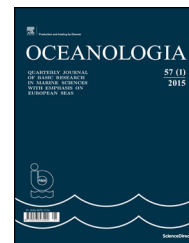




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ORIGINAL RESEARCH ARTICLE

# Determination of antibiotic residues in southern Baltic Sea sediments using tandem solid-phase extraction and liquid chromatography coupled with tandem mass spectrometry

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**Summary** The main objective of this study was to adapt analytical procedures for determining antibiotic residues in solid and aquatic samples to marine sediments and to investigate the occurrence of 9 sulfonamides, trimethoprim and 2 quinolones in southern Baltic Sea sediments. The analytical procedure was applied to sediment samples characterized as sand and silty sand. The validation results showed that a sensitive and efficient method applying tandem solid-phase extraction (SPE) and liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) was obtained. Analytes were determined in the lower  $\text{ng g}^{-1}$  range with good accuracy and precision. The proposed analytical procedure was applied to the analysis of 13 sediment samples collected from the Baltic Sea along the Polish coast. Concentrations of antibiotic residues in environmental samples were calculated based on external matrix-matched calibration. Residues of nine out of twelve of the above antibiotics were detected in sediment samples in a concentrations of up to  $419.2 \text{ ng g}^{-1}$  d.w. (dry weight). Sulfamethoxazole and sulfachloropyridazine were the most frequently detected compounds (58% of the analyzed samples). The

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occurrence frequency of trimethoprim was 42% and it was always detected simultaneously with sulfamethoxazole. Preliminary studies on the spatial distribution of the analyzed antibiotics indicate a high level of antibiotics occurring in the Pomeranian Bay and close to the mouths of Polish rivers. The study is the first one to demonstrate the occurrence of antibiotic residues in sediments of the Polish coastal area. The obtained results suggest that sediment can be an important secondary source of antibiotic residues in the marine environment.

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## 1. Introduction

At the end of the second half of the twentieth century scientists started to treat pharmaceutical residues as environmental contaminants (Daughton and Ternes, 1999; Hirsch et al., 1999). The development and common use of sensitive analytical instruments like liquid or gas chromatographs coupled with mass spectrometers allowed the detection of trace concentrations of these compounds in different environmental matrices (Kot-Wasik et al., 2007; Mutavdžić-Pavlović et al., 2007). Special attention should be paid to antibiotic residues. In 2002, Wise estimated the world use of antibiotics at between 100 and 200 thousand tonnes per year. According to data published by Boeckel et al. (2014), global consumption of antibiotic drugs increased by 36% between 2000 and 2010. The main sources of antibiotics in the environment are animal farms, agriculture, and urban, municipal and hospital wastewaters (Boxall, 2008a; Hörsing et al., 2011; Kümmerer, 2008a; Łuczkiwicz et al., 2013; Minh et al., 2009; Sarmah et al., 2006). These bioactive compounds have only been detected in low concentrations in environmental samples, nonetheless, given their important, continuous input and only partial degradation, they are considered as 'pseudo-persistent' pollutants (Khetan and Collins, 2007). Prolonged exposure of organisms to antibiotic residues may strongly affect bacterial populations and induce biological effects in non-target organisms, potentially disrupting ecosystem processes (Arnold et al., 2014; Capone et al., 1996; González-Pleiter et al., 2013; Halling-Sørensen et al., 1998; Kotlarska et al., 2015; Kümmerer, 2008b; Molander et al., 2009; Nikolaou et al., 2007). Therefore, it has become of great importance to evaluate concentration levels of antibiotic residues and to understand their environmental fate.

Many studies have demonstrated that antibiotic residues are widespread in treated wastewaters, soils, groundwaters, river and lake water and sediments (Boxall et al., 2002; Kemper, 2008; Li et al., 2012; Sacher et al., 2001; Vazquez-Roig et al., 2012; Yang et al., 2010). The availability of data on antibiotic concentrations and their ecotoxicological properties in marine waters is still limited, while seas can be seen as the final sink of the most persistent antibiotic residues (Chen and Zhou, 2014; Claessens et al., 2013; McEneff et al., 2014). Once discharged into coastal waters, antimicrobial residues, like other contaminants, can undergo biotic and abiotic transformations (including degradation), sorb to suspended particulate matter and sediment, or accumulate in the tissues of organisms (Gaw et al., 2014; Ramirez et al., 2009). The fate of antibiotic residues varies depending on the physicochemical properties of compounds and

matrices, in addition to environmental parameters also playing an important role. Freshwater and marine ecosystems differ significantly in terms of physicochemical conditions e.g. salinity, pH and organic matter content. Therefore, the conclusions generated for freshwater ecosystems on the environmental fate of antibiotics may not necessarily be transferable to marine environments (Weigel et al., 2002). The mobility of compounds greatly depends on water solubility, the octanol–water partitioning coefficient, and  $pK_a$  values governed by their chemical structure. Antibiotics are mostly hydrophilic compounds and should be present with relatively high frequency and concentrations in marine waters. This statement can be confirmed by several studies reporting the presence of these emerging contaminants in seawater (Borecka et al., 2013, 2015; Na et al., 2011; Nödler et al., 2014; Wille et al., 2010; Zhang et al., 2013). However, Bu et al. (2013) suggest that antibiotics could also accumulate in sediments, which could thus serve as a sink and secondary source of antibiotics in the aquatic environment. Several complex processes can be involved in the sorption mechanism of antibiotics in sediments. These comprise not only hydrophobicity but also cation bridging, cation exchange, hydrogen bonding and surface complexation (Kim and Carlson, 2005). All these factors may play important roles in retaining antibiotic residues on a sediment matrix. The sorption of antibiotics like sulfonamides is also governed by the property to ionize numerous compounds from this class depending on the pH of a medium. The  $\log K_{ow}$  coefficients of ionizing compounds change considerably in a pH range around the  $pK_a$  (Mutavdžić-Pavlović et al., 2012).

According to data published by Gaw et al. (2014) and Pazdro et al. (2016), until now only around twenty studies have evaluated the presence of antibiotics residues in marine sediments. Their presence has been reported in some coastal regions of the Pacific (mainly in China) and Atlantic Ocean (Beretta et al., 2014; Lara-Martín et al., 2014; Moreno-González et al., 2015; Na et al., 2013; Shi et al., 2014; Stewart et al., 2014; Yang et al., 2010; Yang et al., 2011; Zhou et al., 2011). As shown above, the information about spatial and seasonal distribution of antibiotic residues concentrations in many coastal areas is still very limited. This is particularly true for the Baltic Sea, a shallow inland sea with a large catchment area. There are only a few publications concerning the occurrence of pharmaceuticals in the Baltic Sea region and these are limited to water and fish (Beck et al., 2005; Borecka et al., 2013, 2015; HELCOM, 2010; Nödler et al., 2014). Borecka et al. (2013, 2015) reported the presence of antimicrobials from the sulfonamide and quinolone groups as well as trimethoprim, at concentrations

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