274$ for K_d; $t = 0.025$; $p = 0.980$ for K_F), clearly indicating that there is no relevant competition among the three sulfonamides for adsorption sites under the experimental conditions of the current study.

3.4. Desorption of the three sulfonamide antibiotics in simple and ternary systems

Similarly to that performed for adsorption, Figure 6 shows desorption percentages for each of the three sulfonamides for the six soils studied, both in ternary systems and in simple systems, and also using both equivalent and different ionic strengths. When equivalent ionic strengths were used, desorption percentages were slightly higher in ternary systems, although showing just very small differences. Specifically, for SDZ the highest reduction in the percentage of desorption took place in soil S1 (going from 35 to 23%), while for SMT it was in soil S4 (from 26 to 20%), and for SCP it took place in soil S5 (from 16 to 5%). However, when the ionic strengths were different, desorption percentages were in most cases higher in ternary systems (unless for SDZ in S4, and for SMT in S2). The highest differences were observed in soils with lower organic matter content, while soils S3 and S6 (with high organic matter content) showed insignificant differences between simple and ternary systems (Figure 6).

Table 6 shows the values of the desorption parameters corresponding to the Linear and Freundlich model for the three sulfonamides in simple systems. Both models satisfactorily described all the experimental data, except for soil S5. In the same way as in the case of adsorption, a paired t-test was performed to compare the values of the K_d and K_F desorption parameters obtained in the simple systems (Table 6) with those obtained in the ternary systems (Table 4). The results of that test indicate that the K_d values obtained for desorption in the simple systems are not statistically different from those obtained in the ternary systems ($t = 1.511$, $p = 0.153$). On the contrary, the K_F values obtained for desorption in the simple systems are significantly higher than those obtained in the ternary systems ($t = 2.327$; $p = 0.035$), indicating that desorption is higher in the ternary than in the simple systems.

4. Discussion

Adsorption curves from ternary systems were type C, which is indicative of a constant distribution of the three sulfonamides between the soil and the solution, also indicating that the adsorption of these compounds did not depend on the amount initially added. This kind of curve is typical of the interaction between hydrophobic compounds (such as sulfonamides) and soil organic matter (Calvet, 1989), which once again suggests that organic matter may have an important influence on the adsorption process of these compounds. Due to the linear nature of the adsorption curves, they were satisfactorily modeled through the Linear and Freundlich equations, with R^2 values close to 1. Similar curves have been previously observed by other authors for SDZ (Hu et al., 2019; Shen et al., 2018), for SMT (Lertpaitoonpan et al., 2009; Pavlović et al., 2014; Srinivasan and Sarmah, 2014), and for SCP (Boxall et al., 2002; Laak et al., 2006; Vieira et al., 2017).

The values of the adsorption parameters K_d and K_F obtained in this work are similar to those from other authors who also studied the adsorption of sulfonamides onto soils (Conde-Cid et al., 2019b, c; Leal et al., 2013; Pavlović et al., 2014; Srinivasan et al., 2014; Vieira et al., 2017), but are clearly lower than those observed for antibiotics of other classes, such as tetracyclines (Teixidó et al., 2012), macrolides (Kodešová et al., 2015) and fluoroquinolones (Álvarez-Esmorís et al., 2020; Leal et al., 2013), indicating that sulfonamides have weaker interactions with binding sites of the soil reactive surfaces and, therefore, higher mobility and bioavailability in soils. This lower interaction of sulfonamides with soils is mainly due to the fact that sulfonamide molecules only have aniline and amide groups, while tetracycline, macrolide and fluoroquinolone molecules have multiple functional groups, whose combined actions induce a high affinity for soil components through multiple adsorption mechanisms, such as cation exchange, surface complexation with metal oxides in soils, cation bridging and hydrogen bonding, among others, which are of little importance in the case of sulfonamides (Hu et al., 2019; Wang and Wang, 2015).

In the current study, K_d and K_F values were highly variable among the different soils, indicating that soil characteristics have marked influence on the adsorption process. In this sense, K_d and K_F were positively and significantly correlated with SOC content, with Pearson's r values being 0.978, 0.970 and 0.968 for the pairs K_d-SDZ, K_d-SMT and K_d-SCP, respectively, and being 0.987, 0.984, and 0.972 for the pairs K_F-SDZ, K_F-SMT, and K_F-SCP, respectively. Similarly, these adsorption parameters were also positively and significantly correlated with TSN contents, with Pearson's r values being 0.974 for K_d-SDZ, 0.969 for K_d-SMT and 0.965 for K_d-SCP, and 0.977 for K_F-SDZ, 0.978 for K_F-SMT and 0.967 for K_F-SCP, with $p < 0.01$ in all cases. Therefore, the affinity of the three sulfonamides for the different soils was strongly dependent on the organic matter content, in agreement with what was observed by other authors, who obtained positive and significant correlations between adsorption parameters and SOC content in the case of SDZ (Conde-

Cid et al., 2019b; Doretto and Rath, 2013; Leal et al., 2013), SMT (Conde-Cid et al., 2019c; Chu et al., 2013; Leal et al., 2013; Lertpaitoonpan et al., 2009), and SCP (Conde-Cid et al., 2019c; Leal et al., 2013).

In order to identify the influence of other edaphic properties on the sulfonamide adsorption process, K_d values were normalized with respect to soil organic carbon content (SOC). The organic carbon normalized sorption coefficient (K_{OC}) values are shown in Table 3. In the case of SDZ and SMT, K_{OC} values were positively and significantly correlated with clay content, with Pearson's r values being 0.823 ($p < 0.05$) and 0.822 ($p < 0.05$) for the pairs K_{OC}-SDZ and K_{OC}-SMT, respectively. This positive role of clay content in the adsorption of sulfonamides is in accordance with that previously obtained by other authors (Conde-Cid et al., 2019b, c; Doretto and Rath, 2013; Leal et al., 2013; Thiele-Bruhn et al., 2004), who reported a higher adsorption of sulfonamides in soils with a higher clay content, indicating that these antibiotics are preferably retained by fine textured soils. In addition, only in the case of SCP, a negative and significant correlation between K_{OC} and pH_{KCl} was obtained ($r = -0.796$, $p < 0.05$). In this sense, a decrease in the adsorption of sulfonamides as the soil pH increases has been widely highlighted in the literature (Białk-Bielińska et al., 2012a; Conde-Cid et al., 2019a; Lertpaitoonpan et al., 2009; Park and Huwe, 2016). Because sulfonamides are amphoteric molecules, with two pK_a values (Table 1), depending on the pH of the medium they can exist in cationic, neutral or anionic form. In this regard, at pH values between 2.5 and ~6 they are predominantly in non-ionized form, while at pH values above ~6 the anionic forms are also relevant. Therefore, at neutral and alkaline pH values, it is expected that electrostatic repulsion will take place between the anionic forms of sulfonamides and the negatively charged soil surface, thus leading to a decrease in adsorption. In this work, the pH effect on the adsorption process was only remarkable in the case of SCP. This is due to the lower value for pK_{a2} of the SCP molecule (5.45, Table 1) compared to those for SDZ and SMT (6.28 and 7.49, respectively, Table 1), leading to a greater presence of anionic forms in the case of SCP compared to SDZ and SMT for the pH range of the studied soils (between 4.5 and 7.1, Table 2).

Furthermore, the affinity of sulfonamides for soils also depended on their octanol-water partition coefficient (K_{OW}). In fact, based on the values of K_d and K_F, the affinity sequence for soils S1, S2, S3 and S6 was: SDZ $\leq$ SMT $<<$ SCP, similarly to what was determined by Leal et al. (2013) (SDZ <sulfamethoxazole <SMT <SCP <sulfathiazole), and by Rath et al. (2019) (SDZ <SMT <sulfadimethoxine <SCP <sulfaquinoxaline) in acid soils of Brazil. In this sense, Rath et al. (2019) attributed this affinity sequence to the degree of hydrophobicity of each of the molecules, with affinity increasing with the degree of hydrophobicity.

However, for soil S5 the sequence was SDZ ~ SCP <SMT, which is different to that obtained in the other soils, as well as to those obtained by other authors (Rath et al., 2019; Leal et al., 2013). This different behavior and adsorption sequences in the different soils can be attributed to pH, because the degree of hydrophobicity of the sulfonamide molecules is strongly dependent on the pH value of the medium. Specifically, soils S1, S2, S3 and S6 are acidic, with pH_{H2O} of 4.8, 4.7, 4.5 and 6.2, respectively (Table 2), while soil S5 is neutral (pH_{H2O} 7.1, Table 2). Relevantly, Carda-Broch and Berthod (2004) experimentally determined the degree of hydrophobicity of different sulfonamides as a function of pH, obtaining $log\ K_{OW}$ values of -0.14 for SDZ, 0.27 for SMT and 0.69 for SCP at pH 5 (Table 1), thus justifying the trend observed in soils S1, S2, S3 and S6, which are acidic. However, at pH 7, the $log\ K_{OW}$ values were -1.05, 0.14 and -0.80 for SDZ, SMT and SCP, respectively (Table 1), with SMT being the most hydrophobic molecule at this pH, thus justifying that this antibiotic is the one with the highest affinity in neutral soils.

The linear nature of the adsorption curves, the strong influence of the organic matter content of the soils and the degree of hydrophobicity of the molecules in the adsorption process, indicate that at pH values lesser than the pKa_2 (Table 1), where the non-ionized from of sulfonamide molecules are dominant, hydrophobic partitioning is the main mechanism that governs the adsorption process of sulfonamides, with organic matter acting as the non-polar phase, in accordance with what was previously indicated by other authors (Chen et al., 2017; Lertpaitoonpan et al., 2009; Rath et al, 2019; Srinivasan et al. , 2014). However, in neutral and alkaline soils, at pH higher than the pk_{a2} values of these molecules (Table 1), where they are mainly present in anionic form, this hydrophobic sorption would be impacted by the electrostatic repulsion between the anionic forms of sulfonamides and the negatively charged soil surface, leading to less adsorption (Lertpaitoompan et al., 2009). At the same time, other adsorption mechanisms may participate in alkaline soils, such as cation bridging, where different polyvalent cations can act as linkers/bridge between anionic sulfonamide molecules and negatively charged clays, non-crystalline compounds and organic compounds present in the soil (Lertpaitoonpan et al., 2009). Likewise, Hu et al. (2019) also indicated that sulfonamides can be adsorbed to soils through hydrogen bonds, electrostatic interactions and π- π interactions, although these adsorption mechanisms do not seem to be predominant in the soils of the current study.

The results of Infrared (FTIR) spectroscopy (see Supplementary material) suggest that the adsorption of the sulfonamide antibiotics onto soils was not only physical, but that there was a process of chemisorption due to the observed structural changes. As per Hu et al. (2019), these changes could be interpreted as the formation of a hydrogen bond, increasing polarity after sorption and π-π interactions between the compounds and soils.

In addition, the values of K_d and K_F obtained for desorption are similar to those reported by other authors (Doretto and Rath, 2013; Hu et al., 2019; Pinna et al., 2012; Sukul et al., 2018; Vieria et al., 2017), and were in all cases consistently higher than those observed for adsorption (which means that desorption was lower than adsorption), indicating the existence of positive hysteresis (Barriuso et al., 1994), signaling that a certain amount of the adsorbed sulfonamides are irreversibly retained, in accordance with what was previously observed by other authors (Doretto and Rath, 2013; Sukul et al., 2008; Vieira et al., 2017). Despite this, the desorption percentages found in the current study were considerably higher than those observed for other classes of antibiotics, such as tetracyclines or fluoroquinolones (Álvarez-Esmorís et al., 2020; Conkle et al., 2010), indicating that sulfonamides adsorb more weakly to soils. In the present study, the K_d and K_F values obtained for desorption also strongly depended on the organic matter content of the soils (as for adsorption). In this sense, K_d and K_F for desorption were positively and significantly correlated with: a) SOC content (r = 0.805 for pairs K_d-SDZ, $p < 0.05$; r = 0.884 for K_d-SMT, $p < 0.05$; r = 0.951 for K_d-SCP, $p < 0.01$; r = 0.907 for K_F-SDZ, $p < 0.05$; r = 0.869 for K_F-SMT, $p < 0.05$; r = 0.972 for K_F-SCP, $p < 0.01$); and b) TSN content (r = 0.825 for pairs K_d-SDZ, $p < 0.05$; r = 0.899 for K_d-SMT, $p < 0.05$; r = 0.954 for K_d-SCP, $p < 0.01$; r = 0.911 for K_F-SDZ, $p < 0.05$; r = 0.882 for K_F-SMT, $p < 0.05$; r = 0.964 for K_F-SCP, $p < 0.01$), indicating that those soils with higher organic matter contents show lower desorption. In addition, the values of the K_d and K_F parameters obtained for adsorption were positively and significantly correlated with those obtained for desorption (r = 0.834 for pairs K_d-SDZ, $p < 0.05$; r = 0.950 for K_d-SMT, $p < 0.01$; r = 0.987 for K_d-SCP, $p < 0.01$; r = 0.925 for K_F-SDZ, $p < 0.01$; r = 0.919 for K_F-SMT, $p < 0.01$; r = 0.950 for K_F-SCP, $p < 0.01$), indicating that those soils with the highest adsorption capacity are also the ones with the least desorption. This means that those soils with lower organic matter contents are the ones that present the least protective potential towards other environmental compartments, also increasing risk of antibiotics being allowed to enter the food chain.

Finally, it should be noted that no competition was observed among the three sulfonamides for the adsorption sites, which is consistent with the linearity of the adsorption curves obtained, as this indicate that the available adsorption sites are not a limiting factor in the range of concentrations studied (Calvet et al., 1989). Even in the absence of equivalent studies focusing on competitive adsorption for sulfonamides in soils, the current results are in agreement with those obtained by Gao and Pedersen (2010), who studied the adsorption of SMT and sulfapyridine in a humic-acid/clay complex and did not observe competition for adsorption sites. However, the simultaneous presence of the three sulfonamides in soils did favor their release, especially in those having less organic matter, as they show lower retention capacity for these antibiotics.

5. Conclusions and environmental significance

The results of the current research demonstrate that the sorption of sulfonamides in soils is governed by both soil properties and antibiotic characteristics. It can be considered of value, as a deep understanding of sulfonamides adsorption/desorption processes is vital to facilitate a correct assessment of the risks due to the presence of these pollutants in the environment, as well as to establish effective measures to mitigate or reduce their possible negative impacts on human and ecological health.

Specifically, in this study organic matter content was the soil property that showed a greater influence in the sulfonamide adsorption process, with higher retention in soils having more organic matter content, whereas clay content and soil pH showed a minor influence.

Hydrophobic partitioning was identified as the main adsorption mechanism in acidic soils with pH values lower than the pK_{a2} of the molecules, where sulfonamides are predominantly in non-ionized form. In addition, it was also obtained that an increase in pH values above pK_{a2} can lead to decreased retention due to electrostatic repulsion between the anionic forms of sulfonamides and the negatively charged soil surface.

Overall, the results obtained indicate that the three sulfonamides here studied have a significant risk of being transported from soils to other environmental compartments, causing potential pollution of receiving water bodies. Therefore, fertilization of soils with manure and/or slurry contaminated with sulfonamides should be controlled. However, the coexistence of different sulfonamides in soils does not appear to significantly increase their mobility and, therefore, their environmental risk.

Although the sulfonamide concentrations used in this investigation are higher than those most frequently detected in the environment, the results obtained in this study allow to identify the main factors that govern the environmental fate of these pollutants. The identification of this factors, in turn, helps to determine which are the most appropriate measures to minimize their negative impacts. In this sense, soil organic matter conservation is of great relevance in order to minimize potential risks related to the transport of these pollutants to other environmental compartments, such as water bodies, or even plant uptake. In addition, different soil management practices, such as organic fertilization or liming, should be applied with caution, since they can lead to an increase in the soil pH, thus increasing the mobility of these pollutants and, consequently, their risks of causing harmful effects on human and ecological health. Therefore, soil management practices should be carried out with precaution.

Acknowledgments

Funding: This work was supported by the Spanish Ministry of Economy and Competitiveness, with FEDER funds [grant numbers [CGL2015-67333-C2-1-R and CGL2015-67333-C2-2-R]. Conde-Cid, M. holds a predoctoral FPU contract (Ministry of Education, Culture and Sports). Fernández-Calviño, D. holds a Ramon y Cajal contract (Ministry of Economy, Industry and Competitiveness). The sponsor had no involvement in the study design, in the collection, analysis and interpretation of data, in the writing of the report, or in the decision to submit the article for publication.

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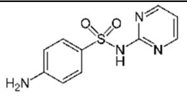
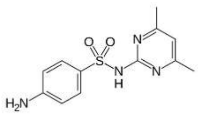
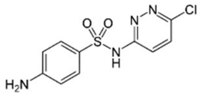
Table 1. Main physicochemical properties of the three sulfonamides studied

	Chemical structure	MW (g mol^{-1})	log K$_{OW}$[a]			pK$_a$[b]	WS[c] (mg L^{-1})
			pH 3	pH 5	pH 7		
SDZ		250.3	-0.1	-0.14	-1.05	2.10-6.28	77
SMT		278.3	0.16	0.27	0.14	2.07-7.49	1500
SCP		284.7	0.68	0.69	-0.8	1.87-5.45	35

MW: molecular weight; WS: water solubility.

[a] Carda-Broch and Berthod (2004)

[b] Babić et al. (2007)

[c] Chen et al. (2015)

Table 2. Main physicochemical properties of the six soils used

Soil sample	Site	pH_{H2O}	pH_{KCl}	Na_e	K_e	Ca_e	Mg_e	Al_e	eCEC	SOC	TSN	Sand	Silt	Clay	Al_{ox}	Al_{pir}	Fe_{ox}	Fe_{pir}
				$cmol_c\ kg^{-1}$						%					$mg\ kg^{-1}$			
S1	AL	4.8	4.3	0.25	1.27	1.53	0.41	0.61	4.08	1.1	0.1	70	12	18	855	614	1150	946
S2	AL	4.7	4.3	0.35	1.00	2.24	0.64	1.68	5.92	3.4	0.3	58	19	22	5040	3342	2585	1652
S3	AL	4.5	4.0	0.42	1.14	5.94	1.48	2.66	11.64	10.9	0.8	49	19	32	2995	2460	1430	2842
S4	S	6.3	5.9	0.36	0.61	12.86	1.13	0.00	14.96	2.0	0.2	22	62	16	18378	9125	56424	21193
S5	S	7.1	6.4	0.28	1.40	9.89	0.97	0.01	12.54	1.8	0.2	27	56	17	15756	7902	42377	11196
S6	S	6.2	5.4	0.41	1.20	12.79	2.88	0.11	17.38	6.9	0.5	40	42	18	50594	44980	73096	39370

pH_{H2O}: pH in water; pH_{KCl}: pH in 0.1 M potassium chloride; Na_e: exchangeable sodium; K_e: exchangeable potassium; Ca_e: exchangeable calcium; M_e: exchangeable magnesium; Al_e: exchangeable aluminum; eCEC: effective cation exchange capacity; SOC: soil organic carbon; TSN: total soil nitrogen.; Al_{ox} and Fe_{ox}: Al and Fe extracted with oxalic acid – ammonium oxalate; Al_{pir} and Fe_{pir}: Al and Fe extracted with sodium pyrophosphate.

Table 3. Fitting of experimental data (from ternary systems) to the Linear and Freundlich adsorption models. K_d (L kg^{-1}): distribution coefficient; K_F (L^n µmol^{1-n} kg^{-1}): Freundlich affinity coefficient; n (dimensionless): Freundlich linearity index; K_{OC} (L kg^{-1}): K_d normalized to organic carbon. R^2: coefficient of determination. Different letters designate significant differences between K_d and K_F values of the different soils according to one-way ANOVA analysis ($p < 0.05$). *Calculated using equations 3 and 4

Soil	Antibiotic	Linear		K_{OC}	Freundlich		
		K_d	R^2		K_F	n	R^2
S1	SDZ	0.52 ± 0.03^{a}	0.980	47.3 ± 2.7	1.03 ± 0.20^{a}	0.81 ± 0.06	0.993
	SMT	0.62 ± 0.04^{a}	0.978	56.4 ± 3.6	1.31 ± 0.21^{a}	0.79 ± 0.05	0.995
	SCP	1.61 ± 0.05^{a}	0.995	146.4 ± 4.5	1.91 ± 0.24^{a}	0.95 ± 0.04	0.997
	SDZ+SMT+SCP*	0.84 ± 0.04^{a}	0.990	76.4 ± 3.6	1.55 ± 0.30^{a}	0.87 ± 0.05	0.996
S2	SDZ	1.22 ± 0.03^{b}	0.998	35.9 ± 0.9	1.48 ± 0.11^{a}	0.94 ± 0.02	0.999
	SMT	1.24 ± 0.06^{b}	0.987	36.5 ± 1.8	1.89 ± 0.35^{a}	0.87 ± 0.06	0.993
	SCP	3.45 ± 0.12^{b}	0.994	101.5 ± 3.5	3.52 ± 0.53^{b}	0.99 ± 0.06	0.995
	SDZ+SMT+SCP*	1.74 ± 0.05^{b}	0.997	51.2 ± 1.5	2.29 ± 0.33^{a}	0.94 ± 0.04	0.998
S3	SDZ	9.43 ± 0.33^{c}	0.994	86.5 ± 3.0	11.31 ± 1.27^{b}	0.92 ± 0.06	0.995
	SMT	11.05 ± 0.28^{c}	0.997	101.4 ± 2.6	12.97 ± 0.79^{b}	0.92 ± 0.03	0.998
	SCP	24.40 ± 1.03^{c}	0.991	223.9 ± 9.4	32.00 ± 0.27^{c}	0.80 ± 0.01	1.000
	SDZ+SMT+SCP*	12.76 ± 0.33^{c}	0.997	117.1 ± 3.0	17.30 ± 1.53^{b}	0.90 ± 0.03	0.998
S4	SDZ	0.67 ± 0.03^{a}	0.991	33.5 ± 1.5	1.04 ± 0.15^{a}	0.87 ± 0.04	0.997
	SMT	0.77 ± 0.07^{a}	0.961	38.5 ± 3.5	1.89 ± 0.37^{a}	0.74 ± 0.06	0.990
	SCP	0.78 ± 0.06^{a}	0.970	39.0 ± 3.0	1.62 ± 0.38^{a}	0.79 ± 0.08	0.987
	SDZ+SMT+SCP*	0.74 ± 0.05^{a}	0.980	37.0 ± 2.5	1.87 ± 0.37^{a}	0.80 ± 0.05	0.995
S5	SDZ	0.40 ± 0.03^{a}	0.977	22.2 ± 1.7	0.92 ± 0.20^{a}	0.78 ± 0.07	0.990
	SMT	0.77 ± 0.04^{a}	0.985	42.8 ± 2.2	1.66 ± 0.16^{a}	0.78 ± 0.03	0.998
	SCP	0.54 ± 0.02^{a}	0.993	30.0 ± 1.1	0.67 ± 0.12^{a}	0.94 ± 0.06	0.995
	SDZ+SMT+SCP*	0.56 ± 0.03^{a}	0.988	31.1 ± 1.7	1.25 ± 0.26^{a}	0.83 ± 0.05	0.995
S6	SDZ	3.92 ± 0.17^{d}	0.990	56.8 ± 2.5	6.27 ± 0.43^{c}	0.84 ± 0.03	0.998
	SMT	4.33 ± 0.21^{d}	0.989	62.8 ± 3.0	6.95 ± 0.57^{c}	0.83 ± 0.03	0.998
	SCP	8.93 ± 0.31^{d}	0.994	129.4 ± 4.5	12.54 ± 1.06^{d}	0.85 ± 0.04	0.997
	SDZ+SMT+SCP*	5.17 ± 0.20^{d}	0.993	74.9 ± 2.9	9.31 ± 0.75^{c}	0.85 ± 0.02	0.999

Table 4. Values of desorption parameters resulting from fitting of experimental data (from ternary experiments) to the Linear and Freundlich models. K_d (L kg^{-1}): distribution coefficient; K_F (L^{n} µmol^{1-n} kg^{-1}): Freundlich affinity coefficient; n (dimensionless): Freundlich linearity index; R^2: coefficient of determination. Different letters designate significant differences between K_d and K_F values of the different soils according to one-way ANOVA analysis ($p < 0.05$). * Calculated using equations 3 and 4

Soil	Antibiotic	Linear		Freundlich		
		K_d	R^2	K_F	n	R^2
S1	SDZ	4.62 ± 0.35^{a}	0.972	5.20 ± 0.46^{a}	0.89 ± 0.12	0.978
	SMT	5.68 ± 0.50^{a}	0.962	7.87 ± 0.42^{ac}	0.68 ± 0.07	0.986
	SCP	5.59 ± 0.39^{ac}	0.977	4.74 ± 0.88^{a}	1.12 ± 0.14	0.984
	SDZ+SMT+SCP*	5.35 ± 0.31^{a}	0.983	6.63 ± 1.36^{a}	0.91 ± 0.10	0.986
S2	SDZ	5.60 ± 0.17^{a}	0.995	5.69 ± 0.39^{a}	0.99 ± 0.06	0.996
	SMT	6.80 ± 0.25^{a}	0.993	7.09 ± 0.49^{a}	0.97 ± 0.06	0.995
	SCP	8.32 ± 0.49^{ac}	0.983	7.56 ± 1.21^{a}	1.08 ± 0.11	0.988
	SDZ+SMT+SCP*	7.01 ± 0.29^{a}	0.992	6.64 ± 1.17^{a}	1.03 ± 0.08	0.993
S3	SDZ	26.02 ± 1.24^{b}	0.989	27.56 ± 1.70^{b}	0.94 ± 0.07	0.992
	SMT	36.86 ± 2.05^{b}	0.985	36.71 ± 2.17^{b}	1.01 ± 0.09	0.988
	SCP	64.59 ± 3.47^{b}	0.986	60.56 ± 1.91^{b}	1.14 ± 0.09	0.990
	SDZ+SMT+SCP*	37.98 ± 1.44^{b}	0.993	37.00 ± 3.92^{b}	1.03 ± 0.06	0.999
S4	SDZ	5.37 ± 0.63^{a}	0.935	8.26 ± 1.34^{a}	0.65 ± 0.22	0.910
	SMT	6.35 ± 0.82^{a}	0.921	10.89 ± 1.24^{c}	0.53 ± 0.16	0.935
	SCP	4.59 ± 0.65^{a}	0.907	5.82 ± 1.97^{a}	0.91 ± 0.37	0.879
	SDZ+SMT+SCP*	5.51 ± 0.58^{a}	0.948	15.39 ± 3.39^{a}	0.54 ± 0.12	0.955
S5	SDZ	16.29 ± 3.79^{c}	0.778	13.85 ± 2.62^{c}	0.31 ± 0.16	0.840
	SMT	14.47 ± 2.74^{c}	0.843	18.68 ± 1.79^{d}	0.37 ± 0.13	0.906
	SCP	11.68 ± 1.61^{c}	0.928	13.77 ± 1.12^{c}	0.43 ± 0.13	0.956
	SDZ+SMT+SCP*	14.14 ± 2.76^{c}	0.863	32.69 ± 4.05^{b}	0.36 ± 0.12	0.942
S6	SDZ	13.20 ± 0.82^{c}	0.981	19.18 ± 0.85^{d}	0.75 ± 0.04	0.996
	SMT	13.89 ± 0.87^{c}	0.981	19.28 ± 0.86^{d}	0.78 ± 0.04	0.996
	SCP	24.38 ± 3.89^{d}	0.885	41.03 ± 3.50^{d}	0.54 ± 0.10	0.956
	SDZ+SMT+SCP*	16.70 ± 1.36^{c}	0.968	33.17 ± 4.14^{b}	0.72 ± 0.06	0.989

Table 5. Fitting of experimental data (from simple systems) to the Linear and Freundlich adsorption models. K_d (L kg^{-1}): distribution coefficient; K_F (L^n µmol^{1-n} kg^{-1}): Freundlich affinity coefficient; n (dimensionless): Freundlich linearity index; R^2: coefficient of determination. Different letters designate significant differences between K_d and K_F values of the different soils according to one-way ANOVA analysis ($p < 0.05$)

Soil	Antibiotic	Linear		Freundlich		
		K_d	R^2	K_F	n	R^2
S1	SDZ	0.60^{a} ± 0.02	0.986	0.42 ± 0.11^{a}	1.08 ± 0.06	0.989
	SMT	0.57^{a} ± 0.03	0.981	1.67 ± 0.12^{a}	0.77 ± 0.02	0.998
	SCP	1.66^{a} ± 0.04	0.994	2.75 ± 0.27^{ab}	0.88 ± 0.03	0.997
S2	SDZ	1.16^{b} ± 0.01	1.000	1.32 ± 0.03^{b}	0.97 ± 0.01	1.000
	SMT	1.24^{b} ± 0.01	0.999	1.24 ± 0.07^{a}	1.00 ± 0.01	0.999
	SCP	3.66^{b} ± 0.04	0.999	2.90 ± 0.16^{b}	1.06 ± 0.02	0.999
S3	SDZ	9.34^{c} ± 0.16	0.997	12.03 ± 0.48^{c}	0.92 ± 0.01	0.999
	SMT	11.31^{c} ± 0.15	0.998	15.79 ± 0.79^{b}	0.90 ± 0.02	0.999
	SCP	27.51^{c} ± 0.51	0.997	24.38 ± 1.36^{c}	1.05 ± 0.03	0.998
S4	SDZ	0.60^{a} ± 0.01	0.999	0.68 ± 0.05^{ab}	0.98 ± 0.02	0.999
	SMT	0.70^{a} ± 0.03	0.988	1.94 ± 0.12^{a}	0.78 ± 0.02	0.999
	SCP	0.95^{d} ± 0.02	0.995	1.63 ± 0.15^{ab}	0.88 ± 0.02	0.998
S5	SDZ	0.46^{a} ± 0.02	0.987	1.30 ± 0.11^{b}	0.78 ± 0.02	0.997
	SMT	0.67^{a} ± 0.03	0.987	2.40 ± 0.35^{a}	0.73 ± 0.04	0.991
	SCP	0.53^{d} ± 0.01	0.995	1.05 ± 0.12^{a}	0.85 ± 0.03	0.997
S6	SDZ	3.67^{d} ± 0.10	0.994	6.90 ± 0.49^{d}	0.84 ± 0.02	0.998
	SMT	3.98^{d} ± 0.09	0.995	7.48 ± 0.64^{c}	0.84 ± 0.03	0.997
	SCP	9.70^{e} ± 0.18	0.997	15.33 ± 0.78^{d}	0.86 ± 0.02	0.999

Table 6. Values of desorption parameters resulting from fitting of experimental data (from simple experiments) to the Linear and Freundlich models. K_d (L kg^{-1}): distribution coefficient; K_F (L^{n} µmol^{1-n} kg^{-1}): Freundlich affinity coefficient; n (dimensionless): Freundlich linearity index; R^2: coefficient of determination. Different letters designate significant differences between K_d and K_F values of the different soils according to one-way ANOVA analysis ($p < 0.05$). na: not adjusted

Soil	Antibiotic	Linear		Freundlich		
		K_d	R^2	K_F	n	R^2
S1	SDZ	8.53 ± 0.33^{a}	0.987	8.41 ± 0.68^{a}	1.01 ± 0.06	0.988
	SMT	8.05 ± 0.40^{a}	0.978	10.03 ± 0.85^{a}	0.88 ± 0.06	0.982
	SCP	7.18 ± 0.29^{a}	0.985	5.80 ± 0.79^{a}	1.08 ± 0.06	0.988
S2	SDZ	8.54 ± 0.26^{a}	0.992	9.93 ± 0.65^{a}	0.93 ± 0.04	0.994
	SMT	8.71 ± 0.13^{a}	0.998	8.40 ± 0.34^{a}	1.02 ± 0.02	0.998
	SCP	10.90 ± 0.48^{a}	0.983	4.88 ± 0.53^{a}	1.31 ± 0.05	0.996
S3	SDZ	33.83 ± 0.98^{b}	0.992	43.21 ± 2.42^{b}	0.88 ± 0.04	0.994
	SMT	33.21 ± 1.77^{b}	0.975	54.63 ± 2.47^{b}	0.75 ± 0.03	0.995
	SCP	132.95 ± 6.44^{b}	0.979	103.96 ± 2.24^{b}	1.33 ± 0.04	0.998
S4	SDZ	9.56 ± 0.34^{a}	0.989	10.99 ± 0.73^{a}	0.91 ± 0.05	0.992
	SMT	9.64 ± 0.36^{a}	0.988	11.97 ± 1.21^{a}	0.90 ± 0.07	0.983
	SCP	6.82 ± 0.27^{a}	0.987	6.25 ± 0.72^{a}	1.05 ± 0.06	0.989
S5	SDZ	na	na	na	na	na
	SMT	na	na	na	na	na
	SCP	na	na	na	na	na
S6	SDZ	15.61 ± 1.05^{c}	0.961	19.60 ± 3.23^{c}	0.90 ± 0.08	0.967
	SMT	17.45 ± 1.18^{c}	0.960	37.68 ± 2.90^{c}	0.66 ± 0.04	0.986
	SCP	21.83 ± 0.98^{c}	0.982	40.71 ± 2.62^{c}	0.73 ± 0.03	0.994

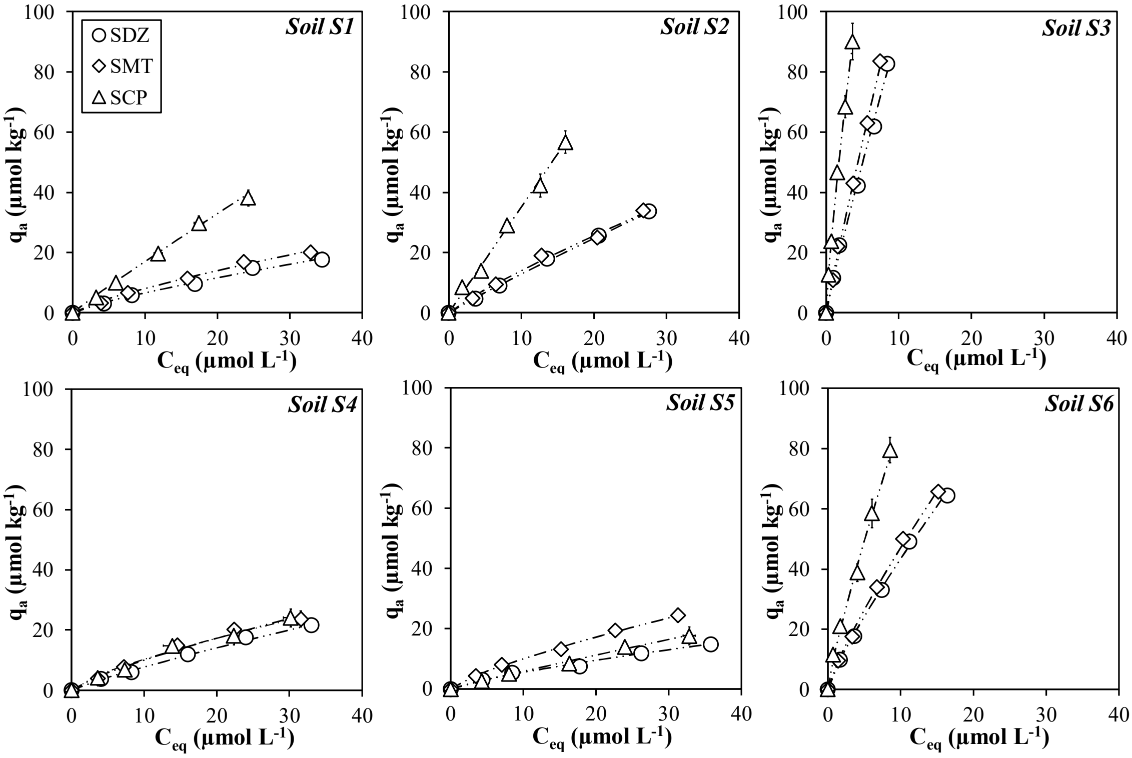


Figure 1. Adsorption curves for each of the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT and sulfachloropyrydazine –SCP) obtained from ternary tests on the six soils studied. q_a: amount of antibiotic adsorbed to the soil; C_{eq}: concentration of antibiotic in the solution at equilibrium. Error bars represent twice the standard deviation of the mean (n = 3). When bars are not visible, they are smaller than the symbols

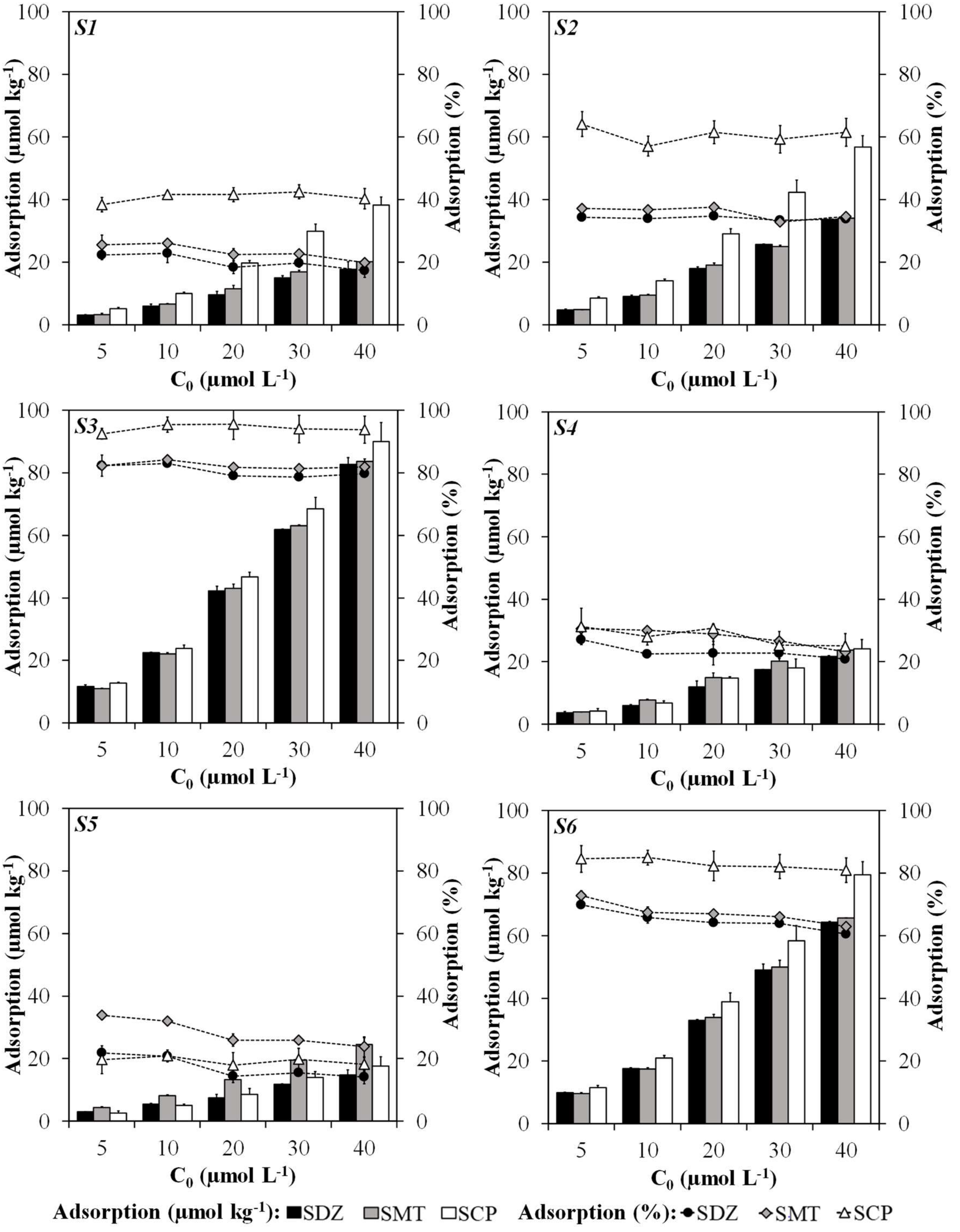


Figure 2. Amounts adsorbed (μmol kg^{-1}) and percentages of adsorption for each of the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT and sulfachloropyrydazine –SCP) obtained from ternary tests in the six soils studied. *C_0*: initial concentration of each of the antibiotics. Error bars represent twice the standard deviation of the mean (n = 3). When bars are not visible, they are smaller than the symbols

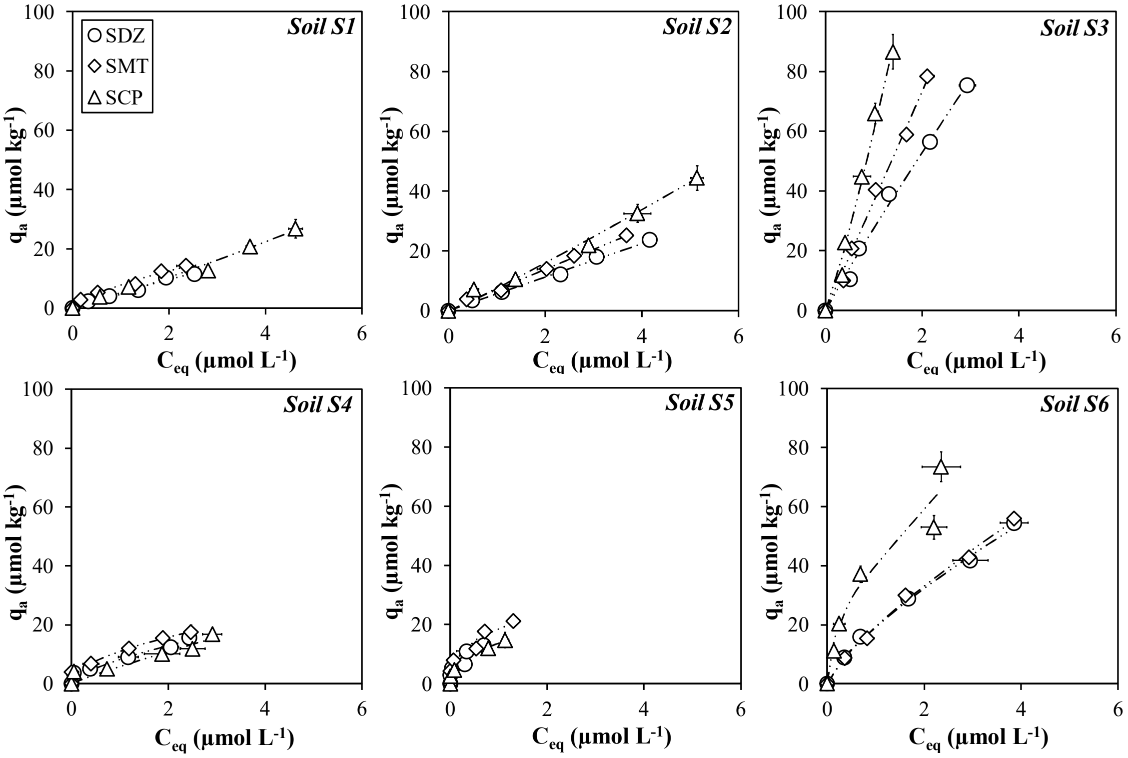


Figure 3. Desorption curves for each of the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT and sulfachloropyrydazine –SCP) obtained from ternary tests on the six soils studied. q_a: amount of antibiotic adsorbed to the soil; C_{eq}: concentration of antibiotic in the solution at equilibrium. Error bars represent twice the standard deviation of the mean (n = 3). When bars are not visible, they are smaller than the symbols

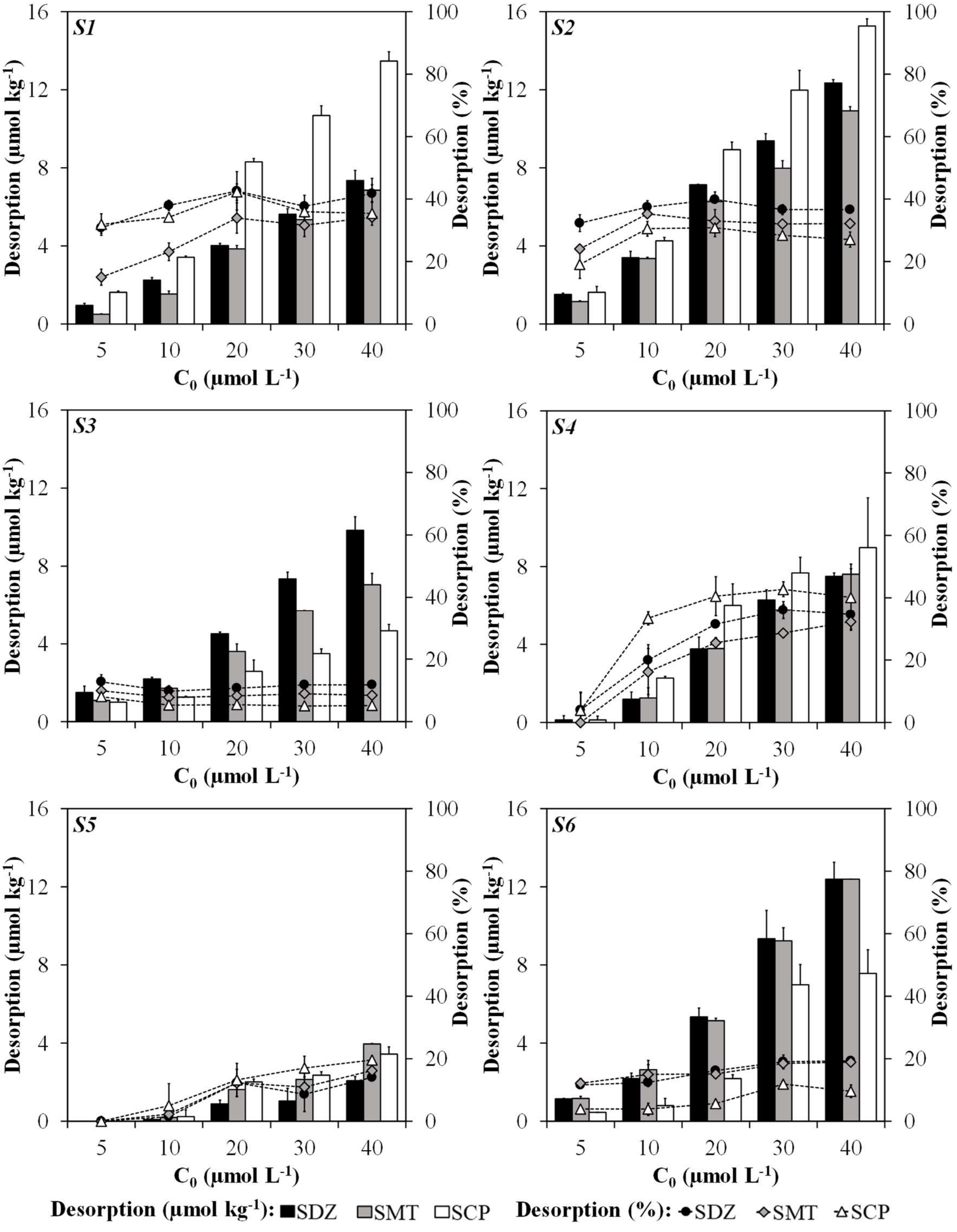


Figure 4. Desorbed amounts (µmol kg^{-1}) and desorption percentages for each of the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT and sulfachloropyrydazine –SCP) obtained from ternary tests in the six soils studied. *C_0*: initial concentration of each of the antibiotics. Error bars represent twice the standard deviation of the mean (n = 3). When bars are not visible, they are smaller than the symbols

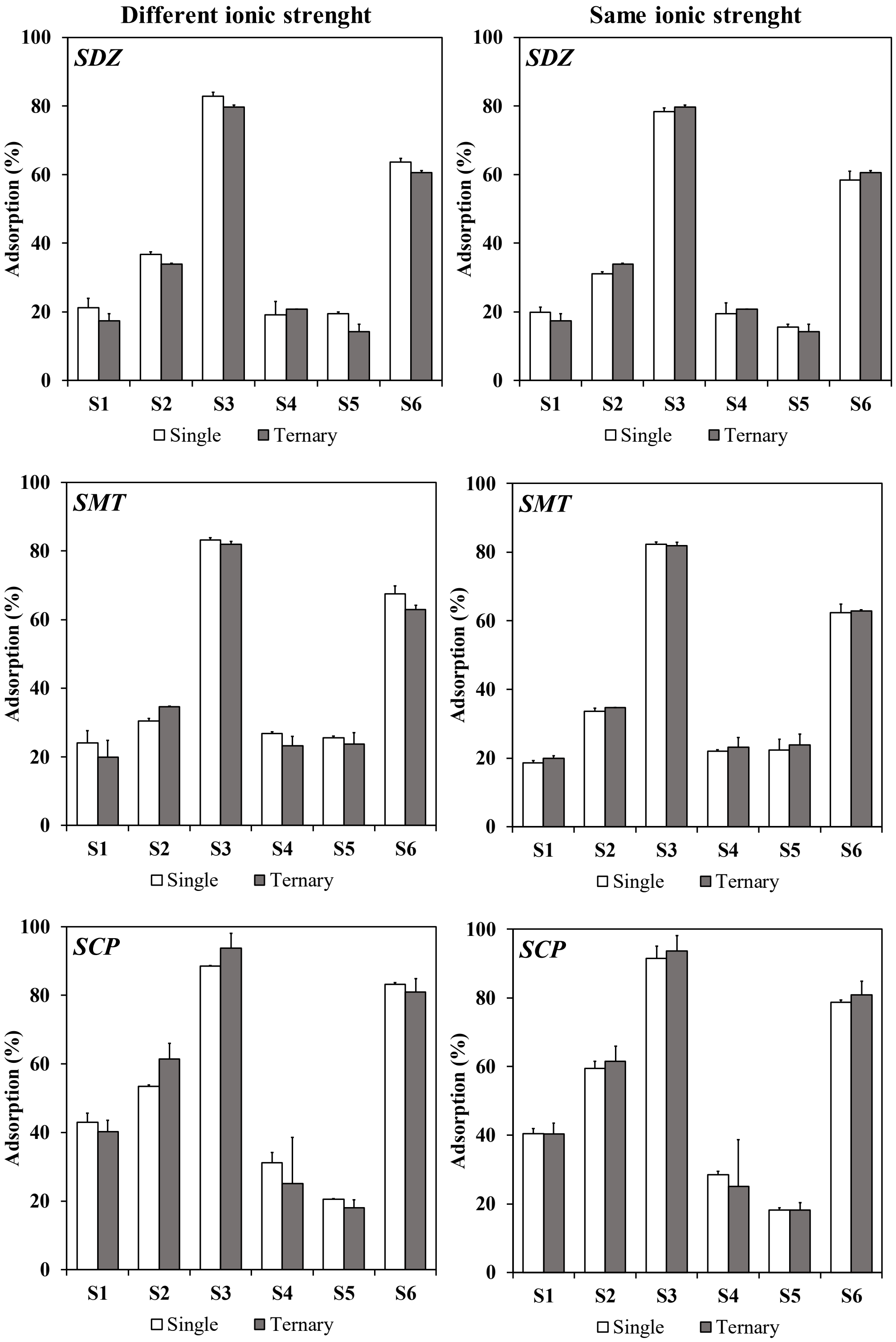


Figure 5. Adsorption percentages for the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT, sulfachloropyridazine –SCP) in the six soils studied, in simple and ternary systems, with different ionic strength and with the same ionic strength. Error bars represent twice the standard deviation of the mean (n = 3)

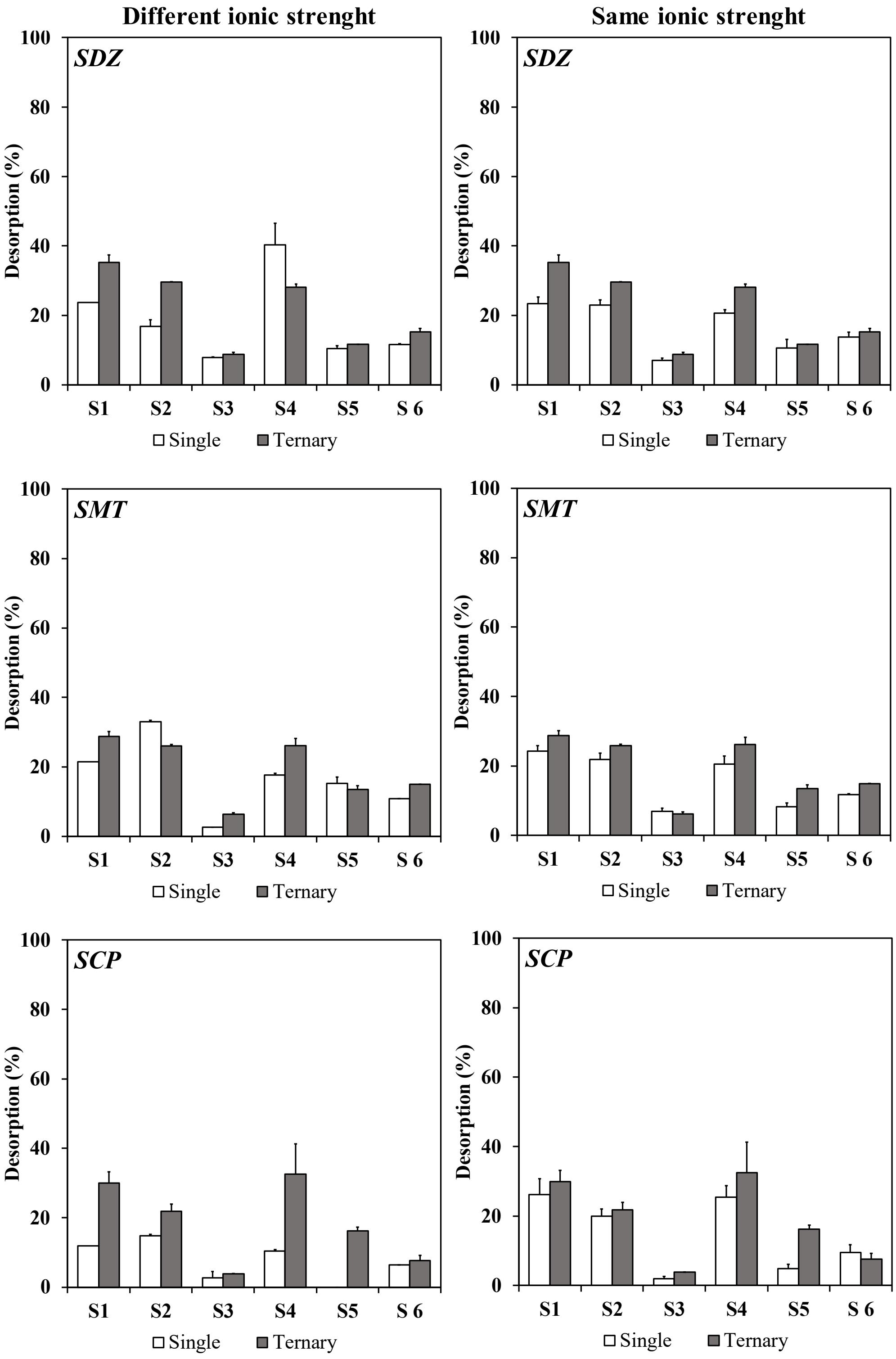


Figure 6. Desorption percentages for the three sulfonamides (sulfadiazine –SDZ, sulfamethazine –SMT, sulfachloropyridazine –SCP) in the six soils studied, in simple and ternary systems, with different ionic strength and with the same ionic strength. Error bars represent twice the standard deviation of the mean (n = 3)