

Responses to the reviews of Hodshire et al.

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in **black text**. Our responses are in regular blue font. We have responded to all the referee comments, and we display our alterations to our paper and supporting information in **bold text**.

At the suggestion of reviewer 2, we have read through the text and have made minor grammatical corrections and minor corrections for clarity throughout the manuscript. These changes may be seen in the tracked-changes version of our submission.

Responses to reviewer 2: page 2

Responses to reviewer 3: page 7

Anonymous Referee #2

Interactive comment on “The potential role of methanesulfonic acid (MSA) in aerosol formation and growth and the associated radiative forcings” by Anna L. Hodshire et al.

The manuscript by Hodshire et al uses a global aerosol model to quantify the role of MSA in the aerosol-climate system. The role of MSA has not been quantified previously, with the majority of current aerosol and climate models making the simple assumption that MSA does not contribute to aerosol loading. The study presents model sensitivity simulations exploring a range of mechanisms that might allow MSA to contribute to aerosol. In doing so, the authors highlight the scarcity of actual observations and lab measurements of MSA, which could be used to constrain the model simulations. When allowing MSA to condense and nucleate in the model, only modest global radiative effects (up to -40 mWm^{-2}) are demonstrated. Regionally (e.g. in the Southern Ocean), larger differences in radiative effects are shown. The study is subject to large uncertainties arising from the lack of measurements, as well as caveats introduced by the modelling approach. These uncertainties notwithstanding, the manuscript is a valid contribution to the field and should lead to further insights about the role of MSA.

Major comments

Please explain the rationale supporting the use multiple anthropogenic NH_3 emissions inventories across different regions. It's not clear why this was done and what impact this may have on the NH_3 concentrations and subsequently the MSA sensitivity tests.

We realized that this section is misleading as it is currently written. We have updated the text regarding inventories in general (below). We use ammonia overwrites as we expect these national and/or regional inventories to be more accurate than the older GEIA inventory.

“Anthropogenic emissions except for ammonia, black carbon, and organic aerosol are from the Emissions Database for Global Atmospheric Research (EDGAR; Janssens-Maenhout et al., 2010). In Europe, Canada, the U.S., and Asia, anthropogenic emissions are overwritten by the European Monitoring and Evaluation Programme (Centre on Emissions Inventories and Projections, 2013), the Criteria Air Contaminant Inventory (<http://www.ec.gc.ca/air/default.asp?lang=En&n=7C43740B-1>), the National Emission Inventory from the U.S. EPA (<http://www.epa.gov/ttnchie1/net/2011inventory.html>), and the MIX (Li et al., 2017) inventories, respectively. Black and organic carbon emissions from fossil-fuel and biofuel combustion processes are from Bond et al. (2007). Grid-box gas-phase concentrations of NH_3 are used in determining the volatility regime of MSA in the MSA parameterization (Sect. 2.2): global anthropogenic, biofuel, and natural ammonia

sources are from the Global Emissions Initiative (GEIA) (Bouwman et al., 1997). Anthropogenic ammonia emissions are overwritten over Europe, Canada, the U.S., and Asia using the same regional inventories discussed above for these regions. Ammonia emission from biomass burning are from FINNv1 (above).”

The comparison method described in Section 2.5 assumes that the total sulphate will be additive between scenarios (i.e. subtracting DEFAULT_NoMSA from the sensitivity simulations leaves the MSA-related contribution). This is an imperfect approach as the additional mass from MSA will grow the aerosol size distribution, and therefore increase rates of dry deposition and nucleation scavenging. This limitation should be noted in the method description. I think the comparison remains useful, however.

We agree with the reviewer that this is an important caveat to point out and have added the following to sect 2.5:

“We compare our sensitivity simulations to the ATom data as follows: we subtract the DEFAULT_NoMSA sulfate mass (that accounts for sulfate and sulfuric acid from DMS/SO₂ oxidation but not MSA) for the months of August (ATom-1) and February (ATom-2) from the sulfate mass for the months of August and February for each sensitivity case that includes MSA for each grid box. The resultant differences in sulfate mass represents the model-predicted contributions of MSA to the total sulfur budget for each case. **This is an imperfect approach, as the additional aerosol mass from the contribution of MSA will change the size distribution, therefore changing rates of wet and dry deposition, and is a limitation of this study.**”

For consistency with the ATom measurements, was the model data used in the comparison also restricted to the sub-micron size range?

This is a reasonable point. We did not use the sub-micron range only; however, an off-line comparison shows that the percent difference between using the entire range (up to 10 μm) and the submicron range is well under 1%. We add the following to the text:

“We then compare the measured and predicted MSA mass by first averaging every ATom data point that falls within a given GC-TOMAS grid box. We then compare each averaged data point to that model grid box. The ATom data used in our analysis lies within 150-180° W (the Pacific ocean basin) and 10-40° W (the Atlantic ocean basin), and thus we use zonal averages of these longitude bands for both the ATom data and the GC-TOMAS output. We note that comparing monthly mean simulated values from 2014 to airborne measurements from a single point in time in 2016 and 2017 contributes to the apparent simulation errors. **We also note that we use the**

full size range (3 nm -10 µm) of sulfate from the model output whereas the ATom data is submicron. However, the model-predicted percent difference in MSA mass between the full range and the submicron mass is well under 1% (not shown).”

Page 11 line 18 refers to 'Table 4', which has not been provided. The data does appear in Figure 8.

Thank you for catching this--table 4 had been removed as it was redundant with the data in Figure 8. We have updated the text and made sure that no other references to Table 4 still exist.

Page 12 line 30 refers to Figure S7, but I think should refer to Figure S6. Please further check labelling of N10 / N80, and for left / right labelling in caption of Figure S6

Thank you for catching these errors, as well. The reference to Fig. S7 has been updated to Fig. S6. The label for Figure S6 has been updated to N80.

Minor comments

There are typographic errors through the manuscript that a thorough read-through should reveal, including some sentences that have redundant words, or fragments from C2 ACPD Interactive comment Printer-friendly version Discussion paper previous iterations. I haven't attempted to highlight them.

We have read throughout the text and corrected what typographical errors we have found.

Page 2 line 29: 'from marine particles' should be 'of marine particles'? Or 'from marine emissions'?

It should be 'of marine particles'--we have updated the text.

Page 3 line 1: VOCs – acronym not defined

Thank you--we have provided the full name along with the acronym.

Page 3 line 5/6: 'are an important source of marine emissions' should be 'are an important contributor to marine aerosol' (or something similar)? 'Aerosol' and 'particles' is being used in the same sense as 'emissions', which is incorrect.

We have updated the text:

“Sulfur-containing organic compounds in the form of dimethylsulfide (DMS; CH₃SCH₃) and organosulfates (Bates et al., 1992, Quinn et al., 2015) are important precursors and contributors to marine aerosol.”

Page 3 line 13: please state the relative yields of each product of DMS oxidation

The relative yields of each product from DMS oxidation are uncertain. We do state in the methods that for this study, we assume that we follow the findings of Chin et al. (1996) and use a branching ratio of 75:25 for SO₂:MSA. However, this is a source of uncertainty. For instance, Chang et al. (2011) states: “The sensitivity of model results to uncertainties in DMS chemistry was also untested. In the oxidation of DMS by OH addition, the branching ratio between SO₂ and methane sulfonic acid (MSA) is uncertain and, following Chin et al.[1996], we used a value of 75:25. Laboratory studies report percent yields of SO₂:MSA of 65:4 [Yin et al.,1990a], 27:6 [Sørensen et al., 1996] and 38:11 [Arsene et al.,2001], for example.”

We add the following to the introduction:

“The main products of DMS from oxidation by the hydroxyl radical are sulfur dioxide (SO₂) and methanesulfonic acid (CH₃S(O)₂OH, MSA) (Andreae et al., 1985). SO₂ can further oxidize to create sulfuric acid (H₂SO₄). The relative yields of SO₂ and MSA from DMS oxidation are still uncertain, with reported branching ratios from oxidation of DMS by OH addition of SO₂:MSA varying across 75:25, 65:4, 27:6, and 38:11 (Yin et al., 1990; Chin et al., 1996; Sørensen et al., 1996; Arsene et al., 2001).”

We also add text in the methods:

“In the standard GEOS-Chem DMS mechanism, DMS reacts with OH through the OH addition pathway to form molar yields of 0.75 SO₂ and 0.25 MSA (Chatfield and Crutzen, 1990; Chin et al., 1996). As discussed in the introduction, laboratory studies have reported variable yields of SO₂ and MSA from DMS oxidation by OH addition. We do not test the sensitivity of our simulations to other pathways, and this is a source of uncertainty.”

Arsene, C., Barnes, I., Becker, K. H. and Mocanu, R.: FT-IR product study on the photo-oxidation of dimethyl sulphide in the presence of NO_x—Temperature dependence, Atmos. Environ., 35(22), 3769–3780, doi:10.1016/S1352-2310(01)00168-6, 2001.

Chang, R. Y.-W., Sjostedt, S. J., Pierce, J. R., Papakyriakou, T. N., Scarratt, M. G., Michaud, S., Lévassieur, M., Leaitch, W. R., and Abbatt, J. P. D.: Relating atmospheric and oceanic DMS levels to particle nucleation events in the Canadian Arctic, J. Geophys. Res., 116, D00S03, doi:10.1029/2011JD015926, 2011.

Chin, M., Jacob, D. J., Gardner, G. M., Foreman-fowler, M. S., Spiro, P. A. and Savoie, D. L.: A global three-dimensional model of tropospheric sulfate acid, , 101, doi:10.1029/ 96JD01221, 1996.

Sørensen, S., Falbe-Hansen, H., Mangoni, M., Hjorth, J., and. Jensen, N. R: Observation of DMSO and CH₃S(O)OH from the gas phase reaction between DMS and OH, J. Atmos. Chem., 24(3), 299–315, doi:10.1007/BF00210288, 1996.

Yin, F., D. Grosjean, R. C. Flagan, and J. H. Seinfeld: Photooxidation of dimethyl sulfide and dimethyl disulfide. II: Mechanism evaluation, J. Atmos. Chem., 11(4), 365–399, doi:10.1007/BF00053781, 1990.

Page 5 line 24: not clear what 'Regional EDGAR overwrites' are

We have updated this section in response to an early comment and refer the reviewer to that response.

Page 6 line 25: for completeness, please clarify whether MSA is assumed to be involved in the binary nucleation process

Thank you, we have added this clarification.

When MSA is assumed to participate in nucleation, it is treated as an extra source of sulfuric acid for the ternary and binary nucleation schemes within the model.

Anonymous referee #3

This manuscript presents a sensitivity study estimating the potential influence of MSA, produced from oceanic DMS emission, on the submicron aerosol population and further on aerosol radiative effects in the global atmosphere. The paper relies on a set of global model simulations that cover the plausible range of parameters anticipated to affect how MSA contributes to the investigated issues. The used model has been evaluated previously in many other applications, so it can be considered appropriate for the purposes of this study. The paper is well organized, and the authors adequately discuss associated uncertainties. The conducted study itself is original and important to the scientific community.

I have a few, rather minor, issues to be considered before accepting this paper for publication.

The last sentence of page 2 (lines 28-31) is strange. Please modify.

We agree and have rewritten this statement as follows:

To improve model estimates of the DRE and AIE, models must account for nucleation and condensational growth of marine particles.

Strictly speaking, primary biological or organic particles should not be called "organic compounds".

We have updated the text:

Biologically productive oceans emit volatile organic compounds (VOCs), primary biological particles, primary organic particles, and halocarbons (Quinn et al., 2015).

Are the latest estimates on the contribution of DMS to biogenic sulfur budget and sulfur precursor emission really as far back in time as from years 1990 and 2006. I also wonder the relative accuracy of the given numbers, i.e. 50% versus 21% (page 3).

We appreciate the reviewer pointing out the outdatedness of these statistics. We have found more appropriate figures and have updated the text and references as follows:

DMS accounts for approximately one-fifth of the global sulfur budget (Fiddes et al., 2017), with DMS flux estimates range from 9 to 35 Tg yr⁻¹ of sulfur (Belviso et al., 2004; Elliott, 2009; Woodhouse et al., 2010; Tesdal et al., 2016), although global DMS fluxes remain uncertain (Tesdal et al., 2016; Royer et al., 2015).

Belviso, S., Bopp, L., Moulin, C., Orr, J. C., Anderson, T. R., Aumont, O., Chu, S., Elliott, S., Maltrud, M. E., and Simó, R.: Comparison of global climatological maps of sea surface dimethyl sulfide, *Global Biogeochem. Cy.*, 18, GB3013, <https://doi.org/10.1029/2003GB002193>, 2004.

Elliott, S.: Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type, *J. Geophys. Res.- Biogeo.*, 114, 1–18, <https://doi.org/10.1029/2008JG000710>, 2009.

Royer, S. J., Mahajan, A. S., Galí, M., Saltzman, E., and Simó, R.: Small-scale variability patterns of DMS and phytoplankton in surface waters of the tropical and subtropical Atlantic, Indian, and Pacific Oceans, *Geophys. Res. Lett.*, 42, 475–483, <https://doi.org/10.1002/2014GL062543>, 2015.

Sheng, J. X., Weisenstein, D. K., Luo, B. P., Rozanov, E., Stenke, A., Anet, J., Bingemer, H., and Peter, T.: Global atmospheric sulfur budget under volcanically quiescent conditions: Aerosol-chemistry-climate model predictions and validation, *J. Geophys. Res.-Atmos.*, 120, 256–276, <https://doi.org/10.1002/2014JD021985>, 2015.

Tesdal, J. E., Christian, J. R., Monahan, A. H., and Von Salzen, K.: Evaluation of diverse approaches for estimating sea-surface DMS concentration and air-sea exchange at global scale, *Environ. Chem.*, 13, 390–412, <https://doi.org/10.1071/EN14255>, 2016.

Woodhouse, M. T., Carslaw, K. S., Mann, G. W., Vallina, S. M., Vogt, M., Halloran, P. R., and Boucher, O.: Low sensitivity of cloud condensation nuclei to changes in the sea-air flux of dimethyl-sulphide, *Atmos. Chem. Phys.*, 10, 7545–7559, <https://doi.org/10.5194/acp-10-7545-2010>, 2010.

The authors use rather old binary and ternary nucleation schemes in their simulations, together with a fixed tuning factor that may or may not be valid in marine environments that are more interesting than continental regions in this study. The authors investigated the sensitivity of their results on different assumptions on whether MSA participates on nucleation or not, but do not discuss whether these results are sensitive to apparent uncertainties in the nucleation scheme itself. I would like the authors to address this point at least by discussing it shortly.

We have added the following discussion to Sect. 2.6 (Study Caveats):

We do not test the sensitivity of our simulations to the binary and ternary nucleation schemes used in this study, including potential sensitivity to the global tuning factor of 10^{-5} that was developed for continental regions (Jung et al., 2010; Westervelt et al., 2013). This source of uncertainty should be tested in future studies, as well.

The authors should discuss more explicitly what part of aerosol-cloud interactions they are attempting to capture in their simulations. Is it the first indirect effect only or something else as well?

We apologize for the lack of clarity here: the aerosol-cloud interactions should be the cloud-albedo AIE, not just the AIE. We have amended the text to read 'cloud-albedo AIE' throughout, and have informed the reader that figure labels of 'AIE' refer to the cloud-albedo AIE, as well.