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Influences of Chemical Pollutants to the Biota of the Caspian Sea

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For 2012 - 2014, has been studied the pollution degree of water of the Caspian Sea of the Azerbaijan sector with the chemical pollutants and their impact on the populations and biomasses of zooplankton. Has been detected that petroleum hydrocarbons at concentrations of 0,05 - 0,5 mg/L, as a rule, do not affect the survival of marine organisms if their toxic effects are not exacerbated by the influence of other toxicants. A minimum development of zooplankton was 63 ind./m^3, and the maximum development marked in the summer 343 ind./m^3. Biomasses changed in a range of 1,799 mg/m^3 - 9,356 mg/m^3. In the contract areas of the «Gunashli», «8 March» and «West Absheron» of the Caspian Sea identified the high level of nutrients in winter, and low in summer, therefore the high level of nitrate compounds was in the interval of 2,998 - 4,082 mg/L, phosphorus compounds are represented in the range of 0,143-0,218 mg/L and silicon in 26,1- 28,2 mg/L, respectively. Given the above, it may be concluded about the current lack of significant negative effects on marine ecosystems and biological resources of the Caspian Sea by oil and gas development.

1. Introduction

Water systems where live aquatic organisms characterized by great diversity of the features of the migration distribution of chemical pollutants such as oil and oil products, pesticides and nutrients. Hydrochemical changes in the aquatic environment disrupt the conditions of existence of organisms, which is reflected in quantitative indicators and in the structure of the population, as well as on changes in the biogeochemical background. Since environmental factors play an essential role in the processes of formation of the resource potential of the Caspian Sea, the deterioration of the quality of the water condition due to external natural and anthropogenic factors and the continuing unstable state of marine biota, the technogenic load will inevitably lead to ecosystem degradation and irreparable damage the biota of the Caspian Sea (Patin, 2008).
Petroleum and petroleum products are related to the most widespread pollutants of the environment, causing significant changes in the chemical composition, properties and structure of water (Sadikhova et al., 2014). The petroleum pollutants reduce the species richness of hydrobionts communities, changing the ratio of species, decreases primary production (Lyushvin et al., 2009). Cladocera and juvenile copepods are the most sensitive to the effects of oil (Minina et al., 2014).
Currently quantify the total flow of petroleum hydrocarbons into the Caspian is very difficult. To do this, it is necessary to hold a series of targeted comprehensive researches, estimate the degree of water pollution by oil hydrocarbons in various parts of the Caspian Sea. This will make it possible to create an objective picture of the Caspian Sea pollution, predict the situation and to compile an integrated monitoring program for transboundary transport of pollutants (Chuikin et al., 2006). The goal of our work is studying the content and dynamics of petroleum products and biogenic elements in water that is an important hydrochemical and environmental issues.

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2. Materials and Methods

2.1 Materials

The collection of samples for the various groups of zooplankton was carried out in 2012 - 2014 from the littoral zone of the Azerbaijan sector of Caspian Sea on the research vessels “MPK - 452” and “M. Suleymanov”. Water samples for analysis were taken by a "Niskin" bathometer volume of 10 liters of a double repetition. Zooplankton was collected by plankton net Jedi and collections were carried out according to standard horizons 0-10, 10-25, 25-50 m. For fixation, Cladocera and Copepoda used 4% formalin solution. For painting hydrobionts in the fixing fluid a small amount of dye «Bengal Rose». (Salahova et al., 2014).

2.2 Methods of analysis

2.2.1. Hydrobiological method

For counting zooplanktons used the method of calculation living specimens in Bogorov's chamber. Identifying and counting species were carried out under a binocular microscope «Mobic» K-500L (USA) (100 - fold increase) and under the microscope «Nicon» B1 series (Japan) (1000 - fold increase). For species, determination mainly used books an "Atlas of Invertebrates of the Caspian Sea" (Birshtein et al., 1968) and "Atlas free-living ciliates" (Alekperov, 2005) as well as a number of other publications.

2.2.2. Gas chromatography method (GC)

Extraction of petroleum products from the liquid phase was carried out by extraction with organic solvents. For the separation of polar from nonpolar compounds, the obtained extracts were passed through a column filled with activated silica gel and sodium sulfate. Determination of the concentration of n-alkanes, PAHs and BTEX was conducted using a gas chromatograph with flame - ionization detector (GC-FID Shimadzu 2010 Plus, Japan) and (Pegasus 4D TOF-MS, USA) that are equipping with the column of Rxi-5ms (Restek).

2.2.3. Spectrophotometric method

The concentration of advanced biogenic elements NO_2^-, NO_3^-, $NH4^+$, PO_4^{3-} and SiO_2 was determined by spectrophotometer Shimadzu UV 1800 with the different optical wavelength λ. For the quality control of all chemical analyzes used different standards.

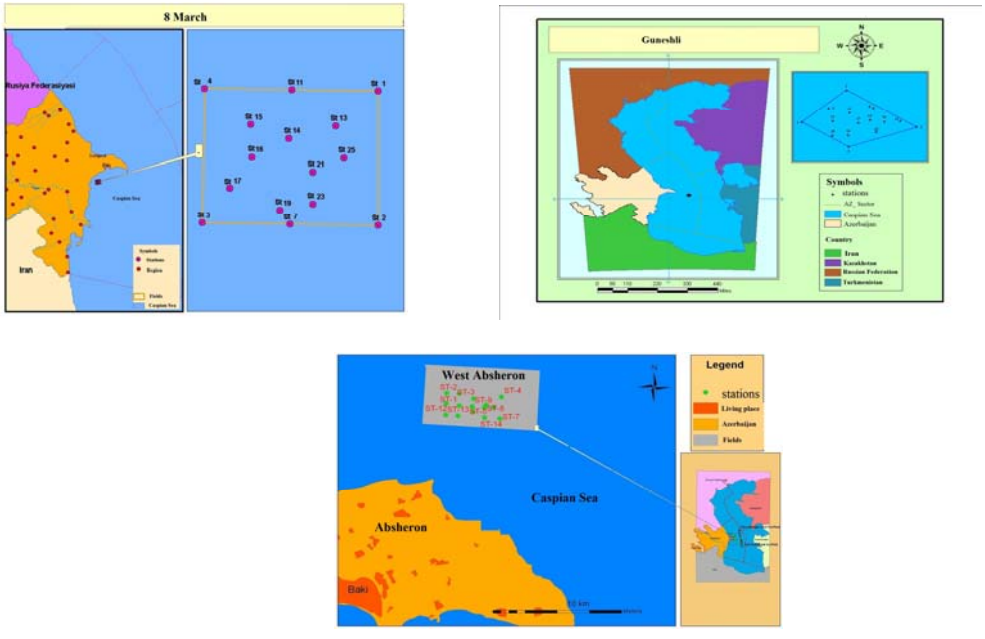

Figure 1. The scheme of the location of investigation fields

3. Results and discussion

We have studied the degree of water pollution with petroleum and petroleum products and its influence on plankton in the areas of direct sampling of hydrobionts. During the investigation years, 243 samples of bottom plankton and for chemical analysis in the areas with stony and muddy bottoms were selected in three oil and gas fields: "West Absheron", "8 March" and "Gunashli". On the territories of "8 March" and Western Apsheron"

all of the samples were taken from 28 stations and on the field of "Guneshli" were sampled from 25 stations with a triplicate repetition for zooplankton and a two-fold repetition for chemical analyzes.

The data regarding to "West Absheron":

The concentration of oil products in the water from 2012 to 2014 was averaged 0,0466 mg/L, whereas the maximum value was varied from 0,064 mg/L in 2012 to 0,054 mg/L 2013 and and exceeded the MPC approximately 1.26 times. In the spring of 2014, the maximum concentration of petroleum hydrocarbons were 0,047 mg/L, but a minimum concentration dropped slightly and was in December of 2014 – 0,028 mg/L.

The lowest concentrations during the investigation period were recorded in winter of 2013, where the average concentration was 0,036 mg/L, a maximum - 0.054 mg/L and a minimum – 0,022 mg/L. In the autumn of 2012 - 2014, the total content of PAHs in the surface layers varied from less than 0,025 μ/L to 9.5 μ/L. On the horizon of 21 m the PAHs content was varied in the range of 0,25 μ/L to 9,52 μ/L, with the averaged value of 4,88 μ/L. Over the study period BTEX content in the water of the Caspian Sea was less than <0,05 mg/L. In this field have been encountered 15 species of zooplankton, to the share of the Cladocera accounting 6 species or 37,5% of the whole fauna. Copepods are also 37,5%, while the others are 18,75%. The highest value of species observed also in autumn (13 species), the lowest in winter (10 species). The dominant species are representatives of the genus of Copepoda - (Podonevadne trigona, Pleopsis polyphemoides, Eurytemora grimmi, Eurytemora minor and Acartia tonsa). The average annual abundance of zooplankton in autumn of 2012 was -178,4 ind./m^3 and the biomass – 4,69 mg/m^3, in winter was 106,5 ind./m^3 and 2,956 mg/m^3. In 2013, the total number of zooplankton was 17 species, to the share of Copepod accounts 41,17% of the whole fauna and represented by 7 species in autumn and 46,15% or 5 species in winter. The maximum number of abundance and biomass falls on September (262 ind./m^3 and 9,356 mg/m^3). The mean value of the zooplankton masses and abundances for 2014 were 4,868 mg/m^3 and 235,5 ind./m^3. The highest biomass was noted at (st.25 – 5,1897 mg/m^3) and the minimum at (st.3 – 1,799 mg/m^3).

The data regarding to "8 March":

In the water area of the "8 March" oil and gas field, we found 15 species of the representatives of mesoplankton. By the number of species were dominated cladocerans (50%), the second place were occupied by copepods (42%), the third was ctenophore (20%) and the fourth - the larvae of mollusks, balanus and copepods a totaling consist 8%. The maximum development of biomass of the mesoplankton at depths of 0 - 50 m was registrated in spring (9,178 mg/m^3). The maximum number of mesoplankton was recorded in August (343 ind./m^3) and the minimum number in November (192 ind./m^3). The maximum concentration of all petroleum hydrocarbons noted in May of 2012 and was 0,0723 mg/L, for 2013 - 2014 the maximum concentrations were also in the range of 0,0614 – 0,049 mg/L, thus it exceeded the MPC almost 1,4 times. However, observed the decreasing in the minimum concentrations during the investigation period, only noted their fluctuations in the intervals from 0,035 to 0,03 mg/L. The average concentrations for 2012 - 2014 also changed and were in the interval from 0,0489 mg/L to 0,0377 mg/L.

The data regarding to "Gunashli":

In 2012 – 2014 in zooplankton community were already 12 species. By the number of species were dominated Copepoda (41,66%), the second place was occupied by the Cladocera (25%), the third - ctenophore (8%) and the fourth by the larvae of the mollusks and balanus (25%). The highest development of mesoplankton biomasses was observed in the summer (6,18 mg/m^3), while in the autumn was observed a decreasing. The maximum abundance of zooplankton was recorded in June (216 ind./m^3 - 229 ind./ m^3), and the minimum was in November (137 ind./m^3). Cladocera predominated in the zooplankton groups. In the summer of 2014, the abundance and biomass of Cladocera and Copepoda decreases; So, if in 2012 - 2013 years the number of Cladocera was 216 ind./m^3, then in 2014 it was 67 ind./m^3, and the total weight of Copepods were dropped 1,39 times and was 4,45 mg/m^3. The maximum concentration of petroleum hydrocarbons in water during the period from 2012 to 2013 was 0,060 mg/L, and in 2014, the total concentration of all hydrocarbons was 0,477 mg/L. Over the researching period of hydrocarbons the minimum concentration climbed, so for instance, if in 2012 it was 0,032 mg/L, in 2014 it was 0,26 mg/L. The average concentration over the period from 2012 to 2014 were in the range of 0,047 and 0,288 mg/L and exceeded the MPC by 9,5 times at (MPC 0.05 mg/L). Thus, zooplankton in the territory of the contract area of "Gunashli" in 2012 - 2014 characterized by the low species abundance and quantitative indicators, that may be related to the effect of oil products, as evidenced by the characteristics of the community on the background section. The results of water analysis for the presence of oil products showed that the concentration of hydrocarbons in the sea water on the studied water areas were 0,022-0,288 mg/L, that is, along with the areas where was not observed excessing, there were also areas where the concentrations of petroleum hydrocarbons exceeded the maximum permissible concentration that is existing in Azerbaijan. Increasing content of petroleum hydrocarbon concentrations noted in some samples in separate seasons is most likely due to the spotted distribution of these in the Caspian Sea. As can be seen from Figure 2., during the observation period from 2012 to 2014 there was a tendency to reduce the concentration of petroleum hydrocarbons in the marine ecosystem, with the exception of the «Gunashli» oil and gas field.

We revealed that the contact of hydrobionts with petroleum at concentrations of 1,25 and 2,5 mg/L led to copepods deaths of 20% and 55%, respectively; however, with a maximum concentration of 100%, mortality was noted on the 10th day of the experiment. The obtained data indicate that in the investigated range (0,5 – 5,0 mg/L) only the minimal concentration did not have a negative effect to the plankton. Thus, based on these data, it can be stated that during the working period of this macro - and microfauna lived in an environment with non-toxic levels of petroleum hydrocarbons.

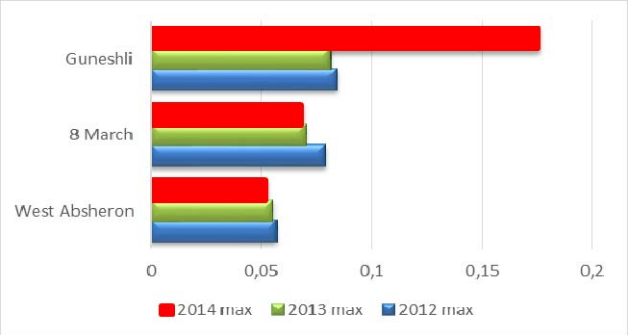

Figure 2. The content of petroleum hydrocarbons in oil and gas fields.

In accordance to the obtained values in 2014, "Gunashli" was the most polluted field, although this trend was not traced in 2012-2013. According to the literature data by the following criteria can be judged the recovery of the biota of the Caspian Sea: 1. In the species composition of zooplankton community must be present more than 1 type; 2. In the absence of pollution, the number of zooplankton must not be less 100 ind./m^3 in spring and 40 ind./m^3 in summer, biomass should not be less 0,065 mg/m^3 in spring and 0,078 mg/m^3 in summer (Mingazova et al., 2014).

Therefore, researching of biological diversity confirms that the toxic effect of oil field pollution is limited on the population level, reduces the quality of the environment condition, but does not yet affect the actual biological diversity (which does not apply to separate local areas), where the level of anthropogenic load exceeds the permissible limits.

Simultaneously, have been analyzed the concentration of biogenic elements in the water and how they affected to the hidrobionts. The biogenic components that are present in natural waters include compounds of nitrogen, silicon and phosphorus, which play a major role in the aquatic ecosystem, determining the biological productivity of water bodies and at the same time serve as one of the indicators of water pollution. Furthermore, some of the compounds of biogenic elements have toxicity when their MPC is exceeded. The presence of nitrogen in water is regulated not only by the intake processes, but also by the consumption of it by hydrobionts. In the reservoir, mineral nitrogen is contained in three forms - ammonium, nitrite and nitrate.

In the distribution of the values of ammonium nitrogen concentration seasonally, can be revealed following main regularities. Over the investigation, the relative maximum was observed in November - December and was 0,32 mg/L, and the minimum value reached 0,225 mg/L in the autumn at the “Gunashli” field. On the "8 March" oil and gas field, the dynamics of distribution of the concentration of ammonium nitrogen was uniformity and amounted were 0,276 mg/L - 0,48 mg/L for 2012 - 2014. The average analytical concentrations in water from 2012 to 2014 decreased from 0,333 mg/L to 0,321 mg/L. The highest values of nitrogen ammonium concentration in the summer of 2013 reached to 0,48 mg/L and the minimum - 0,11 mg/L. In September of 2014, the maximum and minimum concentrations of ammonium nitrogen were in the interval of 0,41 - 0,13 mg/L. The lowest concentration of ammonium nitrogen for the observed periods recorded in autumn 2013 where the average concentration was 0,335 mg/L (maximum - 0,48 mg/L, min - 0,11 mg/L).

One of the main elements, which take part in the formation of quantitative indicators of zooplankton of the Southern Caspian, are organic and mineral compounds of nitrogen and phosphorus. The number of zooplankton during the investigation period averaged 235,5 ind./m^3, and the biomass was 4,87 mg/m^3. The basis of the quantitative composition of mesoplankton was Cladocera and Copepoda, accounting for 82,6% of the abundances and 96,8% of the biomasses of all zooplankton. During the period of research 2012 - 2014, the largest amount of zooplankton was 343 ind./m^3 in 2014 in the oil and gas field “8 March". The natural predominant species were species such as Eurytemora grimmi, Eurytemora minor, Acartia tonsa and Polyphemis exignus. Increasing the abundances and biomasses of zooplankton in 2014 does not coincide with the maximum concentrations of phosphorus and nitrogen compounds (0,276 mg/L and 3,25 mg/L), which is observed in winter. The biological processes in water were most intensively influenced to the concentration of

nitrates; in this case nitrates are most actively absorbed by hydrobionts. Therefore, their content drops to an analytical zero in the summer. Gradually, with a decreasing of abundances and biomasses of zooplankton (respectively, with the decreasing of the consumption of nitrates), the concentration of nitrates increased gradually. In addition, with a lack of oxygen, proceeded the nitrification process, that is leading to the transition of ammonium nitrogen to nitrates and nitrites . Some oil and gas fields such as "Guneshli" were represented by weaker development of zooplankton and their abundance was 216 - 67 ind./m^3. In winter, in the water of the territoty of "8 March" was observed the high level of nitrate content from 2,998 to 4,082 mg/L and phosphorus compounds are represented by phosphate ions - from 0,143 - 0,218 mg/L, which is due to the decay of the organic matter accumulated over the summer (phyto - and zooplankton). In May, during the flood recession, concentrations of nitrates and phosphates decreased and in summer, in the period of intensive vegetation of algae, contuning a further decreasing in the content of nitrates and phosphates occurred. During this period, was observed the minimum content of these substances. In autumn, with the onset of mass decomposition of organic substances and as a result of additional intake with rain floodwaters were observed a second maximum peak in the content of nitrates and phosphates. In November - December, the concentrations of biogenic elements (phosphates, sometimes nitrates) increased sharply, reaching the spring level, and in some cases even exceeded it. This increasing concentrations is presumably associated with an increasing the role of washout of dissolved substances from the surface of the catchment.

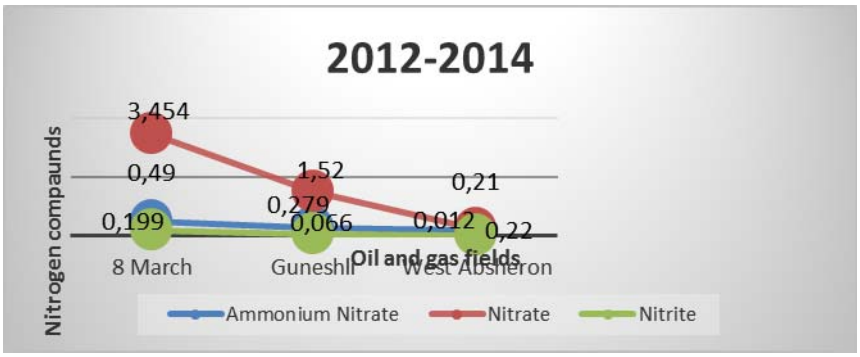

Figure 3. Long-term concentrations of nitrogen compounds in the investigated field.

Unlike other biogenic elements, silicon is always present in sea water in significant quantities. Moreover, the amount of unused silicon is usually higher than the nitrogen and phosphorus. It is not redused to zero even in the zone of photosynthesis and does not limit the development of life processes in the sea. The source of silicon is carried out by its continental runoff, the dissolution of various mineral suspensions and rocks, which form the bottom of the sea, the transition silicon into a solution from organic suspensions, underground ionic runoff and the activity of underwater volcanoes. Silicon is necessary for many planktonic algae, as it is an integral part of their shells, bristles, scales, cysts. With depth, the content of silicon increases, reaching a maximum in the bottom layer. So the content of silicon and ion silicate in the water of the Caspian Sea is shown in detail in Table 1.

Table 1. Maximum and minimum content of nutrients, oil products and abundance of zooplanktons in the three oil and gas fields.

		8 March			Guneshli			West Absheron		
		a	b	c	a	b	c	a	b	c
Zooplankton (ind./m3)	max	198	258	343	216	229	67	262	291	323
	min	132	156	192	115	137	51	124	109	184
Oil products (mg/l)	max	0.0723	0.061	0.049	0.060	0.042	0.477	0.064	0.054	0.047
	min	0.035	0.035	0.03	0.032	0.029	0.26	0.032	0.022	0.028
Nitrogen compounds (mg/l)	max	3.939	3.704	4.751	1.78	1.865	1.22	0.741	1.188	2.407
	min	2.439	2.155	3.28	1.372	1.417	0.852	0.462	0.843	1.381
Phosphorus (mg/l)	max	0.199	0.193	0.276	0.179	0.143	0.218	0.184	0.297	0.193
	min	0.21	0.122	0.129	0.056	0.041	0.083	0.048	0.056	0.032
Silicon (mg/l)	max	26.1	28	28.2	18.87	18.69	16.48	15.47	16.49	15.28
	min	18.7	16.6	18.6	15.38	15.19	13.4	14.12	14.54	14.23

where: a - 2012; b - 2013; c – 2014

The Table 1 shows that maximum and minimum content of nutrients, oil products and abundance of zooplanktons in the three oil and gas fields. From our analysis, follows that by increasing the content of all biogenic elements observed decreasing in abundances and biomasses of zooplankton.

4. Conclusion

Have been revealed, that currently there is no noticeable negative impact of the development of oil and gas fields on the marine ecosystems and bioresources of the Caspian Sea;

Biochemical studies on the territory of the contract areas of the «Gunashli», «8 March» and «West Absheron» fields of the Caspian Sea detected that the high level of nutrient were in winter and low in summer; while a high level of nitrate content was in the range of 2,998 - 4,082 mg/L, phosphorus compounds are represented in the range of 0,143 - 0,218 mg/L and silicon in the range of 26,1- 28,2 mg/L;

Analysis of the data on the qualitative and quantitative development mesoplankton showed that the minimum development of all hydrobionts were observed in the winter and up to April – (67-137 ind./m^3.), and the maximum observed in August and September – (262- 343 ind./m^3.)

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