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## **BIOCHEMICAL TRANSFORMATION OF PETROLEUM HYDROCARBONS IN THE WATERS OF WEST SIBERIA\***

*SUMMARY. Biochemical transformation processes in petroleum hydrocarbons and nitrates are investigated in the 127 lakes (from the tundra to the forest-steppe zone) in the West Siberia (WS) territory. The main anthropogenic sources of pollution by oil products and nitrates are exploitation of petroleum and gas fields and burning of associated gas. For the majority of the WS lakes, located rather far from anthropogenic pollution sources, the self-purification capacity of water bodies during the summer period provides the reduction of the contents of oil products and nitrates to the values below the maximum allowable concentration (MAC) for fisheries. However, the contents of organic carbon ( $C_{org}$ ) and organic nitrogen ( $N_{org}$ ) considerably increase. For WS natural zones, the median  $C_{org}$  value varies from 4.38 to 26.6 mg/dm<sup>3</sup>, the median  $N_{org}$  value varies from 0.17 to 1.52 mg/dm<sup>3</sup>. The biochemical transformation of oil products includes the anaerobic process of humification and the aerobic process of mineralization. In the lakes of the northern and middle latitudes of WS (higher than 58° latitude) the humification is 80%, the mineralization is 20%; in the lakes of the southern latitudes of WS (lower than 58° latitude) the humification is 30%, the mineralization is 70%. The anaerobic oxidation of hydrocarbons and organic residues is accompanied with the restoration of nitrate to nitrite and ammonium. The amination of intermediate products of organic compounds oxidation leads to the increase of organic nitrogen and humic substances content. Considerable amount of ammonium is accumulated in the waters of the lakes in the natural zones ranging from the northern to middle latitudes (tundra, forest-tundra, northern taiga, middle taiga), that predetermines the dominance of the humification process of organic substance over its mineralization. In the natural zones of the southern latitudes (southern taiga, forest-steppe) the humification process is practically limited by complete depletion of ammonium. The molar ratio of carbon and nitrogen in aquatic humic substances is C:N = 23,4:1.*

*KEYWORDS: Petroleum hydrocarbons, nitrogen forms, biochemical transformation, mineralization, humification.*

The key problem of the lakes in West Siberia (WS) is the considerable oil pollution caused by the presence of more than 500 oil and gas fields.

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In addition to emergencies (blowouts, leakages from pipelines, tank ruptures, etc.) that cause, as a rule, large-scale oil pollution of the environment, the organic substances leakage beyond the industrial sites occurs due to the migration and scattering even during normal functioning of oil-field facilities. Besides, the influx of oil pollutants from the lower levels is possible [1].

Large amounts of petroleum hydrocarbons entering the environment while developing oil and gas fields result in the fact, that such type of pollution begins to predominate in the north of West Siberia.

Special attention has to be drawn to the problem of associated gas flaring. Over a number of years, flares in oil fields are the sources of chronic air pollution in vast areas. When flaring, carbon, saturated hydrocarbons (alkanes), phenols, benzo(a) pyrene, carbon monoxide, oxides of nitrogen and sulfur, hydrogen sulfide, heavy metals (vanadium and nickel) and other substances are emitted into the atmosphere. The large scale of nitrogen oxides (NOX) pollution during fuel combustion processes is determined by the formation of these oxides not only through the interaction of O<sub>2</sub> in the air with the nitrogen in fuel, but also through the interaction of O<sub>2</sub> in the air with the nitrogen in the air [2-4].

Simultaneous nitrogen and sulfur oxides emissions cause acid rains. From the total amount of acids fallen down with the rains in central Europe, approximately the 2/3 of them is sulfuric acid and 1/3 is nitric acid. However, such ratio may vary depending on the particular place or region [4]. Accordingly, we can expect that for West Siberia, especially in the North, where the largest number of flare sites is concentrated, the contribution of nitric acid to the acid rains will be more significant.

Most of the pollution caused by the presence of oil and gas deposits and their exploitation is toxic. In assessing the capacity of water bodies for self-purification and the background pollution typical for this region, studying chemical composition of water samples from the West Siberia lakes located far from the main sources of anthropogenic effects is a matter of considerable interest.

The purpose of this research was to determine the regularities of hydrocarbon biochemical transformation and specific features of its influence on the biogenic elements status, as well as the formation of humic substances in the lakes of West Siberia.

**The experiment.** The results of the extensive exploration of 127 small lakes in West Siberia (from the tundra zone to the forest-steppe zone) formed the basis of this paper. The work was carried out according to the investigation principles, stated in [5-6]. The principle of remoteness of lakes from any direct anthropogenic load was kept; simultaneity and seasonal comparability were ensured; and modern analytical equipment was used, as well as internal measurements quality control was carried out.

The content of residual oil products in the WS lake waters was determined by means of spectral methods. We used the *Oil Product (OP)* concept, which means a mixture of non-polar and low-polar hydrocarbons soluble in hexane and unadsorbed in alumina, in our chemical analytical control of oil pollution in natural environments.

To increase the accuracy of analysis, alkyl components content analysis was carried out by means of IR-spectrophotometric method with FSM 1201 FSM 1201IR-

Fourier-spectrophotometer, whereas aryl components content analysis was carried out by fluorometric method with Shimadzu RF-5301PC device applying universal six-component calibrating mixture [7].

The colour of water was determined by spectrophotometric method according to the chromium-cobalt scale of colours at wavelength of 380 nm (UNICO spectrophotometer).

Total nitrogen, total carbon and organic carbon contents were determined by elemental analysis method with the Vario TOC, Elementar apparatus. Mineral carbon (water-soluble forms) was calculated as the difference between total carbon and organic one.

Mineral nitrogen forms (ammonium, nitrates, and nitrites) were determined by ionic chromatography method with DIONIX ICS-2100 ionic chromatograph by means of electrolytic sample preparation and eluent generation, i.e. by means of the techniques, developed to apply electrolytically-generated eluents for any isocratic and gradient separation types in ionic chromatography with conductometric detecting. Organic nitrogen was calculated as the difference between total and mineral nitrogen, i.e. the sum of ammonium, nitrates and nitrites.

**Results and Discussion.** According to the Le Chatelier-Broun principle of stability, if a system in equilibrium is affected from outside by changing any steady-state condition, then the processes targeted to the compensation of external action are intensified. The concentration variation of one or more components (deviation from the equilibrium value) is one of the variants of such external effect [8].

Thus, the introduction of the excess quantity of hydrocarbons (HC) to ecosystems must be accompanied by their biological transformation intensification.

**The content of residual oil products** is defined as a balance between their supply and consumption in oxidative degradation process. It should be noted, that petroleum HC, which are mostly characteristic for oil pollutions, are not alien to natural ecosystems, since large amounts of native hydrocarbons are produced by flora and fauna. There are all necessary conditions in natural water bodies for the oil products oxidative degradation — UV-radiation, the presence of oxygen dissolved in water, moreover, natural bacteriocenoses are genetically conformed to the oil products decomposition [9-10].

The residual oil products tests carried out in autumn at the water temperature of 4°C, when the rate of any supplies and consumption determinative processes decreases, allow estimating water-body self-purification capability from oil products in summer.

Oil product content (median values) in the lakes of various WS natural zones is presented in Table 1.

Table 1

**Oil product content ( $X_{op}$ ) in the lakes of various West Siberia natural zones: the numerator is the median; the denominator is the content limit**

Natural zone	Tundra	Forest-tundra	Northern taiga	Middle taiga	Southern taiga	Forest-steppe
n	36	10	21	33	16	11
$X_{op}$ , $\mu\text{g}/\text{dm}^3$	<b>41</b> 8÷555	<b>32</b> 8÷177	<b>36</b> 8÷392	<b>20</b> 13÷53	<b>18</b> 14÷36	<b>20</b> 14÷32

According to the data given in Table 1, the content of residual oil products and, consequently, the efficiency of hydrocarbon biochemical transformation depend on the location of certain lakes in various climatic and vegetation zones, changing with the latitude and absolute altitude of a certain locality. Lower values of average annual temperature and other features of WS natural zones that define the conditions of the oil pollution supply, its expansion, and transformation can determine higher residual oil content in the northern zones. Probably, such variability of values for different samples within the range of a certain natural zone depends on the distance between the sampling point and the oil-and-gas fields or traffic arteries.

The median values of residual oil contents for all natural zones do not exceed MAC for fisheries (lower than  $50 \mu\text{g}/\text{dm}^3$ ) [11]. The residual oil contents for a half of the examined lakes located far from the main sources of anthropogenic pollution in autumn in the southern natural zones reduces approximately to  $20 \mu\text{g}/\text{dm}^3$  which can be actually considered a baseline value.

**The residual nitrate content** in natural waters is determined by the balance between the supply of nitrates and their consumption in the processes of denitrification and dissimilation. As stated in [12], microorganisms within the nitrogen cycle are stimulated to grow when affected by oil pollution in small doses, due to the supply of a new organic matter into the soil.

As the result of nitrate denitrification, either  $\text{NH}_4^+$  or  $\text{N}_2$  flows into the air. This process occurs with evolving  $\text{NO}$  and  $\text{N}_2\text{O}$  as by-products, which also flow into the air.

Nitrate is reduced to nitrite due to molybdenum comprising enzyme of nitrate reductase. There are two ways of nitrite reduction [14]:

$\text{NO}$ -forming nitrite reductase reduces nitrite to form nitric oxide (II). It is one of the stages of denitrification.

$\text{NH}_3$ -forming nitrite reductase reduces nitrite to form ammonium ion, which is the final stage of dissimilation reduction of nitrate to ammonium, it is also referred to as dissimilation or respiratory ammonification. Such respiration competes with energetically more advantageous aerobic respiration but it is inhibited by oxygen.

The results of analysing the nitrate, nitrite, and ammonium ions contents (median values) in the lake waters for various WS natural zones are presented in Table 2.

Table 2

**Nitrogen mineral form contents in the lakes of various West Siberia natural zones: the numerator is the median, the denominator is the content limit**

Natural zone	Tundra	Forest-tundra	Northern taiga	Middle taiga	Southern taiga	Forest-steppe
n	36	10	21	33	16	11
$\text{NO}_3$ , mg /dm <sup>3</sup>	1.11 0.005-8.95	0.68 0.072-1.91	0.94 0.046-2.35	0.35 0.019-6.84	1.90 0.017-7.82	0.27 0.12-4.48
$\text{NO}_2$ , mg /dm <sup>3</sup>	0,009 0-0.75	0,008 0.002- 0.011	0,010 0.002-1.72	0,011 0-0.26	0,002 0.001-0.22	0,76 0.004-1.57
$\text{NH}_4$ , mg /dm <sup>3</sup>	0.13 0.010-0.41	0.078 0.010-1.11	0.14 0.011-1.53	0.26 0.011-1.23	0.025 0.011-0.73	0.022 0-1.34

According to the data given in Table 2, all the obtained data for the nitrate content are considerably less than MAC for fisheries (less than 40 mg/dm<sup>3</sup>); the median values for all natural zones are less than MAC for Baikal Lake (less than 5 mg/dm<sup>3</sup>). In some lakes, the nitrite and ammonium contents exceed MAC for fisheries (more than 0.08 mg/dm<sup>3</sup> and 0.5 mg/dm<sup>3</sup>, respectively). The median values of the nitrite and ammonium contents are lower than MAC, except the median nitrite content in the forest-steppe zone.

The lowest median values of the ammonium ion content are observed in the southern zones of the southern taiga and forest-steppe zones (Table 2). In these zones, the natural climatic conditions are likely to be more favorable for the aerobic oxidation of organic substrates in comparison with the anaerobic oxidation, when compounds alternative to oxygen — nitrates and nitrites — are used as the electron acceptors. Nevertheless, the considerable amount of nitrates remains in the southern taiga zone, but in the forest-steppe zone, nitrates are mainly reduced to nitrites (Table 2).

**The organic substance content** in natural waters depends on the efficiency of the humification process of hydrocarbons and dead biota organic residues. During such processes, humic substances (HS) which have a polymeric structure and, hence, are quite resistant to decomposition and oxidation are formed.

The Total Organic Carbon (TOC) is a rather reliable indicator of the organic substance content for water, equal to approximately 50% of the organic substance weight. Another important indicator is organic nitrogen (N<sub>org</sub>). The C<sub>org</sub> and N<sub>org</sub> contents (median values) in the lake waters for various WS natural zones are presented in Table 3.

Table 3

**Contents of organic carbon and organic nitrogen in the lakes of various natural zones in West Siberia: the numerator is the median, the denominator is the content limit**

Natural zone	Tundra	Forest-tundra	Northern taiga	Middle taiga	Southern taiga	Forest-steppe
n	36	10	21	33	16	11
C <sub>org</sub> , mg/dm <sup>3</sup>	4.38 1.25-10.8	12.1 8.18-14.6	<u>7.27</u> 2.21-24.1	<u>11.4</u> 1.52-20.3	<u>13.7</u> 7.04-20.7	<u>26.6</u> 19.0-39.4
N <sub>org</sub> , mg/dm <sup>3</sup>	<u>0.17</u> 0.0001-0.86	0.35 0.15-0.69	0.28 0.004-0.70	0.27 0.001-0.73	0.79 0.002-0.99	1.52 1.06-2.57

It should be noted that the contents of organic carbon and organic nitrogen in the WS natural zones (Table 3) subjected to pollution by oil products are higher than in the natural zones of the European territory of Russia [6].

The results obtained correspond to the published data. For example, when examining the underground water samples from Bashkiria, Ukhta, Central Asia, the Kuban area, etc., the values specific for waters in oil-bearing regions including the contents of organic carbon and organic nitrogen exceeding the baseline values that increase on drawing near an oil pool were determined [15].

The most important stage of the humic substance (HS) formation including the formation of fulvic and humic acids is the process of polycondensation of hydroxy carboxylic acids and amino acids which have different structures. Their ratio is the possible reason of the variation of the molar C:N ratio in HS.

The correlation ( $R^2 = 0.63$ ) between the organic nitrogen content and the organic carbon content with an approximate ratio about 0.0497 mgN/ 1 mgC (Fig. 1) is observed for the West Siberia lake waters which corresponds to the molar ratio C:N = 23.4:1 in the water-soluble organic matter.

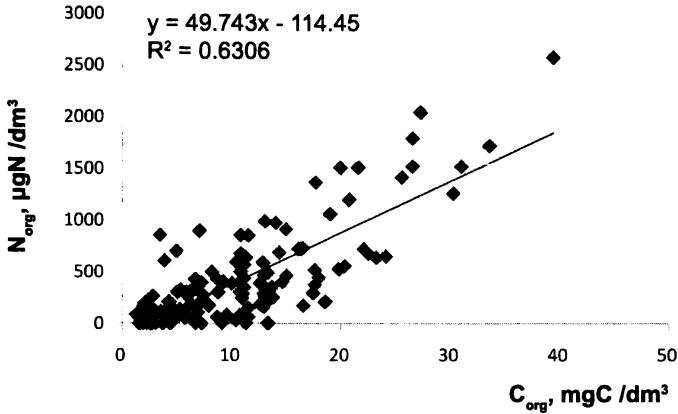


Fig. 1. The organic carbon content ( $C_{org}$ ) versus the organic nitrogen content ( $N_{org}$ ) in the WS lakes

The obtained ratio is rather well correlated with the values of average elemental composition of the humic (HA) and fulvic acids (FA) isolated from the natural waters [16]. The calculation of the data for the element mass content allows us to assess the molar ratio for HA (n=56): C:N = 23:1; for FA (n=63): C:N = 23.7:1.

The water colouring in the WS lakes located in northern and middle latitudes correlates quite well with the  $C_{org}$  content (Fig. 2).

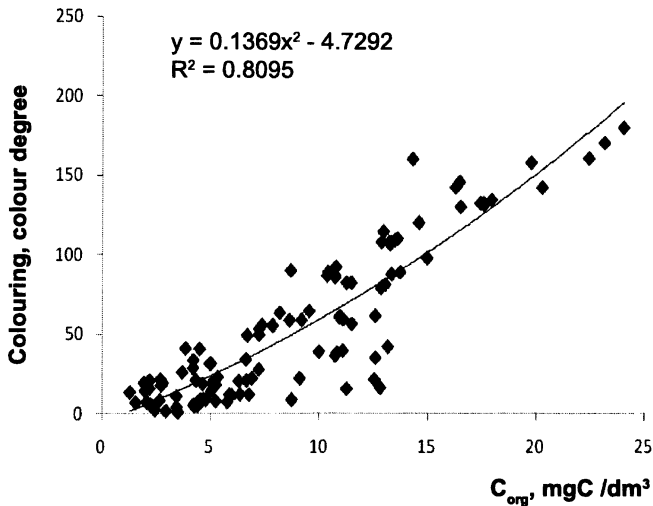


Fig. 2. The colouring of waters versus the organic carbon content ( $C_{org}$ ) in the WS lakes located in northern and middle latitudes.

**The mechanisms of the biochemical transformation of oil products in natural waters.** The gas-liquid chromatography method experimentally proved that oil products are transformed through the reactions of hydrogenation, dehydrogenation, hydroxylation, oxosynthesis (hydroformylation), carboxylation, decarboxylation, esterification, hydrolysis, and condensation, the combination of which results in the hydrocarbon substrate degradation [17]. In the process of oxidative degradation, the intermediate hydrocarbon oxidation products (alcohols, aldehydes, ketones, carboxylic acids, esters) and bifunctional compounds (aldehyde acids, keto acids, etc.) can be formed. It should be noted that in natural conditions microorganisms realize oxidation processes through both aerobic respiration, and anaerobic one [13].

The complete oxidation of hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (the mineralization process) with the following removal of  $\text{CO}_2$  to the atmosphere, or to the lithosphere in the form of carbonate compounds would be the optimal method of the hydrocarbon excess elimination. However, if  $\text{CO}_2$  is formed in water, it actually dissolves, which results in increasing the mineral carbon content ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) in water.

Moreover, the process of the humification of intermediate hydrocarbon oxidation products is also an effective method of the biochemical transformation of oil hydrocarbons. In [18] the author proposes the oil-contaminated soil recovery concept based not on the contaminant removal by destruction to the form of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , but on the transformation of oil compounds into non-toxic humic compounds, that allows to speed up the remediation period for disrupted biocenosis.

The humification process can occur due to the fact, that in the conditions when there is a shortage of oxygen dissolved, the anaerobic hydrocarbon oxidation by nitrates and nitrites with the ammonium formation is possible. The reductive amination of the intermediate products of hydrocarbon oxidation with forming the nitrogen-comprising organic compounds, including amino acids, predetermines the possibility of excessive carbon to be introduced into the composition of water-soluble organic matter (the humification process).

Such a mechanism, through which amino acids are synthesized from  $\alpha$ -keto acids and ammonia, was called *transreamination* by A.E. Braunstein. The essence of this process is the reductive amination of  $\alpha$ -ketoglutaric acid with forming the glutamic acid (glutamate dehydrogenase catalyzes the reaction) and the following glutamate transamination with any  $\alpha$ -keto acid. As a result, L-amino acid corresponding to the initial keto acid is formed, and  $\alpha$ -ketoglutaric acid, which can accept a new ammonia molecule, becomes free again. This system of including ammonium nitrogen into organic compounds with amino groups as the transferor is created and used by many bacteria and plants in those cases, when the ammonium ion concentration in the environment is very low (less than 1 mM/l), as well as if  $\text{N}_2$  is fixed [19]. It can be also noted, that the discovery of the *Corynebacterium glutamicum* bacteria evolving L-glutamic acid initiated a new era in the industrial use of the partial oxidation of carbohydrates and hydrocarbons for the amino acid synthesis [20].

The ratio between the processes of mineralizing (an aerobic process) and humifying (an anaerobic process) the hydrocarbons and organic remnants of dead biota can be estimated with the contents of the mineral ( $\text{C}_{\text{min}}$ ) and organic ( $\text{C}_{\text{org}}$ ) carbon in water.

The contents of organic and mineral carbon in the WS lakes in the latitudinal gradient are presented in Fig. 3.

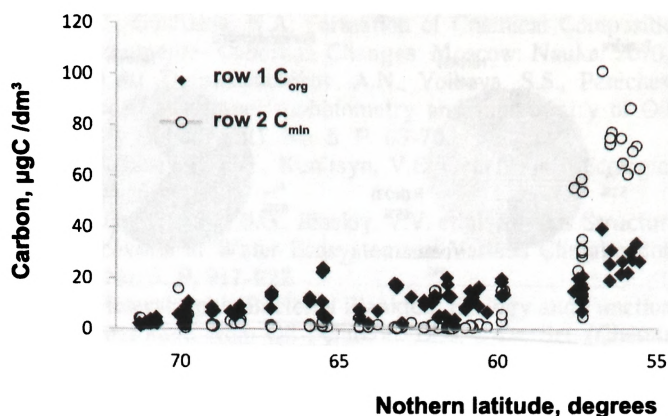


Fig. 3. The contents of organic carbon ( $C_{org}$ ) and mineral carbon ( $C_{min}$ ) in the WS lakes in the latitudinal gradient

Taking into account the data obtained (Fig. 3), we can divide the whole range of WS latitudes explored into two areas: the northern and middle latitudes (NML) (higher than  $58^\circ$ ) and the southern latitudes (SL) (lower than  $58^\circ$ ). In the NML lakes, the humification process dominates the mineralization process ( $C_{org} > C_{min}$ ); the average humification is 80%, the average mineralization is 20%. In the SL lakes, the mineralization process dominates the humification process ( $C_{org} < C_{min}$ ); the average humification is 30%, the average mineralization is 70%.

Thus, the natural and climatic conditions and the dissolved oxygen content in the NML lakes are more favorable for anaerobic processes, but in the SL lakes they are more favorable for aerobic ones.

The efficiency of the amination process for the intermediate products of organic compounds oxidation and, consequently, of the humification process depends on the content of ammonium ion formed in the process of nitrate dissimilated reduction and anaerobic oxidation of hydrocarbons and organic residues. According to the data given in Table 2 and Fig. 4, the considerable amount of ammonium is concentrated in the lake waters of the NML natural zones (tundra, forest-tundra, northern taiga, middle taiga) that predetermines the dominance of the humification process of organic substance over the mineralization one.

In the SL natural zones (southern taiga, forest-steppe), the humification process is actually limited by the complete depletion of ammonium.

**Conclusion.** Our research of the petroleum hydrocarbon contents in the waters of the lakes located far from the sources of pollution demonstrated low residual contents of oil products for all the natural zones of West Siberia. It has been stated that, due to the specific features of anthropogenic pollution of the WS lakes, the combined biochemical transformation of petroleum hydrocarbons and nitrates can occur with forming the humic substances, the element composition of which corresponds to the natural one. The natural and climatic conditions of the northern natural zones are favorable for humifying organic substances, and the conditions of the southern natural zones are favorable for mineralizing them.



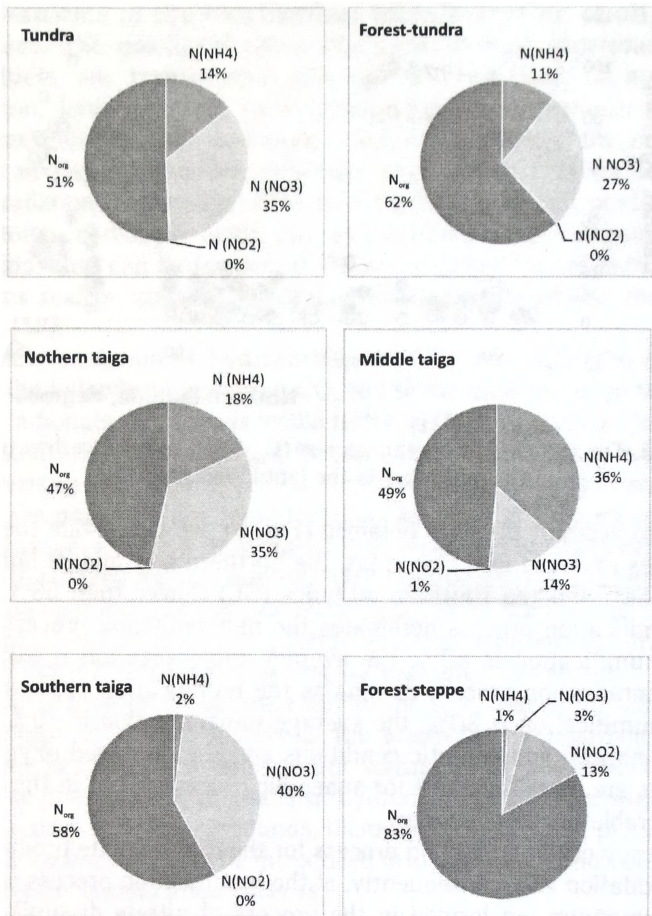


Fig. 4. Relative amount of nitrogen in various forms in the lake waters of WS natural zones

## REFERENCES

1. Oborin, A.A., Khmurchik, V.T., Illarionov, S.A., Makarova, M.Y., Nazarov, A.V. *Polluted Biocenosis*. Perm: Ural Department of Russian Academy of Science; Perm State University; Perm State Technical University, 2008. 511 p.
2. Vasilyev, A.A., Matveyev, N.I., Lukinykh, V.B. *Ecological Techniques of West Siberia Oil Producing Companies // Environmental Management & Ecology: Ecology and the Industry of Russia*. 2004. No. 5. P. 16-17.
3. Abrosimov, A.A. *Ecology of Hydrocarbon System Processing*. Moscow: Khimiya, 2002. 608 p.
4. Goldovskaya, L.F. *Chemistry of Environment*. Moscow: Mir; BINOM, Laboratory of Knowledge, 2007. 295 p.
5. Moiseyenko, T.I., Panicheva, L.P., Larin, S.I., Pologrudova, O.A., Volkova, L.A. *Research Techniques for Chemical Composition of Waters in Small Lakes for Determining Regional Features // Tyumen State University Herald*. 2010. No. 7. P. 175-190.

6. Moiseyenko, T.I., Gashkina, N.A. Formation of Chemical Composition in the Lake Waters under the Environmental Condition Changes. Moscow: Nauka, 2010. 268 p.
7. Kudryavtsev, A.A., Znamenshchikov, A.N., Volkova, S.S., Panicheva, L.P. Model Mixture of Hydrocarbons for IR-Spectrophotometry and Fluorimetry of Oil Products // Tyumen State University Herald. 2011. No. 5. P. 63-70.
8. Trukhin, V.I., Pokazeyev, K.V., Kunitsyn, V.E. General and Ecological Geophysics. Moscow: Fizmatlit, 2005. 576 p.
9. Koronelli, T.V., Dermicheva, S.G., Ilinskiy, V.V. et al. Species Structure of Hydrocarbon-Oxidative Bacteriocenosis in Water Ecosystems of Various Climatic Zones // Microbiology. Vol. 63. 1994. No. 5. P. 917-922.
10. Ilyinskiy, V.V. Heterotrophic Bacterial Plankton: Ecology and Functioning in Natural Purification of the Environment from Oil Pollution. Diss. ... Dr. Sci. (Chemistry). Moscow. 2000. 603 p.
11. Water Quality Standards for Fisheries. Approved by the Order of Russian Ministry of Fishery 18.01. 2010. No. 20.
12. Orlov, D.S., Ammosova, Y.M. Monitoring Methods of Soils Contaminated with Oil Products // Soil and Environmental Monitoring. Moscow: Moscow State University Press, 1994. P. 219-231.
13. Lysak, V.V. Microbiology. Minsk: Byelorussian State University Press. 2007. 426 p.
14. Modern Microbiology. Prokaryotes. Translated from English / Ed. by Y. Lengler, G. Drevs, and G. Shlegel. Moscow: Mir, 2005.
15. Shvets, V.M. Organic Matter of Underground Waters as Oil Exploration Indicators. // Organic Matter and Microorganisms of Underground Waters, and their Oil Exploration Significance. Russian Research Institute of Hydrogeology and Geological Engineering. Issue 26. Moscow, 1970. P. 6-29.
16. Perminova, I.V. Analysis, Classification, and Prediction of Humic Acids Properties. Diss. ... Dr. Sci. (Chemistry). Moscow, 2000. 359 p.
17. Odintsova, T.A. Ecological and Geochemical Aspects of the Organic Matter Transformation in Oil Polluted Geosystems // Modelling of Strategy and Development of Geological Resources. Proceedings. Perm: Mining Insitute, Ural Department of Russian Academy of Science. 2003. P. 241-245.
18. Illarionov, S.A. Petroleum Hydrocarbons Transformation in Soils of the Humid Zone. Diss. ... Dr. Sci. (Biology). Syktyvkar. 2006. 359 p.
19. Braunshtein, A.E. On the Way to Studying the Reaction and the Enzymes of Amino Group Transfer // Plenary Session Report in the 3<sup>rd</sup> USSR Biochemical Congress. Moscow. 1974. 37 p.
20. URL: <http://micro.moy.su/publ>.