

THE INFLUENCE OF THE ANTHROPIC FACTORS ON THE BLACK SEA STATE

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ABSTRACT

The paper proposed herewith aim is to present a synthesis of the existing data in the literature on the main environmental problems of the Black Sea: pollution, introduction of invasive species, irrational fishing, etc.

The most important aspects that are presented refer to the sources of pollution, the nature of the pollutants, the coastal areas on the Black Sea affected by pollutants, the effects of pollution on the marine ecosystem, the loss of habitats and the biodiversity loss.

Keywords: Black Sea coastal area, inorganic nitrogen, phosphorus loads, discharges of nutrients, petroleum products

1. INTRODUCTION

The Black Sea is one of the most remarkable regional seas of the world. It is enclosed by land, with brackish waters, whose area of 423,000 km² represent 3% from the Planetar Ocean surface, having a water volume of 537,000 km³ and over 2200 meters deep. Its catchment covers an area of 1,9 million km² (one-third of continental Europe), including parts from 22 countries, in which live over 160 million inhabitants [1], [2], [3]. The Sea has six coastal countries: Romania, Bulgaria, Georgia, Russia, Turkey and Ukraine. The length of Black Sea coastline is 43338 km, from which Ukraine has longest coast (1628 km) and Romania the shortest (225 km) [1]. The Black Sea is supplied with fresh water from major European rivers: Danube, Dnieper, Dniester, Bug, Don, Kulan and a number of smaller rivers. The Danube contributes with 59% of the fresh water discharge into the Black Sea, Dnieper 15%, Dniester 3%, Bug and Don 1.5%. The total influx of fresh water is estimated to be 350 km³/year [4]. The Black Sea is linked by the ocean through the Mediterranean that communicates through the Strait of Bosphorus, and in the north by the Strait of Kerch communicates with the Sea of Azov. The communication with the Mediterranean Sea through the Bosphorus determine the existence of two layer flow: a bottom layer with salinity of about 37⁰/₀₀ carrying about 300 km³ of sea water to the Black Sea from Mediterranean and an upper layer with salinity of about 18⁰/₀₀ with twice volume to the Mediterranean from the Black Sea [2].

The most characteristic in the Black Sea hydro-dynamical structure is the remarkable stability in stratification. This stability is largely due to river runoff, which provides a

continuous source of fresh water, diluting the upper basin layer and overcoming the supply of salt through Bosphorus. One of the direct consequences of this fact is that the Black Sea is the world's largest anoxic basin [5]. Only 10% of sea water, representing the surface layer of water with depth up to 150-200 m is oxygenated, which runs all aerobic biotic processes, and the remaining of 90% (in the 150-200 m depth) is devoid of oxygen and therefore lifeless. The forecasts predict the volume expansion anoxic (contains no oxygen) the interface between the oxygenated upper layer and the anoxic lower layer, rich in H₂S, rising above increasingly, phenomenon at which can contribute the eutrophication of water [2]. The Black Sea abiotic environment influences the qualitative and quantitative structure of marine flora and fauna.

The Black Sea is the most isolated marine ecosystem of Europe and one of the most sensitive to the human activities.

The purpose of the present work is to highlight some aspects of water pollution in the Black Sea and the consequences of the pollution on marine ecosystems.

2. ENVIRONMENTAL ISSUES IN THE BLACK SEA

In the last 45 years, the Black Sea basin is subjected almost continuously to a process of pollution that has destructive effect on the marine ecosystem and water quality, being a hazard on human health for the people living closed to the coastal environment.

At the same time, were introduced invasive species in the Black Sea and it has been practiced overfishing, which emphasized the marine ecosystem degradation and reducing the native biological diversity in the Black Sea.

The coastal protection in the Black Sea become in the last years a very important issue and the wave energy farms may become very effective from this perspective, see for example [6], [7], [8], [9], [10].

An environment very similar with the Black Sea is the Caspian Sea as presented in [11].

2.1 Main factors of pollution in the Black Sea

Pollution is produced by the introduction from human operators of pollutants due to negligence, intentionally or accidentally into the sea. Some threats are introduced by marine transport, in particular transport of petroleum products, the penetration of invasive species, over fishing or destructive fishing techniques.

The pollution sources for the Black Sea are multiple. These are coming mainly from land based human activities of the coastal and from non-coastal states of its basin through rivers flowing into the sea.

The largest amounts of pollutants are introduced in the sea by the large rivers, particularly by the Danube. They collect large quantities of pollutants from its whole basin including numerous large urban centers and wide range activities. The river flow provides suspension, organic material, an elevated quantity of nutrient, but also oil-components, detergents, pesticides and phenols.

In the coastal areas live a great number of people. The total population is estimated 20 millions without Istanbul and 30 millions Istanbul included. The impact of these populations is felt through agglomerations human, industrial activities, intensive farming, tourism, port infrastructure which damaged aquatic ecosystems [1]. They generate large amounts of waste and wastewater, which if not properly processed reach in the sea with large amounts of pollutants.

Pollutants reach in the sea from point and diffuse land-base sources.

Substances that pollute the Black Sea have a great diversity: nutrient (N, P, Si), heavy metals (Mn, Fe, Cu, Cd, Pb), total hydrocarbons, persistent organic pollutants, pesticide,

oil, sediments (suspended particulate matter), artificial radionuclide (^{90}Sr , ^{137}Cs), parasite and saprophyte fungi, litter etc.

The most sea water's problems are: nutrient pollution, organic pollution, hazardous substances pollution.

2.1.1 Nutrient pollution

Eutrophication is the most ecological problem of the coastal Black Sea regions, this as regards its extension and impact over the ecosystems [12]. It is caused by the excess of nutrients, in principal nitrogen and phosphorus compounds. Eutrophication is widespread in the Black Sea, but its effects are more pronounced on some areas, especially for its northwestern and west areas. In the southwestern and southern and central western of the Black Sea the nutrient concentrations in water are lower [13], [14].

The main resource of nutrients in western Black Sea coastal area was identified the River Danube. It discharges about 65-80% of the nutrient load input to this of the Black Sea [15]. In the North, the effects are intensified by influence of Rivers Dniester and Dnieper. The nutrients in rivers coming from point sources with untreated waste water discharges or inadequate treated settlements from urban, industrial, agricultural and diffuse sources particularly from livestock farming and fertilizer use.

The observed (2000-2002) nitrogen (dissolved in organic nitrogen) and phosphorus loads, from the ICEPEDR's monitoring network (TNMN=Transnational monitoring network) discharged by the Danube to the Black Sea, show that these are approximately 410 kt/yr nitrogen and 12 kt/yr phosphorus [16]. Using MONERIS model and monitoring the data on nutrient concentrations in the Danube, Schreiber et al (2003) have found that about 65% (450 kt N/yr) of the nitrogen emission and 35% (25 kt P/yr) of the phosphorus emission to the rivers system are discharged by River Danube to the Black Sea [17].

During the period 2003-2005, from the total amount of nutrients of 362, 545 t/yr brought by the rivers flowing into the Black Sea, the Danube intake was 86%. The other two great rivers Dnieper contribute with 7% and 1% Dniester [1].

The eutrophication has strongly affected the coastal waters from the north-western and western of the Black Sea since 1970s to the early 1990s.

Since 1990 nutrient input of Danube River decreased (Fig. 1), which had made that the eutrophication to decrease.

As shown in Figure 1, the DIN (dissolved inorganic nitrogen) intake of the Danube to the Black Sea decreases in 2005 as compared to that of the year 1989, by more than 20%, while the intake of P decreases by 70% in the same period. Likely cause for a higher DIN flux may be despite changes in N-fertilizer application, the big nitrogen stocks (soil, groundwater) in the Danube catchment, which have slow down effects on diffuse N-emissions to the river system.

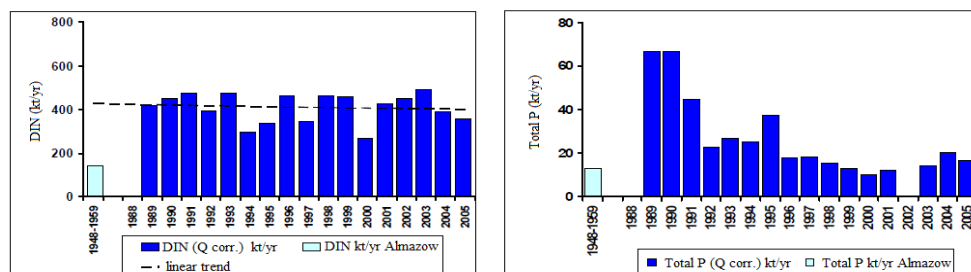


Fig. 1. River Danube annual inorganic nitrogen and total phosphorus loads to the Black Sea (1989-2005) (from [1])

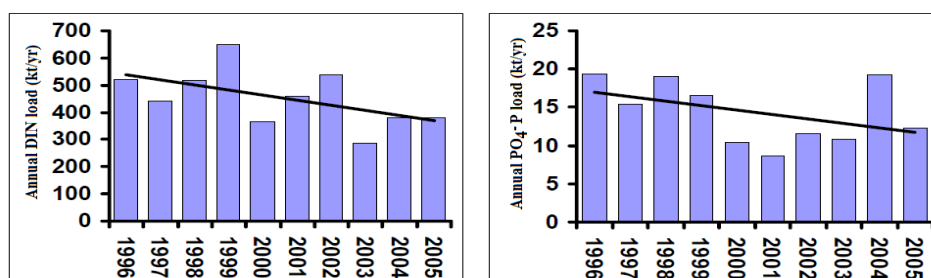


Fig. 2. Trends in river nutrient loads to the Black Sea, 1996-2005 (from [1])

Also, total river loads of nutrient decreased from 1996-2005 (Fig. 2).

A linear regression of the nutrient loads suggests a decrease of over 30% for river-borne nutrient entering the Sea during the period 1996-2005.

The decrease in river nutrient loads following the early 1990s is due to the decline in agricultural intensity (the closure of ineffective large animal farms), reduction of fertilizer production related of nutrient discharging, introduction of phosphorus free detergents in a lot of countries. Also, the nutrient removal from waste water was improved in the countries along the Danube River [13].

Pollution from the coastal area is due to the fact that a part of the population and a few industrial plants are not connected to the system of waste collection and discharged of waste waters directly or waste waters are insufficiently treated before being discharged into the Sea or in the public sewer systems, that increases the nutrient quantity and organic substances discharged. A coastal population of some 7 million inhabitants is connected to sewerage systems discharging directly into the Sea, the proportion being from about 53% in Russia through 70% in Turkey (excluding Istanbul) to more than 90% in Bulgaria [1] and 52% in Romania [18].

In summer, due to tourism, the number of inhabitants on the coast increases considerably (by 25-50% and more) than winter resident population. In order not to increase the amount of pollutants discharged into the sea, a need is to build sewerage systems and treatment work that can cope with the peak seasonal demands placed on them [1].

In Romania, in the coast area there are 15 agglomerations > 2,000 PE of which in 2007 only 8 were connected to wastewater treatment plant. Nutrient discharges into surface waters in 2007 by agglomerations are shown in Table 1.

Table 1. Discharges of nutrients (total N, total P) from agglomerations of the coast and the Danube Delta in Romanian waters (from [19])

Agglomerations	Coastal area		Danube Delta	
	N total, t/yr	P total, t/yr	N total, t/yr	P total, t/yr
> 100000 PE	438,597	102,344	110,145	25,833
10000-100000 PE	69,468	10,437	0	0,225
2000-10000 PE	0	0	9,741	0,781
<2000 PE	0	0	0	0
Total	508,065	112,761	113,197	26,732

In 1996, TDA (Transboundary Diagnostic Analysis) has identified 47 hot-spots in the Black Sea coastal area, the majority (31) of these being municipal sources.

On the Romanian coast were found six hot-spots: Rompetrol Refinery, Fertilchim, Petromidia-Constanta, Constanta South WWTP (Waste Water Treatment Plants), Constanta

North WWTP, Eforie South WWTP and Mangalia WWTP, municipal sources spilling over 62 millions m³/yr. All these wastewater treatment plants are now upgraded including tertiary treatment stage (reducing the content of N and P) [1], [19]. Significant source of nutrient pollution is represented by industrial facilities, in special the chemical sector, important contributor along with the food industry and pulp and paper industry. They contribute to water pollution through untreated or inadequately treated waste water discharge and through pollution from accidents.

Also, agriculture is a contributor to pollution the Black Sea from livestock farming and fertilizer use. After the 1990s, the number of livestock farms and inorganic fertilizers quantities used have dropped dramatically in most of countries by the Black Sea, except in Turkey where fertilizer application rates were substantially higher [1].

In Romania, after 1989 the use of fertilizers in agriculture decreased substantially, in 2003 the consumption of N and P fertilizer having shrunk from 68.2 kgN/ha to 26.8 kgN/ha and from 34.1 kgP/ha to 10.1 kgP/ha (Fig. 3).

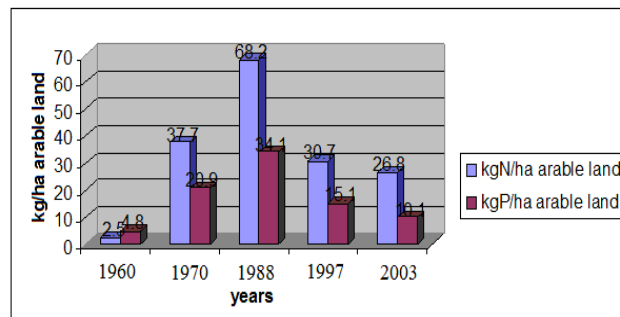


Fig. 3. Application of the inorganic fertilizers in Romania (1960-2003) (from [1])

A small contribution to the water eutrophication in the Black Sea belongs to the atmospheric depositions. Containing nitrogen oxides, atmospheric emissions contribute indirectly to discharge nutrients into the Black Sea. Contribution from major sources to the nutrient pollution of the Black Sea is presented in Table 2. From Table 2, it follows that the highest weight of nutrient intake in the Black Sea it has the rivers that flow into the sea, and the smallest, the atmospheric deposition.

Table 2. Estimates of annual nutrient load to the Black Sea (tons) (from [1])

Pollution source	DIN	PO ₄ -P(phosphate)
Direct discharges from municipal waste water treatment plants serving >5000 people	6120	2150
Direct discharges from industrial sources discharging > 1000 m ³ /day	1180	250
River loads	362.545	17.799
Atmospheric deposition	203-431	-

Black Sea coastal areas affected by nutrients

Nutrient concentration varies along the Black Sea coast from one sector to another, both in surface waters and in sediment depending on the position to the rivers flowing into the sea and coastal development. Also, it has a temporal distribution.

The average concentration of nitrate and phosphate in the coastal waters of the Black Sea, provided of the second Black Sea Transboundary Diagnostic Analysis (2007), for the period 2004-2005 are presented in Fig. 4.

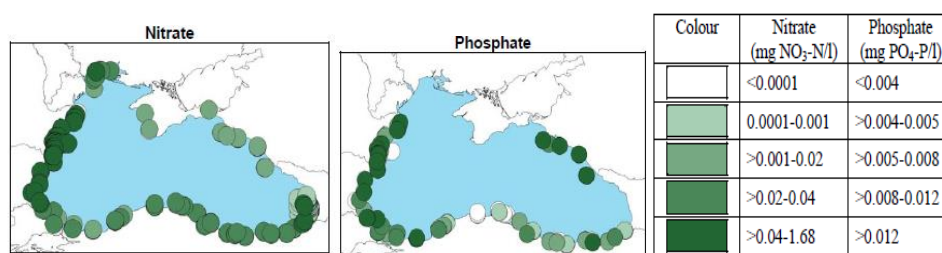


Fig. 4. Mean concentrations of nitrate and phosphate in surface water (0-10 m depth) of the Black Sea, 2004-2005 (from [1])

As shown in Figure 4, a high concentration of nutrient, both nitrate and phosphate in surface water are along the western edge of the sea. Around Odessa, at Georgian border and at a small number of sites offshore of the Turkey are high levels of nitrate. Along of the Turkey coast are moderate levels of nitrate, but the concentration of phosphates in isolates sites is big, presumably due to local discharges.

2.1.2 Organic pollution

The organic pollution of the Black Sea, expressed as BOD₅ (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand), is given by organic substances brought by rivers flowing into the sea, especially the Danube and Dniester and the ones brought by land-based sources, by the discharge of the waste water from point or/and diffuse sources. Organic materials are found in untreated municipal sewages, and in agricultural sources such as large livestock operations, food processing industries, and pulp and paper mills.

Land based sources of organic matter contribute to organic enrichment of coastal waters and sediments, while the rivers pollute waters entering the Sea.

The rivers introduce into the sea large quantities of organic substances. The average value of the organic matter quantities during 2004-2005 was by 573 kt/year (Fig. 5).

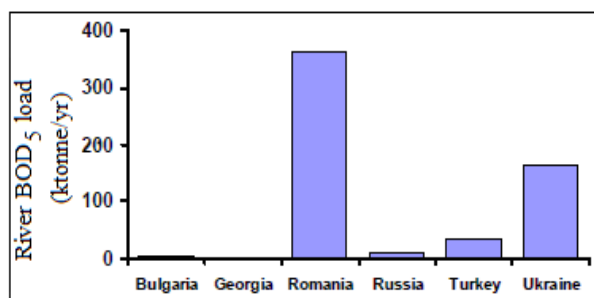


Fig. 5. Average river BOD₅ loads to the Black Sea, 2004-2005 (from [1])

The values from Romania are those from the Danube representing 63% of the total river borne BOD₅ load (361 kt/year), from Ukraine BOD₅ load was 29% of the total river borne (166 kt/year), while for the other countries of the Black Sea coast the amounts of BOD₅ brought by rivers were much lower (Georgia and Bulgaria 1.85 kt/year).

A main contributor to the organic pollution is the agglomerations which have no or insufficient waste water treatment.

Figure 6 presents the amounts of BOD₅ for the six Black Sea countries for 2004-2005 periods, taking into account 48 WWTP serving a population of > 5000 people. Total average load was of 15, 448 t/year.

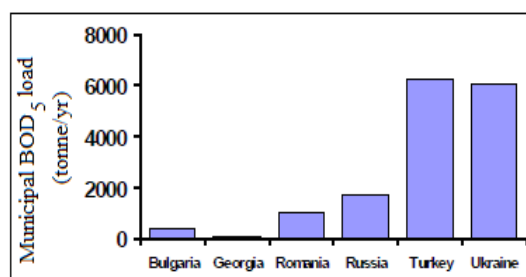


Fig. 6. Average municipal BOD₅ loads to the Black Sea 2004-2005 (from [1])

The largest amounts of BOD₅ belong to Turkey (about 6, 200 t/year) and Ukraine (about 6,000 t/year) and lowest Georgia; where over 90% of coastal populations (1.7 millions people) are connected to sewer system. Romania (920 t/year) is among the countries with the lowest amounts of BOD₅, after Georgia (60 t/year) and Bulgaria (310 t/year).

The industrial waste waters discharges are important because often these waste waters are insufficiently treated or are not treated at all before being discharged into the surface waters or into the public sewer systems [20].

For the period 2004-2005 the total average load of BOD₅ for industrial discharge for the 6 countries bordering the Black Sea was 2,837 t/year, of which Turkey had the highest quantities discharged (about 1,780 t/year), followed by Bulgaria (650 t/year).

For the Romanian coast and the Danube Delta the quantities of organic substances discharged into surface waters from agglomerations are shown in Table 3.

Table 3. Discharges of organic matter from agglomerations in the coastal zone and the Danube Delta in coastal waters, 2007 [19]

Agglomerations	Coastal area		Danube Delta	
	COD, t/yr	BOD ₅ , t/yr	COD, t/yr	BOD ₅ , t/yr
> 100000 PE	3463.019	1240.632	1528.901	644.079
10000-100000 PE	288.461	100.668	8.343	1.673
2000-10000 PE	0	0	115.057	23.607
<2000 PE	0	0	4.095	0.507
Total	3751.48	1341.3	1568.332	651.192

Today the situation is much improved in the coastal area by upgrading WWTP from Constanta, Mangalia, Eforie and Petromidia.

In the Danube Delta, there are 13 agglomerations > 2,000 PE with a degree of connection in the collection systems of 40-95%. Of these in 2007, 11 such of localities had not treatment plants, and from the two existing stations only one had tertiary treatment stage.

Given that in the last years in the middle and lower Danube region, the primary and secondary biological waste water treatment are increasing, and also the tertiary treatment (N and P removal) is being applied to a large number of new waste water treatment plants, it is expected that the pollution with organic substances of the Black Sea to drop.

Organic substances are also present in the suspensions introduced in the Black Sea. They consist mainly of mineral particles, most of them from erosion, but also from organic matter and phytoplankton particle. After Shimus and Trimonis 1974, the suspensions from the Black Sea basin are constituted from inorganic substances in proportion of 25-85%, the organic suspensions representing about 30%, but function of conditions they can vary

between 15-75% [21]. An important part of these suspensions comes from the erosion of the coasts, but most of them are brought by the rivers flow and among them the Danube plays the most important roll. The amount of suspensions brought by the rivers varies depending on the reception area of the tributaries and their flow.

The distribution of particulate matter in the Northwestern Black Sea is influenced by the seasonal thermocline and the salinity of the coastal waters, which is controlled by the transport of riverine waters [5].

It was found that, the concentration of suspended solid and turbidity in the Southeastern Black Sea coastal is higher near to the coast and decrease from the coast toward offshore. It is believed that this is mainly due to the suspended solids transport by rivers to the coastal region, but and due to the receipt of drainage waters by nearshore coastal water from land, activities of the port, discharge of city's sewage and material from erosion [22].

Particulate matter has property to adsorb strongly pollutants, especially heavy metals. A great importance it has the grain size distribution of bottom sediments since finer grained sediments tend to accumulate higher levels pollutant.

2.1.3 Hazardous substances pollution, including oil

In the Black Sea, large amounts of hazardous substances annually enter. The most common hazardous substances discharged in the Black Sea are pesticides, herbicides, insecticides, polyaromatic, hydrocarbons (PAHs), petroleum hydrocarbons (TPHs), heavy metals, surfactants. Annually, the Black Sea receives 206,000 tons petroleum and petroleum products, 48,000 tons surfactants, 90,000 tons iron, 12,000 tons zinc, 67,000 tons manganese, 4,500 tons lead, 2,800 tons cooper, 900 tons cadmium and 80 tons mercury [23].

The most important sources of pollution with hazardous substances are: industry, agriculture, municipal sewage, and navigation and harbor activities, directly from the coast and indirectly by rivers flowing into the sea. Industry and mining are responsible of most discharge of hazardous substances, very broad range of industries produce effluents with hazardous substances, both organic and inorganic. Industry contributes to pollution with metals (extraction and processing industry, chemical industry) and dangerous organic micro-pollutants (organically chemical industry, oil industry).

The accidental pollution from operating industrial facilities may be also significant.

The implementation of the urban waste water treatment contribute to the reduction of the hazardous pollution from urban waste water and indirect from industrial discharges.

The intensive agricultural activities may be a source especially as regards the pesticide pollution. About 300-500 different active agents of pesticides have been used.

Also, insecticides fumigants and antibiotics may be used in intensive livestock farming, and its waste is discharged to surface waters, with full, partial or no treatment.

Vessels and especially tankers of oil have an important contribution on the oil pollution. Ships transiting the Black Sea pollute evacuating in water wastes such: used oil, bilge oil, bilge water, wash water contaminated with oil and fuel residues. Also, local pollution is produced due to the small spills at terminals and dockyards. Accidental spillages of major oil spill at Sea are the major sources of the Sea pollution. Such accidents in the Black Sea are of around 10-30/year, the total amount of oil spilled into the Black Sea being generally, less than 50 tones/ year. The risk of producing both illegal discharges and oil spills increase due to of the increased oil transportation. This amount increased from the 150 millions tone in 2010 up to the 160 millions tons in 2013 [24].

The largest contribution to the sea pollution with oil it have the shipping activities and have oil transport (45%) and domestic and industrial discharge directly or via rivers (36%), the remaining of 19% being produced by offshore oil extraction (2%), atmosphere (9%) and natural hydrocarbon seeps (8%) (Fig. 7) [24].

Both illegal discharges and oil spills increase due to the increase of oil transportation.

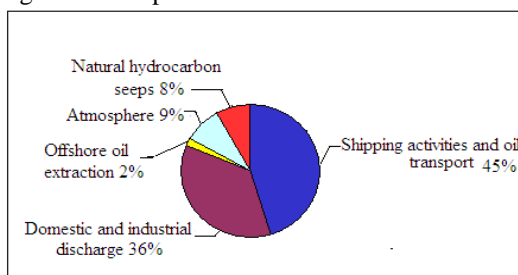


Fig. 7. The contribution of different activities to the Black Sea pollution with oil (from [24]).

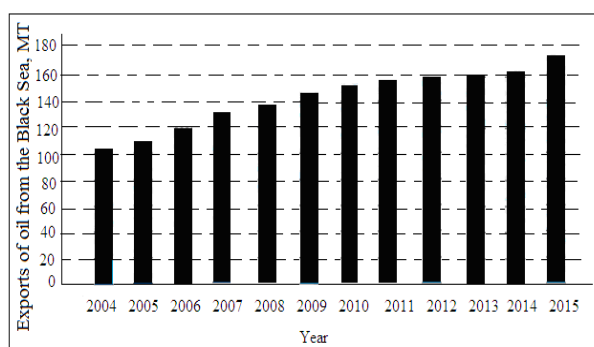


Fig. 8. Increasing oil forecast through the Bosphorus and Dardanelles straits (from [24]).

Pollution level with hazardous substances, including oil

The present level of oil pollution is not high in the open Sea but is high in many coastal areas.

Oil pollution in the Black Sea is predominantly concentrated in the coastal around the river mouths sewage outfalls, harbors and industrial plants [18].

For the period 2000-2004, using remote sensing imagery, the EC Joint Research Centre have observed the concentration of oil spills along the shipping routes Odessa-Istanbul and Novossiysk-Istanbul and also in the north area of the Bosphorus Strait. The annual of likely number of oil spills/illicit discharges is shown in the figure 9.

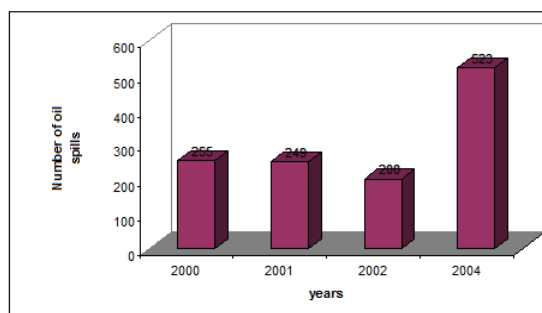


Fig. 9. Number of oil spills detected for 2000-2004 (from [1])

The monitoring in the south-eastern of the Black Sea coastal have shown that generally, the highest oil and grease level was recorded in summer and especially around the Rize harbor than other parts of investigated area in the Black Sea [22].

Achieved studies using satellite images SAR (Synthetic Aperture Radar) from the north-eastern of the Black Sea, in period 2006-2008, have shown that 184 events of Sea surface oil pollution as a result of ship discharges (Fig. 10).

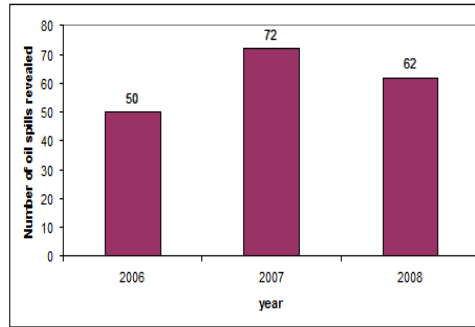


Fig. 10. Number of revealed oil spills (processed from [24])

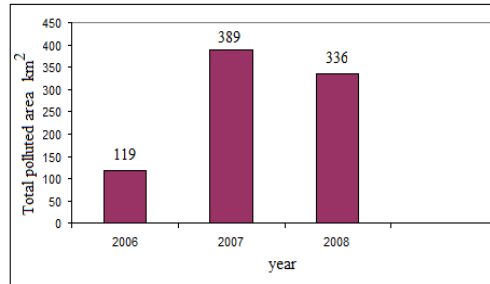


Fig. 11. Total polluted area (sq. km) (processed from [24])

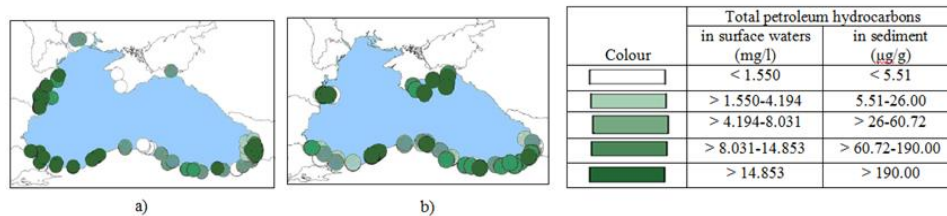


Fig. 12. Mean concentrations of total petroleum hydrocarbons (processed from [1])
 a) in surface waters (0-10 m depth) of the Black Sea, 2000-2005
 b) in sediments of the Black Sea, 1996-2006

Total polluted areas were 844 km² (Fig. 11). Sharp growth of polluted area in 2007-2008 is due a catastrophic oil spills in the Kerch Strait. Such accidents might happen also in the future, taking into account the routes of oil transports from the Caspian Sea towards Europe on the Black Sea.

Concentration of *total petroleum hydrocarbons (TPHs)* as measure of oil pollution in period 1996-2006, is shown in figure 12 [1].

As results from Figure 12, total petroleum hydrocarbons levels are highest in three distinct areas: of the Georgian coast, the West Turkish coast and at several point along the Romanian coast. This situation may be a result of local spills from ships at ports (On the Georgiana coast there are the ports Ponti, Kobuliti and Batumi with an important oil terminal) and discharges from waste water systems of large cities.

In sediment, the contamination with petroleum hydrocarbons has a similar distribution to that of water, being higher along the Romanian coast.

The analysis of total petroleum hydrocarbons in the Romanian transitional (Sulina-Gura Buhaz) and coastal waters (Vama Veche-Constanta) shows the presence of the pollutant load in water. In 2004-2009 period, the concentration of TPHs had an increasing trend, from an average of 244.4 $\mu\text{g/l}$ in 2004 to 568.9 $\mu\text{g/l}$ in 2009, but it decreased noticeably in 2010 to smaller values than 200 $\mu\text{g/l}$ (the limit for good ecological status).

In contrast, in sediments, the concentrations of TPHs in 2004-2010 periods have had a decrease trend (Fig. 13).

Heavy metal pollution affects generally the coastal areas, which do not represent a problem for the entire Black Sea basin.

The heavy metal concentration in coastal waters of the Black Sea is generally lower than admissible levels, except some hot-spot regions, where in sediment have been highlighted relatively high concentration levels of heavy metal.

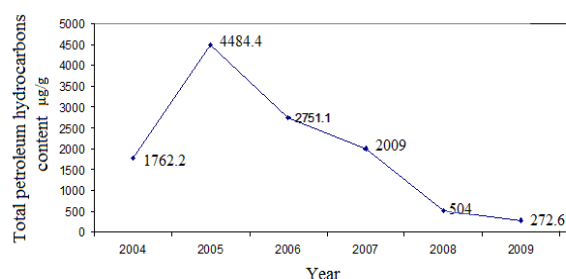


Fig. 13. The average concentration of TPHs ($\mu\text{g/g}$) in sediment from the Constanta south station, in 2004-2009 period (processed from [25])

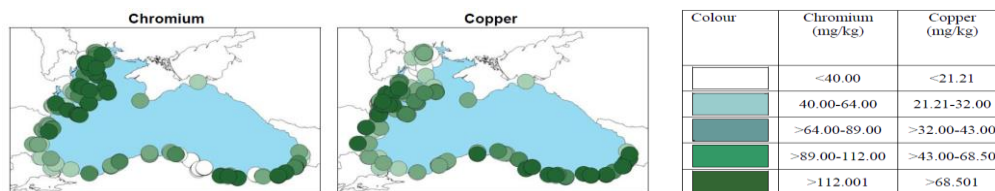


Fig. 14. Mean concentrations of chromium and copper, in sediments of the Black Sea, 1996-2006 (processed from [1])

Figure 14 shows that the concentrations of chromium and copper are similar.

They are elevated along the western-central area of the Black Sea shelf, where the Danube and Dniester Rivers enter the Sea, and also along the eastern area of Turkey (possibly due to the agricultural and industrial activities, especially the mining activities), the southern Georgian coast and Bulgarian coast (possibly due to river-borne or direct municipal/industrial discharges).

Some scientific information [26], [27] showed that the concentrations of dissolved metals registered in the Romanian coastal waters are comparable with other coastal regions (Crimea/Ukraine).

Data provided by the National Institute for Marine Research and Development Constanta show that, the annual average values for heavy metals concentrations in transitional waters, coastal and marine Romanian in the period 2006-2010 have, in general, a downtrend for copper and chromium and ascending one for lead and the nickel and cobalt concentrations oscillate around the values from 2006, with the tendency of stabilization.

In open sea most metals concentrations were slightly lower than in coastal area.

In sediment, in transitional, coastal and marine areas the average values and variation ranges of heavy metal concentrations, in 2010, were comparable, but they have slightly increased compared to the range of multiannual averages for the period 2006-2009.

Distribution of concentrations from heavy metal showed significant differences between different geographical areas. Higher concentrations in sediments and water were measured in front of the Danube mouth, and in the Constanta harbor, comparison to central and southern sectors [28].

According to water quality standards recommended by national and European legislation, the amounts of heavy metals concentrations were within generally below the limit. There are some values that exceeded the quality standards. These values refer to lead in water and cadmium and sometimes copper and nickel in sediments.

Pesticides continue to pollute hot-spot of coastal water of Black Sea. The levels of pollutants such DDT, polychlorinated diphenyls (PCBs), hexachlorohexanes (HCHs) and hexachlorobenzen (HCB) appear to be quite high in sea water and sediments in some coastal regions. They come mainly from agriculture, industry and municipal sewage [18].

The concentrations of DDT in 1996-2006 periods are alarmingly high in one Ukrainian coastal site and also off Romanian coastal.

Other pesticides, such linden and HCH isomers are low in waters from Ukrainian coast line, Russian Federation and Turkey, HCB were found in sediments at much lower concentrations than the water compounds.

In Romanian coastal waters, the concentrations of the total organochlorinate pesticides (HCB, lindane, heptachlor, aldrin, dieldrin, endrin, pp'DDE, pp'DDD, pp'DDT) in 2010 varied within the range of 0.2523-0.3978 µg/l, with an average of 0.3231 µg/l. These values are lower than the average recorded in the period 2006-2009, of 0.625 mg/l.

By monitoring the sediments it has been observed that the total organochlorinate pesticides registered downward trend in period 2006-2009 and continued in 2010, the average being of 0.0925 µg/l.

Polynuclear aromatic hydrocarbons (PAHs) are water hazardous substances that polluted sea water. They have been found in bottom sediment near Odessa, the Danube coastline and in Sochi (Russia). In marine waters, the Black Sea Commission (2002) has reported high concentration of PAHs in different areas [18].

In sediments, the total polynuclear aromatic hydrocarbons average concentration was of 0.629 µg/g. The maximum and average concentration in 2010 recorded the lowest values compared with those in period 2006-2009, in recent years registering a downward trend (Fig. 15).

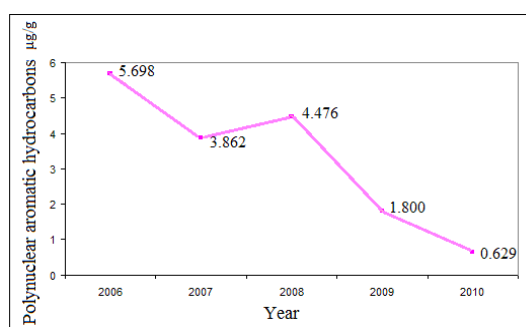


Fig. 15. The average concentration of total polynuclear aromatic hydrocarbons (µg/g) in sediment on Romanian coast in 2006-2010 period (processed from [28])

In Romanian coastal waters, the results of PAHs monitoring in 2010 showed the presence of 16 priority hazardous organic contaminants. Their average concentrations in water are of 1.344 µg/l, being situated within the specific range for the period 2006-2009 [28]. However, the low molecular weight PAHs (anthracene, phenanthrene, benzo (a) anthracene, and crysene) is insignificant concentrations.

The concentration of *phenol* in the southeastern coastal region of the Black Sea, whose main sources are waste water from fossil fuel, refineries, pharmaceuticals and pesticides, reached from 7.1 µg/l in nearshore to 1.6 µg/l, in offshore water, and from surface to depth [29]. More recent data show values of phenol of 1.00 up to 18.72 µg/l, in this area [22].

For the *anionic surfactant*, the data provided by the study carried out by Guven et al. (2010) during period of 2004-2007 showed that the concentration of anionic surfactant in southeastern part of the Black Sea ranged from 30.52 µg/l to 86. 88 µg/l. In northwestern part, this was over 100 µg/l and reached to 1200 µg/l in the discharge area of Danube River [30].

2.2 The introduction of invasive species

Invasive species are one of the great problems of the Black Sea. Some of these species had a negative impact on native communities in marine water ecosystems affecting biodiversity [31], [32].

The establishment of alien species in the Black Sea has been encouraged by the low salinity, eutrophication of the coastal area, as well as the high trade rate in the same area [47]. Most species are accidentally introduced from ships' hulls and in ballast water while other species are introduced for aquaculture and mariculture.

At the Romanian Black Sea coast, about 60% of the alien invasive species were accidentally introduced with ballast water and about 33% in fouling associations [33].

The development of marine transportation will lead to the increase the flow of ballast water into the sea and the risk of alien species introduction.

First record of most alien invasive species in the Black Sea basin is mentioned in the north-western and north-eastern part of the basin, in the vicinity of Odessa, Sevastopol and Novorossiysk harbors [31].

The Black Sea is invaded by some alien species of crab, jellyfish, annelid worm, mollusks and algae. Nearly 10% of the established alien species in the Black Sea and coastal aquatic habitat are considered to be highly invasive and 16% as moderately invasive.

The most spectacular event is the intrusion and afterwards the development of mass populations of the ctenophore *Mnemiopsis leidyi*, have been mentioned in early 1990s. This species of jellyfish is an invasive species with the highest impact on the associations of zooplanktonic and neritic species in the Black Sea [34]. She played an important role in the collapse of many fish species of great economic value, consuming the food, the larvae and juvenile species of these [2].

After the year 2000, the number of reported invasive species decreases.

The Black Sea ecosystems affected by invasive species are the pelagic and benthic associations from 0 to 50 m depth, both on rocky and sandy bottom.

2.3 The unsustainable fishing

Besides of the nutrient and chemical pollution, the habitat change and invasive alien species, a negative effect on marine biodiversity it also was unsustainable fishing (overexploitation and destructive fishing practices).

Due to overfishing in the early 1970s-1980s, the structure of catches has been modified significantly. Also, fish stock has declined drastically causing considerable economic losses to the fishing industry in the region. At the decrease of the fish stock the pollution and

habitat loss has contributed. The stocks of predatory species as bonito (*Sarda sarda*), horse mackerel (*Trachurus trachurus*) and bluefish (*Pomatomus saltatrix*) have been decreased and the stocks in non-predatory species such as anchovy (*Engraulis encrasicolus*) and sprat (*Sprattus spratus*) have increased [1]. Anchovy and sprat are the main commercial species in the Black Sea, today. Sturgeon fisheries have been dramatically depleted.

Thus, during this period the number of commercially exploited fish species declined from twenty to only five, and the yield of 800,000-900,000 tons/year in the mid 1980s decreased to about half of this amounts in the mid 1990s (Fig. 16).

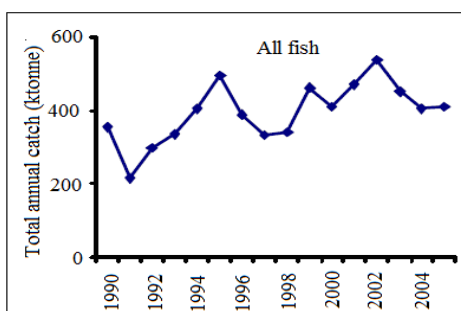


Fig. 16. Trends in Black Sea fish catches, 1990-2004 (processed from [1])

From Figure 16, it results that, since the early-mid 1990s, total fish catches have increased in the Black Sea, intimating that the resource has been recovered, but remain below compared with the estimated maximum sustainable yield.

In the Romanian Black Sea sector the fish stocks have increased in the period 2005-2010, both the small species (sprat, anchovy, whiting, goby) and the large ones (turbot, shark) (table 5), while the total catch has declined especially after 2006 (Fig. 17).

Table 5. The value of stocks (tons) for the main species of fish from the Romanian Black Sea sector (from [28])

Species	2005	2006	2007	2008	2009	2010
sprat	45,000	14,750	60,000	60,000	60,000	60,000
hitting	8,000	7,000	6,000	8,500	10,000	11,000
anchovy	19,000	20,000	20,000	20,000	-	-
goby	600	600	600	500	-	500
turbot	1,080	1,150	1,300	2,356	1,500	1,350
dogfish	1,650	2,000	4,300	1,450	2,500	2,500

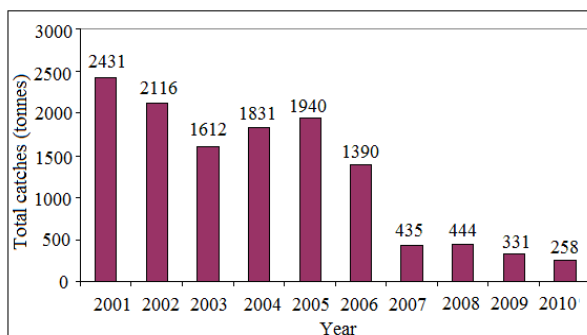


Fig. 17. Total catches (tons) carried out in the Romanian sector of the Black Sea, in 2001-2010 period (processed from [28])

The rehabilitation of the fish stocks is the result of a slow but continuous process of improvement in ecosystem of the Black Sea detected after 1990, as show the Transboundary Diagnosis Analysis (2007) and ex-ante Evaluation Report of the Joint Operational Programme for the Black Sea basin (2013).

2.4. Pollution consequences

The main consequences of the pollution of the Black Sea are: water quality degradation, the decline of biodiversity, living resources change (Mostly fish stocks), habitat destruction.

Eutrophication represents the main cause of the ecological imbalance of the Black Sea. This phenomenon is characterized by algal blooms chronically, oxygen deficiencies, modifying specific component of phytoplankton, zooplankton and zoobenthos, the simplification of the trophic chains, and drastically reduction of the biodiversity [35].

The measurements of the zooplankton in the Romanian nearshore showed its decrease from north to south (Fig. 18). In the north of the Romanian nearshore the considerably greater densities of zooplankton show the important role of the Danube in the pollution process.

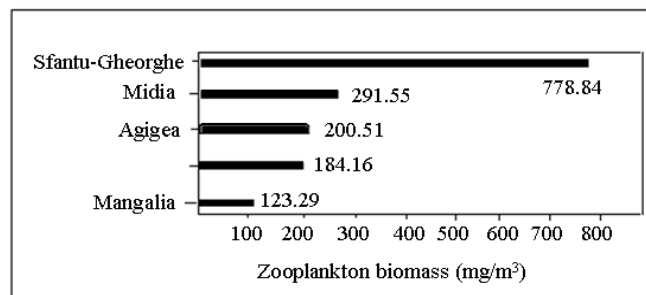


Fig. 18. Distribution of the zooplankton in the Romanian zone with shallow water (processed from [36])

From the early 1970s through the 1990s excess nutrient to the western made that tens of thousands of square kilometers to be under hypoxic conditions (depleted oxygen) [16].

Gomoiu, referring to the state of the Black Sea benthic ecosystems, at least for those on the northwestern continental shelf, shows that it is characterized by: drastic decrease of the specific diversity, decrease of the numeric abundance and biomass of benthic populations, simplification of vegetal and animal benthic communities structures [37].

Over the past 20 years due to reduced nutrient input, eutrophication levels have decreased with an improvement of the near bottom oxygen regime, regeneration of phytoplankton and zooplankton [15].

In the western Black Sea the number of benthic species observed in the early 2000s was 1.5-2 x higher than levels found in the late 1980s, but still more than 1.5 x lower than conditions in the 1960s [16] (Fig. 19).

As noted by the Development Research Institute of Marine from Constanta, there is a return tendency of the plankton and benthic populations to the state of existence many years ago. However, it is believed that the return to the existing ecological condition with 50-60 years ago the Black Sea is extremely slow and questionable [2].

Other pollutants such metals, pesticides and herbicides contribute to the deterioration of sea water quality with long-term effects in the marine ecosystems.

The heavy metals have been accumulated by mollusks and fish. When they are accumulated in large quantities, they can have toxic effect on consumers in food chains, such as humans, birds and marine mammals.

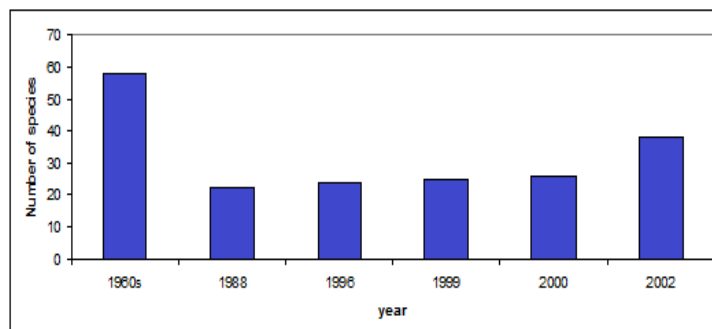


Fig. 19. Number of macro benthic species in front of the Danube Delta (processed from [16])

Studies regarding the concentration of the metals in *Mytilus galloprovincialis* in the period 1999-2008, along the Romanian coast of the Black Sea have shown a decrease in the accumulation of cadmium and stabilization for lead and copper in relation to the previous period. The order of the bioaccumulation metals in the downward sense of the values were:

$$\text{Zn} > \text{Mn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cd} > \text{Cr}$$

Investigations on the metal bioaccumulation in mussels in different areas of the Black Sea showed values comparable to those observed on the Romanian Black Sea coast [38].

Accumulation of metals to the fishes depends on a number of factors: the level of exposure (water, food), physiological factors (age, metabolic activity), and environmental factors [39].

Studies on the distribution of heavy metals in different organs of fish showed that metals accumulate in higher concentrations in the gills and digestive tract and less in the muscle tissue. Worrying is that some metals have penetrated beyond the maximum limits in the tissue of some species [40].

Also, the petroleum products spilled into the sea are toxic for the aquatic organisms, the effects can be immediate or long-term [2].

Major oil spills and those from offshore drilling-extraction are the most dangerous because they usually occur in estuaries and along the coast, areas that are the most productive ecosystems that serve as spawning place and as nests for many economically important species. The oil pollution is a serious threat to the riverine ecosystems because the oil contains a whole series of chemical components, some of which are toxic to the micro fauna and micro-flora of the aquatic ecosystems.

Oil pollution affects especially large species, like sea water birds and mammals and fish health [41] [42] [43] [44].

Besides the direct effect, the petroleum products affects the aquatic ecosystem due to the formation of the surface film that inhibits photosynthesis and the gases exchange between air and water resulting in decreased concentration of dissolved oxygen in water. This causes behavioral and functional changes of all planktonic and benthic populations.

Organic pollution causes heterotrophic growth, which consumes the available dissolved oxygen and the increase of the frequency/severity of hypoxic events.

Hypoxic phenomena were signed in the Ukrainian sector of northwestern coastal waters and on the Romanian sector of the Black Sea, frequently in the 1970s and sometimes in 2001 and 2010.

By assessing the degree of impact of various pollutants, Gomoiu (2004) shows that for the Black Sea the main cause of biological imbalance is the increase of the concentration of organic matter over the ability of ecosystems to mineralize of it. It is followed by the impact of pesticides and heavy metals, a less impact having the oil pollution [37].

An improvement in the quality of sea water can be achieved by reducing the pollution of the Danube and other rivers flowing into the sea, the connecting of a large number of coastal industries and inhabitants to the collection systems and upgrading sewage treatment plants, the pollution reduction from port activities and from diffuse sources [45]. At these actions must attend all the countries of the Black Sea basin [46].

3. Conclusions

In the last 40 years, the Black Sea basin is continuously subjected to a significant pollution process that has destructive effect on the marine environment.

The changes in the water quality take place due to discharges into the sea of numerous pollutant substances coming from the land based human activities of the coastal and non-coastal states of its basin.

The most important problems affecting marine ecosystems are: nutrient pollution, organic pollution, hazardous substances pollution.

A great ecological problem of the coastal Black Sea regions is eutrophication that is caused by the excess of nutrients, especially nitrogen and phosphorus compounds.

The main polluters are agglomerations, industry, agriculture and transport. Pollution is caused mainly by municipal and industrial waste water discharges which are only partially treated or even untreated, from livestock farming and fertilizer use in agriculture, navigation and harbors activities. Vessels, especially tankers have an important contribution on the oil pollution. Some threats are induced by the penetration of invasive species, over fishing or destructive fishing techniques.

The pollution of marine environment has destructive effect on the biological resources, of marine flora and fauna, and also a serious impact on human health for the people living in the coastal area of the Black Sea and for the activities that depend on good sea water quality (capture, fisheries, aquaculture, and coastal tourism).

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