DOI: http://doi.org/10.21698/simi.2019.fp25

IMPACT OF TERRESTRIAL AND MARINE POLLUTION ON THE BLACK SEA QUALITY OF WATER

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Abstract
Black Sea represents a direct link between the European Union, EU candidate countries and some Asian countries such as Russia, Georgia, etc. During the last decades, the Black Sea has been confronted with unexpected environmental problems. In the south part of the Romanian seashore has appeared erosion, in the North-East part of the Black Sea appeared a massive algae development, followed by modification of the maritime biological balance. In parallel, the maritime water parameters have been changed, partly due to the water discharged from the main rivers as Danube, Dnieper, Dniester, partly from the amount of freshwater from deep currents new appeared in the last decades, and partly due to the impact of the pollutant sources. Firstly, are mentioned some data, based on the local measurements and registered data, which underlines the actual situation, referring at the existing sources of pollution, the hydrocarbons and ions concentration, etc. with immediate consequences on the local equilibrium of the marine bio-system. The registered Turkish accidents with spilled oil briefly mentioned, were followed in a short term by a process of nitrification, with many consequences. Next are presented the appeared modifications, registered in the Black Sea fauna, some endangered species, correlated with the simultaneous apparition of some invasive species. Finally, some conclusions and references are presented.

Keywords*: Biodiversity, Environmental factors, Environmental monitoring Marine pollution, Sea measurements.*

Introduction

The Black Sea is a zone of particular interest for the European Union because represents the eastern border, a connection between the EU and Asian countries. The Black Sea also has strategic importance in energetic infrastructure, being a zone which confronts with political conflicts (peninsula Crimea), permanent discussion referring to the marine traffic, fishing quotas, etc. Anyway, members or non-members of UE, each country which is bordering the Black Sea should maintain the regional ecologic equilibrium, and respect the treaties of excellent proximity and the regulatory environment rules (Protocol on Protection of the Marine Environment of the Black Sea from Land-Based Sources and Activities 2009), (Strategic Action Plan for the Environmental Protection and Rehabilitation of the Black Sea 2009).
In the last decades, in the Black Sea environment, marine biology and the water characteristics have recorded some changes, affecting the entire ecosystem. The

south part of the Romanian Black Sea shore has confronted with massive erosion, with several cliffs collapsed, sometimes more than 4-5 m. The main cause was considered the registration of many small earthquakes near the border with Bulgaria, for Romania the zone between resorts Venus and Vama Veche. In time, a Bulgarian team registered the apparition of a freshwater current, with a significant flow rate.

Moreover, new environmental and social problems appeared mainly due to mismanagement of the main rivers flowing in the Black Sea, Danube, Dnieper, Dniester, etc. with significant input of wastewater, solid waste from the industrial activities, and contaminated water due to improper utilization of fertilizers on agricultural lands. This year, confronted with many floods, has transported supplementary solid waste. The chemical fertilizers often used in Danube meadow are another responsible factor in marine water contamination, but the leading causes remain the existent shipyards and the industrial activities. Any changes in the ecological balance affect the standard of living in this zone. The beaches width has decreased in Eforie, Mangalia, 2 Mai, and Vama Veche, reducing significantly the number of tourists, which have turned to outbound tourism.

The Black Sea has specific characteristics because over 90% of its deep-water is anoxic. In natural conditions, without any perturbations, the interaction between the water-rich in oxygen from the surface and the anoxic deep one is minimal. With specific measurements was observed that the Black Sea has a layering structure, with significant consequences on the biologic diversity. The newly registered current in deep water interferes between these layers, with impact on the ecosystems. The Black Sea is almost a close body of water, with the fauna diversity approximately three times smaller, compared with that one from the Mediterranean Sea.

Starting 1997 there were registered three accidents in Turkish shipyards and their vicinity, with oil spills. One of them due to the massive oil spilled in the Black Sea water has been followed by some chemical and biological modifications, especially massive felt on the seaside from Ukraine and Georgia. In 2005 and 2007 the Romanian shore was also affected. In Mamaia, Mangalia, and near the Bulgarian border, for more than three weeks in full season during the summer holidays, massive quantities of dead fish and jellyfish have appeared on the sea surface, followed by a vast amount of destroyed marine vegetation.

In the local analysis of the Romanian Black Sea coastal water should be considered both the source of pollution from waste-waters discharged by sewage pipes from municipal and industrial treatment plants but also the coastal water nearby the discharges from the agricultural lands. There are four domestic waste-water treatment plants, Constanta North, Constanta South, Eforie South, and Mangalia, a petrochemical industrial waste-water treatment plant in Petromidia, and a shipyard in Mangalia. All these factors have major influences in the marine environment and local ecologic balance.

Experimental Materials

The Black Sea represents a region of particular interest because it is rather sensitive to climate and anthropogenic influences. It is considered a deep sea, as the maximum depth is about 2200 m. The Black Sea receives drainage from almost one-third of the continental free water flow of Europe, being meanwhile an isolated sea. It is the reason why it is regarded as a vulnerable water basin, being permanently

monitored, Fig. 1-a; green–marine currents, blue-temperature, red-water parameters, cyan-biologic registration. The purple line represents the territorial waters. Since 2002 a total of 37 boats have been deployed in the Black Sea, with 11 permanently active with cycles of 5 days for monitoring and marked depths, between 200-1000 m. Most ships alternate the average depth with maximal profiling depths between 700 and 1500 m. Fig. 1-b presents the routes of the ships for two months.

Figure 1. a- Monitored points on 20 March 2019, b-Routes for March-April 2019

Internationally, a report created jointly by the countries bordering the Black Sea has highlighted the main factors for water pollution, Table 1.

Table 1. Types and pollutant sources in the Black Sea

Types of pollution	Sources of pollution				
	1	2	3	4	5
Contamination with chemicals:					
• nutrients and organic matter	+	+	+	+	+
• oil and petroleum products	+	+	+	+	+
• persistent organic pollutants	+	+	+	+	+
• trace elements	+	+	+	+	+
Radioactive contamination		+		+	
Marine litter (solid waste) pollution	+	+	+	?	+
Biological pollution:					
• microbial/faecal contamination	+	+	+		+
• introduction of exotic species					+

[1] – Industrial liquid wastes and insufficiently treated or untreated sewage from coastal cities and settlements;
[2] – Inputs from the agriculture, industry, mining, and municipal sewage from the whole Black Sea drainage area;
[3] – Inputs from the agriculture, animal husbandry and non-managed tourism mainly through the run-off from land (coastal pluvial effluents and ground waters);
[4] – Inputs from various sources of air pollution (smokes, fumes, dust, and exhaust gases) no matter where in the world;
[5] – Dumping of the solid waste, and dredged matter; discharge of untreated sewage and ballast waters; oil spills; lost fishing nets; introduction of alien marine organisms owing to the bio-fuel.

To establish the influence of the waste-water discharges by the municipal sewage stations in Romania, have been analyzed the chemical and bacteriological pollutants, identified in samples from the waste-water, collected inside the sewage treatment plants, before being discharged into the sea. There were compared with the values obtained in seawater samples as to be determined the level of pollutants within the footprint of the profile weirs at 0 m, 5 m, and 20 m. In 2017 the collected samples

from the municipal wastewater treatment plants, after the refurbishments carried out during 2007-2010, showed levels of total hydrocarbons within the range of 82-503 μg/l, values accepted by The Commission on the Protection of the Black Sea Against Pollution. The only amount that has exceeded the permitted limit was registered in the station Petromidia, Table 2, where CN-Constanta North, CS-Constanta South, ES- Eforie South, M-Mangalia, P-Petromidia

Table 2. Average values of the hydrocarbons concentration

	CN	CS	ES	M	P
Waste water	82	88	503	280	1840
Sea 0 m	145,4	154,7	180,6	810	884
Sea 5 m	122	195,6	150,3	640	819
Sea 20 m	101,8	118	120,2	224	740

The spatial distribution of the hydrocarbons pollutant confirms the petroleum dispersion on the east direction, along the discharge channel in the marine environment. At level 20 m, the load of the total hydrocarbons determined in seawater decreased at four stations in the direction of the waste-water treatment plants. There were analyzed the concentration levels of heavy metals Cu, Cd, Pb; there are within the accepted range 9.45-32.06 μg/l for Cu, 8.05-14.9 μg/l for Cd, and 0.91-9.54 μg/l for Pb, Table 3.

Table 3. Average values of metals concentration

		Wastewater	Seawater 0 m	Seawater 5 m	Seawater 20 m
CN	Cu	11,3	14,4	11,3	10,1
	Cd	14,8	7,8	6,3	5,9
	Pb	2,33	2,1	1,7	1,6
CS	Cu	9,5	19,7	11,4	8,2
	Cd	8,4	6,4	5,3	2,14
	Pb	1,1	6,8	5,32	4,84
ES	Cu	34,9	12,8	7,84	6,8
	Cd	16,6	14,1	8,6	5,4
	Pb	9,14	5,73	4,82	3,7
M	Cu	19,4	16,7	12,3	11,2
	Cd	9,23	7,4	5,4	2,8
	Pb	3,47	12,5	10,8	8,3
P	Cu	32,3	38,4	27,3	23,1
	Cd	14,8	12,8	12,7	13,9
	Pb	4,83	5,1	5,3	5,6

If there are compared the measured values for heavy metals, with those recorded in 2000-2005 the values constantly have decreased until 2007. After the accidents registered in 2005, 2007, and 2009 in Ukraine and Turkey, the concentrations increased again (Final ¨Diagnostic Report¨ to guide improvements in the Black Sea environment 2010), (Zaitsev 2006). In the mentioned period in Romania was tested the concentration of the poly-aromatic hydrocarbon. Of the five poly-aromatic compounds investigated from samples of the wastewater treatment plants have been

identified three compounds in Petromidia, Eforie Sud, and Mangalia, and two compounds in Constanta South and Constanta North, Table 4.

Table 4. Content of poly-aromatic hydrocarbons

Poly-aromatic	CN	CS	ES	M	P
Naphthalene	0	0	69,3	74,8	493
Acenaphthene	0	0	5,4	2,43	0,688
Fluorine	0	0	2,1	2,4	0,378
Acenaphthylene	0,29	0,32	0	0	0
Benzopyrene	0,31	0,28	0	0	0

The highest concentration of poly-aromatic hydrocarbons was recorded at 5 m depth, of 124,3 ng/l, which is 5 times higher than at 20 m. In three points of measurements near Constanta North, Constanta South, and Mangalia, from the southern part of the Romanian seaside where there are more farmlands have been investigated eight types of pesticides organic-chlorides, Table 5.

Table 5. Average HCB and Lindan

	CN		CS		M	
	HCB	Lindan	HCB	Lindan	HCB	Lindan
2000	430	47,9	68,5	1042,4	118,4	86,7
2001	520	85,2	112,7	894,7	143,7	132
2002	617	221,7	314,7	1247	212,2	473,6
…..	…..	…..	…..	…..	…..	…..
2017	780	714,5	714,5	1770	690,6	706,4

The highest level of pesticides is recorded at the level 20 m in seawater, with an average of 473,8 ng/l, value about 32% greater than the value recorded near the seashore. The superior load of the organic chlorine pollutants recorded in deep seawater is the result of cumulative effects between the concentration of the pollutants of fluvial origin, domestic urban, but also produced by the marine currents, that bring polluted water mainly from the southern. The pollution with pesticide was made due to the fungicides HCB and lindan in high concentrations in water, offshore, between 270 ng/l and 1774 ng/l, exceeding about of nine times the maximum allowed value by the European normative of 200 ng/l. From the recorded data could be observed that three monitored wastewater treatment plants, Constanta South, Eforie South, and Mangalia contain large amounts of feces, with maximum values of 1.7×10^7 germs/100 ml for the indicators total coliforms CT, and CF fecal coliforms, and $2 \cdot 10^5$ for SF- fecal streptococci. The highest level was found in the Eforie South station. The realized measurements prove that the southern coastal waters are insufficiently treated, downloading in the marine environment large amounts of germs, including pathogens.

Results and Discussion

The oil spills by accidents or by common industrial activities have produced the main disturbances in the last decades, followed by chemical and biological modifications, with effects in the nitrification process. The maximum values recorded for the nitrates were reached in 1997 and 2009. The values for the

Romanian marine waters involved in the eutrophication process was determined based on the measurements recorded at station Constanta and showed a monthly average of N = 372 mg/l. In the south part of the Romanian seashore it has increased dramatically, N = 3024 mg/l, (Boltachev & Karpova 2006), (Dobrovolov et al. 2003). In Fig. 2-a, the affected areas by eutrophication are illustrated. As it may be observed the Romanian shore is affected, mainly due to Ukrainian pollution. As a consequence of the supplementary freshwater amount, the water salinity from the Black Sea was changed, Fig. 2-b, followed by modification of the temperature, and biologic structure.

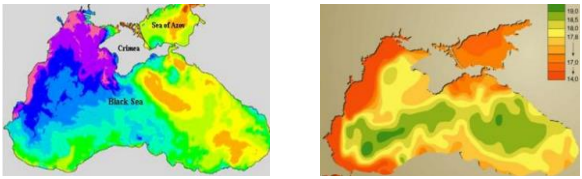

Figure 2. Affected area: a- by eutrophication, b- salinity modification

Special marine conditions characterize the areas where the hypoxia and the anoxia were registered: vertical gradients of density in 6 conventional units, salinity variation of 6%/m, and temperature variations of 15º C, with an important role in the eutrophication process. However, in the spring of 2016, water was over-saturated with the oxygen of 170%, and the pH level on the surface has reached 9.25, (O'Higgins et al. 2014). In these conditions, in the bottom layer, the pH of water has decreased to 7.8. As a consequence, a destructive process has appeared: the constant speed of the organic matter oxidation exceeds by 3-5 times and the BOD-Biochemical Oxygen Demand value reaches 2-4 mg/l. All these modifications recorded in the water's composition, causes a removal of the fish from the shore, causing it to stay only in deep water, a decrease of fish quantity, and an increase of the amount and sizes of the jellyfish. In 2016 for the Romanian sea-fishing was recorded one of the smallest quantity from the last 30 years.

The Black Sea is now confronted nowadays with some invasive species. As eutrophication's consequence has evolved the saprophytic bacterial plankton, suddenly increasing, mainly the cocci and bacilli. This is a consequence of high levels of organic matter dissolved particles, being an additional source for nutrition for the saprophytic microorganisms. The populations of bacteria, especially the pathogenic organisms, have reacted at changes appeared in marine conditions, increasing the organic matter in the water volume and bottom sediments. The most advantaged species in these eutrophic conditions are the plankton of small sizes, such as Euglenoids, Coccolithophores, and Dinoflagellates. The phytoplankton species composition is represented by 148 species and subspecies. The unfavorable conditions, such as intense solar radiation recorded in the last years have provoked also massive development of algae.

Intensive algae development has induced a sharp decline of the dissolved oxygen and has increased the bio-sedimentation of the decaying plants. The light penetration and transparency of the marine waters have decreased. Consequently, an important modification of the zooplankton communities was determined by massive increasing of species as Cassiopea Andromeda and Cotylorza tuberculate, the largest ones in

the Black Sea, but also Aurelia aurita and Rizzhosstoma Pulmo. These four species have large dimensions, are poisonous, and newly developed in the Black Sea, Fig. 3.

Figure 3. Invasive poisonous species of jellyfish

In the Black Sea, there are about 200 fish species, more than 500 mollusks and many macrophytes water plants, as the green, red, blue, and brown algae. Among the recorded fish species, economic value is represented by about two dozens of species representing 98% of the catches from the last two decades. Between them, must be mentioned the Pontic shad, gray mullets, and sturgeons. In the last years, the number of Pontic shad permanently decreases. But the main threat for all species remains the over-fishing. By exclusive international agreements, this aspect may be solved. The problem remains with critically endangered species, Fig. 4 due to:

- Eutrophication: as the angel shark, starry sturgeon, and beluga
- Salinity modifications: as the sea horse, thorn-back ray, crabs
- Oil pollution, the European eel, and smooth hammerhead.

By making a comparison, the situation of shad's stock is better than the sturgeon, due to the natural abilities of shad to more rapid recovery. As an example of over-fishing: it is recommended the sturgeon capture of 10 trawlers/year; in 2017 were registered 15 trawlers and in 2016, 18 trawlers. It can be seen that only in recent years has been fished almost two times more than the recommended amount of sturgeon; but the problem is repeated with mackerel, turbot, etc.

Figure 4. Endangered species a- beluga, b- sea horse, c-angel shark

Unfortunately, in the Black Sea region, there is not a regional fisheries management organization. Each riparian country promotes its regulatory framework in fisheries, even for the migratory species. The EU Scientific, Technical, and Economic Committee for Fishery try to solve the problem by creating international projects and committees with sub-commission of the stock's assessment for species like sprat, turbot, anchovy, whiting, mackerel and shark from the Black Sea.

Conclusions

The Black Sea represents a transit route (more than 50000 ships, including 10000 oil tankers) for the oil and gas exports, which means that there are risks associated with these activities, such as oil spills and accidental pollution. Signed in 2015, the BS-SAP an updated Strategic Action Plan for rehabilitation and protection of the Black Sea represents a new step in the ecologic rehabilitation, by solving any trans-boundary environmental problems. It contains realistic objectives, including legal

and institutional reforms, suggestions for necessary investments in solving the ecological issues, as diminishing the insufficient treated waters and pollution from priority sources, eutrophication, surveillance of traces for metals and radio-nuclides, to avoid the chemical pollution. Several projects developed by international teams have restored partially some environmental aspects. Introducing in 2018 the Beroye ovata, which is feeding with *Mnemiopsis leidyi* (invasive species), has been observed a decrease of the algae number and biomass. The problem of the venomous jellyfish is remaining; they become more significant in number and dimensions. The increase of fodder zooplankton is followed by an increase in the stocks of small pelagic fish, but national efforts and international cooperation in the framework of the MSFD brought the first signs of recovery of the Black Sea ecosystem.

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