Organic Matter Distributions in the Eastern North Atlantic –
Azores Front Region

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Abstract

Temperate, transitional and subtropical waters of the remote Azores Front region east of Azores (24–40°N, 22–32°W) were sampled during three cruises conducted under increasing stratification conditions (April 1999, May 1997 and August 1998). Despite the temporal increase of surface temperature (by 5°C) and stratification (by 2.1 min⁻²), as well as the thermocline shoaling (by ~15 m), dissolved organic carbon (DOC) and nitrogen (DON) in the surface layer were not significantly different for the early spring, late spring and summer periods, with average concentrations of 69±2 µM-C and 5.2±0.4 µM-N, respectively. The surface excess of semilabile DOC, compared with the baseline DOC concentration in the deep ocean (47±2 µM-C), represents 33% of the bulk DOC concentration and as much as 85% of the TOC (=POC+DOC) excess. When compared with the winter baseline (56±2 µM-C), the seasonal surface DOC excess is 20% of the bulk DOC concentration and 87% of the seasonal TOC excess. These results confirm the major role played by DOC in the carbon cycle of surface waters of the Azores Front region. The total amount of bioreactive DOC transported from the temperate to the subtropical North Atlantic by the Ekman flux between March and December represents only ~ 15% of the average annual primary production, and ~ 15% and ~ 30% of the measured sinking POC flux + vertical DOC eddy diffusion during early spring and summer, respectively. Vertical eddy diffusion is 35% and 2% of the spring and summer sinking POC flux, respectively. On the other hand, DOC only contributes 13% to the local oxidation of organic matter in subsurface waters (between the pycnocline and 500m) of the study region.

Keywords: dissolved organic carbon and nitrogen, suspended organic carbon and nitrogen, Azores Front, Eastern North Atlantic.

1. Introduction

Phytoplankton primary production is the main source of dissolved organic carbon (DOC) and nitrogen (DON) in surface open ocean waters (Kirchman et al., 1993). The fate of these materials include *in situ* recycling, seasonal accumulation, horizontal export to the surrounding ecosystems, and downward export to deep waters by turbulent diffusion (stratification) or convective overturning (winter mixing; e.g. Carlson et al., 1994; Legendre and Le Fèvre, 1995; Hansell and Waterhouse, 1997). Direct release of semi-labile compounds (Kirchman et al., 1993), photochemical transformation of labile into less reactive molecules (Benner and Biddanda, 1998), and ‘malfunctioning’ of the microbial loop (Thingstad et al., 1997) are the processes leading to the observed dissolved organic matter (DOM) excess in the surface ocean compared with the waters below. Nitrogen-rich compounds (amino acids, proteins, etc) are recycled faster than carbon-rich compounds (mono- and polysaccharides, lipids, etc) in surface ocean waters (Sambrotto et al., 1993), so C/N ratios of DOM are more than double the average C/N ratio of the products of synthesis and early degradation of marine phytoplankton (6.6 mol-C mol-N⁻¹; Anderson, 1995). Accurate data on DOC and DON in open ocean waters are limited to a few studies conducted in the Pacific Ocean (Hansell and Waterhouse, 1997; Doval and Hansell, 2000), the Atlantic Ocean (Carlson et al., 1994; Hansell and Carlson, 2001) and the Mediterranean Sea (Copin-Montégut and Avril 1993; Doval et al., 1999). Moreover, the contribution of suspended organic matter (POM) to recycling and export processes has been considered in few DOM studies (Carlson et al., 1998; Doval et al., 1999).

The thermohaline, chemical and biological uniformity of vast regions of the surface ocean is dramatically disrupted at the thermohaline fronts that separate ocean biogeochemical provinces (Longhurst et al., 1995). Frontal systems tend to be associated with a sharp increase in phytoplankton biomass and with enhanced primary production rates (LeFevre, 1986). Oceanic fronts, and specially subtropical fronts, are characterised by their large extension and persistence. They have been widely studied from the physical viewpoint, although comparatively little attention has been paid to their chemical and biological implications. This is specially true for the case of DOM in the AF, the northern boundary of the North Atlantic

subtropical gyre (Gould, 1985; Siedler et al., 1985). Some studies have assessed the biological response of this highly dynamic system during the springtime (Platt et al., 1983; Fasham et al., 1985; Kahru et al., 1991; Jochem and Zeitzchel, 1993; Fernández and Pingree, 1996). Maximum Chl-*a* concentrations between 0.1 and 1 mg-Chl m⁻³ and primary production rates from 0.1 to 0.9 g-C m⁻² d⁻¹ have been reported in the area. However there is a lack of studies about DOM.

In this paper, we infer for the first time the DOM dynamics in the remote temperate, transitional and subtropical waters of the NE Atlantic east of Azores, from the distributions of DOC and DON. DOC and DON variability is related to the observed thermohaline and biological (Chl-*a*) fields in the area during three cruises conducted under increasing stratification conditions. In addition, suspended organic carbon (POC) and nitrogen (PON) pools measured during the Azores-I cruise allow us to study the POM/DOM partitioning under stratification conditions.

2. Materials and Methods

Samples for the analysis of Chl-*a*, dissolved and suspended organic carbon and nitrogen were collected during the Azores-I cruise, aboard 'R/V Hesperides' in August 1998. Three quasi-meridional transects crossing the AF were occupied: lines *A*, *B* and *C* at 22°, 28° and 32°W respectively (Fig. 1). A cold eddy detached from the main current was also surveyed: line *D*, at 23°W. Line *A* was also occupied during cruises AMT-4, aboard 'RRS James Clark Ross' in May 97, and Azores-II, 'R/V Hespérides' in April 99. Finally, a second cold eddy was sampled during the Azores-II cruise: line *E* at 28°W (Fig. 1). Only Chl-*a*, DOC and DON were determined during the AMT-4 and Azores-II cruises. During the three cruises, samples were drawn from 12 litre PVC Niskin bottles mounted on a rosette sampler.

2.1. Thermohaline parameters

Continuous vertical profiles of salinity and temperature were recorded with calibrated conductivity-temperature-depth (CTD) probes attached to the rosette samplers, as described by

Bale et al. (1997) for AMT-4, Pérez et al. (accepted) for Azores-I and Mouriño et al. (accepted) for Azores-II. Water column stability at 5m depth intervals was quantified by means of the square of the Brunt-Väisälä frequency (N^2):

$$N^2 = \frac{g}{\rho} \cdot \left(\frac{\Delta \rho}{\Delta z} \right) \quad (1)$$

g is the gravity acceleration. ρ is the average density over the 5m depth intervals (Δz), obtained from the CTD salinity and temperature profiles with the equation of state of seawater (UNESCO, 1985). $\Delta \rho / \Delta z$ is the corresponding density gradient. The pycnocline, depth of maximum N^2 , separates the DOM-rich surface layer from the DOM-poor water below. N^2 profiles in the AF area were not characterised by a single well-defined maximum at a given depth. On the contrary, several maxima were observed between z_1 and z_2 , the top and bottom depth of the ‘pycnocline layer’.

The stability at the pycnocline, $N^2(p)$, controls the downward transport of the surface DOM excess to the waters below by turbulent diffusion. This is the main physical mechanism of downward transport of dissolved materials operating under stratified conditions. The turbulent diffusion flux of DOC across the pycnocline layer (F_{DOC}) can be roughly estimated as:

$$F_{\text{DOC}} = -K_Z \cdot \frac{\Delta \text{DOC}}{\Delta z} = - \left(\frac{\varepsilon \cdot R}{N^2(p) \cdot (1 - R)} \right) \cdot \left(\frac{\overline{\text{DOC}}_2 - \overline{\text{DOC}}_1}{z_2 - z_1} \right) \quad (2)$$

The turbulent diffusion coefficient (K_Z) can be calculated from the dissipation rate (ε), the Richardson number (R) and the square of the Brunt-Väisälä frequency at the pycnocline. ε and R can be set to constant values of $10^{-8} \text{ m}^2 \text{ s}^{-3}$ and 0.2 respectively for open ocean waters (Copin-Montégut and Avril, 1993). Consequently, K_Z variability just depends on the inverse of $N^2(p)$. The DOC gradient across the pycnocline ($z_2 - z_1$) is calculated as the difference between the average DOC concentration from z_2 to 200 m ($\overline{\text{DOC}}_2$) minus the average DOC concentration from 0 m to z_1 ($\overline{\text{DOC}}_1$).

*2.2. Chlorophyll-*a*, suspended and dissolved organic matter*

Chl-*a* was measured fluorometrically, following the procedures described by Bale et al. (1997) for AMT-4, Pérez et al. (accepted) for Azores-I and Mouriño et al. (accepted) for Azores-II.

POM was determined in the upper 200m during the Azores-I cruise. Seawater was drawn from the Niskin bottles into 2 litre polycarbonate flasks. It was immediately filtered using an oil-less vacuum filtration system (filtration pressure $<0.3 \text{ kg cm}^{-2}$) to collect the particulate material on precombusted GF/F filters (450 °C, 4 hours). The filters were dried over silica gel and then kept frozen at -20°C until analysis in the laboratory. Suspended organic carbon (POC) and nitrogen (PON) measurements were carried out using a 'Perkin Elmer 2400 CHN' analyser. Acetanilide was used to calibrate the system. The analytical error of the method was $\pm 0.1 \text{ }\mu\text{M-C}$ for POC and $\pm 0.04 \text{ }\mu\text{M-N}$ for PON.

Samples for the analysis of DOM were collected in precombusted 10 ml glass ampoules (450 °C, 12 hours) during the three cruises. After acidification with H_3PO_4 to pH <2 , the ampoules were heat-sealed and stored in the dark at 4°C, until analysed in the laboratory. Full-depth profiles were collected during the Azores-I cruise and the upper 2000 meters were sampled during the AMT-4 and Azores-II cruises. A nitrogen specific 'Antek 7020' nitric oxide ($\text{NO}\bullet$) chemiluminescence detector was coupled in-series with the carbon specific Infra-Red Gas Analyser (IRGA) of a 'Shimadzu TOC-5000' organic carbon analyser. After decarbonation of the sample, 200 μl were injected into the vertical furnace of the 'Shimadzu TOC-5000', filled with 0.5% Pt coated Al_2O_3 catalyst at 680°C. Quantitative production of CO_2 and $\text{NO}\bullet$ occurs from the dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in the sample. High purity synthetic air carried the combustion products through a series of scrubbers before the dried gas mixture entered the measuring cell of the IRGA. The combustion gases are then routed to the 'Antek 7020' detector by pulling with a diaphragm vacuum pump at the exit of the reaction chamber. Following Álvarez-Salgado and Miller (1998), a T-piece was installed before the 'Antek 7020' and the flow through it was set to ~75% of the total flow

(=150 ml min⁻¹) by means of an ‘Swagelock’ extra-fine Nupro metering valve. The remaining ~25% (= 37.5 ml min⁻¹) was vented to the atmosphere. The system was calibrated daily with a mixture of potassium hydrogen phthalate and glycine. The concentration of DOC and TDN was determined by subtracting the system blank area from the average peak area (3–5 replicates) and dividing by the slope of the standard curve. The system blank —obtained by frequent injection of UV-Milli-Q water— was equivalent to 10 µM-C and 0.4 µM-N. Precision of both simultaneous measurements was about ±1 µM-C and ±0.3 µM-N. The accuracy of our DOC measurements were tested daily with the reference materials provided by J.H. Sharp (University of Delaware) with very satisfactory results. We obtained an average concentration of 45.1±0.7 µM-C (n= 50) for the DEEP OCEAN and 0.4±0.6 µM-C (n= 50) for the BLANK reference material. Nominal values are 44.0±1.5 and 0.0±1.5 µM-C respectively. Dissolved organic nitrogen (DON) concentration in the samples was obtained by subtracting the independently measured NO₃⁻ to the HTCO-TDN. Since the analytical error of NO₃⁻ measurements was ±0.1 µM-N, the precision of DON estimation was ±0.3 µM-N ($= \sqrt{(\pm 0.1)^2 + (\pm 0.3)^2}$).

3. Results

3.1. Hydrographic conditions

The physical setting (water masses, fronts, eddies) influences the distribution of dissolved and suspended organic materials in the water column. Accordingly, we will examine first the hydrographic conditions during the summer cruise (Azores-I, August 98), when the AF area between 20° and 33°W was sampled in detail (Fig. 1). Then, we will compare the contrasting hydrographic settings along the quasi-meridional transect at ~20°W, performed under increasing stratification conditions (Azores-II, April 99; AMT-4, May 97; and Azores-I, August 98). Finally, we will study two cold eddies detached from the AC and intercepted during Azores-I and Azores-II. Temperate (north of the AF), transitional, and subtropical (south of the AF) waters of the study region will be differentiated in the three cruises. Special attention will

be paid to the development of the seasonal thermocline and the conspicuous distribution of water masses in the three zones.

3.1.1. Spatial variability: the summer cruise (Azores–I, August 98)

The large and meso-scale hydrographic variability during the summer cruise has been described in detail by Pérez et al. (accepted). Here we summarise those of their results that are relevant to this study. The AC has been usually identified by the position of the 16°C isotherm at 200m depth (Gould, 1985). This isotherm is highlighted in Figure 2, allowing us to identify the temperate and subtropical waters to the north and south of the front, respectively. Note that the upper 100m has been expanded x 4 in order to better show the variability in surface ocean waters. A steep change was observed in the depth of the 16°C isotherm in the westernmost line C, west of the Azores Isles (Figure 2e). The transitional area between the temperate and subtropical regimes (delimited by the vertical dashed lines in Figures 2 to 5) extended over less than 1 degree in latitude and, although it was intensively sampled, did not display any meso-scale activity (Pérez et al., accepted). In contrast, lines A and B, east of Azores (Figure 2c, d), were characterised by a broad transitional area (about 3 degree wide) and meanders or eddies of the AC were present. The water masses analysis of Pérez et al. (accepted) indicate that central waters of the temperate zone are quite uniform from 22° to 32°W, and consist mainly of Eastern North Atlantic Central Water (ENACW; Ríos et al., 1992). In contrast, a progressive eastward increase in salinity converted Sargasso Sea Water (SSW; Gould, 1985) into Madeira Mode Water (MMW; Siedler et al., 1987) in the subtropical zone.

Surface waters above the seasonal thermocline ($<z_1$) were characterised by high temperatures ($>23^{\circ}\text{C}$), showing a clear westward increase (Figure 2c, d, e; Table 1). A distinct thermocline layer separated the surface waters, in which POM (Figure 5) and DOM (Figure 6) accumulate, from the central waters below. The top of the pycnocline depth (z_1) is shown in Figure 2 (black dots). Line A (Figure 2c) illustrated the expected meridional evolution of z_1 : it progressively deepens from the temperate (20 ± 4 m) to the subtropical (45 ± 8 m) domain. The same tendency was observed in line B (Figure 2d), where the smooth equatorward extension of

the surface layer was interrupted by the abrupt deepening of the thermocline at stn 16 ($z_1 = 78\text{m}$). The stability of the seasonal thermocline, $N^2(p)$, was high ($>2.3 \text{ min}^{-2}$), specially along line C (Table 1) in parallel with the observed spatial variability of surface temperature. It contributed to the prevention of the downward transport of materials accumulated in the surface layer. The meridional evolution of $N^2(p)$ showed a slight southward decrease from the temperate to the subtropical domain along lines A and B.

3.1.2. Temporal variability: contrasting stratification conditions along 20°W

Comparison of the meridional evolution of temperature profiles along line A during the early spring (Azores–II, Figure 2a), late spring (AMT–4, Figure 2b) and summer cruises (Azores–I, Figure 2c) illustrated the expected seasonal increase of surface temperatures. $\overline{T}_1$ (average temperature in the $0\text{--}z_1$ depth range) from 30° to 38°N (latitudinal range of the Azores–I line A) increased from $\sim 18.5^\circ\text{C}$ to $\sim 23.5^\circ\text{C}$ (Table 2). Accordingly, the seasonal thermocline was much weaker during the spring cruises: average $N^2(p)$ of 1.0 min^{-2} and only 0.2 min^{-1} were recorded during late and early spring, respectively (Table 2). The surface layer extended deeper during the spring cruises, specially on the northern side of the study section where it was twice as deep as during the summer. In contrast to the summer cruise, the spring cruises showed a clear equatorward increase of surface temperature between 30–38°N increasing by about 1°C during Azores–II and 2°C during AMT–4.

The 16°C isotherm at 200m is used again to locate the AF, differentiating the temperate, transitional and subtropical domains. During the early spring cruise, the equatorward deepening of the 16°C isotherm was very smooth compared with the summer cruise. Steep gradients were observed at stns 9–10 and 5–6, which delimit the northern and southern ends of the transitional area. Meanders or eddies of the AC were observed at stns 6 and 8 (Pérez et al., accepted). The poor spatial resolution of the late spring cruise did not allow to observe the any probable meso-scale activity of the area and only a vertical dashed line is depicted to indicate the position of the AF. The presence of ENACW at the northern end of Azores–I (stn 1) and AMT–4 (stn 31)

cruises and MMW at the southern end of Azores–I (stns 7–9), Azores II (stns 3–5) and AMT–4 (south of 34°N), respectively, was denoted by the temperature and salinity distributions.

Hydrographic lines *D* and *E* crossing the Azores–I and –II eddies were occupied (Figure 1; Pérez et al., accepted; Mouriño et al., accepted). The surface temperature and the deepness of the surface layer (Figures 3 a & d) showed the expected seasonal trend from 20 to 24°C and from 38 to 33m, respectively. Accordingly, the seasonal thermocline was markedly weaker during the spring cruise (0.24 min^{-2}) than during the summer cruise (2.3 min^{-2}). The thermohaline structure of the two cold cyclonic eddies sampled in April and August showed the expected isotherm doming (see the reference 16°C isotherm). However, the two eddies presented some differences. The top of the pycnocline (z_1) shoaled by ~25m at the core of the spring eddy, whereas it remained at a constant depth in the summer eddy, as a consequence of the higher stratification conditions. In addition, ENACW advected from the northern side of the AF was found in the summer eddy (Pérez et al., accepted), whereas a tongue of SSW was observed in the spring eddy.

3.2. Chlorophyll-*a*, suspended and dissolved organic matter distributions

3.2.1. Chl-*a*, POM and DOM during the summer cruise (Azores–I, Aug 98)

Chl-*a* profiles in the upper 200m (sampling range) along the three quasi-meridional lines occupied during the summer cruise (Figures 4c, d, e) were characterised by extremely low surface values ($<0.1 \text{ mg m}^{-3}$) and a marked deep Chl-*a* maximum (DCM) centred at ~100m depth. The DCM was observed in the temperate, transitional and subtropical regions of the three study lines. Chl-*a* levels in the DCM ranged from 0.3 to 1.0 mg m^{-3} , showing a striking variability. As a general trend, Chl-*a* levels at the DCM were inversely correlated with the DCM depth, z_{DCM} ($r = -0.78$, $p < 0.01$, $n = 31$) in agreement with the results found previously by Fasham et al. (1985) and Agustí and Duarte (1999) in the AF area and central Atlantic Ocean, respectively. z_{DCM} and Chl-*a* tend to decrease and increase westwards, respectively: average values were 100m and 0.55 mg m^{-3} along line *A* and 85m and 0.87 mg m^{-3} along line *C* (Table 1). This trend was parallel to the westward increase of $\overline{T_1}$ and $N^2(p)$, which can affect the

position (and magnitude) of the DCM. In fact, the direct correlation of Chl-*a* at the DCM with $\overline{T_1}$ ($r = +0.78$, $p < 0.01$, $n = 31$) and $N^2(p)$ ($r = +0.68$, $p < 0.01$, $n = 31$) was high. In any case, it should be highlighted that z_{DCM} is much deeper than z_1 , precluding the transference of fresh organic materials produced at the DCM to the surface layer.

Despite the fact that POC is being derived from phytoplankton primary production, its vertical distribution during the summer cruise (Figure 5a, b, c) contrasted with the distributions of Chl-*a*. High POC levels were observed from the surface layer (where Chl-*a* levels are minimum) to z_{DCM} and decrease monotonically from z_{DCM} to 200m (sampling range), where POC levels were $< 3 \mu\text{M-C}$. Average POC along the three study lines varied from 4.3 to 4.7 $\mu\text{M-C}$ (average $4.3 \pm 0.6 \mu\text{M-C}$) in the surface layer ($\overline{POC_1}$) and from 3.7 to 3.9 $\mu\text{M-C}$ (average $3.8 \pm 0.5 \mu\text{M-C}$) in the z_1 –200m depth layer ($\overline{POC_2}$; Table 1). Differences between the hydrographic lines were not significant. POC maxima were not observed at the DCM. The dissimilarity between profiles of Chl-*a* and POC resulted in POC/Chl-*a* ratios ranging from $72 \pm 20 \text{ g-C g-Chl}^{-1}$ at the DCM to $540 \pm 70 \text{ g-C g-Chl}^{-1}$ in the surface layer. Considering the average phytoplankton carbon estimated from cell volumes in the area (12–16%; Fernández et al., 1994) and the high suspended organic C/Chl-*a* ratio during the Azores I cruise, most of the 4–5 $\mu\text{M-C}$ of POM accumulated in the surface layer seems to consist of microheterotrophs and mainly detritus (Fasham et al., 1985).

PON distributions (not shown) were coupled to POC throughout the upper 200m. The linear regression for all samples was relatively high ($r = +0.82$, $p < 0.01$, $n = 186$) considering the limited PON (from 0.1 to 0.7 $\mu\text{M-N}$) and POC ranges (from 1.7 to 6.0 $\mu\text{M-C}$). The slope of the linear regression (Model II; Sokal and Rohlf, 1995) was $8.3 \pm 0.3 \text{ mol C mol N}^{-1}$. The origin intercept of the regression, *i.e.* the fraction of POC which does not covary with PON was $0.7 \pm 0.1 \mu\text{M-C}$ and represented 17% of the average POC. If these calculations are restricted to the DCM, then the correlation coefficient is increased ($r = +0.88$, $p < 0.01$; $n = 32$) and the slope is reduced to $6.7 \pm 0.6 \text{ mol-C} \cdot \text{mol-N}^{-1}$, the Redfield C/N ratio of phytoplankton biomass (Anderson, 1995). The origin intercept was $1.0 \pm 0.3 \mu\text{M-C}$, which represents 25% of the

average POC at the DCM. Accordingly, the direct C/N molar ratios of POM were 11 ± 1 and 9 ± 2 at the surface layer and the DCM, respectively.

DOC profiles during the summer cruise were also characterised by maximum values ($>65 \mu\text{M-C}$) in the $0-z_{\text{DCM}}$ depth range (Figure 6c, d, e). The variability, with concentrations $>70 \mu\text{M-C}$ in the surface layer ($0-z_1$) of several stations (1, 9, 11, 12, 16, 18 and 21), was high and cannot be directly related to the variability observed in temperature, Chl-*a* or POM. No significant meridional (temperate, transitional and subtropical domains) or zonal differences were observed in $\overline{DOC_1}$ (Table 1). The same is applicable to $\overline{DON_1}$. Average $\overline{DOC_1}$ and $\overline{DON_1}$ during the summer cruise were $70 \pm 3 \mu\text{M-C}$ (average $\pm$ SD) and $5.0 \pm 0.4 \mu\text{M-N}$, producing a C/N molar ratio of 14 ± 2 . This ratio is $\sim 30\%$ higher than the C/N ratio of $\overline{POM_1}$ and $>100\%$ higher than the C/N ratio of the products of synthesis and early degradation of marine phytoplankton (6.6).

According to previous studies in the area (Robinson et al., 1979; Fasham et al., 1985; Jochem and Zeitzchel, 1993) the winter mixed layer was 150–200m deep, which is similar to that observed at the BATS stations in the Sargasso Sea (Hansell and Carlson, 2001). Therefore, we can consider the average DOC and DON concentration at 200m depth, $56 \pm 2 \mu\text{M-C}$ and $4.0 \pm 0.5 \mu\text{M-N}$, as the expected level in the surface layer during the winter mixing period. Accordingly, the DOC excess of labile and semi-labile material in the surface layer compared with the winter baseline (seasonal excess; $\overline{\Delta DOC_1s}$ and $\overline{\Delta DON_1s}$) was $14 \pm 2 \mu\text{M-C}$ and $1.0 \pm 0.5 \mu\text{M-N}$, *i.e.* $\sim 20\%$ of $\overline{DOC_1}$ and $\overline{DON_1}$. Equivalent calculations for POM yielded average concentrations of $2.5 \pm 0.4 \mu\text{M-C}$ and $0.22 \pm 0.04 \mu\text{M-N}$ at 200m depth and a $\overline{\Delta POM_1s}$ excess of $2.0 \pm 0.6 \mu\text{M-C}$ and $0.2 \pm 0.1 \mu\text{M-N}$, *i.e.* $\sim 45\%$ of $\overline{POC_1}$ and $\overline{PON_1}$. Differences in average DOC and DON levels from the thermocline to 200m depth between the three study lines (Table 1) were not significant, although a slight eastward increase was observed. The average $\overline{DOC_2}$ for the summer cruise was $63 \pm 2 \mu\text{M-C}$, with an average C/N molar ratio of

14±2 (Table 1). $\overline{DOC_2}$ at every station exceeded from 2 to 5 $\mu\text{M-C}$ the expected concentration from the conservative mixing of surface and 200m–depth waters. Temperature was used as a conservative tracer to run this simple mixing calculation. The correlation between DOC and temperature in the z_2 –200 m depth range was relatively high ($r = +0.74$, $p < 0.01$, $n = 164$), indicating that ~55% of the variability of DOC can be explained by temperature. The multiple correlation with temperature and POC ($r = +0.77$, $p < 0.01$, $n = 153$) increased the percentage of explained variance of DOC up to 60%. Turbulent diffusion fluxes of DOC across the seasonal thermocline (F_{DOC}) were quite limited, ranging from 0.9 to 8.7 $\text{mg-C m}^{-2} \text{ d}^{-1}$. Significantly higher values were recorded in subtropical (average $3.8 \pm 1.4 \text{ mg-C m}^{-2} \text{ d}^{-1}$) compared with temperate waters (average $2.0 \pm 0.4 \text{ mg-C m}^{-2} \text{ d}^{-1}$), due to the higher K_z values and DOC gradients. These numbers represented $< 0.2\%$ of $\overline{\Delta DOC_1}$, indicating that turbulent diffusion was not an important mechanism for the downward transport of the DOC excess in surface ocean waters. Low F_{DOC} values were due to both the reduced K_z (0.3 – $1.5 \text{ m}^2 \text{ d}^{-1}$), characteristic of summer stratification, and the limited DOC gradients across the pycnocline (0.1 – 1.6 mg-C m^{-4}).

Below 200m, DOM decreased monotonically due to the conservative mixing with the baseline concentration of highly refractory material ($47 \pm 1 \text{ } \mu\text{M-C}$ and $3.4 \pm 0.5 \text{ } \mu\text{M-N}$) in deep ocean waters ($> 500\text{m}$). Comparison of $\overline{DOC_1}$ with the concentration of refractory material produced a total DOM excess ($\overline{\Delta DOC_1}$ and $\overline{\Delta DON_1}$) of $23 \pm 4 \text{ } \mu\text{M-C}$ and $1.6 \pm 0.5 \text{ } \mu\text{M-N}$, *i.e.* ~33% of $\overline{DOC_1}$ and $\overline{DON_1}$. DOC was inversely correlated with total inorganic carbon, normalised to salinity 35.0 (NC_T), in the z_2 –500m depth range ($r = -0.77$, $p < 0.01$, $n = 94$). NC_T was also corrected for CaCO_3 precipitation–dissolution using the term $-0.5 \times (\text{NTA} + \text{NO}_3^-)$, being NTA the normalised total alkalinity and NO_3^- the nitrate concentration (Broecker and Peng, 1982). Since NC_T has been CaCO_3 –corrected, the DOC/NC_T slope indicates the relative contribution of degradable DOC oxidation to NC_T production in subsurface waters above 500m. However, DOC and NC_T variability is partly due to water masses mixing, which affects the slope of the correlation. To remove the effect of water masses mixing, a multiple regression of

DOC with temperature and NC_T has been conducted ($r=0.80$, $p<0.01$, $n=94$) and the resultant temperature-independent DOC/ NC_T slope was -0.13 ± 0.01 . This means that DOC only contributed to 13% of the carbon demand in subsurface waters, when the whole z_2 –500m depth-range is considered. Just for comparison, the temperature-independent slope of the multiple regression of apparent oxygen utilisation (not shown), with temperature and NC_T for all samples between z_2 and 500m was $1.4\pm0.1 \text{ mol-O}_2 \text{ mol C}^{-1}$ ($r=0.95$, $p<0.01$, $n=94$) This value indicates that the oxidation of organic matter occurs according to the classical Redfield stoichiometry (Anderson, 1995). Carbon system, nutrients and oxygen data were taken from Ríos, et al. (accepted).

3.2.2. Temporal variability of Chl-*a* and DOM along 20°W

A DCM, characteristic of nutrient-poor open ocean waters (Menzel and Ryther, 1960; Agustí and Duarte, 1999), was observed during the three cruises (Figure 4a, b, c). All of them were conducted in post spring-bloom conditions, even the early spring Azores-II cruise. Accordingly, surface Chl-*a* concentrations $<0.1 \text{ mg m}^{-3}$ were observed, except at the northern (stn 31) and southern (stns 22–23) ends of AMT-4. Remnants of the spring bloom at 40°N and the possible influence of waters exported from the adjacent NW Africa coastal upwelling system at 24°N could be the reasons behind these higher surface Chl-*a* levels. Within 30°–38°N latitudes, the DCM deepened from 70 to 110m and increased from 0.3 to 0.6 mg-Chl m^{-3} from early spring to late summer (Table 2). z_{DCM} was always well below the seasonal thermocline (z_1) and there was also an increase of the difference between z_{DCM} and z_1 from early spring (22m) to late summer (77m). The temporal increase of Chl-*a* at the DCM parallels the increase of $\overline{T_1}$ and $N^2(p)$, observed in the study of the spatial variability during Azores-I (section 3.2.1). The temporal deepening of the DCM was previously assessed both in the Azores (Fasham et al., 1985) and Sargasso Sea waters (Michaels and Knap, 1996). However, only few reports study the temporal variation of Chl-*a* at the DCM depth in this region. Fasham et al. (1985) showed a temporal increase within the transitional and subtropical areas, and similar values within the temperate area. On the other hand, Marañón et al. (2000) found similar values for spring and

autumn cruises in the three stations sampled in this region. Local Chl-*a* maxima were recorded at the northern end of the 20°W transect in all cruises, in agreement with some previous studies of phytoplankton in this area (Fasham et al., 1985; Kahru et al., 1991). Chl-*a* maxima were also observed in the southern end of AMT-4 (stn 22), and within the transitional zone in Azores-I (stn 5). In general, there was little evidence of increased Chl-*a* associated with the front in the sampled area. Considering all studies of phytoplankton distribution within this area, a relatively broad range of Chl *a* maximum values ($\sim 0.1\text{--}1 \text{ mg Chl } a \text{ m}^{-3}$) in spring have been reported in different years, which suggest interannual variability is important in this oligotrophic region.

As observed during the summer cruise (section 3.2.1), the distribution of DOC concentration contrasts with that of Chl-*a* concentration. Maximum DOC concentrations ($>65 \mu\text{M-C}$) were also recorded in the upper layer, between the surface and the DCM depth, during AMT-4 and Azores-II (Figure 5a, b). DOM levels were similar to those found at the BATS station in the Sargasso Sea (31° 40'N, 64° 10'W): average annual surface concentrations were 60–70 $\mu\text{M-C}$ and 4.0–5.5 $\mu\text{M-N}$ (Carlson et al., 1998; Hansell and Carlson, 2001). The broader latitudinal range covered during the spring cruises allows to observe a conspicuous equatorward increase of $\overline{DOC_1}$, in parallel with the $\overline{T_1}$ increase (Figure 2a, b). $\overline{DOC_1} > 73 \mu\text{M-C}$ was observed in the Subtropical domain. The latitudinal variability of either $\overline{DOC_1}$ or $\overline{T_1}$ was more reduced during the summer cruise (Figure 2c). Considering the common 30°–38°N latitudinal range, $\overline{DOC_1}$ and $\overline{DON_1}$ were not significantly different between the three cruises although $\overline{T_1}$ and $N^2(p)$ increased by 5°C and 2.1 min^{-2} from early spring to the summer (Table 2). Average $\overline{DOC_1}$ and $\overline{DON_1}$ within this latitudinal range were $69 \pm 2 \mu\text{M-C}$ and $5.2 \pm 0.4 \mu\text{M-N}$ respectively, with a C/N molar ratio of 13 ± 1 . Since DOC and DON at 200m were not significantly different for the three cruises, $56 \pm 2 \mu\text{M-C}$ and $4.3 \pm 0.4 \mu\text{M-N}$, average $\overline{\Delta DOC_1s}$ and $\overline{\Delta DON_1s}$ resulted $13 \pm 2 \mu\text{M-C}$ and $0.9 \pm 0.4 \mu\text{M-N}$. It should be noticed that the thickness of the surface layer decreased from 52m in April to 33m in August, which produced contrasting DOC accumulation values in g-C m^{-2} despite the fact that $\overline{DOC_1}$ remained

constant. Since $\overline{DOC}_2$ and $\overline{DON}_2$ did not show a significant seasonal variation (Table 2), F_{DOC} was mainly controlled by K_z , *i.e.* by the thermal stratification. Average F_{DOC} decreased from 54 mg-C m⁻² d⁻¹ in the early spring cruise to 2.3 mg-C m⁻² d⁻¹ in the summer cruise. In any case, it represented <0.6% of $\overline{\Delta DOC}_{1s}$. As for the summer cruise, DOC below 200m decreased monotonically due to conservative mixing with deep waters (>500m) with an average DOC concentration of 47±2 µM-C (n= 33). These deep DOC values were slightly higher than those recorded at BATS (44±2 µM-C for >1000m; Hansell and Carlson, 2001), and similar to those obtained in the NE Atlantic (~50 µM-C; Álvarez-Salgado XA & Miller AEJ, unpub) and in the western equatorial Atlantic (12–16°W; 46±7 µM-C; Thomas et al., 1995).

Chl-*a* distributions showed DCMs of 0.3 and 0.6 mg m⁻³ at ~90 and ~107m during the spring and summer eddies, respectively (Figure 3b & e). Significant Chl-*a* increase was found in association with the uplift of z_{DCM} at the centre of the spring eddy, whereas a more homogeneous Chl-*a* distribution was observed in the summer eddy with maximum Chl-*a* values at the south and centre of it. Average surface DOC values were ~67 µM-C in both eddies (Figure 3c & f). This DOC concentration was similar to that found in other stations sampled during these cruises (Tables 1 & 3). In both cases, surface DOC distributions were not strongly affected by the presence of eddies, pointing to a lag time between Chl-*a* and DOM accumulation and/or low DOM production rates by the assemblage of organisms within the eddies.

4. Discussion

4.1. Biochemical significance of the surface DOC excess

Seawater for DOC analysis was drawn directly into the 10ml ampoules, so it contains part of the POC which otherwise would have been retained on the GF/F filters. Two litres of sample were filtered to collect the POC material, so POC is representative for particles in the 0.8–200 µm size range. On the other hand, only 200 µl of sample are analysed for DOC content. This volume is representative for particles, say, <2 µm. Therefore, the DOC analysis includes particles between 0.8 and 2 µm. How much carbon does it represents?. For the case of

phytoplankton, with a surface concentration of 0.08 mg C m^{-3} and considering that organisms $<2 \text{ }\mu\text{m}$ represent $\sim 70\%$ of Chl-*a* in the area (Herbland and Le Bouteiller, 1981) it would represent $0.5 \text{ }\mu\text{M-C}$, a concentration below the detection limit of the DOC analyser. So, considering that microheterotrophs and detritus are $>2 \text{ }\mu\text{m}$, let us assume that POC does not interfere our DOC measurements.

The surface DOC excess in the AF region, represents 85% of the observed summer TOC (POC+DOC) excess. Similar POC/DOC partitioning ratios has been observed in the Sargasso Sea (Carlson et al., 1998) and the Mediterranean Sea (Copin-Montégut and Avril, 1993; Doval et al., 1999), confirming the relevance of the DOC pool in nutrient limited ecosystems. The surface DOC excess compared with the baseline concentration of deep waters is similar in the three study cruises (about 33% of the total surface DOC), showing only slightly higher values in the early spring cruise (Azores-II; Table 2). Similarly, the annual cycle of DOC in the BATS station shows slightly higher DOC values during, or just after, the spring bloom (Carlson et al., 1998; Hansell and Carlson, 2001). These authors have addressed the importance of the winter mixing process (and the associated nutrient entrainment) in the subsequent spring–summer DOC production and export. Therefore, the annual variations in the winter mixed layer depth should have a first order effect on phytoplankton, new production and TOC export in oligotrophic gyres (Michaels and Knap, 1996; Hansell and Carlson, 2001). Homogeneity of surface DOM during the spring–summer period in the study region could be related with the relative abundance of semilabile materials **1**) formed during the spring bloom (Carlson et al., 1994), **2**) advected from the Sargasso Sea area or **3**) continuously produced by efficient transformation of new nutrients (Fasham et al., 1985; Jochem et al., 1993; Malone et al., 1993), which are either transported upwards by turbulent mixing, mesoscale eddies and microzooplankton (Doney et al., 1996; Steinberg et al., 2000) or southwards by Ekman pumping (Williams et al., 2000). Ekman pumping can transport DOC from the surface temperate to the surface subtropical NE Atlantic. The Ekman flux in the upper 30m across 36°N , from 22° to 32°W , calculated by Williams et al. (2000) using average 1958–98 wind–stress values, is $23.1 \text{ } 10^{12} \text{ m}^3$ from March to December (average, 0.89 Sv). Considering the $14 \text{ }\mu\text{M-C}$ excess of DOC

in the spring and summer upper mixed layer compared with the DOC concentration at 200m (section 3.2.2), the total amount of bioreactive DOC transported southwards by the Ekman flux from March to December is $3.9 \cdot 10^{12}$ g-C or $32 \text{ mg-C m}^{-2} \text{ d}^{-1}$ in the $0.41 \cdot 10^{12} \text{ m}^2$ ruled area in Figure 1 (32–36°N, 22–32°W). For comparison, this amount represents ~ 20 and 30% of the measured spring and summer sinking POC flux at 100m (0.15 and $0.1 \text{ g-C m}^{-2} \text{ d}^{-1}$, respectively; R. Anadón, pers. comm.) and only ~15% of the average primary production ($\sim 0.2 \text{ g-C m}^{-2} \text{ d}^{-1}$; Maraño et al., 2000; F.G. Figueiras, pers. comm.). In any case, the bioreactive DOC transported by Ekman pumping from the temperate to the subtropical North Atlantic seems not to be the reason behind the net heterotrophy (carbon consumption exceeds *in situ* production) of the study area suggested by Duarte et al. (2001).

Vertical eddy diffusion is the main physical mechanism injecting DOC into deep waters under stratified conditions (Copin-Montégut and Avril, 1993; Carlson et al., 1994). However, eddy diffusion fluxes in the AF region are extremely low when compared with the average surface DOC excess, confirming that stability keeps the DOC within the surface layer and that turbulent diffusion is not an important route to inject semilabile DOC in subsurface waters. The amount of DOC exported downwards by turbulent diffusion during early spring and summer cruises (53 and $2.3 \text{ mg-C m}^{-2} \text{ d}^{-1}$) was 35% and 2 % of the sinking POM flux at 100m, respectively. Zooplankton vertical migration has also been proposed as a mechanism to inject DOC into subsurface and deep layer (Longhurst and Harrison, 1988; Steinberg et al., 2000 and references therein). This mechanism could be important in areas where relatively abundance of migratory zooplankton has been documented, as the Sargasso Sea and Azores regions (Angel, 1989; Steinberg et al., 2000). However, the average DOC excreted by migrant zooplankton in the subsurface layer only account for 2% of the annual DOC export by physical mixing in the Sargasso Sea (Steinberg et al., 2000).

4.2. Organic matter mineralisation in subsurface waters

The temperature independent NC_T/AOU slope for all samples in the z_2 –500 m depth range ($1.4 \pm 0.1 \text{ mol-O}_2 \text{ mol-C}^{-1}$) indicated that the oxidation of organic matter occurs according

to the classical Redfield stoichiometry, this is with a C/N ratio of 6.6 mol C mol N⁻¹ (Anderson, 1995). However the C/N ratios of POM and DOM in the surface layer were 11±1 and 14±2 mol-C mol-N⁻¹. Comparable C/N ratios of POM were measured in the sinking material collected in shallow sediment traps at ~100 m, deployed during the same cruise (R. Anadón, pers. comm.), and in the sinking POM (150m) at the BATS station in the Sargasso Sea (≥10; Bates et al., 1996) and the ALOHA station in the North Pacific (8; Karl et al., 1996). Similar C/N ratios of DOM were measured by Hansell and Carlson (2001) at the BATS station. In the case that ~15% of POC in the surface layer consists of phytoplankton (Fernández et al., 1994), with an average C/N molar ratio of 6.6, the remaining 85% should have a C/N ratio of 12.5±1.0, which is very close to the average C/N ratio of surface DOM. The disagreement between the composition of the material accumulated in the surface layer, which will be eventually transported downwards, and the material mineralised at depth, has been already observed in the eastern South Atlantic (Álvarez-Salgado et al., 2001). In addition, it should be highlighted that DOC represents a minor fraction of the mineralised organic matter in several regions. When comparing the whole upper 500m, the contribution of DOC to the total mineralised organic matter in the AF region (this study), the South Atlantic (Álvarez-Salgado et al., 2001), the western South Pacific and central Indian Ocean (Doval and Hansell, 2000), was, respectively, 13%, 9% and 10%. These observations suggest that oxygen consumption in subsurface water is mainly due to large organic particles not accounted for in DOC analyses. This is the case of sinking aggregated detritus, with high C/N ratios (Verity et al., 1996). If this semi-labile material constitutes a major fraction of the mineralised organic matter, then nitrogen should be processed much faster than carbon to eventually produce the observed Redfield mineralisation ratio. Alternatively, it has been suggested that the flux of organic matter to the deep ocean is dominated by fast-sinking labile organic matter of Redfield composition produced by sporadic highly productive events (Anderson and Sarmiento, 1994).

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Table 1. Average $\pm$ SD values of the main hydrographic and biochemical parameters along the quasi-meridional transects *A*, *B* and *C* during the summer cruise (Azores I, August 1998)

	Transect <i>A</i> (20–23°W)	Transect <i>B</i> (27–29°W)	Transect <i>C</i> (31–33°W)
$\overline{T_1}$ (°C)	23.4 $\pm$ 0.3	24.5 $\pm$ 0.7	26.1 $\pm$ 0.3
$\overline{T_2}$ (°C)	17.6 $\pm$ 1.2	18.4 $\pm$ 0.9	17.9 $\pm$ 0.6
$N^2(p)$ (min ⁻²)	2.3 $\pm$ 0.6	2.5 $\pm$ 0.6	3.7 $\pm$ 0.7
F_{DOC} (mg-C m ⁻² d ⁻¹)	2.3 $\pm$ 0.7	2.7 $\pm$ 1.8	1.8 $\pm$ 0.5
z_1 (m)	33 $\pm$ 11	41 $\pm$ 20	27 $\pm$ 4
z_{DCM} (m)	110 $\pm$ 10	95 $\pm$ 13	85 $\pm$ 6
Chl <i>a</i> -DCM (mg m ⁻³)	0.55 $\pm$ 0.05	0.72 $\pm$ 0.13	0.87 $\pm$ 0.16
$\overline{POC_1}$ (μM-C)	4.3 $\pm$ 0.6	4.2 $\pm$ 0.6	4.7 $\pm$ 0.8
$\overline{PON_1}$ (μM-N)	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	0.5 $\pm$ 0.1
$\overline{POC_2}$ (μM-C)	3.8 $\pm$ 0.7	3.7 $\pm$ 0.5	3.9 $\pm$ 0.5
$\overline{PON_2}$ (μM-N)	0.3 $\pm$ 0.1	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1
$\overline{DOC_1}$ (μM-C)	70 $\pm$ 1	70 $\pm$ 4	71 $\pm$ 3
$\overline{DON_1}$ (μM-N)	5.3 $\pm$ 0.7	4.8 $\pm$ 0.4	4.7 $\pm$ 0.2
$\overline{DOC_2}$ (μM-C)	65 $\pm$ 2	64 $\pm$ 2	62 $\pm$ 2
$\overline{DON_2}$ (μM-N)	4.7 $\pm$ 0.4	4.5 $\pm$ 0.5	4.4 $\pm$ 0.3

$N^2(p)$, stability at the pycnocline; z_1 and z_2 , upper and lower limit of the pycnocline; z_{DCM} , depth of the deep chlorophyll maximum; $\overline{POC_1}$ and $\overline{POC_2}$, average POC between 0 and z_1 and between z_2 and 200m, respectively; the same notation is used for $\overline{PON}$, $\overline{DOC}$ and $\overline{DON}$; F_{DOC} , eddy diffusion flux of DOC from surface to waters below the thermocline depth.

Table 2.– Average±SD values of the main hydrographic and biochemical variables along transect A (30–38°N; 20–23°W) during the Azores II, AMT4 and Azores I cruises

Transect A (30–38°N; 20–23°W)	Azores II (April 99)	AMT-4 (May 97)	Azores-I (August 98)
$\overline{T_1}$ (°C)	18.4±0.7	19.0±0.9	23.4±0.2
$\overline{T_2}$ (°C)	17.7±0.6	16.6±1.1	17.6±1.0
$N^2(p)$ (min ⁻²)	0.16±0.03	1.0±0.3	2.3±0.7
F_{DOC} (mg-C m ⁻² d ⁻¹)	53±22	16±8	2.3±0.7
z_1 (m)	52±8	37±6	33±11
z_{DCM} (m)	70±10	80±10	110±10
Chl a-DCM (mg m ⁻³)	0.3±0.1	0.5±0.1	0.6±0.1
$\overline{DOC_1}$ (μM-C)	68±2	69±5	70±2
$\overline{DON_1}$ (μM-N)	5.0±0.2	5.1±0.4	5.3±0.6
$\overline{DOC_2}$ (μM-C)	63±3	61±5	65±5
$\overline{DON_2}$ (μM-N)	—	4.5±0.6	4.7±0.4
DOC _{z>500} (μM-C)	48±3	47±2	47±1
$\overline{\Delta DOC_1}$ (gC m ⁻²)	9.5	8.3	7.1

$N^2(p)$, stability at the pycnocline; z_1 and z_2 , upper and lower limit of the pycnocline; z_{DCM} , deep chlorophyll maximum depth; $\overline{DOC_1}$ and $\overline{DOC_2}$, average DOC between 0 and z_1 depth and between z_2 and 200m; the same notation is used for $\overline{DON}$; F_{DOC} , eddy diffusion flux of DOC from surface to waters below the thermocline depth; $\overline{\Delta DOC_1}$, surface excess DOC compared to refractory DOC level at >500m. No POM data was included because it was not available for AMT4 and Azores II cruises.

FIGURE CAPTIONS

Figure 1. Map of stations sampled during the Azores–I (black circles), AMT–4 (open triangles) and Azores–II (open circles) cruises. From north to south; Azores–I cruise: line *A* (stns 1–9), line *B* (stns 11–17), line *C* (stns 36–33, 30, 27, 25, 21, 19, 18) and line *D* (stns 37, 39, 41, 43, 45); AMT–4: line *A* (stns 22–25, 27–31); Azores–II : line *A* (stns 1, 2, 4, 6, 8, 10, 11) and line *E* (stns 17–23). The average position and direction of the Azores Current is indicated by the grey arrows (taken from Klein and Siedler, 1989). The ruled area (32°–36°N, 22°–32°W) has been considered for the calculation of DOC Ekman fluxes in section 4.2.

Figure 2. Vertical distribution of temperature (°C) along line *A* during the Azores II, AMT–4 and Azores–I cruises (a, b and c) and along lines *B* and *C* during the Azores–I cruise (d and e). The vertical dashed lines delimit the transitional area. Black points indicate the thermocline depth (z_1). Note that the upper 100 meters are expanded x4 compared with the 100–500m depth range.

Figure 3 Vertical distributions of (a, d) temperature (°C), (b, e) Chl-*a* (mg m⁻³) and (c, f) DOC (μM-C) along lines *D* and *E* during the Azores–I and Azores–II cruises (a, b, c, d, e and f). Black points indicate the thermocline depth. Note that the upper 100 meters are expanded x4 compared with the 100–500m depth range.

Figure 4. Vertical distribution of Chl-*a* (mg m⁻³) along line *A* during the Azores II, AMT–4 and Azores–I cruises (a, b and c) and along lines *B* and *C* during the Azores–I cruise (d and e). The vertical dashed lines delimit the transitional area. Black points indicate the thermocline depth. Note that the upper 100 meters are expanded x4 compared with the 100–200m depth range.

Figure 5. Vertical distribution of POC (μM-C) along lines *A*, *B* and *C* during the Azores I cruise (a, b, c). The vertical dashed lines delimit the transitional area. Black dots represents sampling depths. Note that the upper 100 meters are expanded x4 compared with the 100–200m depth range.

Figure 6. Vertical distribution of DOC (μM-C) along line *A* during the Azores II, AMT–4 and Azores–I cruises (a, b and c) and along lines *B* and *C* during the Azores–I cruise (d and e). The vertical dashed lines delimit the transitional area. Black dots represents sampling depths. Note that the upper 100 meters are expanded x4 compared with the 100–500m depth range.

AZORES-I

a)

AZORES-II

d)

b)

e)

c)

f)

latitude

latitude