

Response to the Referee #2:

This study investigates the degassing volcanic SO₂ emissions to global sulfur budgets using a Hemispheric CMAQ. The sensitivity simulations were conducted with and without the volcanic SO₂ emissions. The model simulations have been verified by the surface sulfate measurements during 2010 around the world. This study indicated that the degassing volcanic SO₂ emissions are an important source impacting airborne sulfur budgets and should be considered in air quality model simulations assessing background sulfate levels and their source attribution. Overall, this is a nice piece of paper with clear objectives and methods. Before considering publication in ACP, major revisions should be made. Some comments and suggestions are listed as follows:

Reply:

We thank the reviewer for the overall positive assessment of the manuscript and appreciate the constructive comments, addressing which have helped improve the manuscript. Detailed below is our responses to specific comments by the reviewer.

Specific comment:

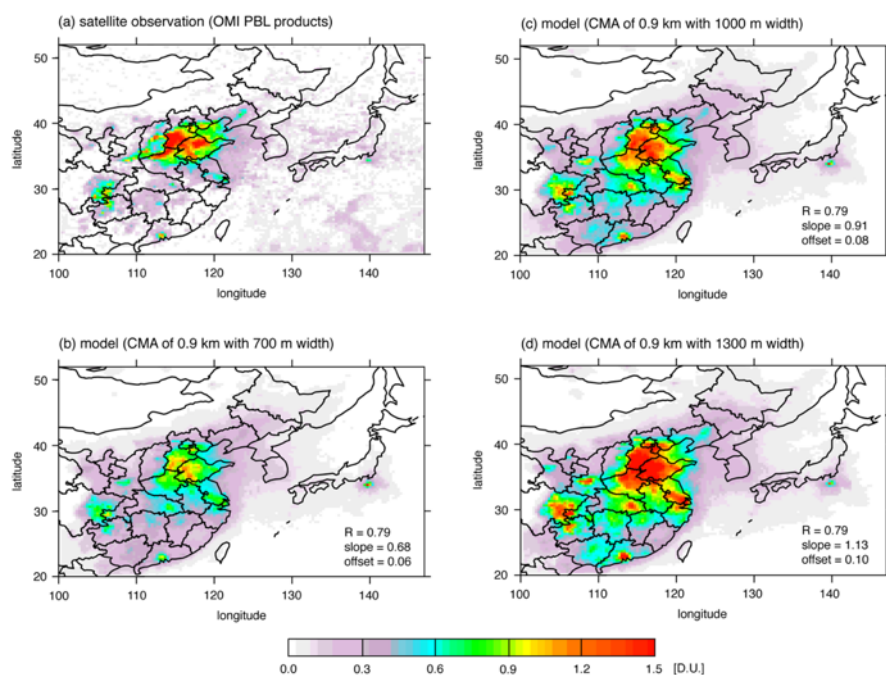
- In model verification, only the measurement of surface sulfate concentration is not enough. Since this study aimed to the sulfur budgets, the observation of deposition as well as VCD from satellite are needed.

Reply:

We appreciate the reviewer's comments on the need for further analysis of sulfur deposition amounts and VCD. In the revised manuscript, we include a supplemental materials section that illustrates the evaluation of surface SO₂ concentration, SO₂ VCD with satellite, and SO₄²⁻ wet deposition.

For SO₂ VCD comparison, the publicly available OMI satellite observation do not include information of the averaging kernel to consider the sensitivity on vertical profile. To overcome this point, our previous study (Itahashi et al., 2017a; see figure below) examined the sensitivity of the modeled VCD to the depth from the center

of mass altitude (CMA), which is set as 0.9 km in the satellite retrieval. The results indicated that the analysis of CMA of 0.9 km with 1 km depth provided the best correspondence between model and satellite observation.



Supporting Figure (taken from Figure S6 of Itahashi et al. (2017)): Spatial distribution of SO₂ column density (a) observed by space-based OMI, and modeled with a CMA of 0.9 km and depths of (b) 700, (c) 1000, and (d) 1300 m. Units are Dobson Units.

Following this methodology, we have evaluated H-CMAQ with OMI satellite measurement. Because of this comparison methodology, only R was evaluated for the base H-CMAQ simulation and the H-CMAQ simulation incorporating the degassing volcanic SO₂ emissions. The results of this evaluation of SO₂ VCD are presented in the Supplement and shown as follows.

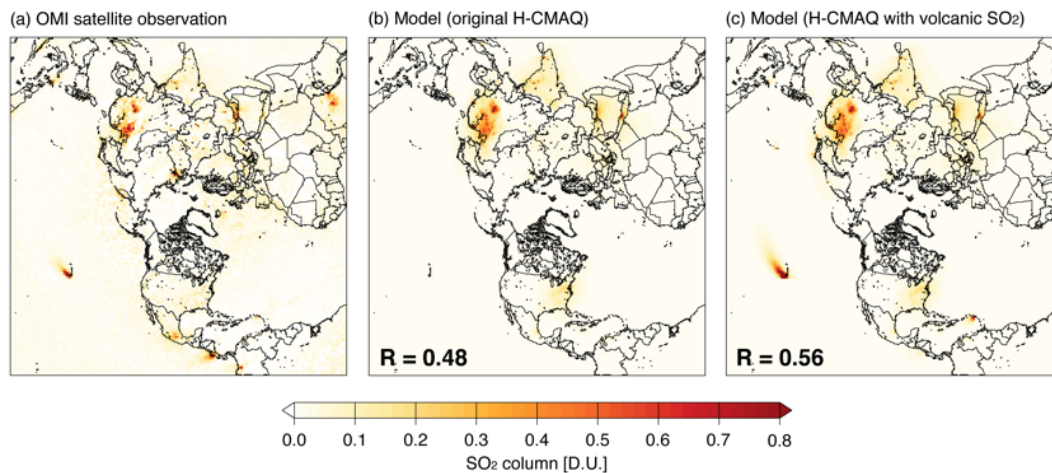


Figure S1. Annual averaged SO₂ column in 2010 of (a) observed by OMI satellite and simulated by (b) original H-CMAQ and (c) H-CMAQ with incorporation of volcanic SO₂ emissions. The spatial correlation coefficient with satellite observation are noted at left-bottom corner of (b) and (c).

Consistent with the distribution of SO₂ emissions shown in Fig. 1, high SO₂ VCD were also found over portions of East Asia, India, and the Arabian Peninsula. High SO₂ VCD over Hawaii are also indicative of SO₂ emissions from the Kilauea volcano. The original H-CMAQ did perform well over high SO₂ VCD areas such as East and South Asia with high anthropogenic SO₂ emissions; however, it did not capture the peak at Kilauea because of missing volcanic emissions. The correlation coefficient (R) between the original H-CMAQ and OMI VCD was 0.48. In contrast, the H-CMAQ simulation incorporating degassing volcanic SO₂ emissions captured the high SO₂ VCD at Kilauea, and also yielded a higher correlation of 0.56. These comparisons indicate that the incorporation of degassing volcanic SO₂ emissions is important for improving the model's ability in representing magnitude and spatial variability of airborne sulfur across the Northern Hemisphere.

For deposition, observed wet deposition data from EANET over Asia and NADP over the U.S.A. was used to further evaluate the model's performance in

representing precipitation chemistry and atmospheric sulfur budgets. These comparisons are tabulated in the Supplement1 and also shown as below.

Table S2. Statistical analysis of modeled SO₄²⁻ concentration in precipitation and wet deposition with observations.

	N	Mean		R	NMB	NME
		Obs.	Model			
SO₄²⁻ concentration in precipitation						
EANET						
–original H-CMAQ	2657	4743.7	1152.5	0.35 ^{***}	–75.7%	81.9%
–incorporation of volcanic emissions			1236.0	0.35 ^{***}	–73.9%	81.6%
NADP						
–original H-CMAQ	7377	842.7	631.5	0.33 ^{***}	–25.1%	61.9%
–incorporation of volcanic emissions			653.1	0.32 ^{***}	–22.5%	61.6%
Precipitation						
EANET	4497	16.6	13.7	0.37 ^{***}	–17.4%	56.3%
NADP	10670	21.4	16.5	0.55 ^{***}	–23.1%	66.9%
SO₄²⁻ wet deposition						
EANET						
–original H-CMAQ	2676	406.7	122.0	0.45 ^{***}	–70.0%	78.7%
–incorporation of volcanic emissions			131.5	0.44 ^{***}	–67.6%	77.9%
NADP						
–original H-CMAQ	8154	160.4	99.3	0.46 ^{***}	–38.1%	68.5%
–incorporation of volcanic emissions			103.6	0.47 ^{***}	–35.4%	68.4%

Note: The unit of mean for observations and simulations is g/L for concentration in precipitation and g/ha for wet deposition. Significance levels by Students’ t-test for correlation coefficients between observations and simulations are remarked as * p < 0.05, ** p < 0.01, and *** p < 0.001, and lack of a mark indicates no significance.

The original H-CMAQ underestimated both SO_4^{2-} concentrations in precipitation and SO_4^{2-} wet deposition. The inclusion of degassing volcanic SO_2 emission helped slightly rectify the negative model bias noted in the base calculation.

The results are presented in the Supplement as one figure and two tables and the relevant discussion was added in the main text. The additional text are as follows. In Section 2.2, the explanation of additional observation are added:

“To further examine the model’s ability to represent the tropospheric sulfur distributions and budget, ambient SO_2 concentration at CASTNET sites and vertically integrated SO_2 column concentration measured by the OMI sensor were also analysed. The OMI measured SO_2 column was taken from the level 3 daily global sulfur dioxide product (OMSO2e) gridded into 0.25° (Krotkov et al., 2015). This gridded data were mapped to the H-CMAQ modeling domain and grid structure.. This product contains the total column of SO_2 in the planetary boundary layer (PBL) with its center of mass altitude (CMA) at 0.9 km, and lacked in the vertical sensitivity. Our previous study indicated that 1 km depth for CMA in the modeled SO_2 column yielded best comparisons with satellite-measured SO_2 column over East Asia (Itahashi et al., 2017a). The observed deficit grids by satellite were also considered in the analysis of modeled SO_2 column. The same approach to compare and evaluate SO_2 column was used in this study. Furthermore, SO_4^{2-} concentration in precipitation, precipitation amount, and SO_4^{2-} wet deposition were also evaluated relative to observations at EANET sites over Asia and the National Atmospheric Deposition Program’s National Trends Network (NADP/NTN) over the U.S.A. (NADP, 2021). Measurements by wet-only sampler are available at 49 EANET sites with daily interval at most sites and weekly or 10-days interval at others sites (EANET, 2020). Observation of volume-weighted concentration in precipitation and total weekly wet deposition are available at 240 NADP sites.”

In Section 3.1, model evaluation for original H-CMAQ are added:

“Comparisons of model estimated SO₂ column distributions with satellite derived values are presented in Fig. S1 in the Supplement. The R value of 0.48 indicated the general agreement for the spatial distribution pattern of SO₂ column over the Northern Hemisphere with higher concentrations in regions with high anthropogenic SO₂ emissions (illustrated in Fig. 1); however, high SO₂ column over Hawaii evident in the satellite retrieval was not captured in the base H-CMAQ simulation due to the lack of volcanic SO₂ emissions.”

In Section 3.2, the impact by incorporating volcanic SO₂ emissions on SO₂ concentration, SO₂ column, and SO₄²⁻ wet deposition are added.

“Both simulations of original H-CMAQ and H-CMAQ incorporating degassing SO₂ emissions showed model overestimation for ambient SO₂ concentration when compared to CASTNET observation as listed in Table S1 in the Supplement. The model performance statistics were comparable for the case incorporating degassing volcanic SO₂ emissions; indicating that additional SO₂ emissions from volcano were fully oxidized to SO₄²⁻ and thus have greater impact on changes in model performance for SO₄²⁻. The overestimation of SO₂ could be attributed to the insufficient oxidation process from SO₂ to SO₄²⁻ in the modeling system, because SO₄²⁻ were still underestimated by incorporating volcanic SO₂ emissions. Coarse grid resolution leading to artificial dilution of SO₂ emissions, could also contribute to overestimation of predicted ambient SO₂ levels relative to measurements at remote locations. The detailed discussion using conversion rate is further presented in next Section 3.3. The comparison of SO₂ column with satellite observation showed the improvement of R value from 0.48 to 0.56 due to improvements in representation of the spatial variability in tropospheric SO₂ distributions resulting from capturing the high SO₂ column in vicinity of active volcanos such as Kilauea as illustrated in Fig. S1 in the Supplement. The evaluation for removal processes such as wet deposition is tabulated in Table S2 in the Supplement. The base H-CMAQ simulation tended to underestimate both SO₄²⁻ concentration in

precipitation and wet deposition. The inclusion of volcanic SO₂ emission sources led to slight improvements in the NMB and R, but the NME was largely unaltered.”

- Since the atmospheric sulfate is connected with nitrate as well as ammonium, analysis on these two species are also needed, especially considering the long-range transport over the remote areas.

Reply:

We appreciate this comment to evaluate other aerosol components such as NO₃⁻ and NH₄⁺. While we acknowledge the connections of the SO₄²⁻-NO₃⁻-NH₄⁺ system and that the gas-particle partitioning of airborne NH_x and total nitrate is dependent on the amounts of airborne SO₄²⁻, we do not believe that biases/errors in predictions of NO₃⁻ and NH₄⁺ provide any additional information on the error/bias in SO₄²⁻ predictions than direct comparisons of modeled and observed SO₄²⁻ levels. Since the primary aim of this study is to assess the impact of degassing volcanic SO₂ emissions on SO₄²⁻ and since the modeling performance in Table 2 showed generally good agreement compared to observations over U.S.A. and Asia, we do not feel that inclusion of model performance for NO₃⁻ and NH₄⁺ would add significantly to the primary goals of the study. We thus would like to keep our focus on SO₄²⁻ concentrations throughout the manuscript.

- The conversion from SO₂ to sulfate should also be discussed, since their different deposition characters (dry deposition velocity, wet scavenging). I would suggest the authors focus on the total S instead of the sulfate only.

Reply:

We agree with the reviewer that given differences in deposition sinks for gaseous and particulate sulfur, from an atmospheric budget perspective it is important to assess the total sulfur as well as the relative amounts of SO₂ and SO₄²⁻. By including additional evaluation of surface SO₂ concentrations and SO₂ VCD as suggested by both reviewers, we believe we now provide a more complete picture of model

performance of both SO_2 and SO_4^{2-} as well as total-S. The CASTNET Florida site reports both SO_2 and SO_4^{2-} , and we have now included additional analysis of conversion rate from SO_2 to SO_4^{2-} at this site. The result of temporal variation of conversion rate is additionally plotted in Fig. 6 (c). Based on this result, we have added the following discussion on Section 3.3.

“At this CASTNET site, EVE419 in Florida, the conversion rate from SO_2 to SO_4^{2-} were further examined. We use the ratio $\text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{SO}_2)$ as an indicator of the S(IV) to S(VI) conversion rate with higher values indicating greater levels of oxidation of SO_2 to SO_4^{2-} . The temporal variation of this conversion rate is plotted in Fig. 6 (b). As expected, in response to seasonal variations in intensity of atmospheric chemistry and oxidant levels, the observed conversion rate was lower in the cool season and higher in warm season, and this general feature was captured by model. The mean of conversion rate through the year was 0.58 in the observation whereas original H-CMAQ was 0.42. By incorporating degassing volcanic SO_2 emissions, the mean of conversion rate increased to 0.43, but still underestimated the observed value. Since data from routine measurement networks are not designed to specifically characterize impacts of volcanic emissions on atmospheric sulfur budgets, these observations are unable to unambiguously quantify any modulation in S(IV) to S(VI) conversion rates due to the presence of volcanic emissions as also evidenced by the small change in the estimated conversion rate between the simulations with and without volcanic degassing emissions.”

- P4, L10. The global SO_2 emission is described here. What about the other species, such as NO_x , NH_3 , etc? Since the conversion from SO_2 to sulfate, dry and wet deposition as well as atmospheric transport should be controlled by the reactions with the other species.

Reply:

As we stated in the original manuscript, a total of 105.8 Tg/yr of SO_2 emissions are emitted over the modeling domain. We have analyzed NO_x and NH_3 emissions in the same manner, and results were 93.5 Tg/yr for NO_x and 45.5 Tg/yr for NH_3

emissions. The basis for the emission estimates for all species used in our calculations are detailed in the references provided in the manuscript and are thus not repeated here. As mentioned in our response to the second specific comment, we believe that it is better to focus on SO₂ emission and SO₄²⁻ concentration within the scope of this study. We thus have not incorporated any revisions in the manuscript in response to this comment.