

Comments from the reviewer are in black; answer to the reviewer are in blue, new adding to the text are in black and italics.

Reviewer 2

General Comments

This manuscript describes a comprehensive set of dissolved reactive gas and microbiological measurements taken on a research cruise from the North Atlantic to the Arctic. The authors extensively discuss the sources and relationships between the measured trace gases and microbiology, and focus their discussion on dimethyl sulfide (DMS) and methanethiol (MeSH). They show that MeSH does not correlate with DMS during the entirety of the cruise. They find that MeSH can contribute on average 20%, and up to 50%, to the total waterside sulfur budget, defined by the sum of DMS and MeSH. Overall, this manuscript is well-structured and presents new findings that are valuable to the biogeosciences and atmospheric chemistry communities and should be published after the following main comments are addressed. My main comment for this manuscript is that a more nuanced discussion of variations in the measured $\text{MeSH}/(\text{DMS}+\text{MeSH})$ ratio and the dominant factors controlling it would be extremely helpful. Little information currently exists on how this ratio varies based on environmental parameters, which has impacts for how we think about SO_2 production.

This dataset provides measurements of MeSH in a region for the first time with varying temperature and salinity, meaning that we now have data to form more accurate models of SO_2 production based on how this ratio scales with different waterside parameters.

We thank the reviewer for the overall positive evaluation of our manuscript and for the useful comments and suggestions. We address the different points in the sections below.

Suggestions for discussion on this topic include:

Addition of a column containing $\text{MeSH}/(\text{DMS}+\text{MeSH})$ to Table 1. Can any trends from the water classifications (salinity, temperature) explain the observed variations?

In line 371-372, it's noted that at 78.6 °N, MeSH contributes up to 50% of total sulfur, but only 20-40% in 70-75°N. What is driving this difference? all this needs more discussion, check in detail

Looking at Fig. 2, it looks like in some regions MeSH and DMS covary (>71°N) and in some regions, there is little correlation (<68°N). Some more statistical analysis and discussion of why there seems to be a correlation in certain water masses/time periods but not others would be useful.

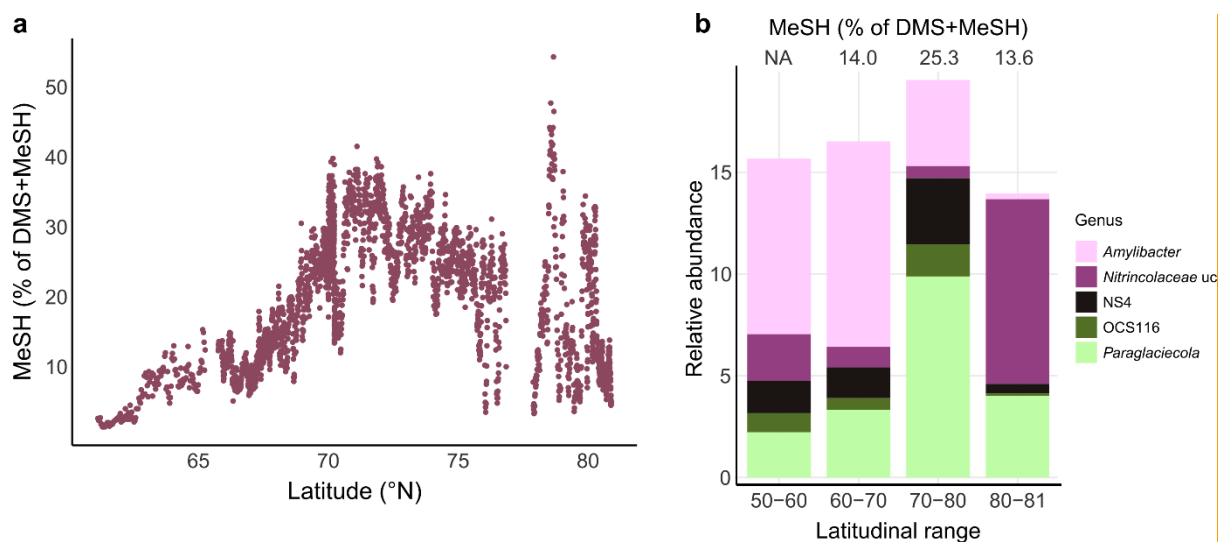
Fig 5 could be revised to provide more information about any environmental parameters controlling this ratio (colored points by salinity, temperature, chlorophyll?) or additional regressions against these variables instead of just latitude.

We thank the reviewer for the suggestions how to improve the discussion on MeSH/(MeSH+DMS). We have added the MeSH / (MeSH +DMS) ratio to Table 1 (see below), showing that this ratio was higher in Atlantic (wAW and fAW) than in Polar waters. However, we did not find any significant global correlation between the ratio and environmental parameters (chl-a, temperature). We have tested coloring the dots in Fig.5 by environmental parameters, but found it provided little additional information. Nevertheless, to highlight the latitudinal variability and possible underlying links, we have added Fig. 5b showing major bacterial genera that vary by latitudinal ranges and their specific MeSH / (MeSH +DMS) ratios. In addition to the figure, we have added the following text (new text in italics and bold):

Comparable to some North Sea locations (Leck and Rodhe, 1991), MeSH contributed up to 40% between 70°N-75°N, with a maximum of 50% at 78.6°N (Fig. 5a). ***This latitudinal variability*** was underlined by shifts in major bacterial genera. ***For instance, Paraglaciecola (Gammaproteobacteria), NS4 (Bacteroidetes) peaked together with the highest MeSH fraction between 70-80°N. Amylibacter decreased towards the north, whereas unclassified Nitrospiraceae prevailed >80°N together with an again smaller MeSH/DMS ratio.*** The overall MeSH contribution of 20% suggests that MeSH represents a considerable fraction of sulphur, being linked to microbial dynamics. Accordingly, we found several correlations with the abundance of specific ASVs. Correlations between *Yoonia-Loktanella* and *Asciidiaceihabitans* ASVs with MeSH reflected the prominent role of *Rhodobacteraceae* in DMSP demethylation (Curson et al., 2011; Moran et al., 2012). The positive link of SAR11 and SUP05 ASVs corresponds to the prevalence of DMSP-metabolizing genes in these taxa (Nowinski et al., 2019; Landa et al., 2019; Sun et al., 2016). The link between cyanobacteria and MeSH was notable, since DMSP-utilizing genes appear to be rare in cyanobacteria (Liu et al., 2018). Hence, there might be indirect effects on other photosynthetic organisms, indicating yet undescribed chemical linkages among primary producers.

| | Acetonitrile (nM) | Acetaldehyde (nM) | Acetone (nM) | DMS (nM) | Methanethiol (nM) MeSH/(MeSH +DMS) | Isoprene (pM) | CO (nM) |
|--|----------------------------|-----------------------------|--------------------------|-------------------------------|---------------------------------------|------------------------------------|-------------------------------------|
| Coastal-influenced/low-salinity Atlantic Water (AWs; $\theta > 5^\circ\text{C}$, $S < 34.4$) | 1.1 ± 0.6 | 19.7 ± 8.0 | 23.3 ± 12.8 | 15.7 ± 7.0 | 0.8 ± 0.7 5.6 ± 7.1 | 2.6 ± 0.8 $23.4 \pm 3.10^*$ | 10.7 ± 3.1 $2.50 \pm 1.70^*$ |
| warm Atlantic Water (wAW; $\theta > 2^\circ\text{C}$, $S > 34.9$) | 0.5 ± 0.2 | 4.8 ± 4.0 | 2.4 ± 5.9 | 11.8 ± 7.0 | 2.9 ± 1.5 21.9 ± 8.7 | 1.4 ± 0.7 $42.5 \pm 49.6^*$ | 5.9 ± 2.8 $3.3 \pm 2.2^*$ |
| freshened Atlantic Water (fAW; $\theta > 1^\circ\text{C}$, $34.4 < S < 34.9$) | 0.9 ± 0.4 | 9.8 ± 5.6 | 14.6 ± 10.8 | 13.1 ± 8.8 | 3.3 ± 1.5 20.7 ± 10.6 | 2.7 ± 1.5 $24.8 \pm 19.1^*$ | 10.2 ± 5.9 $3.4 \pm 2.4^*$ |
| cold Polar Water (cPW; $\theta < 0^\circ\text{C}$, $S < 34.7$) | 0.3 ± 0.1 | 1.0 ± 2.3 | BDL | 30.0 ± 9.3 | 2.8 ± 0.8 9.1 ± 2.3 | 1.2 ± 0.5 | 5.0 ± 2.8 |
| warm Polar Water (wPW; $\theta > 0^\circ\text{C}$, $S < 34.4$) | 0.2 ± 0.1 | 0.3 ± 0.9 | BDL | 34.7 ± 8.5 | 3.5 ± 0.3 9.6 ± 2.0 | 1.1 ± 0.3 | 7.8 ± 2.1 |
| Polar waters (PW) (cold+warm) | 0.3 ± 0.1 | 0.8 ± 2.1 | BDL | 31.2 ± 9.3 | 3.0 ± 0.7 9.2 ± 2.2 | 1.2 ± 0.4 $14.5 \pm 11.5^*$ | 5.9 ± 2.9 $6.5 \pm 3.2^*$ |
| Surface water at sea-ice stations $> 80^\circ\text{N}$ (range) | 0.3 ± 0.1 (0.2-0.5) | 7.2 ± 4.4 (0.3-14.2) | 2.3 ± 2.8 (0-6.9) | 11.2 ± 10.9 (1.6-31.9) | 0.1 ± 0.2 (0.02-0.5) | 3.2 ± 2.1 (0.9-7.3) | 1.5 ± 1.7 (0.2-4.3) |

New Table 1



New Fig. 5, with added panel Fig. 5b: Relative abundance of selected bacterial genera by latitudinal range and associated MeSH/DMS ratio. NA: not available; uc: unclassified.

Specific Comments – Manuscript

Line 19: It would be helpful to make it clear somewhere in the abstract that all gas measurements are in the dissolved phase in the seawater and not in the air. Potentially could also add “dissolved” to title.

Dissolved has been added to the title (and “concentrations” replaced by “variability” to answer a suggestion of reviewer 3). The new title reads:

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

Line 39: Instead of “rapidly oxidized”, can you state the atmospheric lifetime of DMS?

Has been changed to:

“DMS is rapidly oxidized once emitted to the atmosphere (average lifetime of 1 day)”

Line 40: It would be useful to add some references to the CLAW hypothesis. Some suggestions:

Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem.*, 14, 315–337, <https://doi.org/10.1007/BF00115242>, 1992.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, 326, 655–661, <https://doi.org/10.1038/326655a0>, 1987.

Line 41: Suggested references for DMSP demethylation producing MeSH:

Kiene, R. P.: Production of methanethiol from dimethylsulfoniopropionate in marine surface waters, *Mar. Chem.*, 54

Kiene, R. P. and Linn, L. J.: The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: tracer studies using ³⁵S-DMSP, *Geochim. Cosmochim. Ac.*, 64, 2797–2810, [https://doi.org/10.1016/S0016-7037\(00\)00399-9](https://doi.org/10.1016/S0016-7037(00)00399-9), 2000b.

Line 42: The atmospheric impacts of MeSH are less well-characterized than DMS, but we do know some about MeSH impacts based on its oxidation and reactivity. See references

below:

Butkovskaya, N. I. and Setser, D. W.: Product Branching Fractions and Kinetic Isotope

Effects for the Reactions of OH and OD Radicals with CH₃SH and CH₃SD, *J. Phys. Chem. A*, 103, 6921– 6929, <https://doi.org/10.1021/jp9914828>, 1999.

Tyndall, G. S. and Ravishankara, A. R.: Atmospheric oxidation of reduced sulfur species, *Int. J. Chem. Kinet.*, 23, 483–527, <https://doi.org/10.1002/kin.550230604>, 1991

Novak, G. A.; Kilgour, D. B.; Jernigan, C. M.; Vermeuel, M. P.; Bertram, T. H. Oceanic Emissions of Dimethyl Sulfide and Methanethiol and Their Contribution to Sulfur Dioxide Production in the Marine Atmosphere. *Atmospheric Chem. Phys.* 2022, 22 (9), 6309–6325. <https://doi.org/10.5194/acp-22-6309-2022>.

Line 49: Isoprene has also been shown to have a photochemical source.

Ciuraru, R.; Fine, L.; Pinxteren, M. van; D'Anna, B.; Herrmann, H.; George, C. Unravelling New Processes at Interfaces: Photochemical Isoprene Production at the Sea Surface. *Sci. Technol.* 2015, 49 (22), 13199–13205. <https://doi.org/10.1021/acs.est.5b02388>.

Line 52-53: Add a citation for OVOCs affecting the oxidative capacity of the remote atmosphere. Potentially this one could work:

Singh et al. (2004). Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. *Journal of Geophysical Research Atmospheres*.

[We thank the reviewer for the suggested references, which have been included in the text.](#)

Lines 55-59: Acetone, methanol, acetonitrile, and acetaldehyde can also be anthropogenic, affecting whether the net flux is positive or negative. It is worth adding this in addition to whether the flux is positive or negative depending on oligotrophic water.

Added

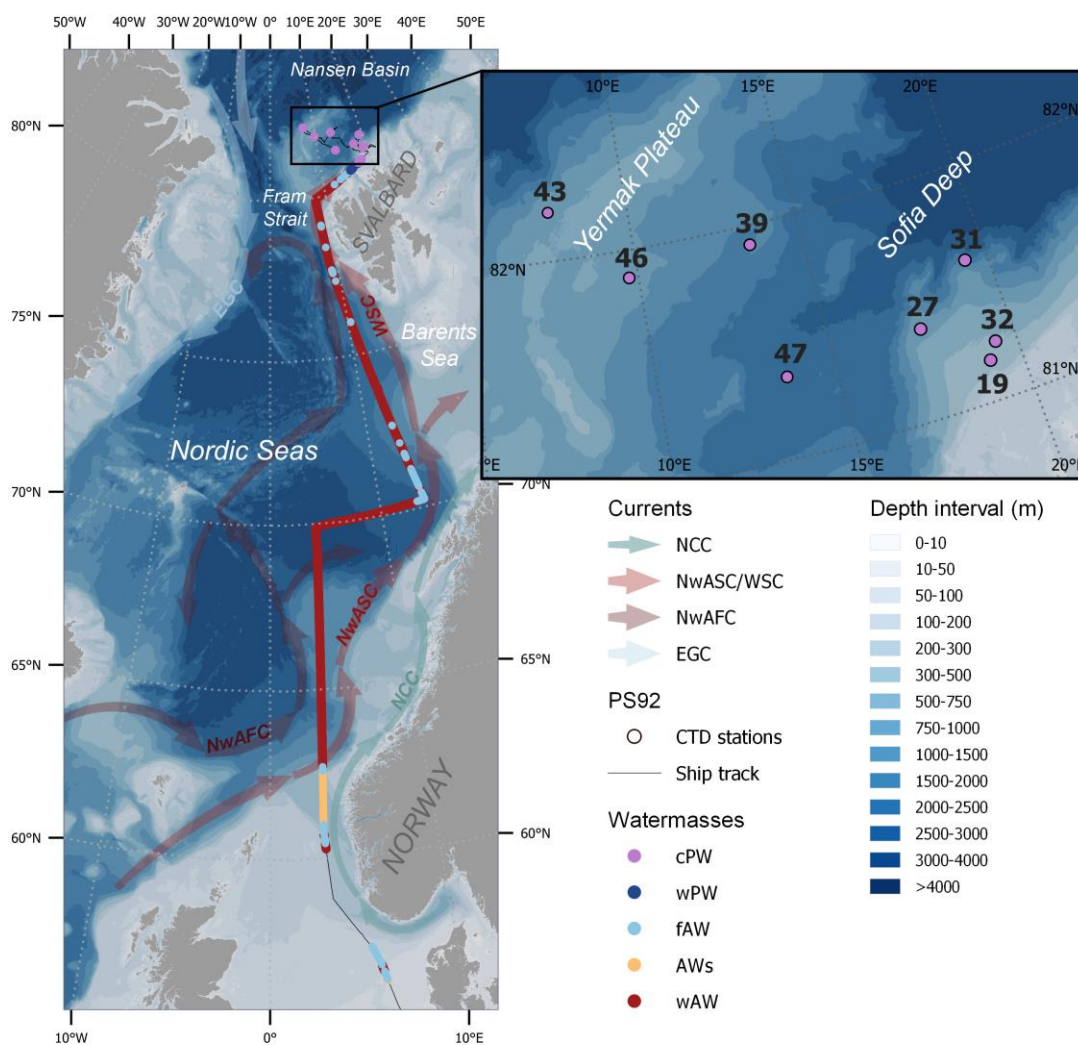
Lines 58-59: Another reference for acetone and acetaldehyde flux.

Phillips, D. P., Hopkins, F. E., Bell, T. G., Liss, P. S., Nightingale, P. D., Reeves, C. E., Wohl, C., and Yang, M.: Air–sea exchange of acetone, acetaldehyde, DMS and isoprene at a UK coastal site, *Atmospheric Chem. Phys.*, 21, 10111–10132, <https://doi.org/10.5194/acp-21-10111-2021>, 2021.

Additional reference was added

Line 115: What do the different blue colors mean in Fig. 1? I suggest adding information about the water classifications to this figure as well, like Fig S6.

We thank the reviewer for this suggestion, which was also suggested by reviewer 1. We have modified Figure1 to now include the main surface currents (arrows) as well as the water masses (colored dots) along the ship track (the latter was earlier shown in Fig S6). It also includes a legend for the bathymetry (background blue colors). The new figure is perhaps a little busy but has the benefit of including all relevant information in one and the same figure, as better support to several parts of the manuscript. Fig S6 has thus been omitted.



New figure 1: The campaign ship track with the sampled range colored by water mass: ‘regular’ warm Atlantic Water (wAW), coastal influenced Atlantic water with low salinity (AWs), fresh Atlantic Water (fAW), warm Polar Water (wPW) and cold Polar Water (wPW), according to the temperature and salinity criteria in Table 1. Surface measurements were sampled by the FerryBox system between 57°N and 81°N while vertical profiles were sampled at eight sea ice stations (black insert and Table S1). The background map shows the GEBCO_2022 bathymetry (GEBCO Compilation Group (2022); doi:10.5285/e0f0bb80-ab44-2739-e053-6c86abc0289c) and a schematic overview of the major currents influencing the surface waters in the study area, as adopted from Skagseth et al. (2022): the northward flowing Norwegian Atlantic Slope Current (NwASC), West Spitsbergen Current (WSC), Norwegian Atlantic Front Current (NwAFC), and Norwegian Coastal Current (NCC) and the southward East Greenland Current (EGC).

Line 152: It has been shown previously that other molecules can be measured in PTR-MS at the unit mass 63 where DMS is measured, such as ethylene glycol. Has this been accounted for in background measurements? Otherwise, if these are measured along this transect, they could artificially inflate the DMS measurements. It should be explicitly stated that all VOC measurements were taken at their unit mass $m/z + 1$ mass.

The $m/z +1$ has been attributed uniquely to DMS (like other studies using a HS-PTRMS in oceanic environments, see for example Wohl et al. 2020, <https://doi.org/10.5194/bg-17-2593-2020>). It is indeed very likely that compounds like ethylene glycol have negligible interference in these oceanic environments. In addition, the strong correlation ($R^2 = 0.93$) observed for m/z 63 with Chl-a on the vertical profiles confirms that m/z 63 can be attributed to DMS only. The text already states that the compounds are measured at their $m/z +1$.

Line 155: Cite Blake et al. (2009) again for the thermodynamics of the proton transfer reaction.

Citation has been added.

Line 155-156: While PTR-MS can be a soft ionization technique, there is still the possibility for fragmentation of larger molecules to affect your measurements, so quantifying at the $m/z +1$ mass may be the protonated molecule in addition to fragments of larger molecules. Have there been control experiments to support quantifying the molecules of interest only at the $m/z+1$ mass?

The reviewer is right to mention the possibility for fragmentation. However, for the masses reported in this paper, the fragmentation of larger molecules are likely not impacting significantly the measured $m/z+1$ of interest. Nevertheless, this is an important point to mention and we have added the following precisions to the revised manuscript (section 2.3.1)

“The soft ionization allowing only small fragmentation, the compounds are directly measured at their corresponding $m/z+1$. *Although we cannot rule out higher molecule fragment on the measured $m/z+1$, interferences from other compounds are likely negligible for the masses presented in this manuscript (Blake et al., 2009; Yuan et al. (2017). An exception could be isoprene, as it can contain fragmentation of 2-methyl-3-buten-2-ol (MBO) or fragmentation of cyclohexanes. However, during the period when the PTRMS was measuring in scan mode, MBO mass (m/z 87) has shown no correlation ($R^2= 0,02$) with m/z 69. In addition, the good correlation ($R^2= 0.77$) between isoprene and Chl a on vertical profiles (see Figure S7) confirms that the measured m/z 69 can be mainly attributed to isoprene. For acetone, the signal corresponds to “acetone + propanal” but it has been noted that propanal can be neglected and m/z 59 be considered as acetone (de Gouw and Warneke, 2007). The PTRMS used for this campaign had been used the year before on a field campaign and some of its characteristics are described here (Zannoni et al., 2016).”*

Line 157-158: What is the residence time in your tubing? Does it affect the measurements of any of your molecules, like acetonitrile?

Thank you for mentioning this. We explain it now in the text as followed:

The estimated residence time of about 30 seconds should prevent any degradation or adsorption of the extracted gases in the system. Furthermore, a series of standards were measured under the same experimental conditions, showing high linearity in the system's response. This observation supports the absence of artefacts in the experimental procedure.

Line 164-164: I don't see information in the SI on how MeSH was calibrated. Was this an assumed equivalent sensitivity as DMS? This calibration should also be included in the SI.

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 2 "surrounding" 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).

This point is now included in the SI, as well as the fact that it represents an additional uncertainty for MeSH concentrations. Nevertheless, the estimated sensitivity for MeSH corresponds to the high range of the determined sensitivity coefficients. Hence, the coefficient could be over-estimated, and which would even result in underestimating the corresponding MeSH concentrations. Thus, we feel very confident in our conclusion that MeSH plays a significant role in the sulphur budget, since we rather under- than overestimating this compound with our method.

Line 194: I don't see any discussion of uncertainty for the trace gas measurements. Some discussion of this should be included either in the methods or in 3.1.1.

We thank the reviewer for pointing this out. The following information has been added in the method description.

The measurement uncertainty with this PTRMS had been estimated at $\pm 20\%$ taking into account errors on standard gas, calibrations, blanks, reproductibility/repetability and linearity (Baudic et al., 2016). The overall uncertainty for dissolved VOC was estimated at $\pm 30\%$.

Line 195: What are your detection limits for acetone and acetaldehyde?

We have added in the supplementary S4 the following information

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 the 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 shown 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). Values have been kept in the figure to show the variability, but a note has been added in the figure caption ("Values below 3 nM are below the detection limit for acetone and acetaldehyde, see S4).

Line 205: I'm curious what's causing the high MeSH between 70 and 73-75 °N?

This could be due to difference in bacteria community. This is now discussed with the new figure 5b (see above).

Line 209: I think this figure can be edited to help the story flow better. My suggestions are:

Since CO presumably has a different source than DMS and MeSH, having it on the same panel is distracting. I'd suggest making this a 4-panel figure with CO on its own.

Can some information about the water masses (info from Table 4) be included? Perhaps as a shaded background.

Can information about the timing of these measurements be included? By plotting against latitude, it is hard to understand how many points are represented at each latitude, especially in the horizontal transect region near 70°N.

We thank the reviewer for all suggestions. The revised figure 2 (see below) now includes a horizontal bar representing the different water masses, as suggested by reviewer 1 too. We have furthermore added an additional X-scale to highlight the timing of the measurements.

We have decided to keep CO on the same panel, for two reasons. As we have already added a bar at the top, adding another panel would limit readability of the figure. Moreover, having CO on the same panel as DMS and MeSH allows to easily visualizing some common features (for example higher values between 73°N and 75°N).

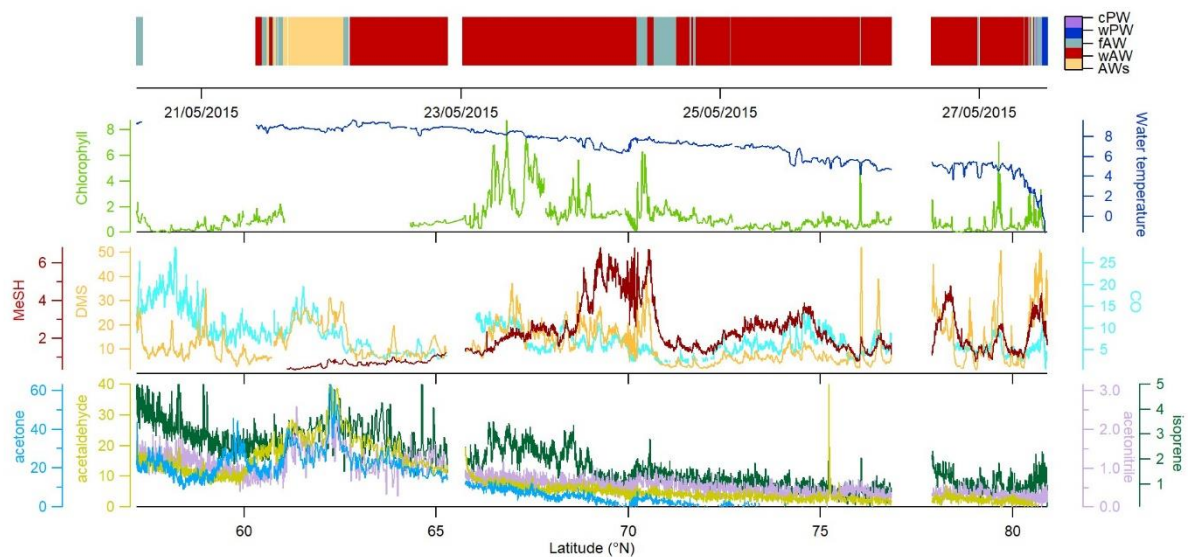


Figure 2: Latitudinal variability of acetone (nM), acetaldehyde (nM), acetonitrile (nM), isoprene (pM), DMS (nM), MeSH (nM), and CO (nM) between 57.2°N to 80.9°N in relation to Chl a ($\mu\text{g L}^{-1}$) and water temperature ($^{\circ}\text{C}$). Due to sensor failure temperature values are missing until $\sim 61^{\circ}\text{N}$. The top X-scale gives the corresponding date. On the top panel, the colored horizontal bar represents the different water masses: warm Atlantic Water with low salinity (AWs), ‘regular’ warm Atlantic Water (wAW), freshened and cooled Atlantic Water (fAW), cold Polar Water (cPW) and warm Polar Water (wPW).

Line 227: I am unclear what MeSH_DMS is on Fig. 3b x-axis? Is this $\text{MeSH}/(\text{MeSH}+\text{DMS})$?

If so, should be updated to read more clearly.

The reviewer is correct. The figure legend has been clarified accordingly:

“MeSH_DMS: ratio between MeSH and DMS, expressed as $\text{MeSH}/(\text{MeSH}+\text{DMS})$ ”

Technical Corrections – Manuscript

Line 35: “source and sink” should be “sources and sinks”

Line 99: “some leads present),” should be “some leads present),”

Line 123: “Chl a l concentrations” should be “Chl a concentrations”

Line 156: “at their at their” should be “at their”

Line 254: “but the here found concentrations” should be “but here the concentrations found”

Line 324: “nm” should be “nM”

All technical corrections have been done.

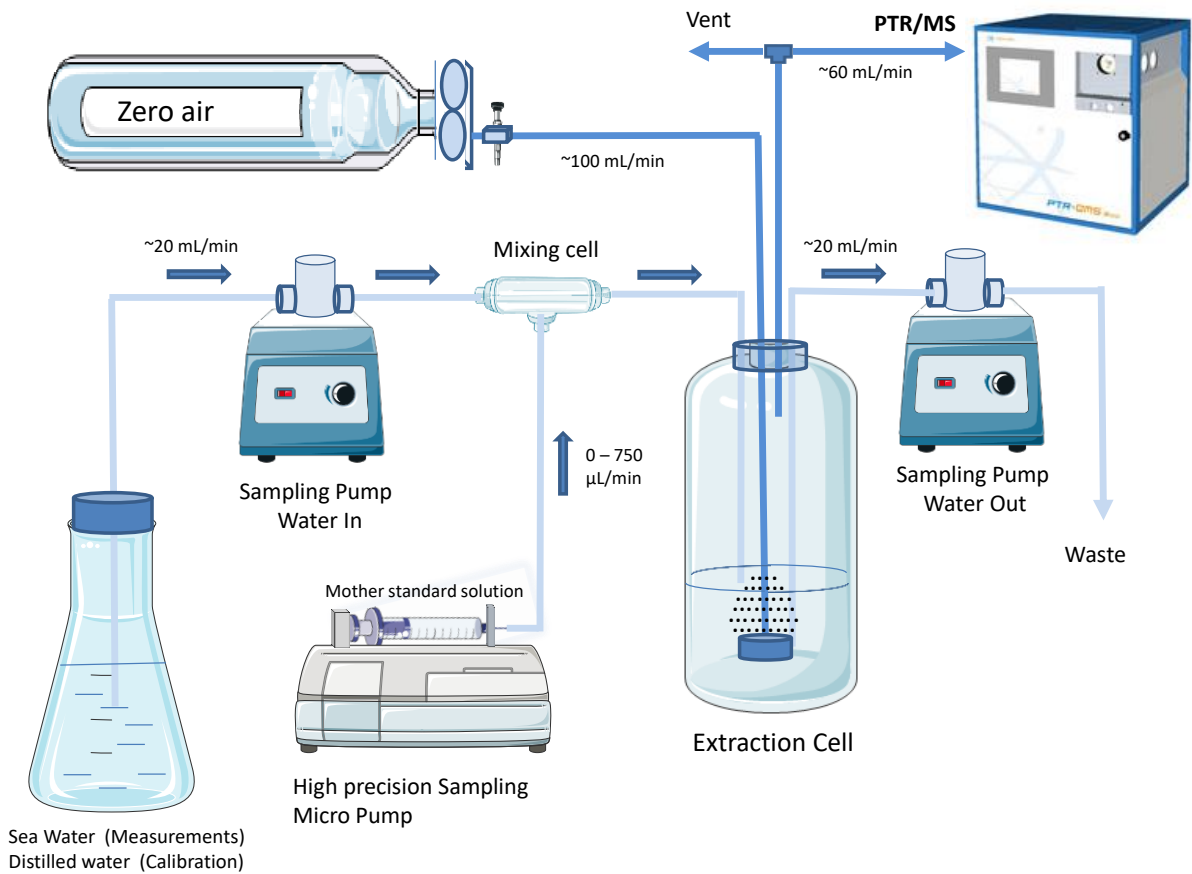
Technical Corrections – Supplemental

Line 8: There is something cut off in the upper righthand corner of Fig. S1.

This was due to a line number partly covering the figure, this does not appear in the version without the line numbering.

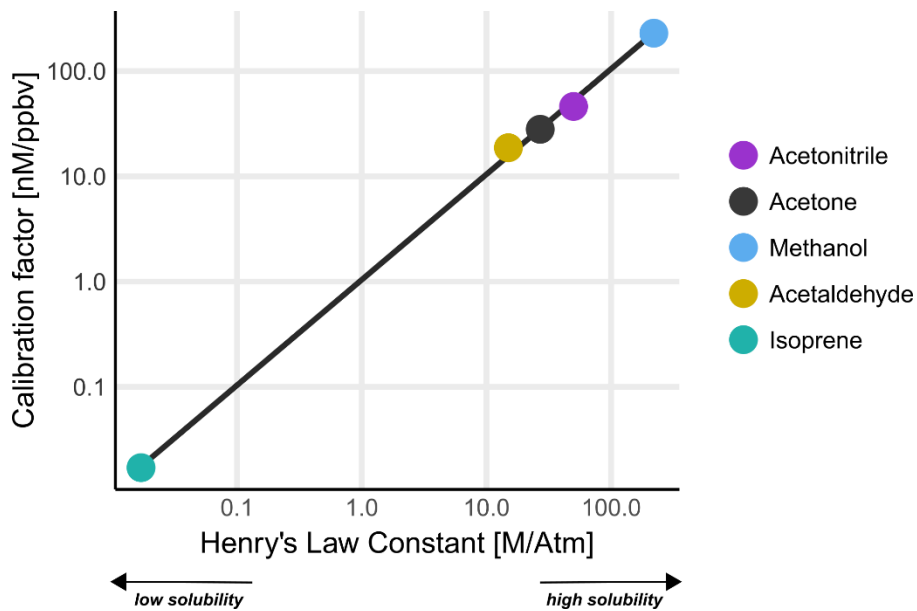
Line 61: Fig. S3 is blurry and hard to read.

A clearer version of the figure is now included



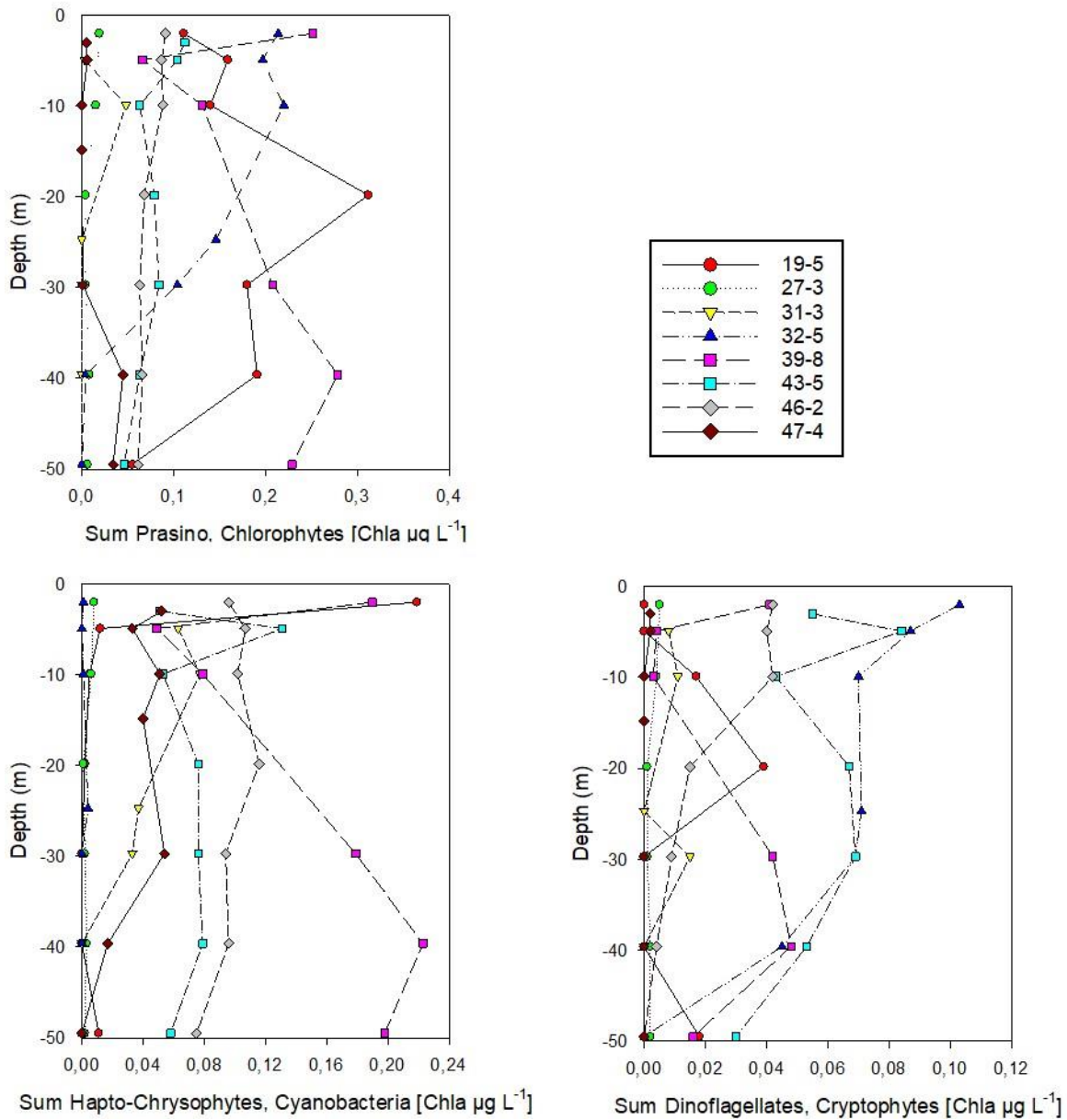
Line 77-79 : I am unclear what it means for the Henry' law constant “whatever the solubility of the compound over 4 to 5 orders of magnitude”

We apologize; there was a problem in the X and Y axis units, which did not allow to see that the units were in log-scale. The new figure is shown below. We hope this has clarified the sentence.



Line 118: Bottom right panel y-axis in Fig. S6 is cut off. What is being plotted on the x-axis – is this both phytoplankton functional group and chlorophyll? Can the x-axis label be adjusted to be more clear?

The new figure S6 (with no more cut-off) is given below. Overall this figure has the same set up as Fig. 4, but we do agree that the x-axes were misleading, since we showed here sums of the various groups and the / might have indicated ratios. We modified this and also to clarify this figure we used a similar figure caption as for Fig. 4:



“Figure S6: 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 various phytoplankton groups is expressed as Chl a concentrations.”

Line 123: Should read “Supplement S7: ”

changed

Lines 131-146: References should be alphabetized and formatting should be consistent.

Done

Line 133: Callahan et al. reference is missing a year

Done