NEW TENDENCY IN NUTRIENTS EVOLUTION FROM ROMANIAN COASTAL WATERS

Adriana COCIASU, Luminita LAZAR, D. VASILIU
National Institute for Marine Research and Development
"Grigore Antipa" Constantza

ABSTRACT

During 1970-1990, Romanian coastal waters have been strongly affected by eutrophication phenomenon characterized by chronically algal blooms, oxygen depletion, huge mortalities of benthic fauna and drastically reduction of biodiversity. This ecosystem degradation was the result of inorganic nutrients excess and Danube River was identified as their main source.

Although, since 1990 the nutrients level considerably decreased and some positive changes in ecosystem were observed mainly as a result of the economical collapse in East European countries, eutrophication still represented an important environmental problem if the ecosystem fragility was taken into account.

The main risk of the next period is represented by economy enforcement of the countries mentioned before and increase of nutrient emissions. Additionally, recent studies emphasize the increase of organic nitrogen and phosphorus levels, which can represent important sources of easy assimilable inorganic nutrients.

Present paper updates data sets regarding inorganic nutrients evolution both in Danube at Sulina just before the river entering the sea and in marine coastal waters at Constanta, with special emphasis within 2000-2005. In the same time, the paper presents new data on organic nutrient concentrations, making an estimation of total content of phosphorus and nitrogen in Romanian coastal waters.

KEY WORDS: eutrophication, nutrients, Danube discharge, coastal waters

INTRODUCTION

The most significant phenomenon degrading the Black Sea has been eutrophication, with dramatic changes on the coastal ecosystem, living resources, tourism and recreation. It is generally assumed that the main cause of eutrophication was the increase of nutrient and organic matter loads of rivers Danube, Dniestr, Dniepr and Bug draining half of Europe and some parts of Asia. More than 75% of this discharge is contributed by the Danube, the second largest and most important river in Central and Eastern Europe. It flows about 2,900 km through 13 countries, draining 817,000 km^2, includes about 300 tributaries, being the main contributor to the nutrient budget of the north-western Black Sea shelf waters.

Mismanagement of nutrients in the Danube Basin has led in last decades to changes of the chemical content of the river waters. According to estimates based on data prior to 1990 the nutrient concentrations were completely different compared with 1960, largely as result of various anthropic pressures (agricultural, industrial and urban activities, dams construction upstream the river and its tributaries etc.).

Between 1970 and 1990, Romanian coastal waters have been strongly affected by eutrophication phenomenon characterized by chronically algal blooms, oxygen depletion, and huge mortalities of benthic fauna and drastically reduction of biodiversity. This ecosystem degradation was the result of inorganic nutrients excess and Danube River was identified as their main source. Although since 1990 the nutrients level considerably decreased and some positive changes in ecosystem were observed mainly as a result of the economical collapse in East European countries, eutrophication still represented an important environmental issue as to ecosystem fragility.

Economy enforcement of the countries mentioned before and the increase of nutrient emissions due to the use of inorganic fertilizers and flowering of animal farms and reactivation of factories that produce fertilizers with P and N as well represent the main risk of the next period. Additionally, the increase of organic nitrogen and phosphorus levels, preferentially used by

some bacteria and phytoplankton species, can represent important sources of easy assimilable inorganic nutrients.

The present paper updates data sets regarding inorganic nutrients evolution in Danube waters and in marine coastal waters with special emphasis on last five years. In the same time, the paper presents recent data on organic nitrogen and phosphorus concentrations, both in Romanian coastal waters and in the Danube at Sulina just before the river entering the sea. For a better evaluation of tendency of eutrophication the previous period was considered for comparison.

METHOD

Constanta area is a reference area of the Romanian shelf. It is located about 70 nautical miles south of the Delta and is subject to the permanent fresh water influence of the Danube which transports more than 2/3 of the river input into the region. For this area a large number of nutrient data with systematic measurement is available. Figure 1 shows the station locations, Sulina station on the Danube and Constanta onshore station are places where water samples were collected daily during 1959-present.

The measurements of nutrients concentration in water samples were analyzed by using analytical methods described by GRASHOFF *et al.* (1976, 1983, 1999), STRICKLAND and PARSONS (1960, 1972).

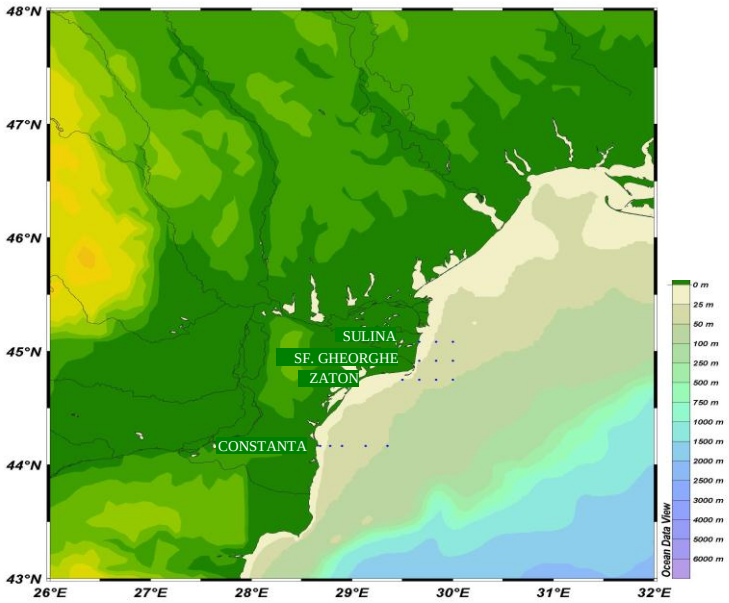


Fig.1 - The network stations

RESULTS AND DISCUSSIONS

The Danube river itself being the main tributary of the Black Sea with a drainage area of 817 000 km^2 has nearly five times larger than the total surface area of the basin. It drains effluents of eight European countries, which undergo ample, industrial, agrarian, urban and demographic developments.

Danube annual discharge is significantly varying following a certain periodicity. In the 1959-1999 period annual mean values ranged between 134.1 Km^3 in 1990 and 295.8 Km^3 in 1970, the average of the period representing 205.6 Km^3. On the whole, annual maximum of the discharge is recorded in April-May and the minimum in September-October. During the last five years annual mean values ranged between 156.4 km^3 in 2003 and 271.8 km^3 in 2005 (Fig. 2).

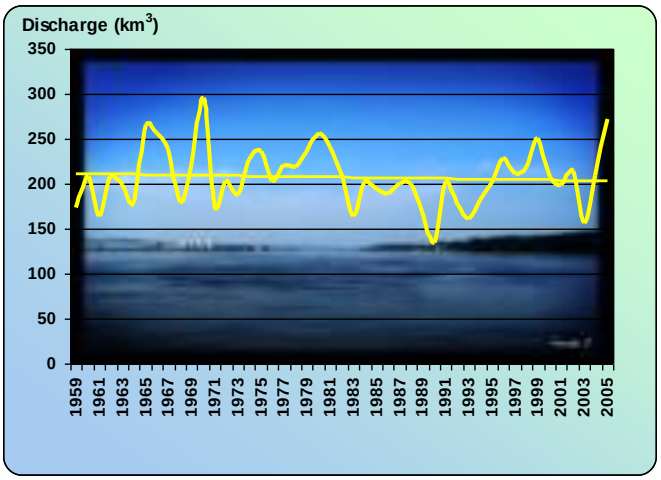


Fig.2 - Annual averages of the Danube discharges

Seasonal evolution was well defined, monthly averages ranging between 6.3 Km^3 in September 2003 and 36.1 Km^3 in May 2005.

According to estimates based on data prior to 1990 the chemical content of Danube waters were completely different from the 60 ies, largely as a result of the various human activities (agricultural, industrial and urban activities, dams construction upstream to river and its tributaries), associated with both the mismanagement of nutrients in the Danube basin and no adequate ecological policy. Reduction in the Danube water discharge since early 70 ies due to river management has been accompanied by an increase in the nitrogen and phosphorus delivery to the Black Sea. At the same period,

silica decreased significantly due to the reduced solid flow after dam constructions.

In the mid and late 90 ies some positive changes related to a decrease in anthropogenic pressure, mainly as aresult of economical collapse in the former East European Black Sea coastal countries (COCIASU, POPA, 2004).

In the analyzed period, nutrients content in Danube water presented a different evolution with a general trend of returning to the condition before eutrophication (Table 1).

Table 1

Danube‘s nutrient concentrations (µM)

Period	$P\text{-}PO_4$	$Si\text{-}SiO_4$	$N\text{-}NO_3$	$N\text{-}NO_2$	$N\text{-}NH_4$
1981-1990	3.46	62.17	298.54*	2.20*	8.93*
1991-1995	3.03	47.24	223.30	1.17	4.44
1996-1999	2.29	62.37	82.11	1.76	6.08
2000-2005	1.62	63.78	51.90	1.67	4.58

*1988-1990

Phosphates recorded a slight but continuous decreasing tendency, the average between 2000 and 2005 being below the ones in the previous periods. The average value for 2005, 1.08 µM, was the lowest registered in the last 25 years (Fig. 3a).

Silicates, opposite to phosphates, recorded a slight increase in the analyzed period. The average between 2000 and 2005 was higher than that between 1981 and 1990 (Table 1). The average value for 2005, 80µM, was the highest mean registered during the last 25 years (Fig. 3a).

The three forms of inorganic nitrogen concentrations recorded between 2000 and 2005 are lower values comparing with the previous period, although nitrates increased slowly and continuously, reaching more than 70µM in 2005. It is important to mention the decreasing of ammonium nitrogen contribution and the trend of recovery to normal condition (Fig. 3b).

The annual nutrient loads, calculated from the monthly averages of the concentrations analysed in the Danube water at Sulina branch and water discharge volume measured upstream the river before it enters the Delta (Ceatal Izmail, Km 85), also display interannual changes.

The average values for 2000 to 2005 were reduced comparing with the previous period, even if in the last year silicates and nitrates input increased at 600.000 tons and 250.000 tons, respectively (Fig.4). Comparing with the reference data published by ALMAZOV 1961, phosphorus loads slightly decreased below ‘60s levels, inorganic nitrogen loads even if follows a

decreasing trend still has a higher level and silicates represent half of reference values (Table 2).

Table 2

Danube nutrients mean flux (t x 10^3)

Period	Discharge (km^3)	$P\text{-}PO_4$	$Si\text{-}SiO_4$	$N\text{-}NO_3$	$N\text{-}NO_2$	$N\text{-}NH_4$
1981-1990	196.0	18.02	341.11	701.24*	5.00*	20.57*
1991-1995	184.4	17.15	266.08	591.95	2.90	11.17
1996-1999	226.9	15.91	405.42	263.81	5.52	18.89
2000-2005	209.4	10.21	396.74	155.01	4.64	12.65
Almazov, 1960	207.8	12.00	790.00	140.00		

* 1988-1990

a)

b)

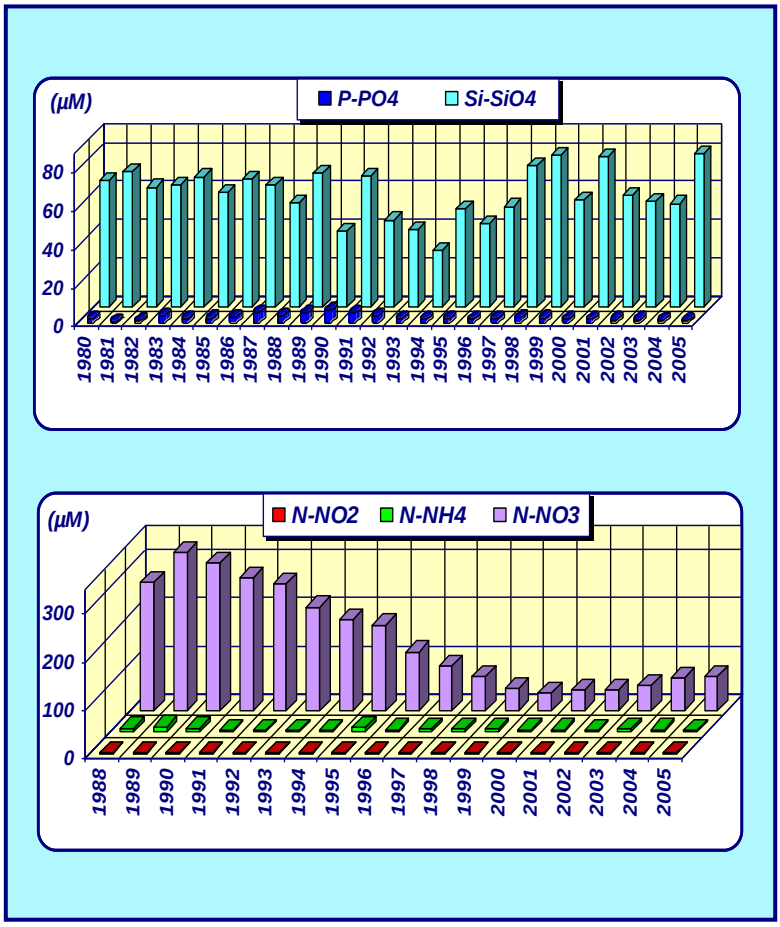


Fig.3 - Evolution of nutrient concentrations in Danube water

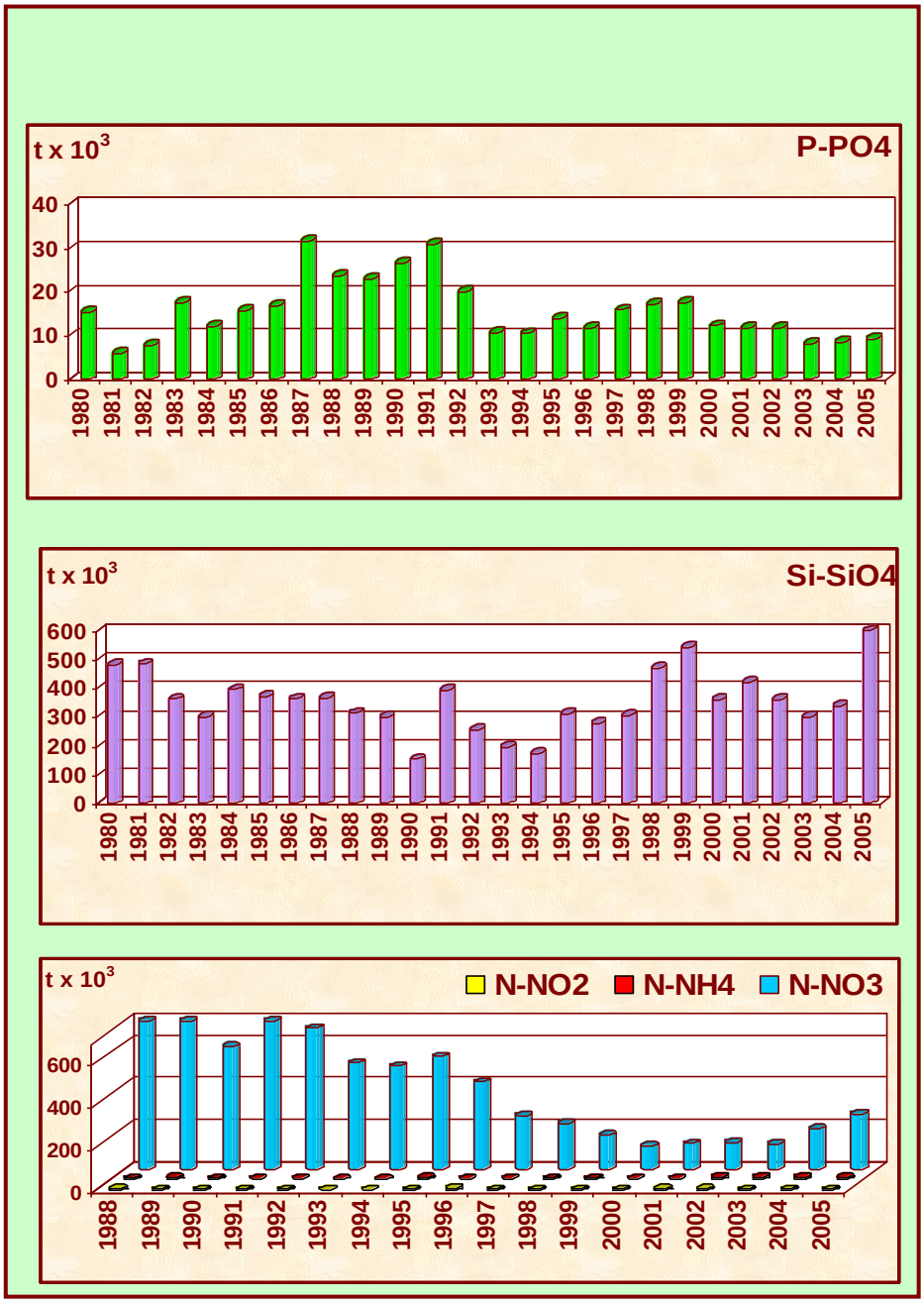


Fig. 4 - Evolution of nutrient loads in Danube water

Ionic ratios presented a general tendency of reaching marine water characteristics, except 2005 when these ratios were higher due to the notable

reduction of phosphorus and also to the increase of nitrogen and silicon (Fig.5).

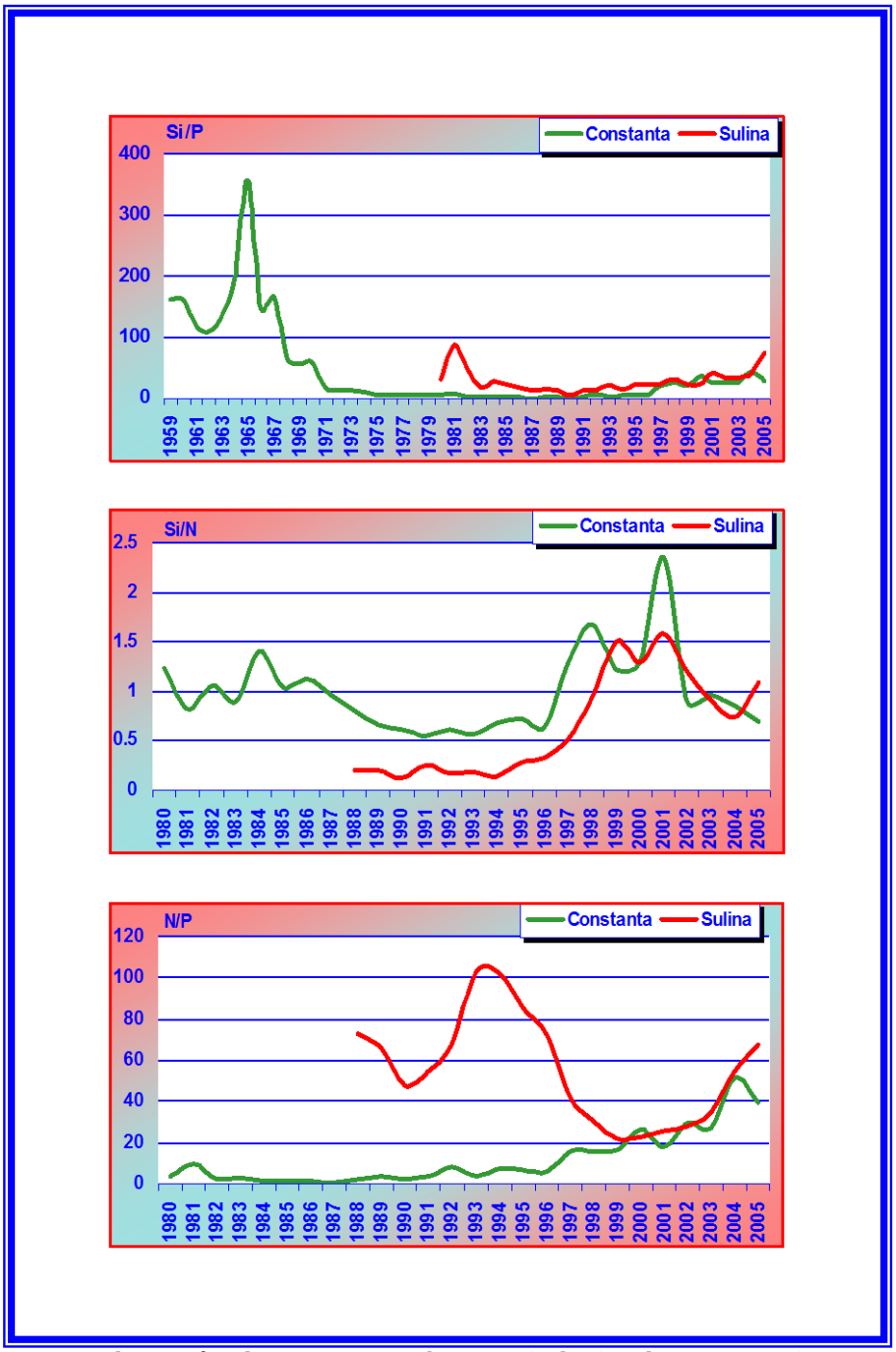


Fig. 5 - Evolution of molar ratios in Danube water (Sulina) and in sea water (Constantza)

On the Romanian shelf the highest concentrations have been observed in the 70', they were considerably decreasing in the 80' and slightly in the 90' (COCIASU *et al*., 1998). During the last five years ***phosphates*** continued their decreasing trend, approaching '60s values. Annual averages ranging between 0.66µM in 2001 and 0.27µM in 2004, period mean being higher than 1959-1968 period (Fig. 6 and Table 3). Frequent cases of inorganic phosphorus diminution below the method detection limit (0.01µM) were recorded in the summer time.

Silicates presented a slightly but continuous increasing trend begun after 90', concentrations being yet much below reference level from 1959-1968 (Fig. 6 and Table 3).

Nitrates level recorded a 30% increase during 2000-2005 compared with previous period, being higher than ammonium level (Fig. 6 and Table 3).

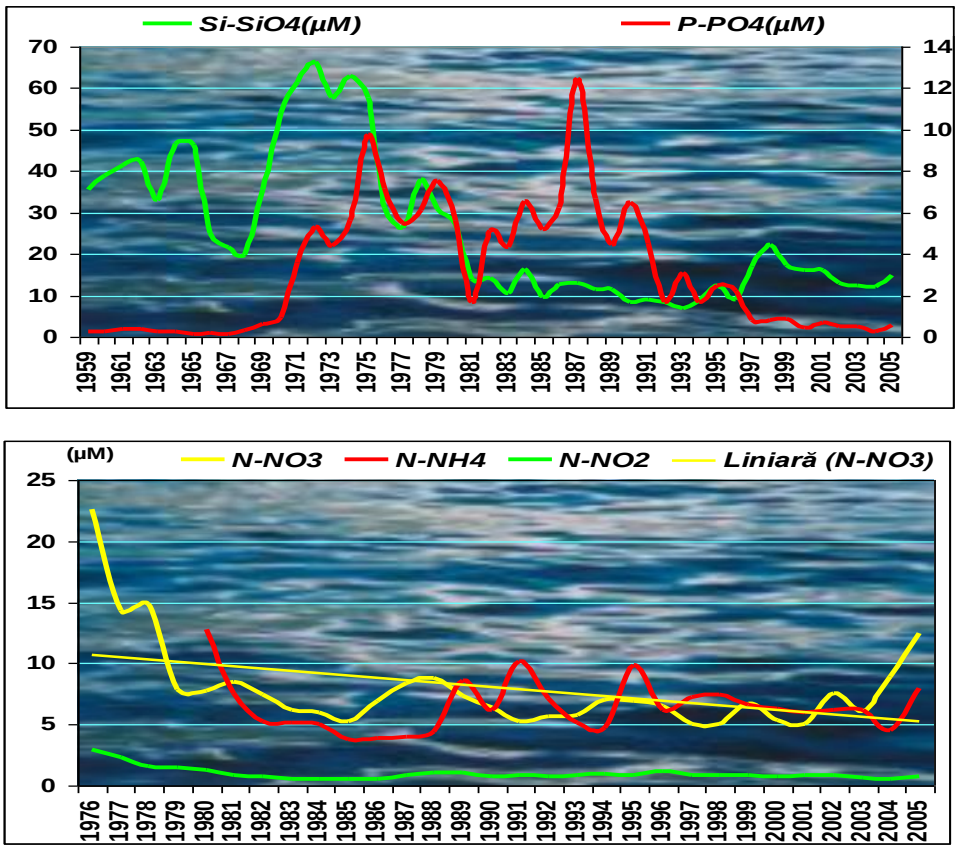


Fig. 6 - Nutrient concentrations in Romanian coastal waters

Table 3

Nutrient concentrations in Romanian coastal waters (µM)

Period	P-PO_4	Si-SiO_4	N-NO_3	N-NO_2	N-NH_4
1959-1969	0.28	35.05	-	-	-
1970-1980	5.59	46.64	7.78*	1.89*	-
1981-1990	5.91	12.11	7.11	0.74	5.36
1991-1999	2.01	12.27	5.96	0.88	7.15
2000-2005	0.48	14.05	7.54	0.86	6.26

*1976-1980

Large N/P ratios during 2000-2005 period strongly suggest phosphorus the nutrient with limiting role for the Romanian waters (Fig. 5).

Seasonal dynamic within 2000-2005, even if the values were lower then previous period, have been better pronounced for silica and phosphorus. Thus, during spring-summer consumption, phosphorus had decreased closely to the 60' concentrations (Fig. 7).

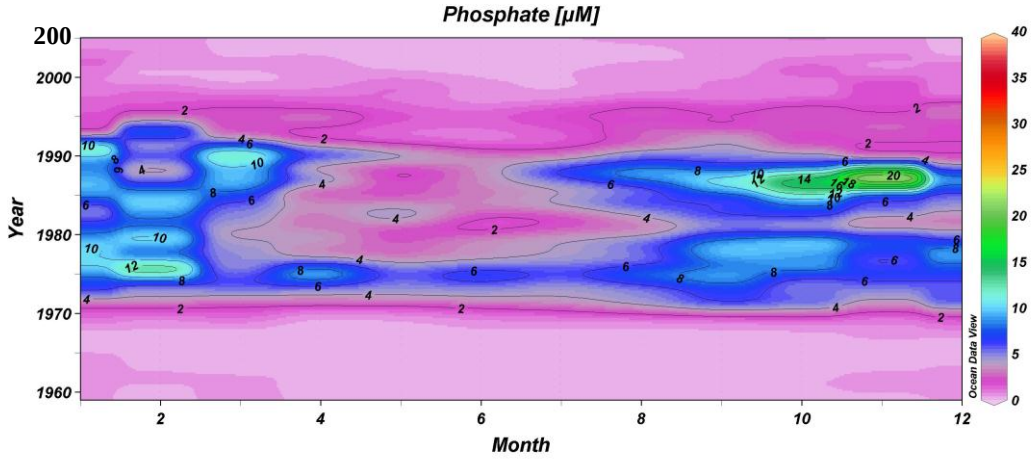


Fig. 7 - Phosphate concentrations in Romanian coastal waters at Constantza within 1959-2005

As regards silicates, we can observe that, quantitatively Within 2000-2005, are still below 1960's values. The seasonal variability was not so accentuated like before 1980 (Fig. 8).

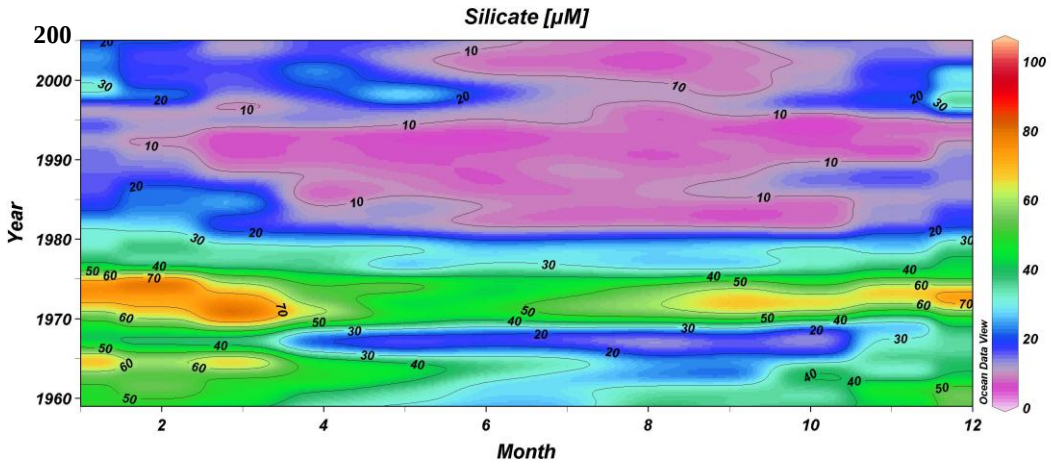


Fig. 8 - Silicate concentrations in Romanian coastal waters at Constantza within 1959-2005

Regarding the inorganic nitrogen within 2000-2005, the most abundant form was nitrate in the year's first part and ammonia in the second part. The year 2005 is an exception, within July –December the two inorganic nitrogen forms were very closely. While nitrite, as an intermediate form, is quantitatively reduced and respects the nitrate distribution (Fig. 9).

Like for the inorganic nutrients, Danube is the most important organic nitrogen and phosphorus source for the Romanian shelf waters. During our observations, the total nitrogen level recorded a pronounced seasonal dynamic, underlined by the winter increased concentrations up to 220 µM in February 2004 and their decreasing during summer close to 70 µM, in July 2005 (Fig.10).

Concerning the total nitrogen fractions, the inorganic one constituted from nitrates, nitrites and ammonia recorded values within 47.5 µM in August 2005 and 113.2 µM in March 2005. The organic form, even with a slowly decreased level, showed a larger range within 13.5 and 130.6 µM with a better delimited annual cycle, particularity given to total nitrogen (Fig. 10).

Total nitrogen quantities determined for these two years indicate slowly increased values in 2005, even if the concentration level was more decreased. This situation is given by the river input, which was higher in 2005 then previous year from March to October (Fig. 11).

The analyze of those two years observations data, shows that in the Danube's waters, maybe due to the higher natural background, the inorganic fraction is preponderant, 58.3 %, only 41.7% organic nitrogen.

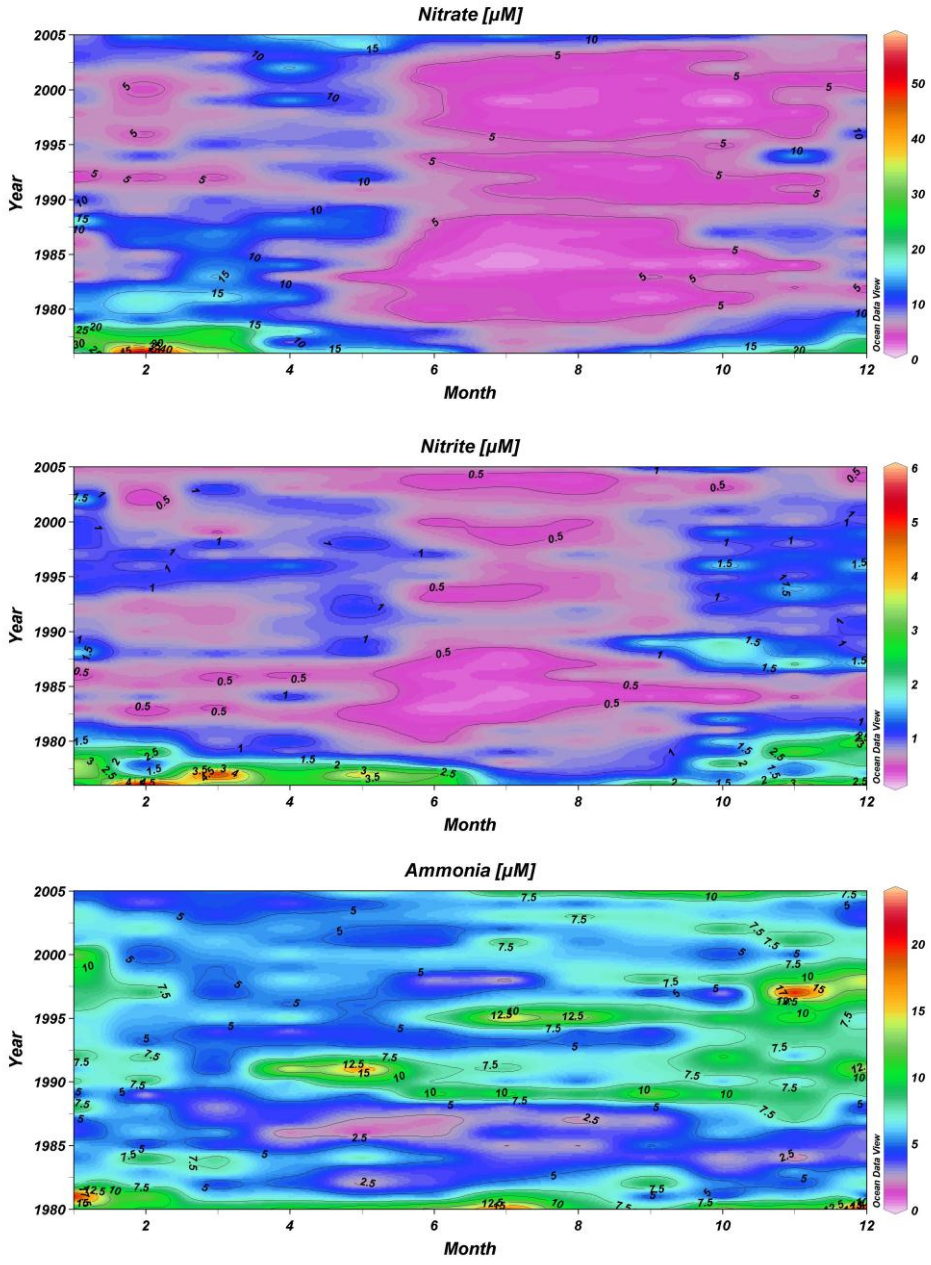


Fig. 9 - Nitrates, nitrites and ammonia concentrations in Romanian coastal waters at Constantza within 1976-2005

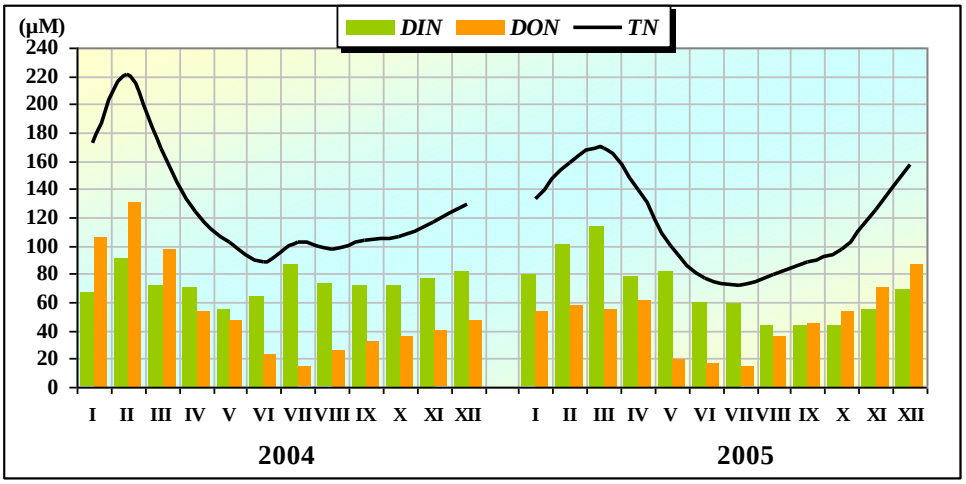


Fig. 10 - Total, inorganic and organic dissolved nitrogen in Danube water (Sulina)

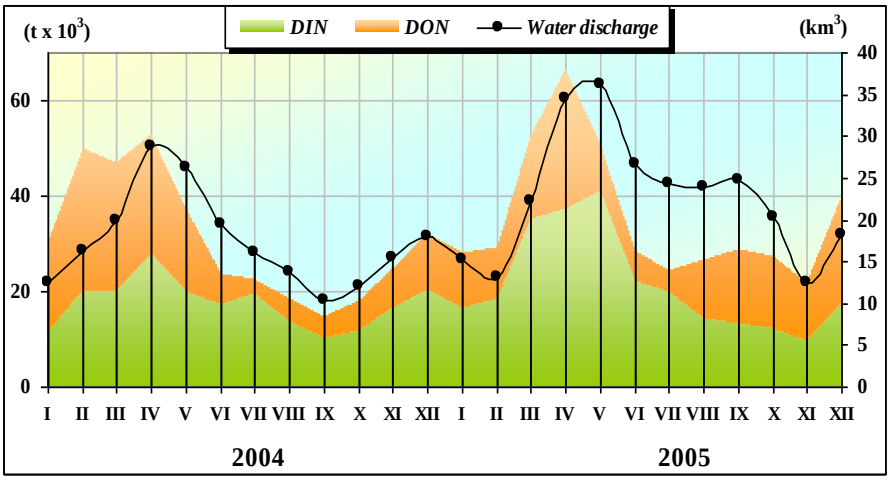


Fig. 11 – Nitrogen fraction loads in Danube water (Sulina)

Regarding phosphorus, sensitive differences have been between years, much lower in 2005 when the seasonal evolution was weak pronounced. Monthly averages values oscillated within 0.45 µM in December 2005 and 4.62 µM in November 2004 for the organic phosphorus (Fig. 12).

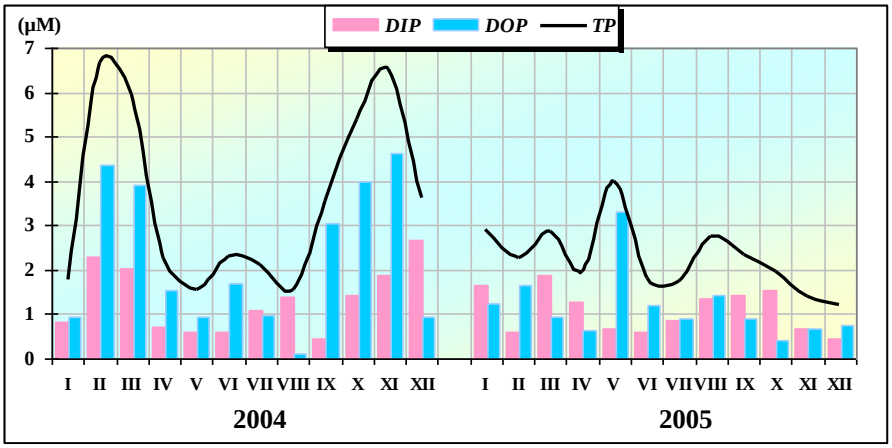


Fig.12 - Total, inorganic and organic dissolved phosphorus in Danube water (Sulina)

Total phosphorus quantities discharged into the sea these two years also presented important variances towards the water discharge and concentration level reached during the observations. It is very important to specify that, in the phosphorus case, preponderant in the Danube's water was the organic fraction with 58,7 % (Fig. 13).

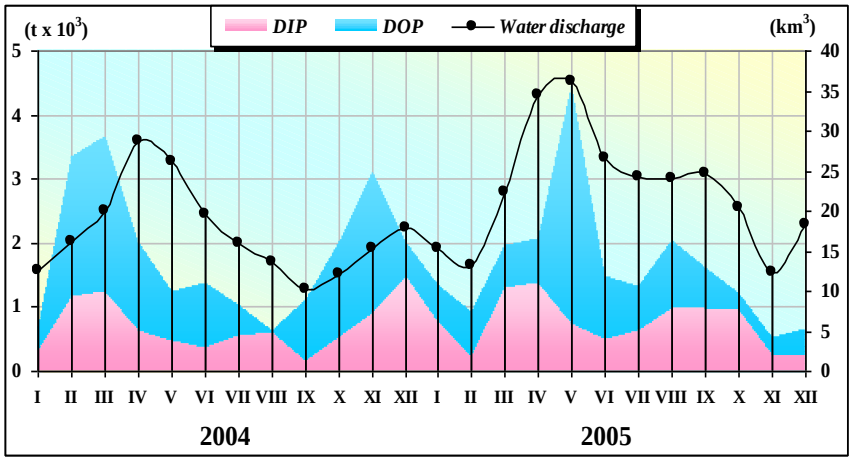


Fig.13 - Phosphorus loads in Danube water (Sulina)

We can assess, from the data analysis, that the Danube has important organic nitrogen and phosphorus loads which are discharged into the sea,

contributing to the Romanian seawater increased nutritive potential. They have annual and seasonal variations influencing either qualitative or quantitative the transitional and coastal waters nutrients background, accordingly determining the biological processes amplitude.

The seawater observations started in 2004 at Constanta area, reference area for the Romanian shelf. Like the inorganic forms, the organic fractions oscillated in wide range usually having higher quantities.

Related to nitrogen, data from 2004 and 2005, at surface, Constanta section, during April to September, shows that, even if total nitrogen had different values, the organic form dominated both situations. In this meaning we mention that, while the inorganic nitrogen concentrations oscillated around 10 µM, the organic form represented within 20-60 µM. Total nitrogen frequently outgrew 40 µM in 2004 and only few cases in 2005 (Fig. 14).

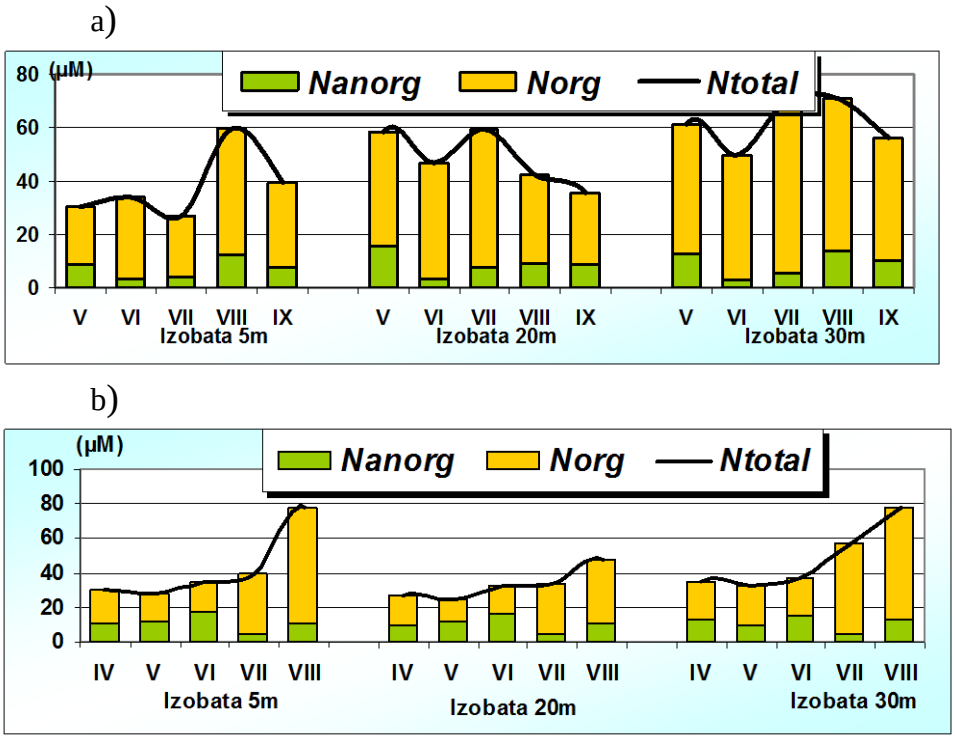
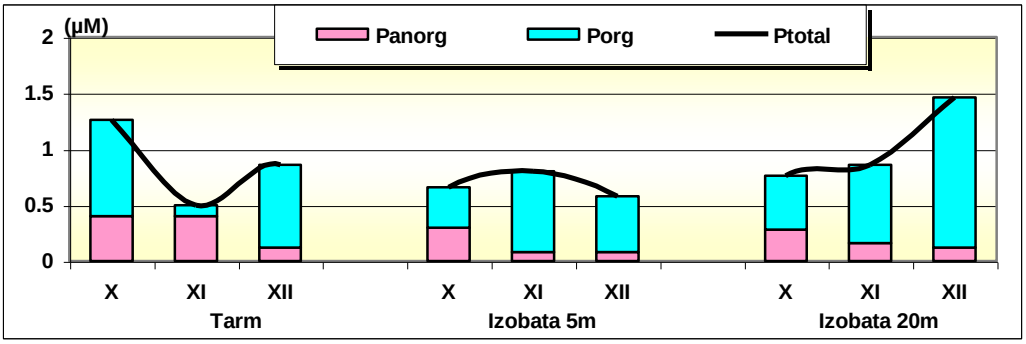


Fig. 14 - Nitrogen concentrations in sea water at Constantza in 2004 (a) and 2005 (b)

Related to phosphorus, either in 2004 or 2005 organic form has been preponderant. While the inorganic form recorded values within 0.05

µM(minimum) and 0.4 µM(maximum), organic phosphorus didn't decrease below 0.1 µM and increased to 2 µM during summer. Like nitrogen, organic phosphorus reached maximum in the warm season generally, when the biological processes are more intense. Total phosphorus oscillated in a wide range, 0.2-2.5 µM, both values of 2005 (Fig. 15).

a)



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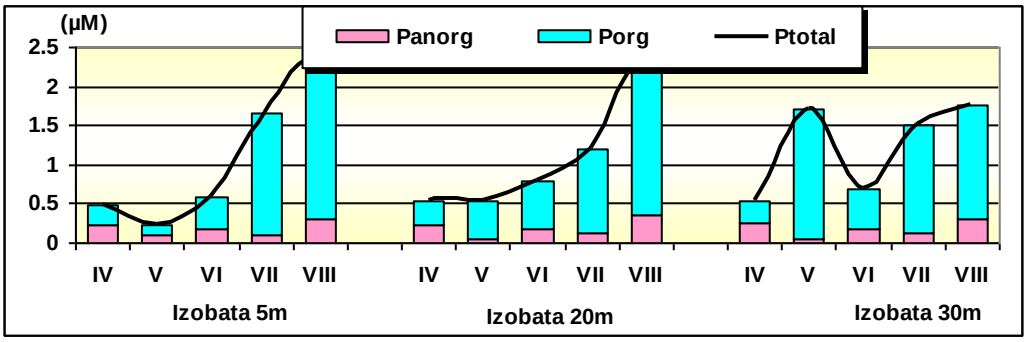

Fig. 15 - Phosphorus concentrations in sea water at Constantza in 2004 (a) and 2005 (b)

The increase of organic nitrogen and phosphorus concentrations both in Danube and coastal waters, accounting for 20% to 90% of the total nitrogen and phosphorus, preferentially used by some bacterium and phytoplankton species, represent potential sources of easy assimilable inorganic nutrients. On the other hand, the greatest part of the particulate organic matter carried from land by rivers and waste waters and the one produced "in situ" falls on the sediment surface where is enzymatically decomposed by microorganism into basic minerals. So, the coastal sediments are considered as extremely dynamic chemical systems, being a potential source of nutrients for the water above, which maintains eutrophication.

CONCLUSIONS

Between 2000 and 2005 the situation in the Romanian coastal area has improved significantly from the ecological environmental point of view. The improvement, which means reduced eutrophication, is caused by reduced nutrient inputs of Danube River, a result of the economic crisis in the former communist countries.

Phosphorus is a limiting nutrient for algae growth and seems to be the main reason for improvement of marine ecosystem state in this area.

The increase of organic nitrogen and phosphorus concentrations can contribute to the transitional and coastal waters eutrophication and cause strong changes in species composition of the marine ecosystem.

The main risk of the next period is the recovery of the economic situation, which potentially results in increasing nutrient loads to the Black Sea, unless sound environmental management is carried out throughout the Danube Basin.

Continued monitoring of the Western Black Sea coastal waters "reference point of the sustainability of nutrient management in Danube basin" is necessary to assess future developments.

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