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**Salahova SZ**

Zoology Institut of ANAS AZ  
1073 Azerbaijan, Baku, passage  
1128, quarter 504.

**Sh Topchieva A**

Zoology Institut of ANAS AZ  
1073 Azerbaijan, Baku, passage  
1128, quarter 504.

## The pollution water and bottom sediments of the Caspian Sea by petroleum products

**Salahova SZ, Sh Topchieva A**

### Abstract

Had been studied the degree of water contamination and bottom sediments of the Caspian Sea with the oil products. For the investigation period in the waters of the oil fields of South Caspian are fixed 66 species of zooplankton. It was revealed that petroleum hydrocarbons in concentrations of 0.05-0.5 mg/l, as a rule, don't affect survival of marine organisms, if their toxic effects are not exacerbated by the action of other toxicants. It is shown that during the study from 2011 to 2013, observing a tendency of decreasing the content of petroleum hydrocarbons in sea water, exception to oil-gas field "Gurgan". It is established the maximum value of abundance and biomass of zooplankton (1331 ind./m<sup>3</sup> and 8.757 mg/m<sup>3</sup>) for the summer season on the field of Oil Rocks. It was noted the current lack of significant negative consequences for marine ecosystems and biological resources of the Caspian Sea from oil and gas development. This may indicate a some improvement and general stabilization of the ecological situation in the entire offshore of the Caspian Sea.

**Keywords:** petroleum pollution, n-alkanes, mono- and polycyclic aromatic hydrocarbon, gas chromatography, hydrobionts, Caspian Sea

### Introduction

The technogenic impact on the environment is manifested in all stages of operation of oil and gas complex and the main pollutants are the petroleum hydrocarbons, chemicals, acid-forming substances, phenols [1]. Of all pollutants released into the Caspian Sea, the main part falls on the oil, oil products, phenols. Petroleum products trapped in the aquatic environment, are exposed to numerous processes and as a result the polluted water bodies is undergoing significant changes. Oil pollution affects negatively to the quality of water and hydrobiont habitat conditions [2]. Zooplankton of water ecosystems is among the most rich nutrient food for juvenile fish. The productivity of the fish depends on the abundance and biomass of zooplankton. Planktonic organisms serve the bioindicators of regime of the waterbodies and pollution [3]. Zooplankton communities of the Caspian Sea are determined by the ratio of the three main groups: rotifers, copepods and Cladoceras [4]. Studying the impact of oil pollution on water ecosystems is relevant in connection with the development of oil producing complex [5].

The goal of this study was to examine the pollution degree of the oil and gas territories of Azerbaijan sector of the Caspian Sea with petroleum hydrocarbons and their impact on the biological diversity of hydrobiont.

### Material and methods

Water samples were collected by using a sampler «Niskin» volume of 10 liters and for a full analysis samples taken with the two-time repetition. There were used samplers "Van – Veen" with an area of 0.1 m<sup>2</sup> for taking sediment and for precise of analysis samples taken with the three-fold repetition. For the extraction of petroleum products from the liquid or solid phase was applied extraction with certain organic solvents. As a solvent have been used hexane, dichloromethane and acetone for gas chromatography (GC). To reduce the pH  $\geq 2$  water samples were oxidized HCl (c) or H<sub>2</sub>SO<sub>4(c)</sub>. For determining the concentration of n-alkanes and monocyclic aromatic hydrocarbons (benzene, toluene, ethyl benzene, m-, p, o-xylene) further extraction was carried out in ratios of 10:1, and for determination of polycyclic aromatic hydrocarbons (PAH) in water further extraction was performed with the samples in the ratios of 5: 1 and repeated twice. For the extraction of sediments samples were taken with weight 2-4 g. with a precision of 0.01 g. When the determining PAH added 12 ml of dichloromethane,

### Correspondence

**Salahova SZ**

Zoology Institut of ANAS AZ  
1073 Azerbaijan, Baku, passage  
1128, quarter 504.

and for determination of n-alkanes and BTEX (benzene, toluene, ethyl benzene, m-, p-, o- xylene) added 30 ml of acetone and hexane in the ratios of 1: 1. For the best shaking samples were placed on a shaker. The obtained eluent was passed through a silica gel column. Extract for the PAH and n-alkanes evaporated to dryness and the dry residue was dissolved in 2 ml of solvent (dichloromethane, hexane). For analysis of purified extracts used the gas chromatography method. Analyses on determination of the concentration n-alkanes, PAH and BTEX were performed using a gas chromatograph with the flame ionization detector FID Shimadzu GC-2010 Plus (Japan), which equipped with a column Rxi - 5ms (Restek). Injection volume of extract for all analyzes was 1 $\mu$ l. To prepare the calibration solutions as a standard was used (Test Standard Mixture of n-alkanes in Hexane, Restek) with a concentration of each component in

the hexane, 50 g/ml, (BTEX Standard, Restek) with a concentration of each component in methanol 200  $\mu$ g/ml, (SV Calibration Mix # 5 PAH Mix, Restek) with a concentration of each component in hexane 2,000  $\mu$ g/ml. For the quality control of all analysis were used blanks, duplicate and replicate samples, for PAH also a certified sample (WEPAL). In the water samples calculation is carried out on 1 liter of water, whereas the sediment is counting on the dry weight.

## Results

In the waters of the oil fields of the South Caspian for the study period are fixed 150 species of zooplankton (Table 1) among them by number of species dominated cladocerans (11 species), the second place is taken by copepods (7 types), and the third place is taken by the larvae of invertebrates (3 species).

**Table1:** The species composition of the zooplanktons on the investigated oil and gas fields.

	Oil Rock	Banka Absheron	Gurgan	SDXZ
<b>Cladocera</b>				
Polyphemus exiguus	+	+	-	+
Pleopis polyp-hemoides	-		-	
Evadne anonyx typica	+	+	+	+
E.anonus prolongata	+	+	+	+
Apagis culindrata	+		-	-
Podonevadne trigona	+	+	-	-
P.trigona typica	+	+	+	+
Podonevadne trigonoides	-		-	+
P.trigona intermedia	-		+	+
Cercopadis pengoi	+	+	+	+
Potonevadne camptonyx	+		-	-
<b>Copepoda</b>				
Helicyclops sarsi	+	+	-	+
Hetercope caspia	+	+	+	+
Limnocalanus grimaldii	+	-	-	-
Calanipeda aquaedulis	+	+	+	+
Eurytemora grimmi	+	+	+	+
Euretemora minor	+	+	+	+
Acartia tonsa	+	+	+	+
Ctenophora				
Mnemiopsis leidyi	+	+	+	+
Others				
Larvae Mollusca	+	+	+	+
Larvae Balanus	+	+	+	+
Larvae Copepoda	+	+	+	+
Total	19	16	14	17

Most of zooplankton for the investigated period found in the area of oil and gas fields Oil Rocks, Sangachal-Duvanna-Khara-Zira, Absheron Banka and least of all on the territory of Gurgan. In the above-mentioned fields spread such species as Podonevadne trigona typical, Podonevadne trigonoides, Evadne anonyx typica, Evadne anonyx prolongata, Eurytemora grimmi, Calanipeda aquaedulis, Hetercope caspia and Acartia tonsa.

Organisms that live in the macrophyte thickets, were located in the thickness of sea water. Considering this, we have studied the levels of oil pollution in water and bottom sediments in areas of direct selection of hydrobionts samples.

During 2011 - 2013 years in areas with stony and muddy bottom were selected in order of 250 - 310 samples of seawater and sediment.

Concentration of petroleum products in water in 2011-2013 ("Banka Absheron") was on average 0,0466 mg/l, whereas the maximum value varied from 0,054 to 0,063 mg/l, but the minimum value was in the range of 0,034 mg/l. The total amount of oil hydrocarbons in sediments was 69 mg/kg, with a

minimum amount of 52 mg/kg. In autumn of 2011- 2013 the total content of PAH in the surface layer was changed from 0.025 to 9.5 g/l. On the horizon of 21 m content of PAH was varied in the range of 0.25 to 9.52 g/l, with a mean of 4.88 mg/l.

In water of the given field encountered 16 species of zooplankton, while a fraction of Cladocerans accounted 6 species or 37,5% of the fauna. Copepods constituted also 37, 5% and the others amounted 18.75%. The highest value of species observed in the autumn (13 species), the lowest - in the winter (10 species). The dominant species were representatives of Copepod - (Eurytemora grimmi, Eurytemora minor and Acartia tonsa). The average annual number of zooplankton for 2011 was 128.4 ind./m<sup>3</sup> in the autumn and biomass - 3.69 mg/m<sup>3</sup>, but in winter - 76.5 ind./m<sup>3</sup> and 2,816 mg/m<sup>3</sup>. In 2012 the total number of zooplankton was represented by 17 species, while at a fraction Copepod accounted 41.17 % of all fauna and was represented by 7 species in autumn and 46.15 % or 6 species of winter. Thus the maximum value of abundance and biomass were in September (212 ind./m<sup>3</sup> and 9,3536

mg/m<sup>3</sup>). The average value of the mass and abundance of zooplankton for 2013 were 4,668 mg/m<sup>3</sup> and 164.53 ind./m<sup>3</sup>. The highest biomass observed at the station 25 – 4, 1897 mg/m<sup>3</sup> and the minimum at the station 3 -1,799 mg/m<sup>3</sup>.

In the coastal waters of "Sangachal Duvanna Khara Zira" investigated 14 species of mezoplankton, among which by number of species the first place occupied Cladocerans (7 types), then Copepods (6 species) and larvae of invertebrates (3 types). The total biomass in 2011-2012 fluctuated between 152 ind./m<sup>3</sup> (st. №2) ÷ 218 ind./m<sup>3</sup> (st. №4), the average biomass of zooplankton was 3.44 mg/m<sup>3</sup>, while the average number was 166,7 ind./m<sup>3</sup>. In 2013, the average biomass was 2,646 mg/m<sup>3</sup>, while the number was 143, 37 ind./m<sup>3</sup>. The maximum value of zooplankton observed in October, 213 ind./m<sup>3</sup>, and the minimum in April, 114 ind./m<sup>3</sup>. The averaged content of petroleum hydrocarbons were 0,050 mg/l. In the summer of 2011 was recorded maximum concentration of 0,069 mg/l, but in November 2013 the maximum concentration decreased and amounted to 0,057 mg/l. Observed a decrease the content of PAHs from 2011 to 2013 on average up to 0,057 mg/l. In the sediments the content of hydrocarbons was a slight decrease from 69 to 55 mg/l.

In 2011-2012, "Gurgan" greeted by 12 species of zooplankton. As the number of species was dominated by copepods (41, 66%), the second place was occupied by cladocerans (25%), third - stenofora (8%) and the fourth - larvae of molluscs, balanus and copepods- (25%). The maximum development of mezoplankton observed in summer (10, 18 mg/m<sup>3</sup>), but in autumn observed a decrease of zooplankton biomass. The maximum number of zooplankton observed in June (216 ind./m<sup>3</sup> - 229 ind./m<sup>3</sup>), and the lowest recorded in November (137 ind./m<sup>3</sup>). From zooplankton groups dominated Cladocera. In summer of 2013 the abundance and biomass of Cladocera and Copepod decreases, so if in 2011-2012 the number of Cladocera was 229 ind./m<sup>3</sup>, in 2013 was 66 ind./m<sup>3</sup>, and the total mass of Copepod decreased 1,3 times and amounted to 8,45 mg/m<sup>3</sup>. Thus, zooplankton on the territory of Gurgan in 2011 - 2013 are characterized by low species richness and quantitative indicators, which could be due to the influence of petroleum products, as evidenced by the characteristics of the community on the background section too. The maximum amount of oil products concentration in 2011-2012 was – 0,060 mg/l, and in 2013 the maximum concentration has reached 0,277 mg/l.

In the water of this field "Oil Rocks" observed 16 species in the summer and 13 species of zooplankton in the autumn, while at a fraction of cladocerans accounted 7 species or 43,75% of the entire fauna. Copepods were 37, 5% and were presented by 6 species, and the others were 18, 75%. The dominant species were representatives of Copepoda - (Eurytemora grimmeri, Eurytemora minor and Acartia tonsa). The average annual number of zooplankton for 2011 in summer was 178 ind./m<sup>3</sup> and biomass - 4, 49 mg/m<sup>3</sup>, but in autumn – 85, 57 ind./m<sup>3</sup> and 3,24 mg/m<sup>3</sup>. In 2012-2013 the total number of zooplankton is represented by 17 species, while on a fraction of Copepod accounted 41, 17% of the entire fauna, which are represented by 7 species. The maximum value of the abundance and biomass accounted for the summer (1331 ind./m<sup>3</sup> and 8,757 mg/m<sup>3</sup>). Distribution dynamics of hydrocarbon concentration is characterized by uniformity and for 2011-2013 is 0,094 mg/l - 0,058, at a mean value 0, 0726 mg/l.

The results of the water analysis for petroleum products content showed that the average content of the oil products in seawater on the investigated area were 0,0029 – 0,0885 mg/l,

that is, were areas where there is no excess and were areas where oil products concentration exceeded MPC existing in Azerbaijan. Increasing the content of the petroleum products, this is noted in some samples in separate seasons, most likely associated with a spotty distribution oil product in the sea. As seen from Fig. 1, during the observation period from 2011 to 2013, there is a tendency reducing the content of the oil petroleum in sea water, except the "Gurgan" field. This may indicate about slight improvement, and general stabilization of the ecological situation in the whole water area of the Caspian Sea.

From the presented data some authors shown [6] that contact hydrobiont with the oil led to a decrease the resistance Calanipeda at concentrations of 1, 25 and 2, 5 mg / l, while the death was 20 and 55% respectively, at the maximum concentration 100% mortality is marked on the 10th day of the experiment. The obtained data suggest that in the investigated range (0, 5-5, 0 mg/l), only a minimum concentration has no negative effect on Calanipeda.

On the whole we might say that during the period of the present work the macro and micro-fauna lived in an environment with low levels of the OH.

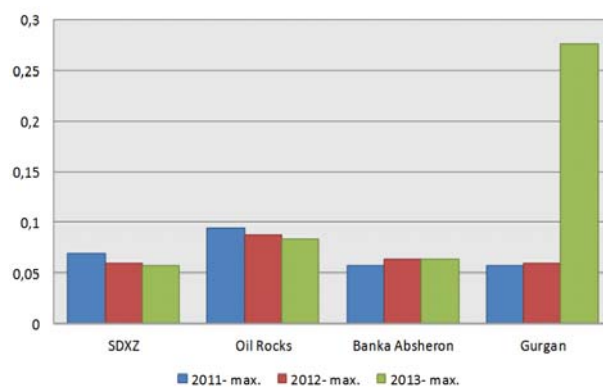


Fig 1: The content of oil hydrocarbon on the oil and gas fields

Zooplankton characterized with the minimum values of quantitative indicators and the broken structure immediately after the entering petroleum products. By obtained values in 2013 the area of Gurgan of the Caspian Sea was most polluted, although in 2011 -2012 these trends were not traced.

In summary, it can be concluded about the current lack of significant negative consequences for marine ecosystems and biological resources of the Caspian Sea from oil and gas development. In the Azerbaijani sector the water area of the sea for a few exceptions was practically cleared. This was facilitated a number of factors, one of which raised its level.

## Conclusions

1. Installed that average content of oil hydrocarbon in seawater on the studied water areas were 0,029 – 0, 0885 mg/l, i.e. there were areas where no excess and were areas where the concentration of oil hydrocarbon exceeded MPC.
2. Revealed that petroleum hydrocarbons in concentrations of 0, 05–0, 5 mg/l, as a rule, don't influence the survival of marine organisms, if their toxic effects are not exacerbated by the influence of other toxicants.
3. It is shown there is a tendency reducing the content of the oil hydrocarbons in sea water, with the exception of the field "Gurgan" in the research period from 2011 to 2013.
4. Revealed the maximum value of zooplankton biomass and number accounted on the summer season on the field Oil Rocks (1331 ind./m<sup>3</sup> and 8.757 mg/m<sup>3</sup>).

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