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SIGNIFICANT CHANGES IN DANUBE NUTRIENT LOADS AND THEIR IMPACT ON THE ROMANIAN BLACK SEA COASTAL WATERS

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ABSTRACT

The paper presents the latest changes of the Danube nutrient loads share and its effect on Romanian Black Sea coastal waters. Monthly averages of the inorganic concentrations and fluxes from Danube river waters at Sulina were computed for the period 1996 - 2002 and monthly concentrations of the inorganic nutrients at Constantza for the same period.
Data analysis proves that although decreasing, both in Danube and coastal waters, nutrients budget is still superior to the one recorded in the years before eutrophication occurrence contributed to new ample blooms.

KEY WORDS : dissolved inorganic nutrients, Danube discharge, Black Sea Romanian coastal waters

INTRODUCTION

Isolation from the flushing effects of the open ocean coupled with its huge catchments, thermohaline stratification and the long residence time of the water masses have made the Black Sea particularly susceptible to increased production of organic matter (eutrophication). This has led in the last three decades to radical changes in the ecosystem, with a major transboundary impact on biological diversity and human use of the sea, including fisheries and recreation.

The main ecological consequence of the increasing eutrophication has been an increase, during the ‘70ies and ‘80ies of planktonic primary production (BODEANU *et al.,* 1998; BOLOGA *et al*., 1999). The algal blooms, a rare phenomenon until the ‘70ies, increased both in frequency and magnitude (for the decade 1981-1990, 47 monospecific blooms). Frequent hypoxia and occasional anoxia phenomena have resulted from eutrophication and led to a severe decline of benthos over broad regions of the continental shelf.

A marked decrease in biodiversity, which has been induced by alien opportunistic species as well, has been recorded. Many species disappeared or decreased in biomass, i.e. the macroalgae *Cystoseira* and *Phyllophora,* the mussel *Mytilus galloprovincialis* and fish species such as sturgeon and turbot. Other species increased explosively in biomass, i.e. the bivalve *Mya arenaria*, the flagellate *Noctiluca scintillans*, the jellyfish *Aurelia aurita* and the comb jelly *Mnemiopsis leidyi* (PETRANU *et al*., 1999). Only six out of the 26 commercially valuable fish species in the ‘60ies remained in exploitable quantities. The main reason for eutrophication and the following disequilibrium of the ecosystem on the north-western Black Sea shelf is the elevated land-based nutrient input lasting already more than three decades. The international rivers Danube, Dniestr, and Dniepr provide the main source with approximately 60% and 67% of the total nitrogen and phosphorus inputs respectively, into the Black Sea. The Danube itself represents the largest freshwater source with 75% of the total water discharge and subsequently carries approximately 50% of the total nutrient input to the north-western part of the basin.

The most affected part of the basin is the northwestern one, especially the Romanian shelf. The pelagic ecosystem of the Romanian shelf shifted from a highly diverse system into an eutrophic plankton culture, which led to unsuitable environmental conditions for most higher organisms (MEE, 1992).

It is assumed that these alterations of the ecosystem were essentially caused by changes in nutrient discharges through major rivers, particularly the Danube, which accounts for more than 75% of the river input into the northwestern continental shelf of the Black Sea (COCIASU *et al.,* 1996; 1997).

METHOD

The paper presents monthly means of inorganic nutrient concentrations and fluxes (PO_4, SiO_4, NO_3, NO_2, NH_4) obtained from daily Danube water samples at Sulina since 1996 until 2002. The annual nutrient loads of the Danube entering into the Black Sea have also discussed. They have been calculated from monthly averages of the concentrations measured in the Sulina branch and water volume discharge measured upstream in the river before it enters the Danube Delta (Ceatal-Izmail, km 85).

Monthly inorganic nutrients averages are analyzed for a better understanding of the trophic current state of the marine coastal waters. Data include also daily observations, in the same period of time at Constantza, as a representative area of the Romanian littoral. The measurements of nutrients in water samples have been done according to standard methods (GRASSHOFF *et al.*, 1999).

For a better evaluation of the environmental factors between 1996 - 2002, the previous period was considered for comparison.

RESULTS AND DISCUSSIONS

The Danube is the main river of the Black Sea basin, and it has essential influence on productivity and biodiversity of the marine ecosystem. Total length of the river is 2860 km, drainage basin - 817000 km^2 it represents approximately 41% of the drainage basin of the whole sea. There are 17 industrial countries with agricultural structure.

Annual mean discharge is significanly varying, following a certain periodicity. During the last 45 years annual mean values ranged between 134.15 Km^3 in 1990 and 295.81 km^3 in 1970, the average of the period representing 205.62 km^3. It is 36% of the fresh water incoming into the Black Sea and more than 75% of the fresh water incoming into the northwestern part of the Black Sea. On the whole, annual maximum of the water discharge is recorded in April-May and the minimum in September-October.

According to estimates based on data prior to 1990 the chemical content of Danube waters were completely different from the ‘60ies, 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 the early ‘70ies 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 '90ies some positive changes related to a decrease in anthropogenic pressure and continuous improvement in the state of the ecosystem were observed, mainly as a result of economical collapse in the former East European Black Sea coastal countries (COCIASU *et al.*, 1998).

Between 1996–2002, the Danube discharge was high, annual averages exceeding 200 Km³ (Fig 1). One can find significant the long term average of the period - 218.2 Km³ - superior to the average value of the last 45 years (205.62 km^3) (Table 1).

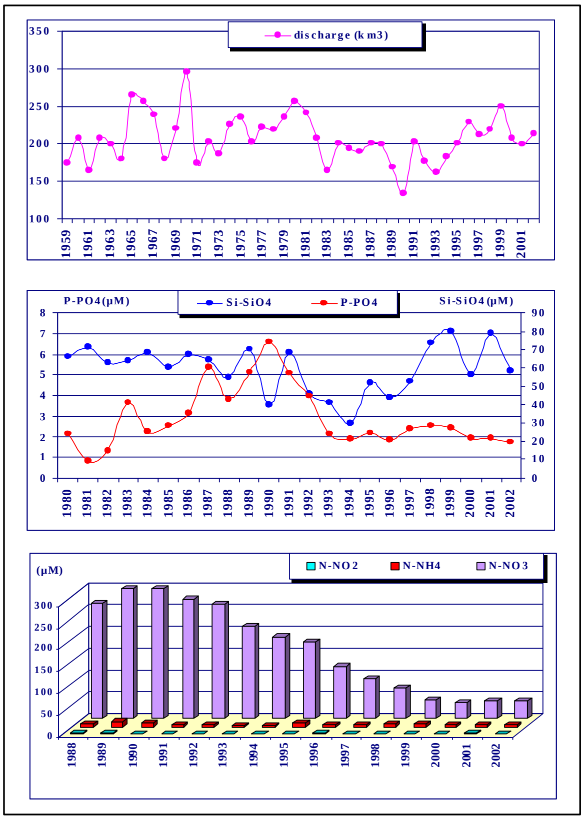

Fig.1 – Evolution of Danube water discharge at Ceatal-Ismail and nutrient concentrations at Sulina station

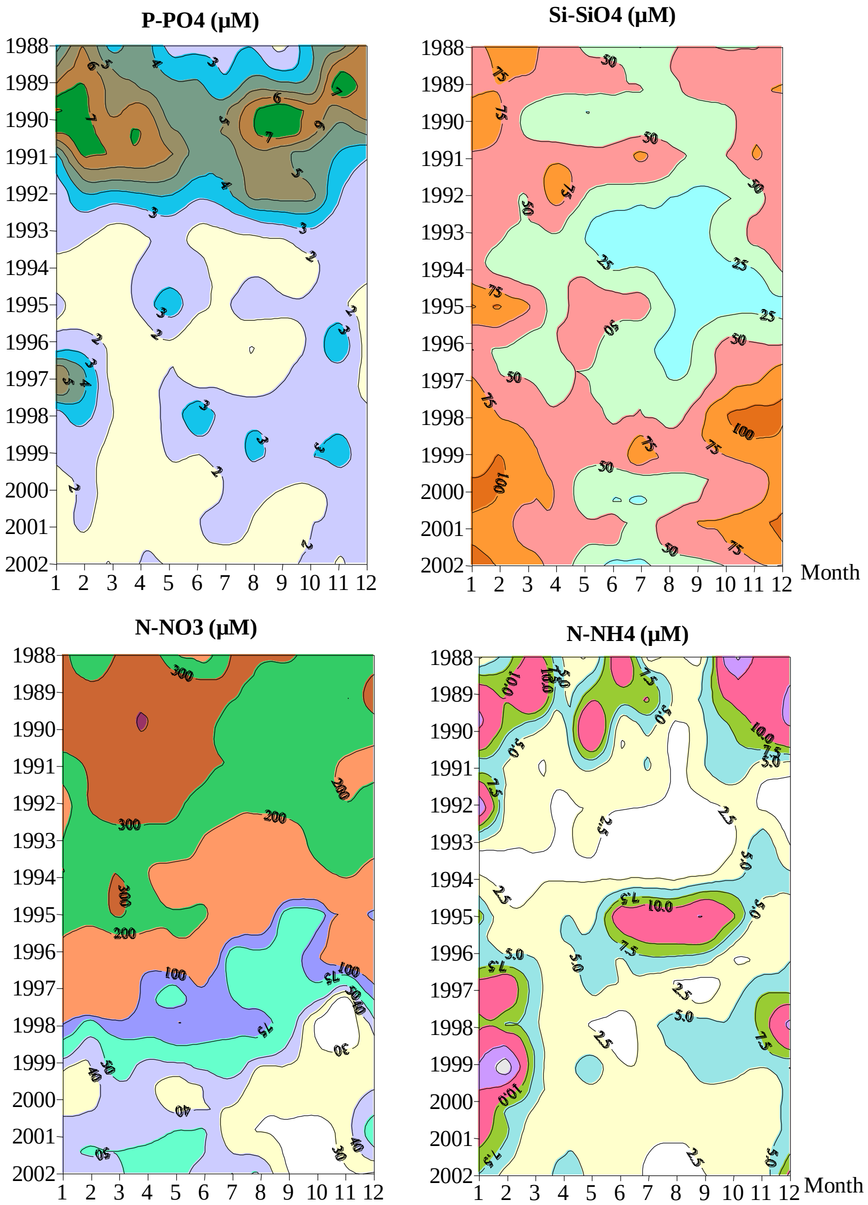

Fig. 2 Seasonal variation of phosphorus, silica, nitrate and ammonia in Danube waters at Sulina station

Table 1

Danube nutrient mean values

Year	Discharge Km^3	P-PO_4 µM	Si-SiO_4 µM	N-NO_3 µM	N-NO_2 µM	N-NH_4 µM
1959-1969	213.4	-	-	-	-	-
1970-1980	223.3	-	-	-	-	-
1981-1990	196.0	3.46	62.17	298.54*	2.20*	8.93*
1991-1995	184.4	3.03	47.24	223.30	1.17	4.44
1996-2002	218.2	2.11	63.28	64.48	1.84	5.45

- only 1988-1990

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Seasonal evolution was well defined, monthly averages ranging between 9.20 km³ in September 2000 and 31.07 km³ in May 1999.

Nutrient content presented a different evolution in the analyzed period. On the whole, phosphates ranged within the limits that were reached in the last ten years, annual averages varying around 2 µM. A slightly but continuous decreasing tendency was recorded, the average for the analyzed period being below the ones in the previous periods (Fig. 1).

Like phosphates, inorganic nitrogen presented a significant decrease in the last ten years, especially since 1997. The decrease was mainly induced by the prevailing nitrates reduction, which reached the lowest level of 37.2 µM in 2000 (Fig. 1). Between 1996 – 2002 nitrates decreased about four times, while the other two forms of the inorganic nitrogen, nitrites and ammonia recorded a slight increase if compared to the previous period (Table 1) .

Opposite to phosphates and nitrates evolution, silicates recorded a slight increase in the analyzed period. Annual averages increased from 43.6 µM in 1996 to 79.6 µM in 1999 (Fig. 1). This increase was very well reflected in the average of the period, that is 63.28 µM, which exceeded with 16 µM the average of the previous period (Table 1).

During the annual cycle, seasonal variations of the time interval 1996 – 2002 have been less significant, especially for phosphorus. Regarding silicates and nitrates, consumption periods were different, summer and late fall respectively, in agreement with the biological cycle of the main phytoplankton groups (Fig. 2) .

River discharge and nutrient concentration changes do influence equally the nutrient loads discharged into the sea, accurately reflecting the changes of the two parameters. In this respect, in the considered period, phosphorus and especially nitrogen stocks were continuously decreasing, while silica ones have significantly increased (Fig. 3). Thus, the lowest nitrates quantity discharged into the sea was estimated to 108.89 thousands tones in 2000 and the highest silica quantity discharged into the sea was estimated to 546.93 thousands tones in 1999 (Fig. 3). In the same time the increase of nitrites and ammonia quantities should be noticed, which tend to increase their share in total inorganic nitrogen.

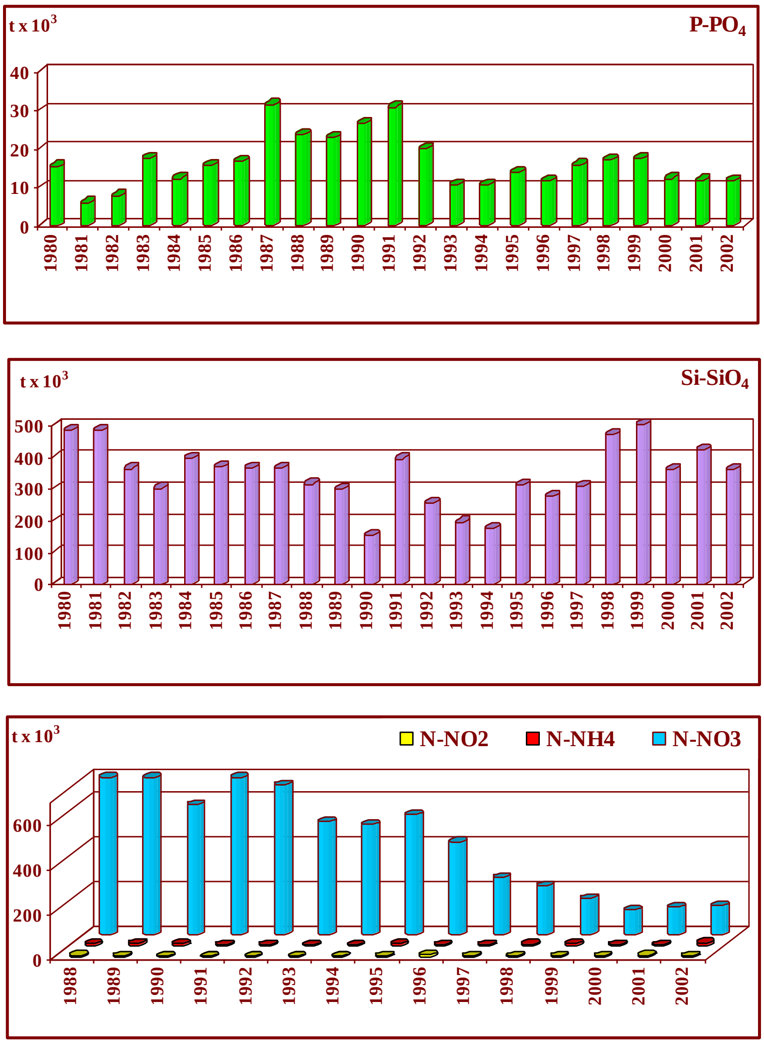


Fig.3 – Evolution of nutrient loads in Danube water at Sulina station

Comparative analysis of the nutrient fluxes discharged into the sea between 1996–2002 reveals that even if a general trend of returning to the normal condition before eutrophication is to be noticed, differences still exist. In this respect, while phosphorus and nitrogen quantities are superior to the ones published by ALMAZOV (1961) for the ’60ies, silica is still a half of the level reached in that reference period (Table 2).

Table 2

Danube nutrients mean flux (t x 10^3)

Year	**P-PO_4**	**Si-SiO_4**	**N-NO_3**	**N-NO_2**	**N-NH_4**
1981-1990	18.02	341.11	701.24*	5.00*	20.57*
1991-1995	17.15	266.08	591.95	2.90	11.17
1996-2002	13.95	390.78	199.85	5.54	16.52
Almazov 1960	12.0	790.0	140.0		

* only 1988-1990

Ionic ratios presented a general tendency of reaching marine water characteristics. Si/P and Si/N ratios increased following phosphorus and nitrogen concentration reduction. N/P ratio decreased significantly until 1999 and a slight increase was noticed after that, due to a more vigorous phosphates reduction in the last three years, to a relatively constant level of nitrogen (Fig. 4).

Former data demonstrated that with time, all the changes in river water concentrations determined correspondent changes in the coastal marine waters, the Danube acting as the main nutrient source. On the Romanian continental shelf, the highest stocks have been estimated in the ‘70ies, they were considerably decreasing in the ‘80ies and slightly in the ‘90ies (COCIASU *et al.*, 1977).

Since 1996 until 2002 all the changes of the Danube water chemical structure were found in the marine coastal waters. Thus, while phosphates and nitrates continued their decreasing trend, silicates recorded a significant increase (Fig. 5). Annual averages of the phosphates ranged between 0.5-1.0 µM, with the mean value of the period 0.90 µM, which keeps them at a high level if compared to the ‘60ies (Fig. 5). Nevertheless, frequent decrease of the phosphorus during summer season below method detection limit demonstrates its role as limitative factor of the primary production.

Silicates, even if twice higher if compared with 1991 to1995, were still at low levels towards the ‘60ies.

Regarding the main inorganic nitrogen forms, both nitrates and ammonia recorded values below the former period. Likewise the former period, ammonia recorded values slightly higher than nitrates, a peculiarity of the marine coastal waters in the ten years.

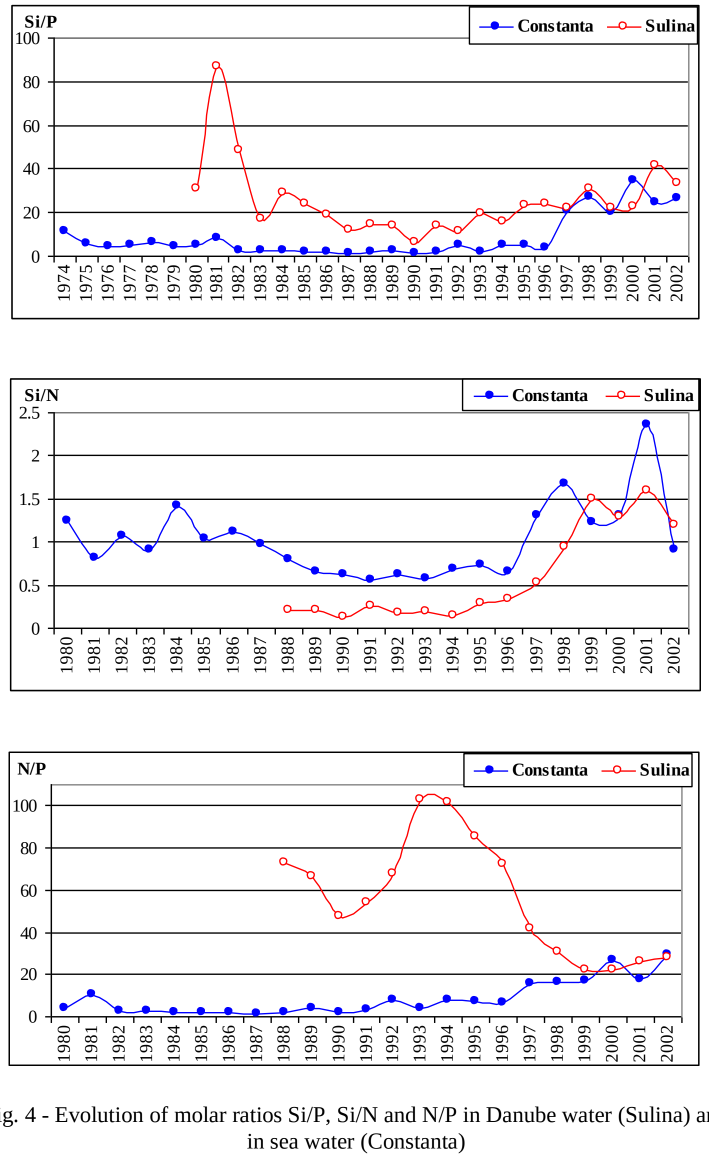


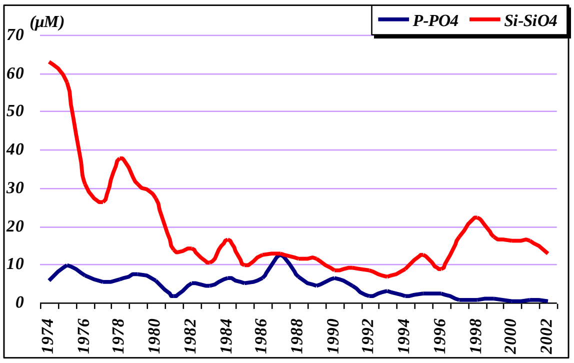
Fig. 4 - Evolution of molar ratios Si/P, Si/N and N/P in Danube water (Sulina) and in sea water (Constanta)

Table 3

Nutrient concentrations and molar ratios at Constantza

Year	P-PO_4 MM	Si-SiO_4 µM	N-NO_3* µM	N-NO_2* µM	N-NH_4 µM	Si/N	Si/P	N/P
1959-1969	0.28	35.05	-	-	-	-	125.21	-
1970-1980	5.59	46.64	7.78	1.89	-	-	8.34	-
1981-1990	5.91	12.11	7.11	0.74	5.36	0.92	2.05	2.24
1991-1995	2.68	8.98	6.10	0.83	7.40	0.63	3.15	5.35
1996-2002	0.90	15.81	5.86	0.87	6.53	1.19	17.57	14.73

* only 1976-1980



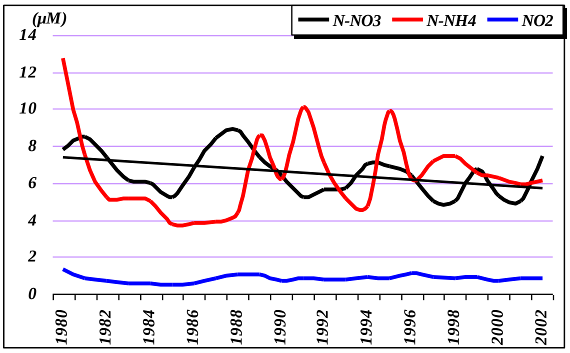


Fig.5 – Evolution of nutrient concentrations in Romanian shallow waters at Constantza station

During the period under consideration, seasonal variations began to be more clearly distinct, due to a sensitive decrease of the concentrations in summer and autumn seasons. This peculiarity was more marked for silica and nitrates (Fig. 6).

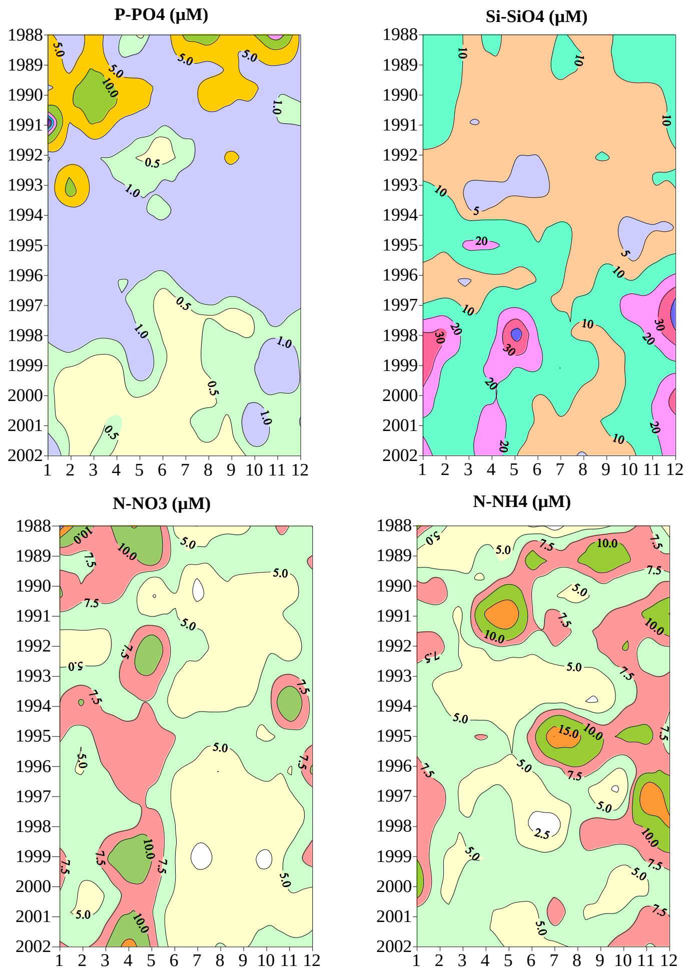


Fig.6 – Seasonal variation of phosphorus, silica, nitrate and ammonia in seawater at Constantza station

Ionic ratios increased against former periods, due to silica increases but mainly due to phosphorus reduction. Both Si/N and N/P ratios were close to 1 and 16 respectively, considered by REDFIELD (1934) as normal ones for the natural background.

CONCLUSIONS

Data sets regarding the nutrients evolution in Danube and marine coastal waters, with special emphasis between 1996 and 2002 are being updated. So the nutrients monitoring was continued, as a need to scientifically substantiate the previsions for eutrophication reduction and ecosystem recovery.

These data are supporting the continuous recovery tendency to the situation during the ‘60ies, before eutrophication. Although inorganic nitrogen and phosphorus concentrations have remarkably decreased and silica level is steadily increasing, the concentration level of the nutrients in the two water bodies still differs vs. to the reference period.

The increase of the ammonia forms at and even over the nitrates level represents a peculiarity of the Romanian coastal waters during the last decade.

Frequent cases of phosphates reduction below detection limit during the summer season grants phosphorus the role of limitative factor of primary production in the marine coastal areas.

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