| Nutrient Levels and Eutrophication of the Romanian Black Sea Waters (2006-2011) - Assessment Related to the Marine Strategy Framework Directive Implementation *(Luminița Lazăr, Laura Boicenco, Valentina Coatu, Andra Oros, Daniela Țigănuș, Maria - Emanuela Mihailov)* | "Cercetări Marine" Issue no. 43 Pages 162-173 | 2013 |
|---|---|---|

# NUTRIENT LEVELS AND EUTROPHICATION OF THE ROMANIAN BLACK SEA WATERS (2006-2011) - ASSESSMENT RELATED TO THE MARINE STRATEGY FRAMEWORK DIRECTIVE IMPLEMENTATION

**Luminița Lazăr, Laura Boicenco, Valentina Coatu, Andra Oros, Daniela Țigănuș, Maria - Emanuela Mihailov**

*NIRDEP - National Institute for Marine Research and Development "Grigore Antipa", 300 Mamaia Blvd., 900581 Constanța, Romania, E-mail: llazar@alpha.rmri.ro*

## ABSTRACT

The assessment of the current nutrient levels and eutrophication of the Romanian Black Sea waters, as part of the Marine Strategy Framework Directive implementation, was based on data acquired during 2006-2011 from the monitoring network stations consisting of 36 stations along the Romanian littoral. Additionally, were collected daily (for chemistry) and bi-weekly (for phytoplankton) data from the Constan'a station. The trends were analyzed based on historical data (1964/1980-2011) from the East Constanța transect. The inorganic phosphorus content is influenced by the Danube's and WWTPs' input. Due to different flows, the fluvial input is more significant. On the long-term, decreased concentrations compared to the values of the 1960s, reference period for the good quality of the Romanian Black Sea waters, were observed. These low values give to phosphorus the feature of a limitative element for the phytoplankton's proliferation. The inorganic nitrogen content is mainly influenced by the Danube's input. Seasonally and on a restricted area, we found in the neighborhood of WWTPs higher ammonia concentrations. On the long-term, we observed the decreasing concentrations up to the level of 1991-1992, when the intensity of the eutrophication started to drop. Therefore, the intensity and number of the monospecific blooms have decreased, the mixed blooms phenomena and the increasing diatoms proportion in the phytoplanktonic populations occurred and, consequently, the eutrophication has been slightly reduced. Dinoflagellates' proportion was reduced, but still, in the summer, they can reach 40% from the total phytoplankton. Thus, the ecosystem recovery is still fragile and could be easily destabilized by the influence of the anthropogenic pressures and climate changes.

**KEYWORDS:** nutrients, eutrophication, Danube, Black Sea

## AIMS AND BACKGROUND

The eutrophication of the NW Black Sea was one of the most problematic environmental issues of the past decades. The area, known as one of the most naturally productive one [1, 2, 3, 4] due to the riverine (freshwater and nutrients) input, was strongly affected by the changes in the nutrients' regime occurred during mid 1970s - end of 1980s [5, 6]. First, the economic collapse of the surrounding socialist republics in the early 1990s resulted in decreased nutrient loading, which has allowed the Black Sea ecosystem to begin to recover [3, 7, and 8]. Added to these were the extensive efforts of the Black Sea riparian countries to permanently adopt legislation and measures to prevent the eutrophication of the area. One of the most important is the Convention on the Protection of the Black Sea against Pollution (Bucharest, 1992), with its Protocols. Of the latter, the most important addressing eutrophication is the Protocol on the Protection of the Marine Environment of the Black Sea from Land-Based Sources and Activities (revised in 2009). Another important step to reduce eutrophication was done through the adoption of the Strategic Action Plan for the Environmental Protection and Rehabilitation of the Black Sea (revised in 2009) which still has, as one of the most relevant Ecosystem Quality Objectives (EcoQOs3), to reduce eutrophication [9].

Only two years after the Bucharest Convention, the countries from the Danube's hydrographic basin adopted the Convention on Co-operation for the Protection and Sustainable Use of the River Danube (Danube River Protection Convention, Sofia, 1994) with one of the main objectives: take measures to reduce the pollution loads entering the Black Sea from sources in the Danube River Basin. And the successful measures taken to reduce nutrient discharges in the upper Danube countries, including dramatic reductions in the use of fertilizers, considerable improvements in the treatment of waste water and the implementation of a ban on polyphosphate detergents in some countries, were the most important steps to reduce eutrophication in the NW Black Sea [10].

Overall, in 2007, Romania and Bulgaria joined EU and together with them, part of the Black Sea had become, legally, a European Sea. Thus, the protection of the Black Sea, relevant to eutrophication, was enhanced by the new legislation like: Urban Wastewater Treatment Directive (1991), Nitrates Directive (1991), Habitats Directive (1992), Water Framework Directive (2000) and the Marine Strategy Framework Directive (2008). The latter is the only particularly addressing to the marine environment and has generous objectives consisting of the protection, preservation and, where practicable, restoration of the marine environment with the ultimate aim of maintaining biodiversity and providing diverse and dynamic oceans and seas which are clean, healthy and productive [11]. In this respect, the Black Sea is one of the fourth marine regions designated for the implementation of the MSFD through two riparian countries and Member States (MS): Romania and Bulgaria. Thus, according to the MSFD, each MS shall develop a strategy to achieve the objectives of the Directive. The first three steps to be followed in the strategy preparation have been already fulfilled by Romania at 15 July 2012 and consisted of: an initial assessment of the current environmental status of the waters and the environmental impact of human activities, a determination of good environmental status and the establishment of a series of environmental targets and associated indicators in accordance with articles 8, 9 and 10.

The aim of this paper is to assess the nutrient levels and other characteristics related to the eutrophication of the Romanian Black Sea waters during 2006-2011 as part of the initial assessment of the environmental status and impact of the human activities.

## MATERIAL AND METHODS

The assessment of the environmental status was done according to Table 1 - Characteristics and Table 2 - Pressures and impacts (Annex III) [11].

The data were acquired during 2006-2011 in the national monitoring program on the network consisting of 36 stations along the entire Romanian coast, between the Danube's mouth pf Sulina and Vama Veche, with 5-30 m bottom depths (Fig. 1). Additionally, we used historical data from the transect East Constanţa, 5 stations (approx. 10 m - 50 m bottom depths) sampled in the water column at standard depths (0 m, 10 m, 20 m, 30 m, 50 m), during 1964-2011 (phosphorus) and 1980-2011 (nitrogen) (Fig. 1).

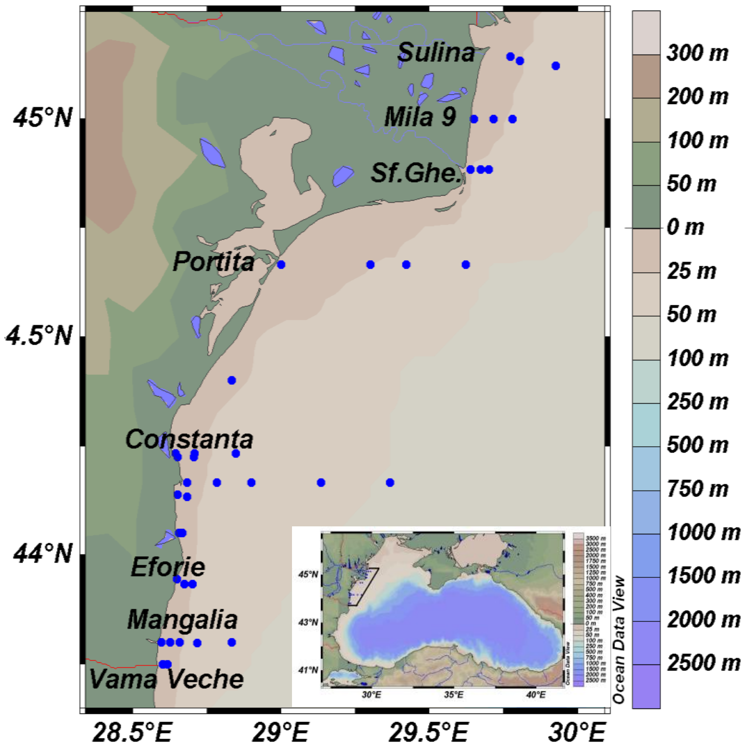


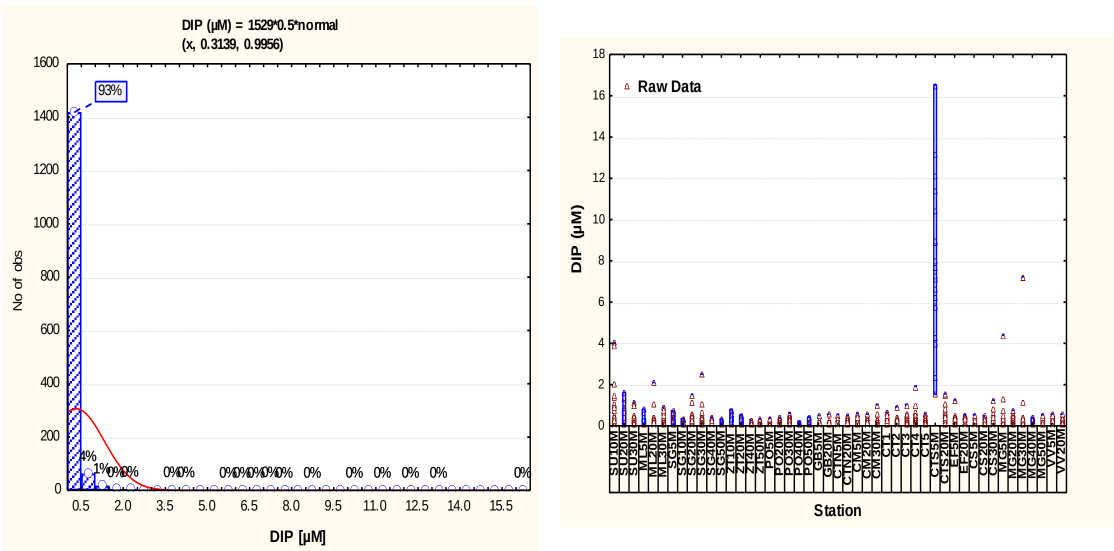

**Fig. 1 - Map of monitoring network stations - Romanian Black Sea**

Nutrient samples were stored frozen at -20ºC until their subsequent analysis in the laboratory. Nutrients were determined according to standard methods for seawater analysis [12]. Phytoplankton samples were preserved with 4% formaldehyde seawater buffered solution. Qualitative and quantitative phytoplankton determinations were performed by prior employment of the sedimentation method (Morozova-Vodyaniskaya, 1954), to concentrate the samples. Data were analyzed with Excel 2010 and ODV [13].

## RESULTS AND DISCUSSION

### *The distribution of inorganic dissolved phosphorus (DIP)*

DIP concentrations (N=1529) ranged within 0.01-16.50 µM (mean 0.31 µM, median 0.15 µM, std. dev. 0.96 µM), with 93% values in the interval "*undetectable*" - 0.05 µM (Fig. 2a). The extreme values, higher than 4.00 µM, are recorded seasonally, in a restricted area, in the influence zone of the Constanţa and Mangalia cities (Fig. 2b).




**(a)** **(b)**

**Fig. 2 - Histogram (a) and spatial variability (b) of DIP concentrations - Romanian Black Sea waters**

During winter, the 0.20 µM isoline marks, at the surface, a slight gradient between transitional and coastal waters. Anyway, the means are homogenous enough and do not allow an evident distinction between fluvial and coastal sources input. In spring, the concentrations decreased, being the lowest throughout the year because of the specific phytoplankton consumption. In summer, the fluvial input become, on average, more significant, but with concentrations in the natural variability. At the end of the warm season, the areas nearby Constanţa and Mangalia cities are delimited by the highest averages of the year. Thus, at the Romanian Black Sea coast, two inorganic phosphorus sources are distinguished: the Danube and the Constanţa South and Mangalia WWTPs. Due to their very different flows/input of the sources, we consider fluvial input as more significant (Fig. 3).

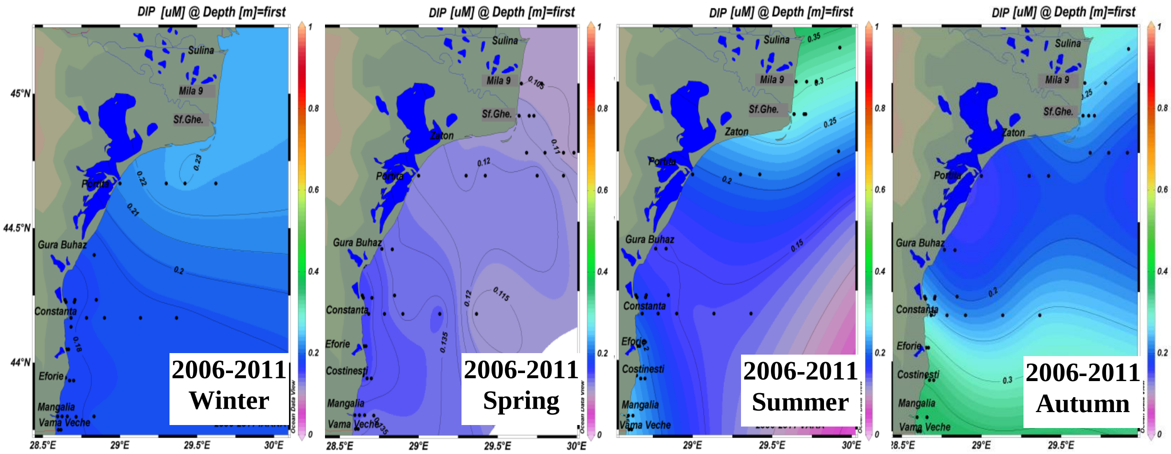



**Fig. 3 - The spatio-temporal distribution of DIP at the surface - 2006-2011, Romanian Black Sea waters**

DIP vertical variation was influenced by the ecosystem's biological activity and physical phenomena. The water column had two distinct layers delimited every season by the 0.2 µM isoline. We found the maximum concentration in winter due to phosphate regeneration from phytoplankton, detritus and dissolved organic compounds. Then, the uptake of the phytoplankton during the specific spring bloom led to minimum concentrations. The end of spring and early summer were characterized by the increasing gradient with depth, with maximum concentrations at 50 m assuming that inorganic phosphorus was accumulated in sediments. In autumn, these values were not found, even if the gradient was still evident, but in a lower range. The DIP vertical distribution was generally characterized by two maxima: the smaller one in the 0-20 m layer and the other at the water-sediment interface (Fig. 4 and 5).

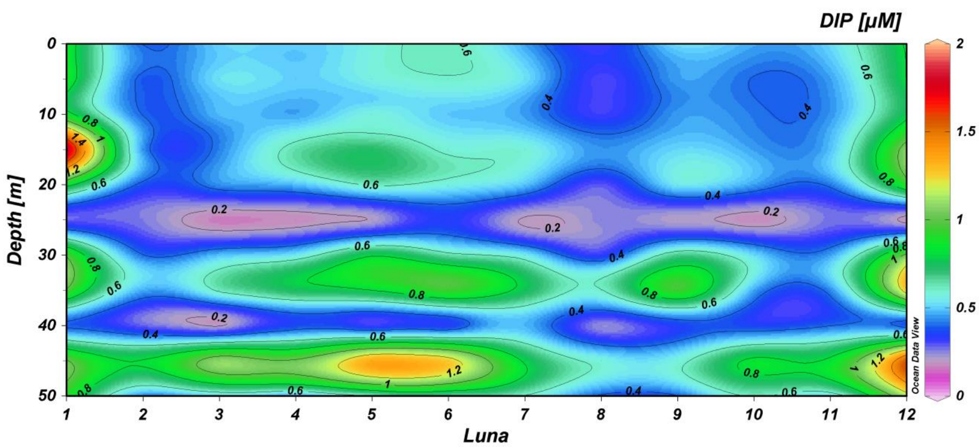
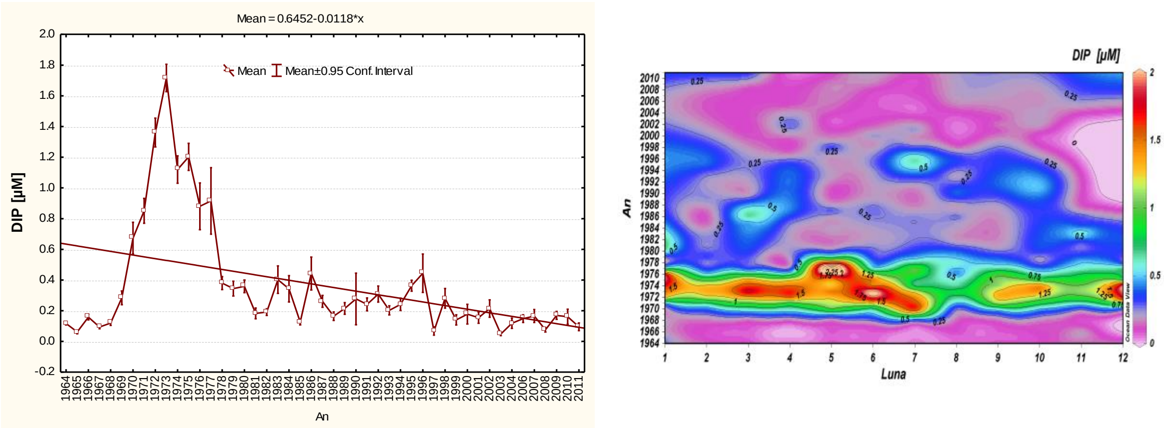



**Fig. 4 - Water column DIP (µM) - multiannual monthly means 1964-2011 - East Constanţa**

On the long-term (1964-2011, N=6964), the DIP concentrations decreasing up to comparable values with the 1960s, reference period for the good quality of the Romanian Black Sea waters, were observed (Fig. 5a and 4b).

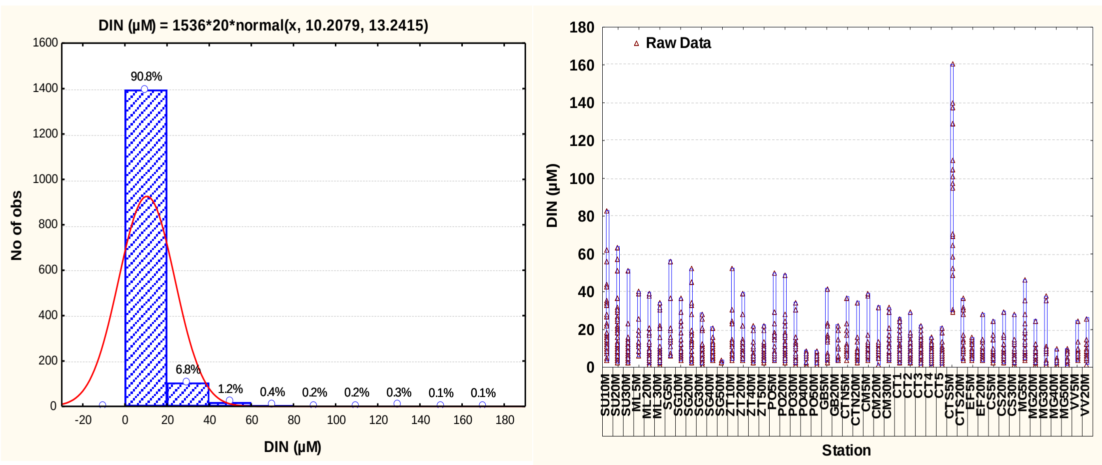



(a) (b)

**Fig. 5 - Annual (a) and monthly (b) DIP means concentrations - East Constanţa**

## *The distribution of inorganic dissolved nitrogen (DIN)*

DIN (as sum of nitrate, nitrite and ammonia) concentrations (N=1536) ranged within 1.14 - 160.04 µM (mean 10.21 µM, median 6.70 µM, std. dev. 13.24 µM), with 90.8% values in the interval "*undetectable*" - 20.0 µM (Fig. 6a). The extremes were, as in the phosphorus case, seasonally and point-like, in the WWTP Constanţa South neighborhood (Fig. 6a and 6b).




(a) (b)

**Fig. 6 - Histogram (a) and spatial variability (b) of DIN concentrations - Romanian Black Sea waters**

The analysis of the general statistics for each inorganic nitrogen chemical species contributing to DIN highlights the comparable level of nitrates and ammonia (Table 1).

**Table 1: General statistics - inorganic nitrogen chemical species contributing to DIN concentrations (µM) - Romanian Black Sea waters, 2006-2011**

| | Min. | Max. | Mean | Median | Std. dev. |
|---|---|---|---|---|---|
| **Nitrates, $(NO_3)^-$** | 0.06 | 73.38 | 5.18 | 3.20 | 6.73 |
| **Nitrites, $(NO_2)^-$** | 0.01 | 46.96 | 0.89 | 0.30 | 3.11 |
| **Ammonia, $(NH_4)^+$** | 0.07 | 150.31 | 4.15 | 2.16 | 9.42 |

Generally, throughout the year, the highest mean concentrations were observed in the northern part of the coast, under the Danube's direct influence. However, in the surface layer we observed seasonal variations as result of the biological activity, more pronounced in the coastal waters. In spring, the 18.00 µM isoline marks, at the water surface, the front between transitional and coastal waters, approx. nearby the Portiţa Station. Unlike phosphate, the inorganic nitrogen input was more outlined in spring and autumn, with the increased precipitations. This input was reduced due to the biological consumption from spring, still limited by phosphorus, and, in summer, the concentrations gradient became decreased from north to south. In the coastal zone, in summer, ammonia became predominant due to the higher WWTP discharges, phytoplankton decomposition, zooplankton and fish excretions etc. In winter, the mean concentrations were homogenous and quite low along the entire coast (Fig. 7).

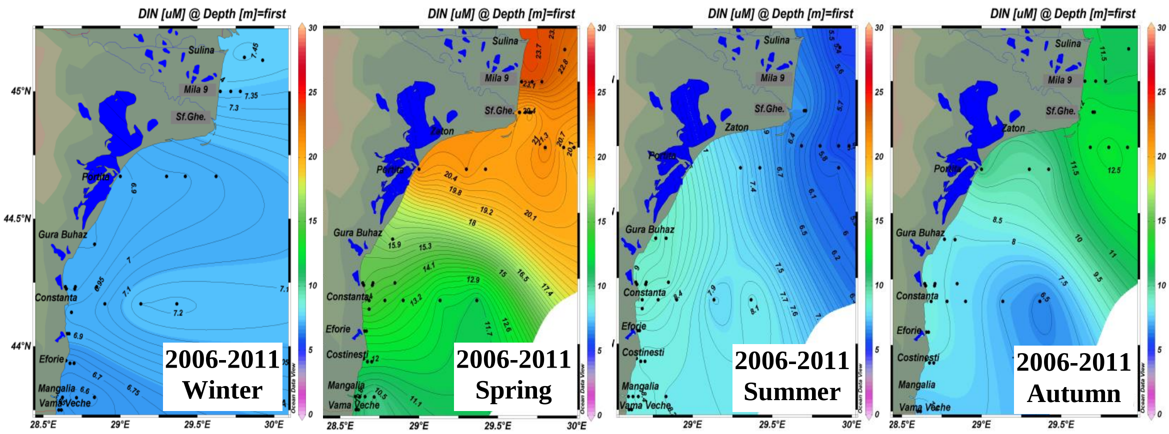



**Fig. 7 - The spatio-temporal distribution of DIN at the surface - 2006-2011, Romanian Black Sea waters**

The DIN vertical variation was influenced by the ecosystem's biological activities, physical and chemical processes. The water column had two distinct layers delimited every season by the 2.0 µM isoline, at 25 m approx. depth. The highest values were found in spring, in the superior layer, due to fluvial and coastal input but also to the seasonal thermocline delineation. Due to the specific biological consumption during spring, the maximum of the superior layer, early summer, was found at 10-30 m depth instead of the surface. Thus, it was emphasized the inorganic nitrogen regeneration in the superior layer, as well as the trend to sedimentation. The end of summer was characterized by the interruption of the inventory regeneration by a second bloom which led to minimum concentrations, whole water column. In November, due to the breaking thermocline and increase of the input from land, the DIN regeneration started and continued during winter (Fig. 8).

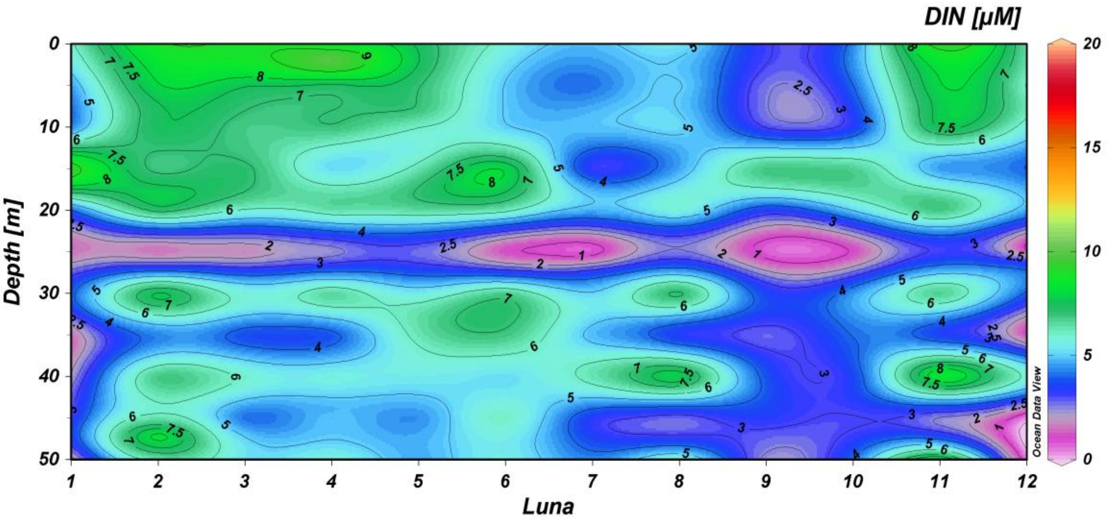
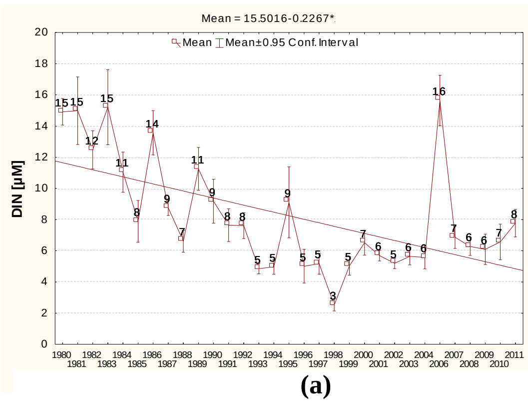
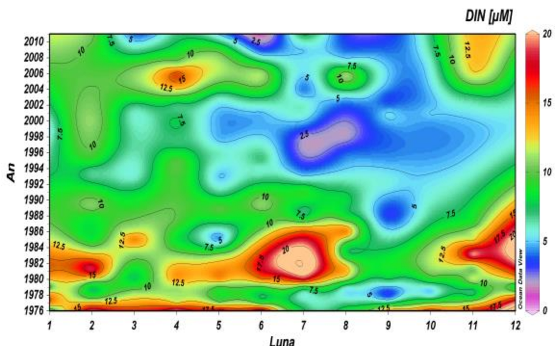



**Fig. 8 - Water column DIN (µM) - multiannual monthly means 1964-2011 - East Constanţa**

On the long-term (1980-2011, N=3914), the decreasing of DIN mean concentrations was generally observed, up to comparable values from 1991-1992, when the eutrophication intensity of the Romanian Black Sea waters started to decrease. However, nowadays, DIN values were slightly increasing compared to the end of the 1990s, when the minimum was observed (Fig. 9a and 9b).




(a)




(b)

**Fig. 9 - Annual (a) and monthly (b) DIN mean concentrations - East Constanţa**

## *Phytoplankton*

Phytoplankton is the first link in the chain of transformations of matter in aquatic basins. Due to its autotrophic character, it is the link that synthetizes organic matter, thereby linking the mineral medium with other organisms living in it [14]. Therefore, it is one of the best assessment indicators for the state of eutrophication, that produces changes of phytoplankton species composition (e.g. from diatoms to dinoflagellates) and increases frequency and/or magnitude and/or duration of phytoplankton blooms [2].

The input of nutrients from land-based sources has nutritional effect on the phytoplankton community, especially in summer, when the water temperature rises. The biological activity and the transport of water masses cause the propagation of land-based input effect beyond 5 m isobaths, so that the maximum density and biomass of phytoplankton are found further from the shore, along 20 m and 30 m isobaths, in front of the Danube mouths, where nutrient concentrations are generally higher. Thus, the role of the river input in the North Western Black Sea (Danube, Dniester etc.) was reinforced. During 2006-2011, only one bloom of over 10 million cells/L, was found in the Constanța South WWTP neighborhood (September 2010) and was dominated by diatoms in proportion of 99.8% (Tables 2 and 3).

**Table 2 - General statistical values of phytoplankton densities in the waters of the Romanian Black Sea coast - comparison land-based pollution sources - offshore, 2006-2011**

| | **Density [thousand cell/L] Land-based sources, N=73** | | | | **Density [thousand cells/L] Offshore, N=188** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Min. - Max.** | **Mean** | **Median** | **Std. Dev.** | **Min. - Max.** | **Mean** | **Median** | **Std. Dev.** |
| Diatoms | 14.6-37014.0 | 1782.0 | 595.2 | 4616.0 | 2.0-39705.2 | 1526.9 | 323.5 | 4153.3 |
| Dinoflagellates | 0.0-544.7 | 42.4 | 23.3 | 73.0 | 0.0-1894.6 | 71.2 | 19.8 | 220.7 |
| Other groups | 1.0-5643.7 | 168.0 | 40.3 | 660.9 | 0.22-896.8 | 65.4 | 30.0 | 105.7 |
| Total | 32.4-37069.9 | 1994.2 | 754.8 | 4645.5 | 42.1-39740.0 | 1663.5 | 424.5 | 4162.9 |

**Table 3 - General statistical values of phytoplankton biomasses in the waters of the Romanian Black Sea coast - comparison land-based pollution sources - offshore, 2006-2011**

| | **Biomass [mg/m$^3$] Land-based sources, N=73** | | | | **Biomass [mg/m$^3$] Offshore, N=188** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Min. - Max.** | **Average** | **Median** | **Std. Dev.** | **Min. - Max.** | **Average** | **Median** | **Std. Dev.** |
| Diatoms | 0.4-16168.0 | 1535.7 | 459.4 | 2731.7 | 7.6-27265.1 | 1429.5 | 382.3 | 3472.0 |
| Dinoflagellates | 0.0-2179.4 | 365.2 | 241.8 | 411.0 | 0.0-10424.9 | 510.4 | 236.7 | 1024.8 |
| Other groups | 0.01-383.3 | 42.0 | 17.1 | 68.7 | 0.01-912.9 | 32.9 | 9.3 | 86.7 |
| Total | 19.3-16433.6 | 1924.8 | 959.0 | 2750.7 | 38.8-27537.8 | 1883.2 | 741.0 | 3402.1 |

The only significant difference between the two areas was recorded for densities for other groups than diatoms and dinoflagellates, which in areas under human influence are, on average, 2.6 times higher than densities recorded offshore. In both cases, the highest values were determined near the mouths of the Danube.

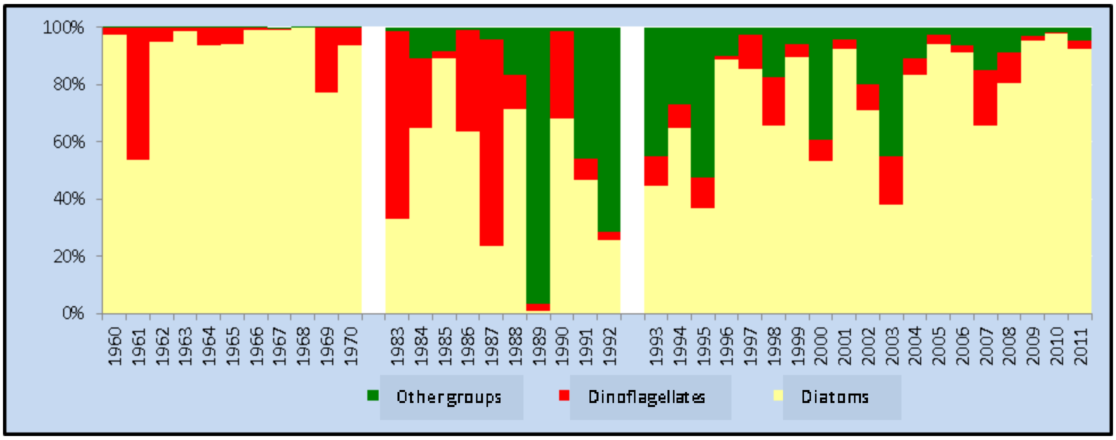



**Fig. 10 - Share in abundance (cells/L) of the main phytoplankton groups**

On the other hand, on the long-term, during the 1990s and the recent years after 2000, important changes occurred, such as a decrease of phytoplankton monospecific blooms and their higher amplitude during summer season and the increase of diatoms dominance in the total phytoplankton abundance (Fig. 10).

## CONCLUSIONS

The inorganic phosphorus content of the Romanian Black Sea waters is influenced by the Danube and WWTP input. Due to their different flow, the fluvial input is more significant. In the water column, the DIP seasonal variation is more influenced by the biological activity and it is characterized by two maxima: the smaller one in the 0-20 m layer and the other at the interface water. On the long-term (1964-2011, N=6964), is was observed that DIP concentrations decrease up to comparable values with the 1960s, reference period for the good quality of the Romanian Black Sea waters. These low values give to phosphorus the feature of a limitative element for the phytoplankton proliferation.

The dissolved inorganic nitrogen content of the Romanian Black Sea waters is mainly influenced at surface by the Danube input. Seasonally and on restricted area, we found in the neighborhood of WWTPs higher ammonia concentrations. DIN seasonal variation in the water column is characterized by two maxima: the smaller one at approx. depth 10 m and the other at the water - sediment interface. On the long-term (1980-2011), even if currently a slightly increasing trend is observed, we observe the decreasing concentrations up to the level of 1991-1992, when the intensity of the eutrophication started to decrease

Discharges of nutrients from land-based sources of pollution rise in the waters from the Romanian Black Sea coast seasonal effects, especially in summer when the input increases. These are found in areas near the mouths of the Danube and wastewater treatment plants and consist mainly of increasing the phytoplankton blooms intensity.

During the 1990s and the recent years after 2000, important changes occurred, such as the decrease of phytoplankton monospecific blooms and their higher amplitude during the summer season and the increase of diatoms dominance in the total phytoplankton abundance

The current state of eutrophication (2006-2011) of the Romanian Black Sea waters confirms the complexity of the phenomenon and its effects on the ecosystem. The lack of the environment homogeneity and many controlling factors (physical, chemical, biological, social) of the eutrophication make the current state different than all previous ones. It seems that the ecosystem will not return to a state identical to the reference and its attempt to recover is not in the same pathway that the imbalance occurred. At the moment, we found a slightly improved state, easily to be destabilized by extreme phenomena governed by factors other than the river input, such as climate change and atmospheric deposition. These phenomena have appeared in acute form, episodically, in 2009 and 2010, only in the warm season.

The emphasized spatial and seasonal variability and the extreme phenomena from the Romanian Black Sea coast makes the current state definable as a moderate - good equivalent of a eutrophic - mesotrophic state which, under the action of climatic factors and human impact more pronounced in the coastal zone, can easily pass to extreme states, unsatisfactory (hypertrophic) or very good (oligotrophic), conditions occasionally encountered in the waters of the Romanian Black Sea Black, often seasonally.

**REFERENCES:**

1. Antipa G., 1941 - Marea Neagră, Vol.I. Oceanografia, Bionomia şi Biologia generală a Mării Negre, Imprimeria Naţională, Bucureşti, pp. 313.
2. BSC, 2008 - State of the environment of the Black Sea (2001-2006/7), Publication of the Commission on the Protection of the Black Sea Against Pollution, pp. 447.
3. Cociaşu A., Varga L., Lazăr L., Vasiliu D., 2009 - Recent data concerning the evolution of the eutrophication level indicators in Romanian seawater, Journal of Environmental Protection and Ecology J.E.P.E.- B.E.N.A, Vol. 10, nr.3.
4. Mee L.D., Topping G., 1999 - Black Sea Pollution Assessment. Black Sea Environmental Series Vol. 10, pp. 380.
5. ICPDR, 2005 - Nutrient management in the Danube basin and its impact on the Black Sea - daNUbs Final report. International Commission for the Protection of the Danube River - http://www.icpdr.org, pp. 69.
6. BSC, 2007 - Black Sea Transboundary Analysis, Publication of the Commission on the Protection of the Black Sea against Pollution, pp. 269.
7. Gomoiu M.-T, 1992 - Marine eutrophication syndrome in the North-Western part of the Black Sea, Science of the total environment, Elsevier, pp. 683-692.
8. Oguz T., Velikova Violeta, 2010 - Abrupt transition of the northwestern Black Sea shelf ecosystem from a eutrophic to an alternative pristine state, Marine Ecology Progress Series, Vol.405, pp. 231-242.
9. http://www.blacksea-commission.org/_bssap2009.asp (18.06.2013)
10. http://www.icpdr.org/main/danube-basin/black-sea-trend-ecological-trend-western-black-sea (18.06.2013)
11. Official Journal of the European Union, 2008, Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive).

12. Grasshoff K., Kremling K., Ehrhardt M., 1999 - Methods of Seawater Analysis, Wiley-VCH, pp. 599.
13. Schlitzer R., 2011 - Ocean Data View, http://odv.awi.de.
14. Bodeanu N., Andrei C., Boicenco Laura, Popa Lucia, Sburlea Alice, 2004 - A new trend of the phytoplankton structure and dynamics in the Romanian waters, Cercetări marine Vol.35, pp. 77-86.
15. Borysova O., Kondakov A., Paleari S., Rautalahti-Miettinen E.,Stolberg F., Daler D., 2005 - Eutrophication in the Black Sea region; Impact assessment and Causal chain analysis, University of Kalmar, Sweden, Global International water assessment, UNEP, pp. 60.
16. Cloern J.E., 2001 - Our evolving conceptual model of the coastal eutrophication problem, Marine Ecology Progress Series Vol.210, pp. 223-253.
17. Gomoiu M.-T, 1981 - Some problems concerning actual ecological changes in the Black Sea, Cercetări Marine, Vol. 14, pp. 109-127.
18. Konovalov S.K., Murray J.W., 2000 - Variations in the chemistry of the Black Sea on a time scale of decades (1960-1995), Journal of Marine Systems 795, pp. 773-795.
19. Lazăr L., Gomoiu M.- T., Vasiliu D., Timofte F., 2010 - Variability of inorganic nitrogen forms in Romanian Black Sea marine and coastal waters- Cercetari Marine, Vol.39, pp.73-87.
20. Yunev O. A., Carstensen J., Moncheva S., Khaliulin A., Aertebjerg G., Nixon S., 2007 - Nutrient and phytoplankton trends on the western Black Sea shelf in response to cultural eutrophication and climate change, Estuarine, Coastal and Shelf Science, Vol.65, pp. 172-190.