

**POLYCYCLIC AROMATIC HYDROCARBONS (PAH)
IN GRAVITY-OPERATED AND SURFACE WATER
FROM AREAS LOCATED NEARBY COKING PLANT
IN DĄBROWA GÓRNICZA
(UPPER SILESIA REGION, POLAND)**

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The paper presents the results of five PAHs contents determination in the surface and gravity-operated water. The samples of gravity-operated water were taken quarterly in 2009 from collectors put in fifteen points in areas located nearby coking plant in Dąbrowa Górnicza (Upper Silesia region, Poland). The results allowed determining the seasonal variability of PAHs concentration in gravity-operated water. Significant differences in concentration of PAHs in the summer and wintertime were observed. Moreover, to check the presence of PAHs contamination in the surface flowing water from selected streams, watercourses and draining system were collected.

Keywords: PAH, gravity-operated water, surface water

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are group of ubiquitous environmental contaminants, produced primarily as a result of incomplete combustion from predominantly anthropogenic sources [1]. PAHs are mainly formed as by-products of incomplete combustion of organic materials. They have been identified in many emission sources, such as vehicle exhausts, power plants, chemical-, coke- and oil-shale industries, urban sewage [2]. Primary natural sources of PAH are forest fires and volcanic activity [3, 4]. Water contaminants, mainly originated from PAHs emission to atmosphere, are entered by atmospheric fallout. Some authors maintain that PAHs get to surface water with dry and wet precipitation together with dust from air [5].

By the reason of this phenomenon, during a rain, in storm sewage even hundred-tuple increase of PAHs contents has occurred [6]. The levels of individual PAH in rainwater ranged from 10 to 200 ng/litre, whereas levels of up to 1000 ng/litre have been detected in snow and fog [5].

According to some authors, PAHs can be created incidentally by aqueous organism activity, which may be concerned as PAHs natural source [7]. Unfortunately, aquatic animals are known to adsorb and accumulate PAH from water [5]. Only small part of PAHs becomes dissolved in water, whereas the rest part is found on solid fraction, creating suspension and colloidal solution [7].

PAHs are quite resistant to degradation [2]. However, in water they are considerably biodegradable by both chemical and biological processes. Principal biodegradation occurs in case of polycyclic aromatic hydrocarbons containing two and three rings (eg. naphthalene, anthracene), which have the highest solubility in water among PAHs compounds [8]. PAHs found in aqueous solution undergo decomposition much easier under the influence of elevated temperature and visible radiation, than PAHs in atmosphere [9]. PAHs can be expected to be photooxidated in water [5].

In the nature those compounds, occur in various structural forms, [10] which are environmentally important because many PAHs show genotoxic, [2] mutagenic and carcinogenic properties [11]. In 1973 a report of International Agency for Research on Cancer (IARC) presented that forty eight PAHs compounds are carcinogenic to, at least nine animal species including humans [10].

Gaseous and particle-bound PAHs can be transported across significant distance before their soil deposition, [12] from where they are may be moved via surface or gravity-operated water to human and animal organisms.

Similarly like the others hydrophobic xenobiotics, PAHs have their own capability to accumulate in adipose tissue and milk fat and then finally found in food products [10]. Therefore United States Environmental Agency (US EPA), recommends to control PAHs contents in main environmental components such as water, soil or plants [13]. When the release of PAHs into the environment exceeds their degradation capacity, a significant accumulation of PAHs is observed. The presence of permanent pollution sources results in the accumulation of PAHs in soil, plants and water bodies [2]. The half-life range for PAHs in soil estimated by different researchers is quite wide depending on the individual compound, from 2 month to 28 years [14].

Diversification of threats connected with environmental contaminants are defined by environmental harmfulness index, which consider series factors such as emission quantity, toxicity, number of endangered population, endanger range, substance stability in the environment, aptitude to accumulation and impact on physical and chemical environment, as well. Toxic substances

ranged according to index values, create the list of the most significant environmental poisons (Tab. 1). For Poland area Environmental Toxicology Commission of Polish Academy of Science placed PAHs on third position: under compounds of sulphur and dust but above pesticides, heavy metals and nitrogen oxides [15].

In many circumstances the environmental occurrence of PAHs has been associated with negative effects on public health [16].

2. PRESENTATION OF INVESTIGATED OBJECT

At first stage of development work seven surface flowing water samples were taken. Representative streams, watercourses and draining systems were determined in 4 km radius west from coking plant in Dąbrowa Górnicza.

As the following step fifteen collectors for gravity-operated water were assembled (Fig. 1). Collectors were spaced within the distance at the least of 85 m from local road with low traffic flow in order to minimize communication route impact on PAHs content in tested samples. Moreover, for limitation PAHs emission impact of households (stoves coal-fired) on samples, the collectors were put within the distance at least 450 m from nearest buildings.



Fig. 1. Sampling of gravity-operated water [8]

The samples of gravity-operated water were taken quarterly in 2009. Points location were assigned with the assistance of global positioning system receiver (GPS) what is presented on a map (Fig. 2). The samples were taken into tight container made from amber glass and transported to laboratory in four hours.

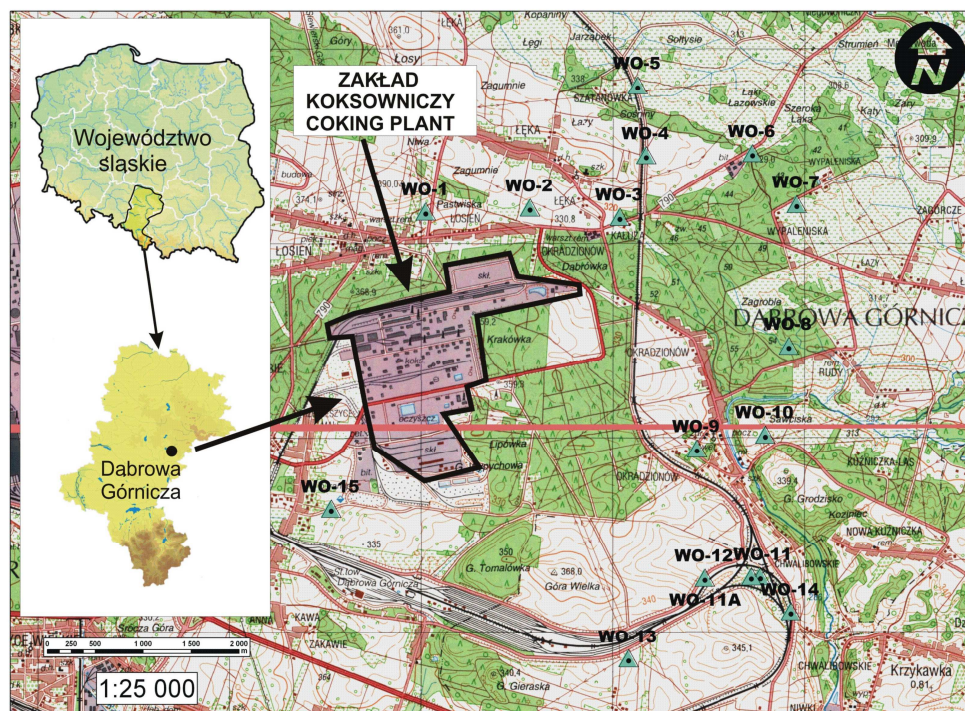


Fig. 2. Location of gravity-operated water sampling points on topographic map [8]

3. MATERIALS AND METHODS

500 ml of each water sample were hexane extracted for 60 min with 15 ml hexane, using magnetic bar stirrer, directly in the same bottle that a sample was taken. This is preventing operation, reducing analyte losses during preparation stages. Then the extracts were dried with sodium sulfate (VI) (Na_2SO_4), next were concentrated in 0,5 ml acetonitrile and were analysed by HPLC method (FLD detector, gradient elution programme).

4. RESULTS AND DISCUSSION

Based on our results, in surface flowing water samples, the very low PAHs contents were found out. The large majority of results received were under determination limit of used method (0,5 ng/L). Low PAH contents possibly are connected with high water flow in watercourse and low suspended matter contents. Thus we discontinued further researches of this water samples as useless in further evaluation.

Environment Minister Regulation applied to water quality doesn't take into consideration gravity-operated water therefore all determination results were compared to limit values of I and II class surface water (Tab. 2).

Polish law rules concerning surface water contaminations standards allows for polycyclic aromatic hydrocarbons (PAHs), i.e. benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3cd)perylene. The PAHs group includes over 200 compounds and was found that 5 of PAHs are particularly harmful for aqueous environment and benzo(a)pyrene is enumerated on first place.

To determine water PAHs contamination degree assessment there are some guidelines which include the classification of surface water uniform parts: stream, flux, torrent, river (including strongly changed water), canal, lakes, strongly changed lakes, other natural and artificial water reservoirs, internal marine water, transitory and coastal water.

Table 2. Polycyclic aromatic hydrocarbons quality standard in surface water [$\mu\text{g/L}$] according to Environment Minister Regulation (2008)

Polycyclic aromatic hydrocarbons (PAHs)	Concentration unit	Quality standard of I and II class surface water*
benzo(a)pyrene	[$\mu\text{g/L}$]	0,1
benzo(b)fluoranthene		$\Sigma=0,03$
benzo(k)fluoranthene		
benzo(g,h,i)perylene		$\Sigma=0,002$
indeno(1,2,3,-cd)pyrene		

* Class I – stream, flux, torrent, river (including strongly changed water), canal;

Class II – lakes, strongly changed lakes, other natural and artificial water reservoirs;

For PAHs group the correspondence should be achieved for each value i.e. benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene sum and benzo(g,h,i)perylene i indeno(1,2,3,-cd)pyrene sum.

Based on achieved results, in tested samples of gravity-operated water we found out that PAHs contents were over quality standard values (according to Environment Minister Regulation) and changed quarter to quarter as we showed in figures 1-4.

In the individual diagrams lack of samples or values under determination limits are marked as blanks.

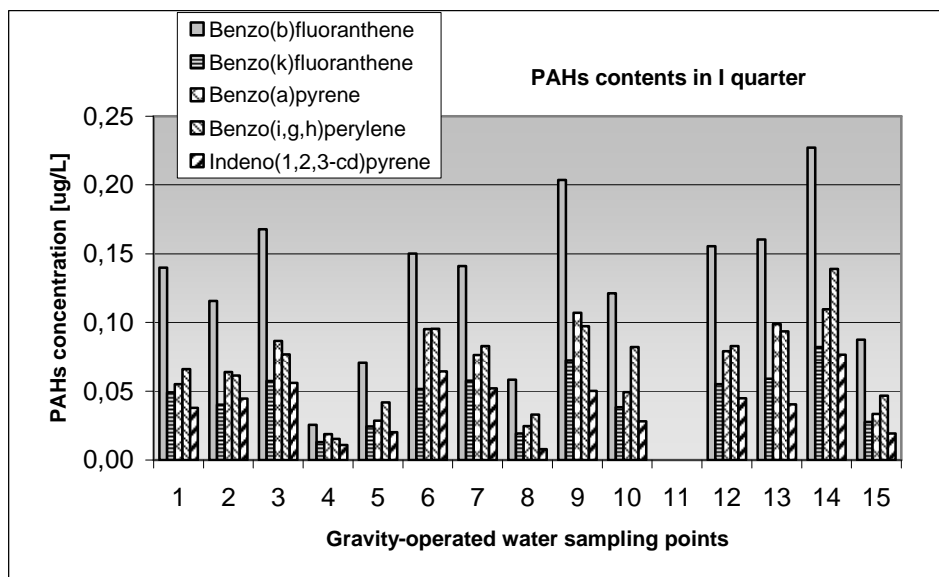


Fig. 1 Diagram of PAHs contents in tested samples taken from 15 sampling points in I quarter 2009

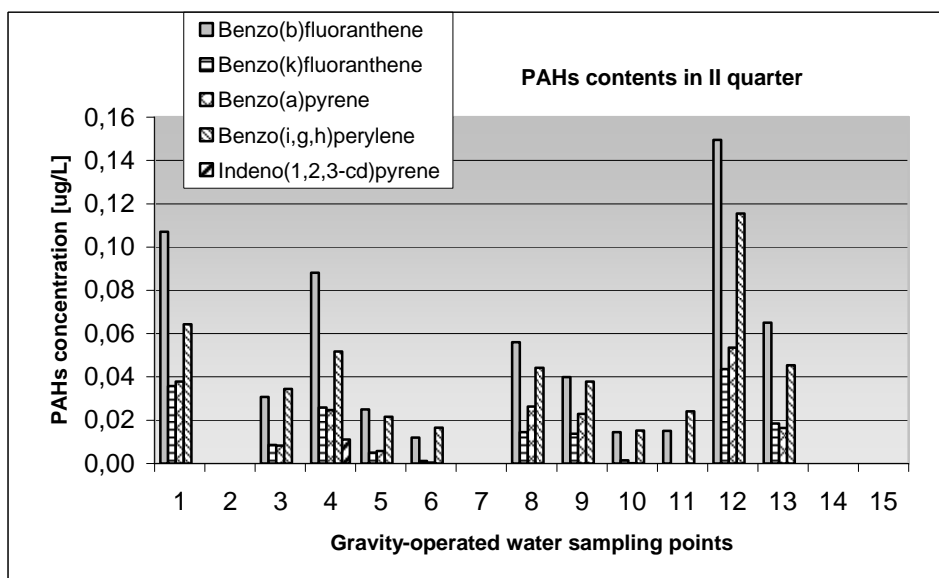


Fig. 2 Diagram of PAHs contents in tested samples taken from 15 sampling points in II quarter 2009

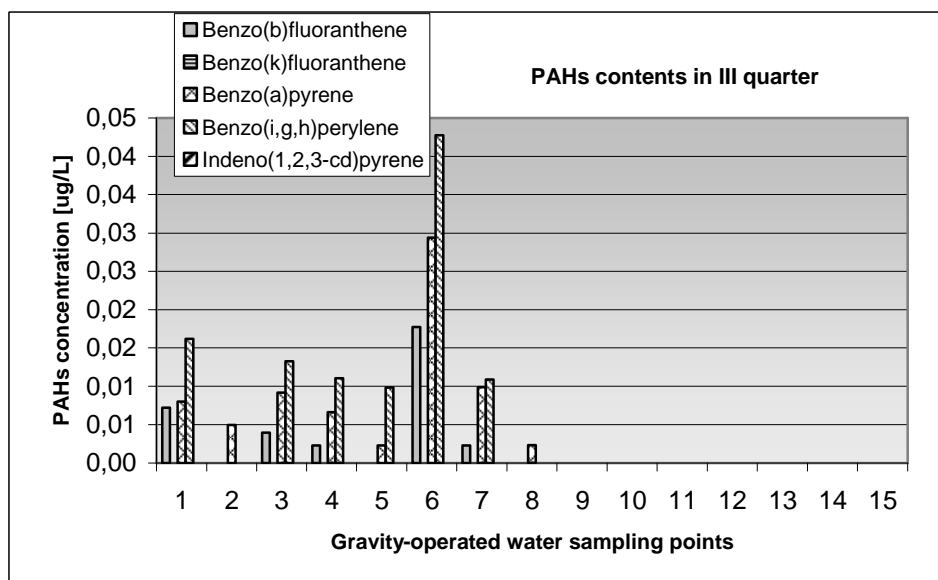


Fig. 3 Diagram of PAHs contents in tested samples taken from 15 sampling points in III quarter 2009

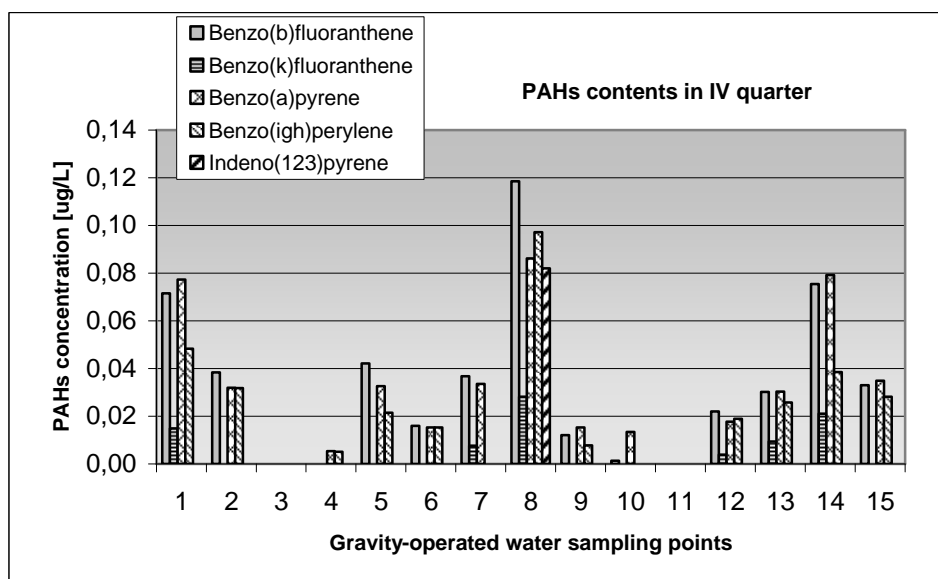


Fig. 4 Diagram of PAHs contents in tested samples taken from 15 sampling points in IV quarter 2009

Analyses results of tested gravity-operated water samples are presented in tables 3-6.

Table 3. Statistical parameters determined for contents of PAH in tested gravity-operated water samples – I quarter, 2009

PAH	Average	Geometric average	Range	Standard deviation	Concentration [µg/L]	Quality standard
Benzo(b)fluoranthene	0,12	0,12	0,02-0,23	0,06	1,9	0,03
Benzo(k)fuoranthene	0,04	0,04	0,01-0,08	0,02		
Benzo(a)pyrene	0,06	0,06	0,02-0,11	0,03	0,93	0,1
Benzo(i,g,h)perylene	0,07	0,06	0,02-0,14	0,03	1,56	0,002
Indeno(1,2,3-cd)pyrene	0,04	0,03	0,01-0,08	0,02		

Table 4. Statistical parameters determined for contents of PAH in tested gravity-operated water samples – II quarter, 2009

PAH	Average	Geometric average	Range	Standard deviation	Concentration [µg/L]	Quality standard
Benzo(b)fluoranthene	0,04	0,03	0,01-0,15	0,04	0,80	0,03
Benzo(k)fuoranthene	0,01	0,01	0,01-0,04	0,01		
Benzo(a)pyrene	0,01	0,02	0,01-0,05	0,02	0,20	0,1
Benzo(i,g,h)perylene	0,03	0,04	0,02-0,10	0,03	0,48	0,002
Indeno(1,2,3-cd)pyrene	0,01	0,01	0,01	-		

Table 5. Statistical parameters determined for contents of PAH in tested gravity-operated water samples – III quarter, 2009

PAH	Average	Geometric average	Range	Standard deviation	Concentration [µg/L]	Quality standard
Benzo(b)fluoranthene	0,002	0,01	0,01-0,02	0,01	0,025	0,03
Benzo(k)fuoranthene	0*	0*	0*	-		
Benzo(a)pyrene	0,005	0,01	0,01-0,03	0,01	0,063	0,1
Benzo(i,g,h)perylene	0,007	0,02	0,01-0,04	0,01	0,104	0,002
Indeno(1,2,3-cd)pyrene	0*	0*	0*	-		

* 0 – below determination limit

Table 6. Statistical parameters determined for contents of PAH in tested gravity-operated water samples – IV quarter, 2009

PAH	Average	Geometric average	Range	Standard deviation	Concentration [µg/L]	Quality standard
Benzo(b)fluoranthene	0,03	0,04	0,01-0,12	0,03	0,58	0,03
Benzo(k)fuoranthene	0,01	0,01	0,01-0,03	0,01		
Benzo(a)pyrene	0,03	0,03	0,01-0,09	0,03	0,47	0,1
Benzo(i,g,h)perylene	0,02	0,03	0,01-0,10	0,03	0,42	0,002
Indeno(1,2,3-cd)pyrene	0,08	0,08	0,08	-		

5. CONCLUSION

During quarterly cycles of gravity-operated water sampling the significant differences in concentration of PAHs in the summer and wintertime were observed. Higher PAHs contents in wintertime and lower in the summertime probably were caused by increased decomposition effect following photooxidation process (intensive insolation and high temperature).

Moreover, it may be bring about specific meteorological conditions in wintertime when adsorbed on dust PAHs cannot be diluted [17].

PAHs get to surface water with wet and dry dustfall from air. Only small part of PAHs becomes dissolved in water, whereas the rest part is found on solid fraction, creating suspension and colloidal solution.

Collectors were spaced within the distance at least 85 m from local road with low traffic flow in order to minimize communication route impact on PAHs content in tested samples. Moreover, for limitation PAHs emission impact from households (stoves coal-fired) the collectors were put within the distance at least 450 m from nearest buildings.

Benzo(a)pyrene contents, which is acknowledged as the most toxic and first of all the most carcinogenic compound of PAH, in all tested samples were on low level. Only in the first quarter its contents were over limit value (0,1 [$\mu\text{g/L}$]) in 14% of tested samples.

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WIELOPIERŚCIENIOWE WĘGLOWODORY AROMATYCZNE (WWA)
W WODACH OPADOWYCH I POWIERZCHNIOWYCH W REJONIE ZAKŁADÓW
KOKSOWNICZYCH W DĄBROWIE GÓRNICZEJ (WOJ.ŚLĄSKIE)

Streszczenie

W pracy przedstawiono wyniki badań zawartości pięciu WWA w próbkach wód opadowych i powierzchniowych. Próbki wód opadowych pobierano kwartalnie w 2009 roku z 15 kolektorów umieszczonych na terenach zlokalizowanych w pobliżu zakładów koksowniczych w Dąbrowie Górniczej (woj. śląskie). Uzyskane wyniki pozwoliły określić zmienność sezonową stężeń WWA w wodach opadowych. Wyraźnie podwyższone stężenia WWA zaobserwowano w sezonie zimowym. Ponadto, w celu sprawdzenia obecności zanieczyszczeń WWA w wodach powierzchniowych, przebadano próbki wód (płynących) powierzchniowych pobranych z wybranych potoków, cieków wodnych oraz rowów melioracyjnych.