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Nutrient (N, P and Si) and carbon partitioning in the stratified NW Mediterranean

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Abstract

The distribution of nutrients and carbon in the different pools present in the three functional layers (the upper, biogenic layer, the thermocline layer, and the deeper, biolythic layer) of the stratified NW Mediterranean Sea was examined. The stoichiometry between dissolved inorganic nutrients, which had low concentrations in the surface waters, indicated a deficiency in nitrogen, relative to phosphorus, and an excess nitrogen relative to phosphorus within the thermocline, as well as a general silicate deficiency relative to both N and P, even extending to the biolythic layer. The dissolved organic matter was highly depleted in N and, particularly, in P relative to C, with average DOC/DON ratios >60 and DOC/DOP ratios >1500 in all three layers. The particulate pool was also depleted in N and P relative to C, particularly in the biolythic layer. The concentration of biogenic silica was low relative to C, N and P, indicating that diatoms were unlikely to contribute a significant fraction of the seston biomass. Most (>80%) of the organic carbon was present as dissolved organic carbon. Total organic N and P comprised 50–80% of the N and P pool in the biogenic layer, and decreased with depth to represent 10–25% of these nutrient pools in the biolythic layer. The high total N:P ratios in all three depth layers (N/P ratio >20) indicated an overall phosphorus deficiency in the system. The high P depletion of the dissolved organic matter must derive from a very rapid recycling of the P-rich molecules within DOM, and the increasing C/N ratio of DOM with depth indicates that N is also recycled faster than C in the DOM. Because of the uniform depth distribution of the total dissolved nitrogen concentration, the increase in the percent inorganic N and the decline in the percent dissolved organic N with depth indicates that there must be biological transformations between these pools, with a dominance of DON production in surface waters and remineralisation in the underlying layers, from which dissolved inorganic nitrogen is supplied back to the biogenic layer. Downward fluxes of DON and DOC were estimated at 200–250 μmol N m^{-2} d^{-1} and 1.4–2.1 mmol C m^{-2} d^{-1}, respectively, while there should be little or no export of P as dissolved organic matter. The downward DON flux exceeded the diffusive DIN supply of about 145 μmol N m^{-2} d^{-1} to the biogenic layer, suggesting that allochthonous N inputs must be important in the region.

Keywords: Nutrients; Silica; DOC; Stoichiometry; NW Mediterranean

1. Introduction

Nutrient, particularly phosphorus, limitation plays an important role in controlling biological processes in the oligotrophic Mediterranean Sea (e.g. Fiala et al.,

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1976; Berland et al., 1980; Bethoux and Copin-Montégut, 1988; Thingstad and Rassoulzadegan 1995). Provided the low nutrient supply, the maintenance of plankton in the Mediterranean depends on nutrient recycling (Thingstad and Rassoulzadegan, 1995; Thingstad et al., 1998; Zweifel et al., 1993; Bethoux et al., 1992), particularly in summer when the development of the seasonal thermocline separates the pelagic ecosystem in three distinct layers, (1) the upper, biogenic layer, where photosynthesis supports the formation of organic matter; (2) the thermocline area, where biogenic processes associated with a deep-chlorophyll maximum established at or near the thermocline coexist with an intense remineralisation of organic matter that supplies nutrient to maintain biogenic processes; and (3) the lower, biolythic layer, where heterotrophic biological processes are maintained by organic matter exported from the overlying layers. These different layers are coupled by the downward transport of particulate and dissolved organic matter (POM and DOM, respectively), and the upward transport of inorganic nutrients from the biolythic layer.

While nutrient supply sets an upper limit to the biological production in Mediterranean waters, the planktonic organisms exert a tight control on the elemental distribution, affecting the chemical composition of both dissolved and particulate matter (Redfield, 1934; Redfield et al., 1963). While the stoichiometry between dissolved inorganic components in the biolythic zone and particulate organic compounds in the biogenic layer appears to be described adequately by the Redfield ratio of 106 C:16 N:1 P, that of dissolved organic matter seems to deviate greatly from the Redfield ratio (Jackson and Williams, 1985; Jackson, 1988; Butler et al., 1979). A reliable account of the total stoichiometry of nutrient elements in the ocean must incorporate the dissolved organic pool (Jackson and Williams, 1985), because this is the major reservoir of both organic carbon and nutrients in the biogenic layer, particularly in oligotrophic waters (Eppley et al., 1977; Butler et al., 1979; Orret and Karl, 1987; Vidal et al. 1999). The labile and semi-labile fractions of DOM can be major sources of N and P for planktonic food webs via bacterial assimilation (Thingstad and Rassoulzadegan, 1995). In addition, the downward fluxes of dissolved organic carbon and nitrogen may comprise an important fraction of the export of new production from the biogenic layer of oligotrophic waters (e.g. Toggweiler, 1989; Vidal et al., 1999), rendering dissolved organic matter an important link between the biogenic and the biolythic layers.

The examinations of nutrient pools in oceanic waters rarely consider all three components (particulate and dissolved organic and inorganic, together with their distribution across the three distinct layers of the stratified ocean) simultaneously. As a consequence, our knowledge on the partitioning of nutrients between these pools is still poor. Our goal here is to contribute to bridging this gap by examining the distribution of C, N, P and Si in their particulate, dissolved organic, and inorganic forms in the three distinct layers of the stratified NW Mediterranean,

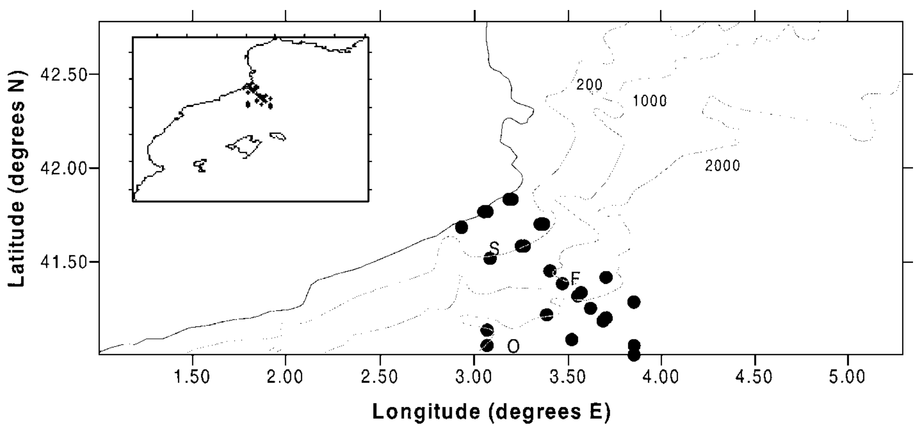

Fig. 1. Map showing the study area, with the position of the stations sampled and that of the stations S (shelf), F (front), and O (Oceanic) studied in greater detail.

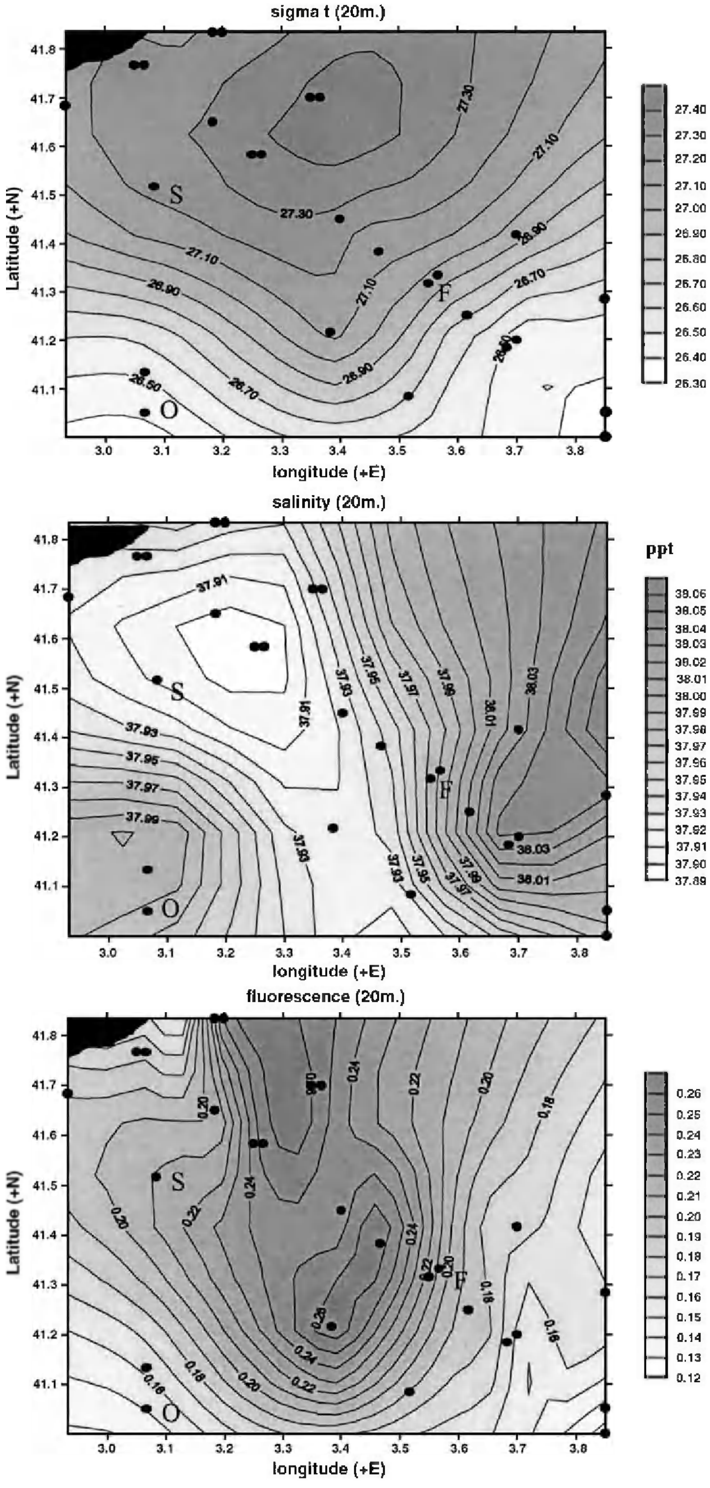

Fig. 2. Contour plot describing the distribution of salinity, density anomaly (sigma t) and fluorescence in subsurface (20 m depth) waters.

where studies concerning all nutrient pools are particularly scarce. We do so based on data collected on a cruise in the NW Mediterranean at the end of the summer of 1996. The examination of the ratios between C, N, P and Si was used to draw inferences on the recycling of nutrients and their possible role as limiting factors for primary production.

2. Methods

The study was conducted in the north-western Mediterranean Sea during the 'FRONTS 96' cruise (September 1996) on board the Spanish research vessel B/O 'Garcia del Cid'. A network of stations along the Catalan-Balearic Sea was occupied (Fig. 1).

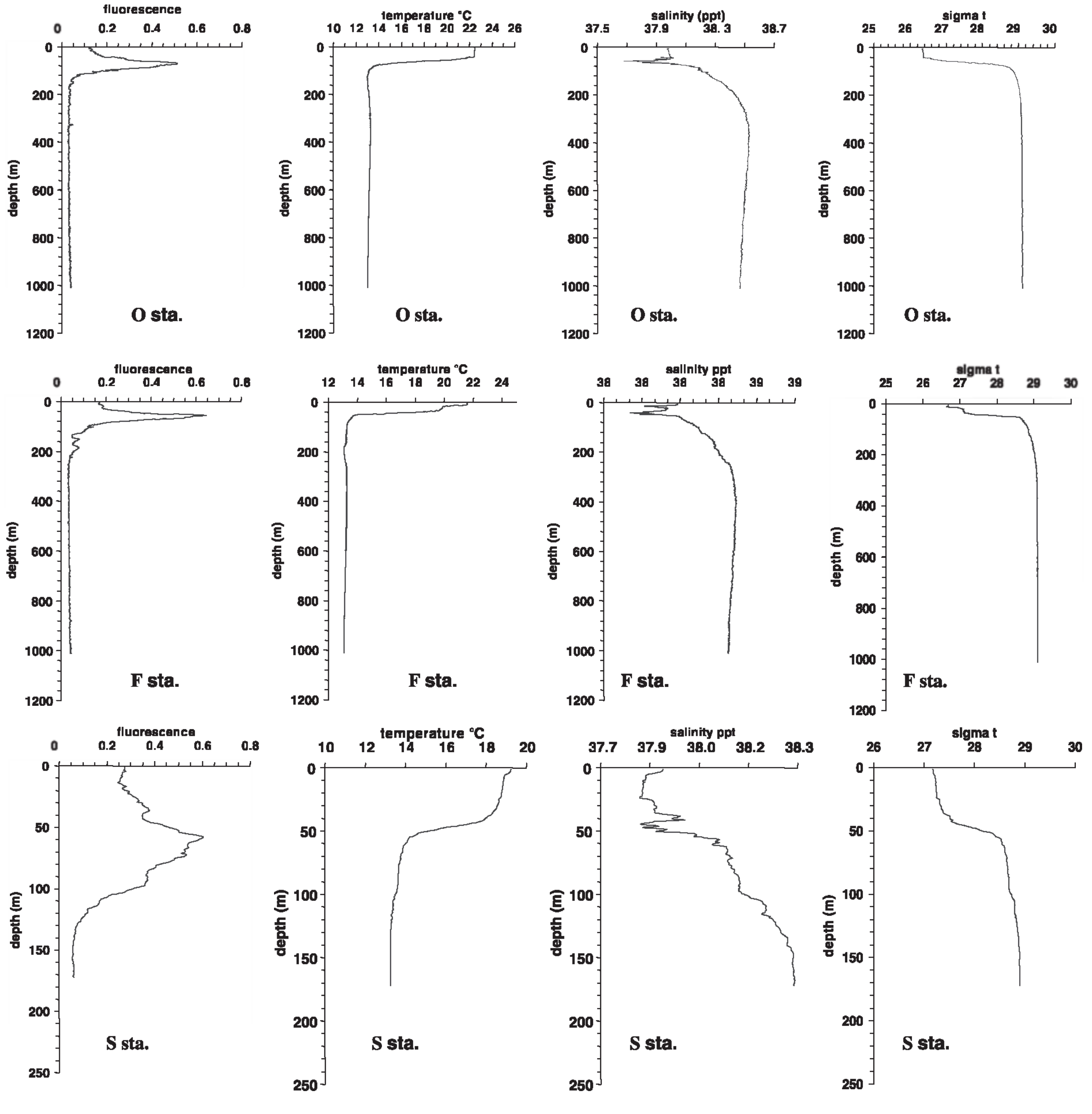

Fig. 3. Vertical profiles of fluorescence, temperature salinity, and density anomaly (sigma t) for O (oceanic), F (frontal) and S (shelf) stations.

Detailed studies were conducted at three stations, each representing the shelf (S station) and oceanic (O station) waters, as well as the frontal (F station) area separating shelf from oceanic waters (Fig. 1).

Conductivity-temperature-pressure (CTD) data were obtained with a vertical resolution of 10 cm. Salinity and temperature estimates derived from CTD casts were calibrated along the cruise using direct salinity measurements from a Guildline Autosal salinometer calibrated with IAPSO standard seawater (34.993 ppt) and a highly accurate reversible thermometer, respectively. Vertical profiles of salinity and temperature derived from the (corrected) CTD data were screened for errors. CTD casts reached near the sediment surface, in shallow stations, or down to a maximum of 1000 m. Water samples were collected using Niskin bottles attached to a rosette system. The depths for discrete water sampling were selected from the features emerging from examination of the CTD and fluorometer profiles and included, at least, the surface mixed layer, the deep Chlorophyll-a maximum (if present), the minimum potential temperature (Mediterranean Winter Water = MWW), and the deep maximum temperature and salinity (Levantine Intermediate Water = LIW). Samples collected below 150 m in the shelf zone and below 375 m in the oceanic zone were located between the LIW and the Mediterranean Deep Water (MDW) (Lacombe and Tcher-

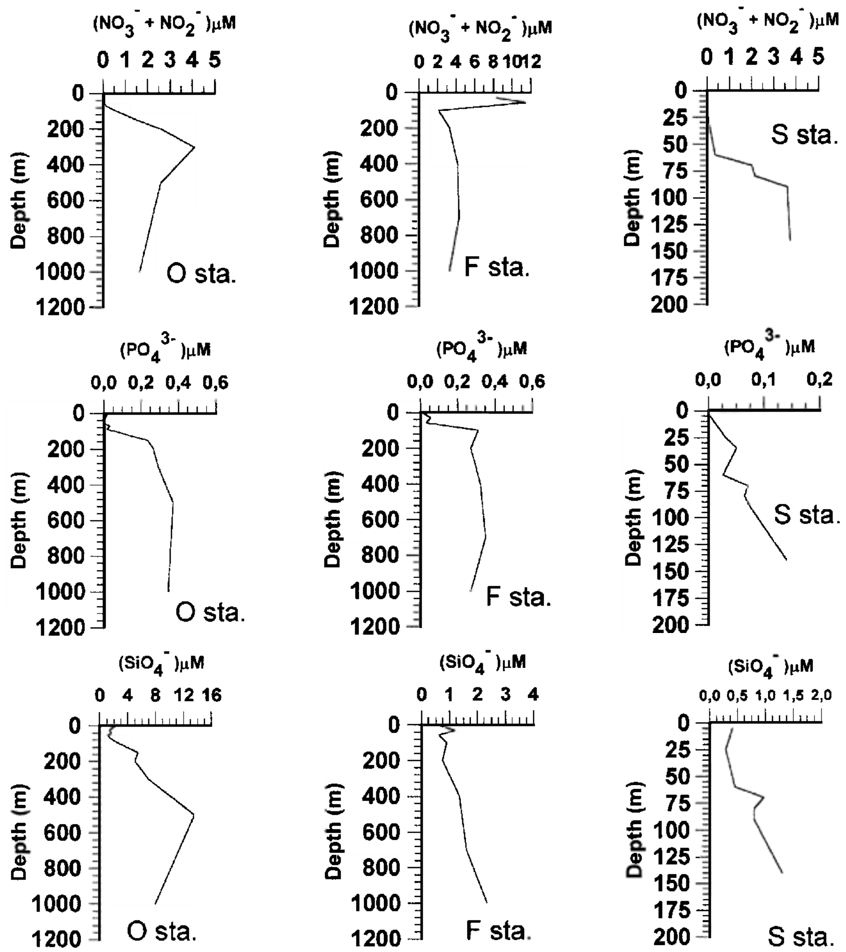

Fig. 4. Vertical profiles of dissolved inorganic nitrogen, phosphorus and silica for O (oceanic), F (frontal) and S (shelf) stations. The maximum depth sampled at the S station was 200 m.

nia, 1972). Subsamples were drawn from the Niskin bottles into pre-cleaned polyethylene bottles. Samples for dissolved inorganic and organic nutrients were preserved with chloroform and immediately frozen for later analysis. Dissolved inorganic nutrients were measured spectrophotometrically using a 10-cm cuvette cell according to standard methods (Hansen and Koroleff, 1999). The detection limit of dissolved nutrient concentrations was 0.01 μM for PO_4^{3-} and $Si(OH)_4$, and 0.02 μM for $NO_3^- + NO_2^-$. Precision was better than 0.05 μM for all nutrients, as indicated by analyses of replicate samples. Samples for particulate organic carbon (POC), nitrogen (PON) and phosphorus (POP) were collected onto pre-combusted (450 °C) Whatman GF/C glass fibre filters and kept frozen. Samples for POC and PON were exposed to concentrated HCl fumes for 30 min to remove the dissolved inorganic carbon, which may interfere with the analysis. Measurements were carried out using a Perkin-Elmer 240 CHN analyser. Samples for POP determinations were oxidised in acidic persulphate solution. The particulate phosphate was then analysed as soluble reactive phosphorus following the methods outlined in Murphy and Riley (1962). Total dissolved phosphorus and nitrogen were measured by the persulphate oxidation method of Murphy and Riley (1962) and the methods of Solórzano and Sharp (1980), respectively. Dissolved organic nitrogen

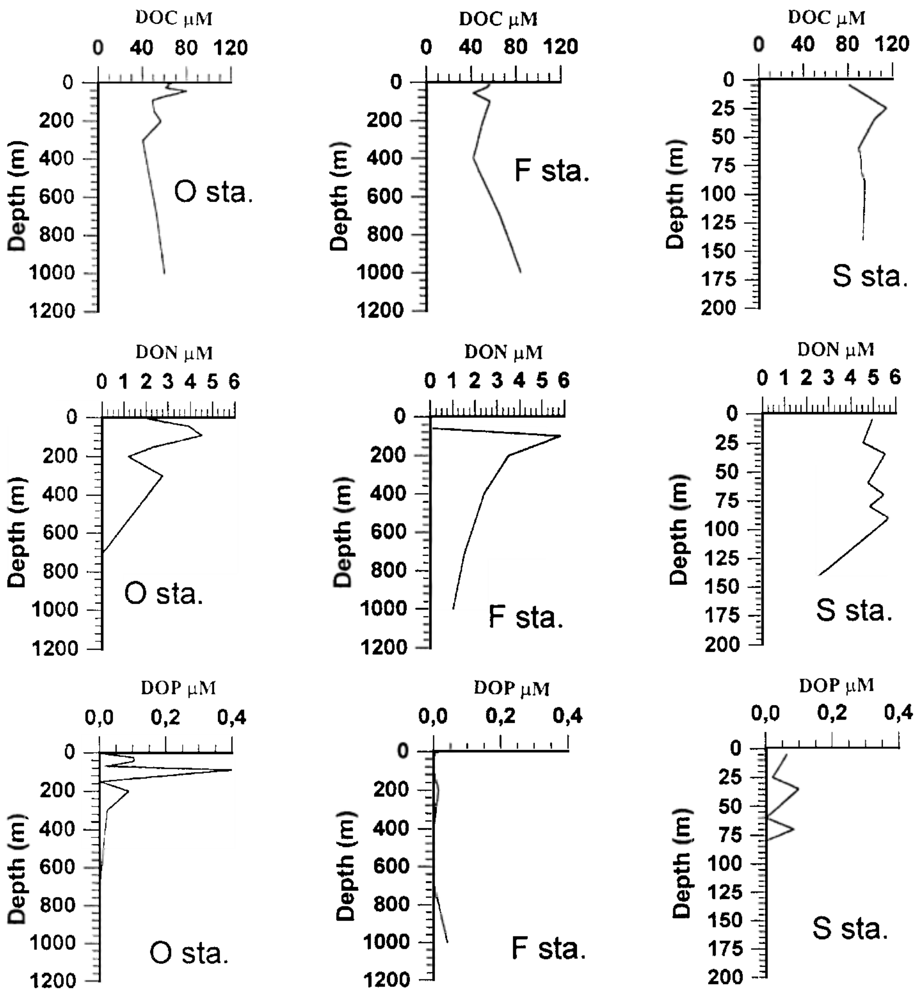

Fig. 5. Vertical profiles of DOC, DON, and DOP for the O (oceanic), F (frontal) and S (shelf) stations.

(DON) and phosphorus (DOP) concentrations were estimated as the difference between the total nutrient and dissolved nutrient concentrations.

Samples to estimate the concentration of silica of biological origin (Si_{bio}) were filtered onto 47 mm polycarbonate Nucleopore filter (0.6 μm pore size) and dried for 12 h at 60 °C. The determination of biogenic silica followed the NaOH/HF digestion method (Ragueneau and Tréguer, 1994). Samples for DOC analyses were immediately filtered (burned Whatman GF/F filters, not washed) and stored in acid-washed, precombusted glass vials. The 10 ml-subsamples were acidified by 40 μl 2 N HCl and sealed with acid-rinsed Teflon lining. The samples were stored in the dark and kept cold. DOC was measured by Pt-catalysed high temperature combus-

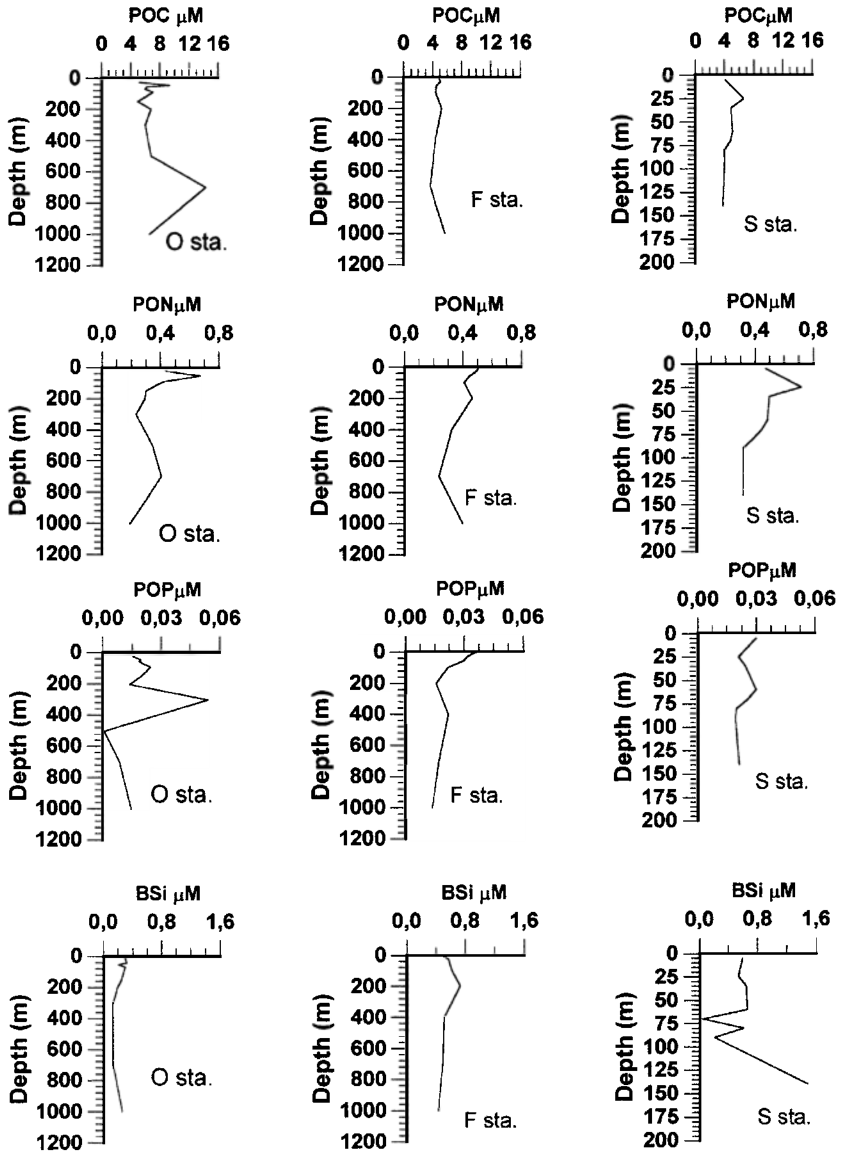

Fig. 6. Depth distribution of the particulate organic matter pool and biogenic silica for the O (oceanic), F (frontal) and S (shelf) stations.

tion in a Shimadzu TOC-5000 with autosampler injection, after being sparged with the carrier gas for 6 min at 75 ml/min (Sharp et al., 1993). A 4-point calibration curve between 50 and 200 μM was prepared for each series of measurements and its slope was used to calculate sample concentrations. Ten blank samples with MilliQ-water and added acid were evenly distributed within each series and the mean blank area of about 750 (CV lower than 15% for 50 μl injections) was subtracted from each sample before calculation. Duplicate samples were analysed with a coefficient of variation lower than 7%. Measurements of DOC in blank and deep ocean water reference materials supplied by J. Sharp (pers. comm., 1997) were included in each series as a quality control. A deviation in concentration of more than 6 μM (n = 3)

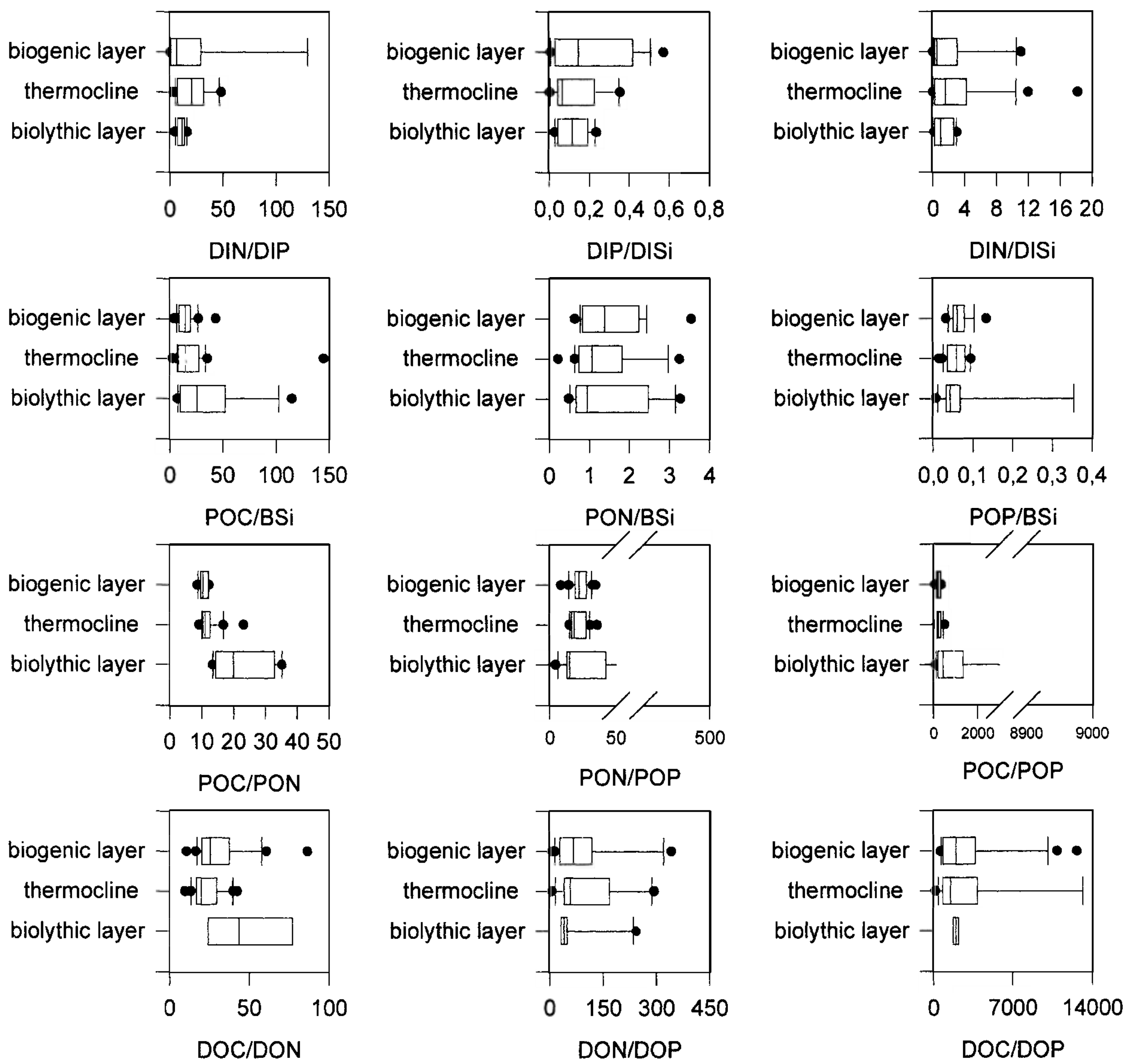

Fig. 7. Box plots showing the distribution of the carbon to nutrient ratios of dissolved inorganic, dissolved organic and particulate organic pools for the biogenic, thermocline and biolythic layers. The central line indicates the median value, the boxes encompass the lower and upper quartiles of the distribution, the lines encompass 95% of the data and the solid circles indicate observations beyond the 95% limits.

from the stated 44 μM in the deep ocean water released a re-run of our samples. Our blank samples had an average area of 117 ± 39 (SD, n = 25) higher than the reference blank. Thus, the presented DOC concentrations are probably underestimated by about 3 μM.

3. Results

The horizontal salinity distribution revealed the presence of a relatively low salinity core (about 37.91 at 20 m) associated to the Palamós Canyon. The locations of the canyon and the Catalan front (Estrada and Margalef, 1988) drive the distribution of the water stratification (Fig. 2). The circulation and upwelling associated with the canyon also contribute to supply nutrients to the euphotic zone (cf. Granata et al., 1999) as indicated by maximum fluorescence values along the northern boundary of the canyon (Fig. 2). The water column was strongly stratified (Fig. 3).

Dissolved inorganic nutrients were generally low in the biogenic layer (Fig. 4), although unusually high nitrate + nitrite concentrations of 8–12 μM were observed in surface waters of the Frontal station, suggesting high nitrogen inputs in the frontal zone prior to the cruise. These nitrate + nitrite concentrations are abnormally high, and a possible contamination cannot be ruled out. Yet, contamination is an unlikely explanation, since analyses of independent samples from adjacent stations (Fig. 1) yielded similarly high nitrate + nitrite concentrations in surface waters. Phosphate was below or near detection limit in the surface waters, and rose to about 0.4 μM in the biolythic layer (Fig. 4). Silicate concentrations varied substantially across stations, with the shelf and frontal waters having lower concentrations (0.4–2 μM) than the oceanic stations, where the concentration reached a maximum of 14 μM below 400 m.

Dissolved organic carbon and nitrogen concentrations were highest in the mixed layer (80–120 μM DOC, 5–6 μM DON) at the shelf and oceanic stations (Fig. 5). DOP concentrations were low at all stations, except for some relatively high (0.4 μM) values just below the thermocline at the oceanic station (Fig. 5). The range of particulate organic nutrients was similar across stations (Fig. 6), although it showed greater variability with depth in the oceanic and shelf stations than at the front. The concentration of Si_{bio} was highest in shelf waters and declined towards the open sea (Fig. 6).

The elemental ratios differed greatly among pools and across layers. The ratio of dissolved inorganic nutrients indicated a deficiency in nitrogen, relative to phosphorus in the biogenic layer — where these estimates are subject to considerable uncertainty due to low concentrations — and, conversely, an excess of nitrogen relative to phosphorus within the thermocline relative to the Redfield N:P ratio of 16, which was found in the biolythic layer (Fig. 7, Table 1). There was, on average, a general silicate deficiency relative to both N and P extending even into the biolythic layer (Table 1), compared to the global ratios of these elements (16 N: 16 Si: 1 P, Redfield et al., 1963; Brzezinski, 1985). The dissolved organic matter was highly depleted in P relative to N and C in all layers (Fig. 7), with average DOC/DON ratios >25 and DOC/DOP ratios >1500 in all three layers of the water column (Table 1). The stoichiometric ratios of the particulate pool also showed evidence of N and P depletion relative to C in all layers, which was particularly high in the biolythic layer, whereas N was present in near-Redfield balance relative to P in the particulate pools of the biogenic and thermocline layers (Fig. 7, Table 1). The concentration of Si_{bio} relative to C, N and P was low (Fig. 7, Table 1), indicating that diatoms were unlikely to contribute significantly to the seston biomass.

The partitioning of the nutrient stocks between different pools is best represented by the percentage of the total stock they comprise (Fig. 8). Most (>80%) of the organic carbon was present as dissolved organic carbon, with POC representing a minor percentage throughout the water column (Fig. 8). In contrast, the importance of organic matter as a reservoir of N and P

Table 1
Average nutrient ratios in the different pools (dissolved and particulate) and layers of the stratified NW Mediterranean considered

zone	DIM N : Si : P	DOM C : N : P	POM C : N : Si : P
biogenic	6 : 7 : 1	1984 : 66 : 1	232 : 22 : 16 : 1
thermocline	20 : 17 : 1	1510 : 58 : 1	220 : 18 : 16 : 1
biolythic	11 : 10 : 1	1974 : 25 : 1	426 : 15 : 25 : 1

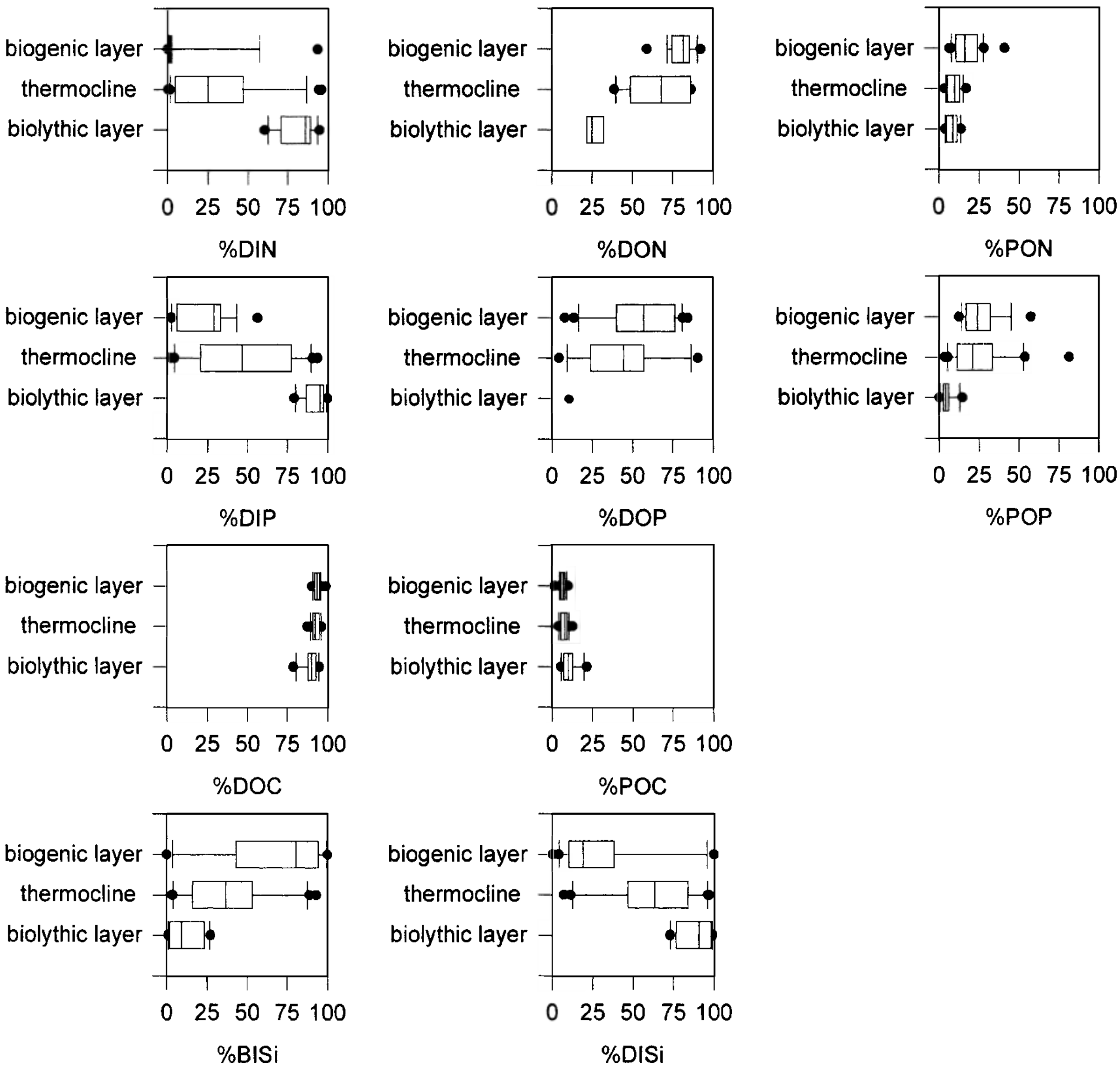

Fig. 8. Box plots showing the distribution of the relative distribution of the total nutrient stock among different pools for the biogenic, thermocline and biolythic layers. The central line indicates the median value, the boxes encompass the lower and upper quartiles of the distribution, the lines encompass 95% of the data and the solid circles indicate observations beyond the 95% limits.

declined greatly with depth, from some 50–80% in the biogenic layer decreasing to 10–25% in the biolythic layer, parallel to the rise with depth of the contribution of importance of dissolved inorganic compounds to the reservoir of N and P (Fig. 8). A similar shift with depth was evident in the partitioning between the particulate and dissolved silica pools (Fig. 8).

4. Discussion

The hydrographic structure during the cruise showed a ridged-shaped elevation of the isopycnals as a result of the divergence between the southwest-flowing coastal current on the Catalan side and a flow to the north-east on the Balearic Islands side, which determines the presence of a dome resulting in a front parallel to the Catalan coast (Font et al., 1988). The origin of the low salinity core on the slope of the Palamós canyon is the advection of shelf water from the Gulf of Lions by the Liguro-Provençal-Catalan (or Northern) Current (Le Vouch et al., 1992). The higher salinity values are formed by upwelling of Levantine Intermediate Water, which is traced by the pattern of fluoresence. A fluorescence maximum was associated with the front area, where doming pycnoclines lead to a high nutrient supply (Estrada and Margalef, 1988). Dissolved inorganic nutrient concentrations were otherwise low, and the results suggested a general silicon deficiency, consistent with the dominance of autotrophs other than diatoms (i.e. picoplankton, Agustí et al., 1998; Agawin et al., 1998) in the stratified NW Mediterranean.

DOC and DON concentrations were comparable to those observed earlier for the NW Mediterranean (Copin-Montégut and Avril, 1993; Doval, 1999), and comprised the bulk of the organic carbon and nitrogen, as observed for other oligotrophic waters (Bethoux and Copin-Montégut, 1988; Minas et al., 1988; Copin-Montégut and Avril, 1993; Doval, 1999; Vidal et al. 1999) and some more productive waters (Søndergaard et al., 2000) in the past. The relatively high DOC concentration of up to 90 μM in the deep (1000 m) waters at the frontal stations is consistent with earlier observations in this area (Cauwet, 1983; Cauwet et al., 1997), suggesting that the acumulation of DOC is a characteristic feature of the deep water mass located in the frontal region.

The total N:P ratios far exceeded the Redfield ratio in all three depth layers (N/P ratio >20), suggesting an overall system phosphorus deficiency, which is consistent with reports of P limitation in the Mediterranean Sea (Minas et al., 1988; Jacques et al., 1973; Thingstad and Rassoulzadegan, 1995; Thingstad et al., 1998). Such P deficiency is, however, not evident from either the dissolved inorganic nutrients, where P is in excess relative to N in the biogenic zone, or the particulate organic matter, where the observed N/P ratios are comparable to the Redfield ratio (Table 1). The P deficiency, however, becomes evident when the highly P-depleted dissolved organic pool (N/P ratio >50) is considered. P depletion of dissolved organic matter has already been reported elsewhere (e.g. English Channel, Butler et al., 1979; Pacific Ocean, Jackson and Williams, 1985; Central Atlantic, Vidal et al., 1999) and seems to be a general feature of dissolved organic matter. Because DOP production rates are high in oligotrophic environments (e.g. Cañellas et al., 2000), the P depletion of the dissolved organic matter must derive from a very rapid recycling of the P-rich molecules within DOM (Orret and Karl, 1987; Thingstad, 1993; Thingstad and Rassoulzadegan, 1995). The increasing C/N ratio of DOM with depth indicates that N is also recycled faster than C in the DOM (Fig. 6).

The distribution of total nitrogen was rather uniform with depth, with PON representing a modest (median < 20%) fraction of the total N pool. Examination of the relative distribution of the nutrient pools revealed an opposite trend in the contribution of the dissolved inorganic and dissolved organic pools with depth (Fig. 7). Because of the uniform depth distribution of the total dissolved nitrogen concentration, this pattern indicates that the net result of biological activity in the waters studied is the production of dissolved organic nitrogen in the biogenic layer and its subsequent remineralisation in the aphotic, biolythic layer. These changes are mediated by the biota contained within the relatively modest particulate organic N pool. High phytoplankton DON and DOP production rates, often exceeding 50% of the N and P uptake (Bronk et al., 1994; Cañellas et al., 2000) have indeed been reported for oligotrophic marine waters, where DOC production rates can also be high, e.g. >30–40% of photosynthetically-produced C (Williams, 1995; Søndergaard et al., 2000). Exudation by healthy cells, representing < 10% of the primary production (Carlson and Ducklow, 1995) does not appear to be sufficient to account for such high DOM production rates, so other processes must be invoked to explain the apparently high DOM production. Recent results point to high phytoplankton lysis rates in oligotrophic marine waters (e.g., 0.8 d^{-1} and 0.45 d^{-1} in the open and coastal NW Mediterranean, Agustí et al., 1998; Agustí and Duarte, 2000, respectively; and 0.95 d^{-1} in the NE subtropical Atlantic, Agustí et al., 2000) as an important source of DOM, which must be accompanied by a relatively inefficient recycling by bacteria to allow its accumulation.

The inorganic nutrients produced upon mineralisation of DON in the deeper water column is re-supplied to the biogenic layer. We hypothesise that DON is an important link between the biogenic and biolythic layer. This was tested by calculating the downward flux of DON by gradient-driven diffusive transport (cf. Lewis et al., 1986; Vidal et al., 1999) as the product between the mean DON gradient across the thermocline in the frontal and oceanic stations (68 and 83 μM N m^{-1}, respectively), and an assumed vertical turbulent diffusion coefficient of 3 m^2 d^{-1} for the stratified NW Mediterranean (Copin-Montégut and Avril, 1993). The calculated downward fluxes (200 and 250 μmol N m^{-2} d^{-1} for the frontal and oceanic stations, respectively) are high compared to the average PON export from the biogenic layer in the NW Mediterranean (140 μmol N m^{-2} d^{-1}, Miquel et al., 1994). In contrast, there was no measurable DOP gradient across the thermocline, indicating the export of P as dissolved organic matter to be small, consistent with results from oligotrophic waters elsewhere (Vidal et al., 1999). These calculations indicate that the downward flux of DON is a dominant source of nitrogen export from the biogenic layer of the NW Mediterranean (about 60% of the downward N transport). Our calculations — using a similar approach of that used to calculate the DON flux — of the downward DOC transport, yielded estimates of 1.4 and 2.1 mmol C m^{-2} d^{-1} for the Frontal and Oceanic stations, respectively, somewhat greater than previous estimates (0.82 mmol C m^{-2} d^{-1}, Copin-Montégut and Avril, 1993), but comparable to the estimates of the average POC export from the biogenic layer (1.08 mmol C m^{-2} d^{-1}, Miquel et al., 1994). These estimates support previous findings that DOC transport comprises half of the organic C export from the biogenic layer of the NW Mediterranean Sea. The sum of the DOC flux estimated here (average 1.7 mmol C m^{-2} d^{-1}) and the average POC flux (1.1 mmol C m^{-2} d^{-1}) in the NW Mediterranean yield an estimate of TOC flux which is in the low range of the estimated new production in the region (4 mmol C m^{-2} d^{-1}, Minas et al., 1988, and 2.7–7.9 mmol C m^{-2} d^{-1}, Bethoux, 1989). This contrast suggests that new production must be much higher during the winter mixing period than that we found during the stratified period, consistent with the nutrient limitation experienced in the stratified period.

Based on the vertical gradient of dissolved inorganic nitrogen of the oceanic station (48 μM N m^{-1}), a supply of 145 μmol N m^{-2} d^{-1} to the biogenic layer was estimated. Hence, the export of N from the biogenic layer appears to exceed the re-supply of inorganic nitrogen across the thermocline, suggesting that allochthonous N inputs must be important in the region. Indeed, the atmospheric N deposition in the NW Mediterranean averages 120 μmol N m^{-2} d^{-1} (Erdman et al., 1994), which would represent about half of the total N supply, and is sufficient to compensate for the excess downward N export as DON. The imbalance of N exchange across the thermocline suggests that there must be lateral export or burial of N. The diffusional phosphate supply to the biogenic layer, based on the vertical gradient of phosphate for the oceanic station was estimated at 7.2 μmol P m^{-2} d^{-1}, which must be balanced by a similar particulate export, since there was no evidence for a downward flux of DOP at the station.

5. Conclusions

Our results show that dissolved organic components dominate the pools of N, P and organic C in the biogenic layer of the NW Mediterranean, shifting to a dominance of dissolved inorganic nutrient pools below the thermocline. These patterns result from the active elemental cycling between dissolved organic and inorganic pools as catalysed by a small pool of living organisms together with gradient-driven vertical fluxes of DOM from the biogenic layer to the biolythic layer and a reverse upward gradient-driven flux of dissolved inorganic nutrients. The downward export of N appears to exceed the upward diffusional flux of dissolved inorganic nitrogen, and is probably balanced by a significant input of atmospheric N to the biogenic layer. In contrast, the downward transport of P is much reduced and limited to the modest particulate flux. P appears to be rapidly and preferentially recycled from DOM. Hence, the system shows clear symptoms of P limitation, so that the high excess export of N from the biogenic layer does not represent a reliable estimate of the new production of the system, which must be estimated in terms of the export of P, the limiting nutrient, in the NW Mediterranean.

Acknowledgements

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