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Contamination of runoff waters with polycyclic aromatic hydrocarbons in the city of Siedlce

Zanieczyszczenie węglowodorami aromatycznymi wód spływnych miasta Siedlce

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Słowa kluczowe: środowisko, wody spływne, analiza, zanieczyszczenie, WWA, HPLC

Abstract

The paper presents the results of the research on content of 16 polycyclic aromatic hydrocarbons in samples of runoff waters collected in Siedlce city. The samples were collected in March, July and October 2015. The highest mean total concentration of 16 PAHs amounting to $12.54 \mu\text{mol}\cdot\text{dm}^{-3}$ was determined in water samples collected at Łukowska Street, whereas the lowest concentrations ($1.90 \mu\text{mol}\cdot\text{dm}^{-3}$) were found in samples collected at Warszawska Street. In some samples, small amounts of benzo(a)pyrene were present; the average content ranged from $0.02 \mu\text{mol}\cdot\text{dm}^{-3}$ at Warszawska Street to $0.20 \mu\text{mol}\cdot\text{dm}^{-3}$ at Garwolińska Street.

Streszczenie

W pracy przedstawiono wyniki badań dotyczące zawartości 16 wielopierścieniowych węglowodorów aromatycznych w próbkach wód spływnych pobranych na terenie miasta Siedlce. Próbki pobierano w marcu, lipcu i październiku 2015 roku. Największe średnie sumaryczne stężenie 16 WWA wynoszące $12,54 \mu\text{mol}\cdot\text{dm}^{-3}$ stwierdzono w próbkach wody pobranych przy ulicy Łukowskiej, zaś najniższe ($1,90 \mu\text{mol}\cdot\text{dm}^{-3}$) w próbkach pobranych z ulicy Warszawskiej. W niektórych analizowanych próbkach występował w niewielkich ilościach benzo(a)piren. Jego średnia zawartość wahała się od $0,02 \mu\text{mol}\cdot\text{dm}^{-3}$ przy ulicy Warszawskiej do $0,20 \mu\text{mol}\cdot\text{dm}^{-3}$ przy ulicy Garwolińskiej.

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1. INTRODUCTION

The diverse forms of human activity cause an increase in the amount of pollutants released into the environment. An increase in the concentration of individual elements, especially when exceeding the limit values, may result in significant effects on the ecosystem balance, which violates the principles of sustainable development. This applies, in particular, to the coexistence of different plant and animal organisms. The most evident effects include the impact of harmful substances on the human organism, hence the need for systematic monitoring of the quality of various environmental components, mainly water, soil, air and food.

Compounds generally referred to as micropollutants represent the major human health risk. One of the most important groups of organic micropollutants is the polycyclic aromatic hydrocarbons and their derivatives. Their complicated structures, difficulties in determination and removal and in particular, properties harmful to the health are the main arguments for their continuous monitoring [Adamczewska et al. 2000].

Microtraces of aromatic hydrocarbons are sufficient to induce cancerous processes [Gadzała, Buszewski 1995]. The main justification for a research on these compounds is the sudden increase in the incidence of neoplastic (tumour) diseases, which are one of the main causes of death. In many cases, a correlation was found between the effect of PAHs and the development of neoplastic diseases [Kluska 2007].

Human economic activity disrupted the equilibrium between the production of polycyclic aromatic hydrocarbons and their degradation, and therefore, it is necessary to determine the concentrations of these compounds in all elements of the human natural environment. Changes in the ecosystem, especially disruption of its balance by agriculture, industry or households lead to continuous contamination of air, water, soil and food. Therefore, due to ecological, social and economic consequences, the integrated nature conservation is necessary. The prevention of progressive degradation involves continuous monitoring of contamination and changes in the ecosystem [Walna et al. 2003]. Runoff waters, often referred to as meteoric waters or wastewaters, are one of the main forms of atmospheric water entering the environment. They are derived from rainfall or meltwater, which wash down impurities from roofs, roads, lawns and canopy of trees, agricultural and forest areas, as well as dumps of municipal and industrial wastes. The threat posed by road transport is mainly related to the emission of different substances into the environment. These substances are produced during the combustion of diesel fuel, emitted in the process of fuel evaporation and derived from power transmission and braking systems, as well as these result from the exploitation of road surfaces, car tires and agents used in road maintenance. The main pollutants resulting from the road transport are as follows:

oxides of carbon, nitrogen and sulphur, aerosols containing soot and lead compounds, aldehydes, hydrocarbons (including aromatic ones), phenols and derivatives of petroleum, fuels, fats and lubricants [Niedziński et al. 1999; Polkowska et al. 2005; Yang et al. 2010; Re-Poppi, Santiago-Silva 2005].

Water is the most important compound in human life; hence, it should be protected from contamination. Prevention of water pollution includes different areas of human activity and has repeatedly helped to avoid irreversible losses, such as human health deterioration, extinction of plant and animal species, or permanent landscape degradation [Stogiannidis, Laane 2014; Song et al. 2011]. Prevention of water pollution is very expensive, therefore prevention by prohibitions is more effective (implemented in accordance with water law), such as prohibition of water contamination with garbage, sewage, discharge of snow removed from polluted areas, collection of wastewaters, chemicals, and other materials which could lead to water contamination. The aforementioned prohibitions are completed by relevant legislation, which governs different aspects of water protection in Poland [Ustawa 2001].

Monitoring of environmental pollution is an open issue, and results from the provisions of the national law and requirements of Water Framework Directive UE 2000/60/WE. According to the directive, the Member States are obliged to rational exploitation and protection of water resources in accordance with the principles of sustainable development [Water ... 2000]. The present study is a continuation of the research on the evaluation of environmental pollution [Chrzęścik et al. 2007a, b]. The objective of the study was to determine the level of content of 16 polycyclic aromatic hydrocarbons in samples of runoff waters collected in Siedlce.

2. EXPERIMENTAL PART

2.1. Description of the sampling area

The city of Siedlce is located on the Siedlce Upland, which is a geographical part of the South Podlasie Lowland, between the Muchawka and Helenka rivers. Siedlce covers an area of 3186 ha and is located at a distance of ca. 90 km from Warsaw (western direction) and ca. 100 km from Terespol (eastern direction). In terms of the population size, Siedlce is the 48th largest city in Poland, and the 4th largest city in the Mazovia Province (after Warsaw, Radom and Płock). The population density is 2399 ind.·km⁻², which makes Siedlce the 10th largest city in the Mazovia region and the 34th one in Poland.

Sites with the highest traffic volume were selected for the analysis, namely, the streets Warszawska, Garwolińska, Łukowska and Starowiejska. In the case of Garwolińska and Łukowska streets, the samples were collected under the railway bridge, in ground depressions which collect runoff waters transported from areas located at relatively large distances (Fig. 1).

2.2. Study methods

The main objective of the study was to determine the content of the following hydrocarbons: naphthalene (Na), acenaphthylene

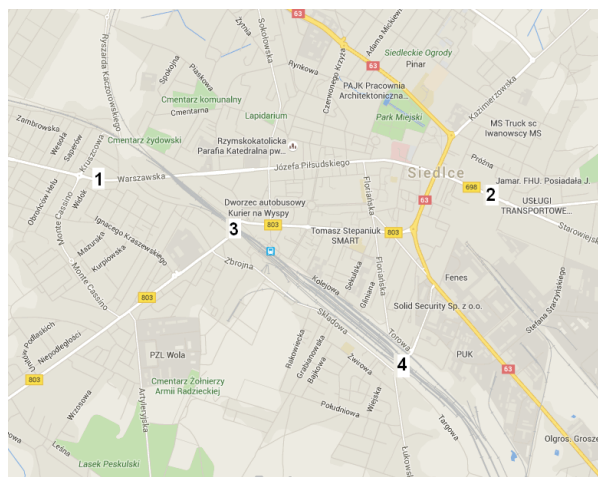


Figure 1. Scheme of Siedlce City from mark the numbers of checkpoints to take samples.

(Ace), acenaphthene (Acn), fluorene (Flu), phenanthrene (Fen), anthracene (An), fluoranthene (Fl), pyrene (Pir), benzo(a)anthracene (B[a]A), chrysene (Ch), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F), benzo(a)pyrene (B[a]P), dibenzo(ah)anthracene (D[a,h]A), benzo(g,h,i)perylene (B[g,h,i]P), indeno[1,2,3-c,d]pyrene (I[1,2,3-c,d]P) in the samples of runoff waters collected in Siedlce. The research covered qualitative and quantitative determination of 16 PAHs. High-performance liquid chromatography with UV/Vis detection (HPLC - UV/Vis) was used in the analysis.

The next day after sampling, the collected samples of runoff waters were analyzed for the content of 16 PAHs. Hyamine in the amount of 1.2 ml (Merck, Germany) was added to 1 dm³ of water, mixed together and passed through the SPE extraction column (BakerBond) prepared beforehand. Water samples selected for the analysis were passed through the extraction columns at a rate of 3–4 drops/sec., and then purged with nitrogen. Hydrocarbons adsorbed on the columns were eluted with dichloromethane (8 ml). Next, 2 ml of acetonitrile was added to the eluate and mixed together. The obtained solutions were concentrated under nitrogen streams at a temperature of 37°C to reach a volume of 0.5 ml. After the process of concentration, water was added to the solutions to reach a volume of ca. 1 ml and analyzed using HPLC at a wavelength of 254 nm, the methanol flow rate of 1 ml · min⁻¹ and temperature of 22°C. Samples of runoff waters were collected in 2015 at four sites of the Siedlce urban area (Fig. 1). The content of the analyzed elements in waters collected at each site were averaged. The described methodology of analysis was similar to the work of Walna et al. 2003 and Zbytniewski et al. 2002.

2.3. Equipment

Extraction columns SPE RP C18 and a HPLC system were used to assess the content of PAHs. The latter consisted of: Shimadzu SPD-6A UV/Vis detector with a wavelength of 254 nm, Shimadzu LC-6A pump, Shimadzu CR 6A Chromatopac data logger (Kyoto, Japan), Rheodyne 7125 injector with a loop volume of 20 µL, columns RP C18 with an internal diameter of 4 mm and a length of 250 mm, POCH Gliwice.

3. RESULTS AND DISCUSSION

The results obtained [according to Konieczka et al. 2004] for the content of 16 polycyclic aromatic hydrocarbons in samples of runoff waters are presented in Tables 1–4. Samples were collected in the urban area of Siedlce, in March, July and October 2015 (Fig. 1). The water sampling sites are characterized by high traffic volume and so-called traffic jams, particularly during peak hours.

It is assumed that benzo(a)pyrene is an indicator of water contamination (including runoff water) with polycyclic aromatic hydrocarbons. In the case of surface-clean waters, the contamination with benzo(a)pyrene is in the range of 0.05–0.25 $\mu\text{mol}\cdot\text{dm}^{-3}$, whereas surface-contaminated waters may even contain up to 13.0 $\mu\text{mol}\cdot\text{dm}^{-3}$ [Michalski, Germuska 2002; Rosik-Dulewska, Michalski 2012; Zbytniewski et al. 2002].

As a result of the performed analyses, as many as 12 aromatic hydrocarbons were determined in water samples collected in March at Warszawska street (out of the total 16 analyzed compounds; Table 1). Their total content ranged from 2.53 to 3.09 $\mu\text{mol}\cdot\text{dm}^{-3}$ (with an average of 2.81). Also the highest content of naphthalene was determined in these samples – from 1.40 to 1.55, on average 1.47 $\mu\text{mol}\cdot\text{dm}^{-3}$. The content of other hydrocarbons was much smaller, for example, phenanthrene (0.43 – 0.47, average 0.45 $\mu\text{mol}\cdot\text{dm}^{-3}$), fluorene (0.14 – 0.19, average 0.17 $\mu\text{mol}\cdot\text{dm}^{-3}$), anthracene (0.13 – 0.17, average 0.15 $\mu\text{mol}\cdot\text{dm}^{-3}$) and pyrene (0.06 – 0.10, average 0.08 $\mu\text{mol}\cdot\text{dm}^{-3}$).

Four hydrocarbons (out of the total 16 analyzed compounds) were not found in the samples, namely, fluoranthene, benzo(g,h,i) perylene, indeno[1,2,3-c,d]pyrene and benzo(k)fluoranthene. On the other hand, benzo(a)pyrene occurred in small amounts.

Samples collected in October at Warszawska Street contained slightly smaller amounts of the analyzed hydrocarbons. Their content ranged from 2.27 to 2.82 $\mu\text{mol}\cdot\text{dm}^{-3}$, on an average 2.53 $\mu\text{mol}\cdot\text{dm}^{-3}$. The smallest average content of 0.03 $\mu\text{mol}\cdot\text{dm}^{-3}$ was determined for benzo(a)pyrene. On the other hand, the highest content was determined for naphthalene and phenanthrene. The content values ranged from 1.11 to 1.25 $\mu\text{mol}\cdot\text{dm}^{-3}$ for naphthalene (with an average of 1.17) and from 0.39 to 0.48 $\mu\text{mol}\cdot\text{dm}^{-3}$ for phenanthrene (with an average of 0.43). In the analyzed samples collected in October, the following five hydrocarbons were absent: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene.

The smallest content values of the analyzed hydrocarbons were determined in water samples collected at Warszawska Street in July. The total content of PAHs ranged from 1.54 to 2.24 $\mu\text{mol}\cdot\text{dm}^{-3}$ (with an average of 1.90). Water samples collected in July at Warszawska Street did not contain the following hydrocarbons: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. Whereas, the highest content was determined for fluorine ranging from 0.27 – 0.37 $\mu\text{mol}\cdot\text{dm}^{-3}$ (with an average of 0.31).

Table 1. Average content [$\mu\text{mol}\cdot\text{dm}^{-3}$] of PAHs determined in water samples collected in 2015 from Warszawska street (1) in Siedlce city (n = 5, SD \leq 5%).

PAHs	March		July		October	
	Min – Max	Average	Min – Max	Average	Min – Max	Average
Na	1.40 – 1.55	1.47	0.70 – 1.03	0.89	1.11 – 1.25	1.17
Ace	0.07 – 0.11	0.09	0.05 – 0.08	0.07	0.04 – 0.06	0.05
Acn	0.06 – 0.10	0.08	0.06 – 0.09	0.07	0.12 – 0.19	0.15
Flu	0.14 – 0.19	0.17	0.27 – 0.37	0.31	0.20 – 0.26	0.24
Fen	0.43 – 0.47	0.45	0.15 – 0.21	0.18	0.39 – 0.48	0.43
An	0.13 – 0.17	0.15	0.15 – 0.19	0.17	0.18 – 0.21	0.19
Fl	–	–	0.02 – 0.05	0.03	0.06 – 0.10	0.08
Pir	0.06 – 0.10	0.08	0.11 – 0.16	0.13	0.08 – 0.11	0.10
B[a]A	0.07 – 0.10	0.08	–	–	–	–
Ch	0.02 – 0.05	0.03	–	–	–	–
B[b]F	0.10 – 0.13	0.12	–	–	–	–
B[k]F	–	–	–	–	0.03 – 0.05	0.04
B[a]P	0.01 – 0.03	0.02	–	–	0.02 – 0.05	0.03
D[a,h]A	0.04 – 0.09	0.07	0.03 – 0.06	0.05	0.04 – 0.06	0.05
B[g,h,i]P	–	–	–	–	–	–
I[1,2,3-c,d]P	–	–	–	–	–	–
Total PAHs	2.53 – 3.09	2.81	1.54 – 2.24	1.90	2.27 – 2.82	2.53

– not detected

Table 2. Average content [$\mu\text{mol}\cdot\text{dm}^{-3}$] of PAHs determined in water samples collected in 2015 from Starowiejska street (2) in Siedlce city ($n = 5$, $\text{SD} \leq 5\%$).

PAHs	March		July		October	
	Min – Max	Average	Min – Max	Average	Min – Max	Average
Na	1.37 – 1.41	1.39	1.24 – 1.27	1.25	1.11 – 1.14	1.12
Ace	0.07 – 0.09	0.08	0.05 – 0.07	0.06	0.04 – 0.05	0.05
Acn	0.06 – 0.07	0.07	0.06 – 0.08	0.07	0.12 – 0.14	0.13
Flu	–	–	0.27 – 0.30	0.29	0.20 – 0.22	0.21
Fen	0.34 – 0.39	0.37	0.05 – 0.07	0.06	–	–
An	1.03 – 1.07	1.05	–	–	–	–
Fl	0.12 – 0.14	0.13	0.15 – 0.16	0.16	0.19 – 0.21	0.20
Pir	–	–	0.11 – 0.13	0.12	0.15 – 0.16	0.16
B[a]A	–	–	0.11 – 0.12	0.12	–	–
Ch	0.07 – 0.11	0.09	–	–	–	–
B[b]F	0.09 – 0.11	0.10	–	–	0.10 – 0.11	0.11
B[k]F	–	–	0.13 – 0.16	0.15	0.08 – 0.10	0.09
B[a]P	–	–	–	–	–	–
D[a,h]A	–	–	–	–	0.11 – 0.13	0.12
B[g,h,i]P	–	–	–	–	–	–
I[1,2,3-c,d]P	–	–	–	–	–	–
Total PAHs	3.15 – 3.38	3.28	2.17 – 2.36	2.28	2.10 – 2.26	2.19

– not detected

Table 3. Average content [$\mu\text{mol}\cdot\text{dm}^{-3}$] of PAHs determined in water samples collected in 2015 from Garwolińska street (3) in Siedlce city ($n = 5$, $\text{SD} \leq 5\%$).

PAHs	March		July		October	
	Min – Max	Average	Min – Max	Average	Min – Max	Average
Na	5.04 – 5.42	5.22	4.41 – 4.43	4.42	4.11 – 4.19	4.15
Ace	2.07 – 2.09	2.08	2.05 – 2.07	2.06	2.04 – 2.05	2.04
Acn	2.03 – 2.05	2.04	1.16 – 1.21	1.18	1.12 – 1.14	1.13
Flu	1.34 – 1.39	1.37	0.87 – 1.00	0.92	0.28 – 0.32	0.30
Fen	0.11 – 0.13	0.12	–	–	–	–
An	0.32 – 0.35	0.33	–	–	0.30 – 0.34	0.32
Fl	0.27 – 0.31	0.29	0.25 – 0.31	0.28	0.15 – 0.16	0.16
Pir	0.19 – 0.22	0.20	0.05 – 0.09	0.07	–	–
B[a]A	–	–	–	–	0.10 – 0.13	0.12
Ch	–	–	0.11 – 0.13	0.12	0.08 – 0.11	0.10
B[b]F	–	–	0.11 – 0.13	0.12	–	–
B[k]F	0.14 – 0.18	0.16	0.14 – 0.16	0.15	0.11 – 0.13	0.12
B[a]P	0.17 – 0.25	0.20	–	–	–	–
D[a,h]A	0.01 – 0.03	0.02	–	–	–	–
B[g,h,i]P	–	–	–	–	–	–
I[1,2,3-c,d]P	–	–	–	–	–	–
Total PAHs	12.69 – 13.18	12.03	9.15 – 9.53	9.32	8.29 – 8.57	8.44

– not detected

Table 4. Average content [$\mu\text{mol}\cdot\text{dm}^{-3}$] of PAHs determined in water samples collected in 2015 from Łukowska street (4) in Siedlce city ($n = 5$, $\text{SD} \leq 5\%$).

PAHs	March		July		October	
	Min – Max	Average	Min – Max	Average	Min – Max	Average
Na	5.34 – 5.41	5.37	4.40 – 4.43	4.42	4.17 – 4.20	4.19
Ace	3.06 – 3.08	3.07	3.06 – 3.07	3.06	3.03 – 3.05	3.04
Acn	–	–	0.16 – 0.18	0.17	–	–
Flu	2.06 – 2.15	2.10	–	–	2.12 – 2.18	2.15
Fen	–	–	0.27 – 0.30	0.29	0.20 – 0.22	0.21
An	0.34 – 0.39	0.37	–	–	–	–
Fl	1.13 – 1.17	1.12	0.15 – 0.19	0.17	1.39 – 1.48	1.43
Pir	–	–	0.09 – 0.12	0.10	0.15 – 0.16	0.16
B[a]A	0.12 – 0.18	0.14	0.11 – 0.14	0.12	–	–
Ch	0.07 – 0.11	0.08	0.10 – 0.12	0.11	0.10 – 0.13	0.12
B[b]F	0.09 – 0.15	0.12	–	–	0.08 – 0.11	0.09
B[k]F	–	–	–	–	–	–
B[a]P	0.14 – 0.19	0.17	–	–	0.11 – 0.14	0.13
D[a,h]A	–	–	0.13 – 0.16	0.14	–	–
B[g,h,i]P	–	–	–	–	–	–
I[1,2,3-c,d]P	–	–	–	–	–	–
Total PAHs	12.35 – 12.83	12.54	8.47 – 8.71	8.58	11.35 – 11.67	11.52

– not detected

A slightly higher content of the analyzed hydrocarbons was determined in water samples collected at Starowiejska Street (Table 2). In March, their total content ranged from 3.15 to 3.38 $\mu\text{mol}\cdot\text{dm}^{-3}$ (with an average of 3.28). The highest content was determined for naphthalene, having an average of 1.39 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the minimum value of 1.37 and the maximum value of 1.41 $\mu\text{mol}\cdot\text{dm}^{-3}$, as well as for anthracene ranging from 1.03 to 1.07 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the mean value of 0.37 $\mu\text{mol}\cdot\text{dm}^{-3}$. On the other hand, fluorene, pyrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene were not recorded. The results confirm the washing surface streets after the winter (March 2015), the accumulation of PAHs in the winter permafrost.

Water samples collected at Starowiejska Street in July contained the highest amounts of naphthalene, in the range of 1.24 – 1.27 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the average content of 1.25 $\mu\text{mol}\cdot\text{dm}^{-3}$. On the other hand, the total content of all analyzed hydrocarbons ranged from 2.17 to 2.36 $\mu\text{mol}\cdot\text{dm}^{-3}$, and their average content was 2.28 $\mu\text{mol}\cdot\text{dm}^{-3}$. Chrysene, anthracene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene were not found. A similar content of the analyzed hydrocarbons was determined in water samples collected in October. The total content of PAHs was in the range of 2.10 – 2.26 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the average value of 2.19 $\mu\text{mol}\cdot\text{dm}^{-3}$. The highest average content of 1.12 $\mu\text{mol}\cdot\text{dm}^{-3}$ was determined for naphthalene. As found in July, the following hydrocarbons were not present: phenanthrene, anthracene,

benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene.

Taking into account all water samples collected at Garwolińska Street in March 2015, the content of naphthalene had the highest values (Table 3) and ranged from 5.04 to 5.42 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the average value of 5.22 $\mu\text{mol}\cdot\text{dm}^{-3}$. The total content of all analyzed hydrocarbons ranged from 12.69 to 13.18 $\mu\text{mol}\cdot\text{dm}^{-3}$; the average value was 12.03 $\mu\text{mol}\cdot\text{dm}^{-3}$. Slightly smaller content was determined in samples collected in July and October – from 9.15 to 9.53 $\mu\text{mol}\cdot\text{dm}^{-3}$ in July and from 8.29 to 8.57 $\mu\text{mol}\cdot\text{dm}^{-3}$ in October. Mean values ranged from 9.32 $\mu\text{mol}\cdot\text{dm}^{-3}$ in July to 8.44 $\mu\text{mol}\cdot\text{dm}^{-3}$ in October. Benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene were absent in all samples of runoff waters collected at Garwolińska street. Benzo(a)pyrene occurred only in the samples collected in March (after the winter). Its content ranged from 0.17 to 0.25 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the average value of 0.20 $\mu\text{mol}\cdot\text{dm}^{-3}$. Samples for the analysis were collected under the so-called Garwolin bridge, where the pollution is transported by rain from long distances, mainly along the roadway.

On the other hand, the highest mean total concentration of 16 analyzed hydrocarbons was recorded in samples collected at Łukowska Street in March (Table 4). Their total content ranged from 12.35 to 12.83 $\mu\text{mol}\cdot\text{dm}^{-3}$, with the average value of 12.54 $\mu\text{mol}\cdot\text{dm}^{-3}$. In the other months of sampling, the average content of the analyzed hydrocarbons was lower, and ranged from 8.58 $\mu\text{mol}\cdot\text{dm}^{-3}$ in July to 11.52 $\mu\text{mol}\cdot\text{dm}^{-3}$ in October. The presence of benzo(a)pyrene was determined in samples collected in March and October. Its content ranged from 0.14

to $0.19 \mu\text{mol}\cdot\text{dm}^{-3}$ (average 0.17) in March and from 0.11 to $0.14 \mu\text{mol}\cdot\text{dm}^{-3}$ (average 0.13) in October. Similarly, as in the samples collected at Łukowska Street, the presence of mainly two hydrocarbons was not confirmed: benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. In all samples collected at Łukowska Street, the content of naphthalene had the highest values – on average from $4.19 \mu\text{mol}\cdot\text{dm}^{-3}$ in October to $5.37 \mu\text{mol}\cdot\text{dm}^{-3}$ in March. It is worth mentioning that the water sampling point was located in a ground depression, which collected pollutants transported from different distances during rainfalls.

Both car traffic and households emit large amounts of pollution into the atmosphere. Atmospheric pollution spreads over different distances and fall on the ground with precipitation, leading to degradation of soils and surface waters. As it appears from the data presented in Tables 1-4, the quality of runoff waters from the analyzed samples is affected mainly by transportation and households. Similar results for surface waters in north-eastern Poland were obtained by other authors [Chrząścik et al. 2007; Stogiannidis, Laane 2014].

Environmental threats considered in this study may contribute to the gradual deterioration of the water quality. Road transport, the intensity of which continuously increases, represents the main threat to the natural, atmospheric and acoustic environment in the study area. Taking into account the results of the analyses presented in Tables 1-4, the impact of pollution on the quality of atmosphere and surface waters becomes perceptible. It is alarming that some of the analyzed water samples contained hydrocarbons with carcinogenic properties. Nevertheless, despite the presence of PAHs, including carcinogens, the acceptable standards valid in Poland were not exceeded in the analyzed runoff-water samples.

4. SUMMARY AND CONCLUSIONS

Protection of surface and ground waters from contamination is an important objective in human life. This concerns both the environmental safety and the principles of sustainable development, and involves mainly reduction, avoidance and elimination of water contamination, and in particular contamination with substances harmful to the environment. These actions aim at environmental protection. In many cases, irresponsible human activities have resulted in the disturbed state of equilibrium between the amount of contamination produced and the capacity of nature for self-cleaning, hence there is a need for monitoring and protection of individual elements of the environment.

Runoff waters contain all kinds of pollutants, which are released directly into the environment. Because runoff waters are discharged into rivers or other water bodies through storm water drains, mainly surface waters are not contaminated, and they represent a source of drinking water. In fact, runoff waters should be directly channelled to wastewater treatment plants.

The presence of a small amount of analyzed carcinogens in the water samples clearly indicates the negative human impact, including the road transport. The presence of carcinogens in the immediate vicinity of man will in the future result in increased cancer incidence and deaths. At present, such a correlation was not found in the city of Siedlce, due to the fact that environmental pollution is still at a low level. The obtained results do not exceed the Polish water quality standards for surface waters [Water ... 2000].

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