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THE IMPORTANCE OF FRESH WATER OUTFLOW ON A STATION SITUATED IN FRONT OF THE PO RIVER (PO DI GORO)

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RIASSUNTO

In questo lavoro viene descritta la situazione della stazione di campionamento S1 nell'Adriatico nord occidentale (44°44'70"N, 12°27'41"E), posta davanti allo sbocco del canale di Po di Goro, nella quale sono stati raccolti dati relativi alle componenti organiche ed inorganiche dell'azoto e fosforo totali disciolti. Questa zona di mare è interessata da importanti apporti fluviali delle acque di origine padana, che contribuiscono in modo determinante allo stato trofico del sistema. Risulta perciò particolarmente interessante mettere in evidenza l'influenza che questi apporti possono avere sui processi biochimici nell'ambiente marino costiero e tentare di fare una stima dell'utilizzo delle varie frazioni di azoto e fosforo rispetto alle quantità immesse nel sistema. Per questo motivo sono stati scelti due periodi di campionamento caratterizzati da diverse situazioni di afflusso di acqua dolce; scarso in aprile 1995 ed elevato in luglio 1995. Dai dati ottenuti si è cercato di evidenziare un bilancio dei flussi di azoto e fosforo nella stazione considerata.

Nel caso dell'azoto, si nota un forte apporto fluviale di nitrato che risulta venire rimosso dal sistema marino rispettivamente per il 30 e il 42 % nei due periodi. Risultano nello stesso tempo evidenziati gli accumuli di ammonio e soprattutto di azoto organico disciolto (DON). Questo ultimo si incrementa nella stazione di campionamento anche del 3120 % rispetto alla quantità immessa dal fiume Po.

Nel caso del fosforo, i dati presentati tendono invece ad indicare come questo potrebbe essere l'elemento carente del sistema. 11 fosfato viene infatti fortemente rimosso, fino al 92 %, mentre il fosforo organico disciolto (DOP), al contrario del DON, non riesce ad accumularsi nell'ambiente marino rispetto all'apporto fluviale.

ABSTRACT

The fractions of dissolved organic and inorganic nitrogen and phosphorus in sea water samples were monitored at the station S1, placed in front of the Po River mouth (44°44'70"N, 12°27'41"E). The aim was to extent our knowledge about the biochemical situation in an area that is highly influenced by fresh water loads by the

largest Italian river, and to estimate the portions of organic and inorganic nitrogen and phosphorus that were lost from the System due to physical and biochemical interactions.

For this purpose, we chose to examine a sampling period with scarce river outflow (April 1995) and one with greater outflow (July 1995). Despite great nutrient loads in both sampling periods, our estimates revealed that almost the whole fraction of inorganic phosphorus (up to 92 % at April) and a part of the inorganic nitrogen (30 % at April and 42 % at July) was readily consumed at the station.

Surprisingly the dissolved organic fraction of nitrogen (DON) was much greater at the station (up to 3120 % in April) than in the river water, and it constituted a conspicuous part of the total dissolved nitrogen in the study area. On the contrary, the dissolved organic fraction of phosphorus (DOP) did not accumulate in the coastal area, compared to the river water.

1. INTRODUCTION

In the years of 1995-96, four PRISMA 1 cruises of the "Biogeochemical Cycles-Project" took place in the north-western part of the Adriatic Sea. Samples were collected, with the aim to extent our knowledge about the biogeochemical situation in an area which is highly influenced by fresh water loads from the largest Italian river, the Po River. This part of the Italian coast is very important for the comprehension of the biogeochemical dynamics of the entire northern Adriatic Sea, and various studies have therefore attempted to describe different biological, chemical and physical situations and processes (Ferrari *et al.*, 1984; Franco *et al.,* 1986; Degobbis *et al.,* 1986; Giordani *et al.,* 1992; Zoppini *et al.,* 1995). The Po River watershed is very large and covers an area that is highly populated and has a very intensive industrial and agricultural activity. It has been estimated that the northern Adriatic receives as much as 50 % of the total nutrient load, and 60-70 % of the total inorganic nutrient load from the Po River (Degobbis & Gilmartin, 1990). Macroalgal blooms, due to massive nutrient loads, and following anoxic conditions have caused severe economical problems for the fishery nearby the Po Delta (Rinaldi *et al.*, 1992).

In this paper we will examine the importance of fresh water loads on the inorganic dissolved fractions of nitrogen and phosphorus (nitrate, nitrite, ammonium and phosphate), and on the concentrations of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). We will present an estimate of the fractions of N and P that were removed from the System passing from the Po River mouth to the station, by the use of a simple model, in order to make a comparison with previous studies by other authors.

For this purpose we have selected the station S1 (Fig. 1) which is directly influenced by the river outflow in order to compare the periods of scarce and great outflow. These periods are corresponding to the sampling periods of April and July 1995.

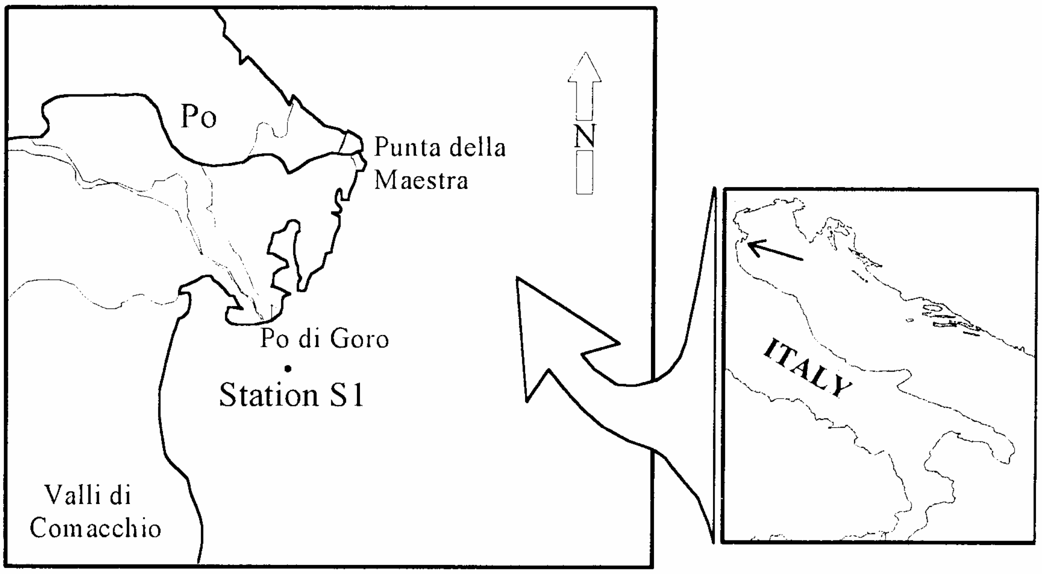


Fig. 1 - Sampling station S1 (44°44'70"N. 12°27'41"E) of the "Biogeochemical Cycles- Project".

2. MATER1AL AND METHODS

Water samples were collected on the 9-10 April 1995 and on the 10-11 July 1995 at the station S1, every 4 hour, in 5 m intervals from the surface to the bottom (20 m), by the use of Niskin bottles of 5 litres. The vertical profiles of temperature, salinity (PSU), fluorescence and light transmission were logged every 2 hour. Sub-samples for the determinations of dissolved oxygen and dissolved organic and inorganic nitrogen and phosphorus, were collected directly from the Niskin bottles Dissolved oxygen was determined according to the Winkler method (Strickland & Parsons, 1972). Samples collected for the determination of the inorganic fractions and of the DON and DOP were filtered on precombusted Whatman GF/F filters.

Nitrates, nitrites, ammonium and phosphates were determined according to the Alpkem-Perstorp *Flow Solution Methodologies* (1992). The concentrations of total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) were determined after photo-oxidation by UV and H_2O_2 (Walsh 1989), and analysed as sum of nitrites and nitrates and as phosphate, respectively. The DON and DOP concentrations were calculated subtracting the value of the total dissolved inorganic fraction from the total dissolved fraction.

3. RESULTS

We chose to consider salinity an indicator of fresh water outflow from the Po River. Sampling periods were of 2 days' intervals, in order to examine the influence of the tides on the water masses. In fact, our hypothesis is that the tide is one of the most important forcing factors which generate horizontal oscillations of the surface layer. One can thus assume that these oscillations, measured at our fixed station S1, are comparable with those one could find examining different stations more or less distant from the river mouth. Therefore, when the tide is low the situation at the station S1 can be considered similar to a situation closer to the river mouth, because it is more influenced by fresh water of Continental origin, while when the tide is high, the situation at the station S1 can be considered more similar to a generic station placed more distant.

3.1. Estimate of fresh water outflow based on salinity

Fig. 2 shows the distribution of salinity in both sampling periods. The Y-axis represents the depth, and the X-axis the time course.

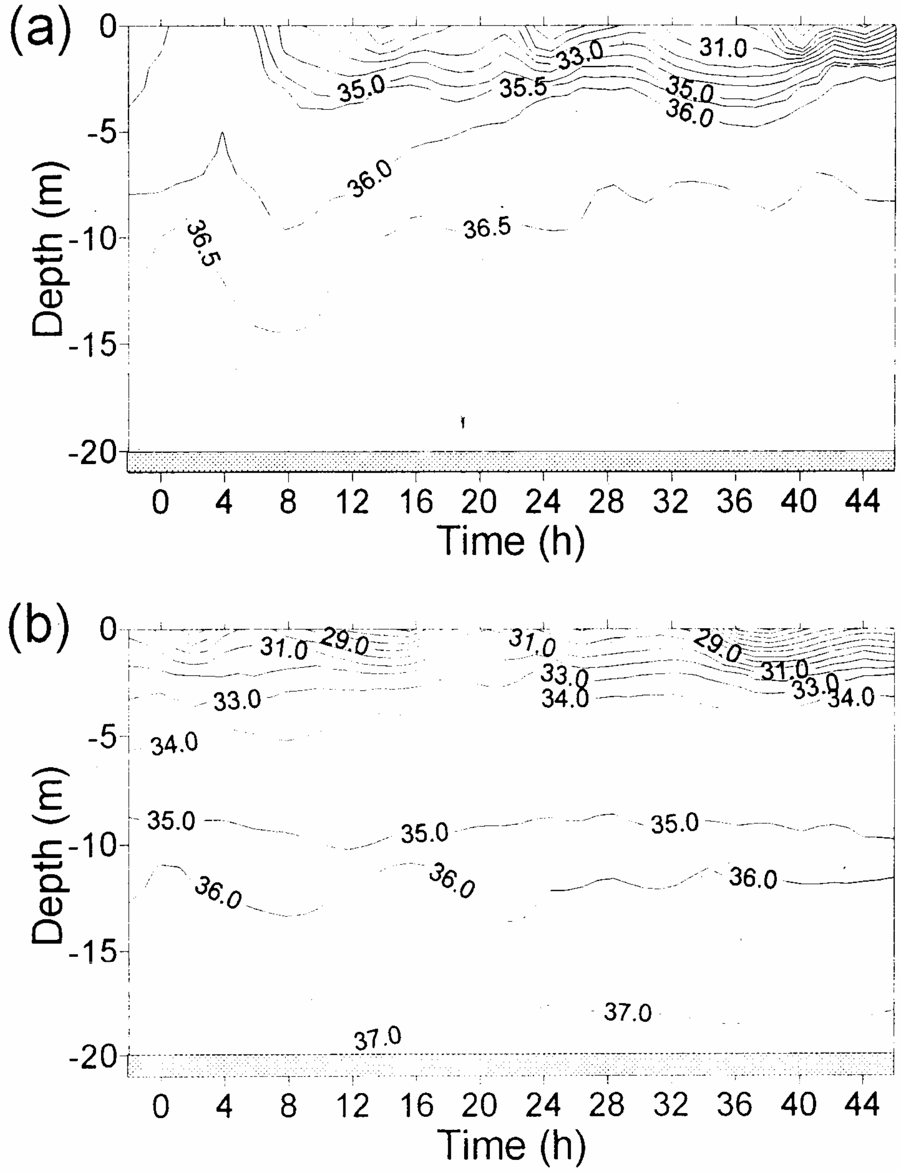


Fig. 2 - Salinity (PSU) at the station S1 during the sampling periods of April (a) and July (b)

In April (Fig. 2a), the layer with lower salinity was mainly confined in the upper water column, from the surface to 3 m of depth, with minimum values reaching 27.44, indicating a rather small fresh water outflow. In July (Fig. 2b) the fresh water penetration was more conspicuous with salinity values reaching 10.54 at the surface, and with a progressive stratification from the surface to the bottom.

The quantity of fresh water at the station, in both sampling periods, can be estimated integrating the salinity profiles of the whole water column. This calculation can be done by assigning a salinity equal to zero to the fresh water, and by assigning a salinity equal to the values found in the bottom layer to the sea water. We have found the quantity of fresh water to be 3 % at April, and 8 % at July.

3.2. Chemical characteristics of the station

In both sampling periods we have found different situations in the surface and in the bottom waters.

In April, the surface waters contained the highest concentrations of nitrates (4.6 - 36.0 µM-N), nitrites (0.32 - 1.09 µM-N) and negative values in apparent oxygen utilisation (-19.29 to -41.08 µM-AOU), indicating a supersaturation of oxygen.

The bottom waters were characterised by lower concentrations of nitrates (3.15 - 4.36 µM-N), nitrites (0.30 - 0.49 µM-N) and positive AOU values (from +12.58 to +28.23 µM). The concentration of phosphate was very low in the whole water column (less than 0.03 µM-P) and did not seem to depend on variations in salinity. Also ammonium did not seem to be directly influenced by fresh water outflow (0.63-3.13 µM-N). The concentrations of DON were higher in the surface waters (5.98 - 20.6 µM-N) than in the bottom waters (4.26 - 8.75 µM-N), while DOP was distributed with low concentrations (less than 0.34 µM-P) in the whole water column, without any apparent correlation with fresh water outflow.

In July, the fresh water outflow was greater and differences in the chemical composition between surface and bottom waters were even more clear. In the surface waters, the concentrations of nitrates (10.8 - 49.5 µM-N) and of nitrites (0.42 - 1.13 µM-N) were higher due to the river outflow. The waters contained low concentrations of phosphates (0.04 - 0.19 µM-P) and were supersaturated with oxygen (from -59.02 to -103.61 µM-AOU). The bottom waters were not saturated with oxygen (+50.76 to +156.44 µM-AOU) and contained higher concentrations of phosphates (up to 0.63 µM-P), nitrites (up to 0.46 µM-N), and especially ammonium (up to 16.52 µM-N), probably due to rimineralization processes.

In July, the concentrations of DON were usually higher (2.20 - 42.6 µM-N) than in April, while DOP concentrations were similar (0.01 - 0.36 µM-P) in both sampling periods.

In both periods, the N:P ratios were very high in the surface waters (469 and 208 respectively), and lower (28 and 29 respectively) in the bottom waters. This might indicate a disequilibrium in the biological availability between nitrogen and phosphorus in the system, probably due to heavy loads from the river.

During the sampling periods, the meteorological conditions were stable (average wind force 3.9 m/s), and the trend of the parameters considered, were influenced by a strong and stable water column stratification, thereby limiting any significant mixing between the surface and the bottom layer.

3.3. Data elaboration

One can try to explain the phenomena earlier described, by the use of graphics that relates the generic chemical parameter X to the salinity, as shown in the theoretical example in Fig. 3. The points at high salinity refer to the bottom waters and those at low salinity to the surface.

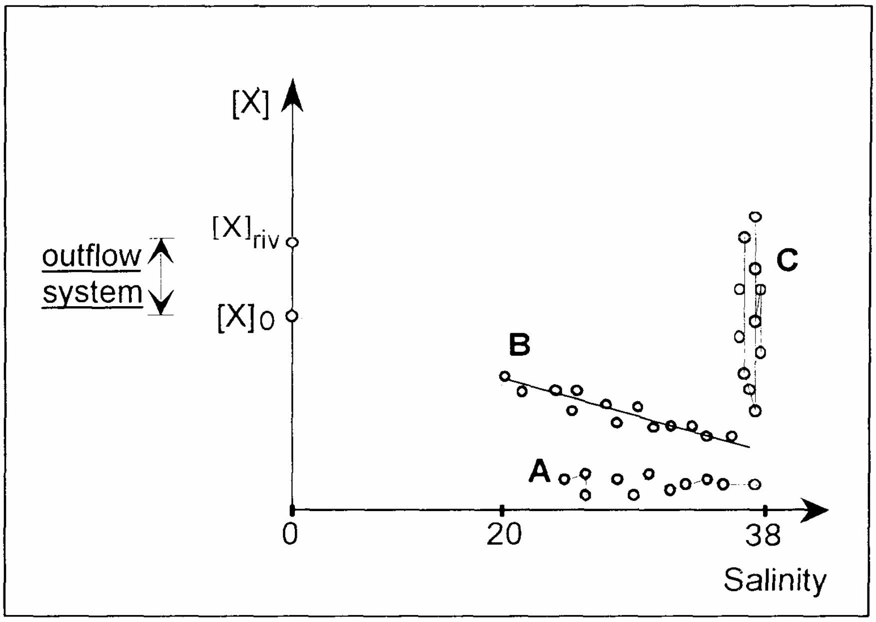
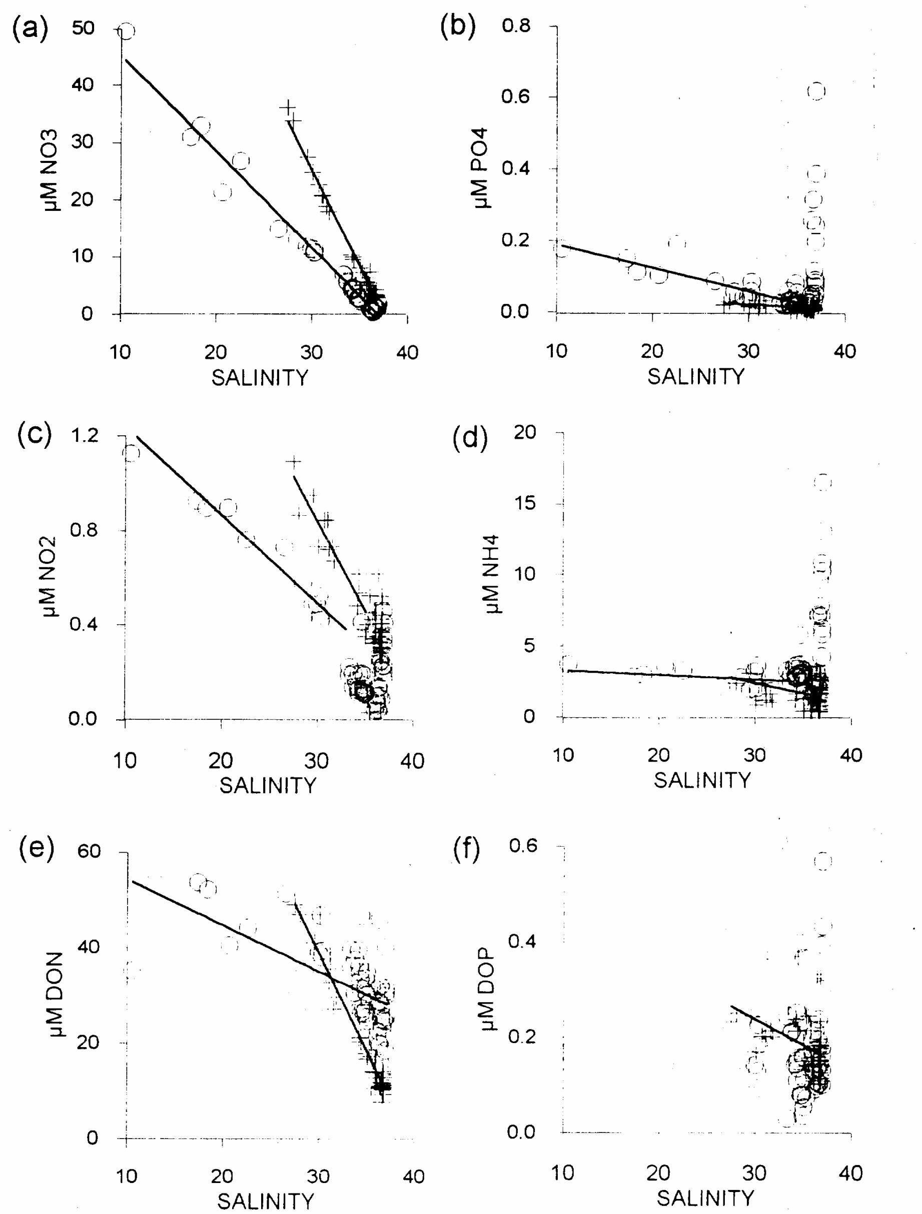


Fig. 3 - Plot of the concentration of the chemical parameter X (= nitrate, nitrite, ammonium phosphate, DON and DOP) vs salinity at the sampling station, where $[X]_{riv}$ is the concentration of X in water samples from the Po River, and $[X]_o$ is the concentration of X estimated by linear regression.

The concentrations of X can be more or less correlated with salinity, depending on physical (water mixing) and biogeochemical (assimilation and release of nutrients) interactions in the System.

In Fig. 3, the cases (A) and (C) are featuring a lack of correlation with salinity, because in (A), although mixing is present, the concentrations do not change and remains low due to assimilation processes, in the second case (C) the concentrations varies a lot in the same water mass, due to re-oxidation of organic matter in the bottom layer. In the intermediate case (B), there is a correlation between the [X] - parameter and the salinity, which can be fitted by a linear regression.



Coefficient of determination, R-squared:

	NO3	PO4	NO2	NH4	DON	DOP
APRIL	0.983	0.134	0.848	0.143	0.910	0.190
JULY	0.977	0.773	0.937	0.164	0.371	-

Fig. 4 - Plots of (a) nitrates, (b) phosphate, (c) nitrites, (d) ammonium, (e) DON and (f) DOP vs salinity, in the two sampling periods of April 95 (+) and July 95 (O)

If we extrapolate the regression line to salinity equal to zero, we will find the $[X]_0$ -value. This value represents the theoretical concentration that X would have in the fresh water fraction at the river mouth, if the factors that modify X behave in a linear way from the sampling station to the river mouth. Although we ignore the things that happens in the first interval of mixing (from salinity 0 to 20 in Fig. 3), the difference between the real X-value measured in the river water ($[X]riv$) and its calculated value ($[X]_0$) represents an estimate of the amount of X that has been lost or gained to the System because of physical and biochemical interactions.

We have elaborated our data in a similar way. The Fig. 4 shows the dissolved organic and inorganic forms of nitrogen and phosphorus vs salinity at the station and the coefficients of determination (r^2) of the regression lines. In all the plots it is possible to distinguish some data-points, that can be fitted by the use of a linear regression technique. These points are usually corresponding to the surface layers that are distinguishable form bottom layers due to the strong stratification of the water column. The only exception is the case of the DOP at July (Fig. 4f) where $[X]_0$ is estimated as a simple average, because of the great dispersion of points.

In April, it is interesting to notice the rather linear appearance of the nitrates (Fig. 4a), in the whole water column (B- type behaviour). The phosphate concentrations are very low with a trend more similar to the theoretical A-type, probably due to strong biological assimilation. In the surface layers, the nitrites (Fig. 4c) are featuring a linear behaviour similar to the B-type, while the ammonium (Fig. 4d) is similar to the A-type. In the same sampling period, also the DON (Fig. 4e) is strongly correlated with the salinity, with a linear appearance that determines a very high $[X]_0$-value. The concentrations of the DOP (Fig. 4f) are low, and are the least correlated with salinity.

At July, one can also notice a very linear appearance of the nitrates (Fig. 4a). The nitrate is in fact the fraction mostly affected by the outflow from the Po River. All the other fractions (Fig. 4b, e, d, e, f) are featuring a similar appearance to the one described in paragraph 3.2, and it is easy to distinguish two different situations: the points of the surface layer are linear with salinity (phosphates, nitrates and DON are of the B-type, and ammonium is of the A-type), while the points of the bottom layers are strongly influenced by biological processes (C-type).

4. DISCUSSION

The Tab. 1 shows the results obtained by the linear regression techniques earlier described. Using these data, one can make a comparison between the real concentrations in the Po River water ($[X]riv$) sampled in the same periods (Camusso, 1RSA Brugherio, *pers. comm.),* and those estimated by linear regression $[X]_{(0)}$. The difference in percent ($\Delta\%$) is calculated using the formula:

$$\Delta\% = \frac{[X]_0 - [X]_{riv}}{[X]_{riv}} \cdot 100$$

In Tab. 1, one can see that at April, the phosphate is almost completely consumed (-92 %), compared to the levels found in the river water, while the DOP concentrations remains Constant in lime. The nitrate is consumed (-30%), but remains always at high concentrations due to the heavy loads from the Po River. It is very interesting to notice that the concentrations of both ammonium and DON increase at the station compared to the river water, the former with 250 %, the latter, even with 3 120 %.

In July the phosphate concentration decreases very much (-69 %), but contrary to April, also the DOP is very reduced (-76%). The nitrate and the ammonium are featuring the same trends as at April, with variations of-42 % and +186 % respectively. In this period, the DON is once again presenting much higher concentrations at the station, than in the river water (+2947 %).

Tab. 1 - Concentrations (μM) of the organic and inorganic fractions of the nitrogen and phosphorus in water samples from the Po River ($[X]_{riv}$), estimated by linear regression at the station ($[X]_o$) and difference in percent (Δ%).

Cruise		PO4 μM-P	DOP μM-P	NO3+NO2 μM-N	NH4 μM-N	DON μM-N
	$[X]_{riv}$	1.19	0.61	183	2.0	5.0
April 95	$[X]_o$	0.1	0.6	128	7	161
	Δ%	-92 %	-2 %	-30 %	+250 %	+3120 %
	$[X]_{riv}$	0.97	0.42	111	1.4	2.1
July 95	$[X]_o$	0.3	0.1(*)	64	4	64
	Δ%	-69 %	-76 %	-42 %	+186 %	+2947 %

(*) average of all data

The estimates in Tab. 1 seems to indicate that the organic fractions of N and P are important for the dynamics in the study area. For this reason, the Tab. 2 shows the organic and inorganic composition in percent, of the total dissolved nitrogen and phosphorus. The data in this table are integrated values of the mean profile of the sampling periods. It is interesting to notice that the DOP and the DON are constituting a conspicuous part of the total dissolved fractions at the station, with values that varies from 47 %, in the case of the DON, to 91 % in the case of the DOP.

Tab. 2 - Organic and inorganic composition (%) of the total dissolved nitrogen and phosphorus with DIP=dissolved inorganic phosphorus. DOP=dissolved organic phosphorus. DIN=dissolved inorganic nitrogen. DON=dissolved organic nitrogen.

Cruise	DIP	DOP	DIN	DON
April 95	9 %	91 %	53 %	47 %
July 95	36 %	64 %	28 %	73 %

5. CONCLUSION

It has already been pointed out by other authors, that the Po River is a very important source of inorganic nitrogen and phosphorus to the Adriatic Sea. Our data are confirming that physical processes, like the river outflow and the tides, are affecting the coastal environment, but they are also indicating that biochemical processes are as important, in determining the dynamics of this area. In this paper we have emphasised particularly on the later aspect. These biochemical processes might determine a rapid decline in the inorganic phosphorus content (reaching -92 %) and in the nitrogen content (reaching -42 %), from the river to the coastal area. The different rate by which the phosphorus and the nitrogen seem to be consumed, is also determined by the strong disequilibrium between their concentrations (N:P ratio up to 469) in the surface layers, more influenced by the river outflow.

Regarding the organic fractions, the concentration of DOP in the coastal area is similar to that found in the river water. Some times it is even less, suggesting a possible consume of the dissolved organic phosphorus due to rimineralization processes. The DON, on the contrary, surprisingly constitutes a conspicuous part of the total dissolved nitrogen at the station, with concentrations much higher than in the river water (up to +3120 %). This accumulation might also be determined by a higher turn-over rate of phosphorus compared to nitrogen in processes related to the phytoplanktonic and bacterial production.

The data presented in this paper are not only suggesting the inorganic nutrients, but also the DOP and the DON are important for the understanding of the dynamics of the coastal area near the Po River. The DON and DOP pools are the product of different biological processes like the phytoplanktonic production of exudates and grazing, and are fundamental! for the bacteriological recycling of N and P in the coastal System. Further studies are needed to fully understand these dynamics, in order to be able to explain the processes of the whole northern Adriatic basin.

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