1 Supplementary Information (SI) of:

2 Dissolved Organic Carbon in the North Atlantic Meridional Overturning Circulation

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10 SI Text

Specifications of the OMP analysis An extended Optimum Multiparameter (eOMP) analysis¹ was used 11 12 to solve the water mass structure of the OVIDE section. OMP analyses are based on the premise that the 13 water mass fractions that constitute a sample can be reproduced by an appropriate mixture of some well-14 known end-member water types, which are characterized by water mass tracers like Θ and S. OMP analyses obtain the water mass fractions (X_i) by solving a system of linear equations by minimization 15 16 through a non-negative least square method. Each equation of the system is weighted in relation to the accuracy of the measured property. The main difference between classical (cOMP)² and extended OMP 17 analyses is that the latter includes both conservative and non-conservative variables. We constrained the 18 19 OMP analysis to the water samples with pressure >100 dbar to avoid the non-conservative behavior of Θ 20 and S in the surface layer due to air-sea interactions after the last maximum of winter convection³. The OMP has been successfully used in previous studies with similar needs for solving water mass mixing $^{3-5}$. 21 22 The system of equations in the first step, the cOMP based on conservative variables, remains as follows:

$$\sum_{i=1}^{n} X_i * \theta_i^{SWT} = \theta^{sample} + R_{\theta}$$
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$$\sum_{i=1}^{n} X_i * S_i^{SWT} = S^{sample} + R_S$$

25
$$\sum_{i=1}^{n} X_{i} * SiO_{2i}^{SWT} = SiO_{2}^{sample} + R_{SiO_{2}}$$

$$\sum_{i=1}^{n} X_i * NO_i^{SWT} = NO^{sample} + R_{NO}$$

$$\sum_{i=1}^{n} X_i * PO_i^{SWT} = PO^{sample} + R_{PO}$$
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$$\sum_{i=1}^{n} X_i = 1 + R_{mass}$$

where Rp is the residual of each property p (Θ , S, SiO₂, NO=10.5*NO₃+O₂ and PO=175*PO₄+O₂ ⁶⁻⁸) measured (p^{sample}) that the OMP tries to minimize and P_i^{SWT} is the property of each SWT_i . The last equation accounts for the mass conservation.

The cOMP analysis is solved for each mixing figure. The mixing figures are groups of SWTs that are susceptible to mix together, and are set considering the vertical characteristics and/or dynamics of the SWTs in the region of study. The analysis is applied to assign the mixing figure where the water sample presents the lowest residuals.

Using the same set-up as the cOMP, an eOMP analysis is solved also considering non-conservative variables (SiO₂, NO₃, PO₄ and O₂). A new unknown has to be considered, ΔO , which refers to changes in O₂ due to the remineralization of the organic matter.

$$\sum_{i=1}^{n} X_{i} * \theta_{i}^{SWT} = \theta^{sample} + R_{\ell}$$

$$\sum_{i=1}^{n} X_i * S_i^{SWT} = S^{sample} + R_S$$

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$$\sum_{i=1}^{n} X_{i} * SiO_{2i}^{SWT} + \Delta O / r_{Si} = SiO_{2}^{sample} + R_{SiO_{2}}$$

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$$\sum_{i=1}^{n} X_{i} * O_{2i}^{0SWT} - \Delta O = O_{2}^{sample} + R_{O_{2}}$$

43
$$\sum_{i=1}^{n} X_{i} * NO_{3i}^{0SWT} + \Delta O / r_{N} = NO_{3}^{sample} + R_{NO_{3}}$$

44
$$\sum_{i=1}^{n} X_{i} * PO_{4i}^{0SWT} + \Delta O / r_{P} = PO_{4}^{sample} + R_{PO_{4}}$$

$$\sum_{i=1}^{n} X_i = 1 + R_{mass}$$

where R_{SiO2} is 12, R_{NO3} is 10.5 and R_{PO4} is 175^{7.8}. The cOMP analysis selects the mixing figure based on conservative water mass tracers; once the mixing figures are selected, the estimates of the X_i are given by the eOMP analysis, which takes into account the effect of the biology in the measured variables. The methodology has been contrasted with available [DOC] data from a section inside the OVIDE box in 2013 (Leg 1 of A16N)⁹. We compare the measured [DOC] (487 samples) with the reconstructed [DOC] result of the combination of the water mass proportions of the A16N section ($X_i^{A16N_2013}$) with the source

52 water types
$$[DOC]_i$$
 of Table 1 through the equation $[DOC]^{A16N_2013} = \sum_{i=1}^{12} SWT_i^{A16N_2013} \times [DOC]_i$.

53 The correlation coefficient (r^2) between the measured and reconstructed [DOC] is 0.75, with a mean 54 difference of 2.3±1.9 µmol·kg⁻¹, which is inside the uncertainty of the measurements.

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Time evolution of the DOC content. To evaluate if the time derivative of DOC storage in the OVIDE box is negligible, we evaluated the inventory of apparent oxygen utilization (AOU) in the OVIDE box from 2002 to 2012 as a proxy of the DOC content (Fig. S1). The range of interannual variation in AOU is tightly constrained around ~124 μ mol·kg⁻¹ between 2002 and 2012, with a standard deviation as low as 60 ± 1.2 μmol·kg⁻¹. Therefore, the assumption of no considerable differences in the interannual variability of 61 DOC transport is also supported by the oxygen that have been respired.



Figure S1. Apparent Oxygen Utilization (AOU, in μ mol·kg⁻¹, \pm standard deviation) at OVIDE line for each of the six cruises (2002–2012).

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Error calculation. Assuming that the OVIDE cruises are repetitions, i.e. they had been performed
 equally and represent a similar oceanographic behavior, the error in the estimate of the DOC transport can
 be calculated simply as follows:

$$errorT_{DOC_{OVIDE}} = \sqrt{\frac{std}{n}}$$

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where *std* is the standard deviation of the computed transports and *n* is the number of cruises between 2002 and 2012 (n=6).

- 69 Analytical computations of errors were performed at the G-I-S sills ($errorT_{DOC_{SILLS}}$) by means of a
- 70 perturbation method. Independent normally-distributed perturbations (n=100 for each input variable) were
- 71 generated using as the standard deviation the published uncertainties in the [DOC] data.
- 72 Budget error quantities in the OVIDE box were also computed through:

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$$BUDGETerror = \sqrt{errorT_{DOC_{OV}}^{2} + errorT_{DOC_{sills}}^{2} + errorDOC_{storage}^{2}}$$

where $errorDOC_{storage}$ is evaluate from the variability of the inventory of DOC in the OVIDE box from 2002 to 2012 using the stoichiometric relationship between AOU and carbon (AOU-C_{eq}) and the proportion of carbon respired from the DOC pool (estimated in the article as $33\pm6\%$).

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Reconstruction of DOC transports at 24.5°N during the RAPID period. To get a robust DOC 78 transport for the RAPID period (2004–2014), we reconstructed the DOC transports at subtropical 79 latitudes (24.5–26.5°N) based on the work of Hansell et al.⁹ and the data of the RAPID-MOC time 80 series¹¹. This is a different approach from that used for the OVIDE section. First, we computed velocity-81 weighted mean [DOC] for each layer ([DOC]_{mean}²98, in μ mol·kg⁻¹) using the volume transports (T₁₉₉₈, in 82 Sv; 1 Sv=10⁶ m³·s⁻¹) and the DOC transports (T₁₉₉₈DOC, in kmol·s⁻¹) of the 24.5°N cruise in 83 January/February 1998 reported by Hansell et al.⁹ (their Table 1). To obtain the same water column 84 separation used for the RAPID-MOC time series¹¹, we restructured Hansell et al.⁹'s data for the upper 85 limb of the AMOC into three layers: Ekman, upper mid-ocean and Gulf Stream. Volume transports and 86 DOC transports for the Ekman layer were taken from Hansell et al.⁹'s Figure 4(c and d). Volume 87 88 transports and DOC transports for the upper mid-ocean layer were obtained by adding the surface and intermediate layers in Hansell et al.⁹'s Table 1 and then removing the transports associated to the Ekman 89 layer. Finally, [DOC]_{mean}'98 was combined with the average volume transport in RAPID-MOC time 90 series¹¹ (T_{RAPID}, in Sv) for the period between 1 April 2004 and 22 March 2014, thus obtaining the 91 reconstructed DOC transports at subtropical latitudes (24.5–26.5°N) (T_{RAPID}DOC, in kmol·s⁻¹). All data 92 required for these computations are given in the following table: 93

	T ₁₉₉₈	T ₁₉₉₈ DOC	[DOC] _{mean} '98	T _{RAPID}	T _{RAPID} DOC	
	(Sv)	$(\text{kmol} \cdot \text{s}^{-1})$	$(\mu mol \cdot kg^{-1})$	(Sv)	$(\text{kmol} \cdot \text{s}^{-1})$	
Ekman	2.72	190.2	67.9	3.57	250	941
Upper mid-ocean	-21.65	-1239.6	55.6	-17.90	-1025	211

Gulf Stream	30.49	1661.3	53.1	31.40	1716.4	
Deep ocean	-15.86	-659.4	40.6	-17.80	-746.4	-702
Deeper than 5000m	4.26	187.1	42.5	1.02	44.7	

The RAPID/MOCHA/WBTS array is a collaborative effort supported through the UK Natural Environment Research Council (NERC) RAPID-WATCH program, the US National Science Foundation (NSF) Meridional Overturning Circulation Heat-flux Array project, and the US National Oceanographic and Atmospheric Administration (NOAA) Western Boundary Time Series project; and transports including error estimates were freely available at <u>www.rapid.ac.uk/rapidmoc</u>





Figure S2. Dissolved organic carbon (DOC, in μ mol·kg⁻¹) vertical distribution modeled along the OVIDE

section from Greenland (left) to the Iberian Peninsula (right) by combining water mass distributions with the source water types $[DOC]_i$ (see article Table 1) through the equation $[DOC]^{year} = \sum_{i=1}^{12} SWT_i^{year} \times [DOC]_i$. The sections were generated using Ocean Data View 4.7.1. Schlitzer, R., Ocean Data View, <u>odv.awi.de</u>, 2015. Note that the depth scale is not linear and the first

become back view, <u>our awree</u>, 2013. Note that the depth scale is not inical and the first hundred meters are excluded. The model is able to reproduce DOC changes in the sections between years based on the variability of the water mass contributions. In this way the model does not need the assumption of the time derivative of [DOC] being zero at OVIDE section. In addition, the model approach has the advantage of filtering any possible bias produced at single-station level. In the vertical distribution of [DOC] (Fig.2), there are some stations in the Iberian Abyssal Plain (east of 22°W) showing a columnar vertical pattern that was not predicted by the eOMP, which means that it does not follow the water mass distributions.

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102 Table S1. Water mass characterization at the Greenland-Iceland-Scotland (G-I-S) sills. Volume transport (in Sv; 1 Sv= $10^6 \text{ m}^3 \cdot \text{s}^{-1}$) from Pérez et al.¹¹ (ENACW, East North Atlantic Central Water; 103 104 MNACW, Modified North Atlantic Central Water; and NIIW, North-Iceland Irminger Water), Nilsson et al.12 (PIW, Polar Intermediate Water), Macrander et al.13 (DSOW, Denmark Strait Overflow Water), 105 Hansen and Østerhus^{14,15} (ISOW, Iceland-Scotland Overflow Water). Positive transports are northward. 106 [DOC] (in μ mol·kg⁻¹) and density (in kg·m⁻³) are taken from Jeansson et al.¹⁶. The exchanges with the 107 108 Nordic Seas are restricted by the G-I-S sill topography. The mean depth of the sill, around 500 m, limits 109 the exchange of deep water with the North Atlantic. The only regions that allow relatively deep overflows are the Denmark Strait and the Faroe Bank Channel. Shallower overflows also occur across the Iceland-110 111 Faroe Ridge, a broad ridge with minimum depths of 300–500 m (deepening at the Faroese end), and the Wyville-Thomson Ridge between the Faroes and the Scotland shelf (depth $\sim 600 \text{ m}$)¹⁵. This bathymetric 112 restriction narrows the variability in annual circulation, so available literature data are well constrained. 113

114 Using data from the following table, we computed the T_{DOC} at the G-I-S sills as 115 $T_{DOC}^{sills} = \sum_{i=1}^{6} T_{SWT_i}^{sills} \cdot [DOC]_i \cdot \overline{\rho}^{SWT_i} \cdot$

Water mass	Volume transport	Density	[DOC]		
water mass	(Sv)	(kg ⋅ m ⁻³)	(µmol∙kg ⁻¹)		
ENACW	3.85 ± 1	1027.3	58 ± 4		
MNACW	3.85 ± 1	1027.4	58 ± 4		
NIIW	0.8 ± 0.2	1027.6	59 ± 4		
PIW	-1.8 ± 0.5	1027.4	70 ± 10		
DSOW	-3 ± 0.3	1027.9	58 ± 6		
ISOW	-3 ± 0.6	1028	53 ± 5		

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117 **Table S2.Volume and DOC transports at OVIDE section.** Volume (in Sv; $1 \text{ Sv}=10^6 \text{ m}^3 \cdot \text{s}^{-1}$) and DOC 118 transports (in kmol·s⁻¹) at OVIDE section separated as surface layer (<100 dbar), the upper limb of the 119 AMOC without the first 100 dbar, and the lower limb of the AMOC. The sum of the three components 120 results in the net transport represented in the row labeled "Total". Northward transports are positive.

	2002		20	04	2006		
	T _{Sv}	T _{DOC}	T _{Sv}	T _{DOC}	T _{Sv}	T _{DOC}	
Surface layer	0.89	84	1.18	119	1.31	41	
Upper limb >100 dbar	15.85	855	15.11	818	11.34	619	
Lower limb	-16.5	-913	-16.35	-927	-11.25	-631	
Total	0.24	26	-0.06	10	1.4	29	

	2008		2010		2012		Mean	
	T_{Sv}	T _{DOC}	T_{Sv}	T_{DOC}	T_{Sv}	T _{DOC}	T _{Sv}	T _{DOC}
Surface layer	1.69	92	1.43	58	1.15	59	1.26	76
Upper limb >100 dbar	16.6	901	17.04	916	15.5	836	15.28	824
Lower limb	-17.37	-933	-17.23	-915	-15.71	-874	-15.73	-866
Total	0.92	60	1.24	59	0.94	21	0.8	34.2

Table S3. Mean water mass volume transports (in Sv; $1 \text{ Sv}=10^6 \text{ m}^3 \cdot \text{s}^{-1}$) for the period 2002–2012 in the 123 upper 100 dbar, the upper limb of the AMOC at depths >100 dbar, the lower limb of the AMOC and the 124 whole water column (Total) at the OVIDE line. ENACW₁₆ and ENACW₁₂: East North Atlantic Central 125 126 Waters; MW: Mediterranean Water; SAIW: Subarctic Intermediate Water; SPMW₈ and SPMW₇: Subpolar Mode Waters of the Iceland Basin and IrSPMW of the Irminger Basin; LSW: Labrador Sea 127 Water; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water; PIW: Polar 128 Intermediate Water; and NEADW_L: lower North East Atlantic Deep Water. Positive transports are 129 northward. 130

$\mathbf{T}_{\mathbf{Sv}}$	<100 dbar	Upper limb >100 dbar	Lower limb	Total
ENACW16	0.066	0.12	0	0.185
ENACW12	1.91	6.69	0.007	8.603
MW	0.00	0.074	0.005	0.08
SAIW	-0.30	3.99	-0.68	2.997
SPMW8	-0.002	1.74	0.28	2.022
SPMW7	0.71	1.78	0.47	2.961
IrSPMW	-1.04	0.2	-8.6	-9.44
LSW	0.013	0.68	-1.34	-0.65
ISOW	0	0.003	-2.71	-2.71
DSOW	0	0	-2.48	-2.48
PIW	-0.08	-0.036	-1.34	-1.45
NEADW _L	0	0.006	0.66	0.665

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