

RC1:

Siegel et al. presented gas-phase and particle-phase measurements of SA, MSA and HPMTF during the full year of 2020 at the Zeppelin Observatory, Ny-Ålesund, Svalbard. They report high gas-phase concentrations of HPMTF between April and September when DMS emissions are high, but observe no significant concentration of HPMTF in the particle-phase. The paper is well written and provides an important insight into the role of HPMTF in the atmosphere. I recommend that the paper be published after addressing the comments below.

The authors thank the reviewer for the positive assessment of our manuscript and the time invested to review it. The authors comment on each of the reviewer's comment (bold) individually. The lines given in the answers refer to the revised document. Figure numbers refer to Figures in the manuscript and Figure letters refer to Figures only provided for the review process.

Specific comments:

Page 1 - line 2: "methanesulfonic acid (MSA) and sulfuric acid (SA) are well-known for participating in the formation and growth of atmospheric aerosol particles". While it is well known that SA contributes to new particle formation, I would not say that MSA is well-known to do so. Recent studies have found it plausible that MSA contributes to NPF, but it has not been definitely established.

The authors thank the reviewer for pointing this out. The authors changed L14-17 to "DMS undergoes oxidation in the atmosphere to form a range of oxidation products, out of which sulfuric acid (SA) is well-known for participating in the formation and growth of atmospheric aerosol particles, and the same is also presumed for methanesulfonic acid (MSA)."

Page 2 - line 29: "Up to 42% of global natural sulfur emissions can be traced back to DMS". This is a low estimate, and other studies have reported that DMS may comprise more than 50% of the global natural sulfur emission. Therefore, I would not use the phrasing, 'up tp 42%'.

The authors rephrased L32-34 to "The global natural DMS emissions vary largely between the southern and the northern hemisphere. On a global average, around 42% of the natural sulfur emissions can be traced back to DMS (Simó, 2001), which is equal to at least 50% of the total amount from anthropogenic sources (Simó, 2001; Klimont et al., 2013)".

Figure 1: I find the schematic for SO₂ and SO₃ production a bit confusing. While SO₂ produces SO₃ which in turn produces SA, SO₃ is also formed directly from CH₃SO₃ (which is the dominant pathway leading to SO₃ and thus SA production from DMS). Consider making an arrow that branches into both SO₂ and SO₃ production to indicate that they are produced from two separate pathways.

The authors modified Fig. 1 accordingly, see below. We also include methanesulfonate (CH₃SO₃⁻) in the schematic, as mentioned by the reviewer, and updated L51-56 to “Main products in the abstraction pathway are the inorganic compound sulfuric acid (SA, H₂SO₄) (via sulfur dioxide, SO₂ or methanesulfonate (CH₃SO₃⁻), and sulfur trioxide, SO₃), and the organic compound methanesulfonic acid (MSA, CH₃SO₃H). The first stable product in the addition pathway is dimethyl sulfoxide (DMSO, CH₃SOCH₃), followed by methanesulfinic acid (MSIA, CH₃S(O)OH) (Barnes et al., 2006). MSIA can either undergo reactive uptake to the particle phase or oxidize further via methanesulfonate to MSA and SA, although the abstraction pathway is normally considered more important for the production of these two species.”.

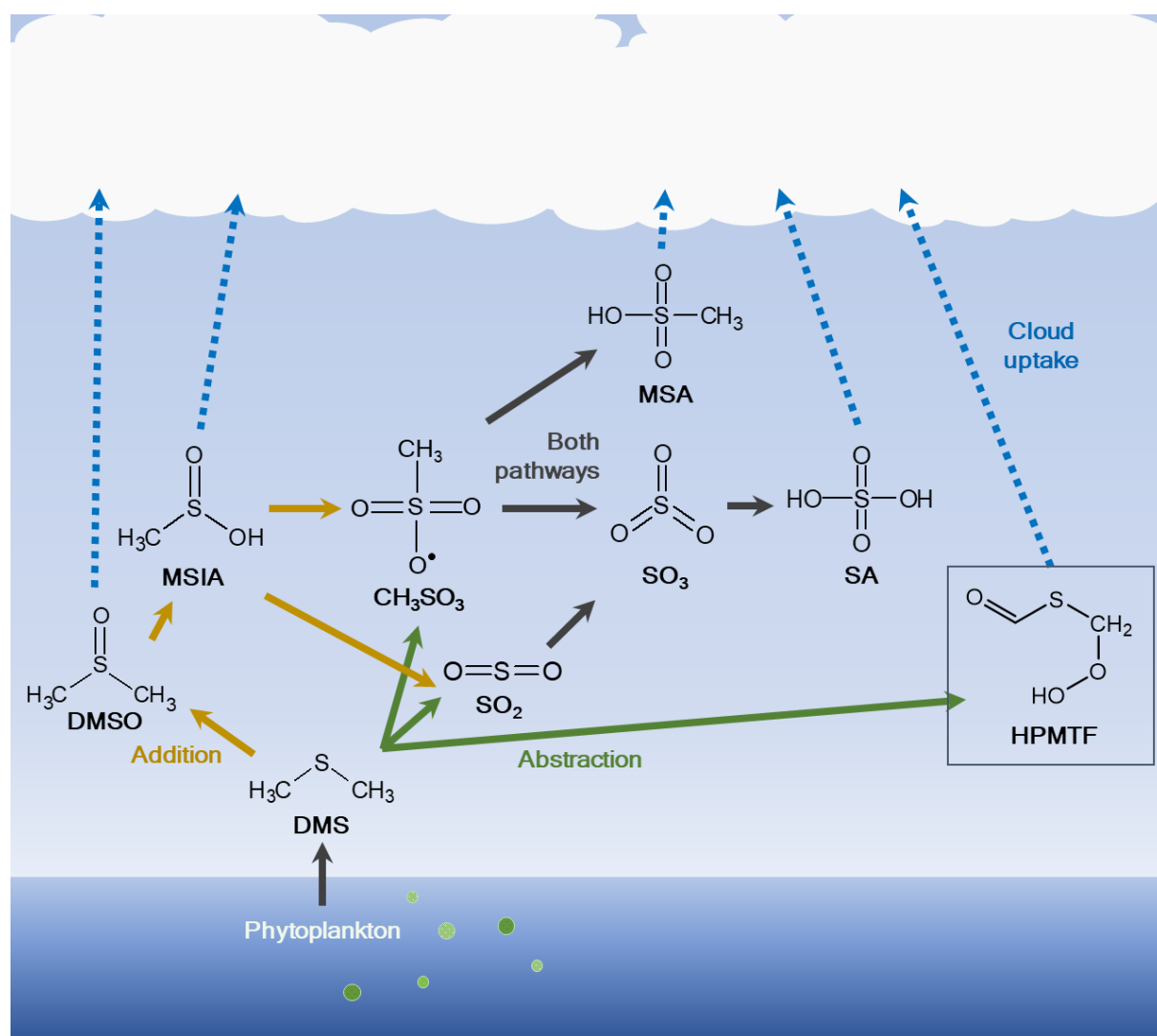


Figure 1. Simplified oxidation scheme of dimethyl sulfide (DMS) in the atmosphere. DMS is produced by microbiological activity in the ocean and emitted to the atmosphere, where it is oxidized through two main routes: 1) *addition* of a radical to produce dimethyl sulfoxide (DMSO) and methanesulfinic acid

(MSIA), and further via methanesulfonate (CH_3SO_3) to methanesulfonic acid (MSA) and/or sulfuric acid (SA) either via sulfur dioxide (SO_2) and sulfur trioxide (SO_3) or via methanesulfonate and SO_3 ; 2) *abstraction* of a hydrogen (H) atom to produce MSA, hydroperoxymethyl thioformate (HPMTF; marked with a box) and/or SA via SO_2 and SO_3 . The figure was created using information from (Barnes et al., 2006 and R. Wu et al., 2015). The addition pathway is shown in orange arrows, the abstraction pathway in green arrows, and DMS oxidation products that are part of both pathways are indicated with black arrows.

Page 15 - line 296: "the summer months are known for higher particle number concentrations due to new particle formation (Tunved et al., 2013), where condensation of SA from DMS oxidation and formation of MSA are the main drivers". Rephrase this statement. It is not the condensation of SA and MSA that drives the increase in PN. It is the new particle formation from SA (and maybe also MSA) that causes an increase in PN.

The authors thank the reviewer for indicating this and rephrased L311-313 accordingly: "However, the summer months are known for higher particle number concentrations due to new particle formation (Tunved et al., 2013), driven by SA (g) with subsequent growth by condensation of SA (g) and MSA (g) (Beck et al., 2021; Xavier et al., 2022)."

Figure 4: Why would you show a combined R2 value for SA and MSA, and not just report R2 for both species?

We show a combined R2 value for SA and MSA to visualize that they can have the same sources and are part of the same reaction processes in the summer months MJJ. Presenting separate R2 values for MSA and SA would only indicate the relation between the gas- and the particle phase for the two compounds individually, which is not what the authors intended to emphasize. This has been made clearer in the new version of the manuscript (L330-337). To better visualize the correlation of the combined MSA and SA data, the authors made the figure below, where no distinction is made between MSA and SA points. A linear relationship then appears more clearly. Please note that the figure below is for the reviewer's information only.

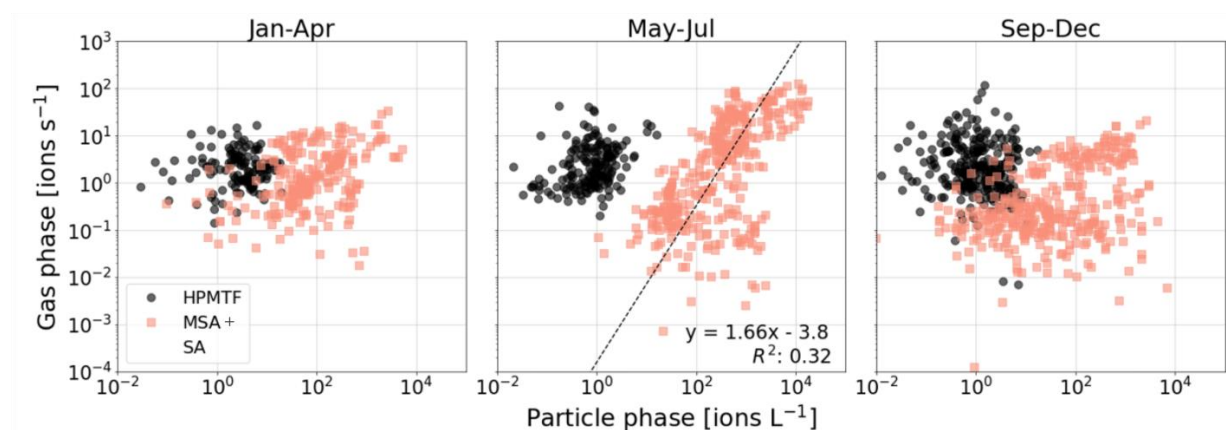


Figure a: Relationship between the gas- and particle phase of MSA, SA, HPMTF per season, where SA and MSA have the same color to show the connection between the combined MSA and SA correlation.

Technical comments:

Figure 2: Consider using (a), (b), (c), (d) instead of upper left, upper right, etc.

Changed as suggested, see updated Fig. 2 below.

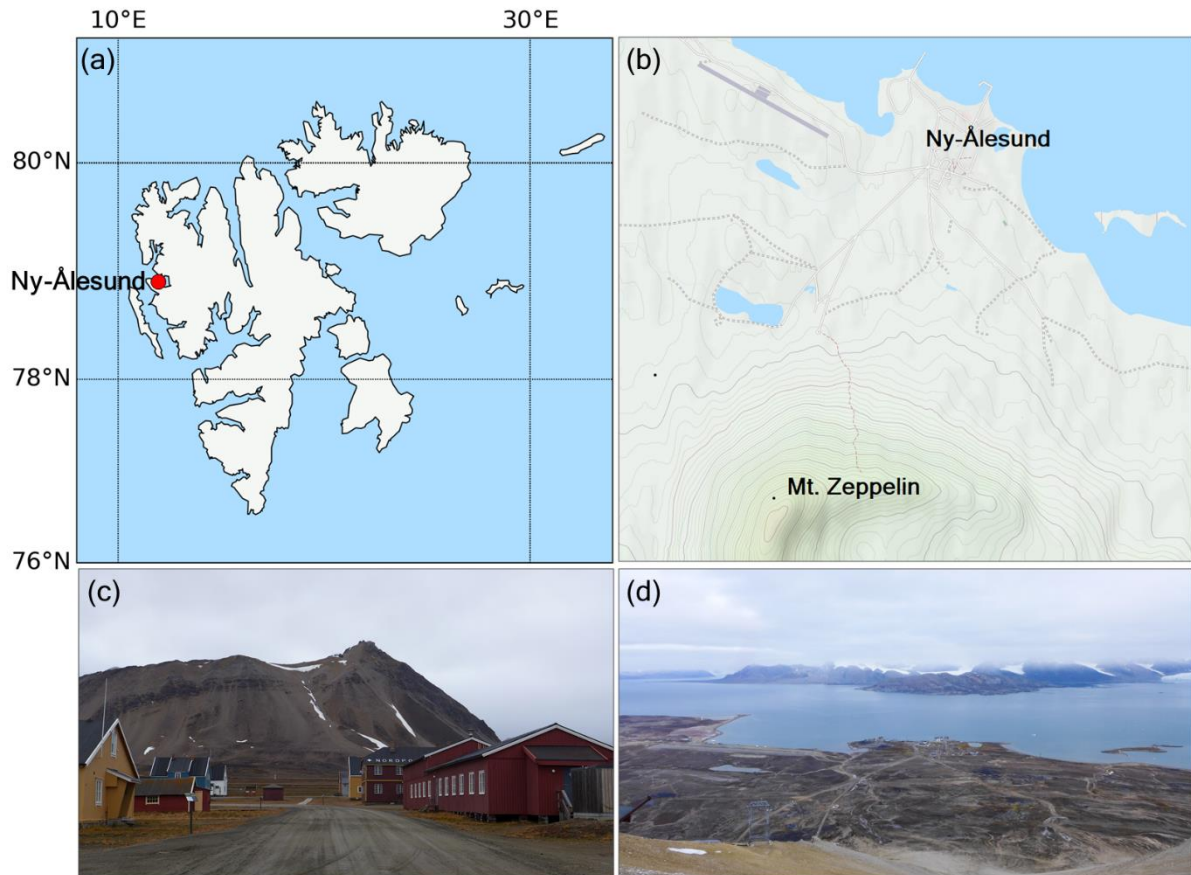


Figure 2. (a) Map of Svalbard, where Ny-Ålesund is marked with a red circle. (b) Mt. Zeppelin with the Zeppelin Observatory in relation to Ny-Ålesund (maps generated using Python's Matplotlib Basemap toolkit and ©OpenStreetMap contributors 2023, distributed under the Open Data Commons Open Database License (ODbL) v1.0). (c) View of Mt. Zeppelin and the observatory from Ny-Ålesund. (d) View of Ny-Ålesund and Kongsfjorden from the Zeppelin Observatory (photos taken in September 2021).

Page 10 - line 218: "to be able to produce DMS". Write, "in order to produce DMS".

Changed as suggested.

Figure 4: No need to have the same y-axis ticks all three plots. Just keep the ones on the left plot.

Changed as suggested, see below.

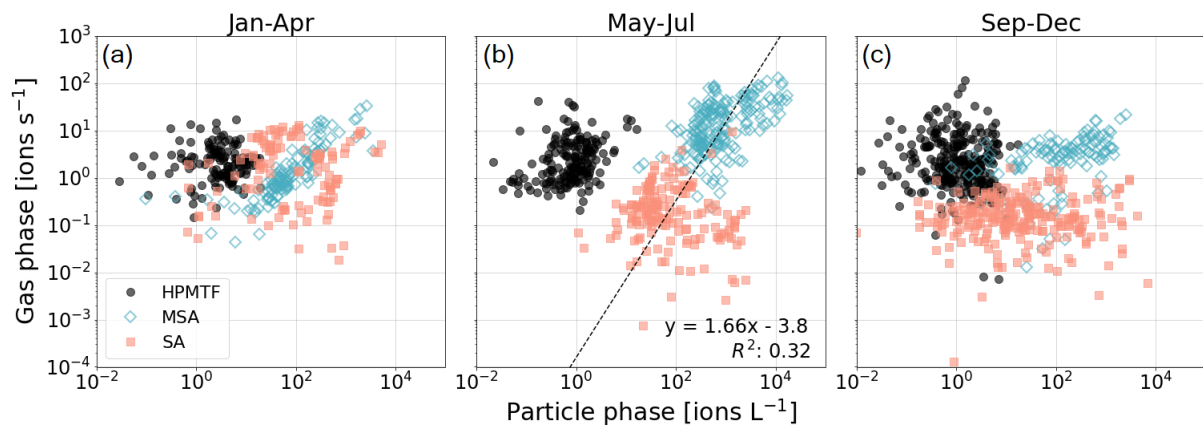


Figure 3. Relationship between gas- and particle-phase MSA, SA and HPMTF per season: (a) January–April (JFMA), (b) May–July (MJJ), (c) September–December (SOND). The black line in panel (b) represents the orthogonal linear regression between the combined logarithmized MSA and SA datasets. The linear equation and correlation coefficient R^2 are shown in the lower right corner.

Figure 4: What is the unit for the gas-phase and particle-phase measurements?

The authors thank the reviewer for indicating that the units are missing in Fig. 4. The unit of the gas phase is ions per second, and the unit of the particle phase is ions per liter. The units have been added to the x- and y-axis label.

Page 19 - line 381: "Although it seems not likely". Write, "Although it seems unlikely".

Changed as suggested.

Page 21 - Line 421: "and the almost unknown HPMTF one". Write, "and the almost unknown one of HPMTF".

Changed as suggested.

References

- Barnes, I., Hjorth, J., and Mihalopoulos, N.: Dimethyl Sulfide and Dimethyl Sulfoxide and Their Oxidation in the Atmosphere, *Chem. Rev.*, 106, 940–975, <https://doi.org/10.1021/cr020529+>, 2006.
- Beck, L. J., Sarnela, N., Junninen, H., Hoppe, C. J. M., Garmash, O., Bianchi, F., Riva, M., Rose, C., Peräkylä, O., Wimmer, D., Kausiala, O., Jokinen, T., Ahonen, L., Mikkilä, J., Hakala, J., He, X., Kontkanen, J., Wolf, K. K. E., Cappelletti, D., Mazzola, M., Traversi, R., Petroselli, C., Viola, A. P., Vitale, V., Lange, R., Massling, A., Nøjgaard, J. K., Krejci, R., Karlsson, L., Zieger, P., Jang, S., Lee, K., Vakkari, V., Lampilahti, J., Thakur, R. C., Leino, K., Kangasluoma, J., Duplissy, E., Siivola, E., Marbouti, M., Tham, Y. J., Saiz-Lopez, A., Petäjä, T., Ehn, M., Worsnop, D. R., Skov, H., Kulmala, M., Kerminen, V., and Sipilä, M.: Differing Mechanisms of New Particle Formation at Two Arctic Sites, *Geophys Res Lett*, 48, <https://doi.org/10.1029/2020GL091334>, 2021.
- Klimont, Z., Smith, S. J., and Cofala, J.: The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions, *Environ. Res. Lett.*, 8, 014003, <https://doi.org/10.1088/1748-9326/8/1/014003>, 2013.
- Simó, R.: Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links, *Trends in Ecology & Evolution*, 16, 287–294, [https://doi.org/10.1016/S0169-5347\(01\)02152-8](https://doi.org/10.1016/S0169-5347(01)02152-8), 2001.
- Tunved, P., Ström, J., and Krejci, R.: Arctic aerosol life cycle: linking aerosol size distributions observed between 2000 and 2010 with air mass transport and precipitation at Zeppelin station, Ny-Ålesund, Svalbard, *Atmos. Chem. Phys.*, 13, 3643–3660, <https://doi.org/10.5194/acp-13-3643-2013>, 2013.
- Wu, R., Wang, S., and Wang, L.: New Mechanism for the Atmospheric Oxidation of Dimethyl Sulfide. The Importance of Intramolecular Hydrogen Shift in a $\text{CH}_3\text{SCH}_2\text{OO}$ Radical, *J. Phys. Chem. A*, 119, 112–117, <https://doi.org/10.1021/jp511616j>, 2015.
- Xavier, C., Baykara, M., Wollesen de Jonge, R., Altstädter, B., Clusius, P., Vakkari, V., Thakur, R., Beck, L., Becagli, S., Severi, M., Traversi, R., Krejci, R., Tunved, P., Mazzola, M., Wehner, B., Sipilä, M., Kulmala, M., Boy, M., and Roldin, P.: Secondary aerosol formation in marine Arctic environments: a model measurement comparison at Ny-Ålesund, *Atmos. Chem. Phys.*, 22, 10023–10043, <https://doi.org/10.5194/acp-22-10023-2022>, 2022.