Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Presence, concentrations and risk assessment of selected antibiotic residues in sediments and near-bottom waters collected from the Polish coastal zone in the southern Baltic Sea — Summary of 3 years of studies

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A R T I C L E I N F O

Keywords:
Antibiotic residues
Near-bottom water
Sediments
Risk assessment
Baltic Sea

A B S T R A C T

Concentrations of selected antibiotic compounds from different groups were measured in sediment samples (14 analytes) and in near-bottom water samples (12 analytes) collected in 2011–2013 from the southern Baltic Sea (Polish coastal zone). Antibiotics were determined at concentration levels of a few to hundreds of ng g^{-1} d.w. in sediments and ng L^{-1} in near-bottom waters. The most frequently detected compounds were sulfamethoxazole, trimethoprim, oxytetracycline in sediments and sulfamethoxazole and trimethoprim in near-bottom waters. The occurrence of the identified antibiotics was characterized by spatial and temporal variability. A statistically important correlation was observed between sediment organic matter content and the concentrations of sulfachloropyridazine and oxytetracycline. Risk assessment analyses revealed a potential high risk of sulfamethoxazole contamination in near-bottom waters and of contamination by sulfamethoxazole, trimethoprim and tetracyclines in sediments. Both chemical and risk assessment analyses show that the coastal area of the southern Baltic Sea is highly exposed to antibiotic residues.

1. Introduction

In recent years, environmental scientists have paid increased attention to the occurrence, fate, transport and effects on organisms of pharmaceutical residues (Arnold et al., 2014; Klatte et al., 2016; Manzetti and Ghisi, 2014). Among these chemicals, special attention should be paid to antibiotics, since the diffusion of these compounds in the environment contributes to the development and dissemination of antibiotic resistance (Carvalho and Santos, 2016; Weber et al., 2016). These bioactive compounds are widely present in the environment matrix due to their extensive and long-term use in human and veterinary medicine (Kümmerer, 2008a). The global annual usage of antibiotics has been estimated at between 100,000–200,000 t and their consumption has been increasing in industrialized and developing countries (Shi et al., 2014; Xu et al., 2014).

In human medicine, besides being used to treat infectious diseases, these compounds are indispensable in transplantations, chemotherapy and surgical interventions (ECDC, 2015). According to The European Centre for Disease Prevention and Control (ECDC), the mean consumption of human antibiotics, expressed as defined daily doses (DDD) in the EU, gradually increased between 2004 and 2008, but in most European countries no significant changes were observed during the period 2008–2013. In 2013, the population-weighted mean consumption in the EU and the European Economic Area (EEA) was 22.9 DDD per 1000 inhabitants and per day, with the highest consumption in Belgium, Cyprus, France and Greece and the lowest consumption in Estonia and the Netherlands. In Poland, mean consumption was comparable to the median European level. In veterinary medicine, antibiotics are used for therapeutic purposes but are also administered for non-therapeutic uses, e.g. as growth promoters in livestock (except the EU countries where it has been forbidden since 2006) (EC, 2003).

The major entrance sources of antimicrobial agents and their byproducts into the environment are municipal, agricultural and industrial wastewaters, since from 30% to up to 90% of antibiotics administrated to humans and animals are excreted via urine and feces, largely unmetabolized. The presence of antibiotics used in human medicine in the environment is mainly attributed to the discharge of treated wastewater, since conventional WWTPs do not effectively remove these compounds (Carvalho and Santos, 2016). Apart from human pharmaceuticals, veterinary pharmaceuticals carry a significant

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http://dx.doi.org/10.1016/j.marpolbul.2017.10.075
Received 30 June 2017; Received in revised form 24 October 2017; Accepted 25 October 2017
0025-326X/

environmental risk, as the active agents and their degradation products enter the environment directly, never passing through a waste water treatment plant systems (Klatte et al., 2016). Van Boeckel et al. (2015) presented the first global map of antibiotic consumption in livestock (228 countries) and conservatively estimated the total consumption in 2010 at 63,151 tons. The authors projected that antimicrobial consumption will rise by 67% by 2030, and will nearly double in some countries, e.g. Russia, India, China and South Africa.

In the last 15 years, due to improvements in analytical methods, considerable research has been performed in different countries to prove the presence of pharmaceuticals in different matrices like soils, river sediments, lakes, groundwaters, drinking water and wastes (Boxall et al., 2002; Kemper, 2008; Sacher et al., 2001; Yang et al., 2010). Despite relatively low concentrations of antibiotic residues in the environment, their continuous input – and prolonged exposure of organisms to them – may affect bacterial populations and induce biological effects in non-target organisms, potentially disrupting ecosystems (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). The load of antibiotic residues may be transported to groundwater, rivers, and finally to the sea. The marine environment is considered to be the ultimate sink for sewage and other anthropogenic activities, yet knowledge about antibiotic concentrations and their ecotoxicological properties in marine or estuarine waters is still very limited (Chen and Zhou, 2014; McEneff et al., 2014). It is well known that marine sediments accumulate organic pollutants of different classes, and contaminant profiles in sediments represent extremely valuable natural archives of environmental contamination by which contaminant sources and historical changes in contaminant input and cycling may be recognized. Sediments may act as sink but also as a secondary source of contaminants, that poses a great potential danger for aquatic organisms (Shi et al., 2014; Xu and Li, 2010). Despite this, so far only a few studies have been conducted on antibiotic residues in marine sediments (Bu et al., 2013, Moreno-González et al., 2015; Na et al., 2013; Shi et al., 2014; Yang et al., 2011; Zhou et al., 2011).

In our previous studies (Siedlewicz et al., 2016, 2014) we published preliminary data about antibiotic residue levels in sediments collected from the southern Baltic Sea. The main objectives of both studies were to adapt certain analytical procedures, which have been used for determining sulfonamide, trimethoprim, quinolone and tetracycline residues in solid and aquatic samples, to analysis of marine sediments. Thus, the validated methods were applied to the analysis of a dozen sediment samples collected from the southern Baltic Sea. These preliminary results showed high concentrations of sulfonamides in sediments collected along Polish coast (Siedlewicz et al. 2016) and tetracyclines in Gulf of Gdansk (Siedlewicz et al. 2014). Therefore we decided to continue sampling and measurements to enlarge the data set which could be used for statistical analyses and for preliminary assessment of the ecological risks related to the presence of these compounds in the Baltic ecosystem. As a consequence, the objectives of this study were: 1) to measure distribution of the concentration levels of certain antibiotics (namely sulfathiazole (ST), sulfapyridine (SP), sulfamerazine (SRZ), sulfamethazine (SMZ), sulfamethiazole (SMT), sulfachloropyridazine (SCP), sulfamethoxazole (SMX), sulfisoxazole (SSX), sulfadimethoxine (SDM), trimethoprim (TMP), oxolinic acid (OA), enrofloxacin (ENR), tetracycline (TC) and oxytetracycline (OTC)) in successive sediment and near bottom water samples from the southern Baltic Sea; 2) to use new and earlier published data and environmental characteristics to study more comprehensively the occurrence and spatial/temporal distribution of these 14 target antibiotics in the investigated area; and 3) to apply the measured concentrations for further ecological risk characterization studies.

2. Materials and methods

2.1. Study area and sampling location

The Baltic Sea is one of the largest brackish water areas in the world, with limited inflows of marine waters through the Danish straits and a water residence time of around 30 years (Kautsky, 2000). Dense populations in the coastal area (16 million people) and intensive industry and agriculture (including farming and animal husbandry) produce large amounts of domestic, industrial and agricultural waste which – in combination with its shallowness, long water residence time and particularly large catchment area – make it susceptible to the accumulation of anthropogenic substances (Bojakowska and Uścinowicz, 2011; HELCOM, 2014; Lundberg, 2005). Our study area was located in the southern part of the Baltic and included the Gulf of Gdańsk, which receives waters from the Vistula river and hosts the Tricity agglomeration on the coast, the Pomeranian Bay with the Szczecin Lagoon and an open sea area along the Polish coast — in the proximity of the mouths of some smaller rivers (e.g. Łeba, Słupia, Parsęta, Wieprza, Dziwna).

The investigated area is naturally divided into two parts. The first one is the southern Baltic open coast, including the Gulf of Gdańsk, and the second one is the Szczecin Lagoon which is the Oder river estuary. The coastal part can be characterized as a wide belt of shallows (depths to 30 m) extending for nearly 20 km along the open coast from the shallow Pomeranian Bay in the west to the Hel peninsula in the east. Depths in excess of 100 m are found only in the central part of the Gulf of Gdańsk, where a depression with an accumulative type of bed has formed. Along the coast the most extensive areas of the seabed to 50–60 m depth are covered by medium and fine grained sands. In areas where the water dynamic is low, sediments are accumulated to form muds and silts in admixture with sand. The sills between seabed depressions are covered by mixed sediments enriched with organic matter. The highest values of near bottom currents (above 50 $cm\ s^{-1}$) are observed in the slopes near the base of the Hel Peninsula and in the western part of the study area — at the edge of the Pomeranian Bay. The lowest water flow values are noted over the flat, deeper bottom of the Gulf of Gdańsk. The hydrology of the shallow near-bottom area is also periodically affected by wind waves. Highest orbital velocities (over 200 $cm\ s^{-1}$) were noted near the base of the Hel Peninsula and in the vicinity of the Vistula River mouth. The lowest values are measured in the sheltered area of the inner Puck Bay (Gic-Grusza et al., 2009). The Szczecin Lagoon is a specific transitionary shallow water body with particular hydrological characteristics. The average depth of this area is 3.8 m: its maximum natural depth is 8.5 m, but dredging in the shipping channel produces depths exceeding 10.5 m. 94% of the water loads discharged into the lagoon are from the Oder river. In the North, the lagoon is connected to the Pomeranian Bay via the three channels. The shallow areas are dominated by eroded sand temporarily covered by a thin and mobile organic-rich fluffy material. Bottom sediments at depths of 4 m and more are dominated by silt. The annual mean temperature of near-bottom water (below 25 m) for the southern Baltic Sea ranges from 7 to 10 °C, and seasonal differences between warm (June–October) and cold (December to April) periods can exceed 15 °C. In the study area the mean annual near-bottom water salinity ranges from 5.5 to 12 PSU, except for the Szczecin Lagoon, where the mean salinity ranges between 0.5 and 2 PSU (Radziejewska and Schernewski, 2003).

The main sources of pharmaceuticals in coastal environments, namely wastewaters, animal husbandry and horticulture located in river catchments and in coastal areas (Pazdro et al., 2016), are fully applicable to the studied area. The catchment areas of the rivers Vistula and Oder are the second and third largest in the Baltic Sea (12% and 8% of the Baltic catchment area, respectively) (HELCOM, 2010). Moreover, these rivers drain densely populated and agricultural areas. Several smaller rivers receiving waters from the Pomeranian coastal area discharge into the sea along the Polish open coast, with smaller city-harbours located in their mouths. The largest point sources of antibiotic