

## The Effects of Dissoluble Oil Products on Chemical Indicators of the Black Sea Water in the Ajarian Littoral Zone

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**ABSTRACT.** The effects of growing concentrations of dissoluble fractions of Chevron oil upon some chemical indicators of the Black Sea water in the Ajarian littoral zone have been studied. Oil and dissoluble oil products have been found to cause an increase in the concentration of carbon dioxide (CO<sub>2</sub>), a reduction in the content of pH and significant growth of the seawater oxidizability at the expense of accumulation of organic matters and their active oxidation. As a result, the seawater's oxygenation is affected and its buffer capacity and chemical composition stability are disrupted. At present, there is no universal method of cleaning seawater from oil pollution; therefore, every oil spill requires an individual approach. ©2008 Bull. Georg. Natl. Acad. Sci.

**Key words:** Black Sea, dissoluble oil products, pH (active reaction), oxidizability, carbon dioxide, Ajarian offshore strip.

From the standpoint of oil pollution, the south-eastern littoral zone of the Black Sea shelf represents an especially vulnerable region. In particular, Batumi, Supsa, Poti, Tuapse and Novorossiisk offshore strip.

The chemical composition of the seawater is characterized by significant stability resulting from its high calorific capacity, large volume and great buffer capacity. Notwithstanding this, mankind armed with up-to-date technology might cause an irreparable damage to the sea. A graphic example of the above is its pollution with oil and dissoluble oil products which are characterized by particular carcinogenicity, cause oncogenic diseases and pollute the offshore strip. Each year, as a result of accidents and catastrophes, up to 12 million tons of oil are spilled in the global ocean which detrimentally affects the sea flora and fauna. Therefore, the oil pollution control has become one of the most urgent problems of today and is being exercised by chemi-

cal, technological and biological means and techniques [1, 2].

**Materials and Methods.** The objective of our study was to investigate the effects of Chevron's oil on some chemical indicators of the Black Sea: pH, CO<sub>2</sub> content and oxidizability. Chevron's oil source is the Tengiz oil field in Kazakhstan. The Tengiz oil is delivered to Batumi oil terminal in transit from Baku; from Batumi it is further transported by oil carriers to different ports of Europe.

The object of the study was the Ajarian littoral zone (Batumi-Kvariati offshore strip). Seawater samples taken there were artificially polluted with growing oil concentrations. The clean seawater of Kvariati offshore strip served as a background (check sample). The concentration of dissoluble oil products was measured by means of gas-liquid chromatography, pH – by the potentiometry technique, free carbon dioxide – by the neutralization technique, and oxidation – by

Table

The effects of growing concentrations of dissoluble oil products on chemical indicators of the Black Sea water

Volume of water-spilled oil, ml/l	In 24 hours				In 10 days			
	Dissoluble oil products concentration, mg/l	CO <sub>2</sub> , mg/l	pH	Oxidizability, mg/l	Dissoluble oil products concentration, mg/l	CO <sub>2</sub> , mg/l	pH	Oxidizability, mg/l
0 Check sample (Kvariati)	0	0.38	8.30	2.1	0	0.38	8.32	2.1
10	30.8	0.77	7.42	4.7	42.8	5.80	7.08	11.2
50	66.3	0.80	7.29	4.9	89.9	6.19	7.07	17.7
100	106.2	0.93	7.20	5.1	164.7	7.35	6.92	30,15

permanganometry [2, 3]. Analyses were conducted in two series: Series I – in 24 hours after the oil spillage; Series II - in ten days after the oil spillage. The experiments' results are given in the table below.

Dissoluble oil products (low-temperature boiling paraffin waxes and naphthenic acids) are oxidized in the seawater with the evolution of carbon dioxide. At the same time, the oil film formed on the seawater surface interferes with the exchange of gases, leading to the accumulation of carbon dioxide in different layers. Naphthenic acids interact with the Ca and Mg bicarbonates, as a result of which large amounts of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) are being delivered and the concentration of carbon dioxide is increased. In wintertime, the sea surface layers contain 1 mg/l free carbon dioxide (CO<sub>2</sub>), while in summertime its concentration makes 0.4 mg/l, which is connected with the summer activation of photosynthesis and the seawater temperature growth [4].

According to the obtained data, the carbon dioxide content in the seawater in the check option (Kvariati) makes 0.39 mg/l in wintertime, which is 2.6-times less against the established standard. In the options polluted by Chevron's oil, an increase of carbon dioxide concentration in the seawater against the check is noted. If such an increase is relatively allowable in 24 hours after the oil spillage, in 10 days after the oil spillage its concentration increases from 5.42 to 6.97 mg/l against the check. Thus, the carbon dioxide content of the oil-polluted seawater exceeds 6-7-times the allowable rates.

The seawater represents a strong buffer system, pH of which is controllable by the carbon dioxide-carbonate system. The seawater pH is a soft alkali and its content in the surface layers makes 8.31 to 8.33 mg/l. With an increase of depth, its concentration reduces to 7.6

mg/l due to the increase in free carbon dioxide in the seawater deeper layers [4]. The seawater pH is a sensitive indicator of its pollution, which may result in a serious change of the sea buffer capacity. According to our study results, under the check option where the seawater was not oil-polluted, its pH made 8.30 to 8.32 and did not exceed the rate fixed for the surface layers. As for the seawater polluted by Chevron's oil, the carbon dioxide increase caused a significant reduction of pH, which becomes more obvious some time after the oil spillage. In the case of 50 ml/l and 100 ml/l oil spillage, the seawater buffer capacity deterioration tendency becomes obvious, which might seriously endanger the ecological condition of the marine gene pool. In the option of the seawater pollution up to 100 ml/l, the seawater pH already represents a soft alkali – 6.92.

Oil enriches the seawater with organic matter, leading thus to an increase in its oxidizability. The seawater oxygen content, which equals the content of the oxidizer (potassium permanganate) spent on the oxidation of the organic matter accumulated in the seawater, is the seawater oxidizing ability. Oxidizability of the Black Sea water surface layers (0 – 100 m) makes 0.61 to 3.72 mg/l.

According to the results of our study, the seawater oxidizability in the check option makes 2.1 mg/l, which meets the allowable rates. In the oil-polluted options, a regular increase in the seawater oxidizability is observed in correspondence with the growth of the dissoluble oil products' concentration. In the option with the least seawater content of oil products (30.8 mg/l), oxidizability exceeds the upper limit of the fixed rates by more than 1.3-times even in 24 hours after the oil spillage. A sharp increase in the oxidizability is observable in 10 days after the oil spillage in the seawater, and its value 3 to

8-times exceeds the admissible rates.

Thus, it may be concluded that:

1. The seawater oxidizability regularly the increases in proportion to an increase in the amount of oil spilled and, at the same time, after passage of definite time. This is caused by the transfer of soluble fractions from crude oil to the seawater.

2. The soluble oil fractions constitute the principal

mass of organic compounds accumulated in the seawater that undergoes chemical and microbiological oxidation. It is just the oxidation process on which free oxygen is spent, a great volume of carbon dioxide being delivered instead.

3. Carbon dioxide delivered in the seawater leads in turn to its oxidizing and significant changes in the seawater stable chemistry.

### ანალიზური ქიმია

## ხსნადი ნავთობპროდუქტების გავლენა შავი ზღვის წყლის ქიმიურ მაჩვენებლებზე აჭარის აკვატორიაში

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აჭარის სანაპირო ზოლში შესწავლილია “შევრონის” ნავთობის ხსნადი ფრაქციების მზარდი კონცენტრაციების გავლენა შავი ზღვის წყლის ზოგიერთ ქიმიურ მაჩვენებელზე. დადგენილია, რომ ზღვის წყლის ჟანგადობა კანონზომიერად იცვლება წყალში ჩაღვრილი ნავთობის მოცულობის მატების პროპორციულად. ეს გამოწვეულია წყალში ხსნადი ნავთობპროდუქტების გადასვლით, რომლებიც შეადგენენ ზღვაში დაგროვილი ორგანული ნაერთების ძირითად მასას. ამ ნაერთების ქიმიურ და მიკრობიოლოგიურ ჟანგვაზე იზარჯება თავისუფალი ჟანგბადი და მის ნაცვლად გამოიყოფა დიდი რაოდენობით ნახშირორჟანგი, რომელიც თავის მხრივ იწვევს ზღვის წყლის მნიშვნელოვან გამჟავიანებას და მისი სტაბილური ქიმიური მაჩვენებლების ცვლილებას.

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