ASSESSMENT OF WATER QUALITY AT THE ROMANIAN BLACK SEA SHORE

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Over the last 40 years the Black Sea recorded a serious degradation of the aquatic ecosystem, mainly due to human pollution. Excessive nutrients concentration in water mass (from agriculture or sewage treatment) caused the apparition of eutrophication in Black Sea. Eutrophication disturbs the aquatic ecosystems and become a risk to organisms that depend on water resource and also to human health.

The occurrence of eutrophication phenomenon in the Black Sea produces big economic losses in tourism and fishing industry. This study investigates, based on experimental observations, the causes and effects of eutrophication occurrence. Furthermore, based on current state of eutrophication indicators in the sea water, this paper tried to identify possible methods of rehabilitation of the marine ecosystem.

Keywords: amenity value, Black Sea, degradation, eutrophication, water quality

1. Introduction

Nowadays marine and oceanic ecosystems undergo great anthropic pressures often manifested by pollution of these water bodies. Anthropic impact on the coastal zone is mainly exerted through riverine nutrient discharge, dependent on land use and watershed management.

Marine coastal eutrophication is characterized by a strong increase of primary production most often restricted to a narrow area along the coast, or within the plumes of large rivers. The main source of nitrogen to European coastal waters is agricultural runoff discharged into the sea via rivers, identified as originating from sources of ammonia evaporation in animal husbandry and partly from fossil fuel combustion in traffic, industry and households. For phosphorus the major sources are treated and untreated discharges to the sea from households and industry as well as soil erosion. Effects of eutrophication on marine ecosystems are: algal blooms resulting in green water; reduced depth distribution of submerged aquatic vegetation; increased growth of nuisance macro algae,

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sedimentation and oxygen consumption, oxygen depletion in bottom water, and sometimes dead benthic animals [1].

Black Sea through its unique characteristics represents an extremely sensitive ecosystem and is exposed to these threats [2]. Thus, during the last four decades, the cultural eutrophication has been identified as a key ecological problem for the North-Western coastal Black Sea region, which is strongly influenced by freshwater input. The Black Sea is one of the most important European seas because its watershed includes 23 countries, among which 6 countries are located in the coastal area [3]. At present, due to the high level of pollution which determines a serious impairment of the aquatic ecosystem, the Black Sea is in a vulnerable situation.

The Black Sea contributes significantly to the regional economy by means of fishing, tourism, transport activities and so on. Now it is estimated that there are substantial economic losses due to occurrence of Black Sea eutrophication phenomenon. Even if in the late years nutrients pollution in the Black Sea region decreased slightly, because the agricultural activities in the riparian countries have been reduced, it is considered that the N-W part of the Black Sea and certain sectors of the Danube, Dnepr and Don Rivers will reach a high rate of eutrophication. For this reason the efforts to rehabilitate the unique Black Sea aquatic ecosystem should be strengthen to implement measures of abating eutrophication.

The aim of this paper is to analyze the trophic state of the Black Sea, to determine the causes of the emergence of this phenomenon, to quantify the effects felt at the ecosystem level and moreover to identify the methods to rehabilitate this ecosystem. In this context, a review of the existing rehabilitation methods will be made, including the possibility of their application for the studied marine ecosystem.

2. Materials and methods

The Black Sea is a semi-closed, inter-continental sea, characterized by a total surface of 451,488 km^2 (out of which about 12% belongs to its annex – the Azov River), a volume of water of 529,950 km^3 and an average depth of 1,282 m. The surface of its hydrographical basin is of 2,405,000 km^2. The Black Sea waters represent a mixture of fresh waters brought by important tributaries which flow into them (the Danube, Don, Dnepr, Dnestr, Bug, Kizil, Irmak and so on) and salty waters from the Mediterranean Sea. The annual share of fresh water at the Black Sea level is estimated at 390 km^3/year out of which half is brought by the Danube River. According to the decision of the International Court of Justice (Hague) from 9 February 2009 regarding maritime delimitation of the Black Sea, the economic area which belongs exclusively to Romania is about 29,700 km^2 [4].

The Black Sea basin, with its limited size and almost complete enclosure, displays unique circulation characteristics and permanent stratification that divides the basin into upper aerobic (comprising only 13% of the total volume of the basin) and bottom anaerobic zones [5]. The Black Sea is a strongly stratified system, thus, this ecosystem is characterized by the existence of two layers: a surface one, with a depth up to 100 m and a deep one up to 2,245 m [6]. The surface layer is supplied from river waters, it has low salinity (17-18%) and it is influenced by climate factors and has a diversified fauna. The deep layer however has greater salinity (22%) and it lacks oxygen, which determines anaerobic decomposition of organic matter with toxic gas (H_2S) release and accumulation. Under these conditions, the deep areas are almost totally devoid of life, since only sulphur bacteria develop here.

Under the influence of winds a circular current forms in the Black Sea, and, in front of the Crimeea Peninsula, is divided into two closed branches: eastern and western. In Bosporus Strait flows a compensation current from the Mediterranean Sea of 193 km^3/year while in Kerch Strait the current from the Azov Sea brings another 95 km^3/year. Large volumes of water are lost from the Black Sea by evaporation (365 km^3 / year - about 44%) and by volumes of water passing to the Mediterranean Sea (392 km^3/year - 47.5%) and the Azov Sea (70 km^3/year - 8.5%) [4].

The Black Sea shows characteristics specific to the aquatic ecosystems in the temperate area regarding the temperature distribution in depth. Thus, if water temperature beyond the 75 m depth is constant to the bottom and equal to 7-8°C, the water temperature in the superficial layers undergoes seasonal and diurnal variations. In the summer time, at the level of the marine ecosystem, a direct stratification takes place, the epilimnion having a 8-10 m depth and a temperature which may reach 26°C. However, during the cold season, a reversed stratification takes place with water surface temperatures which may drop even below 0°C, so that the sea may freeze. Mean annual Black Sea water temperature on the Romanian sector varies between 12° C and 14° C, while transparency does not exceed 15 m. In the Black Sea the amount of oxygen decreases close to the seacoast down to the 50 - 100m depth, while at depths greater than 150-200 m, the waters are anoxic due to the absence of convection currents in the depth [4]. Dissolved oxygen availability is reflected in the biodiversity of this ecosystem.

Since the late 1960s, increased eutrophication has been reported, reaching a maximum during 1980 -1995 period, and having negative effects on the coastal ecosystem of the Black Sea [7]. The most affected area is the northwestern Black Sea, especially the Romanian coastal shelf zone, which receives water from the rivers Dnieper, Dniester and the Danube [8] (Fig. 1).

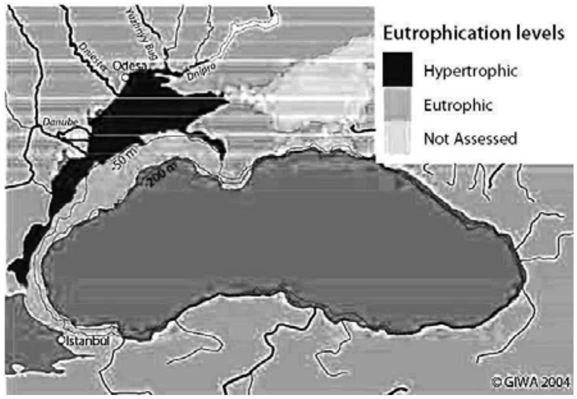

Fig. 1. Eutrophication level for Black Sea [8].

The main causes of severe environmental degradation in the Black Sea are pollution loads discharged by the important tributaries, dumping of toxic wastes, over-fishing, intensive shipping activity, mineral exploitation, the introduction of non-native species and the damming of tributaries [9], [6]. Regarding this situation, many specialists have estimated that perpetuation of this pollution level will lead to an ecological disaster. Ecological changes in open-sea regions of the Black Sea have received less attention than those of coastal regions [5]. But in the framework of the political changes at the beginning of the '90, changes were recorded in the marine ecosystem behavior characterized by a slight but continuous improvement of water quality. After 1990 the eutrophication has felt more seldom mostly due to the reduction of economic activities in the European countries within the Danube River basin and upgrading of water treatment plants, which led to a major reduction of nutrients concentration discharged into the aquatic ecosystems [8]. The present state of the Black Sea is characterized by a fragile balance, so that any significant intervention may have disastrous effects over this ecosystem.

3. Results and discussion

The physical-chemical indicators analyzed for estimating the degree of eutrophication in the Black Sea are: temperature, transparency, dissolved oxygen, nutrients and chlorophyll a. The values of these parameters were measured by the "Grigore Antipa" National Institute for Marine Research and Development and were taken over from the environmental reports published for the study period 2000-2010.

Changes in the water temperature regime can fundamentally alter a sea's water quality. For instance, chemical reactions and algal growth rates are temperature dependent. The duration and depth of temperature stratification also can affect the time and volume of water that is isolated during the summer, affecting anoxia and ammonia production and accumulation in the ecosystem's hypolimnion. Values of the water temperatures recorded along the Romanian seashore for the study period ranged between 0.8 0C (February) and 27.8 0C (September) [10], which allow the consideration that from the thermal point of view the Black Sea fluctuate within the normal variation limits for marine ecosystems in the temperate areas (Fig. 2.). The annual (yearly) mean values for the water temperature at Constanta vary significantly for the last decade (Fig. 3.). Thus, if this value was 10.0°C in 1985, in 2002 it was- 14.3°C.

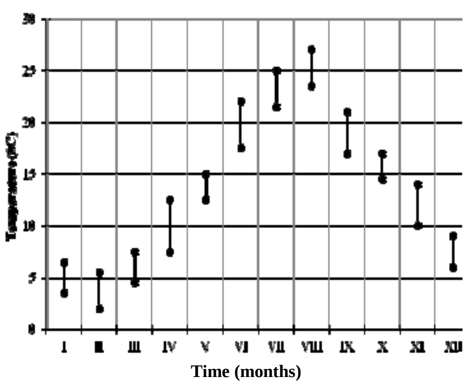

Fig. 2. Monthly multiannual mean values of temperature in Black Sea waters in Constanta shore area.

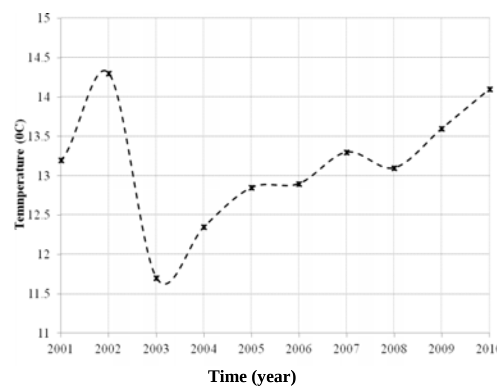

Fig. 3. Annual mean values of temperature in Black Sea waters - Constanta shore area.

Evolution of the dissolved oxygen saturation of the sea water in Constanta has showed great variations correlated mainly with air temperature evolution (Fig. 4.). Thus, the values recorded ranged within a minimum value in July 87% and a maximum one of 107% in May, which allows us to consider that the waters are well oxygenated taking into consideration that all the values determined in 2009 exceed the value (80%) recommended by regulation [11]. The lowest values of dissolved oxygen were recorded in the summer period, especially in July and August. Both in summer 2009 and in 2010 along the Romanian coast extreme situations appeared, characterized by decreased dissolved oxygen concentrations below the hypoxia limit even if the water temperature was within normal levels for this time of year (Fig. 5.).

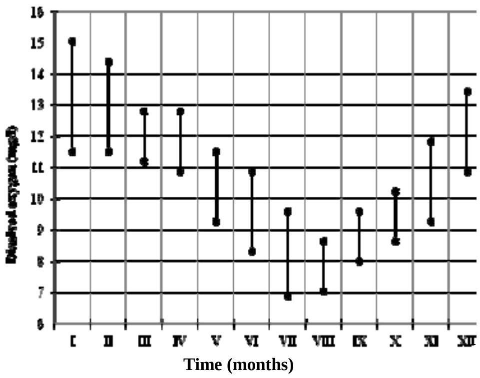

Fig. 4. Monthly multiannual values of dissolved oxygen concentration in waters in Constanta shore area.

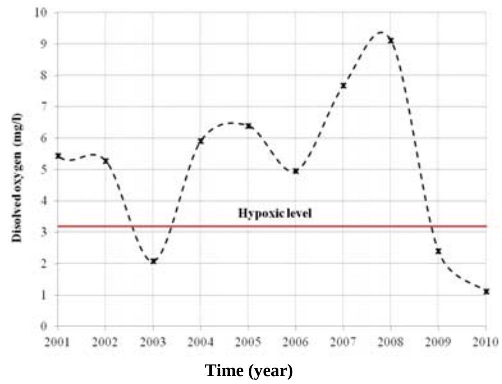

Fig. 5. Minimum annual values of dissolved oxygen concentration in waters - Constanta shore area.

The phenomena recorded near the shore were caused by high oxygen consumption in the water column due to oxidative decomposition of organic matter from algal flowering and by the upwelling process favored by winds. Thus, the water masses near the shore moved towards offshore, being replaced by water masses from the lower layers of small depth 10 to 20m. This way, a strong but episodic hypoxia phenomenon appeared in the water near the shore.

The mean total inorganic nitrogen monthly concentrations in the Romanian coastal waters are directly correlated with Danubian mean monthly discharge. Regarding the multiannual evolution an increase of the concentration of these compounds were recorded for 2005, 2006 and 2008 in comparison with the rest of the study period, however, a return to the normal is noticed for the year 2009 and 2010 [10]. Thus, total inorganic nitrogen concentrations have recorded values between 0.2 to 1.5 mg/l (Fig. 6).

Of the three total inorganic nitrogen compounds the largest amount is represented by nitrates and ammonia nitrogen. In the last 10 years, fluctuations in terms of these two compounds share in total inorganic nitrogen content were registered. Thus, if in the beginning of 2000 the ammonia nitrogen prevails, in 2003 its share was equal with the nitrates one, then the nitrates almost double its quantity until 2010, when the ammonia nitrogen prevail again (Fig. 7). The abundance of ammonium in sea water is justified by the regeneration of this compound in water mass, by decomposing organic matter or to anthropogenic sources contribution, represented by Danube's water and treatment plants. In terms of nitrogen, it usually decreases during summer due to biological consumption and sedimentation. But both nitrate and ammonia nitrogen concentrations are largely consistent with the average monthly flow of the Danube.

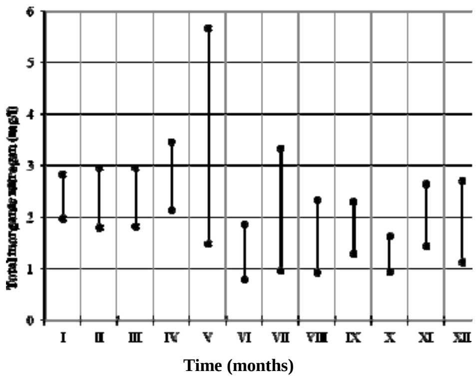

Fig. 6. Monthly multiannual values of inorganic nitrogen concentration in waters - Constanta shore area.

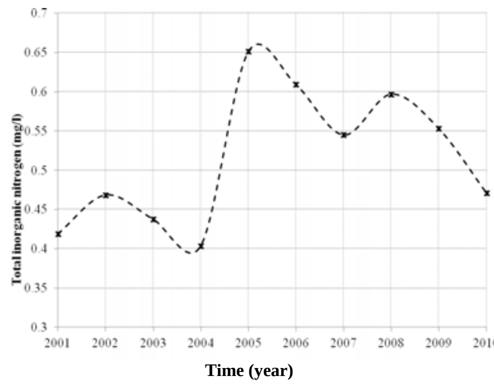

Fig. 7. Annual mean values of inorganic nitrogen concentration in waters - Constanta shore area.

For the study period the orthophosphate concentrations have recorded values between 0.0095 and 0.123 (Fig. 8), meaning that most of them were within the permissible limit (0.1 mg/l) for ecological status and the impact area of anthropogenic activity. Exceptions in terms of exceeding the limit values are due to anthropogenic influences on coastal water or to river intake for marine and transitional waters. In conclusion, in the coastal area of Constanta, phosphate concentrations have been very low, comparable to those of the 60s, but with a larger seasonal variability. For the study period the values of the mean multiannual soluble reactive phosphorus concentrations present a decreasing tendency, by reaching a minimum value in 2008 (Fig. 9).

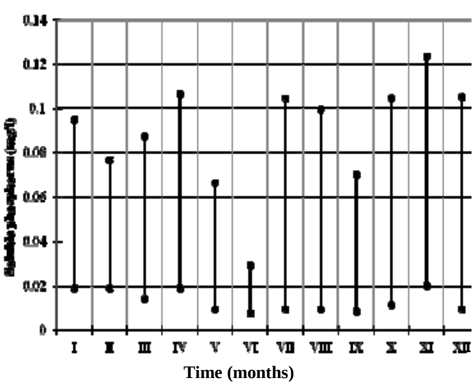

Fig. 8. Monthly multiannual mean values of orthophosphate concentration in Constanta shore area waters.

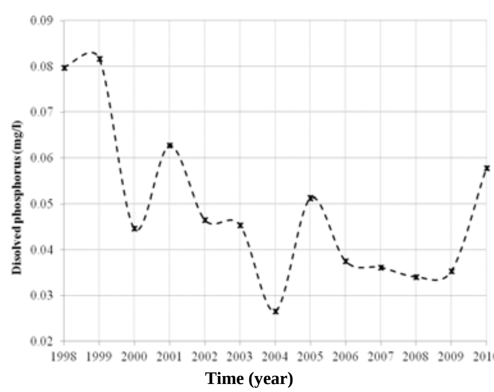

Fig. 9. Annual mean values of orthophosphate concentration in waters - Constanta shore area.

Considering the tendency of the last years (2006 -2009) it can be said that the levels of the phosphate concentrations in the coastal waters, in Constanta area, are comparable with the mean multiannual values of the 1960-1970, which represent the reference period for good quality of the waters in the marine environment [10].

The content of chlorophyll-a determined in Constanta, in the shore area, varied between 0.95 to 50.63 mg/m3 (Fig. 10). The mean multiannual monthly values of chlorophyll-a concentration have recorded a substantial increase in 2006 followed by a period of decrease (Fig. 11). Thus, for 2006 the greatest value was recorded in April due to an extensive algal bloom, but for a very short period of time. Moreover, the high values of the mean monthly concentration, over the mean annual ones (5.56 g/m^3), were determined in February (8.61 mg/l), May (9.13 mg/l), respectively, as a result of the precocious diatoms bloom in these periods of the year [10]. In 2009 the mean annual chlorophyll-a content in the seashore waters have recorded a higher value than in 2008 (5.56 g/ m^3 in 2009, in comparison with 4.55 g/ m^3 in 2008), but below the annual mean determined between 2001 and 2009 (5.92 g/m^3), confirming thus the tendency of restoring the ecological state of the coastal ecosystem in the Black Sea Romanian waters recorded in the last years [10].

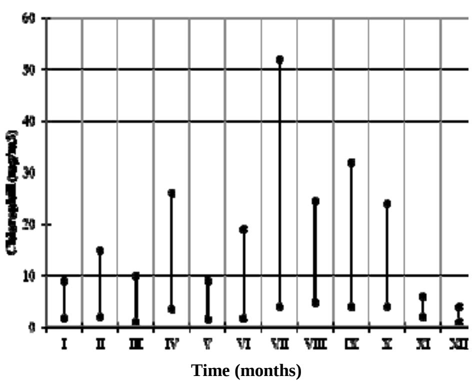

Fig. 10. Monthly multiannual mean values of chlorophyll-a concentration in Constanta shore area waters.

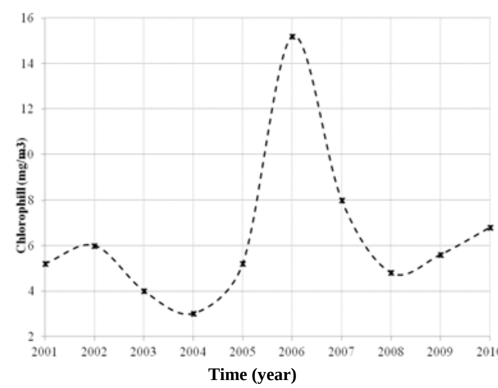

Fig. 11. Annual mean values of chlorophyll-a concentration in waters - Constanta shore area.

Chlorophyll-a content in the shallow waters of the Romanian seaside presented in 2010, a high seasonal variability, with values ranging between 0.66 to 58.47 µg/l. Seasonal distribution of chlorophyll-a presented a first maximum at the end of winter (early March), according to the annual cycle of diatoms development, during this period being recorded the annual maximum also. After the end of the spring, characterized by low concentrations of chlorophyll-a, high flows of the Danube, associated with unusually high temperatures of the surface layer of the sea, led to a significant increase in chlorophyll levels during the summer, with a peak in August. Chlorophyll-a concentrations remained high until the autumn middle, as a result of a favorable thermohaline regime. Starting with the end of autumn, the chlorophyll-a values dropped suddenly.

The quantities of nitrogen, phosphorus, and other biologically useful nutrients are the primary determinants of aquatic systems trophic state index (TSI). The trophic state is defined as the total weight of biomass in a water body at a specific location and time. Carlson's index is one of the more commonly used trophic indices and it uses the algal biomass as an objective classifier of a lake or other water body's trophic status [12]. This index provides a way to rate and compare lakes according to their level of biological activity on a scale from 0 to 100. This scale goes from 0 to 100, with 0 being corresponding to oligotrophic systems and 100 corresponding to hypereutrophic system [12]. The TSI values obtained for period 2006 – 2009 on Black Sea (Fig. 12.) indicate that the ecosystem is in large proportion in meso-eutrophic status regarding the concentrations of nitrogen and chlorophyll-a.

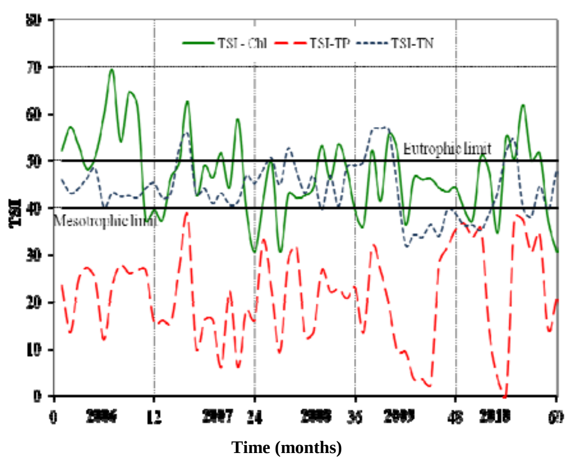

Fig. 12. The TSI values in Black Sea (Constanta shore area) between 2006 –2010.

During the eutrophication a series of complex processes take place. Therefore, the concentrations of nutrients increase, so the primary production of organic matter rise and thus the amount of organic material in a state of decomposition in water increase, all those processes having a major effect on marine water quality. Thus, effects of Black Sea eutrophication affect the ecosystem by reducing the commercial value, the biodiversity and recreational and amenity value of the water body and by apparition of negative ecological effects on biota [13]. The increase of the amplitude and frequency of algal blooms is a significant ecological consequence of the accumulation of nutrients in sea water. Since 1970, in Black Sea the blooms are no longer exceptional phenomena. Therefore, in the 1980's alone, 46 blooms were recorded in the Romanian littoral waters. The numerical density of the main species increased from the levels of the 1960's, for 66% of the species in the 1970's, and for 78% of the species in the 1980's. Thus, due to the changes in the nutritive basis changes in quantitative proportions of the main algal groups in Black Sea appeared. These changes include the diminution of the ratios Si:N and Si:P (which is detrimental to diatoms), and the increase of organic matter. Thus, between 1983 and 1990 the average biomass of phytoplankton in Romanian coastal waters was more than 8 times higher than that assessed between 1959 and 1963 [3]. Due to increase of water turbidity, apparition of unpleasant odors and the algal blooms, the recreational and amenity value of Black Sea are loss [14]. Such blooms are more frequent for the Romanian littoral and they are unpleasant, with green slimy margins to the water, or toxic if blue-green algae are present, affecting the touristic activity. In the same time in the Romanian littoral there is a tendency of qualitative and quantitative decline of algal flora.

One of the main research directions in the restoration of aquatic ecosystems domain is the limitation of the eutrophication phenomenon. The restoration strategy is difficult to be chosen because the eutrophic aquatic ecosystem restoration is a very complex process, which consists in bringing the system to a state according with its use. The ecological restorations of aquatic ecosystems aim to bring the ecosystem to an autonomous state, by actions onto physical, chemical and biological factors. Techniques to restore aquatic ecosystems affected by eutrophication are many but unfortunately few of them are effective for a long term. Consequently, the best way to combat the marine eutrophication is to reduce nutrients amount from point and diffuse sources [15], [13]. Therefore, the most efficient methods to prevent and control the eutrophication consist in actions on wastewater discharged into the marine ecosystems or interventions on the marine catchment area. The first type of action consists in wastewater treatment before discharging them into aquatic ecosystems. The main purpose is to improve the quality of water to a level at which it can be discharged into the environment without harming flora and fauna. Because this type of action aims mainly to reduce the nutrient content of wastewater, is recommended to treat water by physicochemical and biological processes, in three stages wastewater treatment plants (primary, secondary and tertiary). The second type of action consists in limiting the use of fertilizers in agriculture in Black Sea catchment. In this way, the amounts of nutrients which comes from flushing agricultural land by the rainfall and arrive into the Black Sea will be reduced, hence would reduce the eutrophication of this ecosystem.

4. Conclusions

Over the last 40 years the environmental quality of the Black Sea has deteriorated due to the water eutrophication, leading to overgrowth of algal biomass. Thus, between 1973 and 1990 the eutrophication consequences have consist in fish deaths, estimated at five million tones, and a diminution of the tourist visits to the Black Sea coast [16]. These effects have resulted in economic losses for the tourist and fishing industry. A study performed within the framework of the Black Sea Environmental Program [8] estimated that for a 10% decrease in the marine environmental quality, the annual economic loss due to the tourism in this region and fishing could be approximately estimated at 500 million USD. It is generally recognized that Danube has a big contribution to the total nutrients load in Black Sea waters and hence to the eutrophication of this ecosystem. The excess nutrients load in the Black Sea which caused the eutrophication come in large proportion from agriculture (80%), from insufficiently treated urban sewage (15%) and 5% from other sources. The nutrients intake is considered to be the primary element, which caused the Black Sea to evolve over the past 30 years from oligotrophic to eutrophic environment.

Regarding the level of the nutrients in Romanian Black Sea coast after 2006 a reduction can be remarked, which is associated with the upgrade of the Constanta treatment plant. Hence, the occurrence of eutrophication process in the Romanian Black Sea coast was strongly diminished. Nitrogen and phosphorus emissions continue to reduce, but their 2000-2010 average values are still higher than their pristine levels at 1955-1965 [6].

Given the current economically and politically state of Romanian society, one of the main causes of eutrophication in the Black Sea results from legal and institutional origin. The authorities still ignore the problems and implementations of environmental technologies economically favorable for long-term environmental problems are missing.

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