

## Pollution of the Volga River basin with petroleum products in the Astrakhan region, Russia

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### ABSTRACT

Water bodies of the delta part of the Lower Volga are extremely important for preservation of biodiversity as feeding and breeding grounds for valuable fish species, including sturgeon species. Meanwhile, the anthropogenic load on these water ecosystems is increasing alongside the growth of oil and gas industry. Thus, the aim of this study is to dynamically assess the pollution of water bodies of the prime grade of fishery importance with petroleum products throughout 2014-2018. The objects of this study are the water bodies exposed to anthropogenic impact of both operating enterprises and formerly active industrial facilities. The content of petroleum products in the samples of water and benthos deposits was defined in accredited laboratories as prescribed by Federal Environment Protection Regulatory Documents (PND F) 14.1:2:4.128-98 and 16.1:2.2.22-98. According to the results of the study, it was found that the content of petroleum products in water exceeds the maximum permitted concentrations (MPC) in all monitored sites, its highest value is 4.2 times the MPC in Kizan River in the vicinity of Sokolovskie Neftyanые Yamy (Sokolovsky Oil Pits), a formerly active industrial facility. Here, the maximum level of pollution of benthos deposits with petroleum products (18719.3 mg kg<sup>-1</sup>) was recorded, and, as a consequence, the degradation of zoobenthos diversity with oligochaeta remaining its only representative was observed.

**Keywords:** Caspian region; Hydrosystem; Sokolovsky Oil Pits; Zoobenthos.

**Article type:** Research Article.

### INTRODUCTION

Anthropogenic pollution of water bodies, including benthic deposits, may seriously jeopardize the ecological systems and human health since pollutants are transferred through the food chains or directly when using untreated water (Shao *et al.* 2020, Ameri Siahouei *et al.* 2020). Monitoring studies for assessing anthropogenic pollution of water bodies are held everywhere in the world (Zabolotskikh & Vasilyev 2017; Islam *et al.* 2018; Costa-Böddekeret *et al.* 2020; Fallah *et al.* 2021). Special attention is paid to the actively developing industrial areas (Domnina *et al.* 2014, Deng *et al.* 2020), water storage reservoirs and intensive agriculture districts (Ojeda Olivares 2020), as well as significant natural areas (nature reserves, wildlife preserves, etc.) (Aligadzhiev *et al.* 2016). The Astrakhan region represents Russia in the strategically-significant Caspian region. In the context of growing energy consumption worldwide the importance of this region as one of the largest sources of raw hydrocarbons is constantly increasing. Herewith, the anthropogenic load on hydro systems of the Lower Volga River, represented by water bodies of the prime grade of fishery importance in the delta part of the river, grows, too (Bazhenova *et al.* 2012). There are about 7000 monitored water discharge outlets, or separate (point) sources of pollution in the Volga River basin. Annually they discharge circa 2.5 cubic kilometers (km<sup>3</sup>) of polluted wastewaters (Russian Ministry of Natural Resources and Ecology 2019).

In spite of the fact that the share of petroleum hydrocarbons in the general structure of water pollution within the borders of the Astrakhan region amounts to 2 percent only (Nature Management and Environment Protection Service of the Astrakhan region 2020), the accelerated development of oil exploration and production may result in its increasing impact on the quality of water and on hydrosystems taken as a whole. In the Lower Volga streams within the boundaries of the Astrakhan region high concentrations of hydrocarbons were revealed by researches carried out in various time periods (Katunin *et al.* 1998, Brekhovskih *et al.* 2011). A number of research works indicates high background concentrations of hydrocarbons in the region (Ostrovskaya *et al.* 2016). Herewith, a tendency of pollutant concentration growth is observed, in the direction from the Volga river bed to the head of the delta (Makarova *et al.* 2009, Brekhovskih & Ostrovskaya 2017), however hydrocarbons concentration decreases downstream from the city of Astrakhan (Nemirovskaya & Lisitsyn 2011). The formerly active business facilities pose a special threat by producing a long-lasting negative impact on water ecosystems (Melnik *et al.* 2015). The aim of this research is to dynamically assess the oil pollution of main water currents within the boundaries of the Astrakhan region throughout 2014-2018, and to study the outcomes of long-lasting impact of such pollution on water ecosystems.

## MATERIALS AND METHODS

The subject of the study are the selected river sites in the delta part of the Lower Volga within the borders of the Astrakhan region (the main bed of the Volga River, Akhtuba, Buzan, Krivaya Bolda, Kamyzyak Arms), which are exposed to anthropogenic load, including that from industrial enterprises of fuel and energy sector, to the utmost. In order to study the outcomes of the long lasting impact on the hydrosystem, a facility of former business activity – Sokolovskie Neftyanye Yamy (Sokolovsky Oil Pits), found in the shore section of Kizan River, in its water-protection zone, was used. The study was carried out in five monitoring spots: control (recreation zone, upstream at a distance of 150 m); by Oil Pits №1; № 2; at distances of 500 m and 1000 m down the stream (Fig. 1). The content of petroleum products in the samples of water and benthos deposits was defined in accredited laboratories of Federal State Institution “SevKasptechmordirekziya” and the testing laboratory of ecological control of Federal State Budgetary Institution “State Center of Agrochemical Service “Astrakhanskiy”, as prescribed by PND F 14.1:2:4.128-98 and 16.1:2.2.22-98. The assessment of the condition of the Kizan River macrozoobenthos structure in Sokolovsky Oil Pits location was held in accordance with commonly-accepted methodologies, therewith the indicators of species abundance and biomass, as well as the proportion of various phyla of benthos communities were used (Vinberg & Lavrent'ev 1984; Abakumov *et al.* 1983). Water quality assessment criteria and methods were picked on the ground of the analysis of the statistically- processed study results. The Student's t-test was used as a criterion for reliability of the results, and the standard errors of the mean were used as the errors of the mean.

## RESULTS

The average content of petroleum products in the Volga River (a water body of the prime grade of fishery importance) within the period between 2014 and 2018 amounted to 0.091 milligram per cubic decimeter ( $\text{mg dm}^{-3}$ ), which corresponds to 1.8 times of maximum permissible concentration (MPC). The maximum content of petroleum products was observed here in 2014 and reached  $0.101 \text{ mg dm}^{-3}$ , which is 2.02 times higher than MPC. The minimum value of the content of petroleum products was registered in 2016, equal to  $0.078 \text{ mg dm}^{-3}$  (1.56 times higher than MPC; Fig. 2). The anthropogenic load upon this water area is impressive, the list of water-consuming enterprises includes Federal State Budgetary Institution “Department of Astrakhanmeliovodhoz”, Municipal Unitary Enterprise of the city of Astrakhan “Vodokanal”, LLC “Agro-industrial complex “Astrakhanskiy”, LLC “LUKOIL-Astrakhanenergo” and so on. The average content of petroleum products in the water area of Akhtuba River within the period between 2014 and 2018 was  $0.089 \text{ mg dm}^{-3}$  (1.78 times higher than MPC). The highest value was recorded in 2018, i.e.,  $0.120 \text{ mg dm}^{-3}$  (2.4 times the MPC), while the minimum was observed in 2017, equal to  $0.069 \text{ mg dm}^{-3}$ , slightly (1.38 times) higher than MPC (Fig. 3). The average content of petroleum products in Buzan River during the period between 2014 and 2018 was  $0.115 \text{ mg dm}^{-3}$  which was much higher than the maximum permissible concentration for water bodies of fishery importance (2.3 times higher). The highest content was recorded here in 2015 ( $0.129 \text{ mg dm}^{-3}$ ), 2.58 times higher than the MPC while the lowest in 2017 (equal to  $0.103 \text{ mg dm}^{-3}$ ), 2.06 times higher than MPC (Fig. 4). The high content of petroleum



products in Buzan River is mainly due to industrial activities of one of the largest transport enterprises in the region, i.e., LLC “Terminal-Buzan”, which uses the water area of 0.3154 km<sup>2</sup> and handles cargoes.

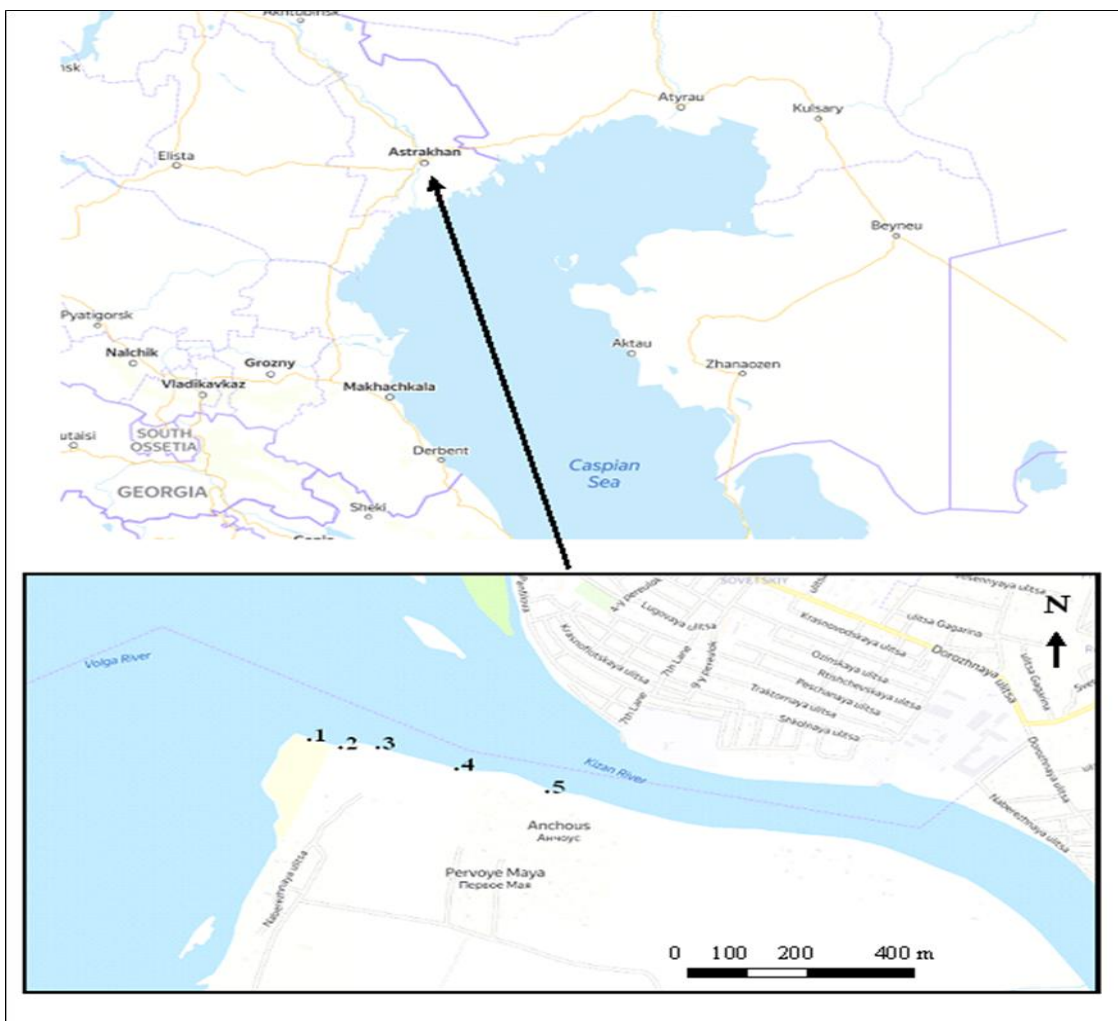


Fig. 1. Geographical location of the study area and the monitoring spots.

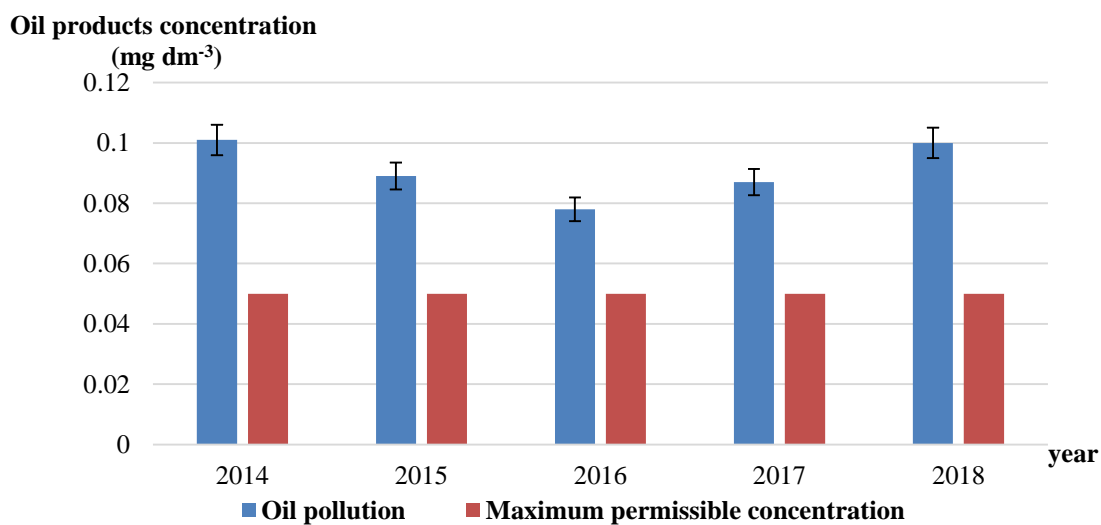


Fig. 2. Dynamics of the Volga River pollution with petroleum products within the borders of the Astrakhan region in 2014-2018.

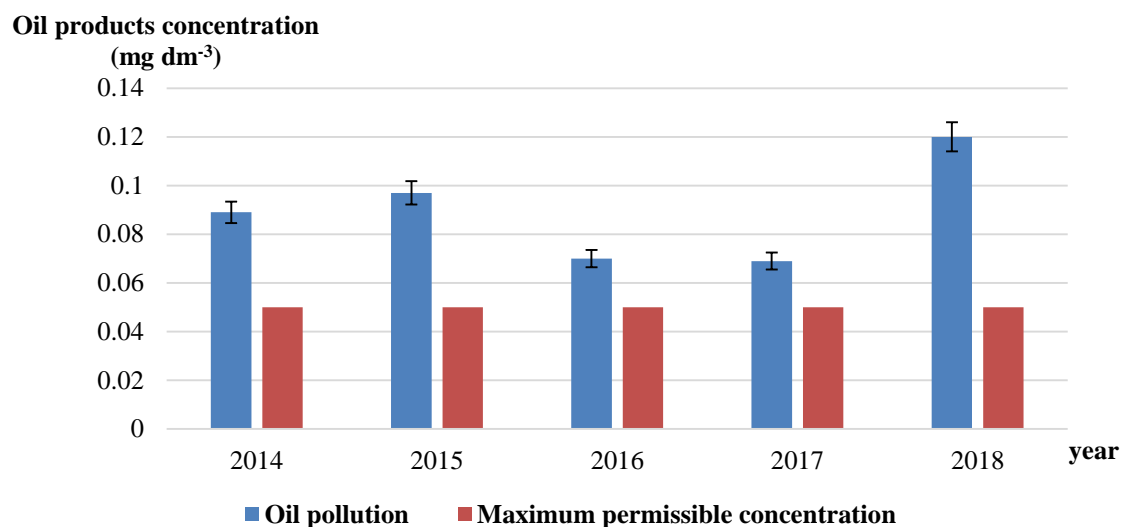


Fig. 3. Dynamics of the Akhtuba River pollution with petroleum products in 2014-2018.

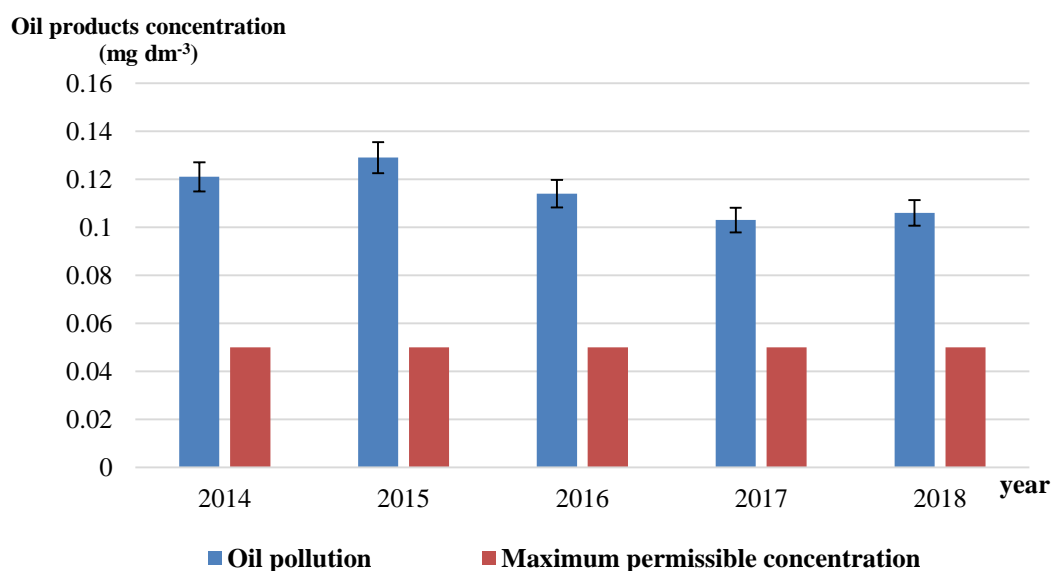
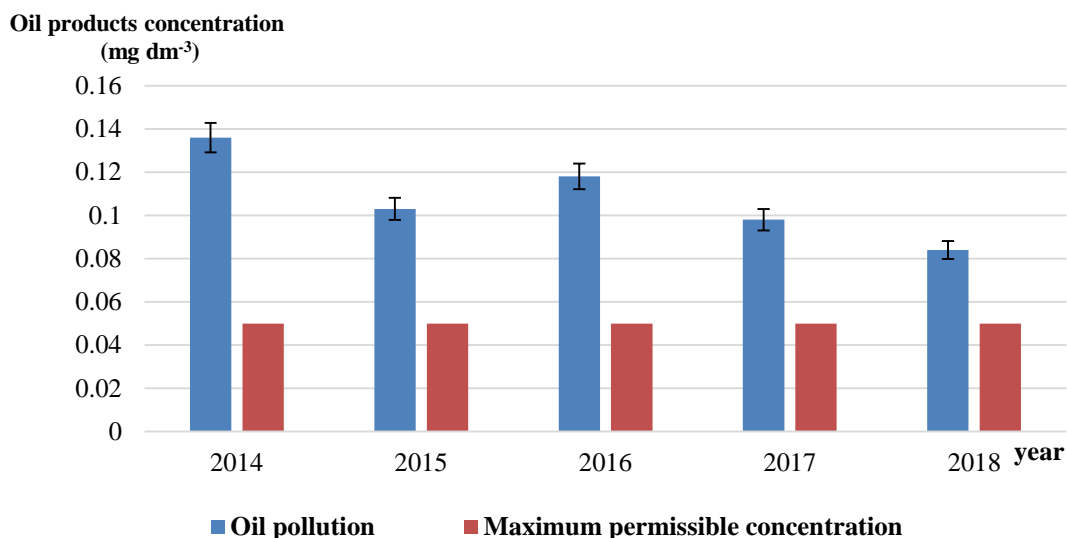


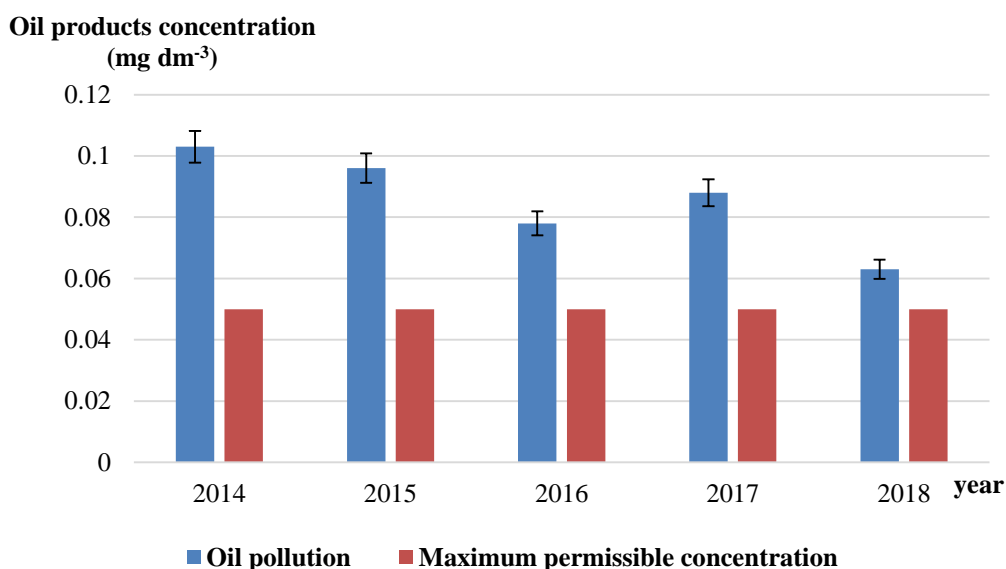
Fig. 4. Dynamics of the Buzan River pollution with petroleum products in 2014-2018.

The analysis of the diagram allows us to conclude that the average content of petroleum products in the samples taken from Krivaya Bolda River during the period between 2014 and 2018 was 0.108 mg dm<sup>-3</sup>, exceeding the maximum permissible concentration by 2.16 times. The maximum average content in the aforementioned river was observed in 2014 (equal to 0.136 mg dm<sup>-3</sup>), which was 2.72 times higher than the MPC, while the minimum in 2018 (0.083 mg dm<sup>-3</sup>), 1.68 times higher than the MPC set for water bodies of fishery importance (Fig. 5). The high rate of pollution in the waters of Bolda River is in large part associated with the activities of the Astrakhan Ship-repairing plant "Zvezdochka" which occupies 10,000 m<sup>2</sup> of the river water area. The plant has been carrying its activities on maintenance and equipping the vessels of the Russian Navy, as well as the ship construction and repair of electrical and mechanical devices since 1984. The average content of petroleum products in Kamyzyak River in 2014–2018 was 0.086 mg dm<sup>-3</sup>, 1.72 times higher than MPC. The highest content in this river was observed in 2014, i.e., 0.103 mg dm<sup>-3</sup>, which was 2.06 times higher than MPC, while the lowest was in 2018 (equal to 0.063 mg dm<sup>-3</sup>), 1.26 times higher than MPC (Fig. 6). The Kamyzyak Arm is of a great fishery importance for the Astrakhan region since this is a place for reproduction and growing of valuable and

commercially-important fish species. The tourism sector based on recreational fishing and other water activities is actively developing in this district.



**Fig. 5.** Dynamics of the Krivaya Bolda River pollution with petroleum products in 2014-2018.



**Fig. 6.** Dynamics of the Kamyzyak Arm pollution with petroleum products in 2014-2018.

The Sokolovsky Oil Pits, a facility of accumulated environmental damage found in the water conservation zone of Kizan River (an arm of the Volga River) are an example of negative impact of oil industry on hydroecosystems in Astrakhan region. This facility started operating at the beginning of the past century, when oil business was just emerging in Astrakhan Province. After numerous changes in ownership, oil pits were abandoned, and their ruined walls were saturated with petroleum products, afterward the formed shore-line of the river was a source of the petroleum products entry into the water basin for many decades. According to the results of the present study, the chemical contamination level of the soils in the shore-line with allows referring them to the “dangerous” and “extremely dangerous” categories. For such soils, the sanitary norms recommend taking measures in order to decrease the level of contamination and to establish and carry out control after the content of toxicants in soils, surface and underground waters (Melnik & Drozdova 2017).

Administratively, the contaminated territory of Sokolovsky Oil Pits facility is found in Privolzhskiy district of Astrakhan region, on the lands of a settlement within the borders of shore-line protecting (50 m) and water

conservation (200 m) zones of Kizan River, which is a source of water supply for economic and household purposes, and at the same time a waterway of the prime grade of fishery importance. The territory of the facility is surrounded by functional zones of agricultural and recreational designation. Alongside its downstream there are dacha settlements, the Kizan sturgeon fish-breeding plant, children's camps and residential areas.

Sokolovsky Oil Pits consist of two pits with the total area of 17536 m<sup>2</sup>: oil pit № 1 occupies 9016 m<sup>2</sup>, whilst № 2 occupies 8520 m<sup>2</sup>. The length of the polluted shore-line is approximately 300 m and the depth of contamination with petroleum products is up to 10 m. According to preliminary calculations, the total area of the water polluted by petroleum products was 30 000 m<sup>2</sup> (Vasileva *et al.* 2019).

The results of the surface waters analyses prove the high level of contamination of the river basin with petroleum products (Fig. 7).

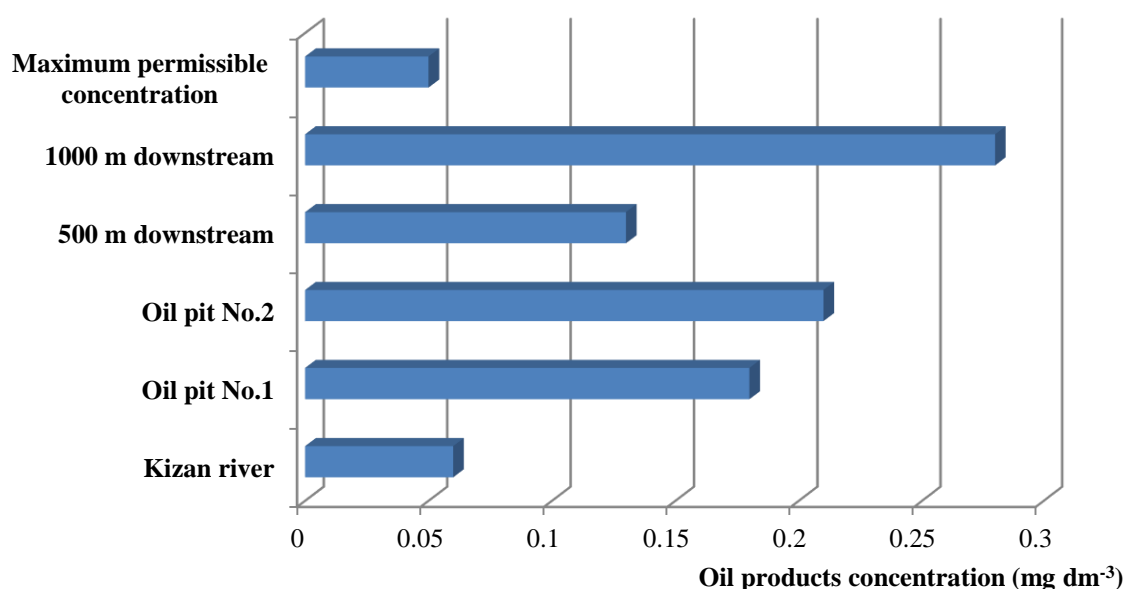


Fig. 7. Contamination of Kizan River with petroleum products beside the Sokolovsky Oil Pits.

Fig. 7 shows that the maximum content of petroleum products (5.6 times higher than MPC) was recorded at downstream of Kizan River at a distance of 1000 m from oil pits, which is apparently conditioned by various vertical and horizontal under-currents. The petroleum products concentrations were 3.6 times higher than MPC by Oil Pit № 1 and 4.2 times by Oil Pit № 2. The 1.2 times-MPC exceedance was recorded in the control sample even (recreation area – beach). In spite of the fact that the recreation area is found upstream at a distance greater than 150-200 m from Sokolovsky Oil Pits, the steadiness of pollution with oil contributes to expanding contaminated area at both downstream and upstream. The chemical composition of benthal deposits, used as a representative indicator of pollution, is an important criterion for assessing the ecological condition of a water body. Fig.8 represents the results of benthal deposits study. The data in Fig. 8 illustrate that the maximum content of petroleum products (18719.3 mg kg<sup>-1</sup>) in benthal deposits was recorded at Oil Pit № 2, representing 36 times higher than the control sample. The minimum value (474.8 mg kg<sup>-1</sup>) was recorded at a distance of 1000 m downstream from the source of pollution, while within the control zone (recreation area) the value was somewhat higher (1.1 times). When assessing the condition of streams, the majority of biological classifications and bioindication systems rely on the analysis of benthos communities (Yanygina 2014). The present study revealed the presence of oligochaeta representatives directly in the areas where oil pits are found. Essentially, they were the only representatives of zoobenthos within the whole period of the study, and solely in September we recorded the presence of crustaceans: *Niphargoides robustoides* and *N. deminutus* (Yessenamanova *et al.* 2020). The received data are confirmed by studies conducted by other hydrobiologists: Oligochaeta is one of the groups that are most resistant to oil pollution, and actively participate in the process of detoxifying petroleum products in benthal deposits (Vorob'ev 2006; Holmogorova 2007).

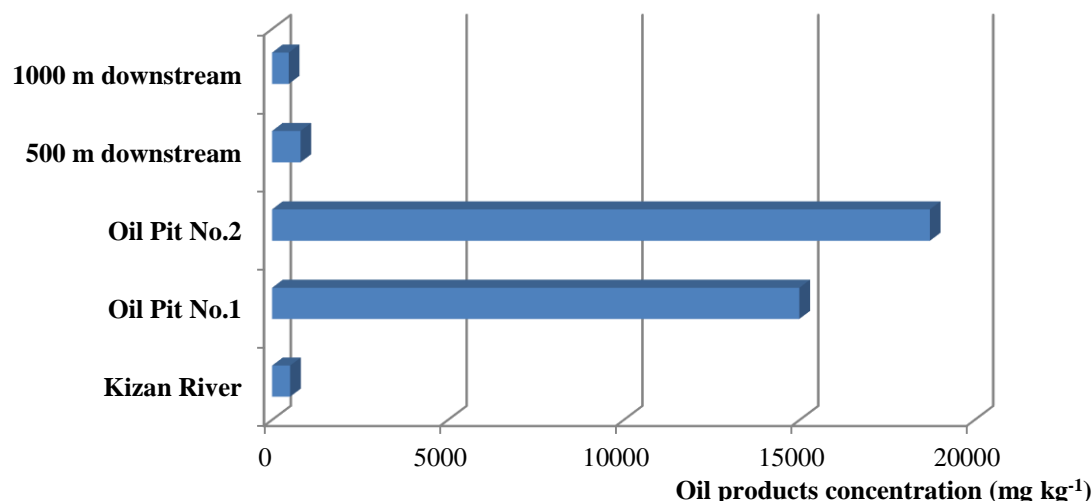


Fig. 8. The content of petroleum products in benthal deposits in Kizan River beside Sokolovsky Oil Pits (the MP Crates).

## DISCUSSION

Oil pollution is distinguished as a separate type of pollution due to the complex composition of oil (hundreds of various hydrocarbon compounds and heterocyclic compounds containing nitrogen, oxygen, sulfur and microelements). Compounds constituting oil have various properties, including solubility and reactivity. Many oil components are toxic. The long-lasting chronic exposure to even low oil concentrations poses an environmental hazard (Kogevin 2001). The problem of pollution of the Volga River basin with oil existed already in the late 19<sup>th</sup> century due to leaks which occurred while transporting the Caspian oil.

Oil and petroleum products form a slick on the surface of water bodies thus impeding normal gas exchange between water and the atmosphere, as well as preventing the access of sunlight to phytoplankton, and also inhibiting photosynthesis. Light fractions dissolve in water and destroy phytoplankton, while heavy fractions settle to the bottom and destroy benthos. One gram of oil, once in a reservoir, pollutes 10 m<sup>3</sup> water. Ten grams of oil, according to some scientists, or 1 dm<sup>3</sup> of oil, according to some others, make 1 m<sup>3</sup> of water highly toxic, unsuitable not only for aquatic organisms, but also for household and drinking use (Lukyanenko *et al.* 2020). As stated in a number of studies, the concentrations of pollutants in water and in benthos deposits may differ by several times (Ostrovskaya *et al.* 2009; Nemirovskaya & Lisitsyn 2011). As a rule, the heavy oil fractions quickly settle down to the bottom of the water body, while in the soil the lighter ones are sorbed on solid particles and, as a result, settle down as well (Kurapov 2006). Benthos deposits are capable of sorption, they may accumulate pollutants for a long time. On the one hand, these processes contribute to the self-purification of water bodies, however, when a certain assimilation potential is exceeded, secondary pollution becomes possible, even in the absence of visible reasons (for example, excess discharge of polluted wastewater). Secondary pollution in this case may be caused by turbidity of the water body, alterations in the hydrological regime, and the influx of additional pollution.

The pollution of bottom sediments by the oil and petroleum products leads to the restructuring benthic communities in both marine and freshwater ecosystems (Milovidova & Kiryukhina 1985; Ruzanova & Vorobiev 1999). At the same time, benthic organisms are much more resistant to oil pollution than plankton ones, which quickly die in oil concentrations in the range of 0.01 - 0.001 mg L<sup>-1</sup> (Kalugina *et al.* 1967; Milovidova 1974). Many structural characteristics of macrozoobenthos - species diversity, abundance, biomass, depend both on the physical properties of the soil and the amount of easily-digestible organic matter converted by bacteria in it, and on the quality of sediments. The quality criteria for bottom sediments should be based on indicators that take into account the level of quantitative development of zoobenthos. Soils with signs of oil pollution are characterized by a poor species composition with a high number and biomass of pollution-tolerant forms, and with severe chronic pollution, the whole community is suppressed, including resistant forms (Vorobiev 2006).

The results of our study confirm this finding too, accordingly, the only representatives of benthos in the area with the maximum level of pollution of bottom sediments with oil products (18719.3 mg kg<sup>-1</sup>) are those of the class Oligochaeta.

The analysis of a water body pollution should be carried out through a comprehensive study on the pollutant concentration in water and in the sediments, and also special attention should be paid to areas subjected to long-term exposure to the pollutant. For each of the water flows under examination, there is a stable excess of the maximum permissible concentration of oil products associated with several reasons. The first reason are the historically high background concentrations of this pollutant typical for the region (Ostrovskaya *et al.* 2016). The values which we use as background values are 0.06-0.07 mg dm<sup>-3</sup>. However, the influence of the anthropogenic factor is the main reason: accidental spills during the transportation of hydrocarbon raw materials, activities for the disinfection and cleaning vessels, transit runoff of the pollutant from other areas located upstream of the Volga River, as well as facilities of former business activities.

## CONCLUSION

In this study, it has been discovered that throughout the whole time period between 2014 and 2018 the petroleum product concentrations in water were higher than the maximum permissible concentrations, averaged 0.115 mg dm<sup>-3</sup> (2.3 times higher than MPC for fish-breeding water bodies), the maximum value was recorded in Kizan River by a formerly-active business facility, i.e., Sokolovsky Oil Pits.

The most contaminated components of the local hydrosystem were the benthal deposits, where the petroleum product concentrations were 36 times higher than the control sample (recreation area). Therefore, we observed the depauperization of zoobenthos biodiversity in the area where oil pits were found. The only zoobenthos representatives here were oligochaeta that are most resistant to oil pollution, and participate actively in the process of detoxifying petroleum products in benthal deposits. The problem of oil pollution requires further studies, systematic monitoring and immediate decision-making. Oil pollution is distinguished as a specific type of pollution due to complex composition of oil and its immediate penetration into environment. Its environmental consequences may cause irreparable damage to biodiversity of water bodies of the prime grade of fishery importance in the delta part of the Lower Volga.

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