New insights on the mineralization of dissolved organic matter in central, intermediate, and deep water masses of the northeast North Atlantic

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Abstract

An optimum multiparameter (OMP) analysis was applied to samples collected during a cruise in the northeast North Atlantic with the aim of objectively defining water mass realms and calculating water mass mixing-weighted average (archetypal) concentrations of dissolved organic carbon (DOC) and nitrogen (DON) and fluorescent dissolved organic matter (FDOM). The profile of archetypal DOC, which retains the basin-scale variability from the formation area of the water masses to the study area, was modeled with a constant initial concentration of $60 \pm 1$ mmol kg$^{-1}$ that decreased linearly with increasing apparent oxygen utilization (AOU) at a rate of $-0.20 \pm 0.03$ mol C per mol of AOU. The archetypal C:N ratio of dissolved organic matter was also modeled with a constant initial molar ratio of $11.5 \pm 0.4$ that increased at a rate of $0.06 \pm 0.01$ per $\mu$mol kg$^{-1}$ of AOU. The profile of archetypal FDOM was modeled with a constant initial humic-like fluorescence of $0.54 \pm 0.07$ quinine sulfate units that increased at a rate of $0.009 \pm 0.001$ g equivalent of quinine sulphate per mol of AOU. Only the Denmark Strait Overflow Water departed from this behavior because of the marked terrestrial influence of Arctic rivers during the formation of this water mass. The variability not explained by the archetypal concentrations, which retain the local variability, suggesting that N-poor DOM was mineralized in the study area, and that the efficiency of the local production of humic-like substances was directly proportional to the ventilation of the corresponding water mass realms.

The role played by dissolved organic matter (DOM) in the metabolic balance of the ocean is still a subject of open debate (Carlson et al. 2010; Hansell et al. 2012). It is currently accepted that DOM is responsible for 10–20% of the oxygen demand in the mesopelagic ocean (200–1000 m; Arı´stegui et al. 2002). For the case of the bathypelagic ocean (1000 m–bottom), considering the 14 m

In the case of the northern North Atlantic, there is a scarce knowledge about the relative importance of the complex mixing pattern of water masses, which form with different preformed DOM levels, compared with the biogeochemical transformations experienced by DOM during that mixing, but see Carlson et al. (2010) and Hansell et al. (2012).

In the present study, we use an optimum multiparameter (OMP) analysis of the thermohaline and chemical characteristics of the water masses that mix in the northeast North Atlantic as an objective tool to define water mass realms, water mass mixing-weighted average concentrations of dissolved organic carbon (DOC) and nitrogen (DON) and humic-like substances and the basin vs. local-scale mineralization patterns of these parameters along the ‘Observatoire de la variabilité interannuelle et décennale en Atlantique Nord’ (OVIDE) line, which intercepts or navigates nearby to the formation area of most of the water masses that circulate in the North Atlantic.

Methods

Sampling program—The cruise OVIDE 2002 was conducted from 19 June to 11 July 2002, on board R/V Thalassa. Ninety-one full-depth hydrographic stations were occupied, from the continental shelf off Greenland to
Lisbon (Fig. 1). Salinity (S), potential temperature (θ), dissolved oxygen (O₂), nitrate (NO₃), phosphate (PO₄), and silicate (SiO₄) profiles were obtained at every station (maximum 30 levels). DOC and DON and fluorescence of fluorescent dissolved organic matter (FDOM) profiles were determined at 30 stations (see black dots in Fig. 1) and selected depths (maximum 15 levels). Samples for DOM analysis were collected in 10 mL precombusted glass ampoules. After acidification to pH 2, the ampoules were heat-sealed and stored at 4°C until DOC and total dissolved nitrogen (TDN) analysis. They were measured with a nitrogen-specific Antek 7020 nitric oxide chemiluminescence detector coupled in series with the carbon-specific Infra-red Gas Analyzer of a Shimadzu Total Organic Carbon 5000 analyzer. The measurement error was ±0.7 μmol kg⁻¹ for carbon and ±0.3 μmol kg⁻¹ for nitrogen. Their respective accuracies were tested with the reference materials provided by D. A. Hansell (University of Miami), which were run once per day just after calibration with a mixed standard of potassium hydrogen phthalate and glycine. We obtained an average concentration of 44.5 ± 1.1 μmol L⁻¹ of C and 21.5 ± 0.3 μmol L⁻¹ of N (n = 17) for the deep ocean reference (Sargasso Sea deep water, 2600 m) minus blank reference materials. The nominal values for TOC and TDN provided by the reference laboratory are 44.0 ± 1.5 μmol C L⁻¹ and 21.1–21.3 μmol N L⁻¹. Nutrient salts were determined onboard by standard segmented flow analysis with colorimetric detection. DON was obtained by subtracting NO₃ from TDN, and the error propagation of the analytical determination of both variables, ± 0.1 μmol kg⁻¹ and ± 0.3 μmol kg⁻¹ of N, respectively, was calculated as \( \sqrt{\text{er}_{\text{NO}}^2 + \text{er}_{\text{TDN}}^2} = 0.32 \mu\text{mol kg}^{-1} \) of N. FDOM was determined on board at the ship lab temperature (20°C) with a Perkin Elmer LS50 spectrofluorometer equipped with a xenon discharge lamp, equivalent to 20 kW for 8 μs duration. Slit widths were fixed to 10 nm for the excitation and emission wavelengths and the scan speed was 250 nm min⁻¹. Measurements were performed at the excitation and emission wavelengths of 320 nm and 410 nm, respectively, characteristic of marine humic-like substances absorbing in the ultraviolet C (Coble 1996). The fluorescence of ultraviolet-radiated Milli-Q at these excitation and emission wavelengths was subtracted from all samples. Factory-set excitation and emission corrections of the instruments were used. Following Coble (1996), the fluorescence intensities were expressed in quinine sulphate units (QSU) by calibrating the instrument at the excitation and emission wavelengths of 350 nm and 450 nm, respectively, against a quinine sulphate dihydrate (QS) standard made up in 0.05 mol L⁻¹ sulphuric acid. The measurement error was ± 0.04 QSU.

Extended optimum multi parameter (OMP) water mass analysis—The water masses present in the northeast North Atlantic have been already identified and evaluated by means of an extended OMP analysis of the World Ocean Circulation Experiment (WOCE) line A25 (Alvarez et al. 2004). The same method has been used here to obtain the proportions of the water masses that mix along the OVIDE 2002 line. Briefly, the OMP analysis consists on quantifying the proportions of the source water types (SWTs) that

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Fig. 1. Chart of the eastern North Atlantic, showing the 91 hydrographic stations occupied during the OVIDE 2002 cruise, aboard R/V Thalassa, from 19 June to 11 July 2002. Black dots are stations where DOC, DON, and FDOM measurements were performed at selected depths throughout the entire water column (maximum 15 levels). IAP is the Iberian Abyssal Plain.
Table 1. Main water masses crossed by the OVIDE 2002 section in the northeast North Atlantic, brief description of their characteristics, and some references where more information about their origin and circulation can be found.

<table>
<thead>
<tr>
<th>Name and acronym</th>
<th>Source</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subtropical eastern North Atlantic central water (ENACW13)</td>
<td>Subtropical gyre</td>
<td>Mode water formed in the area of the Azores Current, θ&gt;13°C and S&gt;35.7, very low nutrient concentration</td>
<td>Pollard and Pu 1985; Rios et al. 1992</td>
</tr>
<tr>
<td>Labrador Sea water (LSW)</td>
<td>Labrador Sea and Irminger Sea</td>
<td>Formed by winter convection, spreads between 1500–2000×10−4 Pa, θ<del>3°C, S</del>34.8, and high oxygen content</td>
<td>Talley and McCartney 1982; Harvey and Arhan 1988; Pickart et al. 2003</td>
</tr>
<tr>
<td>Iceland Scotland overflow water (ISOW)</td>
<td>Norwegian Sea and sills of Faroe Bank Channel</td>
<td>Formed in the sills by entrainment on the Norwegian overflow, it spreads in the Northern North Atlantic at 2750×10−4 Pa, θ&gt;2°C and S&gt;34.94, high oxygen and low nutrient signature</td>
<td>Sugi and Talley 1995</td>
</tr>
<tr>
<td>Denmark Strait overflow water (DSOW)</td>
<td>Arctic Ocean and Denmark Strait</td>
<td>Same formation mechanism as ISOW, well-ventilated water, very low temperature, θ&lt;2°C, and S from 34.8 to 34.9, high oxygen and low nutrient content</td>
<td>Tsuchiya et al. 1992; van Aken and de Boer 1995</td>
</tr>
<tr>
<td>Lower deep water (LDW)</td>
<td>Antarctic Ocean</td>
<td>Warmed Antarctic Bottom water entering at the Vema fracture. In the Iberian basin, θ and S have a linear relation, very high silicate signature</td>
<td>Lee and Ellet 1967; McCartney et al. 1991; McCartney 1992; Dickson and Brown 1994</td>
</tr>
</tbody>
</table>

where $x_{ij}$ is the proportion of the SWT i in sample j; $\theta_j$, $S_j$, $SiO_{4j}$, $O_{2j}$, $NO_{3j}$, and $PO_{4j}$ are the thermohaline and chemical characteristics of sample j; $\theta_i$, $SiO_{4i}$, $O_{2i}$, $NO_{3i}$, and $PO_{4i}$ are the thermohaline and chemical characteristic of the SWT i in its formation area; $\Delta O_{2j}$ is the oxygen anomaly of sample j due to the respiration of organic matter, which is very close to the apparent oxygen utilization (AOU) because $O_{2i}$ is assumed to be near

$$SiO_{4j} = \sum_i x_{ij} \times SiO_{4i}$$

$$O_{2j} = \sum_i x_{ij} \times O_{2i} - \Delta O_{2j}$$

$$NO_{3j} = \sum_i x_{ij} \times NO_{3i} + \Delta O_{2j}/R_N$$

$$PO_{4j} = \sum_i x_{ij} \times PO_{4i} + \Delta O_{2j}/R_P$$
The thermohaline and chemical characteristics of the source water types (SWTs) introduced in the optimum multiparameter (OMP) analysis of the water masses that mix in the northeast North Atlantic are shown in Table 2. The selected SWTs are eastern North Atlantic central water of 15°C (ENACW$_{15}$), 12°C (ENACW$_{12}$), and 8°C (ENACW$_{8}$), Subarctic intermediate water (SAIW), diluted Antarctic intermediate water (AIW), Mediterranean water (MW), Labrador Sea water (LSW), Iceland-Scotland overflow water (ISOW), Denmark Strait overflow water (DSOW), and lower deep water (LDW). ENACW$_{12}$ corresponds to the mode water defined by Harvey (1982) and ENACW$_{8}$ to the so-called subpolar mode water (SPMW). Eqs. 1–7 were weighted according to the variability of the thermohaline and chemical properties in the formation region and the analytical precision of each measurement (see row W in Table 2). A weight of 100 was set to Eq. 1, in such a way that mass was always accurately conserved. For each sample j, the system of linear mixing Eqs. 1–7 contains 11 unknowns (10 $x_{ij}$ for each SWT, and $\Delta$O$_2$), but a maximum of 7 SWTs can be considered simultaneously. This inconvenience was solved assuming some reasonable vertical constraints to the water mass mixing following Álvarez et al. (2004). Initial $R_N$ and $R_P$ values of 10 mol O$_2$ mol N$^{-1}$ and 150 mol O$_2$ mol P$^{-1}$, respectively, were tested and iterated to obtain the minimum residuals of Eqs. 1–7. The retained $R_N$ and $R_P$ values were 9.4 ± 0.3 mol O$_2$ mol N$^{-1}$ and 162 ± 5 mol O$_2$ mol P$^{-1}$, respectively.

The OMP analysis has been able to reproduce with a high confidence the thermohaline and chemical fields along the OVIDE line, as indicated by the determination coefficients ($R^2 > 0.985$) between the measured and the predicted values of the different tracers and the low standard deviation of the corresponding residuals (SD res), which remained slightly higher than the analytical error of the measurements (Table 2).

Water mass mixing-weighted average concentrations of chemical parameters in the water masses of the northeast North Atlantic—On basis of the concentration of any chemical parameter (N) and the proportions of the 10 SWTs identified in this study, the water mass mixing-weighted average concentration of N in each SWT (hereinafter, the archetypal concentration of N) was obtained as follows:

$$<N_i> = \frac{\sum x_{ij} \times N_j}{\sum x_{ij}} \quad (8)$$

Where $<N_i>$ is the archetypal concentration of N in SWT i; $N_j$ is the concentration of N in sample j; and $x_{ij}$ is the proportion of SWT i in sample j. The standard deviation (SD) of the estimated archetypal concentration of N was calculated as

<table>
<thead>
<tr>
<th>Source water type*</th>
<th>$S_i$ (mol kg$^{-1}$)</th>
<th>$\theta_i$ (°C)</th>
<th>$\zeta_i$ ($\times 10^{-4}$ Pa$^{-1}$)</th>
<th>VOL$_i$ (%)</th>
<th>O$_i$ (mol kg$^{-1}$)</th>
<th>PO$_i$ (mol kg$^{-1}$)</th>
<th>SD res</th>
<th>SD res</th>
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<tr>
<td>ENACW$_{15}$</td>
<td>35.02</td>
<td>14.80</td>
<td>1.8</td>
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<td>SAIW</td>
<td>34.67</td>
<td>14.00</td>
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<td>2.1</td>
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<tr>
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<td>11.93</td>
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<td>0.03</td>
<td></td>
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<tr>
<td>ISOW</td>
<td>34.89</td>
<td>10.43</td>
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<td>2.5</td>
<td>0.2</td>
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<td>DSOW</td>
<td>33.44</td>
<td>10.14</td>
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<td>LDW</td>
<td>35.11</td>
<td>9.19</td>
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<tr>
<td>MW</td>
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<td>10.43</td>
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<td>2.5</td>
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<td>0.03</td>
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<tr>
<td>DSOW</td>
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<td>10.14</td>
<td>2.6</td>
<td>2.6</td>
<td>0.2</td>
<td>0.03</td>
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* ENACW$_{15}$, subtropical eastern North Atlantic central water of 15°C; SAIW, Subarctic intermediate water; ENACW$_{12}$, ENACW of 12°C; AIW, diluted Antarctic intermediate water; SPMW, Subpolar mode water; MW, Mediterranean water; LSW, Labrador Sea water; ISOW, Iceland–Scotland overflow water; DSOW, Denmark Strait overflow water; and LDW, Lower deep water.
Application of Eq. 8 to the longitude (LON), latitude (LAT), and pressure (Z) of the samples allowed the calculation of the corresponding archetypal values for each SWT (\(<\text{LON}_i>, <\text{LAT}_i>, \text{and} <\text{Z}_i>\)). These archetypal values represent the center of mass (i.e., the SWT proportion-weighted average location of each SWT).

Therefore, the archetypal concentration of N for SWT i, \(<\text{N}_i>\), would represent the average concentration of N in the center of mass of SWT i in the study site (\(<\text{LON}_i>, <\text{LAT}_i>, \text{and} <\text{Z}_i>\)); in our case, the OVIDE 2002. Conceptually, \(<\text{N}_i>\) would retain the following: the variability of N related to the conservative mixing of SWT concentrations in their formation areas, \(N_0\); plus the variability related to the basin-scale mineralization processes from the formation area of each water mass to its center of mass.

Finally, the proportion of the total volume of the sampled section occupied by SWT i (\(<\%\text{VOL}_i>\)) was simply calculated as

\[
<\%\text{VOL}_i> = 100 \times \frac{\sum x_{ij}}{n}
\]

where \(n\) is the number of samples (1937 for LON, LAT, Z, O\(_2\), NO\(_3\), PO\(_4\), and SiO\(_2\), and 333 for DOC, DON, and FDOM). The values of \(<\text{LON}_i>, <\text{LAT}_i>, <\text{Z}_i>, \text{and} <\%\text{VOL}_i>\) for each SWT are summarized in Table 2.

**Mixing model of dissolved organic matter**—Once the SWT proportions of each sample (\(x_{ij}\)) have been calculated, the contribution of water mass mixing plus the basin-scale mineralization from the formation area of the water mass to their respective centers of mass along the OVIDE 2002 line to the total variability of any chemical variable (N) can be assessed following the method proposed by P\(\text{é}\)rez et al. (1993). It consists of performing a multiple linear regression of \(\text{N}_i\) with the SWT proportions (\(x_{ij}\)) calculated in the previous section. A system of \(n\) linear equations (one per sample) with 10 coefficients (one per SWT) has to be solved for each chemical variable:

\[
\text{N}_j = \sum_j x_{ij} \times z_i \quad \text{j = 1 to n samples}
\]

where \(z_i\) (\(\geq 0\)) is the linear fitting parameter of SWT i. The determination coefficient \((R^2)\) and the standard deviation of the residuals (SD res) of this non-negative least-squares analysis are summarized in Table 3.

**Mixing-biogeochemical model of dissolved organic matter**—Given that the relationship between any pair of non-conservative chemical parameters (\(N_1, N_2\)) depends upon the mixing of SWTs, the basin-scale mineralization from the formation area to the center of mass of each SWT in the study line and the local-scale mineralization around the respective centers of mass, the following linear equation allows modeling the relationship between \(N_1\) and \(N_2\):

\[
\text{N}_1 - \sum_j x_{ij} \times z_{1i} = \beta \times \left(\text{N}_2 - \sum_j x_{ij} \times z_{2i}\right)
\]

or

\[
\text{N}_1 = \sum_j x_{ij} \times (z_{1i} - \beta \times z_{2i}) + \beta \times \text{N}_2
\]

\(j = 1 \text{ to } n\) samples

where \(N_{ij}\) and \(N_{2j}\) are the concentrations of \(N_1\) and \(N_2\) in sample \(j; z_{1i}\) and \(z_{2i}\) are the linear fitting parameter of \(N_1\) and \(N_2\) for SWT i, respectively; and \(\beta\) is the fitting parameter of the relationship between \(N_1\) and \(N_2\) independent of the mixing, assuming that such a relationship is linear and homogeneous (i.e., \(\beta\) does not vary) in all the study area. Again, a system of \(n\) linear mixing equations (one per sample) was solved with 11 unknowns in this case: \(10 \times z_{1i} - \beta \times z_{2i}\) parameters (one per SWT) and \(\beta\). As for the case of Eq. 11, the goodness of this linear mixing-biogeochemical model was tested using the determination coefficient \((R^2)\) and the standard deviation of the residuals of the least-squares analysis (SD res). These numbers are also summarized in Table 3. In this work, we have studied the mixing-biogeochemical relationships between DOC and AOU, DOC and DON, FDOM and AOU, and FDOM and DOC.

**Results**

**Distributions of water masses in the northeast North Atlantic**—Six of the ten SWTs were present in > 5% of the sampled water in the OVIDE 2002 section (see \(<\%\text{VOL}_i>\) in Table 2). They were ordered according to their archetypal pressure: ENACW12, SPMW, MW, LSW, ISOW, and LDW. These six SWTs represented 92% of the total volume of water sampled. The remaining four SWTs (ENACW15, SAIW, AIW, and DSOW) contribute marginally to the OVIDE 2002 line. Figure 2 shows the realms of the subtropical thermocline waters (ENACW15 + ENACW12, \(\theta > 12.30\text{C}\)), subpolar thermocline waters (ENACW13 + SPMW + SAIW, \(\theta < 12.30\text{C}\)), Mediterranean water (MW), Labrador Sea water (LSW), dense overflow waters (DSOW + ISOW), and lower deep water (LDW). We define the realm of SWT i as the region where \(x_{ij}\) is > 50%. Briefly, LSW was the dominant SWT, which represented 39.0% of the total volume of water sampled and extended all along the OVIDE 2002 line at an archetypal depth of 1516 \(\times 10^{-4}\text{ Pa}\) (Table 2), although it was the dominant water mass from the surface to about 2000 \(\times 10^{-4}\text{ Pa}\) north of 59°N (Fig. 2). The subpolar thermocline waters represented all together 27.1% of the total volume of water sampled, and they were the dominant water masses in the upper 1000 \(\times 10^{-4}\text{ Pa}\) south of 51°N. An isolated core of subpolar thermocline waters was observed around 58°30’N, 30°W, in between the two branches of LSW that entered the Irminger and Iceland basins, to the west and east of the Reykjanes ridge, respectively. This core was extensively described in Thierry et al. (2008). A small volume of Mediterranean water was observed in the southern end of the section (Fig. 2), where
Table 3. Parameters of the linear mixing (Eq. 11) and mixing-biogeochemical (Eq. 12) models. $R^2$, determination coefficient; SD res, standard deviation of the residuals of the estimation; % SD reduction, percentage of reduction of the SD res of the mixing-biogeochemical as compared with the corresponding mixing model; $\beta$, fitting parameter of the relationship between $N_1$ and $N_2$ independent of the mixing; SD($\beta$), standard error of the estimation of $\beta$; $p$, significance level of the estimation of $\beta$. Results are presented for all samples and for the six water mass realms defined in Fig. 2. Only 29 of 333 samples did not belong to any realm, because they do not have $\geq 50\%$ proportion of any of the 6 SWTs or groups of SWTs defined in Fig. 2. Numbers in parentheses are the contribution of each SWT in each of the study water mass realms.

<table>
<thead>
<tr>
<th>N1</th>
<th>N2</th>
<th>$R^2$</th>
<th>SD res</th>
<th>% SD reduction</th>
<th>$\beta$</th>
<th>SD($\beta$)</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>DON</td>
<td>0.62</td>
<td>3.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>DON</td>
<td>DOC</td>
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<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<td>DOC</td>
<td>0.87</td>
<td>10.6</td>
<td>—</td>
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<tr>
<td>DOC</td>
<td>AOU</td>
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<td>3.0</td>
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<tr>
<td>DOC</td>
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<td>2.80</td>
<td>10%</td>
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<tr>
<td>FDOM</td>
<td>AOU</td>
<td>0.84</td>
<td>0.08</td>
<td>18%</td>
<td>0.0086</td>
<td>0.0006</td>
<td>0.0000</td>
</tr>
<tr>
<td>FDOM</td>
<td>DOC</td>
<td>0.76</td>
<td>0.10</td>
<td>0%</td>
<td>—</td>
<td>—</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

Subtropical thermocline waters realm (ENACW15 + ENACW12 > 50%; n = 38)

| DOC    | DON    | 0.01  | 3.9    | 1%             | —       | —           | 0.2429 |
| DOC    | DON    | 0.15  | 3.6    | 8%             | 13      | 5           | 0.0102 |
| FDOM   | AOU    | 0.08  | 10.1   | —              | —       | —           | —    |
| FDOM   | DOC    | 0.05  | 0.15   | 0%             | —       | —           | 0.6447 |

Subpolar thermocline waters realm (ENACW12 + SAIW + SPMW > 50%; n = 98)

| DOC    | DON    | 0.35  | 3.3    | 5%             | -0.27   | 0.08        | 0.0012 |
| DOC    | DON    | 0.47  | 3.0    | 15%            | 11      | 2           | 0.0000 |
| FDOM   | AOU    | 0.79  | 13.0   | —              | —       | —           | —    |
| FDOM   | DOC    | 0.56  | 0.10   | 2%             | —       | —           | 0.0327 |

Mediterranean water realm (MW > 50%; n = 14)

| DOC    | DON    | 0.53  | 1.8    | 40%            | 13      | 3           | 0.9184 |
| DOC    | DON    | 0.33  | 0.06   | 2%             | —       | —           | 0.5116 |
| FDOM   | DOC    | 0.21  | 0.06   | 0%             | —       | —           | 0.9285 |

Labrador Sea water realm (LSW > 50%; n = 108)

| DOC    | DON    | 0.53  | 2.4    | 10%            | -0.45   | 0.09        | 0.0000 |
| DOC    | DON    | 0.45  | 2.6    | 3%             | —       | —           | 0.0141 |
| FDOM   | AOU    | 0.76  | 0.05   | 13%            | 0.009   | 0.002       | 0.000  |
| FDOM   | DOC    | 0.68  | 0.06   | 0%             | —       | —           | 0.2400 |
it was the dominant water mass in the Iberian basin at a narrow depth interval centered around 1255 $\times 10^{-4}$ Pa (Table 2). The dense overflows waters, which represented 11% of the total volume of collected water, dominated the bottom layer of the Irminger and Iceland basins (Fig. 1). Whereas the ISOW meandered anticyclonically around the Reykjanes ridge, the DSOW concentrated on the eastern Greenland slope in the Irminger basin. Finally, the LDW, which is the diluted Antarctic bottom water (AABW) that enters the eastern North Atlantic across the Vema fracture at about 11° N (McCartney et al. 1991), was the dominant water mass from 3000 $\times 10^{-4}$ Pa to the bottom, south of 53° N (Fig. 2). It represented 13% of the total volume of water sampled. A detailed description of the water masses’

**Table 3.** Continued.

<table>
<thead>
<tr>
<th>N1</th>
<th>N2</th>
<th>R²</th>
<th>SD res</th>
<th>% SD reduction</th>
<th>β</th>
<th>SD(β)</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dense overflows waters realm (DSOW + ISOW &gt; 50%; n = 15)</strong></td>
<td></td>
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<tr>
<td>SWTs involved: ISOW (52%), LSW (27%), DSOW (14%), LDW (4%), and SPMW (3%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>DOC</td>
<td>—</td>
<td>0.11</td>
<td>2.7</td>
<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
<tr>
<td>DON</td>
<td>—</td>
<td>0.13</td>
<td>0.47</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FDOM</td>
<td>—</td>
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<td>—</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AOU</td>
<td>DOC</td>
<td>0.99</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DOC</td>
<td>AOU</td>
<td>0.02</td>
<td>2.7</td>
<td>0%</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
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<td>2.7</td>
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<tr>
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<td>AOU</td>
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<td>0%</td>
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</tr>
<tr>
<td>FDOM</td>
<td>DOC</td>
<td>0.03</td>
<td>0%</td>
<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
</tbody>
</table>

| **Lower deep-water realm (LDW > 50%; n = 33)** |
| SWTs involved: LDW (76%), ISOW (14%), LSW (9%), and MW (1%) |
| DOC | — | — | 3.0 | — | — | — | — |
| DON | — | — | 0.53 | — | — | — | — |
| FDOM | — | — | 0.12 | — | — | — | — |
| AOU | DOC | 0.73 | 2.2 | — | — | — | — |
| DOC | DON | 0.12 | 3.0 | 2% | — | — | — |
| DON | DOC | 0.09 | 2.9 | 6% | 11 | 5 | 0.0386 |
| FDOM | AOU | 0.12 | 0% | — | — | — | — |
| FDOM | DOC | 0.12 | 0% | — | — | — | — |

**Fig. 2.** Distribution of northeast North Atlantic water masses along the OVIDE 2002 section. Samples with > 50% of subtropical thermocline waters (ENACW15 + ENACW12) subpolar thermocline waters (ENACW12 + SPMW); Mediterranean water (MW); Labrador water (LSW); dense overflows waters (DSOW+ISOW); and deep water (LDW) are shown. Solid vertical lines indicate changes of orientation of the section.
Distributions of chemical parameters in the northeast North Atlantic—The distributions of NO\textsubscript{3}, DON, and FDOM along the OVIDE 2002 section are presented in Fig. 3. Trends in the water mass distributions described in Fig. 2 can also be observed in the variability of these chemical tracers. For the case of NO\textsubscript{3} (Fig. 3a), the subtropical thermocline waters south of 49\textdegree N or the dense overflows waters around the Reykjanes ridge were characterized by NO\textsubscript{3} concentrations lower than the surrounding waters. The isolated volume of subpolar thermocline waters around 58\textdegree 30'N, 30\textdegree W that coincided again with the absolute NO\textsubscript{3} maximum and DON absolute maximum concentrations in the LDW realm that was characterized by NO\textsubscript{3} concentrations above 20 \mu mol kg\textsuperscript{-1}. For the case of DON (Fig. 3b), relatively low (< 3 \mu mol kg\textsuperscript{-1}) concentrations were clearly associated with the MW and LDW realms, and DON minima were also observed in the area of the dense overflows waters. On the contrary, LSW and especially the thermocline waters were characterized by relatively high DON levels. Finally, for the case of FDOM (Fig. 3c), there were marked similarities with NO\textsubscript{3} and DON, such as the minimum FDOM in the subtropical thermocline waters coinciding with minimum NO\textsubscript{3} and maximum DON concentrations; the isolated maximum of subpolar thermocline waters around 58\textdegree 30'N, 30\textdegree W that coincided again with a NO\textsubscript{3} minimum and DON maximum; or the absolute maximum concentrations in the LDW realm that coincided with the absolute NO\textsubscript{3} maximum and DON minima.

DOM characterization of the water masses of the northeast North Atlantic—The vertical profile of archetypal concentrations of DOC (Fig. 4a) shows that the shallowest thermocline waters of the northeast North Atlantic, between 12\textdegree C (ENACW\textsubscript{15}; centered at 44\textdegree N, 280 \times 10\textsuperscript{-4} Pa) and 15\textdegree C (ENACW\textsubscript{12}; centered at 42\textdegree N, 128 \times 10\textsuperscript{-4} Pa), were characterized by maximum concentrations ranging from 54.8 \pm 0.6 \mu mol kg\textsuperscript{-1} to 57.1 \pm 1.2 \mu mol kg\textsuperscript{-1}. These concentrations were significantly higher (p < 0.05), from 1.4–3.7 \mu mol kg\textsuperscript{-1} to 10.7–13.0 \mu mol kg\textsuperscript{-1}, than the archetypal DOC of the other water masses. On the contrary, the archetypal DOC of the deepest SWT, LDW (centered at 44\textdegree N, 3700 \times 10\textsuperscript{-4} Pa), 44.1 \pm 0.5 \mu mol kg\textsuperscript{-1}, was significantly lower (p < 0.005) than the others. At the intermediate waters realm (1000–2000 \times 10\textsuperscript{-4} Pa), it was remarkable that the archetypal DOC of the MW (centered at 41\textdegree N, 1255 \times 10\textsuperscript{-4} Pa), 47.3 \pm 0.7 \mu mol kg\textsuperscript{-1}, was significantly lower (p < 0.01) than for LSW (centered at 54\textdegree N, 1516 \times 10\textsuperscript{-4} Pa), 48.9 \pm 0.3 \mu mol kg\textsuperscript{-1}. The profiles of archetypal DOC and AOU (Fig. 4b) were opposite. In fact, the linear relationship with <DOC\textsubscript{i}> (Fig. 5a) explained 88\% of the variability of <DOC\textsubscript{i}>:

\[
<\text{DOC}_i> = 60(\pm 1) - 0.20(\pm 0.03) \times <\text{AOU}_i>
\]

\[R^2 = 0.88, n = 10, p < 0.001\]

Note that, according to our conceptual model, the archetypal AOU retained the variability due to organic matter oxidation from the area of formation of the different SWTs to their respective centers of mass (<\text{LON}_i>, <\text{LAT}_i>, and <\text{Z}_i>; Table 2) along the OVIDE line. Therefore, Eq. 13 indicates a tightly coupling between DOC and dissolved oxygen consumption at the northeast Atlantic basin-scale.

For the case of DON, we obtained a constant archetypal concentration of 2.9–3.0 \mu mol kg\textsuperscript{-1} for the water mass realms below 1000 \times 10\textsuperscript{-4} Pa, except for the case of LSW, which exhibited a significantly higher (p < 0.01) archetypal concentration of 3.4 \pm 0.2 \mu mol kg\textsuperscript{-1} (Fig. 4c). As for DOC, the highest concentrations were obtained in the shallowest thermocline waters, ranging from 4.2 \pm 0.1 \mu mol kg\textsuperscript{-1} to 4.7 \pm 0.2 \mu mol kg\textsuperscript{-1}. The profile of archetypal DON explained 94\% of the variability of the profile of archetypal DOC (Fig. 5b):

\[
<\text{DOC}_i> = 26(\pm 2) + 6.9(\pm 0.6) \times <\text{DON}_i>
\]

\[R^2 = 0.94, n = 9, p < 0.001\]

Again, Eq. 14 indicates a tight coupling between DOC and DON at the northeast Atlantic basin-scale. An exception to this rule was the DSOW realm, with an unexpectedly high archetypal DOC, although this value was uncertain (see the large standard deviation of the estimate) because the DSOW represented only 1\% of the sampled volume of water (Table 2).

The archetypal C : N ratio of DOM (<\text{DOC}_i> : <\text{DON}_i>; Fig. 4d) increased monotonically with depth, from a minimum of 12.1 \pm 0.1 mol C mol N\textsuperscript{-1} for the shallowest (ENACW\textsubscript{15}) to a maximum of 15.4 \pm 0.1 mol C mol N\textsuperscript{-1} for the deepest SWT (LDW; Fig. 5c). <\text{DOC}_i> : <\text{DON}_i> in the northeast North Atlantic can be reasonably modeled with the following power function of the archetypal pressure:

\[
<\text{DOC}_i> = 10.3(\pm 0.4) \times (<\text{Z}_i> - 100)^{0.050\pm 0.006}
\]

\[R^2 = 0.91, n = 8, p < 0.001\]

This means that the C : N molar ratio of DOM at the base of the photic layer (100 \times 10\textsuperscript{-4} Pa) would be 10.3 \pm 0.4 and that it would increase with pressure with a power-fitting parameter of 0.050 \pm 0.006, independently of the water mass. An exception to this rule was the MW realm, with an archetypal C : N molar ratio of 15.9 \pm 0.1, which was significantly higher (p < 0.001) than the other intermediate water mass, the LSW, characterized by an archetypal C : N molar ratio of 14.5 \pm 0.3. A second exception was the DSOW, with a high archetypal C : N molar ratio of 17.1 \pm 1.5.

The behavior of MW compared with LSW can be straightforwardly explained on basis of their contrasting archetypal AOU: 47 \pm 2 \mu mol kg\textsuperscript{-1} for LSW vs. 76 \pm
Fig. 3. (a) Distributions of nitrate (NO₃) in μmol kg⁻¹; (b) dissolved organic nitrogen (DON) in μmol kg⁻¹; and (c) fluorescence of dissolved organic matter (FDOM) in QSU along the OVIDE 2002 section. Solid vertical lines indicate changes of orientation of the section.
In this case, DSOW was excluded from the analysis. Therefore, the DOM exported to the northeast Atlantic through the Denmark Strait was exceptionally carbon-rich in origin.

The profile of archetypal concentrations of FDOM (Fig. 4e) also resembled \( <\text{DOC}_i> \) (Fig. 4a) and \( <\text{AOU}_{i}> \) (Fig. 4b), with a minimum value of 0.65 \( \pm \) 0.04 QSU for the shallowest and a maximum value of 1.23 \( \pm \) 0.2 QSU for the deepest one. The linear relationships with \( <\text{DOC}_i> \) (Fig. 5e) and \( <\text{AOU}_{i}> \) (Fig. 5f) explained 99% and 83% of the variability of \( <\text{FDOM}_i> \), respectively.
Fig. 5. X–Y plots of (a) archetypal dissolved organic carbon ($\langle \text{DOC}_i \rangle$) vs. archetypal apparent oxygen utilization ($\langle \text{AOU}_i \rangle$); (b) $\langle \text{DOC}_i \rangle$ vs. archetypal dissolved organic nitrogen ($\langle \text{DON}_i \rangle$); (c) archetypal C:N ratio of DOM ($\langle \text{DOC}_i : \langle \text{DON}_i \rangle \rangle$) vs. archetypal pressure ($\langle \text{Z}_i \rangle$); (d) $\langle \text{DOC}_i \rangle$, $\langle \text{DON}_i \rangle$ vs. $\langle \text{AOU}_i \rangle$; (e) archetypal fluorescence of dissolved humic-like substances $\langle \text{FDOM}_i \rangle$ vs. $\langle \text{DOC}_i \rangle$; and (f) $\langle \text{FDOM}_i \rangle$ vs. $\langle \text{AOU}_i \rangle$. 

North Atlantic dissolved organic matter
3.1 residuals (SD res) of the mixing model (Eq. 11), was 2002 line, respectively (Table 3). The standard error of the variability of DOC, DON, and FDOM along the OVIDE analytical error of the determination of this variable.

- Exported to the northeast Atlantic through the Denmark typal FDOM was remarkably high. Therefore, the DOM basin-scale mineralization retained by the archetypal North Atlantic—distribution of chemical parameters in the northeast water masses plus the basin-scale mineralization retained by the fitting parameter 

\[
\text{DOC, DON, and FDOM were measured. The mixing of water masses to the study OVIDE 2002 line is responsible for more than a half of the total variability of AOU and the SD res, }\]

\[
\text{AOU) models showed SD res reductions > 10\%, with }\beta\text{-values of } -0.45 \pm 0.09 \text{ mol C mol } O_2^{-1}\text{ and } -9 \pm 2 \times 10^{-3} \text{ g equivalent of QS mol } O_2^{-1}\text{. In the dense overflows of the northern North Atlantic, the mixing-biogeochemical model did not improved significantly the predictions of the mixing model alone, likely because only 11 of the 333 samples belong to this realm, a reduced number of data points for our statistical approach. Finally, in the lower deep water realm, only the (DOC, DON) model experienced a substantial reduction of the SD res, and the obtained }\beta\text{ was } 11 \pm 5 \text{ mol C mol } N^{-1}\text{. Therefore, depending on the pairs of variables, specific values of }\beta\text{ can be obtained for the different water mass realms.}

Discussion

The statistical method applied in this work allowed us to objectively separate the effect of water mass mixing and basin-scale mineralization from the formation area to the center of mass of the 10 SWTs intercepted along the OVIDE 2002 line (retained by the mixing model) from the effect of local mineralization around the center of mass of each SWT (retained by the fitting parameter }\beta\text{ of the mixing-biogeochemical model).
54.8 μmol kg\(^{-1}\), respectively, were quite comparable to those reported by Carlson et al. (2010). Regarding the LSW and ISOW, our archetypal concentrations were 5–6 μmol kg\(^{-1}\) higher, probably because the OVIDE 2002 line was much closer to the formation area of these water masses than the Climate Variability lines studied by Carlson et al. (2010). The difference was even larger, 9 μmol kg\(^{-1}\), for the case of the DSOW. The high DOC concentration, C:N ratio of DOM, and humic-like fluorescence of this water mass will receive particular attention in the following sections. Finally, regarding the LDW, our archetypal concentration, 44.1 ± 0.5 μmol kg\(^{-1}\), was 3.6 μmol kg\(^{-1}\) above the DOC of Antarctic bottom water (AABW) reported by Carlson et al. (2010), but note that whereas the archetypal depth of our LDW was 3700 ± 159 10\(^{-4}\) Pa, the average depth of AABW was 5019 10\(^{-4}\) Pa. Regarding the archetypal DOC concentration of MW, 47.3 ± 0.7 μmol kg\(^{-1}\), it was significantly lower than the expected concentration of 48.8–49.3 μmol kg\(^{-1}\) obtained when mixing the Mediterranean overflow water (MOW) of the Strait of Gibraltar (45–46 μmol kg\(^{-1}\); Dufner et al. 2001) with the SPMW (50.5 ± 0.6 μmol kg\(^{-1}\); Fig. 4a) in a MOW:SPMW proportion of 0.25–0.34 to form the MW (Rogerson et al. 2012). These numbers indicate that intense mineralization of DOM occurs during the subduction of MOW and the entrainment of SPMW to form MW.

The excellent linear relationship between the archetypal concentrations of DOC and AOU (Fig. 5a) suggests that the basin-scale mineralization of DOM from the formation area of the SWT to their respective centers of mass along the OVIDE 20202 line in the northeast North Atlantic can be modeled assuming a quasi-constant concentration of DOC of 60 ± 1 μmol kg\(^{-1}\) (y-intercept of Eq. 13) at the time of formation of the different SWTs (AOU = 0.0 μmol kg\(^{-1}\)), which decreased with increasing AOU at a rate of 0.20 ± 0.3 mol C mol O\(_2\)\(^{-1}\). Considering the Redfieldian R\(_N\) and R\(_P\) values of 9.4 ± 0.3 mol O\(_2\) mol N\(^{-1}\) and 162 ± 5 mol O\(_2\) mol P\(^{-1}\) maintained by the OMP analysis, a −O\(_2\):Corg stoichiometric ratio (R\(_C\)) of 1.4 mol O\(_2\) mol C\(^{-1}\) (Redfield et al. 1963; Anderson and Sarmiento 1994) can be used to estimate a basin-scale contribution of DOC to the oxygen demand of the northeast North Atlantic of 28% ± 4% from the slope of 0.20 ± 0.3 mol C mol O\(_2\)\(^{-1}\) (Eq. 13). Considering the water mass realms defined in Fig. 2 individually, AOU improved the prediction of the distribution of DOC only for the subpolar thermocline waters and Labrador Sea water realms. In the case of the subpolar thermocline waters, the value of β suggests that 40% ± 10% of the local oxygen demand around the center of mass of this water mass was covered by DOC; and in the case of the Labrador Sea water realm, the contribution of DOC increased to as much as 60% ± 10%. Our estimate of the basin-scale contribution of DOC to the oxygen demand of the northeast North Atlantic is in the upper end of the calculations of Aristegui et al. (2002) for the global mesopelagic ocean and those of Carlson et al. (2010) for the whole North Atlantic basin. This is an expected result considering that the OVIDE line was very close to the formation areas of the LSW, DSOW, ISOW, and MW, and intercepted the formation areas of the ENACW and SPMW. The closer a water mass is to its formation area, the higher is the contribution of DOC to the oxygen demand on the realm of that water mass because the concentration of DOC is higher and probably more bioavailable. Thus, 30–40% of the microbial respiration at intermediate depths of the North Pacific was due to the oxidation of the DOM transported downward by the North Pacific intermediate water (Doval and Hansell 2000; Hansell et al. 2012). In the North Atlantic, Carlson et al. (2010) obtained that the export and subsequent mineralization of DOC explained 9–19% of the oxygen demand in the NADW, when it explained <10% in the deep Pacific and Indian Oceans (Doval and Hansell 2000). The case of MW merits attention because DOC does not contribute significantly to the oxygen demand. As indicated above, this SWT is composed of the diluted Levantine intermediate water (LIW) that crosses the sill of the Strait of Gibraltar and subducted North Atlantic thermocline waters (Álvarez et al. 2005). Considering the relatively high respiration rates measured by La Ferla and Azzaro (2004) in the LIW, from 4 μmol C kg\(^{-1}\) yr\(^{-1}\) in the Levantine basin to 1 μmol C kg\(^{-1}\) yr\(^{-1}\) in the Strait of Gibraltar, it is likely that most of the mineralization of the DOM carried by the MW, which results in its high DOC : DON ratio (Fig. 4d), has occurred within the Mediterranean Sea. In fact, Santinelli et al. (2010) reported that DOC contributed to 38% of the oxygen demand on the LIW realm. In addition, intense mineralization seems to occur during the entrainment of the Mediterranean overflow water and North Atlantic thermocline waters to form the MW (see previous paragraph).

**Stoichiometry of the mineralization of dissolved organic matter in the northeast North Atlantic**—Although the C:N ratios of DOM (Fig. 4d) were comparable to the average global deep ocean ratio of 14.7 ± 2.8 mol C mol N\(^{-1}\) compiled by Bronk (2002), the exceptional linear relationship obtained between the archetypal concentrations of DOC and DON (Fig. 5b) is remarkable. The regression slope of 6.9 ± 0.3 mol C mol N\(^{-1}\) indicates that the C:N ratio of the DOM mineralized at the basin scale from the formation areas of the SWT to their respective centers of mass along the OVIDE 2020 line does not differ significantly from the Redfieldian ratio of 6.7, characteristic of the mineralization of fresh fast-sinking phytagenic particles (Redfield et al. 1963; Anderson and Sarmiento 1994). The preferential use of the N-rich compounds of particulate organic matter is well-documented from the increasing C:N ratio of the material collected on sediment traps with depth (Schneider et al. 2003) or the study of inorganic nutrient ratios (Brea et al. 2004; X. A. Álvarez-Salgado unpubl.). Our work provides evidences that the DOM consumed in the dark ocean follows the same pattern, supporting observations made in ocean margins and central ocean gyre environments that indicated that DOM is mineralized with a C:N:P stoichiometry substantially lower than for bulk pools (Hopkinson and Vallino 2005; Álvarez-Salgado et al. 2006). Hopkinson and Vallino (2005) reported that although the C:N:P
stoichiometry of DOM mineralization is lower than for the bulk DOM, it is greater than the Redfield ratio. Their open ocean profiles were collected in central gyres; therefore, it seems that the Redfield stoichiometry found in the OVIDE 2002 line could be characteristic of intermediate and deep ocean ventilation sites. This basin-scale DOM consumption with a C:N molar ratio of 6.9 produced a highly significant ($p < 0.001$) increase of the archetypal C:N ratio of DOM with increasing AOU (Fig. 5d), which results in aged water masses being characterized by high C:N ratios of DOM because of preferential consumption of the more labile N-rich DOM compounds (Hopkinson and Vallino 2005; Kramer et al. 2005). Accordingly, the evolution of the C:N ratio of DOM in the northeast North Atlantic result from a quasi-constant ratio of 11.5 ± 0.4 mol C mol N$^{-1}$ (y-intercept of Eq. 16) at the time of formation (AOU = 0.0 $\mu$mol kg$^{-1}$) of the different SWT that mix in the OVIDE line, which increases with increasing AOU at a rate of 0.06 ± 0.01 (mol C mol N$^{-1}$) per mol of AOU. Only the DSOW was clearly apart from that straight line (Fig. 5d).

Considering the whole data set ($n = 333$), it resulted that the mixing-biogeochemical model improved the prediction of the distribution of DOC when DON is considered as an explanatory variable (Table 3), which means that not only the basin-scale but also the local-scale processes in the surrounding of the mass center of each water mass along the OVIDE line are necessary to describe the DOM distributions. Interestingly, the value of the corresponding $\beta$ parameter indicates that the C:N ratio of local DOM mineralization around the mass center of the water masses that mix along the OVIDE line increased to a significantly higher ($p < 0.001$) value of 13 ± 2 mol C mol N$^{-1}$. The C:N molar ratios of local mineralization in the subtropical (13 ± 5) and subpolar (11 ± 2) thermocline, Mediterranean (13 ± 3), and Lower Deep Water (11 ± 5) realms did not differ significantly. This is consistent with the mineralization of fresh dissolved and fast-sinking biogenic materials close to the formation area of the water masses (retained by the mixing model), where they suddenly sink from the surface to their respective archetypal depths (Brea et al. 2004; X. A. Álvarez-Salgado unpubl.). By contrast, local mineralization (retained by the fitting parameter $\beta$ of the mixing-biogeochemical model) would be supported by slow-sinking suspended materials and aged DOM transported downward from the upper mixed layer.

Production of marine humic-like substances in the northeast North Atlantic—Marine humic-like substances in the dark ocean are a by-product of the microbial respiration of biogenic organic matter, either dissolved or particulate (Yamashita and Tanoue 2008; Jorgensen et al. 2011). Therefore, the positive linear relationship found between archetypal FDOM and AOU (Fig. 5f) was sound, and the slope of this correlation can be used as an indicator of the recovery of marine humic-like substances from the degradation of organic matter. A good correlation was also observed between archetypal FDOM and DOC (Fig. 5e), which suggests that both fast-sinking fresh biogenic particles and DOM contribute to the basin-scale production of humic-like materials in the water masses that mix in the northeast North Atlantic. Using a $RC$ of 1.4 mol O$_2$ mol C$^{-1}$, it results that the rate of FDOM production to organic carbon mineralization—either dissolved, suspended, or sinking—would be $-13 \pm 3 \times 10^{-3}$ g equivalent of QS mol C$^{-1}$ ($= -9 \pm 2 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$ $\times 1.4$ mol O$_2$ mol C$^{-1}$). For comparison, the rate of FDOM production to DOC mineralization was $44 \pm 2 \times 10^{-3}$ g equivalent of QS mol C$^{-1}$. Multiplying this rate by the contribution of DOC to the basin-scale oxygen demand of the northeast North Atlantic, 28% ± 4%, yields a rate of $-12 \pm 2 \times 10^{-3}$ g equivalent of QS mol C$^{-1}$, which is not significantly different from the value $-13 \pm 3 \times 10^{-3}$ g equivalent of QS mol C$^{-1}$. Therefore, the rate of FDOM formation is not dependent on the aggregation state of the mineralized organic matter. Again, only the DSOW was clearly apart from that straight line. The DOM exported to the northeast Atlantic through the Demark Strait is carbon- and humic-rich in origin, likely due to a larger terrestrial influence. Note that the DSOW (salinity 34.88; Table 3) is 0.3% fresher than the ISOW (salinity 34.98). Following Amon et al. (2003) and Benner et al. (2005), surface waters of the Arctic Ocean have the highest concentrations of DOM and terrigenous DOM (from Arctic rivers) of all ocean basins, and these materials are exported to the ocean interior preferentially in the DSOW. Furthermore, lignin phenols of terrestrial origin (Benner et al. 2005) are the likely cause of the enhanced archetypal humic-like fluorescence of the DSOW (Amon et al. 2003; Osburn and Stedmon 2011).

Regarding the production of humic-like substances during the local degradation of organic matter, the value of $\beta$ for the whole data set ($n = 333$), $-8.6 \pm 0.6 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$, was not significantly different from the value obtained for the basin-scale mineralization (Eq. 18). However, the efficiency of humic-like substance production depended on the water mass realm. The parameter $\beta$ for the Labrador Sea water was not significantly different from the $\beta$ for the whole set of samples; this is an expected result considering that LSW was the most densely sampled water mass, appearing in 33% of the 333 samples collected. However, the $\beta$ of the subtropical thermocline waters ($-15 \pm 1 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$) was significantly higher ($p < 0.001$), and the $\beta$ of the subpolar thermocline waters ($-7.0 \pm 0.7 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$), was significantly lower ($p < 0.005$) than the reference value of $-8.6 \pm 0.6 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$. Note that the archetypal AOU of ENACW$_{12}$ (31 ± 3 $\mu$mol kg$^{-1}$), the dominant SWT in the subtropical thermocline waters realm, was significantly lower ($p < 0.001$) than the archetypal AOU of the LSW (47 ± 2 $\mu$mol kg$^{-1}$), and the latter was significantly lower ($p < 0.001$) than the archetypal AOU of the SPMW (52 ± 4 $\mu$mol kg$^{-1}$), the dominant SWT of the subpolar thermocline waters realm. Therefore, it seems that the efficiency of the local production of humic-like substances from the consumption of biogenic materials is directly proportional to the ventilation of the corresponding SWT realms. This hypothesis is confirmed by the low conversion factors, $-4.7$ to $-4.9 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$, that Yamashita and Tanoue (2008) obtained in the very aged thermocline (AOU, 25–300 $\mu$mol kg$^{-1}$) and abyssal (AOU, 150–300 $\mu$mol kg$^{-1}$) waters of the Pacific Ocean. Conversely,
Yamashita et al. (2007) obtained higher conversion factors of $-6.4 \pm 1.0$ and $-6.8 \pm 0.8 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$ for the more ventilated subantarctic mode water and Antarctic intermediate water in the Pacific sector of the Southern Ocean. Finally, in the Iberian upwelling system, Castro et al. (2006) obtained a conversion efficiency of $-7.8 \pm 0.4 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$ for the central waters off northwestern Spain, and Nieto-Cid et al. (2006) obtained a value of $-8.1 \pm 0.9 \times 10^{-3}$ g equivalent of QS mol O$_2^{-1}$ for the same waters once they have upwelled into the rías, the large coastal embayments of the Galician coast. Consequently, the estimate made by Yamashita and Tanoue (2008) of the global production of FDOM in the ocean interior, 13–17 $\times 10^{12}$ g equivalent of QS yr$^{-1}$, is probably underestimated by one-third.

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References


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