© LARISA P. PANICHEVA[1], TATYANA A. KREMLEVA[2], SVETLANA S. VOLKOVA[3]

[1]Dr. Chem. Sci., Professor,
Department of Organic and Ecological Chemistry, Institute of Physics and Chemistry
Tyumen State University (Tyumen)

[2]Cand. Chem. Sci , Associate Professor,
Department of Organic and Ecological Chemistry,
Institute of Physics and Chemistry, Tyumen State University (Tyumen)

[3]Senior Researcher,
Department of Organic and Ecological Chemistry,
Institute of Physics and Chemistry, Tyumen State University (Tyumen)

lpanicheva@list.ru, kreml-ta@yandex.ru, svolkova2008@mail.ru

UDC 556.461

ACCUMULATION OF PETROCHEMICALS BY BOTTOM SEDIMENTS IN THE BACKGROUND WATER RESERVOIRS OF WEST SIBERIA

SUMMARY. This article determines the degree of oil pollution of waters and bottom sediments due to the processes of atmospheric and water migration for 22 small background lakes in various natural zones of West Siberia. It is shown that the oil content in the bottom sediments of the background lakes may be 218 ÷ 24667 times higher than in water. The capacity of bottom sediments to accumulate petroleum hydrocarbons depends on the content of organic matter in them. According to the results of the studies of the distribution of petroleum products between water and bottom sediments, a mechanism of co-deposition of colloidal forms of oil products and slightly soluble humus substances sparingly formed during the biochemical transformation of organic matter in the water phase of the pond has been offered. The reverse process of desorption of oil products from bottom sediments by peptizing small fraction of particles of the solid phase and the return of hydrocarbons in the water phase as micro emulsion is only possible due to performing additional work. However, petrochemical content in water having a contact with bottom sediments, in which significant amounts of petroleum products are deposited, cannot be lower than their molecular solubility.

KEY WORDS. natural waters, bottom sediments, pollution, petroleum hydrocarbons.

Introduction. Geochemical studies of objects of the environment in various anthropogenic landscapes of West Siberia (WS) have their relevance due to both the need of theoretical generalizations on chemical pollution of the environment and the need for environmental assessment and forecast of its adverse changes in the conditions of existing and planned anthropogenic influences.

In the context of intensive oil and gas exploration of West Siberia, deterioration of water quality is possible not only in waters subject to anthropogenic pollution, but

also in those lying sufficiently distant from the sources of pollution. This is caused by the involvement of significant amounts of organic pollutants, including petroleum hydrocarbons, in the global flow of migration [1]. While respecting the fundamental principles of research of background lakes in West Siberia [2], including the principle of remoteness from any direct anthropogenic impacts on the lakes, simultaneity and seasonal comparability of results, the results of measurements of residual oil content in water samples from 127 background lakes of West Siberia showed that the median values for all natural areas (from tundra to forest-plain) do not exceed the maximum permissible concentration (MPC) for fishery water bodies, but for a number of lakes in the tundra and northern taiga, the 7-10 times excess of MPC was observed [1].

The assessment of oil pollution of sediments is of special interest in cases where anthropogenic pressure on a lake is small, and due to self-purification capacity, the residual oil content in the water is low. Sediments accumulate pollutants coming from the water catchments for a long period of time, they can be considered as an indicator of the ecological state of the territory, a kind of integral index of the level of contamination [3].

The purpose of this study was to determine the level of oil pollution of bottom sediments in West Siberian water ponds that are sufficiently distant from the sources of pollution, and to study the peculiarities of distribution of petroleum hydrocarbons between water and sediments.

Materials and Methods. Simultaneous sampling of water and sediments in the background lakes of various natural zones of West Siberia was held in autumn of 2011 in accordance with the procedure [4]. Total carbon and organic carbon in the water samples was determined by elemental analysis with the use of "vario TOC" and "Elementar" devices, the number of organic matter content in sediments was measured photometrically by Tyurin's method [5]. The determination of residual oil content in the water and sediments of lakes of West Siberia was conducted with the use of spectral methods. The proposed in [6,7] combined procedure of determining the mass of oil products by IR spectrophotometry and fluorimetry based on known methods for detection of oil products in natural water samples by IR spectrometry (PND F 14.1:2:4.168-2000, 2004) and by fluorimetry (PND F 14.1:2:4.128-98, 2007); soil and sediments by infrared spectrometry (PND F 16.1:2.2.22-98, 2005) and by fluorimetry (PND F 16.1:2.21-98, 2007).

Results and discussion. For a complex comprehensive study, 22 small lakes located in different natural zones of West Siberia were selected. The results of determining the content of oil products (OP) in water and sediments, organic carbon (C org) with the use of elemental analysis in water and organic matter (OM) samples by Tyurin's method in the sediment samples are presented in Table 1.

Given the fact that the studied "background" water ponds are remote from the sources of contamination, it can be assumed that the residual oil content in the water must not be large. According to the data (Table 1.), the water in 19 of 22 lakes studied is relatively clean – the oil content is less than MPC for fishery ponds (50 mkg/dm^3), 2 lakes exceed the MPC for oil products in water and one lake has OP = MPC.

Regarding the oil pollution of sediments (soil of water bodies), the situation is ambiguous. The median for the content of oil products in sediment is 30 mg/dm^3, quartile (0.75) – 79 mg/dm^3.

Table 1

The content of oil products (OP), organic carbon (Corg) and organic matter (OM) in the samples of water and sediments of West Siberian lakes

No	Natural zone	WATER		SEDIMENTS			$(OP)_{SED}/(OP)_{WAT}$
		OP, mg/dm^3	C org, mg/dm^3	OP, mg/kg	OM, g/kg	OP/ OM,%	
1	tundra	0,070	4,2	31,0	5,8	0,54	443
2	tundra	0,030	3,5	19,5	3,3	0,60	651
3	tundra	0,050	3,4	10,9	4,1	0,26	218
4	tundra	0,040	2,7	81,0	40,0	0,20	2025
5	tundra	0,020	10,8	80,8	48,6	0,17	4041
6	tundra	0,040	6,9	629,0	95,6	0,66	15725
7	tundra	0,060	6,3	16,1	5,2	0,31	268
8	tundra	0,010	6,6	218,0	83,6	0,26	21800
9	north taiga	0,040	7,2	50,7	12,0	0,42	1267
10	middle taiga	0,020	5,2	10,5	2,6	0,40	525
11	middle taiga	0,021	5,3	9,4	2,3	0,41	450
12	middle taiga	0,015	13,4	7,4	2,5	0,30	496
13	middle taiga	0,019	15,0	9,6	2,6	0,38	504
14	middle taiga	0,019	13,8	10,0	29,9	0,03	1579
15	south taiga	0,021	13,5	51,9	3,6	1,42	2471
16	south taiga	0,021	19,8	43,5	3,4	1,29	2071
17	south taiga	0,036	14,0	11,4	3,0	0,38	318
18	forest-plain	0,018	33,5	350,0	83,2	0,42	19444
19	forest-plain	0,015	27,3	370,0	76,8	0,48	24667
20	forest-plain	0,021	26,5	30,0	23,5	0,13	1429
21	forest-plain	0,035	26,6	27,0	17,1	0,16	771
22	forest-plain	0,024	19,0	79,0	14,6	0,54	3292

It should be noted that the problem of MPC for oil content in sediments, as well as in soils, is practically unresolved. Therefore, in [8], it is proposed to assess the level of oil pollution of soil by the excess of oil content above the background value in a particular area and a particular territory. At the same time, in particular, it is pointed out that for areas not involved in oil extraction, the background level of oil products in soil is 40 mg/kg, and for the oil-producing areas it amounts 100 mg/kg. However, to classify the degree of oil contamination of sediments, more stringent criteria are usually used.

According to the classification of V.I. Uvarova [9], by the content of petroleum hydrocarbons (mg/kg of dry soil), soils can be divided into: pure -0 ÷ 5.5, slightly polluted -5.5 ÷ 25.5, moderately polluted -25.6 ÷ 55.5, contaminated -55.6 ÷ 205.5, dirty — 205.6 ÷ 500, very dirty — more than 500. If we adhere to this classification,

then the 22 samples of sediments of the studied West Siberian lakes (Table 1) are as follows: clean — 0; slightly polluted — 9 (41%), moderately polluted — 6 (27.3%); contaminated — 3 (13.6%) , dirty — 3 (13.6%), very dirty — 1 (4.5%).

As noted by I.A. Kuznetsov and A.N. Tszyuban [10], bacterial communities accurately identify the "concentration limits" of oil pollution of sediments below which microbial cenoses water-soil still cope with the incoming hydrocarbons in sediments and stabilize the situation — 40 ... 60 mg/kg of dry soil.

According to these data, in 7 of the 22 studied sediment samples (31.7%) the "concentration limits" of oil pollution are exceeded (dirty and very dirty by the classification of V.I. Uvarova), although the water in the corresponding lakes does not exceed the MPC in terms of the content of oil products (Table 1).

As shown in Figure 1, correlation of data on the content of oil products and the organic matter in sediments is observed ($R^2 = 0.7684$).

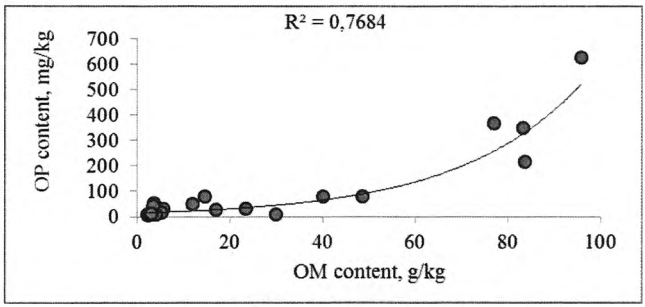

Figure 1. Dependence of the content of oil products on the content of organic matter in sediments of West Siberian lakes

Thus, the sorption of oil in the sediments is predominantly carried out by organic matter.

However, the mechanism of sorption is not consistent with the mechanism of equilibrium of adsorption-desorption of molecules of oil products at the interface of "water-sediments". This is confirmed by the fact that the correlation between the content of OP in sediments and OP content in water is virtually absent ($R^2 = 0.0128$). Correlation between the OP content, deduced by the content of OM $(OP/OM)_{SED}$, in sediments and oil content in water $(OP)_{WAT}$ is small ($R^2 = 0.1924$). Correlation between the data on the content of organic matter (OM) in sediments and the content of organic carbon (C org) in water is also practically absent ($R^2 = 0.0746$).

This may be due to the fact that the oil received in the water pond as a result of surface and underground runoff from the water catchment, is molecularly dissolved in small quantities due to the low solubility of hydrocarbons in water. Large quantities of hydrocarbons are present in the water as microemulsion (the absence of visible droplets of macroemulsion and membranes) and are adsorbed on the surface of the suspended solids, i.e. form stable colloidal systems.

The sediment organic matter in a pond, due to hydrophobic interactions, can contribute to sedimentation of suspended particles together with adsorbed molecules of OP and to coalescence of microemulsion droplets at the interface "water-sediment." However, a more efficient is the process of co-precipitation of colloidal forms of oil products and sparingly soluble humic substances that are formed during the biochemical transformation of organic matter in the aqueous phase of the water pond. The long-term process of simultaneous accumulation of organic matter and mineral oil at the bottom of the water pond allows explaining the correlation between the content of OM and OP in the sediments. In this case, the reverse process of desorption of OP from sediments by peptizing of fine fraction of particles of the solid phase and the return of hydrocarbons in the aqueous phase in the form of microemulsion can occur only when making additional work, such as sediment resuspension.

This process usually results in a "secondary pollution" of the aqueous phase with erosion of sediments in rivers, it depends on the diameter of sediment particles and the velocity of the river flow. However, in small lakes in relatively static conditions a "burial" of OP occurs predominantly in sediments, where they are biodegradable, mainly on the interface of "water-sediment," but with a significantly lower rate than in the aqueous phase.

The role of molecular desorption processes of OP from sediments into the water is greater in those cases where as result of biochemical degradation in water, the colloidal fraction of the OP disappears. Further biotransformation will be accompanied by molecular desorption of OP from sediments to the water to saturate the solution with hydrocarbon molecules. Consequently, even in cases where the highest efficiency of the processes of self-purification of water from oil products, in the presence of contact with sediments, in which significant amounts of OP are deposited, the OP content in the water cannot be lower than their molecular solubility.

The minimum content of OP in water lakes of various natural zones of West Siberia is $8 \div 13$ mkg/dm^3, within the measurement error of spectral methods with the use of the composite procedure [1].

Conclusion. Thus, these data suggest that the background lakes in West Siberia that are distant from sources of pollution are subject to oil pollution due to the processes of atmospheric and water (aboveground, underground) migration. Also, the first stage of purification of natural waters from oil products is the accumulation of petroleum hydrocarbons in sediments. The ability of sediments to accumulate petroleum hydrocarbons depends on their level of content of organic substance.

REFERENCES

1. Panicheva, L.P., Moiseenko, T.I., Kremleva, T.A., Volkova, S.S. Biochemical transformation of petroleum hydrocarbons in the waters of Western Siberia. *Vestnik Tjumenskogo gosudarstvennogo universiteta — Tyumen State University Herald.* 2012. № 12. Series «Ecology». Pp. 38-48. (in Russian).

2. Moiseenko, T.I., Panicheva, L.P., Larin, S.I., Pologrudova, O.A., Volkova, L.A. Methods for studying the chemical composition of waters of small lakes in order to identify

regional characteristics of its formation. *Vestnik Tjumenskogo gosudarstvennogo universiteta — Tyumen State University Herald.* 2010. № 7. Pp. 175-190. (in Russian).

3. Moskovchenko, D.V., Valeeva, Je.I. The study of the bottom sediments of the lower Ob river basin (within the Khanty-Mansi Autonomous Okrug). *Vestnik jekologii, lesovedenija i landshaftovedenija — Ecology, Forestry and Landscape Science Herald.* 2001. Issue 2. Pp. 138-142. (in Russian).

4. *Kompleksnoe gidrohimicheskoe i biologicheskoe issledovanie kachestva vodi sostojanija vodnyh i okolovodnyh jekosistem: Metodicheskoe rukovodstvo. Chast' 1. Polevye issledovanija* [Comprehensive hydrochemical and biological study of water quality and the state of aquatic and semi-aquatic ecosystems: Methodological Guide. Part 1. Field studies] / Ed. T.I. Moiseenko. Tyumen, 2011. 128 p. (in Russian).

5. *Kompleksnoe gidrohimicheskoe i biologicheskoe issledovanie kachestva vodi sostojanija vodnyh i okolovodnyh jekosistem: Metodicheskoe rukovodstvo. Chast' 2. Kameral'nye raboty* [Comprehensive hydrochemical and biological study of water quality and the state of aquatic and semi-aquatic ecosystems: Methodological Guide. Part 2. Laboratory works] / Ed. T.I. Moiseenko. Tyumen, 2012. 304 p. (in Russian).

6. Znamenshhikov, A.N. *Opredelenie strukturno-gruppovogo sostava i obshhego soderzhanija uglevodorodov v neftjah i neftjanyh zagrjaznenijah spektral'nymi metodami* (diss. kand.) [Determination of structural-group composition and total hydrocarbons content in the oils and oil pollutions by using spectral methods (Cand. Diss.)]. Tyumen, 2012. 133 p. (in Russian).

7. Kudrjavcev, A.A., Znamenshhikov, A.N., Volkova, S.S., Panicheva, L.P. Hydrocarbon mixture model for IR spectrophotometry and fluorimetry of oil products. *Vestnik Tjumenskogo gosudarstvennogo universiteta — Tyumen State University Herald.* 2011. № 5. Series «Chemistry». Pp. 63-70. (in Russian).

8. Rogozina, E.A. Topical issues of oil-contaminated soils cleaning. *Neftegazovaja geologija. Teorija i praktika — Petroleum Geology. Theory and practice.* 2006. № 1. Pp. 1–11. URL: http://www.ngtp.ru. (in Russian).

9. Uvarova, V.I. Current state of water and soil pollution level of the Ob-Irtysh basin // *Sb. nauch. tr. GosNIORH. Vyp. 305.* [Collection of scientific papers. GosNIORH]. Issue 305. 1989. Pp. 23-33. (in Russian).

10. Kuznecova, I.A, Dzjuban, A.N. Microbiological assessment of the effects of water bodies oil pollution [Mikrobiologicheskaja ocenka posledstvij neftjanogo zagrjaznenija vodoemov]. *Sovremennye problemy gidrobiologii Sibiri: Tez. dokl. Vsesojuz. konf.* (Modern Problems of Hydrobiology of Siberia: The All-Union Conference Abstracts). Tomsk, 2001. Pp. 123–124. (in Russian).