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## A comparative study on the abundance and elemental composition of POM in three interconnected basins: the Black, the Marmara and the Mediterranean Seas

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## Abstract

The abundance and elemental composition of suspended particulate organic matter in the upper layers of the interconnected Mediterranean, Marmara and Black Seas having different ecosystems were determined in 1990-1998. The aim was principally to compare the C:N:P ratio of seston and understand factors controlling the seston composition in near- and off-shore waters of these seas. In the Marmara Sea, euphotic zone average particulate concentrations varied regionally and seasonally between 10-35  $\Box M$ for POC,  $0.4-4.5 \square M$  for PON and  $0.05-0.45 \square M$  for PP. These concentrations are mostly above the offshore Black Sea values but much greater than those measured in the open waters of the north-eastern Mediterranean whose near-shore data are comparable with the seston content of the deep Black Sea.

Comparison of C:N:P ratios of seston reveals that atmospheric and land-based phosphorus input influences the C:P and N:P ratios in the near-shore waters. Apparent nutrient deficiencies observed in the water column were not as remarkable in the elemental composition of seston. Unexpectedly, in the NE Mediterranean, N:P ratios from regression analyses of particulate data are very low (7-9) in the coastal region but slightly increase to levels of 10-15 in the open sea. In the Sea of Marmara, the N:P ratios (7-12) of seston are as low as in the Mediterranean, being consistent with the particulate ratios of the Black Sea inflow and NO3:PO4 ratios of the Marmara sub-halocline water. The Black Sea seston is relatively rich in carbonaceous compounds with N:P ratio ranging merely between 15-17 in the open sea but 9-27 in coastal waters where riverine discharges markedly influence the stoichiometry of seston.

Keywords: Black, Mediterranean, Marmara Seas, POM concentration, C:N:P ratio.

## Introduction

Suspend particulate organic matter elemental composition (C:N:P ratio) of (POM; also called seston) in the marine POM produced photosynthetically in the environments is the relatively slow-sinking, bulk fraction of total POM and consists of expected to have a nearly invariant chemical phytoplankton, microzooplankton, aggregates of bacteria and detrital material. The

sea under optimal growth conditions is 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). Since it is principally produced and mostly oxidised in the upper layer of the oceans, suspended POM is of critical importance to bio-mediated chemical processes and thus cycling of many chemicals in the water column having different biogeochemical properties and redox conditions (COPIN-MONTEGUT & COPIN-MONTEGUT, 1983), besides the estimations of biomass and trophic states of marine ecosystems (VOSTOKOV, 1996).

The aim of this study is to contribute to further understanding of the abundance and elemental composition of seston in the landlocked Black, Mediterranean and Marmara Seas having different ecosystems. In the course of the present study, the major components (C,N,P) of seston collected from the upper layer waters were determined so as to understand the variations in abundance and elemental composition of POM with season and region, and ultimately to compare the composition of bulk POM produced in the euphotic zones of these three seas.

The Black Sea is a relatively productive, very deep, land-locked basin connected to the Aegean basin of the eastern Mediterranean through the Sea of Marmara via Bosphorus the straits of and Dardanelles. It is the unique marine environment possessing the oxygenated waters in the surface and anoxic, sulphide bearing waters in the deep basin throughout the year. A permanent halocline below 50-70 m from the surface separates these two layers during the year. The halocline waters below the winter mixing zone have similar chemical properties at similar density surfaces due to relatively strong lateral flows over the deep basin (TUGRUL et al., 1992; MURRAY et al., 1995). Since the halocline limits the ventilation of deep waters, transport of biogenic one of the oligotrophic seas over the world,

particles from the productive surface layer keep the sub-halocline waters anoxic and sulphidic during the year (SOROKIN,1993). The Black Sea receives large amounts of nutrients via rivers which have been heavily polluted by industrial and domestic waste discharges during the last 30 years (MEE, 1992; COCIASU et al., 1997). Such a large riverine input has resulted in intense eutrophication especially in the wide northwestern shelf waters flowing cyclonically towards the Bosphorus region. Consequently, the Black Sea ecosystem has changed dramatically in recent decades (MEE, 1992).

Since there exists a large salinity difference between the exchange flows of Marmara and Black Sea in the straits, a twolayer ecosystem is formed permanently in the Sea of Marmara (BESIKTEPE et al., 1994). A sharp halocline of 15-20 m thick separates the upper and lower waters throughout the basin. The brackish upper layer is relatively thin (10-15 m) and always occupied by the Black Sea water, with seasonally variable hydro-chemical properties (POLAT et al., 1998). It is further contaminated by waste discharges from the city of Istanbul to the Bosphorus (ORHON et al., 1994) and by intrusion from the Marmara sub-halocline waters at the Marmara-Bosphorus junction (Polat & Tugrul, 1995; Tugrul & POLAT; 1995). Solar irradiance occasionally penetrates down to the lower boundary of the halocline in summer months and thus primary production is always confined to in the upper layer waters including the halocline depths during the less productive periods. The Marmara upper layer is renewed twice per year by the nutrient-rich Black Sea inflow via the Bosphorus. Recent flux estimates indicate that the natural input of nutrients from the Black Sea exceeds the total annual (industrial + domestic + rivers) discharges from land into the Marmara ecosystem (TUGRUL & POLAT, 1995).

The eastern Mediterranean is known as

due to limited nutrient input to its surface waters from external and internal sources (BETHOUX, 1981; DUGDALE & WILKERSON, 1988). However, in the cyclonic Rhodes region where the nutricline is located at the base of the euphotic zone (45-80 m), diffusive processes and vertical mixing in winter introduce dissolved inorganic nutrients from the lower layers into the productive zone and sustain primary productivity at certain levels during the year (EDIGER et al., 1999). On the other hand, the nutricline is generally thicker and located far below the euphotic zone of anticyclonic regions and their peripheries in the eastern Mediterranean. Therefore, even during winter mixing, only limited amounts of nutrients are supplied from the lower layers to the euphotic zone and the annual primary production is relatively less in these waters where solar irradiance can penetrate down to 100-120 m (1% light depth) during spring-autumn period.

### Methodology

Water samples for biochemical measurements were collected from the staions shown in Figure 1, using 51 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 & TUGRUL, 1995). Briefly, the POC and PON filters were dried at 50-60 °C overnight and then exposed to hydrochloric



Fig.1: Sampling stations visited in Black, Marmara and Mediterranean Seas during 1990-1998.

acid fumes to remove all inorganic carbonates. Re-dried filters were analysed using a Carlo Erba 1108 CHN analyser. The filters for PP analysis were combusted at 500° C for 3 hours, treated with 12 ml of 0.5 N HCl and filtered. After adjusting the pH to 8, the total phosphorus in the digested solution was determined by following the conventional colorimetric method (POLAT & TUGRUL, 1995). Between 1990-1998, about 180, 250 and 350 POM samples, collected from the stations shown in Figure 1, were analysed for summer, autumn and spring periods, respectively. Related hydrographic and biochemical parameters, such as dissolved inorganic nutrients (NOx, PO<sub>4</sub>), dissolved oxygen (DO), chlorophll-a (CHL-a), temperature, salinity and light penetration were determined simultaneously at the same locations, following the conventional methods (YILMAZ et al., 1998; POLAT et al., 1998, EDIGER et al., 1999). A Licor, Model 185 quantameter was used to measure the light penetration. 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 and Riemann (1978).

## **Results and Discussion**

The Southern Black Sea: Particulate data obtained in off- and near-shore waters between 1990-1998 indicate remarkable variations with season and region. The depth-averaged concentrations for the euphotic zone of the southern Black Sea ranged seasonally between 28.6-5.55 µM for POC, 3.1-0.69 μM for PON, 0.115-0.034 μM for PP. These mean values are comparable to those measured in different regions of the open Black Sea in the last decade (Lyutsarev & Shanin, 1996; Burlakova et al., 1997; KRIVENKO et al., 1997). As shown in typical summer profiles in Figure 2, the particulate concentrations decrease markedly below the euphotic zone to background levels of 1-4  $\mu$ M for POC, 0.1-0.3  $\mu$ M for PON and 0.01-0.03  $\mu$ M for PP in the oxic/anoxic transition (suboxic) zone. Interestingly, the particulate profiles display a coherently rising trend again in the suboxic-anoxic interface of both open and near-shore regions and reach the peak levels in the upper boundary of sulphide-bearing waters. The deep layer particulate maxima are more pronounced for PP, especially in the rim-currents where a fine particle layer (mainly of non-biogenic origin) selectively enriched with phosphorus is formed throughout the year (KEMPE *et al.*, 1991).

In the seasonally stratified surface waters of the Black Sea, CHL-a profiles display a sub-surface maximum at the base of the euphotic zone (Fig. 2) where the rate of primary production was very low due to insufficient light intensity (YAYLA *et al.*, 1999). Since the observed summer CHL-a maximum does not coincide with POC profile, POC/CHL-a ratio declines at the base of the euphotic zone. It is principally due to less organic carbon synthesis per CHL-a by shade-adapted cells (COBAN-YILDIZ *et al.*, 1999).

Figure 3 shows the seasonal variations of depth-averaged POM data in the euphotic zone of the studied three seas. In the open Black Sea, relatively low spring concentrations (mostly measured in April-May) may have been due to effective removal of photosynthetic particles by sedimentation and grazing pressure after bloom. The spring particulate concentrations in the near-shore surface waters including rim-currents of the Black Sea display pronounced regional and inter-annual variations in 1990-1998 (Fig.3). This seasonal trend is consistent with the increasing influence of riverine inputs on the coastal water ecosystems during the spring months.

Not unexpectedly, seasonal changes in the NOX:PO4 ratio of the euphotic zone (Table 1) were much more pronounced than in the PON:PP ratio (Fig. 4) because phytoplankton uptake dissolved inorganic nutrients



*Fig. 2:* Typical vertical profiles of POC ( $\bullet$ ); PON ( $\diamond$ ); PP( $\blacktriangle$ ) and CHL-a (+) in Black, Marmara and Mediterranean Seas.

with much less variable proportions for its metabolism even in the nutrient-depleted surface waters. During the spring-autumn period of 1990-1998, the surface waters of cline, where dissolved nutrients accumulate the open Black Sea possessed low nitrate  $(0.02-1.97 \ \mu\text{M})$  and phosphate  $(0.02-1.15 \text{ estimated from the above individual meas-$ 

 $\mu$ M) concentrations. The higher ratios were observed in such locations that the base of the euphotic zone coincides with the nutridue to remineralisation. NOx:PO4 ratios



*Fig. 3:* Euphotic zone seasonal averages of POC ( $\bullet$ ), PON ( $\bullet$ ), and PP ( $\blacktriangle$ ) concentrations in Black, Marmara and Mediterranean Seas, measured during 1990-1998, with sample standard deviations.

urements range seasonally between 1 and 10 which are much lower than the Redfield ratio of 16 and thus, strongly suggest nitrogen-limited algal production in the offshore Black Sea. However, the NOx:PO4 molar ratio in the near-shore water appeared to vary markedly from 2 to 40, the most variable ratios being observed in spring, depending on river fluxes and nutrient-uptake efficiency of phytoplankton. The results of limited number of bio-assay experiments indicate nitrogen-limited primary production in the open sea, which is consistent with the lower NOx:PO4 ratios, whilst the phosphorus-limited production proceeded in the near-shore water of the southern Black Sea in July 1997, March-April 1998 and September 1998 (YAYLA et al., 1999). Seasonal averages of PON:PP ratios of seston were in the range of 13 and 16 in the open waters of the Black Sea, being quite comparable with the Redfield ratio. This finding indicates the importance of labile

DON for phytoplankton production, especially in the seasons when the surface waters were poor in dissolved inorganic nutrients. The existence of vertically migrating phytoplankton species such as *Rhizoselenia alata* (E. EKER, unpublished data) could be another source for the transportation of dissolved inorganic nutrients input to the euphotic zone. The PON:PP ratios of seston were more variable in the near-shore waters, seasonal averages ranging between 15-21.

Regression analyses of particulate data enable us to understand the extent of correlation between the C, N, and P components of suspended POM in the euphotic zone (Table 2). In the open Black Sea, PON-PP correlation is insignificant in spring, when the POM concentrations were quite variable. On the other hand, in summer and autumn, PON:PP ratios derived from the slopes of the linear regressions are respectively 15.6 and 14.5, being comparable with Table 1

| REGION 🔶                         |        | OFF-SHORE |           | NEAR-SHORE |           |           |
|----------------------------------|--------|-----------|-----------|------------|-----------|-----------|
| DATA                             | SEASON | BL.SEA    | MED.SEA   | BL.SEA     | MED.SEA   | MAR.SEA   |
|                                  | Spring | 0.02-1.13 | 0.04-2.95 | 0.02-4.14  | 0.04-3.61 | 0.07-4.11 |
| $NO_X$                           | Summer | 0.02-0.87 | 0.03-2.79 | 0.02-0.79  | 0.07-1.22 | 0.02-0.95 |
| (µM)                             | Autumn | 0.03-1.97 | 0.04-2.01 | 0.04-1.53  | 0.17-0.48 | 0.06-0.73 |
|                                  | Spring | 0.02-1.15 | 0.02-0.19 | 0.02-0.21  | 0.02-0.04 | 0.02-0.25 |
| ΡΟ <sub>4</sub><br>(μΜ)          | Summer | 0.02-0.14 | 0.02-0.04 | 0.02-0.21  | 0.02-0.04 | 0.04-0.2  |
|                                  | Autumn | 0.02-0.96 | 0.02-0.07 | 0.02-0.22  | 0.02-0.11 | 0.02-0.21 |
| NO <sub>X</sub> /PO <sub>4</sub> | Spring | 1-7       | 2-16/38   | 6-40       | 1-27      | 2-12      |
|                                  | Summer | 2-10      | 5-8       | 2-12       | 1-24      | 1-6       |
|                                  | Autumn | 2-8       | 2-6       | 2-8        | 2-16      | 2-7       |

1990-1998 period NOx-PO4 concentration and ratio ranges in the euphotic zones of Black, Marmara and Mediterranean Seas.

the Redfield ratio of 16. The open sea POC:PON ratio is relatively high in summer; but the spring and autumn values approach the conventional planktonic ratio of 6.7. POC:PP ratios estimated from the regressions are variable and much above the Redfield ratio of 106.

In the near-shore waters of the Black Sea the slopes of the regressions vary remarkably with season, indicating the influence of riverine input on the chemical composition of suspended POM (Table 2). Markedly high POC:PP and POC:PON ratios indicate that carbonaceous rich organic compounds dominate the seston abundance. Interestingly, high negative intercepts appeared in the linear regressions of the spring and autumn POC-PP and PON-PP data sets, obtained in the near-shore waters. Moreover, the seasonal averages of the PON:PP ratios in Figure 4, calculated from the individual measurements, apparently differ from the slopes of the PON-PP regressions in Table 2. This difference may have originated from the increasing contribution of non-biogenic phosphorus in the seston as PP concentrations drop to the background levels in the euphotic zone. This factor results in misleading conclusions in the regression analysis of particulate data.

<u>The Sea of Marmara:</u> Since primary production is confined to the less saline upper layer and sustained by both new and regenerated nutrients, suspended POM content of this layer is apparently higher than in the Black Sea (Fig. 3). The depth-averaged particulate concentrations for the euphotic zone ranged regionally and seasonally between 13-35  $\Box$ M for POC, 0.4-4.5  $\Box$ M for PON and 0.08-0.45  $\Box$ M for PP. No apparent POM accumulation was observed within the steep halocline located at the bottom of the euphotic zone (Fig. 2). Halocline also limits particle snow to the subhalocline waters as compared to vertical fluxes in the other seas where the density stratification is relatively weak.

The particulate concentrations measured in the deep basin of the Marmara Sea, reaching the peak values in spring, are greater than in the Black Sea inflow at the strait exit, where PP concentrations generally exhibited higher inter-annual variations than POC and PON values (Fig. 3). In the Marmara upper layer, the greatest standard deviation were observed in the spring data due to measurements during both bloom and post-bloom periods (POLAT et al., 1988). In the euphotic zone of the Marmara Sea, PON:PP ratios were variable and generally low while POC:PP and POC:PON ratios were higher than or comparable with Redfield ratio (Fig. 4). This indicates an apparent nitrogen deficiency in photosynthetically produced particulate matter as confirmed clearly by PON-PP regression

#### Table 2

| SEASON | OFF-SHOR             | C:N:P  |      |          |
|--------|----------------------|--------|------|----------|
|        | POC=7.1 PON+1.9      | R=0.82 | N=40 |          |
| SPRING | POC=172 PP+1.39      | R=0.63 | N=30 | 123:17.1 |
|        | insignificant        |        |      |          |
|        | POC=11.8 PON-0.06    | R=0.95 | N=49 |          |
| SUMMER | POC=172 PP-0.28      | R=0.93 | N=37 | 172:16:1 |
|        | PON=15.6 PP+0.0      | R=0.92 | N=37 |          |
|        | POC=7.1 PON+4.1      | R=0.83 | N=56 |          |
| AUTUMN | POC=132 PP+2.3       | R=0.75 | N=32 | 132:15:1 |
|        | PON=14.5 PP-0.09     | R=0.79 | N=32 |          |
| SEASON | NEAR-SHORE BLACK SEA |        |      | C:N:P    |
|        | POC=10.0 PON-1.1     | R=0.99 | N=46 |          |
| SPRING | POC=249 PP-4.3       | R=0.96 | N=31 | 249:27:1 |
|        | PON=27.3 PP-0.5      | R=0.95 | N=31 |          |
|        | POC=13.3 PON-1.36    | R=0.91 | N=21 |          |
| SUMMER | POC=128 PP+2.95      | R=0.82 | N=18 | 128:9:1  |
|        | PON=8.5 PP+0.42      | R=0.87 | N=17 |          |
|        | POC=8.2 PON+2.5      | R=0.89 | N=29 |          |
| AUTUMN | POC=222 PP-3.3       | R=0.95 | N=7  | 222:26:1 |
|        | PON=25.7 PP-0.71     | R=0.91 | N=7  |          |

Regression equations of particulate variables in the euphotic zone of the southern Black Sea.

slopes (Table 3). Regression equations depicted in Table 3 indicate relatively weak correlations between PON-PP data sets for the spring and summer as experienced in spring Black Sea (Table 2), which was attributed to the randomly variable contribution of inorganic phosphorus to PP in some samples. We should note that the intercepts of POC-PON regression equations in Table 3 are apparently high and variable, whereas their slopes are in the range of 6.5-8.7 and much below the seasonal averages of POC:PON ratios obtained from individual measurements (Fig. 4). These findings suggest that the Marmara suspended POM was relatively rich in background carbonaceous compounds (representing about 15-40% of total Marmara Seas (Figure 2), the particulate

POC). However, the suspended POM concentrations of the upper layer increase with POC:PON ratios, similar to the conventional planktonic ratio. The basin-wide POC and CHL-a data have indicated that about 50% of bulk seston was composed of living phytoplankton when the Marmara surface water was more productive and relatively rich in biogenic POM. The abundance and elemental composition of seston in the Marmara euphotic zone were comparable with those in the Black Sea inflow which renew the Marmara upper layer twice a year, on average.

The North-eastern Mediterranean Sea: In contrast to the profiles in the Black and

Table 3

Regression equations of particulate variables in the euphotic zone of the Sea of Marmara.

| SEASON | THE S            | THE SEA OF MARMARA |      |         |  |
|--------|------------------|--------------------|------|---------|--|
|        | POC=8.7 PON+4.6  | R=0.91             | N=61 |         |  |
| SPRING | POC=94 PP+7.8    | R=0.76             | N=40 | 94:9:1  |  |
|        | PON=8.5PP+1.18   | R=0.57             | N=40 |         |  |
|        | POC=7.1 PON+9.2  | R=0.68             | N=23 |         |  |
| SUMMER | POC=112 PP+0.5   | R=0.81             | N=24 | 112:7:1 |  |
|        | PON=7.3 PP+0.33  | R=0.57             | N=24 |         |  |
|        | POC=6.5 PON+4.6  | R=0.91             | N=61 |         |  |
| AUTUMN | POC=86 PP+4.6    | R=0.71             | N=19 | 86:12:1 |  |
|        | PON=11.6 PP+0.02 | R=0.92             | N=19 |         |  |



*Fig. 4:* Euphotic zone seasonal averages of POC:PON ( $\bullet$ ), POC:PP ( $\blacktriangle$ ), and PON:PP ( $\diamond$ ) molar ratios, calculated from individual data of 1990-1998 period in Black, Marmara and Mediterranean Seas, with sample standard deviations.

concentrations reached the peak values at the base of the euphotic zone of the cyclonic regions when the surface layer is seasonally stratified 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. The depthaveraged concentrations of POC, PON and PP in the euphotic zone of the Levantine basin between 1990-1998 were respectively in the ranges of 1.44-5.18, 0.06-0.68, 0.01-0.037 mM. POM concentrations in the open Mediterranean Sea are at least 3-4 times less than the values in Black and Marmara Seas, whereas near-shore data were comparable with the seston content of deep Black Sea (Fig. 3).

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, but they are consistent with the ratios in the Black and Marmara Seas. On the other hand, the PON:PP ratios were generally low (Fig. 4) although primary production in the Mediterranean Sea is known to be potentially limited by reactive phosphate because the water masses below the euphotic zone have always high NO3:PO4 ratios (YILMAZ & TUGRUL, 1998). As depicted in Table 1, NOx:PO4 ratios 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. 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 ses-

#### Table 4

| SEASON | OFF-             | C:N:P  |       |          |
|--------|------------------|--------|-------|----------|
|        | POC=8.0 PON+1.2  | R=0.91 | N=113 |          |
| SPRING | POC=105PP+0.84   | R=0.78 | N=108 | 105:11:1 |
|        | PON=11PP+0.03    | R=0.73 | N=94  |          |
|        | POC=7 PON+0.82   | R=0.94 | N=48  |          |
| SUMMER | POC=113 PP+0.79  | R=0.64 | N=41  | 113:15:1 |
|        | PON=15 PP+0.01   | R=0,71 | N=41  |          |
|        | POC=5.3 PON+0.78 | R=0.77 | N=45  |          |
| AUTUMN | POC=109 PP+0.60  | R=0.92 | N=11  | 109:10:1 |
|        | PON=9.5 PP+0.04  | R=0.81 | N=9   |          |
| SEASON | NEAR             | C:N:P  |       |          |
|        | POC=6.4 PON+3.9  | R=0.95 | N=9   |          |
| SPRING | POC=51.5 PP+7.3  | R=0.94 | N=8   | 52:9:1   |
|        | PON=9.4 PP+0.35  | R=0.94 | N=9   |          |
|        | POC=9.3 PON+0.12 | R=0.94 | N=20  |          |
| SUMMER | POC=77 PP+4.9    | R=0.77 | N=21  | 77:7:1   |
|        | PON=7.0 PP+0.54  | R=0.70 | N=21  |          |
|        | POC=9.7 PON-0.14 | R=0.96 | N=16  |          |
| AUTUMN | POC=64 PP+2.6    | R=0.97 | N=11  | 64:7:1   |
|        | PON=7 PP+0.23    | R=0.94 | N=11  |          |

Regression equations of particulate variables in the euphotic zone of the northern Mediterranenan Sea.

ton. Though the near-shore and open water POM concentrations are seasonally variable (Fig. 3), the depth-averaged POC:PON ratios of bulk seston are nearly constant during year (Fig. 4). Interestingly, 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. However, the regression slopes of the open sea seston are below the seasonal averages of the individual ratios but mostly comparable with the average POC:PON and POC:PP ratios for the oceanic phytoplankton (see Table 4 and Fig. 4). 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 Figure 4, but comparable with the conventional Redfield ratio.

Estimates of POC:CHL-a ratios, from slopes of the regression equations were

mostly in the ranges of 45 and 201 in the northeastern Mediterranean (EDIGER, 1995; EDIGER *et al.*, 1999; COBAN, 1997), 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*. The lower POC:PON ratios of the seston from this zone, together with the decreasing ratios of the relative abundances of carbohydrate to protein markers from the surface to the DCM depths (Y. COBAN-YILDIZ, unpublished data), corroborate the suggestion.

## Conclusions

Unfortunately, no winter data were available to evaluate pre-bloom conditions in the three interconnected seas. The ranges of inter-annual variations of seasonally averaged data for the 1990-1998 period were lowest in the open Mediterranean, and in the Black Sea inflow to the Marmara. Regional and seasonal differences in the euphotic zone seston concentrations become less pronounced during the summer-autumn period (including late spring) when the surface layer is stratified and depleted in biologically labile nutrients and riverine discharges are consumed mostly in shelf regions. The POC:PON ratios calculated from the individual measurements appeared to be relatively high in the euphotic zone of the studied land-locked seas with different trophic status, indicating that the seston was mainly composed of non-living biogenic particles (detritus) and rich in carbonaceous compounds. 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 NOx:PO4 ratios and bioassay experiments were not as apparent in the elemental composition of seston.

In the Black Sea, near-shore surface water is relatively rich in seston with the largest inter-annual changes in the spring while offshore spring data, mostly obtained during post-bloom periods, appeared to be less than the summer and autumn concentrations. The seston of the deep Black Sea, which is relatively rich in carbonaceous compounds, PON:PP ratios derived from individual measurements and regression analyses were almost invariant and comparable with the Redfield ratio, although production is limited by nitrogen due to anomalously low NO3:PO4 ratio in the oxic/anoxic transition zone. However, in the near-shore regions where riverine discharges markedly influence both the abundance and the stoichiometry of seston during the year, PON:PP ratios were much more variable and could deviate from the classical ratio whilst the long-term changes in the POC:PON values have been observed to be very limited.

The Sea of Marmara, which connects the brackish Black Sea to the more saline eastern Mediterranean, has the highest concentrations of suspended POM among the three interconnected seas visited seasonally in 1990-1998. Relatively high PP content of seston in the Marmara upper layer has been observed to lower the NO<sub>3</sub>:PO<sub>4</sub> ratios to levels of 8-12 in the sub-halocine waters. Very low PON:PP ratios derived from the slopes of regression equations suggest apparent nitrogen limited primary production. Relatively weak correlation between PON and PP, and euphotic zone averaged PON:PP individual ratios, still being lower than the Redfield ratio indicate a remarkable contribution of non-biogenic phosphorus to the total PP pool.

The nutrient-depleted offshore waters of the NE Mediterranean are relatively poor in seston as compared to the near-shore waters, which contain more PP than POC and PON. Thus the POC:PP and PON:PP ratios derived from the regression analyses of the near-shore data are much below both the open sea and the conventional Redfield ratios, due presumably to the accumulation of non-biogenic particulate phosphorus in the surface waters. However, the average PON:PP ratios for the open sea are relatively high but much lower than the NO<sub>3</sub>:PO<sub>4</sub> ratio (26-28) of the deep waters, suggesting other source or sink terms for biologically labile nitrogen and phosphorus in order to reach such anomalously high N:P ratios in the deep waters.

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