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Polycyclic Aromatic Hydrocarbons In Bottom Sediments Of Donuzlav Lake (Black Sea)

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ABSTRACT

Lake Donuzlav, located in the western part of the Crimean Peninsula is a water body undergoing anthropogenic load, which cannot but affect the state of its bottom sediments. The content and composition of polycyclic aromatic hydrocarbons (PAH) are representative indicators of the degree and character of an anthropogenic impact in natural habitats. The aim of the work was to assess the level of PAH content in the bottom sediments, to identify potential sources and to assess the toxicity of bottom sediments. It was established that the average content of ∑PAH in the sediments amounted to 806±380 ng/g, with the values of this parameter ranging over 34–4036 ng/g. At five out of ten stations in Lake Donuzlav, PAH values, average for the Black Sea, were exceeded. These stations were grouped along both banks in the inner part of the reservoir. Fourteen PAHs were identified: Nap, 2mNap, Flu, Phe, Ant, Fla, Py, TrPhe, Chr, BbF, BkF, BaP, DBA, BghiP. The main share falls on the binuclear Nap and 2mNap, which indicate the presence of fresh oil pollution. The average share of these compounds over the water area was 60±5%, and at stations with elevated levels of ∑PAH it was 74±4%. There was a close correlation between the content of all polyarenes, which coefficient averaged 0,88. The presence of geochemical relationships between polyarenes entering from different sources was probably due to the functioning of natural mechanisms aimed at the transformation of pollutants, which served to restore the dynamic balance of the system.

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INTRODUCTION

Lake Donuzlav, or Donuzlav Bay, is located in the western part of the Crimean Peninsula and, in the past, underwent a significant anthropogenic transformation. For several centuries it existed as a closed and hypersalted reservoir, separated from the sea by a sandy bank. In the 60s of the 20th century, due to the construction of naval facilities, a channel was dug out trough the sandbar separating the lake from the Black Sea. After 1980, a naval base with the necessary infrastructure was built on the shore.

The system of currents in the Donuzlav Bay, after the construction of a navigable channel, is such that, depending on the direction and strength of the wind, currents are observed in which water is driven out of the bay or, conversely, enters it. The flow velocities in the lower water layer are usually higher than in the upper one. Eddy currents in the channel area, the drift of

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terrigenous material from the upper reaches of Lake Donuzlav and a slight introduction of sandy material from the seashore are observed in the lake. The peculiarities of the hydrodynamics of the reservoir indicate that the polluted waters of the lake can flow through the channel freely into the open sea and be involved further in the general circulation system (Tikhonenkova et al., 2010; Kovrigina and Nemirovsky, 1999).

The anthropogenic load on the bay coast is uneven. There are large settlements, fleet infrastructure facilities and a port in the southeastern part of the Donuzlav. In the bay estuary there is a quarry for underwater sand mining. Near these sources of anthropogenic impact, the coastal water area is polluted with household and industrial wastes (Kotelyanets et al., 2019; Ivanyutin, 2020). For the most part there are agricultural lands and some recreation centers on the north-western shore of the reservoir. This section of the reservoir is less susceptible to the anthropogenic load, unlike the south-eastern shore, where almost all man-made objects of this area have been concentrated. On the one hand, the north-western coast is not subject to anthropogenic load, on the other, it may be exposed to the local sources of pollution located on the opposite shore of the reservoir.

Due to its features, Lake Donuzlav is widely used for mariculture purposes. It has a number of advantages as compared with the open areas of the Black Sea, namely, favorable natural conditions (absence of storms and strong currents), a high level of biological productivity, and, according to mariculture researchers' assessment, the absence of sources of anthropogenic pollution (Vyalova, 2019). The conditions of Lake Donuzlav fully satisfy the needs of farmed shellfish, which ensures good growth and development of mussels. There are several mussel and oyster farms in the waterbody. In particular, a large farm for the cultivation of Black Sea mussels and oysters is located near the village of Novoozernoye. The hydrological regime and trophic activity of the lake also ensure good growth of mollusks (Kochergin et al., 2017; Nemirovsky and Kovrigina, 2000). According to seafood producers, the level of pollution of the lake's waters does not exceed maximum permissible concentrations, so mussels, being filtrators, do not accumulate such an amount of harmful substances that can threaten the health of consumers (Yakovleva and Grebennikov, 2020).

Lake Donuzlav can be characterized as a reservoir with an average level of bottom sediments pollution caused by pollutants of priority classes (Kotelyanets et al., 2019). At the same time, there is a number of data indicating that its ecological state and that of the adjacent water area of the Black Sea are unfavorable (Kochergin et al., 2017; Ivanyutin, 2020). It is found that most of the studied elements of hazard classes I and II (Pb, Cu, Ni, Cr, Mo) reached abnormal concentrations exceeding background values and European standards. Patterns have been identified in the distribution of anomalies in the lake, which are primarily associated with the spread of silty sediments and their proximity to shallow parts of the lake (Ivanyutin, 2020). The data of the YugNIRO (Zhugaylo et al., 2018) confirm the ongoing contamination of certain sections of the estuary with heavy metals, petroleum products (PP) and organochlorine compounds. If we compare the concentrations of PP with European standards, it turns out that these values exceeded the standard by 21.4 in 1999, and by 5.8 times in 2015.

The content and composition of polycyclic aromatic hydrocarbons (PAHs) is an informative indicator of the degree and nature of anthropogenic impact in natural environments (Koshovskii et al., 2017). The study of PAHs is an urgent task which is enhanced by the fact that many individual PAHs are priority pollutants with a carcinogenic effect. Their sources in the environment are high-temperature effects on organic matter during anthropogenic activities, as well as natural lithogenic and biogeochemical hydrocarbon flows (Koshovskii et al., 2017). Despite the importance of this characteristic of the ecological state of coastal waters, PAH pollution of Lake Donuzlav has not been studied earlier.

Bottom sediments are a depot of pollutants, including PAHs, in which traces of chronic pollution inevitably remain. For this reason, PAHs are considered the most reliable indicator of the safe water area. The total content of polyaromatic compounds in bottom sediments, as well as their individual composition, is a source of information on quantitative indicators of pollution, its potential sources, as well as the toxicity of the surrounding aquatic environment.

The aim of the work was to assess the level of PAH content in the bottom sediments of Lake Donuzlav, to identify potential sources of formation of these compounds, as well as to assess the toxicity of the bottom sediments of the reservoir under discussion. To study the content of PAHs being priority carcinogenic compounds is a particularly urgent task in the region of mariculture development and the adjacent water areas.

MATERIAL AND METHODS

The bottom sediments of Lake Donuzlav were sampled during the expedition conducted by researchers of A.O. Kovalevsky Institute of Biology of the Southern Seas in July 2021. Sampling stations (Fig. 1) were selected along the coast, taking into account the water's edge (because the shores of lake Donuzlav are steep and up to two meters high), local water circulation and transport of bottom sediments (Fomin and Ivanov, 2006). Due to the fact that detritus is carried over from the upper part to the estuarine areas of the reservoir (Tikhonenkova et al., 2010), there also occurs a concomitant movement of pollutants. In accordance with the models of water circulation and sediment transport (Fomin and Ivanov, 2006), and with run-up and run-down phenomena along the axis of the bay, the relatively isolated zones of bottom sediment circulation and transport also form. As a result, some geochemical specificities can be assumed in certain

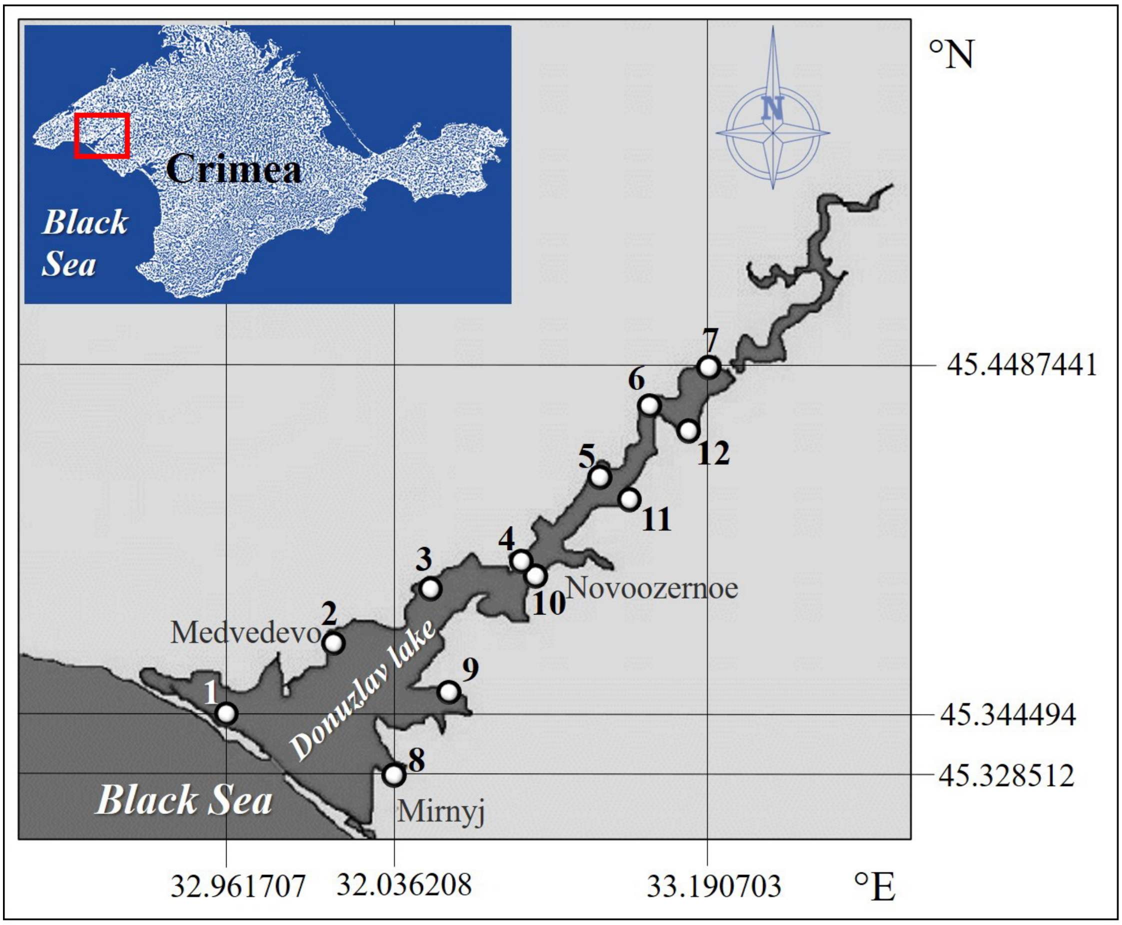

Fig. 1. Layout of bottom sediment sampling stations in Lake Donuzlav (July, 2021)

areas of the water body. The presence of these circulation zones, along with accessibility and relatively uniform distribution along the lake shore appeared to be an important factor when choosing the location of sampling stations. At the same time, this scheme does not pretend to a detailed geochemical description of the area that was not the aim of the research.

Samples (layer 0–5 cm) were taken by a manual sampler. Sampling at each station was carried out in three replicates. For the analysis, an averaged sample of bottom sediments was used, in which the pH and Eh values were measured *in situ* by a Neutron pH meter-thermometer. To determine the PAH content, only the central part of the sample was taken, which was not in contact with the walls of the sampler. The sample was cleaned of macro inclusions (stones, shells, algae, etc.) and placed in hermetically sealed containers for further transportation to the laboratory. The bottom sediments were stored in a refrigerating chamber up to the analysis, dried to an air-dry state under natural conditions, then ground in an inert mortar with a pestle and sieved through a sieve with a mesh diameter of 0,25 mm.

Determination of PAHs in bottom sediments was carried out according to Methodology for measuring the mass fraction of polycyclic aromatic hydrocarbons in samples of soils and bottom sediments of freshwater and marine water bodies (FR.1.31.2007.03548). It is based on the extraction of polycyclic aromatic hydrocarbons from bottom sediments and soils by a mixture of hexane and acetonitrile (10:1), concentration of the extract, and chromatographic separation of the hydrocarbon fraction in a thin layer of aluminum oxide. Identification and determination of individual polycyclic aromatic hydrocarbons in bottom sediments were carried out on an EKOM Beta-10US liquid chromatograph with a luminescent detector (RF-5301 PC) and a Yanapak ODS-T column.

The standard error was applied as an indicator of the variation of mean values. The correlation dependence was estimated based on the Pearson correlation coefficient ($p=0{,}05$). Data processing was performed using Microsoft Excel software packages.

RESULTS AND DISCUSSION

The bottom sediments of the area studied were represented by silts and/or silts with an admixture of sand. The hydrogen index of bottom sediments was in the range of 7,79–8,46, which corresponded to their granulometric composition. The redox potential was mainly of a reduction kind and varied from −225 to −137 mV.

The average content of ∑PAH in the water body was 806±380 ng/g, with the values of the parameter ranging over 34–4036 ng/g (Fig. 2A), i.e. the spread of values was of the second order. Its average value for the Black Sea basin is about 200 ng/g (Readman et al., 2002). According to our data, the content of ∑PAH on the outer roadstead of Lake Donuzlav was low and amounted to 41 ng/g. Low values of ∑PAH were also noted in the southeastern Bay (Stations 1-3, 8, 9), far from large settlements and port infrastructure. Thus, at five of twelve stations in Lake Donuzlav, the figures, average for the Black Sea, were exceeded. These stations were grouped on both banks in the inner part of the reservoir. Increased values of pollutants in the coastal areas, especially in port waters, were expected and are widely described in the literature (Chen Ch.-W. and Chen Ch.-F., 2011; Nemirovskaya, 2013; Vitali et al., 2019).

High concentrations of ∑PAHs (>1000 ng/g) were typical of areas with a constant supply of pollutants (Baumard et al., 1998). Values exceeding that conditional indicator were recorded at three stations (Stations 6, 10, 11 – Fig. 2 A, B) located in the central part of the reservoir. Station 10, where maximum values of PAH were found, was located in the center of the urban-type settlement of Novoozernoye, in the water area of the town beach. Elevated levels of various pollutants at the Station were also associated with the functioning of outdated sewage treatment plants discharging untreated municipal wastewater into the waters of the bay (Ivanyutin, 2020). The other two stations were far from the settlements and the port (for instance, Station 6 is

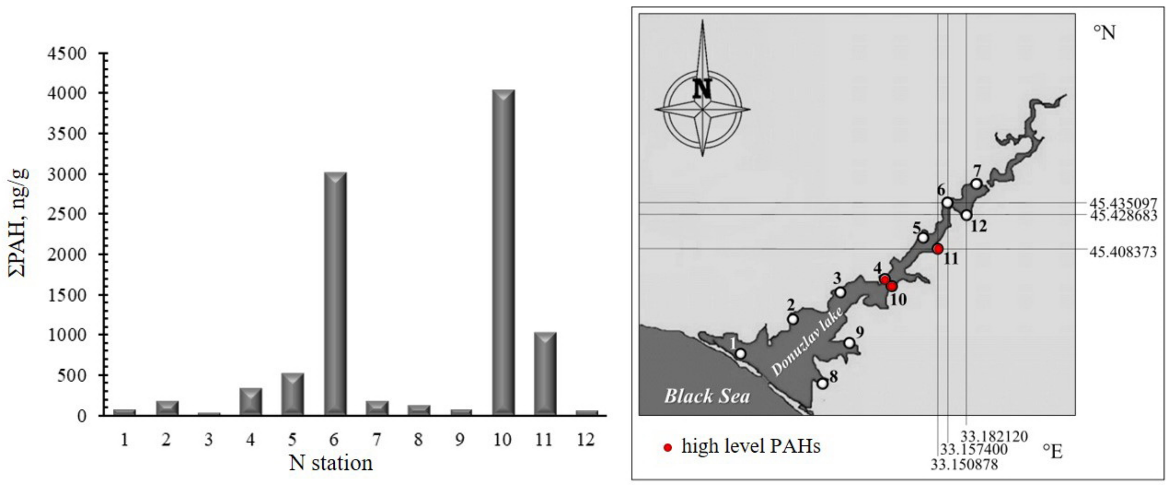

Fig. 2. Total content of PAH (ng/g) in bottom sediments at sampling stations in Lake Donuzlav (A); areas with increased content of PAH (B), 2021

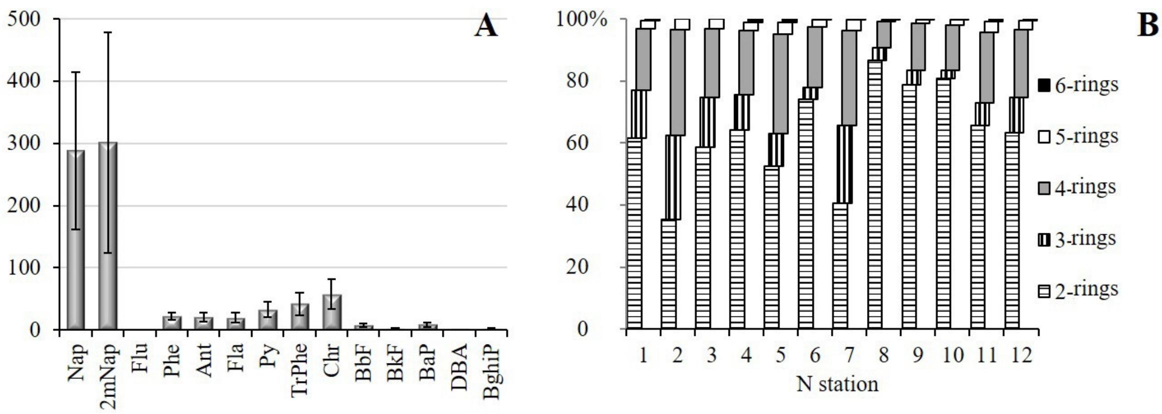

Fig. 3. The content of individual PAHs in the bottom sediments of Lake Donuzlav: A – the average content of individual PAHs (ng/g) with an indication of a standard error; B – the proportion of different PAHs at sampling stations in Lake Donuzlav (%), 2021

adjacent to the lands of the national reserve). Despite this, it can be noted that there have been constant sources of PAH intake in these areas.

In the bottom sediments of Lake Donuzlav there were identified 14 PAHs: naphthalene (Nap), 2-methylnaphthalene (2mNap), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), triphenylene (TrPhe), chrysene (Chr), benz(b)fluoranthene (BbF), benz(k)fluoranthene (BkF), benz(a)pyrene (BaP), dibenz(a,h)anthracene (DBA), benz(g,h,i)perylene (BghiP). At the same time, only trace concentrations of Flu were found at all sampling stations. This compound belongs to the PAHs of the geochemical background, and is often formed in the sediments rich in humus (Rovinskiy et al., 1988; Nemirovskaya, 2013). The main share of individual PAHs in the bottom sediments of Lake Donuzlav (Fig. 3A) falls on binuclear Nap and 2mNap, which are markers of the presence of fresh oil pollution (Yunker et al., 2012). The average proportion of these compounds in the water area amounted to 60 ± 5%, and at stations with high levels of PAH it was 74 ± 4%, which may evidence a connection between the increased content of polyarenes and oil pollution.

In the whole water area (Fig. 3B), the share of binuclear compounds was 64% (35–81%), tri-nuclear compounds amounted to 12% (3-27%), tetra-nuclear to 22% (8–34%), penta-nuclear to 3% (1–4%), and hexa-nuclear compounds amounted to 0.4 % (0.0–1.0 %). At stations with increased ∑PAH concentrations, the proportion of binuclear compounds was higher, while that of tri-nuclear and tetra-nuclear ones was lower. The proportion of anthropogenic toxic 5- and 6-nuclear PAHs did not differ on average (Fig. 3B).

The physico-chemical parameters of the medium, in particular pH and Eh, along with other factors, influence both the accumulation and further transformation of PAHs in bottom sediments (Verâne et al., 2020). The study of the correlation relationship between the pH of sediments and the content of ∑PAH and its individual components showed that there was a weak negative correlation of ∑PAH (r = –0,56), as well as of all the components of the mixture (r = –0.63...–0.51). It is believed that high pH levels in bottom sediments contribute to the accumulation of PAHs (Hussain et al., 2016), since, as shown in the experiments, the degradation rate of polyaromatic compounds decreases somewhat at pH>6 (Hung et al., 2020). In our case, the opposite trend is noted, which is probably the result of the predominant influence of other factors. In general, the relationship of these parameters, among other things, can be explained by complex interactions in the PAH–pH–microbial community system (Ghosal et al., 2016, Wu et al., 2017). PAH contamination leads to changes in the diversity, succession processes and functioning of the microbial community (Leys et al., 2004; Sawulski et al., 2014; Ren et al., 2015; Liang et al., 2016). The vital activity of bacteria and the processes of biodegradation of organic substances underlie the formation of the pH value of bottom sediments. The influence of Eh on the content of PAHs is also specified (Hussain et al., 2016), unfortunately, such a correlation could not be established on the data set studied, probably due to the relatively narrow range of Eh changes.

If we evaluate the toxicity of bottom sediments by individual components, then for Nap, 2mNap and Ant at stations with elevated levels of PAH, there were recorded levels exceeding background levels but not causing negative effects. Only at Station 10, with the maximum ∑PAH, the level of Nap content (>1000 ng/g) was observed that could have had a negative impact on biota under prolonged exposure. Conditional standards for the most toxic compounds have not been exceeded (Savinov et al., 2011).

An important generally accepted indicator of the toxicity of bottom sediments is BaP (Israel and Tsyban, 1989; Opekunov et al., 2015). On average, its share in the lake accounted for about 1 % of ∑PAHs with a fluctuation in the range of 0,3–1,7 %. According to the data of (Barabashin et al., 2020), that indicator varied in different parts of the Crimean coast from 0,5 to 1,1 %, with an average of 0,7 %. These values were slightly lower than in the waters of Lake Donuzlav. The conditional standard (25 ng/g (Neue..., 1995)) was exceeded at Station 6 (32 ng/g) and at Station 10 (32 ng/g), where the maximum values of ∑PAH were found.

BaP is also a conditional unit for assessing PAH toxicity. The toxicity of the amount of PAHs in bottom sediments is estimated by using the toxic equivalent (TEQ), the unit of measurement of which is the toxicity of BaP. It is calculated by the formula:

$TEQ = \sum (Ci \times TEFi)$, (Petry, 1996; Pufulete M., 2004)

where TEF is a toxic equivalent factor of individual PAHs (relative to the carcinogenic effects of BaP);

Ci is the concentration of individual PAHs in the mixture.

The obtained values of toxic equivalents of bottom sediments ranged from 0.6 to 62.5 ng/g (Fig. 4). Their increment was closely associated with an increase in the total content of PAHs in bottom sediments (r=0,98) (Fig. 4). The calculated level of PAH toxicity is relatively low. For example, in the waters of the Kola Bay, the average indicator was 438 ng/g (Zhilin and Plotitsyna, 2011). In water areas with a high technogenic load, it can reach 1964 ng/g or more (Chen Ch.-W. and Chen Ch.-F., 2011). The main contribution to the formation of bottom sediment toxicity

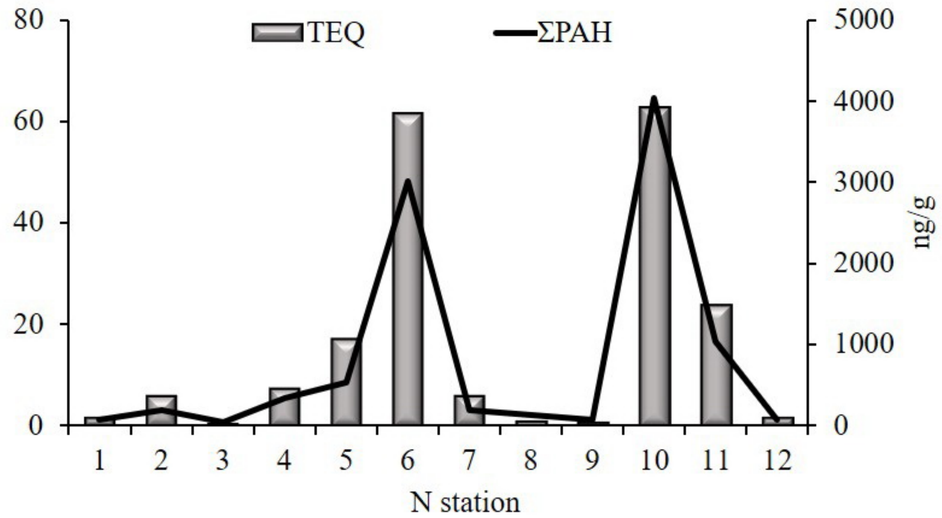

Fig. 4. The value of toxic equivalents (TEQ) and ΣPAHs of bottom sediments at the sampling stations of Lake Donuzlav (ng/g), 2021

Table 1. Values of molecular indices for PAHs of pyrolytic and pyrogenic origin

Index	Mean (min-max)	Origin		References
		pyrolitic	petrogenic	
Nap/2mNap	1,82 (0–5,55)	<1,0	<1,0	Transportation…, 2003; AMAP, 2007
Phe/Ant	1,17 (0,40–7,81)	<10,0	>15,0	Baumard et al., 1998; Yanker et al., 2002
Flu/Py	1,21 (0,33–3,51)	>1,0	<1,0	Baumard et al., 1998; Yanker et al., 2002, 2012
Flu/(Flu +Py)	0,43 (0,18–0,75)	<0,5	>0,5	Yunker et al. 2002; 2012
Py/BaP	3,26 (1,90–6,44)	<1,0	>1,0	Soclo, 2000
Ant/(Ant+Phe)	0,54 (0,11– 0,71)	>0,1	<0,1	Yunker et al. 2012
∑(2-4)/∑(5-6)	41,46 (9,08–83,72)	<1,0	>1,0	Soclo, 2000

was accounted for by TrPhe and BaP, 34% and 45%, respectively. Both compounds are mainly the product of incomplete combustion processes in the atmosphere of engine exhaust gases, whose compounds appear later in the hydrosphere.

Calculated diagnostic molecular indices that allow one to identify potential sources of PAH intake in the bottom sediments of Lake Donuzlav are shown in Table 1.

As it was mentioned above, the presence of elevated concentrations of Nap and its methylated homologues is a sign of oil pollution (Nemirovskaya, 2013; Yan et al., 2019). Moreover, in the case of fresh oil input, the Nap/2mNap ratio should be lower than 1, since methylated compounds predominate in oil (AMAP, 2007). On average in the water area, this ratio exceeded 1 (Table 1), which is most likely a consequence of the more active microbial destruction of 2-methylnaphthalene, compared with its holonuclear homologue (Wammer and Peters, 2005). The values of this index were below 1 at Stations 6 and 10, where elevated levels of PAH were observed, which indicates the main source of formation of such levels, i.e. the input of oil and petroleum products. The ratio of light and heavy PAHs also indicates the predominance of oil pollution (Table 1).

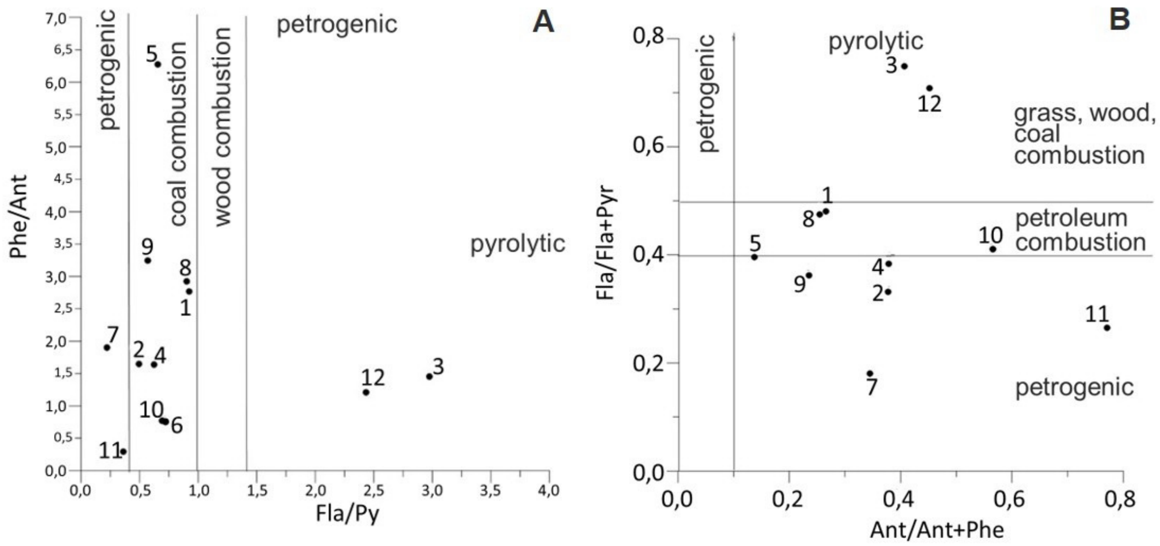

Fig. 5. Graph of double PAH ratios: A –Fla/RuiRhe/Ant; B –Ant/ (Ant+Phe) and Fla/ (Fla+Py).

The ratios of Py/BaP and Ant/Ant+Phe in all cases indicated the predominance of petrogenic components in pollution. The Phe/Ant ratio shows a significant presence of pyrolytic components.

As a result, the use of a single diagnostic ratio of PAHs may not be sufficient to determine the source of oil input. Therefore, researchers used graphs of the ratio of PAH biomarkers with two sources or cross graphs to differentiate PAH sources (Yunker et al. 2002, 2012, 2015; Wagener et. al., 2010). The ratios marked on the abscissa axis (Fig. 5) are completely in the range of values characteristic of the pyrolytic pathway of PAH formation. In accordance with the indices located along the ordinate axis, the values obtained do not always unequivocally characterize the sources of PAH input. The cross graphs in Fig. 5 show, judging by the profiles obtained, that at most stations (Stations 2, 4, 5, 7, 9, 11), we can talk about the mixed (both petrogenic and pyrogenic) origin of PAHs. At Stations 6 and 10, the predominant source of pyrogenic PAHs was burning, judging by the Fla/Py ratio of oil, and by the Fla/ (Fla+Py) ratio of wood. At Stations 3 and 12, the most likely source of PAHs was coal burning. Profiles of Stations 1 and 8 may be associated with the burning of oil (0,4<Fla/ (Fla+Py) <0,5), and Fla/Py>1,5 showed the presence of crude oil.

All analyzed indices indicate a mixed origin of PAHs in the bottom sediments of Lake Donuzlav. Some inconsistencies in the results of the index analysis may be related to both the variety of sources of PAH input and their further degradation in the environment. It should be noted that there was a close correlation between the content of all polyarenes, averaging 0,88, not falling below 0,55 in the case of BaP and 2mNap, which have different natures. The presence of geochemical relationships between polyarenes coming from different sources is probably due to the functioning of natural mechanisms for the conversion of pollutants, which serves to restore the dynamic equilibrium of the system (Nemirovskaya, 2013). Accordingly, the PAH mixture recorded during the study is the result of both natural and anthropogenic processes of genesis and the destruction of this class of organic compounds.

In general, Lake Donuzlav is a water body undergoing anthropogenic stress, which affects the state of its bottom sediments. The detected PAH contamination of the bottom sediments of the reservoir has traces of both pyrolytic and petrogenic compounds, which is typical for areas with human economic activity. It is possible to identify individual areas where anthropogenic impact is critical. There, the indicators of the content of toxicants are ten times higher than the background ones. As to these areas, in particular, Stations 6 and 10 with elevated levels of PAH content, it is possible to state the presence of fresh oil pollution as the main source of PAH. At other stations, oil pollution is present, but it is of a chronic nature, and its components are partially transformed. The results of our research give the idea on the content of PAHs in the coastal areas of Lake Donuzlav. At the same time, it should be noted that the level of pollution of bottom sediments in the middle part of the lake is greater compared to other parts of the water body, which is due to the higher sorption capacity of the marine bottom sediments containing a larger amount of fine fraction (Zhugaylo et al., 2018). Thus, in deeper water areas adjacent to the studied ones, an increased content of PAH can be expected. At the same time, areas with higher levels of PAH in bottom sediments are located near the large mussel-oyster farm. Based on this, it is possible to recommend studying the content of this class of substances in the tissues of seafood grown on the mariculture farms mentioned.

CONCLUSIONS

The average content of ∑PAH in the water area was 806±380 ng/g, while the range of values of this indicator was 34–4036 ng/g. At five out of ten stations in Lake Donuzlav, the average figures for the Black Sea were exceeded. These stations are grouped on both banks in the inner part of the water body. No reliable correlation has been revealed of the PAH content with the physico-chemical parameters (pH, Eh) of bottom sediments.

Fourteen PAHs have been identified in the bottom sediments of Lake Donuzlav: Nap, 2mNap, Flu, Phe, Ant, Fla, Py, TrPhe, Chr, BbF, BkF, BaP, DBA, BghiP. The main share is accounted for by binuclear Nap and 2mNap, which indicate the presence of fresh oil pollution. The average proportion of these compounds in the water body was 60 ± 5%, and at stations with elevated levels of ∑PAH it was 74 ± 4%. There was a close correlation between the content of all polyarenes, the correlation coefficient of which averaged 0,88. The presence of geochemical relationships between polyarenes coming from different sources was probably due to the functioning of natural mechanisms for the conversion of pollutants, which served to restore the dynamic balance of the system.

On average in the water area, the share of benz(a)pyrene BaP, which characterizes the toxicity of bottom sediments, accounted for about 1% **∑**PAH ranging over 0,3–1,7 %. The conditional standard, 25 ng/g, was exceeded at the stations where the maximum PAH values were registered. The obtained values of toxic equivalents of bottom sediments ranged from 0.6 – 62,5 and their growth was closely associated with an increase in the total PAH content in bottom sediments (r=0,98). The main contribution to the formation of toxicity of bottom sediments was made by pyrogenic TrPhe and BaP, 34 % and 45 %, respectively.

Lake Donuzlav is a water body undergoing anthropogenic stress, which affects the state of its bottom sediments. The detected PAH contamination of the bottom sediments of the reservoir has traces of both pyrolytic and petrogenic compounds, which is typical for areas with human economic activity. It is possible to identify individual areas where anthropogenic impact is critical. There, the concentrations of toxicants are orders of magnitude higher than the background ones. For these areas, the fresh oil pollution should be considered as the main source of PAHs. However, at other stations, the available oil pollution is of a chronic nature, moreover, its components have undergone some transformation processes.

GRANT SUPPORT DETAILS

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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