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# The relationship between the black carbon and bisphenol A in sea and river sediments (Southern Baltic)

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ABSTRACT

This study was derived from field investigations to assess bisphenol A (BPA) concentrations in the sea and river sediments of the Gulf of Gdansk. Black carbon (BC) and total organic carbon (TOC) were identified as influencing factors on the accumulation. As a result of the transportation of BC with organic matter *via* rivers into the Gulf of Gdansk, the highest mean concentrations (11.26 ng BPA/(g dry weight (dw))), were determined in the sediments of river estuaries. Sediments in coastal stations were characterized by the lowest mean concentrations (5.73 ng BPA/(g dw)). TOC content below 0.1% determined the sorption of BPA on BC particles in sediments, and statistically significant correlation between the concentration of BPA and the BC/TOC ratio was found in these cases. In addition, dependency between the concentration of BPA and the content of BC was discovered in sediments where the BC/TOC ratio was >0.33.



## Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) belongs to the group of so-called Endocrine Disrupting Compounds, which interfere with the functioning of the hormonal system in living organisms. In animals, BPA leads to feminization or hermaphroditism, while in humans it causes obesity, abnormal functioning of thyroid hormones, fertility problems and increased risk of cancer, including breast and prostate cancer (Flint et al., 2012).

Since the 1950s, BPA has been widely used in the production of synthetic materials, mainly polycarbonate and epoxide resins. BPA is found for example in products that come into contact with food (resins lining most metal tins, containers), in products of everyday use and in various components found in *e.g.*, cars and homes (construction elements, films covering various surfaces, such as CDs, mobile phones, varnishes and paints, water drainpipes, sport equipment, hulls of boats), in medical products (medical equipment, dental fillings, prosthetic limbs), *etc.* In foods and cosmetics, BPA is often used as an antioxidant (ECHA, 2008).

The first restrictions limiting the use of BPA in the EU were introduced in March 2011. The production, transportation and sale of baby bottles containing BPA is now forbidden as a result of a European Committee decision. However, the use of BPA in Europe amounts to 30% of global production (about 1.6 million tonnes). Annual production in the EU countries is the biggest in the Netherlands with 425, Germany 400, Spain 340 and Russia 150 thousand tons/year (ICIS Chemical Business, 2008). Production in the drainage area of the Baltic Sea is at a lower level. The most significant production takes place in Poland in Kędzierzyn Koźle, and can be estimated at about 18–20 thousand tons/year (ICIS Chemical Business, 2008; http://www.pccsynteza.pl).

The few available studies prove that despite the lowest production and use of bisphenol A of the European countries, this compound is present in the drainage area of the Baltic Sea in concentrations reaching up to several μg/(kg dry weight (dw)) in plankton organisms, mussels, fish (herring, perch and

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flounder), and gulls (HELCOM, 2010; Staniszewska et al., 2014). The omnipresence of this compound in the environment of the Baltic Sea represents a potential problem. In addition, slow decomposition of synthetic materials and the extraction of their components may result in a several decade-long processes of BPA release from polycarbonate debris into the environment. The fact that the problem is on a global scale is highlighted by papers on the leaching of additives from polymers into oceanic waters from plastic debris (Teuten et al., 2009). These researchers point to nanoparticles of synthetic materials as carriers of organic pollutants, such as phenol derivatives, transporting them to benthic organisms.

Owing to its uses, the main sources of BPA in the environment are debris and wastewater. From the land, BPA is transported eolically and *via* watercourses, ending up first in water and then in bottom sediments of water basins. The BPA concentrations in the near-bottom water of the coastal zone in the Gulf of Gdansk ranged from <5.0 to 152.6 ng/L, indicating its presence in sediment (Staniszewska et al., 2015). In sediments, BPA has higher sorption than is indicated by the relatively low octanol/water partition-coefficient ($\log K_{o/w}$ = 3.3–3.5; European Commission, 2014). Kang et al. (2006) attribute this to physical–chemical conditions that are favorable for BPA longevity in sediments: low oxygen content and no light. The high affinity of BPA for hydrophobic zones in the sea is confirmed by high enrichment factors that were noted for the surface microlayer of the Gulf of Gdansk, amounting to 4.4 (Staniszewska et al., 2015). However, the main factor responsible for high sorption of BPA in sediments is probably the presence of black carbon (BC). BC comes mainly from the combustion of fossil fuels (exhaust fumes, industry and home heating), waste burning and biomass burning. Long-term research has shown that BC is characterized by between 10 and 1000 times higher sorptive ability than organic matter (humic and fulvic acids) for hydrophobic compounds such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins and polybrominated diphenylethers (Bärring et al., 2002; Jonkers and Koelmans, 2002; Bucheli and Gustafson, 2003; Koelmans et al., 2006).

There is no available information on the levels of BPA concentrations in surface sediments of the Southern Baltic. Therefore, the aim of the present paper was to gauge the level of BPA pollution in the surface sediments of the Gulf of Gdansk and to determine the factors influencing these concentrations. Owing to the fact that the role of black carbon in the sorption of bisphenol A is not fully understood, a focus was placed on clarifying the dependency between BPA and black and total organic carbon concentrations in sediments.

## 1. Materials and methods

### 1.1. Sample collection

The study material was collected in 2011 and 2012 in three different seasons (spring, summer, and autumn). The stations were located in the coastal zone of the Gulf of Gdansk: 3 in river estuaries, 4 on the coast close to urbanized areas, and 5 offshore in the Gulf of Gdansk (Fig. 1).

The Gulf of Gdansk forms the catchment of several rivers in the Pomerania region, the most significant of those being Poland's longest river — the Vistula (ST1) (average flow: 1046 $m^3$/sec). This river measures 1047 km, and has a drainage area of 194,424 $km^2$. The Kacza (ST2) is a watercourse flowing through Gdynia (measuring 14.8 km), whose drainage area (53.8 $km^2$) consists of marshy areas, densely covered with bushes and woods. The main sources of pollutants are the nearby urbanized areas. The Gizdepka (ST6) is a small river (11.8 km) flowing mainly through agricultural areas. It receives pollutants through surface run-off from cultivated fields and farms and flows into Puck Bay near Oslonino. Samples of bottom sediment from rivers were collected at a short distance (5–10 m) from their outlets into the Gulf of Gdansk.

The Orlowo Pier (ST3), the Seaside Boulevard in Gdynia (ST4) and Mechelinki (ST5) are all located close to beaches and recreational sites, frequented by large numbers of tourists, particularly during summertime. In addition, the Seaside Boulevard is adjacent to a marina and the Mechelinki station (ST5) is located close to one of the largest water purification plants in the Tri-city agglomeration (Gdansk, Sopot and Gdynia: total population around one million). Station ST3 was located in the outlet of the Kacza River, in the vicinity of the wooden pier in Gdynia, and station ST7 was in Swarzewo, a holiday destination also featuring a water purification facility (Fig. 1).

The offshore stations were located from 1 to 19 km from the coast. UW station was located 7 km to the North-East of the Vistula estuary, 40 m below sea level; SP station was located 7 km away from Orlowo Pier, 17 m below sea level; GDY station was located 4 km away from the entrance to Gdynia Harbor, 12 m below sea level; GN station was located 19 km to the North-West of the Vistula estuary, 37 m below sea level; and ME station was located about 1 km away from the coast, 4 m below sea level (Fig. 1).

5-centimeter-thick surface layers of sediments were collected using a Nemistö sediment corer. Samples were then frozen, and subsequently lyophilized and homogenized. The following physicochemical properties were determined in the sediment samples as well as BPA concentrations: wetness (W), loss-on-ignition (LOI), total organic carbon (TOC), BC and granulometric composition.

### 1.2. Determination of BPA

All solvents (water, acetonitrile and methanol) were HPLC grade and were purchased from Merck. 70% perchloric acid (VII) –$HClO_4$ and ammonium acetate (analytically pure) were purchased from POCh. High purity (>97%) BPA was obtained from SIGMA-ALDRICH®. Stock and working solutions (respectively: 1 mg/mL and 10, 25, 50, 75, 100 ng/mL) of each compound were prepared in methanol.

In order to determine BPA, 2.0 g of sediment was extracted by mixture of 2 mL of 0.01 mol/L ammonium acetate, 8 mL methanol and 100 μL perchloric acid(VII) in an ultrasonic bath (10 min, 20°C). The supernatant after centrifugation was supplemented to a volume of 20 mL of 0.01 mol/L ammonium acetate. It was then purified on Oasis HLB (Waters) glass cartridges (5 mL/200 mg) according to the procedure set out by Staniszewska et al. (2014). Extraction columns were

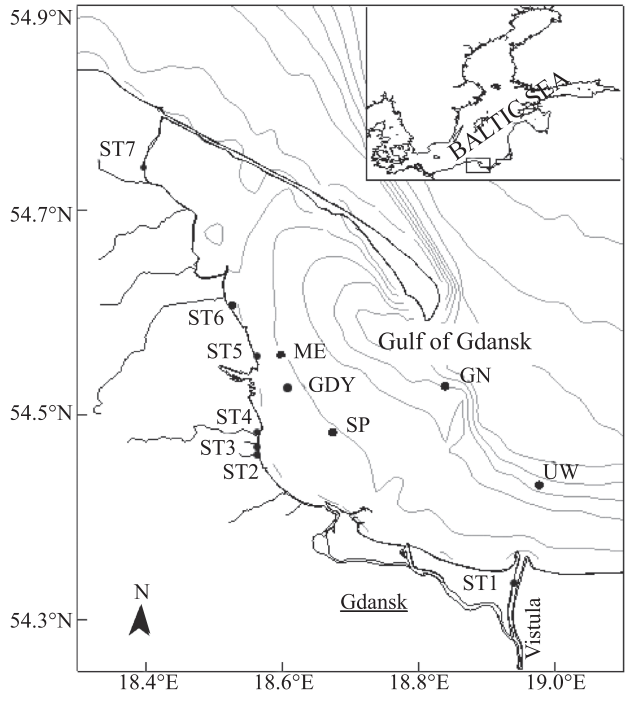


**Fig. 1 – Locations of sediment sampling sites in river outlets and in the Gulf of Gdansk in 2011–2012.**

preconditioned by washing with 10 mL of methanol followed by 5 mL of water and ammonium acetate (0.01 mol/L) at the flow rate of 1 mL/min. Next, the sample was passed through the column bed at the flow rate of 5 mL/min. After the enrichment step, the bed was dried under vacuum for 5 min. BPA was eluted from the columns with methanol (2 × 4 mL). The obtained extractions were dried through evaporation, and the dry remnants were dissolved in 200 μL of acetonitrile. The final determinations were performed using high-performance liquid chromatography with fluorescence detection (Dionex; excitation at λ = 275 nm and emission at λ = 300 nm). Chromatographic separation was conducted on a HYPERSIL GOLD reversed phase column (Thermo Scientific) with a mobile phase at 1 mL/min (acetonitrile and water) under gradient conditions: 70% $H_2O$ and 30% acetonitrile for 1 min; ACN from 30% to 65% from 1 to 12 min, ACN from 65% to 100% from 12 to 17 min, 100% ACN for 4 min and return to baseline conditions in 3.5 min.

All operations at the BPA collection and determination stages were carried out using tools and containers made of glass, Teflon or metal. Glass vessels were thoroughly cleaned prior to use, etched in a 3.5 mol/L nitric acid solution (V) for 24 hr and then rinsed in deionized water and dried at a temperature of 200°C.

The linear correlation coefficient (*r*) of the analytical curves was >0.999. The average amount of BPA recovered, determined through a quintuple analysis of samples containing an added known amount of the standard, was 91%. The achieved precision (variation coefficient) was <13%. The limit of quantification (LOQ) was determined as ten times the signal to noise ratio for a sample with very low analyte content and amounted to 0.08 ng/g dry weight. The background for the blank sample was checked every time a new batch of columns was used and the obtained "background" values for BPA were <LOQ.

### 1.3. Physicochemical properties of sediments

The wetness of sediments was determined by measuring the loss of wet sediment mass after 24-hr drying session at 105°C until constant mass was reached. Granulometric analysis was performed by sifting dry sediment through a set of metal sieves of the following mesh dimensions: 2.00; 1.00; 0.5; 0.125; and 0.063 mm. Loss-on-ignition was determined as the change in dry sediment mass after igniting at 550°C until constant mass was reached (Heiri et al., 2001).

Carbon forms (TOC and BC) were determined using a 2400 Series II CHNS/O, Perkin Elmer, USA through combustion of a dry sediment sample. When analyzing total organic carbon, the sample have previously been acidified (1 mol/L HCl) in order to remove carbonates (*i.e.*, Hedges and Stern, 1984). BC was analyzed with the chemothermal oxidation method, as described by Gustafsson et al (1997) and Elmquist et al. (2004). When analyzing BC, an additional stage was implemented following carbonate removal and consisted of ignition at 375°C for 18 hr with constant air flow. To ensure quality, the samples were always repeated three times. Reproducibility (replicate analysis of the samples) of carbon measurements was better than 5% at concentrations above 0.1 wt.%, but was on the order of 15% at concentrations less than 0.05 wt.%. The limit of BC detection was 0.03 μg in 1 mg of sample.

### 1.4. Statistical analysis and data normalization

Statistical analysis, as well as a visual representation of the obtained results, was carried out using the STATISTICA 10 program by Stat Soft. The normality of data distribution was checked using the Shapiro–Wilk test ($p < 0.05$). Most results were of a non-parametric nature, so the Kruskal–Wallis test was used to determine the significance of differences ($p < 0.05$). The dependencies were determined using the Spearman's correlation coefficient (*r*), adopting a confidence interval of 95%.

It can be stated that hydrophobic organic contaminants or black and organic carbon are mainly adsorbed onto the particles of small grain size sediments (Ø < 0.063 mm), which have large surface area (Mayer, 1993; Keil et al., 1994). In order to compare and determine the dependencies between BPA concentrations and BC, TOC content, BPA, BC and TOC results were normalized to the smallest fraction of Ø < 0.063 mm based on the following equation (Beldowski and Pempkowiak, 2007):

$$A_{\varnothing} = \frac{A}{10^{-2} \times (\varnothing < 0.063\text{mm})}$$

where, $A_{Ø}$ is the concentration/content normalized to the smallest sediment fraction, *A* is the concentration/content, and Ø < 0.063 is the percentage of the finest fraction of sediment.

In our work normalizing BPA, BC, and TOC to the sediment fraction Ø < 0.063 mm in 66 samples, statistically significant correlation was found between the concentrations of BPA, BC, TOC and the smallest fraction ($r = 0.72$; $r = 0.79$; $r = 0.61$ $p < 0.05$).

## 2. Results

### 2.1. The characterization of bottom sediments from the study area

The mean wetness of the sediments collected in the Gulf of Gdansk amounted to 21%, and the organic matter content (LOI) was 2%. More than 90% of the samples collected in the Gulf of Gdansk contained sand sediments. Only 3% contained silt (stations GN and UW), and had a high mean content of the smallest sediment fraction with particles of <0.063 mm in diameter (29.6% and 79.7% respectively) (Table 1). By contrast a sample from the station located in the vicinity of the water purification plant in ME had a 400 times lower content of the smallest sediment fraction. However, the smallest content of the finest fraction was determined in the bottom sediments collected in the Kacza River estuary, which were of a gravelly nature, and loss-on-ignition was the highest (6.9%). The sediments from the station in the Vistula Estuary (ST1) and those located to the north of its outlet had two times lower organic matter content. Among the sediments from the coastal stations, the highest average content of the mean sediment fraction was found in the Swarzewo area (ST7) at 0.2%, this also being the most hydrated sediment (22.2%). Sediments collected from the Mechelinki station (ST5) and from the Gdynia Boulevard (ST4) were characterized by similar contents of the finest fraction <0.07% (Table 1).

### 2.2. Bisphenol A, organic and black carbon

BPA was assayed in all the analyzed sediment samples, and the mean BPA concentration for all sediments amounted to 7.24 ng/(g dw). The average contents of total organic carbon and BC were 0.23% and 0.05% respectively (Table 1). Having categorized the results according to station locations, it was found that the highest mean (11.26 ng/g) BPA concentrations came from the river outlets (ST1, ST2, ST6). The sediments originating from coastal stations had the lowest mean BPA concentrations, amounting to 5.73 ng/g dw. The highest individual BPA concentration recorded at any station was noted in sediment collected in the Vistula Estuary (ST1) (60.20 ng/(g dw)), while the lowest average concentration was determined in a sample from the Gizdepka Estuary (ST6) (2.64 ng/(g dw)). That sediment (ST6) was characterized by the highest contents of both TOC (0.18%) and BC (0.04%) among river estuary sediments. The smallest total organic carbon content was determined for sediment from the ME station (0.07%), and it was an order of magnitude smaller than that of the sediment from the UW station, where the BC content was at its highest among offshore stations. Sediment from the UW station had the highest average total organic carbon and black carbon contents, at a level of 0.90% and 0.17% respectively.

## 3. Discussion

### 3.1. The pollution of sediments in the Gulf of Gdansk by BPA

BPA concentrations in the sediments of the Gulf of Gdansk were low in comparison with other regions of the world (Table 2).

BPA, possessing endocrine-like properties, can have a negative effect on marine organisms inhabiting bottom sediments. In order to determine the danger posed by the presence of BPA in the sediments of the Gulf of Gdansk, the obtained concentrations were compared to the PNEC (predicted no effect concentration). According to the European Commission (2010) the BPA concentration limit that is safe for organisms is 36 ng/g dw. The results for sediments from the Gulf of Gdansk suggest that the levels of BPA found there do not pose a threat to organisms. Only one sediment sample from the Gulf of Gdansk (station ST1) exceeded the concentration limit, but it was only by as much as 60%. In the literature, more highly polluted sediments can be found, for example in the river sediments of the Elbe or the Mediterranean Sea by the Italian coast, where BPA concentrations were up to 10 times higher than the PNEC value. There are also areas (Anzali Wetland in Iran, the Pearl River in China, and 39 American Streams in the USA) where BPA concentrations were not higher than the accepted safe concentration value for bottom organisms (Table 2).

### 3.2. The influence of black and total organic carbon on BPA concentration in sediments

Tsai et al. (2006) and Sun et al. (2010) pointed to condensed organic matter: non-hydrolyzable carbon (NHC) and black carbon (BC), as two factors responsible for the sorption of 3.2 BPA in sediments. In the sediments from the Gulf of Gdansk, however, no statistically significant correlation was found between the BPA concentration and BC content in relation to the smallest sediment fraction in all analyzed samples. A statistically relevant correlation between BPA concentration and BC content in relation to the smallest sediment fraction appeared only for sediments characterized by a BC/TOC ratio over 0.33 ($n = 31$; $r = 0,75$; $p < 0.05$). With sediments where the BC/TOC ratio was lower than 0.33, there was no statistically significant correlation. This is confirmed by results obtained by Zeng et al. (2006), which indicated a non-linear sorption isotherm in sediments low in BC.

The present studies have shown that an important role in the sorption of BPA onto sediment samples from the Gulf of Gdansk is played not only by the concentration of BC itself, but also by the co-presence of organic matter expressed as TOC concentration. It has been observed in several studies that BC plays a decisive role in the sorption of PAHs in sediments that are high in black carbon and low in organic carbon (Staniszewska et al., 2011). In sediments that are high in organic carbon, the predominant phenomenon may be that of organic matter competing against BPA for hole-filling in elemental carbon, which as a result weakens the sorptive abilities of BC in relation to BPA (Tian et al., 2009). Zeng et al. (2006) reported a higher sorptive capacity (about 30%) in

**Table 1 – Wetness (W), loss of ignition (LOI), content of the smallest fraction <0.063 mm (Ø); total organic and black carbon (TOC, BC) and bisphenol A (BPA) average concentrations in samples of sediments collected from river outlets, coastal stations and stations located at the depth > 4 m.**

| | | Sampling station | W (%) | LOI (%) | TOC (%) | BC (%) | BPA (ng/g dw) | Ø (%) |
|---|---|---|---|---|---|---|---|---|
| River outlets | ST6 | Gizdepka River | 17.67 ± 4.51 | 0.48 ± 0.20 | 0.18 ± 0.20 | 0.04 ± 0.01 | 2.64 ± 4.89 | 0.17 ± 0.12 |
| | ST2 | Kacza River | 15.33 ± 2.36 | 6.90 ± 9.36 | 0.09 ± 0.08 | 0.02 ± 0.04 | 9.86 ± 12.90 | 0.04 ± 0.02 |
| | ST1 | Vistula Swibno | 12.45 ± 9.41 | 3.48 ± 2.89 | 0.12 ± 0.04 | 0.03 ± 0.01 | 21.25 ± 21.01 | 1.17 ± 0.71 |
| Costal station | ST7 | Swarzewo | 22.25 ± 3.70 | 0.90 ± 0.88 | 0.19 ± 0.19 | 0.02 ± 0.03 | 3.39 ± 5.67 | 0.17 ± 0.09 |
| | ST5 | Mechelinki | 16.20 ± 3.51 | 0.29 ± 0.14 | 0.04 ± 0.01 | 0.02 ± 0.01 | 7.81 ± 9.99 | 0.07 ± 0.04 |
| | ST4 | Gdynia Seaside Boulevard | 14.37 ± 4.43 | 0.49 ± 0.17 | 0.04 ± 0.02 | 0.01 ± 0.01 | 5.47 ± 6.26 | 0.05 ± 0.03 |
| | ST3 | Orlowo Pier | 17.98 ± 1.37 | 1.3 ± 2.34 | 0.03 ± 0.02 | 0.01 ± 0.01 | 4.70 ± 6.80 | 0.14 ± 0.10 |
| Offshore station | ME | | 18.40 ± 2.87 | 2.69 ± 5.29 | 0.06 ± 0.02 | 0.02 ± 0.01 | 6.40 ± 5.88 | 0.22 ± 0.15 |
| | SP | | 19.58 ± 2.55 | 0.60 ± 0.30 | 0.11 ± 0.12 | 0.02 ± 0.01 | 3.51 ± 2.96 | 0.60 ± 0.47 |
| | GDY | | 23.45 ± 6.74 | 1.42 ± 0.95 | 0.35 ± 0.55 | 0.05 ± 0.08 | 5.08 ± 5.38 | 1.46 ± 1.03 |
| | GN | | 24.98 ± 18.16 | 2.58 ± 4.21 | 0.67 ± 0.97 | 0.17 ± 0.37 | 10.41 ± 6.83 | 14.94 ± 35.55 |
| | UW | | 34.47 ± 19.01 | 3.81 ± 6.29 | 0.90 ± 0.98 | 0.17 ± 0.27 | 6.39 ± 5.88 | 40.32 ± 44.02 |

Data are presented as average content ± standard deviation

relation to BPA in sediments thermally deprived (at 375°C) of organic matter. They attributed this to the opening of pores in BC and mineral components of the sediment that had been previously blocked by organic matter.

The strong sorption of BPA onto BC is conditioned by the aromatic structure of the particle and bonding of the π–π type occurring between BPA and BC (Zhu et al., 2004; Pan et al., 2008; Sun et al., 2010). Pan et al. (2008) indicate even stronger BPA sorption on small particles of carbon nanomaterials than in the case of typical hydrophobic compounds such as PAHs, owing to the fact that the phenolic group is a good electron donor and makes it possible for strong π–π donor–acceptor bonds to be formed between BPA and a carbon particle. In the case of PAHs, where only benzene rings are present, such strong connections are not formed. However, the main BPA sorption mechanism in BC, as stated by Braida et al. (2003), is the penetration by BPA, which measures 0.43 nm in diameter, into available micropores and submicropores (0.3–0.5 nm) in the surface of BC. This results in competition with other compounds of suitable dimensions to fill the micropores. Xing and Pignatello (1997) proved the non-linear sorption for compounds with a tendency to penetrate into the micropores, particularly at small BC concentrations when most sorption sites are already filled by other compounds.

In the coastal zone of the Gulf of Gdansk, the low organic matter content promotes the sorption of BPA onto BC, which results from deposition to sediments *via* the atmosphere. This is confirmed by a high positive correlation coefficient between BPA concentration and the BC/TOC ratio determined in relation to the finest sediment fraction ($n = 56$; $r = 0{,}88$; $p = 0.02$) in all the collected sediments. The highest BPA concentrations in the fine fraction were found in rivers and the coastal zone, where the BC/TOC ratio was at its highest. The stations located in the vicinity of the Debogorze water purification plant (ME, ST5), in the outlet of the River Kacza (ST2), at the Seaside Boulevard (ST4) and at the Orlowo pier (ST3) stood out in this respect. At those stations the mean BC/TOC ratios were 2 times higher and BPA concentrations per smallest sediment fraction were 7 times higher than at other stations (Table 3). The low organic matter content at these stations derives from the type of sediment (sands), while the high content of BC results from proximity to uncontrolled burning areas.

Organic carbon content, which controlled the BPA sorption onto BC in sediments from the Gulf of Gdansk, was determined

**Table 2 – Concentrations of BPA in surface sediments in the Gulf of Gdansk compared with concentrations in other regions of the world.**

| Area of study | | Sediment type | BPA (ng/g dw) | Quantity of samples > PNEC (%) | References |
|---|---|---|---|---|---|
| Rivers sediment | Pearl River (China) | Silt | 0.58–2.16 | 0 | Peng et al. (2006) |
| | Elbe (Germany) | Silt | <LOQ-380 | 33 | Stachel et al. (2003) |
| | Beijing-Wenyu (China) | Silt | 0.6–59.6 | 6 | Lei et al. (2008) |
| | 39 American Streams | Sand | <LOQ-15 | 0 | Kolpin et al. (2002) |
| | Baden-Wurttemberg (Germany) | Sand | <50.0–272.0 | 0 | Bolz et al. (2012) |
| | Gulf of Gdansk | Silt | 0.2–60.2 | 3 | This study |
| Marine sediment | North Sea (Holand) | Sand | 5.6–56 | 13 | Vethaak et al.(2005) |
| | Mediterranean Sea (Italy) | Sand | 2.0–118.0 | 33 | Pojana et al. (2007) |
| | Masan Bay (Korea) | Sand | 2.7–50.3 | 5 | Khim et al. (1999) |
| | Anzali Wetland (Iran) | Silt | 1.0–6.97 | 0 | Mortazavi et al. (2012) |
| | Tokyo Bay (Japan) | Sand | 5.20–48 | 0 | Hashimoto et al. (2005) |
| | Gulf of Gdansk | Sand | 0.1–32.2 | 0 | This study |

PNEC: predicted no effect concentration.

to be below 0.1%. For sediments containing TOC < 0.1%, a statistically significant correlation was found between bisphenol A concentration and the BC/TOC ratio in relation to the finest sediment fraction ($n$ = 43; $r$ = 0,67; $p$ = 0.02,), while for sediments with TOC content > 0.1% no such correlation was determined.

An additional factor that is favorable to BPA sorption onto BC is the weak BPA bonding with organic carbon. This is confirmed by a high negative correlation coefficient between the concentration of bisphenol A in the sediments of the Gulf of Gdansk and total organic carbon content in relation to the finest sediment fraction ($n$ = 71; $r$ = −0.81, $p$ = 0.02). In an experiment conducted by Tian et al. (2009), strong bonding was indicated between BPA and mineral components of sediment such as kaolinite, illite and montmorillonite, but not with organic matter. Zeng et al. (2006) observed a linear sorption isotherm for sediments containing only mineral particles. On the other hand, as shown by Sun et al. (2010), the interaction between humic acids – a significant component of organic matter – and compounds like BPA, 17-alpha-ethinyl estradiol and 17-beta-estradiol, decreases with the number of phenolic groups in an endocrine compound. In the abovementioned experiment, BPA interacted the least with humic acids. This interaction was indicated in the study by Tian et al. (2009) by a dramatic decrease in pH above 8.34 when BPA transferred to its anionic form and became more negatively charged. Samples from the near-bottom water layer (Staniszewska et al., 2015) were characterized by pH in the range 7.0–8.6, and only three samples had a pH value above 8.34. So we can say that the pH is not a decisive factor in the lack of affinity of BPA for marine sediments in the Gulf of Gdansk.

After applying the Kruskal–Wallis test, there were no statistically significant differences found between the values of the BC/TOC ratio normalized to the finest fraction of the sediment Ø < 0.063 mm collected from all offshore stations ($H$ = 5.2486; $n$ = 30; $p$ = 0.0895) (Fig. 2a). However, the station ME stands out slightly as compared to other stations. After grouping sediment collected from the other four stations (GN, GDY, SP, UW) and comparing with the station ME, a statistically significant difference is seen ($H$ = 8.422; $n$ = 30; $p$ = 0.0374) (Fig. 2b). A similar analysis for the concentration of BPA showed that there were also statistically significant differences between the concentration of BPA normalized to the smallest fraction of sediment collected from offshore stations compared with the station ME ($H$ = 7.5466; $n$ = 30; $p$ = 0.006) (Fig. 2c). This result confirmed the hypothesis of the influence of the BC/TOC ratio on BPA sorption. The station that stood out was one located close to the Debogorze purification plant (ME), which was characterized by the lowest total organic carbon content (one order of magnitude lower), a 3 times higher BC/TOC ratio and 5 to 336 times higher BPA concentration normalized to the finest fraction Ø < 0.063 mm in comparison to the other stations (UW, GN, SP, GDY) (Table 3).

Separation of stations: UW, GN, SP, and GDY may suggest a common source of BPA, BC and organic matter at those stations (Fig. 2b and c). BC may come from various sources, such as car exhaust fumes, oil burning and biomass combustion. It was found that black carbon of anthropogenic origin has a higher capacity for the sorption of organic pollutants than black carbon of natural origin (Jonker and Koelmans, 2002). BPA and BC at stations SP and GDY, located close to urbanized areas, might have originated mainly from combustion processes (Sidhu et al., 2005; Fu and Kawamura, 2010). BPA and BC could have travelled to stations located further off into the gulf *via* atmospheric transport and with the River Vistula waters (UW, GN). In the case of station ME, the predominant BPA source was most likely the water purification plant, which together with the relatively low content of organic carbon in the sediments, may be conducive to high accumulation of BPA on the BC. However, the source of BC is located outside the wastewater, most likely being combustion processes.

**Table 3 – Mean BC/TOC ratios and BPA concentrations normalized to the finest sediment fraction in samples collected from river outlets, coastal stations and stations located at depth > 4 m.**

| | Sampling station/ variable | | $BC_{Ø}$/ $TOC_{Ø}$ | $BPA_{Ø}$ (ng/g dw) |
|---|---|---|---|---|
| River outlets | ST6 | Gizdepka River | 0.18 ± 0.13 | 2695.5 ± 5536.6 |
| | ST2 | Kacza River | 0.29 ± 0.14 | 12411.7 ± 8427.9 |
| | ST1 | Vistula Swibno | 0.32 ± 0.10 | 6635.2 ± 12737.4 |
| Coastal station | ST7 | Swarzewo | 0.11 ± 0.13 | 9356.8 ± 15386.1 |
| | ST5 | Mechelinki | 0.46 ± 0.02 | 16279.9 ± 38238.8 |
| | ST4 | Gdynia Seaside Boulevard | 0.30 ± 0.21 | 31467.6 ± 57129.2 |
| | ST3 | Orlowo Pier | 0.36 ± 0.14 | 15384.4 ± 35028.1 |
| Offshore station | ME | | 0.32 ± 0.22 | 3894.4 ± 4420.3 |
| | SP | | 0.27 ± 0.14 | 943.8 ± 1312.9 |
| | GDY | | 0.20 ± 0.12 | 268.3 ± 211.4 |
| | GN | | 0.11 ± 0.12 | 971.8 ± 1143.6 |
| | UW | | 0.18 ± 0.16 | 423.1 ± 621.3 |

Data are presented as average content ± standard deviation.

The variability of BPA concentrations in the surface sediments of the Gulf of Gdansk was related to the seasonal variability of the BC/TOC ratio. There were no statistically significant differences between the seasonal changes in the BC/TOC ratio and BPA concentrations normalized to the smallest fraction of the sediment for all seasons and stations (Kruskal–Wallis test, $H$ = 7.9241; $n$ = 56; $p$ > 0.05). This indicates similar seasonal variability for both parameters. The highest BPA concentrations were obtained in the summer and the lowest in spring and autumn in river outlets, coastal and offshore stations (Fig. 3). A similar seasonal variability of BC/TOC ratio values was obtained, especially from offshore stations. A similar profile of seasonal variability for both parameters confirms the deep relation between them. It may also indicate a common source of BC and BPA.

Additional factors influencing the highest BPA concentrations in sediments, obtained in summer, were the physicochemical qualities of the water and anthropogenic BPA sources. Similar conclusions were arrived at by Kitada et al. (2008), who found higher bisphenol A concentrations in sediments in summer, compared to the winter–spring period. According to Sajiki and Yonekubo (2003), higher water

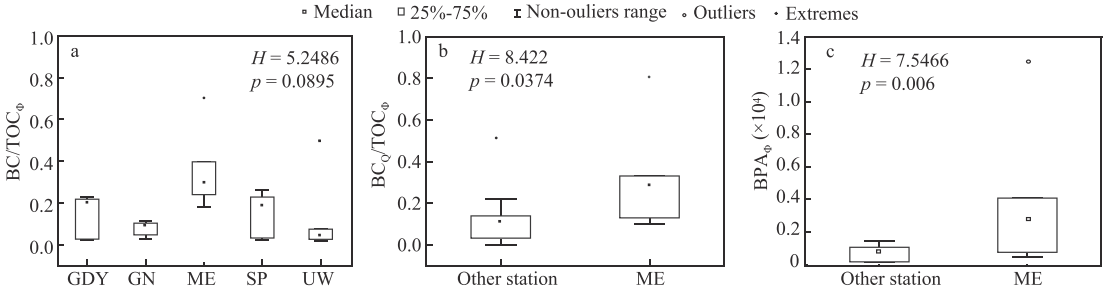


**Fig. 2 – Kruskal–Wallis test for BC/TOC ratio (a, b) and mean BPA concentration (c) normalized to the finest fraction Ø < 0.063 mm conducted for offshore stations.**

temperatures facilitate the leaching of BPA from synthetic materials. In experimental research, the speed of BPA leaching was 1.6 ng/(mL·day) at 20°C, while at 37°C this value was an order of magnitude higher (11 ng/(mL·day)).

In the coastal zone, the increased BPA content in water and sediments results from the widespread use of BPA in various areas of the paint industry (plasticizers, paints and epoxy resins), paper production and the chemical industry (Furhacker et al., 2000) and the leaching of this compound from the lining of water drainpipe walls (Imoaka et al., 2006). Increased shipping traffic and tourism in the summer period are also of significance here. Every summer more than 3 million tourists visit the Tricity alone, taking advantage of the city beaches and polluting the environment with, for example, cosmetics and synthetic materials containing BPA (Fig. 3c). In the case of river sediments, the highest mean BPA concentrations occurred in summer and could have been heavily influenced by runoff from the entire drainage area of the Vistula River (the largest Polish river) into the Gulf of Gdansk. The other two rivers, despite being small and slow-flowing, are also potential suppliers of BPA into the Gulf of Gdansk, due to the urbanized drainage area of the Kacza River and the agricultural drainage area of the Gizdepka River (Fig. 3c and d).

Similar anthropogenic sources of BC and BPA in coastal sediments of the Gulf of Gdansk were indicated by values of BC/BPA ratios equal to 1 in the finest sediment fraction from the outlets of small rivers (Gizdepka (ST6) and Kacza (ST2)) and sites located at some distance from the outlet (Swarzewo (ST7), Orlowo (ST3)) (Fig. 4). A characteristic feature of those sediments was a similar content of total organic carbon. A different situation was observed when comparing the BC/BPA ratio from the Vistula outlet (ST1) to a station located at sea further away from the outlet (UW). Station UW demonstrated a higher proportion of total organic carbon, as much as 6 times that of sediments in the Vistula estuary (ST1), and this was probably caused by lower BPA sorption in the sediments at that station.

Stronger bonding between BC and BPA in sediments at offshore stations than in coastal stations and in river outlets is indicated by the BC/BPA ratios calculated for those stations, ranging between $0.2 \times 10^6$ and $1.2 \times 10^6$. In addition, sediments collected in autumn at offshore stations were characterized by a statistically significant correlation coefficient between the

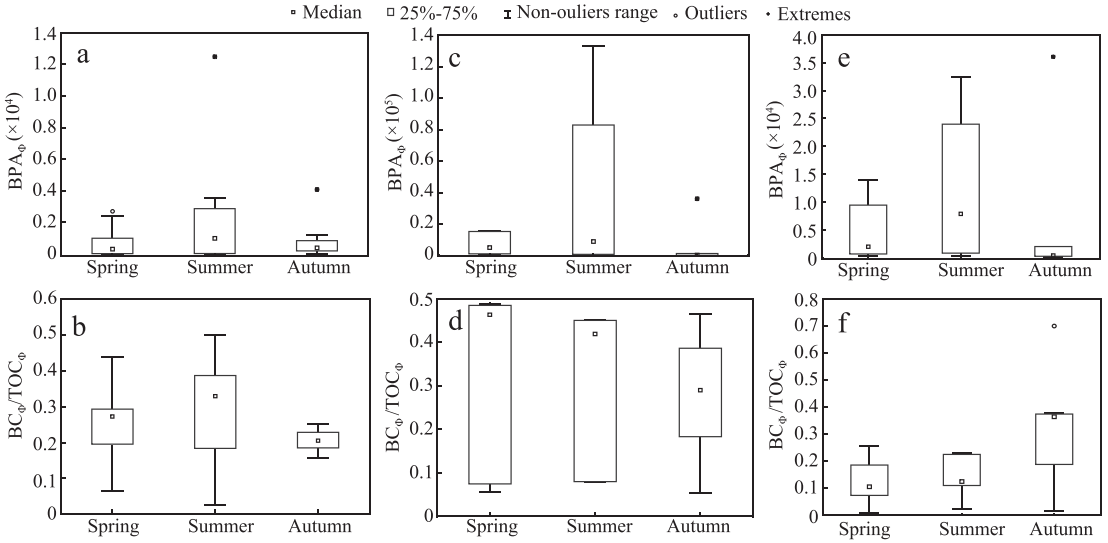


**Fig. 3 – Seasonal variability of BPA concentrations in relation to the smallest sediment fraction and the BC/TOC ratio in sediments collected from offshore stations (a, b), coastal stations (c, d), and river outlets (e, f).**

concentration of bisphenol A and the BC/TOC ratio in relation to the finest sediment fraction ($n$ = 10; $r$ = 0.87; $p$ = 0.02). This suggests a common origin of BC and BPA from combustion processes.

In autumn, the BPA formed in combustion processes (involving plastic debris) undergoes occlusion onto soot and carbon particles, and can thus be transported *via* the atmosphere and deposited further away from the coastal zone (Lewandowska et al., 2010). Sidhu et al. (2005) reported significant emissions of BPA from uncontrolled burning of domestic waste. A strong bonding between BPA and BC at offshore stations in autumn is additionally confirmed by the highest BC/BPA ratios being obtained then, which were found to be on order magnitude higher than in the spring–summer season. Earlier studies conducted by Lewandowska et al. (2012) indicated a statistically significant correlation ($n$ = 60; r = 0.5; $p$ = 0.02;) between the concentration of BPA and BC in small aerosols of <2.5 μm of diameter. This seems to confirm the relationship between those two parameters, indicating similar sources of origin. High bisphenol A concentrations recorded during the home-heating season in 2012 over Gdynia, ranging from 0.1 ng/m$^3$ to several ng/m$^3$ in small aerosols <2.5 μm, also point to the atmospheric transport of BPA adsorbed onto BC (Lewandowska et al., 2012). Such high concentration of BPA may come from combustion processes. It is possible that people may conduct uncontrolled burning of plastic waste in Gdynia and in the surrounding cities or villages, where coal-fired furnaces are common (Lewandowska et al., 2012).

## 4. Conclusions

In the sediments from the Gulf of Gdansk area (Southern Baltic), the highest mean concentrations of 11.26 ng/(g dw) were found in river outlets, while the lowest (5.73 ng/(g dw)) were noted in marine sediments at coastal stations. Compared to results found in literature from around the world, the concentrations do not indicate high contamination of the coastal area of the Gulf of Gdansk.

Studies showed that the presence of black carbon and organic matter both played an important role in BPA sorption onto the particles of sediments from the Gulf of Gdansk. The dependency between BPA concentration and black carbon manifested itself only in sediments where the BC/TOC ratio was >0.33. The highest BPA concentrations in the finest sediment fraction (Ø < 0.063 mm) were determined in rivers and in the coastal zone, where the BC/TOC ratio was at its highest. The seasonal variability of BPA concentrations in surface sediments of the Gulf of Gdansk was also connected to the variability of the BC/TOC ratio. 0.1% was accepted as the limit of organic matter content that was significant for BPA sorption onto BC. Weak bonding of BPA with organic carbon was indicated by the negative correlation coefficient between the concentration of BPA in the sediments from the Gulf of Gdansk, and total organic carbon content in relation to the finest sediment fraction.

High correlation between BPA concentration and the BC/TOC ratio in relation to the smallest sediment fraction at offshore stations was probably determined by BPA and BC emission from combustion processes, especially from uncontrolled burning of plastic waste, which in Northern Europe increases in autumn.

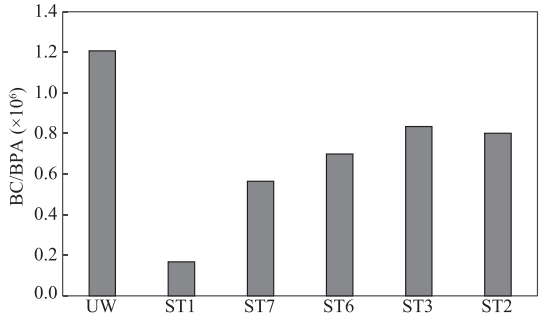


**Fig. 4 – Mean BC/BPA ratios in sediment samples collected in river outlets and stations situated the closest to the river outlets: Vistula River (ST1), UW, Gizdepka River (ST6), Swarzewo (ST7), Kacza River (ST2), and Orlowo Pier (ST3).**

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