1 **Observationally constrained analysis of sulfur cycle in the marine atmosphere with NASA**
2 **ATom measurements and AeroCom model simulations**

4 Huisheng Bian[1,2], Mian Chin[2], Peter R. Colarco[2], Eric C. Apel[3], Donald R. Blake[4], Karl Froyd[5], Rebecca S.
5 Hornbrook[3], Jose Jimenez[6,5], Pedro Campuzano Jost[6,5], Michael Lawler[5,7], Mingxu Liu[8], Marianne Tronstad Lund[9],
6 Hitoshi Matsui[8], Benjamin A. Nault[6,5,10,11], Joyce E. Penner[12], Andrew W. Rollins[5,13], Gregory Schill[7], Ragnhild B.
7 Skeie[9], Hailong Wang[14], Lu Xu[15,16], Kai Zhang[14], and Jialei Zhu[17]

9 [1]Goddard Earth Sciences Technology and Research (GESTAR) II, University of Maryland at Baltimore County,
10 Baltimore, MD, USA.
11 [2]NASA Goddard Space Flight Center, Greenbelt, MD, USA.
12 [3]Atmospheric Chemistry Observations & Modeling Laboratory, National Center for Atmospheric Research,
13 Boulder, CO, USA,
14 [4]Department of Chemistry, University of California Irvine, CA, USA.
15 [5]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA.
16 [6]Department of Chemistry, University of Colorado, Boulder, CO, USA.
17 [7]NOAA Chemical Sciences Laboratory, Boulder, CO, USA.
18 [8]Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan.
19 [9]CICERO Center for International Climate Research, Oslo, Norway.
20 [10]Now at: Department of Environmental Health and Engineering, Whiting School of Engineering, The Johns
21 Hopkins, Baltimore, MD, USA
22 [11]Now at: Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc., Billerica, MA, USA
23 [12]Dept. of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, Michigan, USA.
24 [13]NOAA Earth System Research Laboratory, Chemical Sciences Division, Boulder, CO, USA.
25 [14]Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, USA.
26 [15]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA.
27 [16]Now at Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis,
28 Missouri, USA.
29 [17]Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, China.

31 *Correspondence to*: Huisheng Bian (huisheng.bian@nasa.gov)

33 **Abstract**

34 The sulfur cycle plays a key role in atmospheric air quality, climate, and ecosystems. In this
35 study, we compare the spatial and temporal distribution of four sulfur-containing species,
36 dimethyl sulfide (DMS), sulfur dioxide (SO_2), particulate methanesulfonate (MSA), and
37 particulate sulfate (SO_4), that were measured during the airborne NASA Atmospheric
38 Tomography (ATom) mission and simulated by five AeroCom-III models to analyze the budget
39 of sulfur cycle from the models. This study focuses on remote regions over the Pacific, Atlantic,
40 and Southern Oceans from near the ocean surface to ~12-km altitude range, and covers all four
41 seasons. These regions provide us with highly heterogeneous natural and anthropogenic source
42 environments, which is not usually the case for traditional continental studies. We examine the
43 vertical and seasonal variations of these sulfur species over tropical, mid-, and high-latitude
44 regions in both hemispheres. We identify their origins from land versus ocean and from
45 anthropogenic versus natural sources with sensitivity studies by applying tagged tracers linking
46 to emission types and regions. In general, the differences among model results can be greater
47 than one-order of magnitude. Comparing with observations, simulated SO_2 is generally low
48 while SO_4 is high, and the model-observation agreement is much better in ATom-4 (April-May,
49 2018). There are much larger DMS concentrations simulated close to the sea surface than
50 observed, indicating that the DMS emissions may be too high from all models. Anthropogenic
51 emissions are the dominant source (40-60% of the total amount) for atmospheric sulfate

52   simulated at locations and times along the ATom flight tracks at almost every altitude, followed
53   by volcanic emissions (18-32%) and oceanic sources (16-32%). Similar source contributions can
54   also be derived at broad ocean basin and monthly scales, indicating that any reductions of
55   anthropogenic sulfur emissions would have global impacts in modern times.
56
57   **1. Introduction**
58   Atmospheric sulfur species have wide-ranging environmental and health impacts. About two-
59   third of sulfur emissions come from anthropogenic activities (Chin et al., 2000); therefore,
60   considerable efforts have been made to reduce these sulfur emissions. For example, acid rain
61   occurs when sulfur dioxide (SO_2) is oxidized to form sulfuric acid and particulate sulfate (SO_4),
62   which fall to the ground with the rain (Bian et al., 1993; Grennfelt et al., 2020) and can wreak
63   havoc on aquatic ecosystems (Josephson et al., 2014; McDonnell et al., 2021). Through the
64   competing neutralization reaction of SO_4 and nitrate with NH_3 and other alkaline species, SO_4
65   affects strongly both particulate nitrate formation (Bian et al., 2017) and aerosol pH (Huang et
66   al., 2020; Nault et al., 2021). Sulfate is a key component of particulate matter (PM), which
67   degrades air quality (Dong et al., 2018; Tan et al., 2018) and directly reflects the sun's rays
68   (Moch et al., 2022; Myhre et al., 2013). Due to its highly hygroscopic nature, sulfate aerosol
69   affects cloud physics (Boucher et al., 2013; Breen et al., 2021; Seinfeld et al., 2016) and thus
70   indirectly radiative forcing (Penner et al., 2016; Wang et al., 2021) through aerosol-cloud
71   interactions. The contribution of aerosols to atmospheric clouds and energy budget remains the
72   largest uncertainty in climate models (Gryspeerdt et al., 2023; Jia et al., 2021, 2022; Klein et al.,
73   2013; Malavelle et al., 2017).
74
75   Unlike other major atmospheric aerosols, a significant fraction (i.e., roughly a quarter) of sulfate
76   in the atmosphere comes from marine biological emissions (Chin et al., 1996). The impact of
77   oceanic sulfate is particularly pronounced on marine shallow clouds, which are characterized by
78   low droplet number concentrations and weak updraft velocities (Rissman et al., 2004). Sulfur
79   research has also focused on the tropical upper troposphere (TUT), where the growth of new
80   aerosol particles and homogeneous nucleation involving sulfuric acid is at a maximum
81   (Williamson et al., 2019), and where deep convective transport allows a small portion of the
82   sources to reach the lower stratosphere. The resulting sulfate aerosols in the stratosphere can
83   persist for years (Holton et al., 1995). Unfortunately, the TUT and above are observation-sparse
84   regions. Acquiring atmospheric composition and its chemical/physical properties over remote
85   oceans is challenging, although satellites can often provide total column constraints of aerosol
86   optical depth.
87
88   The NASA Earth Venture Suborbital (EVS-2) Atmospheric Tomography (ATom) airborne
89   mission provided abundant measurements of gases and aerosols over the world's oceans (Hodzic
90   et al., 2020; Thompson et al., 2021). In particular, a suite of instruments integrated on the NASA
91   DC-8 aircraft made measurements of many important sulfur species including dimethyl sulfide
92   (DMS), SO_2, particulate methanesulfonate (MSA) and SO_4 over the Pacific and Atlantic Oceans
93   in both hemispheres and the Southern Ocean in all four seasons. This comprehensive sulfur
94   dataset provides us with unprecedented opportunities to assess sulfur source, transport,
95   chemistry, deposition, and particle activation and growth represented in the global aerosol
96   models, and to estimate the extent of anthropogenic influence on remote oceanic atmospheric
97   composition and cloud properties.

98
99   This study has two specific scientific goals. First, we explore the vertical and seasonal variation
100 of sulfur species (i.e., DMS, SO_2, MSA, and SO_4) using ATom measurements and simulations
101 from five global models that participated in the AeroCom-ATom model experiments. AeroCom
102 is an international initiative of scientists aiming at the advancement of the understanding of the
103 global aerosol and its impact on climate (https://aerocom.met.no/). Here we focus on remote
104 regions over the Pacific, Atlantic, and Southern Oceans, from near the surface to an altitude of
105 about 12 kilometers, covering all four seasons. Second, we determine whether the produced SO_4
106 originated from land or ocean sources and from anthropogenic or natural sources by using tagged
107 tracers associated with emission types and regions.
108
109 The structure of this paper is as follows. Section 2 describes the ATom measurements and the
110 AeroCom models used in this study. Section 3 presents the ATom-AeroCom sulfur comparison
111 from different perspectives, namely the overall comparison in Sect. 3.1, the vertical profiles in
112 Sect. 3.2, and the regional and seasonal analysis in Sect. 3.3. The sulfur budget analysis is given
113 in Sect. 4. We further present investigations of source origins for aerosol SO_4 along flight tracks
114 and over oceans in Sect. 5. Finally, we summarize our findings in Sect. 6.
115
116 **2. Data**
117 **2.1 ATom measurements**
118 ATom was a NASA-funded Earth Venture Suborbital project designed to study the effects of air
119 pollution on chemically reactive gases, aerosols, and greenhouse gases in the remote atmosphere.
120 ATom deployed a large suite of gas and aerosol measurement instruments on the NASA DC-8
121 aircraft for systematic sampling, covering an extended region of the globe from 85°N to 85°S
122 over the Pacific and Atlantic Oceans, with vertical profiles from near-surface to near-tropopause
123 (i.e., ~0.2-12 km) (Thompson et al., 2021). Four ATom deployments (ATom-1 to -4) were
124 executed over each of the four seasons from 2016 to 2018, and their flight paths are shown in
125 Fig. 1. The extensive aerosol and gas measurements made during ATom include inorganic and
126 organic aerosols, precursor gases, particle size distributions and particle composition. Table 1
127 lists the instruments for ATom sulfur species observations used in this study including the
128 relevant sampling details needed for the model comparison.
129
130 We use SO_4 and MSA that had been measured by two instruments, the University of Colorado
131 Aerodyne high-resolution time-of-flight aerosol mass spectrometer (AMS, Canagaratna et al.,
132 2007; Guo et al., 2021), and the NOAA Particle Analysis by Laser Mass Spectrometry (PALMS,
133 Froyd et al., 2019). The latter one makes in situ measurements of the chemical composition of
134 individual aerosol particles. Furthermore, AMS measured submicron aerosols while PALMS
135 provided mass mixing ratio and size distribution up to 3 μm in dry diameter (Brock et al., 2019).
136 It is worth noting that AMS data were independently processed and reported at both 1-s and 60-s
137 time resolutions by instrument PI (Jimenez et al., 2019). The detection limit varied with different
138 averaging time resolutions, and they were provided directly for each sampling point in AMS
139 datasets. Some negative measurements were also presented in AMS datasets, and this is normal
140 for measurements of very low concentrations in the presence of instrumental noise. The AMS
141 data at 60-s resolution is recommended owing to more robust peak fitting at low concentrations
142 (Hodzic et al., 2020). Given the complex data overlays (i.e., starting, ending, and frequency)
143 reported from multiple instruments, the ATom team also provide a 10-s merged dataset to

144   facilitate users' applications. In this study, we evaluate data reported in different time
145   resolutions, using AMS as an example, to ensure the quality of merged data that are exclusively
146   used as the primary dataset in this work.
147
148   Two instruments, the California Institute of Technology Chemical Ionization Mass Spectrometer
149   (CIMS) and the NOAA Laser Induced Fluorescence (LIF), were used for SO_2 measurements
150   (Table 1). The CIMS uses CF_3O^- as a reagent ion which reacts with SO_2 via fluoride ion transfer
151   chemistry. The product ion is detected by a compact time-of-flight mass spectrometer (CToF).
152   The precision of the CIMS SO_2 measurement decreases with increasing water vapor
153   concentration (Eger et al., 2019; Huey et al., 2004; Jurkat et al., 2016; Rickly et al., 2021),
154   making it challenging to measure SO_2 in remote ocean regions. In these regions, the ambient
155   water vapor may be sufficiently high that the CIMS SO_2 precision at 1-s resolution (~130 parts
156   per trillion by volume, pptv) is insufficient for measuring ambient SO_2 value there (<100 pptv).
157   To address this shortcoming, the ATom science team added a new instrument, the NOAA LIF, to
158   the ATom-4 payload. The NOAA LIF instrument uses red-shifted laser-induced fluorescence to
159   detect SO_2 at very low ppt levels (Rickly et al., 2021; Rollins et al., 2016). Both instruments
160   report negative values and the detection limit of the LIF instrument is about 2 pptv.
161
162   DMS was measured during ATom by two instruments, the University of California, Irvine
163   Whole Air Sampler (WAS), and the NCAR Trace Organic Gas Analyzer (TOGA). The WAS
164   reported DMS for all four ATom deployments, while the TOGA reported data for ATom-2 to -4
165   and not for ATom-1 due to possible issues associated with the TOGA inlet (the inlet was
166   changed for ATom-2 to -4). Both instruments have comparable detection limit (1 pptv) and
167   accuracy (~15%). However, the sampling time interval of WAS (variable but ~180s) was longer
168   than TOGA (~120s).
169
170   **2.2 AeroCom models**
171   Five global aerosol models participated in an AeroCom-ATom model experiment
172   (https://wiki.met.no/aerocom/phase3-experiments): CAM-ATRAS, E3SM, GEOS, IMPACT,
173   and OsloCTM3. The experiment required all participating models to (1) conduct three-year-
174   simulations of 2016-2018 (i.e., covering the whole ATom observation period); (2) use or nudge
175   meteorological data for the simulation period; and (3) use the same pre-defined emission fields
176   for precursor gases and aerosol tracers. The suggested emissions are the Coupled Model
177   Intercomparison Project Phase 6 (CMIP6) (Feng et al., 2020) for anthropogenic source, daily
178   biomass burning emission (such as The Global Fire Assimilation System (GFAS)), a dataset
179   based on satellite volcanic SO_2 observations from the OMI instrument on the Aura satellite (Carn
180   et al., 2016, 2017) for outgassing and eruptive volcanic emission, and DMS concentration in sea
181   surface from Lana et al. (2011). Wind-driven emissions, such as dust and sea salt, are calculated
182   online by each model. Following the experimental protocol, all models provided results for all
183   AToms except for OsloCTM3 that omitted data in ATom-4. Unlike traditional AeroCom
184   experiments that used gridded daily/monthly averaged data, modelers are required to interpolate
185   model results along flight track every 10-s (see more discussion in Sect. 3.1) using three-
186   dimensional high frequency (e.g., hourly or even less depending on the models' time step) data
187   to facilitate the comparison. It is worth noting that the models do not have any actual information
188   at 10-s time resolution, given their time steps are at least 10× greater and their spatial resolutions
189   are coarse. However, the interpolation methodology suggested here provides the best model

190 information at their current configuration to compare with aircraft measurements. Table 2
191 summarizes the detailed model characteristics and input datasets relevant to this study.
192
193 The AeroCom-ATom experiment also designed three sensitivity simulations by tracking gas and
194 aerosol emissions to anthropogenic, biomass burning, and volcanic sources to attribute the origin
195 of sulfur sources on sulfur simulations over remote oceans. These experiments were conducted
196 with the Goddard Earth Observing System (GEOS) model. The setup of the GEOS model
197 followed the experiment protocol generally, but GEOS used its own daily biomass burning
198 emissions that were derived from the Quick Fire Emissions Dataset (QFED) developed based on
199 MODIS fire radiative power and calculated in near real-time at 0.1° resolution (Darmenov and
200 da Silva, 2015; Pan et al., 2020). Emissions from biogenic sources were calculated using the
201 Model for Emissions of Gases and Aerosols from Nature (MEGAN) embedded in the GEOS
202 model.
203

3. ATom-AeroCom comparisons of sulfur species
205 This section presents a comparison of sulfur species between ATom measurements and
206 AeroCom model simulations. The consistency and diversity of data across remote regimes, both
207 horizontally and vertically, help us understand the effects of emissions, transport, and chemical
208 transformations, and shed light on improving the processes in models to best represent the ATom
209 observations.
210

3.1 Overall comparison
212 The overall performance of SO_4 PDF distribution observed from the AMS and PALMS
213 instruments and simulated by five AeroCom models for four ATom deployments is presented in
214 Fig. 2. Also shown in Fig. 2 are the corresponding various percentiles, namely, 0th (minimum),
215 25th, 50th (median), 75th, and 100th (maximum), and the mean for statistical analyses. As
216 mentioned in Sect. 2.1, we have AMS data at three sampling intervals (i.e., 1-s, 60-s, and 10-s).
217 The 10-s merged dataset were deliberately provided by the ATom observation team for
218 integrating data from various instruments to a unified temporal resolution. We intend to use this
219 dataset for investigation on regional and seasonal bases. Before applying it, however, we first
220 evaluate the quality of the 10-s data. Previous studies (Hodzic et al., 2020) indicated
221 measurement precision improved with the square root of the number of sampling points. In other
222 words, averaging data over a 60-s interval is better than averaging over 1-s or 10-s intervals
223 because there are more sample points in a 60-s interval. This also applies to the detection limit
224 (DL) as it is just 3 times the precision. DL flags are assigned to convey semi-quantitative
225 information when sampling conditions are beyond the instrument detection range and the
226 measurements are not quantifiable. Despite the differences, the three PDFs of AMS SO_4 (red,
227 using all relevant data including negatives) are nearly identical. Statistical analyses were further
228 performed on the AMS 60-s, 10-s, and 1-s data sets by (1) all sampling points, even negative
229 values, as indicated by the dot-dash box-and-whisker (approach 1), and (2) sampling points when
230 their values exceeded DL as shown by solid box-and-whisker (approach 2). The SO_4 median
231 (and mean) values of 60-s are closer to 10-s' but lesser than 1-s' by 0-10% in approach 1. There
232 is slightly greater diversity (~30%, solid box-and whisker) between these statistical values in
233 approach 2, and the data in 60-s and 10-s are also relatively close, with a difference less than
234 ~20%. These comparisons of the PDFs with noise and signal tell us that, on average, SO_4 is high
235 enough in the ATom background to be unaffected by noise at any resolution. A similar analysis

236   (not shown here) of SO_2 and DMS measurements also showed agreement between the 10-s
237   interval dataset and the original dataset. Thus, the use of the 10-s data is acceptable in our study,
238   given the significant differences in tracer statistics between model simulations and between
239   model and observation.

241   We use 10-s merged data where observations above DL throughout the main text unless
242   otherwise stated. When multiple instruments measured the target field, only points where all
243   instrument measured above DL values were included in analysis, as AMS 10-s in orange and
244   PALMS 10-s in grey in Fig. 2. All model results were sampled mimicking flight observations
245   (see Sect. 2.2), and only data with measurements available were used in comparison. This
246   approach ensures that model evaluation is based on high-quality measurements. It is worth
247   noting that the given statistical values in this method represent more regions having high tracer
248   concentration or mixing ratio. In the supplementary material, we further give a model-
249   observation comparison for all available measurement data including negatives. The observed
250   and simulated PDF distributions are presented separately in Fig. 2.

252   Most observed and simulated SO_4 exhibit highest probability density around SO_4 values of 10-
253   100 ng sm^{-3}. With the exception of GEOS and CAM-ATRAS, the model SO_4 PDFs show higher
254   tails beyond 100 ng sm^{-3}, which explain the higher median and mean SO_4 simulated by the
255   models. Clearly, the diversity among model simulated SO_4 is high. Although the mean of
256   PALMS SO_4 is generally about 10-50% higher than AMS SO_4, this difference is much smaller
257   than the difference between models that can easily exceed several orders of magnitude. The
258   lower SO_4 of AMS than PALMS may be due at least in part to the fact that the sample size range
259   of AMS (~0.75 µm) is smaller than that of PALMS (~3 µm), as mentioned in Sect. 2.1. In
260   general, nearly all measurements and models indicate that SO_4 concentrations on a global ocean
261   basis are lowest (or highest) during the Northern Hemisphere (NH) summer (or spring) season.
262   Similar analysis was also performed on all (e.g., both positive and negative) measurement data
263   (Fig. S1), the median/mean values of observations are naturally smaller than those in Fig. 2 by 8-
264   20%, but the PDF distributions are almost identical between the two treatments.

266   Figure 3 shows the PDF distribution and statistics for SO_2. All observed and simulated data were
267   reprocessed by including points above the detection limit (2 pptv) only. Both instruments (CIMS
268   and LIF) were deployed during ATom-4. Despite CIMS being less precise than LIF (Rollins et
269   al., 2016), both instruments agreed within 95% and CIMS measured SO_2 concentrations were
270   consistently 3-7% lower than LIF measurements. This difference is within the combined
271   uncertainties of the two measurements, but it suggests a systematic calibration error in one or
272   both instruments that is currently unresolved (Rickly et al., 2021). Meanwhile, the width of
273   CIMS SO_2 PDF (measured at half-height) is narrower in ATom-4, with peak heights around 10
274   pptv and is more consistent with LIF measurements and model simulations. In contrast, the
275   distribution of SO_2 measured by CIMS during ATom-1 to -3 is spread much wider than the
276   models. This wider distribution needs to be examined given the degree of seasonal variation in
277   the SO_2 PDF. CIMS adjusted its CToF between ATom-3 and -4 to improve resolution, and
278   thereafter managed to fit SO_2 and formate-H_2O independently, which was practically impossible
279   for ATom-1 to -3. Throughout ATom periods, models, especially E3SM, GEOS, and
280   OsloCTM3, show higher peak heights and narrower peak widths. Statistics indicate lower model
281   SO_2 medians and higher simulated mean/median ratios than those of observations (see

282   corresponding values given in the figure). The model-observation agreement is much better in
283   ATom-4 among the four ATom deployments. Figure S2 presents the corresponding analysis,
284   including the measured negative values. Compared to Fig. 3, the observed median and mean
285   values drop substantially (up to 50%), but the model statistics change relatively small.
286
287   Atmospheric DMS observations are scarce, especially on a global scale. Thus, DMS
288   measurements by the two instruments (WAS and TOGA) during the four ATom deployments
289   provide an unprecedented opportunity to investigate biological DMS over global remote oceans
290   and evaluate model DMS simulations on spatial and temporal distributions. By excluding points
291   with measured values below detection limit (i.e., 1 pptv), the overall DMS comparison in Fig. 4
292   indicates TOGA has higher data peaks and probability densities when DMS ranges from 3-10
293   pptv. However, this does not appear to be consistent with the lower median and mean values of
294   TOGA, indicating a higher tail in the WAS DMS PDF. Likewise, although the peak of WAS
295   DMS PDF is significantly higher than all models from 3-10 pptv (~5-20 pptv for ATom-3), the
296   median and mean of the WAS DMS are lower, suggesting an even higher tail in model DMS
297   PDF. Overall, there is a big gap between the WAS and TOGA DMS measurements, and both are
298   surprisingly low compared to the models. Statistical analysis performed on selected percentiles
299   indicates that multi-model DMS medians are about 4.9 (ATom-1), 8.6 (ATom-2), 6.6 (ATom-3),
300   and 7.7 (ATom-4) times higher than observed, while model GEOS has a better performance (i.e.,
301   1.2, 2.7, 2.3, and 2.8 correspondingly). Even though the model DMS median is mostly higher
302   than the observed value, the degree of overestimation is not as serious as the mean value that can
303   be more than tenfold, indicating a few points are simulated with extraordinarily high DMS
304   values. Based on what we know about DMS sources and sinks, these very large simulated DMS
305   appear most commonly in the boundary layer (BL). Indeed it is confirmed in Fig 4c,f,i,l by
306   looking at the ratios of DMS median values between model simulations and observations. The
307   analyses are performed on four vertical ranges (e.g., the entire vertical column, the BL 0-1.5 km,
308   the low-middle free troposphere 1.5-6 km, and the upper troposphere 6-12 km). The last column
309   "MMM/MOM" refers to multi-model median to multi-observation median. Apparently, the high
310   ratio stems mostly from the BL, above which the consistency is much better. Meanwhile, the
311   PDF distribution and statistics of the models agree better with the WAS measurement than with
312   the TOGA measurement. We should also acknowledge that this is a very limited set of
313   observations we used here, and that there are some longer-term DMS observations near the
314   surface that were used as input for the parameterization of DMS emissions. More DMS
315   observations near the ocean surface are needed to make a confident comparison.
316
317   DMS measurement is uniquely having a fraction of measured values in "-888". An instrument
318   typically has an operational detection range, which is defined by the lower limit of detection
319   (LDL) and upper limit of detection (UDL). The flag for measured value less than the LDL is "-
320   888" for TOGA and WAS data used in this study. The number of "-888" is not meaningless. It
321   means that we know the value of a given measurement is below a known quantity, but we are not
322   able to quantify that value precisely. Fig. S3 shows a similar DMS PDF analysis as Fig. 4, but
323   instead of excluding the "-888" measurements, these are replaced with "0" as suggested by the
324   instrument PIs. The percentage (P) of the measured "-888" is given for TOGA and WAS
325   measurement data in the figure. These Ps for all AToms range 65% - 91%, which means majority
326   of measured values are below LDL and the medians of both TOGA and WAS data are zero.
327   Correspondingly, the multi-model average median (0.22, 1.13, 1.10, and 1.34 pptv for ATom-1

328   to -4 respectively) are much lower than those in Fig. 4. The ratio of means between model and
329   observation for all AToms is 9.1 in Fig. S3, which is ~44% higher than 6.3 in Fig. 4.
330
331   **3.2 Vertical profiles**
332   Vertical profiles of ATom-1 to -4 for observed and modeled SO_4, SO_2, DMS, and MSA are
333   shown in Figs. 5-8, respectively, for five latitude bands (from the north to the south) and for both
334   the Pacific and Atlantic Ocean basins. Again, the profiles include equal amounts of data for each
335   measurement and model result. In other words, all comparisons show only available points
336   where the two observed values (i.e., AMS vs. PALMS for SO4 and MSA, CIMS vs. LIF for
337   SO2, and TOGA vs. WAS for DMS) are greater than their detection limits, and where the model
338   values are extracted.
339
340   The average and range of sulfur tracers for ATom-1 to -4 are shown in Figs. 5-8 and their
341   corresponding details in each ATom are further given in Figs. S4-7. As shown in Fig. 5, the SO_4
342   measured by the two instruments are close to each other and lie generally within the span of
343   modelled SO_4 throughout the ATom periods. The spread of modeled SO_4 concentrations is large,
344   easily exceeding an order of magnitude, especially in the upper troposphere. Despite that
345   improvements are needed, the models are able to capture the shape of the SO_4 profile generally.
346   These five models can generally be divided into three groups according to their SO_4 vertical
347   profiles: 1. CAM-ATRAS and GEOS, 2. E3SM, and 3. IMPACT and OsloCTM. Over tropical
348   and northern hemisphere oceans, Group 1 captures the SO_4 vertical profile well, while Group 3's
349   vertical profile does not decrease enough at higher altitudes. The CAM-ATRAS model recently
350   reported an improvement of aerosol wet scavenging processes, which allow efficient removal of
351   aerosols by convective clouds and precipitation in the tropical and mid-latitude troposphere,
352   while trace gases such as SO_2 to reach the upper troposphere (Liu and Matsui's 2021). In the free
353   troposphere at high southern latitudes, SO_4 is too low for Group 1 and too high for Group 3.
354   Group 2 (i.e., E3SM) has SO_4 simulations between the other two groups.
355
356   Figure 6 shows generally lower modeled SO_2 volume mixing ratios compared to the CIMS
357   observations for most altitudes and latitude bins. The spread among modeled SO_2 values exceeds
358   an order of magnitude, but around the measured SO_2. SO_2 is better simulated by model IMPACT
359   in the NH and by models CAM-ATRAS and OsloCTM3 in the Southern Hemisphere (SH). The
360   tropical Pacific appears to be an interesting region where all models need to improve SO_2
361   simulations from the surface to 400mb. Basically, the observed SO_2 is high at the surface, falls
362   rapidly in the BL, and then gradually decreases above the BL, except for ATom-1, during which
363   a second peak appears just above the BL (see Fig. S5 for the details of ATom-1 to -4 separately).
364   These observations indicate a strong local source for SO_2 in all seasons and a transport source in
365   the low free-troposphere NH summer (ATom-1). Like observations, the model GEOS provides a
366   local source for SO_2 at the surface, but it misses the plume above the BL in ATom-1, and its
367   vertical SO_2 convection is consistently too weak. Since only one flight was in ATom-1, more
368   observations are needed to confirm whether GEOS has been failing to catch the plume there
369   during the NH summer. All other models miss the strong local source and simulate SO_2 transport
370   in the low free-troposphere, which is only shown to a lesser extent in ATom-1 observation.
371   Figure S5 also shows an excellent agreement of SO_2 profiles measured by the CIMS and LIF
372   during ATom-4 and models agree with measurements better in ATom-4 as well. Modeled SO_2
373   volume mixing ratios are generally lower compared to the CIMS observations for most altitudes

374   and latitude bins in ATom-1 to -3, which may be partially owing to the CIMS measurement issue
375   discussed in Sect. 3.1.
376
377   DMS measurements fill in another piece of the puzzle for the atmospheric sulfur budget. As
378   shown in Fig. 7, all five AeroCom models generally overestimate DMS in the BL, particularly
379   for models CAM-ATRAS and OsloCTM3. This large bias close to the surface requires us to
380   revisit the DMS emissions employed in our models. In these five models, DMS emissions from
381   CAM-ATRAS, E3SM, and IMPACT are directly derived from climate emissions inventories.
382   GEOS calculates DMS emissions based on monthly climatological DMS concentrations in ocean
383   water (Lana et al., 2011) and modeled sea surface wind and temperature. OsloCTM3 oceanic
384   DMS is parameterized as in Nightingale et al. (2000). The parameterization converts the monthly
385   DMS ocean concentration, which is taken from Kettle and Andreae (2000), a climatology based
386   on observations, to a flux based on wind speed from the meteorological data. It is worth to note
387   that even the latest climatological database by Lana et al., (2011) was constructed by compiling
388   measurements before 2000, so the potential long-term change of DMS emission caused by
389   environment change could be missed (Barford, 2013). Also, although the data used by Lana et al.
390   (2011) is large (i.e., ~47,000 seawater concentration measurements), interpolation and
391   extrapolation techniques were still necessary in creating a global monthly climatological DMS
392   emission. Gali et al. (2018) reported updated oceanic DMS levels on a global scale using remote
393   sensing satellite data. However, much effort is still needed to accurately establish global rates of
394   change in order to create global DMS emissions for climate modeling.
395
396   Meanwhile, the modeled DMS vertical gradient is generally steeper than the observed one,
397   implying slower vertical transport or faster chemical conversion of DMS to SO_2 in the model.
398   The data collected from the AeroCom models did not provide us with enough information to
399   tease out the determinants. Currently, GEOS and OsloCTM3 account for two products from the
400   oxidation of DMS (i.e., SO_2 and MSA) but only GEOS output MSA results. The other models
401   consider DMS oxidation products only as SO_2. These chemical processes in the model may also
402   need to be revisited. Previous studies proposed other chemical reactions for DMS loss in the
403   atmosphere. For example, halogen chemistry represented 71% of the DMS loss in the study of
404   Hoffmann et al., (2016). Veres et al. (2020) estimated that about 30% of DMS in the atmosphere
405   was oxidized to a sulfur compound, hydroperoxymethyl thioformate (HPMTF), reported only in
406   ATom-4. To this end, the HPMTF serves as a new reservoir of oceanic sulfur and its life cycle in
407   the atmosphere is unknown. The new finding indicates that important components of Earth's
408   sulfur cycle are not yet been fully understood and urges us to reassess this fundamental marine
409   chemical cycle. However, including these chemical DMS losses further reduces DMS above the
410   surface, making DMS in the models even lower at high altitudes.
411
412   Of the five models, only GEOS reports MSA (Fig. 8). The GEOS MSA matches observations in
413   the lower troposphere. In the upper troposphere (UT), the GEOS MSA tends to decrease slowly
414   or even increase with altitude. These behaviors are inconsistent with observations, and this
415   inconsistency can be explained at least partially by the MSA phase stages defined in the model
416   and observations. AMS and PALMS only measure the particle phase of MSA, but GEOS MSA
417   is the total MSA and is not accurately represented by observations, especially in UT. Yan et al.
418   (2019) reported that the ratio of MSA to SO_4 can be reduced by 30% when calculations do not
419   consider methanesulfonic acid in the gas phase (MSAg) at low temperatures.

420
3.3 Regional and seasonal analysis
422 Further analyses on regional and seasonal basis are given in Figs 9-11 for SO_4, SO_2, and DMS,
423 respectively. Only multi-model median is shown here to highlight any common problems in the
424 models. Further details of each individual model are given in Figs. S8-10 and discussed in
425 supplementary material. Each model in this study has its anomalous behavior at a specific time
426 and location. With this knowledge, modelers can further explore the simulation to identify
427 potential causes of model anomalies.

428
429 High SO_4 concentration regions vary across seasons (Fig. 9). In free-troposphere, these regions
430 cover the tropics to mid-latitudes in summer and winter (i.e., ATom-1 and ATom-2) and shift to
431 mid- to high-latitudes in spring and autumn (i.e., ATom-3 and ATom-4). The most high
432 concentration areas appeared in the SH high-latitudes during ATom-3 (SH spring) and the NH
433 high-latitudes during ATom-4 (NH spring). Things are a bit more complicated in the BL, but the
434 tropical atmospheric SO_4 concentration appears to be always elevated, and SO_4 concentration
435 levels and SO_4 interregional variation are more pronounced in ATom-1 (NH summer). Among
436 all AToms, the performance of the model SO_4 simulation is best for ATom-4 and worst for
437 ATom-1 (NH summer). Compared to observation, the free tropospheric atmosphere simulated by
438 the models tends to be more polluted. SO_4 concentration levels in simulated and observed worlds
439 can differ significantly in certain areas of each ATom. Differences may be caused by majority
440 models or a few individual models, and more discussion is given in the Supplement.

441
442 Atmospheric SO_2 (Fig. 10) is most abundant in the BL of NH mid-latitude Pacific Ocean during
443 ATom-1 (NH summer) and the tropical Pacific BL during ATom-3 (NH autumn), and pollution
444 affects the atmosphere above. Areas where free tropospheric SO_2 pollution is relatively polluted
445 do not necessarily follow the example of the BL. For instance, the SH mid-latitude Atlantic free
446 troposphere appears to be more polluted than other regions in ATom-4, but not in the BL,
447 implying a potential source of horizontal transport. The interregional variation of SO_2 in BL is
448 much larger than in the free troposphere, from which local oceanic sources of SO_2 can be
449 inferred. In terms of model-observation comparison, model simulated SO_2 in the free troposphere
450 is generally lower, which is opposite to the case of SO_4. A rapid SO_2 to SO_4 chemical conversion
451 in models could be one of reasons.

452
453 Surface DMS (Fig. 11) is generally higher in the tropics when the ocean is warm and in mid-high
454 latitudes when the hemisphere is in spring (e.g., ATom-3 SH spring and ATom-4 NH spring). A
455 remarkable pattern of high model DMS values in the BL is revealed throughout the ATom cycle.
456 This phenomenon also occurs in the free lower troposphere, but not necessarily in the upper
457 troposphere, suggesting a potential slower vertical transport or faster DMS chemical loss in
458 models. The high model DMS in BL can be attributed to (1) too high DMS emission, (2) too
459 slow DMS chemical loss, and (3) too slow DMS vertical transport from BL to free troposphere.
460 The convoluted effort can be somehow alleviated by focusing on remote high-latitudes, for
461 example SH high-latitude (40S-70S) Pacific, where land source impacts are limited. Thus, the
462 higher simulated SO_2 there in the BL ruled out a chemical cause due to low DMS loss. The
463 extremely high surface DMS is also not due to the slow vertical transport giving simulated DMS
464 is also high in the layers above the BL. A large model DMS emission is likely responsible for the
465 simulated high surface DMS.

4 Sulfur budget from AeroCom models

Table 3 summarizes the global sulfur budgets for emissions, wet/dry deposition and chemistry from the five models. Clearly, the largest source of sulfur (~70 TgS/yr) is SO_2 emitted directly from anthropogenic (~78%), biomass burning (~2%), and volcanic sources (~20%). Biogenic DMS (~15-30 TgS) produced and outgassed from decomposition of marine organic molecules provides the largest natural source of sulfur to the atmosphere. A small amount of SO_4 (< 3%) is emitted directly from anthropogenic sources.

DMS is oxidized in the atmosphere by OH and NO_3 radicals to form SO_2 and MSA. This biological source of SO_2, along with SO_2 emitted directly from other sources, reacts with hydroxyl radicals (OH) in the gas phase and hydrogen peroxide (H_2O_2) and ozone (O_3) in the aqueous phase to produce sulfuric acid (H_2SO_4) and eventually sulfate particles, which play an important role in the formation of clouds over the oceans.

In the five models, DMS has the shortest global average lifetime (0.6-2.0 days), followed by SO_2 (1.1-1.8 days), and SO_4 the longest lifetime (3.1-5.6 days). Among them, GEOS has the lowest global burden and shortest lifetime for all sulfur species. The magnitudes of global burdens and lifetimes shown here support the model performance shown in Figs. 2-8. For example, models CAM-ATRAS and OsloCTM3 emit highest DMS, which is consistent with the highest DMS value (Fig. 4 and S10) and longest lifetime simulated by the two models.

The key budget items include DMS emission, SO_2 emission, sulfate source or total deposition (source and deposition are pretty much the same as they should be), lifetime (reversely proportional to the loss rate), and total atmospheric mass load. From the multi-model mean and standard deviation, the "diversity" can be calculated. Figure 12 shows the global mean budget items in the percentage deviation of each model from the multi-model mean, following the same concept shown in Schulz et al., 2006 and Gliss et al., 2021. It reveals the processes causing model differences. For example, E3SM and GEOS have approximately the same SO_2 emissions and total sulfate sources, but the sulfate lifetime is much shorter in GEOS (implying faster removal rates) thus smaller sulfate burden that is consistent with lower sulfate concentrations in GEOS than in E3SM. At the same time, the lower total sulfate source in E3SM is compensated by longer lifetime compared to CAM-ATRAS, resulting in a comparable global burden of SO_4 in the two models.

It is worth pointing out that the much lower atmospheric SO_4 mass loading of the GEOS simulations is not necessarily related to the poor performance of the GEOS SO_4 simulations, as revealed by the model-measurement comparison in Figs 2, 5 and S8. Although the multi-model mean (or median) often represents the best simulation in the modeling domain, common modeling problems or too small model sample can compromise this effort.

5. Source origins for aerosol SO_4 along flight track and Ocean basins

In this section, we perform an analysis of source attribution by tagging the sulfur source types using the GEOS model. This model is the only one that provides tagged data. Our goal is to understand the sources (anthropogenic, biological, volcanic) of sulfate aerosols in remote regions

511   and how chemistry, transport, and removal processes determine the vertical distribution of
512   sulfate aerosols across seasons and ocean locations.

513

514   Figure 13a presents a quantitative summary of the source attribution of aerosol SO_4 sampled
515   along the ATom flight tracks. The analysis was performed over four seasons, spanning the
516   troposphere and three vertical layers (i.e., marine boundary layer, free troposphere and upper
517   troposphere). Overall, anthropogenic emissions were the dominant source (40–60% of the total)
518   of simulated tropospheric SO_4 along the ATom flight tracks for almost all altitudes and seasons,
519   followed by volcanic (18–32%) and oceanic sources (16–32%). Anthropogenic pollution
520   prevailed over remote oceans most in spring and autumn (ATom-3 and -4). The overall
521   contributions from volcanic and oceanic sources are comparable during the ATom periods.
522   Meanwhile, the ocean source contribution has an obvious seasonal variation which is most active
523   during the SH summer (ATom-2), when marine biochemical activity in the vast Southern Ocean
524   is at its most active. Volcanos show the largest contribution in the NH summer 2016 (ATom-1)
525   during the four ATom deployments. Given the irregular and event character of eruptions, the
526   volcanic contribution deserves further discussion below.

527

528   In the vertical direction, SO_4 from anthropogenic emissions contributes more than 50% to the
529   free to upper troposphere. Even in the marine boundary layer, anthropogenic sources of SO_4 still
530   account for the largest fraction, except in the SH summer (ATom-2) where and when oceanic
531   source became dominant. The relative importance of volcanic and marine sources varies not only
532   seasonally but also vertically. Oceanic sources understandably make up a significant fraction
533   (26-42%) of SO_4 in the boundary layer. In the free troposphere, its contribution drops off
534   sharply, reflecting its local surface source characteristics. On the other hand, SO_4 from
535   anthropogenic emissions expands in the free troposphere, suggesting that the source originated
536   from distant continental areas. Volcanic SO_4 remains nearly constant throughout the troposphere,
537   making volcanoes the second largest source there. Meanwhile, the contribution of biomass
538   burning to SO_4 over remote oceans is relatively small (< 3%).

539

540   The sources of SO_4 discussed above are deduced from the location and timing of the ATom's
541   flight path. Conclusions about the total contribution of the ocean needs caution, as there may be
542   representativeness issues using such narrow-band and instantaneous sampling. There might be a
543   situation where, for example, volcanoes provide a very large signal but only account for a small
544   measured area, and in most regions, volcanoes play a very minor role. Whereas oceanic sources
545   in the marine boundary layer perhaps were the dominant source for a much wider region but the
546   SO_4 concentration resulting from the DMS was overall a smaller amount compared to other
547   sources where near a volcanic or anthropogenic source. To address this representation issue, we
548   perform one more analysis with the model data averaged over a wider oceanic region (the shaded
549   orchid area in Fig. 1) and over a longer period (i.e., monthly mean over ATom periods). Such
550   source attributions are given in Fig. 13b.

551

552   Qualitative conclusions drawn from source attribution along the flight tracks generally apply to
553   the ocean basin source attribution, albeit to a slightly different extent. This confirms that
554   continental man-made sources dominate tropospheric SO_4 even over oceans. It has a clear
555   seasonal variation in oceanic contribution, which is largest in austral summer (ATom-2)
556   followed by boreal summer (ATom-1). There are two types of volcanic emissions. Volcanic

557 degassing emissions tend to remain nearly constant throughout the year and are equivalent to
558 about 20% of SO_2 global anthropogenic emissions. This degassing emission ensures that
559 volcanoes contribute more than 20% to SO_4 over the oceans. Due to the irregularity of volcanic
560 eruptions in terms of different eruption locations, magnitudes, and times, explosive volcanic
561 eruptions can cause severe fluctuations in SO_4 in the atmosphere. Compared with the source
562 attribution along the flight trajectory, the volcanic contribution decreased over a larger spatial
563 and temporal domain (i.e., ocean basin and monthly mean) in the NH winter 2017 by 32%
564 (ATom-2) and increased in all other three seasons by 14-33%, especially in the NH spring 2018
565 (ATom-4), when the massive Kilauea eruption in Hawaii began on 3 May 2018. Contrarily, the
566 anthropogenic contribution increased in the NH winter (ATom-2) by 5% and decreased in other
567 seasons by 7-21%.
568
569 **6. Conclusions**
570 This study investigates sulfur in remote tropospheric regions at global and seasonal scales using
571 ATom measurements and AeroCom models. The goal is to understand the atmospheric sulfur
572 cycle over the remote oceans, each model's behavior and the spread of model simulations, as
573 well as the observation-model discrepancies. Such understanding and comparison with real
574 observations are crucial to narrow down the uncertainty in model sulfur simulation. Even after
575 decades of development, models are still struggling to accurately simulate sulfur distributions,
576 with differences between models often exceeding an order of magnitude. On the other hand, the
577 agreement between instruments is usually much better. Differences between modeled SO_4 are
578 particularly large in the tropical upper troposphere, where deep convective transport allows a
579 small portion of sulfur sources to reach the lower stratosphere where resultant sulfate aerosols
580 can persist for many years. Compared with observations, simulated SO_2 is generally low while
581 SO_4 is high, and the model-observation agreement is much better in ATom-4. Modeled DMS
582 values are typically an order of magnitude higher than observed DMS near the surface, pointing
583 to a need to revisit the DMS emission inventories and/or the biogeochemical modules used to
584 predict DMS emissions. Our work also suggests investigating three other potential corresponding
585 processes: whether the chemical conversion from SO_2 to SO_4 is too rapid, whether DMS-
586 generated free tropospheric SO_2 is too low, and whether the vertical transport of SO_2 from BL to
587 free troposphere is too low. This further investigation requires atmospheric oxidant fields and the
588 ability to track SO_2 production and loss using tagged tracers.
589
590 We investigate source attribution of SO_4 over remote oceans seasonally and vertically. Sampled
591 at the location and time of ATom measurements, anthropogenic emissions were the dominant
592 source (40–60% of the total) of simulated tropospheric SO_4 at almost all heights and seasons,
593 followed by volcanic (18–32%) and oceanic sources (16 – 32%). These contributions changed to
594 34-56%, 17-37%, and 19-37% when extended to the broad Pacific and Atlantic during the
595 months of ATom deployment. This survey confirms that anthropogenic sources from land
596 dominate tropospheric SO_4 even over oceans. Given that we find DMS source to be
597 overestimated in the models, the anthropogenic sources overall are a larger portion of the budget,
598 and biogenic is likely smaller than volcanic. Volcanic degassing throughout the year contributes
599 about 20%, and this proportion is increased by explosive eruptions that vary in location and
600 timing. The oceanic contribution has obvious seasonal variation, the largest in the Southern
601 Hemisphere summer, followed by the Northern Hemisphere summer.
602

603 It is understood that anthropogenic sulfur emissions currently offset a significant portion of
604 greenhouse gas warming, but they are rapidly declining through emissions controls. As these
605 anthropogenic emissions decrease, natural sources of sulfur, particularly bio-derived sulfur
606 compounds discharged from the world's oceans, will increase their relative contribution.
607 Therefore, more efforts are needed to understand the sulfur cycle in remote environments. On the
608 other hand, our study shows that anthropogenic emissions remain a major source of sulfate
609 aerosols generated over remote oceans during the ATom deployment periods, suggesting that
610 any limitation of anthropogenic sulfur emissions would have modern global implications.

611
612 *Code availability.* The GEOS Earth System Model source code and the instructions for model build are available
613 at https://github.com/GEOS-ESM/GEOSgcm/ (Last accessed: 28 August 2023).

614
615 *Data availability.* The AeroCom model outputs needed to reproduce the results described in this paper are
616 publicly available for download at https://acd-ext.gsfc.nasa.gov/anonftp/acd/tropo/bian/ATom-AeroCom-Sulfur/.
617 The ATom data was obtained from their ESPO Data Archive: https://espo.nasa.gov/atom/content/ATom, last
618 accessed: 28 August 2022.

619
620 *Author contributions.*
621 BH and MC conceptualized ATom-AeroCom experiment. BH performed analysis and wrote the manuscript. BH,
622 PRC, MLi, MTL, RBS, HM, JEP, HW, KZ, and JZ provided AeroCom model results and ECA, KF, RSH, JJ, PCJ,
623 MLa, BAN, AWR, GS, and LX contributed to ATom measurements. All authors contributed to the editing of the
624 manuscript.

625
626 *Competing interests.*
627 At least one of the co-authors is a member of the editorial board of Atmospheric Chemistry and Physics.

628

629 *Acknowledgements.*
630 HB, MC, and PRC acknowledge the GEOS model developmental efforts at Global Modeling and Assimilation
631 Office (GMAO). This work was supported by NASA's Aura STM and ISFM programs and ACMAP award
632 (80NSSC23K1000). The computing resources supporting this work were provided by the NASA High-End
633 Computing (HEC) Program through the NASA Center for Climate Simulation (NCCS).
634 ECA and RSH acknowledge the support of the National Center for Atmospheric Research, which is a major facility
635 sponsored by the National Science Foundation under Cooperative Agreement No. 1852977.
636 ML acknowledges the support of JSPS Postdoctoral Fellowships for Research in Japan (Standard).
637 HM was supported by the Ministry of Education, Culture, Sports, Science, and Technology and the Japan Society
638 for the Promotion of Science (MEXT/JSPS) KAKENHI grants (JP19H05699, JP19KK0265, JP20H00196,
639 JP20H00638, JP22H03722, JP22F22092, JP23H00515, and JP23H00523); by the MEXT Arctic Challenge for
640 Sustainability II (ArCS II) project (JPMXD1420318865); and by the Environment Research and Technology
641 Development Fund 2-2003 (JPMEERF20202003) and 2-2301 (JPMEERF20232001) of the Environmental
642 Restoration and Conservation Agency.
643 KZ and HW acknowledge support by the U.S. Department of Energy (DOE), Office of Science, Office of Biological
644 and Environmental Research, Earth and Environmental Systems Modeling program. The Pacific Northwest National
645 Laboratory (PNNL) is operated for DOE by Battelle Memorial Institute under contract DE-AC05-76RLO1830.
646 LX thanks Michelle Kim, Hannah Allen, John Crounse, and Paul Wennberg for operating the CIT CIMS instrument
647 during ATom. LX acknowledges NASA grant NNX15AG61A.
648 MTL thanks Marit Sandstad (CICERO) for assistance with the model post-processing and acknowledges
649 the National Infrastructure for High Performance Computing and Data Storage in Norway (UNINETT) resources
650 (grant NN9188K).
651 RBS acknowledges funding from the Research Council of Norway (grant number 314997).

652
653 **References**

654   Abdul-Razzak, H. and Ghan, S.: A parameterization of aerosol acivation, 2. Multiple aerosol
655   types, J. Geophys. Res. Atmos., 105, 6837–6844, https://doi.org/10.1029/1999JD901161, 2000.

656   Allen, H. M., Bates, K. H., Crounse, J. D., Kim, M. J., Teng, A. P., Ray, E. A., and Wennberg,
657   P. O.: H_2O_2 and CH_3OOH (MHP) in the Remote Atmosphere: 2. Physical and Chemical
658   Controls, J. Geophys. Res. Atmos., 127, e2021JD035702,
659   https://doi.org/10.1029/2021JD035702, 2022.

660   Bacmeister, J., Suarez, M., and Robertson, F. R.: Rain Reevaporation, Boundary-Layer,
661   Convection Interactions, and Pacific Rainfall Patterns in an AGCM, J. Atmos. Sci., 63, 3383–
662   3403, https://doi.org/10.1175/JAS3791.1, 2006.
663
664   Barahona, D. and Nenes, A.: Parameterizing the competition between homogeneous and
665   heterogeneous freezing in cirrus cloud formation – monodisperse ice nuclei, Atmos. Chem.
666   Phys., 9, 369–381, https://doi.org/10.5194/acp-9-369-2009, 2009.
667
668   Barahona, D., Molod, A., Bacmeister, J., Nenes, A., Gettelman, A., Morrison, H., Phillips, V.,
669   and Eichmann, A.: Development of two-moment cloud microphysics for liquid and ice within
670   the NASA Goddard Earth Observing System Model (GEOS-5), Geosci. Model Dev., 7, 1733–
671   1766, https://doi.org/10.5194/gmd-7-1733-2014, 2014.
672
673   Barford, E.: Rising ocean acidity will exacerbate global warming, Nature,
674   https://doi.org/10.1038/nature.2013.13602, 2013.
675
676   Bian, H., Luo, C., and Li, X.: Numerical modeling of air pollutant and rainfall effect on acid wet
677   deposition, ACTA Meteorol. Sin., 7, 3, 273–286, 1993.
678
679   Bian, H., Chin, M., Hauglustaine, D. A., Schulz, M., Myhre, G., Bauer, S. E., Lund, M. T.,
680   Karydis, V. A., Kucsera, T. L., Pan, X., Pozzer, A., Skeie, R. B., Steenrod, S. D., Sudo, K.,
681   Tsigaridis, K., Tsimpidi, A. P., and Tsyro, S. G.: Investigation of global nitrate from the
682   AeroCom Phase III experiment, Atmos. Chem. Phys., 17, 12911–12940,
683   https://doi.org/10.5194/acp-17-12911-2017, 2017.
684
685   Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V.-M.,
686   Kondo, Y., Liao, H., Lohmann, U., Rasch, P., Satheesh, S., Sherwood, S., Stevens, B., and
687   Zhang, X.: in: Climate Change 2013: The Physical Science Basis, in: Contribution of Working
688   Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change:
689   Clouds and Aerosols, edited by: Stocker, T., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.,
690   Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P., Cambridge University Press,
691   Cambridge, UK and New York, NY, USA, 571–657, 2013.
692
693   Breen, K. H., Barahona, D., Yuan, T., Bian, H., and James, S. C., Effect of volcanic emissions on
694   clouds during the 2008 and 2018, Atmos. Chem. Phys., 21, 7749–7771,
695   https://doi.org/10.5194/acp-21-7749-2021, 2021.
696

Brock, C. A., Williamson, C., Kupc, A., Froyd, K. D., Erdesz, F., Wagner, N., Richardson, M., Schwarz, J. P., Gao, R.-S., Katich, J. M., Campuzano-Jost, P., Nault, B. A., Schroder, J. C., Jimenez, J. L., Weinzierl, B., Dollner, M., Bui, T., and Murphy, D. M.: Aerosol size distributions during the Atmospheric Tomography Mission (ATom): methods, uncertainties, and data products, Atmos. Meas. Tech., 12, 3081–3099, 2019.

Carn, S. A., Clarisse, L., and Prata, A. J.: Multi-decadal satellite measurements of global volcanic degassing, J. Volcanol. Geotherm. Res., 311, 99–134, http://dx.doi.org/10.1016/j.jvolgeores.2016.01.002, 2016.

Carn, S. A., Fioletov, V. E., McLinden, C. A., and Krotkov, N. A.: A decade of global volcanic SO_2 emissions measured from space, Sci. Rep., 7, 44095, https://doi.org/10.1038/srep44095, 2017.

Chin, M., Rood, R. B., Lin, S. J., Müller, J.-F., and Thompson, A. M.: Atmospheric sulfur cycle simulated in the global model GOCART: model description and global properties, J. Geophys. Res. Atmos., 105, D20, 24671–24687, https://doi.org/10.1029/2000JD900384, 2000.

Colarco, P. R., da Silva, A., Chin, M., and Diehl, T.: Online simulations of global aerosol distributions in the NASA GEOS-4 model and comparisons to satellite and ground-based aerosol optical depth, J. Geophys. Res. Atmos., 115, D14207, https://doi.org/10.1029/2009JD012820, 2010.

Crounse, J. D., McKinney, K. A., Kwan, A., J. and Wennberg, P. O., Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry, Anal. Chem., 78, 19, 6726–6732, https://doi.org/10.1021/ac0604235, 2006.

Darmenov, A. and da Silva, A.: The Quick Fire Emissions Dataset (QFED) - Documentation of versions 2.1, 2.2 and 2.4, NASA TM-2015-104606, Vol. 38, 183 pp., 2015.

Dentener, F., et al. (2006). "Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom." Atmospheric Chemistry and Physics 6: 4321-4344.

Dong, X., Fu, J. S., Zhu, Q., Sun, J., Tan, J., Keating, T., Sekiya, T., Sudo, K., Emmons, L., Tilmes, S., Jonson, J. E., Schulz, M., Bian, H., Chin, M., Davila, Y., Henze, D., Takemura, T., Benedictow, A. M. K., and Huang, K.: Long-range transport impacts on surface aerosol concentrations and the contributions to haze events in China: an HTAP2 multi-model study, Atmos. Chem. Phys., 18, 15581-15600, https://doi.org/10.5194/acp-18-15581-2018, 2018.

Eger, P. G., Helleis, F., Schuster, G., Phillips, G. J., Lelieveld, J., and Crowley, J. N.: Chemical ionization quadrupole mass spectrometer with an electrical discharge ion source for atmospheric trace gas measurement, Atmos. Meas. Tech., 12, 1935–1954, https://doi.org/10.5194/amt-12-1935-2019, 2019.

Feng, L., Smith, S. J., Braun, C., Crippa, M., Gidden, M. J., Hoesly, R., Klimont, Z., van Marle, M., van den Berg, M., and van der Werf, G. R.: The generation of gridded emissions data for CMIP6, Geosci. Model Dev., 13, 461–482, https://doi.org/10.5194/gmd-13-461-2020, 2020.

744
745 Fountoukis, C. and Nenes, A.: Continued development of a cloud droplet formation
746 parameterization for global climate models, J. Geophys. Res. Atmos., 110, D11212,
747 https://doi.org/10.1029/2004JD005591, 2005.
748
749 Galí, M., Levasseur, M., Devred, E., Simó, R., and Babin, M.: Sea-surface dimethylsulfide
750 (DMS) concentration from satellite data at global and regional scales, Biogeosciences, 15, 3497–
751 3519, https://doi.org/10.5194/bg-15-3497-2018, 2018.
752
753 Gliß, J., Mortier, A., Schulz, M., Andrews, E., Balkanski, Y., Bauer, S. E., Benedictow, A. M.
754 K., Bian, H., Checa-Garcia, R., Chin, M., Ginoux, P., Griesfeller, J. J., Heckel, A., Kipling, Z.,
755 Kirkevåg, A., Kokkola, H., Laj, P., Le Sager, P., Lund, M. T., Lund Myhre, C., Matsui, H.,
756 Myhre, G., Neubauer, D., van Noije, T., North, P., Olivié, D. J. L., Rémy, S., Sogacheva, L.,
757 Takemura, T., Tsigaridis, K., and Tsyro, S. G.: AeroCom phase III multi-model evaluation of the
758 aerosol life cycle and optical properties using ground- and space-based remote sensing as well as
759 surface in situ observations, Atmos. Chem. Phys., 21, 87–128, https://doi.org/10.5194/acp-21-87-
760 2021, Jan., 2021.
761
762 Grennfelt, P., Engleryd, A., Forsius, M., Hov, Ø., Rodhe, H., and Cowling, E.: Acid rain and air
763 pollution: 50 years of progress in environmental science and policy, Ambio, 49, 849–864,
764 https://doi.org/10.1007/s13280-019-01244-4, 2020.
765
766 Gryspeerdt, E., Povey, A. C., Grainger, R. G., Hasekamp, O., Hsu, N. C., Mulcahy, J. P., Sayer,
767 A. M., and Sorooshian, A.: Uncertainty in aerosol-cloud radiative forcing is driven by clean
768 conditions, Atmos. Chem. Phys., 23, 4115–4122, https://doi.org/10.5194/acp-23-4115-2023,
769 2023.
770
771 Guo, H., Campuzano-Jost, P., Nault, B. A., Day, D. A., Schroder, J. C., Kim, D., Dibb, J. E.,
772 Dollner, M., Weinzierl, B., and Jimenez, J. L.: The importance of size ranges in aerosol
773 instrument intercomparisons: a case study for the Atmospheric Tomography Mission, Atmos.
774 Meas. Tech., 14, 3631–3655, 2021.
775
776 Hodshire, A. L., Campuzano-Jost, P., Kodros, J. K., Croft, B., Nault, B. A., Schroder, J. C.,
777 Jimenez, J. L., and Pierce, J. R.: The potential role of methanesulfonic acid (MSA) in aerosol
778 formation and growth and the associated radiative forcings, Atmos. Chem. Phys., 19, 3137–
779 3160, 2019.
780
781 Hodzic, A., Campuzano-Jost, P., Bian, H., Chin, M., Colarco, P. R., Day, D. A., Froyd, K. D.,
782 Heinold, B., Jo, D. S., Katich, J. M., Kodros, J. K., Nault, B. A., Pierce, J. R., Ray, E., Schacht,
783 J., Schill, G. P., Schroder, J. C., Schwarz, J. P., Sueper, D. T., Tegen, I., Tilmes, S., Tsigaridis,
784 K., Yu, P., and Jimenez, J. L.: Characterization of organic aerosol across the global remote
785 troposphere: a comparison of ATom measurements and global chemistry models, Atmos. Chem.
786 Phys., 20, 4607–4635, 2020.
787
788 Hoffmann, E. H., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R. and Herrmann, H., An
789 advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl

790   sulfide chemistry, Proc. Natl. Acad. Sci. USA, 113, 11776–11781,
791   https://doi.org/10.1073/pnas.1606320113, 2016.
792
793   Holton, J. R., Haynes, P. H., McIntyre, M. E., Douglass, A. R., Rood, R. B., and Pfister, L.:
794   Stratosphere-troposphere exchange, Rev. Geophys., 33, 403–439,
795   https://doi.org/10.1029/95RG02097, 1995.
796
797   Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., et al.
798   (2018). Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the
799   Community Emissions Data System (CEDS). Geosci. Model Dev., 11,
800   369–408. https://doi.org/10.5194/gmd-11-369-2018.
801
802   Huang, R-J., Duan, J., Li, Y., Chen, Q., Chen, Y., Tang, M., Yang, L., Ni, H., Lin, C., Xu, W.,
803   Liu, Y., Chen, C., Yan, Z., Ovadnevaite, J., Ceburnis, D., Dusek, U., Cao, J., Hoffmann, T., &
804   O'Dowd, C. D., Effects of NH3 and alkaline metals on the formation of particulate sulfate and
805   nitrate in wintertime Beijing. Sci. Total Environ., 717, 137190,
806   https://doi.org/10.1016/j.scitotenv.2020.137190, 2020.
807
808   Huey, L. G., Tanner, D. J., Slusher, D. L., Dibb, J. E., Arimoto, R., Chen, G., Davis, D., Buhr,
809   M. P., Nowak, J. B., Mauldin III, R. L., Eisele, F. L., and Kosciuch, E.: CIMS measurements of
810   HNO$_3$ and SO$_2$ at the South Pole during ISCAT 2000, Atmos. Environ., 38, 5411–5421,
811   https://doi.org/10.1016/j.atmosenv.2004.04.037, 2004.
812
813   Jia, H., Ma, X., Yu, F., and Quaas, J.: Significant underestimation of radiative forcing by
814   aerosol–cloud interactions derived from satellite-based methods, Nat. Commun., 12,
815   https://doi.org/10.1038/s41467-021-23888-1, 2021.
816
817   Jia, H., Quaas, J., Gryspeerdt, E., Böhm, C., and Sourdeval, O.: Addressing the difficulties in
818   quantifying the Twomey effect for marine warm clouds from multi-sensor satellite observations
819   and reanalysis, Atmos. Chem. Phys., 22, 7353–7372, https://doi.org/10.5194/acp-22-7353-2022,
820   2022.
821
822   Moch, J. M., Mickley, L. J., Keller, C. A., Bian, H., Lundgren, E. W., Zhai, S., and Jacob, D. J.:
823   Aerosol-radiation interactions in China in winter: Competing effects of reduced shortwave
824   radiation and cloud-snowfall-albedo feedbacks under rapidly changing emissions, J. Geophys.
825   Res. Atmos., 127, e2021JD035442, https://doi.org/10.1029/2021JD035442, 2022.
826
827   Josephson, D. C., Robinson, J. M., Chiotti, J,, Jirka, K. J., and Kraft, C. E.: Chemical and
828   biological recovery from acid deposition within the Honnedaga Lake watershed, New York,
829   USA, Environ. Monit. Assess., 186, 4391–4409, https://doi.org/10.1007/s10661-014-3706-9,
830   2014.
831
832   Jurkat, T., Kaufmann, S., Voigt, C., Schäuble, D., Jeßberger, P., and Zireis, H.: The airborne
833   mass spectrometer AIMS – Part 2: Measurements of trace gases with stratospheric or tropo-
834   spheric origin in the UTLS, Atmos. Meas. Tech., 9, 1907–1923, https://doi.org/10.5194/amt-9-
835   1907-2016, 2016.

836
837 Kettle, A. J. and Andreae, M. O.: Flux of dimethylsulfide from the oceans: A comparison of
838 updated data sets and flux models, J. Geophys. Res. Atmos., 105, 26793–26808,
839 https://doi.org/10.1029/2000JD900252, 2000.
840
841 Klein, S. A., Zhang, Y., Zelinka, M. D., Pincus, R., Boyle, J., and Gleckler, P. J.: Are climate
842 model simulations of clouds improving? An evaluation using the ISCCP simulator, J. Geophys.
843 Res. Atmos., 118, 1329–1342, https://doi.org/10.1002/jgrd.50141, 2013.
844
845 Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp,
846 L., Saltzman, E. S., Stefels, J., Johnson, J. E., and Liss, P. S.: An updated climatology of surface
847 dimethlysulfide concentrations and emission fluxes in the global ocean, Global Biogeochem.
848 Cy., 25, GB1004, doi:10.1029/2010GB003850, 2011.
849
850 Liu, M. and Matsui, H.: Improved simulations of global black carbon distributions by modifying
851 wet scavenging processes in convective and mixed-phase clouds, J. Geophys. Res. Atmos., 126,
852 e2020JD033890, https://doi.org/10.1029/2020JD033890, 2021.
853
854 Lund, M. T., Myhre, G., Haslerud, A. S., Skeie, R. B., Griesfeller, J., Platt, S. M., Kumar, R.,
855 Myhre, C. L., and Schulz, M.: Concentrations and radiative forcing of anthropogenic aerosols
856 from 1750 to 2014 simulated with the Oslo CTM3 and CEDS emission inventory, Geosci. Model
857 Dev., 11, 4909–4931, https://doi.org/10.5194/gmd-11-4909-2018, 2018.
858
859 Malavelle, F. F., Haywood, J. M., Jones, A., Gettelman, A., Clarisse, L., Bauduin, S., Allan, R.
860 P., Karset, I. H. H., Kristjánsson, J. E., Oreopoulos, L., Cho, N., Lee, D., Bellouin, N., Boucher,
861 O., Grosvenor, D. P., Carslaw, K. S., Dhomse, S., Mann, G. W., Schmidt, A., Coe, H., Hartley,
862 M. E., Dalvi, M., Hill, A. A., Johnson, B. T., Johnson, C. E., Knight, J. R., O'Connor, F. M.,
863 Partridge, D. G., Stier, P., Myhre, G., Platnick, S., Stephens, G. L., Takahashi, H., and
864 Thordarson, T.: Strong constraints on aerosol–cloud interactions from volcanic eruptions,
865 Nature, 546, 485-491, https://doi.org/10.1038/nature22974, 2017.
866
867 McDonnell, T. C., Driscoll, C. T., Sullivan, T. J., Burns, D. A., Baldigo, B. P., Shao, S., and
868 Lawrence, G. B.: Regional target loads of atmospheric nitrogen and sulfur deposition for the
869 protection of stream and watershed soil resources of the Adirondack Mountains, USA, Environ.
870 Pollut., 281, 117110, https://doi.org/10.1016/j.envpol.2021.117110, 2021.
871
872 Matsui, H.: Development of a global aerosol model using a two-dimensional sectional method: 1.
873 Model design, J. Adv. Model. Earth Syst., 9, 1921–1947,
874 https://doi.org/10.1002/2017MS000936, 2017.
875
876 Matsui, H. and Mahowald, N.: Development of a global aerosol model using a two-dimensional
877 sectional method: 2. Evaluation and sensitivity simulations, J. Adv. Model. Earth Syst., 9, 1887–
878 1920, https://doi.org/10.1002/2017MS000937, 2017.
879
880 Molod, A.: Constraints on the Total Water PDF in GCMs from AIRS and a High Resolution
881 Model, J. Climate, 25, 8341–8352, https://doi.org/10.1175/JCLI-D-11-00412.1, 2012.

882

883   Moorthi, S. and Suarez, M. J.: Relaxed Arakawa-Schubert. A parameterization of moist
884   convection for general circulation models, Mon. Weather Rev., 120, 978–1002,
885   https://doi.org/10.1175/1520-0493(1992)120<0978:RASAPO>2.0.CO;2, 1992.

886

887   Myhre, G., Samset, B. H., Schulz, M., Balkanski, Y., Bauer, S., Berntsen, T. K., Bian, H.,
888   Bellouin, N., Chin, M., Diehl, T., Easter, R. C., Feichter, J., Ghan, S. J., Hauglustaine, D.,
889   Iversen, T., Kinne, S., Kirkevåg, A., Lamarque, J.-F., Lin, G., Liu, X., Lund, M. T., Luo, G., Ma,
890   X., van Noije, T., Penner, J. E., Rasch, P. J., Ruiz, A., Seland, Ø., Skeie, R. B., Stier, P.,
891   Takemura, T., Tsigaridis, K., Wang, P., Wang, Z., Xu, L., Yu, H., Yu, F., Yoon, J.-H., Zhang,
892   K., Zhang, H., and Zhou, C.: Radiative forcing of the direct aerosol effect from AeroCom Phase
893   II simulations, Atmos. Chem. Phys., 13, 1853–1877, https://doi.org/10.5194/acp-13-1853-2013,
894   2013.

895

896   Nightingale P. D., Malin G., Law C. S., Watson A. J., Liss P. S., Liddicoat M. I., et al. In
897   situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile
898   tracers. Global Biogeochem. Cy. 14, 373–387, https://doi.org/10.1029/1999gb900091, 2000.

899

900   Penner, A., Prather, J. E., Ramanathan, K. A., Ramaswamy, V., Rasch, V., Ravishankara, P. J.,
901   Rosenfeld, A. R., Stephens, D., and Wood, R.: Improving our fundamental understanding of the
902   role of aerosol–cloud interactions in the climate system, P. Natl. Acad. Sci. USA, 113, 5781–
903   5790, https://doi.org/10.1073/pnas.1514043113, 2016.

904

905   Rasch, P. J., Xie, S., Ma, P. -L., Lin, W., Wang, H., Tang, Q., Burrows, S. M., Caldwell, P.,
906   Zhang, K., Easter, R. C., Cameron-Smith, P., Singh, B., Wan, H., Golaz, J.-C., Harrop, B. E.,
907   Roesler, E., Bacmeister, J., Larson, V. E., Evans, K. J., Qian, Y., Taylor, M., Leung, L. R.,
908   Zhang, Y., Brent, L., Branstetter, M., Hannay, C., Mahajan, S., Mametjanov, A., Neale, R.,
909   Richter, J. H., Yoon, J.-H., Zender, C. S., Bader, D., Flanner, M., Foucar, J. G., Jacob, R., Keen,
910   N., Klein, S. A., Liu, X., Salinger, A. G., Shrivastava, M., and Yang, Y.: An Overview of the
911   Atmospheric Component of the Energy Exascale Earth System Model, J. Adv. Model. Earth
912   Syst., 11, 2377–2411, https://doi.org/10.1029/2019MS001629, 2019.

913

914   Rickly, P. S., Xu, L., Crounse, J. D., Wennberg, P. O., and Rollins, A. W.: Improvements to a
915   laser-induced fluorescence instrument for measuring SO_2 – impact on accuracy and precision,
916   Atmos. Meas. Tech., 14, 2429–2439, https://doi.org/10.5194/amt-14-2429-2021, 2021.

917

918   Rienecker, M., Suarez, M., Todling, R., Bacmeister, J., Takacs, L., Liu, H.-C., Gu, W.,
919   Sienkiewicz, M., Koster, R., Gelaro, R., Stajner, I., and Nielsen, J.: The GEOS-5 Data
920   Assimilation System – Documentation of Versions 5.0.1, 5.1.0, and 5.2.0., Vol. 27 of Technical
921   Report Series on Global Modeling and Data Assimilation, NASA Goddard Space Flight Center,
922   Greenbelt, MD, USA, 2008.

923

924   Rissman, T. A., Nenes, A., and Seinfeld, J. H.: Chemical amplification (or dampening) of the
925   Twomey effect: Conditions derived from droplet activation theory, J. Atmos. Sci., 61(8), 919–
926   930, https://doi.org/10.1175/1520-0469(2004)061<0919:CAODOT>2.0.CO;2, 2004.

927

Rollins, A. W., Thornberry, T. D., Ciciora, S. J., McLaughlin, R. J., Watts, L. A., Hanisco, T. F., Baumann, E., Giorgetta, F. R., Bui, T. V., Fahey, D. W., and Gao, R.-S.: A laser-induced fluorescence instrument for aircraft measurements of sulfur dioxide in the upper troposphere and lower stratosphere, Atmos. Meas. Tech., 9, 4601–4613, https://doi.org/10.5194/amt-9-4601-2016, 2016.

Schueneman, M. K., Nault, B. A., Campuzano-Jost, P., Jo, D. S., Day, D. A., Schroder, J. C., Palm, B. B., Hodzic, A., Dibb, J. E., and Jimenez, J. L.: Aerosol pH indicator and organosulfate detectability from aerosol mass spectrometry measurements, Atmos. Meas. Tech., 14, 2237–2260, 2021.

Seinfeld, J. H., Bretherton, C., Carslaw, K. S., Coe, H., DeMott, P. J., Dunlea, E. J., Feingold, G., Ghan, S., Guenther, A. B., Kahn, R., Kraucunas, I., Kreidenweis, S. M., Molina, M. J., Nenes, A., Penner, J. E., Prather, K. A., Ramanathan, V., Ramaswamy, V., Rasch, P. J., Ravishankara, A. R., Rosenfeld, D., Stephens, G., and Wood, R.: Improving our fundamental understanding of the role of aerosol–cloud interactions in the climate system, P. Natl. Acad. Sci. USA, 113, 5781–5790, https://doi.org/10.1073/pnas.151404311, 2016.

Schulz, M., Textor, C., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Dentener, F., Guibert, S., Isaksen, I. S. A., Iversen, T., Koch, D., Kirkevåg, A., Liu, X., Montanaro, V., Myhre, G., Penner, J. E., Pitari, G., Reddy, S., Seland, Ø., Stier, P., and Takemura, T.: Radiative forcing by aerosols as derived from the AeroCom present-day and pre-industrial simulations, Atmos. Chem. Phys., 6, 5225–5246, https://doi.org/10.5194/acp-6-5225-2006, 2006

Simpson, I. J., Colman, J. J., Swanson, A. L., Bandy, A. R., Thornton, D. C., Blake, D. R., and F. S. Rowland, F. S.: Aircraft Measurements of Dimethyl Sulfide (DMS) Using a Whole Air Sampling Technique, J. Atmos. Chem., 39, 191-213, https://doi.org/10.1023/A:1010608529779, 2001.

Slingo, J.: The development and verification of a cloud prediction scheme for the ECMWF model, Q. J. Roy. Meteor. Soc., 113, 899–927, https://doi.org/10.1002/qj.49711347710, 1987.

Smith, R. N. B.: A scheme for predicting layer clouds and their water content in a general circulation model, Q. J. Roy. Meteor. Soc., 116, 435–460, https://doi.org/10.1002/qj.49711649210, 1990.

Søvde, O. A., Prather, M. J., Isaksen, I. S. A., Berntsen, T. K., Stordal, F., Zhu, X., Holmes, C. D., and Hsu, J.: The chemical transport model Oslo CTM3, Geosci. Model Dev., 5, 1441–1469, https://doi.org/10.5194/gmd-5-1441-2012, 2012.

Tan, J., Fu, J. S., Dentener, F., Sun, J., Emmons, L., Tilmes, S., Flemming, J., Takemura, T., Bian, H., Zhu, Q., Yang, C.-E., and Keating, T.: Source contributions to sulfur and nitrogen deposition – an HTAP II multi-model study on hemispheric transport, Atmos. Chem. Phys., 18, 12223–12240, https://doi.org/10.5194/acp-18-12223-2018, 2018.

974 Tiedtke, M.: Representation of clouds in large-scale models, Mon. Weather Rev., 121, 3040–
975 3061, https://doi.org/10.1175/1520-0493(1993)121<3040:ROCILS>2.0.CO;2, 1993.
976
977 Wang, H., Easter, R. C., Zhang, R., Ma, P., Singh, B., Zhang, K., Ganguly, D., Rasch, P. J.,
978 Burrows, S. M., Ghan, S. J., Lou, S., Qian, Y., Yang, Y., Feng, Y., Flanner, M., Leung, L. R.,
979 Liu, X., Shrivastava, M., Sun, J., Tang, Q., Xie, S., and Yoon, J.: Aerosols in the E3SM Version
980 1: New Developments and Their Impacts on Radiative Forcing, J. Adv. Model. Earth Syst., 12,
981 e2019MS001851, https://doi.org/10.1029/2019MS001851, 2020.
982
983 Wang, D., Zhu, B., Wang, H., and Sun, L., Simulation study on the indirect effect of sulfate on
984 the summer climate over the eastern China monsoon region, Sci. Rep., 11, 8295,
985 https://doi.org/10.1038/s41598-021-87832-5, 2021.
986
987 Williamson, C. J., Kupc, A., Axisa, D., Bilsback, K. R, Bui, T. P., Campuzano-Jost, P., Dollner,
988 M., Froyd, K. D., Hodshire, A. L., Jimenez, J. L., Kodros, J. K., Luo, G., Murphy, D. M., Nault,
989 B. A., Ray, E. A., Weinzierl, B., Wilson, J. C., Yu, F., Yu, P., Pierce, J. R., and Brock, C. A.: A
990 large source of cloud condensation nuclei from new particle formation in the tropics, Nature,
991 574, 399–403, https://doi.org/10.1038/s41586-019-1638-9, 2019.
992
993 Thompson, C. R., Wofsy, S. C., Prather, M. J., Newman, P. A., Hanisco, T. F., Ryerson, T. B.,
994 Fahey, D. W., Apel, E. C., Brock, C. A., Brune, W. H., Froyd, K., Katich, J. M., Nicely, J. M.,
995 Peischl, J., Ray, E., Veres, P. R., Wang, S., Allen, H. M., Asher, E., Bian, H., Blake, D.,
996 Bourgeois, I., Budney, J., Paul Bui, T., Butler, A., Campuzano-Jost, P., Chang, C., Chin, M.,
997 Commane, R., Correa, G., Crounse, J. D., Daube, B., Dibb, J. E., Digangi, J. P., Diskin, G. S.,
998 Dollner, M., Elkins, J. W., Fiore, A. M., Flynn, C. M., Guo, H., Hall, S. R., Hannun, R. A., Hills,
999 A., Hintsa, E. J., Hodzic, A., Hornbrook, R. S., Greg Huey, L., Jimenez, J. L., Keeling, R. F.,
1000 Kim, M. J., Kupc, A., Lacey, F., Lait, L. R., Lamarque, J.-F., Liu, J., Mckain, K., Meinardi, S.,
1001 Miller, D. O., Montzka, S. A., Moore, F. L., Morgan, E. J., Murphy, D. M., Murray, L. T., Nault,
1002 B. A., Andrew Neuman, J., Nguyen, L., Gonzalez, Y., Rollins, A., Rosenlof, K., Sargent, M.,
1003 Schill, G., Schwarz, J. P., St. Clair, J. M., Steenrod, S. D., Stephens, B. B., Strahan, S. E., Strode,
1004 S. A., Sweeney, C., Thames, A. B., Ullmann, K., Wagner, N., Weber, R., Weinzierl, B.,
1005 Wennberg, P. O., Williamson, C. J., Wolfe, G. M., and Zeng, L.: THE NASA ATMOSPHERIC
1006 TOMOGRAPHY (ATom) MISSION: Imaging the Chemistry of the Global Atmosphere, Bull.
1007 Am. Meteorol. Soc., 103, E761-E790, https://doi.org/10.1175/BAMS-D-20-0315.1, 2022.
1008
1009 Zhang, K., Zhang, W., Wan, H., Rasch, P. J., Ghan, S. J., Easter, R. C., Shi, X., Wang, Y.,
1010 Wang, H., Ma, P.-L., Zhang, S., Sun, J., Burrows, S. M., Shrivastava, M., Singh, B., Qian, Y.,
1011 Liu, X., Golaz, J.-C., Tang, Q., Zheng, X., Xie, S., Lin, W., Feng, Y., Wang, M., Yoon, J.-H.,
1012 and Leung, L. R.: Effective radiative forcing of anthropogenic aerosols in E3SM version 1:
1013 historical changes, causality, decomposition, and parameterization sensitivities, Atmos. Chem.
1014 Phys., 22, 9129–9160, https://doi.org/10.5194/acp-22-9129-2022, 2022.
1015
1016 Zhu, J., Penner, J. E., Lin, G., Zhou, C., Xu, L., and Zhuang, B.: Mechanism of SOA formation
1017 determines magnitude of radiative effects. Proceedings of the National Academy of Sciences of
1018 the United States of America, 114, 12685–12690, https://doi.org/10.1073/
1019 pnas.1712273114, 2017.
1020

1021 Zhu, J., Penner, J. E., Yu, F., Sillman, S., Andreae, M. O., and Coe, H.: Decrease in radiative
1022 forcing by organic aerosol nucleation, climate, and land use change. Nature Commun, , 10, 423,
1023 https://doi.org/10.1038/s41467-019-08407-7, 2019.

1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066

1067 Table 1. ATom sulfur measurements used in the study

	SO₄		SO₂		MSA		DMS	
Instrument	AMS[a]	PALMS[b]	CIMS[c]	LIF[d]	AMS	PALMS	TOGA[e]	WAS[f]
ATom deployment(s)	1 to 4	1 to 4	1 to 4	4	1 to 4	1 to 4	2 to 4	1 to 4
Frequency	60 s	180 s	1 s	1 s	1 s	180 s	120 s	Variable but ~180 s
Accuracy	±35% (2s)	±60% at 10 ng m-3 ±20% at 1 µg m-3	±25%	± 9% (1s)	±35% (2s)	±70%	15% or better	15%
precision			130pptv					10%
Detection limit	5-15 ng sm⁻³	~10 ng sm⁻³		2 pptv	2.5 ng sm-3 (60 s)	~15 ng sm⁻³	1 ppt	1 ppt
Cut-off size (dry diameter)	~0.75 µm	0.1-3 µm			~0.75 µm	0.1-3 µm		
Primary Investigator(s)	Jose Jimenez and Pedro Campuzano Jost	Karl Froyd and Gregory Schill	Paul Wennberg	Andrew Rollins	Jose Jimenez and Pedro Campuzano Jost	Karl Froyd and Gregory Schill	Eric Apel	Donald Blake
References	Guo et al., 2021; Schueneman et al., 2021	Froyd et al., 2019	Allen et al., 2022; Crounse et al., 2006	Rollins et al., 2016	Hodshire et al., 2019	Froyd et al., 2019	Apel et al., 2015	Simpson et al., 2001

1068 [a]AMS: Aerosol Mass Spectrometer
1069 [b]PALMS: Particle Analysis by Laser Mass Spectrometry
1070 cCIMS: Chemical Ionization Mass Spectrometer
1071 [d]LIF: Laser Induced Fluorescence
1072 [e]TOGA: NCAR Trace Organic Gas Analyzer
1073 [f]WAS: Whole Air Sampler

1074
1075
1076 Table 2. AeroCom Models used in this study

Model Abbreviation	Model Version	Nominal Resolution	Vertical Levels	Meteorological Fields	Ocean Surface Temperature Data	Interactive Aerosol-Meteorology	Endogenous Oxidants	Endogeous DMS Emission	Aerosol Module	Anthropogenic Emission	Volcano Emission	Key References
CAM-ATRAS	CAM5-ATRAS2	1.9° × 2.5°	30	MERRA-2	HadSST	Yes	Yes	No	Microphysics, 12 sectional size bins, and internal mixing of aerosol constituents in each bin.	CEDS (Hoesly et al., 2018),	Degassing (Andres and Kasgnoc, 1998), Eruption (Neely and Schmidt, 2016)	Liu and Matsui 2021; Matsui 2017; Matsui and Mahowald, 2017
E3SM	v1.0	1° × 1°	72	ERA-Interim	HadSST	Yes	No	No	Microphysics, MAM4, internal mixing within a mode, external mixing between modes	CEDS (Hoesly et al., 2018)	Continous emission (Denener et al., 2006). No eruptive emissions.	Rasch et al., 2019; Wang et al., 2020; Zhang et al. 2022
GEOS	Icarus-3_3_p2	1° × 1°	72	MERRA-2	MERRA_sst	Yes	No	Yes	GOCART, Bulk, external mixing	CEDS (Hoesly et al., 2018)	Carns et al., 2016, 2017	Bian 2017; Colarco et al., 2010; Chin et al., 2000
IMPACT		1.9° × 2.5°	30	Open IFS ECMWF	HadSST	No	Yes	no	Microphysics, internal mixing within a mode, external mixing between modes	CEDS (Hoesly et al., 2018)	AeroCom volcanic emissions	Zhu et al., 2017; Zhu et al., 2019
OsloCTM3	OsloCTM3v1.02	2.25° × 2.25°	60	Open IFS ECMWF	Open IFS ECMWF	No	Yes	Yes	Bulk, external mixing	SSP245 with linear interpolation for 2017	AeroCom volcanic emissions (busing TOMS- and OMI-based estimates), continuous from Dentener (2006)	Lund et al., 018; Søvde et al., 2012

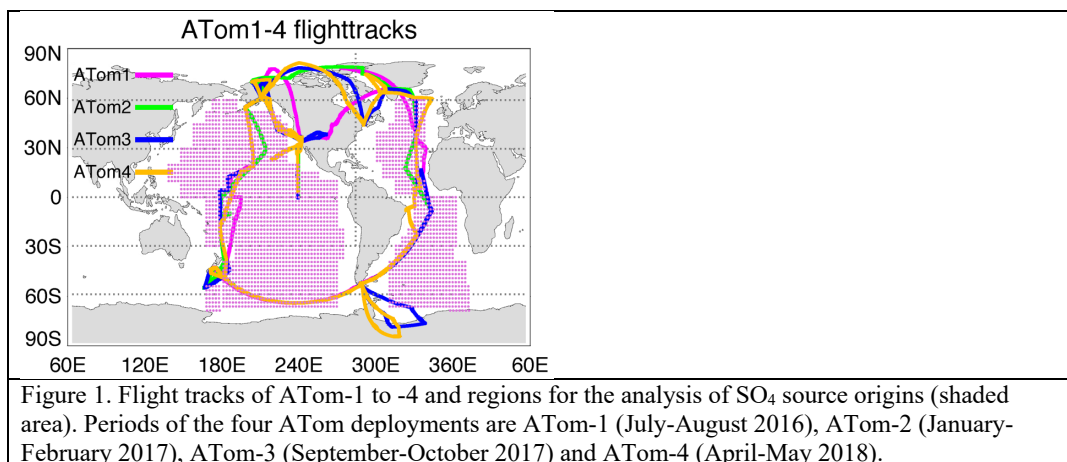
1077
1078
1079
1080
1081
1082
1083
1084

1085   Table 3. Global sulfur budget in 2017

		Emission	SUPSO2[1]	SUPMSA	SUPSO4	Dry	Wet	TotalSource	Burden	Lifetime
		TgS/yr	TgS/yr	TgS/yr	TgS/yr	TgS/yr	TgS/yr	TgS/yr	TgS	days
CAM-ATRAS	DMS	26.05	-26.05	--	--	--	--	26.05	0.13	1.8
	SO2	68.67	26.05	--	-55.67	-39.05		94.72	0.445	1.7
	SO4	1.76	--	--	55.67	-4.72	-53.23	58.09	0.67	4.2
E3SM	DMS	19.43	-19.40	--	--	--	--	19.43	0.0658	1.24
	SO2	67.92	19.40	--	-38.56	-48.76		87.32	0.3825	1.60
	SO4	1.74	--	--	38.56	-6.95	-33.31	40.31	0.6183	5.60
GEOS	DMS	15.57	-14.84	-0.74	--	--	--	15.57	0.0252	0.59
	SO2	67.06	14.84		-37.49	-32.93	-11.39	81.90	0.3488	1.55
	SO4	1.68	--	--	37.49	-5.27	-33.90	39.17	0.3269	3.05
	MSA	--	--	0.74	--	-0.10	-0.64	-.74	0.0063	3.11
IMPACT	DMS	18.22	-18.22	--	--	--	--	18.05	0.0369	0.75
	SO2	64.76	18.22	--	-51.44	-31.29	--	82.98	0.4134	1.82
	SO4	1.36	--	--	51.44	-3.48	-49.32	52.80	0.7502	5.19
OsloCTM3	DMS	26.93	-26.93	--	--	--	--	26.93	0.1496	2.03
	SO2	52.80	26.93	--	-49.23	-29.01	-1.49	79.73	0.2346	1.08
	SO4	1.053	--	--	55.49	-6.35	-50.29	56.54	0.8681	5.60

1086   [1]SUPSO2: chemical production for SO2

1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118

Figure 1. Flight tracks of ATom-1 to -4 and regions for the analysis of SO₄ source origins (shaded area). Periods of the four ATom deployments are ATom-1 (July-August 2016), ATom-2 (January-February 2017), ATom-3 (September-October 2017) and ATom-4 (April-May 2018).

1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150

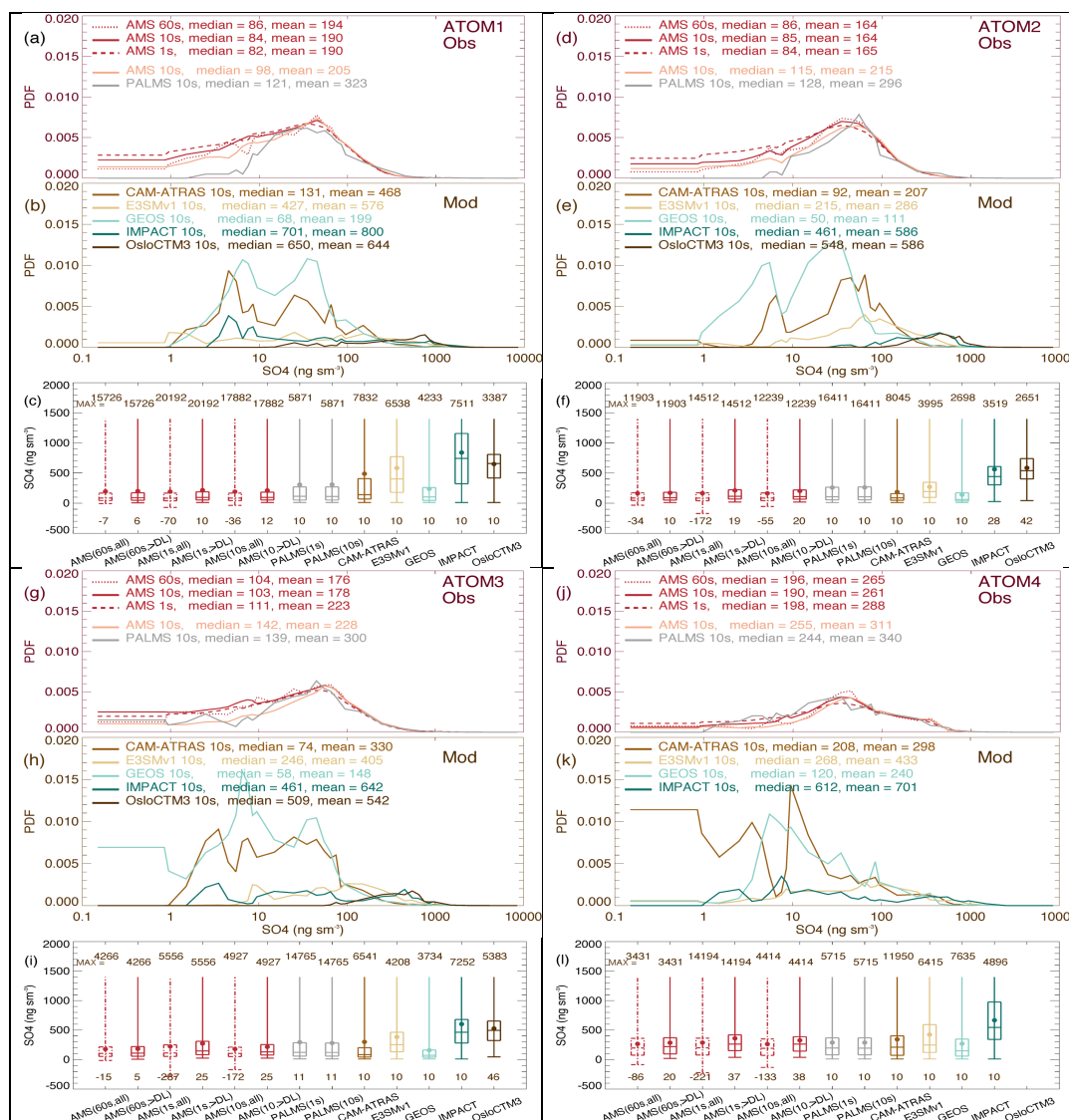



Figure 2. Probability density function (PDF) of SO$_4$ from AMS and PALMS observations (a, d, g, j) and five model simulations (b, e, h, k), as well as their statistical values shown in box-and-whisker plot (c, f, i, l) for four ATom deployments. PDF analyses include AMS SO$_4$ reported in three-time frequencies (1-s, 10-s, and 60-s) in red. Data for all other colors are sampled at 10-s points where all instrument measurements are available. The median/mean values listed are calculated when the measured values are above the detection limit. Statistical values include the range of data from the minimum to the maximum values, the three levels in boxes for 25th, 50th (aka median value), and 75th percentiles, and the filled circles for mean values. Box-and-whisker in red dot-dash is for all AMS sampling points including negative values, and in red solid is for sampling points when AMS values exceeded detection limit (DL).

1151

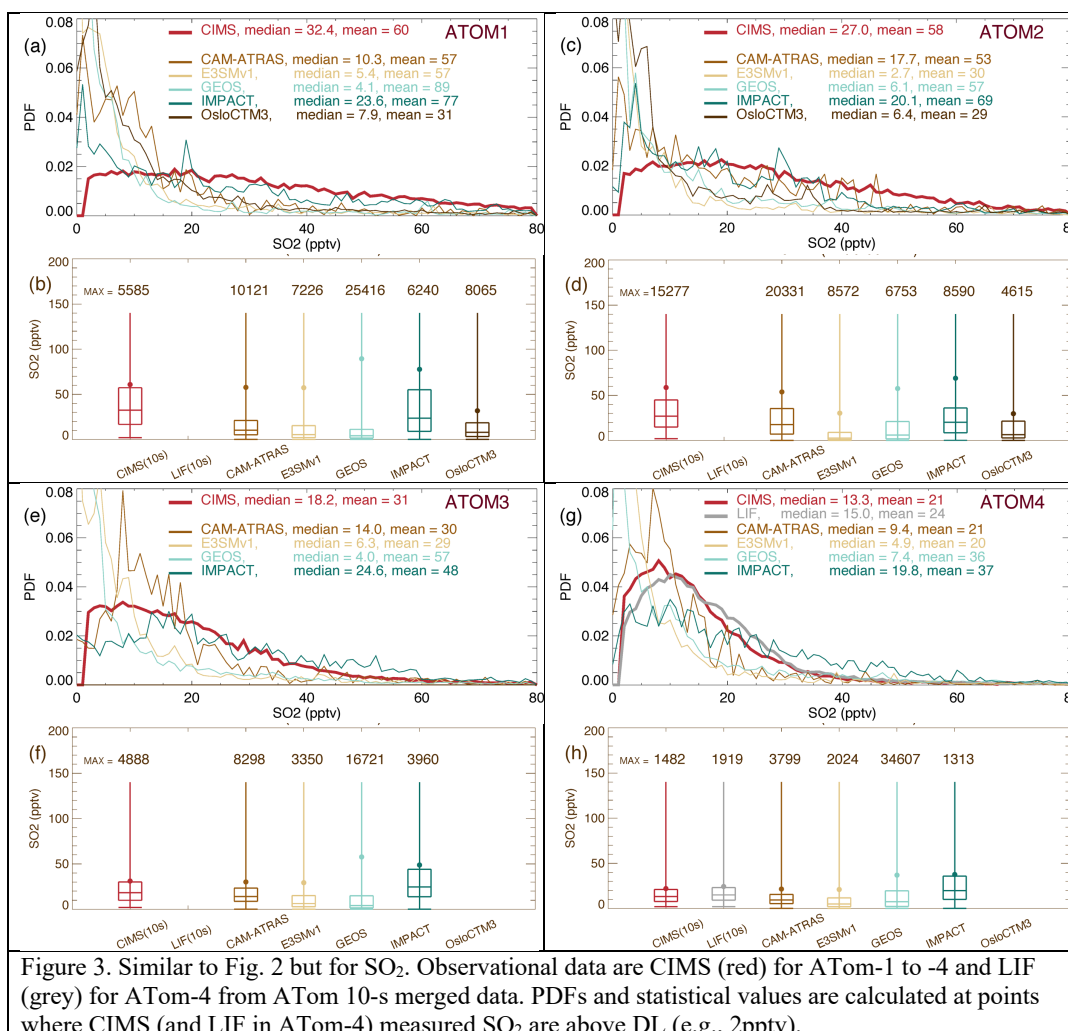



Figure 3. Similar to Fig. 2 but for SO₂. Observational data are CIMS (red) for ATom-1 to -4 and LIF (grey) for ATom-4 from ATom 10-s merged data. PDFs and statistical values are calculated at points where CIMS (and LIF in ATom-4) measured SO₂ are above DL (e.g., 2pptv).

1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163

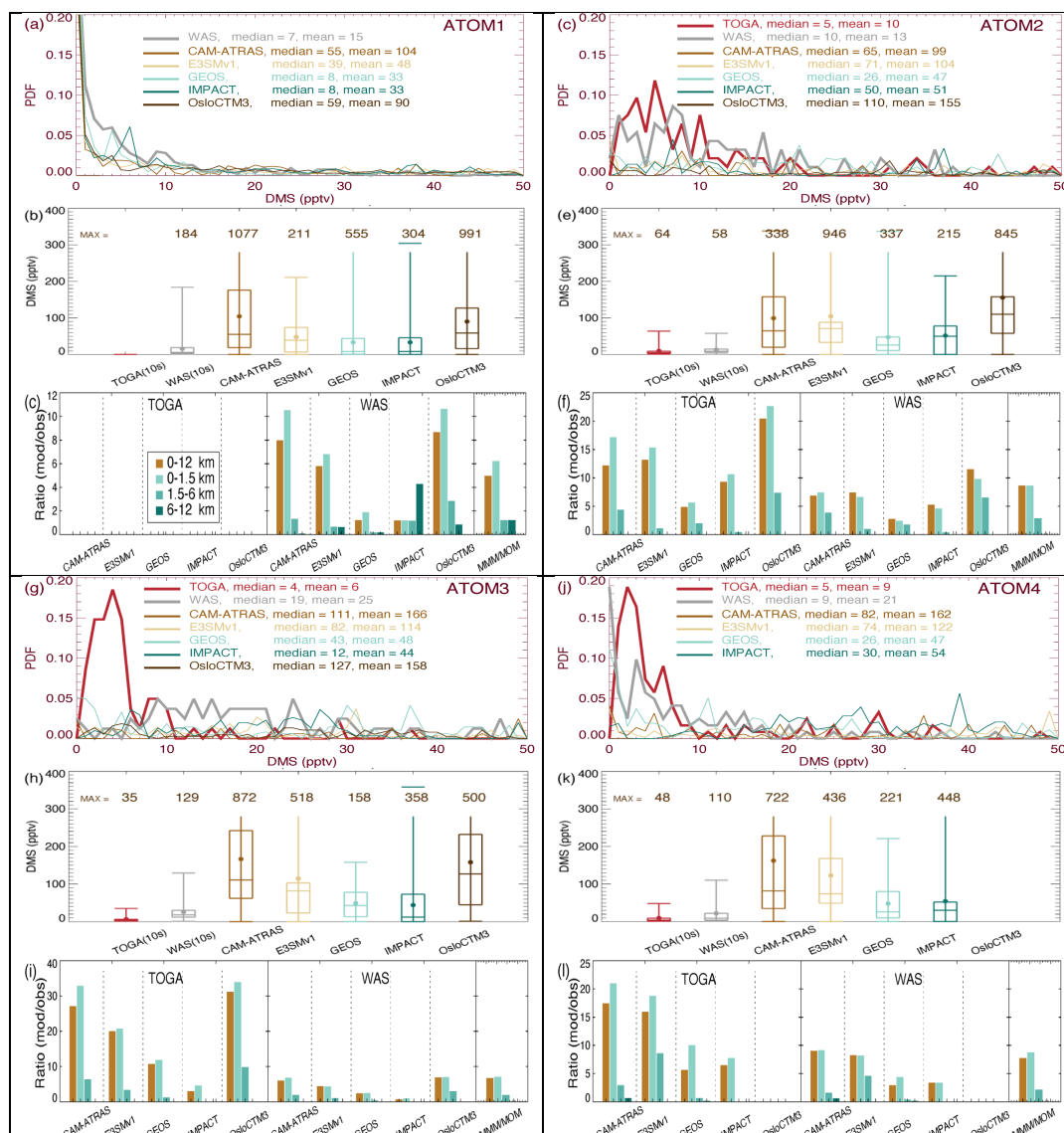



Figure 4. Similar to Fig. 2 but for DMS for ATom-1 (a,b), ATom-2 (d,e), ATom-3 (g,h), and ATom-4 (j,k). (c, f, i, and l) Ratio of DMS median values between model simulation and observation for four ATom deployments. Ratio analyses are performed on four vertical ranges as shown in four colors (see legend in (c)). The last column "MMM/MOM" refers to multi-model median to multi-observation median. The original data reported by TOGA and by WAS have also been converted to 10-s frequency. Data included in PDF and statistical analysis are on 10-s points where DMS measured by both TAGO and WAS are above DL (i.e., 1 pptv).

1164
1165

Figure 5. Observed and modeled vertical profiles of SO$_4$ in 1-km vertical bins averaged for four ATom deployments (lines) and variation across the four AToms (shaded area for measurements and horizontal bars for simulations). ATom measurements are shown in black (AMS) and light grey (PALMS) while model results are shown in other colors. Comparisons are conducted only when both observational measurements above detect limitation are available. Comparisons are separated into five latitude bands from the northern to the southern hemisphere, and into Pacific and Atlantic Basins.

1166
1167
1168
1169
1170
1171

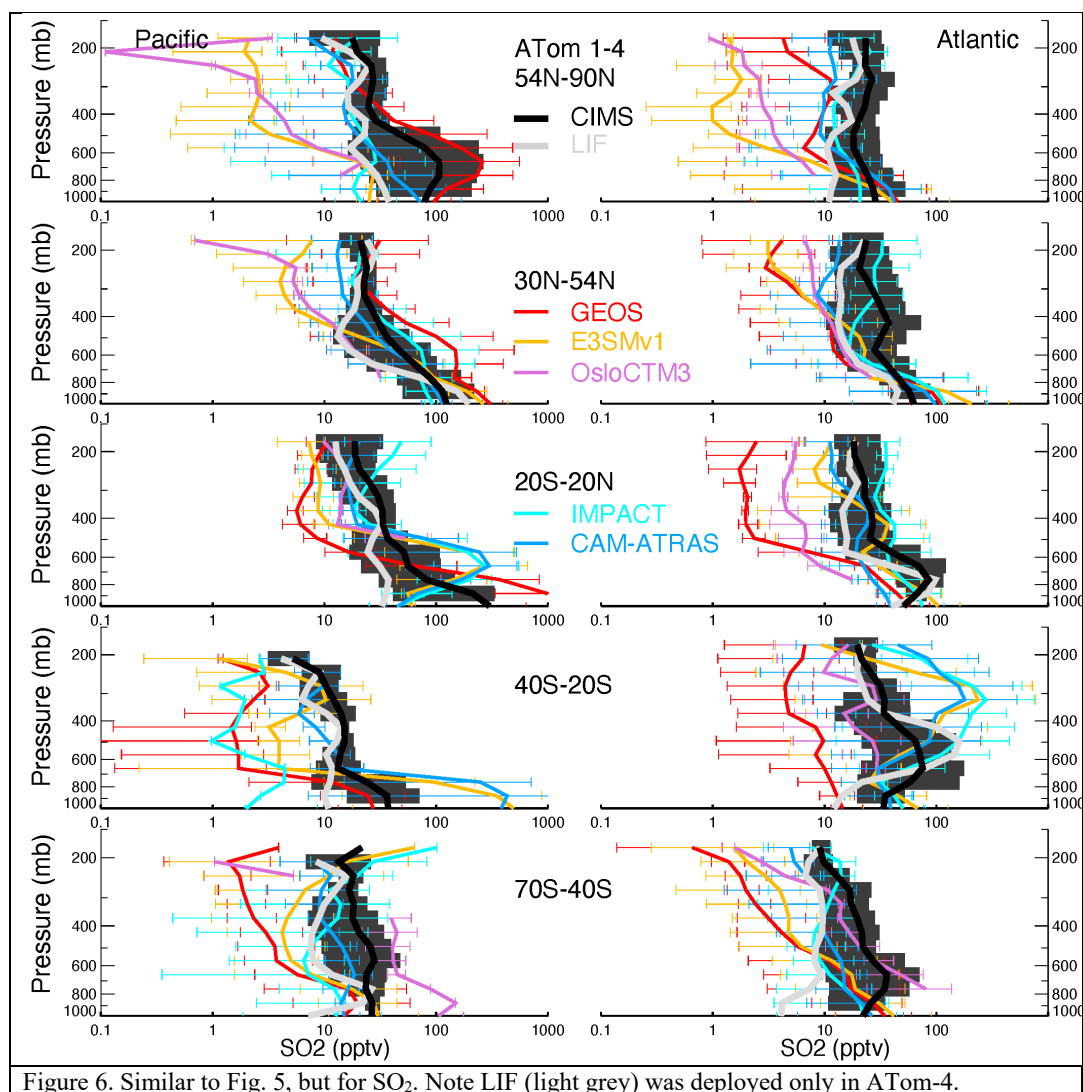



Figure 6. Similar to Fig. 5, but for SO$_2$. Note LIF (light grey) was deployed only in ATom-4.

1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182

Figure 7. Similar to Fig. 5, but for DMS.

1183
1184
1185
1186

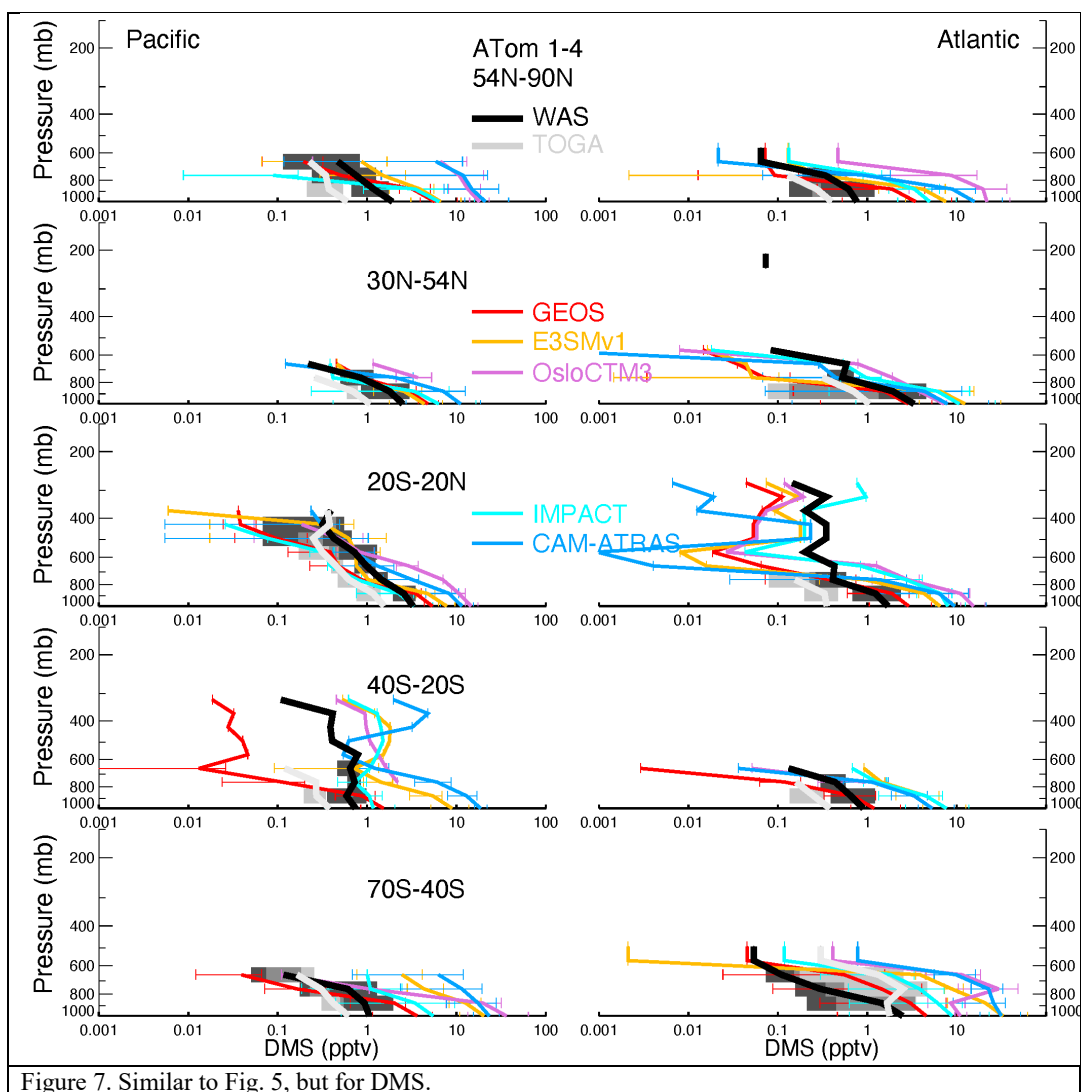
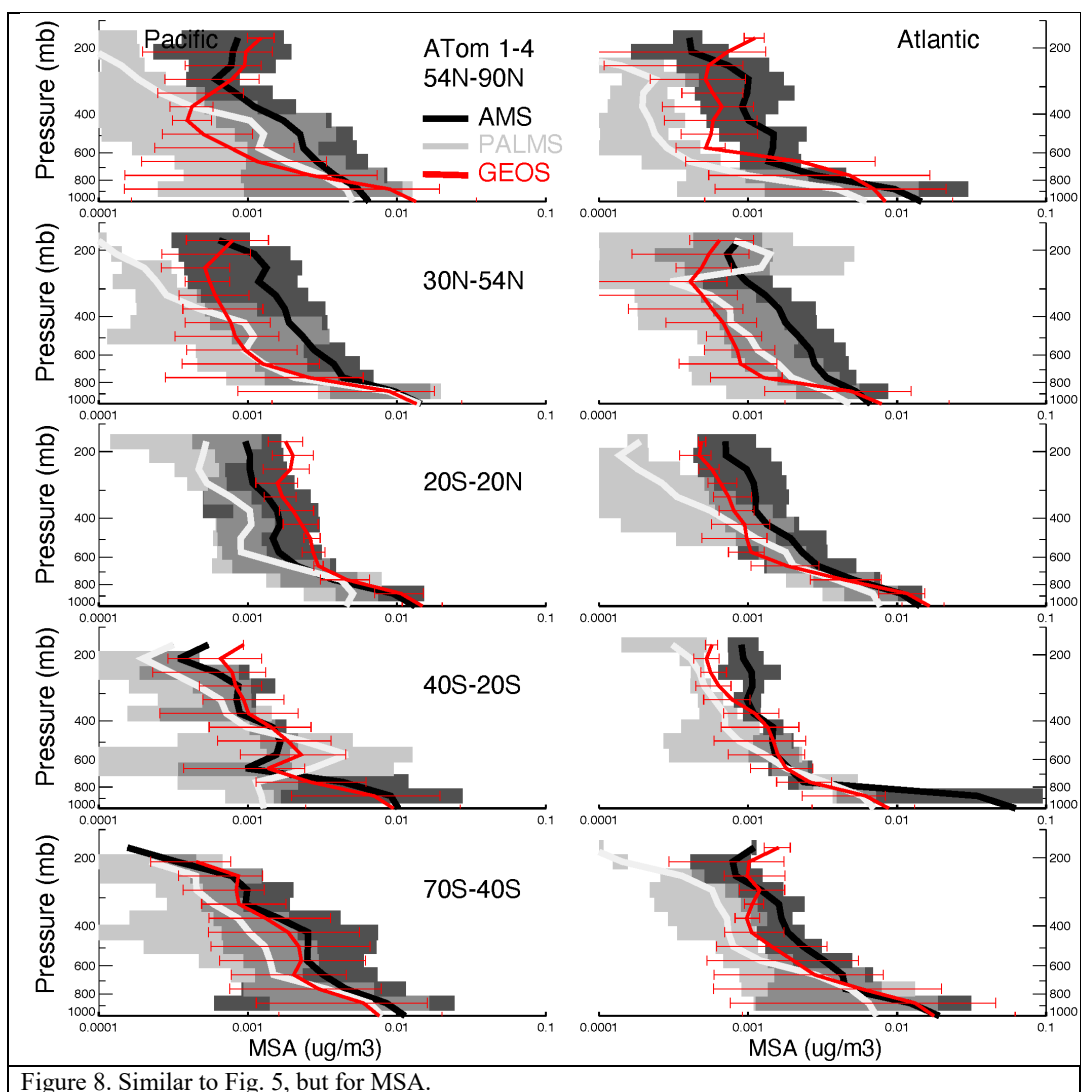
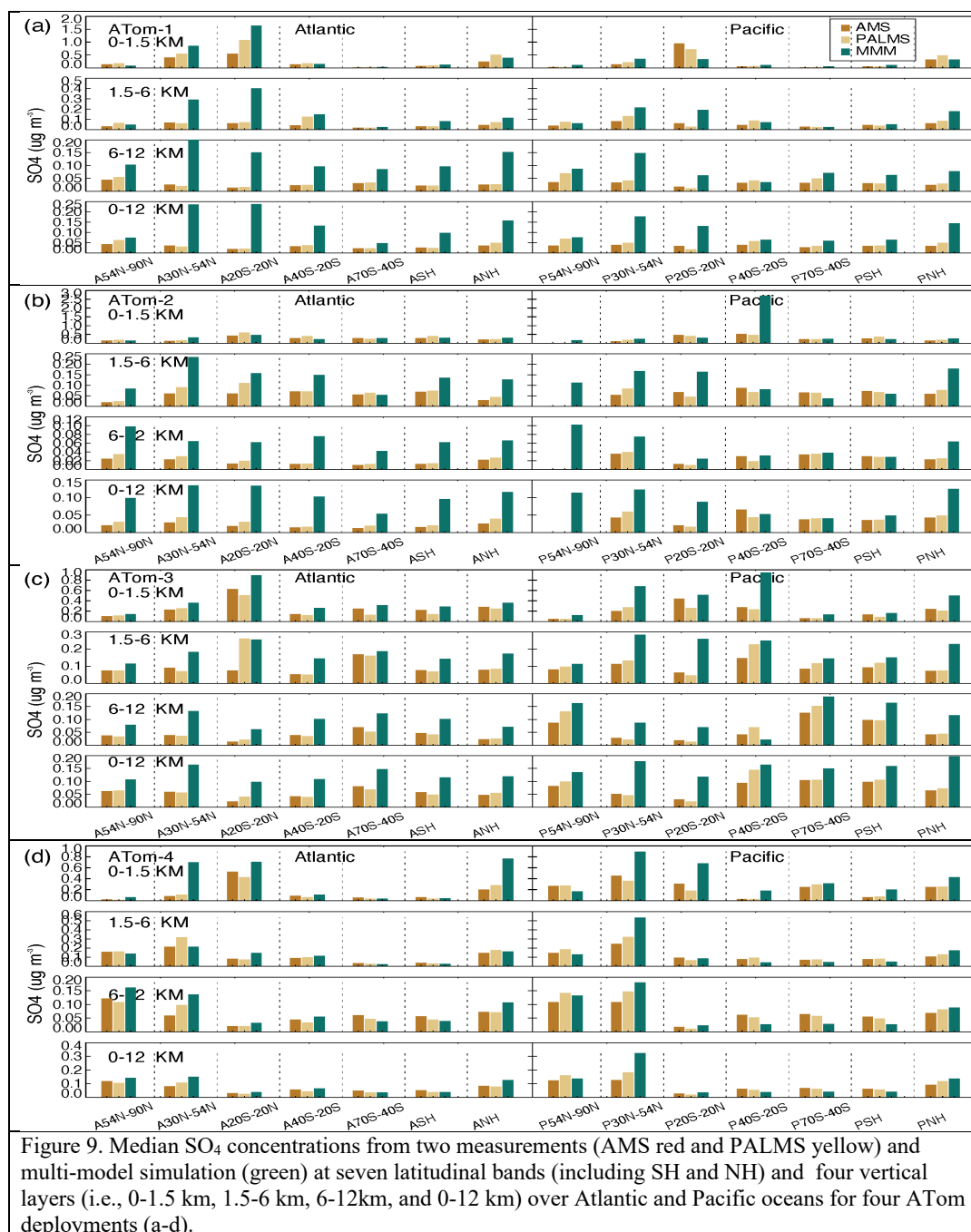
Figure 8. Similar to Fig. 5, but for MSA.

1187
1188
1189
1190
1191
1192
1193

Figure 9. Median SO$_4$ concentrations from two measurements (AMS red and PALMS yellow) and multi-model simulation (green) at seven latitudinal bands (including SH and NH) and four vertical layers (i.e., 0-1.5 km, 1.5-6 km, 6-12km, and 0-12 km) over Atlantic and Pacific oceans for four ATom deployments (a-d).

1194
1195
1196

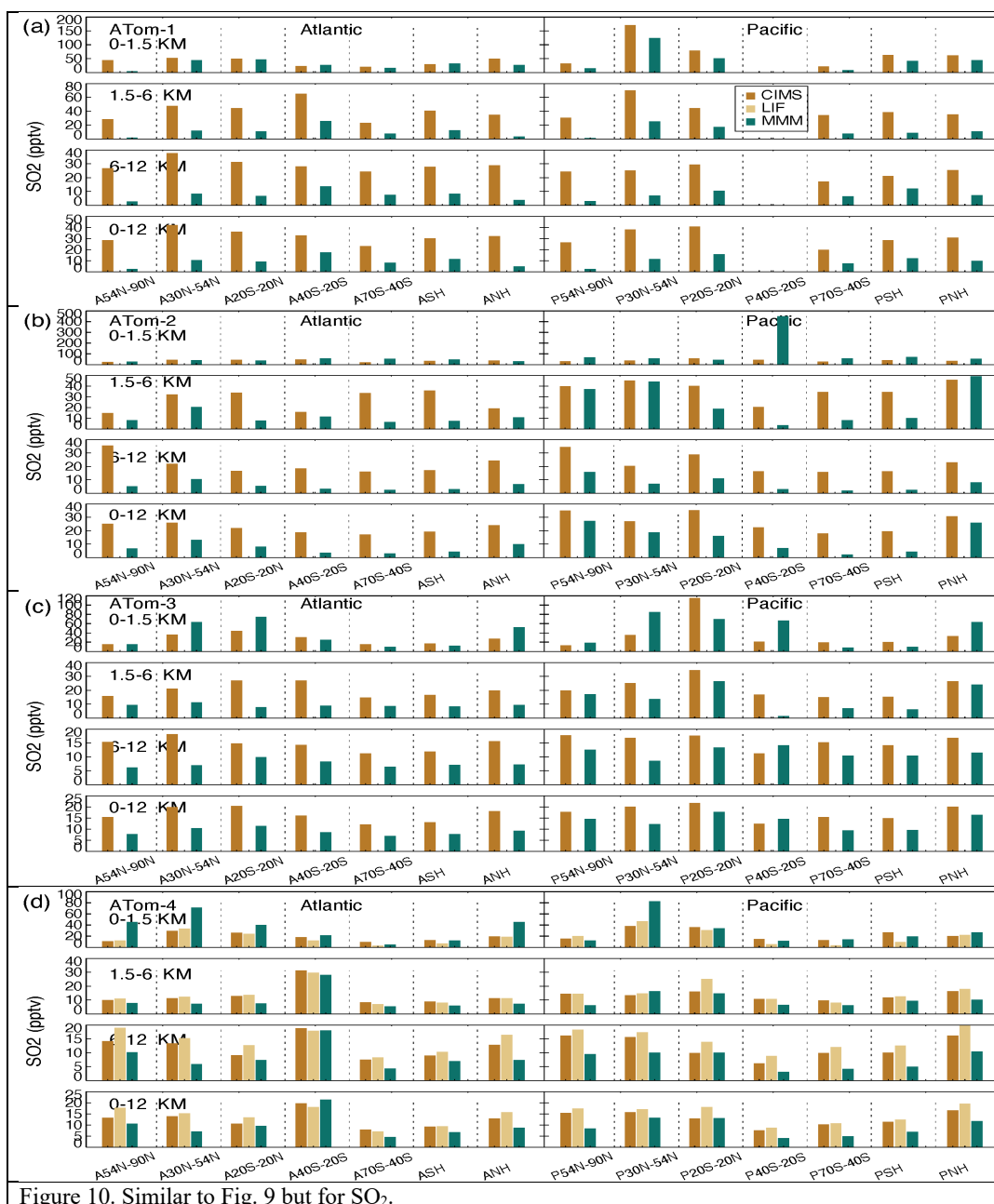



Figure 10. Similar to Fig. 9 but for SO$_2$.

1197
1198
1199
1200
1201

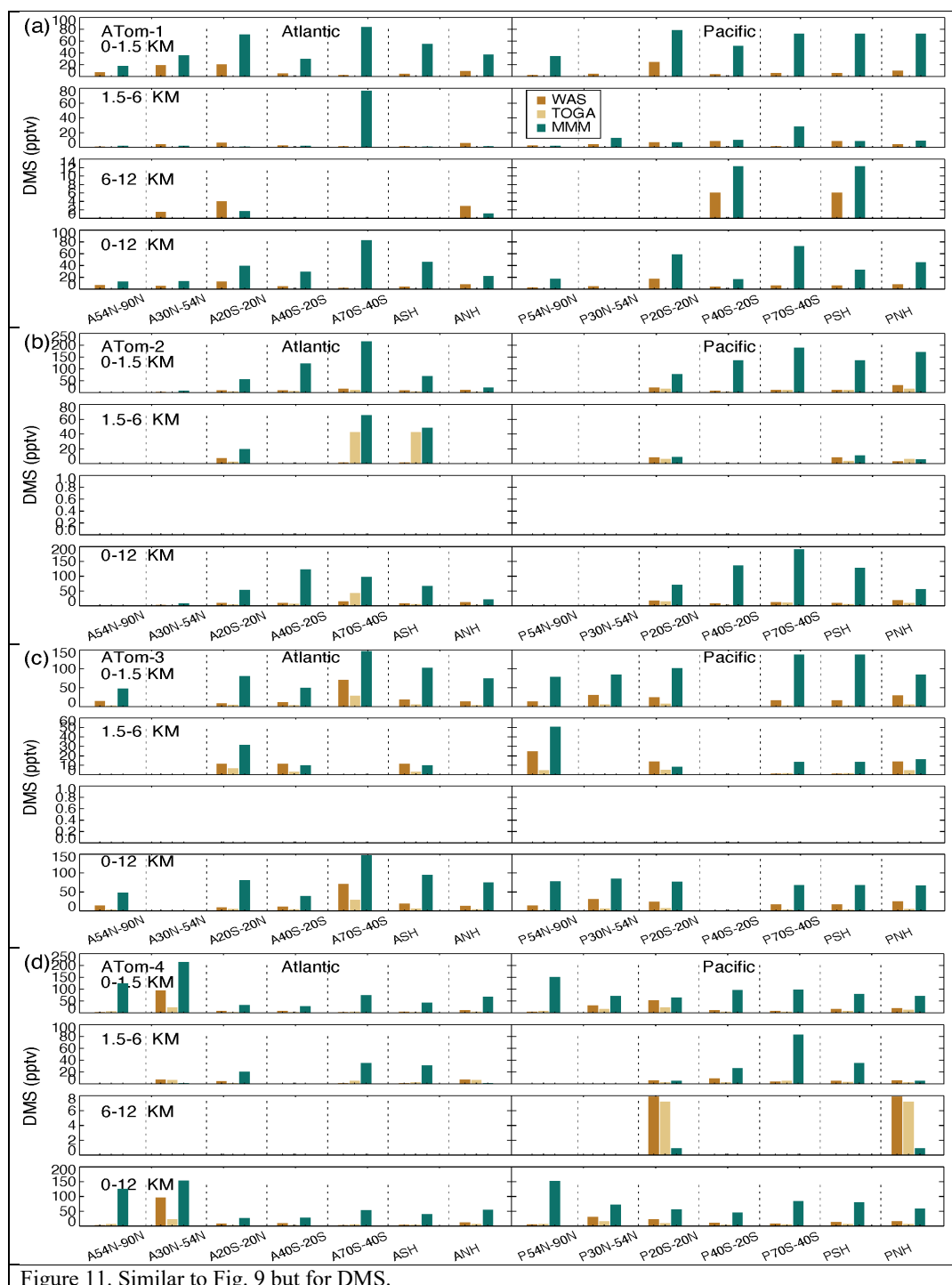



Figure 11. Similar to Fig. 9 but for DMS.

1202

Figure 12. Deviation from multi-model mean for key budget items in sulfur study include DMS emission, SO$_2$ emission, sulfate source or total deposition, sulfate lifetime, and total sulfate atmospheric mass load.

Figure 13. Source origins in percentage (%) for aerosol SO$_4$ along flight tracks (a) and for a wide oceanic area (b) based on the results from GEOS. Source origins are identified as anthropogenic (AN), biomass burning (BB), volcanic (VOL), and oceanic (OCN). Ocean basins include shaded region shown in Fig. 1.