# Supplementary Material

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**Table S1.** Location and occupation dates of stations, including selected physical and biological parameters from the underway flowthrough surface seawater system and meteorological station(s) during the North Atlantic Aerosol and Marine Ecosystems Study (NAAMES) field campaigns. Data presented are the mean for each station. Measurements that were not collected at a particular station are denoted with '-' and all other abbreviations are defined below.

Cruise	Station	Date(s)	Latitude	Longitude	SAL	T_sea	T_air	Rain	RH	WS	WD	PAR_max	Chl_a	POC	NPP	Polarity
			(degrees)	(degrees)	(PSU)	(°C)	(°C)	$(mm h^{-1})$	(%)	(m s <sup>-1</sup> )	(degrees)	(µmol m <sup>-2</sup> s <sup>-2</sup> )	(mg m <sup>-3</sup> )	(mg C m <sup>-3</sup> )	(mg C m <sup>-3</sup> d <sup>-1</sup> )	
N1	<b>S</b> 1	2015-11-12	51.046	-43.624	35.5	13.4	4.1	0.34	60.3	10.6	296	218	0.24	54	4.04	Anticyc
	S2	2015-11-14/15	54.075	-40.170	34.7	5.7	2.7	0.02	66.9	6.8	246	735	0.38	44	4.77	NE
	<b>S</b> 3	2015-11-16	51.134	-40.076	34.2	7.4	7.0	1.23	86.9	11.5	87	134	0.73	65	7.93	Cyclone
	S4	2015-11-18	46.205	-37.872	35.9	15.6	11.2	0.07	74.7	5.9	97	1103	0.24	22	2.13	Anticyc
	S5	2015-11-20	43.825	-37.510	35.9	16.4	14.7	0	80.8	12.3	60	455	0.06	14	6.21	NE
	S5b	2015-11-20	43.642	-38.417	35.8	16.9	14.5	9.20	84.6	13.0	84	0.19	-	-	-	NE
	<b>S</b> 6	2015-11-21/23	43.211	-40.243	35.7	17.3	16.9	0.14	87.3	12.1	127	581	0.09	15	12.3	Anticyc
	<b>S</b> 7	2015-11-24/25	40.610	-40.472	36.1	18.7	19.0	0.12	84.8	10.9	152	822	0.09	18	13.9	Cyclone
N2	S0	2016-05-17	54.445	-46.153	34.6	4.6	4.5	0.02	90.3	8.8	140	1751	1.24	132	-	NE
	<b>S</b> 1	2016-05-18/19	56.324	-46.011	34.8	4.2	3.7	0.03	86.7	4.7	106	787	1.56	138	23.1	Cyclone
	S2	2016-05-19/21	53.528	-42.227	34.6	6.2	5.7	0	82.9	8.4	276	1747	3.02	269	38.8	Anticyc
	<b>S</b> 3	2016-05-22/23	50.091	-43.903	34.9	9.0	7.5	0.01	81.2	8.0	290	1942	3.68	242	51.4	Anticyc
	S4	2016-05-23/27	47.459	-38.716	36.1	15.7	13.8	0.16	81.3	7.1	218	1553	0.70	68	41.3	Anticyc
	S5	2016-05-28/31	44.471	-43.298	35.5	15.6	11.9	1.82	78.0	14.0	203	2102	0.97	159	-	Cyclone
N3	S1a	2017-09-04	42.245	-44.733	35.3	23.4	17.7	0	64.5	4.6	265	2145	0.14	23	-	NE
	<b>S</b> 1	2017-09-04/05	42.387	-42.907	36.4	22.5	18.8	0	59.6	3.3	145	2105	0.08	25	6.07	Anticyc
	S1.5	2017-09-05	43.712	-42.929	33.1	17.4	21.2	0	67.8	8.2	221	2047	0.15	59	-	NE
	S2	2017-09-06/07	44.364	-43.339	33.4	18.4	17.0	0	90.8	4.8	265	1662	0.16	45	6.31	Cyclone
	<b>S</b> 3	2017-09-08/09	47.028	-40.111	35.6	19.6	18.4	0	91.4	6.2	234	1514	0.16	35	8.34	Mode
	S3.5	2017-09-09	48.044	-39.240	34.6	16.4	17.8	0	94.0	7.8	232	2006	-	-	-	NE
	S4	2017-09-10/11	48.638	-39.129	34.3	16.9	17.4	0.01	94.6	7.3	229	1400	0.18	53	19.6	Cyclone
	S4.5	2017-09-11	50.153	-39.264	33.9	15.8	15.1	0.67	94.2	5.5	291	484	0.35	73	-	NE
	S5	2017-09-12/13	51.718	-39.574	31.4	14.3	10.7	0	68.5	5.8	225	1382	0.33	72	23.0	NE
	S5.5	2017-09-13	52.653	-39.601	34.2	12.2	11.5	0	83.1	13.4	119	794	0.85	125	-	NE
	S6	2017-09-13/17	53.376	-39.542	34.0	11.7	11.6	0.08	89.1	8.8	212	1170	0.83	124	22.9	NE

N4	S1	2018-03-27	39.405	-43.455	36.2	18.8	16.0	0.07	69.3	10.0	66	1790	0.62	64	28.4	NE
	S2	2018-03-28	39.279	-41.211	36.1	17.7	17.7	0	86.1	5.4	148	1955	1.00	111	59.5	NE
	S2.1	2018-03-29	42.115	-42.187	36.6	18.8	18.4	0.002	81.6	13.6	192	1708	0.37	39	-	NE
	<b>S</b> 3	2018-03-30	43.493	-42.167	35.3	18.6	13.6	0.006	75.2	14.1	261	1749	0.42	36	16.9	NE
	S4	2018-03-31/ 2018-04-01	44.471	-38.293	34.6	14.2	12.2	0.003	78.8	12.7	288	1853	0.61	56	21.7	NE
	S2RD	2018-04-03/04	40.009	-39.898	36.2	17.9	14.2	0.03	69.6	12.2	272	1961	0.67	70	-	NE
	S2RF	2018-04-05	39.195	-40.086	36.5	18.1	12.7	0	58.3	8.4	303	2221	0.65	53	22.6	NE

Abbreviations: SAL, sea surface salinity; T\_sea, sea surface temperature; T\_air, atmospheric temperature; Rain, rain intensity; RH, relative humidity; WS, true wind speed; WD, true wind direction; PAR\_max, maximum photosynthetically available radiation; Chl\_a, chlorophyll-a concentration estimated from absorption spectra; POC, particulate organic carbon estimated from beam attenuation; NPP, net primary production; Polarity, presence/absence of eddy water masses; Anticyc, anticyclonic eddy; Cyclone, cyclonic eddy; Mode, mode water; NE, station not located within an eddy; N1-4, NAAMES cruise 1-4 (N1=November 2015, N2=May 2016, N3=September 2017, and N4=March 2018).



**Figure S1.** Equipment set-up on the *R/V Atlantis* illustrating how the polycarbonate dynamic stripping chambers were coupled with proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF/MS) to quantify net VOC production rates.

#### Section 1. Data analysis

#### PTR-ToF/MS data processing

Raw PTR-ToF/MS .h data files were pre-processed using PTR-Viewer version 3.2.8.0 software (IONICON Analytik GmbH, Innsbruck, Austria). ToF/MS data was first mass calibrated against ions of known mass (nitrosonium, NO<sup>+</sup>, at m/z 29.998 and 1,3-diiodobenzene at m/z 203.943 and m/z 330.848) contained within each spectrum using the following criteria: 3-point calibration mode, cycle 200, 0.2 m/z search range, and 3 spectra averaging. NO<sup>+</sup> is a parasitic ion formed within the ionization source and 1,3-diiodobenzene was continuously introduced into the sample drift tube by way of a permeation tube maintained at 60 °C. The accuracy of the mass calibration was confirmed against alternate ions of known mass contained within each spectrum (hydronium ions,  $H_3^{18}O^+$ , at m/z 21.022, <sup>18</sup>O.O<sup>+</sup> at m/z 33.990, hydrated water cluster,  $H_2O.H_3^{18}O^+$ , at m/z 39.035, and acetone (optional) at m/z 59.049).

Next, Gaussian parameters were fitted to each target peak in the averaged mass spectrum of each experiment for integration and subsequent quantification at each time point (Table S2). A mass scale calibration file and peak fitting file was prepared each day and applied to all corresponding samples collected the same day.

Target VOC	Gauss Center	Gauss Height	Gauss Width	Gauss Percent	Multiplier	k Rate	
	(m/z)	(cps)	(a.m.u.)	(%)		$(x10^{-9} \text{ cm}^3 \text{ s}^{-1})$	
${\rm H_{3}}^{18}{\rm O^{+}}$	21.02425	169	0.02314	100	487	2.00	
$H_2O.H_3{}^{18}O^+$	39.03645	21.2	0.03703	99.5	250	2.00	
methanol	33.03209	5.50	0.03651	58.9	1	2.33	
acetonitrile	42.03238	0.24	0.06017	88.6	1	4.74	
acetaldehyde	45.02328	2.40	0.05606	58.4	6.173	3.36	
methanethiol	49.01449	0.57	0.05451	100	1	2.00	
acetone	59.05274	1.48	0.06069	99.8	1.214	3.00	
dimethylsulfide	63.03042	1.20	0.06326	99.7	1.229	2.24	
isoprene	69.06930	0.13	0.10000	98.7	3.891	1.94	

**Table S2.** Gaussian parameters used for the quantification of target VOCs. This is a representative peak table from 16 September 2017. Multiplier values shown in bold are calculated calibration response factors (explained in the text below). Where literature collision (k) rate values (Zhao and Zhang, 2004; Cappellin et al., 2010) were not available, a default k rate of  $2.00 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>, recommended by the manufacturer, was used.

Widely accepted methods (Lindinger et al., 1998) were used to calculate mixing ratios, based on primary ion counts originating from  $H_3O^+$  and the hydrated water cluster ( $H_2O.H_3^{18}O^+$ ), due to the high humidity introduced by bubbling seawater. Where collision rate constants for reactions occurring in the drift tube were available in the literature (Zhao and Zhang, 2004; Cappellin et al., 2010), the literature value was used, otherwise the default collision rate constant of  $2.00 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>, recommended by the manufacturer, was selected. Concentration data and instrumental parameters were exported from PTR-Viewer into a .txt file for each experiment to undergo further manipulation in R Studio, version 1.1.463 (Boston, MA). For each measurement period (defined as one 60-sec measurement per chamber), the first 30 seconds of data and final

data point were excluded to account for sorption within the tubing and the response time for gases to travel from the dynamic stripping chambers into the PTR-ToF/MS inlet.

#### Background concentrations from autoclaved artificial seawater

Autoclaved and pre-purged artificial carbon-free seawater (ASW, i.e., "VOC-free" seawater) was used to determine background concentrations of VOCs arising from the experimental setup (Figure 2). ASW was prepared and autoclaved in advance, then purged (i.e., bubbled) and measured fresh daily during the March 2018 field campaign. ASW (100 mL) was added to an empty chamber and bubbled in the same manner as for samples, while the daily calibration was performed (~15-30 min, details outlined in the main manuscript). Following completion of the calibration, ASW concentrations were monitored for a further ~15-30 min to establish the background concentrations arising from the experimental setup. The temperature of the incubator during background ASW measurements was set to the ambient sea surface temperature at the start of the calibration measurement and ranged between 12.9 and 24.9°C across the March 2018 campaign. Due to the observed temperature dependence of the background concentrations, linear regressions were fitted to the ASW data for each target VOC (Figure S2) and background concentrations were subsequently computed for each experiment with natural seawater based on the surface seawater temperature at the time of collection (see Figure 2 and Table 1 in the main manuscript). We applied the temperature regressions obtained during the March 2018 cruise across all samples and all years because the measurement protocol was modified during the March 2018 campaign (the fourth of four campaigns). During the first three cruises, ASW concentrations were monitored prior to the calibration procedure without the ~30-60 min bubbling. The 30-60 min bubbling ensured a truer "VOC-free" seawater and experimental background. Thus, the background concentrations from autoclaved, bubbled (i.e., "VOC-free") ASW provide appropriate, conservative thresholds for natural seawater bubbled with synthetic air.



**Figure S2.** Linear regressions for each target VOC were used to account for the temperature dependence observed in background concentrations obtained by bubbling autoclaved ("VOC-free") ASW during the March 2018 field campaign.

#### Recipe for artificial seawater (ASW) media

The ASW recipe was based on standard f/2 media, with the exclusion of organic carbon compounds. The following salts were added and completely dissolved in 2 L of MilliQ water in the following order: 0.04 g SrCl<sub>2</sub>·6H<sub>2</sub>O, 0.06 g H<sub>3</sub>BO<sub>3</sub>, 0.2 g KBr, 1.4 g KCl, 2.9 g CaCl<sub>2</sub>·2H<sub>2</sub>O, 8 g Na<sub>2</sub>SO<sub>4</sub>, 21.6 g MgCl<sub>2</sub>·6H<sub>2</sub>O, 47 g NaCl, and 0.4 g NaHCO<sub>3</sub>. The media was stored in acid-washed polycarbonate carboys, autoclaved for 45 min, and allowed to cool before use.

#### *Temperature-dependence and computation of VOC loss rates in abiotic controls*

Abiotic controls were prepared to remove the biological processes involved in VOC production and consumption and retain the existing VOCs present in the sample. Thus, the abiotic controls were used to account for the physical removal ("stripping") of VOCs from the seawater due to the bubbling process (Figure 2). Abiotic controls (0.22 µm gravity filtered natural seawater) were concurrently run with each experiment during the September 2017 and March 2018 field campaigns, which covered a wide spatial and temporal range. Abiotic controls were prepared by gravity filtration of natural seawater, collected immediately prior, through a 0.22 µm Sterivex filter. The filtration was achieved by securing the bottle of natural seawater at a height ~2 m above the collection bottle for the filtrate. Both the supply and collection bottles were 500 mL polycarbonate with two-port lids, one of which was fitted with a PTFE filter and open to the ambient laboratory air and the other was connected to the fluid path. All bottles and tubing were blackened to prevent reactions with light. A siphon flow was established using suction provided by a syringe at the lower end of the tubing, into which a Sterivex filter was installed. Approximately 50-100 mL of seawater was allowed to flush through the filter and was discarded, following which, the collection bottle was attached to the back end of the Sterivex to collect the filtrate ("abiotic control"). On average, 10-20 min was required to filter 200-500 mL of seawater. Abiotic controls had also been prepared during the November 2015 and May 2016 field campaigns, but with different filter types and filtration setups that either released significant background concentrations of VOCs, particularly acetone, and/or caused noticeable stress responses and signals from the phytoplankton. Our revised gravity filtration approach with Sterivex filters avoided these unwanted signals.

The abiotic controls exhibited logarithmic declines in most target VOCs with time and no consistent trends with temperature. However, dimethylsulfide and methanethiol showed noticeable temperature dependencies. Thus, to account for the temperature-dependence of these two compounds, the abiotic controls from 5-m surface water collected at dawn and the early afternoon local time across both field campaigns were grouped by seawater temperature into three categories ("low" <14 °C; "mid" 14-20 °C, and "high" >20 °C). An average abiotic control loss rate was calculated for each target VOC and/or temperature category by fitting the data with regression models producing the highest  $r^2$  values (Table S3). No abiotic control was applied for isoprene, which produced a linear regression with a slope equal to zero. Thus, it was only possible to calculate positive net production rates for isoprene. The abiotic controls for methanol were treated separately for the September and March field campaigns, due to the large disparities observed in the concentrations between the two field campaigns. Experiment-specific abiotic control concentrations were then calculated using the relevant incubation time-based regression models listed in Table S3. For all compounds, except methanol, the regression models were applied to sample data across all cruises. For methanol, the 2017 regressions were used for the 2016-2017 cruises and the 2018 regressions were applied to the 2015 and 2018 sample data.

**Table S3.** Regression equations used to calculate abiotic control concentrations for each target compound at "low" (<14 °C), "mid" (14-20 °C), and "high" (>20 °C) temperatures, where y = concentration in air (ppbv) and x = time (min). Abiotic controls were not applied for isoprene because the regression slope was zero.

VOC	Cruise	Temperature	Abiotic control regression equations
Acetaldehyde	All cruises	all	$y = -0.125 In(x) + 1.13 (r^2 0.07)$
Acetone	All cruises	all	$y = -0.146 In(x) + 0.871 (r^2 0.23)$
Acetonitrile	All cruises	all	$y = -0.007 In(x) + 0.0931 (r^2 0.07)$
Dimethylsulfide	All cruises	low	$y = 8.65 \cdot x^{-1.04}$ ( $r^2 0.62$ )
		mid	$y = 5.04 \cdot x^{-0.946}$ ( $r^2 0.63$ )
		high	$y = 3.38 \cdot x^{-0.713} (r^2 \ 0.68)$
Isoprene	All cruises	all	_
Methanethiol	All cruises	low	$y = 0.692 \cdot x^{-0.299} \ (r^2 \ 0.14)$
		mid	$y = 0.428 \cdot x^{-0.206}  (r^2 \ 0.08)$
		high	$y = 0.252 \cdot x^{-0.038}$ ( $r^2 0.008$ )
Methanol	May 2016 + Sept. 2017	all	y = -0.857 In(x) + 27.3 ( $r^2$ 0.003)
	Nov. 2015 + Mar. 2018	all	$y = -0.350 \text{ In}(x) + 3.94 \ (r^2 \ 0.02)$

Day	November 2015 May 2016							September 2017				March 2018							
	Date	Ald	Ace	Isop	Date	Ald	Ace	DMS	Isop	Date	Ald	Ace	DMS	Isop	Date	Ald	Ace	DMS	Isop
Ave		1.254	0.844	1.685		1.332	1.313	1.531	3.326		1.332	1.346	1.337	3.299		1.332	1.489	1.380	4.980
1										20170829	1.332	1.346	1.337	1.570	20180320	1.332	1.489	1.380	4.980
2					20160512	1.332	1.156	1.164	3.326	20170830	1.332	1.346	0.942	3.299	20180321	1.524	1.718	1.337	4.484
3					20160513	1.189	1.214	1.397	3.326	20170831	1.426	1.391	1.337	2.632	20180322	1.372	1.392	1.513	3.892
4					20160514	1.189	1.211	1.397	3.077	20170901	1.322	1.348	1.290	2.551	20180323	1.358	1.538	1.363	4.425
5					20160515	1.164	1.130	1.311	2.959	20170902	1.303	1.312	1.215	2.688	20180324	1.399	1.610	1.252	4.651
6	20151112	1.254	0.844	1.685	20160516	1.273	1.330	1.414	3.247	20170903	1.192	1.145	1.241	2.584	20180325	1.307	1.399	1.538	4.274
7	20151114	1.254	0.844	1.685	20160517	1.248	1.269	1.439	3.077	20170904	1.322	1.279	1.285	2.865	20180326	1.386	1.580	1.307	4.808
8	20151115	1.254	0.844	1.685	20160518	1.264	1.314	1.420	3.165	20170905	1.192	1.174	1.355	2.632	20180327	1.319	1.508	1.497	4.762
9	20151116	1.109	0.838	1.582	20160519	1.282	1.287	1.567	3.175	20170906	1.383	1.372	1.271	3.195	20180328	1.372	1.590	1.479	5.291
10	20151117	1.149	0.853	1.621	20160520	1.273	1.266	1.326	3.165	20170907	1.303	1.332	1.314	3.058	20180329	1.345	1.515	1.502	4.950
11	20151118	1.391	1.014	1.901	20160521	1.260	1.211	1.650	3.135	20170908	1.393	1.404	1.342	3.460	20180330	1.259	1.513	1.351	5.155
12	20151119	1.314	0.893	1.818	20160522	1.308	1.351	1.642	3.268	20170909	1.139	1.100	1.337	3.106	20180331	1.270	1.359	1.575	4.831
13	20151120	1.164	0.763	1.592	20160523	1.365	1.350	1.572	3.356	20170910	1.332	1.346	1.229	3.299	20180401	1.319	1.536	1.475	5.319
14	20151121	1.247	0.887	1.672	20160525	1.332	1.313	1.531	3.326	20170911	1.332	1.346	1.337	1.969	20180402	1.430	1.484	1.216	5.291
15	20151122	1.188	0.786	1.534	20160526	1.437	1.418	1.969	3.497	20170912	1.473	1.460	1.456	3.571	20180403	1.214	1.391	0.940	5.128
16	20151123	1.318	0.879	1.818	20160527	1.421	1.406	1.605	3.425	20170913	1.404	1.479	1.395	4.255	20180404	1.372	1.558	1.709	5.405
17	20151124	1.225	0.847	1.658	20160529	1.448	1.427	1.664	3.436	20170914	1.461	1.449	1.471	4.292	20180405	1.460	1.739	1.504	6.061
18	20151125	1.233	0.759	1.555	20160530	1.332	1.313	1.531	3.326	20170915	1.275	1.370	1.325	4.329	20180406	1.300	1.382	1.529	5.329
19	20151126	1.224	0.765	1.592	20160531	1.331	1.258	1.531	3.226	20170916	1.118	1.214	1.229	3.891	20180407	1.307	1.370	1.656	5.405
20	20151127	1.304	0.832	1.678	20160601	1.459	1.404	1.701	3.731	20170917	1.362	1.364	1.447	4.762	20180408	1.270	1.502	1.412	5.848
21	20151128	1.287	0.821	1.667	20160602	1.482	1.387	1.730	3.861	20170918	1.461	1.488	1.595	5.263	20180409	1.332	1.489	1.380	4.980
22	20151129	1.475	0.912	1.946	20160603	1.437	1.361	1.684	3.559	20170919	1.332	1.346	1.337	3.299	20180410	1.115	1.326	1.155	5.263
23	20151130	1.254	0.844	1.685	20160604	1.437	1.422	1.754	3.546	20170920	1.449	1.555	1.669	3.299	20180411	1.332	1.489	0.834	3.125

**Table S4.** Calibration factors for the quantification of target VOCs during each field campaign. On days where there were issues with the calibration or it was not run, the average calibration factors for each compound and cruise were used (shown in bold).

**Table S5.** Compilation of mean  $\pm$  standard error (SE) of net biogenic VOC production rates (in units of nmol L<sup>-1</sup> h<sup>-1</sup>) during each field campaign. The ranges of observed values are shown in parentheses and the number of measurements above the detection limits and used in SE determinations are also displayed. The total number of measureable samples for each month is displayed in the header.

VOC	Nov	<i>n</i> = 14	Mar	<i>n</i> = 56	May	<i>n</i> = 50	Sept	<i>n</i> = 74	
Acetaldehyde	$-0.922 \pm 0.5$	4	$-0.358\pm0.6$	10	$1.73\pm0.7$	50	$-0.468 \pm 0.3$	61	
	(-2.76 – 1.61)	4	(-3.24 – 9.08)	10	(-3.47 – 14.4)	30	(-3.55 – 5.31)	01	
Acetone	10.2	1	$16.0 \pm 3$	6	$14.7 \pm 2$	20	$0.326\pm0.5$	16	
	-10.5	1	(-0.913 – 36.7)	0	(1.99 - 80.2)	30	(-1.82 – 13.7)	10	
Acetonitrile	$0.381\pm0.08$	$-0.186 \pm 0.02$	$-0.186 \pm 0.02$	50	$0.770\pm0.06$	50	$-0.0416 \pm 0.02$	71	
	(0.148 - 1.18)	14	(-0.289 – 0.268)	30	(0.0940 - 1.42)	30	(-0.232 - 0.283)	/4	
Dimethylsulfide	2 22	1	$2.02 \pm 0.5$	27	$14.7 \pm 2$	50	$3.30\pm0.5$	16	
	5.52	1	(-2.33 – 9.83)	(-0.958 - 43.3)		30	(-1.12 – 15.5)	40	
Isoprene	$2.11 \pm 0.4$	4	$2.96 \pm 0.3$	24	$8.19\pm0.7$	50	$1.17\pm0.04$	16	
	(1.09 - 3.91)	4	(1.25 - 10.3)	24	(1.79 - 26.3)	50	(0.828 - 1.65)		
Methanethiol	$3.08 \pm 0.3$	14	$1.51 \pm 0.3$	51	$1.79 \pm 0.1$	40	$2.42 \pm 0.3$	72	
	(1.90 - 4.87)	14	(-1.19 – 7.86) 54		(0.605 - 3.15)	49	(-0.0671 - 7.01)	13	
Methanol	$-140 \pm 2$	10	-116 ± 7	1 4	$127 \pm 6$	40	$203 \pm 22$	71	
	(-149 – -130)	10	(-1538.46)	14	(58.0 - 211)	48	(-3.16 - 859)	74	



**Figure S3.** Measurement locations and spatial overlap during the four NAAMES field campaigns (November 2015, May 2016, September 2017, March 2018). Months are displayed in pairs for ease of comparison. Note that there is no overlap between the transect in May with either March or September.



Figure S4 (continued below).



**Figure S4.** A) Measurement locations during four field campaigns in the North Atlantic Ocean, where month is indicated by color and shape. Grey boxes in the left-hand panel indicate the data range selected to investigate north-to-south gradients (between 44 and 38 °W) and west-to-east gradients (between 40 and 44 °N). B) Net production rates of our target VOCs along a north-to-south transect. Data is only shown for the May and September field campaigns due to the lack of latitudinal variability and overlap obtained during November and March. C) Net production rates for the same compounds along a west-to-east gradient. Data is not shown for May due to the limited number of measurements. Net rates of zero are indicated by the dotted grey vertical lines in panels B and C. Where >50% of the concentrations for a given rate measurement were below detection limits, rates were not calculated, and the locations of these samples are represented by '×'.

VOC	Net production rates, this study (nmol L <sup>-1</sup> h <sup>-1</sup> )	Net production rates (nmol L <sup>-1</sup> h <sup>-1</sup> )*	References
Acetaldehyde	-3.55 - 14.4	-0.23 - 1.8	(Dixon et al., 2013)
microbial	-	-310.78	(Dixon et al., 2013;
oxidation			Beale et al., 2015; de
			Bruyn et al., 2017)
Acetone	-10.3 - 80.2	-0.13 - 1.55	(Dixon et al., 2013)
microbial	-	-0.0420.001	(Dixon et al., 2013,
oxidation			2014)
Acetonitrile	-0.289 - 1.42	-	-
Dimethylsulfide	-2.33 - 43.3	-0.1 - 0.3	(Royer et al., 2016)
microbial	-	-0.37 - 0.0008	(Hopkins and Archer,
oxidation			2014) and references
			therein
Isoprene	0.828 - 26.3	1-7 pM 10 <sup>6</sup> cells <sup>-1</sup> d <sup>-1</sup>	(Milne et al., 1995)
Methanethiol	-1.19 - 7.86	-	-
Methanol	-153 - 859	-19 - 7.8	(Dixon et al., 2013)
microbial	_	-11.20.09	(Dixon et al., 2011a,
oxidation			2011b, 2013; Sargeant
			et al., 2016)

**Table S6.** Ranges of reported target VOC production rates (*and microbial oxidation rates*) in natural seawater (<200 m) during this study and available in the literature.

<sup>\*</sup> Dixon et al. (2013) report daily net production rates (nmol  $L^{-1} d^{-1}$ ) from the sum of incubations under 12-h light and 12-h dark conditions, respectively. Here, we report the range of net production rates from individual 12-h incubations on a per-hour basis. The same is also true for microbial oxidation rates originally reported from 24-h incubation periods. Note the different units for net isoprene production. **Table S7.** Ranges of target VOC concentrations in seawater (<200 m) reported in the literature. A more detailed list of references and a breakdown of locations can be found in Table 4 (Wohl et al., 2020) – we only provide additional references not included therein.

VOC	Concentrations in seawater (nM)	Additional references(Wohl et
		al., 2020)
Acetaldehyde	1-37	
Acetone	1.4-67.8	(Dixon et al., 2014)
Acetonitrile	4-12	(Williams et al., 2004)
Dimethylsulfide	0-316	(Williams et al., 2004; Srikanta
		Dani et al., 2017)
Isoprene	0.001-0.541	(Dani and Loreto, 2017)
Methanethiol	0.02-2	(Eyice et al., 2017)
Methanol	7-361	



**Figure S5.** Monthly medians and range of ancillary nutrient and plankton metrics collected during stations on each of the NAAMES field campaigns. Abbreviations are as follows:  $PAR_{max} = daily$  maximum photosynthetically active radiation,  $T_{air} = atmospheric temperature$ ,  $T_{sea} = sea$  surface temperature, NPP = net primary productivity, Phyto\_total = total phytoplankton abundance (sum of nanoeukaryotes, picoeukaryotes, prochlorococcus, and synechococcus cells), BP = bacterial production, BA = bacterial abundance, DOC = dissolved organic carbon, POC = particulate organic carbon, and TDN = total dissolved nitrogen.



**Figure S6.** Spearman's rank correlations with ancillary data collected during the NAAMES campaigns. Values of  $r_s$  are displayed and represented by the colour shading (red = positive correlation, blue = negative correlation) and those in bold were statistically significant (p < 0.05). Abbreviations are as follows: T\_sea, sea surface temperature; PAR, photosynthetically active radiation; BA, bacterial abundance; BP, bacterial production; NPP, net primary production; Phyto\_total, total phytoplankton abundance; NANO\_pcnt, percentage abundance of nanoeukaryotic cells (and subsequently PICO, picoeukaryotes; PRO, prochlorococcus; SYN, synechococcus); Chl.a, chlorophyll-a concentration; DOC, dissolved organic carbon; POC, particulate organic carbon; Ace\_sw, sea surface concentration of acetone; DMS\_sw, sea surface concentration of dimethylsulfide; and DMS\_air, atmospheric concentration of dimethylsulfide.



**Figure S7.** Sea surface temperature and inline chlorophyll-a concentrations (A), seawater acetone concentrations (B), and bacterial productivity and abundance (C) against latitude during the May 2016 cruise.



**Figure S8.** Latitudinal gradients of nutrients across each of the NAAMES field campaigns. Note the different concentration units for DOC. Abbreviations are as follows: DOC = dissolved organic carbon, TDN = total dissolved nitrogen, NH4 = ammonium, PO4 = phosphate, SiO4 = silicate,  $NO2_NO3 = nitrite$  to nitrate, and NO2 = nitrite.

**Table S8.** Selected physico-chemical properties of our target VOCs at 25 °C. All values were estimated using the EPI (Estimation Programs Interface) Suite (US EPA, 2017) software developed by the United States Environmental Protection Agency.

VOC	Vapor pressure (Pa)	Henry's constant (Pa m <sup>3</sup> mol <sup>-1</sup> )	Water solubility (mg L <sup>-1</sup> )
Acetaldehyde	$1.2 \times 10^5$	6.87	$2.6 \times 10^5$
Acetone	$3.1 \times 10^4$	5.02	$2.2 \times 10^5$
Acetonitrile	$1.2 \mathrm{x} 10^4$	3.10	$1.4 \mathrm{x} 10^5$
Dimethylsulfide	$6.7 \times 10^4$	79.6	$2.2 \times 10^4$
Isoprene	$7.3 \times 10^4$	12400	$3.4 \times 10^2$
Methanethiol	$2.0 \times 10^5$	265	$2.9 \times 10^4$
Methanol	$1.7 \mathrm{x} 10^4$	0.43	$1.0 \times 10^{6}$

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