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THE OCCURRENCE AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN BOTTOM SEDIMENTS OF THE WISŁOK RIVER

Sabina Książek, Małgorzata Kida, Piotr Koszelnik

Department of Chemistry and Environmental Engineering
Rzeszów University of Technology

Key words: bottom sediments, Wisłok river, micro-contaminants, PAHs, contamination sources.

Abstract

The work presents analysis and assessment of the degree contamination of bottom sediments of the Wisłok river with polycyclic aromatic hydrocarbons (PAHs). The samples of the bottom sediments were taken in the summer in 2012 in 6 research points by Environmental Authorities under the State Monitoring for Environment. The concentration of the sum of 17 PAHs in the bottom sediments ranged from 0.218–8.437 mg kg^{-1} of dry weight. Among PAHs surveyed, 4-ring congeners had the largest share, and 3-ring ones had the smallest share. The highest concentration was registered in the case of fluoranthene, also four-cyclic benzo(a)anthracene and pyrene had a large share. Whereas the lowest concentration was registered for acenaphthene, acenaphthylene and fluorene. The work also identifies possible sources of PAHs in the bottom sediments analysed. The method used to identify the source of origin of PAHs in bottom sediments is comparison of the quotient of concentrations of compounds characterised by L/H low and high molecular masses and comparison of measured concentrations of analysed PAHs, e.g. Phe/Ant, Flt/Py, Flt/(Flt+Py), Ant/(Ant+Phe) as well as IndP/(IndP+BghiP). The values of indicators used for this purpose indicated contamination with compounds from the PAHs group of pyrolytic origin.

WYSTĘPOWANIE WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W OSADACH DENNYCH RZEKI WISŁOK

Sabina Książek, Małgorzata Kida, Piotr Koszelnik

Zakład Inżynierii i Chemii Środowiska
Politechnika Rzeszowska

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Address: Sabina Książek, Rzeszów University of Technology, 35-959 Rzeszów, al. Powstańców Warszawy 6, phone: + 48 (17) 865 10 65, + 48 (17) 865 24 07, e-mail: sabina_ksiazek@outlook.com

Abstrakt

W pracy przedstawiono analizę i ocenę stopnia zanieczyszczenia osadów dennych rzeki Wisłok wielopierścieniowymi węglowodorami aromatycznymi (WWA). Próbki osadów dennych pobrała w sezonie letnim w 2012 r. w 6 punktach badawczych Inspekcja Ochrony Środowiska w ramach Państwowego Monitoringu Środowiska. Stężenie sumy 17 WWA w osadach dennych wynosiło 0,218–8,437 mg kg^{-1} s.m. Wśród badanych WWA największy udział miały kongenery 4-pierścieniowe, najmniejszy 3-pierścieniowe. Najwyższe stężenie odnotowano w przypadku fluorantenu, duży udział miał także czteropierścieniowy benzo(a)antracen i piren. Najniższe stężenie odnotowano natomiast dla acenaftenu, acenaftylenu i fluorenu. W pracy zidentyfikowano również prawdopodobne źródła WWA w analizowanych osadach dennych. Metodą stosowaną do określenia źródła pochodzenia WWA w osadach dennych jest porównanie ilorazu stężeń związków charakteryzujących się małymi i dużymi masami cząsteczkowymi L/H oraz porównanie oznaczonych stężeń analizowanych WWA, np. Fen/Ant, Flu/Pir, Flu/(Flu+Pir), Ant/(Ant+Fen) oraz IndP/(IndP+Bper). Wartości wykorzystanych w tym celu wskaźników wskazały na zanieczyszczenia związkami z grupy WWA pochodzenia pirolitycznego.

Introduction

Bottom sediments constitute an important, dynamic and integral part of the water ecosystem. Return reactions occur between bottom sediments and water, and the character of exchange of organic substances, mineral substances, and gases is highly complicated. Above all it is a result of participation of a number of opposing or overlapping biological and physicochemical processes which are divided most generally into the processes that decide on precipitating components from water into the bottom sediment (sedimentation, physicochemical and biochemical precipitating dissolved and colloidal compounds from water, sorption of ions from water through the sediment sorptive complex) and the processes that cause substances to penetrate from the bottom sediment to water (dissolving sediment components and diffusion to water, desorption, mineralization of sediments organic components, etc.) (STARMACH et al. 1976, HELIOS-RYBICKA and ALEKSANDER-KWATERCZAK 2009).

As a consequence of that, the bottom sediments enable to keep trace of transformations which occur in the environment, and also to supply enough relevant information on the causes of these changes. On account of higher concentrations of organic contaminants in the bottom sediments, by comparison with their content in water, the bottom sediments chemical analysis enables to detect and observe changes in their contents even with a relatively low degree of environmental pollution (GAWLIK and BILEK 2006, SZLACHTA 2009).

Among organic contaminants of water ecosystems, polycyclic aromatic hydrocarbons constitute a significant group. PAHs are compounds formed in biosynthesis processes, nevertheless to a large extent they are a result of human activity, mainly of incomplete combustion processes. Smelting and coking industry, combined heat and power plants, waste incineration plants, farms, rubber, carbon electrodes production plants, car engines are the centre of their emission to the atmosphere. PAHs settle the most often on surfaces of soot particles, and then they fall directly on soil and water surfaces. Apart from that, they get into water bodies together with surface flows from contaminated areas. Areas in the immediate vicinity of industrial plants, roads and combined heat and power plants are exposed the most (SAPOTA 2002, KALETA 2005, KOCIOŁEK-BALAWEJDER and STANISŁAWSKA 2012, WŁODARCZYK-MAKUŁA 2014). Generally sources of PAHs may be divided into pyrogenic ones-connected mainly with combustion processes and petrogenic sources, connected with petroleum and its products penetrating into the environment (WOLSKA et al. 2014).

The tool used to identify the source of origin of compounds from the PAHs group in bottom sediments is comparison of the concentrations of compounds with low and high molecular masses and analysis of the quotients of concentrations of selected PAH (ROGOWSKA et al. 2013).

The purpose of the work was to determine the degree of contamination with compounds from the PAHs group and to identify the sources of their origin in the bottom sediments of the Wisłok river.

Survey Area

The area where the samples to be analysed were taken was the Wisłok river, located in the south-eastern part of Poland. The Wisłok river is a typically mountain river, classified into changeless and average rivers, according to the classification by length and continuity of their feed. It is a left-bank tributary of the San river with the length of 220 km and the river basin of 3,528 km^2. The sources of the Wisłok river are located in Beskid Niski, in the vicinity of the Slovak border. In the region of Rzeszów, it flows into Pradolina Podkarpacka, being distinguished by a dense waterway network and wide areas of wetlands (KOSZELNIK et al. 2004, MADEYSKI et al. 2008, SANOCKA and WIŚNIOS 2012).

The samples of bottom sediments were taken from 6 research points: 1st sampling point – Boguchwała, 2nd – Besko, 3rd – Wojaszówka, 4th – Czarna, 5th – Tryńcza, 6th – Zarszyn.

Survey Scope and Methodology

Surveys of the contents of polycyclic aromatic hydrocarbons in the bottom sediments of the Wisłok river were conducted by the Environmental Authorities under the State Monitoring for Environment. Samples of the bottom sediments were taken in the summer in 2012 in 6 research points. The scope of the bottom sediments surveys conducted included determination of concentrations of 17 PAHs congeners with the use of gas chromatography coupled with mass spectrometry, by applying an internal method of the State Inspectorate for Environmental Protection.

Until 2012, in Poland there was only one legal act on the quality of sediments. It was the Ordinance of the Minister for the Environment (OME) of 16 April 2002 on types and concentrations which cause output contamination (Rozporządzenie Ministra Środowiska z 16 kwietnia 2002 r... Dz.U. no. 55, item 498). Currently, since 2013 surveys in the subsystem of Monitoring of bottom sediments have been conducted based on only eco-toxicological criteria for organic compounds and geochemical ones for metals.

Contaminants threshold contents – lower TEL (Threshold Effect Level) and upper PEL (Probable Effects Levels) as well as PEC (Predicted Environmental Concentration) values – are used to assess a negative effect of polycyclic aromatic hydrocarbons contained in the sediments on water organisms. The PEC value is treated as a predicted concentration in the water environment. The TEL level corresponds to the content of a chemical element or compound

Table 1

Acceptable contents of PAHs in bottom sediments, based on (*Stan środowiska*... 2009, ROSIŃSKA 2010, ROSIŃSKA and DĄBROWSKA 2011)

PAHs	Concentration [mg kg^{-1} dw]			
	OME	TEL	PEL	PEC
Acenaphthene	–	0.00671	0.089	–
Acenaphthylene	–	0.00587	0.128	–
Anthracene	–	0.0469	0.245	0.845
Fluorene	–	0.0212	0.144	0.536
Phenanthrene	–	0.0867	0.544	1.170
Fluoranthene	–	0.113	1.494	2.23
Chrysene	–	0.108	0.862	1.29
Pyrene	–	0.153	0.875	1.5120
Benzo(a)anthracene	≥ 1.5	0.0748	0.385	1.05
Benzo(b)fluoranthene	≥ 1.5	–	–	–
Benzo(k)fluoranthene	≥ 1.5	–	–	–
Benzo(g.h.i)perylene	≥ 1.0	–	–	–
Benzo(a)pyrene	≥ 1.0	0.032	0.782	1.45
Dibenzo(a.h)anthracene	≥ 1.0	0.00622	0.135	–
Indeno[1.2.3–cd]pyrene	≥ 1.0	–	–	–
Σ PAHs	–	–	5.683	22.80

below which the contaminants toxic effect occurs rarely, whereas with values above PEL a harmful effect on the organisms is often observed (Table 1) (*Stan środowiska*... 2009, ROSIŃSKA 2010, ROSIŃSKA and DĄBROWSKA 2011).

Results of the Surveys and Discussion

The concentrations of 17 detected congeners of polycyclic aromatic hydrocarbons (PAHs) and their sums in the bottom sediments of the Wisłok river are presented in Table 2.

Table 2

The concentrations of the PAHs (mg kg^{-1} dw) in the bottom sediments from the Wisłok river in 2012

PAHs		Research points						Mean
		1	2	3	4	5	6	
Acenaphthene	Ace	0.003	0.005	0.007	0.0005	0.003	0.007	0.0043
Acenaphthylene	Acft	0.004	0.006	0.012	0.0005	0.0005	0.018	0.0068
Anthracene	Ant	0.032	0.078	0.126	0.001	0.008	0.058	0.0505
Benzo(a)anthracene	BaA	0.213	0.414	0.722	0.015	0.08	0.389	0.3055
Benzo(a)pyrene	BaP	0.227	0.424	0.712	0.02	0.105	0.549	0.3395
Benzo(b)fluoranthene	BbF	0.26	0.415	0.71	0.025	0.134	0.634	0.363
Benzo(e)pyrene	BeP	0.18	0.3	0.503	0.019	0.099	0.483	0.264
Benzo(k)fluoranthene	BkF	0.121	0.223	0.382	0.011	0.057	0.282	0.1793
Benzo(g.h.i)perylene	BghiP	0.175	0.309	0.505	0.019	0.107	0.483	0.2663
Chrysene	Chry	0.195	0.374	0.656	0.016	0.08	0.398	0.2865
Dibenzo(a.h)anthracene	DBA	0.039	0.078	0.124	0.0025	0.023	0.105	0.0619
Fhenanthrene	Phe	0.117	0.223	0.459	0.006	0.025	0.292	0.187
Fluorene	Fluo	0.006	0.011	0.023	0.0005	0.002	0.035	0.0129
Fluoranthene	Flt	0.392	0.769	1.472	0.028	0.135	0.684	0.58
Iindeno[1.2.3-cd]pyrene	InP	0.172	0.309	0.508	0.018	0.105	0.457	0.2615
Perylene	Per	0.115	0.162	0.259	0.012	0.062	0.24	0.1417
Pyrene	Py	0.333	0.651	1.257	0.024	0.121	0.609	0.4992
Σ 17 PAHs		2.584	4.751	8.437	0.218	1.1465	5.723	3.8099

The bottom sediments taken from 6 research points were highly diversified in terms of the content of polycyclic aromatic hydrocarbons. The concentration of the sum of 17 PAHs in bottom sediments ranged from 0.218–8.437 mg kg^{-1} of dry weight. The PAHs compounds contamination was the lowest in the point located in the town Czarna, where in most forests and wastelands occur, and the highest in Wojaszówka – mainly agricultural lands.

One can assess the degree of bottom sediment contamination based on the concentration of 16 priority PAH, determined by USEPA. Sediments may be classified as heavily contaminated when the concentration of Σ16 PAHs is above 0.5 mg kg^{-1} of dry weight, moderately contaminated when this concentration is from 0.25 to 0.5 mg kg^{-1} of dry weight and weakly contaminated when the concentration monitored is below 0.25 mg kg^{-1} of dry weight. Except for the point located in Czarna (about 0.218 mg kg^{-1} of dry weight), according to this division the sediments surveyed may be classified as heavily contaminated (GUO et al. 2009). Nevertheless relating to the classification of the level of contamination of sediments by PAHs (low level: 0–0.1 mg kg^{-1} of dry weight, moderate level: 0.1–1 mg kg^{-1} of dry weight, high level: 1–5 mg kg^{-1} of dry weight and very high level: > 5 mg kg^{-1} of dry weight) proposed by BAUMARD et al. (1998), the bottom sediments surveyed are characterised by a changeable level, from the moderate one to the very high level of PAHs contaminants.

Analogous scopes of concentrations of the sum of PAH in bottom sediments were registered in the San river. The content of polycyclic aromatic hydrocarbons in 1995, 1998 and 2009–2014 ranged from < 1 mg kg^{-1} to over 11 mg kg^{-1}. When analysing the results of the surveys of bottom sediments conducted in the area of West Pomeranian Voivodeship under the State Monitoring for Environment in 2010–2011, diversified levels of contamination with PAHs compounds were also shown. The content of the sum of 17 PAHs in the surveyed sediments of rivers in the area of this Voivodeship was from 0.0655 to 9.2050 mg kg^{-1} of dry weight. An increased concentration of the sum of 17 PAHs was observed in the bottom sediments of the Wieprza river in Stary Kraków and of the Odra river in Gryfin. A maximum concentration was registered in 2011 in the Dzierżęcinka river in Koszalin. Whereas the content of 17 PAHs in the surveyed sediments of lakes was higher than in the bottom sediments of rivers and was from 0.076 to 21.375 mg kg^{-1} of dry weight. An increased content of PAHs compounds was observed in the Wielke Dąbie, Morzycko, Starzyc and Trzesiecko lakes. Furthermore, concentration values exceeding even 100 mg kg^{-1} of dry weight were registered in the bottom sediments of the Odra and Przemsza rivers [Report on the environmental situation 2010–2011, Bojakowska 2006]. Nonetheless, relating to literature data on the degree of contamination of bottom sediments of rivers located in other countries, considerable diversification in the contents of polycyclic aromatic hydrocarbons is observed. For example, the concentration of the sum of 16 PAHs in bottom sediments in Italy was within the range from 0.92 to 279.38 mg kg^{-1} of dry weight (PERRA et al. 2009). Whereas in the Kor river in Iran within the range of 167.4–530.3 mg kg^{-1} of dry weight (KAFILZADEH et al. 2011).

Among the PAHs surveyed, the highest concentration was observed in the case of fluoranthene (0.028–1.472 mg kg^{-1} of dry weight), four-cyclic benz(a)anthracene and pyrene, and also five-cyclic benzo(b)fluoranthene and benzo(a)pyrene also have a large share. Whereas the lowest concentration was registered for acenaphthene, acenaphthylene and fluorene (Figure 1). Nonetheless, among polycyclic aromatic hydrocarbons it is the presence of benzo(a)pyrene (BaP) which has the strongest effect on the quality of bottom sediments, mainly because of high toxicity. Furthermore, BaP being identified in any element of the environment shows share in it of also other compounds from this group. The concentration of benzo(a)pyrene in the taken samples of bottom sediments was within the range of 0.02–0.712 mg kg^{-1} of dry weight and exceeded neither the PEL, PEC threshold values, nor the values determined by the Ordinance of the Minister for the Environment of 16 April 2002 on types and concentrations of substances which cause output contamination (Rozporzadzenie Ministra Środowiska z 16 kwietnia 2002 r. Dz.U no. 55, item 498). However, these values exceeded the TEL threshold value (0.032 mg kg^{-1} of dry weight). Exception was the bottom sediments taken from Czarna, where the concentration of BaP in bottom sediments was 0.02 mg kg^{-1} of dry weight. In the same year an average concentration of this compound of 150 Polish lakes was several times higher by comparison with the bottom sediments of the Wisłok river (BOJAKOWSKA et al. 20120).

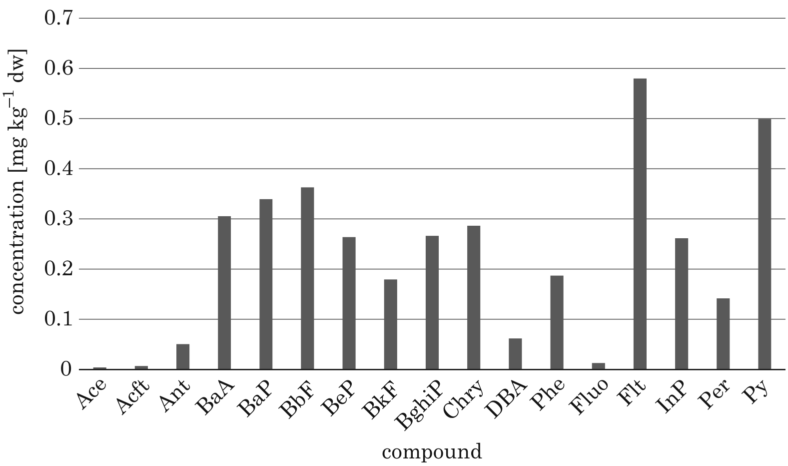

Fig. 1. The mean concentrations of PAHs in the bottom sediments in the Wisłok river in 2012

Depending on the number of aromatic rings, PAHs are divided into four groups: 3-, 4-, 5- and 6-ring. Average shares of the individual groups of compounds are presented in Figure 2. Four-ring PAHs (44%) have the largest share, then 5-ring ones (35%), 3-ring compounds (7%) had the smallest share.

Difference in the share of individual groups of PAHs is apparently a result of their dissimilar susceptibility to decomposition by micro-organisms, which is

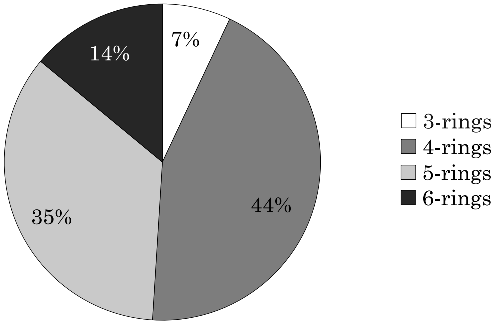

Fig. 2. The percentage of individual groups of compounds of PAHs in the bottom sediments in 2012 depending on the number of rings in the molecule

strictly connected with the number of rings in molecules of individual congeners. PAHs with lower molecular masses, such as naphthalene and phenanthrene, are quickly degraded in bottom sediments, whereas compounds with the higher number of rings, such as pyrene, fluoranthene, benzo(a) anthracene and benzo(a)pyrene are more resistant to biodegradation (OBAYORI and SALAM 20100. The diversified contents of individual groups of PAHs are also connected with the (K_{ow}) octanol/water distribution coefficient. The solubility of polycyclic aromatic hydrocarbons decreases with the increase in molecular mass, and therefore with the increase in the K_{ow} coefficient. As a consequence of that, compounds with greater molecular mass settle on constant molecules which, in turn, involves greater concentration of them in bottom sediments (DJOMO et al. 1996).

The presence of polycyclic aromatic hydrocarbons in the environment is a result of different processes, both natural, and anthropogenic ones. The main source of PAHs in the environment are combustion processes – pyrogenic sources, e.g. combustion of fossil fuels, forest fires, grass and bush burning as well as contamination with petroleum and its products – petrogenic sources. These compounds penetrate into the water environment as a result of dry or wet deposition. The share of treated sewage being introduced to waters directly from sewage-treatment plants is still unspecified (WOLSKA et al. 2014, ROGOWSKA et al. 2013). The method used to identify the source of origin of compounds from the PAH group in bottom sediments is comparison of the quotient of concentrations of compounds characterised by low and high molecular masses and comparison of the measured concentrations of analysed PAHs. The concentrations ratio of selected polycyclic aromatic hydrocarbons may indicate the source of emission and the environmental fate prior to depositing them in bottom sediments (ROGOWSKA et al. 2013).

PAH with the higher number of aromatic rings are considered to be technogenic character contaminants, whereas 2- and 3-cyclic ones belong to natural origin substances. The ratio of the sum of PAHs with low molecular mass (L), to which 2- and 3- cyclic compounds belong, to the sum of PAHs with high molecular mass (4-6 rings) was calculated for all samples. The L/H value < 1 indicates PAH compounds contamination of pyrolytic origin (MAGI et al. 2002). The L/H indicator values of the surveyed bottom sediments for all points are lower than 1 and are within the range from 0.035 to 0.080 (Figure 3). Possible sources of emission of PAHs found in the bottom sediments of the Wisłok river are thus combustion processes. The L/H indicator lowest value was found in the point located in Tryńcza. Whereas, the largest L/H ratio was in Wojaszówka, where contamination with these compounds was the highest. The L/H indicator for PAHs may differ considerably depending on the season. For example, these compounds in winter occur in higher concentrations, it concerns both congeners with the lower, and higher number of rings. Nonetheless in the summer lower contents of 2- and 3- ring PAHs, which effortlessly escape from contaminated sediments due to lower boiling points, are observed (CHEN et al. 2012, GARCIA-FALCON et al. 2006). The samples of the surveyed bottom sediments of the Wisłok river were taken in July, therefore compounds containing 4-6 aromatic rings dominated in the bottom sediments surveyed.

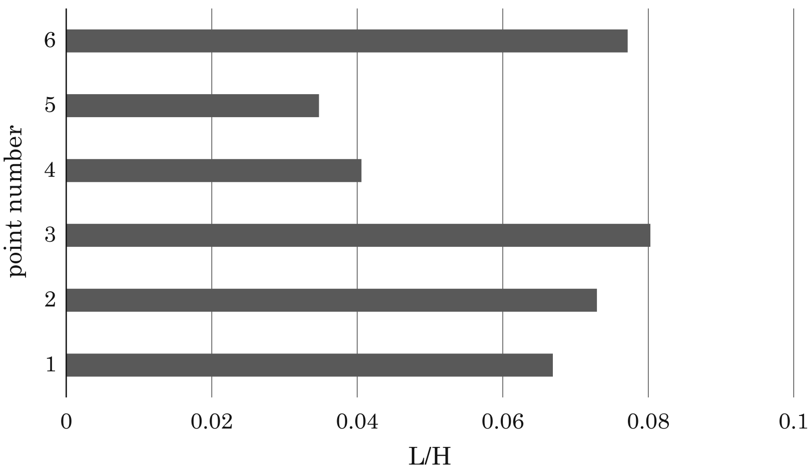

Fig. 3. The ratio L/H for individual research points

Another indicator used to identify sources of polycyclic aromatic hydrocarbons may also be the ratio of concentration of phenanthrene to anthracene (Phe/Ant) and fluoranthene to pyrene (Flt/Py). On the whole, PAHs of petrogenic origin are characterised by the Phe/Ant ratio above 10, whereas for combustion processes Fen/Ant is < 10. In the case of the Flt/Py ratio, values greater than 1 indicate pyrolytic origin, and values lower than 1 – petrogenic origin (NEKHAVHAMBE et al. 2014). In the bottom sediments analysed, the values of the quotient of Phe/Ant concentrations were 3.66, 2.82, 3.64, 6.00, 3.13, 5.04, and the values of the Flt/Py indicator: 1.18, 1.18, 1.17, 1.17, 1.12, 1.12. The Phe/Ant and Flt/Py ratios suggest that PAH in the Wisłok river in all sampling points originate from pyrolytic sources (Figure 4).

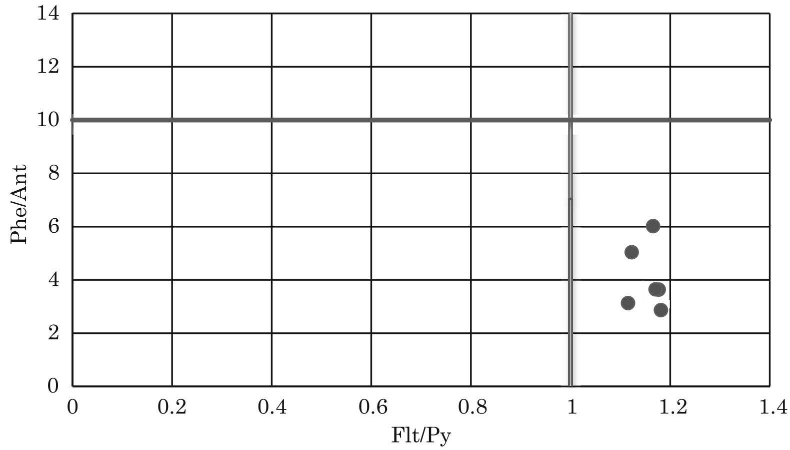

Fig. 4. Identification of sources of PAHs based on the ratio Phe/Ant and Flt/Py

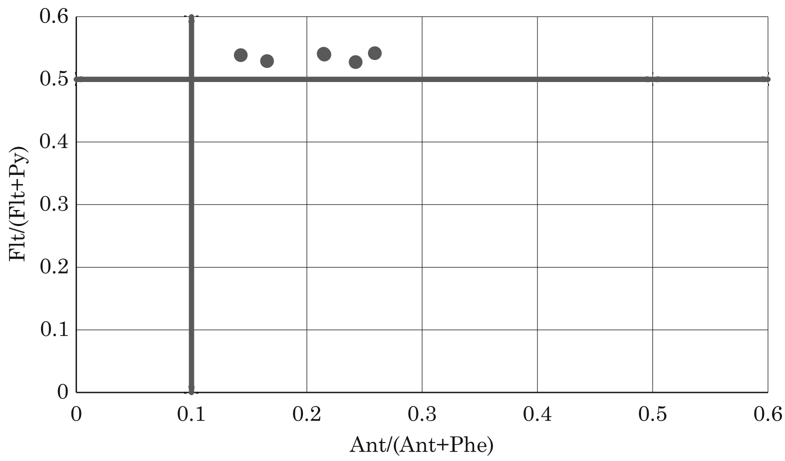

Fig. 5. Identification of sources of PAHs based on the ratio Flt/(Flt+Py) and An/(An+Phe)

The Flt/(Flt+Py) concentrations ratio may also be used to identify the origin of PAHs in the environment. The indicator with the value of > 0.5 is characteristic of grass, wood and coal burning, within the range from 0.4 to 0.5 characteristic of petroleum combustion and < 0.4 indicates petrogenic sources (YUNKER et al. 2002). This indicator confirms pyrolytic origin of PAHs contained in the bottom sediments of the Wisłok river (Figure 5). Furthermore, based on the Ant/(Ant+Phe) and IndP/(IndP+BghiP) indicators, the sources of PAH may be classified into the pyrolytic sources (Figure 5 and Figure 6). It is proved by the Ant/(Ant+Phe) concentrations ratio > the value of 0.1 and IndP/(IndP+BghiP) being within the range from 0.2 to 0.5.

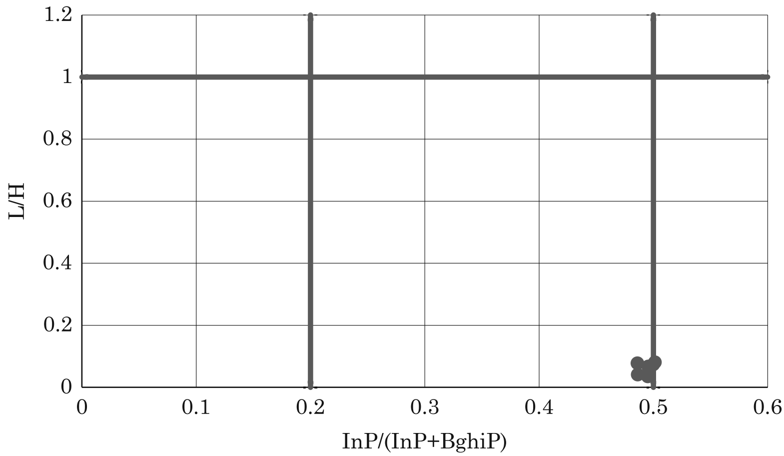

Fig. 6. Identification of sources of PAHs based on the ratio L/H and InP/(InP+BghiP)

Conclusions

As a result of the surveys conducted, the following conclusions were drawn:

1. The content of the sum of 17 measured PAHs in the surveyed bottom sediments in 2012 was within the range from 0.218 to 8.437 mg kg^{-1} of dry weight.

2. Exceeding the PEL threshold value for Σ WWA, indicating that bottom sediments often harmfully affecting the water organisms occur, was registered in the bottom deposits taken from Wojaszówka and Zarszyn. Whereas, exceeding the PEC value was not registered.

3. Fluoranthene (0.028–1.472 mg kg^{-1} of dry weight) dominated across the spectrum of measured PAHs, four-ring benz(a)anthracene and pyrene, and also five-ring benzo(b)fluoranthene and benzo(a)pyrene also had a large share.

Whereas the lowest concentration was registered for acenaphthene (0.0005–0.007 mg kg^{-1} of dry weight), acenaphthylene (0.0005–0.018 mg kg^{-1} of dry weight) and fluorene (0.0005–0.035 mg kg^{-1} of dry weight).

4. The concentration of benzo(a)pyrene in the samples of bottom sediments taken was within the range of 0.02–0.712 mg kg^{-1} of dry weight and exceeded neither the PEL, PEC threshold values, nor the values determined by the Ordinance of the Minister for the Environment of 16 April 2002 on types and concentrations of substances which cause output contamination (Rozporządzenie Ministra Środowiska z 16 kwietnia 2002 r... Dz.U no. 55, item 498).

5. Domestic and worldwide diversification in the occurrence of PAHs in bottom sediments was observed. The chemical composition of bottom sediments is a result not only of the land geomorphology and climatic conditions, but also of the manner lands along rivers are developed and used.

6. The concentrations ratio of selected PAHs may indicate the source of emission and the environmental fate prior to depositing them in bottom sediments.

7. The comparison of the quotient of concentrations of compounds characterised by L/H low and high molecular masses and the comparison of the measured concentrations of analysed PAH, e.g. Phe/Ant, Flt/Py, Flt/(Flt+Py), Ant/(Ant+Phe) and IndP/(IndP+BghiP) showed that the main source of PAHs in the bottom sediments of the Wisłok river are combustion processes (pyrogenic sources).

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