UDK 504.5: 574

THE IMPACT OF HYDROCARBON POLLUTION ON BIOCHEMICAL CHARACTERISTICS OF AQUATIC ECOSYSTEMS

H.Kh.Khalilova

International Ecoenergy Academy, Baku
M.Rahim str.,5, Az 1073, Baku, Azerbaijan
e-mail: khalilova@rambler.ru

The paper discusses the status of pollution and biochemical characteristics of aquatic systems that had long been subjected to the anthropogenic impact of oil industrial activities. Laboratory analyses have revealed increased concentrations of toxic hydrocarbons in surface water, seawater and sediment samples in the territory of oil fields of Absheron peninsula – the main industrial region of Azerbaijan. Concentrations of total petroleum hydrocarbons in the majority of surface samples varied from 1796 to 53580 mkg/l that exceeded the permissible level by ten orders of magnitude. The results of biochemical and microbiological analyses aimed at evaluating the effect of hydrocarbon pollution on aquatic ecosystems showed that long-term anthropogenic impact has significantly changed the quality of water resources on the study site.
Keywords: *hydrocarbons, pollution, BOD, COD, seawater, sediment, ecosystem*

Introduction

Among the other components of ecosystem, water resources are frequently subjected to anthropogenic impact. Oil and oil products, phenols, surface active agents and heavy metals are the most dangerous pollutans of aquatic systems. Pollution of water systems can be caused by natural factors, including acid rains, flooding and physico-chemical properties of water, as well as by various anthropogenic sources, such as industrial operations, farming, manufacturing plants and domestic discharges,etc.

Polluton of the environment by toxic chemicals is largely widespread in the regions dealing with hydrocarbon production. Considering that significant amount of hydrocarbon losses and industrial discharges fall to the share of water basins, pollution of surface waters has become a serious concern in oil bearing regions, including the Absheron peninsula of the Republic of Azerbaijan.

Rapid urbanization, agricultural and industrial activities, including intensive offshore and onshore oil-field developments have led to pollution of water basins in the peninsula by various organic and inorganic pollutants degrading their natural quality.

Given that per capita share of water resources in Azerbaijan is about 1000 m^3 per year, which is several times lower than in neighboring countries, protection of available water resources is one of the major problems. Long-term contamination by crude oil, produced water and drill cuttings, as well as consequent environmental impact led to changes in geochemical, hydrological, geophysical and biological conditions of ecosystem in the Absheron region as referred to by a number of authors [1-5]. In this respect, the studies dealing with the impact of anthropogenic waste of various etiologies on ecological conditions of the Caspian Sea and other water basins are of significant importance.

Pollution of water systems by oil and other toxic substances has led to reducing the productivity of food base and fish species. Due to oil pollution, the intensity of photosynthesis has been significantly decreased in the coastal waters, where the number of hydrobionts and their productivity are lesser than in unpolluted zones. The fauna of the Absheron lakes suffered from continuous adverse effect of chemical substances. Self-purification

capacities of many water basins have been significantly reduced. Currently, they are not suitable for reproduction of fish and other aquatic communities. Apparent changes have been observed in the number of macrobenthos and zooplankton species [6-9].

The quality criterion of water can be described in terms of its physical, chemical and biological characteristics. In order to assess the risk posed by toxic substances in aquatic systems, it is necessary to determine the pollution degree of bottom sediments.

Hence, the main goal of the research is to determine the pollution of surface water, seawater and bottom sediments by organic wastes and examine its influence on biochemical properties of water systems.

Materials and methods

Seawater and marine sediments were sampled in the Caspian Sea, on offshore shelf of the Contract area. The samples were collected from water and bottom sediments of each sampling point by a vessel using bathometer and grabs. Surface water samples were taken from coastal sites adjacent to this area. The data considered here are results arising from the analysis of, at least, 5 samples out of 15 sampling locations consisting of 10 onshore and 5 offshore stations of the study area. Stations 11, 12 and 13 were located at distances 5, 3 and 2 km from seacoast, respectively. Stations 14 and 15 were located within relatively shallow water sections.

The samples were analyzed for total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAH) including USEPA 16 PAHs and 2-6 rings PAHs, total naphthalene, phenanthrene and dibenzo-thiophene (NPHD) and undecomposable complex mixture basically constituting of cycloalkanes (UCM). In order to assess the impact of hydrocarbon pollution on the water systems' quality in the study site, the biological oxygen demand (BOD) and chemical oxygen demand (COD) and microbiological properties were determined in both water and sediment samples. The studies were carried out to comply with generally accepted test methods [10].

The following methods were used to analyze water and sediment samples:

- TPH - aliphatic, alicyclic and aromatic hydrocarbons were analyzed by gas chromatography method;
- PAHs – USEPA 16 PAHs and 2-6 rings PAHs were analyzed by gas chromatography –mass spectroscopy method ;
- BOD – BOD was determined by incubating microorganism in diluted water samples at 20-25°C for 5 days and then measuring the absorbed oxygen;
- COD - COD was determined calorimetrically through dichromate oxidation;
- Standard methods were used for the determination of microbiological properties including the numbers of saprophytes, hydrocarbon oxidizing and phenol degrading microorganisms [11].

The results of studies were compared with the water quality standards shown in Table 1 [5].

Table 1. Permissible levels of the studied parameters

Pollutants	Sanitary water quality standards	Fishery water quality standards
Oil and petroleum products (mg/l)	0.1 – 0.3	0.05
BOD	3.0	
COD	15	

RESULTS AND DISCUSSION

Laboratory measurements revealed the presence of a large number of different organic chemicals in water and sediment samples. In surface water, for example, TPH, 2-6 rings PAHs, NPHD and UCM each had highest concentrations (Table 2). Measurable levels of USEPA 16 PAHs were also detected in several surface water samples (Stations 2,3,5,8, 9 and 10).

Results obtained indicated that the concentrations of hydrocarbons in the majority of samples exceeds the maximum permissible concentration (MPC) by tens orders of magnitude. Increased pollution levels were detected in oil industrial wastewaters (Stations 2 and 3). The highest level of pollution occurred at a surface runoff in the oil fields area. The content of TPH in all samples at coastal locations of the study site exceeded the MPC by several times. That testifies to the migration of wastewater into the sea aquatory.

Comparative analysis of the hydrocarbon content in seawater and marine sediments showed that the concentration of TPH in all samples was higher than the established standards.

Table 2. Content of hydrocarbons in surface water, seawater and sediment samples in the study site

Sampling stations	Surface water samples (mkg/l)				
	TPH	2-6 rings PAHs	USEPA 16 PAHs	NPHD	UCM
1.	128.1	1.45	0.10	1.30	95.4
2.	53580	1096	36.56	1019	40420
3.	6023	98.9	3.12	89.17	4990
4.	1796	4.8	0.86	0.74	1659
5.	4756	176	3.18	166.4	4078
6.	20.9	0.41	0.07	0.28	1.7
7.	68.2	0.42	0.05	0.35	24.3
8.	5749	184.9	4.91	166.4	5030
9.	1890	62.1	3.53	53.7	1511
10.	333.1	21.7	1.50	21.0	37.5
Seawater (mkg/l) and sediment (mkg/g) samples					
11-water	155.5	0.22	0.03	0.19	136.1
11-sediment	1140	4.3	1,2	1,0	1060
12-water	148.0	0.27	0.03	0.24	127.5
12-sediment	1197	7.2	0.9	2.9	1096
13-water	154.1	0.21	0.03	0.16	143.5
13-sediment	128.8	0.6	0.1	0.5	113.6
14-water	2041	7.14	0.32	5.11	1836
14-sediment	246.7	5.1	0.2	4.3	227.1
15-water	1340	4.90	0.20	3.85	1225
15-sediment	1230	19.7	0.40	17.4	1128

The content of TPH in marine sediments at Stations 11 and 12 is considerably higher than the content of those in seawater samples. These stations are exposed to the wastewater flowing from a discharge channel. Stations 11 and 15 are located at different distances from seacoast. According to the results, the content of

hydrocarbons in seawater samples considerably decreases depending on the remoteness of stations from seacoast, whereas, significantly increased levels were detected in sediments even at 5 km distance. This indicates that the exposure to a discharge channel has greatly contributed to the pollution of a large area by oil products within the study site. The level of pollution extended up to 5 km offshore. Relatively lower pollution level was detected at Station 13. However, the results showed that the degree of pollution at this station exceeds the MPC about 3 times.

The studies revealed that USEPA 16 PAHs in all sediment samples are detected at significantly increased levels as compared to those taken from upper horizons of the same stations (with exception of Station 14). The content of USEPA 16 PAHs in marine sediments at Stations 11 and 12 is up 19 and 27 times from the content of those in water samples. This testifies to long-term accumulation of high carcinogenic compounds in marine sediments due to the migration of wastewater into deeper sections. In most cases, the degradation of these compounds under this condition is impossible [1].

A series of laboratory analyses were carried out to study the impact of hydrocarbon pollution on biochemical properties of water systems.

BOD is an indicator of the quantity of materials consumed for the growth of microorganisms in water systems. Usually, in the spring and summer seasons the values of BOD is high that is observed to be lower in the autumn and winter months. In the hydrocarbon polluted environment BOD can be reduced regardless of the season. In the environment having high concentrations of oil, phenols, Fe^{2+} , H^{+} ions and many reducing substances the BOD values may be lower. BOD characterizes easily oxidizing pollutants as of communal-domestic, plant and animal origins.

COD is a parameter determining the quantity of oxygen required for chemical oxidation of petroleum hydrocarbons and other substances. The value of COD is high in the waters polluted by hydrocarbons.

As is seen from Table 3, elevated values were derived from COD and BOD analyses. The results showed that the wastewater inflow to the Caspian sea is rich in industrial and domestic discharges.

Usually, ground and river waters have from 1 to 60 mg O_2/l COD, and wastewater has more than 100 mg O_2/l COD. According to the COD value, the pollution level of wastewater in the Absheron oil fields territory can be classified as:

1. Low -70-200 mg O_2/l;
2. Medium -200-300 mg O_2/l;
3. Very polluted- more than 300 mg O_2/l

The measurements showed that majority of surface waters of the study area can be characterized with medium or very polluted levels. The wastewaters discharged to the environment are contrary to quality standards and result in carrying significant amount of toxic substances into the sea coast.

According to the standards and norms set for aquatic systems, the category of wastewater is established on the basis of biochemical index expressed by BOD/COD ratio. Clean water has a 1/1ratio, and the biologically degradable water has a ratio - ≤2/1. The BOD/COD ratio of industrial waters varies between 0,05 to 0,3 [12].

Table 3. Biochemical and microbiological parameters of oil polluted samples

№№	BOD_5, mgO_2/l	COD, mgO_2/l	BOD_5/ COD	Number of microorganisms		
				Saprophytes	Hydrocarbon oxidising	Phenol degrading
1.	320	70	4.6	10^9	10^5	10^4
2.	480	410	1.02	10^8	10^6	10^4
3.	320	1070	0.29	10^6	10^4	10^5

4.	320	280	1.14	10^6	10^6	10^5
5.	320	127	2.5	10^6	10^6	10^5
6.	240	320	0.75	10^6	10^5	10^4
7.	238	192	1.24	10^6	10^3	10^2
8.	314	230	1.36	10^9	10^6	10^5
9.	200	1200	0.16	10^7	10^6	10^5
10.	180	1270	0.14	10^6	10^6	10^5
11-water	48	21	2.3	10^6	10^5	10^4
11-sediment	72	24	3.0	10^6	10^3	10^3
12-water	40	11	3.6	10^5	10^4	10^5
12-sediment	64	60	1.06	10^4	10^3	10^3
13-water	40	35	1.1	10^6	10^5	10^4
13-sediment	57	44	1.3	10^3	10^2	10^2
14-water	56	36	1.5	10^5	10^4	10^4
14-sediment	68	37	1.8	10^4	10^3	10^3
15-water	42	31	1.35	10^5	10^4	10^4
15-sediment	53	33	1.6	10^4	10^3	10^3

As is seen from Table 3, biochemical indexes of samples taken out of the first point (station 2) and the end (station 3) of the study site shows that the wastewaters discharged to the environment from various anthropogenic sources are additionally polluted by industrial effluents. According to the data in the table above, the samples taken from the most polluted surface waters (9 and 10) are characterized by lower amounts of phytoplanktone and degradable organic substances. They are categorized as industrial wasterwaters due to the high concentration of chemical pollutants.

The results derived from this study demonstrated that:

1. As a result of long-term production, transportation and processing of hydrocarbon resources the levels of oil pollution of surface waters, seawater and sediments in the oil industrial territories of the Absheron peninsula is very high and sometimes reach 53580 mkg/l, 1340 mkg/l and 1230 mkg/g, respectively.
2. Oil contaminated wastewaters contain considerable quantity of toxic hydrocarbons – USEPA 16 PAHs, 2-6 rings PAHs, NPHD and UCM, which concentrations exceed the established permissible levels.
3. Results of researches showed that hydrocarbon pollution significantly influences the biochemical and microbiological conditions of aquatic ecosystems. According to the BOD/COD ratio, the most part of the surface waters of the study area are categorized as industrial wasterwaters. Very low values of saprophytes, hydrocarbon oxidizing and phenol degrading microorganisms indicate that these waters are incapable of natural biological self-purification.

REFERENCES

1. Aliyev F.G., Khalilova H.Kh. The anthropogenic impact on surface water resources in Azerbaijan. *J. Energy &Environment.* 2014, v.25., № 2. p. 343.
2. Khalilov Sh.B., Aliyeva A.A. Pollution of the Absheron lakes by oil products. *Proceedings of the Scientific-methodological conference "Environment and Ecology".* Baku, 1997, p. 117 (in Azerbaijan).
3. Aliyev Ch.S., Zolotovitskaya T.A., Podoprigorenko M.V. Radionuclide pollution of the environment during oil fields

development. *Azerbajdzhanskoe neftjanoe hozjajstvo - Azerbaijan Oil Industry,* 1996, no. 7, p. 46. (In Azerbaijan).
4. Mekhtiev A. Sh., Gul A. K. *Tehnogennoe zagrjaznenie Kaspijskogo morja* [Technogenic pollution of the Caspian Sea]. Baku: Elm Publ., 2006, 180. (In Azerbaijan).
5. Khalilova H.Kh. Pollution of water systems by toxic chemicals in the Contract area. Kimya Problemleri - Chemical problems. 2007, №1, p. 32.
6. Mammadov V.A., Alosmanov M.S. Formation, transformation and assessment of the ecological status of the Absheron lakes. *Proceedings of the 2nd Caspian International Water Technologies Conference,* Baku, 2014, p.470. (in Azerbaijan).
7. Kasimov A.H., Askerov F.S. Biodiversity: Oil and biological resources of the Caspian Sea. Baku: "Print Studio" publishing house, 2001, 326 p. (in Azerbaijan).
8. Mamedov R.G., Nadirov I.A. Ecology of the Absheron peninsula: Management of the regime of water basins in urbanized territories. Baku: "Chashioglu" publishing house, 1998, 139 c. (in Azerbaijan).
9. Aliyev S.I., Aliyev A.R. Hydrobiological description of some lakes of the Absheron peninsula. *Proceedings of the 9th Baku International Congress "Energy, Ecology, Economy".* Baku, 2007, p. 424. (in Azerbaijan).
10. Standard methods for examination of water and wastewater, American Public Health Association/ American Water Works Association/ Water Environment Federation, 19th edition 1995, Washington DC.
11. Khalilova H. The impact of oil contamination on soil ecosystem. *J. Biological and Chemical Research.* 2015, vol. 2, № 3, pp. 133-139.
12. Water Quality Criteria (WQC). A Report of the Committee on Water Quality Criteria. / NAS, Washington DC 1972, p.593.

NEFT KARBOHİDROGENLƏRİ İLƏ ÇİRKLƏNMƏNİN SU EKOSİSTEMLƏRİNİN BİOKİMYƏVİ XÜSUSİYYƏTLƏRİNƏ TƏSİRİ

H.X.Xəlilova

Beynəlxalq Ekoenerji Akademiyası
Az 1073, Bakı, M.Rahim küç., 5; e-mail: khalilova@rambler.ru

Məqalədə uzun müddət neft sənayesinin antropogen təsirinə məruz qalan su sistemlərinin biokimyəvi xassələrinə neft karbohidrogenləri ilə çirklənmənin təsirindən bəhs olunur. Tədqiqat nəticəsində Azərbaycanın əsas sənaye bölgəsi olan Abşeron yarımadasının neft yataqları ərazisində səth suları, dəniz suyu və dib çöküntülərində toksik karbohidrogenlərin yüksək miqdarı qeydə alınmışdır. Müşahidələr zamanı əksər səth suları nümunələrində neft karbohidrogenlərinin ümumi migdarının yol verilən həddən 10 dəfələrlə artıq olması, 1796 mkg/l-dən 53580 mkg/l-ə qədər dəyişdiyi məlum olmuşdur. Karbohidrogenlərlə çirklənmənin su sistemlərinə təsirinin qiymətləndirilməsi məqsədilə aparılmış analizlər uzun müddət antropogen təsirə məruz qalmaları ərazidəki su hövzələrinin keyfiyyətinin xeyli dəyişməsinə səbəb olduğunu göstərir.

Açar sözlər: *karbohidrogenlər, çirklənmə, dəniz suyu, dib çöküntüləri, ekosistem*

ВЛИЯНИЕ УГЛЕВОДОРОДНОГО ЗАГРЯЗНЕНИЯ НА БИОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ ВОДНЫХ ЭКОСИСТЕМ

Х. Х. Халилова

Международная Академия Экоэнергетики
Az 1073, Баку, ул.М.Рахима, 5; e-mail: khalilova@rambler.ru

В статье рассматривается вопрос влияния загрязнения углеводородами на биохимические характеристики водных экосистем, которые долгое время были подвергнуты антропогенному воздействию нефтяной промышленности. В результате анализов высокие концентрации токсичных углеводородов были обнаружены в образцах поверхностных и морских вод, а также донных отложений на территории нефтяных месторождений Абшеронского полуострова - основного промышленного региона Азербайджана. В большинстве пробах поверхностных вод концентрации нефтяных углеводородов превышали предельно-допустимой нормы в десятки раз, варьируя от 1796 мкг/л до 53580 мкг/л. Исследования, проведенные для оценки влияния загрязнения углеводородами на биохимические характеристики водных систем, показали, что длительное антропогенное воздействие существенно изменило природные качества водных ресурсов исследуемой территории.

Ключевые слова: *углеводороды, загрязнение, морская вода, донные отложения, экосистема.*

Поступила в редакцию 26.03.2016.