Introduction

The natural environment has become the recipient of persistent organic pollutants. The types of pollutants and wastes vary with industrialization levels. As a consequence of extensive environmental studies following the degradation of the natural surroundings, the list of substances whose presence requires strict monitoring has been extended, which poses a new challenge to analytical chemists [1]. This group of substances includes polybrominated diphenyl ethers (PBDEs). Under the regulations currently in force, polybrominated diphenyl ether is to be categorized as a top priority substance covered by environmental quality standards and has been listed as a quality indicator of the sediments.
PBDEs have been manufactured since 1965 [5] and used as additives to chemically harden plastics and in manufacturing of office equipment (telephones, copying machines, electric devices and electronics (computers, TV sets, household goods, domestic appliances). They also find use in manufacturing of polyurethane foam widely used in industries. Three dominant commercial mixtures of these compounds are: penta- octa- and deca- mixes of congeners differing in the number of bromine atoms in the molecule. In the early 21st century the world production of PBDEs would approach 67,000 tons (penta-PBDE – 7,500 tons, octa PBDE – 3,790 tons and deca-PBDE – 56,100 tons). The US would account for 49% of the use of PBDEs, in Asia the figure is 37%, and in Europe 12%. The environmental impacts are still significant since used and scrapped electronic devices are often exported to developing countries to be dumped or dismantled and recycled [3, 6].

The use of PBDEs is Poland has been restricted since 2004, when a regulation came into force banning the use of certain substances produced in the electronics sector and potentially harmful to the environment, in accordance with WE Directive 2002/95 implemented at that time. Under this regulation and under the new Regulation of 8 May 2013 [7] the maximal admissible concentration of PBDEs in homogeneous materials measured by weight is 0.1%. The use of deca-PBDEs was restricted in 2008. These restrictions differ between countries, for example in China the use of deca-PBDEs is not regulated in any way [8]. Restrictions relating to quality of commercial products led to the reduction of the amounts of PBDEs, though products containing those substances are still present in the environment.

**Description and Applications of PBDE**

PBDEs are organic compounds, derivatives of diphenyl ethers in which 1 to 10 atoms of hydrogen in aromatic rings are substituted by bromine. Theoretically, 206 PBDE congeners are possible [3]. These compounds have a high temperature of ignition, hence they are widely used as inhibitors of combustion. They belong to the group of additive antipirenes since they are retained in polymer through physical interactions rather than by chemical bonds and therefore are easily released to the environment. PBDEs are persistent and lipophilic compounds while present in the ecosystem, and they tend to bioaccumulate in fat tissues of animals and humans. Under the Stockholm Convention [4] they are listed as persistent organic pollutants. PBDEs display a variety of physico-chemical and toxic properties. Since they were categorized as potential carcinogens and endocrine disruptors, their presence is the environment is perceived as a major threat [5]. The stability of PBDEs is associated with the bromine substitution. Lighter PBDEs tend to be more stable. Transformations of PBDEs congeners are triggered by natural factors, both physical and chemical, and thus formed products may prove to be even more toxic. Debromination gives rise to the formation of PBDEs, whose molecules contain a smaller number of bromide atoms and polibrominated dibenzen furans, brominated phenols, and bromobenzenes.
of atmospheric transport of pollutants. PBDE concentrations in areas distant from local sources of pollutants are of the order of several pg/m³. The highest concentrations were registered in the neighbourhood of the electronics recycling plants. Selected atmospheric PBDE concentrations in areas differing in the land development and industrialization levels are summarized in Table 1.

### Atmospheric Deposition

Atmospheric PBDEs return to the ground in the form of dry and wet deposition. Measurements taken in Europe show the atmospheric deposition of about 10 ng/m² per day. Select examples of atmospheric deposition of PBDEs world-wide are summarized in Table 2.

### Landfills and Dumping Sites

PBDE concentration levels determined in landfill leachate vary by several orders of magnitude (Fig. 1). The concentration is found to increase with the industrialization level and population figures [25]. The PBDE congener profile is diverse too, which is associated with the waste type and the dumping strategy. Relatively low levels registered in Japan may be attributable to the incineration of nearly 80% of municipal waste. PBDE contents in leachate approached 4 ng/L [26]. Fig. 1 shows the concentrations of widely detected congeners in dumping sites in various countries. The points given correspond to maximum levels.

### Wastewater Treatment Plants

Many organic pollutants are present in municipal wastewater [27]. PBDEs determinable by available methods are present in influents and effluents from the treatment plants (Fig. 1). Significant amounts of PBDEs are registered in the summertime and when there is more industrial than municipal waste [28]. The preliminary treatment can cause their

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#### Table 1. PBDEs in outdoor air samples.

<table>
<thead>
<tr>
<th>Area</th>
<th>PBDE</th>
<th>Range (median) [pg/m³]</th>
<th>Country/region</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baltic Sea</td>
<td>∑PBDE</td>
<td>(8.6)</td>
<td>Sweden, Gotska Sandom Island</td>
<td>[11]</td>
</tr>
<tr>
<td>Artic region, offshore</td>
<td>∑PBDE</td>
<td>0.78-48 (6.2)</td>
<td>Canada, Alert, Nunavut</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>BDE-47</td>
<td>0.21-18 (1.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BDE-99</td>
<td>0.19-22 (1.30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BDE-209</td>
<td>0.091-9.8 (0.89)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rural site</td>
<td>∑PBDE (without 209)</td>
<td>2.84±4.23</td>
<td>UK, West Midlands</td>
<td>[13]</td>
</tr>
<tr>
<td>Peri-Alpine lake</td>
<td>∑PBDE</td>
<td>26.3-405.5</td>
<td>Switzerland Tun Lake</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>BDE-47</td>
<td>22.9-405.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban site</td>
<td>∑PBDE</td>
<td>16.2-100</td>
<td>USA</td>
<td>[15]</td>
</tr>
<tr>
<td>Urban site</td>
<td>∑PBDE</td>
<td>40.5±33.5 – 202±213.2</td>
<td>Northern China</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>BDE-209</td>
<td>27.3±38.3 – 171.2±211.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rural-field site</td>
<td>∑PBDE</td>
<td>22±20.6 – 57.2±4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BDE-209</td>
<td>11.9±14.6 – 32±20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicinity of a wastewater treatment plant</td>
<td>∑PBDE</td>
<td>34.0-95.9</td>
<td>Italy</td>
<td>[17]</td>
</tr>
<tr>
<td>Vicinity of the electronics recycling plants</td>
<td>∑PBDE</td>
<td>884-2791</td>
<td>China, Taizhou</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>∑PBDE</td>
<td>5397-47187</td>
<td>China, Guiyi</td>
<td>[19]</td>
</tr>
</tbody>
</table>
amount to be reduced by 70% [28] and in the case of more advanced treatment strategies by 90-98% [29, 30]. Better performance is achieved when combined biological and chemical treatments are employed, biological methods produce slightly poorer results [30]. The major determinant of PBDE reduction efficiency is sorption of sewage sludge. The efficiency of PBDE removal is correlated with the level of reduction of conventional parameters of polluted waters: biological oxygen demand and the sum of solid components [28]. Similar to sewage sludge, PBDE levels in sewage water (Fig. 1) vary by several orders of magnitude (Fig. 2).

<table>
<thead>
<tr>
<th>Area</th>
<th>PBDE</th>
<th>Range ng/m² per day</th>
<th>Country, region</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campus</td>
<td>∑BDE</td>
<td>2±1</td>
<td>Sweden, Lund</td>
<td>[11]</td>
</tr>
<tr>
<td>Alps Monte Rosa Massif</td>
<td>∑BDE</td>
<td>1.38</td>
<td>Swiss-Italian border</td>
<td>[21]</td>
</tr>
<tr>
<td>Vicinity of Lake Maggiore</td>
<td>∑BDE</td>
<td>17.61</td>
<td>Italy</td>
<td>[22]</td>
</tr>
<tr>
<td>Rural site</td>
<td>∑BDE</td>
<td>27.67-64.6</td>
<td>South Korea</td>
<td>[23]</td>
</tr>
<tr>
<td>Urban site</td>
<td>∑BDE</td>
<td>63.0-243.83</td>
<td>Taiwan</td>
<td>[24]</td>
</tr>
<tr>
<td>Rural site</td>
<td>∑BDE</td>
<td>13.44-41.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban site</td>
<td>∑BDE</td>
<td>32.95-60.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicinity of the electronics recycling plants</td>
<td>∑BDE</td>
<td>3,835.62-11,780.82</td>
<td>China, Taizhou</td>
<td>[18]</td>
</tr>
</tbody>
</table>

PBDEs in Soils and Aquatic Environments

Surface and Ground Waters

PBDE concentrations are relatively low compared to inorganic micro-components. Points indicated in Fig. 1 correspond to the maximal determined concentrations. Apart from waters in lakes and rivers, results are given that were determined in firm core from Colle Gnifetti in the Monte Rosa Massif in the Swiss-Italian Alps [21]. The maximal concentration levels registered over the years 1996-2008 do not exceed several ng/L, though they are not lower than in rivers. In the peri-alpine Thun Lake (Switzerland) the concentration of PBDEs ranged from 22.8 to 78.3 pg/L, the predominating congeners being BDE-57 and 209. Similar amounts were registered in the Kander River flowing into the lake [14]. In Lake Ontario (Canada) the total concentration of PBDEs varied from 4 to 13 pg/L, the predominating formulations being BDE-47 and 99 [56]. In Lake Michigan the concentration of ΣPBDEs rose from 31 pg/L in 1997 to 158 pg/L in 2003 [57]. The PBDE concentration determined in the San Francisco estuary was 513 pg/L [58], with the predominating congeners BDE-209, 47, 99. In the Predecelle River in the suburbs of Paris the concentration of ΣPBDEs ranged from 2.3 to 2.7 ng/L, while the level of BDE-209 was 2.1 to 2.48 ng/L [39]. In the Aire River (UK) flowing mainly through industrial regions the concentration of BDE-209 varied from 17 to 295 ng/L [51]. In surface waters in regions with a well-developed electronics industry the concentrations of ΣPBDEs were 22.4 ng/L, including BDE-209 in the amount of 7.3 ng/L. These levels were higher than in highly industrialized areas within the same
geographic region in China, where the concentration of $\Sigma$PBDEs was 18.9 ng/L, the concentration of BDE-209 being 7.3 ng/L [49].

As regards the contamination of ground waters with PBDEs, the major concern is exposed geological features. In the aquifer in eastern Ontario (Canada) the maximal concentration level of $\Sigma$PBDEs was 94 ng/L (the average value being 12.6 ng/L). Slightly higher concentrations were determined in all positive samples collected in the summer. Infiltration of atmospheric precipitation may have caused the reduction of $\Sigma$PBDEs, or it may be attributed to seasonal variations of PBDE concentrations in atmospheric air. The highest concentrations were found for BDE-209, 47, and 99 (Fig. 1). The strong correlation of PBDE levels with concentrations of nitrogen compounds and the analysis of the land development features indicate that potential sources of PBDE contamination are cesspools, organic fertilizers and deposition of airborne substances [41].

Soils and Aquatic Sediments

The receptors of man-made organic pollutants are commonly soils and sediments on the bottoms of rivers and water reservoirs. Typically, PBDE concentrations in soils are of the order of several ng/g. In soils near Bratislava the concentrations of $\Sigma$PBDEs ranged from 0.087 to 0.627 ng/g [54]. In rural areas and woodlands in UK and Norway, the concentrations of $\Sigma$PBDEs ranged from 0.065 to 12 ng/g [59].

On a local scale the increase in the PBDE levels was detected in flooded areas and in agricultural regions (up to several hundred ng/n), where the sewage sludge is used [45, 60] or where the land is irrigated with treated effluents [36]. Concentrations of $\Sigma$PBDEs in woodlands in the Guiyi region (China) ranged from 2.0 to 6.22 ng/g, the proportion of BDE-209 being 63-81%. In the rice fields the levels were 45.1-102 ng/g and in the vicinity of the dumping site of dismantled and incinerated electronic devices they ranged from 85.0 to 201.0 ng/g. At the incineration and dumping site the concentration of $\Sigma$PBDEs varied from 2906 to 44473 ng/g [61]. In soils in agricultural regions the concentration of $\Sigma$PBDEs varied from 2.96 ng/g to 200 ng/g, the predominant congener being BDE-209 [18].

Bottom sediments are a vital component of the aquatic ecosystem, used in monitoring surface water quality [62, 63]. PBDE concentrations in bottom sediments are typically higher than in soils. For example, the $\Sigma$PBDE concentrations determined in rivers are: from 0.29 to 10.4 in the Danube River (Austria) [64] and from 1.0 ng/g to 281.1 ng/g in Czech rivers [49]. The concentration of PBDEs (excluding BDE 209) determined in the estuary of the Vistula River in Poland was 0.2±0.1 ng/g [65]. PBDE concentrations tend to increase gradually over the river course and as the rivers flow into industrial regions. Concentrations registered below the local pollution sources are higher by several orders of magnitude. In the bottom sediments of the Lusatian Neisse River (The Czech Republic) the concentration of $\Sigma$PBDEs downstream from the carpet manufacturing factory was 490 ng/g and the level of 328 ng/g was registered downstream from the hazardous waste incineration plant [53]. The concentration of $\Sigma$PBDEs in the sample collected from the Vero River (Spain) 5 m below the industrial park was 14,395 ng/g and one kilometre further – 5,531 ng/g [66].

Lake sediments and peat bogs are “natural archives” of long-term changes in the quality of the natural environment on a local and regional scale [67]. The concentrations of $\Sigma$PBDEs in the sediments of Lake Mjosa (Norway) ranged from 0.6 to 27 ng/g [68], in Lake Thun (Switzerland): from 0.1 to 5.1 ng/g [14], in Lake Maggiore (Italy): from 1.6 to 18.6 ng/g [69]. In most cases the predominant congener was BDE-209, accounting for 50%-90% of the total amount. Deca-BDE concentration in Lake Thun and Greifen increased over the years 1980-2000 [14]. The $\Sigma$PBDE concentration (excluding BDE 209) in the bottom sediments in the souther part of the Baltic Sea (off the Polish coast) ranged from 2.41±0.78 ng/g to 6.22±1.26 ng/g [70].

Highly variable and extremely high concentrations were determined in bottom sediments in rivers in the Shenhun region (China). The lowest levels of $\Sigma$PBDEs (excluding BDE 209) registered in the region were in the range from 0.18 to 26.5 ng/g. In rural areas the concentrations ranged from 2.08 to 169 ng/g, in urban areas from 10.1 to 2212 ng/g. In the region dominated by electronic industry the concentration of $\Sigma$PBDEs (excluding BDE-209) ranged from 1,528 to 49,000 ng/g. The maximal concentration of BDE-209 in rural areas was 680 ng/g, in urban areas 2,673 ng/g, and in the areas where the electronics industry is located 135,000 ng/g [52]. These amounts correspond to the range of PBDE concentrations in the floor dust in the electronic equipment dismantling plants, where $\Sigma$PBDE levels ranged from 1960 to 340,710 ng/g, including BDE-209, whose amounts vary between 910 and 320,400 ng/g [71].

PBDEs in Surface Waters of Poland

The relevant regulation [72] specifies the admissible level to be 0.5 ng/L of PBDEs as the year-average concentration in homogeneous waters and 0.2 ng/L for homogeneous parts of coastal and flowing waters. It is assumed that the year-average values provide a certain safety margin to protect from short-term increases in PBDE concentrations during the regular discharges, while the admissible maximal concentrations are equal to year-average values. The environmental quality standard specifies the sum of concentrations of congeners 28, 47, 99, 100, 153, and 154 contained in penta-PBDE as a product.

PBDE concentrations determined in surface waters in Podlasie Province were: <0.1 ng/L and <0.05 ng/L [73]. The $\Sigma$PBDE concentrations in rivers and lakes in Zachodniopomorskie Province does not exceed the levels set forth in relevant standards. Significant amounts (about 1 μg/L) were registered in transitional and coastal waters in the province, for example in the estuaries of the Dziewna and Świna rivers, in Kamieński Lagoon, and in coastal rivers [74]. The exceeded admissible levels of $\Sigma$PBDEs were not included in the assessments chiefly because the determinations were too scarce [75]. The relationship was
established between the PBDE concentrations and those of total nitrogen (Fig. 3) and fluoranthene (Fig. 4).

Determining PBDE concentrations (and other organic pollutants) has been included in the National Environmental Monitoring program for 2013-15. The concentrations shall be determined at select points among several hundred locations included in the basic program [76].

**Conclusion**

The factors responsible for PBDE presence in the environment are manufacturing and disposal of products containing PBDEs. Major differences between PBDE concentrations determined in the environment are associated with land development levels, which is best illustrated by the example of China. No restrictions imposed upon the use of PBDEs and the largest market of imports and recycling of electronic goods world-wide pose a major threat to the natural environment. This condition is revealed by elevated PBDE concentrations in various ecosystems in relation to other world regions [18, 19, 52].

PBDEs leak to surface and ground waters with discharges from wastewater treatment plants and through wet and dry deposition. Still higher concentrations were detected in rivers in industrial regions [39, 51]. PBDE concentrations in river sediments tend to increase gradually over the river course and when flowing through industrial regions. [53, 66]. Apart from areas affected by local emission sources, long-range atmospheric transport of pollutants and atmospheric deposition are the main sources of their occurrence. PBDEs can be atmospherically transported over long distances and even to high mountain regions. PBDEs can also leak to local water intakes, threatening the areas at some distance from the source of pollution [21].

Due to the scarcity of information about PBDE concentrations in ground waters, this problem has not yet been fully investigated. It is reasonable to suppose that, similar to other anthropogenic contamination, the problem will be most acute in unconfined aquifers [41], particularly those in exposed geological formations in urban areas.

The amounts of detected PBDEs in the environment are now higher than in previous years and the effects of bans restricting the use of PBDEs are now becoming apparent. PBDE deposition is estimated based on the samples of the firm core in the alpine region in 2003-07 is found to be lower than in the years 1997-2001 [21]. The increasing mass of electronic waste is still the main source of PBDE emissions, even though their actual content is rather low (<0.1%).

The presence of deca-PBDE (BDE-209) being its main component also poses a threat to the environment, as illustrated by research data summarized in this text. In the process of debromination, deca-PBDE becomes a source of lighter yet more persistent congeners.

As regards the amounts of PBDEs in the aquatic environment (Fig. 1), it is reasonable to expect that the admissible limits specified in the relevant Regulation can be exceeded. In Polish conditions the threat to the water ecosystem seems real. However, the current status of research in this field is still insufficient to allow a reliable assessment of the scale of the problem.

Because of its persistent character and short-time (in terms of geology) presence in the environment (manufacturing began after 1965) and industrial origins, PBDE levels have become a reliable anthropogenic indicator of environment quality in the last four decades.

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