



Concentration of chosen organic micropollutants in surface water

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ABSTRACT

Surface water are highly vulnerable to pollution. Many of them contain compounds that are highly toxic and harmful for living organisms. Organic micropollutants are a group of substances with negative impact on people's health and their lives. It is necessary to constantly monitor and estimate their concentration in those surface water, which may after purification process be intended for human consumption. The aim of this research was the assessment of concentrations of chosen organic micropollutants such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) and organic carbon with its fractions in surface water samples taken in Poland and Germany. Sixteen PAH listed and seven PCB congeners listed by Environmental Protection Agency were analyzed. Water samples were taken from the reservoir located in Silesian Voivodeship in Poland and from Rhine River in the city of Kleve located in the North Rhine-Westphalia state in Germany. Both regions are highly industrialized with their main types of industry being mining, chemical, power, and electrical industry. Samples were taken in the similar weather conditions and ambient temperature. Solid phase extraction (SPE) method has been applied to separate PAH and PCB from water samples. The method was applied using 500 mg Octadecyl C₁₈ 6 mL Bakerbond extraction columns and SPE apparatus. Standard mixture of 16 PAH by RESTEK company (U.S, Benner Circle, Bellefonte, PA) and standard mixture of 9 PCB by DR EHRENSTORFER company (Germany, Augsburg) were used. The capillary gas chromatography (CGC) method has been used to analyze their concentrations and composition. Total organic carbon (TOC) analyzer was used to determine the concentration of total organic carbon. TOC, dissolved organic carbon, and biodegradable dissolved organic carbon concentration in water samples were also analyzed using TOC analyzer multi N/C 2100. PAH concentrations varied from 0.61 to 24.52 ng/L in the reservoir and from 0.41 to 10.20 ng/L. None of the PAH standardized in the Council Directive were detected in any of the samples. Also none of the analyzed PCB congeners were detected in any of the samples. It is necessary to extend the amount of samples and sampling period to obtain the full image of the surface water quality in those areas.

Keywords: Surface water; Organic micropollutants; Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls; Organic carbon; Drinking water

1. Introduction

Surface water are considered highly vulnerable to contamination. Their quality may have huge impact on mankind and other living organisms. Organic micropollutants presence in these water affects their quality [1–3]. Many of them are toxic and hazardous. It is necessary to spread awareness of the dangers connected with surface

water polluted with organic compounds and take actions to stop their quality from worsening [1–4]. The wide group of these chemical substances is present in surface water. This group includes compounds such and PAH or PCB [4]. PAH is an enormous group of substances. There are over 300 compounds included in it. To help with the monitoring of these substances in the environment, The Environmental Protection Agency listed 16 PAH that are highly toxic and

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it is necessary to monitor their concentration [2,5–7]. The compounds from the PAH group are present in the environment as an effect of pyrolysis. Their sources may be natural, for example, wildfire, volcanic activity, or anthropogenic, for example, industry of all kinds [4,5,8,9]. Their presence is always as a mixture, not separately [10–12]. Although their concentrations in surface water are low, it is still a danger for living organisms because of their toxic, mutagenic, and carcinogenic nature [5,9–15]. PCB are another big group of organic micropollutants that are highly toxic and carcinogenic with bioaccumulation ability. There are no natural sources of those compounds in the environment. Their only source is the industry. After discovering their toxic and carcinogenic character their production was stopped, but many of them are still present in the environment. The Environmental Protection Agency listed seven PCB congeners that must be monitored in the environment [16]. They may cause many illnesses such as liver disease or cancer [17–21]. Besides the organic micropollutants, surface water may contain other organic matter. The concentration of organic matter in water describes TOC which contains many different fractions. Substances dissolved in water are determined as dissolved organic carbon (DOC). The part of dissolved organic matter which has an ability of biochemical decomposition is determined as biodegradable dissolved organic carbon (BDOC). It has an impact on bacteriological quality of the water due to its role as the source of carbon and energy to microorganisms and is an important parameter considering drinking water treatment and distribution [2,22]. The aim of this research was the assessment of concentrations of chosen organic micropollutants such as PAH and PCB and organic carbon with its fractions in surface water samples taken in Poland and Germany. Sixteen PAH listed by Environmental Protection Agency (EPA) were analyzed: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, and dibenzo(a,h)anthracene. Seven PCB congeners also listed by EPA were analyzed: 28, 52, 101, 118, 138, 153, and 180 [16]. It is the part of further research considering the micropollutants concentrations in surface water and the dangers related to their presence in water prepared for drinking.

2. Materials and methods

2.1. Materials

For the research water samples from the reservoir located in Silesian Voivodeship in Poland and from Rhine River in the city of Kleve located in the North Rhine-Westphalia State in Germany were used. Both regions are known as industrial areas. Silesian Voivodeship economy is based on rich sources of coal and minerals, therefore it is home for many industries like mining, power, chemical, or textile industry. North Rhine-Westphalia is a region that, same as Silesia, has grown to economic importance by coal extraction. Now, as a result of substantial structural changes, it is home to chemical and plastics industry followed by electrical engineering and electronics. Considering the fact

that both areas are highly industrialized and are a home to similar types of industries, they were chosen for assessment of the concentrations of analyzed substances in surface water, which appearance in the environment is strictly connected to human activities (anthropogenic impact) like different kinds of industry [25–27].

Water from the reservoir supplies the water treatment plant which belongs to the Upper Silesian Water Supply company. The reservoir was built over the period of 1935–1939, and then adapted to water supplying purposes in the years 1948–1951. The area of the reservoir cover approximately 6 km² and its volume is approximately 17 mln m³. Purified water from the reservoir is supplied to few major cities of Upper Silesia [25,26].

Rhine is one of the major rivers in Europe. Its length is approximately 1,233 km from which 865 km is within the borders of Germany. It enters the North Sea near the Rotterdam in Netherlands. About 50 million people inhabit its catchment. North Rhine-Westphalia state where the samples were taken is home to many companies in chemical and plastic industry and the river itself is considered highly contaminated [28].

2.2. Analytical procedure

The depth of water sampling in both cases was approximately 0.5 m and both samples were taken approximately 1 m from the bank, where in case of a river the current is strong. The temperature of the samples taken from the reservoir was around 7°C and from the river around 4°C. The water samples from both sources were taken in the same season (fall) with the similar weather conditions and ambient temperature. For PAH and PCB extraction from the water samples, the solid phase extraction (SPE) method was applied, using 500 mg Octadecyl C₁₈ 6 mL Bakerbond extraction columns and SPE apparatus. For the purpose of PAH extraction, 0.5 L of water was taken. Petroleum ether and dichloromethane were added to the samples in the ratio 3:2. The water was passed through SPE extraction columns preconditioned using 6 mL of hexane, 6 mL of methanol and 6 mL of distilled water. After that, the columns with PAH trapped on sorbent were dried in vacuum for approximately 30 min. PAH were then eluted from the columns filling using 3 × 1 mL of hexane. Extracts were condensed to the volume of 1 mL and analyzed with the use of gas chromatography and mass spectrometer (GC-MS) [15,25]. Standard mixture of 16 PAH by RESTEK company (U.S, Benner Circle, Bellefonte, PA) was used and 0.002 mL of extract were injected on DB-5 column using microsyringe. Helium was used as a carrier gas.

For the purpose of PCB extraction, 1 L of water was taken and passed through SPE extraction columns preconditioned using 2 mL × 6 mL of hexane and 6 mL of methanol. After that the columns were dried for 30 min in vacuum. To elute PCB trapped on columns filling, 6 mL of hexane were passed through the columns. Again extracts were concentrated to 1 mL and analyzed with the use of gas chromatography and mass spectrometer (GC-MS) [18,19]. Standard mixture of nine PCB by DR EHRENSTORFER company (Germany, Augsburg) was used. The same as before 0.002 mL of extract were injected on DB-5 column using microsyringe. Helium was used as a carrier gas.

TOC analyzer multi N/C 2100 was used to determine the concentration of TOC and DOC in the water samples. For this purpose, 50 mL of water were taken. To analyze DOC the samples were passed through 0.45 µm membrane filters. For the purpose of BDOC analysis, Joret method was applied. It relies on observations of DOC loss in the water [22,29].

Determination of all analyzed compounds was performed in triplicate. To eliminate the error as a result of sample taking method, the water samples were averaged. These representative samples were put under further procedures. Six-point calibration were performed using serially diluted PAH and PCB standards. Method limits of detection were determined as a concentration of analyte in a sample that give rise to peaks with a minimal signal to noise ratio of 3. The detection limits varied from 0.3 to 1.7 ng/L for PAH. Analytes identification confirmation relied on GC retention time and qualifier ions [30]. Peaks with acceptable ion ratios were integrated to be later quantified. Because of this the main error impacting the variation of concentration of analyzed compounds in the samples is analytical error.

3. Results and discussion

The results of chosen PAH concentration in water samples taken from the reservoir and from the river and their standard deviations are presented in Table 1.

For the purpose of the results discussion, PAH were divided into following groups:

- PAH standardized in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption: benzo(a)pyrene, the sum of PAH (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) [31],
- 2-ring PAH: naphthalene,
- 3-ring PAH: acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene,
- 4-ring PAH: fluoranthene, pyrene, benzo(a)anthracene, and chrysene,
- 6-ring PAH: dibenzo(a,h)anthracene.

In the water taken from the reservoir, none of the PAH standardized in the Council Directive was detected. The research previously performed on the samples taken from this reservoir shows that those substances were present in high concentrations. Literature data shows that the amount of benzo(a)pyrene (123 ng/L) was much higher than the acceptable concentration standardized in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (10 ng/L) [31]. Also, the sum of PAH included in the regulations was above the permissible level [32]. The concentration of 2-ring naphthalene amounted to 24.52 ng/L which is the highest concentration of all the compounds detected in this sample. It is also the highest concentration of all the compounds considering both analyzed samples, taken from the reservoir and from the river. Analyzing the group of 3-ring PAH, the highest concentrations detected in case of fluorene (4.03 ng/L) and phenanthrene (7.10 ng/L).

The concentration of other compounds in this group such as acenaphthylene, acenaphthene, and anthracene amounted to 0.76, 3.00, and 0.61 ng/L. In the group of 4-ring PAH the presence of all compounds was noted. The concentration amounted to 2.07 ng/L in case of fluoranthene, 1.26 ng/L in case of pyrene, 1.94 ng/L in case of benzo(a)anthracene, and 1.55 ng/L in case of chrysene. The presence of 6-ring PAH, that is, dibenzo(a,h)anthracene in analyzed sample taken from the reservoir was not detected. Considering literature data there were few substances that were not detected in the samples before, but were currently present (acenaphthylene, acenaphthene, fluoranthene, and pyrene).

In the water taken from Rhine river similar to the previously discussed sample, none of the PAH standardized in the Council Directive was detected. The concentration of naphthalene amounted to 10.20 ng/L which is also the highest concentration of all the compounds detected in this sample and second highest considering both samples. In the group of 3-ring PAH, the presence of acenaphthylene and anthracene was not noted. The concentration of acenaphthene amounted to 1.00 ng/L, fluorene to 1.15 ng/L, and phenanthrene to 2.15 ng/L. The presence of 4-ring PAH, that is, benzo(a)anthracene and chrysene was not detected and in case of fluoranthene and pyrene the concentration was low and amounted to 0.49 and 0.41 ng/L. The presence of 6-ring dibenzo(a,h)anthracene in the sample taken from the Rhine river was also not detected. Comparison of the concentration of PAH in the water samples taken from the reservoir and from the river shows that all the analyzed compounds had higher concentration in the reservoir water which might be surprising considering the fact that the research shows that Rhine water is highly polluted [28]. Literature data shows that the typical concentrations of PAH in Rhine River in Germany may vary from 10 to 730 ng/L [33]. Ten of 16 analyzed PAH were not detected in the river water and the others showed in low concentrations. In case of the sample from the reservoir only six compounds were not detected.

For the purpose of this research, nine PCB were analyzed in both water samples (PCB 28, PCB 52, PCB 101, PCB 105, PCB 118, PCB 138, PCB 153, PCB 156, and PCB 180) but none of them was detected in neither of the samples. This might be surprising considering the fact that both, the reservoir and the river, have history of high concentrations of PCB. Literature data shows that the samples taken from the reservoir contained those substances in the amount from approximately 700 to 2,700 ng/L. Permissible level according to EPA amount to 500 ng/L [34]. In case of Rhine literature data shows that in the area of sample taking, PCB concentrations amounted to 100 ng/L in average [35].

The results of TOC, DOC, and BDOC concentration in water samples taken from the reservoir and from the river and their standard deviations are presented in Table 2.

In the water taken from the reservoir the concentration of TOC amounted to 8.659 mg/L. DOC concentration in this sample amounted to 7.733 mg/L. In case of BDOC the concentration was really low and amounted to 0.351 mg/L. Literature data shows the concentrations of those substances in this reservoir on a similar level [36]. In the water taken from the river the concentration of TOC was much lower, it amounted to 1.797 mg/L. DOC concentration amounted to

Table 1
PAH concentration in water samples

Compound	Reservoir		Rhein River	
	Concentration in water sample (ng/L)	Standard deviation (ng/L)	Concentration in water sample (ng/L)	Standard deviation (ng/L)
Naphthalene	24.52	1.19	10.20	0.39
Acenaphthylene	0.76	0.06	nd	–
Acenaphthene	3.00	0.37	1.00	0.05
Fluorene	4.03	0.49	1.15	0.07
Phenanthrene	7.10	0.79	2.15	0.02
Anthracene	0.61	0.15	nd	–
Fluoranthene	2.07	0.27	0.49	0.05
Pyrene	1.26	0.11	0.41	0.03
Benzo(a)anthracene	1.94	0.14	nd	–
Chrysene	1.55	0.17	nd	–
Benzo(b)fluoranthene	nd	–	nd	–
Benzo(k)fluoranthene	nd	–	nd	–
Benzo(a)pyrene	nd	–	nd	–
Indeno(1,2,3,-cd)pyrene	nd	–	nd	–
Dibenzo(a,h)anthracene	nd	–	nd	–
Benzo(ghi)perylene	nd	–	nd	–

nd – not detected.

Table 2
TOC, DOC, and BDOC concentration in water samples

Compound	Reservoir		Rhine river	
	Concentration in water sample (mg/L)	Standard deviation (mg/L)	Concentration in water sample (mg/L)	Standard deviation (mg/L)
TOC	8.659	0.083	1.797	0.025
DOC	7.733	0.008	1.587	0.001
BDOC	0.351	0.062	0.076	0.001

1.587 mg/L and BDOC to 0.076 mg/L. According to the Council Directive, the parametric value of permissible TOC level stands for “no abnormal changes” [31].

4. Conclusions

Organic micropollutants like PAH and PCB concentrations were analyzed in water samples taken from surface water located in highly industrialized regions. Comparing those results, we can observe the differences in concentrations of PAH in the reservoir and in the river located in the areas with comparable surrounding conditions. Also referring the results to the previous ones obtained in those areas we can note large variations. It is necessary to extend the amount of samples and sampling period to obtain the full image of the surface water quality in those areas.

Conducted research allows to draw the following conclusions:

- Both analyzed water samples contained PAH.

- All of the analyzed PAH had higher concentration in the water sample taken from the reservoir.
- The highest concentration of the substance from the PAH group considering both taken water samples was noted for naphthalene (24.52 ng/L) in the water from reservoir.
- None of the PAH standardized in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption was detected in any of the samples.
- 10 out of 16 analyzed PAH were not present in the Rhine river water.
- 6 out of 16 analyzed PAH were not present in the reservoir water.
- None of the samples contain any of the analyzed compounds from the PCB group.
- TOC, DOC, and BDOC have much higher concentration in water sample taken from the reservoir.
- Considering the analyzed substances, water taken from Rhein River has better quality than water taken from the reservoir in Poland.

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