

Concentrations of Polycyclic Aromatic Hydrocarbons in the Dnipro River and other Natural Water Systems

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The article presents and generalizes the results of monitoring of polycyclic aromatic hydrocarbons (PAHs) in the surface water of the Dnipro River and establish trends in change of their concentrations for the period 2010-2021. It is shown that the levels of PAHs in the water of the Dnipro River increased significantly during the study period. The average total concentration of PAHs was 181.76 ± 111.42 ng/dm³. The maximum concentration of PAHs was determined in 2020 and exceeded 300 ng/dm³. For the purpose of comparison, similar trends in change of PAH concentrations were established for other water systems of the World. In the natural waters of the rivers of Southern and Central Italy, the Tyrrhenian Sea, the Elbe River, the Ganga River, the Yangtze River, the Pearl River Delta the average total concentrations of PAHs for the indicated years were respectively, ng/dm³: 878.93 ± 275.76 ; 690.95 ± 415.78 ; 93.05 ± 22.98 ; 6911 ± 4068 ; 173.51 ± 145.85 ; 132.87 ± 74.69 . The high relative standard deviation, that amounted 24.7-84.1 %, may be explained by the use of data obtained in different years and by different authors. For most water systems, there is a tendency to decrease of the total PAH concentration. From the analysis of the ratios between individual PAHs in natural waters, it follows that the emission of PAHs is mainly of anthropogenic origin and is related to the processes of combustion of organic substances. The main sources of pollution are vehicle emissions, coal burning, operation of coke ovens, leakage of petroleum products, etc.

Keywords: concentration, monitoring, organic ecotoxics, polycyclic aromatic hydrocarbons, Dnipro River

Концентрації поліциклічних ароматичних вуглеводнів в р. Дніпро та інших природних водних системах

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Наведено й узагальнено результати моніторингу поліциклічних ароматичних вуглеводнів (ПАВ) у поверхневій воді р. Дніпро та встановлено тенденції у зміні їхніх концентрацій за період 2010-2021 рр. Показано, що рівні вмісту ПАВ у воді р. Дніпро значно зросли за період дослідження. Середня загальна концентрація ПАВ становила $181,76 \pm 111,42$ нг/дм³. Максимальну концентрацію ПАВ встановлено 2020 р., яка перевищила 300 нг/дм³. Для порівняння аналогічні тенденції у зміні рівнів вмісту ПАВ були встановлені для інших водних систем світу. В природних водах річок Південної та Центральної Італії, Тіренського моря, р. Ельба, р. Ганг, р. Янцзи, дельти р. Перлинна середні сумарні концентрації ПАВ за вказані роки становили відповідно, нг/дм³: $878,93 \pm 275,76$; $690,95 \pm 415,78$; $93,05 \pm 22,98$; 6911 ± 4068 ; $173,51 \pm 145,85$; $132,87 \pm 74,69$. Високі значення середньоквадратичного відхилення, що близько 24,7-84,1 %, можна пояснити використанням даних, отриманих у різні періоди та різними авторами. Для більшості водних систем спостерігається тенденція щодо зниження загальної концентрації ПАВ. З аналізу співвідношень між індивідуальними ПАВ у природних водах випливає, що емісія ПАВ має, в основному, антропогенний характер і пов'язана з процесами горіння органічних речовин. Основними джерелами забруднення є викиди автотранспорту, спалювання вугілля, робота коксових печей, витік нафтопродуктів тощо.

Keywords: концентрація, моніторинг, органічні екотоксиканти, поліциклічні ароматичні вуглеводні, р. Дніпро

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic substances whose molecules consist of two or more aromatic rings forming different configurations. The main source of their emission into the environment is the incomplete combustion of organic substances. There are natural and anthropogenic sources of PAH emission. Natural are forest fires and volcanic processes, anthropogenic include processes of burning coal, firewood, gas, household and industrial waste, car exhaust gases, cigarette smoke, as well as oil leakages [1].

Distinctive properties of PAHs are hydrophobicity, thermal stability and stability in the environment. The compounds of this class are highly toxic, mutagenic, carcinogenic, teratogenic and immunotoxicogenic for various life forms. Since PAHs are similar in their properties to such organic xenobiotics as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), they can also be included to the list of persistent organic pollutants (POPs) [2].

The US Environmental Protection Agency (US EPA) recommends monitoring 16 priority PAHs in environmental objects: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. The most toxic compounds from this list are benzo(a)pyrene and other five- and six-cyclic hydrocarbons [3].

Since the toxic and carcinogenic properties of benzo(a)pyrene are the most studied of all PAHs, it is used as an indicator of contamination by compounds of this class in general [4]. Table 1 shows the toxicity equivalence factors (TEFs) of priority PAHs relative to benzo(a)pyrene. TEFs represent the relative toxicity of an individual PAH compared to benzo(a)pyrene and is used to calculate the total toxicological equivalent (TEQ) of PAH mixtures. The given coefficients are rather conditional, since they take into account only the carcinogenic effect, but do not reflect other types of toxicity and persistence in the environment. According to the US EPA, the following compounds are considered carcinogenic: benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(b)fluoranthene,

benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(a)anthracene, chrysene.

In most countries, among the 16 priority PAHs, only benzo(a)pyrene has a clearly established maximum allowable concentration (MAC) in water. For example, for drinking water in the EU and Ukraine, the MAC for benzo(a)pyrene is 10 ng/dm³ [5, 6]. In some countries, regulations also apply to some other compounds. According to the Turkish Legislation (Regulation on Water Intended for Human Consumption) implemented in line with the directive of the European Union, five PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene) should be determined in drinking water. This regulation also stipulates that benzo(a)pyrene concentration should not exceed 10 ng/dm³ while the concentration for the other four PAHs should remain below 100 ng/dm³ [7].

According to the article [8], the total global emission of PAHs in 2007 was 5.04·10⁵ tons. Among the total emissions of PAHs, 6.19 % were in the form of high molecular weight carcinogenic compounds. South, East and Southeast Asia were the leading regions in terms of PAH emissions. They accounted for about half of the global emission of PAHs.

The article [9] states that countries such as China (1.14·10⁵ tons), India (9·10⁴ tons) and the USA (3.2·10⁴ tons) are the leaders in terms of PAH emissions. Emission of heavy five- and six-cyclic PAHs in Germany in 2010 was 191.5 tons. In Great Britain, total annual anthropogenic emissions of 16 priority PAHs in 2010 amounted to 621 tons, including 3.23 tons of benzo(a)pyrene [10]. As a result of long-distance transboundary atmospheric transport, PAHs can spread regionally and even intercontinentally.

The procedure of PAH determination in the objects of water systems is quite complex, time-consuming and expensive. It includes such stages as selection, concentration, fractionation and purification of the obtained extracts in order to achieve the necessary enrichment factor to ensure the sensitivity of the detectors in the physicochemical methods of analysis of the target components. At present, the number of studies on the determination of PAHs in natural waters is increasing, but the information on the levels of these compounds is partial and requires generalization.

Table 1. TEFs of priority PAHs.

PAH	TEF	PAH	TEF
Acenaphthylene	0.001	Chrysene	0.01
Fluorene	0.001	Benzo(b)fluoranthene	0.1
Phenanthrene	0.001	Benzo(k)fluoranthene	0.1
Anthracene	0.01	Benzo(a)pyrene	1.0
Fluoranthene	0.001	Dibenzo(a,h)anthracene	5.0
Pyrene	0.001	Indeno(1,2,3-cd)pyrene	0.1
Benzo(a)anthracene	0.1	Benzo(g,h,i)perylene	0.01

During the last decades, a number of complex studies were carried out on the determination of PAHs in the objects of water systems of Ukraine, in particular the river Dnipro. Their results are presented in the monograph [1], as well as in articles [11–15].

According to their physicochemical properties, PAHs are non-polar, semi-volatile, low-soluble organic compounds. For compounds of this class, the logarithm of the octanol-water partition coefficient (hydrophobicity coefficient) is 3.01–7.19 [16]. The water solubility decreases from naphthalene 31 mg/dm³ to benzo(g,h,i)perylene 2.6·10⁻⁴ mg/dm³ [17].

As a result, PAHs in natural systems tend to bind (associate) with suspended particles. The results of determination of the dispersed-phase distribution of these ecotoxins between the aqueous phase and different fractions of suspended particles are given and summarized in articles [18, 19]. They indicate that in the surface water of the Dnipro River, most of PAHs (on average – 56%) are in a bound state with suspended particles. It was established that the water-soluble fraction of individual PAHs decreases with an increase of the hydrophobicity coefficient.

As a result of settling of suspended particles, PAHs accumulate in bottom sediments. Resuspension of bottom sediments is a source of secondary contamination of natural water by organic xenobiotics. Some information on the content of PAHs in bottom sediments of water systems of southern Ukraine is available in articles [20, 21]. According to the results given in [20], the total concentration of priority PAHs in bottom sediments of Black Sea estuaries ranged from 91.7 to 107.7 µg/kg dry weight. Higher levels of PAHs were found in bottom sediments in the Dnipro River reservoirs (Kremenchuk, Zaporizhzhia, Kakhovka regions). Their total concentration was 1215, 4919, and 3896 µg/kg dry weight, respectively [22].

Since heavy five- and six-cyclic hydrocarbons are mainly accumulated in bottom sediments, it is more appropriate to analyze surface water to assess the trend in change of total pollution levels over a long period of time.

The purpose of this study is to generalize the results of PAH monitoring in the surface water of the Dnipro River and other river systems of the World, establish trends in change of total pollution levels during the last decades, and analyze possible sources of emission of these ecotoxins to aquatic ecosystems.

Results and discussion

Analysis of PAHs was carried out in surface water samples collected from the Dnieper River near Kyiv during 2010–2021. Monitoring points were located along an extended urban section and represent typical conditions of the river's middle course in a city environment. Sampling was performed at a depth of 0.5–1 m using standard bathometers. Collected samples were analyzed by a methodology consisting of their extraction, concentration, fractionation, purification and quantification by the method of high performance liquid chromatography with fluorescence detection. A complete and detailed methodology is given in the monograph [1] and articles [11–14, 19].

The results regarding the concentration of priority PAHs in the surface water of the Dnipro River were obtained for the period 2010–2021 [1, 11–15]. The averaged data are presented in Table 2. The average total PAH concentration was 181.76 ± 111.42 ng/dm³. The notably low values were recorded in 2010, 2011 and 2014 (<25 ng/dm³). These anomalous values may reflect interannual differences in hydrological conditions and other environmental factors affecting PAH transport and distribution, although the available data do not allow the exact causes to be identified. Excluding these years, the average amount of PAHs was 243.22 ± 43.37 ng/dm³. The maximum total concentration of PAHs was observed in 2020, and reached 303.90 ng/dm³.

As trend analysis shows, there was a steady increase of the PAH content in the Dnipro River during the period under study (Fig. 1). This trend can generally be attributed to increasing anthropogenic pressure on the river basin, including emissions from transport, industrial enterprises, thermal power plants, gas stations, and oil depots. Other potential anthropogenic sources of PAHs include episodic events such as large-scale ammunition explosions, which have been reported to release PAHs into the environment [23–25].

If the above trend continues, the total level of PAH will be approximately 425 ng/dm³ in 2027 and it will exceed 500 ng/dm³ in 2030. At the same time, if one does not take into account the anomalous values of 2010, 2011 and 2014, the trend is more gradual, and the forecast values will be 321.60 and 345.12 ng/dm³ for 2027 and 2030 respectively.

Table 2. Average total concentrations of priority PAHs in surface water of the Dnipro River.

Year	Season	C, ng/dm ³	Year	Season	C, ng/dm ³	Year	Season	C, ng/dm ³
2010	Spring	28.27	2014	Autumn	14.20	2019	Spring	274.96
2011	Autumn	11.12	2016	Spring	230.00	2020	Autumn	303.90
2012	Spring	213.42	2017	Spring	269.76	2021	Autumn	269.30
2013	Autumn	212.35	2018	Autumn	172.03	Average		181.76±111.42

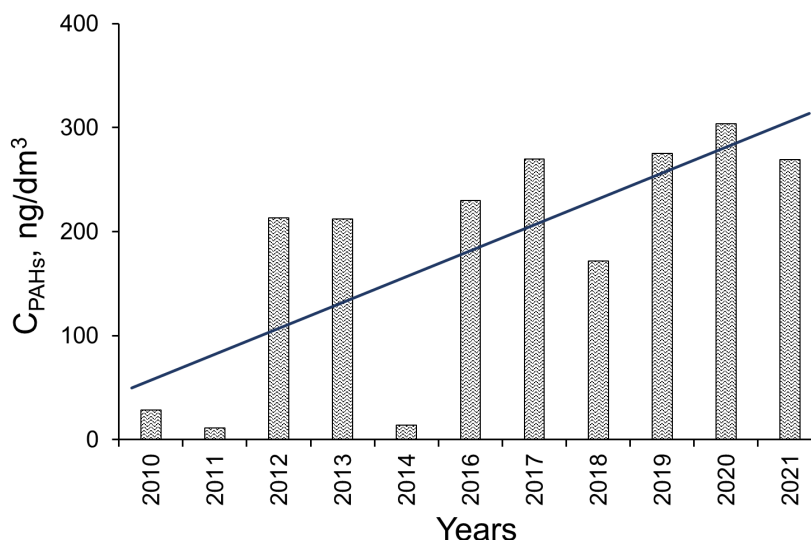


Fig. 1. Trend in change of total PAH concentration in surface water of the Dnipro River.

The total PAH concentration is calculated as the sum of the concentrations of individual priority PAHs measured in the water samples. The average relative percentage contribution of all priority PAHs to the total concentration is given in Table 3. The water of the Dnipro River is dominated by light two-four-cyclic PAHs, which are characterized by higher solubility in water and are less toxic compounds. Their share is 79.20 %. In most water samples, the highest concentrations were determined for naphthalene, phenanthrene and fluoranthene. The proportion of most toxic and carcinogenic compounds benzo(a) pyrene and dibenzo(a,h)anthracene was insignificant and in total did not exceed 2 %. The proportion of six-cyclic PAHs, which are characterized by the greatest stability in the environment, was 12.68 %. The total share of all carcinogenic PAHs according to the US EPA classification amounted to 15.42 %.

Main anthropogenic sources of PAHs in surface waters are pyrogenic, i.e. associated with high-temperature combustion of organic substances (coal, wood, gasoline, diesel, etc.), and petrogenic, caused by leakage of oil and petroleum products that have

not undergone thermal decomposition. Since the temperature and conditions of formation determine which PAHs are created and in what quantities, one may obtain some information about the source of pollution analyzing the ratio of individual PAHs in natural water. Table 4 shows some ratios between individual PAHs, which can be used to assess the source of pollution [26].

In the surface water of the Dnipro River, the marker ratios of anthracene / (anthracene+phenanthrene); fluoranthene / (fluoranthene+pyrene); benzo(a) anthracene / (benzo(a)anthracene+chrysene); were 0.09; 0.88; 0.50, respectively. The last two ratios indicate that the Dnipro River is characterized by the predominance of the man-made component in the PAHs structure caused by the combustion of organic substances. However the ratio of anthracene / (anthracene+phenanthrene) was <0.1, which may indicate that PAH emission into the Dnipro River caused by a leak of oil products. In addition, a low value of this ratio may indicate pollution associated with low-temperature combustion, where the formation of phenanthrene dominates compared to anthracene.

Table 3. Average relative percentage contribution of individual compounds to the total PAH concentration in surface water of the Dnipro River.

PAHs	Number of cycles	Relative contribution, %	PAHs	Number of cycles	Relative contribution, %
Naphthalene	2	27.23	Benzo(a)anthracene	4	3.20
Acenaphthylene	3	3.25	Chrysene	4	3.20
Acenaphthene	3	2.43	Benzo(b)fluoranthene	5	5.70
Fluorene	3	1.03	Benzo(k)fluoranthene	5	0.98
Phenanthrene	3	18.28	Benzo(a)pyrene	5	0.68
Anthracene	3	1.88	Dibenzo(a,h)anthracene	5	0.78
Fluoranthene	4	16.45	Indeno(1,2,3-cd)pyrene	6	0.88
Pyrene	4	2.28	Benzo(g,h,i)perylene	6	11.80

Table 4. Diagnostic Ratios considered for identifying sources of PAHs.

Marker ratios	Diagnostic ratio	Sources
Anthracene/ (anthracene+phenanthrene)	< 0.1	Petrogenic
	> 0.1	Combustion
Fluoranthene/ (fluoranthene+pyrene)	< 0.4	Petrogenic
	0.4–0.5	Fuel combustion
	> 0.5	Coal, grass, and wood burning
Benzo(a)anthracene/ (benzo(a)anthracene+ chrysene)	< 0.2	Petrogenic
	0.2–0.35	Fuel combustion
	> 0.35	Coal, grass, and wood burning

This process occurs in car engines (especially diesel engines). In some samples, a high contribution of benzo(g,h,i)perylene to the total PAH concentration was established, which is characteristic of natural water systems in large cities and is associated with intensive traffic [1, 11–15].

For comparison, information on the PAH content in other water systems in the World was analyzed. The total concentrations of PAHs in the water of the rivers of Southern and Central Italy and the Tyrrhenian Sea [27–30] were quite high and averaged 878.93 ± 275.76 and 690.95 ± 415.78 ng/dm³, respectively. The concentrations of PAHs in these water systems remained approximately at the same level. In the water of the rivers of Southern and Central Italy, a certain increase of the content of PAHs was observed (Fig. 2a). The opposite trend was established for the Tyrrhenian Sea (Fig. 2b). High concentrations of PAHs in these water systems can be explained by significant anthropogenic load in this region. For example, in the Sarno River basin (Naples region) there are many powerful industrial enterprises, one of which is the pharmaceutical plant of Novartis Pharma, that is one of the largest in the World. The Tiber River basin also passes through large industrial cities in central Italy, that contain steel mills (the city of Terni), chemical plants, paper mills, etc.

The water phase from the rivers of Southern and Central Italy and the Tyrrhenian Sea is characterized by the predominance of light PAHs. For example, for the Sarno River [27] and the Tiber River [28], the part of heavy five- and six-cyclic PAHs was only 11 and 19 %, respectively. However, in the suspended phase matter, the part of heavy PAHs is more significant and for the Sarno River and the Tiber River was 36 and 64 %, respectively. It should be noted separately that the concentration of benzo(a)pyrene was quite high and ranged from 12.2 to 63.9 ng/dm³.

From the analysis of marker ratios, it was concluded that the pollution of these water systems is mainly of pyrolytic origin and is associated with combustion of fossil fuels, waste incineration, operation of internal combustion engines, petroleum cracking, production of coke, tar, asphalt, etc. In addition to anthropogenic sources, PAHs can originate as a result of natural

processes. Thus, perylene is formed as a result of the degradation of biogenic precursors. In Italian water systems, the contribution of perylene to the total PAH amount was insignificant, which indicates the anthropogenic nature of the pollution.

In paper [31], long-term trend in changes of the concentration of PAHs in the water of the Elbe River (Germany) was evaluated. The results are presented in Fig. 2c. The average total PAH concentration was 93.05 ± 22.98 ng/dm³. It is estimated that during the period 2001–2016, the PAH content decreased by 38 %.

Light PAHs prevailed in the water of the Elbe River. However, the part of heavy five- and six-cyclic were quite high and amounted to an average of 26 %, while its growth was established for the period 2001–2016. The contribution of benzo(a)pyrene to the total concentration was significantly high and amounted to 6.0 %. The total share of all carcinogenic PAHs according to the US EPA classification was 34.58 %.

A positive matrix factorisation receptor model was used to identify the sources of PAHs. It was calculated that vehicular emissions from gasoline- and diesel-powered engines were the main PAH sources in the Elbe River, contributing approximately 42 % of the total mass overall. In addition, coal combustion made a lower but significant contribution (27 % on average). A smaller proportion of PAHs are associated with work of coke ovens and cement plants.

During the past decades, there has been a slight decrease of the PAH concentrations in the water of the Ganga River (India) (Fig. 2d). According to [26, 32–34], the total concentration of PAHs ranged from 1894 to 10330 ng/dm³. On average – 6911 ± 4068 ng/dm³. High concentrations of PAHs are explained by the rapid growth of industrial production in this region, which caused an increase of the emission of pollutants. In 2004, the emission of PAHs in India amounted to $9.0 \cdot 10^4$ tons. According to this indicator, India is among the three world leaders.

Based on data for 2019 the three-cyclic PAHs were more dominant in water samples from the Ganga River followed by the four-cyclic PAHs and contained about 67 % and 28 % of the total PAHs concentration. Acenaphthylene and benzo(a)anthracene were

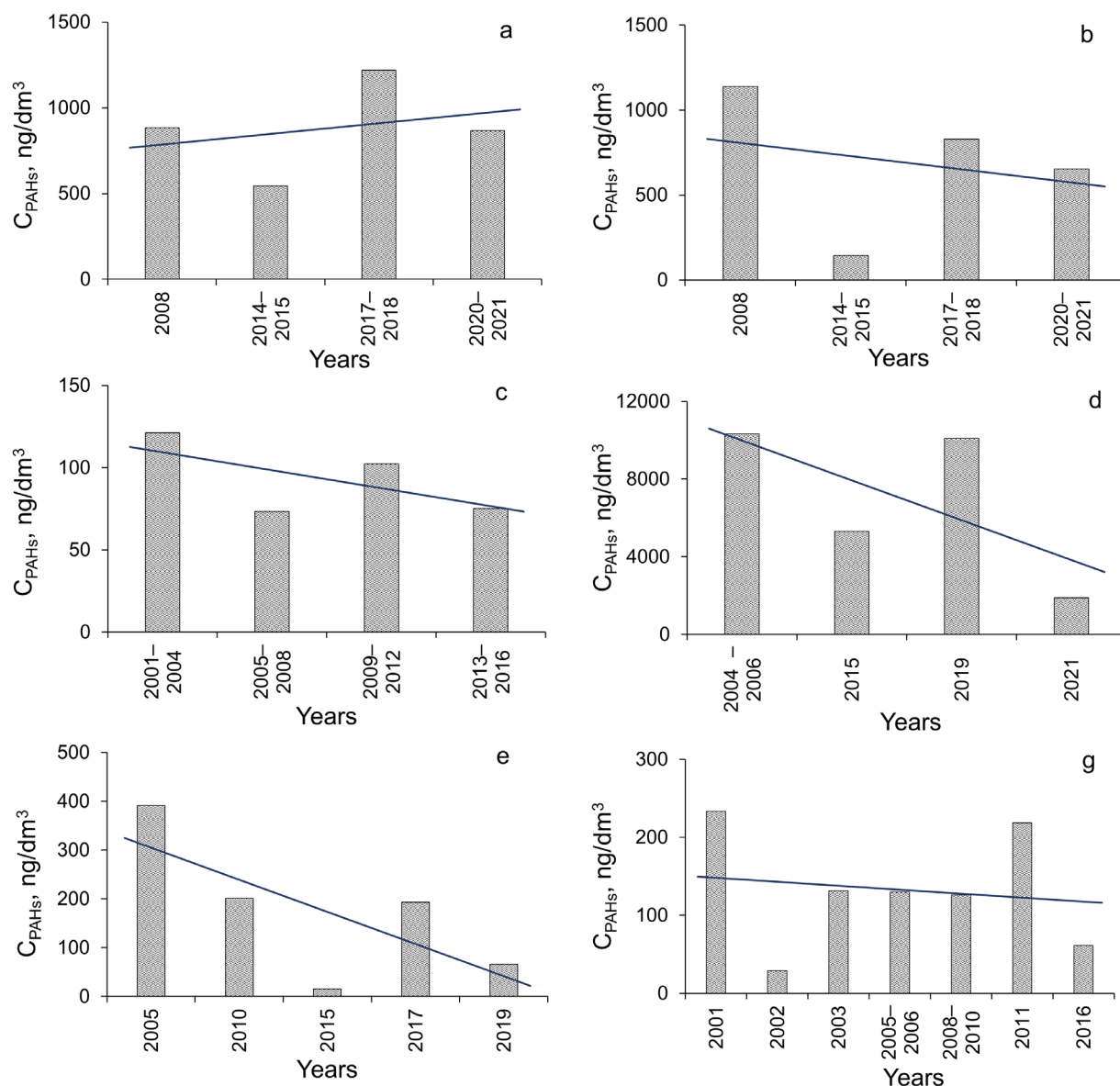


Fig. 2. Average total concentrations of PAHs in surface water of the rivers of Southern and Central Italy (a), the Tyrrhenian Sea (b), the Elbe River (c), the Ganga River (d), the Yangtze River (e)*, the Pearl River Delta (g). * – total concentrations are indicated excluding naphthalene. A trend line is a graph of an approximating function that can be used for predictions based on statistical data.

dominant in most surface water samples. The share of heavy five- and six-cyclic compounds did not exceed 1% [26]. According to data obtained for 2021, the share of heavy PAHs was also insignificant and amounted to 3.86% [34].

For most samples, the marker ratios of anthracene / (anthracene+phenanthrene) and benzo(a)anthracene / (benzo(a)anthracene+chrysene) > 0.1 and 0.35, indicating the pyrogenic nature of the pollution. At the same time, for 93% of the samples, the ratio of fluoranthene / (fluoranthene+pyrene) < 0.4, that indicates that the PAH emission is related to the leakage of petroleum products. From this it can be concluded that the pollution of this water system is caused approximately equally by both pyrogenic and petrogenic factors [26].

The total PAH concentrations in the water system of China the Yangtze River [35–39] (Fig. 2e) and the Pearl River Delta [40–45] (Fig. 2g) averaged 173.51 ± 145.85 and 132.87 ± 74.69 ng/dm³, respectively. For the Yangtze River, there was a tendency to decrease of the PAH concentration in the water. In the water of the Pearl River Delta, the concentration of PAHs did not change significantly during the study period. The stabilization and some reduction of PAH concentrations in China's water systems can be attributed to the decrease of the coal part for energy production. Instead, there was an increase of the use of natural gas, which ultimately reduces the emissions of PAHs.

Pollution of the Yangtze River is mainly associated with three- and four-cyclic PAHs [38]. Their share

accounted for 58.2 and 13.9% of the total amount, respectively. Similar results are given in the article [37]. The relative content of carcinogenic PAHs was 15.6%.

To determine the sources of PAH emission, the principal component analysis coupled with multiple linear regression model was used. It is estimated that 67% of emissions are caused by coal combustion and coke production. The rest of the pollution is related to gasoline and diesel vehicles, natural gas [38].

In the water of the Pearl River Delta the highest concentrations were determined for naphthalene, phenanthrene and fluoranthene. The part of heavy PAHs did not exceed 10%. Part of benzo(a)pyrene accounted for 3.45% of the total PAH content [45]. In the same aquatic system, the proportion of benzo(a)pyrene in sediments was found to be two times higher (7.15%), which confirms the assertion that bottom sediments are a source of secondary water pollution with heavy carcinogenic PAHs.

In paper [43], with usage of the principal component analysis coupled with multiple linear regression model contributions to the total PAHs emission from various types of activity were calculated. The parts from coal and wood burning, coke production, vehicle exhaust, and oil leakage were 28, 25, 22, and 21%, respectively. Only 4% of the emission of PAHs is associated with natural processes.

So, of the seven considered water systems, in five there is a tendency to decrease of the total content of PAHs. The concentrations of PAHs in the water of the rivers of Southern and Central Italy remained at approximately the same level. A clearly expressed tendency to increase the content of PAHs was established only for the Dnipro River. This fact points to the need of PAHs monitoring in Ukrainian water systems and implement measures to limit their emissions. In general, the overall levels of PAHs in the water of the rivers of Southern and Central Italy, the Tyrrhenian Sea, and the Ganga River are significantly higher than in the Dnipro River. In the water of the Elbe River (c), the Yangtze River (e), and the Pearl River Delta (g), the concentrations of PAHs are approximately at the same level as in the Dnipro River.

Conclusions

The article examines and analyzes the results of PAH monitoring in the surface water of the Dnipro River, obtained for the period 2010–2021. The calculated average PAH concentration was 181.76 ± 111.42 ng/dm³. Two- to four-ring PAHs, which are characterized by higher solubility in water and are less toxic compounds, prevailed. A trend in an increase of PAH levels in the water has been established. The maximum concentration of PAHs was observed in 2020 and reached 303.90 ng/dm³.

For comparison, data on PAH monitoring in some water systems of the World are given. The average total PAH concentrations in the water of the rivers

of Southern and Central Italy, the Tyrrhenian Sea, the Ganga River turned out to be higher than in the Dnipro River and amounted to 878.93 ± 275.76 ; 690.95 ± 415.78 ; 6911 ± 4068 ng/dm³. The following values were obtained for the Elbe River, the Yangtze River, the Pearl River Delta – 93.05 ± 22.98 ; 173.51 ± 145.85 ; 132.87 ± 74.69 ng/dm³, which are close to the Dnipro River.

For most of water systems of the World, there is a tendency to decrease of the total PAH concentration. The most clearly expressed trend is established for the Ganga River and the Yangtze River. In the water of the Tyrrhenian Sea, the Elbe River and the Pearl River Delta, PAH levels decreased slightly. PAH concentrations in the water of the rivers of Southern and Central Italy remained at approximately the same level.

The main sources of PAH emission are vehicle emissions, coal burning, operation of coke ovens, leakage of petroleum products, etc. The PAH emission associated with natural processes is insignificant. It follows that with the help of measures aimed at limitation of the PAH emission, it is possible to achieve a decrease of their concentration in natural waters.

Authors' contributions

M.V. Milyukin: conceptualization, methodology, validation, supervision; M.V. Gorban: formal analysis, software, writing – original draft, writing – review and editing.

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Conflicts of interest

The authors declare no conflict of interests.

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