

Supplementary Materials for

Oceanic efflux of ancient marine dissolved organic carbon in primary marine aerosol

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Supplementary Materials for

Table S1. Blank-corrected mPMA sample masses and ^{14}C abundances. Values reported as Fraction modern (Fm), $\Delta^{14}\text{C}$, and ^{14}C age. Measurement uncertainties (± 1 standard deviation) were propagated from the uncorrected mPMA samples (Table S3) and the means and standard errors of the sample handling blank (Table S3). Each sample is reported with the date on which it was collected. All seawater was drawn from 5 m to generate mPMA.

Laboratory ID (UCI AMS #)	Date	Mass * ($\mu\text{g C}$)	Fm	$\Delta^{14}\text{C}$ (‰)	Age (^{14}C yr)
<i>GB, Georges Bank</i>					
199542 †	9/18/16	15.7 \pm 0.8	0.867 \pm 0.023	-140 \pm 23	1150 \pm 220
199543 ‡	9/19/16	6.7 \pm 0.8	0.829 \pm 0.056	-177 \pm 56	1500 \pm 550
192361	9/20/16	7.1 \pm 0.8	0.819 \pm 0.047	-188 \pm 47	1610 \pm 470
<i>SSW, Sargasso West</i>					
199546	9/24/16	18.4 \pm 0.8	0.841 \pm 0.020	-166 \pm 20	1390 \pm 190
<i>SSN, Sargasso North</i>					
192368	10/6/16	5.1 \pm 0.8	0.858 \pm 0.069	-149 \pm 69	1230 \pm 650
<i>BI, Coastal Rhode Island</i>					
192369	10/10/16	37.1 \pm 0.8	0.957 \pm 0.011	-50 \pm 11	350 \pm 90
192370	10/11/16	14.1 \pm 0.8	1.002 \pm 0.029	-6 \pm 29	Modern
<i>Near-surface Averages excluding observations from BI</i>					
Mean (n = 5)		10.6	0.843	-164	1370
Standard deviation of measurements		\pm 6.0	\pm 0.020	\pm 20	\pm 190
Propagated standard deviation of the mean		\pm 0.4	\pm 0.021	\pm 21	\pm 210

* Mass of organic carbon collected on the central disc (38 mm diameter) of each filter

† mPMA generated during daytime (between sunrise and sunset)

‡ mPMA generated during nighttime (between sunset and sunrise)

Table S2. Globally averaged rates of RDOC transfer from the ocean to the atmosphere via PMA formation. Transfer rates were based on published PMA OM production rates and the ^{14}C -based fractions of RDOC in mPMA generated from near surface waters (5 m) assuming that RDOC is entirely fossil carbon ($\Delta^{14}\text{C} = -1000 \text{ ‰}$, $X_{\text{RDOC/PMA}} = 19 \%$) or identical to bulk DOC from deep seawater (depth = 2500 m, mean $\Delta^{14}\text{C} = -457 \pm 8 \text{ ‰}$ ($n = 3$), $X_{\text{RDOC/PMA}} = 40 \%$).

Global PMA OM production rates (Tg C yr ⁻¹)	Production rate references	PMA RDOC production rates (Tg C yr ⁻¹)	
		19 % RDOC (Fossil)	40 % RDOC (Deep sea)
50	Roelofs et al. (23)	10	20
35	Roelofs et al. (23)	7	14
29	Long et al. (22)	6	11
22.3	Gantt et al. (21)	4	9
8	Spracklen et al. (24)	2	3

Table S3. Published sources and losses of marine RDOC. Values converted into consistent units of Teragrams (Tg) and years (yr), given that 1 mol C = 12.011 g C and 1 Pg = 10³ Tg = 10¹⁵ g.

Process	Global Rate (Tg C yr ⁻¹)	Turnover time (yr)	% of total Sources or Losses *
All Sources †	43	16,000	100
All Losses ‡	326 to 1394	450 to 1,900	100
Photochemical Degradation §	300 to 1300	500 to 2,300	76 to 98
Incorporation into POC	25 to 50	13,000 to 25,000	1.8 to 14
Biological Degradation ¶	≤ 43	≥ 15,000	≤ 12
Hydrothermal Circulation #	1 to 1.4	440,000 to 700,000	0.07 to 0.44

Difference = All Sources – All Losses = -283 to -1351

* Minimum percentages assume the process proceeds at the minimum reported global rate while all other processes proceed at their maximum reported rates; maximum percentages assume the process proceeds at the maximum reported global rate while all other processes proceed at their minimum reported rates.

† Global rate (0.043 Pg C yr⁻¹) and turnover time (16,000 yr) from Hansell (2).

‡ Turnover time (with respect to All Losses) = global mass / All Losses, assuming a 630 Pg C global mass of RDOC (2).

§ Range of turnover times (500 yr to 2300 yr) from Mopper et al. (9) and Anderson and Williams (25).
Global rates = turnover times / global mass, assuming a 630 Pg C global mass of RDOC (2).

|| Global rates (0.025 to 0.05 Pg C yr⁻¹) from Hansell et al. (8) and Druffel and Williams (10).
Turnover times = global mass / global rates, assuming a 630 Pg C global mass of RDOC (2).

¶ Upper limit (0.043 Pg C) from Hansell (2) based on global correlations between DOC concentrations and DIC Δ¹⁴C values and the assumption of a primarily biological sink.

Total global rates are reported as losses during transit through cooler off-axis systems (0.8 to 1.2×10¹¹ mol DOC yr⁻¹) (13), which exceed reported losses through high temperature systems by one to three orders of magnitude (7×10⁹ to 1.3×10¹¹ g C yr⁻¹) (11, 12). Turnover times = global mass / global rate, assuming a 630 Pg C global mass of RDOC (2).

Table S4. mPMA handling blank masses and ^{14}C abundances. Values reported with individual measurement uncertainties (± 1 standard deviation), and associated Z-Scores. Each blank is reported with the date on which it was collected.

Laboratory ID (UCI AMS #)	Date	Mass* ($\mu\text{g C}$)	Fm	$\Delta^{14}\text{C}$ (‰)	Age (^{14}C yr)	Z-Score [†] (mass)	Z-Score [†] (Fm)
<i>GB, Georges Bank</i>							
199541	9/18/16	5.4 ± 0.6	0.332 ± 0.059	-671 ± 59	8860 ± 1420	-0.31	-1.44
187986	9/22/16	4.0 ± 0.6	0.559 ± 0.024	-445 ± 24	4670 ± 350	-0.32	0.79
<i>SSW, Sargasso West</i>							
199545	9/24/16	5.4 ± 0.6	0.328 ± 0.059	-674 ± 59	8940 ± 1440	-0.31	-1.48
192363	9/26/16	9.0 ± 0.6	0.559 ± 0.024	-445 ± 24	4670 ± 350	-0.29	0.79
<i>SSN, Sargasso North</i>							
192366 [‡]	10/2/16	504 ± 1.0	0.530 ± 0.007	-474 ± 7	5100 ± 110	2.85	0.50
192401	10/3/16	4.0 ± 0.6	0.459 ± 0.041	-545 ± 41	6260 ± 730	-0.32	-0.19
192367	10/5/16	6.0 ± 0.6	0.524 ± 0.027	-480 ± 27	5190 ± 420	-0.31	0.44
<i>BI, Coastal Rhode Island</i>							
192374	10/12/16	4.0 ± 0.6	0.469 ± 0.042	-535 ± 42	6090 ± 720	-0.32	-0.10
192371	10/13/16	4.0 ± 0.6	0.394 ± 0.044	-609 ± 44	7470 ± 900	-0.32	-0.83
192372	10/13/16	2.0 ± 0.6	0.633 ± 0.103	-372 ± 103	3670 ± 1320	-0.33	1.52
<i>Summary, excluding UCID 192366</i>							
Mean, excluding UCID#192366 (n = 9)		4.9	0.47	-531	6202		
Standard deviation of measurements		± 1.9	± 0.11	± 105	± 1881		
Propagated standard deviation of the mean		± 0.2	± 0.02	± 17	± 317		
Standard error of the mean		± 0.6	± 0.04	± 35	± 627		
Uncertainty-weighted error of the mean [§]		± 0.2	± 0.01	± 12	± 187		

* Mass of organic carbon collected on the central disc (38 mm diameter) of each filter

† Z-score = (value – mean)/standard deviation, for all measurements of mass or Fm (n = 10)

‡ By Chauvenet's Criterion, the Z-score for UCID 192366's mass exceeded a two-tailed critical value of $1.96 = 1 - 1/4n$ for normally distributed data (n = 10), and therefore was excluded from further analyses.

§ Single standard deviation when observations are weighted by their inverse variances, such that $\sigma = (1/\sum(1/\sigma_i^2))^{1/2}$

Table S5. Uncorrected mPMA sample masses and ^{14}C abundances. Values reported with individual measurement uncertainties (± 1 standard deviation). Each sample is reported with the date on which it was collected.

Laboratory ID (UCI AMS #)	Date	Depth (m)	Mass* ($\mu\text{g C}$)	Fm	$\Delta^{14}\text{C}$ (‰)	Age (^{14}C yr)
<i>GB, Georges Bank</i>						
199542 †	9/18/16	5	20.6 \pm 0.6	0.7723 \pm 0.0087	-234.0 \pm 8.7	2080 \pm 100
199543 ‡	9/19/16	5	11.6 \pm 0.6	0.6774 \pm 0.0189	-328.1 \pm 18.9	3130 \pm 230
192361	9/20/16	5	12.0 \pm 0.6	0.6763 \pm 0.0123	-329.2 \pm 12.3	3140 \pm 150
<i>SSW, Sargasso West</i>						
199546	9/24/16	5	23.3 \pm 0.6	0.7630 \pm 0.0086	-243.3 \pm 8.6	2170 \pm 100
<i>SSN, Sargasso North</i>						
192368	10/6/16	5	10.0 \pm 0.6	0.6680 \pm 0.0139	-337.4 \pm 13.9	3240 \pm 170
192365 §	10/1/16	5	15.0 \pm 0.6	0.8251 \pm 0.0117	-181.6 \pm 11.7	1540 \pm 120
<i>GB, Coastal Rhode Island</i>						
192369	10/10/16	5	42.0 \pm 0.6	0.9006 \pm 0.0044	-106.7 \pm 4.4	840 \pm 40
192370	10/11/16	5	19.0 \pm 0.6	0.8647 \pm 0.0077	-142.3 \pm 7.7	1170 \pm 80

* Blank-corrected mass of organic carbon collected on the central disc (38 mm diameter) of each filter

† mPMA generated during daytime (between sunrise and sunset)

‡ mPMA generated during nighttime (between sunset and sunrise)

§ Filter visibly contaminated with dark brown residues after loading into the combustion tubes, and therefore excluded from further analyses

Table S6. Seawater DOC concentrations, $\delta^{13}\text{C}$ values, and ^{14}C abundances. Values reported with individual measurement uncertainties (± 1 standard deviation). Each sample is reported with the date on which it was collected.

Laboratory ID (UCI AMS #)	Date	Depth (m)	[DOC] (μM)	$\delta^{13}\text{C}$ (‰)	Fm	$\Delta^{14}\text{C}$ (‰)	Age (^{14}C yr)
<i>GB, Georges Bank</i>							
192390	9/18/16	5	93 \pm 1	-21.0 \pm 0.2	0.7480 \pm 0.0014	-258.0 \pm 1.4	2330 \pm 15
192378	9/19/16	5	86 \pm 1	-21.4 \pm 0.2	0.7676 \pm 0.0012	-238.6 \pm 1.2	2125 \pm 15
<i>SSW, Sargasso West</i>							
192384	9/25/16	5	74 \pm 1	-21.1 \pm 0.2	0.7147 \pm 0.0011	-291.0 \pm 1.1	2700 \pm 15
192381	9/24/16	2000	40 \pm 1	-20.8 \pm 0.2	0.5700 \pm 0.0010	-434.6 \pm 1.0	4515 \pm 15
192386	9/25/16	2500	44 \pm 1	-21.9 \pm 0.2	0.5442 \pm 0.0010	-460.2 \pm 1.0	4890 \pm 15
<i>SSN, Sargasso North</i>							
192387	10/2/16	5	73 \pm 1	-20.5 \pm 0.2	0.7651 \pm 0.0012	-241.1 \pm 1.2	2150 \pm 15
192392 *	10/6/16	5	69 \pm 1	-21.0 \pm 0.2	0.7713 \pm 0.0012	-234.9 \pm 1.2	2085 \pm 15
192393 †	10/6/16	5	71 \pm 1	-20.8 \pm 0.2	0.7786 \pm 0.0013	-227.7 \pm 1.3	2010 \pm 15
192379	10/1/16	2500	47 \pm 1	-21.8 \pm 0.2	0.5411 \pm 0.0010	-463.2 \pm 1.0	4935 \pm 15
192388	10/1/16	2500	47 \pm 1	-21.8 \pm 0.2	0.5565 \pm 0.0010	-448.0 \pm 1.0	4710 \pm 15
<i>BI, Coastal Rhode Island</i>							
192380	10/10/16	5	92 \pm 1	-21.3 \pm 0.2	0.7821 \pm 0.0012	-224.2 \pm 1.2	1975 \pm 15
192391	10/10/16	5	91 \pm 1	-21.4 \pm 0.2	0.7762 \pm 0.0012	-230.1 \pm 1.2	2035 \pm 15
<i>Deep ocean (2500 m) averages</i>							
Mean (n = 3)			46	-21.8	0.547	-457	4840
Standard deviation of measurements			± 2	± 0.1	± 0.008	± 8	± 120
Propagated standard deviation of the mean			± 1	± 0.1	± 0.001	± 1	± 15

* Seawater from *Endeavor's* clean pumping system that was sampled immediately upstream of the aerosol generator's inlet

† Seawater sampled from the aerosol generator's outlet

Table S7. Seawater DIC concentrations, $\delta^{13}\text{C}$ values, and ^{14}C abundances. Values reported with individual measurement uncertainties (± 1 standard deviation). Each sample is reported with the date on which it was collected.

Laboratory ID (UCI AMS #)	Date	Depth (m)	[DIC] (μM)	$\delta^{13}\text{C}$ (‰)	Fm	$\Delta^{14}\text{C}$ (‰)	Age (^{14}C yr)
<i>GB, Georges Bank</i>							
187983	9/19/16	5	2245 \pm 24	1.2 \pm 0.1	1.0269 \pm 0.0016	18.7 \pm 1.6	> Modern
187984	9/19/16	5	2154 \pm 24	1.2 \pm 0.1	1.0278 \pm 0.0017	19.6 \pm 1.7	> Modern
<i>SSW, Sargasso West</i>							
187982	9/25/16	5	2122 \pm 24	0.8 \pm 0.1	1.0531 \pm 0.0018	44.7 \pm 1.8	> Modern
187981	9/25/16	2500	2263 \pm 24	1.1 \pm 0.1	0.9511 \pm 0.0013	-56.4 \pm 1.3	400 \pm 15
<i>SSN, Sargasso North</i>							
187987	10/2/16	5	2069 \pm 24	1.0 \pm 0.1	1.0496 \pm 0.0015	41.3 \pm 1.5	> Modern
187985	10/1/16	2500	2276 \pm 24	1.0 \pm 0.1	0.9684 \pm 0.0014	-39.3 \pm 1.4	260 \pm 15
187986	10/1/16	2500	2134 \pm 24	0.9 \pm 0.1	0.9675 \pm 0.0014	-40.2 \pm 1.4	265 \pm 15
<i>BI, Coastal Rhode Island</i>							
187988	10/10/16	5	2138 \pm 24	0.8 \pm 0.1	1.0333 \pm 0.0015	25.1 \pm 1.5	> Modern
187990	10/10/16	5	2139 \pm 24	0.8 \pm 0.1	1.0293 \pm 0.0015	21.1 \pm 1.5	> Modern