

## ***Interactive comment on “Summertime sources of dimethyl sulfide in the Canadian Arctic Archipelago and Baffin Bay” by E. L. Mungall et al.***

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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 mea-*

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*surements 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.”

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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

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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

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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  $k_{DMS}$  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.

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**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  $R^2 = 0.35$  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.

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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".

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**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  $80 \pm 30$  cps pptv<sup>-1</sup>. 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

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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%) water-side 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

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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<sub>sw</sub> 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.”

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**AC17:** This section was removed from the text.

**RC18:** *"p. 35564. Line 22, east of Baffin Bay"*

**AC18:** 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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