INTRODUCTION

The key contribution of dissolved organic matter (DOM) to carbon cycling and the implications for the role of the oceans in the regulation of the anthropogenic CO₂ excess have been issues of renewed interest during the last decade (Toggweiler, 1989; Bascatow and Maier-Reimer, 1991; Sambrotto et al., 1993; Legendre and Le Fèvre, 1995). An excess of degradable DOM in surface ocean waters - generated in situ by biological processes (Kirchman et al., 1993; Thingstad et al., 1997) - is a commonly observed world-wide trend (Copin-Montégut and Avril, 1993; Carlson et al., 1994; Pakulski and Benner, 1994; Chen et al., 1996). This DOM excess seems to be composed of a minor fraction of fast-cycling, highly-labile material (Carlson and Ducklow, 1995), which constitutes the substrate for the microbial loop organisms (Azam et al., 1983; Kirchman et al., 1991). The major component of the observed excess appears to be phytogenic semilabile material, either directly released or resulting from photochemical transformation of labile molecules into less reactive compounds. A reduction in the bioavailability of surface water DOM after exposure to natural UV radiation levels has recently been demonstrated, and is probably due to photomineralisation of bioavailable DOM and the phototransformation of DOM to biorefractory substrates (Benner and Biddanda, 1998; Obernosterer et al., 1999). Conversely, accumulation of labile DOM in surface ocean waters could take place as a result of low
growth and biomass of bacteria, caused by competition with phytoplankton for nutrients and predation respectively (Thingstad et al., 1997) or photochemical inhibition of bacterial ectoenzymes (Herndl et al., 1993). In areas where convective mixing follows summer stratification, accumulated DOM is locally exported downwards during winter mixing and contributes to the in situ oxygen consumption in subsurface waters (Copin-Montégut and Avril, 1993; Carlson et al., 1994). Alternatively, horizontal transport to areas where the DOM excess can be recycled (Hansell and Waterhouse, 1997) or where winter mixing occurs could be the final fate of the DOM produced in vast regions of the open ocean (Legendre and Le Fèvre, 1995). Therefore, Eppley and Peterson’s (1979) concept of ‘new production’ needs to be revised because of the major contribution of DOM to organic carbon export, either vertically or horizontally (Bronk et al., 1994; Peltzer and Hayward, 1996). Regarding deep ocean waters, although some authors had suggested a contribution of DOM to oxygen consumption (Sugimura and Suzuki, 1988), the earlier statement that it is very old (4-6 Kyr) and resistant to degradation is currently accepted (Williams and Druffell, 1987, Bauer et al., 1992). However, Hansell and Carlson (1998) have demonstrated that ‘refractory’ is not synonymous with ‘eternal’: DOM in deep ocean waters decreases by 30% from the recently formed deep waters of the North Atlantic (48 µmol C l⁻¹) to the 2 Kyr older deep waters of the North Pacific (34 µmol C l⁻¹).

There are several recent studies on the spatial and seasonal variability of dissolved organic carbon (DOC) at local scales (ca. 10¹² km; e.g. Copin-Montégut and Avril, 1993; Carlson et al., 1994; Chen et al., 1996; Peltzer and Hayward, 1996), but there is a lack of studies covering the basin scale (ca 10³⁻¹⁴ km), apart from the recent works by Hansell and Waterhouse (1997) and Doval and Hansell (2000) in the Indian and Pacific Oceans. The present work reports a limited number of DOC measurements in surface, thermocline and deep ocean waters in the 5500 km long WOCE (World Ocean Circulation Experiment) line A14, in the eastern South Atlantic.

The South Atlantic connects the northern sources of North Atlantic Deep Water (NADW) with the Antarctic, Pacific and Indian Oceans and allows the Intermediate (AAIW), Circumpolar (CDW) and Bottom (AABW) waters of Antarctic origin to penetrate the North Atlantic (Reid, 1989). Complex mixing of these water masses flowing opposite at different levels occurs (Peterson and Whitworth, 1989). In the upper ocean, the climatologically driven circulation (Fig. 1) imposes several contrasting zones, with crucial implications for carbon biogeochemistry. From north to south, A14 started in the Equatorial upwelling. Then, the section crossed the cyclonic Subequatorial gyre, up to the South Equatorial Current (SEC). Further south, the section enters the anticyclonic Subtropical gyre, a vast oligotrophic area. Finally, after the Subtropical Front, the section entered the Subantarctic zone and finished at the northern end of the Subantarctic Front (Peterson and Stramma, 1991).

MATERIAL AND METHODS

Sampling programme

During Leg 1 of cruise CITHER-3 (R/V l’Atalante, January 13 to February 16, 1995), the meridional WOCE line A14 was occupied east of the Mid-
dle Atlantic Ridge, from 4°N to 45°S (Fig. 1). Conductivity-temperature-depth (CTD) data were calibrated and dissolved oxygen and nitrate were collected and determined following standard procedures (Le Groupe CITHER-3, 1998).

Seawater samples for total organic carbon (TOC) analysis were collected at 10 selected depths at 6 stations spaced ∼800 km apart. Samples were directly drawn from the 10 litre Niskin bottles into 100 ml acid-washed glass containers, after rinsing three times. They were subsequently acidified to pH ∼2 with H₂SO₄, covered with a Teflon top, and stored in the dark until analysis in the laboratory. Chen and Wangersky (1996) showed that acidification and dark cold storage is a convenient and practical method for DOC preservation, although it will not completely prevent the slow oxidation of labile materials. In this sense, Sharp et al. (1995) demonstrated that quick freezing and freezer storage in Teflon-sealed vials is very suitable for deep ocean sample preservation. Low particulate organic carbon (POC) levels in open ocean waters (<5% of TOC) prevented us from filtering the samples (Carlson and Ducklow, 1995; Peltzer and Hayward, 1996).

The analytical system

TOC samples were analysed in the base laboratory by high temperature catalytic oxidation (HTCO), with a commercial Shimadzu TOC-5000. The acidified samples were decarbonated by vigorous stirring with high purity air for ~20 min, and injected onto a pre-conditioned 0.5% Al₂O₃ catalyst at 680°C, under an atmosphere of high purity air. The combustion products (CO₂, H₂O, etc.) subsequently passed through: 1) a solution of 25% H₃PO₄; 2) an electronic dehumidifier; and 3) a halogen scrubber. Quantitatively produced CO₂ gas was measured with a Non-Dispersive Infra-Red (NDIR) detector and the resulting area was estimated with an in-built peak integrator. Catalyst conditioning consisted of washing the catalyst with a large volume of UV irradiated MilliQ water (Copin-Montégut and Avril, 1993).

Potassium Hydrogen Phthalate (KHP) was used for calibrating the system. A 4-point calibration curve prepared in UV-MilliQ water was performed every day. The correlation coefficient (r²) for the individual calibration curves was 0.9997. A single regression line was used for the whole set of calibrations, the coefficient of variation (CV) of the slope being 0.6% and r²= 0.9994. The ‘system blank’ (= ‘instrument blank’ + TOC in UV-MilliQ water) was low and stable, equivalent to 10.3±0.4 µmol C l⁻¹ (average±SD) for the whole set of blanks analysed (one every ten samples). UV-MilliQ water has near-zero DOC and is suitable for blank correction (Sharp et al., 1995; Peltzer et al., 1996). TOC concentrations were calculated by dividing the average area of the 3-5 replicate injections of 200 µl by the slope of the average regression line and subtracting the average ‘system blank’. The average CV of the peak area was ~1 %, i.e. equivalent to ±0.8 µmol C l⁻¹. In addition, 2 replicate analyses of inorganic carbon (optional in the Shimadzu TOC 5000) were performed to check for complete decarbonation. Just after analysing the CITHER-3 samples, we ran the set of 14 samples distributed as part of the ‘2nd stage of the large community methods comparison of DOC’ by Prof. J.H. Sharp (Univ. of Delaware), who reported that our results were within the permitted ±10% limits (J.H. Sharp, personal communication). In December 1996, Prof. J.H. Sharp distributed BLANK and DEEP OCEAN reference materials among the DOC analysts. We tested the accuracy of our DOC measurements with these reference materials daily in 1997-98, with very satisfactory results. Using essentially the same method as with the CITHER-3 samples, we obtained an average concentration of 45.8±1.1 µM-C (n= 40) for the DEEP OCEAN reference (Sargasso Sea deep water, 2600 m) and 0.4±0.7 µM-C (n= 43) for the BLANK reference material. The nominal values provided by the reference laboratories are 44.0 ±1.5 and 0.0±1.5 µM-C respectively.

RESULTS AND DISCUSSION

Water mass variability

The full-depth θ-S diagrams for the selected stations (Le Groupe CITHER-3, 1998) clearly show contrasting water masses along line A14 (Fig. 2). Stns 16 (0°S), 31 (8°S) and 46 (15°S) are characterised by higher salinity for a given temperature within the thermocline, which is distinctive of South Atlantic Central Water (SACW) in the eastern South Atlantic north of the SEC (Gordon and Bosley, 1991). On the other hand, stn 76 (30°S) is in the eastern limb of the Subtropical gyre, stn 91 (38°S) is within the Subtropical Front (STF) and stn 106 (45°S) is at the northern end of the Subantarctic Front (SAF), as can be drawn from the θ-S charac-
characteristics of the upper layer (Peterson and Stramma, 1991). Clear zonation within the intermediate, deep and bottom waters is also observed: the purest fractions of the low-salinity AAIW and AABW occur south of the SEC. On the other hand, the high-salinity NADW appears strongly diluted compared with the core of this water mass north of the SEC (Reid, 1989; Gordon and Bosley, 1991).

**Dissolved oxygen and nutrient salt distributions**

Full-depth nitrate and apparent oxygen utilisation (AOU) profiles for the selected stations (Fig. 3a and b) illustrate the contrasting contribution of advection and organic matter oxidation along the 5500 km-long line A14. Stations south of the SEC (76, 91, 106) are characterised by maximum AOU (>135 µmol kg⁻¹) and nitrate levels at ~1500 m depth, associated with the northward penetration of the upper Circumpolar Deep Water (UCDW), advected from the eastward-flowing Antarctic Circumpolar Current (Reid, 1989). The presence of the nutrient-rich purest fractions of
AABW is observed below 2500 m at stn 106. A clear poleward increase in nitrate occurs in thermocline waters. North of the SEC (stns 16, 31, 46), the most striking feature is the AOU maximum (>190 µmol kg⁻¹) at ~200-400m (Gordon and Bosley, 1991). According to Reid (1989), the cyclonic field centred at 10-15°S, together with the Ekman divergence and upwelling providing nutrients to the euphotic zone and the associated fallout of oxidizable organic matter into the subsurface waters trapped in the flow, must be the reasons for the massive local oxygen consumption that is observed. The multiple linear regression with θ and AOU for all samples where organic matter oxidation is dominant (i.e. AOU > 0) in the upper 1000 m explains 97% of the observed variance in the nitrate distribution (Eq. 1). The simple regression with temperature only retains 65% of the variance.

\[
\text{NO}_3^- = 24.9 - 1.31\theta + 0.099 \text{AOU}
\]

\[r^2 = 0.97 \quad n = 65 \quad p < 0.001 \quad (1)\]

The AOU coefficient coincides with the expected value of the stoichiometric ratio \(1/R_N = \text{∆NO}_3^- /\text{∆O}_2^- \approx 0.10\) from the literature (Broecker, 1974; Anderson and Sarmiento, 1994), indicating that: 1) θ removes the effect of water mass mixing on the nitrate and AOU distributions in the upper 1000 m; and 2) AOU in subsurface waters is related to the oxidation of phytopetric organic nitrogen to nitrate at the basin-scale of the eastern South Atlantic. This result confirms Broeker’s (1974) observation of a linear relationship between the conservative tracer ‘NO’ (= O₂⁺RN · NO₃⁻) and θ.

**TOC in deep waters**

Despite the complex advection and mixing patterns of waters of southern (AAIW, CDW and AABW) and northern (NADW) origins (Fig. 2) - with extremely different degrees of ventilation along A14 (Fig. 3) - TOC levels below 500 m are quasi-constant at 55±3 µmol C l⁻¹ (Fig. 4). These are the only TOC values reported for the remote Eastern South Atlantic to date. Following the recent study by Hansell and Carlson (1998) on TOC levels in deep waters of the World Ocean, we should expect a concentration of 44-45 µmol C l⁻¹ in the deep South Atlantic. This is the concentration that they obtained in the Western North Atlantic. Other reported concentrations in the deep North Atlantic are 50 µmol C l⁻¹ in the Gulf of Mexico (Guo et al., 1994), ~50-55

\(\mu\text{mol C l}^{-1}\) in Georges Bank (Chen et al., 1996),

50±3 \(\mu\text{mol C l}^{-1}\) near Bermuda (Pakulsky and Benner, 1994), 51±4 \(\mu\text{mol C l}^{-1}\) in the Bay of Biscay (X.A. Alvarez-Salgado and A.E.J.M. Miller, unpubl.) and 46±7 \(\mu\text{mol C l}^{-1}\) in the Equatorial Atlantic (Thomas et al., 1995). Therefore, our values are at the top end of previous studies and could even exceed the permitted ±10% limits. However, we do not find any strong reason for rejecting the data. Major evidences have been presented in the Material and Methods section on the accuracy of our instrument against an international reference for analytical quality. It should be highlighted that the critical ‘system blank’ correction produces values of the BLANK reference material that are not statistically different from zero. Contamination during storage seems unlikely considering the consistency of the profiles in Figs. 4 and 5. We avoided exposure of the samples to any source of volatile organic contamination during storage, which could affect all samples uniformly. However, we also have no argu-
ments to explain a TOC excess in deep waters of the eastern South Atlantic. In any case, the study of the significance of physical and biological processes on TOC distributions in thermocline waters presented below is not dependent on the accuracy of TOC concentrations in the deep ocean.

Fig. 5. – Potential temperature (θ), apparent oxygen utilisation (AOU) and total organic carbon (TOC) profiles in the upper 1000 m for the six stations where TOC was sampled along A14.
TOC in thermocline waters

An excess of non-degraded TOC compared to the refractory deep-water baseline is observed in surface waters of the Equatorial (stns 16), Subequatorial (stns 31 and 46) and Subtropical (stns 76 and 91) regions (Fig. 5). Average TOC in the upper 100 m is 76 µmol C l⁻¹ (excess of 25 g C m⁻²) at stn 16 and 82-87 µmol C l⁻¹ (excess of 32 to 38 g C m⁻²) at stns 31-91, which are within the expected DOC excess ranges in marine systems world-wide (see review by Thingstad et al., 1997). The observed accumulation of phytopgenic carbon represents a considerable fraction of the annual primary production in these remote areas. According to Berger and Herguera’s (1992) synthetic map, annual productivity integrated over the surface 100 m must be ~60-90 g C m⁻² y⁻¹ at stns 16 and 31, ~40-60 g C m⁻² y⁻¹ at stns 46 and 91 and ~25-30 g C m⁻² y⁻¹ at stn 76. These numbers indicate that the observed TOC excess could represent from 25-40% of the annual primary productivity in the eastern Equatorial Atlantic to as much as 100% in the oligotrophic Subtropical gyre. These percentages are only for reference, as we do not know about the net formation rates of the TOC excess or even how much of the actual excess has been advected to the study sites, but they indicate that the pool of non-degraded TOC seems to be a key transient sink for the phytopgenic carbon all along the temperate eastern South Atlantic. By contrast, at the SAF (stn 106; surface θ and nitrate, 9°C and 15 µmol kg⁻¹ respectively), the average TOC falls dramatically to 62 µmol C l⁻¹ (excess of only 9 g C m⁻²).

TOC profiles in the upper 1000 m are essentially parallel to temperature at all the study sites along A14 (Fig. 5). Temperature, an index of water mass mixing, retains >80% of the variance observed in the individual TOC profiles (n = 6-7, p < 0.001), except at stn 106, where the direct correlation was lower (r² = 0.63, n = 5, p < 0.001) because of the limited ranges of both variables (2.6-9.0°C, 67-54 µmol C l⁻¹). The direct correlation for the six TOC profiles collectively was r² = 0.70 (n = 36, p < 0.001), indicating the dominance of mixing of accumulated TOC produced in the warm upper waters with refractory TOC in cold deep waters (Carlson et al., 1994; Guo et al., 1995; Hansell and Waterhouse, 1997). However, TOC seems to be lower than expected by mixing in the very aged subsurface waters of the Equatorial and Subequatorial South Atlantic (stns 16, 31 and 46), where a maximum apparent oxygen utilisation (AOU) of >190 µmol kg⁻¹ at ~200-400 m is perceived (Fig. 3). TOC and AOU exhibit a good correlation (r² > 0.75) for all the individual profiles (n = 6-7, p < 0.001), except for stn 106 (r² = 0.49, n = 5, p = 0.19). The correlation for the whole dataset in the upper 1000 m, excluding the southernmost station, is:

TOC = 81 - 0.13 AOU
r² = 0.76   n = 31   p< 0.001    (2)

This indicates a clear relationship between the two variables, either at the local or the basin scales, with a slope (-∆TOC/∆AOU ratio) of 0.13±0.01 mol C mol O₂⁻¹. Recent reliable DOC data have revealed some degree of covariance between DOC (or TOC) and AOU in the upper few hundred meters of the ocean (Kepkay and Wells, 1992; Guo et al., 1994; Thomas et al., 1995; Peltzer and Hayward, 1996), as previously suggested by Ogura (1970). These authors obtained slopes of <0.25 mol C mol O₂⁻¹, instead of the 0.72 mol C mol O₂⁻¹ expected from the Redfield stoichiometry (O₂:C:N:P= 148:106:16:1; Anderson, 1995). If a direct cause-and-effect relationship between DOC and AOU occurred, DOC would contribute <35% to the observed bulk oxygen consumption. However, most of these authors also suggested that the correlations could be partly due to the dependence of both DOC and AOU on water mass mixing, as proposed by Menzel and Ryther (1968). The observed correlation of temperature with TOC (r² = 0.76, n = 31, p < 0.001) and AOU (r² = 0.51, n = 67, p < 0.001) for the upper 1000 m in our limited database makes it necessary to consider the effect of mixing. As previously demonstrated, temperature is a suitable tracer for correcting the effect of water mass mixing in the upper 1000 m of the eastern South Atlantic. Therefore, the multiple correlation of TOC with temperature and AOU will give a -∆TOC/∆AOU ratio independent of water mass mixing. The corresponding linear equation (excluding stn 106) is:

TOC = 70 + 0.6 θ - 0.09 AOU
r² = 0.81   n = 31   p< 0.005    (3)

Consequently, TOC oxidation is linked to oxygen consumption in the upper 1000 m, although the -∆TOC/∆AOU= 0.09±0.02 only represents ~13% of the Redfield demand. A comparison of Eqs (2) and (3) indicates that water mass mixing tends to overestimate the contribution of DOC to...
AOU in the eastern South Atlantic. Therefore, rather than from TOC (suspended+dissolved organic carbon), it is logical to suggest that oxygen consumption in subsurface thermocline waters of the study sites is mainly from large organic particles not accounted for in TOC analyses, such as sinking aggregated detritus. The $-\Delta NO_3/\Delta O_2$ ratio of $\sim0.10$ obtained from Eq. (1) agrees with the mineralisation at depth of fresh organic matter of Redfield composition (C/N ratio of 6.6; Anderson, 1995) exported from surface ocean waters. Detritus, which partially originates from DOM aggregation, has much higher C/N ratios (Verity et al., 1994; Guo, 1993). Consequently, the square of the Brunt-Väisälä frequency, $B^2 = \frac{g}{\rho} \left( \frac{\partial \rho}{\partial Z} \right)$, and the Richardson number ($R_i = \frac{\Delta \rho}{\rho} \left( \frac{\partial \rho}{\partial Z} \right)^2$) have been set to constant values of $10^{-2}$ m$^2$ s$^{-3}$ and 0.2 respectively, following Copin-Montégut and Avril (1993), and low bacterial activity in nutrient-limited ecosystems (Williams, 1995; Thingstad et al., 1997). Nitrate levels in the upper 100 m are 0.0-0.5 µM-N in the DOC-rich waters of the Equatorial, Subequatorial and Subtropical eastern South Atlantic.

The build up of DOC in surface waters seems to develop from a fairly intricate assortment of biological and photochemical processes. The combination of an excess production of C-rich DOM such as mono- and polysaccharides (Kirchman et al., 1991; Benner et al., 1992; Pakulski and Benner, 1994), and low bacterial activity in nutrient-limited ecosystems (Williams, 1995; Thingstad et al., 1997) could greatly contribute to the observed DOC accumulation. This conjecture is supported by the multiple correlation of TOC with temperature and AOU for samples where AOU < 0 ($r^2 = 0.64$, n= 13). The $-\Delta$TOC/$\Delta$AOU ratio (independent of temperature) is 1.0±0.4 mol C mol O$_2$$^{-1}$ (p< 0.01), a value compatible with the net production of carbohydrates in the euphotic layer. This number must be taken with care: the slope could be overestimated because loss to the atmosphere of the excess oxygen produced has not been considered. Other processes contributing to the accumulation of phyotogenic DOM in surface ocean waters could also be phototransformation to biorefractory materials (Benner and Biddanda, 1998; Obernosterer et al., 1999) or photochemical inhibition of bacterial growth (Herndl et al., 1993).
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REFERENCES

Chen, W. and P.J. Wangersky. – 1996. Rates of microbial degrada-
Scient. ed.: P.J. Wangersky