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Insights on Environmental Changes

Where the World is Heading

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The Influence of Matrix Effects on Trace Analysis of Pharmaceutical Residues in Aqueous Environmental Samples

Marta Borecka, Anna Białk-Bielińska, Grzegorz Siedlewicz, Piotr Stepnowski and Ksenia Pazdro

Abstract Pharmaceuticals are a class of emerging environmental contaminants. They are manufactured to be biologically active and to be persistent against biodegradation. This makes them more risky for the environment, as they can have negative impact on living organisms. However, still there are many problems in reliable analysis of these compounds due to low amounts and complexity of the environmental samples. The technique widely used for this purpose is liquid chromatography coupled with tandem mass spectrometry. One of the main drawbacks of this technique is the change in ionization efficiency—phenomenon known as the matrix effect. Matrix effects heavily influence both qualitative and quantitative analyses. Therefore, it also has impact on the quality of the obtained results. Thus the main aim of the present study was to investigate the influence of six different aqueous environmental matrices on the solid-phase extraction efficiency and the final determination of twelve selected sulfonamides by LC-MS/MS technique. The obtained results showed that both were strongly affected by the matrix composition. The more complicated the matrix was, the greater influence was observed (matrix effects in tap water were in the range from 8.77 to −16.49 % and in wastewater influents from −63.67 to −97.43 %). Extraction efficiency of selected drugs decreased from 94.9 to 41.5 % for tap water samples to from 31.6 to 0 % for wastewater influents. Thus, it is of high significance to use an approach to correct effects caused by matrix components. The proper calculation of the real concentrations of pharmaceuticals in the environment is required for determining the consequent risk to living organisms.

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1 Introduction

Interest in the presence of pharmaceutical residues in the environment has increased significantly over the last decade. These compounds comprise one of the few groups of chemicals specifically designed to act on living cells, which presents a special risk when these contaminants enter, persist and disseminate in the environment. Pharmaceuticals have been detected throughout the world, especially in wastewater, surface water, groundwater, marine water and also drinking water. The concentrations of these compounds in the water are low—in the range from ng L^{-1} to μg L^{-1} (Daughton and Ternes 1999; Halling-Sørensen et al. 1998). There exists very well documented evidence that some drugs may affect microorganisms and wild life in severe and unexpected ways. Aquatic organisms are particularly important targets, as they are exposed over their whole life time (Carlsson et al. 2006; Santos et al. 2010).

Since pharmaceutical residues have been widely recognized as new emerging pollutants and simultaneously occur in extremely low concentrations, there has been increasing interest in the development of more selective and sensitive methods for their monitoring in the environment (Buchberger 2011; Kostopoulou and Nikolaou 2008; Kot-Wasik et al. 2007). The number of papers on analysis of drugs in water is significant, but still there are many problems related to the improvements in analytical procedures. These problems could cause inaccurate quantification when analyzing real samples.

Liquid chromatography coupled with tandem mass spectrometry, due to its high sensitivity and selectivity, is one of the most popular and appropriate techniques for trace analysis of pharmaceutical residues (Antignac et al. 2005). However, in the case of very complex matrices (like environmental samples), this technique is highly susceptible to the influence of co-extracted components. This has been widely reported in literature (Renew and Huang 2004; Kloepfer et al. 2005; Hao et al. 2007; Lacey et al. 2008; Madureira et al. 2009; Marín et al. 2009). Unfortunately, little is known about the influence of sample matrix complexity on results through the determination of matrix effects and also extraction efficiency.

It should be noticed that matrix effects are unseen in the chromatogram but they have vast impact on methods accuracy and sensitivity because coeluting substances can affect analyte ionization process leading to a signal increase (enhancement) or signal decrease (suppression) (Taylor 2005). This phenomenon was first described by Tang and Kebarle (1993). The authors examined how the signal of the analyte ion recorded with the mass spectrometer depended on the concentration of the analyte ion in the solution and also how this signal was susceptible to the presence of ions of other compounds in the studied solution. They showed that as

the concentrations of other compounds increased the electrospray responses of the analytes decreased. Many authors have studied this phenomenon, but its exact mechanism is still unknown (King et al. 2000; Trufelli et al. 2010). There are different mechanisms proposed in literature to explain the suppression or the enhancement of the signal, e.g., it probably originates from the competition between an analyte and the coeluting, undetected matrix components (Taylor 2005).

Matrix effects are caused by compounds which can be subdivided into two groups: endogenous components (naturally occurring in environmental samples and still present after sample pre-treatment or extraction) and exogenous components (introduced during sample collection or during the pre-treatment/extraction processes or reagents added to the mobile phase to improve chromatographic resolution) (Hall et al. 2012). Different substances can be able to induce matrix effects. Potential ion suppressors are ionic species (inorganic electrolytes, salts), polar compounds (phenols, arylsulfonates) and organic molecules (like carbohydrates, amines, urea, lipids and peptides) (Gosetti et al. 2010; Hall et al. 2012). This applies especially to those compounds or metabolites which chemical structure is similar to the target analyte, as well as to the compounds which are present in analyzed samples extracts at high concentrations (Marín et al. 2009; Gosetti et al. 2010). The physicochemical properties of the analytes can also influence the degree of enhancement or suppression of their ionization. Bonfiglio et al. (1999) reported that highly polar compounds generally appeared to be affected to a greater ion suppression than less polar molecules.

Environmental matrices represent high sample composition variability and it is difficult to find samples that have the same composition, even if the samples belong to the same type of matrices (Marín et al. 2009). Therefore, the main aim of the present study was to investigate the influence of different aqueous environmental matrices on the solid-phase extraction efficiency and final determination of twelve selected pharmaceuticals (described in Table 1) using LC-MS/MS technique. The estimation of extraction efficiency and matrix effects leads to better measurement reliability and renders data from inter-laboratory studies comparable. A detailed study was carried out on six different water samples (tap, lake, river and sea water, effluent and influent wastewater).

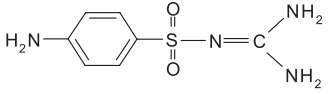
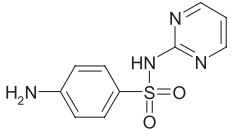
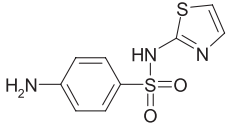
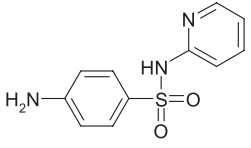
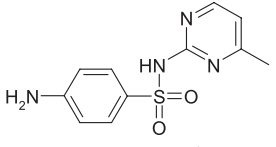
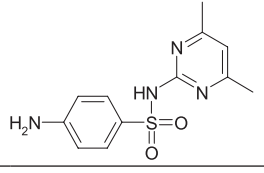
2 Materials and Methods

2.1 Chemicals

Sulfamethazine and sulfapyridine were purchased from Serva (Weissensberg, Germany). All other standards (Table 1) were obtained from Sigma–Aldrich (Steinheim, Germany).

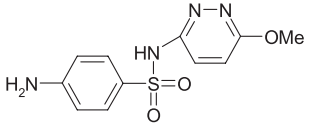
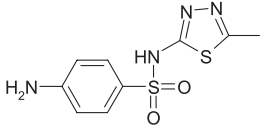
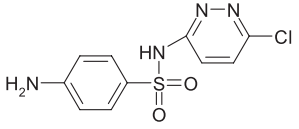
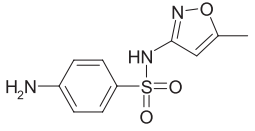
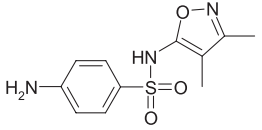
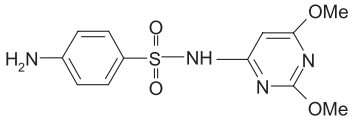
Methanol (MeOH) and acetonitrile (ACN) of HPLC grade were obtained from POCH S.A. (Gliwice, Poland). Acetonitrile (LC–MS Chromasolv®) was purchased from Sigma–Aldrich (Steinheim, Germany). Deionized water was

Table 1 Characteristic of studied pharmaceuticals

Name	CAS number	Chemical structure	Molecular weight (g mol^{-1})	pK_a
Sulfaguanidine	68-67-0		214.2	11.3
Sulfadiazine	68-35-9		250.3	6.5
Sulfathiazole	72-14-0		255.3	7.1
Sulfapyridine	144-83-2		249.2	8.4
Sulfamerazine	127-79-7		264.3	8.0
Sulfamethazine	57-68-1		278.3	7.4

(continued)

Table 1 continued

Name	CAS number	Chemical structure	Molecular weight (g mol^{-1})	pK_a
Sulfamethoxypyridazine	80-35-3		280.3	7.2
Sulfamethiazole	144-82-1		270.3	5.5
Sulfachloropyridazine	80-32-0		284.7	5.5
Sulfamethoxazole	723-46-6		253.3	5.7
Sulfisoxazole	127-69-5		267.3	5.0
Sulfadimethoxine	122-11-2		310.3	5.9

produced by the HYDROLAB System (Gdańsk, Poland). Ammonium acetate (NH_4Ac) and acetic acid (AcH) both of analytical reagent grade were purchased from Chempur (Piekary Śląskie, Poland).

Standard stock solutions of each compound were prepared by dissolving 50 mg in 100 mL of methanol obtaining a final concentration of 500 $\mu g\ mL^{-1}$. All standards were stored in the dark at −18 °C. The stock solutions were mixed and diluted with methanol to prepare working solution (20 $\mu g\ mL^{-1}$). To prepare calibration curves, working solution was diluted with mobile phase A to a proper concentration.

2.2 Sample Collection and Storage

The experiments were conducted with the use of tap, lake, river and sea water, as well as effluent and influent wastewater. Drinking water was collected from the tap of a private home in Gdańsk. Lake water was collected from the lake Fiszewo (54°6′ N, 17°42′ E). River water was taken from river Wda (54°04′ N, 17°40′ E). Sea water was collected from the Gulf of Gdańsk (Baltic Sea) close to the mouth of the Vistula (54°22′ N, 18°57′ E). Wastewater samples were obtained from a wastewater treatment plant located in Gdańsk ("Gdańsk-Wschód" Saur Neptun Gdańsk).

Samples were collected in glass bottles pre-rinsed with ultrapure water. Immediately after collection the samples were filtered through 0.45 μm glass fiber filters (Macherey—Nagel) and then stored at 4 °C in the dark until analysis.

2.3 Solid Phase Extraction Procedure

The solid phase extractions were performed with the use of Strata-X Polymeric Reversed Phase cartridges (3 mL/200 mg, Phenomenex Inc.). The cartridge was sequentially preconditioned with 3 mL MeOH, 6 mL ACN:MeOH (50:50, v/v), 6 mL H_2O:MeOH (95:5, v/v) and 10 mL deionized water. Each of 500 mL sample was transferred through the cartridge at the rate of 5 mL min^{-1}. After sample loading, the cartridge was rinsed with 3 mL H_2O:ACN (95:5, v/v) and then dried under the vacuum for 10 min. Sulfonamides were eluted with 6 mL MeOH:ACN (50:50, v/v). The obtained extracts were evaporated to dryness under a stream of nitrogen and reconstituted in 1 mL mobile phase A and analyzed by LC-MS/MS.

2.4 LC-ESI-Tandem MS Analysis

Chromatographic separation of analytes was performed using an Agilent 1,200 Series LC system (Agilent Technologies Inc., Santa Clara, USA) equipped with