Supplement of Atmos. Chem. Phys., 24, 1717–1741, 2024
https://doi.org/10.5194/acp-24-1717-2024-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

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

Huisheng Bian et al.

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

Supplementary Material

SO_4 PDF distributions observed from AMS data at three sampling intervals (i.e., 1-s, 60-s, and 10-s) are shown in Fig. S1. The 10-s merged dataset were deliberately provided by the ATom observation team for integrating data from various instruments to a unified temporal resolution. We use this dataset for investigation on regional and seasonal bases. Before applying it, however, we first evaluate the quality of the 10-s data. Previous studies (Hodzic et al., 2020) indicated measurement precision improved with the square root of the number of sampling points. In other words, averaging data over a 60-s interval is better than averaging over 1-s or 10-s intervals because there are more sample points in a 60-s interval. This also applies to the detection limit (DL) as it is just 3 times the precision. DL flags are assigned to convey semi-quantitative information when sampling conditions are beyond the instrument detection range and the measurements are not quantifiable. Despite the differences, the three PDFs of AMS SO_4 (red, using all relevant data including negatives) are nearly identical. Statistical analyses were further performed on the AMS 60-s, 10-s, and 1-s data sets by (1) all sampling points, even negative values, as indicated by the dot-dash box-and-whisker (approach 1), and (2) sampling points when their values exceeded DL as shown by solid box-and-whisker (approach 2). The SO_4 median (and mean) values of 60-s are closer to 10-s' but lesser than 1-s' by 0-10% in approach 1. There is slightly greater diversity (~30%, solid box-and-whisker) between these statistical values in approach 2, and the data in 60-s and 10-s are also relatively close, with a difference less than ~20%. These comparisons of the PDFs with noise and signal tell us that, on average, SO_4 is high enough in the ATom background to be unaffected by noise at any resolution. A similar analysis (not shown here) of SO_2 and DMS measurements also showed agreement between the 10-s interval dataset and the original dataset. Thus, the use of the 10-s data is acceptable in our study, given the significant differences in tracer statistics between model simulations and between model and observation.

We further analyze observations and simulations, similar to Figs. 2–4, but include all measurements of SO_4, SO_2, and DMS in Figs. S2–4, respectively. Specifically, the negative values measured by AMS, CIMS, and LIF were included. Of course, the observed median and mean values (Table S2) dropped substantially, by 17% and 13% for SO_4, and by 34% and 34% for SO_2. However, the model statistics (Table S2) vary relatively small, 4% and 13% for SO_4 and 12% and 15% for SO_2.

DMS measurement is unique because it has a fraction of measured values in "-888". An instrument typically has an operational detection range, which is defined by the lower limit of detection (LDL) and upper limit of detection (UDL). The flag for measured value less than the LDL is "-888" for TOGA and WAS data is examined in Fig. S4. The number of "-888" is not meaningless. It means that we know the value of a given measurement is below a known quantity, but we are not able to quantify that value precisely. Fig. S4 shows a similar DMS PDF analysis as Fig. 4, but instead of excluding the "-888" measurements, these are replaced with "0" as suggested by the instrument PIs. The percentage (P) of the measured "-888" is given for TOGA and WAS measurement data in the figure. These Ps for all AToms range 65% - 91%, which means majority of measured values are below LDL and the medians of both TOGA and WAS data are zero. Correspondingly, from Fig. 4 to Fig. S4, the median value of model DMS decreases from 56.6 pptv to 0.7 pptv while the mean decreases by 76%. The ratio between model mean and observation mean for all AToms in Fig. S4 is 9.1, which is approximately 44% higher than the 6.3 in Fig. 4.

The observed and simulated vertical profiles in each ATom are further shown in Figs. S5-8 to reveal details of seasonal changes. For example, the SO_2 values measured by LIF in Fig. 7 are lower than the average SO_2 values measured by CIMS, but the two SO_2 profiles shown in Fig. S6 in ATom-4 are in good agreement when the LIF was onboard. This means that the SO_2 measured by CIMS during ATom-1 to -3 is higher than the SO_2 measured during ATom-4. A discussion of some seasonal characteristics has been given in main text Sect. 3.2.

Overall model performance has been demonstrated in Figs 10-12. The performance of each model on a regional and seasonal basis is further provided in Figs S9-11 to help modelers identify strengths and weaknesses of the model's sulfur simulations. Also, the mean values shown in the figures add information about extreme pollution. Pollution levels in the model world and the observed world can differ substantially in certain regions of each ATom, and this difference can be caused by the majority of models or a few individual models. Each model performs better or worse than the others at every time and place and examples have been given in the main text.

The mean values of SO_4, SO_2, and DMS are generally higher than the median values at most times and locations, and the ratio of mean-to-median value in the boundary layer (BL) is even greater than that in the free troposphere. Sometimes the ratio is very high (e.g., > 10), which means that extreme contamination has been identified.

Table S1. Median and mean values (calculated when measured values are above the detection limit) of measurements and simulations during four ATom deployments.

	ATom-1		ATom-2		ATom-3		ATom-4	
	median	mean	median	mean	median	mean	median	mean
SO4 (ng sm^{-3})								
AMS	98	205	115	215	142	228	255	311
PALMS	121	323	128	296	139	300	244	340
CAM-ATRAS	131	468	92	207	74	330	208	298
E3SMv1	427	576	215	286	246	405	268	433
GEOS	68	199	50	111	58	148	120	240
IMPACT	701	800	461	586	461	642	612	701
OsloCTM3	650	644	548	586	509	542	–	–
SO2 (pptv)								
CIMS	32.4	60	27.0	58	18.2	31	13.3	21
LIF	–	–	–	–	–	–	15.0	24
CAM-ATRAS	10.3	57	17.7	53	14.0	30	9.4	21
E3SMv1	5.4	57	2.7	30	6.3	29	4.9	20
GEOS	4.1	89	6.1	57	4.0	57	7.4	36
IMPACT	23.6	77	20.1	69	24.6	48	19.8	37

OsloCTM3	7.9	31	6.4	29	–	–	–	–
DMS (pptv)								
TOGA	–	–	5	10	4	6	5	9
WAS	7	15	10	13	19	25	9	21
CAM-ATRAS	55	104	65	99	111	166	82	162
E3SMv1	39	48	71	104	82	114	82	162
GEOS	8	33	26	47	43	48	74	122
IMPACT	8	33	50	51	12	44	26	47
OsloCTM3	59	90	110	155	127	158	30	54

Table S2. Similar to Table S1 but median and mean values calculated as long as the measurements are available even the values are negative.

	ATom-1		ATom-2		ATom-3		ATom-4	
	median	mean	median	mean	median	mean	median	mean
SO4 (ng sm^{-3})								
AMS	88	190	94	183	120	201	193	257
PALMS	106	298	105	257	119	268	185	283
CAM-ATRAS	131	492	88	196	74	306	183	283
E3SMv1	419	579	299	279	241	389	241	403
GEOS	66	196	48	111	57	142	116	223
IMPACT	691	558	452	366	458	485	530	464
OsloCTM3	650	610	543	557	506	524	–	–
SO2 (pptv)								
CIMS	16.1	33	20.2	43	10.6	17	10.5	17
LIF							11.7	19
CAM-ATRAS	10.3	47	16.8	60	13.5	33	8.8	20
E3SMv1	5.3	46	2.6	34	6.2	30	4.8	19
GEOS	4.1	62	6.1	55	3.9	47	6.3	32
IMPACT	23.8	70	20.5	75	23.3	48	16.9	33
OsloCTM3	7.6	26	6.4	30	–	–	–	–
DMS (pptv)								
TOGA	–	–	0.00	1.49	0.00	0.60	0.00	1.40
WAS	0.00	3.57	0.00	1.63	0.00	2.91	0.00	2.67
CAM-ATRAS	0.28	32.29	1.17	25.22	0.98	24.33	0.36	34.84
E3SMv1	0.02	12.12	0.14	15.68	0.47	17.67	0.20	28.71
GEOS	0.02	7.32	0.11	11.60	0.07	5.74	0.03	7.53
IMPACT	0.26	8.18	1.95	14.05	1.83	10.11	0.76	12.00
OsloCTM3	0.52	22.58	2.39	62.71	2.03	29.47	–	–

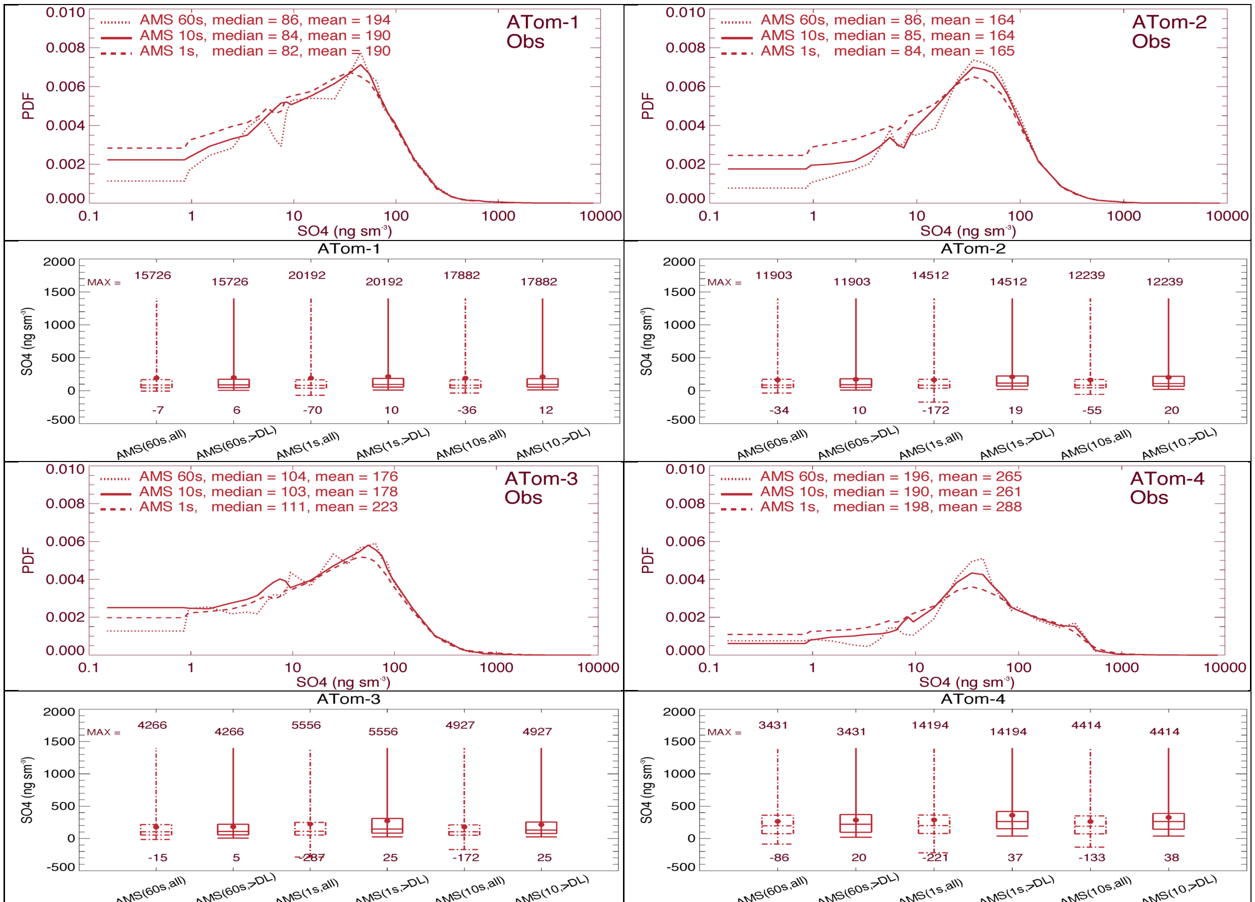

Figure S1. SO_4 PDF distributions reported in three-time frequencies (1-s, 10-s, and 60-s) for four ATom deployments. Statistical values shown in dashed box-and-whisker include all reported data, while in the solid box-and-whisker include data above detection limit (DL). Statistics give the range of data from the minimum to the maximum values, the three levels of 25th, 50th (aka median value), and 75th percentiles in the box, and the mean values (filled circles).

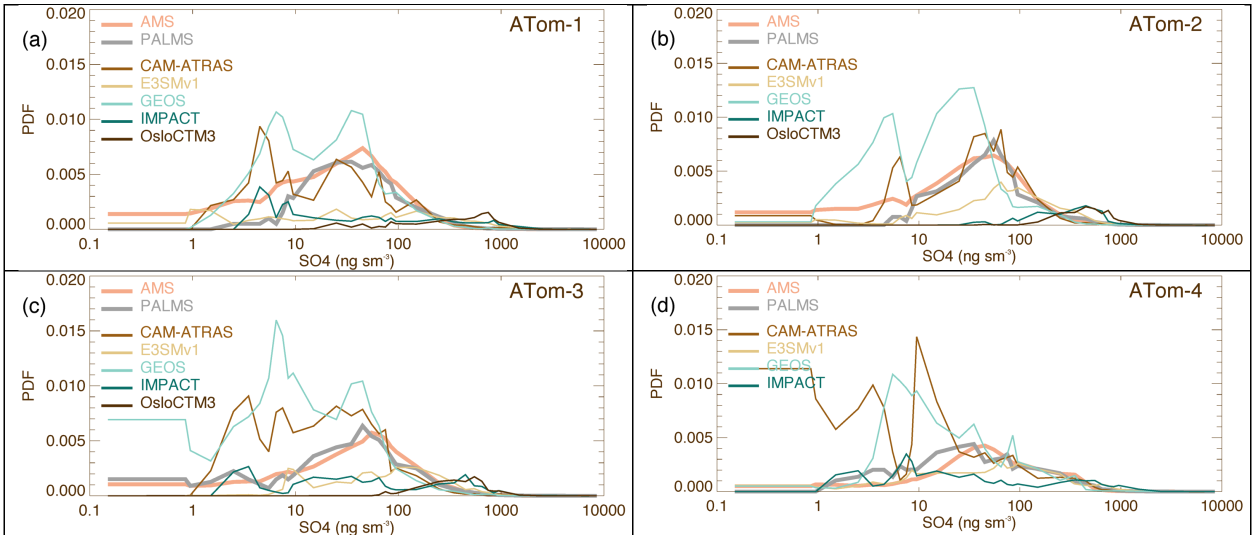

Figure S2. Similar to Fig. 2 but the median/mean values are calculated as long as the measurements are available even the values are negative.

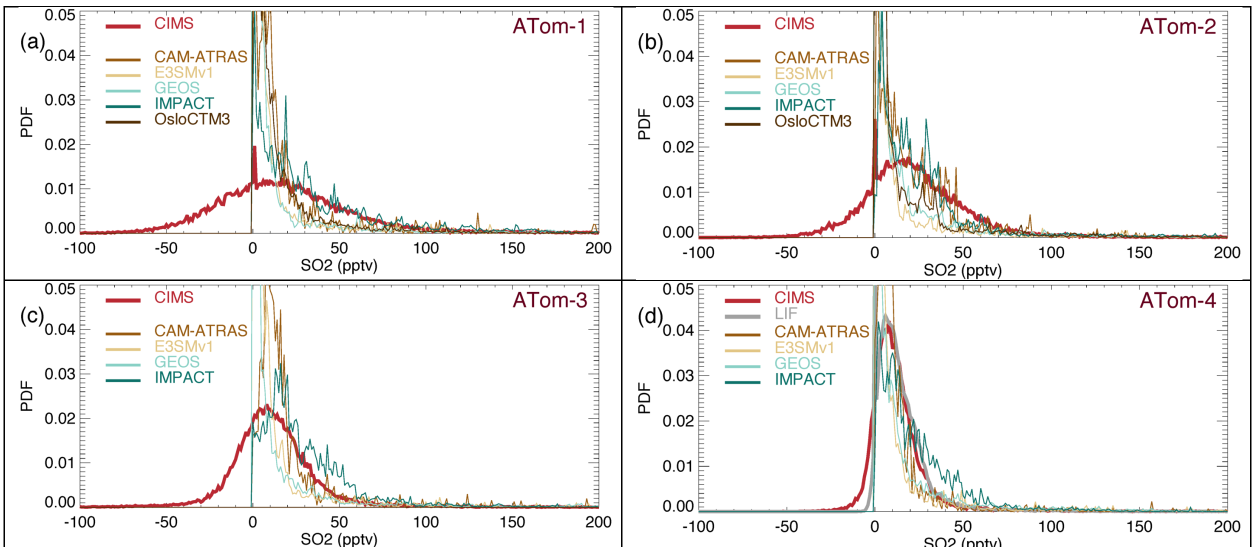

Figure S3. Similar to Fig. 3, but the median/mean values are calculated as long as the measurements are available even the values are negative.

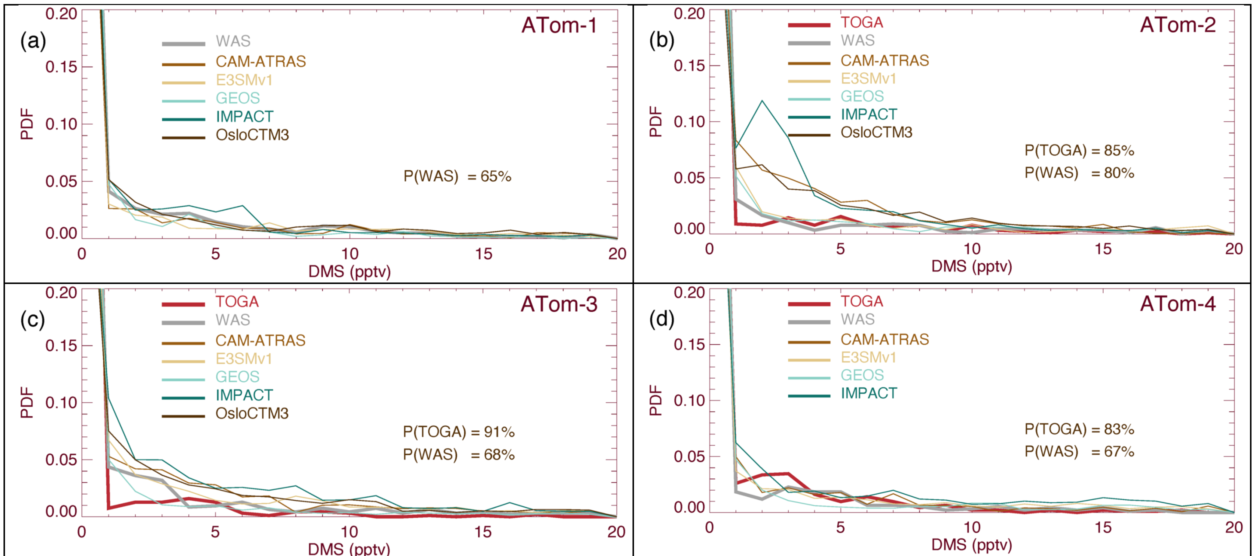

Figure S4. Similar to Fig. 4, but instead of excluding the "-888" measurements, these are replaced with 0 as suggested by the instrument PIs. The percentage (P) of the measured "-888" is given for TOGA and WAS measurement data. Model median/mean values are calculated when measurements including these "-888" are available.

93

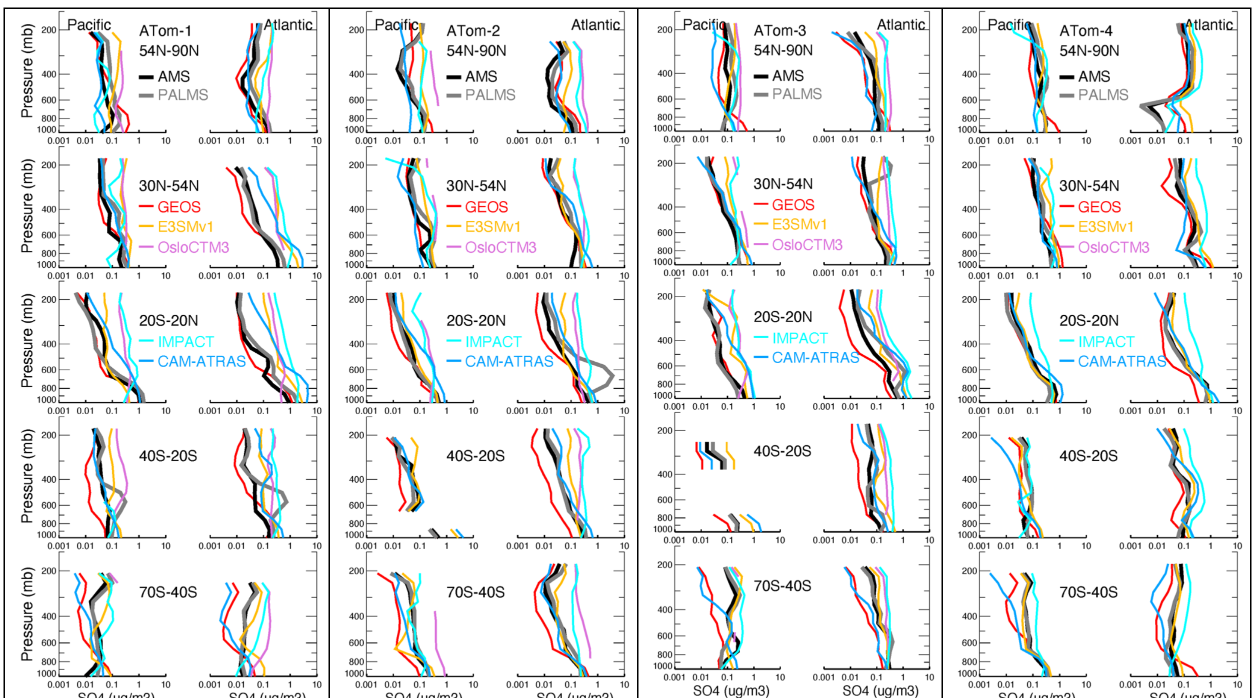

Figure S5. Observed and modeled vertical profiles of SO_4 in 1-km vertical bins for four ATom deployments shown from left to right. ATom measurements are shown in black and grey lines while model results are shown in color lines. Comparisons are conducted only when both observational measurements above detect limitation are available. Comparisons are separated into five latitude bands from the Northern to the Southern Hemisphere, and into Pacific and Atlantic Basins.

94

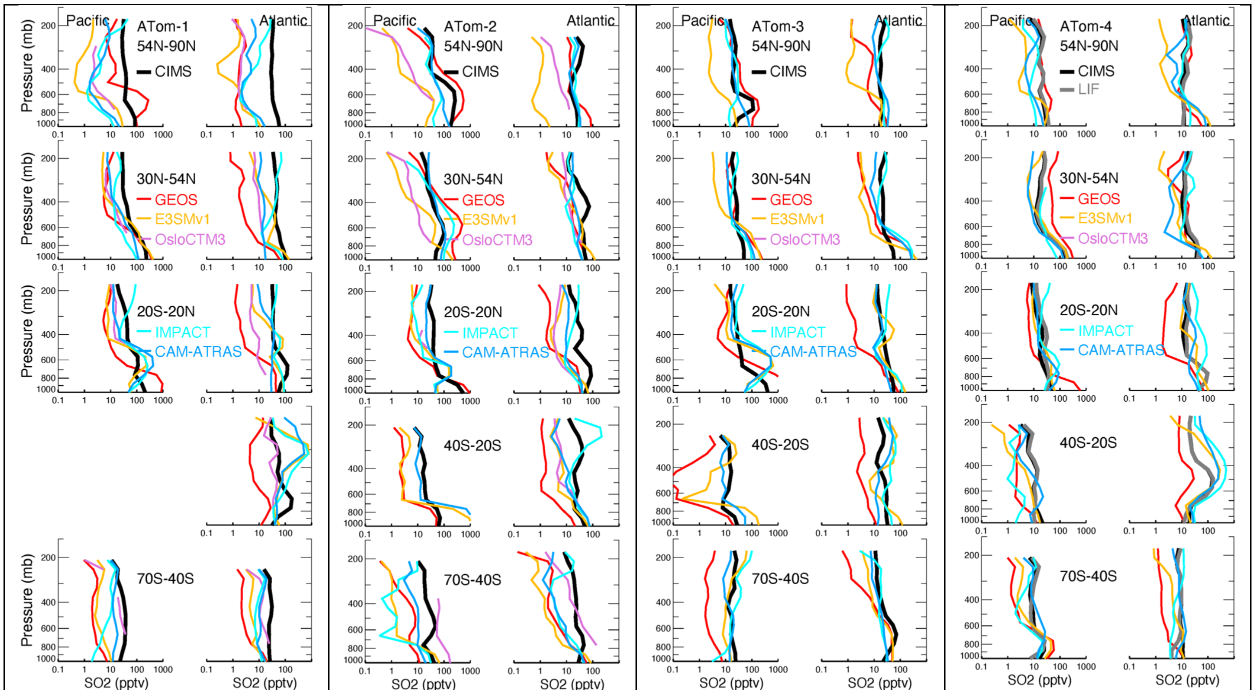

Figure S6. Similar to Fig. S5 but for SO_2.

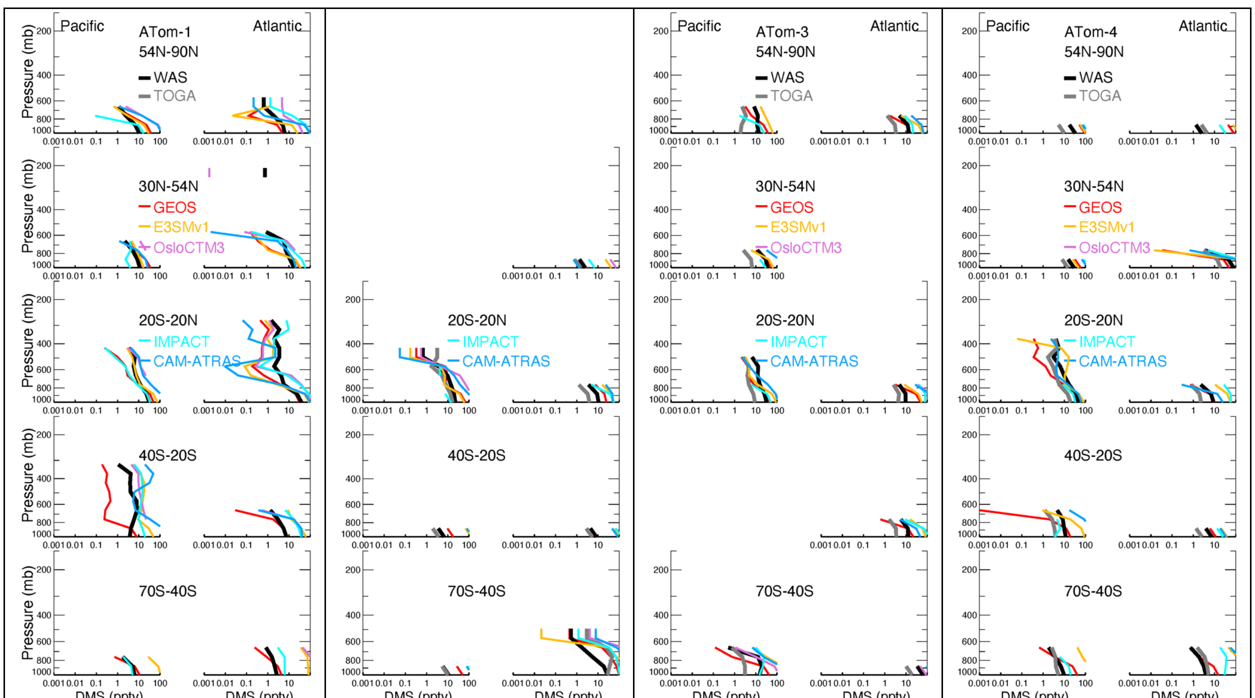

Figure S7. Similar to Fig. S5 but for DMS.

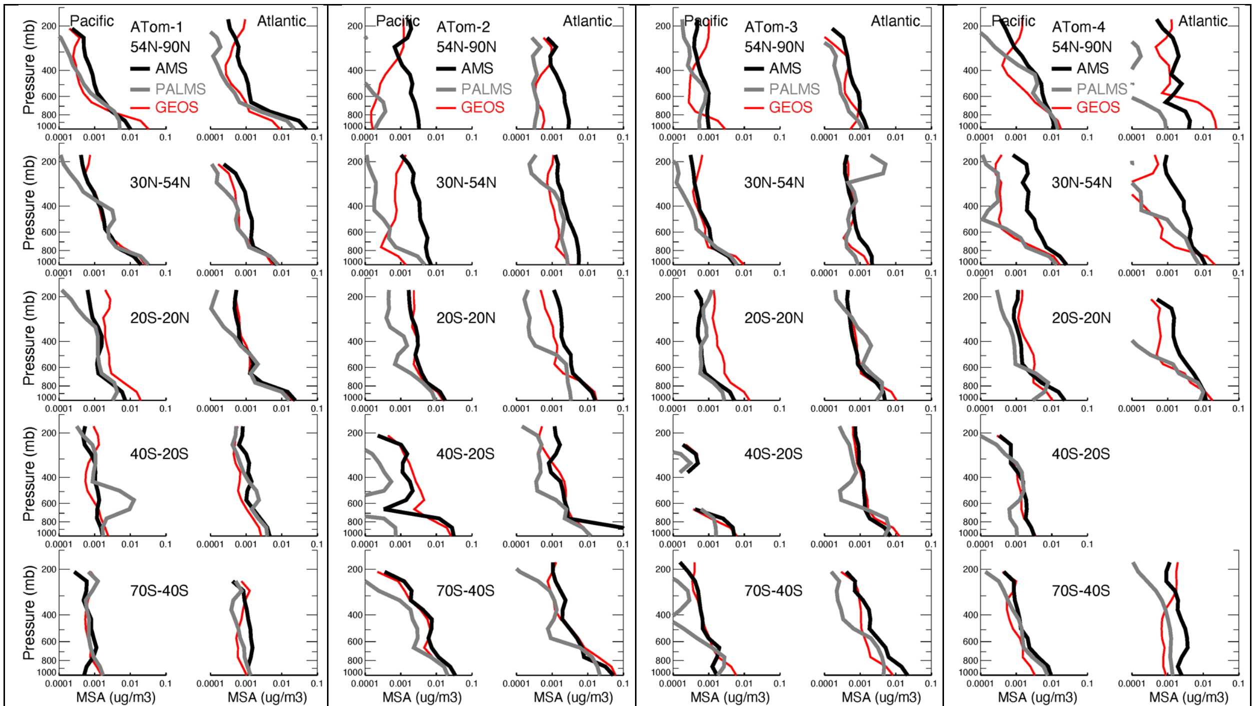

Figure S8. Similar to Fig. S5 but for MSA.

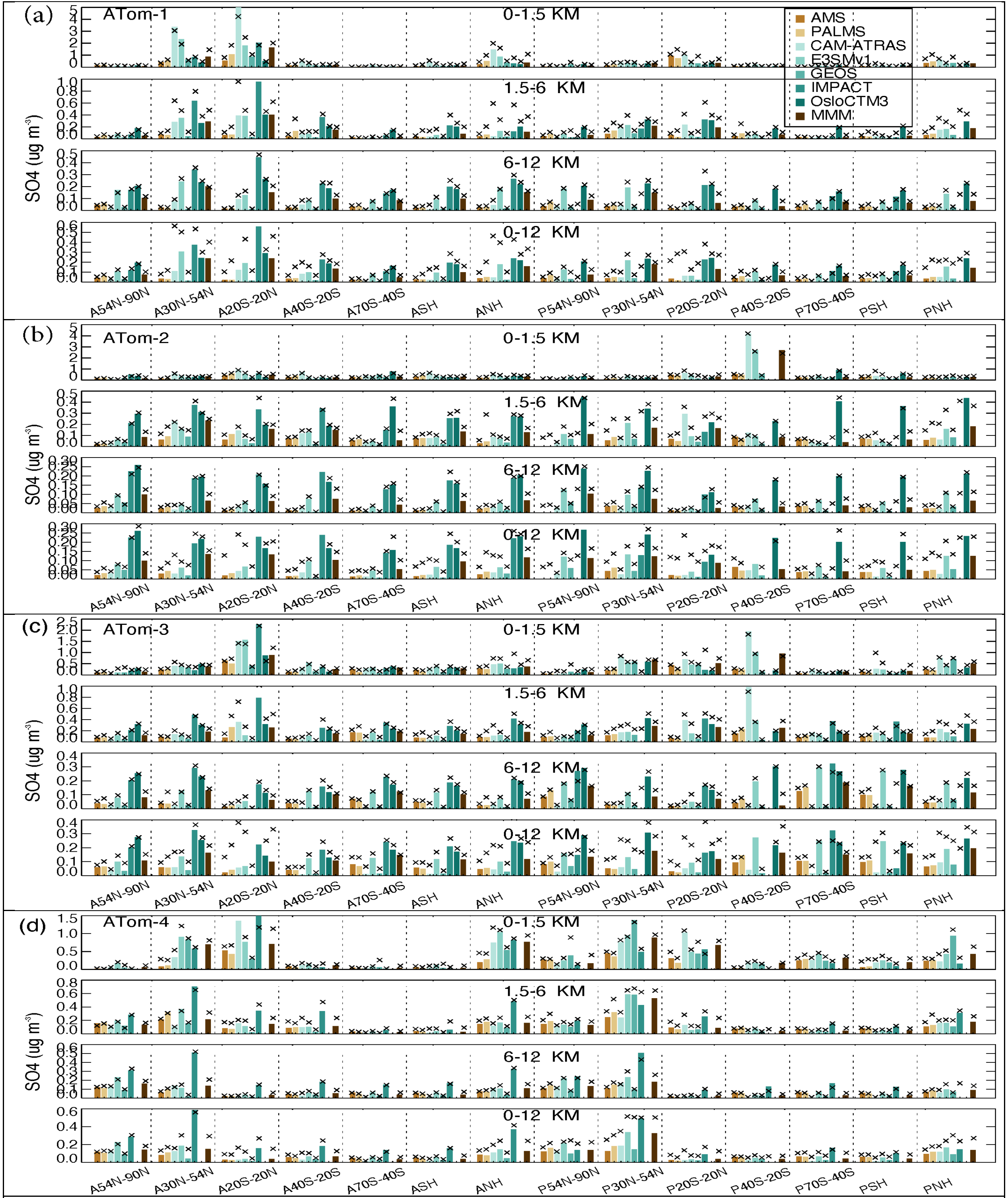

Figure S9. Median (histogram) and mean (symbol x) values of SO_4 from two measurements (orange and yellow), five model simulations (other bluish colors), and multi-model simulation (black) analyzed over five latitudinal bands and SH and NH over Atlantic and Pacific oceans in four vertical layers (i.e., 0-1.5 km, 1.5-6 km, 6-12km, and 0-12 km) for four ATom deployments (a-d).

124

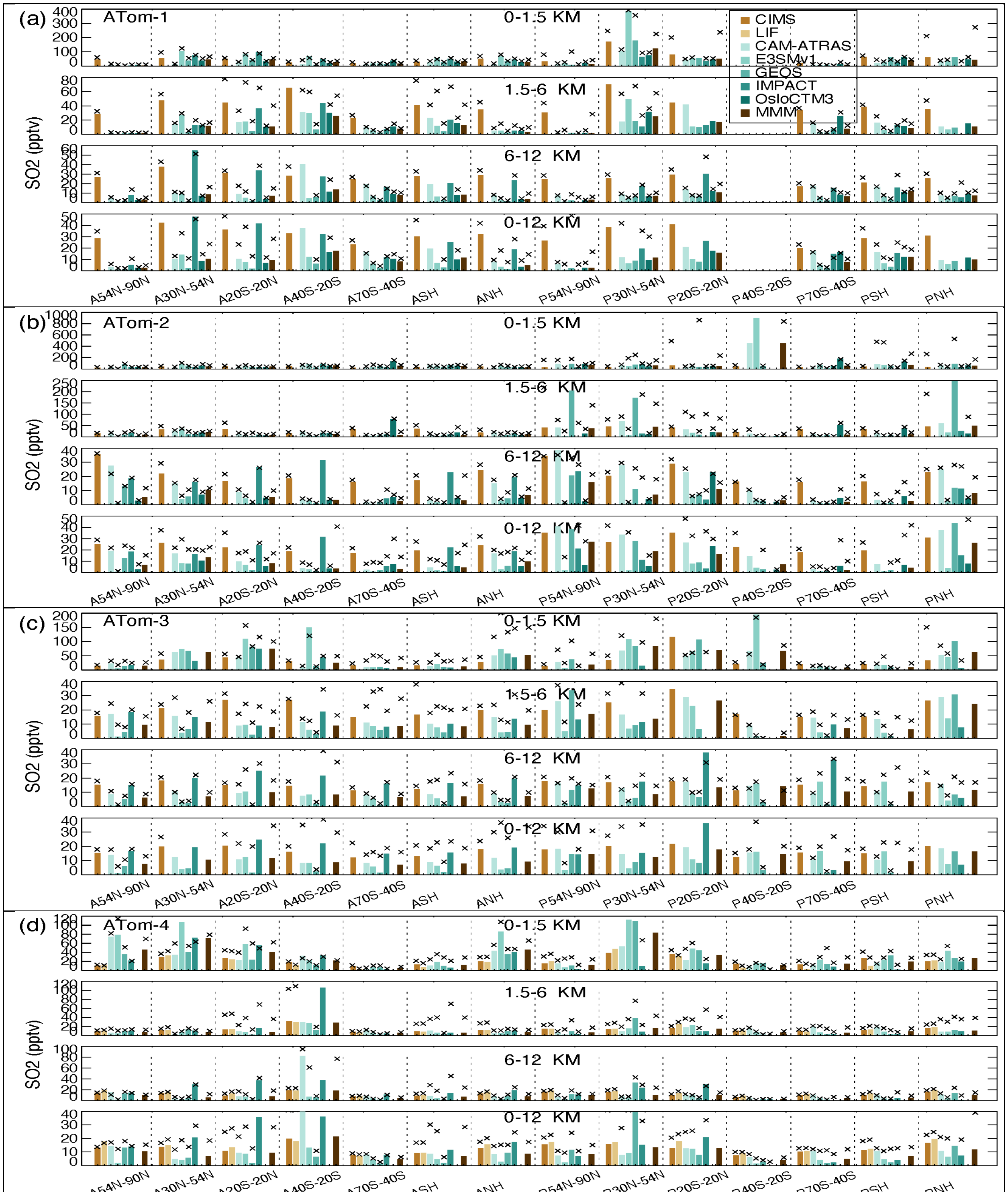

Figure S10. Similar to Fig. S9 but for SO_2.

125

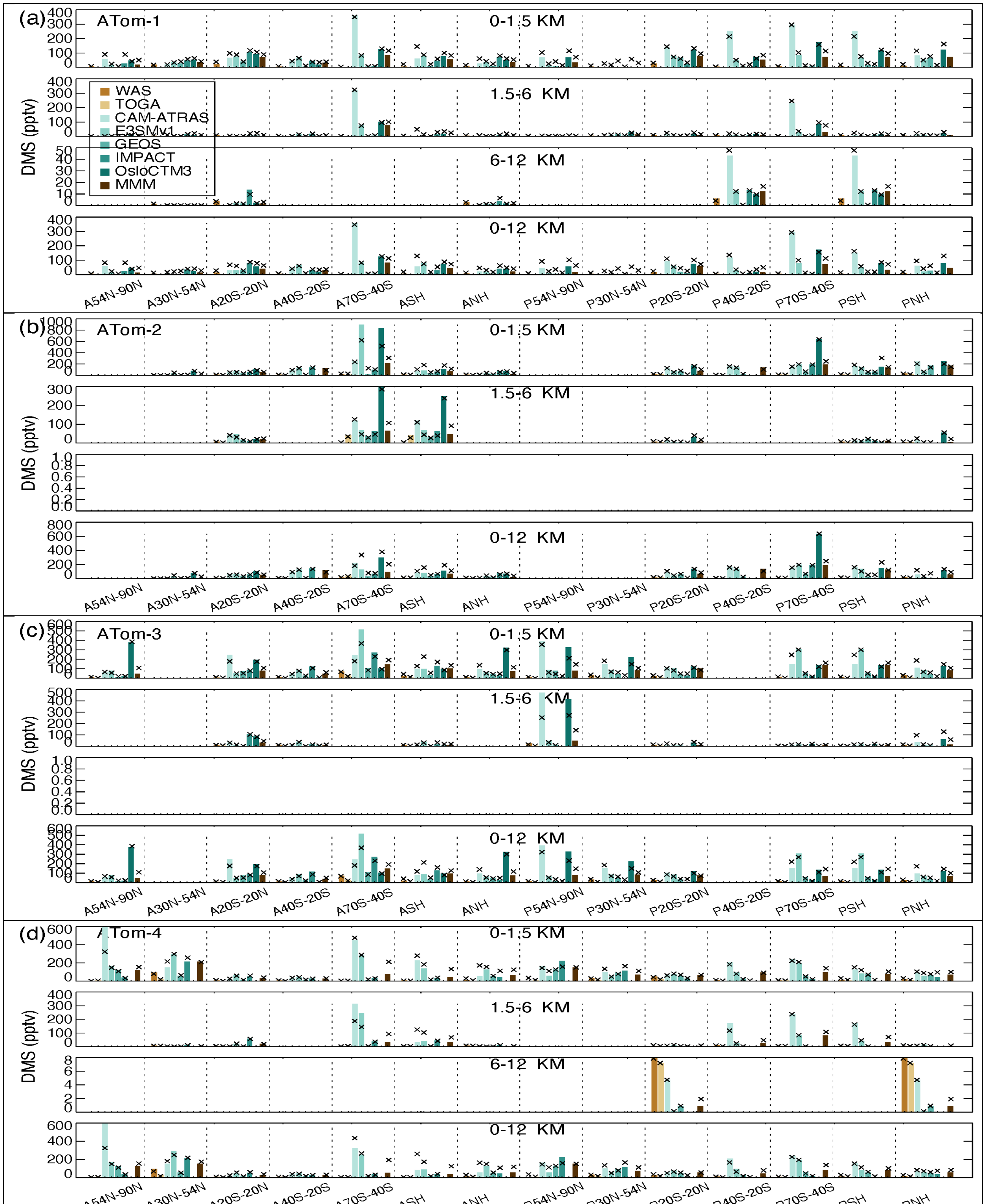

Figure S11. Similar to Fig. S9 but for DMS.