



Supplement of

Concentrations of dissolved dimethyl sulfide (DMS), methanethiol and other trace gases in context of microbial communities from the temperate Atlantic to the Arctic Ocean

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Supplement S1

Table S1: Sea-ice stations north of 80°N where vertical profiles were obtained

Station	Date/Time (UTC)	Latitude	Longitude	Sampling depths (m)
PS92/19_05	28/05/2015 06:28	81° 10.43' N	19° 08.07' E	0.5-10-20-30-40-50
PS92/27_03	31/05/2015 06:52	81° 23.13' N	17° 35.13' E	0.5-10-20-30-40-50
PS92/31_03	03/06/2015 11:44	81° 37.20' N	19° 25.64' E	0.5-10-25-30-40-50
PS92/32_05	06/06/2015 20:04	81° 13.76' N	19° 26.63' E	0.5-10-25-30-40-50
PS92/39_08	11/06/2015 15:05	81° 55.04' N	13° 27.55' E	0.5-10-20-30-40-50
PS92/43_05	15/06/2015 04:45	82° 12.67' N	07° 35.30' E	0.5-10-20-30-40-50
PS92/46_02	15/06/2015 04:45	82° 12.67' N	07° 35.30' E	0.5-10-20-30-40-50
PS92/47_04	19/06/2015 12:03	81° 20.80' N	13° 36.56' E	0.5-10-20-30-40-50

Supplement S2

Biological measurements

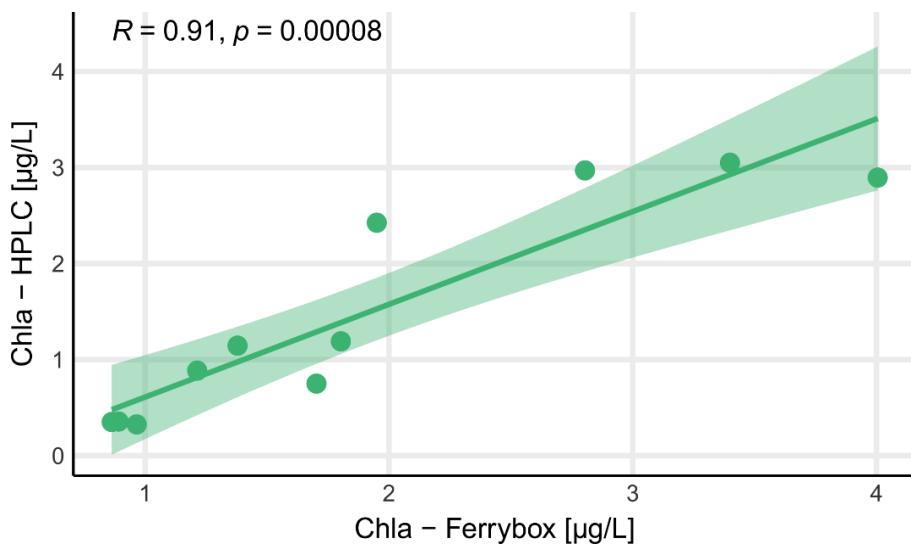


Figure S1: Relationship between chlorophyll a concentrations obtained from HPLC and Ferrybox.

Bacterial community analyses

16S rRNA gene amplicon libraries were prepared according to the standard instructions of the 16S Metagenomic Sequencing Library Preparation protocol (Illumina, San Diego, CA). The hypervariable V4–V5 region was amplified using primers 515F (GTGYCAGCMGCCGCGTAA) and 926R (CCGYCAATTYMTTTRAGTTT). Sequences were obtained on an Illumina MiSeq platform in 2x300 bp paired-end runs at CeBiTec (Bielefeld, Germany). Primer were clipped using cutadapt, and reads processed into amplicon sequence variants (ASVs) following the standard DADA2 workflow at <https://benjineb.github.io/dada2/tutorial.html>. Filtering settings were truncLen=c(230,195), maxN=0, minQ=2, maxEE=c(3,3) and truncQ=0, followed by merging using minOverlap=10, chimera removal and taxonomic classificaton using the Silva v138 database. Data was processed in RStudio using R v4.1.1 and packages phyloseq, vegan, iNEXT, tidyverse, psych and scico, with aesthetic modifications of figures using Inkscape (<https://inkscape.org>). We obtained on average 85,000 quality-controlled, chimera-filtered reads per sample (Table S2) sufficiently covering community composition (Fig. S2). The complete amplicon workflow is available under <https://github.com/matthiaswietz/transsiz>.

Table S2: Amplicon-sequenced samples, showing read counts at each step of the DADA2 pipeline.

sample_title	Date	Lat	Lon	input	filtered	denoised	merged	nochim	tabled
PS92 Auto2	21.05.2015	60.35920	3.29927	118097	98967	98357	82764	82764	80333
PS92 Auto3	21.05.2015	62.38333	3.35833	92223	78393	78082	70022	70022	67872
PS92 Auto4	22.05.2015	64.52022	3.55040	131377	110858	110483	93018	93018	90123
PS92 Auto5	22.05.2015	64.94027	3.58943	129259	109748	109459	104074	104074	98374
PS92 Auto6	22.05.2015	65.90325	3.64348	159876	139180	138735	126581	126581	122124
PS92 Auto7	22.05.2015	66.35847	3.72702	94039	79638	79452	66107	66107	64204
PS92 Auto8	22.05.2015	66.76948	3.76842	147626	123900	123608	98729	98729	94205
PS92 Auto9	23.05.2015	67.31610	3.82471	88694	75721	75541	64079	64079	61492
PS92 Auto10	23.05.2015	67.89882	3.88550	103359	83813	83655	69791	69791	66430
PS92 Auto11	23.05.2015	68.33135	3.91565	85213	72459	72343	59608	59608	57793
PS92 Auto12	23.05.2015	68.68500	3.97063	130307	108826	108595	95159	95159	91516
PS92 Auto13	23.05.2015	69.28850	4.01345	80729	67543	67404	55925	55925	54072
PS92 Auto14	23.05.2015	69.49642	4.01595	121385	104120	103898	93522	93522	89969
PS92 Auto15	24.05.2015	70.00000	10.00000	102120	86176	85987	77672	77672	74763
PS92 Auto16	24.05.2015	70.22695	13.14900	114758	98526	98230	87839	87839	83624
PS92 Auto17	25.05.2015	73.25000	12.25000	128590	108477	108250	91623	91623	88079
PS92 Auto18	25.05.2015	74.13037	11.69167	138591	116132	115847	104990	104990	100890
PS92 Auto19	25.05.2015	74.84322	11.20822	108687	91919	91697	87735	87735	82825
PS92 Auto20	26.05.2015	75.51768	10.72912	179367	152923	152479	146291	146291	137753
PS92 Auto21	26.05.2015	76.76033	9.78639	137058	115973	115657	109506	109506	104299
PS92 Auto22	26.05.2015	77.27977	9.35135	164814	141216	140814	129011	129011	124403
PS92 Auto23	27.05.2015	80.87068	18.44780	123060	102837	102585	96182	96182	91236
PS92 Auto24	27.05.2015	81.01718	19.84131	111661	93595	93043	84908	84908	79382
PS92 Auto25	28.05.2015	81.17000	19.13450	133543	112984	112116	103696	103696	97757
PS92 Auto26	28.05.2015	81.19041	19.09177	143276	122930	122362	107995	107995	102390
PS92 Auto27	29.05.2015	81.20624	18.69745	87506	74860	74472	61118	61118	58023
PS92 Auto28	29.05.2015	81.22513	18.58100	158441	138134	137782	129089	129089	121849
PS92 Auto31	30.05.2015	81.23292	18.76116	107153	91266	91018	81765	81765	77238
PS92 Auto33	01.06.2015	81.32160	17.30839	146149	124768	124324	111819	111819	107371
PS92 Auto34	02.06.2015	81.52571	19.44756	122832	105891	105552	95344	95344	89608
PS92 Auto35	03.06.2015	81.55412	19.51593	89976	73560	73331	57493	57493	55347
PS92 Auto36	04.06.2015	81.52757	18.65566	81157	68831	68620	62260	62260	58519
PS92 Auto38	11.06.2015	81.90915	13.40468	72012	59645	59380	49796	49796	48994
PS92 Auto39	15.06.2015	82.20975	7.38825	97048	82690	82426	70980	70980	69627

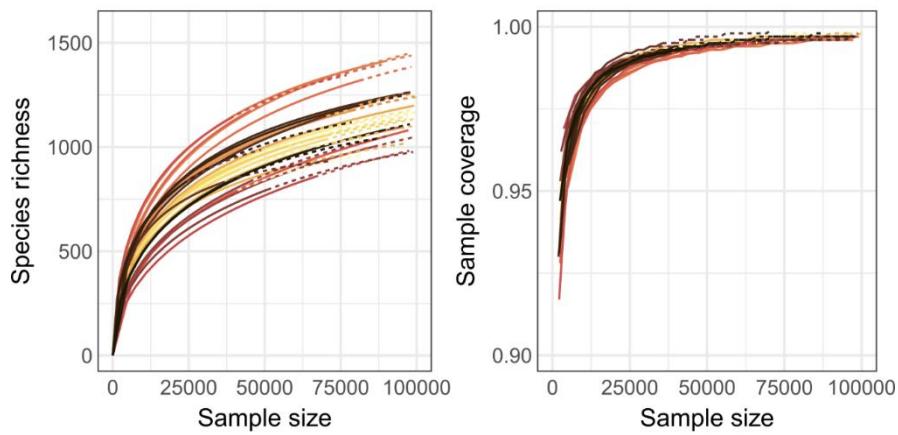


Figure S2: Rarefaction (left) and coverage (right) analyses of amplicon sequence variants, showing that community composition was sufficiently covered. Each coloured line corresponds to an individual sample.

Supplement S3

Extraction system

Dissolved gases in seawater were quantified in the headspace of a glass cell, where gases were extracted by stripping with zero air at a flow rate of 100 mL/min. Three mini-water liquid diaphragm pumps KNF (type FEM 1.02.KT.18S. KNF (KNF Neuberger, IncTrenton, New Jersey USA) were used for the injection and circulation of seawater in the cell at 20 mL/min. Before entering the extraction cell, the water went through a mixing cell which was used for injection of a calibrated solution. For calibration, secondary standard liquid solutions were injected at a flow rate of 250 μ L/min via a fine metering pump (World Precision Instruments; Hitchin, Hertfordshire, UK), and diluted in an identical flow of 20 mL/min of pure distilled water. Figure S3 shows a schematic view of the extraction device.

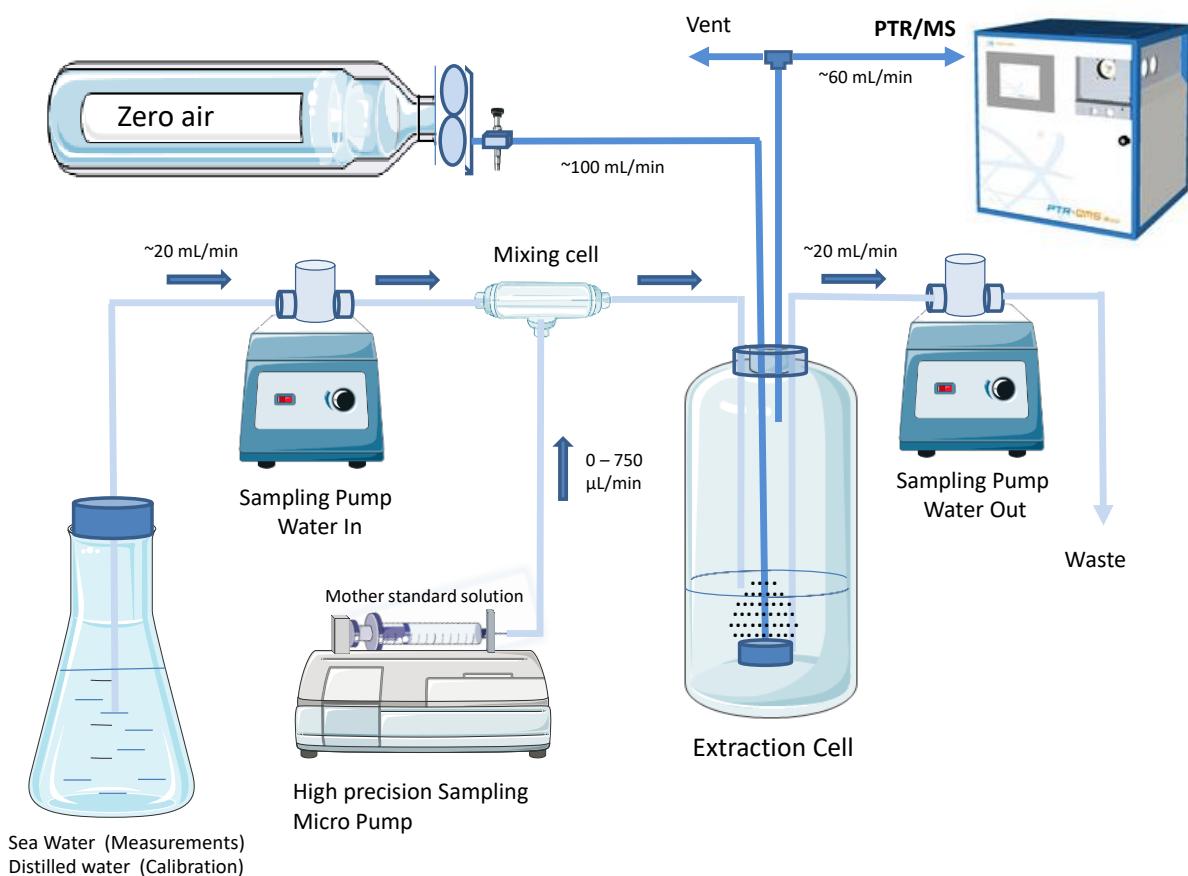


Figure S3: Schematic view of the extraction system

Supplement S4

Calibration procedure, detection limit and evaluation of uncertainties

For the calibration, stock solutions were prepared from pure substances (Sigma Aldrich) diluted in distilled water: isoprene (1.0×10^{-4} M), dimethylsulphide (2.7×10^{-3} M), acetaldehyde (8.95×10^{-3} M), acetone (2.73×10^{-2} M), acetonitrile (7.67×10^{-3} M), and methanol (1.24×10^{-1} M), all stored at 4°C . Secondary standard liquid solutions were prepared immediately before the calibrations from a dilution of 2×10^{-4} (0.2 mL/L) in distilled water. The injection of liquid standard was achieved by dilution of stock solution in distilled water by a high-precision micropump. The calibration factor was expressed as the ratio of the concentration of a given VOC in water (nmol/L or pmol/L) to the concentration in the head space (ppbv) measured by PTR/MS. An example is given for the calibration for acetone (Fig. S4), with excellent linearity between the PPB measured in the headspace by PTRMS and the concentration in water. Experimentally this calibration factor is very close to the Henry's law constant (expressed in mol/L per atmosphere) irrespective of a compound solubility over 4 to 5 orders of magnitude (Fig. S5). Therefore, knowing the Henry's law constant, measurements can be reasonably extrapolated to new compounds detected in water which have not been previously calibrated (such as methanethiol).

Concerning the gas-phase calibration, a complete calibration had been done one month before the campaign in the laboratory using a calibration unit (Ionicon Analytik) and by injecting different amounts of a calibration gas mixture (Ionicon), allowing to derive sensitivity ncps/ppb for all compounds contained in the standard (methanol, acetaldehyde, acetonitrile, acetone and isoprene were of interest for this study). On the same day, a gas cylinder has been measured and brought on-board in order to check the stability of the detection (at the beginning and in the middle of the campaign). As lab- and ship-based results (in ncps) were congruent, the lab-determined calibration coefficients were used for the campaign. As the standard did not include DMS, the calibration was done directly on water using the relation between ncps of DMS and concentrations of compounds in the injected standard. The sensitivity of MeSH (m/z 49) has been determined by taking an average sensitivity factor (13.4 ncps/ppb) between the sensitivity from the two "neighbouring" compounds (m/z 45, acetaldehyde and m/z 59, acetone) with similar sensitivity (within 6%, 13.0 ncps/ ppb and 13.8 ncps/ppb respectively).

During the campaign, a blank of the system was determined by injecting only the extraction gas through the system, taking into account the instrumental background noise from the instrument and potentially residual VOCs in the extraction gas. This value was subtracted from all measurements. The detection limit was estimated as 3 sigma of the blank variability, varying from 0.3 nM (for acetonitrile) to 3 nM (for acetone and acetaldehyde). Some values in Fig. 2 are below the estimated detection limit for acetone and acetaldehyde; which is due to the subtraction of the blank (the measured signal was above the detection limit).

A complete estimation on the gas-phase measurement of this PTRMS has been performed in Baudic et al. (2016). This estimation, based on the ACTRIS measurement guidelines VOC 2014 (see Debevec et al., 2017), calculates the expanded uncertainty of $U(X)$ as

$$U(X) = k \times u(X) + DL_x/3$$

With k being the coverage factor (here 2), $u(X)$ the combined uncertainty in X , and DL_x the detection limit of the species X . The combined uncertainty includes errors on standard gas, calibrations, blanks, reproducibility/repeatability, linearity, and relative humidity parameters. This expanded uncertainty has a maximum of 21% (21%, 18%, 9% and 10% for m/z 42, 45, 59 and 69 respectively). We do not give here the detailed contribution of each factor, as those calculations were not done specifically for this campaign. Nevertheless, we note that the two main sources contributing to the overall uncertainty were due to linearity error and to the uncertainty of VOC concentrations in the calibration standard gas. An additional uncertainty is the conversion of gaseous ppb into nM (based on the error of the calibration linearity, see calibration example for acetone in S4a). The overall uncertainty was then estimated at 21%, 32%, 11% and 11% for m/z 42, 45, 59 and 69 respectively. Therefore, the uncertainty for the calibrated compounds (including DMS, which was not present in the gas-phase standard but which has been calibrated with a liquid standard) has been estimated at about 30%.

As MeSH has been quantified using a sensitivity coefficient based on the average of the sensitivity of acetaldehyde and acetone, we assessed the uncertainty by comparing (i) to an averaged sensitivity coefficient, and (ii) to an estimated DMS sensitivity coefficient. For (i), the average sensitivity coefficient of 9.4 ncps/ppb represents the mean of 10 sensitivity coefficients (determined for m/z 33, 42, 45, 59, 69, 71, 73, 79, 93 and 107). If applying such a sensitivity coefficient to MeSH, it would increase concentrations by a factor of 1.43. As mentioned, DMS was not present in the standard that we had at that time. Recently, we have purchased a NPL (National Physics Laboratory, Teddington, UK) standard containing a series of compounds, including acetaldehyde, acetone and DMS. We have performed three calibrations (on different days) in the laboratory with the same PTRMS used during TRANSSIZ. Taking into account the ratio of the DMS sensitivity (14.4 ncps/ppb) compared to an average of acetaldehyde-acetone sensitivity (21.2 ncps/ppb) we obtained a value of 1.47, hence almost identical to the first evaluation. Overall, we conclude that due to the absence of a calibrated standard for MeSH, concentrations reported in this paper might be underestimated by a factor of ~1.5.

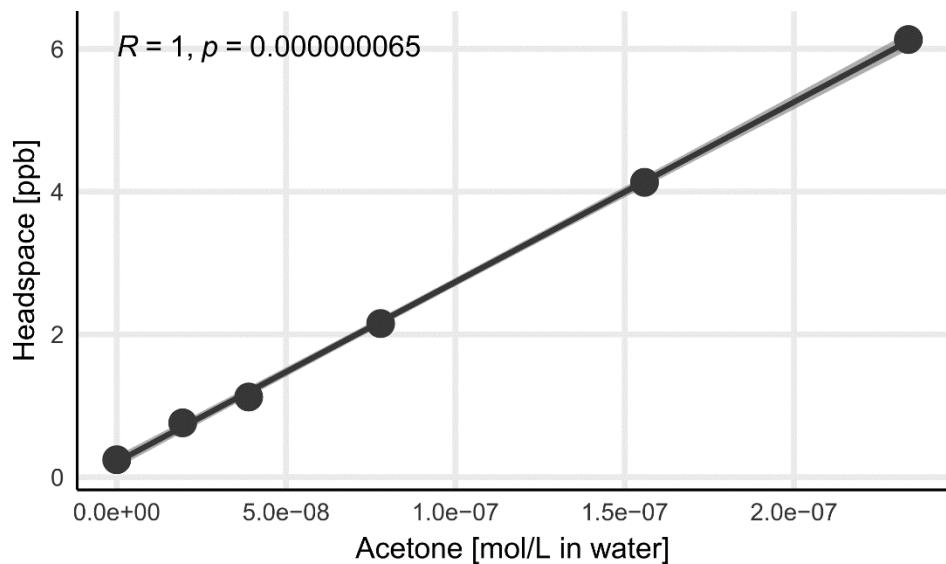


Figure S4a: Calibration of acetone performed on-board

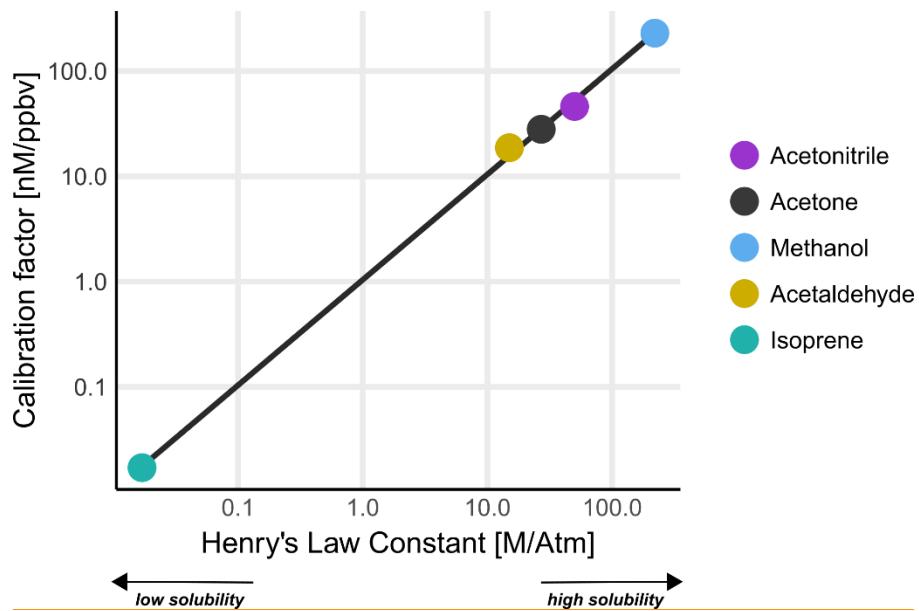


Figure S4b: Calibration factor against Henry's law constant

Supplement S5

Vertical profiles of selected phytoplankton groups

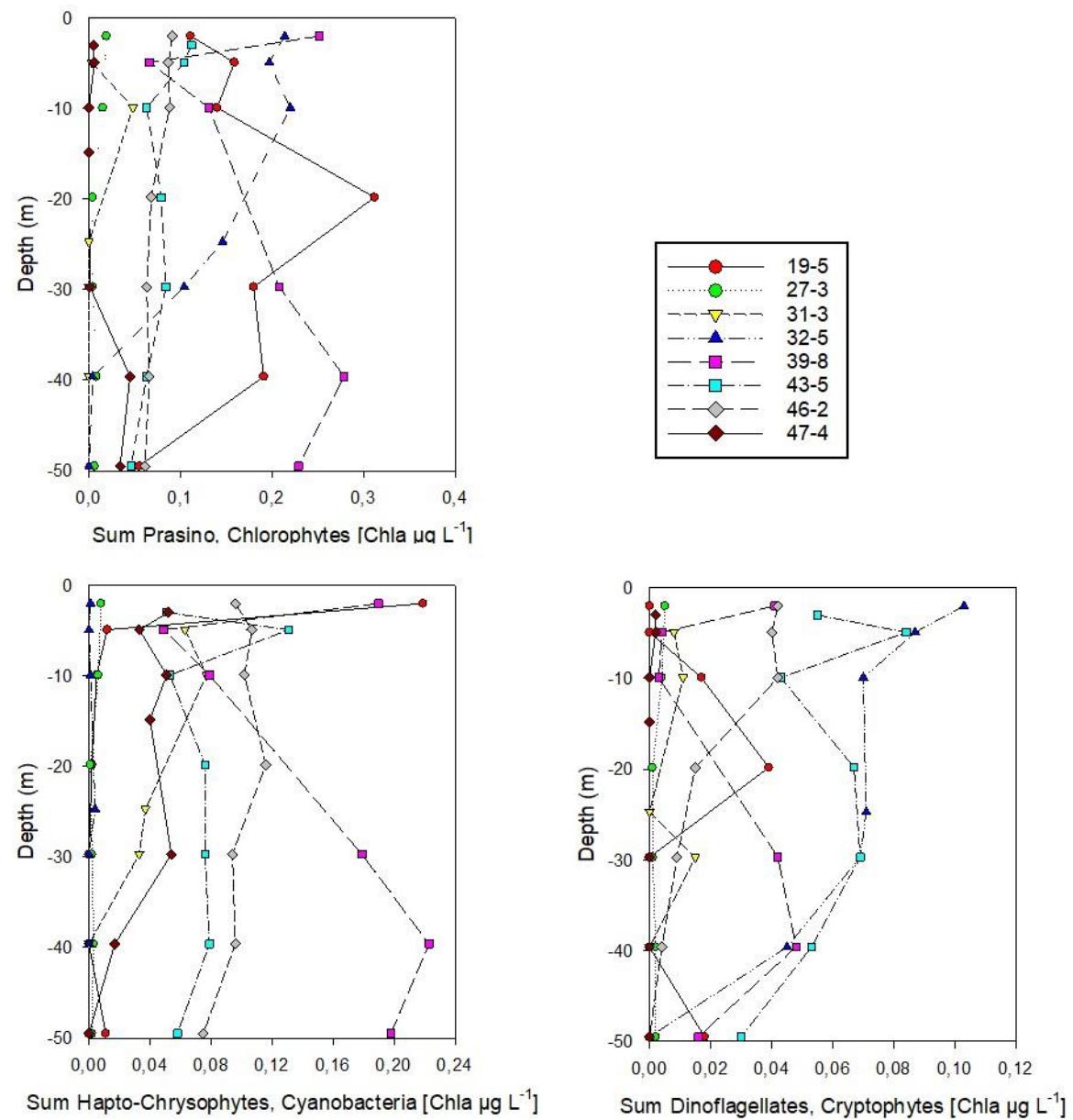


Figure S5: Vertical distribution (0-50 m depth) of selected phytoplankton groups at sea-ice covered stations north of 80°N. According to Dybwad et al., (2021) stations 39, 43, 46 (Yermak Plateau) were in pre-bloom phase, while all other stations were in a bloom phase. Stations 19 and 32 were shelf stations. The contribution of the phytoplankton groups is expressed as Chl a concentrations. Data are available at Peeken et al. (2023).

Supplement S6

Correlation between selected trace gases and Chl a

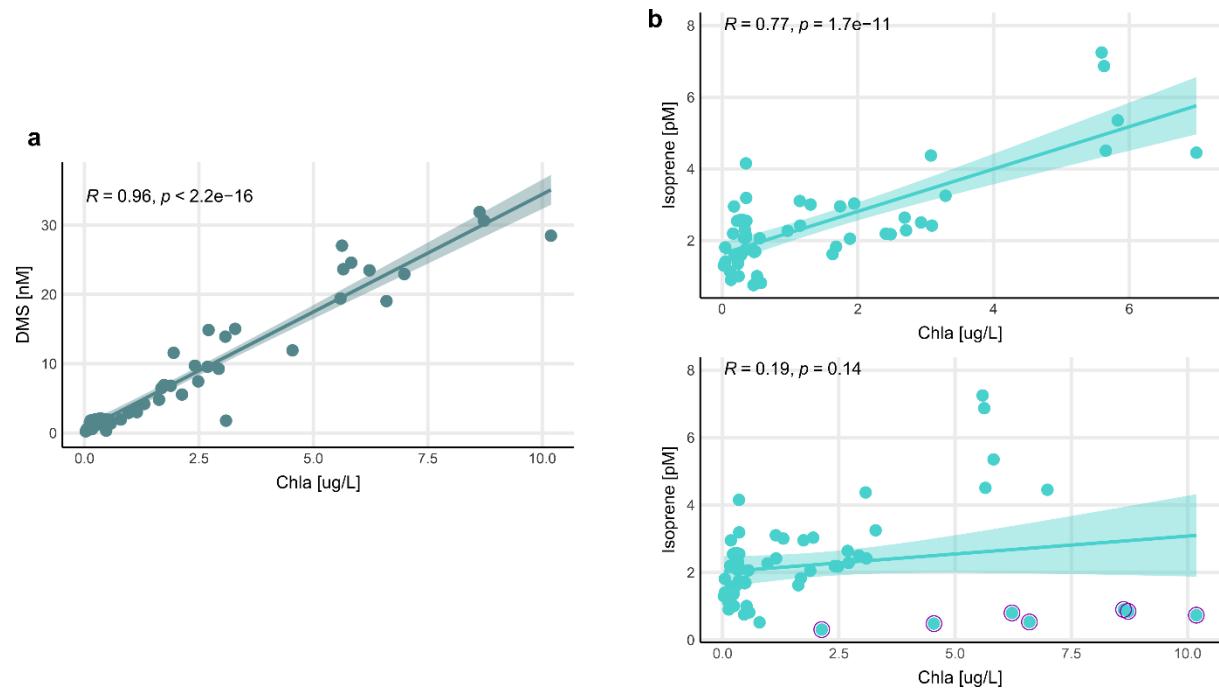


Figure S6: Correlations of DMS (a) and isoprene (b) with Chl a at sea-ice stations north of 80°N. Correlations with isoprene were only significant when excluding station 19 (upper panel; see explanation in the main text). The lower panel includes all data points north of 80°N. Data from station 19 are encircled in purple.

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