

Dear Anonymous Referee #1,

Thank you for your thoughtful and constructive criticism of our work. We have reread and revised our manuscript according to the insightful suggestions you provided, and have added some key references. The most substantial revision may consist of correcting our wind speed to 10m height, and of adjusting references and describing certain aspects of our methods more completely. Please find responses to each of your points, below. We have done our best to address each statement carefully, and look forward to your responses. An updated manuscript is also available.

Best,
Tereza Jarnikova
PhD Student, UBC

Interactive comment on “The distribution of methylated sulfur compounds, DMS and DMSP, in Canadian Subarctic and Arctic marine waters during summer, 2015” by Tereza Jarníková et al.

Anonymous Referee #1

Received and published: 4 October 2017

This manuscript presents DMS/P data measured in Canadian waters using two techniques, a MIMS and an automated GC-PFPD. The authors were able to use the fine resolution spatial distribution of sulfur compounds measured to examine the influence of frontal features and other small scale hydrographic changes on DMS/P. The authors provide a comprehensive introduction to DMS/P cycling and their importance in both the ocean and the atmosphere. They note that high latitude DMS emissions may be especially important for aerosol formation and polar climate. However, the number of measurements in these high latitude regions is scarce, compared to the mid- and low latitudes. The difference between findings in the Antarctic (high values of sulfur compounds) vs. the Arctic (moderate level of sulfur compounds) motivated this study and the authors are particularly interested in the role Arctic sea ice plays on regulating DMS/P distributions. This manuscript is an important contribution to the DMS/P database and should be published after the following minor changes have been made.

Specific comments:

Lines 119-120: Is this Gabric reference the most updated reference on the feedback between ice albedo and DMS emissions?

>We have added a reference to a quite recent modelling study by Cameron-Smith et al, run for the Southern Ocean, that also demonstrates a remarkably strong DMS emission response to loss of sea-ice albedo. Becagli et al (2016) (<http://dx.doi.org/10.1016/j.atmosenv.2016.04.002>) also observed a robust correlation between DMS-sourced aerosol concentration and sea-ice melt, though we did not add this citation as the section focuses on modelling studies of future polar regions.

Line number in Tracked Changes (TC) manuscript: 130

Lines 199-216: What is the LOD for the MIMS?

>A line has been added here - 2nM, reference Tortell 2005.

Line number in TC manuscript: 232

Line 211: Perm tubes are highly sensitive to constant temperature and flow conditions. How reliable are these as primary standards when taken to sea?

>Both these sensitivities are thoroughly addressed - the temperature of the perm tube is kept constant by use of a circuit-controlled heating pad, and the flow through it is kept constant via a flow gauge. We now explicitly state this in our manuscript.

Line number in TC manuscript: 225-230

Line 264: Why are your fluxes computed with N00, when more evidence is coming online that DMS k values should be linearly dependent on wind speed?

>We used this flux computation because it is consistent with the one used by the main global DMS climatology, Lana et al, and still widely used. However, we are aware that newer computations have been published, eg. Bell et al. It would be possible to use these, though we have not done so at present.

Lines 269-270: What your wind speed corrected to 10 m height?

>This is an oversight on our part - the initial data were not corrected to 10m. However, we have made the correction in the present iteration. A supporting figure showing the slight difference in windspeed is added.

Line number in TC manuscript: 289

Line 291: Do the authors mean Table 3 here instead of Table 4?

>Thank you! This has been fixed

Line number in TC manuscript: 310

Lines 305-306: The measured range reported is way below the LOD. The authors discuss this much later, but maybe here there should be a statement about 22% of these are below the LOD.

>For maximum clarity, a line has been added here briefly discussing this, and alluding to the more extensive discussion further down.

Line number in TC manuscript: 325

Line 329: Do the authors mean Figure 4 here instead of Figure 5?

>Thank you! This has been fixed

Line number in TC manuscript: 349

Line 379: Typo, remove of

>Thank you! This has been fixed

Lines 410s: Are there no possible scenarios in which the MIMS values are too low?
E.g. peak resolution not achieved because MIMS is too slow?

>We are not aware of any reason that the MIMS should under-estimate DMS. We use a ~30 second dwell time to ensure good peak resolution for DMS at m/z 62.

Lines 449-451: The top figure in this graph would be more instructive if we could see the comparison between this study and previous studies. The bottom figure helps with this, but does not give an idea of the spatial comparison.

>The top panel in this figure does show a comparison between the current study and previous studies both in terms of concentration distribution and spatial distribution. We have made the symbols clearer to help clarify the presentation of different data sources.

Line number in TC manuscript: Figure 6

Lines 455-rest of paragraph: Why is there no comparison to the Lana climatology here?

>The Lana climatology is based on the PMEL measurements, which we compare with directly. Any information present in the Lana climatology that is not present in the PMEL data results simply from interpolations, and thus (we feel) are not worth comparing. There is almost no data in the PMEL database in our observational region (the Canadian Arctic) - almost all PMEL measurements in the Boreal Polar Longhurst province come from the Atlantic sector. Therefore, according to Lana's methodology, the Lana climatology presents only a rough "first guess" of concentrations in the studied region.

Line number in TC manuscript: 465

Section 4.3: There is only one reference here (Tremblay et al., 2011) related to DMS/P and fronts. Are there no others to corroborate the authors' findings?

>Here we are focusing on the idea that frontal zones may be regions of enhanced productivity, and we then argue that this may lead to increased DMS production. This idea is well-established in the literature - eg Lutjeharms 1985 and others. We chose the Tremblay reference because it is from a similar region from a similar time of year.

Line number in TC manuscript: 532

Lines 533-535: There are no obvious trends in the data between MLD and sulfur compound concentrations. I am not sure that the following explanation is justified by the data.

>We have changed the wording here somewhat to reflect the lack of an overall statistical trend.

Line number in TC manuscript: 565

Line 537: There appears to be something wrong with the numbers here. The shallowest MLD is 2.1 m in Table 2.

*>This was a typo; I have rewritten this sentence.
Line number in TC manuscript: 565*

Lines 552-563: Are there no possible other explanations beside PFTS? Was there more bacterial activity? Or more cell lysis?

*>We agree that these factors are important, though it is not possible for us to estimate them from our observational data. We have added a comment about these factors in this section.
Line number in TC manuscript: 598*

Lines 565-566: Are there no citations for this sentence? Is this considered common knowledge?

*>We now cite a review paper published by Levasseur in 2013, which gives a good overview of the relevant literature.
Line number in TC manuscript: 605*

Line 576: Typo, extra space between study and comma

>Thank you, this has been fixed.

Line 585: What is 30a? Is this a citation typo?

*>This has been corrected - this is a reference to the Galindo 2014 paper.
Line number in TC manuscript: 631*

Lines 590-592: In Table 2, I can see the highest sulfur:chl for stations BB2 and CAA7 for DMS. BB3 and CAA6 are for DMSP only.

*>We have changed this sentence to reflect DMSP only. In this way, the section makes a better link between DMSP:chl ratios and sea ice cover.
Line number in TC manuscript: 637*

Figure 1: Caption – GD should be GL

>Corrected – thank you.

Figure 2: No description of red dots.

>Corrected – thank you.

Dear Anonymous Referee #2,

Thank you for your thoughtful and constructive criticism of our work. We have reread and revised our manuscript according to the insightful suggestions you provided, and have added some key references. The most substantial revision may consist of a reworking (and slight shortening) of our Discussion section in response to your points - we aim to be more cohesive and clear when placing our work in the context of other studies performed in the Arctic. Please find responses to each of your points, below. We have done our best to address each statement carefully, and look forward to your responses. An updated manuscript is also available.

Best,
Tereza Jarnikova
PhD Student, UBC

Interactive comment on “The distribution of methylated sulfur compounds, DMS and DMSP, in Canadian Subarctic and Arctic marine waters during summer, 2015” by Tereza Jarníková et al.

Anonymous Referee #2

Received and published: 15 October 2017

General comments.

The study reports high spatial resolution measurements along a cruise track that passes through a number of distinct regions around the western Arctic. This is interesting on two counts, one is the high spatial resolution of the data that illustrates spatial gradients generally not observed using other approaches, and the second is the contribution to the comparatively few measurements of DMS/P that have been carried out in the Arctic in general and particularly in this region. These high resolution seawater measurements of DMS and DMSP are generated using MIMS and an OSSCAR system that is probably unique to this group and the two systems have seldom been applied simultaneously (e.g. Asher et al. 2015). This is an important data set and may well be useful to those trying to model DMS emissions in Arctic waters and the role that DMS may play in aerosol and cloud formation over the Arctic. Despite the uniqueness and quality of this data, in general, I think the authors fail to make full use of the high spatial resolution data and supporting information. For instance, much of the manuscript, including 3 tables, is dedicated to trying to identify the phytoplankton sources of DMSP and DMS from a limited dataset (9 stations along a 10,000 km transect) of pigment concentrations. It would be much more informative in my view, to concentrate on the unique high resolution data over the very long transect; especially what may be causing the large gradients neatly illustrated in Figure 4 and whether there are areas of particularly high or low DMS sea to air flux. I think the Discussion in particular needs to be more focused on the results from this dataset and what they might mean to DMS emissions in the regions.

Specific Comments

Abstract.

This could be tightened-up so that it really represents the finding in the main

manuscript. At the moment it does little to convey the real relevance of the project.

>We feel that the abstract quite clearly conveys the main results of the paper. However, we have revised it to better reflect the broader significance of the work.

L21-22. What does the conclusion that a range in concentrations of DMS (~1 nM to 18nM) and DMSP concentrations (~1 nM to 150 nM) was consistent with previous observations in the Arctic Ocean really mean? This would apply to almost any large stretch of ocean wouldn't it?

*>Thank you, we agree and have removed this part of the sentence.
Line number in tracked changes (TC) manuscript: 23*

L23. The comment about Baffin Bay is interesting but I do not see a focus on it in the actual manuscript, maybe there should be?

>We agree that the Baffin Bay DMS concentrations are interesting, and wish to highlight them. We discuss the sharp increase in DMS Baffin Bay concentration from lines 347-357 (line 364 in track changes manuscript), and contrast them with the rest of the transect.

Introduction.

L41. The uncertainty in the CLAW hypothesis should also be made clear.

*>We have added a reference to the Quinn and Bates paper, stating that this mechanism remains the subject of debate.
Line number in TC manuscript: 47*

L48. Stefels et al. 2007 is now 10 years old, it might be worth considering whether more recent studies have thrown new light on the topics?

*>Though we agree the Stefels paper is older, it remains one of the most comprehensive reviews of the DMS cycle, which makes it very suitable for a general reference such as the one called for here. We cite more recent papers when discussing specific aspects of our findings.
Line number in TC manuscript: 53*

L60. I don't think Zubkov et al. 2001 directly addresses stimulation of DMS production by grazing or viral lysis.

*>We switched this reference to Evans 2007, who directly compares the relative significance of grazing and viral lysis in DMS production in an *E. huxleyi* culture study.
Line number in TC manuscript: 65*

L68. Several modelling studies also suggest a limited role for DMS in cloud formation in the Arctic and should be mentioned (e.g. Carslaw et al 2012, Browse et al 2014).

>We have added a line stating this, and have cited the Browse 2014 study, as well as citing Carslaw's 2013 paper that highlights the importance of quantifying uncertainty natural aerosol contribution to climate forcing.

Line number in TC manuscript: 73

L80 It is not clear what the relevance of this comparison between Arctic and Antarctic measured DMS values is, both datasets are regionally and seasonally biased making it difficult to conclude anything from the comparison of the full datasets.

>We respectfully disagree - we feel that it is important to point out the different controls on DMS production in the two polar regions, which otherwise share a number of physical characteristics, including seasonally varying sea ice cover and insolation. The difference between these two polar regions is critical to understanding potential drivers of DMS cycling in these regions, and this provides context for our work in the Arctic.

L89-102. The relevance of the comparison of Arctic and Antarctic DMS concentrations and controls on that production is not clear at this point. This is not a component of either the Results or Discussion. Maybe this comparison would be more interesting and relevant as an aspect of the Discussion?

>See above - we believe that a brief discussion of the different DMS dynamics of the two polar regions provides context for our work in the Arctic. It is a fact that there has been a hugely disproportionate effort towards understanding DMS/P dynamics in south polar regions. The relative lack of data from the northern polar regions is a main motivating factor for our work.

Methods

L159+ It would be useful to know why the data from the OSSCAR system does not cover the full transect, maybe I have missed that in the manuscript?

>We experienced technical difficulties with the OSSCAR system in the early part of the expedition. This is now explicitly mentioned in the manuscript.

Line number in TC manuscript: 211

L181. It would be useful to include the concentration of the point standard as this would provide context for the standard error of 0.55 nM that is deemed the level of precision. Was this not concentration dependent?

>We agree - this inline standard was 20 nM, and this has been noted in the text.

Line number in TC manuscript: 189

L266. Flux estimates: possibly understandably the authors use a fairly simplistic parameterization to compute DMS exchange rates, but it should be noted that the Nightingale 2000 parameterization has now consistently been shown to overestimate flux at higher wind speeds. At some point we as a community are going to have to start using a more realistic parameterization. Plus the scaling exponent (0.4) derived from Loose et al. 2009, requires more explanation. Does this account for flux through the ice or

for enhanced exchange due to turbulence generated by the ice etc.? A short section, possibly in the Discussion, is required to make this uncertainty clear.

>We agree - this point about the Nightingale parameterization has been brought up by Reviewer 1 as well. We used it to be consistent with Lana et al and much of the literature. We have also added a brief comment about the Loose et al scaling, which is experimentally derived in a laboratory setting and does not account for turbulence generated by sea ice melt - we have now stated this.

Line number in TC manuscript: 284

L269. Was the wind corrected to U10 as is generally used in the Nightingale 2000 parameterization and was it corrected for ship speed?

>This was an oversight on our part - the original ship data we used was corrected for ship speed but not corrected to U10, but we have obtained U10 data from collaborators and have corrected it in the revised manuscript.

Line number in TC manuscript: 286

Results

L364. It would be useful to have an indication of what distance the subjective 100 points refers to over which the gradients are calculated.

>In our dataset, a radius of 100 points corresponds to a mean radius of around 25 km; this has been clarified in the revised text.

Line number in TC manuscript: 384

Figures. In general, the figure legends could be made more informative.

>We have added additional details to the legends for figures 1,2,5, and 6, but it wasn't clear what the reviewer was exactly looking for.

Discussion.

L406. Could this be caused by carryover of NaOH from DMSP analysis to DMS analysis? High concentrations of NaOH are difficult to wash off with only MQ water, was this tested with DMSP standards at all, i.e. purging of a DMSP standard following a DMSP analysis with NaOH addition.

>Prior to the cruise, we did test the thoroughness of our rinse cycle by testing DMSP standards with no NaOH added, following a DMSP analysis with NaOH addition, and these blanks were clean – a note about this has been added to the text. Nevertheless we want to state this possibility.

Line number in TC manuscript: 424

L451. This comparison of DMS flux does not 'prove' anything really without access to the modeled information.

>We agree and have removed this sentence.

Line number in TC manuscript: 471

L462. Do you mean 'sulfur accumulation', or what does sulfur accumulation mean?

*>The statement 'DMS and DMSP concentrations' is more exact here. We have rephrased this.
Line number in TC manuscript: 483*

L477. It's not clear what point is being made here, I think the logic may be reversed?

*>The purpose of this section is to discuss seasonal patterns in phytoplankton biomass, productivity and DMS/P concentrations, as observed by fellow researchers in the region. It serves to provide a context for the results we obtained in our study. We are not clear which logic the reviewer sees as reversed.
Line number in TC manuscript: 497*

L481. Again, it is not clear what point is being made in this paragraph and whether it is necessary?

>See above comment.

L492. The Simo and Pedros-Alio (1999) study was based on experiments in the North Atlantic, so also not restricted to lower latitudes, and many studies have confirmed the 'summer paradox' seasonal pattern extends beyond low latitude waters.

*>We have rephrased this to reflect observations beyond the low latitudes.
Line number in TC manuscript: 512*

L497. I think this section would be made more interesting if it was considered in terms of trying to develop a seasonal model that included DMS emissions. Is there sufficient information (Table 5 and this study) to start to develop such a model? If not, what is needed; seasonal studies in different regions of the Arctic or more transects throughout the year?

We believe that a seasonal model of DMS in the Arctic is being developed by our colleagues at University of Victoria, (Dr. Steiner's group). We have not focused on model construction in the Discussion as we feel that it is beyond the scope of the paper, but a comparison of seasonal studies in different regions of the Arctic would certainly be helpful in model construction.

L502. 'decorrelation length scales' needs more explanation, especially as the authors then go on to point out co-occurring gradients.

*>Decorrelation length scales provide information on the spatial scale of processes driving the majority of variability in DMS concentrations. We have added an explanatory line to the text. .
Line number in TC manuscript: 524*

L510. I'm not sure whether the argument is consistent - why should high primary production drive increased DMS - as pointed out earlier in the text, high nutrient periods on a seasonal basis are associated with low DMS.

>We can appreciate the apparent contradiction with our earlier discussion of seasonal changes, and have rewritten this section.

Line number in TC manuscript: 535

L523. I'm not sure where this paragraph goes, other than to highlight a different study by these authors? Are there regions identified in this region of the Arctic where understanding the processes would be particularly useful and how might that be achieved?

>We agree – as we are not conducting isotope-based experiments in this research, we have removed this paragraph.

Line number in TC manuscript: 547

L532/Section 4. This section starts off discussing areas of shallow mixed layer depth then merges into a discussion comparing DMSP:chl a ratios generally in the Arctic. What point(s) is being conveyed?

>Here, we aim to characterize the general structure of our observations - to state that we observed elevated DMSP:chl in shallow MLD regions with a mixed assemblage, under potential light stress. We also want to compare these observations with others made in the region, for context.

L552. Again, it is unclear what point is being made here - the range in DMSP:chl is > 3-fold, (52 - 182), why does the final sentence conclude low variability in DMSP:chl?

>We have rephrased this section to better reflect that we cannot draw conclusions on the role of taxonomy in controlling DMSP:Chl a ratios - though the variability in DMSP:chl is relatively high, the variability in taxonomy appears low.

Line number in TC manuscript: 590

L564. This section could be usefully focused. It would be more relevant to focus on what this dataset shows. The paragraph from L565 simply reviews previous studies and seems superfluous. As it stands, it is unclear what the authors conclude. The correlation between sea ice cover and DMS/P is negative but station-specific data suggests enhanced DMSP:chl ratios near the ice edge?

>We have re-written this paragraph to focus the ideas presented. We start with a brief overview of some previous results examining potential ice effects on DMS/P cycling, and use this to provide a context for our work. We have significantly shortened the paragraph to focus on the most important messages.

Line number in TC manuscript: 605

L558. Does the MIMS data pick-up ice edge effects on DMS concentration, i.e. is DMS related to salinity when passing through marginal ice zones or ice edges, over shorter distances than the whole dataset?

>We have now clarified that the ice-edge effects on DMS were observed using MIMS.

Line number in TC manuscript: 636

L605 Again this section reads very much like a review, with little focus on what this particular study demonstrates.

>We agree and have removed this short section, as it does not speak to our specific results.

Minor points

L144 - use CAA instead of Canadian. . .

>Thank you, this has been corrected.

L196 –should read 'convert DMSO to DMS'

>Thank you, this has been corrected.

L266, more correctly A is proportion of sea ice cover, rather than percentage.

>Thank you, this has been corrected.

Figure 1. GL - Greenland not GD; and please define CAA

>Thank you, this has been corrected.

Figure 2. please explain what the red dots are on the DMS graph, possibly station measurements? This would strengthen the suggestion made on L595+

>I have added the note that these are station measurements.

Figure 3. please explain what the red dots are?

>I have added the note that these are station measurements.

Figure 6. Some more information in the legend would be useful, for instance, how are the data compiled, what exactly is illustrated? The total number of points for each dataset would also be useful.

>We have updated this figure legend to reference the data sources and the total number of points.

Dear Anonymous Referee #3,

Thank you for your thoughtful criticism of our work. We have reread and revised our manuscript according to the corrections you provided, including recalculating our wind data to a height of 10 meters. Please find responses to each of your points, below. We have done our best to address each statement carefully, and look forward to your responses. An updated manuscript is also available.

Best,

Tereza Jarnikova,
PhD student, UBC

Interactive comment on “The distribution of methylated sulfur compounds, DMS and DMSP, in Canadian Subarctic and Arctic marine waters during summer, 2015” by Tereza Jarníková et al.

Anonymous Referee #3

Received and published: 1 November 2017

1. General Comments In this paper, authors measured the concentrations of DMS and DMSP in the surface seawater from the Labrador Sea to the Canadian Arctic Archipelago during the summer of 2015. In addition to the distributions of DMS/P concentrations with information of seawater parameters (hydrographic parameters, taxonomic compositions, and sea ice cover) in this area, they detected the abrupt increases in the DMS concentration at the front of hydrographic parameters by measurement with fine spatial resolution. The data obtained from this observation contributes to the accumulation of database in the Canadian Arctic waters and to discussion on the response of DMS to changes occurring in the Arctic Ocean. This paper would be acceptable if the authors reconsider and correct the part described in Specific Comments and

Technical Corrections.

2. Specific Comments

(1) Authors conclude that the results obtained from this cruise (shallow MLDs and mixed phytoplankton assemblages) support the results of previous studies by Gabric et al. (2004) and Lavoie (2013). I wonder whether the spatial changes such as the differences between the sea-ice free area and the locations where sea ice has just melted can be compared with the result caused by sea ice reduction in future Arctic waters.

>We do not believe that it is possible to compare recent sea-ice melt regions with a highly-stratified ice-free Arctic - it is likely that the processes governing DMS production in a recent ice-melt region (eg ice diatom water column release) are quite different from those in the stratified ocean. However, interestingly, we believe that our technique may be able to capture ice-melt effects.

(2) The authors discuss the sharp increase in DMS concentration obtained from the measurement of high spatial resolution. Then what happened where the DMS concentration sharply decreased for example at 2600km, 3600km, 4000km, and 7600km?

>As these are transect measurements, our paper suggests that the areas of sharp increase correspond to encountering watermasses with high DMS production - we discuss the potential

role of fronts in DMS production later in the paper. The regions mentioned here are directly after the spikes in DMS - it may be inferred that the ship left the high-DMS zones at this time.

(3) L262: In Equation (1), do you need to include the DMS concentration in the surface atmosphere? When you use this equation, you need to mention about omitting this.

We do not include any surface atmosphere DMS in our calculation. We mention that we are assuming no surface DMS in the revised manuscript.

Line in track changes manuscript: 279

(4) L269: The exchange coefficient of the flux calculation is a function of the wind speed at the 10m height from the sea surface. Please note that the height of the anemometer. And if the height is far from 10m, then you need to mention about the influence of the height difference.

>This is an issue that has been brought to our attention. We have corrected the wind data to 10m above the surface and recalculated flux accordingly. The supporting data for the manuscript includes a figure showing the slight difference between the two windspeeds and fluxes.

Line in track changes manuscript: 289

3. Technical Corrections

(1) When reading bg-2017-337.pdf, I found the following typing mistakes. I think that there are other typing mistakes in this draft, so reread and fix them.

(2) About the use of "Figure" and "Fig", if "Figure" is used at the beginning of a sentence and "Fig." is used in sentences, "Figure 3" at L317 is not at the beginning of the sentence, is this correct?

>To minimize stylistic problems, I've written out the word "Figure" everywhere.

(3) Figure 5 is referred (L329) prior to Figure 4 (L368). You need to swap Figure 4 and Figure 5.

> Thank you, this has been fixed.

C2

(4) Table 4 is referred prior to Table 3. You need to swap Table 3 (L375) and Table 4

>Thank you, this has been fixed.

(L291). The order of Table 3 and Table 4 is also the same

>Thank you, this has been fixed.

(5) Is the writing style "km 7000" in L309 correct? This notation can be found in several other places such as L309, L322, L326, L331, L334, L336, L343, L346, L386, L403, L590, and L598.

>This style is commonly used in geographic survey literature. We use it consistently in this paper as we believe it to be both concise and unambiguous.

(6) In "Reference list", journal names written by full notation and abbreviations are mixed.

>This has been corrected using the standard abbreviations.

(7) In Figure 2, gray shaded areas denote not only the part of sharp increase in DMS concentration, but also the part of its high concentration (and its sharp decrease). If you want to highlight only the part of its sharp increase, carefully mark the part only where the DMS concentration increases.

>Our approach was to highlight localized regions of DMS accumulation, which include both sharp increases and decreases. We believe that showing the entire signal for each DMS pulse helps the reader visually compare coherence between DMS features and other hydrographic variables

(8) List of technical errors L53: Is "three order" correct?

>This is written as "can vary by three orders of magnitude", and a citation is provided.

L59: At the end of L59, not period but comma.

> Thank you, this has been fixed.

L70~L71: Invalid way to cite the references written in L70-L71; DMS emissions (Chang et al., 2011), (Mungall et al., 2016) ==> DMS emissions (Chang et al., 2011; Mungall et al., 2016)

> Thank you, this has been fixed.

L92: mixed layer depth => mixed layer depth (MLD) L234, L280, L290, L534, L615,

> We have added the abbreviation MLD into instances of mixed layer depth mentions.

L914: mixed layer depth => MLD

>We believe it is correct to have both the full name and the abbreviation in this case, as it is a table caption.

L128, L155, L200: The notation of "membrane inlet mass spectrometry (MIMS)" is to be used only at the first quotation, and the abbreviation (MIMS) should be used at subsequent citations.

>Thank you, we have changed this.

L130, L156 The notation of "OSSCAR" is same as my comment for "MIMS".

We have changed this.

L138: "(July 10-August 20, 2015)". Is parenthesis "()" necessary?

>We have adjusted this stylistically.

L147: shallow, narrow straits => shallow and narrow straits

>We would prefer to keep "shallow, narrow" straits.

L263: Where => where

>Thank you! Fixed.

L306: 18nM => 18 nM

>Thank you! fixed.

L316, L317: 29nM => 29 nM, insert half-size space after "29" 52.31mmol => 52.31 nmol

>Thank you! fixed.

L314: Is "(measured with OSSCAR)" necessary? If so, () is necessary?

>Though this is implied by our instrumental setup, we've opted to remind the reader that DMSP is measured by OSSCAR here to emphasize the source of the data.

L331: sea-air flux observed => sea-air flux calculated (or estimated)

>We have changed this to 'calculated'.

L348: (Fig 2c) => (Fig.2c) insert period after "Fig".

>We have opted to write out "Figure" everywhere.

L360: Is (G) in "Gradients (G) for each variable" necessary here?

>We believe that this links the text to the formula shown, and have opted to keep it.

L416: Quotation "Wolfe et al (2002)" at the end of L416 and the same author's quotation at the end of the sentence of L418 are duplicated (the latter is unnecessary).

>Thank you! Fixed.

L444: Fig 6a,=> Fig. 6a

>We have opted to write out "Figure" everywhere.

L446: Insert a half-size space between "(Fig. 6b)." and " The result,,,,".

>Thank you! Fixed.

L459: heavily => mainly

>Thank you! Fixed.

L461: drawn => obtained

>Thank you! Fixed.

L474: in the Northwest Subarctic => in the northwest subarctic

>Thank you! Fixed.

L474: Lizotte et al (2012) => Lizotte et al. (2012)

>Thank you! Fixed.

L500: Either "Previous" in L500 or "previously" in L501 is unnecessary.

>Thank you! Fixed.

L514: (Tremblay et al., 2011) in the end of sentence should be deleted.

>Thank you! Fixed.

L540: (Matrai et al. 1997) => (Matrai et al., 1997) Need comma after "et al."

>Thank you! Fixed.

L553, L554, L556: nM ug-1 => nmol ug-1

>Thank you! Fixed.

L560: DMSP:Chl and HPLC => insert "a" after chl in italic. DMSP:Chl a and HPLC C4

>Thank you! Fixed.

L585: [30a] Reference?

>Thank you! Fixed.

L601-L602: Gali et al. (Gali et al., 2010) => Gali et al. (2010)

>Thank you! Fixed.

L613: Gabric et al (2005): Need period after “et al”. Year of publish of this paper is 2004, not 2005.

>Thank you! Fixed.

L616: DMSP:Chl a ratios :Chl a should be italic.

>Thank you! Fixed.

L844: 20244. => 20244 (Delete period after 20244.)

>Thank you! Fixed.

L885: Adapted from (Coupel et al. 2015). => Adapted from Coupel et al. (2015).

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L997: show denote =>Choose either "show" or "denote".

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L1024-L1025: What are the grey area in these figures? Are the same as Fig.2?

>Thank you! Fixed.

L1040-L1041: Explain the panel (a) and (b).

>Thank you! Fixed.

1 **The distribution of methylated sulfur compounds, DMS and DMSP, in**
2 **Canadian Subarctic and Arctic marine waters during summer, 2015**

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16 **Abstract**

17 **We present seawater concentrations of dimethylsulfide (DMS), and**
18 **dimethylsulfoniopropionate (DMSP) measured across a transect from the Labrador**
19 **Sea to the Canadian Arctic Archipelago, during summer 2015. Using an automated**
20 **ship-board gas chromatography system, and a membrane-inlet mass spectrometer,**
21 **we measured a wide range of DMS (~1 nM to 18nM) and DMSP (~1 nM to 150 nM)**
22 **concentrations. The highest DMS and DMSP concentrations occurred in a localized**
23 **region of Baffin Bay, where surface waters were characterized by high chlorophyll *a***
24 **(chl *a*) fluorescence, indicative of elevated phytoplankton biomass. Across the full**
25 **sampling transect, there were only weak relationships between DMS/P, chl *a***
26 **fluorescence and other measured variables, including positive relationships between**
27 **DMSP:chl *a* ratios and several taxonomic marker pigments, and elevated DMS/P**
28 **concentrations in partially ice-covered areas. Our high spatial resolution**
29 **measurements allowed us to examine DMS variability over small scales (<1 km),**
30 **documenting strong DMS concentration gradients across surface hydrographic**
31 **frontal features. Our new observations fill in an important observational gap in the**
32 **Arctic Ocean, and provide additional information on sea-air DMS fluxes from this**
33 **ocean region. in this study constitute a significant contribution to the existing**
34 **Arctic DMS/P dataset, and provide a baseline for future measurements in the region.**

35 **1. Introduction**

36 The trace gas dimethylsulfide (DMS), a degradation product of the algal
37 metabolite dimethylsulfoniopropionate (DMSP), is the largest natural source of sulfur to
38 the atmosphere, accounting for over 90% of global biogenic sulfur emissions (Simó,
39 2001). Atmospheric DMS is rapidly oxidized to sulfate aerosols that act as cloud
40 condensation nuclei (CCN), backscattering incoming radiation, increasing the albedo of
41 low-altitude clouds and potentially cooling the Earth (Charlson et al., 1987). The seminal
42 CLAW hypothesis proposed by Charlson et al. (1987) suggests that this negative radiative
43 forcing will have cascading effects on marine primary productivity, leading to a DMS-
44 mediated climate feedback loop. Although more recent work has disputed the mechanism
45 of this biologically-mediated climate feedback (Quinn and Bates, 2011), the CLAW
46 hypothesis has provided motivation for the widespread measurement of DMS in the
47 global ocean over the past thirty years.

48 Beyond their potential role in regional climate forcing, DMS and DMSP also play
49 critical ecological roles in marine microbial metabolism and food-web dynamics (for a
50 complete overview; see Stefels et al., 2007). DMSP is believed to serve numerous
51 physiological functions in phytoplankton, with suggested roles as an osmolyte, an anti-
52 oxidant, and a cryoprotectant under different environmental conditions. Sunda et al.
53 (2002) suggested that oxidative stressors, such as high solar radiation or iron limitation,
54 may stimulate DMSP production in certain phytoplankton species. The production of this
55 molecule is largely species-dependent, and can vary by three orders of magnitude among
56 phytoplankton groups, with the highest intracellular concentrations typically reported in

57 dinoflagellates and haptophytes, and lower concentrations in diatoms (Keller, 1989).

58 After synthesis, DMSP can be cleaved to DMS and acrylate within algal cells, or
59 by heterotrophic bacteria acting on the dissolved DMSP (DMSP_d) pool in the water
60 column (Zubkov et al., 2001). The release of DMSP into the water column is believed to
61 be enhanced in physiologically stressed or senescent phytoplankton (Malin et al., 1998),
62 and can be stimulated by zooplankton grazing and viral lysis (Evans et al., 2007).
63 Bacteria can also utilize DMSP_d as a sulfur source for protein synthesis (Kiene et al.,
64 2000), but this pathway does not lead to DMS release. The DMS yield of bacterial
65 DMSP metabolism (i.e. the fraction of consumed DMSP that is converted to DMS) varies
66 significantly, and may be influenced by the relative supply and demand of reduced sulfur
67 and carbon for bacterial growth (Kiene and Linn, 2000).

68 In environments with low anthropogenic aerosol concentrations, understanding
69 the impact of natural aerosol sources on cloud formation is critical to correctly estimating
70 climate forcing (Carslaw et al, 2013). Modeling studies have suggested that DMS
71 emissions could exert a particularly significant influence on CCN formation and regional
72 climate in polar regions, due to the low background concentrations of atmospheric
73 aerosols at high latitudes (Woodhouse et al., 2010) The effect of aerosol emissions on
74 cloud formation remains subject to some debate, with a modelling study (Browse et al
75 2014) suggesting only weak CCN response to Arctic organic aerosol flux. Nevertheless,
76 direct observations have demonstrated a link between sea surface DMS emissions and
77 particle formation events in the Arctic atmosphere (Chang et al., 2011; Mungall et al.,
78 2016), motivating further quantification of marine DMS emissions in Arctic regions.

79 To date, logistical constraints have limited the measurements of surface water
80 properties in many high latitude regions, and these areas remain relatively sparsely
81 sampled for DMS/P concentrations. Indeed, of the approximately 50,000 data points in
82 the global Pacific Marine Environmental Laboratory (PMEL) database of oceanic DMS
83 measurements (<http://saga.pmel.noaa.gov/dms/>), only 5% have been made in either Arctic
84 or Antarctic waters (~ 1600 and 1000 data points, respectively). Despite the relatively
85 limited sulfur observations in high latitude waters, an examination of the available data
86 reveals large differences in the water column DMS distributions of the Arctic and
87 Antarctic regions. While the summertime mean DMS concentration in the Arctic Ocean is
88 3.0 nM (close to the global mean value of 4.2 nM, derived from the PMEL data), the
89 mean summertime DMS concentration in the Southern Ocean is ~ 3 times higher at 9.3
90 nM. Moreover, several areas of extraordinarily high DMS concentrations (>100 nM) have
91 been observed in various regions of the Southern Ocean (DiTullio et al. 2000; Tortell et
92 al. 2011), whereas no study to date has observed DMS concentrations above 25 nM in
93 Arctic waters. The available data thus suggest contrasting dynamics of DMS/P
94 production in the two polar regions (i.e. Arctic vs. Antarctic).

95 Although Arctic and Antarctic regions share several key physical characteristics,
96 most notably strong seasonal cycles in sea ice cover and solar irradiance, there are some
97 critical differences. Much of the pelagic Southern Ocean is an iron-limited, High
98 Nutrient Low Chlorophyll (HNLC) regime, with large seasonal changes in mixed layer
99 depths (MLD) (Boyd et al., 2001). Low iron conditions, and seasonally-variable mixed
100 layer light levels may induce oxidative stress (particularly in ice-influenced stratified

101 waters) and thus promote high DMS production (Sunda et al., 2002). In addition, parts of
102 the Southern Ocean are characterized by extremely high biomass of *Phaeocystis*
103 *antarctica* (Smith et al., 2000), a colonial haptophyte that is a prodigious producer of
104 DMSP and DMS (Stefels et al., 2007). By comparison, the salinity-stratified surface
105 waters of the Arctic Ocean are believed to be primarily limited by macronutrient (i.e.
106 nitrate) availability (Tremblay et al., 2006), with a maximum phytoplankton biomass that
107 is at least an order of magnitude lower than that observed in the Southern Ocean (Carr et
108 al., 2006). Despite the relatively low phytoplankton biomass over much of the Arctic
109 Ocean, reasonably high summertime DMS levels (max ~ 25 nM) have been observed in
110 some regions. It is also important to note that significant Arctic phytoplankton biomass
111 and primary productivity may occur in sub-surface layers (Martin et al. 2010), and in
112 under-ice blooms (Arrigo et al., 2012). The quantitative significance of these blooms for
113 DMS production is unknown at present (Galindo et al., 2014).

114 Quantifying the spatial and temporal distribution of DMS and DMSP in the Arctic
115 Ocean is particularly important in light of the rapidly changing hydrographic conditions
116 across this region. Rapid Arctic warming over the past several decades has been
117 associated with a significant reduction in summer sea ice extent, resulting in higher
118 mixed layer irradiance levels and a longer phytoplankton growing season (Arrigo et al.,
119 2008). Arrigo et al (2008) suggested that continued warming and sea-ice loss could lead
120 to a three-fold increase in primary productivity over the coming decades. The effects of
121 these potential changes on DMS/P concentrations and cycling remain unknown, but it has
122 been suggested that future changes in Arctic Ocean DMS emissions could modulate

123 regional climatic patterns (Levasseur, 2013). Indeed, modeling work has suggested that
124 cooling associated with increased DMS production and emissions in less ice-covered
125 polar regions may help offset warming associated with loss of sea-ice albedo (Gabric et
126 al., 2004; Cameron-Smith et al., 2011) The important climatic and biological roles of
127 reduced sulfur compounds, combined with altered marine conditions under a warming
128 environment, provide the motivation for a deeper understanding of the distribution and
129 cycling of DMS and related compounds in Arctic waters.

130 In this article, we present a new data set of DMS and DMSP concentrations in
131 Arctic and Subarctic waters adjacent to the Canadian continental shelf. We used a
132 number of recent and emerging methodological approaches to measure these compounds
133 in a continuous ship-board fashion. In particular, we used membrane inlet mass
134 spectrometry (MIMS) to measure DMS with extremely high spatial resolution (i.e. sub-
135 km scale), and the recently developed organic sulfur sequential chemical analysis robot
136 (OSSCAR), for automated analysis of DMS and DMSP. Our goal was to utilize the
137 sampling capacities of the MIMS and OSSCAR systems to make simultaneous
138 measurements of DMS/P in Subarctic Atlantic and Arctic waters, in order to expand the
139 spatial coverage of the existing DMS/P dataset, and identify environmental conditions
140 leading to spatial variability in the concentrations of these compounds.

141 **2. Methods**

142 **2.1 Study Area**

143 Our field study was carried out on board the *CCGS Amundsen* during Leg 2 of the 2015
144 GEOTRACES expedition to the Canadian Arctic, from July 10 to August 20, 2015. We

145 sampled along a ~ 10,000 km transect from Quebec City, Quebec, to Kugluktuk,
146 Nunavut. Data collection commenced off the coast of Newfoundland, and included
147 waters of the Labrador Sea, Baffin Bay and the Canadian Arctic Archipelago (Figure 1).

148 The cruise transect covered two main distinct geographic domains – the Baffin
149 Bay/Labrador Sea region, and the Canadian Arctic Archipelago (CAA). The majority of
150 the surface water in the CAA is from Pacific-sourced water masses, as a shallow sill near
151 Resolute restricts the westward flow of Atlantic-sourced water (Michel et al., 2006). Flow
152 paths through the CAA are complex. The region is characterized by a network of shallow,
153 narrow straits that are subject to significant regional variability in local mixing and tidal
154 processes, and strongly influenced by riverine input, which drives stratification (Carmack
155 et al, 2011). In contrast, both Atlantic- and Pacific-sourced waters mix in the Baffin Bay
156 and Labrador Sea regions, and this confluence drives a strong thermohaline front, leading
157 to lower stratification than in the CAA (Carmack et al, 2011).

158 **2.2 Underway sampling systems**

159 We utilized two complementary underway sampling systems to measure reduced
160 sulfur compounds; MIMS (Tortell, 2005), and OSSCAR (Asher et al., 2015). Detailed
161 methodological descriptions of these systems have been published elsewhere ((Tortell,
162 2005, 2011), (Asher et al., 2015), and only a brief overview is given here.

163 **2.2.1 OSSCAR**

164 The OSSCAR instrument consists of an automated liquid handling / wet
165 chemistry module that is interfaced to a custom-built purge-and-trap gas chromatograph
166 (GC) equipped with a pulsed flame photometric detector (PFPD) for sulfur analysis. A

167 custom LabVIEW program is used to automate all aspects of the sample handling and
168 data acquisition. During analysis, unfiltered seawater (3 - 5 ml) from an underway supply
169 (nominal sampling depth ~ 5 m) is drawn via automated syringe pump into a sparging
170 chamber. DMS is then stripped out of solution (4 minutes of 50 ml min⁻¹ N₂ flow) onto a
171 1/8" stainless steel trap packed with carbopack at room temperature. Rapid electrical
172 heating of the trap (to ~260°C), causes DMS desorption onto a capillary column (Restek
173 SS MXT, 15m, 80 °C, 2 ml min⁻¹ N₂ flow) prior to detection by the PFPD (OI Analytical,
174 Model 5380). Light emitted during combustion in the PFPD is converted to a voltage and
175 recorded by a custom built Labview data acquisition interface. Following the completion
176 of DMS analysis, 5 N sodium hydroxide is added to the sparging chamber for 14 minutes
177 to cleave DMSP in solution to DMS, following the method of Dacey and Blough (Dacey
178 and Blough, 1987). The resulting DMS is sparged out of solution and measured as
179 described above. The sparging chamber is then thoroughly rinsed with Milli-Q water,
180 and the process can be repeated. As we used unfiltered seawater for our analysis, it is
181 important to note that we measured total DMSP (DMSP_t) concentrations, which represent
182 the sum of dissolved and particulate pools.

183 We measured an in-line standard (20 nM) every 4-5 samples (at most every 3
184 hours) to ensure that the system was functioning correctly, and to correct for potential
185 detector drift. The mean standard error of daily point standards was 0.55 nM, and we
186 consider this to represent the precision of our emerging method (significant efforts are
187 underway to increase this precision). To correct the underway data for instrument drift,
188 point standard measurements were smoothed with a 3-pt running mean filter, interpolated

189 to the time-points of sample measurements, and compared to the known standard
190 concentration to provide a drift correction factor for every seawater data point. Six-point
191 calibration curves were performed every two days, using DMS standards (ranging from 0
192 to 18nM), produced from automated dilutions of a primary DMS stock and Milli-Q water
193 (see Asher et al., 2015). The limit of detection of the system was calculated from the
194 calibration curve using the formula $C_{LOD} = 3s_{y/x} \div b$, where C_{LOD} is the concentration limit
195 of detection, $s_{y/x}$ is the standard error of the regression, and b is the slope of the
196 regression line. With this approach, we derived a mean limit of detection of 1.4 nM. The
197 mean linear calibration curve R^2 value, taken over all calibration curves, was 0.9887.

198 The OSSCAR system is designed to automate the collection of seawater for
199 sequential analysis of DMS, DMSO, and DMSP in a single sample. During our cruise,
200 however, we experienced problems with the DMSO reductase enzyme used to convert
201 DMSO to DMS for analysis, and we therefore configured the instrument to run only
202 DMS and DMSP at sea, with one cycle requiring roughly 30 minutes. We experienced
203 general technical difficulties with the instrument during the early phases of the cruise,
204 and no OSSCAR data are thus available for the first half of the transect.

205 **2.2.2 MIMS**

206 We used MIMS to obtain very high frequency measurements (~ several data points per
207 minute) of DMS concentrations and other gases in surface seawater. Using this system,
208 seawater from the ship's underway loop was pumped through a flow-through sampling
209 cuvette, attached, via a silicone membrane, to a quadrupole mass spectrometer (Hiden
210 Analytical HPR-40). DMS was measured by detecting ions with a mass to charge ratio of

211 62 (m/z 62) every ~30 seconds. To achieve constant sample temperature prior to contact
212 with the membrane, seawater was passed through a 20 foot coil of stainless steel tubing
213 immersed in water bath held at 4 °C (Tortell et al. 2011). The system pressure (as
214 measured by the Penning Gauge) remained stable during operation ($\sim 1.3 - 1.5 \times 10^{-6}$
215 Torr). The DMS signal was calibrated using liquid standards that were produced by
216 equilibrating 0.2 μm filtered seawater with a constant supply of DMS (m/z 62) from a
217 calibrated permeation device (VICI Metronics). The primary effluent from the
218 permeation tube (held at 30 ± 0.1 °C in a custom-built oven) was split among several
219 capillary outflows and mixed into a N₂ stream controlled at 50 ml min⁻¹ using a pressure
220 regulator and fixed length / diameter tubing. This system enabled us to achieve a range
221 of DMS / N₂ mixing ratios that were bubbled into standard bottles held in an incubator
222 tank supplied with continuously flowing seawater. Concentrations of DMS in the
223 standard bottles were cross-validated by measuring discrete samples using the OSSCAR
224 system. The limit of reliable detection of the MIMS is ~ 2nM (Tortell 2005).

225 **2.3 Post-processing of DMS data**

226 Raw data outputs (voltages) for both OSSCAR and MIMS measurements were processed
227 into final concentrations using MATLAB scripts. For OSSCAR data, raw voltages were
228 captured with a sampling frequency of 5 Hz. Sulfur peaks eluting off the GC column
229 were integrated using a custom MATLAB script, with correction for baseline signal
230 intensities. DMS concentrations were derived from peak areas using the calibration
231 curves as described above.

232 **2.4 Ancillary seawater data**

233 Shipboard salinity, temperature, wind speed, and chlorophyll *a* (chl *a*)
234 fluorescence measurements were collected using several underway instruments. We used
235 a Seabird Electronics thermosalinograph (SBE 45) for continuous surface temperature
236 and salinity measurements, and a Wetlabs Fluorometer (WetStar) to measure chl *a*
237 fluorescence, as a proxy for phytoplankton biomass. We note that the chl *a* fluorescence
238 data are subject to significant diel cycles associated with light-dependent fluorescence
239 quenching. All sensors were calibrated prior to and following the summer expedition.
240 Conductivity Temperature Depth (CTD) profiles were used to measure vertical profiles of
241 salinity and potential temperature at 17 stations, from which we computed density using
242 the Seawater Toolbox in MATLAB. The mixed layer depth (MLD) was defined as the
243 depth where density exceeded surface values by 0.125 kg m^{-3} . Sea ice concentrations
244 were obtained from the AMSR-E satellite product (Cavelieri et al. 2006) with a spatial
245 resolution of 12.5 km. The percent ice cover along the cruise track was derived from a
246 two dimensional interpolation of the ship's position in time and space against the daily
247 sea ice data.

248 All correlation analyses (Pearson's *r*) were computed in MATLAB, using the
249 `corrcoef` function. Sample sizes were as follows: 33,250 data points in the MIMS DMS
250 dataset, 344 in the OSSCAR DMS dataset, and 318 in the OSSCAR DMSP dataset.

251 **2.5 Phytoplankton biomass and taxonomic composition**

252 In addition to underway data, samples for the quantification of photosynthetic and
253 accessory pigments (Table 1) were collected at a number of discrete oceanographic
254 stations (see Table 2). For each station, duplicate samples (250-500 mL) for chl *a* analysis

255 were filtered onto pre-combusted 25 mm glass fiber filters (Whatman GF/F) using low
256 vacuum pressure (<100 mm Hg). Filters were stored at -20 °C and chl *a* was determined
257 within a few days of sample collection using fluorimetric analysis following the method
258 of Welschmeyer (Welschmeyer 1994). Duplicate 1-2 L samples were filtered onto pre-
259 combusted 25 mm GF/F for pigment analysis by reverse-phase High-Performance Liquid
260 Chromatography (HPLC). Filters were dried with absorbent paper, flash frozen in liquid
261 nitrogen and stored at -80 °C until analysis following the method of Pinckney et al
262 (1994). We used several diagnostic pigments as markers for individual phytoplankton
263 groups, as described by Coupel et al (2015) (see Table 1). Following HPLC pigment
264 processing, data were interpreted with the chemotaxonomy program CHEMTAX V1.95,
265 using the pigment ratio matrix described by Taylor et al (2013).

266 **2.6 DMS Sea-Air Flux**

267 We derived sea-air fluxes of DMS from MIMS measurements of DMS
268 concentrations, as these data had higher resolution and spatial coverage than OSSCAR
269 observations. We computed sea-air flux as:

$$270 \quad F_{\text{DMS}} = k_{\text{DMS}} (\text{DMS}_{\text{sw}}) (1 - A)^{0.4} \quad (1)$$

271 where DMS_{sw} is the concentration of DMS in the surface ocean (surface atmospheric
272 DMS is assumed to be zero) and k_{DMS} is the gas transfer velocity derived from the
273 equations of Nightingale et al. (2000), normalized to the temperature and salinity-
274 dependent DMS Schmidt number of Saltzman et al. (1993). The term *A* represents the
275 proportion of sea ice cover, and the scaling exponent of 0.4 accounts for the effects of sea
276 ice on gas exchange and is derived from the laboratory work of Loose et al. (2009). (We

277 note that this scaling does not capture all processes present in sea-ice dominated regimes,
278 such as turbulence generated by sea ice melt.) Sea surface salinity and temperature
279 measurements described in section 2.5 were used in the calculations. Wind speed data
280 were obtained from the ship's anemometer (AAVOS data, Environment Canada),
281 corrected to a height of 10 m above the sea surface.

282 **3. Results**

283 **3.1 Oceanographic setting**

284 Figures 1 and 2 show the distribution of hydrographic properties across our cruise
285 survey region. Over our sampling area, surface water temperatures varied between -1.2
286 and 10.2 °C, while surface salinity ranged from 10.7 to 34.7 psu (Figure 1). The warmest
287 and most saline waters were found in the Labrador Sea, with cold fresher waters in
288 Hudson Strait and the Canadian Arctic Archipelago. Underway chl *a* fluorescence varied
289 between 0.04 and 2.96 $\mu\text{g L}^{-1}$, averaging 0.20 $\mu\text{g L}^{-1}$. The highest chl *a* fluorescence was
290 observed in a localized region within Baffin Bay, in the vicinity of a sharp temperature
291 and salinity frontal zone (Figure 1). Mixed layer depth (MLD) ranged from ~ 5 - 50 m,
292 and were deepest in the Labrador Sea and shallowest in the stations of the Canadian
293 Arctic Archipelago. Sea ice cover was variable across the survey transect, with ice-free
294 waters in the Labrador Sea, and significant ice cover in the northern Hudson Bay and
295 parts of the Canadian Arctic Archipelago (Figure 2).

296 **3.2 Phytoplankton biomass and taxonomic distributions**

297 Using measurements of accessory photosynthetic pigments, we examined spatial patterns
298 in the taxonomic composition of phytoplankton assemblages (see Table 1 for a

299 description of HPLC marker pigments and their associated phytoplankton taxa). The
300 distribution of pigments across our sampling stations is presented in Table 2, along with
301 measurements of mixed layer depth and ice cover, while CHEMTAX-derived assemblage
302 estimates are shown in Table 3. In order to remove large potential differences in total
303 phytoplankton biomass, we normalized pigment concentrations to total chl *a*
304 concentrations measured using HPLC (see Methods, section 2.5).
305 CHEMTAX pigment analysis shows that all stations in the study area were diatom-
306 dominated, although haptophyte, dinoflagellate, and prasinophyte markers were detected
307 in varying quantities at all stations (see Table 3). Total HPLC-measured chl *a* was
308 relatively low throughout the study area, ranging from 0.11 to 0.56 $\mu\text{g L}^{-1}$.

309 **3.3 Observed DMS/P concentration ranges**

310 The DMS data shown in Figure 1 are derived from MIMS measurements, since
311 these have wider geographic coverage and greater spatial resolution than OSSCAR data.
312 DMS concentrations measured with MIMS ranged from 0.2 nM to 12 nM, averaging 2.7
313 (± 1.5) nM. The highest values were observed in the northern Labrador Sea, Baffin Bay
314 and Hudson Strait, with lower values through much of the Arctic Archipelago.

315 Figure 3 shows the distribution of DMS, measured by both MIMS and OSSCAR,
316 along the cruise track. DMS concentrations measured with OSSCAR ranged from 0.1 to
317 18 nM, averaging 3.2 ± 2.4 nM. As described in the discussion, 22% of our derived DMS
318 concentrations fell below the limit of detection. In general, we observed reasonably good
319 coherence between DMS measurements made by our two analytical systems, with similar
320 absolute values of data and spatial patterns. There were, however, notable offsets in the

321 early August measurements (~ km 7000 cruise track, Figure 3a), when OSSCAR DMS
322 data were consistently higher than MIMS data. Notwithstanding this offset (for which
323 potential reasons are addressed in the discussion), the coherent spatial patterns in data
324 derived from these independent methods is encouraging, particularly given the rather low
325 precision of our current OSSCAR system.

326 The spatial distribution of DMSP concentrations (measured with OSSCAR) along
327 the cruise track is also shown in Figure 3. Concentrations ranged from <1 nM to 160 nM,
328 and averaged 30 ± 29 nM. DMSP:chl *a* ratios measured from HPLC chl *a* data ranged
329 from 52.31 nmol μg^{-1} to 181.4 nmol μg^{-1} . Examination of the data in Figure 3
330 reveals that high DMS concentrations were sometimes, but not always, accompanied by
331 high DMSP concentrations. For example, a sharp increase in measured DMSP
332 concentrations (around 7000-7400 km) on the cruise track was accompanied by a sharp
333 increase in DMS measured by both instruments, while low-DMS waters observed around
334 km 9400 along the transect also showed very little DMSP. Over the portion of the
335 transect where measurements of both DMS and DMSP were available, the OSSCAR-
336 measured concentrations of these compounds exhibited a statistically significant positive
337 correlation ($r = 0.52$, $p < 0.001$). There were, however, a number of regions where
338 increased DMS concentrations were not accompanied by increases in DMSP (e.g. ~ km
339 10,000).

340 **3.4 Sea-Air Flux**

341 Figure 4 shows DMS sea-air fluxes as computed from MIMS-measured DMS seawater
342 concentrations, wind speed and sea ice cover. DMS sea-air fluxes ranged from < 1 to 80

343 $\mu\text{mol S m}^{-2} \text{ day}^{-1}$, with peak sea-air flux calculated around km 5500 on the cruise track.
344 Sea-air flux is highly dependent on wind speed and sea ice cover, with the result that even
345 high concentrations of seawater DMS yielded low sea-air flux when low wind and/or
346 high sea ice was present (e.g. km 2100, 7200, 8300). Conversely, very high sea-air fluxes
347 were observed when moderately high DMS concentrations coincided with high wind
348 speeds and ice-free waters (e.g. km 5400).

349 **3.5 Comparison of gradients in DMS data with hydrographic features**

350 The high sampling frequency of MIMS measurements allows the comparison of
351 DMS observations with other underway environmental variables, and enables the
352 quantification of small-scale DMS concentration gradients in near real-time. Figure 2
353 shows a cruise track record of MIMS-measured DMS concentrations in relation to
354 salinity, temperature, chl *a* fluorescence, and ice cover. Several sharp increases in DMS at
355 around kms 2100, 3300, and 3800 along the cruise track were accompanied by strong
356 gradients in temperature and, to a lesser extent, salinity (Figure 2). These regions
357 correspond to areas in the Labrador Sea and Baffin Bay. An increase in DMS
358 concentrations in Baffin Bay around km 7200 in the cruise track (Figure 2a) was
359 associated with a simultaneous drop in sea-surface temperature and salinity, in close
360 proximity to a sharp increase in chl *a* fluorescence along the cruise track (Figure 2c) (see
361 Figure 1). As shown in Figure 3b, this localized region exhibited the highest
362 concentrations of DMSP along the transect. Interestingly, this area was also characterized
363 by strong gradients in sea ice concentrations, and the low salinity waters are indicative of
364 localized ice melt. Figures 1d and 2d also show the large-scale salinity gradients in the

365 Hudson Bay and the Canadian Arctic Archipelago, highlighting the freshwater influx in
366 these near-shore areas. In contrast to our observations in Baffin Bay, DMS
367 concentrations showed relatively little variability across these salinity gradients.

368 In order to more closely examine small-scale variability in DMS and other surface
369 water variables, we calculated spatial gradients in the data to examine the coherence of
370 frontal features in DMS, salinity, temperature and chl *a* fluorescence. For this analysis,
371 we computed gradients in each oceanographic variable within a neighborhood of 100
372 points surrounding each point. Gradients (*G*) for each variable (DMS, SST, chl *a*, and
373 salinity) were calculated at each point *x* as follows:

$$374 \quad G_x = \frac{V_{x+50} - V_{x-50}}{D_{x+50} - D_{x-50}} \quad (2)$$

375 Here, *G* is gradient (in units of change per km), *V* is the value of the variable at a
376 point, *x*, and *D* is the cruise track distance at *x*. A neighborhood of 100 points,
377 corresponding to a distance of ~25 km, was subjectively chosen because it best captured
378 the observed variability in the data, representing an intermediate value between a
379 localized neighborhood (e.g. 10 points), which would only consider changes close to the
380 point, and a large neighborhood (e.g. 1000 points), which would smooth the features. The
381 results of this analysis (Figure 5) qualitatively demonstrate a coherence of DMS gradients
382 with salinity, chlorophyll, and sea surface temperature.

383 **3.6 Correlation with ancillary oceanographic variables**

384 We computed Pearson correlation coefficients of DMS and DMSP with underway
385 measurements of salinity, sea surface temperature, chl *a* fluorescence, and sea ice cover.
386 We also examined the potential relationships between DMS concentrations and MIMS-

387 derived $p\text{CO}_2$, and $\Delta\text{O}_2/\text{Ar}$ (Tortell et al., in preparation). The results can be seen in Table
388 4. Only correlations significant at the 0.05 level are included. Only weak correlations are
389 seen between MIMS-measured DMS data and ancillary variables, and OSSCAR DMS
390 data did not exhibit any significant correlations with any ancillary variables, including
391 measured of phytoplankton taxonomic distributions. A significant positive correlation (r
392 = 0.66, $p < 0.001$) was found between DMSP and underway chl a fluorescence. Over the
393 whole transect, we observed a weak negative correlation between DMS/P and sea-ice
394 cover ($r = -0.26$ for DMS, and $r = -0.34$ for DMSP, $p < 0.001$ in both cases). A weak
395 positive correlation was found between DMSP/chl a and ice cover ($r = 0.52$, $p < 0.04$),
396 suggesting potential roles for sea-ice microalgae in DMSP production at the sampled
397 stations. It is interesting to note that elevated chl a fluorescence and DMSP
398 concentrations often occurred in areas of intermediate ice cover (km 3300, 7300 and 9200
399 along the cruise track), potentially reflecting the influence of ice-edge blooms or under-
400 ice phytoplankton assemblages. Potential mechanisms for these features are addressed in
401 the discussion.

402 **4. Discussion**

403 Our results provide a new dataset of reduced sulfur compounds in an under-
404 sampled region of the Arctic Ocean, enabling an examination of DMS/P variability in
405 relation to various oceanographic properties on a range of spatial scales. Below, we focus
406 our discussion on the observed relationship between gradients in DMS and other
407 oceanographic variables, and discuss the comparability of the two DMS measurement
408 methods utilized. We compare our results to previously published measurements in the

409 Arctic, situating our results in the context of the changing hydrography and
410 phytoplankton ecology of the Arctic Ocean.

411 **4.1 Comparability of MIMS and OSSCAR measurements**

412 The OSSCAR and MIMS instruments have previously shown good agreement in
413 measured DMS concentrations in the Subarctic Pacific Ocean (Asher et al. 2015).
414 Similarly, we observed relatively good coherence between the two methods (Figure 3)
415 over much of our cruise track. The largest exception to this occurred around km 7000,
416 when DMS measurements measured by OSSCAR were significantly higher than those
417 measured by MIMS. This region was characterized by very high DMSP measurements
418 (often one order of magnitude higher than the DMS measurements). If small amounts of
419 DMS remained in the OSSCAR system after DMSP analysis, sample carry-over could
420 contribute to higher measured concentrations in the subsequent DMS analysis. In order
421 to minimize this potential artifact, the system was thoroughly rinsed with MilliQ water
422 after every run. The effectiveness of this rinse was tested by subsequently purging DMSP
423 standards without NaOH, and no carryover was observed. It is possible, however, that
424 this approach was not entirely efficient. Another potential cause of the higher OSSCAR
425 DMS measurements may be due to cell breakage during the sparging process in
426 OSSCAR. In this scenario, there is the potential for release of intracellular DMSP and
427 DMSP lyase into solution, which would lead to artificially high measured DMS
428 concentrations. It is not possible for us to quantify the magnitude of such a potential
429 artefact, but we note that its magnitude would likely depend on the taxonomic
430 composition of phytoplankton assemblages. Wolfe et al (2002) showed that sample

431 sparging led to an increase in DMS production by both the haptophyte *Emiliana huxleii*
432 and the dinoflagellate *Alexandrium*. Unfortunately, due to limited coverage of discrete
433 sampling, we do not have any estimates of phytoplankton community composition in the
434 region where MIMS and OSSCAR showed the greatest discrepancies. Notwithstanding
435 these potential caveats, we suggest that the two methods show strong promise to provide
436 complementary information on DMS/P (and DMSO) concentrations in surface ocean
437 waters.

438 One challenge going forward is to increase the reproducibility and sensitivity of
439 OSSCAR measurements, and this is an area of active work in our group. The version of
440 our system used in 2015 had a detection limit of roughly 1.4 nM, and was thus far less
441 sensitive than many conventional GC methods, which can achieve sub-nM detection
442 limits. Our detection limit was of only minor consequence for DMSP measurements,
443 given that 72% of measured DMSP concentrations were higher than 10 nM, and less than
444 3% fell below 1.4 nM. The relatively low sensitivity was somewhat more problematic
445 for DMS, with approximately 22% of our OSSCAR-measured DMS values below 1.4
446 nM. Nonetheless, as discussed below, we believe that the OSSCAR data, in combination
447 with our MIMS data, provide useful information on the spatial distribution of both DMSP
448 and DMS in Arctic waters.

449 **4.2 Towards a regional Arctic data base of DMS/P concentrations**

450 Figure 6 shows a comparison between our Arctic DMS measurements (made by
451 OSSCAR) and other summertime Arctic DMS data in the PMEL database. For this
452 comparison, only PMEL measurements made above the Arctic circle (66.56° N) in June-

453 August are included, resulting in a total of 415 data points. As shown in Figure 6, the
454 majority of available summertime PMEL DMS/P measurements are found in the Atlantic
455 region of the Arctic, and in the Bering Sea, with limited data in the Canadian Archipelago
456 (for an overview of Arctic DMS/P studies performed to date, see Levasseur, 2013). For
457 the sake of visual clarity, the presentation of data in Figure 6a is based on DMS
458 measurements made by OSSCAR, whereas both sets of data were included in the
459 frequency distribution analysis (Figure 6b). The results presented in Figure 6 suggest that
460 our measurements are representative of the broader Arctic context, with generally similar
461 data frequency distributions (Figure 6b) for all three DMS datasets (MIMS, OSSCAR,
462 and PMEL). From the map, we see that the spatial footprint of our measurements
463 complement the existing summer data, helping to expand the spatial coverage of DMS
464 observations in the Arctic Ocean.

465 In addition to complementing the existing PMEL DMS database, our new
466 observations also build on a number of other reduced sulfur measurements in the
467 Canadian Sector of the Arctic Ocean. Observations of DMS and DMSP derived from
468 several past Arctic and subarctic Atlantic surveys are summarized in Table 5. This table
469 focuses mainly on DMS and DMSP measurements made in the Canadian sector and
470 Greenland waters, serving to provide context for our measurements performed in similar
471 environments. The data presented in Table 5 are obtained from different times of year,
472 and from phytoplankton assemblages of varying taxonomic composition, allowing us to
473 examine DMS and DMSP concentrations in surface waters under a range of
474 environmental and ecological conditions. For example, Bouillon et al. (2002) observed

475 low DMS concentrations ($<1\text{nM}$) during a large spring diatom bloom ($\sim 15 \mu\text{g L}^{-1}\text{chl } a$)
476 in the North Water region. In contrast, higher DMS concentrations have been reported
477 later in the season when total phytoplankton biomass is lower, and taxonomic
478 composition has shifted away from diatom-dominance. Working in the same geographic
479 region as Bouillon, Motard-Côté et al. (2012) reported higher late summer (September)
480 DMS levels (maximum = 4.8nM), which were accompanied by moderate chl *a*
481 concentrations ($0.2\text{-}1 \mu\text{gL}^{-1}$), while Luce et al. (2011) reported very low DMS ($<1\text{nM}$)
482 associated with moderate chl *a* concentrations ($0.2\text{-}2 \mu\text{gL}^{-1}$) in a flagellate dominated
483 community in late fall (October-November), with DMS decreasing towards the later
484 months. A similar pattern was observed in the northwest subarctic Atlantic by Lizotte et
485 al. (2012), who associated elevated reduced sulphur (DMSP) production with flagellate
486 and prymnesiophyte communities in midsummer and fall, in contrast to early-season
487 diatom blooms with little associated DMSP and DMS. This seasonal decrease in DMS
488 levels may be potentially attributable to light limited primary productivity, and
489 diminishing capacity for light-induced oxidative stress, which has been shown to increase
490 DMS/P production (Sunda et al., 2002).

491 To date, the highest recorded Arctic water column measurements of DMS (25nM)
492 and DMSP (160 nM) have been observed during mid-summer blooms of the haptophyte
493 *Phaeocystis* at the ice edge (see Matrai and Vernet, 1997; Gali and Simo, 2010). Our mid-
494 season (July-August) study of similar areas shows moderately high DMS (up to 18 nM)
495 accompanied by relatively low chl *a* ($0.11\text{-} 1.06 \mu\text{gL}^{-1}$) in a mixed community where
496 flagellates and prasinophytes are present.

497 Together, the available data (Table 5 and our measurements) are consistent with a
498 seasonal cycle in Arctic and subarctic reduced sulfur distributions. Early season diatom-
499 dominated blooms exhibit high biomass and primary productivity but low DMS/P
500 accumulation, while mid-summer phytoplankton assemblages dominated by haptophytes
501 and dinoflagellates display lower phytoplankton biomass but higher reduced sulfur
502 accumulation. This pattern is similar to the summertime 'DMS paradox' reported in a
503 number of temperate and sub-tropical waters (Simo and Pedrós-Alió, 1999). In the fall,
504 both Arctic primary productivity and DMS/P production decrease with the onset of lower
505 temperatures and increased ice cover. Our data are consistent with this general scenario,
506 representing a mixed-species assemblage with moderate biomass and DMS/P
507 accumulation.

508 **4.3 Gradients in DMS and hydrographic frontal structures**

509 The high resolution afforded by the MIMS dataset allows for the observation of
510 fine-scale variability in DMS concentrations at the sub-kilometer scale. Previous studies
511 (Tortell, 2005; Tortell et al., 2011) have quantified fine-scale variability in DMS
512 concentrations, demonstrating de-correlation length scales on the order of 10s of Km, and
513 often shorter than that of other oceanographic variables such as temperature and salinity.
514 These length-scales provide information on the spatial scale of processes driving the
515 majority of variability in DMS concentrations. Figures 2 and 5 clearly demonstrate that
516 gradients in DMS and chl *a* fluorescence often co-occur with strong gradients in
517 temperature and salinity. This suggests a potential role for hydrographic fronts in driving
518 changes in DMS concentrations. Several potential mechanisms may explain this

519 phenomenon. For example, the frontal mixing of distinct water masses, driven by
520 currents, wind, or melting ice, may introduce nutrients into a low-nutrient water column,
521 stimulating localized primary productivity (Tremblay et al. (2011) and potentially
522 increasing DMS/P production. Note that this localized increase in productivity and
523 potential DMS/P production would operate independently of the overall seasonal
524 progression towards increased DMS/P production during the latter summer growth
525 season. Mixing of water masses may also potentially expose water column phytoplankton
526 to light shock or osmotic stress by mixing them upwards in the water column or
527 introducing an abrupt salinity gradient. Both of these factors could contribute to elevated
528 DMSP production, given its hypothesized role as an intracellular osmolyte and anti-
529 oxidant (Stefels et al., 2007). Although our data do not allow mechanistic interpretation
530 for the underlying causes of DMS variability in surface waters, the high resolution
531 afforded by MIMS measurements enables real-time observations of DMS gradients,
532 which may be useful in the design of future process studies examining the driving forces
533 for elevated DMS accumulation.

534

535 **4.4 Influence of phytoplankton assemblage composition and mixed layer depth**

536 Previous work has addressed the role of phytoplankton taxonomic composition
537 and irradiance levels (Stefels et al, 2007) in driving the cycling of DMS/P in marine
538 waters. Here we discuss the potential influence of these factors across our survey region.
539 The majority of the sampled stations were characterized by very shallow mixed layer
540 depths (MLD; Table 2) resulting from strong salinity-based stratification of surface

541 waters. Light stress associated with shallow MLD may contribute to elevated DMSP : chl
542 *a* ratios, and previous studies (Vallina 2007) have shown high correlation between solar
543 irradiance and surface DMS concentrations. In our dataset, however, there was no
544 overall correlation between MLD and DMSP : Chl ratios. We did, however, observe
545 elevated DMSP concentrations at two stations (BB3 and CAA6) with shallow MLDs.

546 The elevated DMSP : chl *a* ratios measured in our study may also reflect the
547 presence of high-DMSP producing taxa, a phenomenon previously reported by other
548 groups (Matrai et al., 1997; Gali et al., 2010; Lizotte et al., 2012). When comparing our
549 DMSP: chl *a* ratios to other measurements, it is important to note that we measured
550 DMSP_t, while many other groups present DMSP_p, without taking into account the
551 dissolved fraction (DMSP_d). As the dissolved DMSP pool typically makes up a small
552 (though highly variable) portion of the total water column DMSP pool, the use of DMSP_t
553 does not likely have a large effect on derived DMSP:chl *a* ratios (Kiene et al., 2000;
554 2006). Despite the potential caveats raised above, the DMSP_t:chl *a* ratios we measured
555 across our sampling stations (52-182 nmol μg⁻¹) were broadly similar to DMSP_p:chl *a*
556 values found by Motard-Côté et al. (15-229 nmol μg⁻¹) in the same region in September
557 (Motard-Côté et al., 2011). In contrast, our measured DMSP_t:chl *a* ratios are significantly
558 higher than those measured by Luce et al. (maximum of 39 nmol μg⁻¹) (Luce et al., 2007)
559 and Matrai and Vernet (maximum 17 nmol μg⁻¹) at diatom-dominated stations in the
560 Barents Sea (Matrai and Vernet., 1997). The higher DMSP : Chl ratios we measured may
561 be attributable to the presence of mixed (rather than diatom-dominated) assemblages
562 present in the study area at the time of sampling. We cannot, however, draw any firm

563 conclusions on the role of taxonomy in controlling DMSP:Chla, as we were unable to
564 detect any significant correlations between DMSP:chl *a* and HPLC pigment markers for
565 different phytoplankton groups.

566 To conclude, our observations do not permit us to establish a firm link between
567 MLD, phytoplankton taxonomy and DMS/P concentrations. Other factors, including
568 bacterial activity and zooplankton grazing are potential contributing factors, but we lack
569 the data needed to examine the importance of these processes.

570 **4.5 The interaction of DMS/P and sea ice**

571 The presence of sea ice exerts a strong control on polar phytoplankton by
572 controlling irradiance levels in the water column (Levasseur 2013), and influencing
573 vertical mixing, stratification and nutrient accumulation. It is thus expected that the
574 presence of sea-ice may affect DMS/P cycling. In a 2010 study, Gali et al (2010) found
575 that Arctic sea ice melt drove stratification of nutrient rich surface water, triggering a
576 sharp increase in primary productivity, with associated elevated DMS and DMSP levels.
577 These authors also showed that experimental exposure of phytoplankton to high light
578 conditions (mimicking those that would follow the breakup of sea ice) led to near-total
579 release of intracellular DMSP, providing one possible explanation for elevated DMSP
580 levels in the water column. A number of studies also show that the ice, itself, can be a
581 potentially significant reservoir of reduced sulfur, associated with bottom ice-algae
582 (Levasseur et al (1994).

583 The weak negative correlation we observed between sea ice cover and DMS/P
584 concentration is consistent with the idea that sea ice cover limits insolation, thereby

585 reducing primary productivity and DMS/P production. In general, the drivers of DMSP
586 and DMS production differ – though DMSP production has been shown to be directly
587 influenced by sea ice melt in under-ice blooms (Galindo et al., 2014), the production of
588 DMS from DMSP is largely dependent on the metabolism of in situ bacterial assemblages
589 (Evans et al, 2007), and may therefore be uncoupled from the influence of ice on
590 phytoplankton activity. It is interesting to note, however, that several sharp increases in
591 DMS (observed with MIMS) occurred simultaneously with the occurrence of small
592 amounts of sea ice (<20% total cover) (Figure 2, kms 3400 and 7200 on the cruise track).
593 Limited station data also indicate high DMSP:chl *a* ratios in areas with a comparatively
594 high sea ice cover, at stations BB3 and CAA6 (Table 2). At the time of our sampling,
595 both of these stations were characterized by very low phytoplankton biomass ($0.11 \mu\text{g L}^{-1}$
596 and $0.20 \mu\text{g L}^{-1}$ chl *a*, respectively) and had particularly high DMSP: chl *a* ratios (129
597 $\text{nmol } \mu\text{g}^{-1}$ and $182 \text{ nmol } \mu\text{g}^{-1}$, respectively). This suggests a potential role for ice-edge
598 effects, either through the melt-induced stimulation of reduced sulfur production in
599 DMSP rich phytoplankton taxa, or through the release of ice-associated DMSP into the
600 water column. Figures 2d and 2e show decreased salinity in partially ice-covered areas
601 (e.g. around kms 4400, 7300, and 9200), suggesting some melt-water stratification
602 effects. Previous groups have also reported elevated DMS and DMSP concentrations in
603 partially ice-covered water and ice-edge regions in the Arctic Ocean (Matrai and Vernet
604 (1997), Gali et al. (2010) and Leck and Persson (1997)).

605 =

606

607 **5. Conclusion**

608 We present a high spatial resolution dataset of reduced sulfur measurements
609 through the Canadian sector of the Arctic Ocean and Subarctic Atlantic. We demonstrate
610 the utility of high-resolution DMS measurements for comparison with other
611 oceanographic variables, and show the coherence of DMS gradients with fine-scale
612 surface hydrographic structure, suggesting elevated DMS production in some
613 oceanographic frontal zones. We also observed elevated DMS/P values in partially ice-
614 covered regions, suggesting that ice-edge effects may stimulate DMS/P production. Our
615 data serve to significantly expand the existing spatial coverage of reduced sulfur
616 measurements in the Arctic, providing a baseline for future studies in this rapidly
617 changing marine environment. Future warming of surface waters and sea-ice melt could
618 lead to increased concentrations and sea-air fluxes of DMS, though significantly more
619 observations will be needed to substantiate this.

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624

625 **Data Availability:**

626 All data are available at the following github repository:

627 [https://github.com/tjarnikova/Jarnikova Canadian Arctic DMS supldata](https://github.com/tjarnikova/Jarnikova_Canadian_Arctic_DMS_supldata) (DOI:
628 [10.5281/zenodo.160225](https://doi.org/10.5281/zenodo.160225))

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906 **Tables**

907

Pigment	Associated Taxa
Chlorophyll c₃	Haptophytes
Peridinin	Dinoflagellates
19'-butanoyloxyfucoxanthin	Haptophyte
Fucoxanthin	Diatoms, Haptophytes
19'-hexanoyloxyfucoxanthin	Haptophytes, Dinoflagellates
Diadinoxanthin	Haptophytes, Dinoflagellates,
	Diatoms
Violaxanthin	Dinoflagellates
Zeaxanthin	Dinoflagellates

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910 **Table 1. HPLC marker pigments and their associated phytoplankton taxa. Adapted**
911 **from Coupel et al. (2015) .**

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Station	Lat(N)	Lon(E)	MLD(m)	% Ice Cover	chl _a (µg L ⁻¹)	DMS/ chl _a (nmol µg ⁻¹)	DMSP/ chl _a (nmol µg ⁻¹)	Perid/ chl _a	19'ButFuc/ chl _a	Fuc/ chl _a	19'HexFuc/ chl _a	Diadino/ chl _a
K1	56.12	-53.37	18.4	<i>nd</i>	0.51	6.6	<i>nd</i>	0.043	0.077	0.184	0.156	0.056
LS2	60.45	-56.55	41.4	<i>nd</i>	0.59	3.4	<i>nd</i>	0.051	0.012	0.277	0.025	0.024
BB3	71.41	-68.59	8.2	19.7	0.12	<i>bdl</i>	129.4	0.049	0.011	0.278	0.051	0.087
BB2	72.75	-67.00	10.3	<i>nd</i>	0.19	21.7	93.3	0.050	0.015	0.312	0.089	0.072
CAA1	74.52	-80.56	32.1	<i>nd</i>	0.56	6.9	52.3	0.015	0.018	0.239	0.023	0.042
CAA5	74.12	-91.49	5.3	6.61	0.16	<i>bdl</i>	114.7	0.078	0.017	0.326	0.020	0.051
CAA6	74.75	-97.47	6.1	16.43	0.21	10.6	181.7	0.054	0.021	0.401	0.015	0.058
CAA7	73.66	-96.53	2.1	13.3	0.13	15.6	81.3	0.109	0.066	0.335	0.057	0.146
VS	69.16	-100.69	8.4	8.23	0.18	10.6	<i>nd</i>	0.029	0.020	0.309	0.032	0.037

935 | **Table 2.** Mixed layer depth (MLD), ice cover, HPLC pigment measurements (ratios of
936 selected marker pigments to chl a), DMS (MIMS) and DMSP (OSSCAR) measurements.
937 Perid = peridinin, 19'ButFuc = 19'-butanoyloxyfucoxanthin, Fuc = Fucoxanthin,
938 19'HexFuc = 19'-hexanoyloxyfucoxanthin, Diadino = Diadinoxanthin. *nd*= no data. *bdl*
939 = below detection limit.

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Station	Diatom	Dinoflag.	Chloro.	Prasino	Crypto.	C-P	c3-Flag.	Hapto-7
K1	37	14	0	17	4	9	1	16
LS2	39	19	0	23	1	3	7	8
BB3	48	15	4	14	8	1	5	5
BB2	44	16	11	14	4	2	1	8
CAA1	47	4	0	39	2	2	4	2
CAA5	50	19	1	10	3	2	14	1
CAA6	52	16	1	8	3	2	17	1
CAA7	46	11	4	17	8	8	0	5
VS	67	8	0	11	3	3	6	3

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942 **Table 3.** CHEMTAX-derived phytoplankton assemblage estimates (numbers given are
943 percent of total chl a) for sampled stations. Diat. = diatoms; Dinoflag = Dinoflagellates;
944 Chloro. = Chlorophytes; Prasino = Prasinophyte (types 2 and 3); Crypto. = Cryptophytes
945 Chryso-Pelago =Chrysophytes/Pelagophytes; c3-flag. = c3-Flagellates; Hapto-7 =
946 Haptophyte type 7. Due to the presence of unidentified phytoplankton taxa, not all
947 assemblage estimates sum to 100%.

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Variable	DMS Correlation Coefficient	DMSP Correlation Coefficient
$\Delta O_2/Ar$	0.22	0.33
Salinity	0.35	0.34
SST	0.29	0.14
Fluorescence	0.32	0.66
pCO_2	0.16	0.12
Ice Cover	-0.26	-0.34

950

951 **Table 4.** Pearson correlation coefficients relating DMS measurements made by MIMS
952 and DMSP measurements made by OSSCAR to other oceanographic variables. Only
953 correlations significant at the $p < 0.05$ level are shown. $\Delta O_2/Ar$ ratios were obtained using
954 MIMS.

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Author	Year	Month	Region	DMS (nM)	DMSP (nM)	Assemblage characteristics
Bouillon et al. 2002	1998	April-June	North Water	0.04-6.7	0.9-53	Diatom dominated assemblage
Matrai et al. 1997	1993	May	Barents Sea	2.8 - 25.3	6-27	Diatom-dominated and <i>Phaeocystis</i> -dominated stations
Lizotte et al. 2012	2003	May-October	Northwest Atlantic	0.1-12	4-101	Nanoflagellate dominated in all seasons
Gali et al. 2010	2007	July	Greenland Sea	0.1 - 18.3	1.4 - 163.6	Haptophyte (<i>Phaeocystis</i>) dominance
Leck et al. 1996	1991	August-October	Greenland Sea	0.04 - 12	--	Not described
Motard-Côté et al. 2012	2008	September	Baffin Bay North Water	0.4-5.2	5-70	
Scarratt et al. 2007	1999	September	Northwest Atlantic	0.2-4.7	0-203	Mixed assemblage
Luce et al. 2011	2007	October-November	High Arctic	0.05-0.8	2- 39	Flagellate-dominated except for diatom-dominated in Baffin Bay

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Table 5. Compilation of published Arctic and Subarctic Atlantic DMS/P data from the

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summer and fall months, focusing on observations from the Western Hemisphere.

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969 **Figures:**

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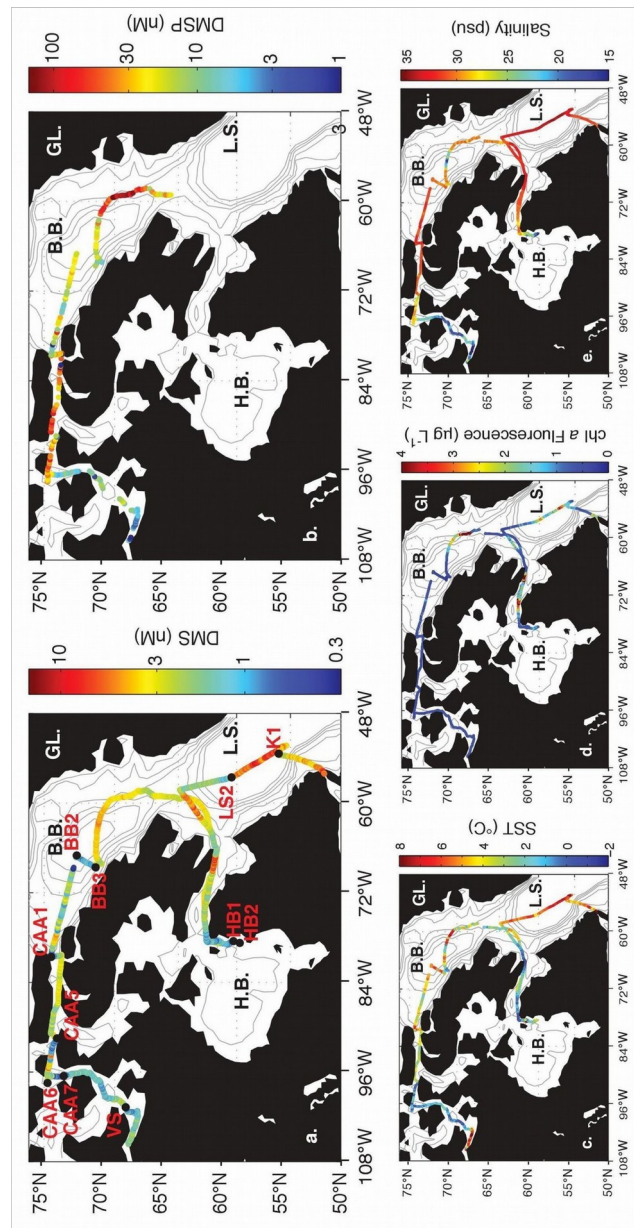
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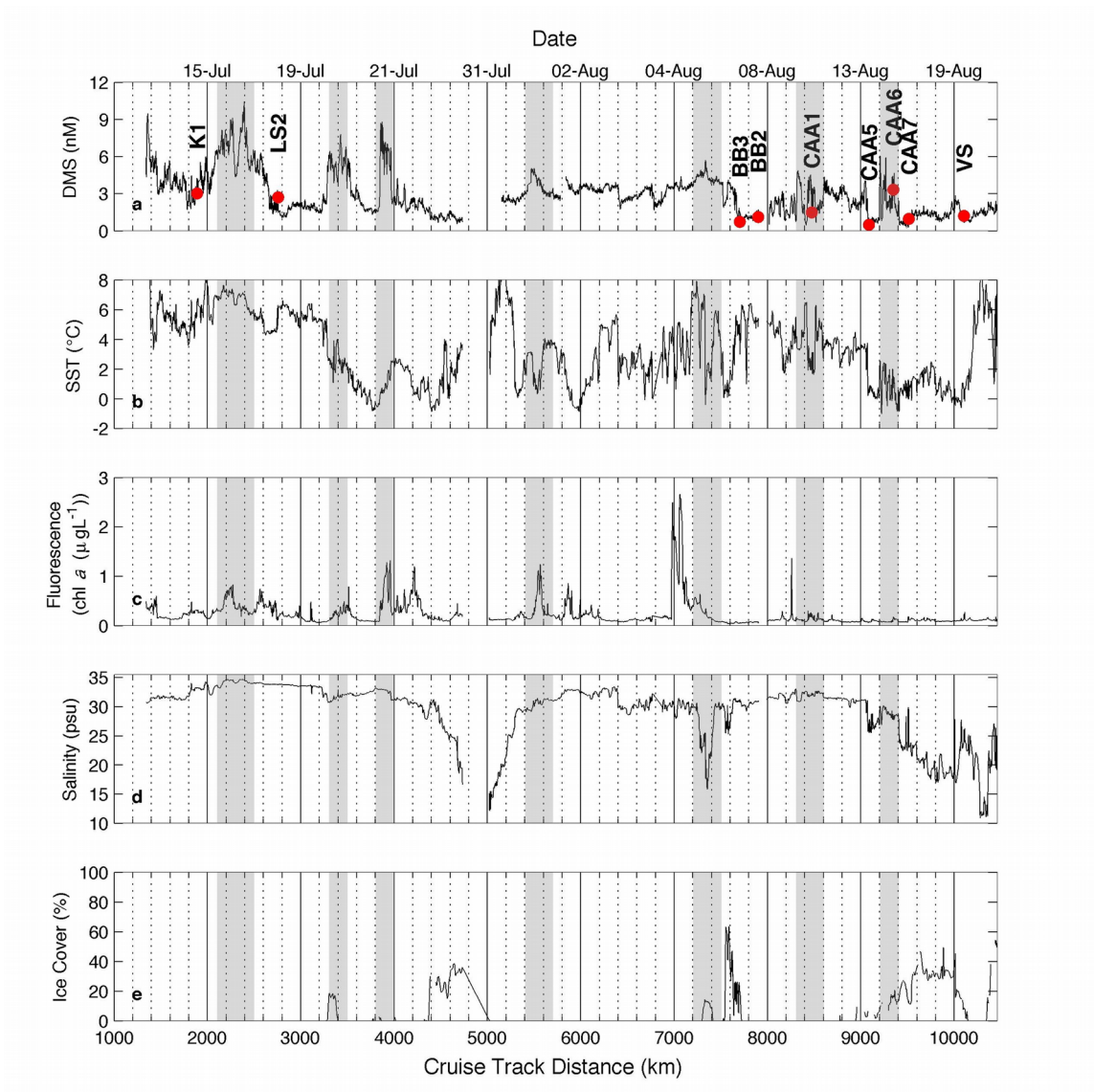
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988 **Figure 1.** Spatial distribution of DMS, DMSP and hydrographic variables. GL. =

989 Greenland, B.B. = Baffin Bay, L.S. = Labrador Sea, H.B. = Hudson Bay, C.A.A. =

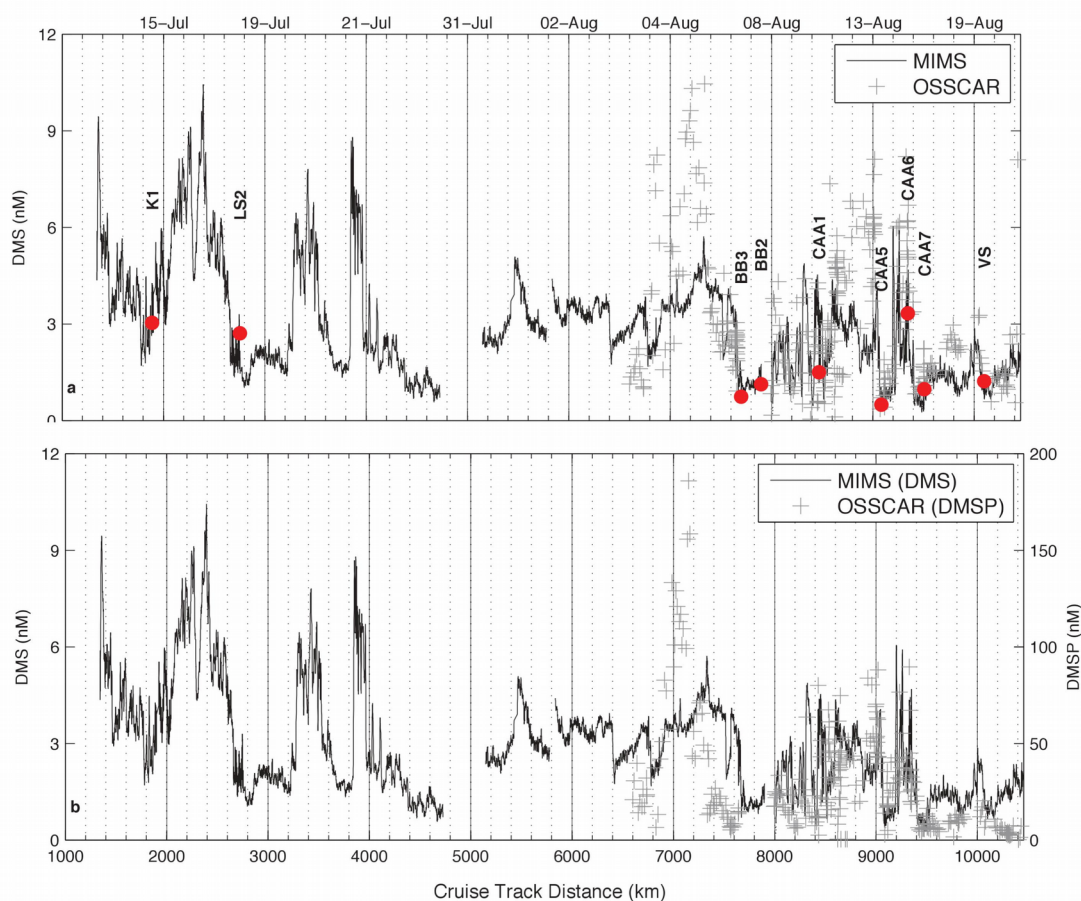
990 Canadian Arctic Archipelago.



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993 **Figure 2.** Distribution of DMS and hydrographic variables along our cruise track. Grey
 994 shaded areas denote regions of sharp increases in DMS. Labeled red dots indicate
 995 sampling stations (see Table 2).

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998 **Figure 3.** Distribution of DMS and DMSP along the cruise track. Panel (a) shows DMS
 999 measurements made by MIMS and OSSCAR. Note that a small fraction (less than
 1000 0.5%) of measurements made by OSSCAR were above 12 nM. Panel (b) shows MIMS
 1001 data with OSSCAR DMSP measurements superimposed on a different y scale (right hand
 1002 side). Labeled red dots indicate DMS concentrations measured at discrete sampling
 1003 stations (see Table 2).

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1021 Figure 4. Distribution of DMS, wind speed, sea ice cover and sea-air DMS flux along the
1022 cruise track.

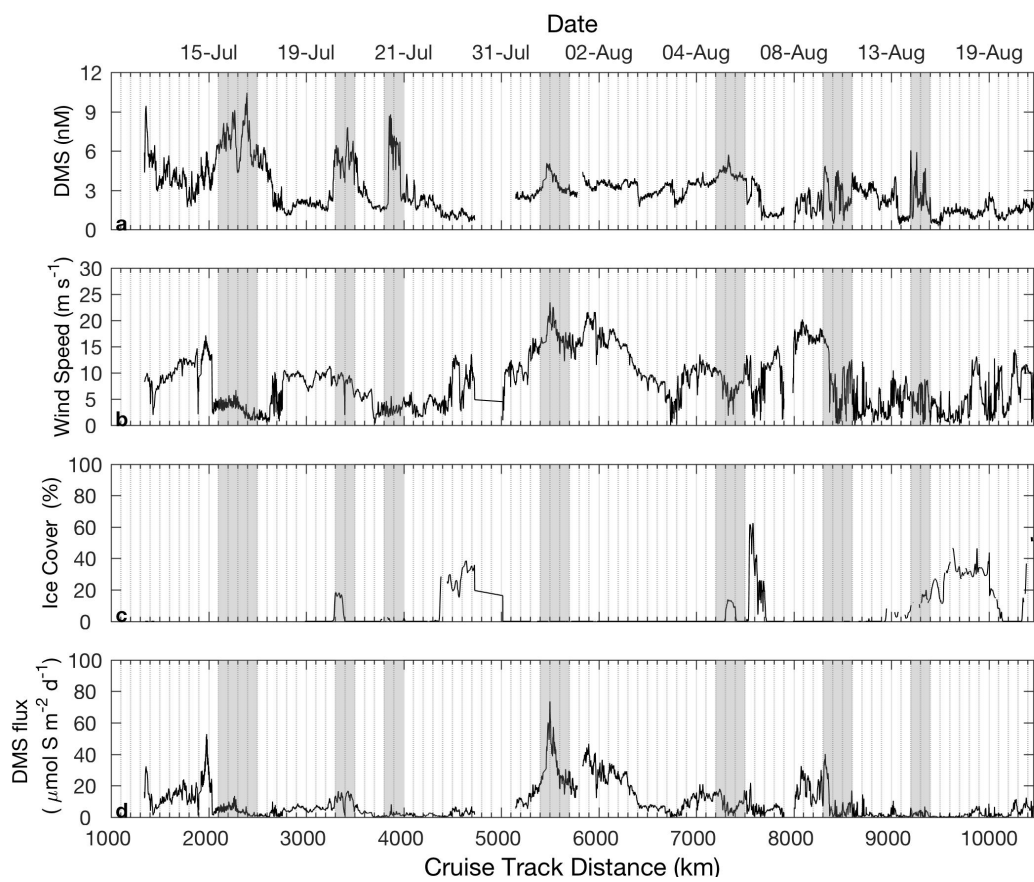
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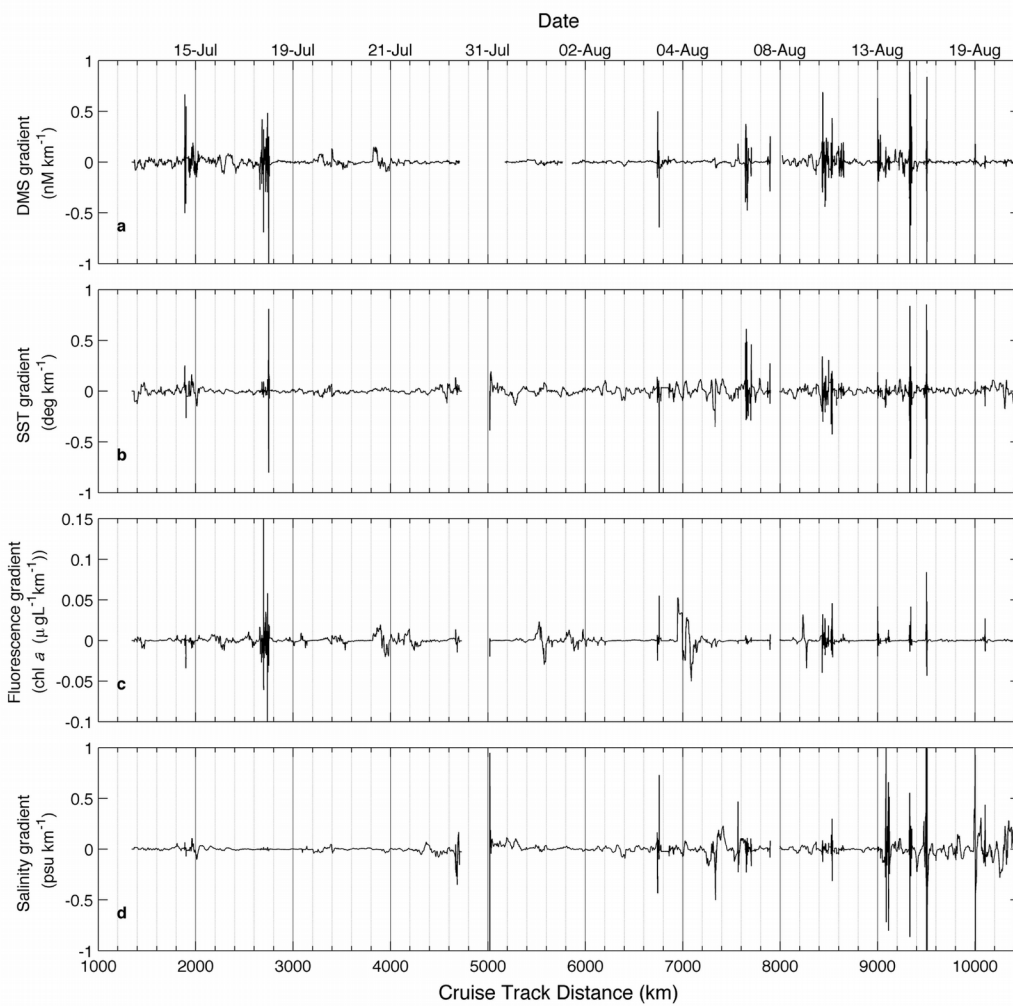


Figure 5. Spatial gradients in DMS (measured with MIMS) and hydrographic variables, calculated from a neighbourhood of 100 data points (~25km).

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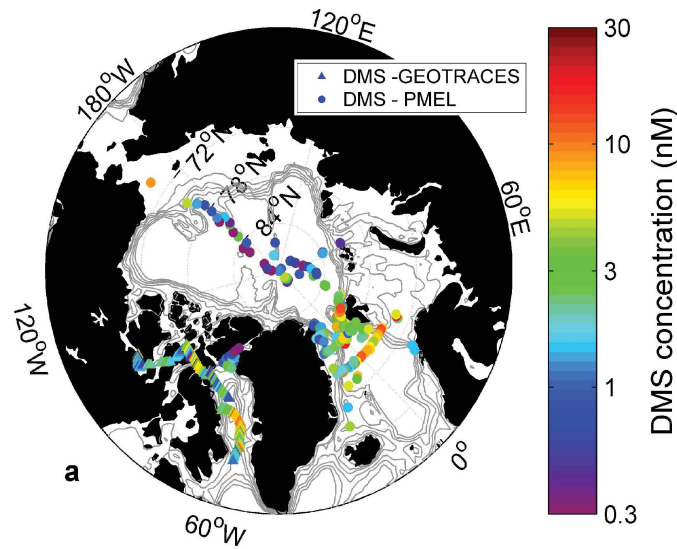
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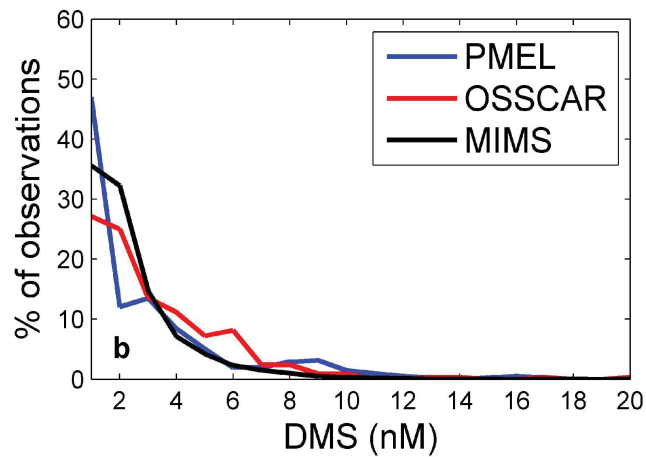
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Figure 6. Comparison of OSSCAR- and MIMS-measured DMS from this study with existing summertime data in the PMEL database. Panel (a) shows the geographic distribution of DMS measurements in the PMEL database and those obtained by this study (using OSSCAR), while panel b) shows a histogram of DMS concentrations in three datasets – the MIMS dataset (33,250 data points) the OSSCAR dataset (344 points), and the PMEL dataset. (415 points).