

Distribution of oil products in bottom sediments of the Irtysh River in the urban area

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Abstract. It was shown that urbanized territories contribute to the pollution of bottom sediments of a watercourse by the example of a large river. It was established that the places of localization of the infrastructure of oil refineries, even after their transfer, continue to pollute the environment with oil products, with a periodic excess of the maximum permissible concentration of $20 \text{ mg} \cdot \text{kg}^{-1}$. The dynamics of the distribution of oil products in the bottom sediments of a watercourse depends on the meandering of the river, the presence of zones of active operation of the fleet and time of year. The smallest concentrations of oil products was observed at the site located upstream from the studied urbanized area adjacent to the city.

1 Introduction

The state of water bodies in the Ob-Irtysh basin is determined by both the natural features of the hydrographic network and economic activity [1, 2]. The main problems in the field of protection and use of water resources of the Irtysh river basin are mainly their low quality and water level. The volume of pollution and the volume of water withdrawal from the Irtysh River have increased over the past 10-15 years. This is due to the development of industry in China, Russia, often without the adequate capacity of treatment facilities. In the south of the Tyumen region in the Irtysh basin, a number of large oil fields have been discovered, which are start operating. It is worth noting that oil companies consider [3–9] the main polluting source of oil and its derivatives in the environment, including transportation [10–13]. Almost 11 million people live in the Irtysh River basin within the Russian Federation, including 75% in cities and urban settlements, 25% in rural areas [14].

The main sources of pollutants of the Irtysh River are companies of oil production and oil refining, engineering, metallurgy, construction, forestry, woodworking, weaving and food industries, the river fleet, communal services, as well as unorganized runoff from residential areas and farmland and cross-border transport from the territory of neighboring regions (Omsk, Sverdlovsk, Kurgan) and the states of China and Kazakhstan [2]. The main pollutants of water and bottom sediments of the Irtysh basin rivers are heavy metals, arsenic, oil products, phenols, biogens, ammonium and nitrite nitrogen, phosphates, iron, saprobic organic substances and stable organic pollutants [2].

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At the same time, the Irtysh River, as an important part of the Ob-Irtysh basin, has significant water biological resources, primarily fish - coregonids, sturgeons, cyprinids, percids and others. In the lower reaches of the Irtysh River there are riverbeds depression that an important role in saving the most valuable kind of fish [15]. The hydrobionts of the river are under a strong anthropogenic pressure - on the one hand, pollution, on the other - illegal (poaching) catch.

In this regard, the aim of the work is to investigate the content of oil products in bottom sediments as one of the priority pollutants in the lower reaches of the Irtysh River.

2 Material and methods

Investigations of the lower Irtysh river were carried out within the Tobolsk and Uvat districts of the Tyumen region during the open water period in 2012-2013 (Western Siberia, Russian Federation). The work was carried out on the site of the Irtysh River (length 179 km) from the village of Abalak to the village of Gornoslinkino. Samples of bottom sediments were taken by the Petersen grab with a capture area of 0.04 m², in the midstream and in the near-bank zones (on the left and right banks) from the motor boat. The total content of oil products was investigated by determining the mass fraction of oil products in bottom sediments by IR spectrometry. The studied section of the river and the location of the sampling sites are shown in Fig. 1. The analysis of the content of oil products was carried out with an indicator of maximum permissible concentration for fishery reservoirs (MPC_f), the value of which as 20 mg·kg⁻¹[16]. Samples were taken at seven sites:

Site No. 1. Located above the village Abalak, at coordinates 58.122276° N.I. 68.577807° E.I. The distance from the mouth of the river is 699 km, the soil on the left bank is clayey, on the midstream it is sandy, and on the right bank it is also sandy.

Site No. 2. Located upstream of the city of Tobolsk, 58.174568° N.I., 68.287937° E.I. The distance from the river mouth is 672 km, the soil on the left bank is silty-sandy, on the midstream and on the right bank it is sandy-silty.

Site No. 3. Located downstream of the city of Tobolsk, at coordinates 58.275693° N.I., 68.223981° E.I. The distance from the mouth of the river is 652 km, the soil on the left bank is muddy, on the midstream and on the right bank it is sandy-muddy.

Site No. 4. Located near of the village Medvedchikova, at coordinates 58.403406° N.I., 68.364583° E.I. The distance from the river mouth is 624 km, the soil along the left bank is muddy, on the midstream it is sandy-muddy, along the right bank also sandy mud.

Site No. 5. Located downstream of the village Bronnikova, at coordinates 58.495204° N.I., 68.394740° E.I. The distance from the river mouth is 608 km, the soil on the left bank is silty-sandy, on the midstream and on the right bank it is sandy-silty.

Site 6. Located near research station "Missiya", at coordinates 58.724245° N.I., 68.685276° E.I. The distance from the mouth of the river is 531 km, the soil on the left bank is sandy, on the midstream - sandy-silty, clayey-sandy on the right bank.

Site No. 7. Located downstream of the village Gornoslinkino, at coordinates 58.777045° N.I., 68.763704° E.I. The distance from the mouth of the river is 520 km, the soil on the left and right banks is clayey-clay, on the midstream - sandy-clay.

3 Results

As a result of studies, it was found that the bottom sediments of the Irtysh River are polluted with oil products. The total content of oil products in bottom sediments during the summer-autumn season of 2012, on average, was the highest in site No. 2 at 29.28 mg·kg⁻¹ and 73.34 mg·kg⁻¹ in summer and autumn, respectively (Fig. 2a).

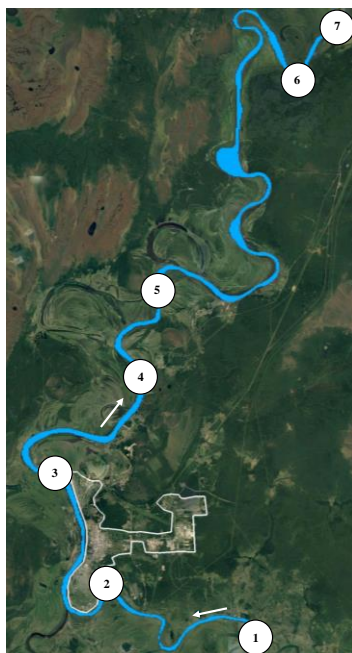


Fig. 1. Satellite image of the studied section of the Irtysh river (numbers - sampling lines, white outline - the borders of the city of Tobolsk, arrows indicate the direction of the river).

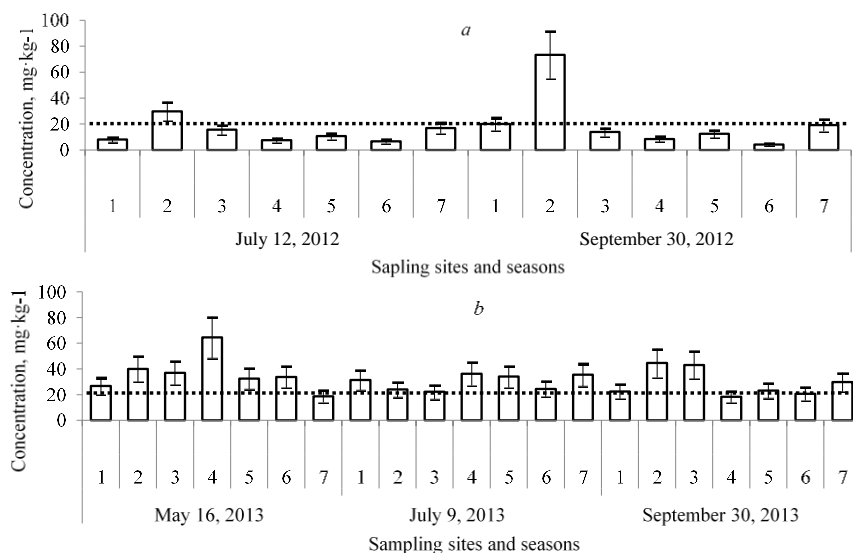


Fig. 2. Dynamics of the total content of oil products in the bottom sediments of the Irtysh River: *a* – 2012; *b* – 2013; (columns - average value, whiskers - average error, dotted line - MPC_f).

The maximum concentrations of petroleum products exceeding the MPC_f in summer were recorded on the midstream and in the right-bank part of the river at site No. 2 - 28 and 48 mg·kg⁻¹, respectively, at site No. 7 in the right-bank part of the river - 33.35 mg·kg⁻¹ (Table 1).

Table 1. The content of oil products ($\text{mg}\cdot\text{kg}^{-1}$) in bottom sediments at the sampling sites of the Irtysh River, 2012-2013.

Sampling points and seasons*			Sampling sites						
			1	2	3	4	5	6	7
a	2012	1	13.34	13.34	6.67	6.67	6.67	6.67	4.00
		2	40.02	20.01	8.00	4.00	4.00	4.67	4.00
	2013	3	33.35	40.02	32.00	46.69	32.00	28.00	4.00
		4	32.75	33.50	33.00	42.00	39.50	14.00	31.50
		5	31.50	37.70	46.00	15.00	37.50	14.00	40.10
b	2012	1	6.67	28.00	20.01	8.00	13.34	6.67	13.34
		2	13.34	80.00	13.34	13.34	20.01	4.00	20.00
	2013	3	26.68	40.02	32.00	73.37	32.00	33.33	12.00
		4	28.00	30.00	28.00	18.00	35.00	29.50	30.00
		5	14.00	45.50	53.00	18.00	18.50	13.00	38.00
c	2012	1	4.00	48.00	20.01	8.00	12.00	6.67	33.35
		2	6.67	120.00	20.01	8.00	13.34	4.00	33.35
	2013	3	20.00	40.02	46.69	73.37	33.35	40.02	40.02
		4	33.50	8.50	5.50	48.50	27.50	29.50	45.00
		5	22.00	50.5	30.00	22.00	13.50	35.00	11.00

Note: a – left bank; b – midstream; c – right bank; 1 – July 12; 2 – September 30; 3 – May 16; 4 – July 9; 5 – September 30;

It should be noted that site No. 2 is located downstream the area where the oil depo was located until 2008, in the water area near of site No. 7 the river fleet is intensively developed and the river pier of floating cranes is located (Gornoslinkino village). In the autumn period, there was an increase in the concentration of oil products in the midstream in almost all sites, in the near bank areas only in certain areas, which is associated with leaching of oil products from the polluted floodplain areas with atmospheric precipitation.

The maximum excess was noted at site No. 2: the midstream - 4 MPC_f (80 mg·kg⁻¹), the right-bank part - 6 MPC_f (120 mg·kg⁻¹).

The excess of MPC_f was also noted in the left-bank part of the river at site No. 1 - 40.02 mg / kg (2 MPC), on the right-bank part of the river at site No. 7 - 33.35 mg·kg⁻¹ (1.5 MPC_f) (Fig. 2b).

During the *spring flood*, there was an increase in the concentration of oil products at the sites and, accordingly, the number of polluted sites increased. The average concentration values were in the range of 18.67-64.48 mg·kg⁻¹ (Fig. 2). The maximum was noted at site No. 4 - 73.37 mg·kg⁻¹ (the midstream and the right-bank part of the river), above this site there are several zones of river piers and ship-repair sections of the river fleet (Fig. 2b, Table 1).

The areas where maximum concentrations were observed that exceeded the MPC_f on average by 1.5–2.5 times are the midstream and the left-bank part of the river sites No. 1–6, and the right-bank part of the river sites No. 2–7 (Table 1).

During *summer*, the content of oil products in bottom sediments was on average 1.5-2 MPC_f; the left bank of the river at sites No. 1-5 and 7, in the midstream at the sites No. 1-3, 5-7, the right bank of the river, sites No. 1 and 4-7. Maximum pollution was observed at site No. 4 in the right-bank part of the river - 48.5 mg·kg⁻¹ (2.5 MPC_f) (Table 1).

In the *autumn period of 2013*, the excess of the MPC_f of oil products in bottom sediments also averaged 1.5-2 times, the concentration was in the range 18.33 - 44.57 mg·kg⁻¹. The most polluted sites were recorded on the midstream at site No. 3 - 53 mg·kg⁻¹, on the right bank part of the river, at site No. 2 - 50.5 mg·kg⁻¹. The MPC_f was not exceeded in the left-bank part of the river at sites No. 4, 6, on the midstream at sites No. 1, 4, 6, in the right bank at sites No. 5, 7 (Table 1).

4 Discussion

The pollution of the bottom sediments of the Irtysh river with specific toxic substances: oil products and heavy metals is associated with the operation of the river fleet, the transportation of oil products, the removal of pollutants from floodplain areas where various enterprises operate, as well as the discharge of polluted sewage into the catchment area of the Irtysh river. The main sources of pollution are [2, 3, 9] industrial companies, the river fleet, agricultural and domestic wastewater, in connection with which the water and bottom sediments of rivers are polluted with oil products.

It was established that under the influence of toxic substances, including oil products in hydroecosystems, changes occur at all levels of the organization: from molecular to ecosystem, significant in terms of environmental consequences for surface water bodies:

molecular - changes in the conformation and activity of enzymes, chromosomal and gene mutations, dysregulation of cellular metabolism, depletion of glycogen depots, hyperglycemia, weakened immunity, impaired lipid, protein and energy metabolism, etc. [12, 17-24];

organismic - decrease in growth rate and survival, morphological malformations, developmental abnormalities, behavior changes, worsening chemotaxis [6, 9, 24-37];

population - a decrease in fertility, a change in biomass, abundance, in particular, an abnormal “outbreak” of a species as an indicator of stability disturbances, changes in the size-weight, sexual, generative and spatial structure, death of the least stable individuals in the population [8, 10, 11, 28, 31, 32, 37-48];

biocenotic - a change in the species, size and trophic structure, type of dominance, violation of interspecific relationships and interpopulation relations [5, 8, 9, 11, 25, 38, 40-45, 47-51];

ecosystem - disruption of the material-energy cycle, imbalance of the biotic cycle, distortion of the information field, change in the direction of production-destruction processes, trophic status of water bodies, self-cleaning processes, unsuitability of the bottom substrate for recolonization [9, 10, 27, 38, 52-54];

In turn, the transboundary transport of pollutants from the southern and western parts of the basin also belongs to the main sources of pollution of the Irtysh River in the lower reaches

[2]. The largest number of determined pollutants in the territory of Russia comes from the Irtysh waters from Kazakhstan. Each year, a large number of basic ions are transferred to the territory of the Omsk region in the border section, which leads to increased mineralization of the Irtysh waters, both easily and difficult to oxidize organic substances, biogens (nitrogen, phosphorus, iron, silicon), specific organic toxicants (phenol, oil products, pesticides) and heavy metals.

In general, for the period 2008 - 2012 were brought from Kazakhstan to Russia: organic matter (1.48 million tons), mineral nitrogen (27.8 thousand tons), silicon (274 thousand tons), oil products (2.78 thousand tons) of copper compounds (295 tons), zinc (928 tons), volatile phenols (70.1 tons), Σ Dichlorodiphenyltrichloromethyl (DDT) (107.3 kg) and Σ Hexachlorocyclohexane (HCCH) (69.2 kg). The average annual amount of pollutants is shown in Table 2.

Table 2. The number of chemicals (thousand tons) transported by the Irtysh River through the border with Kazakhstan (village of Tatarka, Omsk Region).

Indicator	Year of observation							X*
	2004	2005	2006	2007	2008	2009	2010	
Organic matter	268	261	396	306	254	322	259	$\frac{254-396}{295}$
Copper	158	134	425	215	63.9	54.4	50.2	$\frac{50.2-425}{157.2}$
Zinc	184	97.4	318	395	250	148	133	$\frac{97.4-395}{218}$
Nikel	24.6	0	0	0	0	0	16.6	$\frac{0-24.6}{5.9}$
Chrome	25.7	17.9	12.9	26.3	14.7	4.13	9.64	$\frac{4.13-26.3}{15.9}$
Oil products	0.59	2.95	1.08	0.97	1.02	0.28	0.33	$\frac{0.28-2.95}{1.08}$
Phenol	23.7	21.7	30	27.2	28	13.4	17	$\frac{13.4-30.0}{23.0}$
Σ DDT	0.101	0.019	0.022	0.012	0	0.022	0.018	$\frac{0-0.101}{0.028}$
Σ HCCH	0.126	0.048	0.033	0.019	0.0017	0	0	$\frac{0-0.126}{0.033}$

Note: numerator-range of values, denominator-average over the years [2, 55]

The monitoring results of the Irtysh River from the border with Kazakhstan to the mouth in 2003 showed that over the entire length, the content of pollutants exceeds the MPC: for Fe - by 1.5-10, Mn - by 7-22, Cu - by 4.8-35, Zn - 1.5-20, oil products - 1.2-8.5, phenols - 2.2-3.8 times. In the site of the village of Tatarka - the border with Kazakhstan: oil products - 6 MPC, Fe and Cu - 4 MPC, Zu - 2 MPC, Mn - 16 MPC [55].

Possible sources of contaminants to the Irtysh River in the area under study are piers and ship-repair sections of the river fleet, releases of sewage treatment facilities in the city of Tobolsk, a site in the floodplain of the river, where until 2008 Sibneft oil depot was located

(right bank of site No. 2), treatment the construction of industrial companies located near the Aremzyanka River (1st-order right-bank inflow), Omsk Oil Refinery Plant, Omsk Tires Plant, Pavlodar Plant “Chemical Industry”, etc.

The main pollutants in the area from Tobolsk to Khanty-Mansiysk are also oil products, phenols, compounds Fe, Mn, Cu, Zn, ammonium nitrogen, the average annual concentration of which exceeds the MPC by 2-18 times. The maximum concentration in the river's water in this section according to 2007 data [2, 55] amounted to: hardly oxidized organic matter (according to the chemical oxygen demand) - 5 MPC; ammonium nitrogen - 3 MPC; nitrite nitrogen – 10.5 MPC; compounds of Fe - 27 MPC; copper - 26 MPC; Zn - 7 MPC; Mn - 30 MPC; oil products - 48 MPC [2, 55].

According to experts [56], Irtysh in terms of pollution is in 3-rd place in the Russian Federation, after the Volga and Kama, and the main pollutants of Lower Irtysh are phenols, oil products, ammonia and nitrite nitrogen, to a lesser extent pesticides, heavy metal ions [57].

5 Conclusion

For samples of bottom sediments from different points of the same section, there is a significant difference in the content of oil products. The distribution of oil products in the bottom sediments of the Irtysh River, in all probability, is due to their flushing and removal from the polluted floodplain areas located on the catchment area of the river. In addition, the distribution of oil products may be associated with the features of the river flow (meandering), the influence of anthropogenic load (shipping), the presence of silt inclusions, prone to the accumulation of organic matter and the location of potential sources of pollution. The dynamics of the concentration of oil products at the river sites is caused by channel erosion processes and sedimentation of solid runoff with polluted soil particles. The urbanized territory of the studied section of the Irtysh River, in addition to the level of pollutants in the watercourse, contributes to the performance of oil products in bottom sediments with periodic excesses of maximum permissible concentrations

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