ARCHIVES OF ENVIRONMENTAL PROTECTION

CONCENTRATION OF PAHs IN MUNICIPAL WASTEWATER IN SELECTED SEWER COLLECTORS OF THE UPPER SILESIAN URBAN AREA, POLAND

FRANCISZEK PISTELOK, IZABELA JURECZKO*

Institute of Environmental Engineering of the Polish Academy of Sciences,
ul. Skłodowskiej-Curie 34, 41-819 Zabrze
*Corresponding author's email: izabela.jureczko@ipis.zabrze.pl

Keywords: PAHs, municipal wastewater, diagnostic ratios for the emissions of PAHs.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of organic compounds that make constant threat to the environment. Their contents from natural sources are low. The processes of incomplete organic fuel combustion are the main sources of PAHs. In Upper Silesia (Poland), large amounts of PAHs are emitted into the air as a result of coal combustion in home furnaces and liquid fuel burning in combustion engines (low emission). PAHs get into surface water because of the surface runoff and point source wastewater discharges from certain industries. The following study presents PAHs concentrations in raw municipal wastewater. The tests were performed out of the heating season. The samples were collected from the combined sewer system. The analyses of PAHs were carried out with gas chromatography coupled with a mass detector (GC-MS). The concentrations of 16 PAHs sum (EPA list) ranged between 1.025 and 3.056 µg/L. Phenanthrene dominated in nearly all the analysed samples. The contents of PAHs, which are priority hazardous substances according to the directive, were high in the analysed samples. The obtained results and the analysis of diagnostic ratios for the emissions of PAHs into the air helped to reach the conclusion that traffic emissions were the main source of PAHs in the examined wastewater.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of organic compounds that contain between a few and several aromatic rings in the molecule. Their occurrence in the environment is common and mainly related to the anthropopressure. They are formed as by-products of incomplete organic fuel combustion. The most important sources of air pollution with PAHs are the low emission (coal combustion in individual home furnaces and traffic emissions) and industrial emission (heavy industry, cogeneration plants). The contribution of particular sources may differ depending on the urbanization level of the area, solutions used for house and flat heating, traffic intensity, etc. Lighter PAHs occur in the air mainly in the gas phase. Hydrocarbons with three or more rings occur partially

in the gas phase and partially on the particulate matter surface. On the other hand, higher hydrocarbons are almost totally adsorbed on the particulate matter surface [3, 8].

The contents of PAHs, principally benzo[a]pyrene, were analysed in particular components of the environment in the 2nd half of the 20th century. Additionally, their impact on humans, animals and plants was examined. Consequently, the cancerogenicity of certain PAHs was found. PAHs enter human body through the respiratory tract (aerosols), skin (water) and digestive system (water and food). Some of them are accumulated in the adipose tissue, kidneys and adrenal glands. They undergo transformations and form metabolites with cellular macromolecules. The couplings can have the character of promutagenic lesions and can initiate carcinogenesis [8].

The occurrence of PAHs in surface water is mainly the effect of the area source pollution related to flue gas emissions into the air. The pollutants enter receivers with stormwater and thaw water as a result of the surface runoff. PAHs washed out from bituminous surfaces, such as roads and car parks (particularly newly built or renovated), make another area source pollution type. PAHs in surface water can come from point sources. Their high concentrations are observed in wastewater from coke, chemical and metallurgic plants, etc. [17].

Most PAHs are insoluble in water. Hydrocarbons with the lower number of rings occur in the solved or colloid forms. Others undergo sorption on the suspension surface [5]. The compounds are classified as xenobiotics and only slightly decompose biologically. Consequently, a significant amount of PAHs in a receiver sediments easily and produces long-term pollution of bottom sediments [1, 2, 5].

The Water Framework Directive (WFD) was approved in 2000. It established the framework for community action in the field of water policy. The Directive introduced the notions of priority substances and priority hazardous substances. The document committed EU member states to take measures to steadily reduce water pollution with priority substances and gradually eliminate emissions, discharges and losses of priority hazardous substances [9]. The Directive 2008/105/EC on environmental quality standards in the field of water policy [10] established the detailed course of action on priority substances in the EU law. It defines permissible contents of such substances in water. It also identifies priority hazardous substances. PAHs are listed in both documents. Fluoranthene, naphthalene and anthracene belong to priority substances whereas priority hazardous substances include benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene [10]. The EU documents are also reflected in the Polish Water Law [24] and the Regulation of the Polish Ministry of the Environment of 9 November 2011 on the classification of surface water bodies and environmental quality standards (EQS) for priority substances [20]. Consequently, the above-mentioned compounds are included in the classification of the flowing surface water. The introduction of these provisions resulted in the deterioration of the surface water classification results in the Silesian Voivodship. Compounds categorized as PAHs, particularly the sum of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, were a decisive factor for the classification in many profiles [22].

RESEARCH OBJECTIVE

The aim of the research was to determine concentrations of PAHs in raw wastewater before its supply into a wastewater treatment plant. Using markers and diagnostic ratios

enables to establish the origins of PAHs. The obtained results can be used to determine potential sources of surface water pollution with PAHs and diagnose the existing situation. Consequently, proper corrective actions can be taken.

RESEARCH METHODOLOGY

Sampling sites

Sampling took place at 4 sewer collectors that supply wastewater to various wastewater treatment plants in the Silesian Voivodship. All of them work for the cities in the Upper Silesian urban area.

Sample 1 comes from the sewer system that serves 50 000 inhabitants. The daily wastewater flow in the collector is 6600–7690 m^3/day. 80% of the system is made up by the separate sewer system built between 2000 and 2005. 20% of the system is constituted by the combined sewer system constructed throughout the 20th century. There are 7 sewage pumping stations in the catchment area of the wastewater treatment plant.

Sample 2 was taken from the sewer collector to which 12 000 inhabitants are connected. The daily wastewater flow is 1370–1750 m^3/day. The catchment area of the wastewater treatment plant is divided between separate sewer (approx. 50%) and combined sewer (50%) systems. There is 1 sewage pumping station. In the area, there are no significant industrial plants.

Sample 3 was collected from the sewer system working for 28 000 inhabitants. The daily wastewater flow is 7500–7809 m^3/day. The separate sewer system dominates the catchment area of the wastewater treatment plant. It was built in the 1970s and 1980s and is used by 65% of the inhabitants. Others use the combined sewer system. There are 2 sewage pumping stations. There are no significant industrial plants.

Sample 4 was collected at the sewer collector that serves 125 000 inhabitants. Additionally, food industry plants are located in the area. The daily wastewater flow is approx. 40 000 m^3/day.

Range of basic wastewater analyses, ATP determination

Basic wastewater analyses included determinations of wastewater temperature, pH, chemical oxygen demand (COD), suspension, Kjeldahl nitrogen, total nitrogen and total phosphorus. Additionally, total contents of adenosine triphosphate (ATP) in water and cellular ATP were studied. Moreover, the biomass stress indicator (BSI) was established. It was given by:

$$BSI\ [\%] = dATP \cdot 100/tATP$$

where: dATP – dissolved, extracellular ATP in raw wastewater, [ngATP/mL,]

tATP – total ATP in wastewater, [ngATP/mlL].

ATP analyses and BSI calculations were performed according to the test manufacturer's instructions [23].

Determining PAHs

PAHs analyses were performed by an accredited laboratory working in the system according to PN-EN ISO/IEC 17025 standard. Samples were prepared according

to laboratory's procedure which applies determination of PAHs in waters by gas chromatography coupled with mass detector.

The research was carried out in a single series of measurements. 500-mL wastewater samples were extracted three times with dichloromethane. The obtained solvent fraction was separated from wastewater in a separator. The obtained extracts were concentrated to 1-mL volume in a rotary vacuum evaporator. Then, they were cleaned in the initially conditioned glass columns with a stationary phase made of aluminium oxide/silica gel (1:1) and a low amount of anhydrous sodium sulphate. The analytes were leached with 70 mL of dichloromethane. The purified extracts were concentrated again to 1-mL volume in the rotary vacuum evaporator. Afterwards, they were filtered through a polytetrafluoroethylene (PTFE) syringe filter. Then, the samples underwent quantitative and qualitative analysis to determine the PAHs contents. It was performed with gas chromatography coupled with mass detector (GC-MS QP-2010 Plus Shimadzu) with the use of the internal standard. The sample was injected in the amount of 0.5 μL per ZB-5MS column (length – 30 m; diameter – 0.25 mm; film thickness – 0.25 μm) with a built-in 5-m pre-column. The analyses were carried out with the application of the temperature – programmable (PTV) injector in the temperature range from 80°C to 280°C. Results were obtained as the average of three times chromatographic analysis of each sample. 16 PAHs were determined in the samples. These included: naphthalene (Np), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), chrysene (Chr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (IcdP) and benzo[g,h,i]perylene (BghiP) [18].

Diagnostic ratios for determining emission sources

The research conducted in recent years helped to establish the so-called characteristic diagnostic ratios for different sources of PAHs emissions into the air. The same ratios are used in the following study. It is based on the assumption that the content of PAHs in raw wastewater has secondary character and results from their emissions into the air. In combined sewer systems, PAHs get into wastewater together with stormwater and thaw water. The study makes use of the following diagnostic ratios:

- fractions of particular PAHs in the total content of PAHs in wastewater, %,
- ΣCWWA/ΣWWA([Fla]+[Pyr]+[BaA]+[BbF]+[BkF]+[BaP]+[IP]+[BghiP])/([Acy]+[Ace]+[Fl]+[Phe]+[Ant]+[Fla]+[Pyr]+[BaA]+[Chr]+[BbF]+[BkF]+[BaP]+[DahA]+[BghiP]+[IcdP]),
- BaA/BaP,
- BbF/BkF,
- Fla/(Pyr+Fla),
- BaA/(Chr+BaA),
- Phe/(Ant+Phe) [13, 14, 19].

PRESENTATION OF RESULTS

The results of the basic analyses were typical for municipal wastewater diluted, to a different degree, with inflow and infiltration water. The COD values ranged between 588 mgO$_2$/L

and 1,380 mgO$_2$/L, whereas the suspension values were 236–424 mg/L. The differences were much lower for total nitrogen and phosphorus and were 89.0–108.4 mgN/L and 8.0–10.2 mgP/L, respectively. The concentration of total phosphorus was higher only in Sample 1. High contents of COD and Kjeldahl nitrogen indicate that wastewater was only slightly diluted in the sewer collectors no. 2 and 3 (Table 1).

The analyses of ATP values and BSI led to a conclusion that no toxic substances which could adversely affect biological wastewater treatment were observed in the analysed wastewater. Low values of the extracellular ATP and BSI were observed. The BSI ranged between 6.0 and 14.5% (Table 2).

The high content of cellular ATP was observed in Sample 1. It shows that it was possible for biochemical transformations to take place in the sewer pipes. The results obtained for the sewer collectors no. 2 and 3 were much better (Tables 1 and 2).

Table 1. Results of the physicochemical analyses of the sampled wastewater

No.	Indicator	Sample 1	Sample 2	Sample 3	Sample 4
	Sampling date	23 July 2012	12 September 2012	12 September 2012	19 October 2012
1	Wastewater temperature, [°C]	21.0	20.4	20.4	n.d.*
2	pH	7.0	7.9	7.9	7.7
3	COD, [mgO$_2$/L]	840.0	1380.0	1220.0	588.0
4	Suspension, [mg/L]	424.0	402.0	360.0	236.0
5	Kjeldahl nitrogen, [mgN/L]	101.5	92.8	88.8	103.4
6	Total nitrogen, [mgN/L]	108.4	93.0	89.0	105.7
7	Total phosphorus, [mgP/L]	19.5	9.1	8.0	10.2

* n.d. no data

Table 2. ATP contents and BSI values in the analysed wastewater

No.	Indicator	Sample 1	Sample 2	Sample 3	Sample 4
1	tATP, [ng ATP/mL]	316.0	78.7	138.0	162.0
2	dATP, [ng ATP/mL]	19.0	9.4	12.7	23.5
3	cATP, [ng ATP/mL]	297.0	69.3	125.3	138.5
4	BSI, [%]	6.0	11.9	9.2	14.5

The values of the 16 PAHs sum for raw wastewater were between 1.025 and 3.056 μg/L. The phenanthrene content was relatively high in all the samples. It was 0.940 μg/L in Sample 1. The values for the remaining samples were similar (0.444–0.484 μg/L). When analysing fractions of particular PAHs, significant differences were observed in the samples. Phenanthrene made approx. 44–47% of the total PAHs content in Samples 1, 3 and 4. The observed contents of fluoranthene and chrysene were also high in these samples (Table 3). The phenanthrene content in Sample 2 was only about 15% of the total PAHs amount. On the other hand, the contents of 5- and 6-ring

PAHs (including the most carcinogenic ones, i.e. dibenzo[a,h]anthracene and benzo[g,h,i]
perylene) were much higher than in Samples 1, 3 and 4 (Fig. 1).

Table 3. Contents of specific PAHs in the analysed samples

Hydrocarbon	Concentration [µg/L]			
	Sample 1	Sample 2	Sample 3	Sample 4
Naphthalene	0.086±0.014	0.132±0.021	< LoQ	0.122±0.020
Acenaphthylene	0.017±0.003	<LoQ	< LoQ	< LoQ
Acenaphthene	0.039±0.006	0.014±0.002	< LoQ	0.034±0.005
Fluorene	0.053±0.010	0,036±0.007	0.036±0.007	0.028±0.005
Phenanthrene	0.940±0.174	0.460±0.085	0.444±0.082	0.484±0.090
Anthracene	0.046±0.009	0.028±0.005	0.023±0.004	0.014±0.003
Fluoranthene	0.207±0.036	0.092±0.016	0.133±0.023	0.118±0.021
Pyrene	0.108±0.017	< LoQ	< LoQ	0.062±0.010
Benzo[a]anthracene	0.050±0,009	0.067±0.012	0.031±0.005	0.020±0.004
Chrysene	0.079±0.012	0.241±0.037	0.064±0.010	0.033±0.005
Benzo[b]fluoranthene	0.099±0.018	0.109±0.020	0.040±0.007	0.024±0.004
Benzo[k]fluoranthene	0.131±0.022	0.261±0.043	0.047±0.008	0.019±0.003
Benzo[a]pyrene	0.051±0.009	0.087±0.016	0.032±0.006	0.023±0.004
Indeno[1,2,3-cd]pyrene	0.035±0.006	0.247±0.040	0.044±0.007	0.033±0.005
Dibenzo[a,h]anthracene	< LoQ	0.633±0.120	0.053±0.010	0.024±0.004
Benzo[g,h,i]perylene	0.062±0.011	0.649±0.118	0.078±0.014	0.032±0.006
PAHs total	2.003	3.056	1.025	1.070

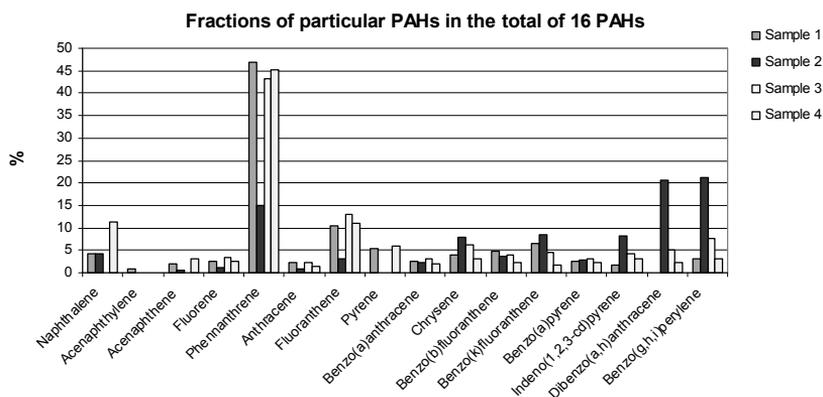<LoQ – result below the limit of quantification

Fig. 1. Fractions of particular PAHs in the total of 16 PAHs, %.

DISCUSSION

The analysis of the wastewater quality showed that the collected samples came from sewer collectors transporting typical municipal wastewater diluted, to a different degree, with inflow and infiltration water. The main reason for the dilution was the significant contribution of combined sewer systems in the particular catchment areas. This solution dominated the Upper Silesian urban area for many years and the majority of the wastewater was supplied to receivers without any treatment. More than 20% of municipal wastewater was supplied in this way in the Upper Silesian area in the mid-1990s. The value dropped to approx. 10% in recent years. The works to put wastewater management into order are still being carried out in some of the Upper Silesian cities [16].

The quality of raw wastewater also depends on other factors that are characteristic for the area. Most sewer collectors designed and constructed before the year 1990 were oversized collectors. According to the population prospects of the late 20th century, the present number of the Silesian Voivodship inhabitants was to exceed 6 million people. What is more, the sewer system installations were designed for much higher wastewater flows. It was assumed that the individual household water consumption was 300 L/M*day [12], whereas the individual household wastewater discharge was approx. 450–500 L/M*day (including inflow water) [6]. At present, the values are significantly lower (daily water consumption: 87–111 L/M*day). The industrial wastewater amount introduced into the municipal sewer system and its dilution are also lower [12].

Mining damages are another specific factor occurring in the catchment areas of the analysed sewer collectors. They cause damage in sewer pipes and produce their unsealing. They also create counter slopes, which negatively affects the wastewater transport. Consequently, sludge sedimentation takes place in sewer pipes, wastewater putrefies and the pollutants contained in wastewater partially decompose. Another side effect of the mining damages is the frequent necessity for sewage pumping.

The obtained values of ATP and BSI indicate that there were no toxic substances that could adversely affect the biological wastewater treatment in the analysed samples [23]. The high content of cellular ATP was observed in the sewer collector no. 1. It probably results from the fact that there are 7 sewage pumping stations equipped with small reservoirs in the catchment area of the wastewater plant. Importantly, the collector drains the area in which coal used to be mined. The part of the sewer system in this catchment area was built in different periods throughout the 20th century and was influenced by mining processes. The ATP values obtained for the collectors no. 2 and 3 indicate that wastewater transport conditions were much better. Slightly worse results were obtained for the sewer collector no. 4 (Tables 1 and 2).

The large participation of the combined sewer system and the lack of plants that could emit PAHs into water lead to a conclusion that the surface runoff is the most probable source of PAHs in the analysed wastewater. Therefore, the pollution is of the secondary character and results from flue gas emissions into the air. PAHs occurring in raw wastewater come from different mixed sources.

As the sampling took place out of the heating season, it is reasonable to expect a relatively minimal impact of home furnace emissions. It seems that traffic emissions mainly influence concentrations and compositions of PAHs. The conclusion is corroborated by the analysis of data on PAHs with different number of rings (Table 4). The values

obtained for Samples 1, 2, 3 and 4 correspond roughly to emissions for the diesel engines. The analysis of the diagnostic ratio values for different sources leads to similar assumptions. The high contents of phenanthrene and the ratios of ΣCWWA/ΣWWA, BaA/BaP, BbF/BkF, BaA/(Chr+BaA) (Table 5) are characteristic for traffic emissions. However, the values for the ratios of Fla/(Pyr+Fla) and Phe/(Ant+Phe) in summer are close to the characteristic values of this ratio set for the combustion of wood and coal [13, 14, 19].

Traffic emissions of PAHs into the air are probably higher than those defined with the records kept by the Institute of Environmental Engineering. According to the data of 2006, approx. 85.46% of PAHs in Poland were emitted from combustion processes in the municipal and residential sectors. The level of PAHs emitted from traffic was only about 1.08% [7, 11]. Different results were obtained in the studies conducted in the urbanized areas of Southern Poland. In Krakow, the contribution of traffic sources in the total emission of PAHs was approx. 45% [3]. Similar values were obtained for the Upper Silesia urban area [13, 19].

Table 4. Fractions of particular hydrocarbons in the total content of PAHs in wastewater, [%]

No.	Hydrocarbons	Sample 1	Sample 2	Sample 3	Sample 4
1	2-ring, [%]	4.29	4.32	0.00	11.40
2	3-ring, [%]	54.67	17.60	49.07	52.34
3	4-ring,[%]	22.17	13.09	22.24	21.78
4	5-ring, [%]	14.03	35.67	16.78	8.41
5	6-ring, [%]	4.84	29.32	11.90	6.07

The values demonstrating the impact of other emission sources were obtained for Sample 2 (Tables 4 and 5). The observed levels of phenanthrene (Table 3) and 3- and 4-ring PAHs (Table 4) were lower. The values for the remaining ratios were also different (Table 5) [13, 14, 19]. What distinguishes this catchment area is the significantly lower level of connections of flats to the district heating systems. The character of buildings is also dissimilar (higher level of lower-standard private housing). It is possible that many inhabitants use furnaces out of the heating season (food preparation, organic waste combustion). The results for this catchment area indicate the possibility of higher PAHs values in the heating season.

Table 5. Ratios of particular PAHs in the analysed samples

No.	Diagnostic ratio	Sample 1	Sample 2	Sample 3	Sample 4
1	ΣCWWA/ΣWWA	0.40	0.56	0.43	0.33
2	BaA/BaP	0.98	0.77	0.97	0.87
3	BbF/BkF	0.76	0.42	0.85	1.26
4	Fla/(Pyr+Fla)	0.66	*n.d.	*n.d.	0.65
5	BaA/(Chr+BaA)	0.39	0.22	0.33	0.38
6	Phe/(Ant+Phe)	0.96	0.94	0.95	0.97

*n.d. no data

For the sum of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, the values in wastewater are 32.5 to over 488.0 times higher than the permissible values defined in the EU directives and in Polish law (Table 6) [10, 20]. The comparison of values leads to the conclusion that even very small percentage of the municipal wastewater introduced into receivers without any treatment can produce a significant increase in the concentrations of the analysed hydrocarbons observed in the water of small watercourses. Consequently, it can influence the results of the water classification performed in accordance with the provisions in force. The problem must be considered in relation to the regulations in force, particularly the Water Framework Directive and Directive 2008/105/EC [9, 10]. It must be also remembered that a motion to tighten the regulations has already been put forward. It is the Proposal for a Directive of the European Parliament and of the Council of 31 January 2012 (COD 2011/0429) [25].

Table 6. Ratios of values in specific samples to standard values in the Directive 2008/105/EC

No.	Ratio	Permissible value [µg/l]	Sample 1	Sample 2	Sample 3	Sample 4
1	Σ benzo[b]fluoranthene benzo[k]fluoranthene	0.030	0.230	0.370	0.087	0.043
	Sample/standard ratio		7.700	12.3	2.9	1.43
2	Σ benzo[g,h,i]perylene Indeno[1,2,3-cd]pyrene	0.002	0.097	0.896	0.122	0.065
	Sample/standard ratio		48.5	448.0	61.0	32.5

A number of actions have been taken to put the sewer systems in the Silesian Voivodship in order. Their main aim is to separate sanitary sewage and drainage systems. Unfortunately, they can also produce the increase in concentrations of PAHs in surface water. PAHs contained in the suspension are easily removed in typical municipal wastewater treatment plants. The separation of municipal and storm wastewater will result in the situation in which part of the stormwater will be directed into receivers without any treatment. It is also difficult to estimate the removal level of PAHs in the normally used oil separators. When taking into consideration trends related to the increase in the traffic intensity, this factor can significantly influence the values of PAHs in water and bottom sediments.

The analysis of the 2011 monitoring data on the flowing surface water in the Silesian Voivodship showed that PAHs, categorized as priority hazardous substances, decided on the water classification. All profiles examined during the diagnostic monitoring demonstrated that all permissible concentrations of the benzo[g,h,i]perylene and indeno[1,2,3,-cd] pyrene were exceeded [22]. The average sum of these compounds varied between 0.0024 and 0.0364 µg/L in particular profiles, which exceeded the permissible values between 1.2 and 18.2 times. Moreover, the permissible sums of benzo[b]fluoranthene and benzo[k] fluoranthene were also exceeded in some samples. High values were observed in highly urbanized and industrialized as well as rural areas. It indicates the significant impact of the area source pollution [26].

CONCLUSIONS

1. The research results are representative for most sewer collectors in the Silesian Voivodship cities. The majority of them discharge typical municipal wastewater that is diluted with inflow water to a different degree. The amount of the industrial wastewater supplied into the sanitary sewer systems is small. Consequently, the content of toxic substances is low and the pollutants contained in wastewater do not influence the biological wastewater treatment.

2. Relatively high concentrations of PAHs were observed in all the samples. These also included benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, both listed as priority hazardous substances.

3. The ratio of the benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene sum in wastewater to their permissible content in surface water was 32.5–448.0. It leads to a conclusion that even small amount of wastewater supplied to receivers without prior treatment can decide on the classification in a given profile.

4. The occurrence of high PAHs contents in all the studied sewer collectors and in water in the diagnostic monitoring profiles of the Silesian Voivodship surface water point to the conclusion that area source pollution decides on the concentrations of PAHs. The pollution has a secondary character and results from emissions of PAHs into the air. It will be difficult to decrease considerably the concentrations of PAHs, particularly benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, within short time.

5. The diagnostic ratios for the emissions of PAHs into the air used in the study lead to a conclusion that the increased values of PAHs result from traffic emissions in most cases. The value seems to be underestimated in the Polish conditions.

6. Analysing the quality of raw wastewater from the sewer collectors took place out of the heating season. It should be expected that concentrations of PAHs in wastewater supplied to treatment plants in the winter season will be significantly higher due to emissions from private housing furnaces.

REFERENCES

[1] Bathi, J.R. (2007). Associations of Polycyclic Aromatic Hydrocarbons (PAHs) with Particulates in the Environment, Proposal for Dissertation Research Topic.

[2] Bathi, J.R., Pitt, R., Findlay, R. & Clark, S.E. (2008). Analyses of PAHs in Urban Stormwater. 11th International Conference on Urban Drainage, Edinburgh, Scotland, UK.

[3] Bilek, M. (2013). Zanieczyszczenie środowiska naturalnego przez wielopierścieniowe węglowodory aromatyczne, www.wssw.krakow.pl.

[4] Bilek, M. (2013). WWA – Wielopierścieniowe Węglowodory Aromatyczne, www.wssw.krakow.pl.

[5] Caban-Pabian, B. (2002). Studies on self-purification of mining waters contaminated with polycyclic aromatic hydrocarbons, *Archives of Environmental Protection*, 28, 4, 57–66.

[6] Cywiński, B., Gdula, S., Kempa, E., Kurbiel, J. & Płoszański, H. (1972). Oczyszczanie ścieków miejskich. Podstawy technologiczne i zasady projektowania oczyszczalni, Arkady, Warszawa 1972.

[7] Czarnowski, K. (2008). Trwałe zanieczyszczenia organiczne w środowisku, Ministerstwo Środowiska, Instytut Ochrony Środowiska, Warszawa 2008.

[8]   Dojlido, J. (1987). Chemia wody, Arkady, Warszawa 1987.

[9]   Dyrektywa 2000/60/WE Parlamentu Europejskiego i Rady z dnia 23 października 2000 r. ustanawiająca ramy wspólnotowego działania w dziedzinie polityki wodnej. Dziennik Urzędowy Unii Europejskiej L 327/1.

[10] Dyrektywa Parlamentu Europejskiego i Rady 2008/105/WE z 16 grudnia 2008 w sprawie środowiskowych norm jakości w dziedzinie polityki wodnej, zmieniająca i w następstwie uchylająca dyrektywy Rady 82/176/EWG, 83/513/EWG, 84/156/EWG, 84/491/EWG, 86/280/EWG oraz zmieniająca dyrektywę 2000/60/WE Parlamentu Europejskiego i Rady. Dziennik Urzędowy Unii Europejskiej L 348/84.

[11] Główny Urząd Statystyczny (2011). Ochrona środowiska (Environment) 2011. Informacje i opracowania statystyczne, Warszawa 2011.

[12] Heinrich, Z. & Jędrzejkiewicz, J. (2007). Analiza zużycia wody w miastach polskich w latach 1995–2005. Analysis of water consumption in Polish cities in the time span of 1995–2005, *Ochrona Środowiska*, 29, 4, 29–34.

[13] Kania, B., Klejnowski, K., Rogula-Kozłowska, W. & Kozielska, B. (2012). Stężenia i równoważniki toksyczności mieszanin WWA związanych z pyłem drobnym i submikronowym w trzech punktach pomiarowych na terenie województwa śląskiego. Concentrations and toxic equivalents of PAH mixtures associated with fine and submicrometer particulate matter in three measurement sites in the Silesian Voivodeship, [In] Ochrona powietrza w teorii i praktyce tom 2, Instytut Podstaw Inżynierii Środowiska, Zabrze 2012.

[14] Khalili, N.R., Scheff, P.A. & Holsen, T.M (1995). PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions, *Atmospheric Environment*, 29, 4, 533–542.

[15] Oleszczuk, P. (2007). Changes of polycyclic aromatic hydrocarbons during composting of sewage sludge with chosen physico-chemical properties and PAHs content, *Chemosphere*, 67, 582–591.

[16] Pistelok, F. (2002). Analiza zależności pomiędzy zanieczyszczeniem ze źródeł komunalnych a jakością wód płynących na obszarach silnie zurbanizowanych na przykładzie zlewni Górnej Wisły, Monografie i Rozprawy Naukowe, Instytut Uprawy Nawożenia i Gleboznawstwa w Puławach, Puławy 2002.

[17] Pośniak, M., Makhniashvili, I. & Kowalska, J. (2000). Wielopierścieniowe węglowodory aromatyczne w procesach stosowania asfaltów, *Bezpieczeństwo pracy nauka i praktyka*, 7–8, 11–13.

[18] Procedura Badawcza własna PB 21. Oznaczanie wielopierścieniowych węglowodorów aromatycznych (WWA) w wodzie metodą chromatografii gazowej z detekcją mas, edycja 2 z dnia 09.01.2012.

[19] Rogula-Kozłowska, W., Kozielska, B., Błaszczak, B. & Klejnowski K. (2012). Rozkład masy względem wielkości cząstek i pochodzenie WWA w punkcie tła miejskiego w Polsce. Size distribution and origin particle-bound PAH at an urban background station in Poland, Ochrona powietrza w teorii i praktyce tom 1, Instytut Podstaw Inżynierii Środowiska, Zabrze 2012.

[20] Rozporządzeniu Ministra Środowiska z dnia 9 listopada 2011 w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych, DZ.U. 2011.257.1545.

[21] Smolik, E. (2001). Wielopierścieniowe węglowodory aromatyczne (WWA). Instytut Medycyny Pracy i Zdrowia Środowiskowego, Sosnowiec, www. ietu.katowice.pl.

[22] Szczygieł, A., Szumowska, A. & Bednarski, G. (2012). Stan Środowiska w województwie śląskim w 2011 roku, Biblioteka Monitoringu Środowiska, Warszawa 2011.

[23] Test Kit Instructions – QuenchGone21 Wastewater (QG21W), www.luminultra.com.

[24] Ustawa z dnia 18 lipca 2001 r. – Prawo wodne (jedn. tekst) Dz.U. 2005.239.2019 z późn. zm.

[25] Wniosek 2011/0429(COD) „Dyrektywa Parlamentu Europejskiego i Rady zmieniająca dyrektywy 2000/60/WE 2008/105/WE w odniesieniu do substancji priorytetowych w dziedzinie polityki wodnej.

[26] WIOŚ Katowice. (2012) Informacje o stanie środowiska w 2011 roku, www.katowice.pios.gov.pl.

STĘŻENIE WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W ŚCIEKACH KOMUNALNYCH W WYBRANYCH KOLEKTORACH AGLOMERACJI ŚLĄSKIEJ

Wielopierścieniowe węglowodory aromatyczne (WWA) stanowią liczną grupę związków organicznych, powodujących trwałe zagrożenie dla środowiska. Ich ilości pochodzące ze źródeł naturalnych są niewielkie. Głównym źródłem WWA są procesy niepełnego spalania paliw organicznych. Na obszarze Górnego Śląska znaczne ich ilości są emitowane do powietrza w wyniku spalania węgla w paleniskach domowych oraz spalania paliw

płynnych w silnikach spalinowych (niska emisja). Do wód powierzchniowych dostają się one w wyniku spływu powierzchniowego, a także ze zrzutów punktowych ścieków z niektórych gałęzi przemysłu. W pracy przedstawiono stężenia WWA występujące w surowych ściekach komunalnych. Badania zostały przeprowadzone poza sezonem grzewczym, zaś próbki pobrane były z kanalizacji ogólnospławnej. Analizę WWA wykonano stosując chromatografię gazową z użyciem detektora masowego (GC-MS). Stężenia sumy 16 WWA (lista EPA) wahały się w granicach 1,070–3,056 µg/l, a związkiem, który dominował niemal we wszystkich analizowanych próbkach był fenantren. W badanych próbkach wysokie były zawartości związków zaliczanych do WWA, które zgodnie z dyrektywą należą do substancji priorytetowych niebezpiecznych. Uzyskane wyniki oraz analiza wskaźników diagnostycznych określonych dla emisji WWA do powietrza doprowadziły do wniosku, że głównym źródłem tych związków w badanych ściekach były zanieczyszczenia komunikacyjne.