

Selected EPs in the water of certain Polish lakes and rivers

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Abstract. Negative and effectively “irreversible” changes in the environment have often been caused by one or more factors including the intensive development of new technologies, progressing urbanisation and – above all – insufficient knowledge of the properties and toxic effects of many chemicals used. Hundreds of non-natural compounds capable of exerting a negative effect on the natural environment have now been identified in it, including within the broad categories of pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. Such new and emerging pollutants pose a serious threat to living organisms on account of their tendency to accumulate in certain parts of the environment. Furthermore, the substances in question may prove toxic and harmful to human beings and the environment even at low concentrations. Work described here thus had as its objective an analysis of the pollution of surface water in Poland in terms of content of organic compounds in general, and the aforementioned emerging organic pollutants in particular. Results confirm the presence in waters of such substances as phthalic esters, polybrominated diphenylethers, and organic tin compounds. Reference to average values for individual parameters in the cases of different rivers and lakes further show that, as of 2014–15, the various Polish surface waters researched were characterised by similar levels of pollution, other than in the case of naphthalene.

1 Introduction

The main reason for adverse changes in rivers and lakes is their pollution. A particularly serious threat is that posed by persistent organic pollutants (POPs) [1]. The presence of organic pollutants in surface waters leads to the poisoning and extinction of aquatic organisms, as well as contamination of organisms making contact with water. Toxicity, persistence and ability to bioaccumulate are the most important characteristics of organic pollutants ensuring their capacity to pose a threat [2]. Some are also included among the priority substances group [3]. Organic substances in surface waters are mainly products of the plastics industry, dyes, plant protection chemicals, chemicals involved in metallurgical industry and petrochemicals [4, 5]. There also remains a large amount of raw or only partially-treated wastewater reaching rivers. Emitted along with these are organic substances

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capable of raising levels of nutrients in water excessively, as well as toxic substances that may accumulate in our bodies and cause a number of diseases. At the same time, work to regulate rivers is being carried out throughout the country, reducing significantly the capacity to self-purify [6, 7]. The development of civilisation also creates new types of pollutants capable of entering waters. These contaminants are called "emerging pollution EPs", and include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, dioxins, pharmaceuticals, and some pesticides [8–10].

The aim of the work is to analyse certain pollutants of Polish rivers and lakes, on the basis of results obtained in the context of State Environmental Monitoring.

2 Research methodology

The analysis presented here was carried out on the basis of data from the Environmental Protection Inspection Service, obtained within the framework of the aforesaid State Environmental Monitoring. The samples concerned were collected and analysed in the years 2014–2015. Selection of rivers and lakes was based on the presence in them, of contaminants, with testing of their levels of pollution carried out on the same day. The analysis of surface-water quality was made on the basis of physico-chemical parameters, as well as the presence of selected organic pollutants (Table 1, Fig. 1). The substances checked for were Anthracene (Ant), Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(ghi)perylene (BghiP), Indeno(1.2.3-cd)pyrene (InP), Fluoranthene (Flt), Naphthalene (Nap), Σ Brominated diphenyl ethers (PBDEs), Σ Chloroalkanes (ChlA), Di(2-ethylhexyl) phthalate (DEHP), and Σ Tributyltin compounds (TBT). The results obtained were set against the relevant limit values for surface waters (Table 2) [11].

Table 1. Number of rivers and lakes.

| Number | River | Number | Lake |
|--------|------------------|--------|------------------------|
| 1 | Kamienica | 11 | Ostrowite |
| 2 | Radunia | 12 | Boruja Duża |
| 3 | Reknica | 13 | Dominickie |
| 4 | Czernica | 14 | Dręstwo |
| 5 | Broczynka | 15 | Wieleńskie-Trzytoniowe |
| 6 | Łupawa | 16 | Niesłysz |
| 7 | Drwęca Warmińska | 17 | Wielgie |
| 8 | Pisa | 18 | Będzin |
| 9 | Świder | 19 | Myśluborskie |
| 10 | Kamienna | 20 | Sierakowskie |

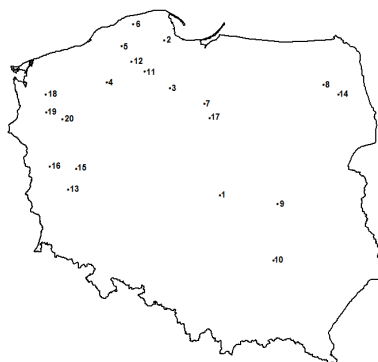


Fig. 1. Locations of measurement points (according to the Table 1).

Table 2. Environmental quality standards for surface water for priority substances and for other pollutants [11].

| Substance | Acceptable concentration - annual average [ng·L ⁻¹] | Maximum acceptable concentration [ng·L ⁻¹] |
|--------------|---|--|
| Ant | 100 | 100 |
| BaP | 0.17 | 270 |
| BbF | ND | 17 |
| BkF | ND | 17 |
| BghiP | ND | 8.2 |
| InP | ND | ND |
| Flt | 6.3 | 120 |
| Nap | 2,000 | 130,000 |
| PBDEs | ND | 140 |
| ChIA | 400 | 1400 |
| DEHP | 1,300 | ND |
| TBT | 0.2 | 1.5 |

ND – no data

3 Results and discussion

Physicochemical analysis of samples taken from the selected Polish rivers under investigation revealed that the latter are contaminated with organic compounds to varying extents (Tables 3, 5). Rivers were characterised by the lowest values for concentrations of brominated diphenyl ethers, tributyltin compounds and some PAHs (Ant, BbF, BkF, Nap). Polybrominated diphenyl ethers (PBDEs) are a class of recalcitrant and bioaccumulative halogenated compounds that have emerged as major environmental pollutants. PBDEs are used as flame-retardants, and are found in consumer goods such as electrical equipment, construction materials, and textiles [12]. In general, TBT compounds are released to the environment from anthropogenic sources. The use of antifouling paints, applied as a coat to the immersed sections of boats and floating structures, represents the major source of TBT finding its way into the aquatic environment [13]. In contrast, polycyclic aromatic hydrocarbons are generally formed via the incomplete combustion of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. PAHs are thus found in coal tar, crude oil, creosote, and roofing tar [14, 15]. In any event, the above-mentioned substances were not found to exceed admissible values in the waters studied. In turn, concentrations of benzo[a]pyrene ranged from 0.5 to 2.4 ng·L⁻¹, as set against the far-lower acceptable annual average concentration of 0.17 ng·L⁻¹. Benzo[a]pyrene is the most studied of the polycyclic aromatic hydrocarbons and is treated as the determinant of the presence of PAHs in general [14]. At 27 ng·L⁻¹, the concentration of fluoranthene noted in the Reknica exceeds the annual average permissible considerably. Levels in the Rivers Broczynka and Kamienna are in turn the subject of slight exceedances. Fluoranthene is one of the U.S. Environmental Protection Agency's 16 priority pollutant PAHs. It is released naturally during the burning of fossil fuels and wood. It is also an ingredient in dyes, pharmaceuticals, and insulating oils [16]. A more major concern is the potential for fluoranthene to build up in aquatic sediments, where it could pose a risk to organisms living on or near the bottom of lakes and rivers [17]. The U.S. Geological Survey (USGS) studied PAHs in three streams in Minnesota. Fluoranthene was in fact the chemical detected most frequently in this study, being found in at least 50% of the samples [18].

Table 3. Average concentration of selected EPs for rivers.

| Substance | Number of river | | | | | | | | | |
|-----------------------------------|-------------------------------------|------|------|------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| | Concentration [ng·L ⁻¹] | | | | | | | | | |
| Anthracene | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 3.7 | 0.5 | 0.5 | 1.3 |
| Benzo(a)pyrene | 0.5 | 0.5 | 1 | 0.5 | 0.5 | 0.5 | 2.4 | 0.5 | 0.5 | 1 |
| Benzo(b)fluoranthene | 0.5 | 0.5 | 1 | 0.5 | 0.5 | 0.5 | 2.4 | 0.5 | 0.5 | 1 |
| Benzo(k)fluoranthene | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 1.3 | 0.5 | 0.25 | 6 |
| Benzo(ghi)perylene | 0.5 | 0.5 | 1 | 0.5 | 0.5 | 0.5 | 2.5 | 2 | 0.5 | 1.4 |
| Indeno(1.2.3-cd)pyrene | 0.5 | 0.5 | 1 | 0.5 | 0.5 | 0.5 | 2.1 | 1 | 0.5 | 1 |
| Fluoranthene | 3.6 | 0.5 | 27 | 4.4 | 7.3 | 5.8 | 6.2 | 0.5 | 1 | 6.9 |
| Naphthalene | 500 | 500 | 500 | 500 | 500 | 500 | 150 | 33 | 100 | 32.4 |
| Brominated diphenyl ethers | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.05 | 0.05 | 0.1 | 0.05 |
| Chloroalkanes | 100 | 100 | 100 | 100 | 100 | 100 | 200 | 200 | 50 | 100 |
| Di(2-ethylhexyl) phthalate | 500 | 500 | 500 | 500 | 500 | 500 | 100 | 100 | 330 | 200 |
| Tributyltin compounds | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.1 | 0.05 |

Rivers were characterised by DEHP concentrations in the range 100–500 ng·L⁻¹, but this did not therefore represent an exceedance of the limit values set out for surface waters. Rainfall transfers phthalate esters in the atmosphere to surface water, and their accumulation there ensures a wide distribution in rivers, lakes and sediments. DEHP is the predominant congener in surface water and sediments as a result of urbanisation and industrialisation. This is usually the caused by phthalate ester, which is produced and used most abundantly [19]. In the literature, concentrations of DEHP in surface water are seen to range from undetected to 97.8 mg·L⁻¹. For example, the maximum concentration reported by Yuan et al. (2002) in Taiwan’s rivers was 18.5 mg·L⁻¹ [20]. In Germany, the maximum DEHP concentration detected in surface water was 97.8 mg·L⁻¹. DEHP has also been noted in groundwater, at concentrations ranging from undetected to 5.661 mg·L⁻¹. This latter maximum was noted in Spain. The distribution of DEHP in groundwater is found to relate to the concentration in surface waters [21].

The average concentration of chloroalkanes in selected rivers was 115 ± 47.3 ng·L⁻¹ (Table 5). This concentration was much less than the maximum permitted. However, while the rivers examined are not significantly contaminated with these compounds, their presence cannot be ignored on account of the way these substances and other organic compounds can tend to accumulate in bottom sediments, ultimately still posing a serious threat to living organisms, on account of their severe toxicity to aquatic life. The chloroalkanes’ persistence, tendency to bioaccumulate, toxicity and occurrence in remote locations all give rise to concerns regarding possible harmful effects on a global scale. All chlorinated paraffins have the potential to form toxic products if heated in a fire; and chloroalkanes are listed as priority hazardous substances and priority substances in the EU’s Water Framework Directive [22].

Concentrations of selected PAHs, brominated diphenyl ethers, chloroalkanes, di(2-ethylhexyl) phthalates and tributyltin compounds in the waters of lakes are given in Tables 4 and 5. Concentrations of individual compounds are in the order of ng/dm³, with higher values for fluoranthene, chloroalkanes and di(2-ethylhexyl) phthalate. Fluoranthene

concentrations in the 10 lakes ranged from 2.7 to 49.4 ng·L⁻¹, with a mean value of 12.3 ± 17.1 ng·L⁻¹. The PAH concentrations in the water from Lake Chaohu (China) are significantly higher than those noted for Polish lakes, except in the case of fluoranthene. Of the 16 priority PAHs, naphthalene was present at the highest concentration (68.8 ng·L⁻¹), anthracene at 2.8 ng·L⁻¹. The concentration of fluoranthene was 9.1 ng·L⁻¹. Among the Polish lakes studied, it was Lake Wieleńskie-Trzytoniowe that reported the highest concentration (49.4 ng·L⁻¹), with the second highest being at site 17, Lake Wielgie. Under Polish regulations, the permissible content for this substance is 6.3 ng·L⁻¹.

Table 4. Average concentration of selected EPs for lakes.

| Substance | Number of lake | | | | | | | | | |
|---|-------------------------------------|------|----|------|------|------|------|------|------|------|
| | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| | Concentration [ng·L ⁻¹] | | | | | | | | | |
| Anthracene | 0.79 | 0.75 | ND | 0.5 | ND | 0.5 | 0.6 | 0.54 | 0.71 | 0.54 |
| Benzo(a)pyrene | 0.54 | 0.5 | ND | 1.03 | ND | 0.68 | 3.51 | 0.63 | 0.75 | 0.54 |
| Benzo(b)fluoranthene+ Benzo(k)fluoranthene | 0 | 0.08 | ND | 2.99 | ND | 0.52 | 5.98 | 0.25 | 0.42 | 0.17 |
| Benzo(ghi)perylene+ Indeno(1.2.3cd)pyrene | 0.33 | 0.42 | 26 | 1.49 | 38.3 | 1.05 | 7.47 | 1.16 | 0.88 | 0.46 |
| Fluoranthene | 5.33 | 3.08 | ND | 9.62 | 49.4 | 2.7 | 33.2 | 1.57 | 2.98 | 3.12 |
| Naphthalene | 5.33 | 3.08 | ND | 9.62 | ND | 7.3 | 1.77 | 1.57 | 2.98 | 3.12 |
| Brominated diphenyl ethers | 0.1 | 0.1 | ND | 0.05 | ND | ND | ND | 0.03 | 0.04 | 0.03 |
| Chloroalkanes | 100 | 100 | ND | ND | ND | ND | ND | 50 | 50 | 50 |
| Di(2-ethylhexyl) phthalate | 425 | 425 | ND | 315 | ND | ND | ND | 188 | 338 | 238 |
| Tributyltin compounds | 0.05 | 0.05 | ND | ND | ND | ND | ND | 0.03 | 0.03 | 0.03 |

ND – no data

Benzo(a)pyrene is often used as a marker for overall exposure to carcinogenic PAHs, as its contribution to the total carcinogenic potential is high [23]. The analyzed lakes were characterised by a concentration of benzo(a)pyrene above the limit value (0.17 ng·L⁻¹). The highest level of benzo(a)pyrene was the 3.51 ng·L⁻¹ detected in Lake Wielgie. Compared with reports from abroad, the benzo(a)pyrene level in Lake Wielgie was, for example, significantly lower than those in the Great Bitter Lake and El Tamsah Lake, Egypt [22]. Benzo(a)pyrene was the dominant PAH found in the saline waters of the latter lakes associated with the Suez Canal, with the average concentration being 3800 ng·L⁻¹.

The PAHs identified can be classified in line with their having a molecular structure of two fused rings (naphthalene), three rings (anthracene), four rings (fluoranthene), five rings (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene) and six rings (indeno(1.2.3-cd)pyrene and benzo(ghi)perylene) [24]. It is the three- or four-ring or low-molecular weight PAHs that are most abundant in the water of the analyzed lakes. This in turn denotes only a more minor presence for the 5- and 6-ring PAHs considered most carcinogenic by the US EPA. As concentrations of benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene, and indeno(1.2.3-cd)pyrene were summed, comparison with permissible maxima is not possible.

Compositional analysis of individual phthalic acid esters (PAEs) can prove helpful in tracking sources of contamination, illustrating fate and transport in a multimedia and multi-component environment. Patterns for different PAEs may indicate different sources. PAEs of low molecular weight, such as DBP, gain wide use in cosmetics and personal care

products. For example, longer alkyl and/or branch-structure PAEs, such as DEHP, are used widely as plasticizers in the polymer industry. DEHP undergoes sorption in sediment more readily, and proves resistant to degradation. Furthermore, for sediments little penetrated by light, photodegradation of PAEs probably loses significance altogether, with biodegradation left as the dominant mechanism for the elimination of PAEs. The concentrations of DEHP in Polish lakes ranged from 188 to 425 ng·L⁻¹, with a mean value of 321 ng·L⁻¹. The concentrations of DEHP measured in Polish lakes are comparable with those obtained in 15 urban lakes of Guangzhou city, China. Sixteen PAE congeners were detected in water and sediments, with DEHP present in all water samples, at detected concentrations in the range 87–630 ng·L⁻¹ [25]. Lakes were characterised by low concentrations of chloroalkanes and tributyltin compounds, however. A correlation between the presence in the environment of benzo(a)pyrene and other substances from the PAHs was observed. On the other hand, no significant dependence between the occurrence of PAHs and other pollutants was observed.

Table 5. Statistical analysis of results.

| Substance | Statistical analysis | | | |
|-----------------------------------|----------------------|------|--------------|------|
| | Rivers (n=10) | | Lakes (n=10) | |
| | Mean | SD | Mean | SD |
| Anthracene | 0.9 | 1.01 | 0.64 | 0.11 |
| Benzo(a)pyrene | 0.79 | 0.60 | 1.02 | 1.02 |
| Benzo(b)fluoranthene | 0.79 | 0.60 | 1.30 | 2.13 |
| Benzo(k)fluoranthene | 1.11 | 1.74 | | |
| Benzo(ghi)perylene | 0.99 | 0.74 | 7.75 | 13.3 |
| Indeno(1.2.3cd)-pyrene | 0.81 | 0.51 | | |
| Fluoranthene | 6.32 | 7.72 | 12.3 | 17.1 |
| Naphthalene | 331.5 | 220 | 4.35 | 2.85 |
| Brominated diphenyl ethers | 0.07 | 0.02 | 0.06 | 0.03 |
| Chloroalkanes | 115 | 47.3 | 70 | 27.4 |
| Di(2-ethylhexyl) phthalate | 373 | 176 | 321 | 96.5 |
| Tributyltin compounds | 0.06 | 0.02 | 0.04 | 0.01 |

In terms of average values for individual parameters in rivers and lakes (Fig. 2, Table 5), Poland's surface waters in 2014–15 can be said to feature rather similar levels of the pollutants considered. The exception was naphthalene, whose average concentration was 75 times higher in rivers than in lakes. In contrast, rivers and lakes alike were characterized by DEHP being present at the highest concentrations of any of the substances studied. In this regard, it should be noted that DEHP is just one representative of a broad class of compounds (the esters of phthalic acid), so the presence of other pollutants of this group in surface waters is anticipated.

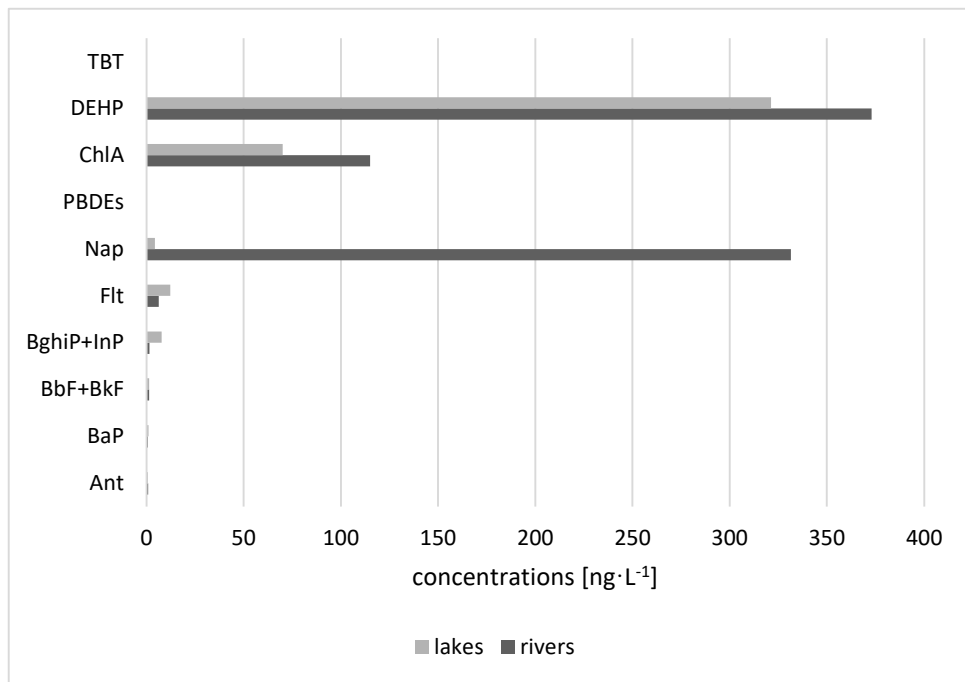


Fig. 2. Average concentrations of selected pollutants in rivers and lakes – comparison.

4 Conclusions

- ✓ Criteria established for environmental quality now relate closely to so-called emerging pollutants, whose quantities and variety in the aquatic environment are seen to be increasing steadily.
- ✓ Concentrations of PAHs and other pollutants in the rivers and lakes under analysis are found to fall within the same range, in the order of $\text{ng}\cdot\text{L}^{-1}$ for individual compounds, albeit with higher values noted in rivers for fluoranthene, chloroalkanes, di(2-ethylhexyl) phthalate and naphthalene.
- ✓ Even where concentrations of organic pollutants in water are low, their presence may not be disregarded, given the tendency of most of the compounds in question to accumulate on solid particles. This leaves it highly probable that higher contents are present in bottom sediments.
- ✓ For surface waters to achieve a more favorable environmental status, it is necessary for emissions of untreated municipal wastewaters to cease.
- ✓ The challenge for the coming years lies in the better understanding of problems with emerging pollutants, not least in regard to their actual concentrations in the environment, and their overall toxic impact there, as well as their impact on particular organisms.

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