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Seasonal fluctuations of DIN/DIP and DON/DOP ratio in the northern Adriatic Sea

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Summary. - Within the frame of PRISMA 1 "Biogeochemical cycles" research project (April 1995 - January 1996) the quantities and the compartments of dissolved nitrogen and phosphorus have been studied in the northern Adriatic basin, considering also the organic pools. The research aimed to provide a better understanding of nutrient availability and to investigate the possible factors which promote the phenomenon of mucilage formation. For this purpose, the availability and the ratios between dissolved nitrogen and phosphorus considering both inorganic and organic fractions have been studied in relation to variations of river outflow and of biological activities. The results obtained reveal the large importance of organic nitrogen (annual average 16 µM) and phosphorus (annual average 0.13 µM) in contributing to the total nutrient availability (annual average total dissolved nitrogen: 29 µM and phosphorus: 0.18 µM) and the pronounced seasonal variability mainly ascribable to biological processes of uptake and remineralization. Furthermore, beside the well documented unbalanced ratio between inorganic nitrogen and phosphorus, the results obtained point out, for the first time, the unbalance also in the organic compartment (ratio between organic nitrogen and phosphorus ranges between 50 and 530), whose consequences might be important in relation to the phenomenon of mucilage formation.

Key words: nitrogen, phosphorus, N/P ratio, northern Adriatic Sea, dissolved organic matter.

Riassunto (*Fluttuazioni stagionali dei rapporti DIN/DIP e DON/DOP nell'Adriatico settentrionale*). - Nell'ambito del progetto di ricerca PRISMA 1 "Cicli biogeochimici" (aprile 1995 - gennaio 1996), sono state studiate le quantità e la ripartizione di azoto e fosforo nel bacino del nord Adriatico, includendo anche le componenti organiche disciolte. La ricerca ha lo scopo di portare ad una migliore comprensione della disponibilità di nutrienti e di investigare i possibili fattori che promuovono il fenomeno della formazione di mucillagini. Per raggiungere lo scopo, sono state prese in considerazione la disponibilità e i rapporti tra azoto e fosforo disciolti, considerando sia le frazioni inorganiche che organiche, in relazione alle variazioni di portata fluviale e alle attività biologiche. I risultati ottenuti rilevano la grande importanza della componente disciolta dell'azoto (media annuale 16 µM) e del fosforo (0,13 µM) nel contribuire alla disponibilità totale di nutrienti (media annuale di azoto organico disciolto: 29 µM e di fosforo: 0,18 µM) e la pronunciata variabilità stagionale, attribuibile principalmente a processi biologici di assunzione e rimineralizzazione. Oltre a rilevare il già noto disequilibrio tra azoto e fosforo inorganico, i risultati ottenuti indicano, per la prima volta, il disequilibrio anche nella componente organica (il rapporto tra azoto e fosforo organico varia tra 50 e 530), le cui conseguenze potrebbero influire sul fenomeno di formazione delle mucillagini.

Parole chiave: azoto, fosforo, rapporto N/P, Adriatico settentrionale, materia organica disciolta.

Introduction

It is commonly accepted [1-3] that unbalanced ratios between dissolved inorganic nitrogen (DIN) and phosphorus (DIP) may be one of the triggering factors which stimulate extracellular polysaccharide release by marine phytoplankton and that, especially in coastal waters, when proper light conditions are met, this phenomenon may be quite significant [2]. This response has been recently described in the northern Adriatic Sea, which represents a typical situation [4, 5] where availability of dissolved inorganic nitrogen and phosphorus determines a DIN/DIP ratio higher than that required for phytoplankton balanced growth [6, 7]. In this particular basin, where phosphorus seems to be the element in deficiency [8, 9], it has been hypothesized that the high load of dissolved organic matter released by phytoplankton is not efficiently utilised and recycled by the natural bacterial community and would allow, therefore, mucus formation [10].

Within this frame of hypothesis, the purpose of this contribution is to present the availability, the seasonal variability and the ratios between dissolved nitrogen (N) and phosphorus (P), in the western part of the northern

Adriatic basin, focusing, for the first time, on the importance of dissolved organic nitrogen (DON) and phosphorus (DOP) pools. The presented data refer to two sampling stations (S1 and S3) monitored during PRISMA 1 "Biogeochemical cycles" research project (April 1995 - January 1996) where the quantities and the compartment of nitrogen and phosphorus between the inorganic and organic pools have been studied, together with the N/P ratios, in order to obtain a clearer idea of nutrient availability in this system and to investigate the possible factors which may trigger increased polysaccharide exudation.

Materials and methods

During PRISMA 1 "Biogeochemical cycles" research project three fixed stations (S1, S2, S3) were monitored seasonally from April 1995 to January 1996 (Fig. 1). Water samples were collected, in each station, at four hour intervals during two days. The presented data refer to two stations characterised by different hydrological conditions: S1 (44°44'70"N, 12°27'41"E) is directly influenced by the Po river outflow (Po di Goro branch) while S3 (44°14'75"N, 12°46'06"E) is located at a farther distance from the coast and is, therefore, more representative of the basin.

Water samples for the determination of dissolved inorganic and organic nitrogen and phosphorus were collected with 5 litres NISKIN bottles. Samples for the analysis of total dissolved nitrogen (TDN) and phosphorus (TDP) were pre-treated with UV + H_2O_2 photo-oxydation [11] and analysed as sum of nitrates + nitrites and as phosphate. TDN, TDP and inorganic nutrients were measured according to Alpkem-Perstorp flow solution methodologies [12,13]. DON and DOP were calculated as differences between TDN and DIN, TDP and DIP respectively.

Results

Table 1 presents a brief review of some mean values of dissolved nitrogen and phosphorus reported for different areas of the Mediterranean Sea compared to the annual mean data obtained during four seasonal campaigns within PRISMA 1 "Biogeochemical cycles" research project.

It has already been revealed that, in the Mediterranean basin, availability and ratio between dissolved nitrogen and phosphorus present some anomalies in comparison with typical oceanic environments where nutrients are

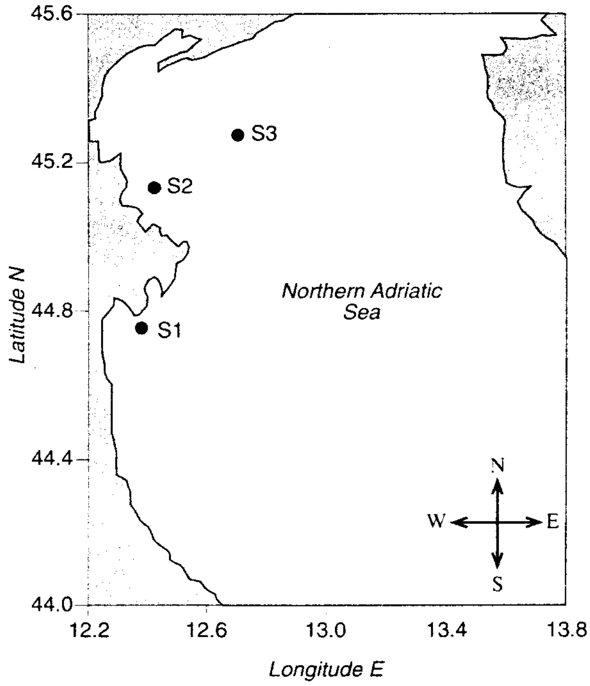

Fig. 1. - Sampling stations of the PRISMA 1 "Biogeochemical cycles" research project in the western part of northern Adriatic Sea.

Table 1. - Review of DIN, DON (μmol l^{-1}-N) and DIP, DOP (μmol l^{-1}-P) available in different areas of the Mediterranean basin

Areas	DIN	DON	DIP	DOP	Reference
Gibraltar Strait (Atlantic water)	4.0	5.5	0.23	0.10	[14]
Gibraltar Strait (Mediterranean water)	8.6	3.0	0.43	0.02	[14]
Provencal Basin	8.2	-	0.39	0.05	[15]
Black Sea	2.1	18.0	0.18	0.15	[16]
Marmara Sea	9.7	3.0	1.00	0.05	[16]
Northern Adriatic Sea	**12.5**	**16.5**	**0.05**	**0.13**	**PRISMA 1**

DIN: dissolved inorganic nitrogen; DON: dissolved organic nitrogen; DIP: dissolved inorganic phosphorus; DOP: dissolved organic phosphorus.

present in quite regular proportion [6]. In this basin, organic components and continental inputs play an important role in determining the N and P content and a DIN/DIP ratio which is higher than the Redfield ratio [6, 14, 15]. However, the data presented in Table 1 show also significant differences among different areas of the Mediterranean basin. The western part of the northern Adriatic Sea reveals, in fact, a high amount of total dissolved nitrogen with a very important DON contribution (16.5 μmol l^{-1}) comparable only with the Black Sea [16], while the high DIN concentration (12.5 μmol l^{-1}) is mainly determined by direct outflow of the Po river, which is the largest Italian river.

Phosphorus seems generally to be the element in deficiency in the whole basin, but the data of the northern Adriatic Sea show a particular low concentration of DIP (0.05 μmol l^{-1}) and a clear predominance of the DOP fraction (0.13 μmol l^{-1}). Furthermore, our data indicate the prevalence, on the annual mean, of the organic fractions in both nitrogen and phosphorus dissolved pools which is not common elsewhere in the Mediterranean waters.

The amounts of TDN and TDP available in different seasons are shown in Fig. 2 which presents the integrated values over the whole water column (mmol m^{-2}) of inorganic and organic nitrogen and phosphorus at S1 and S3 sampling stations.

As far as nitrogen is concerned, the Po river contribution is evident in station S1, as revealed by the high amounts of DIN, ranging from 170 up to 750 mmol m^{-2}, and by the high seasonal variability. On the other hand, being distant from direct continental inputs, station S3 is characterised by a lower and more constant availability of DIN (about 100 mmol m^{-2}), and by a higher percentual weight (from 62 up to 88%) of the organic fraction. The amount of DON is not directly ascribable to continental inputs but rather to biological processes within the basin. The annual mean DON in the Po river (14.3 μmol l^{-1}) is, in fact, only about 7% of TDN in river water (200 μmol l^{-1}, Camusso, IRSA Brugherio, personal communication) while the bar graph shows that in both stations DON always represents a quite conspicuous percentage of TDN in seawater (from 47% up to 88%), with the highest value in the station S3 (670 mmol m^{-2}).

Considering phosphorus, a clear continental input of DIP is present in S1 ranging from 0.3 up to 8 mmol m^{-2}, while S3 presents lower concentrations (less than 1.3 mmol m^{-2}) and a higher importance of the organic fraction which, in the most extreme case, constitutes almost 100% of TDP (April 1995). Both stations show a sharp decrease of DIP related to an increase of the DOP pool as a consequence of biological activity related to phytoplankton bloom when passing from winter to spring.

The N/P ratios calculated for both the inorganic and the organic fractions from the mean values of all data of DIN, DIP, DON and DOP concentrations reveal a clear seasonal fluctuation which is common to both stations. Fig. 3 presents the temporal evolution of the DIN/DIP and DON/DOP ratios in stations S1 and S3 in comparison to the ratio in the Po river waters, expressed as annual average (Camusso, IRSA Brugherio, personal communication).

It is evident that already the freshwater of the Po river outflow presents an unbalanced N/P ratio, revealing a higher nitrogen content, especially in the inorganic fraction (DIN/DIP = 108).

In winter, usually characterised by reduced biological activity, DIN/DIP and DON/DOP ratios in both stations appear quite similar to those reported for the riverine contribution.

In concurrence with the beginning of spring algal bloom, DIN/DIP ratio sharply increases (up to 683 in S1 station, up to 6171 in S3 station), mainly due to limited availability of DIP which is almost depleted (Fig. 2) particularly in S3 station. According to the classical evolution of the phenomena which link primary production, nutrient uptake and subsequent dissolved organic matter release, the spring phytoplankton bloom has determined a clear shift from DIP to DOP pool. In the same season, in both stations DON/DOP ratio remains low (49 and 60 respectively) and close to the winter ratio, probably because DON has not yet accumulated through biological processes (Fig. 2), and DOP is, on the contrary, present in relatively high amounts.

In summer DIN/DIP ratio lowers in both stations (218 and 181) because of increased availability of phosphate, probably due to the decline of the spring bloom and to faster turnover rate of DIP regeneration in comparison to nitrogen. DON/DOP ratio presents, on the contrary, a sharp increase (314 and 529) due to DON accumulation in the system as a consequence of phytoplankton bloom, which does not seem to be balanced by recycling processes through the microbial community.

In autumn both ratios decrease, tending to winter values; this season seems, therefore, to be mainly characterised by regenerative processes which lead to remineralization of dissolved organic matter.

Conclusions

The inclusion of DON and DOP in the dissolved nutrient pool shed a new light upon the real availability of nitrogen and phosphorus in the western part of the northern Adriatic. The organic fractions may, in fact, represent up to 80% and 100% of total dissolved nitrogen and phosphorus, respectively, reaching concentrations up to 40 μmol l^{-1} of DON and 0.4 μmol l^{-1} of DOP, in the

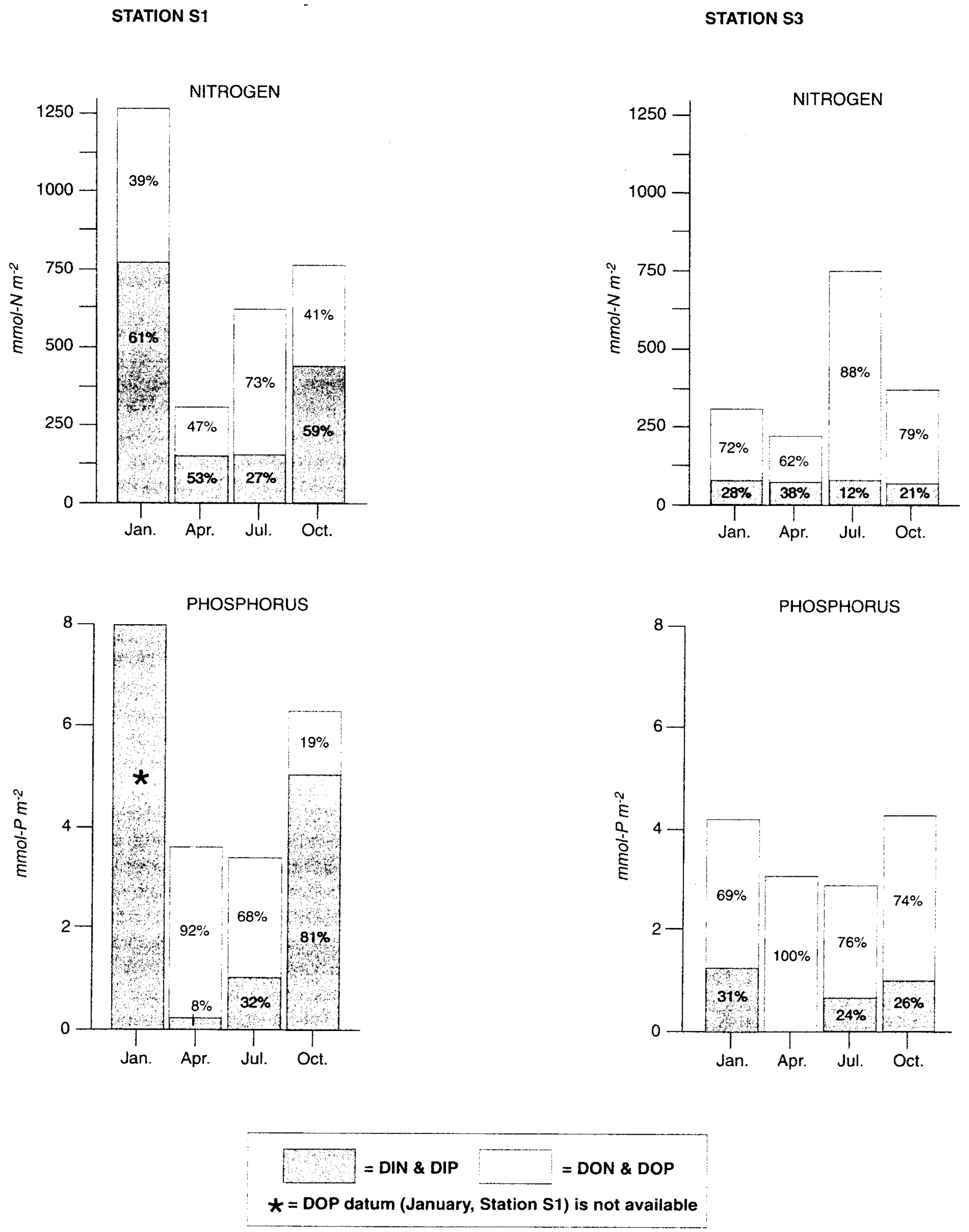

Fig. 2. - Column integrated amounts of dissolved nitrogen and phosphorus in inorganic and organic compartments, expressed in mmol-N m^{-2} and mmol-P m^{-2} respectively, measured in station S1 and S3 of the PRISMA 1 "Biogeochemical cycles" research project. DIN: dissolved inorganic nitrogen; DIP: dissolved inorganic phosphorus; DON: dissolved organic nitrogen; DOP: dissolved organic phosphorus.

station far from direct continental inputs. This high organic content can be encountered, in the Mediterranean basin, only in some peculiar environments such as the Black Sea, which is known as the world's largest permanent anoxic basin due to high river input, strong vertical stratification and limited water exchange [17]. On the other hand, the prevalence, on the annual mean, of the organic fractions in both nitrogen and phosphorus dissolved pools, and the scarce availability of DIP are important peculiarities of the northern Adriatic Sea in comparison to rest of Mediterranean basin.

The temporal trends of N/P ratios of inorganic and organic fractions seem quite correlated with the classical succession of biological processes characterised by an initial phytoplankton bloom which causes inorganic nutrient consumption, in some cases depletion, and leads to the production of high amounts of particulate and dissolved organic matter which form the main substrate for successive bacterial activity [18,19]. It is already well documented how DIN/DIP ratios influence the classical trophic web; the present work points out, for the first time, that there is also an "unbalance" in the DON/DOP ratio, whose consequences must still be considered.

In conclusion, as the northern Adriatic Sea represents a typical example of high DON and DOP availability, a significant seasonal trend and high N/P ratio, further research is needed in order to achieve a better understanding of the effects of these characteristics on the classical food web, on the microbial activity and thereby also on the phenomena of mucilage formation.

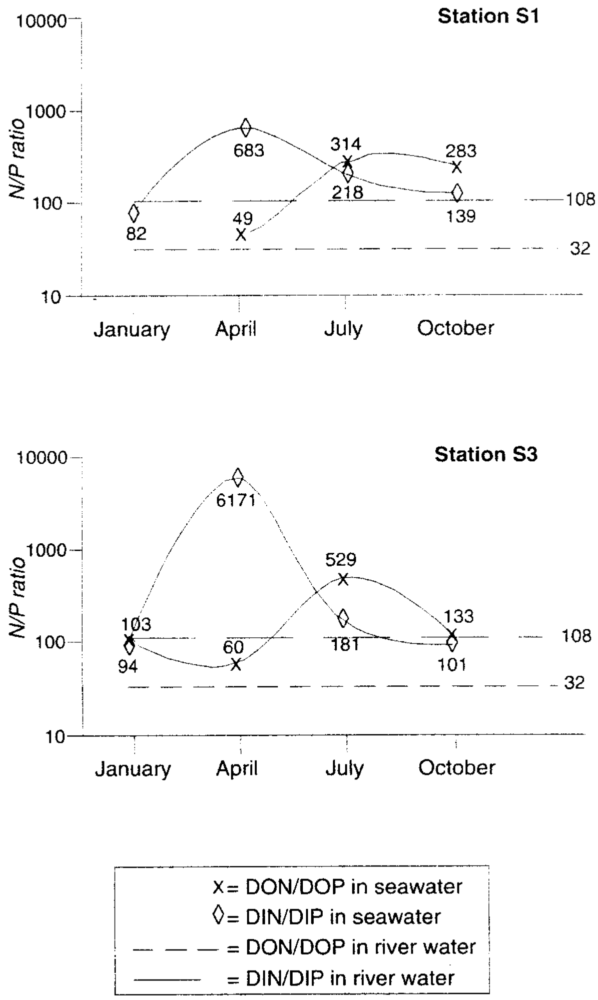

Fig. 3. - N/P ratio in the northern Adriatic Sea. Seasonal fluctuations of DIN/DIP and DON/DOP ratios measured in station S1 and S3 of the PRISMA 1 "Biogeochemical cycles" research project. DIN: dissolved inorganic nitrogen; DIP: dissolved inorganic phosphorus; DON: dissolved organic nitrogen; DOP: dissolved organic phosphorus.

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