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Distribution of phenol derivatives by river waters to the marine environment (Gulf of Gdansk, Baltic Sea)

by

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Abstract

The aim of this study from 2020 was to identify the role of rivers, including those with low water flow and a constant inflow of bisphenol A (BPA), 4-tert-octylphenol (4-t-OP) and 4-nonylphenol (4-NP) to the marine environment. Water samples were collected from the small rivers flowing into the Gulf of Gdańsk and from the Vistula River. Final assays were performed using high-performance liquid chromatography with a fluorescence detector (HPLC-FL). The highest concentrations of phenol derivatives were found in summer, most likely due to higher consumption of products containing phenol derivatives. Another factor may be the type of development in the catchment area. The measurements did not exceed the PNEC, though this does not mean that the amounts of phenol derivatives introduced into the Gulf of Gdańsk by rivers can be ignored. Mean loads of xenobiotics introduced to the sea via rivers have been calculated as over 320 kg y^{-1} of BPA and about 55 kg y^{-1} of 4-t-OP and 4-NP each.

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1. Introduction

Along with the development of industry, more and more new toxic substances of anthropogenic origin are entering the environment. In recent years, the attention of scientists has been drawn to endocrine-disrupting compounds (EDCs). According to the definition of the US Environmental Protection Agency (EPA), they are exogenous factors that interfere with the proper functioning of the hormones responsible for homeostasis, reproduction and developmental processes of the body. EDCs are therefore a group of compounds defined not by their chemical structure, but by their biological activity. These xenobiotics, even at low but environmentally relevant concentrations, can lead to changes in behaviour, reproductive and developmental disorders and even to malformation and the development of genital cancers (Sohoni et al. 2001, Matsumoto et al. 2005, Oehlmann et al. 2009, Chaube et al. 2013, Bhandari et al. 2015, Sharma et al. 2017, Abdel-Tawwab et al. 2018).

These compounds include phenol derivatives such as 4-nonylphenol (4-NP), 4-tert-octylphenol (4-t-OP) and bisphenol A (BPA). These xenobiotics are bioavailable for organisms, i.e. they exist in a form that allows them to travel through the surface of cell membranes in the skin, the epithelium of the gills or the intestines (Pazdro 2007). This phenomenon is additionally intensified by their moderate hydrophobic properties, which give them affinity in adipose tissue. A measure of the hydrophobicity of a given chemical is the octanol/water partition coefficient ($K_{o/w}$), amounting to 3.3 for BPA, 5.3 for 4-t-OP and 5.9 for 4-NP (Ahmed et al., 2018). These properties allow phenol derivatives to undergo bioaccumulation, bioconcentration and biomagnification in living organisms. We assayed phenol derivatives in organisms from all trophic levels in the Gulf of Gdańsk environment, including phyto- and zooplankton, mussels, fish, seals and birds and found that these compounds can bioaccumulate in the trophic chain (Staniszewska et al. 2014, 2015; 2016a, 2016b; Falkowska et al. 2017; Nehring et al. 2017, 2018; Bodziach et al. 2020). Phenol derivatives pose a threat not only to single organisms, but also to entire populations. Therefore, they should be treated as particularly dangerous substances. Phenol derivatives do not occur naturally in the environment, but are widely distributed there as a result of high production, use and processing of products containing these compounds. They can be released into the environment during the manufacture of plastics, including the processing, use and degradation of polycarbonates and epoxy resins (Health Canada, 2008), non-ionic surfactants and detergents or antioxidants.

In the marine environment, the problem mainly concerns rubbish lying on the beaches of the coastal zone, but also riverine input. Plastics are generally stable and it is believed that only small amounts of phenol derivatives are introduced into the environment through the above-mentioned processes. However, this only applies to new polycarbonate materials, as the chances of phenol derivatives being released into the surrounding environment increases as the material ages and deteriorates due to waves, solar radiation and wind. This has been confirmed by the research of Staniszewska et al. (2016a), who showed that the concentration of BPA in water with an admixture of plastic granules was approx. 100 ng dm^{-3} after 20 days, increasing to approx. 700 ng dm^{-3} after 60 days. While investigating bisphenol A in polluted rivers in Japan, Matsumoto (1982) concluded that the compound comes mainly from industrial products such as epoxy and polycarbonate resins and their decomposition products. The emission of phenol derivatives from plastics into food, drinking water and toiletries has also been demonstrated (Teuten et al. 2009, Santhi et al. 2012, Colin et al. 2014, Hahladakis et al. 2018).

The ultimate recipients of phenol derivatives are the seas and oceans, which these compounds enter mainly through surface runoff via rivers and through water discharged from industrial and municipal wastewater treatment plants, where they do not undergo complete degradation (Ahel et al. 1994, Staples et al. 1998, Flint et al. 2012, Corrales et al. 2015, Acir et al. 2018).

Bearing in mind that rivers are considered to be one of the main sources of marine pollution, it is important to fully recognise the pollution status of riverine water. Coastal ecosystems that receive the greatest amount of pollution from rivers are very favourable places for the accumulation of the pollutants, and thus the toxic effect on organisms is increased there. In Poland, the longest river flowing into the Baltic Sea is the Vistula, which is the second largest river in the Baltic basin. However, beside the Vistula, a number of smaller rivers flow into the Gulf of Gdańsk. The chemical status of water is good in only 0.6% of these rivers. The general condition of the Gizdepka, Kacza and Martwa Wisła rivers has been assessed as bad, and the chemical condition below good (Statistics Poland, 2019; GIOŚ, 2019). It is important to note that little is known about the pollution of rivers flowing into the Southern Baltic with phenol derivatives. Therefore, one of the goals of the study was to check whether the poor condition of small rivers may also translate into significant roles in the pollution of sea waters with endocrine-active phenol derivatives. The authors also attempted to estimate the threat to marine organisms that may be posed by the annual influx of phenol derivatives into the coastal ecosystem of the Gulf of Gdańsk.

2. Materials and methods

2.1. Sampling

Water samples were collected during one year in three different seasons (spring – March, summer – June and autumn – October), near the sources and at the outlets of the small rivers flowing through Pomerania, and from the estuary of the Vistula River (Fig. 1). A total of 24 samples were taken and each of them was divided into 3 subsamples. Surface water was taken from the middle part of the stream. The samples were kept in a refrigerator (+4°C) until analysis and were analysed within 72 hours. Three samples were taken at a time from each collection point, which were then analysed in the laboratory for the presence of phenol derivatives. The characteristics of individual stations are presented in Table 1.

2.2. Determination of BPA, 4-t-OP and 4-NP

To assay the concentrations of phenol derivatives in the water, the method previously described by Staniszewska et al. (2016a) was used. For this purpose,

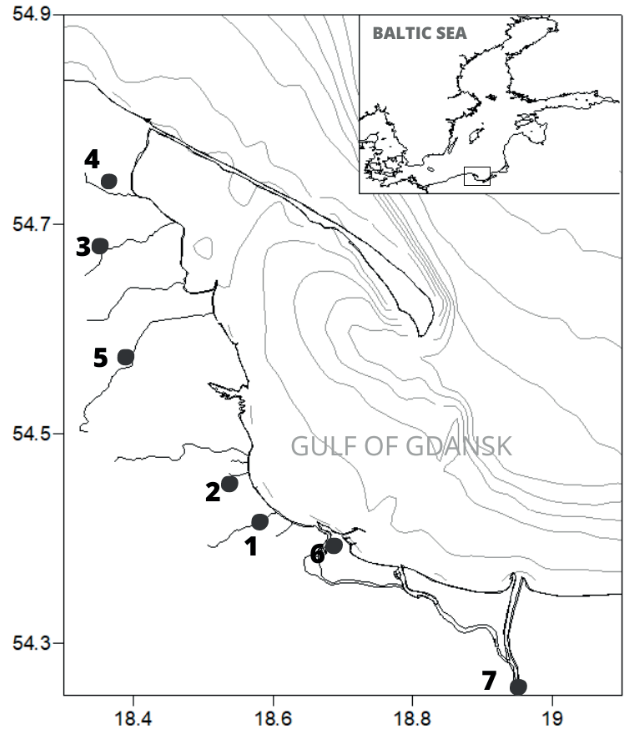

Figure 1

Location of the rivers included in the research

Numbering in Table 1

100 cm^3 of water was passed through columns with Oasis HLB (Waters) (200 mg, 5 ml). The columns were conditioned with 6.0 cm^3 of a 50/50 DCM/methanol mixture (v/v) and activated with 3.0 cm^3 of methanol

Table 1

Characterisation of the sampling sites

Name/location in Fig. 1	Source	Outlet	Length (km)	Flow (m^3 s^{-1})	Catchment development	References
Oliwa Brook [1]	140 m above sea level	In the town of Sopot	10	0.29	Nature reserves, parks, forests and a zoo	Saniewska et al. 2014
Kacza River [2]	150–190 m above sea level	In the town of Gdynia	14.8	0.13	Nature reserves, forests and urban areas	Saniewska et al. 2014
Gizdepka River [3]	forest area	Puck Bay	13.3	0.17	Agricultural areas (47.5%), forests (45.9%) and waters (5.1%)	Wojciechowska et al. 2018
Reda River [4]	backwoods, 49 m above sea level	Puck Bay	51	4.2	Forests (> 50%), recreational areas and urbanised areas	IMGW, 2019
Zagórska Struga River [5]	lake, 153 m above sea level	Gulf of Gdańsk	28	1.3	Forest and agricultural areas. Within the catchment there is a trout farm.	RZGW, 2012
River Vistula [6]	Beskid Śląski mountain range, 1107 m above sea level	Gulf of Gdańsk	1047	1059	Agricultural areas (66%), forests (29%) and urbanised areas (3%). The river flows through the entire country. The estuary is dominated by urbanised areas.	IMGW, 2019
Martwa Wisła River [7]	Estuarial section of the Vistula in Gdańsk	Gulf of Gdańsk	12	178	Urbanised areas	Cieśliński 2017

and 3.0 cm^3 of water. The analysed compounds were eluted with 6.0 cm^3 (2 × 3 cm^3) of the DCM/methanol mixture. The resulting extracts were evaporated until dry and topped up with acetonitrile to 0.2 cm^3.

The final assays of phenol derivative concentrations in both of the analysed matrices were carried out using high-performance liquid chromatography with a fluorescence detector and a Thermo Scientific HYPERSIL GOLD C18 PAH chromatographic column (250 mm / 4.6 µm) with a generated excitation wavelength of λ = 275 nm and emission at the wavelength of λ = 300 nm. The chromatographic separation process was performed using a mobile phase (water: acetonitrile) under gradient conditions (Table 2).

Table 2

Chromatographic separation conditions

Time (min)	H_2O (%)	CH_3CN (%)
0	70	30
0	70	30
12	35	65
17	0	100
21	0	100
21.3	70	30
25	70	30

The background was monitored by checking the centrifuge every 20 times the SPE column was used. The 'background' values for BPA, 4-NP and 4-tOP recorded in this procedure were all lower than the limit of quantification (LOQ).

2.3. Method validation parameters

All tools and vessels used at each stage, i.e. collection, transport, storage and concentration assays, were made of glass, metal or Teflon in order to avoid contact between the samples and plastics, thus avoiding potential contamination.

The linear correlation coefficient (r) of the analytical curves was > 0.999. The average amounts of BPA, 4-NP and 4-t-OP recovered, as determined through a quintuple analysis of samples containing an added known amount of the standard, were 101.0% (BPA), 80.1% (4-t-OP) and 83.5% (4-NP). The accuracy (variation coefficient) was below 2% for each of the compounds. The LOQ was determined as a tenfold signal-to-noise ratio for a sample with a very low analyte content; it amounted to 5.0 for BPA, 1.0 for 4-t-OP and 4.0 ng dm^{-3} for 4-NP.

2.4. Load of endocrine-active phenol derivatives carried by rivers

The loads of BPA, 4-t-OP and 4-NP carried via rivers to the sea were calculated from the concentrations of phenol derivatives measured in the samples and the flow of water in the estuaries of individual rivers provided in literature. The following formula was used:

$$F\left[ng\ s^{-1}\right] = \frac{C_w\left[ng\ dm^{-3}\right]}{0.001} \times P\left[m^3\ s^{-1}\right]$$

$$F\left[g\ year^{-1}\right] = F\left[ng\ s^{-1}\right] \times 10^{-9} g \times A$$

where F is the riverine flux of EDCs (ng s^{-1}), C_w is the concentration of EDCs in riverine water (ng dm^{-3}), P is the water discharge in the estuary (m^3 s^{-1}) and A = 31,536,000 is the number of seconds in a year.

3. Results

The concentrations of phenol derivatives were measurable in approximately 80% of the analysed river water samples. Bisphenol A had the highest rate of detection (100%), while the detection rate was lower for alkylphenols, about 67% for 4-t-OP and 81.5% for 4-NP. Few (30%) of the water samples collected in autumn had a 4-t-OP concentration above 1 ng dm^{-3}. BPA concentrations were higher than those of 4-tert-octylphenol or 4-nonylphenol. The highest BPA concentration was measured in a water sample taken from the source section of the Kacza River in summer (546.16 ng dm^{-3}). It was 10 times higher than that assayed in the sample collected from the same place in spring, and 18 times higher than the concentration in autumn. On the other hand, the lowest average concentrations of bisphenol A were found in the water collected from the estuary section of the Zagórska Struga (Table 3).

Compared to bisphenol A, alkylphenols were present in a narrower concentration range. For 4-NP they ranged from values below the quantification level (< 4.0 ng dm^{-3}) to the maximum value of 35.13 ng dm^{-3}, which was found in a sample from the source of Zagórska Struga. 4-tert-octylphenol concentration was within a range of < 1 to 35.82 ng dm^{-3}. The maximum value for 4-t-OP was measured in spring at the source of the Kacza River and was an outlier, as the remaining concentrations did not exceed 12.7 ng dm^{-3}.

Table 3

Mean concentrations (ng dm^{-3}) of bisphenol A, 4-tert-octylphenol and 4-nonylphenol in water collected from rivers in spring, summer and autumn 2020

	Season	Spring			Summer			Autumn		
	Compound	BPA	4-t-OP	4-NP	BPA	4-t-OP	4-NP	BPA	4-t-OP	4-NP
Station		ng dm^{-3}								
Source	Kacza River	56.1	35.8	17	546.2	5.0	9.3	30.8	< LOQ	17.3
	Zagórska Struga River	27.1	7.1	< LOQ	64.7	7.1	35.1	7.9	< LOQ	< LOQ
	Reda River	19.8	< LOQ	12.1	31.8	18.8	17.4	26.2	< LOQ	3.8
	Gizdepka River	15.9	3.5	25.8	78.4	12.7	18.6	3.6	< LOQ	< LOQ
Outlet	Oliwa Brook	7.6	< LOQ	< LOQ	38.3	< LOQ	12.6	2.6	< LOQ	27.8
	Kacza River	27.2	1.5	13.1	14.1	0.9	12.5	NA	NA	NA
	Zagórska Struga River	15.5	< LOQ	10.2	27.2	3.1	10.5	19.3	2.5	9.8
	Gizdepka River	NA	NA	NA	17.3	9.6	10.3	22.1	8.0	13.0
	River Vistula	80.3	5.3	< LOQ	74.5	11.1	10.6	29.0	< LOQ	12.0
	Martwa Wisła River	89.1	10.5	16.4	43.2	1.5	11.3	59.1	2.5	< LOQ

Symbols: < LOQ – below the limit of quantification: 5.0 ng dm^{-3} for BPA, 1.0 for 4-t-OP and 4.0 for 4-NP; NA – no result

In this study, BPA concentrations measured in summer were fourfold higher than those measured in autumn (22.3 ng dm^{-3}). Even when this extreme concentration is not taken into account, the highest concentrations were still found during the warmest part of the year. Alkylphenols, on the other hand, were characterised by similar concentration levels throughout the year, except in autumn, when the lowest average concentrations were determined for 4-tert-octylphenol and the rate of detection was also low (30%). After averaging the results obtained from the analysis of all water samples, it was observed that the mean annual BPA concentration in the Vistula water exceeded the mean concentrations in all of the other rivers apart from the Kacza, where the highest value was found. On the other hand, the concentrations of alkylphenols did not show a clear trend and were similar for all rivers, regardless of size (Fig. 2). The coefficient of variation of the results was not greater than 10%.

4. Discussion

4.1. Changes in concentrations of phenol derivatives in water at the source and mouth of the river

Each of the small rivers considered in this study is no longer than 60 km, but differences in BPA, 4-t-OP and 4-NP concentrations can be observed between the water collected at the source and at the outlet. At the sources, the riverine water had concentrations of phenol derivatives that were 1.5 to 7 times higher than at the outlets (Table 3). The highest ratio of the mean BPA concentration measured at the source to the concentration at the estuary (38.62) was found in summer for water from the Kacza River (Table 4). This finding indicates that water is more heavily contaminated with bisphenol A at the source than at the outlet. This may be related to the increased

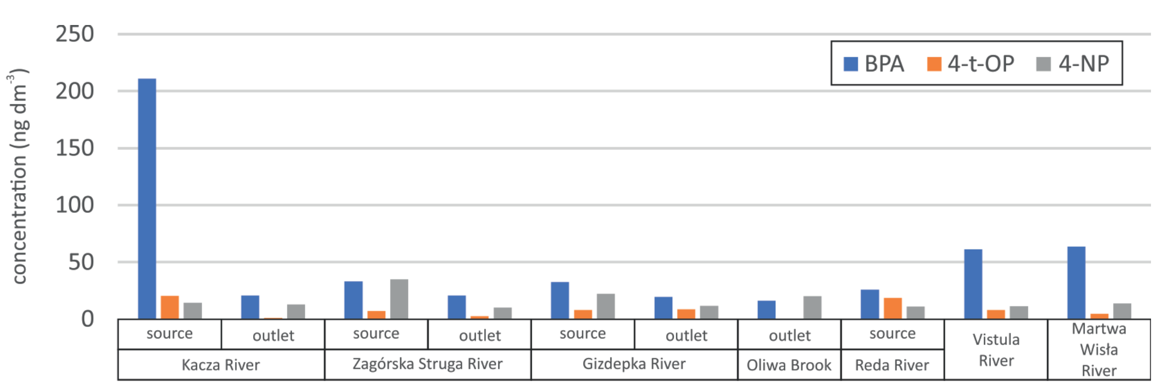

Figure 2

The mean concentrations of bisphenol A (BPA), 4-tert-octylphenol (4-t-OP) and 4-nonylphenol in the water samples collected at the sources and outlets of rivers in 2020

Table 4

Mean ratios of phenol derivative concentrations at the sources to concentrations at the outlets of rivers flowing into the Gulf of Gdańsk, for samples collected in 2020

Season	spring			summer			autumn		
Station	compound								
	BPA	4-t-OP	4-NP	BPA	4-t-OP	4-NP	BPA	4-t-OP	4-NP
Kacza River	2.06	23.88	1.30	38.62	5.8	7.74	-	-	-
Zagórska Struga River	0.57	0.14	2.35	2.37	2.33	3.35	0.41	0.41	0.41
Gizdepka River	-	-	-	4.54	1.33	1.81	0.16	0.13	0.31

amount of silty sediments in the downstream section of a river. The load of phenol derivatives is adsorbed by the suspended particles, causing the particles to sink to the bottom. Thus, phenol derivatives undergo sedimentation and the concentrations in surface water are lower (Li et al. 2004). The development of the riverside is not without significance. There are residential areas with detached houses and small farms in the vicinity of the Kacza source. The lowest source/outlet ratios were determined for samples collected in autumn from the Zagórska Struga and the Gizdepka (0.16 – 0.41). In autumn there is usually more precipitation, which results in increased leaching of pollutants which have accumulated over the summer, causing them to travel from the soil to the surface water. Near the outlets of the rivers there are beaches and recreational areas, where people discard plastic rubbish. In addition, agricultural land covers a significant proportion of the catchment area. Therefore, xenobiotics can be delivered by surface runoff from fields or farms, along with food remains or animal excrement (Stewart 2005). Leaching from the soil is also favoured by more intense weather phenomena, as strong winds cause more turbulence of bottom sediments in shallow rivers and re-suspension of the pollutants accumulated there. This may lead to higher water pollution towards the outlet.

4.2. Load of phenol derivatives introduced to the sea via rivers

It should be remembered that the concentration value alone does not reflect the extent to which riverine waters pollute coastal waters with phenol derivatives. Therefore, the average load of phenol derivatives carried by rivers to the Gulf of Gdańsk was calculated, taking into account the average water flow at the mouth of each individual river (Table 5). The authors tried to find the latest available data on the flows of individual rivers. The average annual water flow was used in these calculations, which means that the results are estimated loads. However, this does not diminish the importance of these results, because the values are significant and worthy of interest, in the opinion of the authors.

The calculated loads clearly show that it is the River Vistula that brings in the majority (99.6%), of phenol derivatives as opposed to smaller rivers. However, this does not rule out the role of smaller rivers in this supply budget. Despite the fact that the mean xenobiotic loads of these rivers are small, high concentrations of phenol derivatives incidentally occur in river water. The research did not involve frequent sampling, which perhaps would have indicated more cases of high concentrations of phenol derivatives.

Table 5

Mean seasonal loads of bisphenol A, 4-tert-octylphenol and 4-nonylphenol carried by rivers to the waters of the Gulf of Gdańsk in 2020

	River	Reda River	Oliwa Brook	Kacza River	Zagórska Struga River	Gizdepka River	Vistula River
	Season	g year^{-1}					kg year^{-1}
BPA	spring	2609.9	69.1	109.8	637.5	26.8	2 700.0
4-t-OP		131.9	9.1	6.1	41.0	5.4	178.3
4-NP		1588.8	36.6	52.8	416.1	21.4	134.5
BPA	summer	4185.3	350.3	57.1	1116.8	92.6	2 505.3
4-t-OP		2478.2	9.1	3.5	125.0	51.3	371.8
4-NP		2289.7	115.3	50.5	428.8	55.2	356.7
BPA	autumn	3302.7	23.5	NA	789.2	118.2	976.7
4-t-OP		131.9	9.1	NA	102.5	42.8	367.1
4-NP		502.1	254.4	NA	403.0	69.8	402.4

NA – no result

The load values for individual rivers in different seasons of the year indicate that the highest supply of endocrine-active phenol derivatives occurs in the summer season. These indicators are several times to several hundred times higher than those calculated for the other seasons. The load of phenol derivatives is highest in summer because of the increase in tourist traffic in the coastal region. The city's beaches are visited by about 3 million beach-goers, who engage in water sports and general recreation from June to September. The 'Tri-City', which is located directly by the sea and whose population numbers in the millions, is also an urban agglomeration with a well-developed coastal industry (shipyards, refineries and pharmaceutical, cosmetics and paint producers). There may also be uncontrolled discharges of sewage from buildings into rivers. In most of the small rivers studied here, the catchment area is covered by forests and farmland. This is of great importance due to the fact that in the literature on the subject phenol derivatives have been reported at measurable levels in bird and pig faeces (Xu et al. 2018, Zhang et al. 2014, Tao et al. 2021). Importantly, 70% to 85% of bisphenol A and alkylphenols in mammals is removed with urine (Tao et al. 2021). In the catchment areas of the small rivers, there are recreational areas where so-called 'wild garbage dumps' are found, often with discarded plastic items or electronics. Such rubbish, decomposed under the influence of weather conditions, is a source of BPA or alkylphenols in the environment (Staniszewska et al. 2015). The intensity of runoff may increase under the influence of heavier rainfall and more frequent flooding (Saniewska et al. 2014).

It should be noted that the authors of the aforementioned studies focussed only on surface water, and that phenol derivatives have a high affinity for organic carbon (Koniecko et al. 2014, Staniszewska et al. 2016b), on which they can sorb and thus accumulate in bottom sediments. Nonetheless, sediments are not the ultimate place of storage for these xenobiotics, especially in shallow water. Due to the size of the rivers, their bottom sediments are not stable, but are sensitive to weather conditions and waves, which may facilitate the re-suspension of these pollutants back into the water column. However, it should be noted that in the remaining seasons, BPA concentrations are also elevated. In autumn, greater rainfall and more dynamic weather conditions increase the inflow of this compound even from further distances. This is related to the ability of phenol derivatives to adsorb on elemental carbon particles (Staniszewska et al. 2016). On the other hand, in spring, when the ice covers thaw, pollutants – including phenol derivatives – are released into the groundwater.

4.3. Risk to marine environment

One parameter which indicates the risk of contamination for aquatic organisms is the predicted no effect concentration (PNEC), which refers to the concentration limit of individual compounds above which adverse effects on organisms may occur. These concentration limits in surface water are 150 ng dm^{-3} for BPA, 10 ng dm^{-3} for 4-t-OP and 330 ng dm^{-3} for 4-NP (EU, 2008). In the literature on the subject, recommendations can be found to tighten BPA PNECs for specific groups of organisms. A PNEC of 60 ng dm^{-3} has been proposed for species such as snails, which are extremely sensitive to the effects of this chemical (Wright-Walters et al. 2011). Currently, the lowest PNEC for BPA is 10 ng dm^{-3}, for its effects on the larvae of the insect *Chironomus riparious* (Selvaraj et al. 2014). Accordingly, based on these acute toxicity values and an assessment factor of 100, a PNEC of 0.88 ng dm^{-3} was obtained (Ministry of the Environment, Japan, 1998).

In addition to PNEC, there are also other indicators related to concentrations of phenol derivatives that are safe for organisms. The Water Framework Directive, created by the European Union, indicates an annual average concentration (AA-EQS) and a maximum allowable concentration (MAC-EQS) for BPA, 4-t-OP and 4-NP.

In this study there were four values that exceeded the PNEC for 4-t-OP. The largest one was more than threefold higher and was found in the Kacza water collected in spring. Samples from other sites (Martwa Wisła, Gizdepka and Vistula) had instances where the limits were exceeded by a few percent each. Interestingly, one PNEC concentration exceedance of bisphenol A was also observed for the water from the Kacza. The catchment area of this river covers a wide urbanised, touristic area where the consumption of plastic products is higher; this may translate into a potentially higher load of phenol derivatives being introduced into the river. If we take into account the proposed lowered PNEC for BPA, due to its toxicity for particular groups of organisms, the number of exceedances will be higher: the concentration of 60 ng dm^{-3} was exceeded in 18.5% of the samples, while the most rigorous level (10 ng dm^{-3}), which is harmful to insects, was exceeded in 89% of the samples. No dangerously high concentrations were observed for 4-nonylphenol. Neither the AA-EQS nor the MAC-EQS were exceeded in any of the environmental water samples (Table 6). Despite the fact that the concentrations measured in collected river water samples can be described as safe for aquatic organisms, it should be remembered that they were single samples. No monitoring or frequent sampling of these concentrations was carried out. Sampling could clearly indicate whether there is a risk connected with phenol derivatives being introduced to the sea via rivers. In summer, when tourist traffic increases in the area of the coastal zone of the sea, concentrations in river water may rise (Staniszewska et al. 2016a). Additionally, the mixture of these three compounds has a greater estrogenic effect on fish reproduction than each compound separately (Brian 2005). Therefore, even the low concentrations found in the small rivers in Pomerania may have chronic effects on aquatic wildlife.

Table 6

Normative values and exceedances of BPA, 4-t-OP and 4-NP in the tested surface waters

Parameter [ng dm^{-3}]	bisphenol A	4-tert-octylphenol	4-nonylphenol
PNEC	150*/60**/10***	10	330
AA-EQS	-	100$^{1)}$/10$^{2)}$	300
MAC-EQS	-	-	2000
rating	1 exceedance	4 exceedances	No exceedance

PNEC – predicted no effect concentration (*European Community, 2008; **Wright-Walters et al. 2011; ***Selvaraj et al. 2014)

AA-EQS – annual average value (WFD-EAF, 2004)

MAC-EQS – maximum allowable concentration (WFD-EAF, 2005)

1) for marine water

2) for freshwater

During studies in 2011 and 2015 in the same area, high concentrations of phenol derivatives were observed in river outlets (in 2011, from < 4 to 55.94 ng dm^{-3} (average: 34.49 ng dm^{-3}) for 4-NP, and from < 1 to 5.64 (3.04 ng dm^{-3}) for 4-t-OP; in 2015, from < 5.0 to 277.9 ng dm^{-3} (56.5 ng dm^{-3}) for BPA, from < 1.0 to 834.5 ng dm^{-3} (42.1 ng dm^{-3}) for 4-t-OP and from < 4.0 to 228.6 ng dm^{-3} (38.8 ng dm^{-3}) for 4-NP (Staniszewska, Falkowska 2011, Staniszewska et al. 2016a). It was shown that small rivers, whose course is about 100 times shorter, bring more concentrated pollutants to sea water. As in the present study, the widest range of concentrations (< 1 – 834.8 ng dm^{-3}) was found in the summer for a sample taken from the Kacza River. In previous years in this region, concentrations of endocrine-active phenol derivatives were also exceeded. The highest number of exceedances was observed for 4-t-OP. In surface water, the PNEC was exceeded in 36% of water samples (on average, the values exceeded PNEC 15.7 times in river water and 3.3 times in sea water). The high exceedances of PNEC limits for 4-t-OP concentrations in riverine water point to land-based sources of phenol compounds (Staniszewska et al. 2016a). It seems that the situation has improved over the years. However, it should not be forgotten that the compared concentrations were short-term . According to the authors, it is crucial to determine the loads of endocrine-active compounds being introduced into sea surface waters. Of course, it makes sense to know the temporary concentrations because of the organisms that live in river waters, but because xenobiotics accumulate in the marine environment, they also pose a great threat to organisms on all trophic levels.

4.4. Comparison with other regions

There is very little data available in the literature on the load of endocrine-disruptive phenol derivatives being introduced into marine waters by rivers. According to Yamazaki et al. (2015), 322 kg year^{1} are delivered to Tokyo Bay by the Arakawa River, the Edogawa River and the Tamagawa River. This suggests that the BPA load carried in spring or summer by the Vistula may be over 8 times higher, despite the fact that less bisphenol A is used in Polish industry. Research by Huang et al. (2020) indicated that the load of bisphenol analogues introduced by tributaries to the Pearl River reached 6,372 kg year^{1}. According to Saniewska (2018), 200 kg year^{1} of mercury – also an endocrine-disruptive substance – enters the waters of the Gulf of Gdańsk with river runoff. Of course, in addition to mercury or phenol derivatives, a number of different pollutants are introduced into sea waters. These may act in synergy, thus increasing their bioaccumulation or biomagnification capacity. After comparing the concentrations obtained in this study with those found in the literature, it can be concluded that the concentrations were in most cases similar or lower. BPA is measured in rivers, water treatment plant waste and effluent from such plants (Santhi et al. 2003, Crain et al. 2007). The highest concentrations of this compound (reaching even hundreds of ng dm^{-3} [Yamazaki et al. 2015, Huang et al. 2020, Wu et al. 2013, Jin et al. 2004]) are found in Asian rivers, often flowing through huge metropolitan areas, where the dense population entails high production of BPA-containing waste and highly developed industry. In Europe, concentrations of these compounds are as much as two orders of magnitude lower. For example, as reported by Cladiere et al. (2013), in the Seine the concentrations of bisphenol A were 154 ng dm^{-3} and were similar to the concentrations of 4-NP (28–157 ng dm^{-3}). In turn, in one of the tributaries of the Rhine in Switzerland, Voutsa et al. (2006) found endocrine-active phenol derivatives within a range of 68–326 ng dm^{-3} for 4-NP, 6–22 ng dm^{-3} for 4-t-OP and 9–76 ng dm^{-3} for BPA. In river water samples in southern Germany, BPA concentration was within a range of 500 pg dm^{-3} to 16 ng dm^{-3}, while 4-nonylphenol concentrations were between 6 and 135 ng dm^{-3}.

5. Conclusions

Rivers are undoubtedly an important inflow route for endocrine disruptive phenol derivatives, i.e. bisphenol A, 4-tert-octylphenol and 4-nonylphenol, into the Southern Baltic. In the case of the Vistula, the second largest river in the Baltic Sea catchment area, over 6000 kg of BPA is introduced annually via this route, and about 900 kg of 4-t-OP and 4-NP each. This may constitute a greater load than in other regions of the world, e.g. in some part of Asia, where the consumption of phenol derivatives is higher than in Europe. Moreover, the load of phenol derivatives is similar or even greater than the load of mercury, another substance with endocrine-disruptive properties introduced by the Vistula. On the other hand, the limited data on the loads of bisphenol A or alkylphenols introduced by other rivers makes far-reaching conclusions difficult, but does indicate that such loads should be taken into account to illustrate the scale of the phenomenon. The research has shown that the outflows of BPA, 4-t-OP and 4-NP via the Vistula constitutes almost 100% of the load of these compounds introduced into the Gulf of Gdańsk. Smaller rivers, with lower flows, have a much smaller contribution, but the short-term concentrations occurring there may exceed the values that are safe for organisms, as shown in both the previous studies in 2011 and 2015 and the present study. The greatest loads and the highest concentrations were recorded in summer. This is undoubtedly related to the tourism in the research area, which is visited by millions of tourists every year, as this increased human presence is associated with the use of a number of products containing phenol derivatives. Unfortunately, it is also the consequence of rubbish that these masses of people leave behind in the environment. An interesting regularity was observed in the research: The concentrations in riverine water were approx. 1.5 to 7 times higher at the source than at the outlet. This phenomenon is interesting because the rivers in question are not long and the flow of water is not high. It is possible, however, that the land development in the catchment area may be important (the proximity to households and farms leads to point runoff of pollutants), as is the type of bottom sediments on which phenol derivatives can sorb (providing some protection for the coastal waters, which consequently receive a limited amount of phenol derivatives). It must not be forgotten, however, that these incidental high concentrations of endocrine-disruptive compounds in the waters of smaller rivers are significant for the organisms living there and may be exceptionally important locally. After all, water from small rivers is often used by breeders to water their animals or water their own crops. In addition, many small bathing areas are located on small rivers. Therefore, the study undoubtedly constitutes a basis for further research, aimed not only at measuring the pollution of river waters with BPA, 4-t-OP or 4-NP, but also determining the total budget for the inflow of these compounds into the Gulf of Gdańsk.

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Conflict of interest

The authors declare that they have no conflicts of interest.

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