The sorption of sulfamethazine on soil samples: Isotherms and error analysis

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HIGHLIGHTS

- The sorption of SMET on eight soil samples was investigated.
- Equilibrium data were tested using linear and non-linear sorption isotherms.
- K_d values indicated that SMET is highly mobile in the soil sample.
- OM content and ionic strength of soil have great impact on sorption of SMET.

GRAPHICAL ABSTRACT
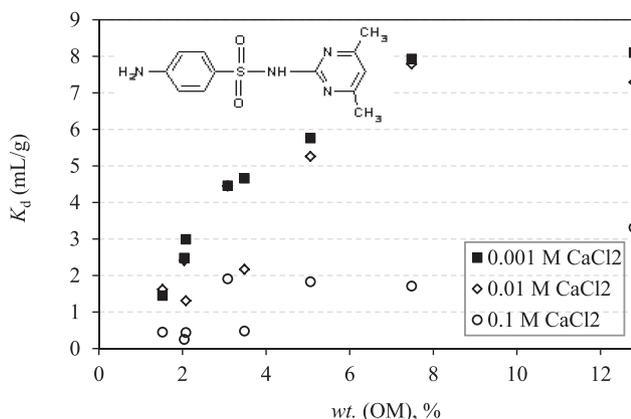
ABSTRACT

In this paper, batch sorption of sulfamethazine on eight soil samples (six from Croatia and two from Bosnia and Hercegovina) with different organic matter contents ranging from 1.52 to 12.8% was investigated. The effects of various parameters such as agitation time, initial concentration, and ionic strength on the sulfamethazine sorption were studied. The experimental data were analysed using a one-parameter model, Linear isotherm, and two two-parameter models, the Freundlich and Dubinin–Radushkevich isotherms. The goodness of fit was measured using the linear regression and the determination coefficient (R^2) value. Also, the equilibrium data of the two-parameter models were analysed using the residual root mean square error (RMSE), the sum of squares of errors (ERRSQ), and a composite fractional error function (HYBRID).

Non-linear regression has better characteristics for analysing experimental data. The obtained sorption coefficients K_d (from 0.25 to 8.10 mL/g) and the Freundlich sorption coefficients K_F (from 1.16 to 7.99 $(\mu g/g)(mL/\mu g)^{1/n}$) exhibited quite low values, which indicated that sulfamethazine is weakly adsorbed on the evaluated soils, is highly mobile, and has a great potential to penetrate and pollute the ground water. The Dubinin–Radushkevich isotherm was used to estimate the apparent free energy of sorption.

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1. Introduction

Pharmaceuticals have been detected in a wide variety of environmental matrices. Among them, a number of compounds belonging to the sulfonamide group have often been found. There is an intense

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interest in developing and applying appropriate analytical methods for the proper identification and measurement of multiple members of the mentioned sulfonamide group. This can be accounted for by their widespread use in human and veterinary applications, their environmental persistence, and their potential for causing the development of resistant strains of bacteria (Shelver et al., 2010). Detection of sulfonamides in a variety of environmentally important matrices is frequently reported in literature (Shelver et al., 2010; García-Galán et al., 2010; Aust et al., 2008).

Sorption is an extremely important process because it may dramatically affect the fate and impacts of chemicals in the environment. It has proven to be a function of many attributes such as CEC, pH, and ionic strength. While hydrophobic partitioning has been regarded as one of the important sorption mechanisms for a range of chemicals in soils, mechanisms such as cation exchange, cation bridging at clay surfaces, surface complexation with metal ions (Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+} or Al^{3+}), and hydrogen bonding also have a role in the sorption of these compounds in soils and sediments (Srinivasan and Sarmah, 2014; Srinivasan et al., 2014; Xie et al., 2014; Kim and Carlson, 2005; Schwarzenbach et al., 2003; Díaz-Cruz et al., 2003). Because of all this, different low-cost sorbents have been used for the removal of various organic contaminants (Ahmaruzzaman, 2012; Ahmaruzzaman and Gayatri, 2010; Ahmaruzzaman, 2009) from wastewater.

The degree of sorption mainly depends on physico-chemical properties (K_d, K_{oc}, K_{ow}, pK_a) of pharmaceuticals, the type of solid matrices (content of organic matter and soil minerals), and environmental conditions (pH, temperature). The distribution coefficient K_d is an important indicator of sorption on solid samples. Considering that the K_d value varies depending on the organic carbon content, it is recommended to use the organic carbon-normalised partition coefficient (K_{oc}) for the prediction of the environmental fate of pharmaceuticals (Díaz-Cruz et al., 2003; Northcott and Jones, 2000). Furthermore, K_{oc} values are easily derived from the octanol–water partition coefficient (K_{ow}) which describes chemical lipophilic and hydrophobic properties (Jacobsen and Berglind, 1988). The degree of sorption for different pharmaceuticals varies to a great extent. These variations could not be explained only by the variation in the soil organic content. The sorption and the consequent accumulation of antibiotics in solid matrices are firmly governed by the ionization property of numerous pharmaceuticals with the pK_a values within an environmentally significant pH range (Hörsing et al., 2011). The sorption of pharmaceuticals onto solid matrices is not only influenced by their pH values but also by the ionic strength (Thiele-Bruhn, 2003).

The physico-chemical properties of sulfonamides (SAs), their dosage, and the nature of the matrix are the factors which are mainly responsible for their distribution in the environment.

The complex sorption behaviour of SAs could be attributed to a number of properties and their interaction with different soil compositions. Because of two pK_as, SAs can exist as anions, neutral compounds, or cations and the charged molecule can be bound to various soil components through ion exchange mechanisms or potentially hydrophobic sorption processes. SAs have relatively high polarity and water solubility, which results in weak sorption affinity to the soil particles and high mobility in the soil (Shelver et al., 2010).

Previous studies confirmed that sulfonamides are present in soil in a concentration of up to 15 μg/kg of soil (Sukul and Spiteller, 2006). Although SAs have been the subject of a number of investigations, few of them have been focused on their behaviour and fate in the environment, including soil (Anskjær et al., 2014; Srinivasan and Sarmah, 2014; Doretto et al., 2014; Vithanage et al., 2014; Srinivasan et al., 2014; Srinivasan et al., 2013; Maszkowska et al., 2013; Lertpaitoonpan et al., 2009; Karcı and Balcıoğlu, 2009). Srinivasan et al. (2014) presented in detail the values of main factors influencing the sorption of sulfonamides in various environmental matrices of soil. All sorption studies on sulfonamides have shown that they are characterised by a low sorption potential. However, even in this case it is difficult to predict their fate

because it really depends on the physico-chemical properties of the investigated soil and experimental conditions.

Since sulfonamides can be ionised, they can be sorbed to the soil organic matter and soil minerals. However, the research done by Kaiser and Zech (1998) has shown that sorption depends to a greater extent on the soil organic matter than on the soil minerals.

Sulfamethazine is a widely used veterinary pharmaceutical drug. That is the reason why it is often found in manures which are used for treating different agricultural areas. Thus, in some studies, it has been found that sulfamethazine can be detected in soil in a period of seven months to a year after fertilization. The amount of 34.5–663 ng/kg of dry matter was found in these studies (Białk-Bielińska et al., 2012). That is the reason why the sorption of sulfamethazine in soil has been selected for the present research.

The goal of this study was to experimentally determine the K_d values (Linear isotherm) for sulfamethazine in eight different natural soil samples different organic matter content (OM), electrical conductivity (EC), cation exchange capacity (CEC), calcium carbonate content, content of affordable microelements (Cu, Fe, Zn and Mn) and particle size distribution. Sorption phenomena were described with a one-parameter model, the Linear isotherm (K_d) (Liao et al., 2014; Białk-Bielińska et al., 2012; Hörsing et al., 2011; Goldberg, 2005), and also with two two-parameter models, the Freundlich (Kim et al., 2012; Liu et al., 2011; Goldberg, 2005; Freundlich, 1906) and the Dubinin–Radushkevich isotherms (Chao et al., 2014; Zhang et al., 2011; Domínguez et al., 2011; Foo and Hameed, 2010). In linear regression analysis, the least squares method was used to predict the parameters. Non-linear regression was performed using the equilibrium data of the two-parameter models (Freundlich and Dubinin–Radushkevich), which were analysed using three non-linear error analysis methods, namely, the residual root mean square error (RMSE) (Hadi et al., 2010), the sum of squares of errors (ERRSQ) (Foo and Hameed, 2010; Ahmaruzzaman and Laxmi Gayatri, 2010) and a composite fractional error function (HYBRID) (Foo and Hameed, 2010; Hadi et al., 2010; Ncibi, 2008). The influence of ionic strength of the sorbate (solution of sulfamethazine) and the sorbent (soil) organic carbon (OC) content on the sorption of sulfamethazine was also investigated. The results from this study may provide information on the likelihood for sulfamethazine to reach groundwater due to soil washouts or soil irrigation by treated wastewater. This is of great importance, especially in areas rich with groundwater and areas where there is high porosity of the soil.
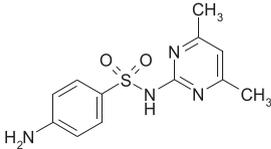
2. Materials and methods

2.1. Materials

The studied pharmaceutical sulfamethazine (SMET) of high purity (>99%) was obtained from Veterina Animal Health Ltd. (Kalinovica, Croatia). The studied pharmaceutical drug and its physico-chemical properties are shown in Table 1. A stock solution of pharmaceutical mixture was prepared by dissolving accurate quantities of powdered standards in the water solution of 0.01 M $CaCl_2$, and stored far away from light at 4 °C. The mass concentration of sulfamethazine in the stock solution was 50 mg/L. Working standard solutions were prepared from this stock by serial dilution. All the chemicals used were supplied by Kemika (Zagreb, Croatia).

2.2. Soil samples

Experiments were carried out using eight natural surface soil samples. The soil samples were collected from different Croatian regions, the Zadar County (soil 2 and soil 4), the Sisak-Moslavina County (soil 7), the Brod-Posavina County (soil 1 and soil 5) and the City of Zagreb (soil 3). The soils 6 and 8 were taken from the territory of Bosnia and Hercegovina. Once in the laboratory, samples were air-dried, ground and passed through a sieve with 2-mm openings. The soils

Table 1
Structure and physico-chemical properties of sulfamethazine.

CAS	Structure	pK_a (Babić et al., 2007)	log K_{ow} (EPIweb)	log K_c (EPIweb)	K_d/l kg^{-1} (Thiele-Bruhn, 2003)	K_{oc}/l kg^{-1} (Thiele-Bruhn, 2003)
57-68-1		$pK_{a1} = 2.5$ $pK_{a2} = 7.4$	0.76	2.28	1.2 (sand) 3.1 (loamy sand)	174 (sand) 125 (loamy sand)

were characterised. The particle size analysis was set out by the Pippete method which is based on the sedimentation of particles by their gravity (Pansu and Gautheyrou, 2006); the organic matter (OM) content was determined by the Kochman method which consists of organic matter oxidation using potassium permanganate and oxalic acid; soil pH values in 0.01 M CaCl$_2$ with a soil to solution ratio of 20 g:50 mL were determined with a pH meter (Mettler Toledo, USA); soil electrical conductivity (EC) values in water with a soil to water ratio of 20 g:50 mL were determined by an inoLab Cond 720 conductometer (Weilheim, Germany); the content of calcium carbonate was measured by volumetric measurements by calcimetry (Pansu and Gautheyrou, 2006), the cation exchange capacity by the cobalt-hexamine (Co(NH$_3$)$_6^{3+}$) method (Renault et al., 2009; AFNOR, 1999), and the content of affordable microelements (Cu, Fe, Zn and Mn) by an AA-6800 Shimadzu atomic absorption spectrometer. Total dissolved solids were calculated from the soil electrical conductivity (EC) by using the following empirical formula (Atekwana et al., 2004)

$$TDS, mg/L = 0.64 \cdot EC, \mu S/cm. \qquad (1)$$

Physicochemical properties of eight investigated soil samples are listed in Table 2.

2.3. Batch sorption experiments

Batch sorption experiments were performed according to the OECD Technical Guideline 106 (OECD, 2000). All experiments were prepared in triplicate. Tests were performed using a laboratory shaker (Innova 4080 Incubator Shaker, New Brunswick Scientific, USA), ensuring constant contact with the soil sample solution containing sulfamethazine. To avoid the photodegradation of sulfamethazine, the experiments were performed in the dark provided by covering the shaker with a piece of dark light-tight cloth.

Selection of optimum soil/solution ratios was based on the calculated percentage of the chemical sorbed on the soil, which should be >20%, and preferably >50%. Based on the OECD procedure and the fact that sulfonamides do not show great affinity to sorption, the ratio for sulfamethazine was 1:2 (w/v) for almost all soil samples except for soil sample 3 (1:5, w/v) which is characterised by a high content of OM (Table 2). For all experiments, 1 g of air-dried soil was equilibrated with 1.8 or 4.5 mL of 0.01 M CaCl$_2$ solution overnight (12 h) before the day of the experiment and then 0.2 or 0.5 mL of the sulfamethazine solution was added to adjust the final volume (2.0 or 5.0 mL). Sodium azide (2 mg) was added into each sample to suppress microbial activity during equilibration. Seven different sulfamethazine solutions (1.0, 2.0, 3.0, 5.0, 10.0, 30.0, and 50.0 mg/L) were used for determining the sorption isotherms. The mixture is agitated for 24 h, according to preliminary experiments. The soil suspensions are separated by centrifugation at 5000 rpm for 10 min and, if necessary, the centrifugate is filtrated by 0.45 μm syringe filters and the aqueous phase is analysed.

Blank samples containing the same amount of soil in contact with 2.0 or 5.0 mL of 0.01 M CaCl$_2$ solution is also included in the analysis. This serves as a backup control during the analysis to detect interfering compounds or contaminated soils.

The influence of external factors on the sorption of pharmaceuticals, e.g. ionic strength, was also investigated. For this purpose, all soils were equilibrated with different CaCl$_2$ concentrations; 0.001 M, 0.01 M and 0.1 M. The whole procedure is identical to the one described above.

2.4. LC–ESI-tandem MS analysis

Sulfamethazine in the filtrate samples from the sorption studies were analysed by LC–MS/MS. The LC analysis was performed using an Agilent Series 1200 HPLC system (Santa Clara, CA, USA) equipped with a Synergy Fusion C18 embedded column (150 mm × 4.60 mm, particle size 4 μm) supplied by Phenomenex. The mobile phase used in the chromatographic separation consisted of a binary mixture of eluent A (0.1%

Table 2
Physico-chemical properties of soil samples.

Parameter	Soil samples							
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8
Coarse sand,%	40.40	56.65	67.60	45.20	42.00	4.40	29.90	2.55
Clay,%	0.05	0.05	0.00	0.10	0.05	0.10	0.05	0.10
Silt, %	0.25	0.10	0.00	0.15	0.30	0.30	0.25	0.25
Fine sand,%	59.30	43.20	32.35	54.55	57.65	95.20	70.50	97.10
pH	5.75	7.25	6.51	7.09	6.37	7.20	6.58	6.45
EC, μS/cm	111.90	44.60	2.90	115.30	149.80	130.80	196.00	352.00
TDS[a], mg/L	71.62	28.54	1.86	73.79	95.87	83.71	125.44	225.28
CEC, mmol/kg	44.81	15.78	70.00	51.06	86.48	91.03	31.36	34.47
OM, %	3.08	1.52	12.8	3.48	7.48	2.08	5.06	2.04
CaCO$_3$, %	0.063	79.71	33.00	9.40	0.44	12.52	3.50	20.30
Zn, mg/kg	2.95	0.66	8.92	0.85	2.41	21.43	27.54	4.52
Cu, mg/kg	5.25	1.25	2.88	1.60	8.40	5.93	9.12	62.90
Fe, mg/kg	143.91	24.56	89.75	20.21	83.05	17.73	167.43	42.44
Mn, mg/kg	37.97	22.57	25.35	9.54	35.16	30.26	106.70	46.40

[a] Total dissolved solids.

formic acid in MilliQ water) and eluent B (0.1% formic acid in acetonitrile). A simultaneous mobile phase gradient programme was used: the elution started with a 4 min linear gradient from 70% A to 60% B, followed by a 4 min linear gradient to 95% B which was maintained for 1 min and then a 0.1 min linear gradient back to 70% of A. After the gradient elution, the column was equilibrated for 2 min before another injection. The flow rate amounted to 0.5 mL/min. An injection volume of 10 μL was applied in all analyses. The tandem MS analyses were carried out on an Agilent 6410 triple quadrupole mass spectrometer equipped with an ESI interface. The analyses were conducted in the positive ion (PI) mode. The parameters for the analyses were as follows: drying gas temperature 350 °C; capillary voltage 4.0 kV; drying gas flow 11 L/min, and nebulizer pressure 35 psi. Sulfamethazine was analysed by MRM, using the two highest characteristic precursor ion/product ion transitions (m/z 279 → 92; m/z 279 → 156).

The optimal collision energy (30 eV) and fragmentor voltage (130) were chosen for the multiple reaction monitoring (MRM) experiment. The instrument control, data acquisition and evaluation were carried out with the MassHunter Agilent 2003–2007 Data Acquisition for Triple Quad B.01.04 (B84) software.

2.5. Modelling of sorption isotherms

Sorption isotherms are preconditions for understanding the nature of interaction between the sorbate (sulfamethazine) and the sorbent (natural soil). In order to describe the mechanism of sulfamethazine sorption on the soil, the data obtained from the sorption experiments were fitted to the Linear isotherm (one-parameter model) (Liao et al., 2014; Białk-Bielińska et al., 2012; Hörsing et al., 2011; Goldberg, 2005), the Freundlich (Kim et al., 2012; Liu et al., 2011; Goldberg, 2005; Freundlich, 1906) and the Dubinin–Radushkevich isotherm (two-parameter models) (Chao et al., 2014; Zhang et al., 2011; Domínguez et al., 2011; Foo and Hameed, 2010). The equation and linearized form of these isotherm models are given in Supplementary information, Table S1.

2.5.1. Linear isotherm

Soil is a complex matrix consisting of a mineral and an organic fraction. The mineral fraction consists of various silicates and various metal oxides/hydroxides of aluminium, iron, and manganese, and the organic reaction of organic matter. The Linear isotherm as a one-parameter model is the simplest model for describing the solute (sulfamethazine) partition in the solution and the surface of the sorbent (soil) in the evaluation of the sorption behaviour. This model obeys Henry's law at low concentration and is expressed with (Hörsing et al., 2011; Yamamoto et al., 2009):

$$q_e = K_d \cdot C_e \qquad (2)$$

K_d (Henry's law constant) is defined as the ratio between the equilibrium of test substance concentrations (sulfamethazine) in a sorbent (soil) and that of its aqueous phase solution and can be calculated with the following formula:

$$K_d = \frac{\text{amount of SMET in sorbent}}{\text{amount of SMET in solution}} \times \frac{V}{m} = \frac{q_e}{C_e} \times \frac{V}{m}$$
$$= \frac{C_0 - C_e}{C_e} \times \frac{V}{m} [\text{mL/g}] \qquad (3)$$

where q_e is the equilibrium sorption capacity in μg/g; C_0 and C_e are the initial and the equilibrium concentration of sulfamethazine in μg/mL; V is the volume of SMET solution in mL and m is the total amount of soil in g.

The linear K_d distribution coefficient was determined from the slope obtained in the low range of the SMET aqueous concentration, where sorption isotherms (C_e vs. q_e) are often linear. In our experiment, K_d

was calculated at the concentration range below 5 μg/mL, where all the isotherms were linear (Estevez et al., 2014).

In the Henry's law range (low equilibrium concentration), the standard free energy change (ΔG°) can be expressed as (Liao et al., 2014; Zhang et al., 2011):

$$\Delta G^\circ = -RT \ \ln K_d \qquad (4)$$

where R is the gas constant (8.314 J/mol K) and T is the solution temperature (K).

Since the organic matter in soils is highly variable, an approach for sorption coefficients which takes into account the organic carbon (OC) was used. A number of studies have demonstrated that the K_d coefficient for the sorption of a single organic contaminant onto a variety of soil materials can be related to the organic content of the sorbent. This observation permits the definition of the organic normalised partitioning coefficient (K_{oc}) (Durán-Álvarez et al., 2012; Kile et al., 1995; Means et al., 1980):

$$K_{oc} = \frac{K_d}{\%OC} * 100. \qquad (5)$$

From the organic matter (OM) content obtained for each soil it is possible to calculate the organic carbon (OC) content using the relationship (Doretto and Rath, 2013; Sabljic, 1989):

$$\frac{\%OM}{\%OC} = 1.724. \qquad (6)$$

2.5.2. Freundlich isotherm

The Freundlich isotherm as a two-parameter model is the earliest known relationship describing the sorption equation. The model applies to sorption onto heterogeneous surfaces with a uniform energy distribution. The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorption centres of the sorbent (Freundlich, 1906). The model can be expressed as:

$$q_e = K_F \cdot C_e^{1/n} \qquad (7)$$

where

q_e is the amount of SMET sorbed per unit of sorbent — soil (μg/g),
C_e is the concentration of SMET at sorption equilibrium (μg/mL),
K_F is the constant indicative of the relative sorption capacity of the sorbent $((\mu g/g)(mL/\mu g)^{1/n})$, and 1/n is the heterogeneity factor.

The linear form of the Freundlich isotherm is shown in Supplementary information, Table S1 and K_F and n can be calculated from the slopes and the intercepts of the plot ln (q_e/C_e) versus q_e.

2.5.3. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm as a two-parameter model was used to estimate the apparent free energy of sorption as well as to make a difference between the physical and the chemical sorption process (Dubinin and Radushkevich, 1947). The above mentioned equation was given by the following relationship:

$$q_e = q_m \exp\left(-\beta \varepsilon^2\right) \qquad (8)$$

where:

q_e the equilibrium solid phase concentration (μg/g),
q_m the theoretical saturation capacity (μg/g),
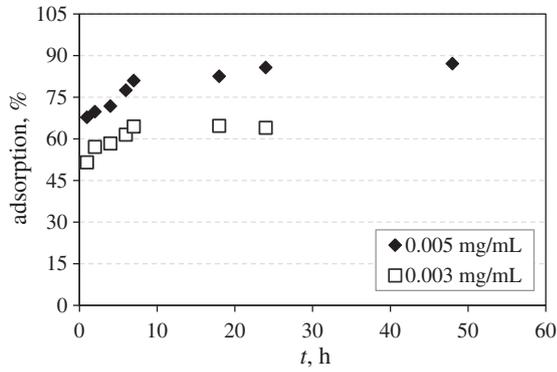β the constant of the sorption energy (mol²/kJ²),

Fig. 1. Kinetics for SMET on the soil samples (soil 3). $T = 25$ °C.

ε the Polanyi potential, which is described in Zhang et al. (2011) as:

$$\varepsilon = RT\ \ln(1 + 1/C_e). \tag{9}$$

The linear form of the Dubinin–Radushkevich isotherm is shown in Supplementary information, Table S1. The values of q_m and β can be calculated from the intercept and the slope of the plot $\ln q_e$ versus ε^2.

The value of sorption energy E (kJ/mol) can be correlated to β by using the following equation (Zhang et al., 2011):

$$E = \frac{1}{\sqrt{-2\beta}}. \tag{10}$$

This parameter gives information about whether the sorption mechanism is physical sorption or ion-exchange. If the value of E is <8 kJ/mol, the sorption process is of a physical nature; if the magnitude of E is between 8 and 16 kJ/mol, the sorption process follows the ion-exchange mechanism (Chao et al., 2014; Zhang et al., 2011; Domínguez et al., 2011).

2.6. Error functions for non-linear regression analysis

Linear regression using the method of least squares was the most commonly used method in determining the isotherm parameters. As an alternative to the linear transformation, nonlinear optimization has also been applied to determine the isotherm parameter values. The optimization procedure requires the selection of an error function in order to evaluate the fit of the isotherm to the experimental equilibrium data. Therefore, in this study, besides the coefficient of determination, (R^2), the residual root mean square error (RMSE) (Hadi et al., 2010), the sum of squares of errors (ERRSQ) (Foo and Hameed, 2010; Hadi et al., 2010; Ahmaruzzaman and Laxmi Gayatri, 2010), and the hybrid fractional error function (HYBRID) (Foo and Hameed, 2010; Hadi et al., 2010; Ncibi, 2008) were applied to confirm the best fitting. The error functions employed and their expressions are presented in Supplementary information, Table S2 (Foo and Hameed, 2010; Hadi et al., 2010; Ahmaruzzaman and Laxmi Gayatri, 2010; Ncibi, 2008). The various isotherms obtained were analysed by the non-linear curve fitting using the MATLAB-7 software.

3. Results and discussion

3.1. Effect of contact time

The effect of the contact time on the sorption of SMET on the soil sample 3 was studied for initial SMET concentrations of 3 and 5 μg/mL (Fig. 1). All experiments were performed in triplicate, and the mean values are reported. Soil sample 3 is selected on the basis of its physico-chemical properties, primarily the organic matter content.

The data obtained from the sorption of SMET on the soil samples (soil 3) showed that a contact time of 24 h was sufficient to achieve equilibrium and the sorption did not change significantly with further increase in contact time (Fig. 1). The time to reach equilibrium conditions appears to be independent of initial sulfamethazine concentrations.

The sorption of sulfamethazine increased from 64 to 85% by increasing the sulfamethazine concentration from 3 to 5 μg/mL. This is in line with expectations as the test concentrations are rather small and they
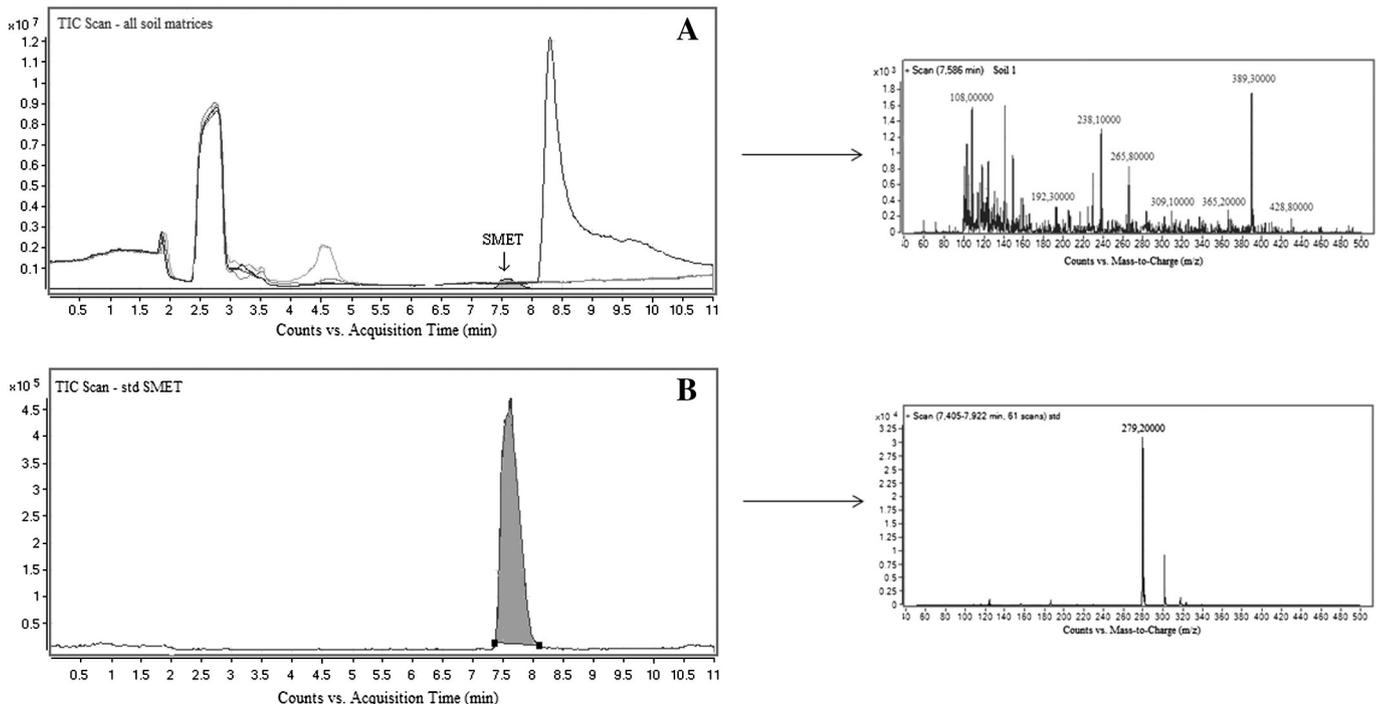

Fig. 2. Total ion chromatogram of A) investigated soil matrices and B) standard solution of SMET with corresponding LC–MS/MS spectra.

do not result in the saturation of the test soil. Further, it was observed that the sorption curves are smooth and continuous, which could indicate a possibility of the formation of sulfamethazine monolayer coverage on the surface of investigated soil. Therefore, we tried to use the Langmuir isotherm to fit the sorption experiments data and a high coefficient of determination was obtained. However, the obtained negative values for the Langmuir isotherm constants for the SMET sorption on the investigated soil samples indicate that the Langmuir sorption isotherm is not suitable for explaining the sorption process since these constants are indicative of the surface binding energy and monolayer coverage. Thus the Linear, Freundlich, and Dubinin–Radushkevich sorption isotherms were used for analyses of SMET sorption on the investigated soil samples.

3.2. Effect of sulfamethazine concentration and ionic strength

The equilibrium aqueous sulfamethazine concentrations used in the sorption experiments ranged from approximately 0.1 μg/mL to 5 μg/mL, which were equivalent to concentrations ranging between 0.5 and 25 mg/kg soil. This concentration range was in accordance with the expected soil concentrations of approximately 0.5–1.5 mg/kg soil in the field, based on a sulfamethazine concentration of 5–15 mg/kg of wet swine manure applied to the soils (Haller et al., 2002). Possible sorption of sulfamethazine on the surface of test vessels, as well as its stability in the solution was evaluated. For this purpose, control samples with highest concentrations (5 μg/mL) of sulfamethazine in 0.01 M CaCl$_2$ were employed and analysed by LC–MS/MS. The results showed that sulfamethazine is stable in the medium during the required time and no sorption onto the vessels occurs. Also, no interferences of the eight different soil sample matrices in the chromatograms were observed under the established experimental conditions, conferring an adequate selectivity to the method. The characteristic chromatograms of the blank soil samples in 0.01 M CaCl$_2$ and 5 μg/mL SMET in 0.01 M CaCl$_2$ are presented in Fig. 2.

From the Fig. 2 is obvious that soil sample 1 did not contain the SMET. Absence of characteristic m/z SMET ion (m/z 279) is a sufficient proof for it. For other soil samples were obtained the same results and therefore not shown their corresponding LC–MS/MS spectra.

The effect of solution ionic strength on the sorption of SMET in soil samples was evaluated at 0.001, 0.01, and 0.1 M CaCl$_2$. The effects of ionic strength on the sorption of SMET isotherms on eight soil samples at 25 °C are shown in Fig. 3. Obtained results indicate that the sorption of SMET on all investigated soil samples depends on the ionic strength; the sorption decreases as the CaCl$_2$ concentration increases.

3.3. Sorption isotherms

The equilibrium data were further analysed using the linearized form of the Linear, the Freundlich and the Dubinin–Radushkevich equation using the same set of experimental data. Calculated values of the distribution coefficient (Henry's law constant) K_d, of the organic normalised partitioning coefficient K_{oc} and of the Freundlich and the Dubinin–Radushkevich model parameters obtained using the linear regression method are summarized in Table 3. All presented values were expressed by its average value of three determinations. Achieved relative standard deviations were lower than 10%.

In most cases, correlation coefficients show slightly higher values in the Linear model than in the Freundlich model, but the lowest value of correlation coefficient was obtained in the Dubinin–Radushkevich model.

The magnitude of the exponent n gives an indication as to the favourability of sorption. From the data in Table 3, n values are about 1, indicating that the sorption of sulfamethazine onto soil samples is favourable (Goldberg, 2005).

The values of sorption energy E (kJ/mol) evaluated from Eq. (8) are from 2.16 ± 0.10 to 4.82 ± 0.23, which indicate that the sorption of SMET on the soil sample is of a physical nature (Chao et al., 2014; Zhang et al., 2011; Domínguez et al., 2011).
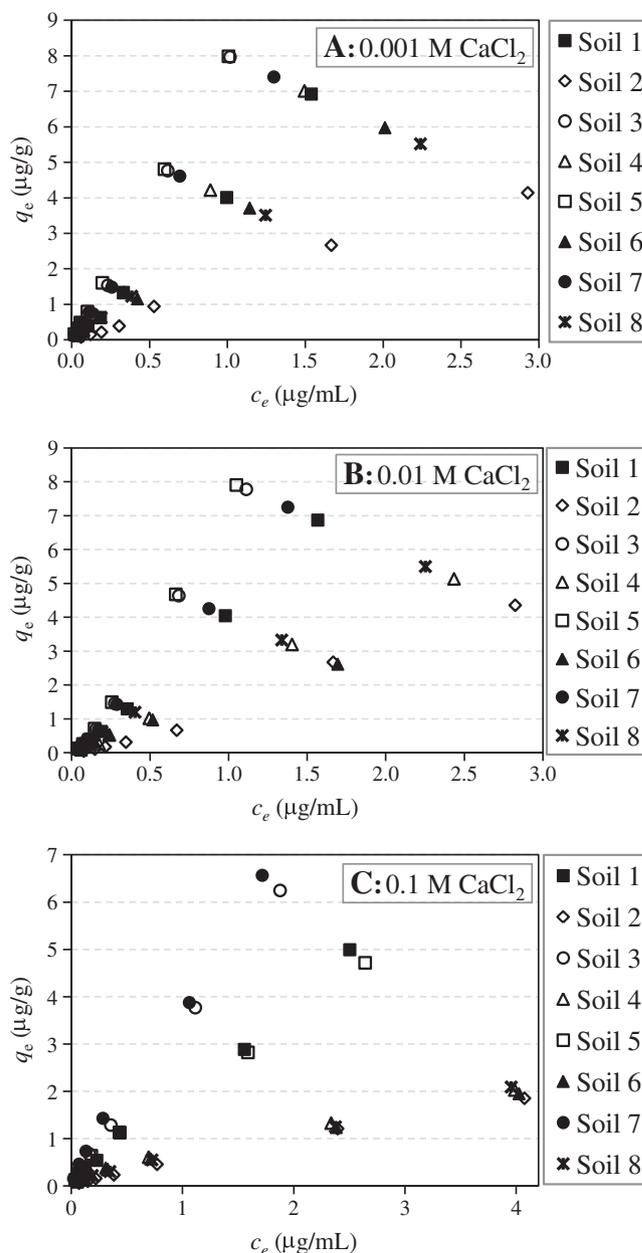

Fig. 3. Equilibrium sorption isotherms of SMET on soil samples at 25 °C at the concentration of CaCl$_2$ (A) 0.001 M, (B) 0.01 M and (C) 0.1 M.

SMET adsorbed differently onto investigated soils. The Freundlich adsorption coefficients ranged from 1.16 ± 0.04 to 7.99 ± 0.31 (μg/g)(mL/μg)$^{1/n}$. The relatively low values obtained for the Freundlich sorption coefficients (K_F) indicate that SMET is most likely highly mobile in soil.

The highest values of the relative sorption capacity (K_F) and the theoretical saturation capacity (q_m) are obtained for sorption experiments performed with the lowest ionic strength (0.001 M CaCl$_2$).

From the results presented in Fig. 4 it is clear that the distribution coefficient (K_d) increased with the soil OM, i.e. with the OC content, and decreased with an increase in ionic strength (concentration of CaCl$_2$).

3.4. Factors influencing the sorption of sulfamethazine by soil samples

The estimated K_d values ranging from 0.25 ± 0.008 to 8.10 ± 0.32 mL/g indicate a low sorption of SMET on all tested soils which were in the same range as the values reported before. According to
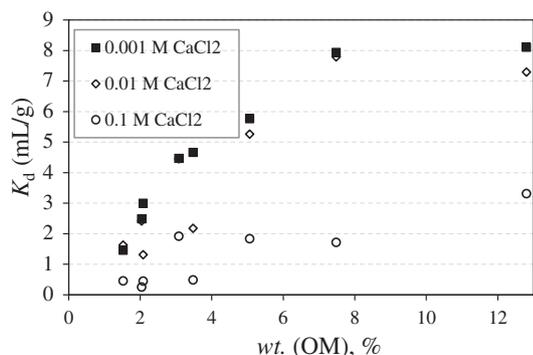
Table 3

The Linear, Freundlich and Dubinin–Radushkevich sorption isotherm parameters obtained using the linear method (K_F ((μg/g)(mL/μg)$^{1/n}$), β(mol^2/kJ^2), q_m (μg/g)).

Soil	Isotherm									
	Linear			Freundlich			Dubinin–Radushkevich			
	K_d, mL/g	K_{oc} mL/g	R^2	n	K_F	R^2	β	q_m	E	R^2
0.001 M CaCl$_2$										
1	4.46	249.64	0.9965	0.92	4.25	0.9984	0.0622	3.94	2.84	0.9099
2	1.45	164.46	0.9929	0.96	1.48	0.9924	0.0773	1.97	2.54	0.8379
3	8.10	109.10	0.9991	0.85	7.99	0.9954	0.0556	4.98	2.99	0.8959
4	4.66	230.86	0.9982	1.13	4.40	0.9925	0.0410	3.52	3.49	0.8654
5	7.93	182.77	0.9999	1.06	7.69	0.9988	0.0381	4.76	3.62	0.9027
6	2.99	247.83	0.9968	1.12	3.04	0.9949	0.0483	2.93	3.13	0.8550
7	5.76	196.25	0.9935	1.15	5.76	0.9947	0.0370	4.18	3.68	0.8964
8	2.48	209.58	0.9941	1.07	2.82	0.9980	0.0571	3.11	3.68	0.9046
0.01 M CaCl$_2$										
1	4.45	249.08	0.9989	0.84	1.16	0.9986	0.0707	2.46	2.66	0.9002
2	1.62	183.74	0.9940	0.77	1.21	0.9982	0.107	1.89	2.16	0.8557
3	7.29	98.19	0.9982	0.78	7.16	0.9979	0.0684	5.08	2.70	0.9154
4	2.17	107.50	0.9973	0.87	2.08	0.9926	0.0843	2.70	2.43	0.9943
5	7.79	179.54	0.998	0.78	7.70	0.9948	0.0664	5.18	2.74	0.9096
6	1.31	108.58	0.9912	1.13	1.63	0.9964	0.0628	2.15	4.82	0.8909
7	5.26	179.21	0.9980	0.90	5.11	0.9978	0.0607	4.35	2.87	0.9169
8	2.41	203.67	0.9989	1.07	2.60	0.9973	0.0561	2.80	2.99	0.8705
0.1 M CaCl$_2$										
1	1.91	106.91	0.9956	1.15	2.14	0.9952	0.0539	2.45	3.05	0.8964
2	0.45	51.04	0.9960	1.16	1.79	0.9987	0.0736	1.16	2.61	0.8140
3	3.31	44.58	0.9994	0.99	3.51	0.9955	0.0610	3.69	2.86	0.9232
4	0.48	23.78	0.9905	1.41	1.31	0.9975	0.0557	1.07	2.99	0.8561
5	1.71	39.41	0.9949	1.21	2.13	0.9933	0.0521	2.51	3.10	0.8899
6	0.44	36.47	0.9932	1.66	1.29	0.9927	0.0430	1.01	3.41	0.8319
7	1.83	62.35	0.9969	1.18	3.99	0.9977	0.0414	3.56	3.48	0.8948
8	0.25	21.13	0.9966	1.38	1.41	0.9975	0.0555	1.03	3.00	0.8098

Table 4

Calculated percentage of ionic forms of the investigated SMET as a function of pH, pK_{a1}, and pK_{a2}.

	Soil pH	Cationic form [%]	Neutral form [%]	Anionic form [%]
Soil 1	5.75	0.06	97.76	2.19
Soil 2	7.25	0.00	58.54	41.46
Soil 3	6.51	0.01	88.58	11.41
Soil 4	7.09	0.00	67.13	32.86
Soil 5	6.37	0.01	91.46	8.53
Soil 6	7.20	0.00	61.32	38.68
Soil 7	6.58	0.01	86.85	13.14
Soil 8	6.45	0.01	89.90	10.09

109.10 ± 3.97 to 249.64 ± 10.43 L/kg at 0.001 M, and the K_{oc} values ranged from 21.13 ± 0.63 to 106.91 ± 6.55 L/kg at 0.1 M CaCl$_2$. The fairly similar K_{oc} values typically indicate the influence of OC on the sorption of organic compounds (Pereira Leal et al., 2013; Lertpaitoonpan et al., 2009).

The shape of the sorption isotherms for SMET in eight investigated soils under varying ionic strengths reveals that the soils behaved differently with increased ionic strength. In literature, a positive influence of ionic strength on sorption results for sulfonamides as well as other organic compounds is recorded. This can be attributed to the replacement of protons from the soil surface as ionic strength increases, causing a slight reduction in pH, and shifting the acidic compound towards neutral forms that are more strongly sorbed than the anionic forms (Srinivasan et al., 2013; Laak et al., 2006; de Jonge and de Jonge, 1999). In the present study, all soils exhibited an opposite and irregular trend in sorptive affinity for SMET, i.e. an increase in ionic strength resulted in decreased sorption coefficients of SMET. Similar trends were also recently observed for sulfadimethoxine and sulfaguanidine in soils from northern Poland (Białk-Bielińska et al., 2012) and could be explained by decreased thickness of the "electrical double layer" of the charged surface. This effect results in a decreasing surface charge, and, finally, in a smaller number of interactions between the protonated form of the compound and the soil surface.

Sulfamethazine is an amphoteric compound with two relevant ionisable groups, the basic 4-amine aromatic ($pK_{a1} = 2.5$) and the acid sulfonamide ($pK_{a2} = 7.4$) moieties (chemical structure of SMET and its protoned and deprotoned form are presented in Supplementary information, Fig. S1). However, only the dissociation constant of the acid group (pK_{a2}) is relevant for our set of soils, which have pH values ranging from 5.75 to 7.25. Due to the natural pH of the tested soils (and soils in general) and to the fact that the neutral species are dominant between pK_{a1} and pK_{a2}, sulfamethazine exists mostly as a neutral molecule (see pK_{a2} and pH of soils in Table 2) rather than in an ionised form, so the "salting out" effect of the soil surface is also possible (Białk-Bielińska et al., 2012). But, in view of SMET properties and soil pH, the percentage of each ionic form can be expressed as a function of pH and pK_a (Sukul et al., 2008), and calculated (Table 4) on the basis of equations given by Schwarzenbach et al. (2003).

literature data, it has been found that the sorption potential and the mobility of a pharmaceutical drug is strongly influenced by the soil physico-chemical properties (pH, OC, CEC, soil texture), the ionic strength of the soil solution, and the physico-chemical properties of tested compounds (Srinivasan et al., 2014; Lertpaitoonpan et al., 2009; Thiele-Bruhn et al., 2004). Therefore, it is very important to determine the factors affecting sorption. All investigated soil samples were sandy structure (Table 2) so the estimated K_d values show a good match with those shown in Table 1. Obtained results (Table 3) of SMET sorption on eight different soil samples indicate that OM and ionic strength are also important adsorbing component of soils. Fig. 4 shows the relationship between the K_d values and the soil OM content at different concentrations of CaCl$_2$ (ionic strength).

To assess the role of organic carbon content, the K_d values were normalised with OC to obtain K_{oc}, as shown in Table 3. The obtained K_{oc} values for the eight investigated soils were fairly similar, ranging from

Table 5

The thermodynamic parameter, $\Delta G°$ at different concentrations of CaCl$_2$ (0.001 M, 0.01 M and 0.1 M).

Soil	$\Delta G°$, kJ/mol		
	0.001 M CaCl$_2$	0.01 M CaCl$_2$	0.1 M CaCl$_2$
1	−3.39	−3.39	−1.47
2	−0.84	−1.09	1.81
3	−4.75	−4.51	−2.72
4	−3.49	−1.76	1.67
5	−4.70	−4.66	−1.22
6	−2.49	−0.61	1.86
7	−3.97	−3.77	−1.37
8	−2.06	−2.00	3.15

Fig. 4. Relationship between K_d values and soil organic matter content (OM) for sorption SMET at different concentrations of CaCl$_2$ (0.001 M, 0.01 M and 0.1 M).
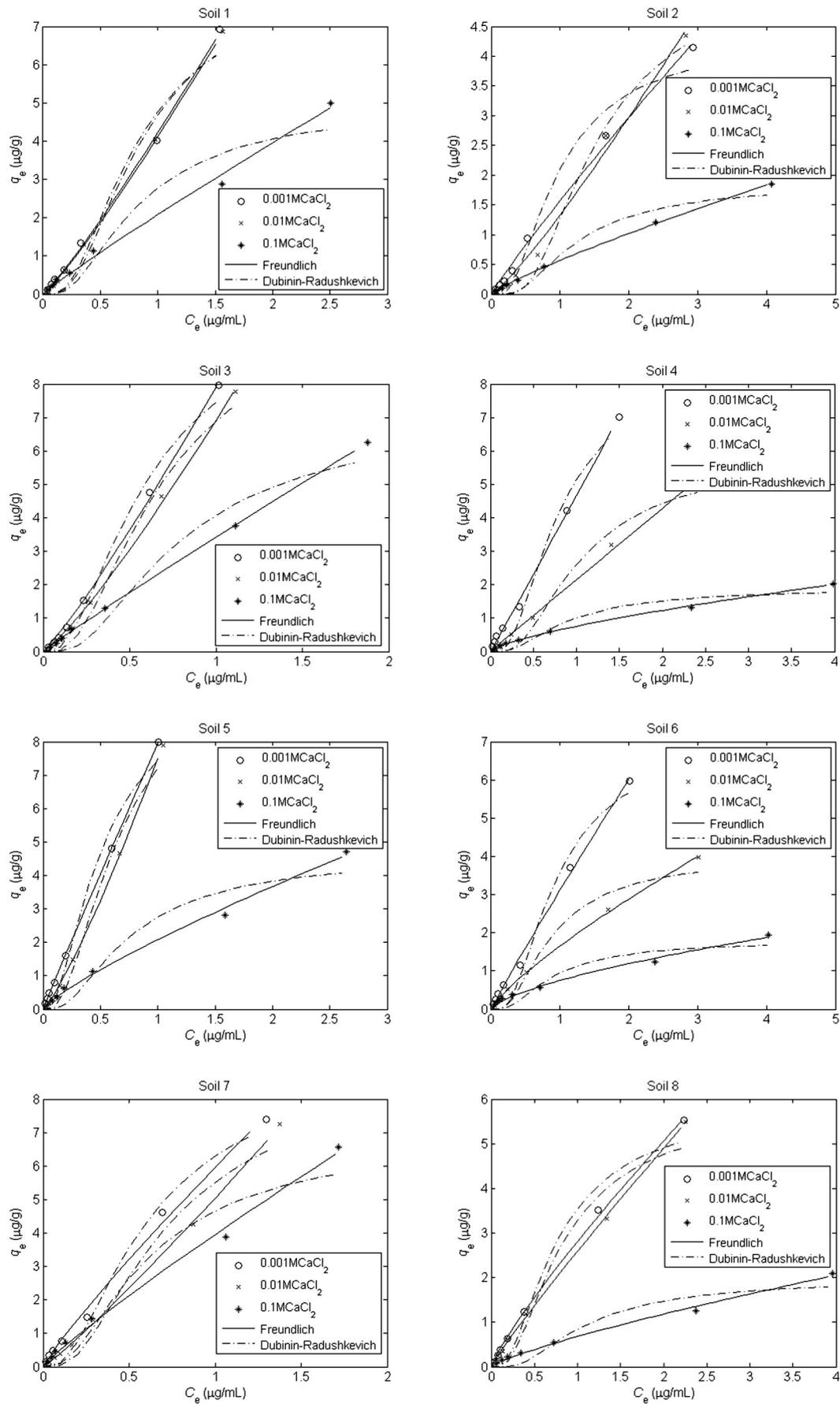
Fig. 5. The Freundlich and Dubinin–Radushkevich isotherms obtained using the non-linear method for the sorption of SMET onto eight soil samples at a temperature of 25 °C and at different concentrations of CaCl₂.

The existence of the anionic form of SMET is becoming more pronounced as the soil pH comes closer to its pK_{a2} value. This form can lead to electrostatic repulsion between the anionic form of SMET and the negative charge of soil surface. Unlike the partition of neutral molecules to solid matrices via the relatively weak van der Waals and electron donor–acceptor interactions, charged species can interact through stronger electrostatic mechanisms, such as cation exchange, cation bridging and complexation (Maszkowska et al., 2013).

3.5. Free energy of sorption

Thermodynamic parameter, the standard free energy change in the sorption process ($\Delta G°$), was calculated according to Eq. (3) and results are shown in Table 5.

$\Delta G°$ is an important parameter that can indicate the characteristics of sorption on soil samples. The negative values of $\Delta G°$ at the 0.001 M and the 0.01 M concentration of $CaCl_2$, for all investigated soil samples, confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for SMET to sorb on soil. Values of $\Delta G°$ slightly increased with the increase concentration of $CaCl_2$ from 0.001 to 0.01 M. On the other hand, by increasing the concentration of $CaCl_2$ (from 0.01 up to 0.1 M), changes in the values of $\Delta G°$ are bigger, and for soil samples 2 and 6 become positive, which indicates that the sorption process has become non-spontaneous.

3.6. Error analysis

Comparison of the Freundlich and Dubinin–Radushkevich isotherms obtained using the non-linear method for the sorption of SMET on soil samples at a temperature of 25 °C are shown in Fig. 5.

The Freundlich and the Dubinin–Radushkevich isotherm parameter as well as error values obtained using the non-linear methods are presented in Supplementary information, Table S3.

According to the data presented in Supplementary information, Table S3, which also include the values of the determination coefficient (R^2), the residual root mean square error (RMSE), the sum of squares of errors (ERRSQ), and the hybrid fractional error function (HYBRID), it is clear that the Freundlich model is more suitable than the Dubinin–Radushkevich model. Higher R^2 values and lower RMSE, ERRSQ and HYBRID values were achieved when the Freundlich model was used for modelling the equilibrium data, both in the linear and the non-linear regression analysis (Tables 3 and S3).

4. Conclusion

This study demonstrated that the sulfamethazine sorption affinity is strongly governed by a multitude of factors (physico-chemical characteristics of the soil samples and physico-chemical characteristics of sulfamethazine). Sorption capacity was found to increase with an increase in initial concentration, agitation time, and OC contents; on the other hand, it decreased with an increase in ionic strength. Linear sorption coefficients (K_d) were highest at the lowest ionic strength tested (at 0.001 M $CaCl_2$), but K_d decreased as ionic strength increased. The sorption of sulfamethazine in this study followed the sorption trend of soil 2 < soil 8 < soil 6 < soil 1 < soil 4 < soil 7 < soil 5 < soil 3 (at 0.001 M $CaCl_2$). The soil with the highest content of OM (soil 3) has the highest sorption potential, thus confirming the theory that the K_d values are directly proportional to the OM of soils. The soil with the lowest sorption potential (soil 2) under the same conditions exhibited almost the lowest content of OM and concentrations of total dissolved solids and also the lowest cation exchange capacity. Sulfamethazine sorption was found to be highly pH dependent, and at the soil pH of 5.75 to 7.25, SMET exists partially as anionic and partially as neutral species. The presence of the neutral species is more favourable for the sorption potential of sulfamethazine.

These results confirmed that sulfamethazine is highly mobile in soil, so all the findings stated above are important from the point of view of groundwater protection and the environment in general, and because of that they will contribute to a better understanding of the environmental fate of sulfamethazine.

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