Comparison of N/P ratios of particulate organic and dissolved inorganic nutrients in the upper layer water of the NE Mediterranean Sea

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Abstract- The Eastern Mediterranean is a typical oligotrophic sea, due to limited nutrient input from internal and external sources with unexpectedly high ratios of dissolved inorganic nitrogen to reactive phosphate. Long-term data on dissolved inorganic nutrients and suspended particulate organic matter (POM) were examined in the north-eastern Mediterranean upper layer between 1991 and 1998. Both dissolved and particulate N:P ratios were calculated in coastal and off-shore areas. C:N:P ratios in POM were also estimated by regression analyses. The aim is to understand factors responsible for the spatial and temporal variations of both the concentrations and N/P ratios of dissolved and particulate nutrients in the upper layer waters, leading to some suggestions for the high N/P ratios in the Mediterranean deep waters.

Keywords- dissolved and particulate N/P molar ratio, Northeastern Mediterranean

Introduction

Suspend particulate organic matter (POM; also called seston) in the marine environments is the relatively slow-sinking, bulk fraction of total POM and consists of phytoplankton, microzooplankton, aggregates of bacteria and detrital material. The elemental composition (C:N:P ratio) of POM produced photosynthetically in the sea under optimal growth conditions is expected to have a nearly invariant chemical composition known as Redfield C:N:P ratio of 106:16:1 (Goldman et al., 1979). However, this conventional ratio varies in space and time, depending on species composition, nutrient availability and light limitation in the marine environments (Goldman et al., 1979; Saksaug et al., 1983). In the Mediterranean deep waters, molar ratios of nitrate to phosphate are anomalously high and range from 22.5 in the western basin (Coste et al., 1984) to 28 in the eastern Mediterranean deep waters (Krom et al., 1991). Seawater leachable fractions of atmospheric deposition have an average (NO_3+NH_4): PO_4 ratio of 133 (Herut, et al., 2002), and the deep water has unusually high NO_3/PO_4 ratio (26-28) (Yılmaz and Tuğrul, 1998). Particulate Organic Carbon (POC), Nitrogen (PON) and Phosphorus (PP) maxima are associated with the Deep Chlorophyll Maximum (DCM) in the Mediterranean and in general the vertical trends coupled in the upper water column (Abdel-Moati, 1990; Ediger et al., 1998; Dovel et al., 1999).

Methodology

Water samples for biochemical measurements were collected from the stations shown in Fig.1, using 5 l Niskin bottles on a rosette system attached to a Sea-Bird Model CTD probe. Sub-samples for particulate organic carbon (POC), nitrogen (PON) and total phosphorus (PP) analyses were filtered through GF/F type filters which were kept frozen until analysis on land (Polat and Tuğrul, 1995). Filters were analysed using a Carlo Erba 1108 CHN analyser. The filters for PP analysis were determined by following the conventional colorimetric method (Polat and Tuğrul, 1995). The automated inorganic nutrient measurements and the spectrofluorometric chlorophyll-a (CHL-a) analyses were carried out by the methods of Grasshoff (1983) and Holm-Hansen et al., (1965).

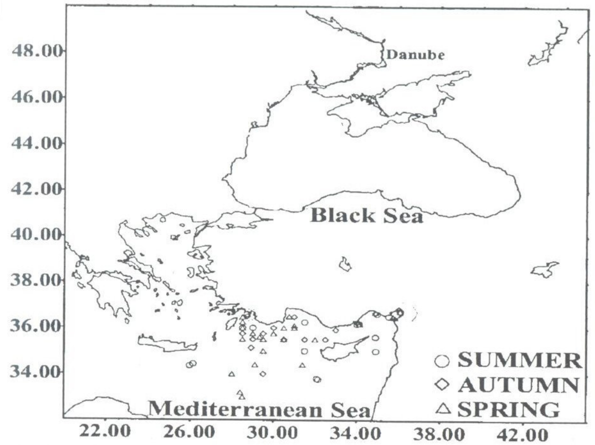

Fig. 1. Sampling stations visited in the Mediterranean Sea during 1991-1998

Results and Discussion

The layer-averaged concentrations of dissolved nutrients and N:P (NO_3+NO_2:PO_4) molar ratios estimated for the euphotic zone are given in Table 1. The water masses below the euphotic zone have always-high N:P ratios (~28) (Yılmaz and Tuğrul, 1998). As depicted in Table 1, N:P ratios as average between 1991 and 1998 in the euphotic zone were low, especially in stratification periods. Whilst the ratio may be as high as 38 when the water column is vertically mixed and nutrient concentrations were relatively high. In the coastal waters dissolved N:P ratios ranging between 1-27 (Table 1).

Depth averaged concentrations and ratios of POM for the euphotic zone are given in Fig. 2. The depth-averaged concentrations of POC, PON and PP in the euphotic zone of the off-shore waters between 1991-1998 were respectively in the ranges of 1.44-5.18, 0.06-0.68, 0.01-0.037 μM (Fig. 2). Vertical distribution of POM and Chl-a in the cyclonic region are given in fig. 3. The particulate concentrations reached the peak values at the base of the euphotic zone, (Fig. 3) when the surface layer is seasonally stratified (as an example oct-1991 and july-1993 in fig. 3) and thus, depleted in nutrients available for photosynthesis. Therefore, the input from nutricline depths enhances the shade-adapted algal production, yielding both particulate and Chl-a maxima at the bottom of the euphotic zone (Fig. 3). The vertical distribution of POM in the euphotic zone in winter appeared to be consistent with that of Chl-a. (Fig. 3). Under the prolonged winter condition of 1992, the Levantine deep waters with their associated chemical properties occupied the surface layer (Ediger et al., 1998). Efficient convective mixing in the upper layer led to the formation of vertically uniform POM and Chl-a profiles in the core of the cyclonic area (Fig. 3).

Table 1. 1991-1998 period NO_3+NO_2 (NO_X)-PO_4 concentration and ratio ranges in the euphotic zone of the NE Mediterranean Sea

REGION		OFF-SHORE	NEAR-SHORE
DATA	SEASON	MED.SEA	MED.SEA
NO_X(µM)	*Spring*	0.04-2.95	0.04-3.61
	Summer	0.03-2.79	0.07-1.22
	Autumn	0.04-2.01	0.17-0.48
PO_4(µM)	*Spring*	0.02-0.19	0.02-0.04
	Summer	0.02-0.04	0.02-0.04
	Autumn	0.02-0.07	0.02-0.11
NO_X/PO_4	*Spring*	2-16/38	1-27
	Summer	5-8	1-24
	Autumn	2-6	2-16

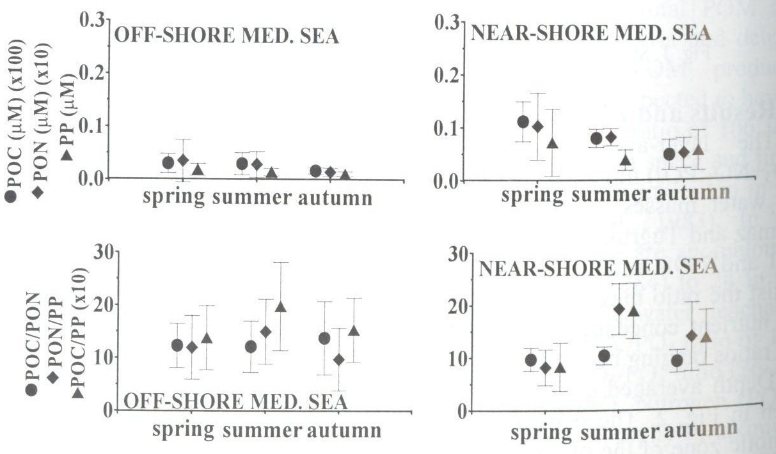

Fig. 2. Euphotic zone seasonal averages of POM concentrations and molar ratios in the NE Mediterranean during 1991-1998

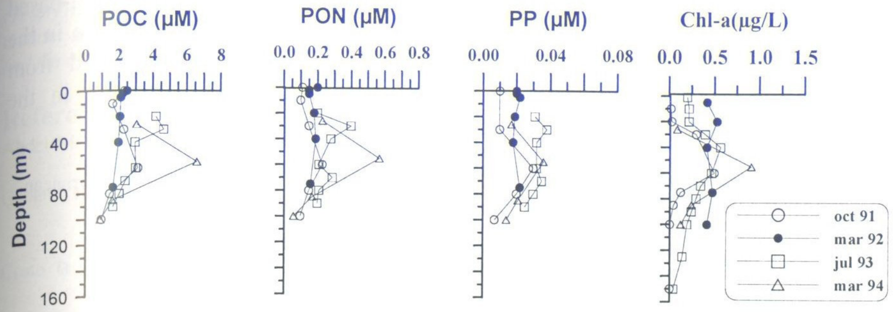

Fig. 3. Vertical profiles of POC, PON, PP and CHL-a in the cyclonic region of NE Mediterranean

The observation of the subsurface peaks in both the POM and Chl-a profiles in the NE Mediterranean (fig. 3) and estimates of POC:CHL-a ratios, from slopes of the regression equations in the area (in the ranges of 45 and 201) (Ediger et al., 1998), suggesting that the abundance of POC in the euphotic zone, especially in near bottom of the euphotic zone, is principally determined by the algal biomass produced *in situ*.

Not unexpectedly, depth-averaged POC:PON and POC:PP ratios of seston in the euphotic zone of the open Mediterranean Sea are mostly greater than the Redfield ratios indicating that the seston was mainly composed of non-living biogenic particles (detritus) and rich in carbonaceous compounds. The depth-averaged POC:PON ratios of bulk seston are nearly constant during year (Fig. 2). Summer and autumn POC:PON ratios of seston are in good harmony with the ratios derived from the POC-PON linear regressions for the coastal waters (Fig. 2 and Table 2). These findings indicate that the abundance of biogenic POM in the euphotic zone has increased with almost constant POC:PON ratios in the near-shore in summer and autumn but with smaller ratios in the spring. However, changes in the seston content of the open sea have occurred with lower POC:PON ratio relative to average composition of seston depicted in Fig. 2, but comparable with the conventional Redfield ratio.

N:P ratio of POM ranging seasonally between 7 and 9, were lower in coastal waters than in the open sea (10-15) (Table 2). On the other hand, the PON:PP ratios were generally low (Fig. 2) although primary production in the Mediterranean Sea was known to be potentially limited by reactive phosphate because the water masses below the euphotic zone have always-high N:P ratios. Unexpectedly low N:P (8.6) ratio of POM was also observed during intense bloom period (March 1992) in cyclonic area of NE Mediterranean. POM is still contained less organic nitrogen as compared to its P components during bloom period. Such low N:P ratio of the bulk seston suggests that POM is exported to the lower depths with much lower N:P ratios than that of N:P (26-28) in the deep water. This contrary view strongly suggests that some fraction of PP measured in the surface water may have been of non-biogenic (most probably atmospheric) origin, which reduces the PON:PP ratio of the seston. Moreover, atmospheric and land-based phosphorus inputs influence the POC:PP and PON:PP ratios of bulk seston in the near-shore waters. Interestingly, such nutrient deficiencies as observed from dissolved N:P ratios and bioassay experiments were not as apparent in the elemental composition of seston.

Table 2. Regression equations of particulate variables in the euphotic zone of the NE Mediterranean

SEASON	OFF-SHORE MED. SEA			C:N:P
SPRING	POC=8.0 PON+1.2 POC=105PP+0.84 PON=11PP+0.03	R=0.91 R=0.78 R=0.73	N=113 N=108 N=94	105:11:1
SUMMER	POC=7 PON+0.82 POC=113 PP+0.79 PON=15 PP+0.01	R=0.94 R=0.64 R=0.71	N=48 N=41 N=41	113:15:1
AUTUMN	POC=5.3 PON+0.78 POC=109 PP+0.60 PON=9.5 PP+0.04	R=0.77 R=0.92 R=0.81	N=45 N=11 N=9	109:10:1
SEASON	NEAR-SHORE MED. SEA			C:N:P
SPRING	POC=6.4 PON+3.9 POC=51.5 PP+7.3 PON=9.4 PP+0.35	R=0.95 R=0.94 R=0.94	N=9 N=8 N=9	52:9:1
SUMMER	POC=9.3 PON+0.12 POC=77 PP+4.9 PON=7.0 PP+0.54	R=0.94 R=0.77 R=0.70	N=20 N=21 N=21	77:7:1
AUTUMN	POC=9.7 PON-0.14 POC=64 PP+2.6 PON=7 PP+0.23	R=0.96 R=0.97 R=0.94	N=16 N=11 N=11	64:7:1

Conclusions

- The nutrient-depleted offshore waters of the NE Mediterranean are relatively poor in seston as compared to the near-shore waters,
- In the coastal waters PON:PP ratios were lower than in the open sea, due to the accumulation of non-biogenic particulate phosphorus in the surface waters,
- POC:PON ratio in the euphotic zone of the open Mediterranean Sea were generally greater than the average ratio of oceanic phytoplankton, due to the contribution of detritus to the POM pool,
- Sinking POM to depths with low PON:PP ratios is unlikely to yield high N:P ratio during its aerobic decomposition in the water column,
- High N:P ratios observed in the deep water might have either originated by the decomposition of dissolved organic nitrogen selectively enriched in the cold waters before sinking at its origin or by selective removal of PO_4 from the deep water by fast-sinking lithogenic particles,

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