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Polybrominated Diphenyl Ethers as the Emerging Contaminants in the Polish Environment

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are organobromine compounds with 209 theoretically possible congeners, including 1 up to 10 bromine atoms, each. They do not occur naturally in the environment but are synthesized as a result of the bromination of diphenyl ether. PBDEs are brominated flame retardants used in products to meet the fire safety requirements (de Wit 2002). Polybrominated diphenyl ethers are so-called emerging contaminants – substances that have recently been detected in the environment, are not included or have been included only recently in the regular monitoring programmes, and yet sufficient information does not exist to determine their potential environmental or public health risk (Naidu et al. 2016).

PBDEs have been used in a range of products:

- plastics, thermoplastic polymers,
- textiles (curtains, carpets, tents, protective clothing, workwear, toys),
- construction materials (insulation panels, insulation foam, wall and flooring panels, foam fillers),
- electric and electronic equipment (computers, office equipment),
- furniture industry (mattresses, upholstered furniture),
- polyurethane foams,
- resins, rubbers, paints, varnishes, impregnates.

Their content in products (polymers, textiles) was on average 5-30% by weight (Alaee et al. 2003).

The commercial mixtures of PBDEs were initially used in the 1960s, and their names are derived from a congener of the highest percentage in the mixture:

- pentabromodiphenyl ether (pentaBDE) – a mixture of, among others, tetraBDE (24-38%), pentaBDE (50-60%) and hexaBDE (4-8%); technical pentaBDE – a total quantity of the following congeners: BDE-47, BDE-99 and BDE-100,
- octabromodiphenyl ether (octaBDE) – a mixture of, among others, hexaBDE (10-12%), heptaBDE (44%), octaBDE (31-35%) and nonaBDE (10-11%); technical octaBDE – a total quantity of the following congeners: BDE-153, BDE-154, BDE-183,
- decabromodiphenyl ether (decaBDE) – a mixture of nonaBDE (< 3%) and decaBDE (97-98%); technical decaBDE – congener BDE-209.

PentaBDE was mainly used in the elastic polyurethane foams (ca. 95% of the applications), which were applied in the furniture and upholstery (60%) and automobile industry (36%) (Alaee et al. 2003). OctaBDE was predominantly used in the ABS plastics (nearly 95% of the applications), in the production of the electric and electronic equipment (office equipment, TV sets). DecaBDE was primarily used in the polymer materials, including the polystyrene parts of the electronic household appliances and in the furniture upholstery.

According to the data from 2010, an annual manufacturing volume of the commercial PBDEs was approximately 67,000 Mg, in that circa 55,000 Mg (82%) decaBDE, almost 9,000 Mg (13%) pentaBDE and 3,000 Mg (5%) octaBDE (Fulara & Czaplicka 2010). Based on the available information, decaBDE is still manufactured in few countries – China, Japan or India (Kukharchyk 2017).

Polybrominated diphenyl ethers have never been manufactured in Poland (Krupanek et al. 2011). The following technical PBDEs mixtures were available for sale: BR 55N, Bromkal 82-ode, DE 83R, Saytex 102 and Tardex 100 (http://www.inchem.org/documents/ehc/ehc/ehc162.htm). The use of pentaBDE and octaBDE in the EU, also in Poland, was prohibited in 2004, and since 2006 a ban on the use of decaBDE in the electric and electronic equipment has been introduced (OJ L 42, 15.2.2003, 45-46; OJ L 37, 13.2.2003, 19-23). Since March 2019, the manufacturing or placing on the market of decaBDE as a substance on its own is prohibited. Pursuant to the Commission Regulation (EU) 2017/227 of 9 February 2017, till 2 March 2027 the ban does not apply to the decaBDE used for the production of spare parts for the machinery produced before 2 March 2019 and for the production of aircraft (OJ L 35 of 10.2.2017, 6-9).

The commercial pentaBDE mixture (tetra- and pentaBDE ethers) and octaBDE mixture (hexa- and heptaBDE ethers) were classified as the persistent organic pollutants and in 2009 included in Annex A (*Elimination*) to the Stockholm

Convention (Journal of Laws of 2009 no. 14, item 76). The use and recycling of the products that contain these compounds were severely restricted. The European Union, as a party to the Convention, registered a specific exemption for hexa-, hepta-, tetra- and pentaBDE, due to a fact, that products, which contain mentioned PBDEs, are still in use and will be recycled in the future. The specific exemptions for PBDEs listed in the Convention will expire in 2030.

Studies related to the PBDEs occurrence in the environmental, food or dust samples show that products containing PBDEs have been and are used in Poland. Analysis of the studies on the occurrence and concentrations of the polybrominated diphenyl ethers in the environment, food, animal organisms, in that humans, will enable to evaluate the PBDEs contamination in Poland and indicate data gaps. Therefore, this study is focused on discussing the results of determination of PBDEs used in commercial mixtures:

- technical pentaBDE (BDE-28, 47, 99, 100),
- technical octaBDE (BDE-153, 154, 183),
- technical decaBDE (BDE-209).

2. PBDEs in the environment

One of the primary emission sources of polybrominated diphenyl ethers to the environment is the use of the products that contain these compounds and subsequent waste management (Krupanek et al. 2011). For Poland, releases to the wastewaters from the industrial sources were estimated, with a great degree of uncertainty, at 1-7 kg/y for pentaBDE and 10 kg/y for decaBDE, and from the municipal wastewater at 0.4 kg/y in the case of pentaBDE and 1.1 kg/y for decaBDE. A volume of the annual release to the environment from the agricultural use of the sewage sludge was estimated at 0.02-0.06 kg for pentaBDE and 43 kg for decaBDE. A deposition volume of pentaBDE from the air, as a result of the use of products, was estimated at 14 up to 20 kg/y, and for decaBDE at 42 up to 130 kg/y, however, these estimations are encumbered with a great deal of uncertainty. The annual emissions of these compounds to the atmosphere and internal air were estimated on the similar levels – 0.08-1.6 kg/y for pentaPDE and 0.4-7 kg/y for decaBDE and 0.07-1.6 kg/y for pentaBDE and 1-23 kg/y for decaBDE, respectively (Krupanek et al. 2011).

2.1. Water and sediments

In Poland, the levels of the following PBDE congeners: BDE-28, 47, 99, 100, 153, 154 are determined in the surface waters and sediments in selected sampling points within the frames of the State Environmental Monitoring (SEM) performed by the Inspection of Environmental Protection (GIOŚ). The PBDEs concentrations in the surface waters can be referred to the environmental quality standards (EQS) for surface waters, expressed by a maximum allowable concentration (MAC-EQS). For PBDEs (the sum of congeners BDE-28, 47, 99, 100, 153 and 154), the MAC-EQS values are (Journal of Laws of 2016 item 1187):

- 0.14 µg/L for inland surface waters (rivers and lakes, and the artificial or significantly changed parts of the waters connected with them),
- 0.014 µg/L for other surface waters.

The PBDEs concentrations in the rivers and lakes' surface waters and sediments detected over a few last years within the frames of the SEM are presented in Table 1.

Table 1. PBDEs (BDE-28, 47, 99, 153, 154) concentrations in the rivers and lakes' surface waters and sediments, determined in 2011-2015 (GIOŚ's unpublished data)

Year	Concentration range (∑PBDEs)			
	Rivers µg/L	Rivers' sediments ng/g dw	Lakes µg/L	Lakes' sediments ng/g dw
2011	*n = 31*		*n = 7*	
	0.00005-0.00127		0.00005-0.00031	
2012	*n = 718*		*n = 17*	
	0.00005-**0.5***		0.00005-0.00025	
2013	*n = 745*	*n =43*	*n = 32*	*n = 22*
	0.000025-0.00036	<50 – < 60000	0.000036-0.00025	<50 – < 50000
2014	*n = 948*	*n = 64*	*n = 52*	
	0 – 0.0018	<0.05 – 64.9	0.000025-0.00025	N/A
2015	*n = 715*	*n = 57*	*n = 68*	*n = 8*
	0.00005-0.00025	<0.05 – 216	0.000025-0.00025	<0.05-86.7
2016	*n =10*	*n = 43*		*n = 1***
	0.011-0.047	<10		<10
2017		*n = 60*		*n = 21*
		< 0.05		< 0.05

* result exceeding the MAC-EQS value for surface waters (0.014 µg/L);
BDE-100 was not included
** sampling point on the Wielkie Dąbie Lake

The data show that over the years 2011-2016, the PBDEs levels in lakes' waters did not exceed MAC-EQS. Regarding rivers' waters, PBDEs concentrations exceeded the MAC-EQS only in 2012 (for 52 out of 718 sampling points). According to the information from the GIOŚ, in the case of sediments, the monitoring of PBDEs started in 2013 in selected rivers and lakes. In 2013, both for rivers and lakes' sediments, PBDE-209 was detected in the highest concentrations (<0.1 - <60,000 ng/g dw in rivers' sediments and <150 - <50,000 ng/g dw in lakes' sediments), as this congener is strongly bonded to sediments (ATSDR

2017). The results for other congeners fluctuated within <50 – <500 ng/g dw. Since the samples were taken in rotational maner (every three years) the possible trend is hard to observe.

In 2010, studies on the occurrence of 7 PBDE congeners in the sediments in the Vistula river estuary, Władysławowskie Fishery and Ustecko-Łebskie Fishery were conducted (Waszak et al. 2012). The fraction <63 µm was used to perform the analysis. The mean concentration of PBDEs in the sediments fluctuated from 0.22 up to 0.61 ng/g dw (Table 2).

Table 2. The mean concentrations of selected PBDE congeners in the sediments, ng/g dw (Waszak et al. 2012)

	Vistula river estuary	Władysławowskie Fishery	Ustecko-Łebskie Fishery
	$n = 3$	$n = 1$	$n = 2$
BDE-28	0.20 ± 0.03	0.05	0.03 ± 0.02
BDE-47	0.15 ± 0.03	0.06	0.05 ± 0.02
BDE-99	0.11 ± 0.03	0.03	0.03 ±0.03
BDE-100	0.05 ± 0.01	0.004	0.005 ± 0.002
BDE-153	0.03 ± 0.02	0.04	0.03 ± 0.02
BDE-154	0.06 ± 0.03	0.03	0.05 ± 0.04
BDE-183	0.03 ± 0.01	0.02	0.02 ± 0.02
∑PBDEs	0.61 ± 0.10	0.22	0.22 ± 0.05

In the sediment samples from the Vistula river estuary, the PBDE concentrations were higher than in the sediments samples from the fisheries, probably due to a greater anthropogenic stress in the Bay of Gdansk. In case of BDE-28 and BDE-47, their concentrations in samples from Gdansk Bay were higher by circa 33% and 22%, respectively. BDE-47, one of the pentaBDE consituents, accounted for 23 up to 27% of the total quantity of all PBDE congeners studied.

Regular monitoring of organobromine compounds in the Baltic Sea has begun in 2012 (Łysiak-Pastuszak et al. 2013). In 2012-2014, the chemical status of all control points in the West Pomeranian Voivodeship – uniform water bodies (JCW) of the transitional waters (JCW of Szczecin lagoon, JCW of Kamieński lagoon, JCW of Dziwna river estuary and JCW of Świna river estuary) and of the coastal waters (JCW of Dziwna-Świna, JCW of Sarbinowo-Dziwna and JCW of Jarosławiec-Sarbinowo) – were assessed as less than good, what was impacted by, inter alia, the exceedances of the average annual values of pentabromodiphenyl ether (Łysiak-Pastuszak et al. 2013; Łysiak-Pastuszak et al. 2014; Zalewska et al. 2015).

2.2. Wastewater and sewage sludges

Occurrence of pentaBDE, octaBDE and decaBDE in wastewater and sewage sludge was investigated within the frame of "*COHIBA: Control of hazardous substances in the Baltic Sea region"* project (Zielonka et al. 2012). In 2009 and 2010, samples of wastewater and sewage sludges were collected, once per two months, from the municipal and industrial wastewater treatment plants (WWTP). Data on the frequency of the occurrence of pentaBDE, octaBDE and decaBDE are presented in Table 3.

Table 3. The frequency of the occurrence of selected polybrominated diphenyl ethers in studied samples, % (Zielonka et al. 2012)

Mixture	Wastewater from the municipal WWTP	Wastewater from the industrial WWTP	Sewage sludges	Surface runoffs	Landfill leachates
pentaBDE	44.4	16.7	50	-	-
octaBDE	-	-	100	50	50
decaBDE	100	100	100	100	100

In effluent from municipal and industrial wastewater treatment plants, concentrations of decaBDE were in all cases above LOD of the method. Moreover, the results of the screening inventory in the Baltic Sea area show that not only point sources (municipal and industrial wastewater treatment plants) but also dispersed sources (field runoffs and use of sewage sludges in agriculture) are responsible for the surface water contamination by PBDEs.

2.3. Air and dust

Due to the wide use of PBDEs in the textiles, furniture and electronic equipment, ingestion of house dust is considered as one of the main exposure routes to PBDEs, especially in the case of infants and small children (Król et al. 2014). In order to investigate the occurrence of congeners used in commercial pentaBDE and octaBDE mixtures, 30 samples of indoor dust (offices, shops with the electronic equipment, computer servicing points, residential houses) were taken in Lublin in 2009 (Staszowska et al. 2012). Results of the study are presented in Table 4.

Table 4. The concentration of selected PBDE congeners in the indoor dust samples, ng/g dw (Staszowska et al. 2012)

Compound	Single-family houses	Offices	Computer servicing points	Electronic equipment shops
	n = 20	*n* = 6	*n* = 2	*n* = 2
BDE-28	<MDL – 8.7	2.4 – 29.4	25.7 – 41.3	32.3 – 27.6
BDE-47	5.1 – 96	7.4 – 111	18.7 – 544	14.6 – 96
BDE-99	<MDL – 74	5.8 – 49	7.1 – 179	6.2 – 75
BDE-100	<MDL – 59.7	5.1 – 33	19.2 – 155	5.4 – 76.9
BDE-153	<MDL – 21.4	6.3 – 24.7	5.9 – 46	6.6 – 34.4

MDL – *method detection limit*

In the majority of the samples, congeners from two PBDE commercial mixtures, with a prevalence of pentaBDE, were detected. The highest concentrations of BDE-28, 47, 99, 100 and 153 were determined in samples collected from the computer servicing points and shops with electronic equipment. However, the maximum concentrations of BDE-47, 99, 100 and 153 in the house dust were comparable with concentrations determined in the dust from offices and electronic equipment shops, and in the case of BDE-99 and BDE-100 were even higher.

In 2012, dust samples were collected from 12 households in Gdańsk and Gdynia, in order to analyse the occurrence and levels of BDE-47, 99, 100, 153, 154, 183, 209 (Król et al. 2014). Results are shown in Table 5.

Table 5. The median, mean and range concentrations of PBDE congeners analysed in dust collected from Gdańsk and Gdynia households, ng/g dw (Król et al. 2014)

Compound	Median	Mean	Range
BDE-28	3.8	3.4	<MDL – 8.2
BDE-47	5.4	9.9	<MDL – 51
BDE-99	1.4	2.2	<MDL – 4.8
BDE-100	<MDL	<MDL	<MDL
BDE-153	<MDL	<MDL	<MDL
BDE-154	<MDL	<MDL	<MDL
BDE-183	3.9	7.5	<MDL – 22
BDE-209	219	241	7.1 – 615
∑PBDEs	232	264	<MDL – 701

*MDL – *method detection limit*

Due to very low water solubility, PBDEs, particularly higher brominated congeners, are strongly associated with the solid phase. It decreases their mobility in the soil, sediments or water, but increases in the atmosphere, where they are associated with solid particles (and dust) suspended in the air (ATSDR 2017). The above is confirmed by the mentioned results – the highest content in dust samples were obtained for the BDE-209 (around 90% of the total concentration of all studied congeners). Concentrations of BDE-100, 153 and 154 were below the MDLs.

3. PBDEs in food and fish potentially intended for human consumption

Food is another main route of human exposure to PBDEs, especially the one that contains significant quantities of animal fat. Therefore, apart from the section dedicated to PBDEs in food, this part of work is also focused on PBDEs concentration in the fish, as potential nutrition source, caught in Polish rivers, lakes, and in the Polish part of the Baltic Sea.

3.1. Content of PBDEs in food

In Poland, the content of PBDEs in the butter, hen eggs, chocolate products, back fat, beef fat and fish meat (carp, cod, salmon) was studied by Wojtalewicz and Wojtalewicz et al. (2008). The total concentration of PBDE congeners with results above detection limit (the sum of BDE-28, 47, 99, 100, 153, 154) was of similar order of magnitude in all products:

- butter: 55-174 pg/g fat,
- hen eggs: 173-391 pg/g fat,
- lard: 38-71 pg/g fat,
- beef fat: 43-68 pg/g fat,
- chocolate products: 55-260 pg/g fat.

Sum of congeners from tetraBDE and pentaBDE mixtures constituted circa 90% of the total amount of PBDEs in the studied products. A high similarity between a congener profile in the analysed samples was observed: BDE-47 and BDE-99 were determined in the highest concentrations (in both cases 42% of the total amount of PBDE), then BDE-153 (6%), BDE-100 (4%), BDE-154 (4%) and BDE-28 (3%). It matches the composition profile of commercial pentaBDE and octaBDE mixtures, in which tetra- and penta-homologues occur in the highest quantities.

In the fish samples, the highest content of all PBDE congeners was detected in the salmon tissues (0.377-5.340 µg/kg ww), with the BDE-47 being the dominant congener. The higher content of PBDEs in the salmon tissues compared to the cod tissues is related to higher fat content in the salmon. The highest content of tetraBDE (BDE-47 and -49) in all fish species confirms that the lower-brominated PBDEs show high affinity to lipids and tendency to bioaccumulation in the aquatic organisms (Siddiqi et al. 2003).

The content of PBDEs was also studied in the cereal products from the Polish market – groats, flakes, flour, pasta, bran, porridges for children, cereal snacks and bread by Roszko et al. (2014). In 191 samples, the mean total content of PBDEs (BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209) was 112±80 pg/g, while the mean total content without the BDE-209 was 15±6 pg/g. Reported data on concentrations of PBDEs in various food items are provided in Table 6.

The levels of PBDEs in the studied cereal products were low. The congener BDE-209 (on average of 97 pg/g dw) was predominant, followed by the congeners BDE-99 (on average 3 pg/g dw) and BDE-47 (on average 2,8 pg/g). The congener BDE-209 accounted for ca 90% of the sum of PBDEs in bran and cereal snacks and for 65% of the sum of PBDEs in groats and flakes.

The content of PBDEs was also studied in the hen eggs from the free-range hens and conventional farms by Roszko et al. (2014). Each sample was composed of at least 8 eggs. 20 samples from the free-range hens and 19 samples from the conventional farms were subjected to the analysis (Table 7).

Congeners BDE-47, 99, 153 and 183 occurred in the highest concentration. The higher PBDEs content was determined in the eggs from the free-range hens, the medians for both groups were similar.

In 2015, the concentrations of 39 PBDEs congeners were determined in the honey samples collected in Wyszyny, Żołędowo, Wągrowiec, Chojna, Mostki, Miłoradzice, Glinica, Nowy Staw, Nidzica, Zalesie Górne, Radzyń Podlaski, Ulanów and Lubaczów (Roszko et al. 2016). For BDE-47, 99, 100 and 183 the highest concentrations were determined. (Table 8). The congeners BDE-118, 47 and 183 accounted for approximately 26.5%, 22% and 13% of the total quantity of all PBDEs, respectively.

Table 6. The concentration of selected PBDE congeners in different cereal products on the Polish market, pg/g (Roszko et al. 2014)

Compound	Concentration	Cereal products							
		Groats	Flakes	Flour	Pasta	Bran	Porridges for children	Cereal snacks	Bread
		n = 35	*n* = 35	*n* = 27	*n* = 14	*n* = 20	*n* = 25	*n* = 15	*n* = 20
BDE-28	Range	0.0-2.9	0.0-0.0	0.0-7.1	0.0-4.0	0.0-105.1	0.0-1.2	0.0-0.7	0.0-0.8
	Mean	0.4	0.0	0.6	0.4	5.7	0.2	0.4	0.2
	Median	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0
BDE-47	Range	0.0-6.3	0.7-12.6	0.0-15.1	0.0-6.8	0.0-13.0	1.7-6.1	2.5-3.3	0.0-9.8
	Mean	1.7	3.2	2.4	2.6	4.3	2.9	2.8	2.4
	Median	1.4	3.0	1.2	2.5	4.0	2.8	2.8	2.0
BDE-99	Range	0.0-8.0	0.0-4.4	0.0-11.4	0.4-29.5	0.2-11.1	1.3-8.4	2.9-4.3	0.0-5.2
	Mean	1.2	1.7	2.1	7.1	3.7	3.4	3.4	1.5
	Median	1.0	1.6	1.2	3.6	3.1	3.4	3.4	1.4
BDE-100	Range	0.0-2.1	0.0-2.2	0.0-13.5	0.0-5.5	0.0-31.4	0.0-1.3	0.0-0.6	0.0-0.6
	Mean	0.3	0.3	1.3	1.1	1.9	0.3	0.2	0.3
	Median	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.4
BDE-153	Range	0.0-1.5	0.0-2.2	0.0-4.8	0.0-5.2	0.0-4.3	0.0-4.0	1.1-1.7	0.0-1.4
	Mean	0.6	0.7	0.7	1.2	1.6	1.4	1.4	0.4
	Median	0.5	0.5	0.3	0.5	1.5	1.5	1.5	0.2

Table 6. cont.

Compound	Concentra-tion	Cereal products							
		Groats	Flakes	Flour	Pasta	Bran	Porridges for children	Cereal snacks	Bread
		n = 35	*n* = 35	*n* = 27	*n* = 14	*n* = 20	*n* = 25	*n* = 15	*n* = 20
BDE-154	Range	0.0-1.9	0.0-3.4	0.0-3.7	0.0-2.2	0.0-1.2	0.0-1.0	0.0-0.8	0.0-0.9
	Mean	0.3	0.4	0.5	0.5	0.4	0.2	0.3	0.3
	Median	0.2	0.3	0.2	0.2	0.4	0.0	0.0	0.2
BDE-183	Range	0.0-9.0	0.5-18.2	0.0-22.1	0.0-5.4	0.0-30.6	0.6-24.1	3.5-7.0	0.1-2.9
	Mean	2.7	3.3	2.0	1.4	6.8	5.5	5.7	1.3
	Median	2.7	2.0	0.5	0.5	4.9	5.6	5.6	1.2
BDE-209	Range	0.0-34.6	0.9-39.2	1.1-961.1	0.5-895.8	17.7-1971.0	23.2-536.8	98.8-163.5	6.7-100.4
	Mean	15.2	18.4	81.0	148.1	248.5	112.8	129.7	22.6
	Median	14.5	19.4	18.3	29.3	59.8	84.4	122.0	17.5
ΣPBDEs	**Range**	8.4-48.6	9.1-59.9	17.4-1002.7	20.0-921.8	37.1-1989.8	34.6-552.4	113.9-178.8	10.2-111.8
	Mean	23.6	29.0	97.2	168.8	274.9	128.4	145.0	29.8
	Median	21.8	28.8	34.2	55.8	88.6	100.5	138.1	25.7

Table 7. The concentration of the sum of PBDEs in eggs, pg/g fat (Roszko et al. 2014)

	Hen eggs from the free-range hens			Hen eggs from conventional farms		
	Mean	Median	Range	Mean	Median	Range
∑PBDEs	164.5	99.4	50.8-735.9	111.1	74.7	21.5-231.6

Table 8. The mean, median and range of concentrations of selected PBDE congeners in the honey samples from Poland, pg/g (Roszko et al. 2016)

PBDE	Mean	Median	Range
BDE-47	3.0	1.9	0.0-12.5
BDE-99	2.7	6.2	0.0-34.6
BDE-100	1.4	4.8	0.0-29.4
BDE-153	0.6	1.8	0.0-10.5
BDE-154	0.9	1.7	0.0-7.5
BDE-183	1.4	1.8	0.0-6.2

The food is the main source of human exposure to organic contaminants, with fish recognized as the most important exposure source (Szlinder-Richert et al. 2010). Therefore, since 2000, the studies on the concentration of PBDEs in the various species of the fresh-water and salt-water fish fished in the Polish waters have been conducted. For brominated diphenyl ethers (the sum of BDE-28, 47, 99, 100, 153 and 154) the environmental quality standard for fish (EQS Flora and Fauna) was determined as 0.0085 μg/kg ww (Journal of Laws of 2016 item 1187), in relation to which the results of presented studies were compared.

Between 2000 and 2008, the studies on the concentration of polybrominated diphenyl ethers (BDE-28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183 and 209) in herrings from Baltic Sea were conducted by Roots et al. (2009). The herring is the species preferred for the purposes of monitoring the PBDEs levels in the Baltic Sea because it is the important commercial species, fished in all parts of the Baltic Sea. The material for the studies was sampled on the open sea, from the Gulf of Finland and the Gulf of Riga. The highest content of PBDEs was detected in the herrings originating from both gulfs. BDE-47, 99, 100, 28, 153 and 154 congeners were detected in the highest concentrations. Over the period 1999-2008, an increase in the PBDEs content in the herrings was not observed. In 2007, the high concentrations of the BDE-209 were determined, however, the reason was not explained.

In 2004-2006, the studies on the PBDEs content (BDE-28, 47, 99, 100, 153, 154, 183) in the fish meat (herring, sprat, salmon) from the southern part of the Baltic Sea were conducted (Szlinder-Richert et al. 2010) (Table 9). The highest content of PBDEs was detected in the salmon meat and the lowest in herring meat. Detected concentrations were similar to the PBDEs content in the herrings originating from the northern part of the Baltic Sea. In the herrings and salmons, the congener BDE-47 which accounted for 55% up to 65% of the total quantity of all PBDEs was detected in the highest quantity. In all studied fishes from the southern Baltic, BDE-183 occurred in the lowest concentrations and accounted for less than 1% of the total quantity of the studied PBDEs. It has to be noted, that all detected concentrations exceeded the EQS level.

In 2010, the studies on the PBDEs content (BDE-28, 47, 99, 100, 153, 154 and 183) in the muscles of the females of flounder species were conducted (Waszak et al. 2012). The study material was collected in the Vistula river estuary, as well as in the area of the Władysławowskie Fishery and Ustecko-Łebskie Fishery. Additionally, in the years 2010 and 2011, the PBDEs concentration in the muscles, liver and gonads of the females of flounder species females fished in the Vistula river estuary were determined. The concentrations of PBDEs in the liver were higher than in the muscles and gonads. Generally, the content of PBDEs was relatively low, the highest in the samples of the flounders from the Vistula river estuary (it results from the higher anthropogenic stress), and the lowest in the samples of the flounders from the Władysławowskie Fishery, however, in the majority of the cases, the environmental quality standard (EQS) was exceeded (Table 10). Similarly, as in the aforementioned studies, the congener BDE-47 occurred in the highest concentrations.

In the years 2010-2012, the studies on the PBDEs concentration, as one of the organic contaminants, in the muscles and liver of the freshwater eel in the Polish waters were performed by Szlinder-Richert et al. (2014). The study material was collected from the Vistula Lagoon ($n = 43$), Szczecin Lagoon ($n = 34$), Bay of Puck ($n = 25$), the lakes: Śniardwy, Mamry, Nidzkie and Jamno ($n = 46$), as well as from the Vistula river near Toruń ($n = 5$). The mean content of PBDEs in the muscles was 1-2 ng/g ww (0.07-8.19 ng/g ww). The content of PBDEs in the muscles of the eels from the Vistula river and Bay of Puck was circa 3-fold higher than in the muscles of the eels from the waters of the Vistula Lagoon, Szczecin lagoon and the lakes. The study results showed the highest content of BDE-47 (0.05-6.4 ng/g w.w.) – it accounted for 50 up to 80% of the sum of PBDEs. The higher content of PBDEs was detected in the liver samples than in muscles (range: 0.19±0.1-1.64±1.6 ng/g w.w.). The highest PBDEs content was determined in the liver of the eel from the Bay of Puck, and the lowest – the eel coming from the lakes. The PBDEs content in the muscles of the freshwater eel fished in the Polish waters significantly exceeded the EQS for fish.

In 2013, the studies on the content of, inter alia, PBDEs in the liver of the Atlantic cod originating from the Baltic Sea were conducted by Roszko et al. (2015). The mean content of the total PBDEs (36 congeners) was 57.857 ng/g fat (*n = 51*, range: 28.592-159.669 ng/g fat). In the profile of the PBDE congeners, the congener BDE-47 prevailed (circa 38% of the total quantity of all PBDEs), and pentaBDE and tetraBDE predominated over the other congeners.

Within the frames of the SEM performed by GIOŚ, data on the content of PBDEs (BDE-28, 47, 99, 100, 153, 154) in the fish from the Polish maritime areas of the Baltic Sea, and from rivers and lakes are collected (Łysiak-Pastuszak et al. 2016). The results are presented in Table 9. In 2015, in the muscle tissue of European flounder fished in the coastal waters of the Gdańsk Basin the lowest content of PBDEs, compared to previous years, was reported – 0.15 ng/g ww. In the case of herring, compared to years 2012-2014, the lower content of PBDEs in the muscle tissues was reported for animals fished in the Gotland Basin and the Bornholm Basin. The content of PBDEs in the muscle tissue of European flounder from the Bornholm Basin was lower than in herring. In the SEM reports, the status of marine waters of the Baltic Sea economic zone regarding the PBDEs concentrations in the years 2012-2015 was qualified as very good. As in 2016, the EQS for fish of 0.0085 ng/g w.w. was introduced, all results from the aforementioned period would qualify the status of the marine waters as poor (exceeding the threshold a few orders of magnitude). It should be pointed out that in the European Union law, this EQS was established already in 2013 (OJ L 226, 24.8.2013).

The results of PBDEs content in the samples of the fish meat (roach, bream, perch, herring and river trout) fished in the Polish rivers, lakes, and transitional and coastal waters, collected within the SEM (GIOŚ unpublished data), are presented in Table 9. Generally, for the same species, for years 2016 and 2017, the lower content of PBDEs was detected in the meat of lake fish compared with the meat of the river fish. For all fish species, fished in the rivers, lakes, and transitional and coastal waters, in 2017 the content of the studied PBDEs was lower compared to the results from 2016. However, results both from 2016 and 2017 exceeded the EQS, and the highest results were obtained for the roach and perch meat fished in the rivers.

Table 9. The mean and range of concentrations of the sum of PBDEs in the fish sampled from Baltic Sea and Polish rivers and lakes, ng/g ww

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Southern Baltic Sea	2004	12	Herring (muscles)	4.2	1.3(*)	Szlinder-Richert J. et al. 2010
	2005	16	Herring (muscles)	4.4	1.2(*)	Szlinder-Richert J. et al. 2010
	2006	15	Herring (muscles)	4.3	1.3(*)	Szlinder-Richert J. et al. 2010
	2004	11	Sprat (muscles)	9.3	2.3(*)	Szlinder-Richert J. et al. 2010
	2005	14	Sprat (muscles)	9.8	1.1(*)	Szlinder-Richert J. et al. 2010
	2006	13	Sprat (muscles)	7.9	1.8(*)	Szlinder-Richert J. et al. 2010
	2004	5	Salmon (muscles)	7.8	4.3(*)	Szlinder-Richert J. et al. 2010
	2005	15	Salmon (muscles)	10.2	2.3(*)	Szlinder-Richert J. et al. 2010
	2006	15	Salmon (muscles)	8.2	2.2(*)	Szlinder-Richert J. et al. 2010
Szczecin Lagoon	2014		Perch (muscles)		0.04(*)	GIOŚ, 2016
	2015		Perch (muscles)		0.07(*)	GIOŚ, 2016
Vistula Lagoon	2014		Perch (muscles)		0.03(*)	GIOŚ, 2016
	2015		Perch (muscles)		0.02(*)	GIOŚ, 2016
Bornholm Basin	2012		Herring (muscles)		0.82(*)	GIOŚ, 2016
	2013		Herring (muscles)		1.39(*)	GIOŚ, 2016
	2014		Herring (muscles)		0.67(*)	GIOŚ, 2016
	2015		Herring (muscles)		0.45(*)	GIOŚ, 2016
	2012		European flounder (muscles)		0.25(*)	GIOŚ, 2016
	2013		European flounder (muscles)		0.20(*)	GIOŚ, 2016
	2014		European flounder (muscles)		0.38(*)	GIOŚ, 2016
	2015		European flounder (muscles)		0.30(*)	GIOŚ, 2016

Table 9. cont.

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Eastern Gotland Basin	2012		Herring (muscles)		0.67(*)	GIOŚ, 2016
	2013		Herring (muscles)		1.29(*)	GIOŚ, 2016
	2014		Herring (muscles)		0.90(*)	GIOŚ, 2016
	2015		Herring (muscles)		0.63(*)	GIOŚ, 2016
Coastal waters of the Gdańsk Basin	2012		European flounder (muscles)		0.22(*)	GIOŚ, 2016
	2013		European flounder (muscles)		0.17(*)	GIOŚ, 2016
	2014		European flounder (muscles)		0.21(*)	GIOŚ, 2016
	2015		European flounder (muscles)		0.15(*)	GIOŚ, 2016
Rivers	2016	115	Roach (muscles)		(0.071-3,5)(*)	GIOŚ.2017 (unpublished)
	2017	301	Roach (muscles)		(0,026-1.146)(*)	GIOŚ,2017 (unpublished)
	2016	30	Bream (muscles)		(0.075-2.7) (*)	GIOŚ.2017 (unpublished)
	2017	95	Bream (muscles)		(0,051-2.48) (*)	GIOŚ,2017 (unpublished)
	2016	8	Perch (muscles)		(0.14-1.8) (*)	GIOŚ,2017 (unpublished)
	2017	54	Perch (muscles)		(0.089-1.276(*))	GIOŚ,2017 (unpublished)
	2017	8	River trout (muscles)		(0.195-.530) (*)	GIOŚ,2017 (unpublished)
Lakes	2016	23	Roach (muscles)		(0.067-0,56) (*)	GIOŚ,2017 (unpublished)
	2017	44	Roach (muscles)		(0,059-0.594) (*)	GIOŚ,2017 (unpublished)
	2016	16	Bream (muscles)		(0.14-0.72) (*)	GIOŚ.2017 (unpublished)
	2017	26	Bream (muscles)		(0.45-0.371) (*)	GIOŚ.2017 (unpublished)
	2016	1	Perch (muscles)		1.6(*)	GIOŚ,2017 (unpublished)
	2017	20	Perch (muscles)		(0.111-0.668) (*)	GIOŚ,2017 (unpublished)

Table 9. cont.

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Transitional and coastal waters	2016	3	Perch (muscles)		(0.11-0.29) (*)	GIOŚ,2017 (unpublished)
	2017	3	Perch (muscles)		(0.091-0.259) (*)	GIOŚ,2017 (unpublished)
	2017	4	Herring (muscles)		(0.804-1.013) (*)	GIOŚ,2017 (unpublished)

(*) result above the environmental quality standard (EQS) – 0.0085 ng/g m.m. (EQS Flora and Fauna)
(**) MDL – method detection limit

4. Human and animal tissues

The samples of the human blood serum, umbilical cord blood serum and human breast milk are the useful biological matrices for the evaluation the adult organism, as well as for the evaluation of a pre- and post-labour exposure to PBDEs of the neonates (Jarczewska et al. 2006). Therefore, the concentrations of selected PBDE congeners in the blood serum and human breast milk were determined during a few studies conducted in Poland. In the years 2002-2005, 89 samples of the umbilical cord blood from the women from Warsaw and the surrounding area were collected, in order to asses the human exposure, inter alia, to PBDEs (BDE-47, 99 and 153) in the prenatal period (Hernik et al. 2013). The average age of the women was 28 years old (16-40 years old), and an average fat content in the blood was of 0.042%. In 2004, the samples of human breast milk from 22 mothers from the Wielkopolska region were collected by Jaraczewska et al. (2006). The average age of the women was 30 years (22-38), and an average fat content in the milk was 2.0%. The results are presented in Table 11.

Table 10. The mean and range of concentrations of individual congeners and the sum of PBDEs in the fish samples from Poland, ng/g (Waszak et al. 2012)

Sampling site	Sampling year	n	Matrix	Fat content [%]	Mean (range) [ng/g w.w.]							∑PBDEs – mean (range) [ng/g w.w.]
					BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	
The Vistula river estuary	2010	23	Flounder (muscles)	1.24	0.03 (0.01-0.06)	0.13 (0.06-0.26)	0.02 (0.006-0.08)	0.05 (0.007-0.15)	0.02 (0.01-0.03)	0.03 (0.01-0.05)	0.01 (0.002-0.02)	0.30 (0.11-0.52)(*)
Władysławowskie Fishery	2010	22	Flounder (muscles)	1.63	0.04 (0.01-0.08)	0.10 (0.03-0.36)	0.02 (0.006-0.06)	0.01 (0.002-0.05)	0.02 (0.01-0.05)	0.03 (0.01-0.06)	0.007 (0.002-0.02)	0.22 (0.08-0.66)(*)
Ustecko-Łebskie Fishery	2010	22	Flounder (muscles)	1.08	0.02 (0.006-0.04)	0.04 (0.01-0.07)	0.009 (0.005-0.02)	0.004 (0.002-0.01)	0.02 (0.008-0.4)	0.02 (0.008-0.3)	0.008 (0.002-0.03)	0.11 (0.08-0.66)(*)
The Vistula river estuary	2010 and 2011	51	Flounder (muscles)	2.0	0.04 (0.01-0.1)	0.2 (0.06-0.4)	0.02 (0.008-0.1)	0.04 (0.008-0.02)	0.02 (0.008-0.03)	0.03 (0.01-0.1)	0.007 (0.002-0.02)	0.3 (0.1-0.6)(*)
The Vistula river estuary	2010 and 2011	39	Flounder (liver)	6.0	0.2 (0.06-0.5)	0.4 (0.1-1.0)	0.07 (0.01-0.5)	0.2 (0.008-0.8)	0.05 (0.01-0.1)	0.06 (0.02-0.1)	<MDL (**)	1.0 (0.3-2.0)(*)
The Vistula river estuary	2010 and 2011	37	Flounder (gonads)	3.0	0.05 (0.007-0.1)	0.1 (0.02-0.2)	0.02 (0.008-0.2)	0.05 (0.008-0.2)	0.03 (0.008-0.1)	0.02 (0.007-0.1)	<MDL	0.3 (0.04-0.6)(*)

(*) result above the environmental quality standard requirements (EQS) – 0.0085 ng/g m.m. (EQS Flora and Fauna)

(**) MDL – method detection limit

Table 11. The mean concentrations (ng/g of fat) of the selected PBDE congeners in the umbilical cord blood (Hernik et al. 2013) and in the breast milk (Jaraczewska et al. 2006) of Polish women

PBDE	Umbilical cord blood *(n* = 89*)*			Human breast milk *(n* = 22*)*		
	Mean content	Standard deviation	Maximum value	Mean content	Standard deviation	Maximum value
BDE-28	-	-	-	0.07	0.08	0.33
BDE-47	1.00	1.20	5.00	1.07	1.03	5.62
BDE-99	0.60	2.25	24.60	0.47	0.13	1.43
BDE-100	-	-	-	0.15	0.13	0.55
BDE-153	0.40	0.89	3.80	0.53	0.27	1.12
BDE-183	-	-	-	0.08	0.07	0.32
∑PBDEs	-	-	-	2.5	1.7	8.4

BDE-47 was detected in the highest concentrations, both in the umbilical cord blood, and human breast milk. In the umbilical cord blood it was detected in 90% of the samples and it accounted for circa 48% of the total quantity of the studied PBDEs. In the umbilical cord blood the lowest concentrations had the congener BDE-153 (15% of the total quantity of the studied PBDEs). A correlation between the concentration of PBDEs in the umbilical cord blood and age of the women was not observed, but it was concluded that human exposure to PBDEs begins already during the foetal period. BDE-47 together with BDE-153 was present in all samples of the human breast milk. The congeners BDE-47, 153, 99, 100, 183 and 28 were circa 45%, 21%, 17%, 6%, 3% and 3% of the total quantity of all studied PBDEs, respectively.

In the years 2002-2004, the blood samples from men (age between 18.5-49.7) from Poland, Ukraine and Greenland (Innuits) were collected, in order to test the concentrations of, inter alia, selected congeners of PBDEs: BDE- 28, 47, 99, 100, 153, 154 and 183 in the blood serum (Lenters et al. 2013). The mean concentrations of the congeners together with the frequency of their occurrence are presented in Table 12.

The concentrations of PBDEs were circa 3-15 times higher in the blood serum of the men from Greenland than men from Poland and Ukraine. In all studied groups, BDE-47 and BDE-153 occurred in more than 95% samples. BDE-47, 99, 100, 153 and -154 accounted for, respectively, 40-58%, 9-23%, 7-9%, 19-40% and 1-3% of the total quantity of all PBDEs. BDE-183 was not determined in any sample.

Table 12. The frequency of occurrence (%) and mean concentrations (ng/g fat) of the selected PBDE congeners in the blood serum of men from Poland, Ukraine and Greenland (Lenters et al. 2013)

PBDE	Poland n = 100		Ukraine n = 100		Greenland n = 99	
	Frequency of occurrence %	Mean blood concentration ng/g fat	Frequency of occurrence %	Mean blood concentration ng/g fat	Frequency of occurrence %	Mean blood concentration ng/g fat
BDE-47	100	0.66	99	0.12	98	1.8
BDE-99	23	-	56	-	74	0.5
BDE-100	19	-	19	-	73	0.43
BDE-153	98	0.58	95	0.32	98	2.8
BDE-154	17	-	22	-	36	-

The use of hair as the biomarkers for the evaluation of human exposure to persistent organic pollutants has started relatively recently. Due to an easy collection, a possibility of the long-term storage and a broad range of the information about the short-term and long-term exposure, hair became commonly used study matrix for the evaluation of human exposure to a wide range of product occurring in the environment (Król et al. 2014). In 2012, the hair samples from 12 inhabitants of Tri-City were collected (women and men aged between 25-30), and the concentrations of 8 PBDE congeners – BDE-28, 47, 99, 100, 153, 154, 183, 209 were tested (Król et al. 2014). From women, hair of 10-30 cm length was collected and from men hair of 1-5 cm (illustrating 10-30 months and 1-5 months of the exposure to PBDEs, respectively. In Table 13, median, mean, and range of concentrations of the individual PBDE congeners are presented.

Table 13. The median, mean and range of the concentrations of the individual PBDE congeners in the hair of the Tri-City inhabitants, ng/g dw (Król et al. 2014)

PBDE	Median	Mean	Range
BDE-28	0.4	0.7	<MDL – 2.8
BDE-47	0.4	0.4	<MDL – 0.65
BDE-99	0.21	0.11	<MDL – 0.42
BDE-100	<MDL*	<MDL	<MDL
BDE-153	<MDL	<MDL	<MDL
BDE-154	<MDL	<MDL	<MDL
BDE-183	<MDL	3.8	3.1-4.6
BDE-209	9.5	12	5.5-25

*MDL – *method detection limit*

BDE-209 was detected in the highest concentrations and it accounted for almost 70% of the total amount of all PBDEs. BDE-183, 28, 47 and 99 accounted for ca. 23%, 4%, 2.1% and 0.8% of the total amount of PBDEs, respectively. The content of BDE-100 and BDE-153 was below the method detection limit. The high content of the congener BDE-209, in relation to the other studied congeners, may result from a fact, that as the main constituent of decaBDE was used in the electric and electronic devices used on the daily basis (TV sets, computers, household appliances, hairdryers, cables or wires) and decorative (curtains) or upholstery (furniture) fabrics.

The sum of the mean concentrations of the studied PBDEs in the women's hair was slightly higher than in the men's hair, but for the congener BDE-209 the result was opposite – the sum of the mean concentrations in the women's hair was of 11 ng/g dw, and in the men's hair – 18 ng/g dw. The concentrations of PBDEs in the non-dyed hair were higher than the concentrations of PBDEs in the dyed hair indicating that hair dying decreases their adsorption properties, or some congeners are subjected to the degradation due to an impact of dying.

The studies on the content of ten BDE congeners in the livers of the predatory birds (barn owl, common buzzard, common kestrel, marsh harrier and Northern goshawk) in Poland during period 2007-2008 were conducted by Czerwiński et al. (2010). The study materials were collected in Tarnowskie Góry (barn owl), Warsaw (common buzzard, common kestrel), Mikołów (common buzzard, marsh harrier) and Biała (Northern goshawk). Studied PBDE congeners were determined in all study samples, and the results were assessed as the high ones. The highest contents of PBDEs were detected in the samples of the liver of common buzzard and marsh harrier. BDE-47, 153 and 99 occurred in the highest concentrations. The maximum concentrations of the particular congeners were of, respectively:

- BDE-28 – 203.1 ng/g fat,
- BDE-47 – 1359.3 ng/g fat,
- BDE-99 – 666.7 ng/g fat,
- BDE-100 – 171.9 ng/g fat,
- BDE-153 – 1035.7 ng/g fat,
- BDE-183 – 89.3 ng/g fat.

The high results may indicate the high potential for bioaccumulation and biomagnification of the PBDEs compounds.

5. Summary

Polybrominated diphenyl ethers have never been manufactured in Poland. In spite of the bans and restrictions put on the use of pentaBDE, octaBDE and decaBDE in the commercial products, which entered into force a decade ago, these chemical compounds are determined in the environment, food and animal and human tissues in Poland. Despite the restrictions on manufacturing, distribution and use, in the following years, the products containing these compounds will end up in the waste stream (waste electrical and electronic equipment, upholstery, end-of-life vehicles, construction materials, wire and cable insulations) and will be released into various environmental matrices (air, water, soil). There, they will be a subject of the bioconcentration in the organisms and bioaccumulation and biomagnification in the food chain.

The scientific, technical, socio-economic and environmental data on PBDEs collected over the years, including the impact on the human health, resulted in the introduction of the environmental quality standards for the surface waters and flora and fauna at European Union and national levels. However, such standards are lacking for soils, food and water intended for human consumption or feeds.

Polybrominated diphenyl ethers are studied within the frames of the regular monitoring studies for a few years only and to a limited extent. Therefore, the available data is insufficient for the assessment of the current status of PBDEs contamination in Poland and for determination of the time trends for these contaminants. However, the measured levels of these compounds in food, which is one of the main sources of human exposure to PBDEs, indicate the need for further studies.

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Abstract

The study focus on the occurrence and levels of polybrominated diphenyl ethers (PBDEs) as contaminants of emerging concern in Poland. In the article, their properties, primary uses and emission sources to the environment were discussed. The review of the available studies on the PBDEs content in the samples of different matrices (groundwaters, surface waters, sediments, air and dust, food, animal and human tissues) was conducted and the results exceeding the available limit values were indicated. It enabled to evaluate the problem of the PBDEs contamination in Poland.

Keywords:
polybrominated diphenyl ethers, PBDEs, water, sediments, wastewater, sludge, air, dust, food, fish, human tissues, animal tissues

Polibromowane etery difenylowe jako nowo pojawiające się zanieczyszczenia w środowisku Polski

Streszczenie

W artykule przedstawiono dane dotyczące występowania i stężeń polibromowanych eterów difenylowych jako nowo pojawiających się zanieczyszczeń w Polsce. W artykule przedyskutowano ich właściwości, wykorzystanie oraz źródła emisji do środowiska. Przeprowadzono przegląd dostępnych badań dotyczących zawartości PBDEs w próbkach różnych matryc środowiskowych (wodach podziemnych, powierzchniowych, osadach, powietrzu i kurzu, żywności, tkanach zwierzęcych i ludzkich) oraz wskazano wyniki przekraczające ustalone wartości graniczne. Pozwoliło to na ocenę problemu zanieczyszczenia środowiska Polski przez PBDEs.

Słowa kluczowe:
polibromowane etery difenylowe, PBDEs, woda, osadu, ścieki, osady ściekowe, powierze, kurz, żywność, ryby, tkanki ludzkie, tkanki zwierzęce