
Dissolved organic carbon, nitrogen and phosphorus in the N-E Atlantic and the N-W Mediterranean with particular reference to non-refractory fractions and degradation

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Abstract:

Dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) measured in deep profiles in the N-E Atlantic and in the N-W Mediterranean in the period 1984–2002 are described. After accurate validation, they show close agreement with those previously published.

Classic profiles were obtained, with concentrations decreasing in deep waters. In the Mediterranean and in the Atlantic comparable concentrations were found in the 1500–2000 m waters, 44–46 $\mu\text{mol l}^{-1}$ DOC, 2.6–2.8 $\mu\text{mol l}^{-1}$ DON and 0.02–0.03 $\mu\text{mol l}^{-1}$ DOP. In the surface layers, DOC concentrations were higher, but DON and DOP concentrations lower, in the Mediterranean than in the Atlantic, leading to higher element ratios in the Mediterranean. In autumn, values were, respectively, DOC:DON ≈ 17 vs. ≈ 14 , DOC:DOP ≈ 950 vs. 500 and DON:DOP ≈ 55 vs. 35. The data suggest an increase in DOC and DON in the North Atlantic Central Water over 15 years, which may be linked to the North Atlantic climatic oscillations.

Refractory DOM found in the 1500–2000 m layer exhibited C:N:P ratios of 1570:100:1. The labile+semi-labile (=non-refractory) DOM (nrDOM) pool was computed as DOM in excess of the refractory pool. Its contribution to total DOM above the thermocline in the open sea amounted to 25–35% of DOC, 30–35% of DON, and 60–80% of DOP. Element ratios of the nrDOM varied among stations and were lower than those of refractory DOM, except for C:N in the Mediterranean: nrDOC:nrDON ≈ 10 –19, nrDOC:nrDOP ≈ 160 –530 and nrDON:nrDOP ≈ 15 –38. The specific stoichiometry of DOM in the Mediterranean led us to postulate that overconsumption of carbon is probably a main process in that oligotrophic sea.

By coupling non-refractory DOM stoichiometry and relationships between the main DOM elements in the water column, the relative mineralization of C, N and P from DOM was studied. Below the thermocline, the preferential removal of phosphorus with regard to carbon from the semi-labile DOM can be confirmed, but not the preferential removal of nitrogen. In the ocean surface layers, processes depend on the oceanic area and can differ from deep waters, so preferential carbon removal seems more frequent. Bacterial growth efficiency data indicate that bacteria are directly responsible for mineralization of a high proportion of DON and DOP in the deep water.

Keywords: Dissolved organic carbon; Dissolved organic nitrogen; Dissolved organic phosphorus; Refractory; Non-refractory; Mineralization; N-E Atlantic; N-W Mediterranean

1 INTRODUCTION

Dissolved organic matter (DOM) is produced and decomposed by microorganisms in the oceans and contributes to the transfer of production in oligotrophic areas and to deep ocean layers (Christensen *et al.*, 1989; Toggweiler, 1989; Copin-Montégut and Avril, 1993; Emerson *et al.*, 1997; Abell *et al.*, 2000). DOM may also constitute a source of nutrients for primary production where inorganic nitrogen and phosphorus become limiting factors (Berman and Chava, 1999). In addition to biological processes, DOM transformation may result from photoreaction in the surface layer and the subsequent production of some biologically labile compounds (Mopper *et al.*, 1991; Moran and Zepp, 1997), but with an overall reduction in bacterial production (Benner and Biddanda, 1998). Therefore, DOM is an essential link in the processes controlling carbon and nutrient cycling. Since it accounts for about 50 % of the organic matter mass, carbon is an ideal tracer of ocean DOM. Consequently, dissolved organic carbon (DOC) has been widely studied over the last decade.

It is well established that concentrations of DOM are higher in the upper layer than in deep water bodies. In deep waters, organic matter is highly refractory to bacterial mineralization and its residence time is on the order of thousands of years (Bauer *et al.*, 1992). Recent studies, which have produced more reliable concentration values, tend to attribute a narrow range of concentrations around 40-50 $\mu\text{mol l}^{-1}$ DOC in deep waters over the world ocean. However, comparison of various areas shows that the deep water DOC concentration actually exhibits gradients throughout the world (Hansell and Carlson, 1998).

Several authors have shown that better understanding of the DOM cycle in the oceans requires the coupling of DOC and dissolved organic nitrogen (DON) pools and dynamics (Kirchman *et al.*, 1991; Carlson *et al.*, 1994; Fasham *et al.*, 1999). The elemental composition of DOM is also an indicator of its bioavailability (Hunt *et al.*, 2000; Sun *et al.*, 1997). In order to obtain more complete information on how DOM behaves, it is preferable to evaluate it using the three elements essential to biological processes: dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP).

Despite the increasing number of studies dealing with dissolved organic matter, those including simultaneous measurements of DOC, DON and DOP are rare. This paper uses data mostly obtained in the 1980s and 90s, when there was considerable concern about the measurement of DOC and DON (Suzuki *et al.*, 1985; Sugimura and Suzuki, 1988; Toggweiler, 1988; Williams and Druffel, 1988; Sharp, 1993). Then international research on DOC, DON and DOP determinations (Special Issue of Marine Chemistry 41, 1993) and subsequent intercomparisons (Sharp, *et al.*, 1995; Peltzer *et al.*, 1996) led to the conclusion that older data could be trusted, provided that methods were carefully corrected for artifacts (mainly blanks) and checked (Sharp, 1997). Accordingly, our results were completely re-examined in the light of recent advance in methods, and now constitute a consistent set of comparable data. It is important to note that, over the study period, DON was measured using a single method, as was DOP, and DOC was measured using two closely intercompared methods. This data set allowed the first comparison of DOM stoichiometry from vertical profiles in the Bay of Biscay (N-E Atlantic) and from the northwestern Mediterranean to be made. These oceanic bodies exchange water through the strait of Gibraltar, and Mediterranean water influences the vertical hydrography in the N-E Atlantic. The paper will focus on several aspects that may influence DOM concentration and stoichiometry, giving particular attention to the non-refractory pool of DOM in terms of concentration and mineralization.

2 MATERIAL AND METHODS

2.1 Study area main characteristics

The area of study and sampling stations are described in Figure 1 and Table 1. DOC, DON and DOP could be measured simultaneously at three profiles in the Atlantic (stations A1, A2 and A3) and one profile in the Mediterranean (station M). Because it is more difficult to measure DOP precisely, additional DOP results are provided from two other profiles in the Atlantic (stations A4 and A5).

Table 1. Characteristics of sampling stations.

Station	Area	Date	Position	Bottom depth m	Deepest sample m	Cruise name
A1	N-E Atlantic Bay of Biscay	10 Sept. 1985	43° 38.0' N 1° 52.2' W	900	850	Intersite 3
A2	N-E Atlantic Bay of Biscay	20 April 2002	46° 45.0' N 5° 59.6' W	4240	4000	Gasprod
A3	N-E Atlantic Bay of Biscay	26 Oct. 1987	46° 00.0' N 6° 01.6' W	4200	3500	Intersite 4
A4	N-E Atlantic Bay of Biscay	24 July 1990	46° 11.9' N 9° 10.0' W	4780	1500	Gastom 3
A5	N-E Atlantic Bay of Biscay	25 July 1990	45° 01.9' N 9° 55.1' W	4875	1500	Gastom 3
M	N-W Mediterranean	13 Sept. 1984	42° 02.4' N 5° 04.8' E	2500	1500	Intersite 2

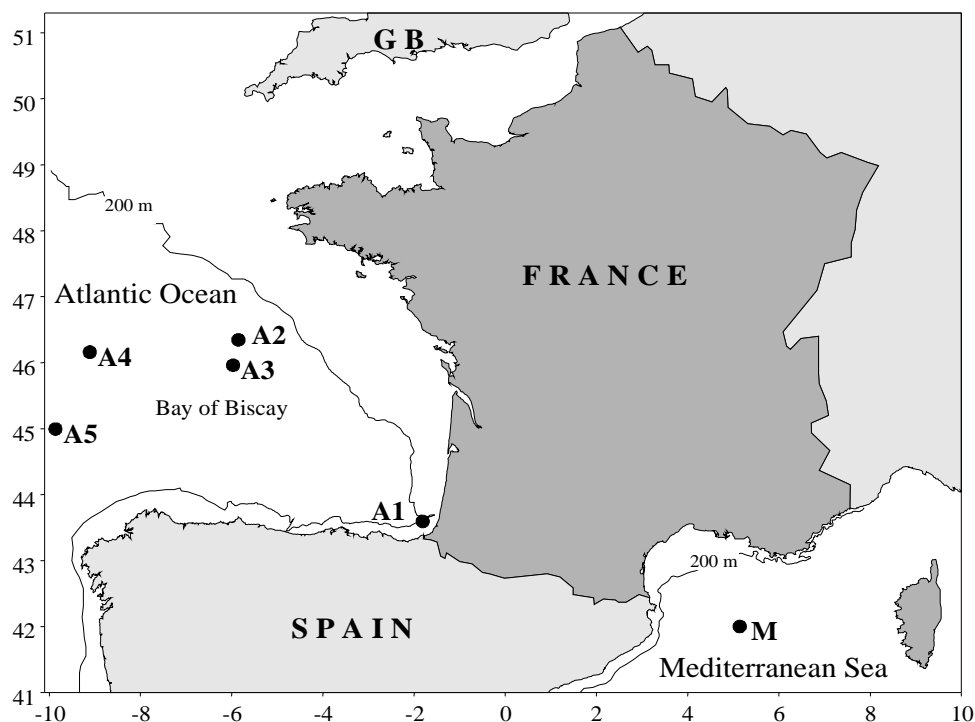


Figure 1. Location of sampling stations.

NE Atlantic

The water masses have been widely described (*e.g.*, Vangrieshem, 1985; Arhan *et al.*, 1994). In winter, the upper layer (0-700 m) of North Atlantic Central Water (NACW) is mixed by intense convection. In spring, NACW begins to be capped by a seasonal thermocline, isolating North Atlantic Surface Water (NASW) of variable salinity and temperature (max. depth 100 m). A marked pycnocline separates NACW from the North Atlantic Mediterranean Water (NAMW) plume identified by the salinity maximum (800-1200 m). Labrador water lies around 1800 m and Norwegian Sea water around 2000 m. Below 2000 m, the North Atlantic Deep Water (NADW) coming from Greenland is influenced by the all-pervading diluted Atlantic Antarctic Bottom Water (AABW).

Mediterranean Sea

The three-layer system found in this sector has been well documented (*e.g.*, Wüst, 1961; Lacombe, 1975). The core water masses are i) the less saline, upper layer (MUL) water of Atlantic origin (~ 0-75 m), ii) the more saline, intermediate water of eastern origin (MIEW; ~ 200-600 m) and iii) the deep Mediterranean water (DMW) below 1500 m.

2.2 Sampling and storage

Water was sampled in 5 or 8 liter Niskin bottles. Subsamples were collected for salinity in glass bottles with rubber sealed porcelain caps and for nutrients in 125 ml polyethylene bottles pretreated with 10 % HCl. For DOM, samples were collected in 500 ml precombusted glass bottles, and subsequently filtered within half an hour onboard the ship. After vacuum (max. 0.3 bar) filtration through precombusted (480 °C) Whatman GF/F glass-fiber filters, the subsamples were collected in precombusted glass bottles stoppered with linerless polyethylene screwcaps (35 ml for DOC measured by high temperature combustion, 125 ml for DOC measured by wet oxidation and 125 ml for DON+DOP). The subsamples for nutrients and DOM were immediately stored in upright position in a freezer (-20 to -25 °C) used only for water samples. Freezing of non-acidified samples of seawater has already been shown to be a reliable preservation technique up to 5-6 months (Walsh, 1989; Williams *et al.*, 1993; Tupas *et al.*, 1994). Analysis was performed in the shore laboratory within a few months of collection, and within one hour after samples were thawed in a cold tap water bath and then well mixed.

2.3 Temperature, salinity and nutrient measurements

Temperature was measured using reversing thermometers before the 1990s, later using in situ probes. Salinity (in PSS78) was measured soon after the cruise with a Guildline 8400 or 8410 salinometer. Ammonium (before the 2002 cruise), nitrate+nitrite (N&N), phosphate and silicate were measured using the classic colorimetric methods adapted to segmented flow analysis (Technicon Autoanalyzer II) according to Tréguer and Le Corre (1975). For the 2002 cruise, ammonium was measured according to K  rouel and Aminot (1997).

2.4 DOC measurement

Measurements were performed up to 1989 using an automated wet oxidation (WO) method including direct intake from the sample bottle (no decanting), automated inorganic carbon removal, hot acidic persulfate plus UV-alkaline oxidations and colorimetric CO₂ determination (Aminot and K  rouel, 1990). The high temperature combustion (HTC) instrument (Shimadzu TOC 500) used subsequently was equipped with an ASI 502 automatic sample injector. Inorganic carbon was eliminated shortly before analysis by adding 250 µl HCl 1.2 mol l⁻¹ directly to the whole sample (30 ml) contained in the sample bottle and bubbling (99.9998 % O₂, 300 ml min⁻¹, 10 min). The sample bottles were then presented one

by one to the automatic injector's syringe, with the carousel removed to avoid sample transfers, and each sample was injected at least three times. The Shimadzu High Sensitivity catalyst (platinized quartz wool, P/N 630-00958, topped with 10 platinum grids) was used. The catalyst was renewed well before it became what Peltzer and Brewer (1993) called "salt-impregnated dust". Since Cauwet *et al.* (1990) and Peltzer and Brewer (1993) suspected that platinized quartz wool (PQW) oxidized less DOC than other catalysts, the performances of PQW and a 4.5 % Pt-alumina catalyst (provided by Shimadzu-France) were compared. Milli-Q water solutions of organic compounds (sulfathiazol, antipyrine, thiourea, L-methionine, L-cysteine, L-tryptophan, nicotinic acid, fulvic acid, humic acid, starch, albumin, chitin, polyethyleneglycol; $\sim 170 \mu\text{mol l}^{-1} \text{C}$) and natural seawater led to comparable ($\pm 3\%$) or even better recoveries (range 80-100 %) with PQW. Additionally, PQW ageing was checked by analyzing 18 natural samples ($40\text{-}80 \mu\text{mol l}^{-1} \text{DOC}$) twice, first after 70 then after 275 seawater analyses (meantime, the samples were stored tightly capped in a closed metal box). At the significance level of $\alpha = 0.05$ a two-sided Student t-test showed that DOC recoveries were identical ($t = 1.4$ compared to critical- $t = 2.1$).

Freshly drawn demineralized water, from a Milli-Q system equipped with an Organex cartridge, was used as blank. In the continuous flow WO method, UV/H₂O₂-treated natural or artificial seawater was used to overcome artifacts, but specific corrections were made to refer to Milli-Q. Compared with UV/H₂O₂-treated water, fresh Milli-Q water was found to be organic-free within the detection limit of our DOC methods ($< 3 \mu\text{mol l}^{-1}$). This agrees with data on Milli-Q water's carbon content (Sharp *et al.*, 1993). In the HTC method, the total blank is mainly a system blank (overall range: $6\text{-}15 \mu\text{mol l}^{-1} \text{DOC}$). Daily blank variations were smooth, with standard deviations $< 2 \mu\text{mol l}^{-1}$. Interpolation of individual sample blanks between blank measurements decreased blank uncertainty to within $\pm 1 \mu\text{mol l}^{-1}$. With blank reference material provided by Dr J.H. Sharp, the DOC equivalent total system signal ranged from 7 to $11 \mu\text{mol l}^{-1}$ (1997 to 2002), while the actual DOC concentration found in the RM was $0.9 \pm 0.8 \mu\text{mol l}^{-1}$ (10 samples). The stability of the HTC response was checked over the period from 1999 to 2002 with the deep ocean reference material provided by J. Sharp: the concentration found was $47.4 \pm 1.9 \mu\text{mol l}^{-1}$ (7 samples).

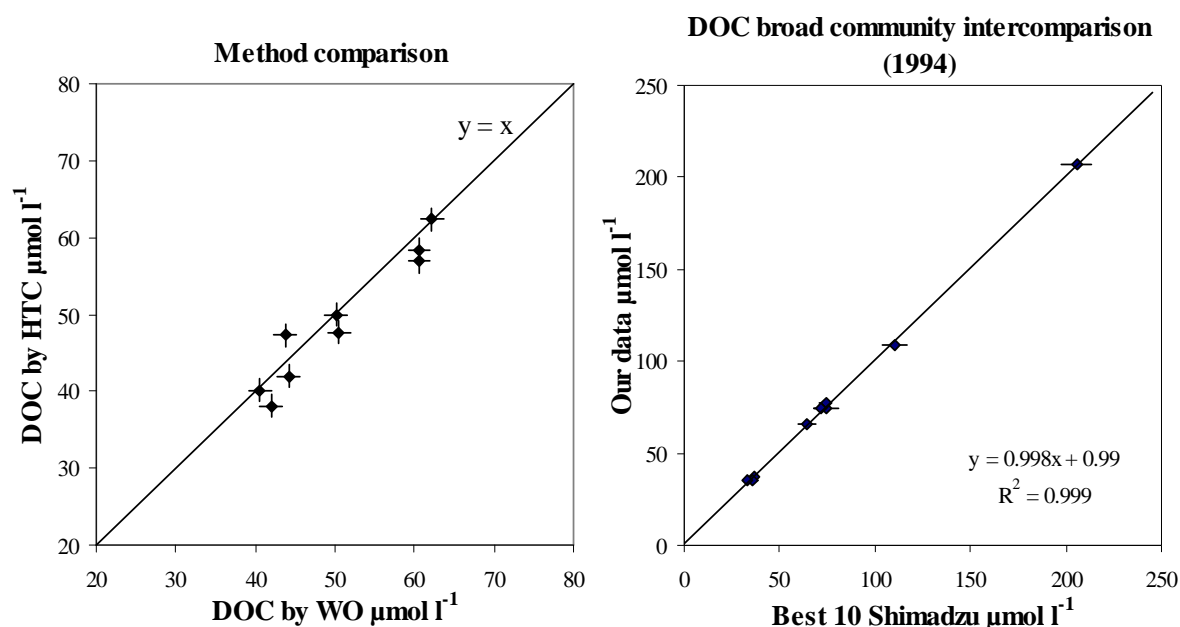


Figure 2. DOC data comparison. Left: laboratory comparison of our WO and HTC results (with standard deviation) using samples from station A3. Right: broad community intercomparison 1994, our data vs the 10 best Shimadzu (with standard deviation).

Our WO and HTC methods were compared using 9 samples from the 1987 deep Atlantic profile A3 (Figure 2). A two-sided Student t-test showed that DOC determinations by WO and HTC did not differ ($t = 1.7$ compared to critical- $t = 2.3$; $\alpha = 0.05$). Our results in the 1994 broad community intercalibration compared well with the ten best Shimadzu averages (Sharp *et al.*, 2002; Figure 2). The comparability of our WO and HTC results, along with the agreement of our HTC results with international data, validates our whole DOC data set.

2.5 DON measurement

The persulfate WO method developed by Solorzano and Sharp (1980) was considered to be the most suitable and reliable for TDN determination, since it ensures complete recovery of nitrogen from recalcitrant compounds. DON resulted from the difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (nitrate + nitrite + ammonium) measured in the same run, just before sample oxidation, from the same sample bottle. The method was applied with the following minor modifications. Using automatic pipettes, aliquots of 10 ml (instead of 40 ml) were used and reagents added proportionally. To resist pressure, screw-cap 25 ml borosilicate glass bottles with PTFE-coated silicone liners (Duran Schott, GL 25) were selected (instead of all Teflon vials). The oxidation vials (new or unutilized for some time) were cleaned as follows: rinsed with Milli-Q water, pyrolyzed at 500 °C, put through a normal procedure run with Milli-Q water as a sample and finally rinsed and capped. Just before use, the reaction vessel was rinsed with freshly drawn Milli-Q water and thoroughly shaken dry. The vials were autoclaved with caps tightly closed (instead of unscrewed) to avoid evaporation and potential contamination from the atmosphere. The last step of the original procedure, buffering before measuring nitrate, was omitted since the high dilution by the buffer reagent in our automated nitrate method (Tréguer and Le Corre, 1975) enabled direct analysis of the acidified samples. Clogging of the Cd-Cu reduction column, which Solorzano and Sharp (1980) attributed to insoluble silica released from glass vials, was not observed because of rapid settling of particles, followed by high dilution of the supernatant in the manifold. These modifications decreased the blank significantly and improved the overall precision of DON data. Determining the nitrate in the non-oxidized and oxidized samples in the same run (same calibration curve) also enhanced reliability.

DON analysis periods started by systematically checking blank repeatability in all the bottles used for that series and repeating the process until the variability stabilized at usual values ($\sim 1-1.5 \pm 0.05-0.1 \mu\text{mol l}^{-1}$). To each daily series of ~ 30 natural samples, several blanks were added, as well as standards of nitrate and/or ammonia and/or urea or amino-acids, in order to check recovery. Many (when not all) samples were analyzed in duplicate.

Walsh (1989) and Bronk *et al.* (2000) reported that persulfate oxidation and HTC can provide reproducible results that are consistent with each other. This was confirmed by a recent international intercomparison (Sharp *et al.*, 2002).

2.6 DOP measurement

The photo-oxidation automated method used for DOP + soluble reactive phosphate (SRP) determination (Aminot and K erouel, 2001) included direct intake from the sample bottle (no decanting), UV-peroxide oxidation and colorimetric SRP determination. DOP was obtained by subtracting SRP measured simultaneously in a parallel channel (according to Tr equer and Le Corre, 1975), from the same sample bottle. Digestion of labile and refractory DOP model compounds was virtually complete when compared with that of the alkaline persulfate oxidation (Koroleff, 1983) as a reference method (K erouel and Aminot, 1996). Freshly drawn Milli-Q water was used as the zero-P reference and the refractive index blank (RIB) was subtracted systematically. For RIB determination, samples were re-run using a

reagent devoid of molybdenum and antimony salts to prevent color development (Tréguer and Le Corre, 1975; Loder and Glibert, 1977).

2.7 Quality control, accuracy and precision

The data set was entirely re-assessed in the light of more recent improvements or knowledge in methods. A few minor blank corrections were subsequently made (in particular for WO-DOC) and uncertainties on DOC, DON and DOP were specifically determined for each series.

Of the many definitions proposed for accuracy (Massart *et al.*, 1988), one generally accepted is “the degree of agreement of a measured value with the true or expected value of the quantity of concern” (Taylor, 1990). There is presently no absolute way of determining the true value of DOC, DON and DOP in seawater, therefore agreement with expected values through intercomparisons is the only recourse. Our DOC results were found to be in satisfactory agreement with international data (Figure 2), but DON and DOP did not benefit from such intercomparisons. The recent TDN broad community intercomparison (Sharp *et al.*, 2002) provided only a partial view of DON, since few participants provided DIN data and a unique DIN value had to be subtracted from participants' TDN data. No broad community intercomparison has ever been specifically undertaken for DOP.

Table 2. Precision of DOC, DON and DOP for the data series taken into consideration.

Parameter	Data	Station (date)				
		A1 (09/85)	A2 (04/02)	A3 (09/87)	A4, A5* (07/90)	M (09/84)
DOC	Method	WO	HTC	WO	-	WO
	Sample number (nb from profile)	19 (3)	18 (18)	16 (16)	-	9 (5)
	Concentration range, $\mu\text{mol l}^{-1}$	46-86	42-78	41-62	-	43-70
	Standard deviation, $\mu\text{mol l}^{-1}$	1.8	1.6	1.4	-	1.2
DON**	TDN < 12 $\mu\text{mol l}^{-1}$					
	Sample number (nb from profile)	12 (2)	10 (5)	10 (2)	-	22 (5)
	Standard deviation, $\mu\text{mol l}^{-1}$	0.07	0.07	0.08	-	0.07
	TDN > 12 $\mu\text{mol l}^{-1}$					
	Sample number (nb from profile)	4 (1)	8 (8)	11 (0)	-	-
	Standard deviation, $\mu\text{mol l}^{-1}$	0.09	0.08	0.11	-	-
DOP**	TDP < 0.5 $\mu\text{mol l}^{-1}$					
	Sample number (nb from profile)	17 (3)	5 (5)	8 (5)	10 (5)	15 (0)
	Standard deviation, $\mu\text{mol l}^{-1}$	0.012	0.004	0.011	0.006	0.009
	TDP > 0.5 $\mu\text{mol l}^{-1}$					
	Sample number (nb from profile)	5 (3)	8 (8)	11 (11)	13 (13)	-
	Standard deviation, $\mu\text{mol l}^{-1}$	0.014	0.005	0.011	0.006	-

* A4 and A5 samples analyzed in the same series.

** Corresponding depths for TDN < 12 $\mu\text{mol l}^{-1}$ and TDP < 0.5 $\mu\text{mol l}^{-1}$: M, whole water column; A1, < 80 m; A2, < 200 m; A3, A4 and A5, < 150 m.

Our data's precision (Table 2) was determined from duplicate analyses of samples as described below, and computed according to Taylor (1990).

For DOC, analyzed samples were re-capped, stored in a clean place then measured again, generally the same day (samples analyzed by HTC were re-bubbled). Comparable standard deviations of about $1.5 \mu\text{mol l}^{-1}$ were found throughout the study period (Table 2).

To obtain DON precision, two aliquots of each sample were submitted to oxidation while nitrate+nitrite (N&N) and ammonium were determined in the remaining sample, then the two oxidized aliquots were measured successively for TDN. Total variance of DON was computed as the sum of the contributions from its individual analytical components (Taylor, 1990). From $\text{DON} = \text{TDN} - \text{N\&N} - \text{ammonium}$, it comes: $s_{\text{DON}}^2 = s_{\text{TDN}}^2 + s_{\text{N\&N}}^2 + s_{\text{ammonium}}^2$. TDN and N&N were measured within the same series, using the same manifold, hence contribution of N&N to uncertainty was restricted to its short-term repeatability component, *i.e.*, $\sim 0.1\%$ of concentration (and $\geq 0.01 \mu\text{mol l}^{-1}$) with our Autoanalyzer (Aminot and K  rouel, 1995). The overall standard deviation of $0.02 \mu\text{mol l}^{-1}$ was used for all N&N concentrations encountered. For ammonium, the uncertainty in the concentration range encountered ($< 0.6 \mu\text{mol l}^{-1}$) was correctly reflected using a standard deviation of $0.02 \mu\text{mol l}^{-1}$ (Aminot and K  rouel, 1995, 1996). DON standard deviations were computed in the low ($< 12 \mu\text{mol l}^{-1}$) and in the high ($> 12 \mu\text{mol l}^{-1}$) TDN range (Table 2). The concentration level did not have a marked effect, and standard deviations did not exceed $0.08 \mu\text{mol l}^{-1}$ and $0.11 \mu\text{mol l}^{-1}$, respectively, in the low and high TDN ranges.

DOP duplicate samples from the same bottle or from two different bottles provided similar precision. Standard deviations computed for DOP (= TDP - SRP) included variability from both TDP and SRP analyses, since these were systematically measured in parallel in each sample using two independent manifolds. DOP standard deviations, computed for the low ($< 0.5 \mu\text{mol l}^{-1}$) and the high ($> 0.5 \mu\text{mol l}^{-1}$) TDP ranges show little influence of the TDP range (Table 2): $\leq 0.012 \mu\text{mol l}^{-1}$ in the low range and $\leq 0.014 \mu\text{mol l}^{-1}$ in the high range. This is attributed to the high repeatability of the Autoanalyzer and the use of the same phosphate standards to simultaneously calibrate the TDP and the SRP channels. Variability decreased at stations A2, A4 and A5 ($\leq 0.006 \mu\text{mol l}^{-1}$) due to computer peak recording and processing (replacing paper recording of older data). Results (in $\mu\text{mol l}^{-1}$) were processed to three decimal figures and then rounded to the second decimal figure in most tables.

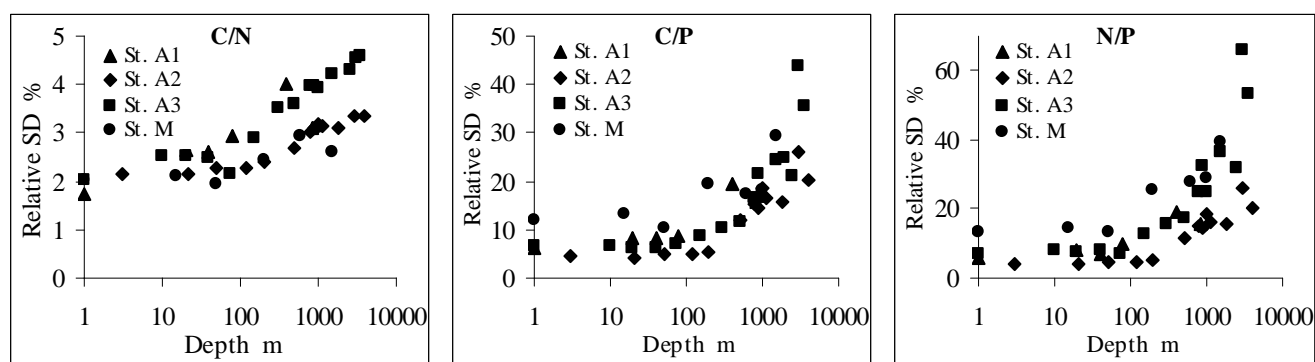


Figure 3. Relative standard deviations of DOM element ratios as a function of depth.

The standard deviations of element ratios (C:N, C:P, N:P) were estimated by the method usually applied to a sample of size 'n' for which two characteristics 'x' and 'y' are measured (Cochran, 1977). Given that $R = \bar{y}/\bar{x}$, the variance is $s_R^2 = (1/n \bar{x}^2)(s_y^2 + R^2 s_x^2 - 2R s_{xy})$. When applied to our results the covariance term ($-2R s_{xy}$) drops since 'x' and 'y' were derived from separate analyses. The variances s_x^2 and s_y^2 were obtained from the series of duplicate analyses. The sample size 'n' here is the number of determinations in each water sample. Since characteristics 'x' and 'y' may or may not have been duplicated, a weighted

sample size, $n = (n_x \cdot n_y)^{0.5}$ had to be used. (Note that n_x and n_y may be weighted values when 'x' and 'y' result from differences, *e.g.*, for non-refractory DOM.) The standard deviations of element ratios increase as a function of the decrease in DOM concentration, *i.e.*, with depth (Figure 3).

Hereafter, significance levels are considered for $\alpha = 0.05$.

3 RESULTS

3.1 Salinity, temperature and nutrients

NE Atlantic

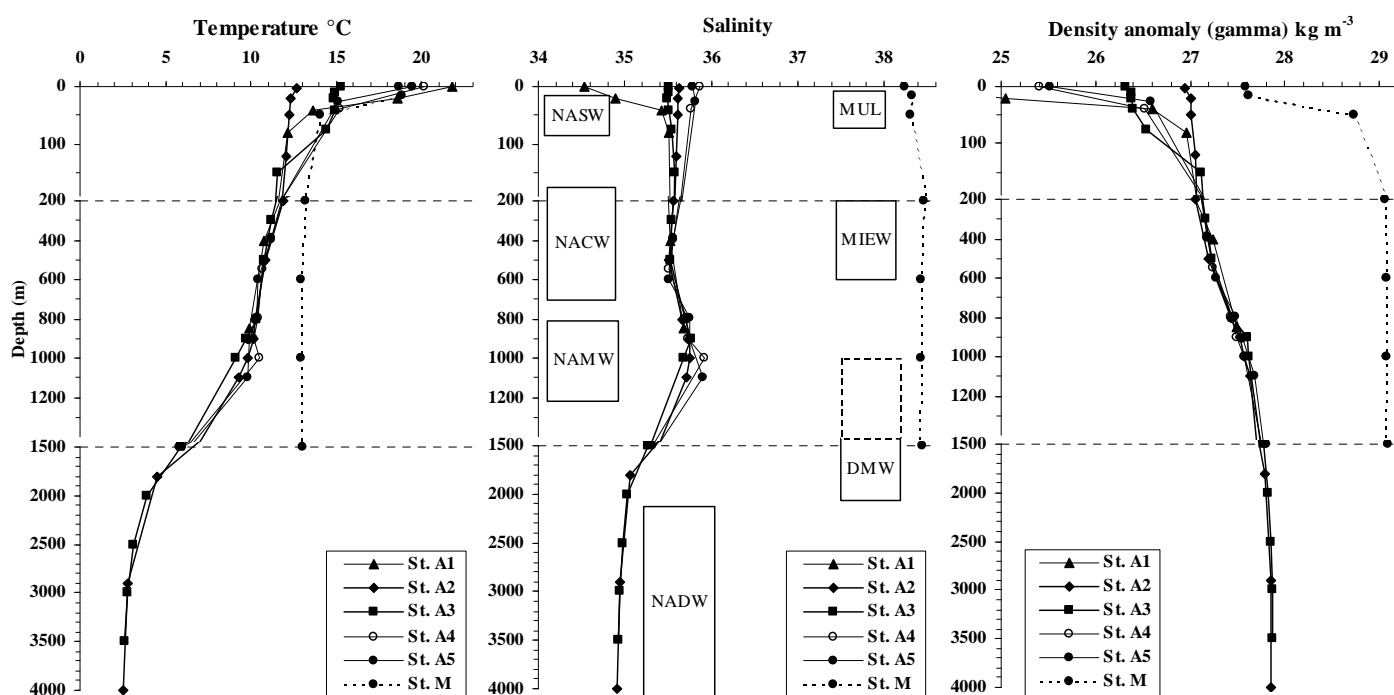


Figure 4. Vertical profiles of temperature, salinity and density anomaly in the N-E Atlantic and in the N-W Mediterranean. Note the different scales as a function of depth. Typical water bodies are given: NASW: North Atlantic Surface Water, NACW: North Atlantic Central Water, NAMW: North Atlantic Mediterranean Water, NADW: North Atlantic Deep Water, MUL: Mediterranean Upper Layer, MIEW: Mediterranean Intermediate Eastern Water, DMW: Deep Mediterranean Water.

A marked thermocline (Figure 4) lay in the 20-50 m layer in summer at the coastal station A1 ($\Delta t \sim 9$ °C) and at open sea stations A4 and A5 ($\Delta t \sim 5$ °C). At station A2 (early spring), the thermocline was starting ($\Delta t \sim 0.3$ °C, 13 m), while at station A3 (early autumn) the thermocline was deeper and disappearing ($\Delta t \sim 3$ °C, 80-100 m). In deeper layers, the temperature decreased continuously, reaching ~ 2.5 °C at 4000 m. In open sea, bottom salinity ($S = 34.9$ at 4000 m) was lower than surface salinity ($S = 35.5$ - 35.9) and the intermediate NAMW maximum at 900-1000 m was marked ($S \sim 35.8$). The influence of continental inputs was noted at station A1 (surface $S = 34.5$). The structure of the water column (Figure 4) showed that vertical advection between water bodies was restricted by two density gradients,

the seasonal upper thermocline and the main pycnocline between NACW and NAMW. The continuous T-S diagram made at station A2 provides a typical example of water mass structure (Figure 5). At the other stations, the T-S diagram differed in the upper layer (> 150 m), with higher temperature (all stations) and lower salinity (st. A1).

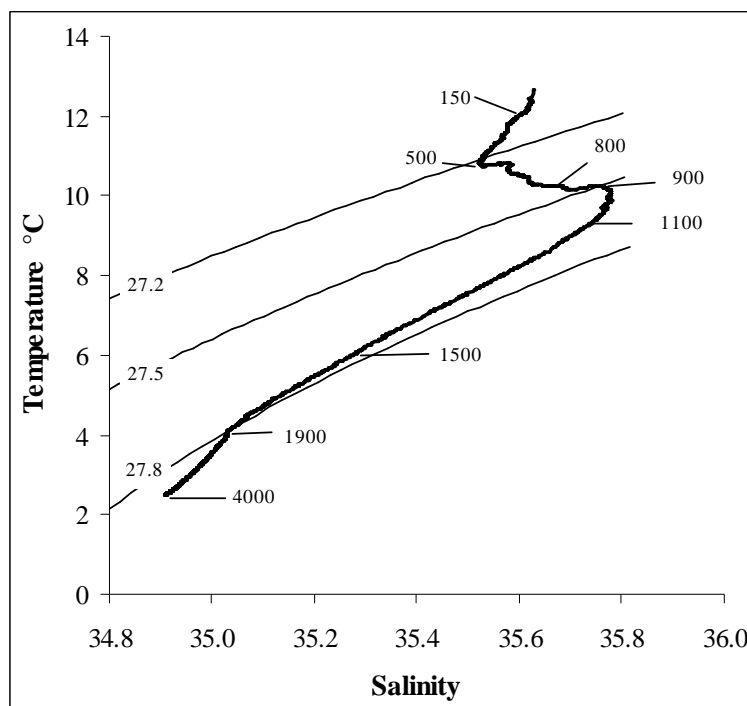


Figure 5. Temperature-Salinity diagram at station A2 in the N-E Atlantic. Some depths are indicated and isopycnal lines are drawn for $\sigma_t = 27.2, 27.5$ and 27.8 kg m^{-3} .

Inorganic nutrients (Figure 6) showed classic profiles with low concentrations above the thermocline and a marked gradient across this boundary. Above the thermocline, nitrate and phosphate concentrations dropped from respectively about $3 \mu\text{mol l}^{-1}$ and $0.2 \mu\text{mol l}^{-1}$ in April to less than $0.3 \mu\text{mol l}^{-1}$ and $0.01 \mu\text{mol l}^{-1}$ in summer. Silicate concentrations increased regularly, moving downward under the influence of the rich Antarctic water ($\sim 120 \mu\text{mol l}^{-1}$). The concentration of $45 \mu\text{mol l}^{-1}$ at 4000 m indicates about 30 % of AABW in NADW.

Mediterranean Sea

The overall cruise was described by El Sayed *et al.* (1994). The seasonal thermocline (Figure 4) was still marked in September in the 15 m upper layer ($\sim 19^\circ\text{C}$). The temperature dropped rapidly down to 50 m ($\Delta t \sim 5^\circ\text{C}$) reaching an almost constant value ($\sim 13^\circ\text{C}$) below 200 m. Salinity (higher than in the Atlantic; Figure 4) showed the classic subsurface minimum and a maximum around 200 m (Lacombe, 1975). The system exhibited an almost constant density anomaly from 200 to 1500 m, which means there was no marked difference between the intermediate water (MIEW) and the deep Mediterranean water (DMW). This agrees with the high degree of homogeneity reported below the intermediate water (Lacombe *et al.*, 1985). Consequently, our 1000 and 1500 m data will be assumed to belong to DMW.

Nutrient profiles (Figure 6) followed the typical variations encountered in the northwestern Mediterranean: very low concentrations in the photic layer, followed by a rapid increase and an almost constant level below 200 m. Concentrations at depths of 1000-1500 m (nitrate $7.9 \mu\text{mol l}^{-1}$, phosphate $0.35 \mu\text{mol l}^{-1}$, silicate $8.4 \mu\text{mol l}^{-1}$) closely agreed with those previously published (McGill, 1965; Karafistan *et al.*, 2002).

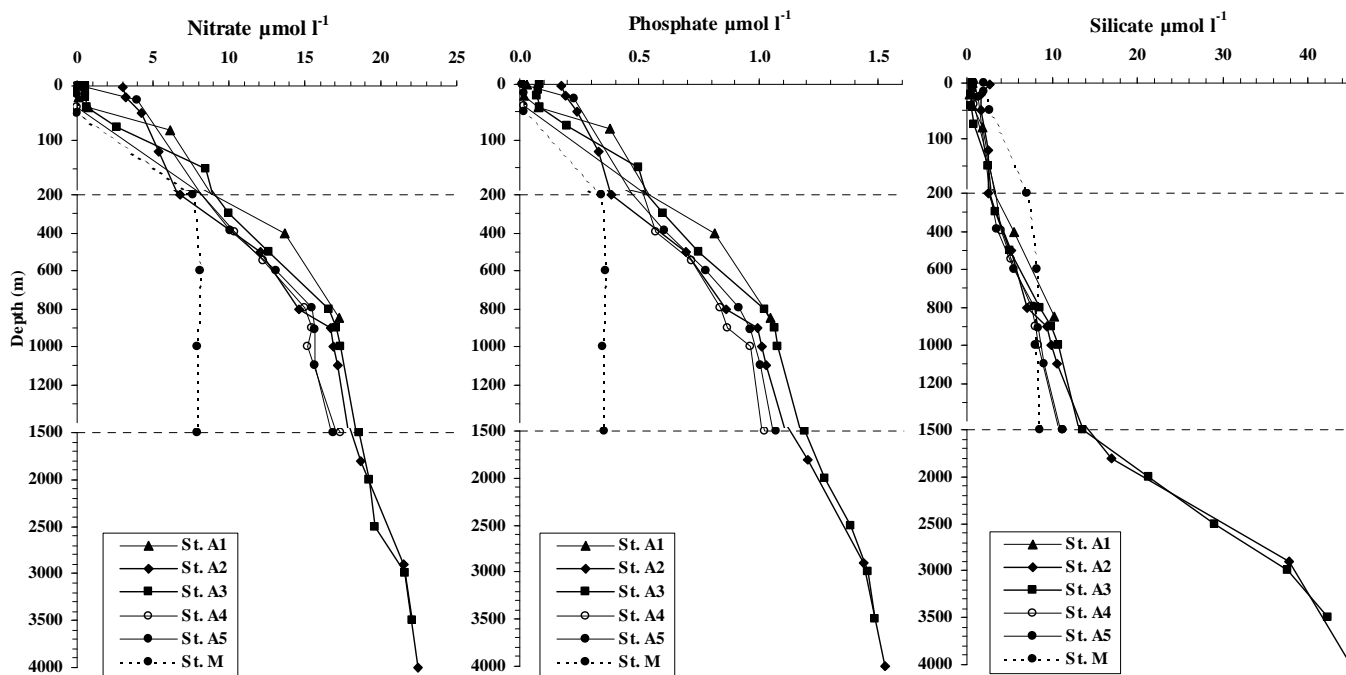


Figure 6. Vertical profiles of nutrients in the N-E Atlantic and in the N-W Mediterranean. Note the different scales as a function of depth. Typical water bodies are indicated in Figure 4.

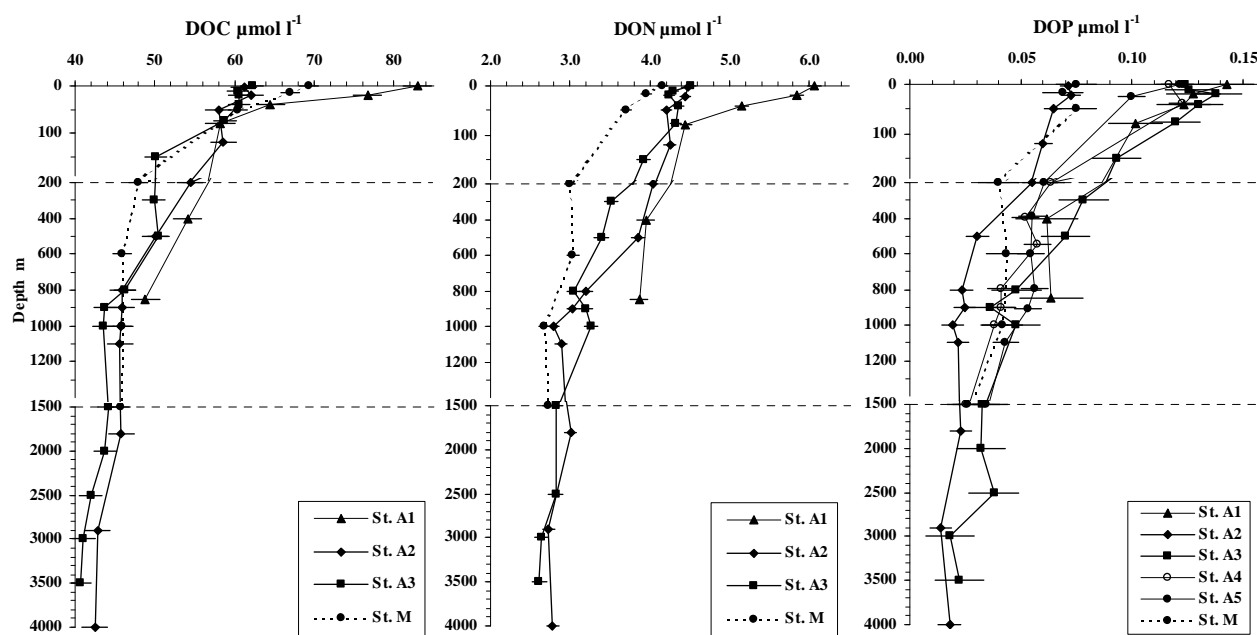


Figure 7. Vertical profiles of DOC, DON and DOP in the N-E Atlantic and in the N-W Mediterranean. Analytical standard deviations are indicated. Note the different scales as a function of depth. Typical water bodies are indicated in Figure 4.

3.2 Vertical distribution patterns of DOC, DON and DOP

Vertical profiles of DOC, DON and DOP concentrations are illustrated in Figure 7 and summarized for the main water masses in Table 3.

Table 3. Summary of DOC, DON and DOP concentration ranges and DOC:DON, DOC:DOP and DON:DOP atomic ratio ranges in the main water masses in the N-E Atlantic (stations A1 to A5) and the N-W Mediterranean (station M). Precision is illustrated in Figures 7 and 8.

Water mass*	Station (date)	n**	DOC $\mu\text{mol l}^{-1}$	DON $\mu\text{mol l}^{-1}$	DOP $\mu\text{mol l}^{-1}$	DOC:DON	DOC:DOP	DON:DOP
Surface layer	A1 (09/85)	2	77-83	5.8-6.1	0.12-0.14	13.1-13.7	580-600	42-46
	A2 (04/02)	1	61	4.5	0.07	13.7	850	62
	A3 (09/87)	4	61-62	4.2-4.5	0.12-0.14	13.8-14.3	440-500	31-36
	A4 (07/90)	1	-	-	0.12	-	-	-
	A5 (07/90)	1	-	-	0.12	-	-	-
	M (09/84)	2	67-69	4.0-4.2	0.08-0.08	16.7-16.9	920-970	55-57
200-600 m	A1 (09/85)	1	54	4.0	0.06	13.7	880	65
	A2 (04/02)	2	50-55	3.9-4.1	0.03-0.05	13.0-13.5	1000-1700	74-130
	A3 (09/87)	2	50-51	3.4-3.5	0.07-0.08	14.2-14.8	640-720	45-49
	A4 (07/90)	3			0.05-0.06			
	A5 (07/90)	3			0.05-0.06			
	M (09/84)	2	46-48	3.0-3.0	0.04-0.04	15.1-16.0	1100-1200	70-76
800-1500 m	A1 (09/85)	1	49	3.9	0.06	12.6	770	61
	A2 (04/02)	4	46-46	2.8-3.2	0.02-0.02	14.4-16.4	1900-2400	120-150
	A3 (09/87)	3	44-46	3.1-3.3	0.04-0.05	13.3-15.2	920-1200	64-88
	A4 (07/90)	3			0.04-0.04			
	A5 (07/90)	3			0.04-0.06			
	M (09/84)	2	46-46	2.7-2.7	0.03-0.04	16.8-17.2	1100-1800	64-106
3000-4000 m	A2 (04/02)	2	42-43	2.7-2.8	0.01-0.02	15.3-15.7	2400-3100	160-200
	A3 (09/87)	2	41-41	2.6-2.6	0.02-0.02	15.5-15.6	1800-2300	120-150

* Corresponding water masses: Surface layer = above thermocline; 200-600 m = North Atlantic Central Water (NACW) or Mediterranean Intermediate Eastern Water (MIEW); 800-1500 m = North Atlantic Mediterranean Water (NAMW; actually, 800-1200 m) or Deep Mediterranean Water (DMW); 3000-4000 m = North Atlantic Deep Water (NADW).

** n = number of results in a water mass.

DOC

The vertical profiles show the classic surface-to-bottom decrease, *i.e.*, an accumulation in the upper productive layer and progressive downward degradation, along with water mass aging. One essential feature is the marked DOM gradients associated with water mass boundaries such as the upper thermocline and the main pycnocline. In the Atlantic, in open sea, the drop between NASW and NACW was $6 \mu\text{mol l}^{-1}$ ($\sim 10\%$) in April (st. A2: 61 to 55 $\mu\text{mol l}^{-1}$) and $11 \mu\text{mol l}^{-1}$ ($\sim 20\%$) in September (st. A3: 61-62 to 51 $\mu\text{mol l}^{-1}$). At station A1, DOC concentrations were markedly higher, with a surface concentration of $\sim 80 \mu\text{mol l}^{-1}$ and a drop below the thermocline by $\sim 25 \mu\text{mol l}^{-1}$ ($\sim 30\%$). In the Mediterranean, DOC dropped by $\sim 20 \mu\text{mol l}^{-1}$ ($\sim 30\%$) from 67-69 $\mu\text{mol l}^{-1}$ in the upper layer to 48 $\mu\text{mol l}^{-1}$ in MIEW.

In the Atlantic, the main pycnocline between NACW and NAMW was associated with a significant decrease of 4-5 $\mu\text{mol l}^{-1}$ DOC in the 500-800 m layer. In the underlying waters (800-1500 m), similar DOC values were measured in open sea in the Atlantic and in the Mediterranean (44-46 $\mu\text{mol l}^{-1}$). These data agree with those previously published for the same areas (Table 4).

Table 4. Main recent literature data for DOC and DON in the area studied compared with the present results.

Layer or water body	Location	DOC $\mu\text{mol l}^{-1}$	DON $\mu\text{mol l}^{-1}$	Reference
NORTH-EAST ATLANTIC OCEAN				
Surface layer	West of Scotland	56-58	3-4	Alvarez-Salgado and Miller, 1998
	Bay of Biscay	61-62	4.2-4.5	This study
200-500 m (NACW)	West of Scotland	51-52	1.9-2.1	Alvarez-Salgado and Miller, 1998
	Bay of Cadiz	48-49	-	Dafner <i>et al.</i> , 1999
	Bay of Biscay	50-54	3.4-4.1	This study
1000-1500 m	West of Scotland	46-48	2.5	Alvarez-Salgado and Miller, 1998
	N-E Atlantic	~ 44	-	Kähler and Koeve, 2001
	Bay of Biscay	43-46	2.8-3.3	This study
MEDITERRANEAN SEA Western basin				
Surface layer	North Corsica	75-85	-	Copin-Montégut and Avril, 1993, fig 2
	Off North of Spain	$\sim 65-75$	$\sim 4-5$	Doval <i>et al.</i> , 1999, fig 4 stations 6-9
	Gulf of Lions	80-100	4.5-5.5	Raimbault <i>et al.</i> , 1999
	Off Gulf of Lions	67-69	4.0-4.2	This study
1000-1500 m	North Corsica	$\sim 50-58$	-	Copin-Montégut and Avril, 1993, fig 2
	Western basin	45-55	-	Cauwet <i>et al.</i> , 1997
	Off North of Spain	$\sim 46-51$	2.9	Doval <i>et al.</i> , 1999, fig 5
	Off Gulf of Lions	46	2.7	This study

Below 1500 m in the Atlantic (stations A2 and A3), DOC concentrations decreased regularly at a rate of 1.5-2 $\mu\text{mol l}^{-1}$ per kilometer to 41-42 $\mu\text{mol l}^{-1}$ at depths > 3500 m. This may be attributed to mixing of NADW with AABW, which contains a lower DOC concentration (Hansell and Carlson, 1998). However, it contrasts with the homogeneity reported by Hansell and Carlson (1998), between 1100 to 4800 m at 48° N ($45.1 \pm 0.4 \mu\text{mol l}^{-1}$; 19 samples).

DON

DON profiles mimic those of DOC. Open sea upper layer DON concentrations were within 4.0-4.5 $\mu\text{mol l}^{-1}$, showing no difference in the Atlantic between station A2 (April 2002) and station A3 (September 1987). Contrary to DOC, DON concentrations in the Mediterranean (station M) tended to be slightly lower than in the Atlantic. The average differences in the top 40-50 m between the two seas (0.2-0.4 $\mu\text{mol l}^{-1}$ DON) were significant.

The DON gradients between the upper layer and the 200-600 m layer were parallel to those observed for DOC. In the Atlantic, DON dropped by 0.5 $\mu\text{mol l}^{-1}$ in April and 0.9 $\mu\text{mol l}^{-1}$ in September, while in the Mediterranean, the drop was greater, 1.1 $\mu\text{mol l}^{-1}$. The continental influence was marked at station A1, with a surface concentration of $\sim 6 \mu\text{mol l}^{-1}$ followed by a drop of $\sim 2 \mu\text{mol l}^{-1}$. The relative differences of DON between the upper and the underlying water masses were quite identical to those calculated for DOC, *i.e.* $\sim 10\%$ at station A2, $\sim 20\%$ at station A3 and $\sim 30\%$ at stations A1 and M.

In NACW, the DON concentration was significantly higher in April 2002 ($\sim 4 \mu\text{mol l}^{-1}$) than in September 1987 ($\sim 3.5 \mu\text{mol l}^{-1}$). Gradients through the main pycnocline between NACW and NAMW were significant, with decreases of 0.4-0.7 $\mu\text{mol l}^{-1}$ DON.

Atlantic and Mediterranean DON values were similar at 1500 m (2.7-2.8 $\mu\text{mol l}^{-1}$), and in the deepest Atlantic waters (3000-4000 m), DON was in the range 2.6-2.8 $\mu\text{mol l}^{-1}$.

Although many papers have dealt with methods for the determination of DON, few deep profiles have been published in the areas studied here (Table 4). A wider scattering of DON data can be noted, compared to DOC data.

DOP

In the upper layer the Atlantic DOP concentrations showed a marked difference between concentrations at station A2 ($\sim 0.07 \mu\text{mol l}^{-1}$; early spring) and at station A3 (0.12-0.14 $\mu\text{mol l}^{-1}$; early autumn). No marked continental influence could be identified at station A1. Variation in DOP concentrations between the upper layer and underlying (200-600 m) water was lower in spring (~ 0.02 -0.03 $\mu\text{mol l}^{-1}$) than in autumn (0.05-0.08 $\mu\text{mol l}^{-1}$; 40-50 % of surface concentration). Nevertheless, in the Mediterranean the concentration in the 200-600 m water layer was consistently about 50 % that of the surface layer.

NACW DOP concentrations measured in 1987-1990 lay in the range 0.05-0.08 $\mu\text{mol l}^{-1}$ while the 2002 values were lower by ~ 0.02 -0.03 $\mu\text{mol l}^{-1}$. Similarly, in the NAMW the average DOP concentration were higher in 1987-1990, *i.e.*, $0.045 \pm 0.007 \mu\text{mol l}^{-1}$ ($n = 9$) than in 2002, *i.e.* $0.022 \pm 0.002 \mu\text{mol l}^{-1}$ ($n = 4$). In contrast, concentrations in deep waters (≥ 1500 m) did not differ significantly with regard to analytical variability (see Figure 7). In the bottom North Atlantic Deep Water (3000-4000 m), DOP was found to be close to 0.02 $\mu\text{mol l}^{-1}$ on average, both in 1987 and 2002.

In the Mediterranean, $\sim 0.04 \mu\text{mol l}^{-1}$ DOP was measured in the intermediate water and $\sim 0.03 \mu\text{mol l}^{-1}$ in the deep water, *i.e.*, similar to that found in the Atlantic at 1500-2000 m.

Despite the increasing number of DOP measurements in the ocean (Karl and Björkman, 2002), information available for the area investigated remains scarce. In surface water, 0.04 to 0.14 $\mu\text{mol l}^{-1}$ DOP were measured in the North Atlantic (Ridal and Moore, 1990; Wu *et al.*, 2000) and 0.06-0.10 $\mu\text{mol l}^{-1}$ DOP in the N W Mediterranean (Raimbault *et al.*, 1999). In deep waters, Ridal and Moore (1990, 1992) found $< 0.05 \mu\text{mol l}^{-1}$ in the North Atlantic and Pacific, while Raimbault *et al.* (1999) reported undetectable levels below 200 m in the Mediterranean.

3.3 Vertical distribution patterns of DOM elemental ratios C:N, C:P and N:P

Elemental ratios for DOM within a water sample are expressed as C:N:P or C:N, C:P and N:P. The corresponding profiles are shown in Figure 8 and Table 3.

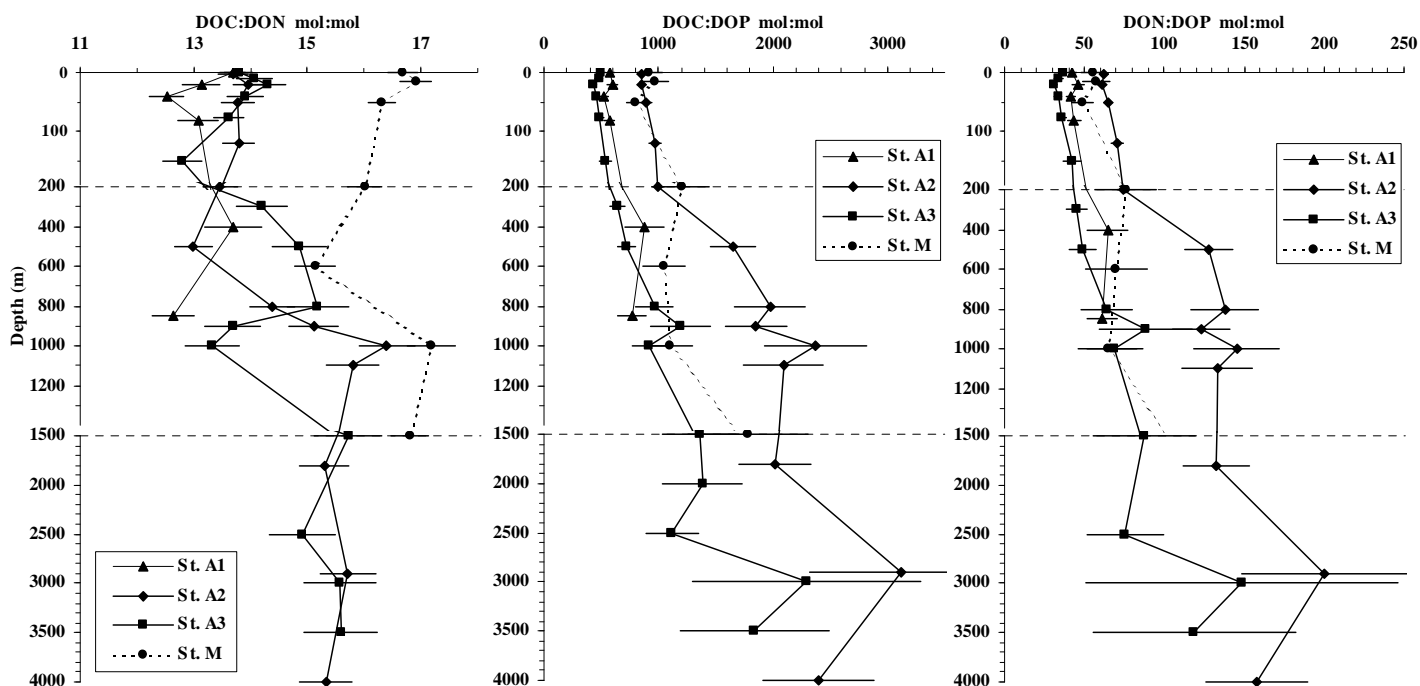


Figure 8. Vertical profiles of DOC:DON, DOC:DOP and DON:DOP atomic ratios in the N-E Atlantic and in the N-W Mediterranean. Standard deviations are indicated. Note the different scales as a function of depth. Typical water bodies are indicated in Figure 4.

DOM C:N ratio

Higher C:N ratios were measured in the deep Atlantic water (1500-4000 m, C:N = 15.4 ± 0.3 , $n = 7$) than in the surface layer (C:N = 13.8 ± 0.4 , $n = 7$). In the Mediterranean, the C:N ratios were higher than in the Atlantic ($\sim 15-17$) and did not show the same tendency to increase with depth.

The C:N ratio exhibited a minimum below the upper layer in early autumn in the Atlantic (st. A1 and st. A3). Another C:N minimum appeared in the NAMW layer in early autumn 1987 (st. A3, 900 and 1000 m). As the two levels showed consistent C:N ratios, the probability of a sampling or analytical artifact is low. However, since such a minimum was not found in April 2002, no simple hypothesis can be suggested for the time being.

DOM C:P ratio

C:P ratios increased by a factor of about 3 from surface to deep waters as a consequence of the more drastic decrease in DOP compared to that of DOC. The average C:P values in the 1500-4000 m water (all stations) was: 1900 ± 600 ($n = 9$). In the Atlantic, upper layer C:P ratios were higher in April (~ 850) than in early autumn ($\sim 450-600$; highest values at st. A1). Early autumn values in the upper layers (0-200 m) also showed that the C:P ratios, like the C:N ratios, were significantly higher in the Mediterranean (900-950) than in the Atlantic.

In contrast with C:N ratios, C:P ratios showed no minima just below the thermocline.

In the intermediate water masses (NACW and NAMW), C:P ratios were higher in April 2002 than in September 1987, essentially due to the lower DOP concentrations.

DOM N:P ratio

Vertical N:P variations closely resembled those of C:P, as a result of almost similar variations of C and N (10 % variation of the C:N ratio versus a factor of 3 for the C:P ratio). The average N:P value in the 1500-4000 m waters from all stations was 130 ± 40 ($n = 8$).

In the Atlantic, upper layer N:P ratios in early autumn were in the $\sim 30-45$ range (highest values at st. A1), while they reached $\sim 60-70$ in April. In early autumn N:P ratios in

the upper layers (0-200 m) were also significantly higher in the Mediterranean (50-75) than in the Atlantic in open sea (station A3).

Although the range of our N:P values is similar to that of Vidal *et al.* (1999) in the central Atlantic Ocean, the decreasing downward trend they found contrasts with our results.

3.4 Relationships of DOC, DON and DOP

The x- and y-axes variables of the relationships of DOC, DON and DOP throughout the water column were selected so that slopes could be easily compared with the C:N:P ratios (Figure 9). The linear regression slopes computed from these relationships reflect alteration of DOM due to relative variations in composition. These will be expressed as $\Delta\text{DOC}:\Delta\text{DON}:\Delta\text{DOP}$ (the composition itself being C:N:P).

The relationships show systematic differences between the upper layers and the underlying waters. Processing in two domains, though it may simplify relationships, gave a satisfactory description of DOM element behavior. The upper domain was found to lie from the surface to the base of the thermocline (or of the winter mixed 500 m layer at station A2) and the hereafter so-called 'deep' domain below this depth. This difference between the two domains was especially marked in the Mediterranean, as well as at the Atlantic station A1. While DOM in the upper domain was typical of each station, all the deep waters at the open sea stations (A2, A3 and M) could be described by a single regression. Because error is associated with components on both axes, model II linear regressions were used.

The main qualitative features are that DOM is richer in nitrogen at the coastal station A1 and richer in carbon at station M than at open sea stations A2 and A3. DOM is also well characterized by its phosphorus content. At stations A1 and M, DOP varied within a restricted range, in contrast with DOC and DON. Between stations A2 (April) and A3 (September), the shift is clearly due to DOP. Straight lines on Figure 9 identify the upper and deep domains. Their slopes are summarized in Table 5.

Table 5. Main parameters of the relationships between DOC, DON and DOP. Data have been omitted when the correlation coefficients were too low.

Layer	Station	Depth m	Nb. obs.	Slope \pm standard error (R^2 ; confidence level)		
				$\Delta\text{DOC}:\Delta\text{DON}$	$\Delta\text{DOC}:\Delta\text{DOP}$	$\Delta\text{DON}:\Delta\text{DOP}$
Upper layer	A1	0-40	3	19.8 ± 2.1 (0.99; $p < 0.01$)	920 ± 450 (0.76; $p = 0.1$)	47 ± 27 (0.66; $p = 0.2$)
	A2	0-500	6	19.2 ± 1.5 (0.98; $p < 0.01$)	284 ± 34 (0.94; $p < 0.01$)	14.8 ± 2.4 (0.90; $p < 0.01$)
	A3	0-150	6	22.3 ± 4.1 (0.87; $p < 0.01$)	282 ± 58 (0.83; $p = 0.01$)	12.7 ± 4.4 (0.51; $p = 0.1$)
	M	0-50	3	20.2 ± 3.7 (0.97; $p = 0.02$)	-	-
Deep layer	A2+A3+M	*	20	10.0 ± 1.7 (0.47; $p < 0.01$)	153 ± 26 (0.46; $p < 0.01$)	15.3 ± 2.5 (0.57; $p < 0.01$)

* Below upper layer for each station.

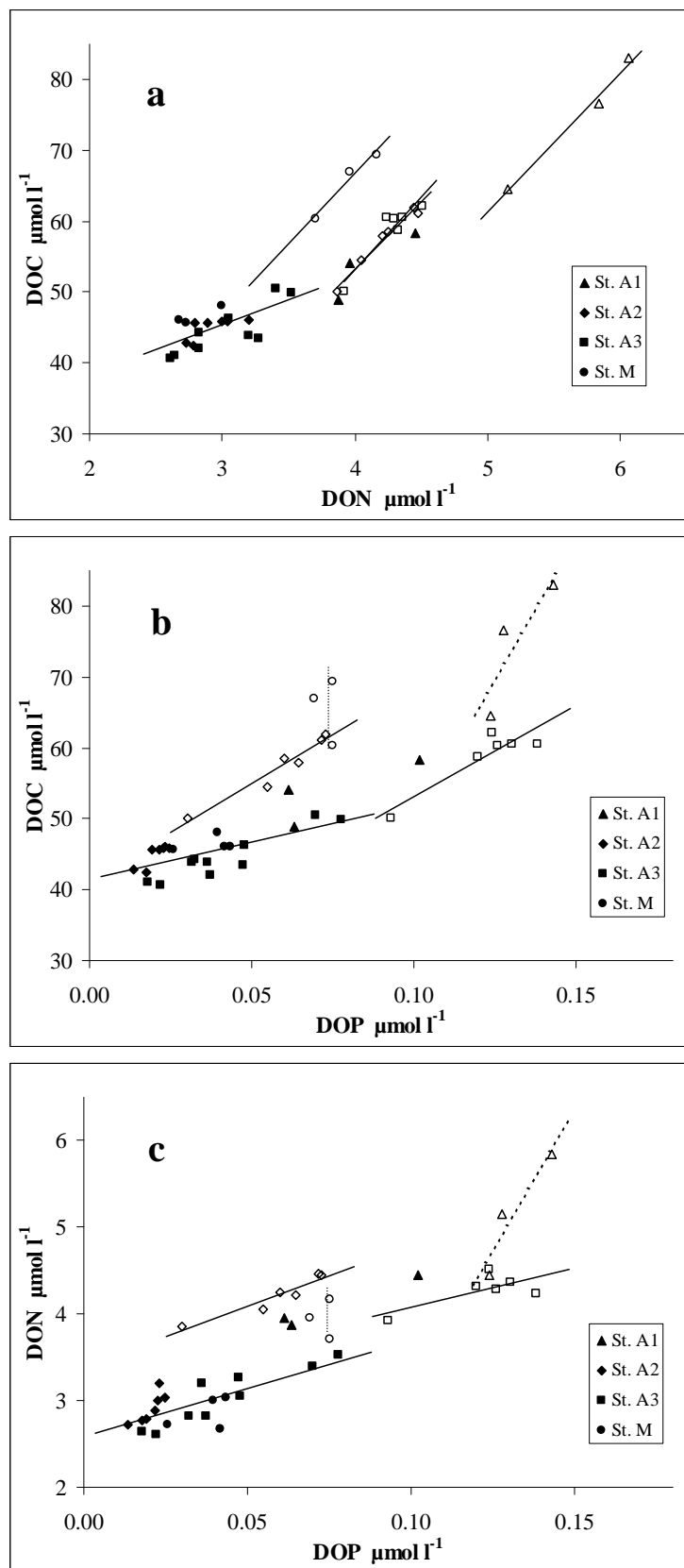


Figure 9. Relationships of a) DOC vs DON, b) DOC vs DOP, c) DON vs DOP in the N-E Atlantic and the N-W Mediterranean. Empty symbols denote the upper layer (from surface to the base of the thermocline). Continuous lines: linear regressions; broken lines: visual data marker.

In the upper layers, the slopes of DOC vs DON relationships lay in a narrow range of $\Delta\text{DOC}:\Delta\text{DON} \sim 19 \pm 2$ to 22 ± 4 and differed significantly from those found in deeper waters (10.0 ± 1.7). For DOC vs DOP, a comparable difference was found at open sea stations in the Atlantic, between the upper layer ($\Delta\text{DOC}:\Delta\text{DOP} \sim 280 \pm 60$ and 280 ± 30) and deep waters ($\sim 153 \pm 26$). The relationships of DON vs DOP show that upper layer values of stations A1 and M deviated from an average behavior characterized by $\Delta\text{DON}:\Delta\text{DOP}$ of $\sim 13 \pm 4$ to 15 ± 2 either in the upper or the deep layers.

Hopkinson *et al.* (1997) determined the overall slopes of the relationships between DOC, DON and DOP in the Georges Bank region, from surface to 1500 m, and obtained values that differed from ours, *i.e.*, $\Delta\text{DOC}:\Delta\text{DON} \sim 10$, $\Delta\text{DOC}:\Delta\text{DOP} \sim 385$ and $\Delta\text{DON}:\Delta\text{DOP} \sim 27$. In the Drake Passage (Antartica) Sanders and Jickells (2000) measured $\Delta\text{TON}:\Delta\text{TOP} = 15.7 \pm 1.7$ and 13.8 ± 1.0 for two different data sets, which is close to our $\Delta\text{DON}:\Delta\text{DOP}$ values.

4 DISCUSSION

4.1 DOM concentrations in the N-E Atlantic

Open sea stations in the N-E Atlantic were sampled at different times of the year and up to fifteen years apart for A2 and A3. Differences in DOC, DON and DOP concentrations may result from seasonal or long term changes. These were marked for DOP in various water masses, but also significant for DON in NACW.

Due to biological activity (planktonic exudation, dissolution from detritus, bacterial decomposition), concentrations of DOM may vary in surface waters. However, studies of annual variations of DOC showed that maximum concentrations are invariably found in autumn within relative variations of 5-10 % (Copin-Montégut and Avril, 1993; Hydes *et al.*, 2001; Carlson *et al.*, 1994). Our samples characterized the beginning (st. A2, April 2002), the middle (st. A4 and A5, July 1990) and the end (st. A3, September 1987) of the productive season. In order to compare DOM in the resulting various stratification conditions, DOC, DON and DOP were integrated over the upper 500 m layer (Table 6), which is the thickness of the upper mixed layer in winter (see Figure 5) and the depth where the main characteristics (temperature, salinity and nutrients concentrations) are quite similar at any time.

Table 6. Integrated DOC, DON and DOP pool in the upper 500 m layer of open sea stations in the N-E Atlantic.

Station (date)	0-500 m integrated pool		
	mmol m ⁻²		
	DOC	DON	DOP
A2 (04/02)	27329	2034	25.2
A3 (09/87)	26144	1884	45.2
A4 (07/90)	-	-	36.4
A5 (07/90)	-	-	33.6

Unexpectedly, the integrated DOC and DON pools were slightly larger (4-7 %) in April than in September. Although the difference is small, it is unlikely to be attributed to

simultaneous analytical biases in DOC and DON. The trend seems large enough to suggest a low-frequency increase of the DOM pool between 1987 and 2002. North Atlantic climatic oscillations are known to generate temperature changes in the upper water masses. Sampling in 1987 corresponded to the end of a period of low temperatures for the northern European surface water. Subsequently, systematically higher temperatures were recorded (Rodwell *et al.*, 1999; OSPAR Commission, 2000). Beaugrand *et al.* (2002) showed that climatic changes have induced strong biogeographical shifts in all copepod assemblages in the eastern North Atlantic Ocean. We postulate from our results that the overall production of organic matter in the North Atlantic could have been affected by this climatic event.

The DOP pool variations, which are reported to be relatively greater than those of DOC and DON, are consistent with the progressive increase in DOP from spring to autumn. Assuming that the 20 mmol m⁻² difference in the DOP pool between st. A2 and st. A3 resulted mostly from spring-summer primary production, the equivalent carbon amount was ~ 2 mol m⁻² (applying the Redfield ratio C:P = 106:1). A yearly carbon production of ~ 4.5-5 mol m⁻² for the North Atlantic (Millero, 1996) together with a net DOP accumulation rate of 10-40 % (turnover time of 60-300 days; Björkman *et al.*, 2000), would lead to accumulations ranging from 4 to 19 mmol m⁻² DOP. Long-term variations of the DOP pool in the 0-100 m layer (up to 10 mmol m⁻² over two years) have been attributed to changes in microplankton communities, a decrease in the DOP pool resulting from a shift from N- to P-limitation conditions (Karl and Tien, 1997; Karl and Björkman, 2002). In the present case, while low-frequency oscillations may be involved in the observed changes in the N-E Atlantic, the seasonal component seemed predominant in the difference observed in DOP pools between early autumn in 1987 and early spring in 2002. Integrated values also confirm that lower April concentrations did not result only from winter mixing with deeper DOP-poor waters, but were mainly a consequence of mineralization.

Station A1, only 35 km off the coast in the Bay of Biscay, offered a typical example of continental influence. Salinity in the upper layer (34.5-34.9) indicates 2-3 % fresh water. Excess surface DOC and DON with regard to offshore values (respectively about 20 and 1.5 µmol l⁻¹) showed a marked (exogenic or endogenic) influence of continental inputs. DOP showed a particular behavior, *i.e.*, there was no excess and an almost constant concentration in the upper 40 m layer. At that period, the inorganic N:P ratio of the main continental input to this area, the French river Adour, was ~ 50-60 (French Government data published in the Water Quality directory), *i.e.*, about 3-4 times the Redfield ratio. Additional concentrations of inorganic nitrogen and phosphorus from fresh water in the surface layer were estimated to be about 3.5 and 0.06 µmol l⁻¹ respectively, however, at the sampling time, the total inorganic pools were almost depleted (N ~ 0.02-0.05; P ~ 0.02-0.03 µmol l⁻¹). To consume excess DIN, phytoplankton had to recycle P from DOM (Cotner *et al.*, 1997; Karl and Björkman, 2002), which prevented accumulation of DOP (in contrast with DOC and DON). In addition, P-limitation in the south of the Bay of Biscay has recently been confirmed (Labry *et al.*, 2002).

4.2 Comparison of Mediterranean and Atlantic open sea DOM

Our results point out that deep water (1500 m depth) DOC, DON and DOP concentrations were similar within analytical uncertainty in the N-E Atlantic and in the N-W Mediterranean. In contrast, concentrations in the open sea upper layer (top 40-50 m) indicate analytically significant differences. While DOC was higher in the Mediterranean than in the Atlantic (resp. 67-69 and 60-62 µmol l⁻¹), the opposite was observed for DON (resp. 3.96-4.06 and 4.24-4.51 µmol l⁻¹) and DOP (resp. 0.07-0.08 and 0.12-0.14 µmol l⁻¹). Concentrations at station M were confirmed by comparable values measured around Corsica (N-W Mediterranean) during the same cruise (DOC: 68-74 µmol l⁻¹; DON: 4.1-4.3 µmol l⁻¹; DOP : 0.06-0.07 µmol l⁻¹; unpublished). Since maximum DOC concentrations are invariably found

in autumn in the N-W Mediterranean and in the N-E Atlantic (Copin-Montégut and Avril, 1993; Hydes *et al.*, 2001) valid comparison can be made of the two areas. The difference between Mediterranean and Atlantic surface waters is illustrated by the relationships between DOC, DON and DOP (Figure 9). Results from other authors tend to confirm this difference. Over an annual cycle, Copin-Montégut and Avril (1993) reported 75-85 $\mu\text{mol l}^{-1}$ DOC northwest of Corsica, while Carlson *et al.* (1994) measured 62-70 $\mu\text{mol l}^{-1}$ in the Sargasso Sea. Unfortunately, values reported by Ferrari (2000) in the vicinity of our stations (Bay of Biscay: 75-187 $\mu\text{mol l}^{-1}$; N-W Mediterranean: 112-141 $\mu\text{mol l}^{-1}$) can be questioned.

As a consequence of these differences, DOM was characterized by higher C:N and C:P ratios in the upper layer in the Mediterranean (resp. ~ 17 and ~ 950) than in the Atlantic (resp. ~ 14 and ~ 450). High C:N ratios of 15.5 ± 0.4 were also measured by Doval *et al.* (1999) in the N-W Mediterranean (Balearic islands), for the whole water column, with ratios exceeding 16 far from the coast. Our results indicate that, in the Mediterranean surface layer, DOM was much poorer in N by about 20 % and in P by about 50 % than in the Atlantic.

The surface water of the western Mediterranean basin results from the spreading of the North Atlantic Surface Water which enters through the strait of Gibraltar. This water moves east- and northeastward according to the general cyclonic surface circulation in the western Mediterranean basin (Lacombe and Tchernia, 1972). If concentrations in water entering the Mediterranean were correctly reflected by our NASW DOM results from the Bay of Biscay, this implies that waters of the N-W Mediterranean were enriched in DOC and impoverished in DON and DOP during their transport. DOC enrichment could be attributed to atmospheric inputs, a process which has been shown to play a major role in the biogeochemistry of the Mediterranean (Martin *et al.*, 1989). However, the simultaneous depletion in DON and DOP implies more consumption or mineralization than production. The N-W Mediterranean is described as an oligotrophic system where phosphorus plays a major role in the limitation of primary production (Berland *et al.*, 1980). Consequently, phytoplankton may need to hydrolyze DOP to grow under low-phosphate conditions (Cotner *et al.*, 1997; Karl and Björkman, 2002), thus maintaining low DOP concentrations. DOM characteristics can also result from the process of carbon overconsumption (*i.e.*, the consumption of inorganic carbon compared to inorganic nitrogen exceeding the Redfield ratio; Williams, 1995). This process, which generates a summer accumulation of DOM with a high C:N ratio in surface waters, particularly in oligotrophic systems (Sambrotto *et al.*, 1993; Kähler and Koeve, 2001; Körtzinger *et al.*, 2001), is liable to occur in the Mediterranean.

4.3 Refractory and labile DOM

Primary production, occurring in the upper photic layer via photosynthetic algae, is the main source of organic matter in the oceans. DOM results from various known mechanisms such as exudation of phytoplankton, excretion, cell lysis, breakdown and dissolution of particles, and bacterial activity (Riley and Chester, 1971). It has been generally accepted that DOM could be regarded as being composed of two major pools. One is recent and labile, resulting from biological excretion and partial bacterial mineralization, while the second is older and refractory (Pomeroy, 1974; Menzel, 1974; Ogura, 1975; Bada and Lee, 1977). In a more detailed approach the bulk pool is divided into three fractions with quite different turnover times: very labile (hours/days), semi-labile (months/seasons) and refractory (hundreds to thousands of years) pools (Kirchman *et al.*, 1993; Carlson and Ducklow, 1995). While differentiation between the labile and semi-labile pools requires specific kinetic studies, it is simple to estimate the two major pools (labile+semi-labile and refractory). Based on the assumption that the refractory pool measured in deep waters (≥ 1500 m) is homogeneously distributed throughout the water column (Carlson and Ducklow, 1995), the excess of DOC,

DON and DOP in the photic layer with respect to the refractory DOM (rDOM) represents the labile+semi-labile DOM (also called non-refractory DOM or nrDOM, hereafter).

In the present study, the decrease of DOM concentrations in 2000-4000 m waters was attributed to mixing of water bodies of different ages. Therefore, the data from 1500-2000 m were considered to be the valid values of refractory DOC, DON and DOP for the subsequent determination of the non-refractory fractions in the overlaying waters. Assuming that rDOM is homogeneous over an oceanic basin, refractory concentrations were obtained by averaging all the 1500-2000 m results, Mediterranean rDOM being considered as from Atlantic origin (the results were not significantly different; Figure 6). Concentrations and element ratios of rDOM are summarized in Table 7. Average C:N:P ratios of 1570:100:1 were found in the refractory DOM. This C:N ratio of 15.7 in rDOM is well within the range of values measured in the deep ocean, *i.e.*, 13-18 with few exceptions (Bronk, 2002).

Table 7. Average characteristics of the refractory DOM found at depths of 1500-2000 m in the N-E Atlantic and in the M-W Mediterranean. Standard deviations are derived from total variance due to analysis and averaging.

Parameter	rDOC $\mu\text{mol l}^{-1}$	rDON $\mu\text{mol l}^{-1}$	rDOP $\mu\text{mol l}^{-1}$	rDOC: rDON	rDOC: rDOP	rDON: rDOP
Nb. of obs.	4	3	6	-	-	-
Range	43.8-45.8	2.73-3.00	0.023-0.034	-	-	-
Average	44.9	2.85	0.029	15.7	1570	100
Std. dev.	1.7	0.17	0.009	0.6	230	16

The characteristics of the non-refractory DOM in the surface layer were obtained by subtracting rDOM from DOM (Table 8). They were determined only for the layer above the thermocline, which is the oceanic area where most of the DOM is produced before being injected in the water column. At the periods of study (early spring or early autumn) nrDOM approximated semi-labile DOM since other investigators have found labile DOM (turnover times of hours to days) to be undetectable when phytoplankton activity was low (Carlson and Ducklow, 1995). Station A1 was disregarded because of the unknown, but significant contribution of terrestrial DOM in the surface layer.

In the open sea upper layer, the proportions of nrDOM with regard to total DOM were approximately 25-35 % for DOC, 30-35 % for DON, and 60-80 % for DOP. In the Atlantic, relative contributions of nrDOM to DOM were on the order of %nrDOC < %nrDON < %nrDOP. The stoichiometry shows that non-refractory DOM was richer in N by ~ 30 % and in P by a factor of 4 to 10, compared with refractory DOM. In the Mediterranean %nrDOC was greater than %nrDON, but 95 % confidence intervals overlap, preventing a clear conclusion. Nevertheless, our figures compare well with measurements taken in the integrated upper 50 m of the Mediterranean in June by Doval *et al.* (1999), *i.e.*, nrDOM amounting to 32 % for DOC (in this study: 34 %) and 33 % for DON (in this study: 30 %). According to these authors, similar proportions of nrDOC were found in other oligotrophic areas.

C:N:P ratios of 380:38:1, 159:15:1 and 530:28:1 were found at stations A2, A3 and M respectively. Elemental ratios of the non-refractory DOM were much lower than those of refractory DOM, except for C:N in the Mediterranean. The element ratios show that the non-refractory DOM in the Mediterranean differed from that found in the Atlantic since it was just three times richer in P than the refractory fraction but 20 % poorer in N. This contrasts with

the results of Doval *et al.* (1999) who found a slightly lower C:N ratio in the non-refractory DOM pool of the upper 50 m compared with the refractory pool.

Table 8. Characteristics of the non-refractory (labile + semi-labile) pool of DOM in the surface layer (above thermocline; number of samples mentioned in Table 3) in the N-E Atlantic (st. A2 to A5) and in the N-W Mediterranean (st. M). Value \pm standard deviation. The standard deviations are derived from the sum of variances of DOM and rDOM components (including analysis and averaging contributions). In parentheses: percent of total DOM element.

Station (date)	nrDOC $\mu\text{mol l}^{-1}$	nrDON $\mu\text{mol l}^{-1}$	nrDOP $\mu\text{mol l}^{-1}$	nrDOC: nrDON	nrDOC: nrDOP	nrDON: nrDOP
A2 (04/02)	16.3 \pm 2.4 (27 \pm 4 %)	1.6 \pm 0.2 (36 \pm 4 %)	0.04 \pm 0.01 (60 \pm 14 %)	10.1 \pm 1.4	380 \pm 70	38 \pm 7
A3 (09/87)	16.0 \pm 2.4 (26 \pm 4 %)	1.5 \pm 0.2 (34 \pm 5 %)	0.10 \pm 0.02 (78 \pm 12 %)	10.7 \pm 1.2	159 \pm 16	14.8 \pm 1.6
A4 (07/90)	-	-	0.09 \pm 0.01 (76 \pm 11 %)	-	-	-
A5 (07/90)	-	-	0.09 \pm 0.01 (77 \pm 11 %)	-	-	-
M (09/84)	23.3 \pm 2.7 (34 \pm 4 %)	1.2 \pm 0.2 (30 \pm 6 %)	0.04 \pm 0.01 (60 \pm 19 %)	19.2 \pm 2.7	530 \pm 100	28 \pm 6

C:N ratios close to the Redfield value of 6.6 (Redfield *et al.*, 1963), can be expected for particulate organic matter issued from primary production and exported toward deeper waters (*e.g.*, Hobson and Menzel, 1969; Doval *et al.*, 1999; Körtzinger *et al.*, 2001). On the contrary, for freshly produced DOM, no single relation between DOC and DON can be found (Kähler and Koeve, 2001). While exudation and excretion of nitrogen-rich compounds like urea (C:N = 0.5) or proteins and amino acids (C:N \sim 4) by microplankton and zooplankton are well documented (*e.g.*, Webb and Johannes, 1967; Schell, 1974; Nagata and Kirchman, 1991), other studies have shown that nitrogen-poor, even nitrogen-free molecules, like carbohydrates and polysaccharides, are also released (Mykkestad and Haug, 1972; Mykkestad *et al.*, 1989; Staats *et al.*, 2000). Proportions of nitrogen-rich or nitrogen-poor DOM are likely to depend on many factors and are highly unpredictable.

Comparison of nrDOM stoichiometry with the Redfield C:N:P ratios (106:16:1) shows that the C:N ratios in the Atlantic surface layer were about 1.5 times the Redfield value, while C:P ranged from 1.5-fold (September) to 3-fold (April). At the end of the productive season, the N:P ratio of DOM (14.8) was close to the Redfield ratio. In comparison, accumulated nrDOM in the Mediterranean was almost two times poorer in N than in the Atlantic (C:N = 19 compared to 11), and 3 times poorer in P (C:P = 530 compared to 160). The stoichiometry of the non-refractory DOM in the Mediterranean suggests that carbon overconsumption (responsible for N- and P-poor DOM) induced by oligotrophy (enhancing DON and DOP recycling) could be a main process in that sea.

Because of the low amounts of nrDOM remaining below the thermocline, its characteristics could not be determined with precision. Nevertheless, taking DOC as the most reliable proxy for DOM, we calculated that 31 % of nrDOC was found in September below the base of the thermocline in the Atlantic but only 13 % in the Mediterranean, although

higher concentrations of nrDOM were measured in the upper layer in the latter area. This suggests that DOM is more actively recycled in the Mediterranean.

4.4 Stoichiometry of DOM dynamics

DOM produced in the surface layer is transferred to the whole water column by water mass transport, advection and diffusion. During these processes, C, N and P atoms are progressively eliminated from DOM by abiotic and biotic processes. Considering DOC as a satisfactory proxy for DOM, the relationships between DOC, DON and DOP (Figure 9) illustrate how DON and DOP vary as a function of the concentration of DOM. There is a general consensus that DON and DOP are selectively mineralized with respect to DOC (Ridal and Moore, 1992; Hopkinson *et al.*, 1997; Clark *et al.*, 1998; Loh and Bauer, 2000; Clark Kolowith *et al.*, 2001). This concept results from observations that C:N:P ratios of DOM increase in aged DOM, *i.e.*, as a function of depth, and that residual concentrations of DOP are very low in deep waters. However, this referred to DOM as a whole, whereas the stoichiometry of the refractory and the degradable fractions of DOM are very different. If the stoichiometry were stable for each fraction, the apparent selective removal of N and P from the total pool of DOM could simply result from the decreasing proportion of the semi-labile pool from surface to deep water. In this study, we specifically focused on the stoichiometry of the non-refractory DOM fraction in order to check the preferential removal concept.

In the areas investigated, the water column was stratified by the upper seasonal pycnocline and, in the N-E Atlantic, by the deep pycnocline (Arhan *et al.*, 1994), minimizing the role of vertical mixing in concentration patterns. Although DOM production and degradation processes generally occur simultaneously, decomposition predominates outside of periods of intense primary production. The periods studied (early spring or early autumn) correspond to low production, therefore relationships between DOC, DON and DOP may be assumed to essentially reflect DOM decomposition (only semi-labile DOM is involved, as previously mentioned). Our discussion was restricted to open sea stations (A2, A3 and M) where the elemental ratio for DOM and regression data sets were most complete. Figure 10 illustrates alteration of DOM by comparing composition (C:N and C:P ratios for DOM) and relative variations ($\Delta\text{DOC}:\Delta\text{DON}$ and $\Delta\text{DOC}:\Delta\text{DOP}$) when changing from the non-refractory surface pool to the deep refractory pool (for the sake of simplification, we disregarded the N:P ratios and slopes which combine the two others).

Regarding the DOC vs DON behavior, we note that the C:N ratio of nrDOM in the Atlantic (stations A2 and A3) was 10-11 while mineralization in the upper layer occurred with a $\Delta\text{DOC}:\Delta\text{DON} \sim 20$. This indicates that carbon is preferentially removed over nitrogen during the first degradation step of nrDOM, or in other words, that nrDOM was enriched in nitrogen. Evidence of such process has been described by Abell *et al.* (2000) in the shallow layers of the subtropical North Pacific. In the Mediterranean, $\Delta\text{DOC}:\Delta\text{DON}$ in the upper layers was equally close to 20, but was comparable there with the nrDOM C:N ratio ($\sim 19 \pm 3$), which means that stoichiometry of DOM is probably not significantly altered during mineralization in the upper layers. In the deeper waters, the overall $\Delta\text{DOC}:\Delta\text{DON} \sim 10$ means that about two times more nitrogen was eliminated with the same amount of carbon compared to the upper layers. In the Atlantic, this mineralization stoichiometry was similar to that of the remaining, more refractory nrDOM which had been slightly enriched in nitrogen (hence with C:N < 11). Within the precision of elemental ratios for DOM and relative variations (regression slopes), the nrDOM which remains below the upper layer appeared to be decomposed according to its stoichiometry, *i.e.*, with no preferential nitrogen removal. In the Mediterranean, the small amount of residual nrDOM below the thermocline, with a high C:N ratio, most likely undergoes preferential nitrogen removal.

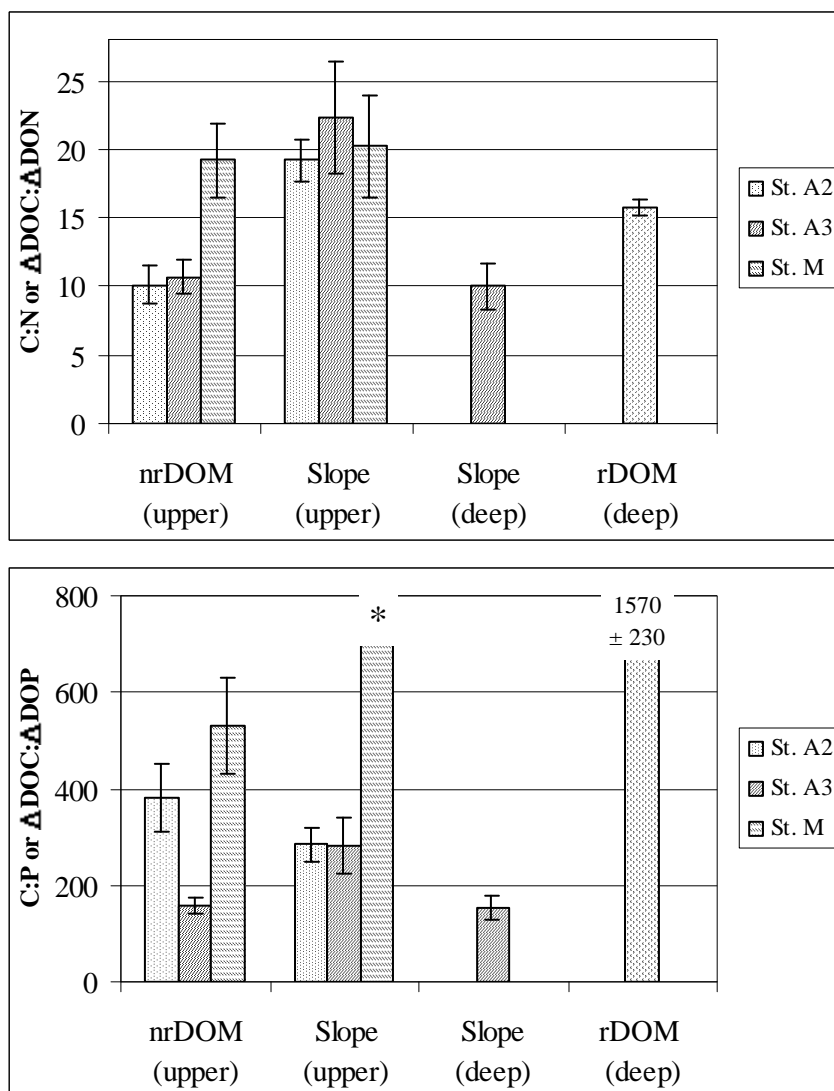


Figure 10. Comparison of C:N and C:P ratios of nrDOM and rDOM with linear regression slopes of DOC vs DON ($= \Delta\text{DOC}:\Delta\text{DON}$) and DOC vs DOP ($= \Delta\text{DOC}:\Delta\text{DOP}$) in the upper and deep layers at the open sea stations in the N-E Atlantic and the N-W Mediterranean. * This bar denotes a high, though not measurable, value of $\Delta\text{DOC}:\Delta\text{DOP}$.

The DOC vs DOP behavior in the Atlantic upper layers showed similar slopes ($\Delta\text{DOC}:\Delta\text{DOP} = 280$) at stations A2 and A3 in spite of significantly different C:P ratios in nrDOM. The figures seem to indicate a slight carbon enrichment ($\Delta\text{DOC}:\Delta\text{DOP} < \text{C:P}$ ratio) for early spring DOM (st. A2) against a slight phosphorus enrichment ($\Delta\text{DOC}:\Delta\text{DOP} > \text{C:P}$ ratio) for early autumn DOM (st. A3). However, because the 95 % confidence intervals of the corresponding slopes and ratios overlap, these trends could not be confirmed. On average, nrDOM C:P ratios and mineralization slopes are similar (~ 270 vs 280), so there was no overall apparent preferential phosphorus removal during the first step of DOM degradation. In the Mediterranean, DOP was almost constant in the upper layer while DOC decreased moving downwards. This particular feature, attributed to the P-limited status of the Mediterranean, indicates preferential mineralization of carbon, hence relative phosphorus enrichment of nrDOM remaining below the thermocline in comparison with surface nrDOM. In the deeper waters, the overall slope decreased by a factor of about 2 compared with the Atlantic upper

layers. Since the nrDOM C:P ratio remained unchanged on average in the Atlantic upper layers, deep water degradation is assumed to occur with preferential removal of phosphorus with regard to carbon ($\Delta\text{DOC}:\Delta\text{DOP} \sim 150$). In the Mediterranean, no mechanism can be inferred for deep water.

The mineralization of DOM mainly occurs through heterotrophic microbial activity (Azam and Hodson, 1977). Bacterial growth efficiency (BGE = the fraction of carbon incorporated into the microbial biomass over the total amount of carbon consumed for both energy production and biomass) is an essential factor which governs the stoichiometry of DOM mineralization, and hence excretion or demand of inorganic compounds by bacteria. Considerable variability in BGE has been reported in the literature (see Carlson *et al.*, 1999). Although a BGE of 0.5 is typical for aerobic bacteria growing on labile DOM, values of 0.1-0.6 have been reported in natural waters (Fenchel *et al.*, 1998). The BGE decreases when DOM is more recalcitrant (Fenchel *et al.*, 1998) and when bacteria are N- and P-limited (Carlson and Ducklow, 1996).

In surface layers, complex processes between biological activity and particulate and dissolved labile organic matter do not allow to infer a relationship between DOM mineralization and BGE from our data. In deep water, the system may be reduced essentially to DOM, as the substrate, and bacteria. Then, typical BGE can be determined for two cases, i) all consumed DON is assimilated, and ii) all consumed DOP is assimilated. Considering an average C:N:P ratios for a bacterial biomass of about 45:8:1 (Fenchel *et al.*, 1998; Goldman *et al.*, 1987), *i.e.*, C:N = 5.6 and C:P = 45 and the average mineralization ratios (Table 5) for DOM of $\Delta\text{DOC}:\Delta\text{DON} = 10$ and $\Delta\text{DOC}:\Delta\text{DOP} = 153$, the corresponding BGE would be ~ 0.6 (5.6:10) and ~ 0.3 (45:153) respectively. According to the literature, BGE for recalcitrant DOM remaining below the thermocline would be in the order of 0.1 or less. Consequently, a large proportion of DON and DOP consumed with DOC must be directly mineralized by bacteria (and not by subsequent bacteria grazing).

By coupling non-refractory DOM stoichiometry and relationships between the main DOM elements in the water column our results confirm the preferential removal of phosphorus relative to carbon from the semi-labile DOM in deep water, but they do not allow us to confirm the preferential removal of nitrogen. They show that processes differ in the upper oceanic layers from those in deep waters, and that they depend on the oceanic basin, with possible preferential carbon removal.

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