



On-line solid phase extraction-ultra high performance liquid chromatography-tandem mass spectrometry as a powerful technique for the determination of sulfonamide residues in soils[☆]



Natália Fernanda Tetzner^a, Milena Guedes Maniero^b, Caio Rodrigues-Silva^a,
Susanne Rath^{a,*}

^a Institute of Chemistry, Department of Analytical Chemistry, University of Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

^b School of Civil Engineering, Architecture and Urban Design, University of Campinas, P.O. Box 6143, 13083-889 Campinas, SP, Brazil

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ABSTRACT

Sulfonamides are antimicrobials used widely as veterinary drugs, and their residues have been detected in environmental matrices. An analytical method for determining sulfadiazine, sulfathiazole, sulfamethazine, sulfamethoxazole, sulfadimethoxine and sulfaquinoxaline residues in soils employing a solid phase extraction *on-line* technique coupled with ultra-high performance liquid chromatography and tandem mass spectrometry (SPE-UHPLC-MS/MS) was developed and validated in this study. SPE and chromatographic separation were performed using an Oasis HLB column and an Acquity UPLC BEH C18 analytical column, respectively, at 40 °C. Samples were prepared by extracting sulfonamides from soil using a solid-liquid extraction method with water:acetonitrile, 1:1 v/v (recovery of 70.2–99.9%). The following parameters were evaluated to optimize the *on-line* SPE process: sorbent type (Oasis and C8), sample volume (100–400 µL), loading solvent (water and different proportions of water:methanol) and washing volume (0.19–0.66 mL). The method produced linear results for all sulfonamides from 0.5 to 12.5 ng g⁻¹ with a linearity greater than 0.99. The precision of the method was less than 15%, and the matrix effect was –27% to –87%. The accuracy was in the range of 77–112% for all sulfonamides. The limit of quantitation in the two soils (clay and sand) was 0.5 ng g⁻¹. The SPE column allowed for the analysis of many (more than 2000) samples without decreasing the efficiency.

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1. Introduction

Antimicrobials are widely used to prevent and treat animal diseases, particularly in intensive farming. In general, antimicrobials are poorly metabolized in animals and are therefore excreted in urine and feces. Antimicrobials have been detected in soil, sediment, surface water and ground water [1–3]. Active antimicrobials can reach the environment from grazing livestock or from manure spread on agricultural soils. After reaching the environment, antimicrobials can sorb onto soils and sediments, be transported to ground or surface waters or be degraded. The presence of antimicrobials in a specific environment, their rate of

spreading and their accumulation at the water-soil interface differs based on the chemical structure of the antimicrobials and the soil properties.

Sulfonamides (SAs) have been used as synthetic antimicrobials since 1937 and are the oldest and most widely employed antimicrobial agents in veterinary medicine because of their low cost and relatively high efficacy for treating bacterial diseases. Nearly 70 different SA formulations are available in the Brazilian market. The main sulfonamides used in veterinary drugs are: sulfadiazine (18 formulations), sulfamethazine (16 formulations), sulfaquinoxaline (12 formulations), sulfamethoxazole (6 formulations), sulfadimethoxine (6 formulations) and sulfathiazole (1 formulation) [4].

Furthermore, Brazil is a major worldwide producer and exporter of animal protein. According to the Brazilian Ministry of Agriculture and Livestock, Brazil will supply 44.5% of the meat required for global consumption in 2020 [5]. In contrast, government agencies

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* Corresponding author.

E-mail address: Susanne.rath@gmail.com (S. Rath).

have not paid attention to the impacts of these veterinary drugs in the environment.

The presence of SAs may affect soil microorganisms and soil functions and raises concerns about the development of resistant pathogenic bacteria genes. It is important to emphasize that the presence of antimicrobials in the environment is not only of concern because of the potential development of resistant bacteria but also because of their potential role in decreasing the activities of different antimicrobial classes due to cross-resistance [6], which may directly affect soil health. Moreover, as reported in our previous study [7,8], the relatively low sorption coefficients of these substances indicate weak interactions between the neutral forms of the molecules and the soil binding sites, which suggests that these antimicrobials could reach surface and ground waters after they are dispersed in the soil. SAs have already been quantified in water matrices in the range of ng L^{-1} [9].

Few studies have reported the presence of SAs in soils [1,10,11], which concentrations are in the pg g^{-1} to ng g^{-1} range. Nevertheless, when manure is applied to agricultural soils, SA concentrations may increase to the $\mu\text{g g}^{-1}$ level [10].

Due to the complexity of the soil matrix and the low concentrations of the target compounds, the analytical method of choice for determining the presence of antimicrobial residues is liquid chromatography with tandem mass spectrometry [12,13]. Even when using a high selective method, sample preparation procedures are required to extract the analyte from the soil, reduce matrix effects and enhance detectability. For extraction, solid-liquid extraction (SLE), ultrasonic-assisted extraction (USE), microwave-assisted extraction (MAE) and pressurized liquid extraction (PLE) have been employed [2,14,15]. For the clean-up and concentration steps, solid-phase extraction (SPE) using more than one cartridge has been used [16,17]. SPE can be performed in *off-line* or *on-line* mode. However, *off-line* SPE is time consuming and requires extensive sample handling, which increases the method uncertainty. Moreover, *on-line* SPE allows large volume injection, which increases the detection sensitivity.

Bordat-Deschamps et al. [18] developed a multiresidue method for determining 13 pharmaceuticals, including two sulfonamides, that uses SPE-UHPLC–MS/MS; however, this method was only validated for aqueous environmental samples. To the best of our knowledge, no reports of the application of *on-line* SPE in a validated method to determine soil SAs are available in the literature.

Based on this scenario, the aim of this study was to develop and validate an *on-line* SPE process coupled with ultra-high performance liquid chromatography and tandem mass spectrometry (SPE-UHPLC–MS/MS) for determining SA residues in Brazilian soils.

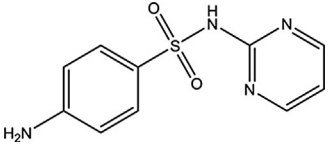
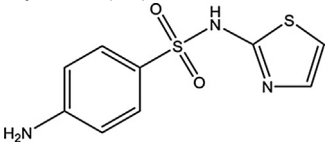
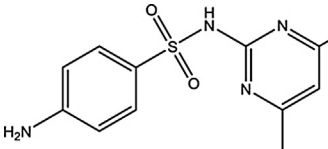
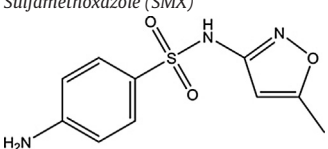
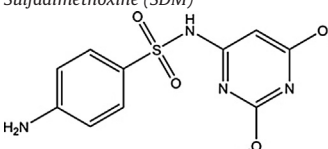
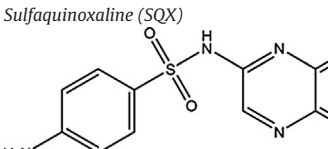
2. Experimental

2.1. Chemicals and reagents

All solvents used in this study were HPLC grade, and all reagents were analytical grade or purer. Formic acid was obtained from Synth (USA), and water was obtained from a Milli-Q purification system (Millipore, USA). Analytical sulfadiazine (SDZ, 99%), sulfathiazole (STZ, 99%), sulfamethazine (SMZ, 99%), sulfamethoxazole (SMX, 99%) and sulfaquinoxaline (SQX, 95%) standards were purchased from Sigma-Aldrich (USA). Sulfadimethoxine (SDM, 99%) and the internal standard sulfachloropyridazine (SCP, 99%) were obtained from Fluka (USA). The molecular structure and some of the physicochemical properties of SDZ, STZ, SMZ, SMX, SDM and SQX are shown in Table 1.

Standard stock solutions (1 mg mL^{-1}) for each of the analytes were prepared in methanol and stored at 4°C . Working solutions and a mixture of the six SAs and the internal standard were pre-

Table 1
Physicochemical properties of sulfonamides.

Sulfonamides	Physical-chemical properties
Sulfadiazine (SDZ) 	Molecular formula: $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$ Molar mass (g mol^{-1}): 250.3 pK_a: 1.6/6.5 Water solubility (mg L^{-1}): 77 K_{ow}: 0.81
Sulfathiazole (STZ) 	Molecular formula: $\text{C}_9\text{H}_9\text{N}_3\text{O}_2\text{S}_2$ Molar mass (g mol^{-1}): 255.3 pK_a: 2.4/7.1 Water solubility (mg L^{-1}): 373 K_{ow}: 1.12
Sulfamethazine (SMZ) 	Molecular formula: $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$ Molar mass (g mol^{-1}): 278.3 pK_a: 2.8/7.6 Water solubility (mg L^{-1}): 1500 K_{ow}: 6.3
Sulfamethoxazole (SMX) 	Molecular formula: $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$ Molar mass (g mol^{-1}): 253.3 pK_a: 1.6/6.4 Water solubility (mg L^{-1}): 610 K_{ow}: 7.8
Sulfadimethoxine (SDM) 	Molecular formula: $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_4\text{S}$ Molar mass (g mol^{-1}): 310.3 pK_a: 1.9/6.1 Water solubility (mg L^{-1}): 340 K_{ow}: 42.7
Sulfaquinoxaline (SQX) 	Molecular formula: $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$ Molar mass (g mol^{-1}): 300.3 pK_a: 2.3/6.0 Water solubility (mg L^{-1}): 120 K_{ow}: 47.9

Source: [10,19].

pK_a : acid/base dissociation constants; K_{ow} : octanol/water partition coefficient.

pared daily by diluting the standard stock solution in the mobile phase (water with 0.1% formic acid and MeOH with 0.1% formic acid, 80:20, v/v).

2.2. Soil samples

Samples obtained from two soils with different textural classes were collected in the state of São Paulo, Brazil: LVe (clay) and RQo (sandy). These two soil types cover approximately 34% of the surface of the state of São Paulo, Brazil.

The soils were collected at a depth of 0–20 cm, air-dried, passed through a 2 mm sieve and stored in plastic bags at room temperature until use. The physical and chemical characteristics of each soil are shown on Table 2.

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