



In Collaboration with
the Netherlands Institute for Sea Research

Journal of Sea Research 49 (2003) 157–170

JOURNAL OF
SEA RESEARCH

www.elsevier.com/locate/seares

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

Anna Lucea^a, Carlos M. Duarte^{a,*}, Susana Agustí^a, Morten Søndergaard^b

^a IMEDEA (CSIC-UIB), Instituto Mediterráneo de Estudios Avanzados, C/Miquel Marqués 21, 07190 Esporles (Islas Baleares), Spain

^b Freshwater Biological Laboratory, University of Copenhagen, Helsingørsgade 51, 3400 Hillerød, Denmark

Received 5 February 2002; accepted 24 October 2002

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.

© 2003 Elsevier Science B.V. All rights reserved.

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.,

* Corresponding author.

E-mail address: cduarte@uib.es (C.M. Duarte).

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,

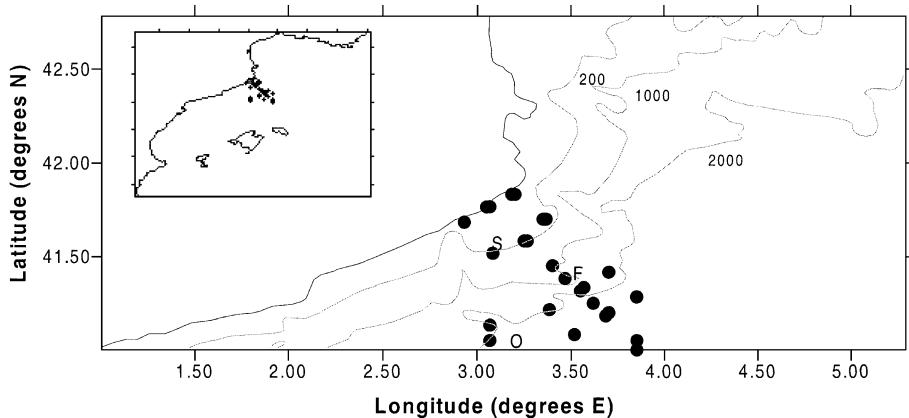


Fig. 1. Map showing the study area, with the position of the stations sampled and that of the stations S (shelf), F (front), and O (Oceanic) studied in greater detail.

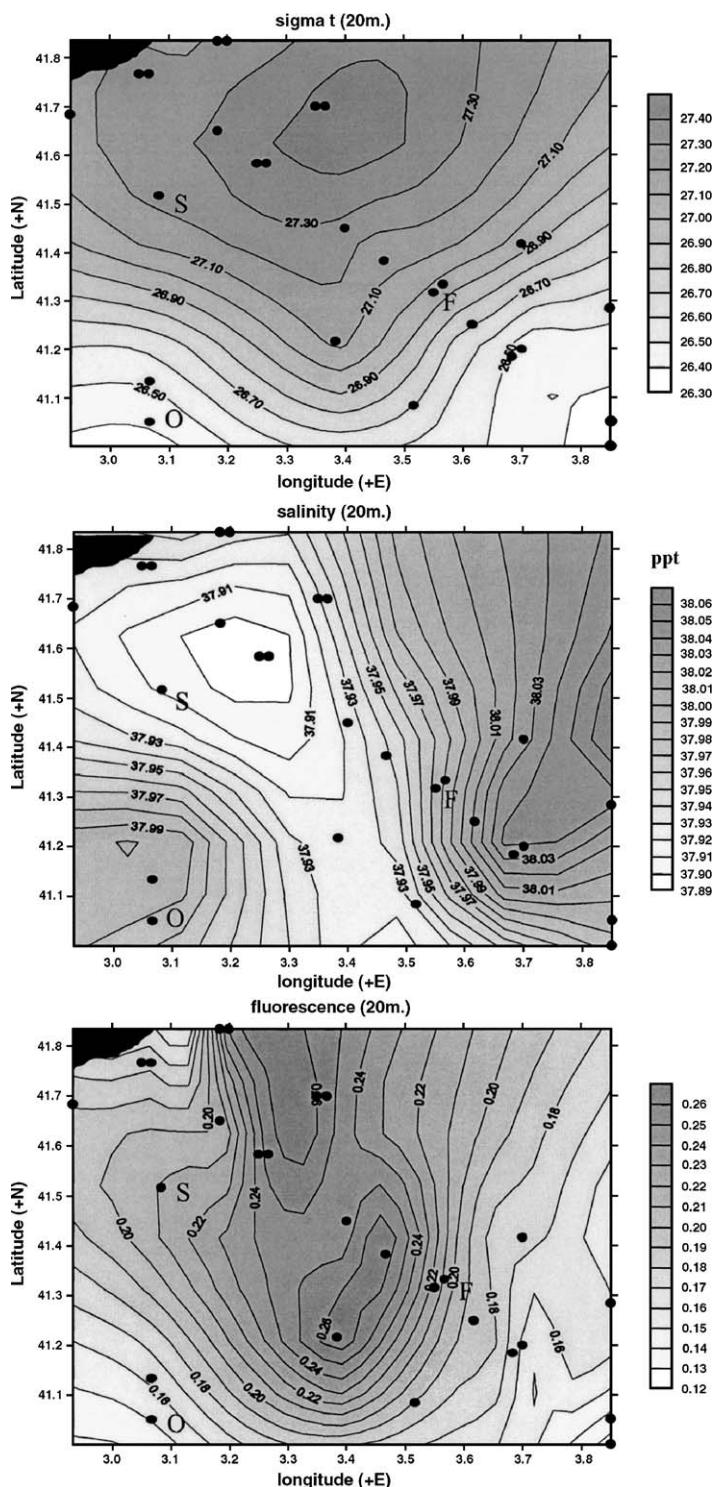


Fig. 2. Contour plot describing the distribution of salinity, density anomaly (σ_t) and fluorescence in subsurface (20 m depth) waters.

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).

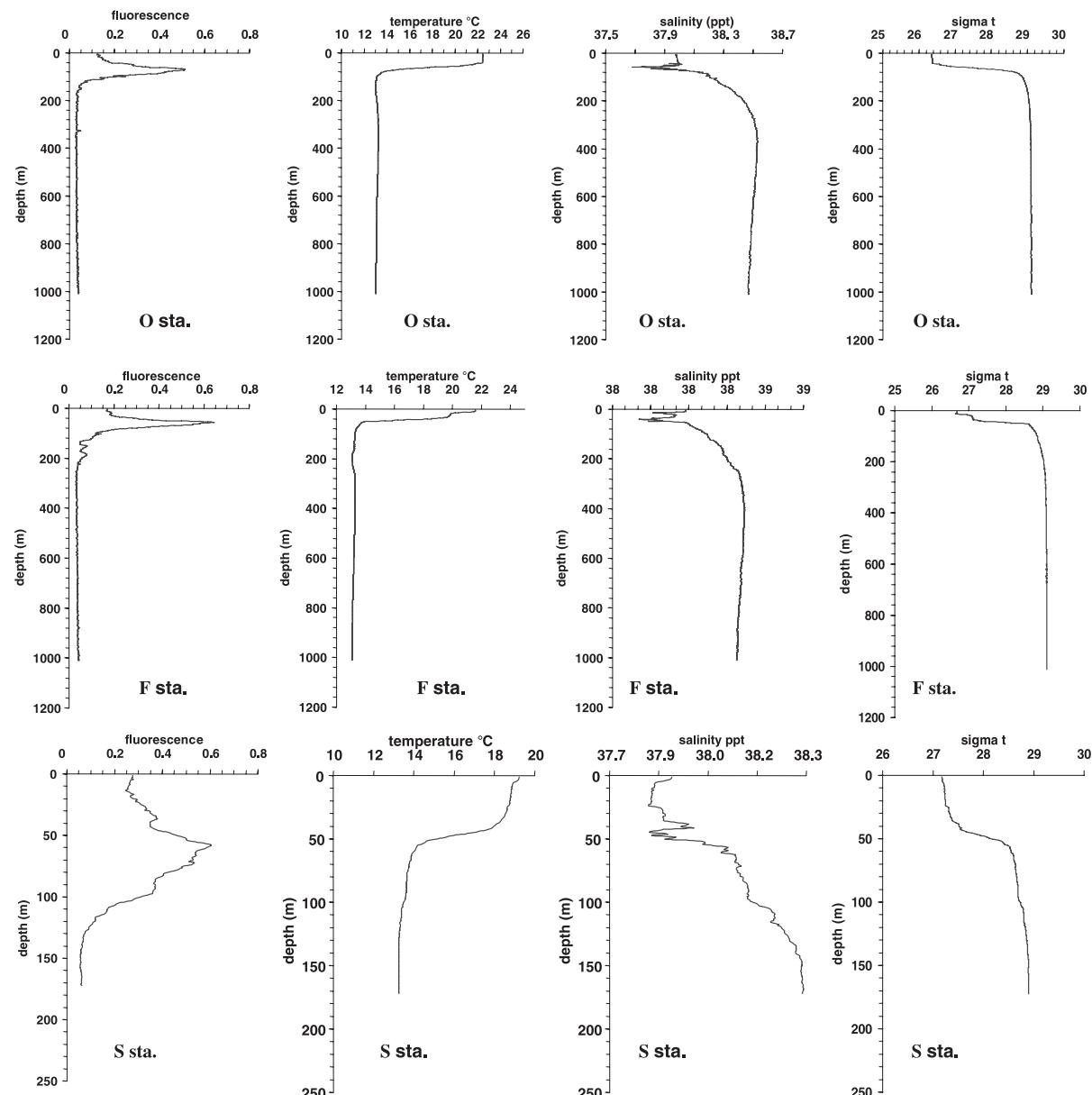


Fig. 3. Vertical profiles of fluorescence, temperature, salinity, and density anomaly (σ_t) for O (oceanic), F (frontal) and S (shelf) stations.

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-

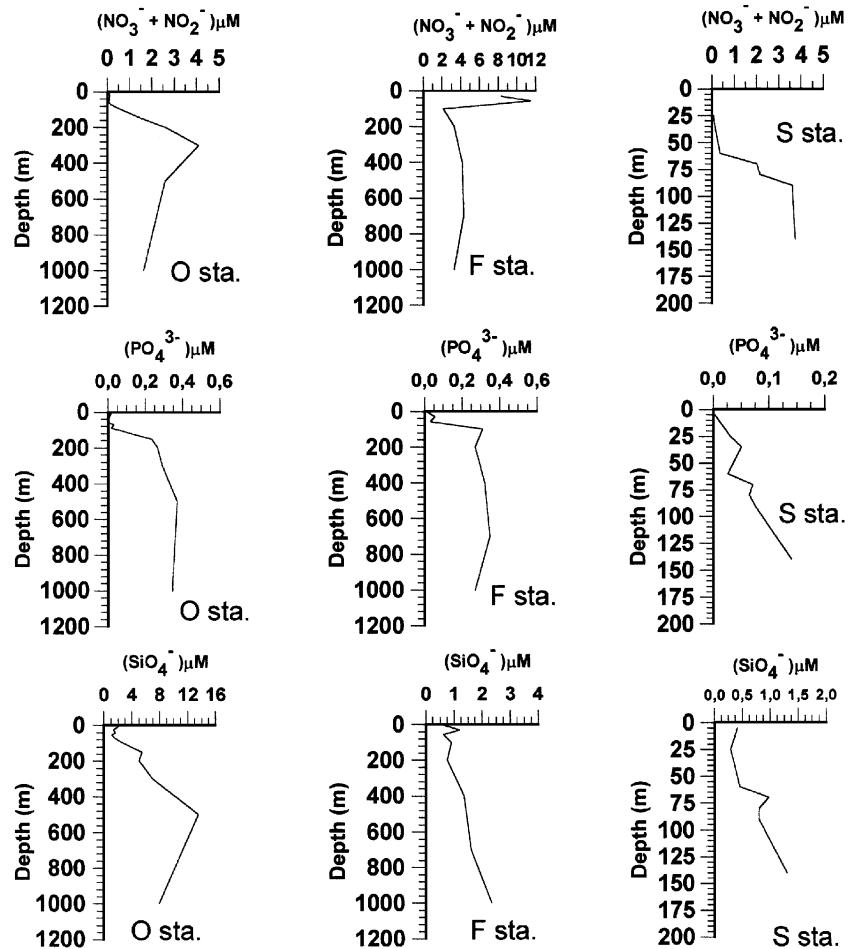


Fig. 4. Vertical profiles of dissolved inorganic nitrogen, phosphorus and silica for O (oceanic), F (frontal) and S (shelf) stations. The maximum depth sampled at the S station was 200 m.

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 $\text{Si}(\text{OH})_4$, and 0.02 μM for $\text{NO}_3^- + \text{NO}_2^-$. 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

$^{\circ}\text{C}$) 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

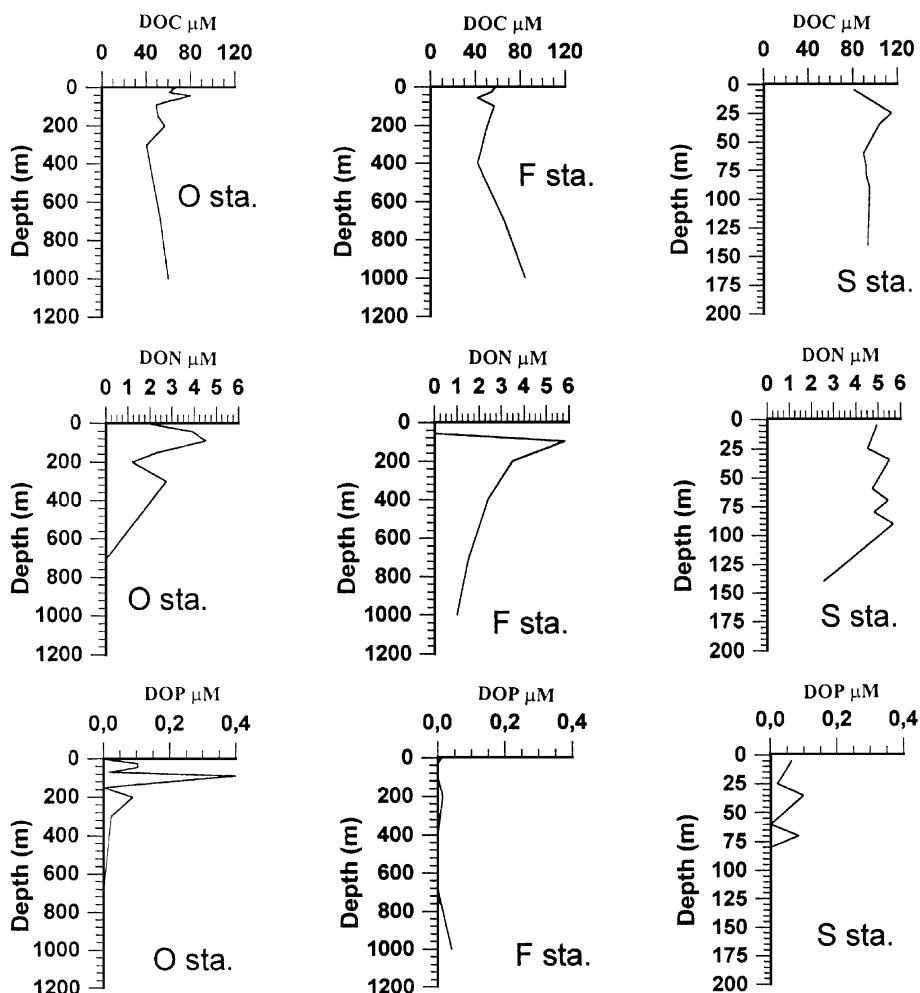


Fig. 5. Vertical profiles of DOC, DON, and DOP for the O (oceanic), F (frontal) and S (shelf) stations.

(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 me-

thod (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-

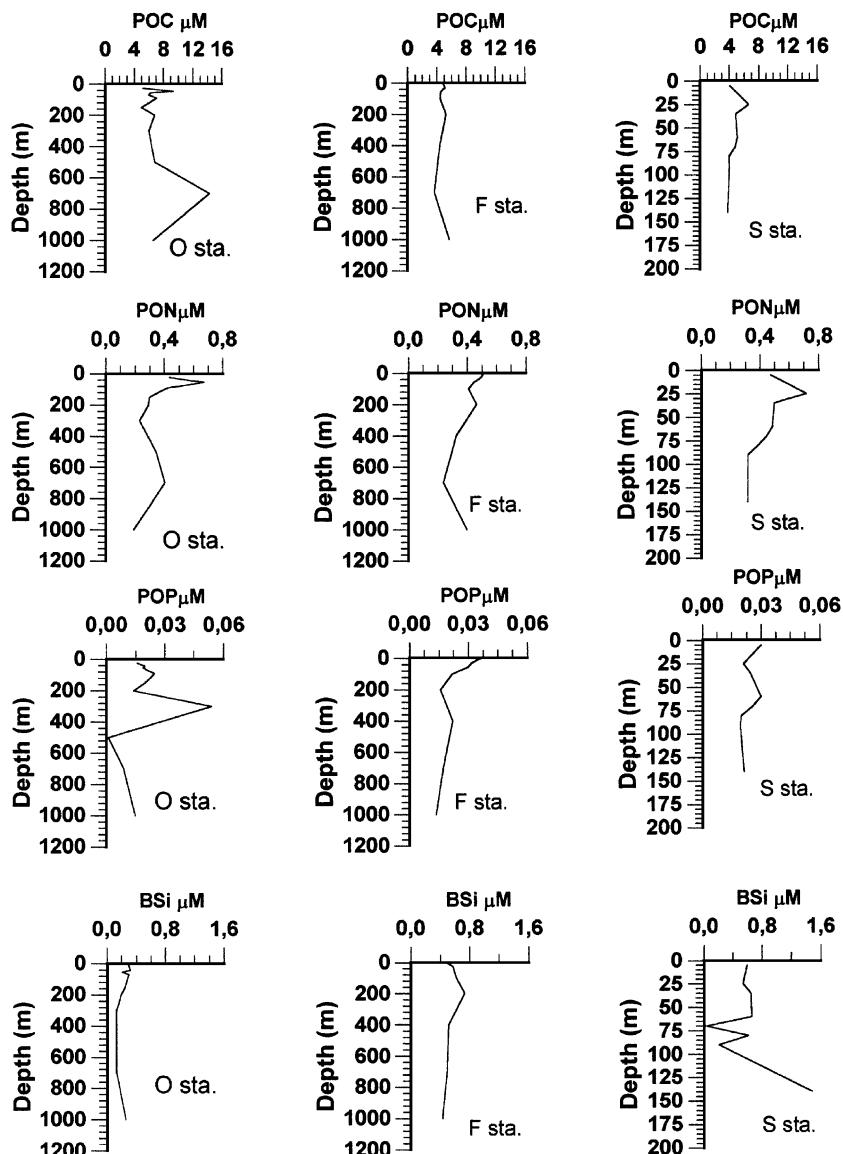


Fig. 6. Depth distribution of the particulate organic matter pool and biogenic silica for the O (oceanic), F (frontal) and S (shelf) stations.

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 ($n=3$)

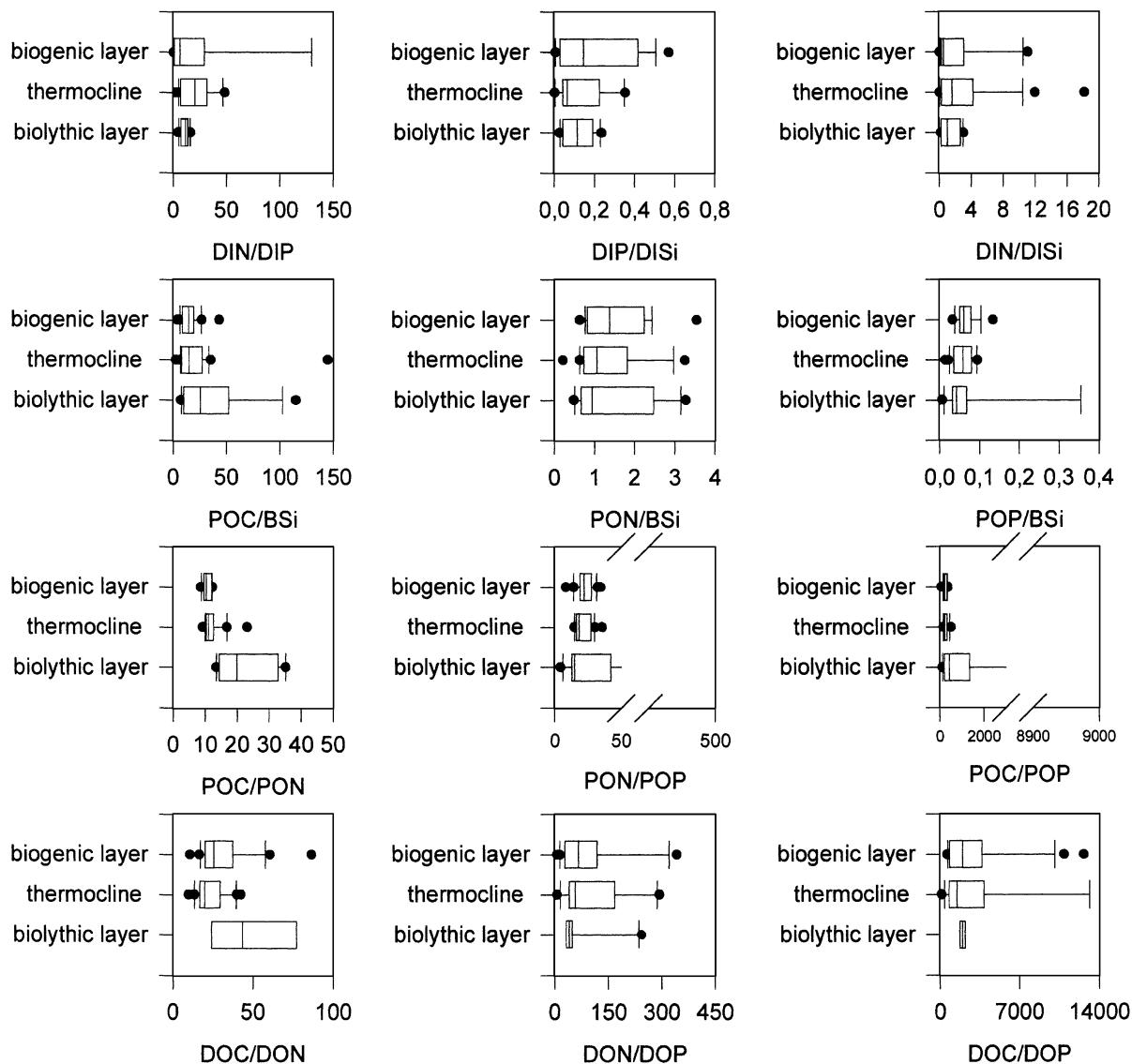


Fig. 7. Box plots showing the distribution of the carbon to nutrient ratios of dissolved inorganic, dissolved organic and particulate organic pools for the biogenic, thermocline and biolythic layers. The central line indicates the median value, the boxes encompass the lower and upper quartiles of the 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	DOM	POM
	N : Si : P	C : N : P	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

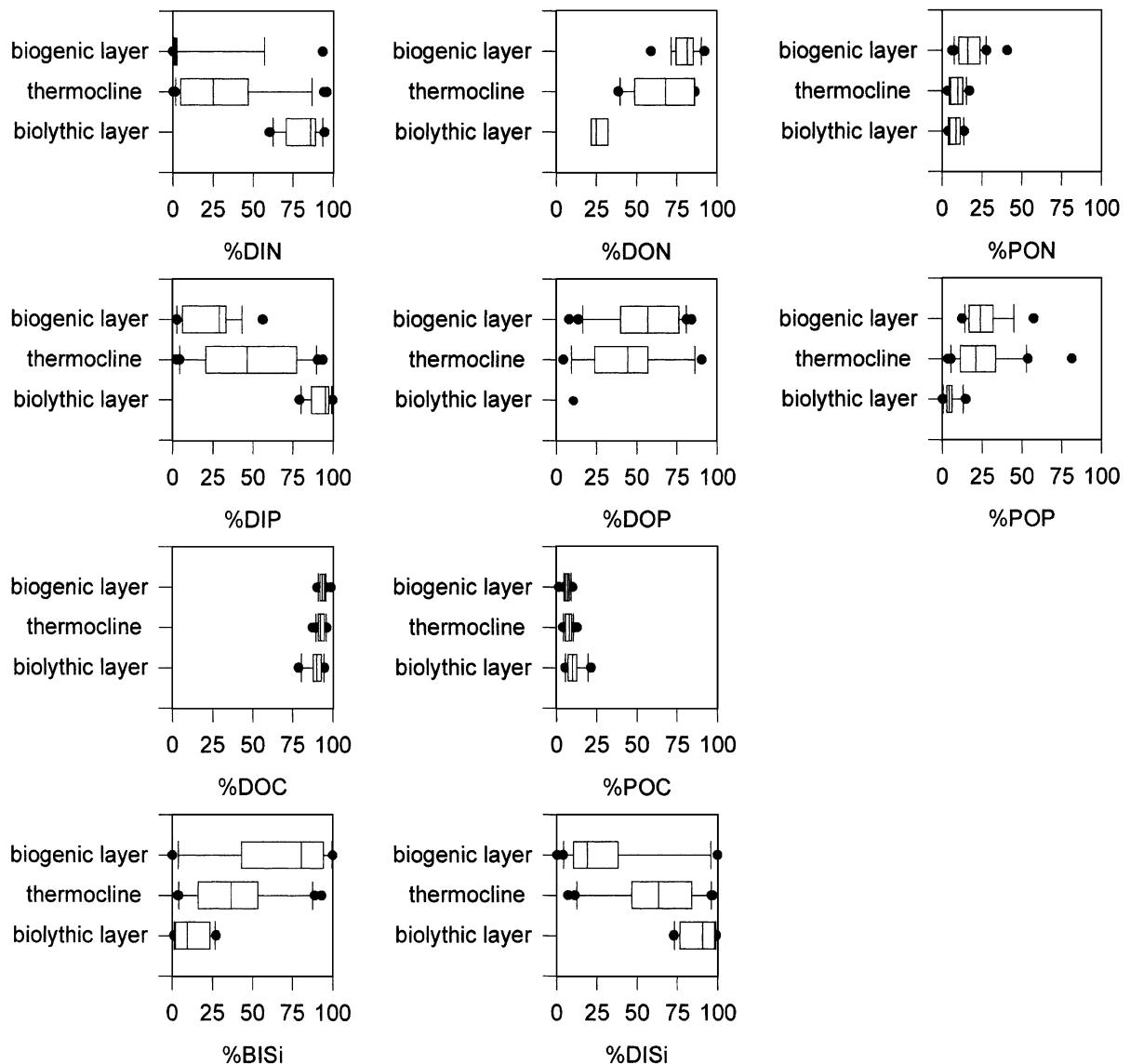


Fig. 8. Box plots showing the distribution of the relative distribution of the total nutrient stock among different pools for the biogenic, thermocline and biolythic layers. The central line indicates the median value, the boxes encompass the lower and upper quartiles of the distribution, the lines encompass 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 fluorescence. 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 accumulation 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 Wil-

liams, 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, biolytic 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 biolytic

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 $\mu\text{M N m}^{-1}$, respectively), and an assumed vertical turbulent diffusion coefficient of $3 \text{ m}^2 \text{ d}^{-1}$ for the stratified NW Mediterranean (Copin-Montégut and Avril, 1993). The calculated downward fluxes (200 and 250 $\mu\text{mol N m}^{-2} \text{ d}^{-1}$ for the frontal and oceanic stations, respectively) are high compared to the average PON export from the biogenic layer in the NW Mediterranean ($140 \mu\text{mol N m}^{-2} \text{ d}^{-1}$, 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 $\text{mmol C m}^{-2} \text{ d}^{-1}$ for the Frontal and Oceanic stations, respectively, somewhat greater than previous estimates ($0.82 \text{ mmol C m}^{-2} \text{ d}^{-1}$, Copin-Montégut and Avril, 1993), but comparable to the estimates of the average POC export from the biogenic layer ($1.08 \text{ mmol C m}^{-2} \text{ d}^{-1}$, 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 $1.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$) and the average POC flux ($1.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$) in the NW Mediterranean yield an estimate of TOC flux which is in the low range of the estimated new production in the region ($4 \text{ mmol C m}^{-2} \text{ d}^{-1}$, Minas et al., 1988, and 2.7 – $7.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$, 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 ($48 \mu\text{M N m}^{-1}$), a supply of $145 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ 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 $120 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ (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 $7.2 \mu\text{mol P m}^{-2} \text{ d}^{-1}$, 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 biolytic 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

This is a contribution to the project ‘Xarxes planctóniques en el mar Catano-Balear’ funded by

the Spanish Interministerial Commission of Science and Technology. We thank B/O 'Garcia del Cid' crew for providing data from CTD casts. M.S. was supported by a grant from the Danish Natural Sciences Research Council.

References

- Agawin, N.S.R., Duarte, C.M., Agustí, S., 1998. Growth and abundance of *Synechococcus* sp. in a Mediterranean Bay: Seasonality and relationship with temperature. *Mar. Ecol. Prog. Ser.* 170, 45–53.
- Agustí, S., Duarte, C.M., 2000. Strong seasonality in phytoplankton cell lysis in the NW Mediterranean littoral. *Limnol. Oceanogr.* 45, 940–947.
- Agustí, S., Satta, M.P., Mura, M.P., Benavent, E., 1998. Dissolved esterase activity as a tracer of phytoplankton lysis: Evidence of high phytoplankton lysis rates in the northwestern Mediterranean. *Limnol. Oceanogr.* 43, 1836–1849.
- Agustí, S., Duarte, C.M., Vaqué, D., Hein, M., Gasol, J.M., Vidal, M., 2000. Food web structure and elemental (C, N and P) fluxes in the eastern tropical North Atlantic. *Deep-Sea Res. II* 48, 2295–2321.
- Berland, B.R., Bonin, S.Y., Maestrini, S.Y., 1980. Azote ou phosphore? Considérations sur le "paradoxe nutritionnel" de la mer méditerranée. *Oceanol. Acta* 3, 135–142.
- Bethoux, J.P., 1989. Oxygen consumption, new production, vertical advection and environmental evolution in the Mediterranean Sea. *Deep-Sea Res. II* 36, 769–781.
- Bethoux, J.P., Copin-Montégut, G., 1988. Phosphorus and Nitrogen in the Mediterranean Sea: specificities and forecasting. *Oceanol. Acta* 9, 75–78.
- Bethoux, J.P., Morin, P., Madec, C., Gentili, B., 1992. Phosphorus and nitrogen behaviour in the Mediterranean Sea. *Deep-Sea Res. II* 39, 1641–1654.
- Bronk, D.A., Glibert, P.M., Ward, B.B., 1994. Nitrogen uptake, dissolved organic nitrogen release, and new production. *Science* 265, 1843–1846.
- Brzezinski, M.A., 1985. The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. *J. Phycol.* 21, 347–357.
- Butler, E.I., Knox, S., Liddicoat, M.I., 1979. The relationship between inorganic and organic nutrients in seawater. *J. Mar. Biol. Assoc. UK* 59, 239–250.
- Cañellas, M., Agustí, S., Duarte, C.M., 2000. Latitudinal variability in phosphate uptake in the Central Atlantic. *Mar. Ecol. Prog. Ser.* 194, 283–294.
- Carlson, C.A., Ducklow, H.W., 1995. Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: daily and fine-scale vertical variations. *Deep-Sea Res. II* 42, 639–656.
- Cauwet, G., 1983. Distribution du carbone organique dissous et particulaire en Méditerranée occidentale. Rapports de la Commission Internationale pour l'Etude Scientifique de la mer Méditerranée (CIESM) 28, 101–105.
- Cauwet, G., Miller, A., Brasse, S., Fengler, G., Mantoura, R.F.C., Spitz, A., 1997. Dissolved and particulate organic carbon in the western Mediterranean Sea. *Deep-Sea Res. II* 44, 769–779.
- Copin-Montégut, G., Avril, B., 1993. Vertical distribution and temporal variation of dissolved organic carbon in the North-Western Mediterranean Sea. *Deep-Sea Res. II* 40, 1963–1972.
- Doval, M.D., 1999. Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean. *Deep-Sea Res. I* 46, 511–527.
- Eppley, R., Sharp, J.H., Renger, M.J., Perry, M.J., Harrison, W.G., 1977. Nitrogen assimilation by phytoplankton and other micro-organisms in the surface waters of the central North Pacific Ocean. *Mar. Biol.* 39, 111–120.
- Erdman, L.K., Sofiev, M., Subbotin, S., Dedkova, I., Afinogenova, O., Chesukina, T., Pavlovskaya, L., Soudine, A., 1994. Assessment of Airbone Pollution of the Mediterranean Sea by Sulphur and Nitrogen Compounds and heavy metals in 1991. MAP Technical Report Series, UNEP/WMO, vol. 85, Athens. 340 pp.
- Estrada, M., Margalef, R., 1988. Supply of nutrients to the Mediterranean photic zone along a persistent front. *Oceanol. Acta* 9, 133–142.
- Fiala, M., Cahet, G., Jacques, G., Neveux, J., Panouse, M., 1976. Fertilization de communautés phytoplanctoniques. I. Cas d'un milieu oligotrophique: Méditerranée nord-occidentale. *J. Exp. Mar. Biol. Ecol.* 24, 151–163.
- Font, J., Salat, J., Tintoré, J., 1988. Permanent features in the circulation of the Catalan Sea. *Oceanol. Acta* 9, 51–57.
- Granata, T.C., Vidondo, B., Duarte, C.M., Satta, M.P., García, M., 1999. Hydrodynamics and particle transport associated with a submarine canyon off Blanes, Spain, NW. Mediterranean. *Cont. Shelf Res.* 19, 1249–1263.
- Hansen, K., Koroleff, F., 1999. Determination of nutrients. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods of Seawater Analysis*, 3rd ed. Wiley-VCH, Weinheim, pp. 159–228.
- Jackson, G.A., 1988. Implications of high dissolved organic matter concentrations for oceanic properties and processes. *Oceanography* 2, 28–33.
- Jackson, G.A., Williams, P.M., 1985. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. *Deep-Sea Res. II* 32, 223–235.
- Jacques, G., Cahet, G., Fiala, M., Panouse, M., 1973. Enrichissement de communautés phytoplanctoniques néritiques de Méditerranée nord occidentale. *J. Exp. Mar. Biol. Ecol.* 11, 287–295.
- Lacombe, H., Tchernia, P., 1972. Caractères hydrologiques et circulation des eaux en Méditerranée. In: Stanley, D.J., et al. (Eds.), *The Mediterranean Sea*. Dowden, Hutchinson and Ross, Stroudsburg, pp. 26–36.
- Le Vouch, J., Millot, C., Castagné, N., Le Borge, P., Orly, J.P., 1992. Atlas des fronts thermiques en Mer Méditerranée d'après l'imagerie satellitaire. *Mém. Inst. Océanogr. Monaco* 16 (VI), 152.
- Lewis, M.R., Harrison, N.S., Oakey, N.S., Hebert, D.L., Platt, T., 1986. Vertical nitrate fluxes in the oligotrophic ocean. *Science* 234, 870–873.
- Minas, H.J., Minas, M., Coste, M., Gostan, P., Nival, P., Bonin, M.C., 1988. Production de base et recyclage; une revue de la problématique en Méditerranée nord-occidentale. *Oceanol. Acta* 9, 155–162.

- Miquel, J.C., Fowler, S.W., La Rosa, P., Buat-Menard, P., 1994. Dynamics of the downward flux of particles and carbon in the open northwestern Mediterranean Sea. Deep-Sea Res. II 41, 243–261.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27, 31–36.
- Orret, K., Karl, D.M., 1987. Dissolved organic phosphorus production in surface seawaters. *Limnol. Oceanogr.* 32, 383–395.
- Ragueneau, O., Tréguer, P., 1994. Determination of biogenic silica in coastal waters: applicability and limits of the alkaline digestion method. *Mar. Chem.* 26, 43–51.
- Redfield, A.C., 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. James Johnstone Memorial Volume. University Press of Liverpool, Liverpool, pp. 176–192.
- Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of seawater. In: Hill, M.N. (Ed.), *The Sea, Ideas and Observations on Progress in the Study of the Seas*, vol. 2. Interscience, New York, pp. 26–77.
- Sharp, J.H., Benner, R., Bennett, L., Carlson, C.A., Dow, R., Fitzwater, S.E., 1993. A re-evaluation of high temperature combustion and chemical oxidation measurements of dissolved organic carbon in seawater. *Limnol. Oceanogr.* 39, 1774–1782.
- Solórzano, L., Sharp, J.H., 1980. Determination of total dissolved phosphorus in natural waters. *Limnol. Oceanogr.* 25, 754–758.
- Søndergaard, M., Williams, P.J.leB., Cauwet, G., Riemann, B., Robinson, C., Malcolm, E., Woodward, S., Worm, J., 2000. Net accumulation and flux of dissolved organic carbon and dissolved organic nitrogen in marine plankton communities. *Limnol. Oceanogr.* 45, 1097–1111.
- Thingstad, T.F., 1993. Microbial processes and the biological carbon pump. In: Evans, G.T., Fasham, M.J.R. (Eds.), *Towards a Model of Ocean Biogeochemical Processes*. Springer-Verlag, Berlin, pp. 193–208.
- Thingstad, T.F., Rassoulzadegan, F., 1995. Nutrient limitations, microbial food webs, and “biological C-pumps”: suggested interactions in a P-limited Mediterranean. *Mar. Ecol. Prog. Ser.* 117, 299–306.
- Thingstad, T.F., Zweifel, U.L., Rassoulzadegan, F., 1998. P limitation of heterotrophic bacteria and phytoplankton in the northwest Mediterranean. *Limnol. Oceanogr.* 43, 88–94.
- Toggweiler, J.R., 1989. Is the downward dissolved organic matter (DOM) flux important in carbon transport? In: Berger, W.H., Smetacek, V.S., Wefer, G. (Eds.), *Productivity of the Ocean: Present and Past*. John Wiley and Sons Limited, Chichester, pp. 65–83.
- Vidal, M., Duarte, C.M., Agustí, S., 1999. Dissolved organic nitrogen and phosphorus pools and fluxes in the central Atlantic Ocean. *Limnol. Oceanogr.* 44, 106–115.
- Williams, J.leB.P., 1995. Evidence for the seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C/N assimilation ratios. *Mar. Chem.* 51, 17–29.
- Zweifel, U.L., Norrman, B., Hagström, A., 1993. Consumption of dissolved organic carbon by marine bacteria and demand for inorganic nutrients. *Mar. Ecol. Prog. Ser.* 101, 23–32.