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WATER QUALITY IN THE COASTAL ZONE OF THE BLACK SEA AND THE PHENOMENON OF MASSIVE ALGAE DEVELOPMENT

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Abstract
Water is recognized worldwide to be the leading source of support of life on Earth; and so the pollution of the seas affects dramatic all of us. A good biological indicator of water quality is the algae and marine biomass. They are also an important agent in combating pollution and We are presenting to you our fundamental researches over the possibilities of marine biomass usage in agriculture as an eco-fertilizer. The usage of marine biomass in agriculture contributes to sustainable development which integrates an environmental, an economic and a social dimension.

Keywords: Water quality, Black Sea coast, algae and marine biomass

1. INTRODUCTION

The Black Sea is a sea of the Atlantic basin, located between Europe and Asia. It has borders with Russia, Ukraine, Romania, Bulgaria, Turkey and Georgia. It communicates with the Azov Sea through the strait Cherci, with the Marmara Sea through the Bosporus and with the Aegean Sea through the Dardanelles. The Black Sea is a remnant of the Sarmatian Sea and presents a number of unique aspects in the world. Every year, the tributary rivers overflow over 350 km3 of water, 85% deriving from the three big rivers: Danube, Dnestr and Dnepr.

Although the Black Sea depth exceeds 2000 m, the marine life unfolds only in the upper 150-200 m, and below that depth live only bacteria which consumes oxygen and so gave birth to the largest "anoxic sea" or an oxygen-poor sea.

The Romanian Black Sea coastline stretches over a distance of about 245 km (153 miles). The marine climate, with hot summers (July average temperature above 22°C) and mild winters make this region attractive throughout the year.

The Black Sea coastal zone is a buffer zone between land and sea, a territory of climatic and biogeographic interference but also a zone of interactions between the natural environment and the human economic interests.

The coastal zone is particularly important in terms of the variety of natural habitats (sand dunes, salty, wetlands, coastal cliffs, etc.) and high diversity of flora and fauna. Due to its specific topoclimate and soil, the coastal zone is a habitat for many rare flora and fauna, some of them characteristic for the coastal area.

A report presented by the Council of Europe shows that thousands of tons of heavy metals and radioactive elements from Chernobyl, Bystroe Canal and the overfishing have caused an ecological disaster in the Black Sea. The discharge of toxic and radioactive residues, the exploitation of resources and the lack of oxygen caused an ecological disaster in the Black Sea.

Only the Danube discharges annually into the Black Sea 280 tons of cadmium, 60 tons of mercury, 4.500 tons of lead, 6.000 tons of zinc, 1.000 tons of chromium and 50.000 tons of hydrocarbons. The other rivers flowing into the sea (Dnestr, Dnepr, Don, Kuban, Youzhny Bela) bring with them 87 tons of cadmium, 1.500 tons of copper and 2.600 tons of zinc, and also an amount of nitrates and phosphates which lead to a development of the plankton and reduce the amount of oxygen in the water (Isac, 2009).

2. METHODS OF ANALYSIS

2.1. Marine water quality - analysis

The water is recognized worldwide as the leading source of support of life on Earth. In the same idea, the waters of the Black Sea have been identified, at least at the regional level as forming a "hydrobiologicum UNICUM". From this, and knowing that at the moment it is one of the world's most polluted sea, we are entitled to acknowledge its great importance at least in terms of the necessity of preserving and rehabilitating it.

The physico-chemical indicators investigated in 2011 for monitoring the quality of transitional waters, coastal and marine from the Romanian littoral of the Black Sea were obtained from the analysis of 149 samples of surface water and the water column (0-50m) taken in two oceanographic expeditions (in May 11 to 14, N = 51 and July 4 to 8, N = 98) on the network which consists of 44 stations located between Sulina and Vama Veche.

There were analyzed the main physico-chemical indicators that characterize and control the eutrophication namely: temperature, transparency, salinity, pH, dissolved oxygen, inorganic nutrients.

Between May and July 2011 along the entire Romanian coast, the water temperature ranged between 5.4 C and 25.0 C. The minimum values are registered in a depth of 10 m of water column. In Constanta, the absolute minimum was -1.0 C on February 4. This was the only negative temperature recorded and the see did not freeze. Absolute maximum, 27.2 C was measured on July 19. The monthly averages of 2011 differ slightly from the 1959-2010 monthly multiannual averages (Environmental Protection Agency).

The transparency (N = 19 in May and N = 34 in July) ranged from 0.5 to 10.8 m (median 3.5 m, dev.std.2, 7m). Both extremes belong to July: the minimum, at Sulina 10m in transitional waters under the direct influence of river intake and the maximum in East station Constanta 3 marine waters.

The salinity of transitional coastal and marine waters has values between 1.72 to 18.91 PSU (PSU 15.68 average, median 16.83 PSU and standard deviation 2.99 PSU). The lowest values were determined in the surface waters due to the intake of freshwater (river or man). The maximum value was found in the southern area of coastal waters where river intake influence is greatly diminished.

At the Romanian seaside, **the dissolved oxygen** concentrations ranged between 152.3 µM (3.41 cm3 / l) and 495.1 µM (11.09 cm3 / l), with the average 306.2 µM (6.86 cm3 / l) median 304.6 µM (6.82 cm3 / l) and standard deviation of 22.3 µM (0.50 cm3 / l).

The phosphate $(PO4)^3$ concentrations, recorded in May and July 2011, values between - 7.30 µM (average 0,22 mm, median 0.10 µM and 0.7 µM standard deviation). With 95 % of values under 0.5 µM phosphate concentrations in the waters of Romanian seaside, are close to the values of the reference period, the ‘60s. Long term monthly averages of 2011 differ significantly (t test, confidence interval 95 %, $p < 0.0001$, t = 7.7741, df = 22, Dev.St. the difference = 0.114) from their multiannual 1960 – 2010 values, due to the low records in 2011.

The nitrate concentrations (NO_3) - recorded values ranging from 1.08 to 70.97 µM; the maximum measured in May, near the WWTP Constanta South. However, unlike phosphate, the main source of nitrate appears to be fluvial intake. The minimum values of nitrate concentrations were determined in July, in the water column. The maximum concentration was recorded in July in transitional coastal and marine northern waters due to river intake, and in May in the coastal waters in areas of influence of WWTP Mangalia and Constanta South. Thus, oppose to phosphate, the main source of nitrate appears to be fluvial intake, the value of 50.33 µM is in the specific area limits.

The average monthly multiannual concentrations (May and July) of nitrates are still comparable with those during intense eutrophication, being the dominant form of inorganic nitrogen compounds. The effects of this nutrient intake are less intense due to reduced phosphate concentrations, limiting factors of phytoplankton proliferation. **It is remarkable the high values in April and May that contributed to the nutritional support of blossoming phenomena.**

In Constanta, monthly multiannual averages 1976-2010 and 2011 monthly averages differ insignificantly (t test, confidence interval 95 %, p = 0.6349, t = 0.4815, df = 22, Dev.St. of difference = 2.565). Long term variation is observed between 4.21 µM (2010) - 22.55 µM (1976) (median 6.89 µM dev.std . 3.66 µM) and the 2011 annual average growth to the value of 10.47 µM.

Nitrites (NO_2) -, intermediate forms of redox processes involving inorganic nitrogen species have concentrations in the range 0.02 -6.17 µM (average 0.63 µM median 0.29 µM and standard deviation 0 , 98µM)

Ammonium (NH_4)+, polyatomic ion in which the nitrogen has the maximum oxidation number 3, is the most easily assimilated form of inorganic nitrogen. Its concentrations recorded values in the "undetectable" -63.94 µM (average 4.62 µM median 2.83 µM and 7.31 µM standard deviation)

The maximum values exceeds in all cases permissible concentration (0.1 mg/dm3 7.14 µM respectively) for both ecological status and for the impact of the human activity. The influence of WWTP Constanta South on coastal waters is found even in May when ammonia has recorded extreme concentration.

Chlorophyll a is one of the most common biochemical parameters determined as an indicator of plant biomass and primary productivity. Due to its importance in the marine ecosystem and the fact that can be measured more easily than phytoplankton biomass, chlorophyll aa was included on the list of indicators for the "Eutrophication" of "Water Framework Directive" of the EU as one of the parameters of impact to be monitored. Chlorophyll content determined in water shores of Constanta ranged between 0.23 and 33.9 mg / L.

Coastal areas represent complex and dynamic systems, subject to natural or anthropogenic influences. Heavy metal contamination of coastal areas can be correlated directly with urban or industrial sources such as factories, power plants, port facilities, water treatment plants. The influence of rivers on coastal aereas is significant, constituting a major source of metals, especially in particulate form, extreme hydrological events (floods) contributing to enhancing its contribution.

Heavy metal concentrations determined over 2011 monitoring stations were within the following areas of variation: 0.24 - 68.70 mg / L copper; 0.02 - 1.35 mg / L cadmium; 0.01 - 51.97 mg / L lead; 0.01 - 30.59 mg / L nickel; 0.01 - 22.94 mg / L chromium. In relation to environmental quality standards in the water field recommended by national legislation, the concentrations of cadmium, nickel and chromium were within the permissible limits, while a rate of about 25% of samples of copper and lead exceeded it (30 mg / L Cu, and 10 mg / L Pb).

2.2. Algae are at the base of what makes a happy, healthy aquatic ecosystem

Establishing ecological status of continental aquatic ecosystems should be based on biological quality elements, taking into account the hydromorphological indicators, chemical, physico-chemical and pollutants that affect specific biomarkers. Evaluation of these items may show the presence of natural conditions, their minor alterations or extent of anthropogenic impact, and also the quality status of water bodies in a certain period of time.

Although so far there are over 13.000 known species of algae, they can be classified into three major classes: red algae, green algae and brown algae. Regardless of the class to which they belong, seaweed fiber structure contains lignin, cellulose, hemicellulose, polysaccharides, proteins and lipids.

Existing studies in the literature (Kumar et al., 2007, Sari & Tuzen, 2009, Montazeri-Rahmati et al., 2011) showed that the highest efficiency in the retention of metal ions from aqueous solutions have brown algae, which have in their structure a high content of polysaccharides, which causes a pronounced ion exchange capacity.

Algae have a number of features that makes them a good biological indicator of water quality: present and abundant in nearly all aquatic habitats. They are very sensitive to changes in the physico-chemical nature of the water and many species present ecological requirements and tolerances well defined. There don't seem to have preference to a certain type of substrate. They have a short development cycle and quickly colonize new habitats, so that changes at the community level show rapid responses to environmental changes.

Searching into the depths of a small entering in the Black Sea with a bathyscaphe, or dressed down in a diving suit, it is discovered that at a distance of 2-12 m from the water surface live 1-5 green algae species, 8-10 species brown algae and 10 to 12 species of red algae. At 25 m depth, green algae are no longer present, of brown algae survive only 5 species, and of the Red survive 8-10 species. If you are studying the water surface to the 2 m, you will find: about 20 species of green algae, 10 species of brown algae and 4-5 species of red algae. This allocation can be assigned to different penetration power through the layer of water of the different light radiation. The red radiation does not pass almost 34 m, while blue and green rays penetrate up to 500 m. But the green algae have a maximum absorption of the red light, and the red ones absorb green light (fig.1).

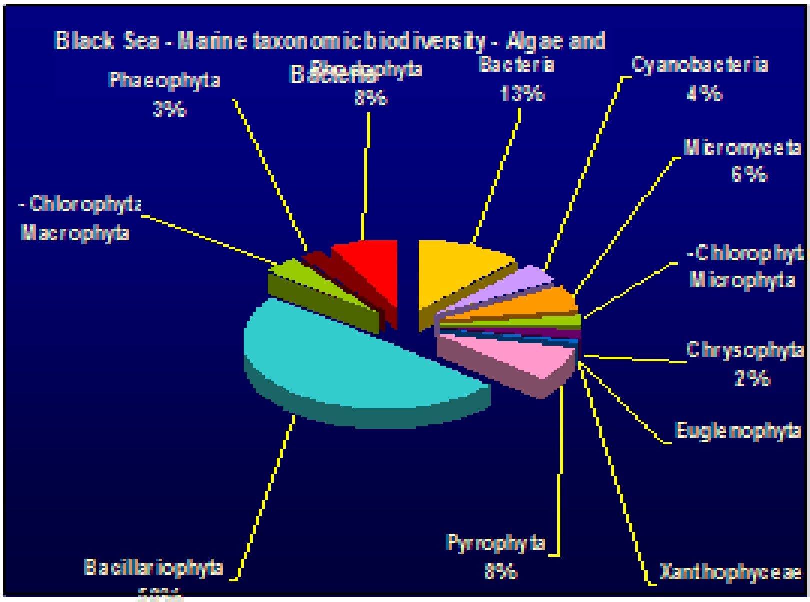

Figure 1. Black Sea Marine taxonomic biodiversity (Skolka et al. 2009)

Comparatively with other seas, the biodiversity of the Black Sea is somehow different. Most of the Black Sea species are immigrants from Mediterranean, who reach the Pontic basin 10000 years ago, after the reopening of Bosphorus strait. Since then, the Black Sea suffers a process of "mediterranisation". A meromictic basin unique in the world, Black Sea is in fact a "pocket" with a particular flora and fauna, originated mostly from Mediterranean. But the number of mediterranean species who settled down in Black Sea and replacing the preexisting ponto-caspian species is small – many Mediterranean species could not survive in the particular conditions of the Black Sea - and the Black Sea ecosystems are more fragile, more sensible to changes comparatively with mediterranean ones (Skolka M., Paraschiv G., Samargiu M.).

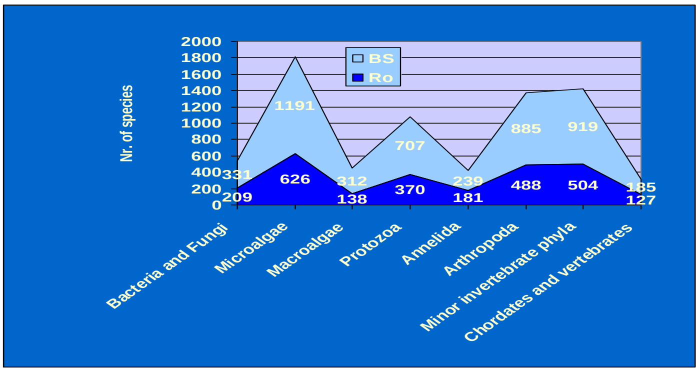

Figure 2. Biodiversity - comparative situation between Black Sea and Romanian coast: dominant groups (Skolka et al. 2009)

The Black Sea is the largest semi-enclosed anoxic basin in the world. In this sea, the most significant pollution problem has been identified as the eutrophication phenomenon. This problem affects especially Romania and Ukraine. The eutrophication of the Black Sea due to excessive loads of nutrients via the rivers and coming directly from the coastal countries has led to radical changes in the ecosystem. This has had a major transboundary impact on biological diversity and human use of the sea, including fisheries, tourism and recreation.

Black Sea has serious environmental problems. It is shallow, mixed surface waters receive river discharges which are heavily loaded with nutrients containing nitrogen and phosphorus and contaminated with agricultural, industrial and mining wastes.

One of the basic sources of these problems of the Black Sea is the agricultural activities. Nitrogen produced by agricultural activities is carried to sea by rivers and soil. Having an increased effect on agricultural production chemical fertilizers are preferred but on the other hand they create a decline on efficiency of soil and have a negative environmental impact. On the other hand chemical fertilizers have reached to the top amount theoretically and cannot provide any more efficiency.

The pollution problem can be approached from the aspect of the agricultural activities. Chemical fertilizers create pollution for both sea and soil and threaten the environment and human health. Mainly biologic alternatives of chemical fertilizers, new compost techniques such as the use of algae, can solve the eutrophication problem and lead to a healthier agriculture. Algae are an important agent in combating pollution and they are already used worldwide for wastewater treatment, especially nitrates and phosphorus removal. Their use has two major advantages over traditional practices: reducing the amount of chemicals and lower energy costs. These plants play an important role in many industries: textile, aquaculture, distillery, tannery, food, chemical, pharmaceutical and metallurgical.

The photosynthesis (also at algae) has three key phases, namely:

- Absorption of light energy by photosynthetic pigments located in chromatophores;
- Transferring this energy, in part to ATP / pyrophosphate, in the "photosynthetic phosphorylation", and in part to the oxidation / reduction, which reduces trifosfopiridin-nucleotide and releases oxygen;
- Assimilation of carbon in a series of reactions that take place in the dark, involving ribose-5-phosphate, ribulose diphosphate and using energy reduction trifosfopiridin-nucleotide and phosphorylation of ATP.

Resuming the basic chemical reactions of photosynthesis result the well-known equation:

$$CO_2 + 2\, H_2O \Rightarrow (CH_2O) + O_2 + H_2O$$

From the algae photosynthesis result the most oxygen used by aquatic animals to breath. It is estimated that the algae produce about 70% of the oxygen in the atmosphere.

We can say that the development of macrophytes is a natural and beneficial phenomenon for the marine ecosystem, they have a very important ecological role as biotic component of the ecosystem, providing a cleaner marine water by removing nutrients and oxygen consumption in the process of photosynthesis.

It also represents a favorable biotope for a range of invertebrates and fish, being a "shelter" and also food for them. It should be noted that the Black Sea records a "comeback" in the sense that the development of marine macroalgae induce both recurrence of macrophyte species in decline over the past 30 years due to eutrophication and especially the recovery of superior organisms dependent on the existence of macroalgae.

But there is the reverse - the development of large quantities may cause a disaster in the sense that what they produce during the day consume by night, but only when they rot - this leads to the phenomenon of hypoxia - asphyxia by lack of oxygen - resulting the death of animals - the fishing mortality. In addition, not less important, affects the tourism activity as it is upsetting both sea and beach and so produce great discomfort. Given the frequency and aggressiveness with which this phenomenon of algal development manifest in recent years, The “Romanian Waters” National Administration set up a monitoring system by daily inspection of shoreline and bathing area. The presence of algae in the water or shoreline is mentioned in the reports that are prepared daily at 8 am, so that the interventions of algae collection and disposal to be organised in the shortest time. The information is transmitted directly to the responsible for the areas of the three branches of the coast: Constanta, Eforie Costinesti and Olimp-Vama Veche.

The total amount of algae collected, of the entire surface of the beaches, including beaches and Navodari Constanta is 28,500 cubic meters, of which the most important quantities were collected from the following areas: Mangalia -11683 m^3, Limanu - 4031 m^3, Eforie -3265 m^3, Costinesti -2959 m^3

3. RESULTS AND DISCUSSIONS

According to the above analysis we point out the pollution which results from high levels of phosphate, nitrates, nitrites and ammonia.

However, the development of massive algae phenomenon produce a number of negative consequences on tourism activities and coastal zone ecosystem.

Because the phenomenon of massive algal growth cannot be predicted accurately, being a natural phenomenon, it is necessary that the intervention of the “Romanian Waters” National Administration to be done urgently, because the negative consequences manifested in a very short time, resulting from aggression and rapidity of the phenomenon.

The Romanian littoral abounds in marine algae that can be improved. Along the year 2009, from the Romanian littoral was collected a quantity of 35.000 tones of algae. Comparative, in the year 2008 were collected 25.000 tones of algae, and in year 2007 – 38.000 tones.

The diversity of marine biomass from Black Sea represents an enormous and unique source for the natural products with potential in the development of the:

- Bio fuel industry (bio diesel),
- the pharmaceutical industry ,
- cosmetics and nutritive supplements industries,
- medicine
- agro-chemicals industry
- Sustainable agriculture.

As a reaction towards this situation and towards the fact that an industry that should produce bio-diesel from the algae is not yet developed, we are developing at the moment fundamental researches over the possibilities of algae and marine biomass usage in other fields then bio-diesel production: pharmaceutics, agro-chemical, and agriculture. One of the important projects developed at this time is researching the possibility of making from algae and marine biomass an eco- fertilizer, for an agriculture which will support the sustainable development. We are studying the possibility of creating a new, innovative compound formed from marine biomass and other biomass waste.

4. CONCLUSIONS

The development of macrophytes is a natural and beneficial phenomenon for the marine ecosystem, they have a very important ecological role as biotic component of the ecosystem, providing a cleaner marine water by removing nutrients and oxygen consumption in the process of photosynthesis, as long as it does not exceed the normal scale. The usage of algae in agriculture contributes to a sustainable development which integrates an environmental, an economic and a social dimension. This new dimension of algae usage can be considered as a key element for a sustainable development and for improving the environment quality because it uses “eco-efficiency” that can empower us to use nature for economic activities (agriculture) necessary for human needs (welfare), and to maintain an equitable access to environment utilization for the present and future generations.

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