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Assessment of the Impact of Oil and Heavy Metal Pollution in the Azov Sea on the Condition of the *Neogobius Melanostomus* (Pallas, 1814)

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Assessment of the Impact of Oil and Heavy Metal Pollution in the Azov Sea on the Condition of the *Neogobius melanostomus* (Pallas, 1814)

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Abstract. This article presents the results of long-term monitoring of the oil pollution in the Azov Sea. Areas with long-term chronic pollution (Arabat and Kazantip bays) are identified. The Azov sea transport routes and the location of natural gas fields can be the reason of the oil pollution. In addition to chronic oil pollution, this area is contaminated with heavy metals in particular in bottom sediments. The biological indicator was chosen for a more accurate analysis - the condition of the bottom-dwelling fish Round goby (*Neogobius melanostomus* (Pallas, 1814)). Comparison of the size-mass characteristics, biochemical indicators and morphophysiological parameters of *Neogobius melanostomus* in different years has shown a decrease in the quality of habitat conditions. This decrease may occur due to contamination of the territory with oil products and heavy metals.

1. Introduction

Marine ecosystems are exposed to the direct and indirect human impacts through accumulation of incoming pollutants with surface runoff and deposition of contaminated precipitation[1]. In this regard, marine ecosystems are the most vulnerable[2]. The critical pollutants to marine ecosystems are oil products, heavy metals, synthetic long-lived radionuclides and chlorinated hydrocarbons[3]. In this connection, the content of oil products and heavy metals in water and bottom sediments was assessed, as well as an assessment of the dynamics of the condition of the bottom hydrobionts based on the condition of bottom-dwelling fish Round goby (*Neogobius melanostomus* (Pallas, 1814)). This assessment was conducted to determine the condition of the ecosystemsouthwestern part Azov Sea.

2. Discussion of the Results

Monitoring of the oil pollution in the water of the western part of the Azov Sea, conducted by the Southern Research Institute of Marine Fisheries and Oceanography from 2001 to 2009, showed that when the concentration of oil products in the water decreased from 2006 to 2009, the concentration of oil products in the bottom sediments was reversed. Thus, in 2009 the minimum content of oil products in water (Fig. 1) and the maximum in bottom sediments were found (Fig. 2)[4].



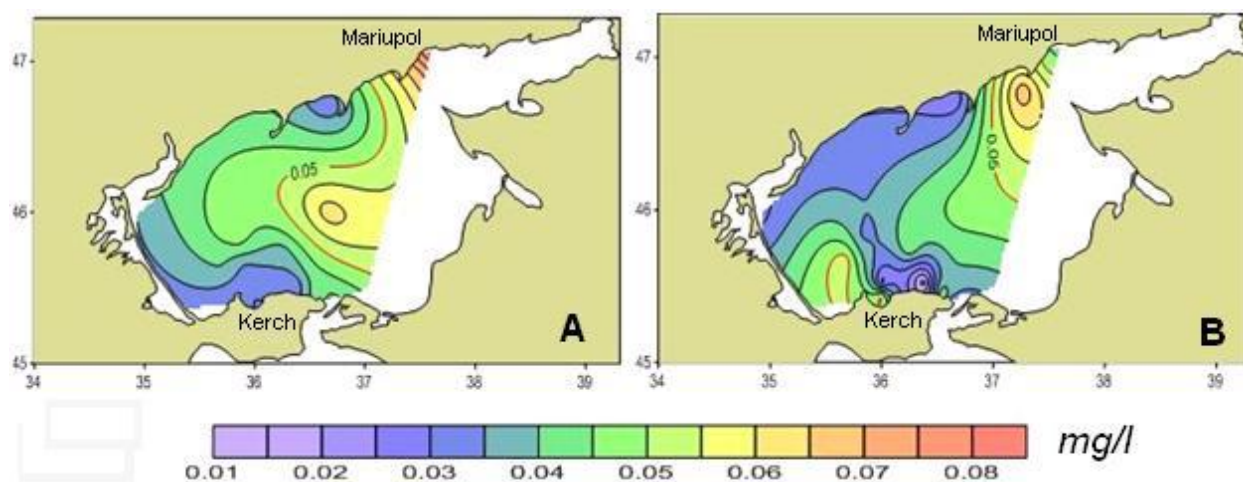


Figure 1. Distribution of oil products in the Azov Sea water in 2009: A - surface horizon; B - bottom horizon [4].

The analysis of water from the surface horizon near the Novootradnoe of the Kerch Peninsula in July 2017 showed the content of oil products = 0.009 mg/l. This analysis carried out by the authors is confirmed the oil products distribution map in the Azov Sea.

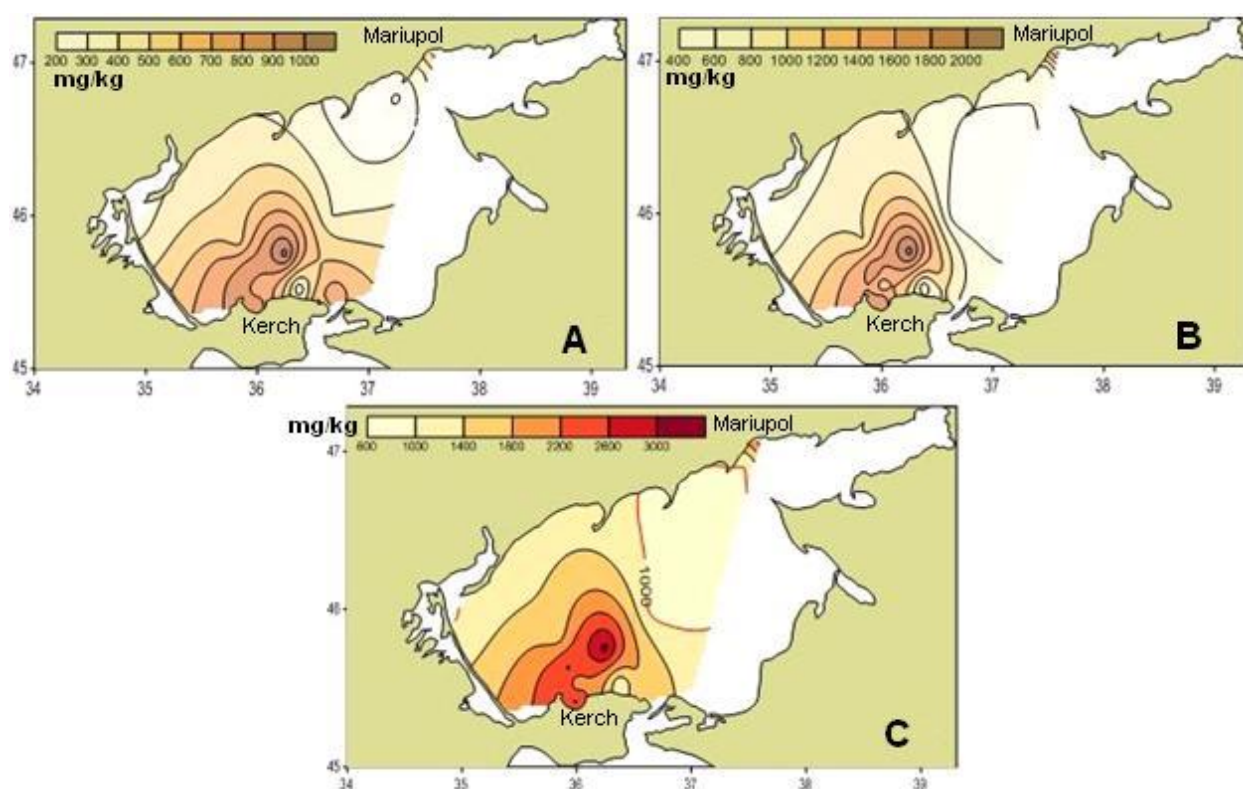


Figure 2. Distribution of oil products in bottom sediments (mg / kg) of the Azov Sea in 2009: A - fraction of resins and asphaltene; B - fraction of oil hydrocarbons; C - total oil products [4].

According to Figure 2, the largest content of petroleum products in the bottom sediments in the western part of the sea was recorded in the Arabatsky Gulf and on the Arabatskaya arrow. This pollution can be associated with the location of existing gas fields (Fig. 3.) and the passage of major sea routes to the large ports of the Azov Sea[5,6].

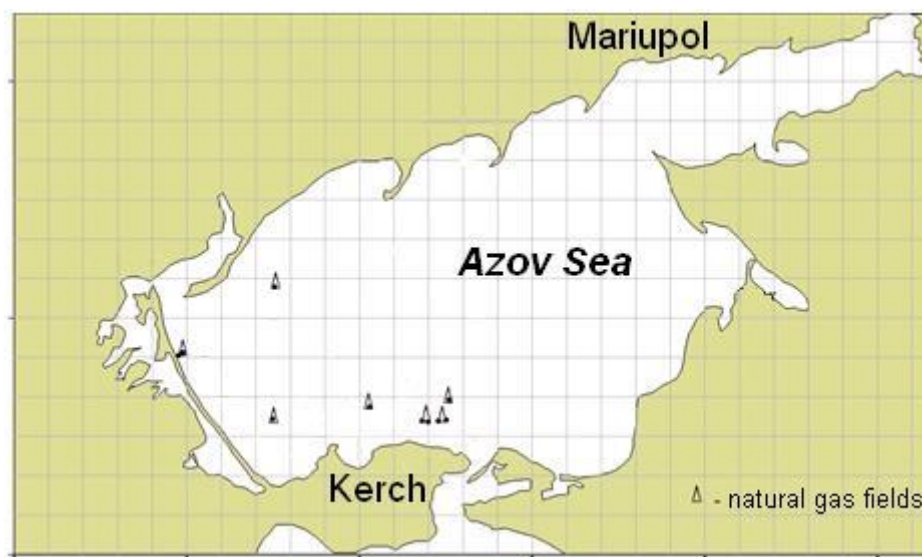


Figure 3. Location of existing natural gas fields in the southern part of the Azov Sea.

In addition to the increased content of petroleum products in the bottom sediments of the southwestern part of the Azov Sea, the following concentrations of heavy metals in the Arabatsky Gulf were detected during the 83rd voyage of the research vessel "Professor Vodnyatsky" in January-February 2016[7].

Table 1. Content of heavy metals in the bottom sediments of the Arabat Gulf [7].

Element	Concentration (mg/kg)
Co	30.8
V	103.7
Cr	98.6
Sr	174.6

The average value of cobalt for bottom sediments is 14 mg/kg[8], so in the Arabat Gulf there is an excess of more than 2 times compared with the average value. The distribution of chromium and cobalt corresponds to each other, and the chromium concentration is also higher than the average concentration (45-90 mg / kg)[7]. An increase in the chromium content is observed in the areas of congestion of vessels and in the water areas of ports, which confirms the significance of the negative impact of the passage of sea routes near the coast of the Kerch Peninsula[9].

The assessment of the certain parameters dynamics of bottom-dwelling fish Round goby was carried out to determine the state of the aquatic organisms in the ecosystem of the southwestern part of the Azov Sea. Round goby feeds on mollusks (Cardium, Corbulomya, Mytilaster, Syndesmia, Dreissena), which are 80-90% of its diet[10]. The mollusks themselves cannot be reliable indicators of bottom sediment contamination in connection with their feature of life activity[11]. Therefore the Round goby was chosen as the indicator.

According to research on the state of Round goby caught from 2011 to 2016 in the Arabat Gulf[12], the following results were obtained:

Table 2. Size-mass, morphophysiological and biochemical parameters of the Round goby in different years[12].

Parameter	2011 (30 units)	2013 (28 units)	2016 (25 units)
Overall length (cm)	18,37±0,37	16,81±0,16	15,45±0,25
Standard length (cm)	14,81±0,3	13,35±0,14	12,71±0,24
Total weight (g)	91,52±5,91	65,32±2,28	48,69±1,93
Body weight (g)	82,1±5,22	58,43±2,1	45,63±2,08
Liver index (‰)	49,19±1,71	49,78±2,02	30,73±2,12
Fatness (%)	2,38±0,034	2,45±0,03	2,25±0,05
Gonadosomatic index (%)	1,01±0,072	1,1±0,12	1,55±0,08
Catalase activity (mg H ₂ O ₂ / mg protein / min)	0,023±0,001	0,027±0,001	0,35±0,002
The activity of peroxidase (unit opt.density/mg protein / min)	0,009±0,0007	0,005±0,0005	0,003±0,0005
The concentration of albumin (g/g protein)	0,325±0,02	0,322±0,02	0,314±0,025

The size-mass and morphophysiological parameters of fish primarily depend on the food base and the habitat condition[13]. Decrease in these parameters may indicate that the organism has to expend energy to remove toxic xenobiotics, which may be oil products and heavy metals contained in bottom sediments. Also, the negative condition of the habitat is indicated by a high value of the gonadosomatic index (low growth rate at high gonad maturation rate)[14,15].

Activity reduction of peroxidase in the liver of a Round goby in 2013 and 2016 may be due to inhibition of enzyme activity by high concentrations of toxicants in the habitat[16,17]. At the same time, the increase in catalase activity in this period is probably an adaptive response of the antioxidant enzyme system in response to increased pollution of coastal waters in this period of research. Also it can be compensatory reaction because catalase performs functions similar to peroxidase – neutralization H₂O₂[18,19, 21].

Reduction of albumin in the liver of fish at a later period is possibly due to a decrease in the protein-synthesizing liver function as a result of ingestion of toxicants and / or a limited feed base[20].

3. Conclusions

1. The chronic pollution of the Arabtsky and Kazantipsky bays of the Azov Sea by oil products was determined in connection with the location of existing gas fields and the passage of major sea routes.
2. The presence of heavy metals in the bottom sediments of the Arabatsky Gulf of the Sea of Azov, exceeding the average concentrations of heavy metals, is also recorded, which also indicates the negative impact of sea transport routes on the territory.
3. A constant decrease in the size and mass characteristics, deviations from the norm of the morphophysiological and biochemical parameters of the Round goby condition are detected. These results also indicate an unfavorable ecosystem condition.

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