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Author comments on "Dimethyl sulfide in the summertime Arctic atmosphere: Measurements and source sensitivity simulations"

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We thank the reviewer for an informed review of the paper. The following point-by-point responses indicate how we have addressed each concern below noting the relevant constraints but at the same time recognizing that this is the first set of DMS measurements for this region during summer. Please note that manuscript page and line numbers in our responses refer to the marked-up version of the revised manuscript.

RC1: *"This paper describes a recent set of DMS measurements (mostly atmospheric, some seawater) from a cruise in the Canadian Arctic. The authors used trajectory analysis and GEOS-Chem model to predict the atmospheric DMS mixing ratios, which were compared to shipboard measurements. Differences between the model and measurements were then attributed to oceanic as well as non-marine DMS sources, such as terrestrial plants, tundra, and melt ponds. The authors were thorough in examining all the possible DMS sources. The use of trajectory/chemical transport modeling for this analysis is appropriate. However, the "end member" emission rates from most of these sources (e.g. melt ponds, biomass burning) are highly uncertain – often times only a single emission value from literature is available. Such large uncertainties mean that the work is less about "attribution" and more a case of sensitivity study."*

AC1: We agree entirely that the simulations, which we conducted to explore the potential source contributions to atmospheric DMS, are sensitivity simulations. We also acknowledge that there are considerable remaining uncertainties. We have made several changes to the manuscript to ensure that these points are clearer in the presentation, including changing the title of the work. Despite these uncertainties, our simulations do present strong evidence that 1) most of the gas phase DMS observed can be explained by local marine sources, and 2) at certain times (e.g. 18-19 and 25-26 July) transport must be invoked to explain the observed levels of atmospheric DMS.

Manuscript Changes:

Changed the title to “Dimethyl sulfide in the summertime Arctic atmosphere: Measurements and source sensitivity simulations” to reflect that these are indeed sensitivity simulations.

p. 1 line 19: “After adjusting GEOS-Chem oceanic DMS values in the region to match measurements, GEOS-Chem reproduced the major features of the measured time series, but was biased low overall (2-1006 pptv, median 72 pptv), although within the range of uncertainty of the seawater DMS source. However, during some 1-2 day periods the model under predicted the measurements by more than an order of magnitude. Sensitivity tests indicated that non-marine sources (lakes, biomass burning, melt ponds and coastal tundra) could make additional episodic contributions to atmospheric DMS in the study region, although local marine sources of DMS dominated.”

p. 4 line 114: Added the phrase “sensitivity studies” to our description of the contents of the manuscript.

p. 7 line 206: Changed “interpret the atmospheric measurements” to “conduct source sensitivity studies”.

p. 12 line 376: Changed the heading for Section 4 from “Source apportionment with GEOS-Chem and FLEXPART” to “Source sensitivity studies with GEOS-Chem and FLEXPART”.

RC2:*“My biggest concern of this paper lies in the fact that there were so few seawater DMS measurements, which are needed to compute the DMS flux along the cruise track and form the principle input parameters for the GEOS-Chem model. A significantly biased seawater DMS field would render most of the analysis on model-measurement comparison in atmospheric DMS moot.”*

AC2: We understand the reviewer’s concern but the question of number of measurements should be assessed in the context of past work. Relative to studies done in other regions of the ocean, we do have fewer seawater DMS measurements. However, the state-of-the-science Lana et al. (2011) was based on DMS data with very limited spatial coverage in the Canadian Arctic Archipelago and Baffin Bay regions. Figure S1 in the Supplementary Information of Lana et al. (2011) shows that the spatial coverage of the DMS measurements used for this database was confined to a very localized region near the mouth of Nares Strait. In contrast, our set of 35 measurements of surface seawater DMS are spread throughout our study region. As a result, we do not have any reason to consider that the seawater DMS field is significantly biased, but rather is an improved model input field for our study region relative to the Lana et al. (2011) climatology.

Additionally, vertical profiles of DMS measurements were conducted at these stations. The profiles showed DMS concentrations in the upper mixed layer (often down to 40 m) that were similar to the surface values used in the paper. This increases our confidence that the surface values were good indicators of the average DMS concentrations in the different water masses at the time of the sampling (M. Levasseur, private communication).

To address this comment we added a discussion in the text about the number and spatial extent of measurement points used for our seawater DMS field relative to the spatial extent of the data used for the Lana et al. climatology. We also added discussion to acknowledge that there are uncertainties in these datasets related to spatial and temporal resolution.

We do not think that the acknowledged uncertainties in the seawater DMS field should render moot the model-measurement comparison for atmospheric DMS. Rather, we consider these comparisons a very valuable indicator of present-day model capabilities in simulation of DMS that will serve to focus future research efforts.

Manuscript Changes:

The most significant changes are in Section 2.2.3 on p. 8

p. 8 line 235: "The GEOS-Chem model uses the monthly mean DMS$_{sw}$ from the climatology of Lana et al. (2011), which was developed based on data with very limited spatial coverage in the Canadian Arctic Archipelago and Baffin Bay as shown by Fig. S1 in Lana et al. (2011). In contrast, our recent DMS$_{sw}$ measurements are spread quite evenly throughout the 21-day ship track and thus have a considerably greater spatial extent throughout our study region than the sources used for the Lana et al. (2011) climatology."

p. 8 line 249: "While our updated DMS$_{sw}$ has improved spatial coverage and is a better temporal match to our study than the Lana et al. (2011) dataset, we acknowledge that there are remaining uncertainties related to spatial and temporal resolution."

p. 13 line 417: "Within these uncertainties, the seawater DMS source could largely account for the measured DMS$_g$. However, there are some notable mismatches that cannot be accounted for by the uncertainties detailed above. These are discussed in the following sections."

RC3: *"Furthermore, the paper seems to implicitly assume that the model gets all the atmospheric transport and the DMS sinks right."*

AC3: In our sensitivity studies we chose to focus on sources and did not conduct sensitivity tests related to transport and sinks. The revised text now explicitly acknowledges this.

Manuscript Changes:

p. 13 line 420: "Since the GEOS-Chem model has very reasonable capabilities in the simulation of transport (Kristiansen et al. 2016) and the chemical sinks of DMS are relatively well understood (Barnes et al. 2006), we chose to keep the transport and sink parameterizations constant for our sensitivity studies and focused on source sensitivity studies due to the considerable source-related uncertainty."

RC4: *"The comment "wind speeds in our GEOS-Chem simulations are generally within a factor of 2 of the observed wind speeds along the ship track time series" is worrying. A factor of 2 error in wind speeds means approximately a factor of 2 error in DMS flux from the ocean (since the kDMS vs U relationship is largely linear). Could it be that the measurements and model predictions (with oceanic DMS only) already agree within the uncertainties?"*

AC4: We have revised this section of text to provide a more careful comparison between the observed and simulated wind speeds. The revised text also now acknowledges that the bias might be zero given the uncertainties. However, given that 1) the median simulated DMS_g was biased low relative to measurements despite instances of large overestimation and 2) there were times when the air mass at the ship had a strong continental origin and had spent very little time over open water, we chose to investigate if other sources could potentially contribute to the DMS along the ship track.

Manuscript Changes:

p. 1 line 20: "…although within the range of the uncertainty of the seawater DMS source …"

p. 13 line 408: "Wind speeds in our GEOS-Chem simulations display considerable scatter about the observed wind speeds along the ship track time series, but show a linear relationship with a slope of 0.95 and $\mathrm{R}^2 = 0.35$ as in Fig. S4."

p. 13 line 417: "Within these uncertainties, the seawater DMS source could largely account for the measured DMS_g. However, there are some notable mismatches that cannot be accounted for by the uncertainties detailed above. These are discussed in the following sections. Since the GEOS-Chem model has realistic capabilities in the simulation of transport (Kristiansen et al., 2016) and the chemical sinks of DMS are relatively well understood (Barnes et al., 2006), we chose to keep the transport and sink parameterizations constant for our sensitivity studies and focused on source sensitivity studies due to the considerable source-related uncertainty."

RC5: *"A comparison of another independent variable might be helpful as verification for the model. For example, the paper shows sea salt, MEK, and CO from GEOS-Chem. Were there other tracers measured on the cruise that could be used to indicate biomass burning (e.g. potassium, acetonitrile), terrestrial biogenic emissions (e.g. methanol, acetone, isoprene, terpenes), pollution (CO, black carbon) etc? The Tof-CIMS with benzene source should be able to detect compounds such as acetone, isoprene, terpenes."*

AC5: We are in complete agreement that other independent variables would be very valuable to this work. Unfortunately, such data is not available to us. No measurements of K, CO, black carbon, or any other recognized tracer of biomass burning or anthropogenic influence were made aboard the ship. This was largely an oceanographic cruise, with a small atmospheric component, and so unfortunately there were strong limitations on the instrumentation we were able to deploy.

The benzene CIMS is indeed able to detect a wide range of oxygenated and unsaturated volatile organic compounds. Unfortunately, we had no choice but to use a zero air generator instead of ultra pure nitrogen for our instrument throughout the campaign, which in conjunction with the smokestack emissions from the ship led to unacceptably high backgrounds for all of the organic compounds such that quantification and often even identification of these compounds were not possible.

While we do not have incontrovertible evidence of continental influence, the work of Wentworth et al. (2016) from the same cruise also suggests a biomass burning influence at certain times (e.g. July 25-26) during the cruise. Taken together with the independent FLEXPART-WRF and GEOS-Chem simulations, we feel confident in our interpretation of the origin of the air arriving at the ship track.

RC6: *"p. 35549. Line 7. DMS emits from the surface ocean to the atmosphere not really because it is "relatively insoluble", but because there's a large air-sea concentration gradient in DMS.*

AC6: We thank the reviewer for noting the need for more careful phrasing of this statement. We have amended the text to reflect that it is not simply solubility, but also volatility, that controls partitioning, as described by the Henry's Law constant of a compound.

Manuscript Changes:

p. 2 line 36: "Due to its low solubility and high volatility (small Henry's Law constant), DMS partitions to the atmosphere after being produced by micro-organisms in surface waters."

RC7: *"p. 35549 Line 15-19 suggest rewrite and add references. For example "more hygroscopic" instead of "more water soluble""*

AC7: A citation was added to the explanation of Kohler theory, and "water soluble" was replaced with the more correct "hygroscopic".

Manuscript Changes:

p. 2 line 46

RC8: *"p. 35549 Line 22-23. Need reference"*

AC8: A citation was added.

Manuscript Changes:

p. 2 line 49

RC9: *"p. 35553. Last line. State the stability/variability of the one-point calibrations. For future deployments, the use of an internal isotopic standard is highly recommended (e.g. see http://www.atmos-meas-tech.net/3/1/2010/ for DMS and http://www.atmoschem-phys.net/14/7499/2014/ for methanol and acetone)"*

AC9: We would have preferred to use an internal standard for DMS, but time constraints around deployment of the instrument meant that it was not possible for this cruise. The text has been amended to include the variability of the calibrations.

Manuscript Changes:

p. 5 line 152: "The average sensitivity measured by one-point calibrations in the field ($\pm 1\sigma$) was 80±30 cps pptv^{-1}. Actual uncertainties on the calibration factor were less as a time-varying calibration factor was applied to the data, as described below."

RC10: *"Also, the authors may want to consider the use of gold beads to blank for DMS or the use of Pt/Pd catalyst to blank for organics in general. It's advantageous to use these methods to blank instead of zero air because doing so doesn't significantly change the water vapor content in the sampled air."*

AC10: We would have preferred to have deployed a more sophisticated background method, but the time constraints were such that the catalyst system we were able to put together actually had slightly worse backgrounds than the zero air generator. In this case, we note that ionization reaction with the benzene reagent ion has such a low relative humidity dependence that we do not expect an error larger than our calibration error.

RC11: *"p. 35554. It's highly unlikely that the moving ship itself will cause enhanced DMS mixing ratio at the foremast. The vast majority of atmospheric DMS just above water level and immediately in front of the ship will blow past the ship before even reaching the sampling height of 16 m."*

AC11: Our concern here was the disturbance of the water in the ship's wake. The sea surface was glassy and smooth during large portions of the cruise, such that the water behind the ship was significantly more turbulent than the adjacent ocean over quite a large distance. This was particularly an issue while we were breaking ice, as the ship's wake essentially constituted an artificial lead, opening an area for air-sea exchange which would not otherwise have been present.

RC12: *"p. 35556. A description of the seawater DMS measurement system?"*

AC12: We have described the seawater DMS measurements in Section 2.1.2.

RC13: *"There is a mistake in Eq. 2. KH should be associated with the ka term in this formulation."*

AC13: We have checked Eq. 2 and it is consistent with the formulation of Johnson et al. 2010.

RC14: *"p. 35558. Bottom of page. Air-sea transfer of DMS is primarily (>90%) waterside controlled, so the choice of the airside transfer velocity (ka) shouldn't make much difference to the predicted sea-to-air flux. If you want to test the sensitivity to ka, you should include the most recent, and one of the only field measurement based parameterizations from Yang et al 2013 (www.pnas.org/cgi/doi/10.1073/pnas.1317840110)."*

AC14: Motivated in part by reviewer comments, we have decided to remove this discussion from the manuscript entirely, since we do not have direct flux measurements with which to compare the results given by the various parameterizations. We rely on published work which suggests a linear wind speed dependence for the DMS transfer velocity to support our choice of the Liss and Merlivat parameterization for our study.

Manuscript Changes:

The figure and table associated with this discussion have been removed.

p. 7 line 222: "DMS emissions are based on the piece-wise linear Liss and Merlivat (1986) sea-air flux formulation (due to recent studies reporting a linear wind-speed dependence for DMS (Huebert et al. 2010, Bell et al. 2013, Bell et al. 2015) and DMS$_{sw}$ concentrations from Lana et al. (2011). "

p. 9 line 295: Removed discussion of transfer velocity parameterizations.

RC15: "p. 35559, line 18. I assume the waterside transfer velocities have been adjusted to the ambient seawater Schmidt number of DMS?"

AC15:. Yes. A sentence has been added to the manuscript to clarify this.

Manuscript Changes:

p. 10 line 307: "[...] adjusted to the ambient seawater Schmidt number of DMS, details are in (Johnson, 2010)."

RC16: “p. 35560, p. 10. Another high latitude cruise with DMS measurements is Yang et al. 2011 (http://onlinelibrary.wiley.com/doi/10.1029/2010JC006526/abstract) from near the South Georgia Islands.”

AC16: Thank you for noting this omission. The related citation was added.

Manuscript Changes:

p. 11 line 340

RC17: “p. 35561, line 12. The Liss and Merlivat 1986 parameterization consists of three piecewise linear terms, rather than a single linear wind speed dependence.”

AC17: This section was removed from the text.

Reviewer Comment: *“p. 35564. Line 22, east of Baffin Bay”*

Author Response: We thank the reviewer for noting the need for correction here. The text has been corrected.

Manuscript Changes:

p. 14 line 471

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Author comments on "Summertime Sources of Dimethyl Sulfide in the Canadian Arctic Archipelago and Baffin Bay"

Emma L. Mungall[1], Betty Croft[2], Martine Lizotte[3], Jennie L. Thomas[4], Jennifer G. Murphy[1], Maurice Levasseur[3], Randall V. Martin[2], Jeremy J. B. Wentzell[5], John Liggio[5], and Jonathan P. D. Abbatt[1]

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RC1: *"This paper reports data and analyses from a recent field campaign made in the Canadian Arctic during the summer, with a particular emphasis on the observations of DMS in air by high time-resolution mass spectrometry, associated with some seawater DMS data obtained by gas chromatography. The authors investigate the role and impacts of oceanic and land sources of DMS in combination with a chemistry-transport model. The data in this region in this season is very valuable to fill the database and to test our understanding of the air-sea sulfur cycle. The measurements are sound and the analyses are thoroughly made. The paper is generally well organized and written. With the above three reasons, I would support publication after minor and technical revision."*

AC1: We thank the reviewer for the very helpful comments and suggestions.

Manuscript change page and line numbers refer to the marked-up version of the revised manuscript.

RC2: *"P35557, L10: The authors use primary productivity as a proxy of DMS in seawater. The first question is why primary productivity not Chl-a? There exist some parameterizations using Chl-a and MLD for the global oceans (Simo and Dachs, GBC, 2002) and SST and SSN for the North Pacific (Watanabe et al., Marine Chem., 2007). A recent paper suggested that primary productivity can be a good proxy in predicting seawater DMS (Kameyama et al., GRL, 2013). It seems to me that the authors' phrase sounds a bit awkward. The authors can be a bit stronger in phrasing this sentence by referring the Kameyama et al. paper. Also I wonder how seawater DMS is parameterized from primary productivity and where this primary productivity data came from (e.g., satellite?). As the model simulations were often used in the analysis later in the paper, the authors are encouraged to elaborate more details here."*

AC2: We thank the reviewer for pointing out these helpful references, which we have used in our manuscript revision. We revised the text to more clearly indicate the source of the primary productivity data and added details about our methodology. The essential point is that very limited information exists regarding DMS$_{sw}$ in the Hudson Bay System, but we felt that a sensitivity test could still provide important information as to its possible role in the sulfur cycle of the summer Arctic.

While we did not use any literature parameterizations in our work, the parameterization of Dachs and Simo gives values that are roughly equivalent to the values we used (less than a factor of 2 difference) if we assume a mixed layer depth of 20 m and use Chlorophyll-a data from the MODIS colour. We do not have enough information to use the parameterization of Kamayama et al., as it would require us to know the net community productivity in the HBS, which to the best of our knowledge is not known.

Manuscript Changes:

p. 8 line 256: “We assumed that a) previously measured primary productivity values were representative of the year of our cruise and b) that the ratio of DMS$_{sw}$ in Baffin Bay to DMS$_{sw}$ in other bodies of water is the same as the ratio of primary productivity in Baffin Bay to primary productivity in other bodies of water. In effect, we assumed a linear relationship between DMS$_{sw}$ and primary productivity. This assumption is in keeping with the Simo and Dachs (2002) parameterization for DMS$_{sw}$. We also note that Kameyama et al. (2013) use a related quantity, net community productivity, to parameterize DMS$_{sw}$, but net community productivity data was not available for the HBS. Ferland et al. (2011) found that the waters of Hudson Strait are as productive as those of the North Water (Northern Baffin Bay), while Hudson Bay and Foxe Basin are about a quarter as productive. Thus for our simulation we set the DMS$_{sw}$ in Hudson Strait to be equal to that measured in the North Water, and the DMS$_{sw}$ in Hudson Bay and Foxe Basin to a quarter of that value. In the absence of measurements, it is not possible to further constrain what the DMS$_{sw}$ values might be in the Hudson Bay System.”

RC3: *“Table 2 and Figure 1b: Clearly indicate atmospheric measurements, please.”*

AC3: We thank the reviewer for drawing our attention to the need for clarification here. Figure 1b has been amended to indicate atmospheric measurements. Table 2 refers to atmospheric mixing ratios and is referenced in the text as pertaining to DMS$_g$.

Manuscript Changes:

p. 28 (Figure 1b)

RC4: *“Section 4.4: Although the investigation of non-marine sources is interesting and worth trying, some parts of the analyses are not strong. I feel better if the authors say ’speculative’. Otherwise, the authors should try to add more robust evidence from the observations or supporting information from the model runs.”*

AC4: We agree that our investigation of non-marine sources should be viewed as sensitivity studies because the related emissions are associated with considerable uncertainty. Throughout the revised manuscript we are now careful to identify uncertainties and indicate that these simulations should be viewed as sensitivity studies.

Manuscript Changes:

p. 2 line 22: "Sensitivity tests indicated that non-seawater sources (lakes, biomass burning, melt ponds and coastal tundra) could make additional episodic contributions to atmospheric DMS in the study region"

p. 4 line 114: "Section 4 presents sensitivity studies with the GEOS-Chem chemical transport model and the FLEXPART-WRF particle dispersion model, which examine the potential of seawater and non-seawater sources to contribute to the measured DMS_g."

p. 7 line 208: "The GEOS-Chem chemical transport model (www.geos-chem.org) was used to conduct source sensitivity studies."

p. 12 line 380: The title of Section 4 was changed to "Source sensitivity studies with GEOS-Chem and FLEXPART"

RC5: *"P35557, L9: In order to assess"*

AC5: We thank the reviewer for noting this error.

Manuscript Changes:

p. 15 line 474: "To assess the impact" was changed to "to investigate the impact that"

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~~Summertime Sources of~~ Dimethyl ~~Sulfide~~ sulfide in the ~~Canadian~~ summertime Arctic ~~Archipelago~~ atmosphere: Measurements and ~~Baffin Bay~~source sensitivity simulations

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Abstract. Dimethyl sulfide (DMS) plays a major role in the global sulfur cycle. In addition, its atmospheric oxidation products contribute to the formation and growth of atmospheric aerosol particles, thereby influencing cloud condensation nuclei (CCN) populations and thus cloud formation. The pristine summertime Arctic atmosphere is ~~a CCN-limited regime, and is thus very susceptible to the influence of~~ strongly influenced by DMS. However, atmospheric DMS mixing ratios have only rarely been measured in the summertime Arctic. During July-August, 2014, we conducted the first high time resolution (10 Hz) DMS mixing ratio measurements for the Eastern Canadian Archipelago and Baffin Bay as one component of the Network on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments (NETCARE). DMS mixing ratios ranged from below the detection limit of 4 pptv to 1155 pptv (median 186 pptv) ~~. A set of transfer velocity parameterizations~~ during the 21-day shipboard campaign. A transfer velocity parameterization from the literature coupled with ~~our atmospheric and coincident~~ coincident atmospheric and seawater DMS measurements yielded air-sea DMS flux estimates ranging from 0.02-12 μmol $m^{-2}d^{-1}$~~, the first published for this region in summer. Airmass~~ . Air-mass trajectory analysis using FLEXPART-WRF and ~~chemical transport modeling using GEOS-Chem~~ sensitivity simulations with the GEOS-Chem chemical transport model indicated that local sources (Lancaster Sound and Baffin Bay) were the dominant contributors to the DMS measured along the 21-day ship track, with episodic transport from the Hudson Bay System. After adjusting GEOS-Chem oceanic DMS values in the region to match measurements, GEOS-Chem reproduced the major features of the measured time series, but ~~remained~~ was biased low overall (~~median 67 pptv). We investigated~~ 2-1006 pptv, median 72 pptv), although within

the range of uncertainty of the seawater DMS source. However, during some 1-2 day periods the model under predicted the measurements by more than an order of magnitude. Sensitivity tests indicated that non-marine sources ~~that might contribute to this bias, such as DMS emissions from~~ (lakes, biomass burning, melt ponds and coastal tundra~~. While the~~) could make additional episodic contributions to atmospheric DMS in the study region, although local marine sources of DMS dominated~~overall, our results suggest that non-local and possibly~~ . Our results highlight the need for both atmospheric and seawater DMS datasets with greater spatial and temporal resolution, combined with further investigation of non-marine ~~sources episodically contributed strongly to the observed summertime ArcticDMS mixing ratios~~DMS sources for the Arctic.

1 Introduction

Despite the established importance of oceanic emissions of biogenic sulfur in the form of dimethyl sulfide (DMS) to aerosol formation and growth in the marine boundary layer (e.g. Charlson et al., 1987; Leaitch et al., 2013), key uncertainties remain about oceanic DMS concentrations and the air-sea flux of DMS (Tesdal et al., 2015). DMS emissions are responsible for about 15% of the tropospheric sulfur budget globally, and up to 100% in ~~the most~~ some remote areas (Bates et al., 1992). ~~DMS is relatively insoluble, so~~ Due to its low solubility and high volatility (small Henry's Law constant), DMS partitions to the atmosphere after being produced by micro-organisms in surface waters~~it escapes to the atmospherewhere it~~ . In the atmosphere, DMS is oxidized to sulfuric acid and methane sulfonic acid (MSA). These oxidation products can then participate in new particle formation (Pirjola et al., 1999; Chen et al., 2015) or condense upon existing particles, causing them to grow larger and changing particle hygroscopicity. The influence of DMS emissions on aerosol concentrations is important since aerosols modify the climate directly by scattering and absorbing radiation, and indirectly by modifying cloud radiative properties by acting as seeds for cloud droplet formation (Charlson et al., 1987; Twomey, 1977; Albrecht, 1989). Both composition and size affect the ability of an aerosol particle to act as a cloud condensation nucleus (CCN), with bigger and more ~~water soluble~~ hygroscopic aerosol particles preferentially activating as CCN ~~. The condensation of the water-soluble products of DMS oxidation on atmospheric aerosol particles thus makes them better CCN through both the composition and size effects.~~

~~Through~~ (Köhler, 1936).

The summer Arctic atmosphere contains very few CCN through a combination of limited local sources and efficient scavenging mechanisms (Browse et al., 2012)~~the summer Arctic atmosphere contains very few CCN~~. At low CCN levels the radiative balance as determined by cloud cover is very sensitive to CCN number (Carslaw et al., 2013). Sea ice cover in the summer Arctic is in rapid decline (e.g. Tilling et al., 2015). With the decline in sea ice comes an enhanced potential for sea-air exchange of compounds such as DMS that may affect aerosol populations in the Arctic. In general, increased numbers of CCN are associated with a cooling effect on climate. However, ~~since~~ portions of the Arctic can reside in a CCN-limited cloud-aerosol regime, with the result that an increase in CCN could have a warming effect ~~on the summer Arctic as an increase in cloudiness could be associated with increased~~ due to increases in cloudiness in turn increasing the trapping of outgoing long-wave radiation (Mauritsen et al., 2011). In order to predict future changes in CCN number, we need to understand the influence of sea-air exchange on ~~aerosols in the summer Arctic~~ summertime Arctic aerosols.

Quantifying present-day atmospheric DMS mixing ratios (henceforth referred to as DMS$_g$) provides an important benchmark for interpreting future measurements. Currently, only a few snapshots of DMS$_g$ in the Arctic exist from a handful of ship-board studies conducted over the last twenty years, none of which captured the most biologically productive time of June and July (Leck and Persson, 1996; Rempillo et al., 2011; Chang et al., 2011; Tjernström et al., 2014). The data span great distances in time and space and provide only a fragmented picture of tropospheric DMS$_g$ levels in the Arctic. Understanding present-day sources of DMS$_g$ is also relevant for predicting how these sources may change in a future climate. ~~The goals of this study are 1) to present ship-board DMS$_g$ measurements taken in the Canadian Arctic during July and August 2014, and 2) to identify sources for the measured DMS$_g$.~~

The ~~intermediate~~ lifetime of DMS$_g$ against OH oxidation of 1-2 days ~~means that whether it travels far~~ suggests that DMS$_g$ may either undergo long-range transport before being oxidized or ~~remains~~ remain in the same area ~~depends strongly on atmospheric transport patterns~~under low wind conditions. Atmospheric transport mixes DMS$_g$ within ~~the~~ a region, effectively smoothing out atmospheric concentration inhomogeneities due to inhomogeneity in the surface water DMS (referred to henceforth as DMS$_{sw}$). Transport can also bring DMS$_g$ from regions further afield. For example, a study by Nilsson and Leck (2002) highlighted the importance of transport in bringing DMS$_g$ from regions of open water to regions covered by sea ice within the Arctic.

Despite the potential for an important role for atmospheric transport, few source apportionment studies for sulfur in the Arctic have been carried out. Previous work has focused almost exclusively on the aerosol phase. ~~A common assumption that all methane~~ Methane sulfonic acid (MSA) in the aerosol phase ~~arises~~ is commonly assumed to arise from oxidation of marine biogenic DMS$_g$ (Sharma et al., 2012). However, Hopke et al. (1995) suggested that terrestrial sources in Northern Canada could also contribute MSA to Arctic aerosol. Previous studies indicate that terrestrial emissions of DMS$_g$ from soils, vegetation, wetlands and lakes are less important than oceanic emissions (Bates et al., 1992; Watts, 2000). However, these studies are based on very few or even no measurements in the Canadian North, and the fluxes for the Canadian tundra and boreal forest, which cover a very large surface area, are highly unconstrained. Much of the Arctic Ocean is in close proximity to land and is more subject to terrestrial influence than the open ocean in other regions of the world (Macdonald et al., 2015).

Sources of DMS$_g$ other than seawater are not typically included in chemical transport and climate models, despite evidence ~~in the literature~~ for several other sources of DMS$_g$. For example, significant levels of DMS have been measured in Canadian lakes (Sharma et al., 1999a; Richards et al., 1994). DMS emissions have also been observed from various continental sources such as lichens (Gries et al., 1994), crops such as corn (Bates et al., 1992), wetlands (Nriagu et al., 1987), and biomass burning (Meinardi et al., 2003; Akagi et al., 2011). Terrestrial plants can be an important source of DMS as demonstrated by DMS levels in the hundreds of pptv range measured from creosote bush in Arizona and from trees and soils in the Amazonian rain forest (Jardine et al., 2010, 2014). One previous study based on sulfur isotopes from Greenland included a pooled biogenic continental and volcanic ~~sources (as their isotopic signatures~~ source (as the isotopic signatures of these two sources are not easily distinguishable) and estimated this continental component to be 44% (Patris et al., 2002). In addition to the possibility of a continental source, melt ponds have been suggested as a potentially important source of DMS to the atmosphere (Levasseur, 2013). These fresh or brackish ponds form from snow melt on top of the sea ice in spring and summer, and have been observed to have an extremely large areal extent, covering 30% of the sea ice on average in midsummer with up to 90% coverage in some regions (Rosel and Kaleschke, 2012). Here we present sensitivity studies to examine the potential importance of these alternative sources of DMS$_g$.

The goals of this study are 1) to present ship-board DMS$_g$ measurements taken in the Canadian Arctic during July and August 2014, and 2) to explore possible sources for the measured DMS$_g$.

Section 2 outlines our measurement methodology. Section 3 presents the measured DMS$_g$ time series along 3 weeks of the cruise. Section 3 also includes concurrent measurements of DMS$_{sw}$ and the calculated DMS air-sea flux estimates for the region. ~~We use~~ Section 4 presents sensitivity studies with the GEOS-Chem chemical transport model and the FLEXPART-WRF particle dispersion model~~to interpret these measurements. Section 4 includes an examination of source regions for~~ , which examine the potential contribution of seawater and non-marine sources to the measured DMS$_g$~~and sensitivity studies related to possible terrestrial sources.~~ .

2 Methods

2.1 Measurements

Measurements of DMS were made during the first leg of the CCGS ~~Amundsen~~ *Amundsen* summer campaign under the aegis of NETCARE (Network on Climate and Aerosols: Addressing Uncertainties in Remote Canadian Environments). The research cruise started in Quebec City on 8 July, 2014 and ended in Kugluktuk on 14 August, 2014. Measurements were made in Baffin Bay, Lancaster Sound and Nares Strait. The ship track is shown in Fig. 1a.

2.1.1 DMS mixing ratios

DMS$_g$ measurements were made using a high resolution time of flight chemical ionization mass spectrometer (HR-ToF-CIMS, Aerodyne). The instrument was housed in a container on the foredeck. The inlet was placed on a tower 9.44 m above the deck at the bow, which was itself nominally 6.6 m above sea level (in total ca. 16 m above sea level). A diaphragm pump pulled air at 30 ~~slpm~~ L min^{-1} through a 25 m long, 9.53 mm inner diameter PFA line heated to 50°C (Clayborn Labs). Flow rate through the line was controlled by a critical orifice. The flow was subsampled and pulled to the instrument inlet through another critical orifice restricting the flow to 2 ~~slpm~~L min^{-1}. The flow through the sealed ^{210}Po source of the HR-ToF-CIMS, also controlled at 2 ~~slpm~~ L min^{-1} by a critical orifice, was supplied by a zero air generator (Parker Balston, Model HPZA-18000, followed by a Carbon Scrubber P/N B06-0263) via a mass flow controller supplying 2.4 ~~slpm~~L min^{-1}. The zero air generator also supplied 9.8 sccm (controlled by a mass flow controller) through a bubbler filled with benzene, which was added to the flow through the radioactive source to provide the reagent ion. The excess went to exhaust. Figure S1 shows a flow schematic.

The use of benzene cations as a reagent ion for chemical ionization mass spectrometry was first proposed by Allgood et al. (1990). This reagent ion was successfully applied to the shipboard detection of DMS~~by the group of Tim Bertram at UCSD (Kim et al., 2015)~~$_g$ by Kim et al. (2015). The ionization mechanism that prevails is the transfer of charge from a benzene cation to an analyte ion which has an ionization energy lower than that of benzene (Allgood et al., 1990). Due to space constraints on board the ship, a zero air generator was used instead of cylinder nitrogen to produce our reagent ion flows. The use of zero air introduced other potential reagent ions to the mass spectrum (O_2^+, NO^+, $C_6H_7^+$, and $H_2O{\cdot}H_3O^+$, shown in Fig. S2). To investigate the effect of this more complicated reagent ion source, calibration experiments were carried out in the laboratory prior to the campaign for both air and N_2 at different sample flow relative humidities and under different CIMS voltage configurations. The calibration curves for DMS (detected as $CH_3SCH_3^+$) showed a linear response under all conditions. We found that the sensitivity of the instrument to DMS did not depend on relative humidity~~, and for operating conditions~~. The average sensitivity measured by one-point calibrations in the field ~~averaged about~~ (±1 σ) was 80±30 cps/pptv~~with detection limits~~. Actual uncertainties on the calibration factor were less as a time-varying calibration factor was applied to the data, as described below. Detection limits were below 4 pptv ~~due to the background being in the~~ as the background was consistently 2-3 pptv~~range~~.

Background spectra were collected in the field by overflowing the inlet with zero air from the zero air generator as shown in Fig. S1. The high mass resolution of the instrument eliminated concern about unit mass isobaric interferences as indicated in Fig. S3. Mass spectra were collected at 10 Hz. One point calibrations were performed nearly every day by overflowing the inlet with zero air and adding a known amount of DMS from a standards cylinder using a mass flow controller (499 ±5% ppb, Apel-Reimer). Peak fitting was performed using the Tofware software package from Aerodyne (version 2.4.4) in Igor Pro. Reported mixing ratios were calculated by first normalizing analyte peak areas to reagent ion peak areas, then subtracting backgrounds, and finally applying calibration factors obtained by linearly interpolating the one-point daily calibrations. Text S1 provides details. ~~The~~ To remove artifacts that might have occurred due to enhanced DMS flux in the ship's wake, the data were filtered such that values were removed when the ship was moving (speed over ground greater than 2 m ~~/s~~s^{-1}) and the wind direction was not within ±90° of the bow. This ~~was intended to remove artifacts that might have occurred due to enhanced DMS flux in the ship's wake. This~~ filtering removed less than 12% of data points.

2.1.2 Surface seawater DMS concentrations

Seawater concentrations of DMS were determined following procedures described by Scarratt et al. (2000) and modified in Lizotte et al. (2012) using purging, cryotrapping and sulfur-specific gas chromatography. Briefly, seawater was gently collected directly from 12L Niskin bottles in gas-tight 24-ml serum vials, allowing the water to overflow. Subsamples of DMS were withdrawn from the 24-ml serum vials within minutes of collection and sparged using an in line purge and trap system with a Varian 3800 gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD). The GC was calibrated with injections of a ~~100nM~~ 100 nM solution of hydrolyzed DMSP (Research Plus Inc.). The full dataset will be presented separately [*Lizotte et al., personal communication*].

2.1.3 Meteorological data

Basic meteorological measurements were made from a purpose built tower on the ship's foredeck. Air temperature (8.2 m above deck), wind speed and direction (9.4 m above deck) and barometric pressure (1.5 m above deck) were measured using, respectively, a shielded temperature & relative humidity probe (Vaisala™HMP45C212), wind monitor (RM Young 05103) and pressure transducer (RM Young™61205V). Sensors were scanned every 2 s and saved as 2 min averages to a micrologger (Campbell Scientific™, model CR3000). Platform relative wind was post-processed to true wind following Smith et al. (1999). Navigation data (ship position, speed over ground, course over ground and heading) necessary for the conversion were available from the ship's position and orientation system (Applanix POS MV™V4). Periods when the tower sensors were serviced or when the platform relative wind was beyond ±90° from the ship's bow were screened from the meteorological data set. Screened periods accounted for less than 20% of total data but up to 45% in some regions.

2.1.4 Sea surface temperature and salinity

Sea surface temperature (SST) was measured with the ship's Inboard Shiptrack Water System, Seabird/Seapoint measurement system. There were no continuous salinity measurements. An average salinity value of 29.7 PSU was used for all calculations since the calculated transfer velocities had very low sensitivity to changes in salinity for our study region.

2.2 ~~Modeling~~Model Descriptions

2.2.1 FLEXPART-WRF

A Lagrangian particle dispersion model based on FLEXPART (Stohl et al., 2005), FLEXPART-WRF (Brioude et al., 2013, website: flexpart.eu/wiki/FpLimitedareaWrf), was used to study the origin of air sampled by the ship. The model is driven by meteorology from the Weather Research and Forecasting (WRF) Model (Skamarock et al., 2005) and was run in backward mode to study the emissions source regions and transport pathways influencing ship-based DMS measurements. Specific details are in ~~another publication arising from the NETCARE Amundsen campaign (?)~~Wentworth et al. (2016).

2.2.2 GEOS-Chem

The GEOS-Chem chemical transport model (www.geos-chem.org) was used to ~~interpret the atmospheric measurements~~conduct source sensitivity studies. We used GEOS-Chem version 9-02 at 2° x 2.5° resolution with 47 vertical layers between the surface and 0.01 hPa. The assimilated meteorology is taken from the National Aeronautics and Space Administration (NASA) Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System version 5.7.2 (GEOS-FP) assimilated meteorology product, which includes both hourly surface fields and 3-hourly 3D fields. Our simulations used 2014 meteorology and allowed a 2-month spin-up prior to the simulation of July and August, 2014.

The GEOS-Chem model includes a detailed oxidant-aerosol tropospheric chemistry mechanism as originally described by Bey et al. (2001). Simulated aerosol species include sulphate-nitrate-ammonium (Park et al., 2004, 2006), carbonaceous aerosols (Park et al., 2003; Liao et al., 2007), dust (Fairlie et al., 2007, 2010) and sea salt (Alexander et al., 2005). The sulphate-nitrate-ammonium chemistry uses the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007), which partitions ammonia and nitric acid between the gas and aerosol phases. The model includes natural and anthropogenic sources of SO_2 and NH_3 (Fisher et al., 2011). DMS emissions are based on the piece-wise linear Liss and Merlivat (1986) sea-air flux formulation ~~and oceanic DMS~~(due to recent studies reporting a linear wind-speed dependence for DMS (Huebert et al., 2010; Bell et al., 2013, 2015)) and DMS_{sw} concentrations from Lana et al. (2011). In our simulations, DMS emissions occurred only in the fraction of the grid box that is covered by sea water and also free of sea ice. Biomass burning emissions are from the Quick Fire Emissions Dataset (QFED2) (Darmenov and da Silva, 2013), which provides daily open fire emissions at 0.1° x 0.1°. Oxidation of SO_2 occurs in clouds by reaction with H_2O_2 and O_3 and in the gas phase with OH (Alexander et al., 2009) and DMS oxidation occurs by reaction with OH and NO_3.

The GEOS-Chem model has been extensively applied to study the Arctic ~~including for aerosol acidity (??)~~atmosphere, in regard to aerosol acidity (Wentworth et al., 2016; Fisher et al., 2011), carbonaceous aerosol (Wang et al., 2011), aerosol number ~~(?)~~(Croft et al., 2016), aerosol absorption (Breider et al., 2014), and mercury (Fisher et al., 2012).

2.2.3 Seawater DMS values in GEOS-Chem

The ~~DMS$_{sw}$ values used in the standard~~ GEOS-Chem ~~are monthly means~~ model uses the monthly mean DMS$_{sw}$ from the climatology of Lana et al. (2011), which was developed based on ~~very few data points~~ data with very limited spatial coverage in the Canadian Arctic Archipelago and Baffin Bay ~~.~~ as shown by Fig. S1 in Lana et al. (2011). In contrast, our recent DMS$_{sw}$ measurements are spread quite evenly throughout the 21-day ship track and thus have a considerably greater spatial extent throughout our study region than the sources used for the Lana et al. (2011) climatology. The Lana et al. (2011) climatology ~~predicts values of~~ contains maximum DMS$_{sw}$ ~~below~~ of 5 nM ~~in this region, while the values measured on board the ship during the campaign were often~~ for our study region. However, the DMS$_{sw}$ measured during our ship-board campaign was generally between 5-10 nM and occasionally higher. Therefore, we used the ~~measured values as input in GEOS-Chem in lieu of the Lana et al. (2011) values for the~~ 35 measured DMS$_{sw}$ values to create an updated DMS$_{sw}$ field for use as a GEOS-Chem input in the study region. The measured values were interpolated using the DIVA web application (http://gher-diva.phys.ulg.ac.be/web-vis/diva.html) and a static field was used for July and August. The Lana et al. (2011) climatology was used for all other ocean regions. While our updated DMS$_{sw}$ has improved spatial coverage and is a better temporal match to our study than the Lana et al. (2011) dataset, we acknowledge that there are remaining uncertainties related to spatial and temporal resolution.

To our knowledge, there ~~exist~~ are no measurements of DMS$_{sw}$ in the Hudson Bay System (comprising Hudson Bay, Foxe Basin and the Hudson Strait; referred to as HBS hereafter). In ~~order the~~ our sensitivity simulations, we assess the potential ~~importance~~ contribution of this source region to DMS$_g$ further north ~~, we used primary productivityas aproxy for~~ by estimating the DMS$_{sw}$ based on primary productivity. We assumed that a) previously measured primary productivity values were representative of the year of our cruise and b) that the ratio of DMS$_{sw}$ ~~for lack of better options. To the best of our knowledge, no accepted proxy for~~ in Baffin Bay to DMS$_{sw}$ in other bodies of water is the same as the ratio of primary productivity in Baffin Bay to primary productivity in other bodies of water. In effect, we assumed a linear relationship between DMS$_{sw}$ ~~exists, and the development of such a proxy, while extremely valuable, is beyond the scope of this work. The work of~~ and primary productivity. This assumption is in keeping with the (Simò and Dachs, 2002) parameterization for DMS$_{sw}$. We also note that Kameyama et al. (2013) use a related quantity, net community productivity, to parameterize DMS$_{sw}$, but net community productivity data was not available for the HBS. Ferland et al. (2011) found that the waters of Hudson Strait are as productive as those of the North Water (Northern Baffin Bay), while Hudson Bay and Foxe Basin are about a quarter as productive. ~~For~~ Thus for our simulation we set the DMS$_{sw}$ in Hudson Strait to be equal to that measured in the

North Water, and the DMS$_{sw}$ in Hudson Bay and Foxe Basin to a quarter of that value. ~~The values chosen here for DMS$_{sw}$ represent what we believe to be a plausible scenario.~~ In the absence of measurements, it is not possible to further constrain what the DMS$_{sw}$ values might be in the Hudson Bay System.

2.3 Flux estimate calculations

~~Concurrent~~ Our 35 concurrent measurements of DMS in the atmosphere and seawater along the ship track in the Baffin Bay and Canadian Arctic Archipelago region allow us to estimate the air-sea flux of DMS. The flux is defined as the rate of transfer of a gas across a surface, in this case the surface of the ocean. For liquid-gas surfaces, the flux is described by Eq. 1,

$$F = -K_W\left(C_g/K_H - C_l\right) \tag{1}$$

where C_g and C_l are the concentrations of the chemical species of interest in the gas phase and liquid phase respectively, K_W is the transfer velocity, and K_H is the dimensionless gas over liquid form of the Henry's law constant (Johnson, 2010). The transfer velocity K_W is described by Eq. 2,

$$K_W = \left[\frac{1}{k_a} + \frac{K_H}{k_w}\right]^{-1} \tag{2}$$

where K_W is composed of the single phase transfer velocities for both the water-side (k_w) and the air-side (k_a), representing the rates of transfer in each phase.

The transfer velocity for each phase encapsulates the physical processes controlling the flux in that phase. For soluble gases, the air-side processes play a more important role, and become increasingly relevant with increasing solubility, while insoluble gases exhibit exclusively water-side control (Wanninkhof et al., 2009). Air-sea fluxes are controlled by many different factors, which has led to the development of a proliferation of transfer velocity parameterizations, each addressing different issues. Some are physically based, i.e. attempt to mathematically describe the processes at play, while others are developed by fitting experimental or field data. It is not clear whether parameterizations developed based on measurements of the flux of a given gas can be applied to other gases. For example, bubbles contribute less to the DMS flux than they do to the CO_2 flux, due to the limited solubility of carbon dioxide in water, and so parameterizations developed for CO_2 might be expected to overestimate the DMS flux (Blomquist et al., 2006). Indeed, recent studies have shown that the wind speed dependence of the DMS transfer velocity is close to linear (Huebert et al., 2010; Bell et al., 2013, 2015).

~~We used multiple transfer velocity parameterizations from the literature together with our measurements of atmospheric DMS mixing ratios, seawater DMS concentrations and wind speed to calculate fluxes. We compared these parameterizations to attempt to clarify the impact of the choice of parameterization on calculated fluxes. These parameterizations are summarized in Table ?? and are referred to by acronyms of the form FXY (F for flux), where X represents the air-side transfer velocity and Y~~

~~represents the water-side transfer velocity. Thus, for example, the transfer velocity parameterization using the~~ Fluxes were calculated according to Eq. 1 using the transfer velocity parameterizations of (Liss and Merlivat, 1986) and (Jeffery et al., 2010) for air-side ~~parameterization of Jeffery et al. (2010) and the water-side parameterization of Liss and Merlivat (1986) is referred to as FJLM. The acronyms referring to the various parameterizations are listed in Table ??. Johnson implemented a wide variety (Table ?? provides details) of both air-side~~ and water-side~~parameterizations (Johnson, 2010), all of which require only wind speed, air temperature, and salinity as inputs. The relationship of the transfer velocity arising from each parameterization with wind speed for~~ , respectively (adjusted to the ambient seawater Schmidt number of DMS, details are in (Johnson, 2010)). Atmospheric concentrations were calculated from measured mixing ratios using measured atmospheric temperature, pressure, and the ~~conditions encountered during the cruise is shown in Fig. S4. Loose et al. (2014) recently published a parameterization specific to the seasonal ice zone, incorporating ice-specific physical processes. This parameterization was used to calculate the water-side transfer velocity whenever the ship was in the marginal ice zone, using estimated sea ice coverage and ice speeds.~~

~~Sea ice~~ Henry's law constant for DMS at the in-situ temperature. Fluxes were multiplied by the fraction of open water in order to account for the capping effect of sea ice (Loose et al., 2014). The sea ice cover near the ship's location was estimated at a 0.5° x 0.5° resolution by plotting the ship's course at hourly resolution on daily ice charts obtained from the Canadian Ice Service (http://www.ec.gc.ca/glaces-ice/). These estimates were cross-referenced with daily photos taken aboard the ship to ensure accuracy. Estimates were made on a scale from 1-10, with no fractional values. ~~Ice speed was estimated using the relationship to wind speed found by (Cole et al., 2014), $u_{\mathrm{ice}} = 0.019\,u_{\mathrm{air}}$.~~

~~Fluxes were calculated according to Eq. 1 as the transfer velocity multiplied by the difference in concentration between the atmosphere and the ocean. Atmospheric concentrations were calculated from measured mixing ratios using measured atmospheric temperature and pressure and divided by the Henry's law constant for DMS at the in situ temperature. Fluxes estimated by all transfer velocity parameterizations that did not explicitly include the effect of sea ice were multiplied by the fraction of open water in order to account for the capping effect of sea ice (Loose et al., 2014).~~

3 DMS mixing ratio observations and estimated fluxes

Figure 1b and Table 1 present the DMS_g mixing ratio data collected along the ship track. ~~These~~ To our knowledge, these are the first ~~published~~ DMS_g ~~values~~ measurements for the Arctic during midsummer (July). These summertime measurements exceed previous measurements made in late summer and early fall by a factor of 3-10 (Table 1). This is consistent with the expectation of higher biological productivity in the summer than in other seasons (Levasseur, 2013). The time series ~~shows~~ exhibits high temporal variability. ~~In particular, three~~ Three episodes of elevated DMS_g

mixing ratios with values of 400 pptv or above occurred along the ship track on 18-20 July, 26 July and 1-2 August. Two episodes ~~of much lower~~ with DMS_g mixing ratios with values below 100 pptv occurred on 22-23 July and 5 August. ~~Comparing these measurements to those made in other regions of the world ocean indicates that our~~ Our values are on the same order (hundreds of pptv) as measurements made at high latitudes under bloom conditions in the Southern Ocean ~~(Bell et al., 2015)~~(Bell et al., 2015; Yang et al., 2011), the North Atlantic (Bell et al., 2013), and the North West Pacific (Tanimoto et al., 2013), but are higher than measurements made in the Tropical Pacific ~~which~~ that were on the order of tens of pptv (Simpson et al., 2014).

Figure 2 presents the time series of DMS_g along the ship track together with ~~the other variables needed to estimate fluxes (wind speedand seawater DMSconcentrations) and shows the flux estimatesas a time series for each transfer velocity parameterization used. Figure **??** shows the regional median DMS air-sea fluxes based on the ship track measurements for the Eastern Canadian Arctic summer.~~ wind speed, DMS_{sw}, and our flux estimates. Previous DMS flux estimates for the Arctic are summarized in Table 2. The only other summertime estimate falls within the same range as in this work of ca. 0-10 $\mu\mathrm{mol\,day}^{-1}\mathrm{m}^{-2}$ (Sharma et al., 1999b). ~~Our values may represent an underestimate of the true regional flux, as wind speeds were low at the times when the highest DMS_{sw} values were observed on 23 and 31 July. It is probable that these high-DMS_{sw} regions experienced higher wind speeds at other times, leading to a larger flux.~~ A better constrained summer flux estimate for this region will require sampling of DMS_{sw} at higher spatial and temporal resolution, and ideally direct continuous flux measurements using a technique such as eddy covariance, but these are challenging measurements rendered more so by the remoteness of Arctic Ocean.

~~Figures 2 and **??** show that the choice of transfer velocity parameterization had little impact on the calculated fluxes the majority of the time, with the exception being times at which wind speeds were high (greater than 10 m/s) during the period of 18-19 July. In particular, the choice of air-side parameterization (the difference between FLL, FLD, FLMY, FLS and FLJ in Fig. **??**) had very little impact on the estimated fluxes, as shown by the similarity of the medians and distributions of the fluxes estimated using these different parameterizations. Without direct flux measurements, we cannot determine which water-side transfer velocity parameterization is the most accurate. However, recent studies have shown that the wind speed dependence of the DMS transfer velocity is close to linear (Huebert et al., 2010; Bell et al., 2013, 2015). As a result we chose to use a linear dependence of transfer velocity on wind speed in our GEOS-Chem simulations following the Liss and Merlivat (1986) parameterization.~~

~~Ultimately, more data is needed in order to evaluate which transfer velocity parameterization is most suited to modeling DMS fluxes, and whether this varies geographically. For example, the FJLo parameterization, which explicitly includes the effects of sea ice in the marginal ice zone, predicts fluxes a factor of 2 larger than the other parameterizations do. This serves as a hint that accounting for the effect of sea ice on air-sea exchange in models (beyond a simple capping effect) may be important~~

~~to modeling emissions of climatologically active gases such as DMS. Even without the additional consideration of regional differences such as sea ice cover, considerable uncertainty concerning transfer velocity parameterizations remains. It is probable that all of the factors controlling air-sea flux are not yet understood (Johnson et al., 2011), and would in any case be very difficult to model. Accurate parameterization of sea-air fluxes is an active area of research, and advances in the field are essential to chemical transport models.~~

4 ~~Source apportionment with GEOS-Chem and FLEXPART~~

~~In order to~~

4 Source sensitivity studies with GEOS-Chem and FLEXPART

In order to explore the provenance of the air masses being sampled on the ship, we used FLEXPART-WRF backward runs as well as GEOS-Chem simulations. Figure 3 summarizes our understanding of the origins of air masses arriving at the ship track. Figure 3A shows the time series of DMS_g from the GEOS-Chem simulation superimposed on the measured DMS_g time series, as well as the GEOS-Chem sea salt (a marine tracer) and methyl ethyl ketone and carbon monoxide (MEK and CO, biomass burning tracers) mixing ratios. Figure 3B shows the main land cover types in the region. Panel C in Fig. 3 shows examples of potential emissions sensitivity plots generated using FLEXPART-WRF that indicate regions the air has passed over before being sampled. Periods highlighted with a gray bar and numbered 1 through 3 were chosen as representative of three types of influence: 1) marine influence from south of the Arctic circle, 2) terrestrial influence from Northern Canada, and 3) regional marine influence from Baffin Bay. Sea salt tracer maxima indicate marine-influenced air and reflect high winds, while MEK and CO maxima indicate an influence from biomass burning. Biomass burning tracers provide a convenient indication of continental influence on the airmass. Figure 3 shows agreement between the sources of the air indicated by FLEXPART-WRF and by the GEOS-Chem tracers. For example, during Period 2 the MEK tracer is high and FLEXPART-WRF shows continental influence, while during Period 3 the sea salt tracer is high and FLEXPART-WRF shows marine influence.

4.1 Model-Measurement Comparison

~~Our~~ Figure 3a shows that our GEOS-Chem simulations reproduce the major features of the measured DMS_g time series, with appropriate magnitudes much of the time and an overall bias of -67 pptv. The poorest model-measurement agreements occur on 1-2 and 6-7 August, as shown in Fig. 4b and Fig. 3a, where GEOS-Chem overestimates DMS mixing ratios by a factor of 2-3. This overestimation coincides with high levels of the accumulation mode sea salt aerosol tracer in GEOS-Chem as shown in Fig. 3b. The overestimation may be due simulation errors related to the

DMS$_{sw}$ ~~values for that time period being too large (given our use of a static fieldbased on only a few measurements), to~~ field, excessive GEOS wind speeds driving too large of a flux during this episode, or ~~to errors in the parameterization used for the transfer velocity~~ the performance of the air-sea transfer velocity parameterization at high wind speeds. Wind speeds in our GEOS-Chem simulations ~~are generally within a factor of 2 of~~ display considerable scatter about the observed wind speeds along the ship track time series, but show a linear relationship with a slope of 0.95 and $R^2 = 0.35$ as in Fig. S4. Overall, GEOS-Chem tended to overestimate DMS$_g$ in Baffin Bay (largely open water at the time of the campaign) and underestimate it in Lancaster Sound (where we encountered between 10-100% ice cover). It is worth noting that the effect of sea ice on sea-air flux as hypothesized by Loose et al. (2014) is to increase the flux at low wind speeds and decrease it at high wind speeds. Implementation of this transfer velocity parameterization might be expected to improve model-measurement agreement. More work is needed to assess how best to parameterize air-sea flux in high latitude regions and the marginal ice zone in particular. Within these uncertainties, the seawater DMS source could largely account for the measured DMS$_g$. However, there are some notable mismatches that cannot be accounted for by the uncertainties detailed above. These are discussed in the following sections. Since the GEOS-Chem model has realistic capabilities in the simulation of transport (Kristiansen et al., 2016) and the chemical sinks of DMS are relatively well understood (Barnes et al., 2006), we chose to keep the transport and sink parameterizations constant for our sensitivity studies and focused on source sensitivity studies due to the considerable source-related uncertainty.

4.2 ~~Local~~ Seawater sources: Baffin Bay and Lancaster Sound as principal oceanic DMS source

Our model-measurement comparisons suggest that as expected, seawater makes the dominant contribution to the measured DMS$_g$. In this section, we examine the potential regional contributions. Figure 4a shows the relative contributions of various marine source regions to the GEOS-Chem simulation of the DMS$_g$ along the ship track. Nearly 90% of the simulated DMS~~was contributed by the areas the ship was traveling through,~~$_g$ could be explained by the DMS oceanic emissions from Baffin Bay and Lancaster Sound when using the DMS$_{sw}$ field based on our in situ measurements. The simulated DMS$_g$ originating from Baffin Bay and Lancaster Sound ~~(~~are shown in blue and purple respectively ~~).~~in Fig.4a. These local emissions also contributed the majority of the highest mixing ratios observed during the campaign on 18 and 20 July. Overall, we conclude that the waters of Baffin Bay and Lancaster Sound acted as a strong local source of DMS$_g$ throughout the campaign.

4.3 Transport from a seawater source: ~~Role~~ role of Hudson Bay System as an additional oceanic DMS source

Figure 4 shows that the simulated influence of the HBS is significant on 18-19 July, contributing up to 60% of simulated DMS$_g$ ~~over~~ towards the end of that time period. This peak in DMS coincided with a ~~storm originating in lower latitudes blowing through~~ synoptic-scale storm system, which originated at lower latitudes and passed over Lancaster Sound, where the ship was located at the time. This transport pattern is visible in the FLEXPART-WRF retroplume for Period 1 in Fig. 3C. These results suggest that DMS emissions from the HBS ~~have the potential to be~~ are potentially an important source of atmospheric sulfur to the Arctic atmosphere during episodic transport events associated with mid latitude storms ~~traveling northward. This result depends~~ travelling northward. Our simulated results depend on the assumption that the DMS$_{sw}$ values in the HBS are similar to ~~levels~~ those observed at higher latitudes. ~~However, the~~ The potential for influence from the HBS is supported by previous reports of high levels of DMS$_g$ in air masses transported northward from the Hudson Bay region (Sjostedt et al., 2012). Measurements of both DMS$_{sw}$ and DMS$_g$ in the HBS are needed to confirm this hypothesis.

4.4 Investigation of possible missing sources

The GEOS-Chem simulated DMS$_g$ time series ~~fails to reproduce the peak~~ underestimates the peaks in measured DMS$_g$ on 17 and 26 July (shown in Fig. 3a). This mismatch coincides with a minimum in the simulated marine tracer (sea salt), suggesting that possibly a non-marine source of DMS$_g$ is not being represented in the ~~model. We expect~~ GEOS-Chem DMS parameterization. Since the emissions of DMS$_g$ and ~~the sea salt tracer to covary in the model as their emissions~~ sea salt aerosol are similarly dependent on wind speed and fraction of open ocean and their lifetimes are similarly short, we expect the DMS$_g$ and sea salt tracers in our simulation to covary if the DMS$_g$ is of marine origin. It is possible that this model-measurement disagreement indicates that the model does not capture the true relationship of DMS$_g$ to wind speed, or that the GEOS-Chem simulation is missing a coastal body of water at a sub-grid scale and that this water body was emitting large quantities of DMS. However, the FLEXPART-WRF retroplumes for 26 July (an example is shown as Period 2 of Fig. 3C) indicate that the airmass had ~~not traveled over very much open water~~ spent most of its time over land surfaces and sea ice before reaching the ship's location. This ~~is~~ continental air-mass origin is further supported by high levels of simulated continental tracers (e.g. MEK, shown in the third panel of Fig. 3a) during these same periods.

The suggestion that DMS$_g$ may have a continental source is not new (Hopke et al., 1995), but ~~it~~ has not received very much attention. The FLEXPART-WRF PES retroplumes indicate that the continental area influencing the air masses sampled by the ship was Northern Canada (primarily, regions to the south and ~~est~~ east of Baffin Bay, including Nunavut and the Northwest Territories).

The land cover in that region is shown in Fig. 3~~B~~ b and is a mixture of tundra, boreal forest, wetlands and lakes. As well, there was a wide spatial extent of melt ponds to the south and west of the ship track (shown in Fig. S5). To ~~assess the impact~~ investigate the impact that each of these sources ~~may~~ could have had on the DMS_g measured during the campaign, we estimated the DMS emission potential of each land cover type (including melt ponds) ~~using published valueswhere possible~~based on existing literature values. We implemented these extra emissions in the GEOS-Chem model and performed sensitivity tests to explore their potential to make additional contributions to DMS_g at the ship positions. These results are presented in the following subsections.

4.4.1 Emissions from melt ponds

Melt ponds form on the surface of sea ice as the snow melts. They cover much of the surface of the sea ice by mid summer and have been suggested as a potentially important source of DMS to the atmosphere (Levasseur, 2013). At the time of the campaign, the sea ice regions to the west and south of our ship track, particularly in Lancaster Sound, had considerable melt pond coverage as shown in Figure S5. The melt pond DMS source was implemented in GEOS-Chem by assuming that 50% of sea ice was covered by melt ponds and treating melt ponds as seawater ~~in the model, that is, using the same flux parameterization as for open ocean (Liss and Merlivat, 1986)~~with a DMS_{sw} concentration of 3 nM (expected to be an upper limit based on Levasseur (2013). The Liss and Merlivat (1986) transfer velocity parameterization was used. The validity of assuming the same flux parameterization applies to a shallow melt pond as to the open ocean is untested, but ~~as discussed previously, the uncertainties associated with parameterizing transfer velocities in general are quite large, so we consider this approximation reasonable~~ is a reasonable approximation for our sensitivity test. ~~The concentration of DMS_{sw} in the melt ponds was set to 3 nM. This value was chosen to provide a reasonable upper limit based on measurements by Levasseur (2013).~~

The blue curve in Fig. 4c shows the ~~modeled DMScontributed by~~ simulated DMS_g contribution for the melt pond source. The simulated melt pond contribution ~~to the simulated DMS_g time series at the ship track~~ was greatest during 18-25 July when the ship was in Lancaster Sound. The ~~melt ponds contributed a maximum of~~ maximum simulated melt pond contribution was about 100% ~~to the total simulated DMS_g at the ship position~~ on 23 July when ~~modeled~~ simulated and measured DMS_g were very low. The strong contribution of the melt ponds at this time was likely due to the ship's position at the ice edge and advection of the arriving airmass over ice-covered regions. The simulated melt pond source contributed an average ~~of close to~~ about 20% ~~of~~ to the total simulated DMS_g over the remainder of the time series. ~~Addition~~ Implementation of this source reduced the overall normalized mean ~~model~~ model-measurement bias by 9%, suggesting that melt ponds could serve to elevate the regional background levels of DMS_g. ~~More~~ Further measurements of DMS concentrations in melt ponds and, ideally, direct measurements of DMS fluxes from melt ponds ~~will further~~ are needed to better constrain the impact this source might have on DMS_g in the Arctic summer.

4.4.2 Emissions from coastal tundra

Previous studies suggest that DMS emissions from lichens (Gries et al., 1994) and from coastal tundra, particularly in regions where snow geese breed (Hines and Morrison, 1992), may be quite large. For lichens to emit reduced sulfur to the atmosphere, they require a source of sulfur. In coastal regions this can be supplied by sea spray. We implemented a tundra DMS source in GEOS-Chem by using the Olson Land Cover data (http://edc2.usgs.gov/glcc/globdoc2_0.php) to calculate the fraction of each GEOS-Chem grid box covered by the land type "barren tundra". We then assumed that 40% of that tundra (to account for inland regions emitting less due to less sulfate being deposited by sea spray) emitted DMS at a rate of 480 nM $m^{-2}h^{-1}$ (Hines and Morrison, 1992). We consider this simulation to give us an upper limit to the potential influence of tundra DMS emissions.

The results are presented as the brown curve in Fig. 4c. The simulated DMS_g at the ship track had the largest contribution from tundra sources during 16-17 July, with a maximum contribution to the simulated DMS_g at the ship position of 6%. The percent contribution was lower than that of the melt pond source because the tundra source acted to increase simulated DMS_g during times when levels were already high, but as can be seen in Fig. 4c the absolute contribution of the ~~modeled~~ simulated tundra source was comparable to or ~~larger~~ greater than the melt pond source contribution. Like the melt pond source, the possible tundra source reduces the overall normalized mean bias (by 14%) and may contribute to the regional background levels of DMS_g. However, neither source can account for the large unexplained peaks in the measured time series.

4.4.3 Emissions from lakes

To evaluate the potential contribution of DMS from lakes, the fresh water fraction in each GEOS-Chem grid box in a rectangular domain spanning 48 to 75°N and -68 to -140°W was calculated using the Olson Land Cover map, ~~which has a resolution of~~ at 1 km x 1 km resolution. Based on the work of Sharma et al. (1999a), we assigned a mean value of 1 nM DMS to the fresh water in that domain. We then applied the same ~~Liss and Merlivat parameterization as was used to represent the air-water flux for the oceans to the~~ Liss and Merlivat (1986) parameterization to the fraction of the grid box with lake coverage. The same caveats apply to the use of transfer velocity parameterizations developed for the open ocean for fluxes from lakes as to the application to melt ponds as discussed above. ~~Under these conditions~~In our simulation, the lake source was ~~regionally~~ only locally important as shown in Fig. 5. ~~It resulted in a modest increase in~~ There was a modest contribution to the absolute magnitude of DMS_g in Northern Quebec and Labrador, and had negligible effects elsewhere. The percent change in surface layer DMS_g in the Northwest Territories was quite large due to there being no other simulated sources of DMS_g in that location~~in GEOS-Chem~~, but the absolute values of DMS_g are very small. ~~The effect on the simulated DMS_g time series along our ship track in the Arctic is negligible.~~ However, as there are ~~so~~ few measurements of DMS concentrations in lakes in

Northern Canada, we cannot exclude the possibility that the actual lake concentrations of DMS_{sw} are much higher than 1 nM and that the unexplained peak in our time series is due to a lake source of DMS_g. This possibility is supported by high chlorophyll-α levels in the lakes of Northern Canada (shown in Fig. S6) and the fact that the measurements of DMS_{sw} in lakes that we used for this sensitivity test were made more than 15 years ago, and the high northern latitudes have warmed significantly since then (IPCC, 2013).

4.4.4 ~~Emissions from forests and soils~~Other potential DMS sources for the study area

Due to the paucity of measurements of DMS emissions from vegetation, boreal soils, and Arctic wetlands, especially during and in proximity to biomass burning events, this potential missing source is ~~by far the most~~ very difficult to evaluate. The correlation between the measurement-model residual and the biomass burning tracers in GEOS-Chem shown in Fig. 3A suggests that ~~the missing DMS~~DMS_g was being co-transported with these biomass burning tracers. The measurement-model difference and the MEK tracer have a similar peak on 26 July as shown in Fig. 3A. The FLEXPART-WRF retroplumes (e.g. Period 2 in Fig. 3) identify this time as being continentally influenced.

DMS emissions have been reported from biomass burning (Akagi et al., 2011; Meinardi et al., 2003)~~and summer~~. Summer 2014 ~~saw~~ was a particularly active wildfire season in Northern Canada (Blunden and Arndt, 2015). The simplest reason for the maxima in biomass burning tracers during the unexplained DMS_g peak on 26 July would be emissions of DMS from biomass burning that are not represented in the model. To gauge the importance of this source to DMS_g in the Arctic, we used the emission factor for DMS from boreal forest biomass burning reported by Akagi et al. (2011). We indexed the simulated DMS emissions to CO emissions, such that 3.66×10^{-5} molecules of DMS are emitted for each molecule of CO emitted~~in GEOS-Chem~~. Figure 5 shows that the biomass burning sensitivity test ~~showed~~ indicated that the biomass burning source of DMS_g had local influence only, like the ~~modeled~~ modelled lake source. The reason for this is that the emission factor for DMS from boreal forest fires is not very large. As a result, this source acted to increase DMS_g in the immediate vicinity of the wildfires in the Northwest Territories, but had a negligible influence on the time series and is therefore not shown in Fig. 4. The biomass burning source of DMS_g was likely not sufficient to directly influence the DMS_g time series at the ship position, unless the emission factor used in the model is an order of magnitude too low. This seems unlikely as the emission factor we used was derived from direct measurements in a biomass burning plume originating from the boreal forest (Akagi et al., 2011)~~, but remains a possibility as much higher~~. Considerably larger DMS emissions have been measured from other types of biomass burning in other locations (Meinardi et al., 2003) ~~.~~

~~Further evidence for~~ but we have no measurement evidence to support a higher emissions factor in our present simulations. We note that in particular, emissions from tundra fires are completely unconstrained and might be quite different from emissions from boreal forest fires due to different vegetation types and different types of burning (e.g. open flames versus smoldering). Further study is required.

Although the available information suggests that direct DMS emissions from fires seem unlikely to explain the bias, support for the hypothesis that DMS$_g$ is being co-transported with biomass burning tracers is given by improved model-measurement agreement indicated by Fig. 3c if we assume the biomass burning plume contains equal amounts of DMS$_g$ and MEK, and ~~then~~ add this DMS$_g$ “source” to the simulated DMS$_g$. ~~The result of this addition is to decrease the~~ This revision reduces the overall measurement-model bias by 24 %~~overall, and to reduce~~ , and reduces the residual by 200 pptv ~~during~~ for the 26 July~~period of interest. The time series of additional DMS$_g$ is shown as the green curve in Fig. 4c.~~ . Alternatively, the air mass observed at the ship could have passed over a strong near-land marine source, which is missing in our simulations. ~~The region air mass passed over, however, was~~ However, the FLEXPART-WRF simulation indicates that the air-mass had travelled over nearly entirely ice-covered ~~at the time, making this an unlikely~~ regions before arriving at the ship, suggesting that a marine source is a less likely explanation for the observed DMS$_g$. ~~These results cannot tell us anything about the nature of the continental source, but they highlight the possibility that a source linked in some way to terrestrial flora could have an important effect on DMS$_g$ in the Arctic summer.~~

Emissions of reduced sulfur species from both soils and lakes are temperature dependent (Bates et al., 1992), ~~opening up the possibility~~ suggesting that the wild fires ~~were indirectly promoting~~ could indirectly promote DMS emissions. Proximity to wild fires ~~would tend to~~ could increase the temperature of the soil as well as changing the ~~quality of the air in a way that~~ air quality, which might stress biota. A mechanism whereby biomass burning increases the emission of reduced sulfur species such as DMS from soils, lakes and vegetation might yield increased emissions but this requires further study and we do not have any information that would allow implementation of this possible effect in our simulations.

5 Conclusions

~~Interpreting our recent shipboard DMS~~ This study presents, to the best of our knowledge, the first measurements of gaseous DMS mixing ratios in the summertime Arctic atmosphere of Baffin Bay and parts of the Canadian Arctic Archipelago. Measured DMS$_g$ ~~measurements~~ values were greater than those measured in fall in the same region (consistent with higher biological productivity in summer) and broadly consistent with measurements in other parts of the ocean. We made flux estimates that fall within the range of existing DMS air-sea flux estimates for the summertime Central Arctic Ocean. The data presented here improve our knowledge of atmospheric DMS levels in the summertime Arctic, but further study is needed to understand spatial, seasonal and interannual variability of DMS both in the ocean and in the atmosphere.

We conducted sensitivity simulations with the GEOS-Chem chemical transport model ~~, we have shown~~ to examine the potential of various sources to contribute to DMS$_g$ measured along the ship track. We found that local oceanic sources can account for a large proportion (70% overall) of the atmospheric surface-layer DMS measured along our ship track in the Canadian Arctic Archipelago and Baffin Bay during summer ~~2014, and that the ocean was acting as a strong local source of DMS$_g$. With~~ 2014. Our GEOS-Chem simulations ~~, we have also shown that~~ indicated that during transport events associated with synoptic-scale storms, marine sources south of the Arctic Circle ~~episodically contribute~~ made strong and episodic contributions (as much as 60%) to DMS mixing ratios in the Canadian Arctic ~~during transport events~~Archipelago region. The role of transport in controlling DMS levels and the potential for aerosol particle formation from DMS$_g$ has been argued convincingly in a global sense by Quinn and Bates (2011). We propose that it may also be important episodically in the Arctic, e.g. transport from the Hudson Bay System or the Northwest Territories. These origins for air at our ship track are also supported by FLEXPART-WRF retroplume analysis.

~~Overall, source apportionment using FLEXPART-WRF and~~ GEOS-Chem ~~indicate that local sources dominate atmospheric DMS in the Canadian Arctic Archipelago and Baffin Bay. However, GEOS-Chem simulations show a low bias of~~ simulations were biased low by 67 pptv over the ship track time series (~~from~~ representing between 10% to 100% of the measured mixing ratios). We investigated several ~~alternative sources that could act to correct this bias and presented evidence that some of these sources make a non-negligible contribution to surface layer DMS mixing ratios. This included sources from~~ additional sources (tundra, forests, lakes and melt ponds), which could contribute to surface layer DMS mixing ratios. Our sensitivity simulations indicated maximum contributions of 6% and 100% from tundra and melt ponds, respectively, to ~~our~~ the simulated total DMS$_g$ ~~time series at the ship position~~for the ship-track time series, suggesting that emissions of DMS from melt ponds and coastal tundra could have important local, regional effects on DMS levels. ~~Given our confidence in marine-based DMS sources, we also estimated as much as 94% of the DMS~~These sensitivity studies also suggest that terrestrial or near-terrestrial sources could make additional contributions to DMS$_g$ ~~at the ship position could be from terrestrial sources (or another source missing from the model) during episodic transport events~~in our study region. These emissions may be related to changes in lake, forest and soil emissions due to the heat and stress associated with biomass burning. Flux measurements from melt ponds and the boreal forest and lakes, particularly when under stress from biomass burning events, are needed to ~~constrain this missing source~~evaluate this hypothesis.

Our findings have implications for our understanding of the sulfur cycle in the summer Arctic and how it has changed in the recent past and will continue to change in the future. For example, much of the discussion surrounding changes in Arctic DMS has focused on the loss of sea ice (Levasseur, 2013), but the loss of permafrost might also have a large impact ~~, by providing nutrients to lakes , for example~~ through changing nutrient levels in lakes (Rhüland and Smol, 1998). The potential ~~of~~

~~the high~~ influence of the observed atmospheric levels of DMS ~~observed during the 2014 campaign to participate in~~ on new particle formation and subsequent growth remains to be explored.

Author contributions

J. Abbatt and M. Levasseur designed the experiments and E. Mungall and M. Lizotte carried them out. J. Murphy, J. Liggio and J. Wentzell facilitated the *Amundsen* campaign. B. Croft and J. Thomas performed the GEOS-Chem and FLEXPART-WRF simulations, respectively. E. Mungall carried out the analysis, and E. Mungall prepared the manuscript with the aid of B. Croft and contributions from all co-authors.

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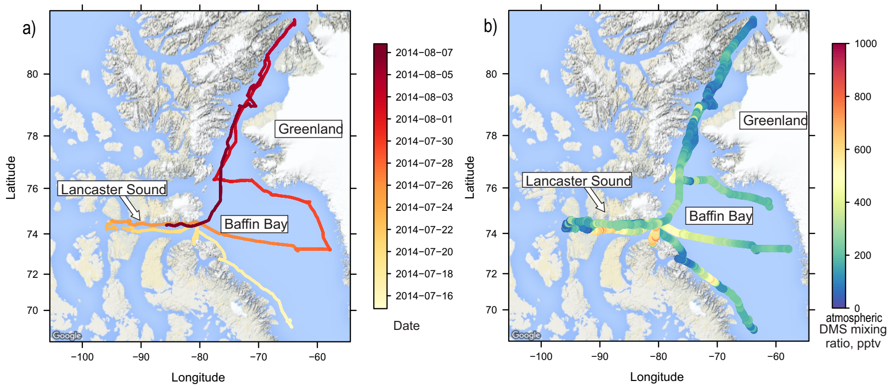

Figure 1. a) The ~~Amundsen~~ *Amundsen* ship position with dates indicated by colours. b) Surface-layer atmospheric dimethyl sulfide (DMS) mixing ratios from ship-based high resolution time of flight chemical ionization mass spectrometer (HR-ToF-CIMS) measurement with colour showing magnitude of mixing ratios.

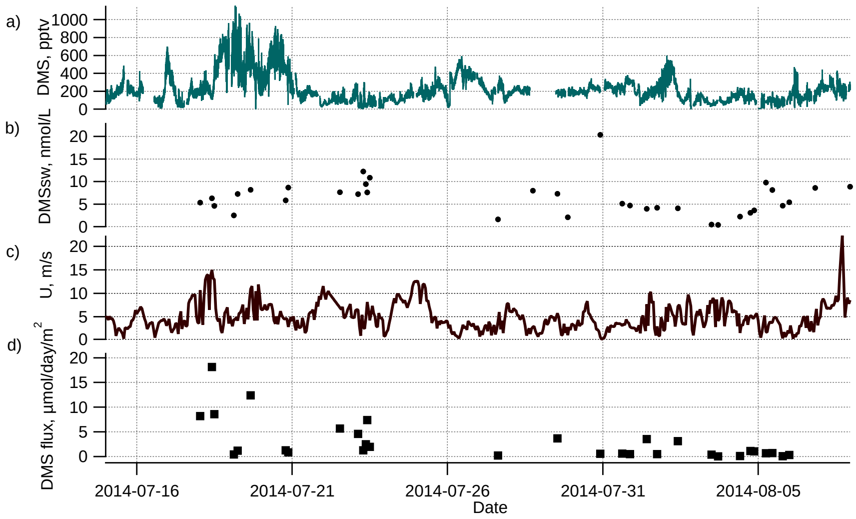

Figure 2. Time series along ~~Amundsen~~ *Amundsen* ship track of a) atmospheric DMS mixing ratio (10 Hz) from HR-ToF-CIMS, b) observed DMS surface seawater concentration, c) hourly-averaged wind speed at ship position, d) DMS water-air flux estimates ~~for all choices of transfer velocity parameterization (symbol acronyms given in Table ??.~~

~~Summary of parameterizations investigated in this workSymbol Reference Brief Description Required InputsAir side D (Duce et al., 1991) Based on micrometeorology, uses molecular weight of the compound compound, uL (Liss, 1973) Based on data from a wind tunnel study uMY (Mackay and Yeun, 1983) Based on data from a wind tunnel study, uses the Schmidt number of the compound compound, u, T S (Shahin et al., 2002) Based on data from an in situ study using a surface water sampling device on an urban rooftop, uses the diffusion coefficient of the compound compound, u, TJ (Jeffery et al., 2010; Johnson, 2010) NOAA~~

~~Regional median DMS flux estimates for all choices of transfer velocity parameterization (symbol acronyms given in Table **??**. The middle line of the box shows the median. The top and bottom box edges show the upper and lower quartiles (1/4 and 3/4 of the data, respectively). The whiskers show the maximum and minimum values, excluding outliers, which are represented by single points. Outliers differ from the upper and lower quartiles by more than a factor of 1.5.~~

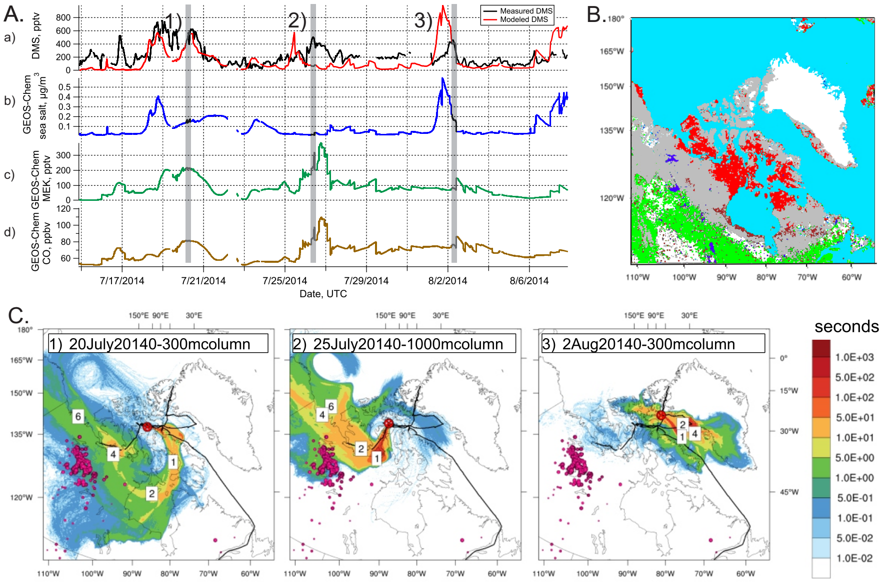

Figure 3. Panel A) Surface-layer atmospheric time series along ~~Amundsen~~ *Amundsen* ship track of a) measured and GEOS-Chem (GC) simulated DMS, b) GC simulation of accumulation mode sea salt mass concentration, c) GC simulation of methyl ethyl ketone (MEK) mixing ratio, d) GC simulation of carbon monoxide (CO) mixing ratio. Panel B) Olson Land Cover map of North America showing low-lying tundra (red), other tundra (gray), forest (green), wetlands and marsh (brown) and inland water (dark blue). Panel C) FLEXPART-WRF potential emissions sensitivity (PES) simulation plots showing the likely origin of the air mass at the ship position. The colour scale in seconds corresponds to time spent in the lower 300-1000 m (marked on each plot) before arriving at the ship position. The three plots correspond to the three periods shown by the numbers and shaded bars in Panel A, showing examples of 1) transport from lower latitudes, including Hudson Bay 2) continentally influenced air 3) local marine influence from Baffin Bay.

~~COARE fully physically based model, modified here to fit better with observations compound, u, T Water side W (Wanninkhof, 1992) Global estimate based on bomb ^{14}C inventory compound, T, u, SL (Liss and Merlivat, 1986) Lake experiments using SF$_6$ and wind tunnel observations compound, T, u, SS (Sweeney et al., 2007) Global estimate based on bomb ^{14}C inventory compound, T, u , SN (Nightingale et al., 2000) Deliberate multi-tracer study (considered the state of the art) compound, T, u, SW97 (Woolf, 1997) Physically based, includes compound-specific bubble effect compound, T, u, S M (McGillis et al., 2000) Cubit fit to field data compound, T, u, SLo (Loose et al., 2014) Fully~~

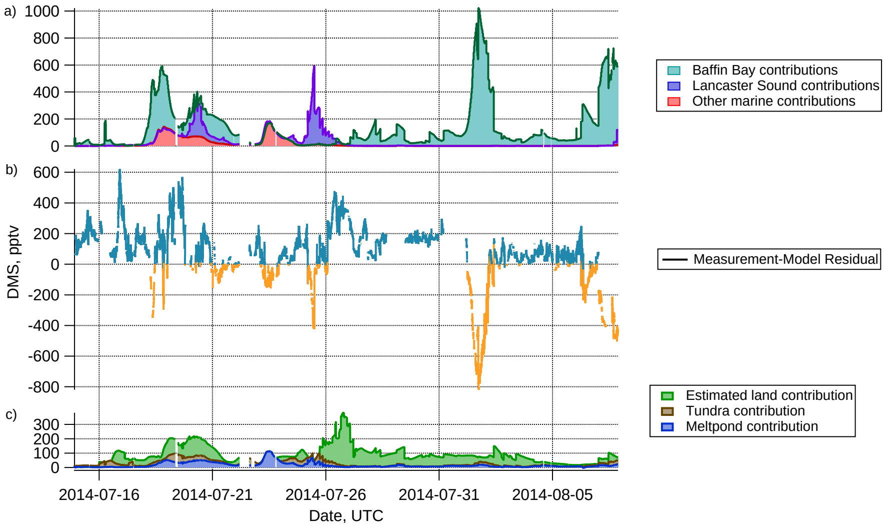

Figure 4. a) GEOS-Chem (GC) simulated ~~of~~ atmospheric surface-layer DMS mixing ratio along ~~Amundsen~~ *Amundsen* ship track as in Fig. 3A, with indication of contributions from Baffin Bay (blue), from Lancaster Sound (purple), and from other marine regions (red). b) Difference between measurement and simulated DMS mixing ratio time series along the ship track showing model over prediction in blue and under prediction in orange. c) GC simulated DMS contributions along ship track from sensitivity tests for additional DMS sources such as melt ponds (blue), tundra (brown), and unknown ~~terrestrial (~~sources possibly including forests, soils, or lakes ~~)/near-terrestrial marine sources~~ in proximity to biomass burning (green).

~~physically based, includes effects of sea ice. Only valid in regions with non-zero sea ice coverage T, u, S,~~ ~~u_{ice}, ice concentration~~

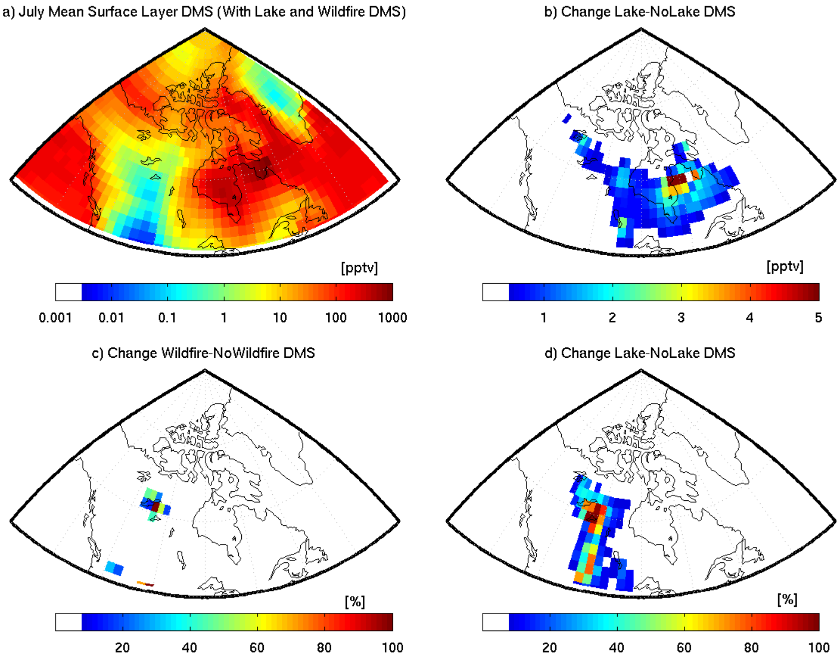

Figure 5. a) GEOS-Chem simulated July mean surface-layer atmospheric DMS in Canada, b) absolute change in simulated surface layer DMS with implementation of lake DMS emissions, c) percent change in simulated Canadian surface layer DMS due to DMS emissions from wildfires, d) percent changes in simulated surface layer DMS with the implementation of lake DMS emissions.

Table 1. Summary of past DMS atmospheric mixing ratio measurements in the Arctic

Study	Leck and Persson (1996)	Rempillo et al. (2011)	Rempillo et al. (2011)	Chang et al. (2011)	Tjernström et al. (2014)	This Work
Cruise Name	IAOE-91	Amundsen 2007	Amundsen 2008	Amundsen 2008	ASCOS 2008	Amundsen 2014
Season	Fall (August, September, October)	Fall (Early October)	Fall (Late September)	Fall (End of August, September)	Fall (August, beginning of September)	Summer (Late July and Early August)
Location	Central Arctic Ocean	Western Canadian Arctic	Eastern Canadian Arctic	Eastern Canadian Arctic	Central Arctic Ocean	Eastern Canadian Arctic
Method	Gas chromatography	Gas chromatography	Gas chromatography	Proton Transfer Reaction Mass Spectrometry	Proton Transfer Reaction Mass Spectrometry	Benzene Chemical Ionization Mass Spectrometry
Measurement Frequency	392 samples in 64 days	9 samples in 3 days	18 samples in 3 days	5 min	1 min	10 Hz
Median	25 (1.1)	10 (0.44)	30 (1.3)	65.9	26	185.8
25th percentile	11 (0.48)			41.2	15	117.8
75th percentile	53 (2.3)			98.9	50	262.5
Minimum	1.1 (0.047)	Below detection (<7 pptv)	Below detection (<7 pptv)	0.3	4.0	Below detection (<4 pptv)
Maximum	380 (17)	30 (1.3)	94 (4.1)	474	158	1155

The studies of Leck and Persson (1996) and Rempillo et al. (2011) report concentrations in nmol/m^3. For purposes of comparison, these have been converted to mixing ratios for an atmospheric pressure and temperature of 101 kPa and 4 ^{circ} respectively. Original (published) concentration values are reported in parentheses following the calculated mixing ratios.

Table 2. Summary of previous air-ocean DMS flux values in the Arctic

Flux	**Date**	**Location**	**Method**	**Authors**
0.02-12 $\mu\text{mol m}^{-2}\text{d}^{-1}$	Summer 2014 (July and August)	Eastern Canadian Arctic	Estimated from measurements	This work
0.1-2.6 $\mu\text{mol m}^{-2}\text{d}^{-1}$	Fall 2007, 2008 (September to November)	Beaufort Sea to Baffin bay through Lancaster Sound	Estimated from measurements	(Rempillo et al., 2011)
0.002-8.4 $\mu\text{mol m}^{-2}\text{d}^{-1}$	Fall 1991 (August to October)	Central Arctic Ocean and Greenland Sea	Estimated from measurements	(Leck and Persson, 1996)
0.007-11.5 $\mu\text{mol m}^{-2}\text{d}^{-1}$	Summer 1994 (July and August)	Central Arctic Ocean East-West transect	Estimated from measurements	(Sharma et al., 1999b)
0.5 $\mu\text{mol m}^{-2}\text{d}^{-1}$	January	North of 60°N	Global model	(Erickson et al., 1990)
4-12 $\mu\text{mol m}^{-2}\text{d}^{-1}$	March-December 1996	Gulf of Alaska	Regional Model	(Jodwalis et al., 2000)