Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean

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ABSTRACT

The distribution of the concentrations of Dissolved Organic Carbon (DOC) and Nitrogen (DON) and Particulate Organic Carbon (POC) and Nitrogen (PON) was studied in a transect perpendicular to the Catalan coast in the NW Mediterranean in June 1995. The transect covered a hydrographically diverse zone, including coastal waters and two frontal structures (the Catalan and the Balear fronts). The cruise was conducted during the stratification period, characterized by the inorganic nutrient depletion in the photic zone and a well established deep chlorophyll *a* maximum. DOC concentrations were measured using a high temperature catalytic oxidation method, and DON was determined directly, with an update of the Kjeldahl method after removal of inorganic nitrogen.

The ranges of DOC and DON concentrations were 44 to 95 $\mu\text{M-C}$ and 2.8 to 6.2 $\mu\text{M-N}$, respectively. The particulate organic matter ranged between 0.9 and 14.9 $\mu\text{M-C}$ and from 0.1 to 1.7 $\mu\text{M-N}$. The DOC:DON molar ratios averaged 15.5 ± 0.4 , while the mean POC:PON ratios was 8.6 ± 0.6 . The distribution of dissolved organic matter (DOM) was inverse to that of the salinity. The highest concentrations of DOM were found in coastal waters and in the stations affected by the Catalan front, located at the continental shelf break.

It was estimated that recalcitrant DOM constituted the 67% of the DOM pool in the upper 50 m. The data suggest that accumulation of DOC due to the uncoupling between the production and consumption mechanisms may occur in the NW Mediterranean during the stratification period and that the organic matter exported from the photic layer is dominated by C-rich bioelements.

INTRODUCTION

Dissolved organic matter (DOM) had been traditionally ignored, in part, due to methodological constraints and also because it was considered biologically inert (Barber, 1968; Williams and Druffel, 1987). Relatively recent data indicate that dissolved organic carbon (DOC) represents quantitatively the most important carbon reservoir in the ocean (Walsh, 1989; Wangersky, 1993; Cauwet, 1994; Bronk et al., 1994; Lefèvre et al., 1996). Thus, DOC may play a major role in the carbon cycle in the planet (Toggweiler, 1989; Copin-Montégut and Avril, 1993; Carlson and Ducklow, 1995; Ducklow et al., 1995), a role mostly attributed to the particulate organic carbon (POC). In addition, dissolved organic nitrogen (DON) appears to be the dominant form of fixed nitrogen in oligotrophic surface waters (Jackson and Williams, 1985; Walsh, 1989). There is no longer doubt that both DOC and DON should be included in biochemical models (Bronk et al., 1994; Kirchman et al., 1994). Nevertheless, very few information is available about the characterization, transformation or even the absolute concentration of DOM in seawater (Sharp et al., 1993a; 1993b).

The oligotrophic waters of the Mediterranean Sea constitute an example of these not well understood areas with regards to the DOM concentration. In the Western Basin, DOC data are only available from the Gulf of Lions and the Ligurian Sea (Cauwet et al., 1990; Copin-Montégut and Avril, 1993; Cauwet, 1994) and estimations of DON concentrations have only been performed in the Alboran Sea (Coste et al., 1988) and the East of Sardinian coast and in the SE Cabo de Palos (Banoub and Williams, 1972). Compared to the rest of the Mediterranean Sea, the areas of the Western Basin are characterized by a relatively increased productivity. The mesoscale hydrographic structures, namely, the Alboran gyres and the mixing chimneys in the

Gulf of Lions, facilitate nutrient inputs to the photic zone (San Feliu and Muñoz, 1971; Minas et al., 1984; Taupier-Lepage and Millot, 1988). The values of DOC in this area were similar to those reported in other oligotrophic areas such as the equatorial Pacific (Carlson and Ducklow, 1995) or equatorial Atlantic (Thomas et al., 1995).

In the Catalano-Balear Sea, located between the Northeastern Spanish coast and the Balearic Islands, the shelf-slope fronts along the continental and insular coasts and the breaking of internal waves at the thermocline play also an important fertilizing role (Estrada and Margalef, 1988). These hydrographic mechanisms and their variability appear to contribute to the maintenance of an otherwise low biomass, specially during the stratification period which extends from April to November (Estrada, 1985). Inorganic nutrients inputs may occur at the level of the thermocline, but both nitrogen and phosphorus are close to the detection limit in the photic zone. It can not be discarded that organic forms may support part of the primary and heterotrophic production in summer. In the vertical dimension, during the stratified period, a well developed deep chlorophyll a maximum (DCM) is present. This formation is due to photoacclimation of cells to low light levels and the availability of nutrients in waters close to the surface (Estrada et al., 1993). For instance, it was estimated that in summer 1983, the phytoplankton of the DCM contributed up to 30% of the total primary production in the water column (Estrada, 1985). Thus, it may be likely that relatively important DOC concentrations occur in this area. Unfortunately, data on DOC and DON concentrations are not available.

In June 1995, during the summer stratification period, a cruise was conducted in the Catalan Sea. The study included a transect perpendicular to the coast of Barcelona, which covered a hydrographically diverse area, from the continental shelf to the open

sea waters. Samples for the simultaneous determination of DOC and DON and, POC and PON concentrations were collected. A main objective was to study the spatial variability in the distribution of both the dissolved and the particulate organic matter related to the hydrography. In addition, we investigated the relationship among the four chemical measurements which will contribute to understand the dynamics of carbon and nitrogen in the NW Mediterranean.

MATERIAL AND METHODS

Sample collection

Samples were collected in June 6, 1995 on board the B/O Hesperides during the "VARIMED'95" cruise (that extended from the 2nd to the 14th of June). Sampling was conducted along a transect between Barcelona and the Mallorca-Menorca channel (Fig. 1). Starting at station #1, nine stations were sampled between 41°20'N 2°17' E and 40°27'N 3°2' E from 5:00 to 10:30 GMT. At each station, temperature, salinity, oxygen and pressure were recorded by means of a CTD (Neil Brown Mark III) probe. Water samples were obtained with a Rosette sampler (12 l Niskin bottles) attached to the CTD system. Discrete samples of O₂ were collected and analyzed by Winkler potentiometric titration (Culberson, 1981) to calibrate the O₂ sensor of the CTD probe.

Water samples were taken at 5, 30, 50, 100, 200, 500, 1000 m depth and at bottom for DOC, POC and PON concentrations and, at 5, 50, 100, 200, 1000 m depth and at bottom for DON concentrations. For chlorophyll *a* concentrations samples were collected at 10 m intervals between surface and 100 m, and at 150 m and at 200 m depth.

The bottles and the filtering system used for the organic matter analyses had been previously soaked on diluted sodium hypochloride, 0.1 N hydrochloric acid and rinsed with Milli-Q water. Samples were drawn into clean 1 L polyethylene containers. Just before filling, the containers were rinsed three times with the water sample. A completely glass filtering system was used to collect the particulate and the dissolved organic matter. Filtration onto Whatman GF/F filters was performed immediately after sampling.

*Particulate organic matter and Chlorophyll *a* determinations*

Particulate organic carbon (POC) and nitrogen (PON) were collected on Whatman GF/F filters, which were dried on silica gel and frozen to -70°C until analysis in the laboratory. Measurements were carried out with a 'Perkin Elmer 2400 CHN' analyzer. Prior to the analyses, carbonates were eliminated from the samples with hydrochloric acid vapour. Combustion to CO₂ and NO_x was performed at 900°C and reduction of NO_x to N₂ at 640°C. The reproducibility of the method was $\pm 0.1 \mu\text{M}$ for POC and $\pm 0.04 \mu\text{M}$ for PON. Aliquots of the filtrate were taken for DOC and DON analyses. The initial filtrate was used to rinse the bottles before filling them with the water sample. For DON and DOC analyses, samples were immediately frozen (-70°C) until analyses.

Chlorophyll *a* concentration was estimated fluorometrically (Strickland and Parsons, 1968). Samples (100 ml) were collected in 25 mm GF/F glass fiber filters and immediately frozen at -70°C. The filters were then left for 12 h in 90% acetone at 4°C in the dark for pigment extraction. The fluorescence of the extract was measured in a

Turner Designs fluorometer calibrated with natural samples collected in the same cruise and measured spectrophotometrically (Jeffrey and Humphrey, 1975).

DOC measurements

DOC analyses were performed (within 2 days) with a commercially available automatic analyzer Shimadzu TOC-5000. This apparatus operates on the principle of high temperature catalytic oxidation (HTCO) of organic compounds in liquid samples. Samples were acidified with 0.5 ml of 2.5 N HCl to pH~2. Intense bubbling of pure synthetic air throughout the sample for 10 min. allowed complete decarbonation. Thus, the measured DOC was not purgable organic carbon. Some volatile organic carbon (VOC) may be lost at room temperature by acidification and purging. Nevertheless, the contribution of the VOC to the DOC value (less than 1%) is considered insignificant (Wangersky, 1993). The decarbonated sample was pumped by a glass syringe and injected into a vertical furnace (combustion quartz tube) which was filled with a 0.5% Pt on Al₂O₃ catalyst. Three to 5 replicate injections of 200 µl were performed per sample. The concentration of DOC was determined by subtracting system blank area from the average peak area and dividing by the slope of the standard curve (Thomas et al., 1995). The system blank is the instrument blank plus DOC in UV-Milli-Q water plus the filtration blank. Measurements made with the high sensitivity catalyst (platinum on silica wool) produced values <2 µM-C for fresh UV-Milli-Q water. The filtration blank (determined by filtering UV-Milli-Q water through the filtration system) was ~5 µM-C. Before sample analyses, the catalyst was washed by injecting UV-Milli-Q, for at least 12 h, until the instrument blank was low and stable. The instrument blank was <8 µM-C; when it was higher, we washed or even replaced the

catalyst. The system was standardized with Potassium Hydrogen Phthalate (KHP). A two-points calibration (0 and 200 $\mu\text{M C}$) was performed routinely every 20 samples with freshly prepared running standards. The coefficient of variation (C.V.) of the peak area for the 3-5 replicates of each sample was $\sim 1\%$.

DON measurements

Most procedures for the determination of the DON are based on the estimation of the total dissolved nitrogen (TDN) from which it is subtracted the independently measured inorganic nitrogen concentration (DIN: nitrate, nitrite and ammonium). Thus, the estimation of DON by this method, accounts for the inaccuracies introduced by the TON and the DIN quantification. In the present study, DON was directly measured by an updated Kjeldahl method (Doval et al., 1997a). A volume of 100 ml of sample was introduced into a 300 ml Pyrex Kjeldahl flask. To eliminate ammonium, 1 ml of 0.5 N NaOH was added and the solution was boiled until the sample volume was reduced by a half. Next, 10 ml of $\text{H}_2\text{SO}_4\text{-FeSO}_4$ reagent were added to concentrate the sample and remove nitrogen oxides. The heating must go on to convert DON to ammonium in acid medium. The residue was diluted with UV-Milli-Q water and carried to a distillation device, where 20 ml of 33% NaOH were added and the resulting ammonia was co-distilled with water vapour until 20 ml were collected over 5 ml of 10^{-3} M HCl. Ammonium concentration on the distillate, directly related to DON in the sample, was finally determined with the SFA system. The average blank was 2 $\mu\text{M-N}$ and it was subtracted from DON values. We analysed duplicate seawater samples, being the C.V. 5%.

RESULTS

Hydrographic conditions

The studied transect covered three main water masses, identified by the salinity distribution, from West to East: coastal water, Local Mediterranean Water and Modified Atlantic Water (Fig. 2A). The Catalan Front was located at the continental slope, around station #3. This continental front separated low salinity (< 38.0) shelf water from the more saline offshore one. The Local Mediterranean Water, extended from stations #4 to #7. At the easternmost part of the transect, the presence of the Balear Front was noticed between stations #7 and #8 at surface. This shallower front separated the Local Mediterranean Water from recent Modified Atlantic Water that has entered the Balearic Basin through the Ibiza channel (Salat and Cruzado, 1981).

All water masses were thermally stratified (Fig. 2B). A marked thermocline extended from approximately 10 to 60 m depth along the transect. Associated to the thermocline, deep chlorophyll *a* maxima (DCM) were found (Fig. 2C). At the depth of the DCM (between 30 and 60 m) chlorophyll *a* concentrations reached 1.4 mg m^{-3} . Close to the coast, chlorophyll *a* concentrations were lower than offshore and the DCM was weak. Within the transect, the highest chlorophyll *a* concentrations were associated to the frontal structures.

Oxygen distribution presented concentration maxima between 30 and 50 m, *i.e.* at the basis of the thermocline (Fig. 2D). Oxygen concentrations were higher at the central zone than at the two extremes of the transect.

Particulate and dissolved organic matter distributions

The distribution of the PON and POC (Figs. 3A and 3B) showed maximum values at the level of the DCM. At this level, stations #3 and #6 presented the highest values of POC (14 and 8 μM , respectively) and PON (1.8 and 1.4 μM , respectively). Station #7 exhibited the lowest concentrations (3 μM -C and 0.4 μM -N). Chlorophyll *a* and POM concentrations were not related; considering all data pairs, the determination coefficient of the linear regression (Model II, Sockal and Rolhf, 1995) was low and not significant ($r^2 < 0.30$). The distribution of the C:N molar ratio of the POM (POC:PON, Fig. 3C) increased specially eastwards. In general, the distribution of the POC:PON ratio showed minimum values (*ca.* 6) at the depth of the DCM. On average the POC:PON molar ratios were 8.6 ± 0.6 ($n=63$, Table 1). POC and PON showed parallel trends, as indicated by the high and significant determination coefficient found, when considering the whole data set (Table 1).

The average concentrations and variation ranges of DOC and DON in the upper 100 m and between 200 m to 2000 m are summarized in Table 2 and 3. In addition, DOC and DON reported by other authors are compared. In general, vertical profiles of DOC and DON presented maximum values at surface, in the photic zone, and decreased with depth (Fig.4A and 4B). At 50 m depth, coinciding with the DCM and the oxygen maxima, slightly minimum concentrations of DON and, specially of DOC, were observed (stn. #2, #3, #4, #7 and #9). Below 500 m the low concentrations were nearly homogeneous. In station #1, where the water column was mixed, DOC and DON were fairly uniformly distributed. An example of the vertical profiles of DOC and DON concentration compared to that of temperature is illustrated for station #7, which also constituted the deepest sampled station (Fig. 5).

The distribution of the DOM (Figs. 4A and 4B) appeared to be inverse to that of the salinity (Fig. 2A). The coastal and Catalan front stations, characterized by low salinity values, presented the highest DON and DOC concentrations. Opposite trends were observed at the central stations. It was worth noting the similarity of the 38.2-38.3 isolines and the 60 $\mu\text{M-C}$ and 4 $\mu\text{M-N}$ isolines, with the characteristic doming at the central stations. Considering the whole data set, DOC and salinity (S) were significantly related following the expression:

$$\text{DOC } (\pm 7.8) = 1669 (\pm 151) - 42 (\pm 4) S$$

$$r^2 = 0.65 \quad n = 63 \quad p < 0.001$$

The lineal regression between DON and S was slightly lower ($r^2 = 0.57$). These regressions increased when the surface values of stations #8 and #9 (with minimum S and different water masses) were not included ($r^2 = 0.74$, $p < 0.001$).

In general, the distribution pattern of the DON and DOC concentrations was very similar and the lineal regression between the two parameters was significant ($r^2 = 0.83$, Table 1). The distribution of the C:N molar ratio of DOM (DOC:DON) increased slightly with depth and eastwards (Fig. 4C). The lowest C:N molar ratios were found in surface waters of the coastal stations (*ca.* 13). DOC:DON ratios oscillated between 13 and 19, with a mean value of 15.5 ± 0.4 ($n = 47$, Table 1). Significant relations were found between DOC and POC and between DON and PON ($r^2 = 0.50$, Table 1). However, DOM and chlorophyll *a* were not significantly related.

DISCUSSION

The hydrographic conditions found during the VARIMED'95 cruise were typical of the stratification season in the open sea waters of the study area (Pérez et al., 1986; Font et al., 1988). During this stratification period, the presence of the Catalan and the Balear fronts appear to play an important role in the fertilization of this area (Estrada and Margalef, 1988; Estrada and Salat, 1989). The doming of the isolines between the two frontal systems is a consistent trend registered in other cruises (Estrada and Margalef, 1988; Estrada and Salat, 1989; Estrada et al., 1993). It is considered that this hydrographic feature helps also to maintain relatively important biomass levels by rising the nutrient rich waters to the surface. This can be evidenced by the increase in the chlorophyll *a* and in the POC and PON concentrations as well, near the frontal structures and at the basis of the thermocline (Figs. 2C and 3A, 3B). The particular distribution of the oxygen maxima, slightly shallower than the DCM agrees with the pattern of vertical distribution of primary production maxima reported in this area (Estrada et al., 1993). In addition, the slightly minimum of DOC concentrations (stn. #2, #3, #4, #7 and #9) agrees with the maximum of biological activity at the DCM.

Nevertheless, the total microplanktonic biomass, estimated from the POC and PON values, did not match chlorophyll *a* concentration distribution. This is due, partly from the different contribution of the phytoplanktonic *versus* the total plankton community (Alcaraz et al., 1985), and the degree of coupling between the autotrophic biomass and the rest of the planktonic organisms in the different zones of the studied transect (Vaqué et al., 1994; Calbet et al., 1996).

The relevant role of the hydrographic conditions in the biogeochemical processes was also noted in the distribution of the DOM. The significant relationship between DOM and salinity suggests that physical processes highly controlled the

mesoscale distribution of DOM in the water column in the studied area. Furthermore, the inverse relationship indicates that, coastal waters, near Catalan front, were a important source of DOM. In the studied area, the river water discharges come from the Arno to Ebro with a maximum river runoff in the inner shelf of the Gulf of Lions, corresponding to the Rhône (Salat 1996 and references there in). Therefore, the low salinity waters must have traveled a long way and they had been mixed with high salinity waters. In the open ocean, only about 10% of the DOC is estimated to be of terrestrial origin (Meyers-Schulte and Hedges, 1986). Thus, the higher concentrations of DOC in surface waters compared to deeper layers are likely the result of the biological activity since the stabilization of the water column. The small scale and biological variability affecting the production and consumption processes of DOC and DON will be reported elsewhere (Berdalet et al., in prep.; Gasol et al., 1998).

This work constitutes a first data set obtained in the Mediterranean Sea with simultaneous determination of DOM and POM. POC and PON concentrations were in the same range as those obtained by other authors in Mediterranean waters (Banoub and Williams, 1972; Copin-Montégut and Copin-Montégut, 1983; Alcaraz et al., 1985).

The DOC values measured in our cruise were in the range reported by other studies in the Western Basin of the Mediterranean Sea (Table 2). With the exception of the data provided by Banoub and Williams (1972) using the peroxidisulfate oxide method, all the available data were obtained by the HTCO technique. The data obtained in our cruise in the open sea waters, fall also in the same range recently reported for other oligotrophic areas (range: 35-110 $\mu\text{M-C}$; Tupas et al., 1994; Thomas et al., 1995; Sharp et al., 1995; Carlson and Ducklow, 1995 and Chen et al., 1996). The range of

DOC values were lower than that obtained from a richer ecosystem, the Ria de Vigo (NW Spain), with average chlorophyll *a* of $6.2 \mu\text{g l}^{-1}$ (average DOC: $107 \mu\text{M-C}$) in the surface layer and $1.1 \mu\text{g l}^{-1}$ (average DOC: $77 \mu\text{M-C}$) in the bottom layer (45 m deep), during summer (Doval et al., 1997b).

The DON concentrations obtained in the VARIMED'95 cruise were close to those estimated using the UV-oxidation method ($\text{DON} + \text{NH}_4^+$) by Banoub and Williams (1972) in the western Mediterranean waters and by Coste et al. (1988) in the Alboran Sea (Table 3). Using the Kjeldahl modified method, Fraga (1966, 1969) measured the same range of DON for Indian waters (2.0-8.0). Finally, similar values were found by Doval et al. (1997a) in the eastern North Atlantic (3.0-11.0).

In the present study, DOC and DON constituted approximately the 90% of the total organic carbon ($\text{POC} + \text{DOC}$) and nitrogen ($\text{PON} + \text{DON}$) in the whole water column. The percentage of DOC was similar to that estimated by Cauwet et al. (1990) in Mediterranean waters. This finding corroborates the important role of DOC as a major form of carbon export in the Mediterranean Sea as first suggested by Copin-Montégut and Avril (1993).

During the stratification period inorganic nutrients are, in general, close to the detection limit in the photic zone (Minas et al., 1988) and this was the case during the VARIMED'95 cruise (Berdalet et al., 1996a; Berdalet et al., in prep). Nevertheless, the C:N molar ratio of the POM, close to 7 in most part of the transect, would agree with the idea that the microplankton communities were not nitrogen limited (Berdalet et al., in prep.), at least during the studied season. Similar high C:N ratios of DOM have been reported by other authors in different areas (Jackson and Williams 1985; Hansell et al, 1993; Williams, 1995; Chen et al, 1996; Doval et al, 1997b), and mechanisms other

than preferential DON over DOC consumption have also been proposed to explain the accumulation of C-rich DOM (Williams, 1995).

A main issue with regards to the dissolved organic matter is its availability to the microorganisms. The bulk DOC pool can be separated into the highly labile, the semi-labile and the refractory pools (Kirchman et al., 1993). Following Carlson and Ducklow (1995), the labile pool consists of biologically available organic matter that turns over on time scales of hours to days; the semi-labile pool turns over on a seasonal time scale; and the refractory DOC, representative of deep waters has an average life time of 6000 years (Williams and Druffel, 1987). In surface waters, all pools are present. The concentration of "new" (*i.e.* non-refractory) DOC depends highly on the balance between its *in situ* production by different biological processes and its consumption within the food web as well.

DOM partitioning has been estimated with a simple 1-D model as used by Carlson and Ducklow (1995) and Cherrier et al. (1996) in oligotrophic gyres. In our study, the average DOC was $78 \pm 7 \mu\text{M}$ at the surface waters, $72 \pm 10 \mu\text{M}$ for waters in the upper 50 m, $62 \pm 9 \mu\text{M}$ at 100 m and $49 \pm 3 \mu\text{M}$ for waters below 500 m. Assuming that the recalcitrant material is homogeneously distributed in the water column (Carlson and Ducklow, 1995), and the DOC pool at depth >500 m is essentially refractory, $49 \pm 3 \mu\text{M}$ would correspond to the recalcitrant DOC concentration. It would constitute the 68% of the total DOC in the upper 50 m or the 63% of surface DOC; *i.e.* the non-refractory DOC or DOC excess (semi-labile + labile) was the 37% of the surface DOC. We could assume the presence of two main fractions of DOC at 100 m depth (refractory and semi-labile), as found by Cherrier et al. (1996) below the DCM in the North Pacific. The semi-labile pool would then account for *ca.* $13 \mu\text{M-C}$, which corresponds

to the 17% of surface DOC. Finally, the remaining 16 $\mu\text{M-C}$ obtained from the difference between average surface DOC and the other two fractions were about the 20% of the surface DOC. But, we only can only calculate two fractions of DOM: excess (semi-labile + labile) and refractory with our data base. It can be considered that DOC excess has been accumulated in surface water since winter mixing.

Similar calculations can be performed for the estimation of the recalcitrant, semi-labile and labile DON pools. The average DON was $5.2 \pm 0.5 \mu\text{M}$ at the surface waters, $4.8 \pm 0.8 \mu\text{M}$ in the upper 50 m, $3.9 \pm 0.5 \mu\text{M}$ at 100 m and 3.1 ± 0.3 below 500 m. The concentrations obtained were: 3.1, 0.8 and 1.2 $\mu\text{M-N}$ for the recalcitrant, semi-labile and labile DON pools, respectively. These concentrations correspond to the 60%, 16% and 24% of the surface DON, respectively. DON excess constitute the 30% of surface DON. The C:N molar ratio of DOM was higher in the refractory pool (~ 16) than in the more labile fraction (~ 13), as expected. It is noted that the C:N molar ratio of the fraction more labile (semi-labile+labile) is similar to the slope of the direct lineal regression between DOC and DON (13.3; Table 1).

The percentage of the recalcitrant DOC (63% of surface DOC or 68% of the upper 50 m DOC) was similar to that estimated by others authors in oligotrophic areas (Carlson and Ducklow, 1995; Thomas et al., 1995 and Chen et al. 1996). A wider range of refractory DOC (50-100%) was found by Copin-Montégut and Avril (1993) in the Northwestern Mediterranean during the annual cycle studied. The amount of semi-labile DOC (about 11 $\mu\text{M-C}$) estimated in the surface waters was similar to the seasonal variability observed in surface waters of the Ligurian Sea by Copin-Montégut and Avril (1993). It has been suggested that grazing pressure on bacteria or nutrient limitation would result in low bacterial activity and thus, DOC accumulation in surface waters

(Williams, 1995; Thingstad and Rassoulzadegan, 1995; Chen et al., 1996). The VARIMED'95 cruise was conducted in June, *i.e.* approximately after three months since the beginning of the stabilization of the water column with the subsequent development of phytoplankton and microbial biomass. Low concentration of labile DOC would have been expected if the production and consumption mechanisms were tightly coupled as it seems to occur in the Equatorial Pacific (Carlson and Ducklow, 1995). Nevertheless, this could not be the case for the NW Mediterranean where phosphorus seems to play a main limiting role (Berland et al., 1980; Thingstad and Rassoulzadegan, 1995; Berdalet et al., 1996b). Detailed studies on bacterial production and respiration yields should allow to properly quantify the highly-labile DOC (Norrman et al., 1995; Giorgio et al., 1997).

The present study was addressed to contribute to the understanding of the carbon cycle in the NW Mediterranean. Nevertheless, many opened questions remain. Further seasonal studies on the temporal and spatial DOM variability should be conducted to know the different magnitude of the biological and physical control of the origin and fate of the organic matter in this area.

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Table 1. Selected lineal regressions among the different variables related to organic matter pools: dissolved organic carbon (DOC) or nitrogen (DON), and particulate organic carbon (POC) or nitrogen (PON)). These coefficients were calculated by minimizing the area $(y_i - y_{im})(x_i - x_{im})$, being y_{im} and x_{im} the average values of y_i and x_i , respectively). Numbers in brackets indicate the standard error of the estimated y-intercept or slope.

Parameters	Average ratio	SD	n	Linear relationship	r^2
POC <i>vs</i> PON	8.6	0.6	63	$y = 0.37 (\pm 0.1) + 7.04 (\pm 0.2)x$	0.96
DOC <i>vs</i> DON	15.5	0.4	47	$y = 8.1 (\pm 3.6) + 13.3 (\pm 0.8)x$	0.83
DOC <i>vs</i> POC	20.3	2.8	63	$y = 43.9 (\pm 2.2) + 3.8 (\pm 0.3)x$	0.53
DON <i>vs</i> PON	12.4	2.4	47	$y = 2.7 (\pm 1.5) + 2.2 (\pm 0.2)x$	0.49

Table 2. Summary of the DOC values (μM) obtained in the present study and comparison with other values reported in Mediterranean waters.

Study area	Depth (m)	Average $\pm$ SD	Range	n	Reference
NW Mediterranean	0-100	68.5 ± 3.6	52-95	35	This study
Sea- summer	200-2000	50.9 ± 1.6	44-63	28	
Western-Mediterranean Sea	0-2000		20-70		Banoub and Williams 1972
Gulf of Lions	0-2000		50-90		Cauwet et al. 1990
“	0-2000		40-200		Cauwet et al. 1997
Ligurian Sea -whole year	0-100		62.5 - 100		Copin-Montégut and Avril 1993
	150-2000		50-60		
Mediterranean Sea	0-200		50-100		Cauwet 1994

Table 3. Summary of the DON values (μM) obtained in the present study and comparison with other values reported in Mediterranean waters.

Study area	Depth (m)	Average $\pm$ sd	Range	n	Reference
NW Mediterranean	0-100	4.5 ± 0.3	3.3-6.2	27	This study
Sea - summer	150-2000	4.0 ± 0.2	2.8-4.7	20	“
Western-Mediterranean	0-100	5.2	3-6.1		Banoub and Williams, 1972
	100-2000	3.3	2.0-4.6		
Alboran Sea	0-100	4.7	3.0-6.3		Coste et al. 1988
	150-800	2.9	2.7-3.1		“

FIGURE CAPTIONS

Figure 1. Study area in the Catalan-Balearic Sea. Numbers indicates the position of the stations sampled in the transect studied.

Figure 2. Distribution of A) Salinity, b) Temperature ($^{\circ}\text{C}$), C) Chlorophyll *a* concentration ($\mu\text{g l}^{-1}$) and D) Oxygen concentration ($\mu\text{mol kg}^{-1}$)

Figure 3 Distribution of A) Particulate Organic Carbon (POC, $\mu\text{M-C}$), B) Particulate Organic Nitrogen (PON, $\mu\text{M-N}$) and C) relation POC:PON

Figure 4. Distribution of A) Dissolved Organic Carbon (DOC, $\mu\text{M-C}$), B) Dissolved Organic Nitrogen (DON, $\mu\text{M-N}$) and C) relation DOC:DON

Figure 5. Example of the vertical profiles of Dissolved Organic Carbon (DOC, $\mu\text{M-C}$), Dissolved Organic nitrogen (DON, $\mu\text{M-N}$) in the upper 200 m (top) and down to 2000 m depth (bottom) at station 7 in the transect studied

(Fig. 1, Doval et al.,)

(Fig.2. Doval et al.,)

(Fig.3. Doval et al.,)

(Fig.4. Doval et al.,)

(Fig. 5. Doval et al.,)