The problem of the Black Sea pollution in Odessa region of Ukraine

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Abstract. The article considers the problem of Black Sea pollution in Odessa region. The researchers made a comparative analysis based on archival and modern materials, statistics on the assessment of pollution of the Black Sea coast around the city of Odessa, as well as adjacent areas to the region. The urgent task of Ukraine as a maritime state is to ensure optimal and sustainable functioning of the maritime complex. The Black Sea has been significantly affected by anthropogenic and man-made activities, which affects its water regime and properties. Therefore, researchers raise the issue of efficient use of natural resources as one of the most important conditions for sustainable social-economic development. In the article we come to the conclusion that the Black Sea ecosystem is affected by the reduction of fresh water, which leads to the influx of inorganic, organic and toxic substances etc. Thus, the researchers highlighted important issues of marine pollution in Ukraine, trying to draw the attention of scientists and the public to address pressing issues and find additional funding for the conservation of the Black Sea ecosystem.

1. Introduction
The environmental problems of the Black Sea are the result of anthropogenic activity, the process of pollution and eutrophication, accompanied by natural variability and climate change. This indicates indecisive changes in its ecology system and resources. Anthropogenic activity is undoubtedly now a powerful factor in changes in the Black Sea ecosystem. On the Black Sea coast there is uncontrolled industrial and domestic waste or. The Black Sea attracted the organization of NATO in 1993. The Global Environment Facility (GEF) funded the Black Sea Environmental Program (BSEP), which was to help the Black Sea countries meet the challenges set by the International Convention for the Protection of the Black Sea against Pollution [1]. The ecological situation in the Ukrainian Black Sea coast is becoming extremely acute, which now permeates all spheres of life and requires comprehensive research. Ukrainian scientists B. Babin, A. Chvalyuk and A. Plotnikov emphasize that the international conflict between Ukraine and the Russian Federation over claims to the Crimean peninsula has caused environmental challenges for the Black and Azov Seas. Scientists are concerned about uncontrolled fishing, discharge of wastewater from the coastal cities of Crimea, significant pollution due to the activities of the Black Sea Fleet and uncontrolled operation of drilling rigs, destruction of the unique seabed of Karkinitsky and Kalamitsky bays, their pollution by chemical industry borders of the marine protected areas adjacent to the Crimea to expand Russia's territorial claims [2].
Within various international organizations, these issues are regulated by a number of international legal instruments. Ukraine is interested in the successful implementation of the goals and objectives of the above agreements, and accordingly in the implementation of international commitments under ratified agreements and international environmental programs. Ukraine's task of preventing pollution of the Black Sea and improving its ecological status is one of the main national priorities in the field of environmental protection and rational use of natural resources. All this indicates a significant urgency of the work.

2. Research Methods
Methodological tools of the study include general and special methods, interdisciplinary approaches. Researchers, first of all, used such general scientific research methods as analysis and synthesis, statistical, method of classification (systematization). The purpose of the work is to address a number of issues, including, in particular, a detailed study of quantitative data on heavy metals and other pollutants in the Black Sea, their distribution, taking into account the dynamics of environmental pollution. The solution of these problems is provided by using the statistical method.

The comparative method is actively involved, because it has a fairly wide field of application, cognitive capabilities. The method was used to compare the pollution of the Black Sea in the late 1980s and the current state of the ecosystem around the Odessa coast.

The aim of the article is to study the ways and prospects of solving the problems of protection of the Black Sea from pollution through the use of world and European experience in the protection of marine waters. The work is based on documents and materials of the State Archives in Odessa region, expeditionary observations of the Ukrainian scientific center of Ecology of SEA (UkrSCES), literature sources and legal documents aimed at protecting the Black Sea from pollution.

3. Literature review
Historiography of the problem of environmental pollution of the Black Sea is represented by significant scientific achievements of foreign and Ukrainian researchers of various specialties from historians, sociologists, ecologists, engineers, public activists, and is of particular interest to scientists representing the Black Sea coast. Turkish researchers Levent Bat, Ayşah Öztekin, Fatih Şahin, Elif Arıcı, Uğur Özsandıkçı [3] in their scientific work considered the problem of pollution of the Black Sea by their country, how Turkey affects the ecosystem on the Black Sea coast. The ecological features of the Black Sea are reflected in the publications of Emma Gileva [4], Kostianoy A.G, Lebedev SA & Tepe Yalçın [5], Ian C. Goulding, Kim A. Stobberup & Tim O’Higgins [6]. Fedun Oleksandra& Zinko Ihor [7], Luminiţa Lazăr, Laura Boicenco, Oana Marin, Oana Culcea, Elena Pantea, Elena Bişinicu, Florin Timofte, Maria-Emanuela Mihaîlov [8], Denha YuM [9], Safranov TA [10], Berlinskyi MA [11], Koval V [12], Mikhno I [13]. However, the issue of environmental pollution of the Black Sea in Odessa region needs detailed attention of researchers.

4. Results and Discussion

4.1. Ecological condition of the Black Sea within the Odessa region in 1980-1990
According to the Law of Ukraine “On Environmental Protection” of 1993, internal marine and territorial waters, natural resources of the continental shelf and the exclusive (marine) economic zone of the Black Sea are natural resources of national (state) importance, control over the protection and use of which within Ukraine is entrusted to the State Inspectorate for the Protection of the Black Sea of the Ministry of Environment of Ukraine [14]. The natural resource potential of the north-western and central regions of the Black Sea is fish stocks, flora and fauna, sea sand as a raw material for building materials and natural gas. Much of the sea coast and the Black Sea coastal strip are used for recreational, health and spa purposes. The sea is largely used for navigation. The north-western part of the Black Sea, which includes the Dnieper-Bug and Dniester estuaries, Karkinitsky Bay, Odessa Bank and the mouth of the Danube, is almost the main industrial area of the sea. Another large industrial area of the Black Sea is the Kerch
Strait. Marine deposits of non-metallic materials (sands) are practically unlimited. The resources of sea sand in the north-western part of the Black Sea are such that with an annual production of 3-5 million tons per year, it will be enough for 10 thousand years. The largest reserves of sand are concentrated in the Odessa bank - about 27 billion tons. In the Black Sea, exploration and production of gas and gas concentrate is carried out, in the 1980s there were 4 offshore stationary platforms and a submarine gas pipeline “Golitsyno-Okunivka” with a length of 75 km.

The natural resources of the Black Sea can be divided into 4 groups: sea water; flora and fauna, fish stocks; non-metallic materials (construction sand); minerals (gas, gas concentrate).

The problem of the use of Black Sea resources and the associated negative consequences should be considered in conjunction with the position of economic and environmental approach to economic activities on land and at sea, for which in each case it is necessary to conduct environmental expertise and monitor these activities. The main direction of development of the Black Sea coast is the construction of residential, social and communal facilities in large and small cities, bases and rest homes, beach area, expansion of health and wellness facilities and water tourism, shipping. This in turn causes the expansion of the bases of the construction industry, increasing the intake of fresh water and discharge of small waters, extraction of sand, including from the sea. With the development of shipping, the replacement of old low-tonnage vessels with modern large-tonnage, there is a need for reconstruction of seaport facilities, increasing the volume of dredging and landfilling (dumping). It is expected to increase the volume of transshipment in the Black Sea ports of bulk cargo and mineral fertilizers and raw materials for them, coal, ore and other substances [15].

In the inspection area, the main sources of pollution of the Black Sea are: - river runoff of major European rivers (Dniester, Danube, Dnieper, Southern Bug), which contributes to the sea more than 80% of all pollution; - discharge of industrial, domestic and stormwater from coastal cities, towns, enterprises, buildings and recreation centers; - coastal runoff from agricultural fields; - shipping. From the monitoring agreed with the Ministry of Environmental Protection of Ukraine, the inspectorate controls the quality of sea water in 115 Black Sea areas, which most typically reflect the picture of sea water pollution. The main components of analytical control are pollution of the marine environment with oxidizing organic substances, phenols, synthetic surfactants (SPAR), petroleum products, pesticides, heavy metals, nutrients. Oil and oil products, such as their leaks from the sunken tanker Delfi in Odessa, continue to be the dominant contaminants today.

In the controlled zone there were tendencies to decrease the level of petroleum products in surface water, which in 1991 and the first half of 1992 in the Odessa Bay reached the level of MPC and below, in the Greater Yalta - below the MPC (in 1989 – 2 MPC). As before, the high level of oil products in sea water in the Sevastopol region is currently 4 MPC, but it should be noted that in 1989 the level of oil products in Sevastopol Bay was 10 times higher than the current level. In the open areas of the Black Sea there is a concentration of SPAR and the level of MPC, while in the areas of impact of wastewater discharge of protective structures of utilities there is a steady trend of pollution of sea water SPAR at 1-3 MPC. Pollution of coastal waters of the Black Sea by phenols is uniform, reaching an average of 1 - 3 MPC, slightly decreasing compared to 1989. The content in the waters of heavy metals (copper, zinc, cadmium, lead, nickel, chromium) does not exceed their average value. in the waters of the seas and oceans, there is a slightly increased compared to the MPC (1.5 - 2 times) the content of iron and mercury [15].

The distribution of nutrients in the controlled zone of the Black Sea, especially mineral forms of nitrogen and phosphorus, in coastal waters is uniform. The highest concentrations of these pollutants are observed in the Black Sea areas exposed to river runoff, due to the leaching of mineral fertilizers from river basins. Despite the cessation of the use of organochlorine pesticides (DDT and its metabolites), the coastal waters of the Black Sea do not reduce the level of pollution by these substances, which indicates the high resistance of these compounds in the environment. The presence of polycyclic aromatic hydrocarbons in coastal waters, especially 3, 4 – bennapyrene and 4, 12 – benfluogen, are carcinogenic compounds. Their appearance in coastal waters is due to the fact that they are intensively washed away through the sewers of urban utilities that do not have local facilities.
Contamination of the Black Sea coastal waters from municipal utilities with insufficiently treated wastewater, as well as from emergency spills from ships and sewers, remains a threat. Throughout the region, there is an excess of suspended solids and BSC5 in the area of impact of wastewater discharges, at the same time it should be noted some tendency to reduce the overall pollution with oxidizing organic matter and nutrients to improve the treatment facilities. In general, in the controlled zone in 1991-1992 there were an improvement in the Black Sea and a reduction in pollution of the marine environment with chemicals, which is confirmed by the absence of algae, the so-called "red tides" observed in recent years. The most detailed study was conducted on the Black Sea coastal strip within the village. South - the coast of Odessa - Illichivsk (now the Black Sea), characterized by a high content of nutrients. The increased content of almost all forms of nutrients is characteristic of the following zones of the Black Sea: - Grigorivsky estuary area - which has a joint influence mainly along the coastal streams (Dnieper, Southern Bug), Southern port and OPZ; - Odessa Bay - the influence of the port of Odessa and stormwater emissions; - the area of beaches from the port of Odessa to the 16th station of the Great Fountain - the joint impact of removal from the Gulf of Odessa with the main along the coastal flow of local unloading of drainage water; - Dry estuary area - the impact of runoff of the Illichivsky River and the port; - dumping area - the impact of the landfill [15].

4.2. Ecological condition of the Black Sea within the Odessa region in 2019

The Ukrainian Research Center for Marine Ecology is a subject of the regional environmental monitoring system of Odessa region and is responsible, within its powers, for monitoring the ecological status of the marine environment (water, biota and sediments). Regular environmental observations of the state of coastal waters throughout the year were conducted at two stations located near Cape Little Fountain and near the beach “Arcadia”, as well as performed once a season in summer in June and autumn in November areas with Kobleve, Adzhalyk estuary, the port "South", the beach "Luzanivka" two stations, the port "Odessa", the beach “Dolphin”. On the Danube coast, seasonal integrated environmental observations were carried out at 12 stations in May and autumn in October at the 12 stations located near the Bystra estuary as part of the economic-contractual theme. According to the international project Emblas +, in July-August, 15 complex ecological stations on the north-western shelf of the Black Sea were constructed in the coastal zone and in the area of the phyllophore field of the JBSS and NMS stations. Also under the international project ANEMONE in August and September, comprehensive environmental observations were conducted once at 8 stations. In total, in 2019, in the territorial sea waters (12 miles) adjacent to the environment of Odessa region, ecological monitoring was carried out at 38 sea stations, and on the north-western shelf of the Black Sea in 2019, observations were made at 47 stations [16].

Eutrophication is a process controlled by the enrichment of water with nutrients, especially nitrogen and phosphorus compounds, which leads to: increased growth of primary products and is one of the main factors of anthropogenic disturbances of the ecosystem of the Black and Azov Seas. The consequences of eutrophication are, of course, the degradation of benthic flora and fauna, which is especially noticeable in the northwestern part of the Black Sea (PZCHM) in the reduction of field area and biomass of phyllophora, mussels and their biocenosis [17]. Adverse and destructive processes associated with the eutrophication of seawater occur as a result of increased nutrients and excessive development of phytoplankton. This in turn leads to the processes of "blooming" of water and reducing its transparency, the development under the pycnocline and in the bottom layers of the shelf zone in the warm season zones of hypoxia and anoxia, which respectively leads to freezing and death of benthic and benthic organisms. The main sources of biogenic pollution of marine waters are considered to be river runoff associated with transboundary anthropogenic impact, and onshore point sources, which primarily include wastewater discharges from various economic entities located in the coastal zone. PZChM rivers account for about 79% of the total flow of rivers in the Black Sea. River runoff from the PZChM comes from the territory of 18 countries located, in whole or in part, in the basins of the Danube, Dnieper, Southern Bug and Dniester. In the conditions of intensification of industrial and sea economic activity on PZChM, one of important and actual ecological tasks is
performance of the National program of protection and revival of the natural environment of the Black and Azov seas. According to the European MSFD Directive, the degree of eutrophication corresponds to the fifth descriptor and good ecological status (DES) is characterized by its minimization due to anthropogenic load of specific substances, biodiversity loss, ecosystem damage, algae blooms and lack of oxygen.

4.3. Hydrochemical state of waters of the Odessa region in 2019

The ecological condition of the Odessa region is significantly influenced by coastal anthropogenic sources associated with the activities of three ports, industrial enterprises, utilities and agriculture. In addition to coastal anthropogenic sources, the quality of sea water is significantly affected by the runoff of transformed river waters of the Dnieper and the Southern Bug. As a result of these factors, the marine environment of this region receives a significant amount of nutrients (BR), which contributes to the eutrophication process and, as a consequence, leads to changes in the hydrochemical regime of water, reducing their quality and environmental degradation [18]. The runoff into the marine environment in the amount of dissolved mineral compounds of nitrogen and phosphorus from anthropogenic sources in the Odessa region is 1.5 times higher than their runoff in the Southern Bug.

Anthropogenic coastal springs together with the river runoff of the BR and together with natural factors determine the formation of the hydrochemical regime of waters, the degree of their trophicity and significantly affect the state of the marine ecosystem of the Ukrainian shelf. Ecological monitoring of the coastal waters of the Odessa region in 2019 was performed by (UkrSCES) on the basis of regular observations (once a week) at Cape Maly Fontan and Arcadia Beach, as well as at seasonal coastal monitoring points along the coast from Koblevo Beach to Zatoko Beach [16].

The oxygen content (O2) in coastal waters during the survey period in June varied in the range from 6.9 to 11.7 mg / dm3, and the relative oxygen saturation ranged from 89.0 to 157.0%. In October, during the survey period, the range of oxygen variability in coastal waters, both absolute and relative values was smaller. Oxygen concentrations in this period ranged from 6.8 to 10.2 mg / dm3, and relative saturation ranged from 67.6 to 106.0%. The average value of oxygen content in June was 8.9 mg / dm3 (115.2% saturation), and during the shooting period in autumn it decreased to 8.5 mg / dm3 (87.4% saturation), are shown in Table 1.

Table 1. Indexes of variability of the hydrochemical state of surface coastal waters of the Odessa region in June and October 2019

| Index | O2 | O2 | Boc5 * | pH ** |
|-------|----|----|--------|-------|
|       | mg / dm³ | % saturation | mg / dm³ | units pH |
| June  | 5 | 5 | 5 | 5 |
| Number of definitions | 11 | 11 | 11 | 11 |
| Middle | 5 | 5 | 5 | 5 |
| Maximum | 11,7 | 157,0 | 6,7 | 8,49 |
| Minimum | 6,9 | 89,0 | 6,7 | 8,15 |
| TSD *** | 1,8 | 25,9 | 2,6 | 0,13 |
| October | 8,5 | 87,4 | 1,4 | 8,23 |
| Middle | 6,8 | 67,6 | 0,9 | 7,89 |
| Minimum | 1,0 | 10,8 | 0,5 | 0,13 |

Note: * – Biological oxygen consumption; ** – Hydrogen index; *** – The standard deviation
In the spatial distribution in absolute terms, the maximum oxygen content in June of 11.7 mg / dm³ was observed in the area of Cape Maly Fontan, at a water saturation of 157% oxygen, which was due to intensive processes of phytoplankton photosynthesis. In October, the absolute value of the maximum oxygen content was observed in the area of the beach “Arcadia” 10.2 mg / dm³ (106.0% saturation) [16].

Table 2. Indexes of variability in the content of nutrients in the coastal surface waters of the Odessa region in June and October 2019

| Index | P(PO4) | TP | N(NO2) | N(NO3) | N(NH4) | TN | Si(SiO3) |
|-------|--------|----|--------|--------|--------|----|----------|
|       | mg / dm³ | mg / dm³ | mg / dm³ | mg / dm³ | mg / dm³ | mg / dm³ | mg / dm³ |
| June  |        |        |        |        |        |        |          |
| Number of definitions | 5 | 5 | 5 | 5 | 5 | 5 |          |
| Middle | 11,1 | 38,3 | 5,6 | 142,3 | 4,8 | 771 | 653 |
| Maximum | 15,7 | 57,4 | 9,1 | 553,0 | 7,6 | 911 | 951 |
| Minimum | <5,0 | 24,1 | 2,7 | 9,2 | <15 | 586 | 451 |
| TSD | 5,0 | 12,2 | 3,2 | 230,9 | 3,4 | 127 | 215 |
| October |        |        |        |        |        |        |          |
| Number of definitions | 11 | 11 | 11 | 11 | 11 | 11 |          |
| Middle | 15,5 | 24,2 | 4,4 | 1144,7 | 5,5 | 2095 | 289 |
| Maximum | 25,1 | 37,2 | 10,4 | 11531,1 | 15,9 | 12731 | 629 |
| Minimum | 10,3 | 19,1 | 1,7 | 5,3 | <15 | 256 | 106 |
| TSD | 5,3 | 5,4 | 2,6 | 3447 | 6,0 | 3621 | 215 |

Concentrations of total phosphorus (the sum of its organic and mineral forms) in the coastal waters of the Odessa region in June and October ranged from 19.1 to 57.4 μg / dm³. The average values of total phosphorus in June were 38.3 μg / dm³, and in October 24.2 μg / dm³. On average, the content of total phosphorus in two surveys in 2019 is 28.6 μg / dm³, which according to the ecological classification of seawater quality corresponds to a high level (<50 μg / dm³. Table 2). Only the maximum concentration of phosphate in June in the waters of the Gulf (57.4 μg / dm³) slightly exceeded this high level and corresponded to a good level (from 50 to 100 μg / dm³) according to the ecological classification of seawater quality. In October, the content of both phosphorus phosphate and total phosphorus relative to June was slightly lower in almost all areas of the Odessa coast, except for the beaches “Dolphin” and “Arcadia” in terms of phosphorus phosphate [16].

The content of nitrite nitrogen in coastal sea waters during the survey of the Odessa coast was in the range from 1.7 to 10.4 μg / dm³. Increased concentrations were observed in June near the beach of the sanatorium “Chkalova” 8.9 μg / dm³ in the area of runoff of drainage water and the Gulf 9.1 μg / dm³ under the influence of the Dniester estuary, and in October in the Koblevo water area 10.4 μg / dm³ and the port “Southern” 6.0 μg / dm³ under the influence of the waters of the Dnieper estuary. The average nitrite nitrogen concentration in the Odessa region was 5.6 μg / dm³ in June and 4.4 μg / dm³ in October. The content of nitrate nitrogen in the coastal waters of the Odessa region, depending on the region during the observation period varied in a very wide range from 5.3 to 553.0 μg / dm³. The maximum concentrations of nitrate nitrogen were observed both in June and in October in the area of the beach of the sanatorium “Chkalova” in the zone of influence of drainage water runoff, the concentration of nitrate nitrogen in which in October reached 11531 μg / dm³. Similar estimates of the impact of drainage water runoff on marine coastal waters have been provided in previous reports. With the exception of the area of influence of drainage waters, the average concentrations of nitrate nitrogen in the study region in June were 39.7 μg / dm³, and in October 106.1 μg / dm³, with maximum
concentrations, respectively, did not exceed 72.9 μg / dm³ (Cape Small Fountain area) and 436.1 μg / dm³ (Dolphin beach area).

The content of ammonium nitrogen in the coastal waters of the Odessa region averaged 4.8 μg / dm³ in June and 5.5 μg / dm³ in October. The maximum concentrations were observed in the zone of influence of drainage water runoff of 7.6 μg / dm³ in June and in Koblevo water area 14.4 μg / dm³, Luzanivka 2 beach 15.9 mcg / dm³ and Zatoka water area 12.9 mcg / dm³ in October. In general, the amount of mineral nitrogen compounds in the coastal waters of the Odessa region varied in the range from 13 to 569 μg / dm³ without taking into account the drainage water runoff zone, with average values in June of 48.6 μg / dm³ and 116.8 μg / dm³ in October. In the coastal waters of the Odessa region, the content of organic forms of nitrogen prevails over the sum of its mineral forms. On average, organic forms of nitrogen exceed the sum of mineral forms by 10 - 40 times. The maximum value of the ratio Norg./N min. = 69 was determined in June in the Gulf of Odessa near the beach "Arcadia", and Norg./N min. = 40 in October in the waters of the Gulf. The content of total nitrogen (sum of mineral and organic forms) varied in the range from 260 to 12731 μg / dm³. The maximum concentrations of total nitrogen were observed in the area of the beach of the Chkalov sanatorium, due to the increased content of nitrates entering the coastal zone with drainage waters. Excluding the impact of drainage waters, the total nitrogen content in the coastal waters of the Odessa region varied in the range from 260 μg / dm³ to 3061 μg / dm³, with an average value of 756 μg / dm³ in June and 1031 μg / dm³ in October. High values of total nitrogen content were observed in the areas of the waters of the port "Southern" 1215 μg / dm³, Koblevo 1968 μg / dm³ and the beach "Dolphin" 3061 μg / dm³ in October [19].

5. Conclusions
The main sources of anthropogenic impact on the Black Sea ecosystem are the following: 1) inorganic, organic and toxic substances come from rivers by reducing fresh water; 2) from agriculture - fertilizers, pesticides; 3) from industry - heavy metals, detergents; 4) from settlements, at the expense of sewage, detergents, oil, pathogenic microorganisms; 5) from the atmosphere precipitation, dust, mercury, lead, nitrates, phosphorus; 6) from shipping - oil, etc.; 7) through ports of water pollution, deepening of the bottom, etc.; 8) from fishing - damage and destruction of bottom ecosystems, overfishing of biological sources; 9) through the beaches of the creation of dead regions; 10) recreation and tourism - microbial pollution of coastal waters, litter of coastal areas; 11) through the territory of the Chernobyl nuclear power plant, which is a terrestrial source of radionuclides, chronic pollution of the Black Sea through the rivers Pripyat and Dnieper.

The best solution to the problem of pollution of the Black Sea in the Odessa region is to reduce the production of ports. Only two EU member states, Bulgaria and Romania, have reduced fishing in the Black Sea. For example, Turkey is trying to create conditions for the use, storage and disposal of chemical waste. Ukraine adheres to environmental standards of European standards for pollution control and support of the maritime strategy. This is especially true of hazardous substances, including heavy metals. However, it is clear that there is significant pollution on the Black Sea coast due to the actions of the Russian Federation on the Crimean peninsula, as Ukraine does not have adequate access to pollution data due to the occupation. The lack of comparable coastal data has made it impossible to assess future pollution trends or to adequately preserve the ecosystem and human health. Therefore, it can be concluded that the situation on the Black Sea requires immediate action. Countries bordering the Black Sea must work together to protect the ecosystem, apply sanctions and penalties for pollutants.

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