

Dear Reviewer,

Thanks for the great comments on the paper. Please find the answers we provided for your comments and questions, below.

Your Sincerely,

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Referee #2:

First, I think the description of the measurement technique needs some clarification, even though it is based on methods described 20 years ago. My main questions to be cleared up: 1) Sample times range from 2 – 11 minutes. What is the flow rate, and what are the resulting sample volumes? 2) Reference to Sharma et al. (1999) as a description of the method seems incorrect as listed. The listed Sharma et al. (1999) paper describes a 10 L sample collected on molecular sieve. The reference Sharma et al. (1997) is a typo and should also be 1999. This appears to be the correct reference to the Tenax method. Sharma (1997) is the MSc thesis, which should contain all of the details but is not easily available which is why some extra detail is needed. The Sharma et al. (1999) paper lists the detection limit as  $\pm 6$  pptv in a 2 L sample (defined as 2:1 S/N), and accuracy and precision of  $\pm 12\%$  (not sure what this means, though). This manuscript refers to a  $\pm 12$  pptv uncertainty (not specified if accuracy or precision). Surely this can't be constant for samples of different volumes. Was this determined based on the triplicate standard measurements, or was this somehow referenced back to Sharma et al. (1999)? Please clarify this, esp. since many of the samples reported seem to be in this range. 4) Sample storage tests: how much standard was loaded onto the cartridge? Were different loadings tested? Please also note the axis of the graph in Figure 3. Is this really the DMS mixing ratio in pptv, or some ratio to initial DMS addition? Is the uncertainty in the stability also considered in assessing the overall uncertainty of  $\pm 12$  pptv?

*1000 mL of samples were collected in 5 mins with a flow rate of approximately 200 mL/min. For few samples the sampling time was shorter or longer than 5 mins, leading to different volume of samples. The uncertainties of DMS mixing ratio were 2 and 3 pptv for the minimum (400 mL) and maximum (2200 mL) of volumes, respectively.*

*We addressed these comments:*

(Page 6, line 1) Sampling collection time was  $300 \pm 5$  seconds with a flow rate of  $200 \pm 20$  mL/min (For few samples the sampling time was shorter or longer than 300 seconds, leading to different volume of samples).

A glass gas chromatograph (GC) inlet liner was used to pack  $170 \pm 2$  mg of Tenax. The Tenax packed in glass tubes was cleaned by heating to  $200^\circ\text{C}$  in an oven with a constant He flow of around 15 mL/min for 5 hours. The DMS samples were analyzed with using a Hewlett Packard 5890 gas chromatograph (GC) fitted with a Sievers Model 355 sulfur chemiluminescence detector (SCD). Two DMS(g) certified standards (1 and 50 ppmv) were used to calibrate the GC-SCD and to determine accuracy of the measurements by checking the standards against each other (for example, 1 microliter of 50 ppmv vs 50 microliters of 1 ppmv). Collection and analysis of samples were based on methods described by Sharma (1997), Sharma et al. (1999) and Rempillo et al. (2011). Uncertainty in the measurements was determined based on the standard deviation ( $\sigma$ ) of DMS(g) standards and was  $\pm 12$  pptv. The detection limit for this method is approximately 7 pptv.

Additional tests were performed to determine if there was significant loss of DMS(g) over time after collection. An experiment was performed to determine how long Tenax is able to store DMS(g) with no significant loss of concentration. This experiment was conducted in triplicate by loading of 50  $\mu\text{L}$  of 1 ppmv DMS(g) standard and storing in a freezer at  $-25^\circ\text{C}$ . In general, Tenax storage tests at  $-25^\circ\text{C}$  showed that DMS losses were approximately 5% and 15% after 10 and 20 days respectively (Figure 3). The DMS(g) mixing ratios summarized in Table 1 are adjusted according to the result of this test.

P7, L.22. The GEOS-CHEM model is certainly widely used for many applications, but as I looked at the Mungall et al., 2016 paper, it seemed that there were significant issues with the DMS emissions specific for the region that was studied, and these conclusions suggest that the GEOS CHEM model needs to be applied with caution for specific locations and seasons for dealing with a highly variable compound such as DMS. Just because it was used is not necessarily an endorsement for its applicability for these measurements, at least without some caveats.

P8, L6. Meteorology and profiles. It is unusual to see the vertical profiles of species averaged for an entire campaign. The DMS measurements need to be related to the atmospheric vertical structure and variability during each flight, or there should be some demonstration that a more suitable analysis is found by taking mission averages.

*As global models often track measurement features but may be slightly off in location or altitude, the model-measurement comparison is more robust if we consider mission averages, particularly in this case where we have limited DMS measurements. We added text on page 12 line 14 to indicate this rationale for the model-measurement comparisons.*

*The O<sub>3</sub>, H<sub>2</sub>O and CO vertical distribution for DMS sampling days are shown in figure S2 and suggest significant uniformity throughout the sampling campaign. We added the uncertainty. The plots are used to compare O<sub>3</sub>, H<sub>2</sub>O and CO during summer and spring. In addition, the O<sub>3</sub> depletion events are reported in Table 1.*

P8, L 16. Please provide the reference(s) to the heterogeneous oxidation of DMS on or within aerosols.

P8, L 24. While sources of DMS and H<sub>2</sub>O are the ocean (though there could be other sources of DMS), different correlations could be observed due to the high spatial and temporal variability of DMS (compared to H<sub>2</sub>O) and effect of temperature on either gas. I assume this discussion of the correlation is related to the argument about the greater presence of clouds in spring vs. summer, and (again) the assertion of a major role of cloud processing of DMS. The presence (note typo on P8, L25) of clouds could potentially have a greater impact on OH production below or above the clouds with subsequent impact on DMS lifetime. Perhaps this was suggested by the statement regarding clouds during transport, but this seems a speculation that could be checked from observations. It is not clear what the authors are saying regarding the effect of clouds: : :reduction of DMS due to heterogeneous O<sub>3</sub> oxidation, or increase of DMS due to slower OH oxidation? Unfortunately, the data is not available to support either impact so this just remains as speculation.

*Correct, the study of aerosol/clouds/CCNs is beyond the scope of this study. Please note that Section 3.1 has been removed.*

P9, L 25. The authors reference again the work reported by Mungall et al., 2016 who measured DMS at the same general location and time period (as far as I can tell) as the airborne data for July,

2014. It would be helpful to discuss the airborne measurements and the impact of the very large variability in DMS emissions that were found in Mungall et al. Perhaps there were times of reasonable overlap between the ship based and airborne measurements that could also be compared. It seems that the large DMS mixing ratios observed during parts of the Mungall et al. cruise were not sampled by the aircraft. Furthermore, the reported range of a factor of 60 in the calculated DMS flux should further raise a cautionary flag about how well climatological models and emission estimates might be applied to the data.

*The Amundsen and Polar 6 measurements occurred during July 2014, but not exactly in the same time and location. We added more information and compared the event during 18-20 July:*

(Page 9, line 5) Mungall et al. (2016) also suggested LRT of DMS from marine regions outside Baffin Bay and Lancaster Sound area, and observed an episode of elevated DMS (g) mixing ratios with values of 400 pptv or above occurred on 18–20 of July. The airborne measurement, showed decline of DMS (g) mixing ratios by height during July 17, and relatively low DMS mixing ratios during July 19<sup>th</sup> and 20<sup>th</sup> (see Table 1).

P10, L 19. Here and elsewhere in the manuscript the possibility of long-range transport of DMS is mentioned. In this context, it would be helpful if the authors could provide some reasonable estimate of the lifetime of DMS and the possible transport times that are considered “long-range” vs. local.

P13, L9. Could the authors make some estimate, based on typical DMS lifetimes, what the source region DMS mixing ratios would need to be to support the observed mixing ratios in spring?

*The life time is assumed to be less than 4 days, and we referred to Sharma et al. (1999):*

(Page 14, line 7) We chose to show the potential emission sensitivity after four days. Sharma et al., (1999) showed that atmospheric DMS(g) lifetime was 2.5 to 8 days in the high Arctic. More details about FLEXPART and the potential emissions sensitivity (PES) could be found in Stohl et al. (2005) and references therein.

Figure 6 shows two examples of FLEXPART-ECMWF PES for 4-day back trajectories in July 2014: an influence from a broad area and especially Lancaster Sound (local region) and north on July 12<sup>th</sup> (Figure 6, left panel), and Hudson Bay, and Baffin Bay (south) on July 19<sup>th</sup> (Figure 6, right panel). A more detailed analysis of PES reveals that the measured air mass descended from >1500 m on July 19<sup>th</sup>, which may explain the low DMS(g) mixing ratios.

Figure 7 shows some examples of FLEXPART-ECMWF PES simulations for 4-day back trajectories during April 2015. For the flights near Alert and Eureka on April 9 and 11, some DMS may have originated from ice-free areas of the Nares Strait and Baffin Bay (Figure 7, upper left and right panels, respectively). For the April 13 flight, the Norwegian Sea, North Atlantic Ocean and Hudson Bay are additional potential source regions (Figure 7, lower left panel). The highest DMS, measured on April 20 near Inuvik is associated with the North Pacific Ocean (Figure 7, lower right panel).

Assuming a DMS atmospheric lifetime of 1 to 4 days, these results suggest that the DMS(g) measured during July 2014 originated primarily from the local region over Baffin Bay and the Canadian Arctic Archipelago. For spring 2015, the DMS(g) sampled was from a range of sources, including Baffin Bay, possibly the Norwegian Sea, the North Atlantic Ocean and the North Pacific Ocean.

P10, L 25. I am not a fan of averaged vertical profiles for variable species (such as aerosols) without some indication of the variability of the measurements over the different profiles. I assume that the higher particle number is associated with the specific profile in July where the measured DMS is about 100 ppt. Or is the higher level of aerosol more widespread? Also, the springtime levels of DMS are even higher than those found in summer, but no significant aerosol production here? This level of discussion and interpretation is incomplete and not particularly informative.

P11, L 3. Thin aerosol layers are common in the Arctic spring. It seems very unlikely that the high altitude peak in aerosol is in any way related to DMS. If the authors really consider the DMS source likely, perhaps some analysis of what sort of conditions might be necessary to produce the observed aerosol abundance.

*Agreed, we removed Fig 5 and discussion about aerosol (study of aerosol is not the focus of this manuscript).*

P11, L 13. Do I understand correctly that the GEOS-CHEM results shown in Figure 6 are compared only for the 2 – 10 minute sample integration time of the measurements? It would be interesting to see some examples of the variability of GEOS CHEM results to perhaps provide a more detailed context for the very limited number of actual samples that were collected. Often models track measurement features, but may be slightly off in time or altitude.

*Correct, We added more information:*

(Page 12, line 13) Caution should be used in interpreting the model-measurement comparisons since these comparisons are conducted over a very limited number of measurement periods and the spatial and temporal resolution of these measurements is a challenge for a global model to simulate.

P11, L 23. I am not sure what the authors want to convey when they claim that the GEOS CHEM data and the measurements are “within their respective uncertainties”. Perhaps “variability” is a better term than uncertainties in this case. There are clearly more uncertainties in the model results beyond just the calculated mixing ratios.

*Yes- We changed “uncertainty” to “variability”.*

P11, L25. From Figure 6, the variability with altitude actually seems less in the summer compared to spring, though the gradient is less in the spring, as noted. Summer range about 20 – 40 ppt at low altitudes, <10 ppt at max altitude; Spring 30 – >50 ppt at all altitudes. Could the authors please quantify the difference in seasonal variability at different altitudes to demonstrate their assertion?

*Thank you- We corrected the text:*

(Page 13, line 2) Both the simulated and measured DMS(g) profiles during spring (~ 30 to >50 pptv) show more variability at all altitude below 4 km than in summer (~ 20 to 40 pptv at low altitudes and <10 pptv at higher altitudes).

P12, L16. 30% difference might also be due to incorrect distribution and intensity of model DMS emissions.

*A cautionary statement is added to the manuscript:*

(Page 13, line 11) The monthly mean seawater DMS field used in our simulations is based on very limited observations from this region (Lana et al., 2011). Datasets of seawater DMS with higher spatial and temporal resolution are needed but are still under development.

P13, L5. I am concerned about the conclusions from the Flexpart analysis where the authors claim a large influence for specific regions. As noted, these analyses suggest where the sampled air spent time in the boundary layer. This analysis must be combined with an emission distribution to provide the source attribution. For example, without additional information, it is misleading to suggest that North Pacific was a significant source of DMS measured in the Arctic. It is a potential source. If the authors have some other data (ocean color, for example) to indicate DMS emission in the North Pacific at that time, then that could be a basis for the claim. Without this emission information, the Flexpart analysis can only indicate “potential” regions.

*Correct: We added word “potential” and more information about FLEXPART to the text:*

(Page 14, line 2) FLEXPART-ECMWF modeling was used to explore the origin of air samples measured along the Polar 6 flight tracks. Figures 6 and 7 show the potential source regions of these air samples four days before the releases along the flight path. More specifically, the response function is shown to all releases of a passive tracer, which in this case has properties of dry air. If

this response function would be folded with an emission flux of the tracer the concentration of this tracer at the release location along, the flight paths could be calculated. We chose to show the potential emission sensitivity after four days. Sharma et al., (1999) showed that atmospheric DMS(g) lifetime was 2.5 to 8 days in the high Arctic. More details about FLEXPART and the potential emissions sensitivity (PES) could be found in Stohl et al. (2005) and references therein.

Figure 6 shows two examples of FLEXPART-ECMWF PES for 4-day back trajectories in July 2014: an influence from a broad area and especially Lancaster Sound (local region) and north on July 12<sup>th</sup> (Figure 6, left panel), and Hudson Bay, and Baffin Bay (south) on July 19<sup>th</sup> (Figure 6, right panel). A more detailed analysis of PES reveals that the measured air mass descended from >1500 m on July 19<sup>th</sup>, which may explain the low DMS(g) mixing ratios.

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P13, L16. The link established in this data set between aerosol formation and DMS is very weak and essentially presented as a given with no detailed analysis. While we all seek global significance of atmospheric chemistry and a potential link to climate, I think that it is an overreach to state that, without much greater data coverage and analysis, the observed vertical variation will significantly impact the Earth's radiation budget.

*Agreed, the discussion of aerosol is removed.*

Figures 1 and 2. These are not particularly helpful figures to identify the sample locations. I would suggest combining each season's flights into several composites that showed 1) a map of flight tracks, 2) an altitude-longitude (and/or latitude) cross-section that identified the location of the samples and the flight tracks. Given only a few flights, a color code could make things relatively easy to follow.

*Figs 1 and 2 show the sampling locations and altitudes. To address this comment, we added more details about the sampling location (Lat/Lon/Alt) in Table 1.*

Figure 3. Already noted. Vertical axis mislabeled?

*The vertical axis shows the DMS mixing ratios, and the mixing ratio of DMS standard used for this experiment is 1 pptv.*

Figure 5. Possible to add shading to each mean profile to show range or std deviation in each bin?

*Fig 5 is removed.*

Figure 7. I could not distinguish the blue lines for the flight tracks. Are these calculated for a single sample or some altitude? Please specify. I certainly do not understand the units for potential emission sensitivities. I thought that these indicated the time spent in the boundary layer (in this case 0 – 200 m) during the period of the back trajectories (4 days here). Is there a factor of 1000 missing here?

*Please note that we added more information about FLEXPART and changed figures 7 and 8.*

Table 1. It would be helpful to add the flight number and altitude to this table.

*Agreed, we added more information to Table 1.*