Response to the Referee #1:

This paper described a straightforward sensitivity study of volcanic SO2 emission using the hemispheric CMAQ. It conducted two runs, with and without the volcanic SO2 emissions, and the results were mainly compared to surface sulfate measurements for year 2010. This surface sulfate-only verification is not sufficient for volcanic SO2 emissions since that sulfate concentration can be affected by other processes, such as wet scavenging. You may need to compare the modeled SO2 concentrations to surface/aircraft measurements and satellite retrievals. This manuscript did not mention the temporal variations of volcanic SO2 emission used here, and it likely used static emission rates. If so, the corresponding discussions are needed to justify the treatment since the volcanos unlikely erupted at constant rates for whole year of 2010.

Reply:

We appreciate the reviewer's constructive comments. To address the reviewer's concerns on model evaluation for SO_2, we have significantly expanded the model evaluation discussion to now also include (1) comparisons of column SO_2 predictions for both model cases – with and without volcanic degassing emissions, with OMI inferred SO_2 column distributions across our Northern Hemisphere domain (in Figure S1 in the Supplement), and (2) comparison of ambient SO_2 predictions with observations at CASTNET monitors in the U.S. (Table S1), and (3) comparison of model predicted SO_4^{2-} concentrations in rainwater, precipitation amounts, and SO_4^{2-} wet deposition amounts with observations from the NADP in the US and EANET in Asia (Table S2). Incorporation of volcanic degassing emissions in the model generally helps improve the performance metrics (slightly in some cases) in these model-observation comparisons and are detailed further in the revised manuscript discussion.

In terms of the temporal variation of SO_2 emission, due to lack of other information, we used a time-invariant emission rate. For clarity, we have revised Section 2.1 as follows with underlined for additional discussion.

"In this study, annual estimates of degassing volcanic SO_2 emissions by Carn et al. (2017) are incorporated into H-CMAQ. The estimated emission of SO_2 from the 50 volcanos within our northern hemisphere modeling domain (Figure 1b) is 12.7 Tg/yr. Considering the characteristics of degassing process from volcanoes and the lack of any other information to accurately specify its temporal variations, we use a constant SO_2 emission rate in H-CMAQ based on the annual SO_2 emission estimates by Carn et al. (2017)."

Please also see our replies to your specific comments.

Specified comments:

Page 4, line 24: "In this study, the entire year of 2010 was simulated". Why choose 2010 as the studied year, or is there any specific reason related to the 2010 volcano eruptions?

Reply:

As already stated in the introduction section, we aimed to understand the impact of SO_2 emissions from degassing volcanoes in this study and did not focus on any specific volcanic eruption event.

P2, L32-33: "The volcanic SO_2 emissions from degassing are relatively stable at 23.0±2.3 Tg-SO_2/yr during 2005-2015, and the highest amount was approximately 26 Tg-SO_2/yr in 2010."

P3, L5-7: "According to the comparison between the degassing and eruptive emissions, Carn et al. (2017) estimated that during 2005-2015, volcanic activity contributed about 23 Tg/yr of SO_2 due from degassing while eruptive SO_2 emissions ranged from 0.2 to 10 Tg/yr of SO_2. Therefore, understanding the behavior of persistent degassing SO_2 emissions and its contributions to airborne SO_4^{2-} levels is important."

Based on these reasons, we choose 2010 as the studied year. To address the reviewer's comment, we stated the reason for selection of 2010 explicitly in page 4, lines 23-26:

"In this study, the entire year of 2010 was simulated to analyze the volcanic emission impacts over the Northern Hemisphere, as the SO_2 emissions from degassing during the 2005-2015 period were highest in 2010. Also note that emission estimates presented in Carn et al. (2017) suggest that degassing dominate over eruptive SO_2 emissions during the same time period."

Page 5, line 7. So the volcano emissions have no plume rise, right? If so, why?

Reply:

Yes, plume rise for volcanic degassing emissions were not treated in this study, and this was because the characteristics of the degassing process. As noted earlier, we aimed to analyze the impact of SO_2 emissions from persistent degassing volcanoes and did not focus on any specific volcanic eruption. As such, a plume rise calculation would require characterization of buoyancy of the degassing plume and thus need information (either observations or estimates) on heat content of the degassing plume. Since these are not readily available, volcanic degassing SO_2 emissions were allocated into the model vertical layer corresponding to the volcano's altitude. In this configuration, the 108 km grid spacing used in CMAQ does not allow the model to adequately resolve localized terrain peaks such as volcanoes and assigning their emissions to the first model layer would not account for the fact that in reality these emissions typically occur above the mixed layer. Therefore, the vertical layer to which volcanic degassing emissions were assigned was determined by first calculating the difference between the altitude of a given volcano (this was listed in Table 1) and the CMAQ terrain height for the cell in which it is located, and then determining the vertical CMAQ layer corresponding to this difference.

Page 6, section 3.1. As commented above, the verification with only surface sulfate is insufficient. Even with the coarse resolution, the SO2 comparisons are still preferred. Or, you can use a high-resolution regional CMAQ to study certain region for a certain period.

Reply:

We agree that comparisons with SO_2 measurements would enable more direct assessments of the impacts of including volcanic SO_2 emissions.

CASTNET has been routinely monitoring SO_2 concentration. To address the reviewer's comment, we evaluated SO_2 predictions against all available observations from CASTNET. The evaluation results are now newly presented in Table S1 in the Supplement along with brief discussions of these results in the main text.

Table S1. Statistical analysis of modeled SO_2 concentration against CASTNET observations.

	N	Mean		R	NMB	NME
		Obs.	Model			
CASTNET						
−original H-CMAQ	**4216**	**1.69**	**2.81**	**0.57*****	**+66.1%**	**94.7%**
−incorporation of volcanic emissions			**2.83**	**0.58*****	**+67.4%**	**94.9%**

Note: The unit of mean for observations and simulations is ppbv. 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.

Because SO_2 concentration did not change in the case of the incorporation of volcanic emissions, this result showed that SO_2 from volcanic sources was fully oxidized to SO_4^{2-} and there was no direct transport of SO_2 itself. To indicate this point, we have explicitly stated within the modeling evaluation at specific site of Florida in Section 3.3, and it was revised as follows.

"CASTNET also provides measurements of weekly-average SO₂ mixing ratios, which are used to evaluate the model's performance for SO₂ prediction, as shown in Table S1. In addition to domain-mean evaluation, we evaluated SO₂ at the EVE419 site in Florida. At this site, the observed annual mean was 0.61 ppbv whereas base H-CMAQ and H-CMAQ with volcanic SO₂ emissions both showed 0.77 ppbv."

Page 8-9, section 3.3. The volcanic SO2 impact is only shown at two surface sites and for sulfate only, which is insufficient.

Reply:

We appreciate this suggestion. It should be noted that we have evaluated model performance for airborne SO_4^{2-} concentration relative to all locations available from the EANET, CASTNET, and IMPROVE networks as listed in Table 2. Within this comparison, total of 1167, 4216, and 18844 observation-prediction data pairs have been evaluated. In addition, according to your comment, we have also evaluated model performance for ambient SO₂ concentration for CASTNET observation as listed in Table S1.

Taking into account this comment, we have re-examined the analysis in Figure 6, and have revised it to include analysis at an additional observation site in the Virgin Islands. We have revised Figure 6 to show detailed analysis over three specific sites that were most affected by the incorporation of persistent volcanic degassing emissions. The updated discussion in Section 3.3 of the revised manuscript is as follows.

"A second location-specific analysis were conducted at sites located in the <u>Virgin Island and</u> in the state of Florida. As seen in the monthly-average spatial distribution patterns (Fig. 5), the influence of volcanic activity of Soufriere Hills located in Montserrat are more prominent during winter. <u>The nearest observational sites from Soufriere Hills are the IMPROVE site VIIS1, and the</u> southernmost measurement location in Florida (see, Fig. 4) is the CASTNET site

EVE419 and comparison of modeled values with observations at these locations are shown in Fig. 6 (b) and (c). At VIIS1 (Fig. 6 (b)), the base H-CMAQ simulation showed invariant concentrations throughout the year with an annual average value of 0.86 μg/m^3. The statistical scores of R showed scattered correspondence between model and observation. NMB showed negative bias because the base H-CMAQ did not capture the episodical peak concentration. By including the degassing volcanic SO$_2$ emissions, the model exhibited improved skill in representing the episodic peaks. The statistical scores showed that the average concentration was 1.75 μg/m^3, and NMB showed +44.6%, and R was dramatically improved to 0.72. The deterioration in the value of NME was found, because of the continuous model overestimation. As also suggested the case in Hawaii, further refinement on emission treatments is required. At EVE419 (Fig. 6 (c)), the seasonal pattern with summer minima was captured by H-CMAQ but underestimated throughout the year. Increased concentrations through the incorporation of volcanic emissions are noted during January, late April to early May and December. The increases during late April to early May were not seen from the monthly-averaged spatial distribution (Fig. 5); hence these could be the episodic long-range transport by southeasterly winds. Because of these increased concentrations, all statistical scores of R, NMB, NME showed improvement compared to the base H-CMAQ."

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 SO_2 concentration, SO_2 VCD with satellite, and SO_4^{2-} wet deposition.

  For SO_2 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 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.
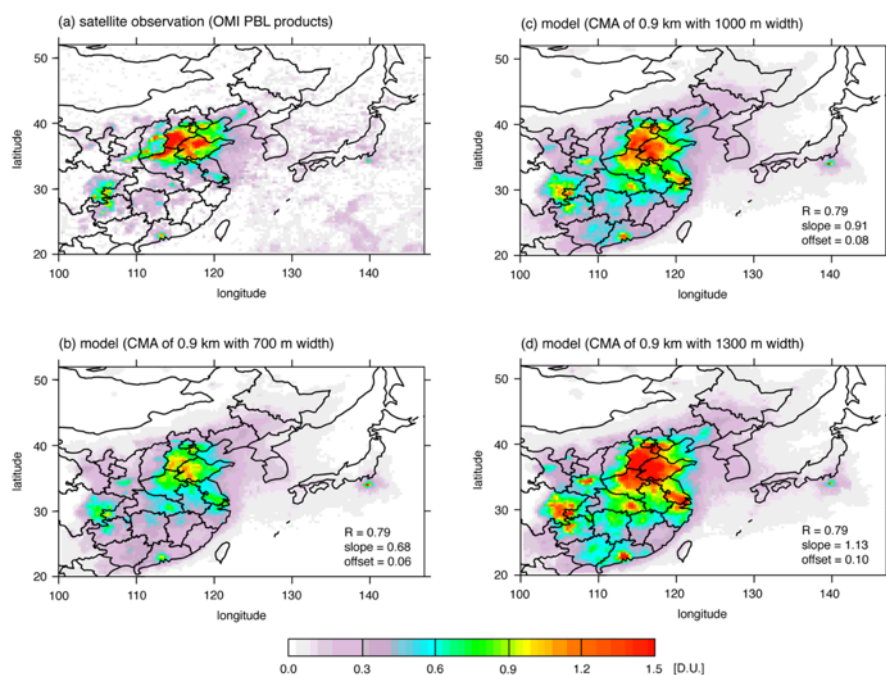
Supporting Figure (taken from Figure S6 of Itahashi et al. (2017)): Spatial distribution of SO_2 column density (a) observed by space-based OMI, and modeled with a CMA of 0.9 km and depths of (b) 700, (c) 1000, and (d) 1300 m. Units are Dobson Units.

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 SO_2 emissions. The results of this evaluation of SO_2 VCD are presented in the Supplement and shown as follows.
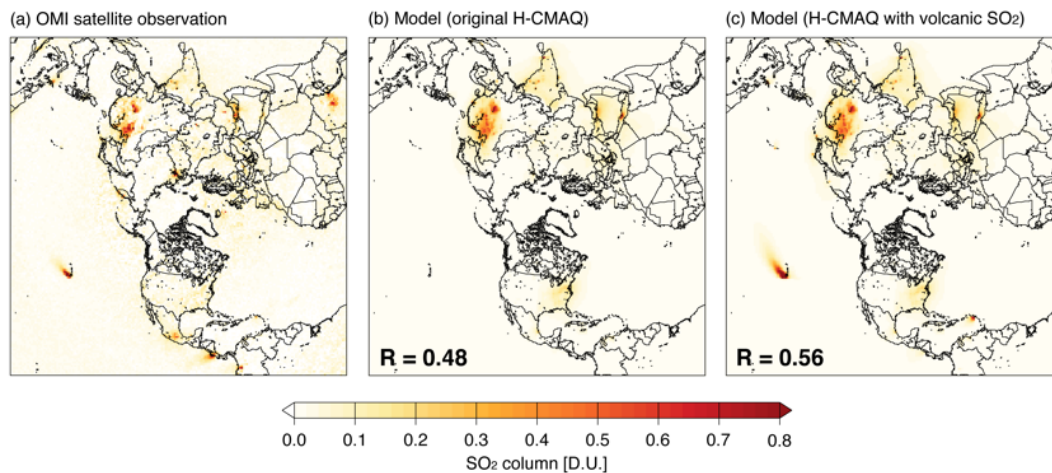
Figure S1. Annual averaged SO₂ column in 2010 of (a) observed by OMI satellite and simulated by (b) original H-CMAQ and (c) H-CMAQ with incorporation of volcanic SO₂ emissions. The spatial correlation coefficient with satellite observation are noted at left-bottom corner of (b) and (c).

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 Supplementl and also shown as below.

Table S2. Statistical analysis of modeled SO_4^{2-} concentration in precipitation and wet deposition with observations.

	N	Mean		R	NMB	NME
		Obs.	Model			
SO_4^{2-} 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%
SO_4^{2-} 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 SO_2 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 SO_2 column over the Northern Hemisphere with higher concentrations in regions with high anthropogenic SO_2 emissions (illustrated in Fig. 1); however, high SO_2 column over Hawaii evident in the satellite retrieval was not captured in the base H-CMAQ simulation due to the lack of volcanic SO_2 emissions."

In Section 3.2, the impact by incorporating volcanic SO_2 emissions on SO_2 concentration, SO_2 column, and SO_4^{2-} wet deposition are added.

"Both simulations of original H-CMAQ and H-CMAQ incorporating degassing SO_2 emissions showed model overestimation for ambient SO_2 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 SO_2 emissions; indicating that additional SO_2 emissions from volcano were fully oxidized to SO_4^{2-} and thus have greater impact on changes in model performance for SO_4^{2-}. The overestimation of SO_2 could be attributed to the insufficient oxidation process from SO_2 to SO_4^{2-} in the modeling system, because SO_4^{2-} were still underestimated by incorporating volcanic SO_2 emissions. Coarse grid resolution leading to artificial dilution of SO_2 emissions, could also contribute to overestimation of predicted ambient SO_2 levels relative to measurements at remote locations. The detailed discussion using conversion rate is further presented in next Section 3.3. The comparison of SO_2 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 SO_2 distributions resulting from capturing the high SO_2 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 SO_4^{2-} 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 NO_3^- and NH_4^+. While we acknowledge the connections of the SO_4^{2-}-NO_3^--NH_4^+ system and that the gas-particle partitioning of airborne NH_x and total nitrate is dependent on the amounts of airborne SO_4^{2-}, we do not believe that biases/errors in predictions of NO_3^- and NH_4^+ provide any additional information on the error/bias in SO_4^{2-} predictions than direct comparisons of modeled and observed SO_4^{2-} levels. Since the primary aim of this study is to assess the impact of degassing volcanic SO₂ emissions on SO_4^{2-} 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 NO_3^- and NH_4^+ would add significantly to the primary goals of the study. We thus would like to keep our focus on SO_4^{2-} 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 SO_4^{2-}. 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 $SO_4^{2-}/(SO_4^{2-} + SO_2)$ 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 SO2 emission is described here. What about the other species, such as NOx, NH3, etc? Since the conversion from SO2 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 SO_2 emission and SO_4^{2-} concentration within the scope of this study. We thus have not incorporated any revisions in the manuscript in response to this comment.

Response to CEC:

Dear authors,

After checking your manuscript, it has come to our attention that it does not comply with our Code and Data Policy.

https://www.geoscientific-model-development.net/policies/code_and_data_policy.html

You have archived your code in GitHub. However, GitHub is not a suitable repository. GitHub itself instructs authors to use other alternatives for long-term archival and publishing, such as Zenodo. Therefore, please, publish your code in one of the appropriate repositories, and include the relevant primary input/output data. In this way, you must include in a potential reviewed version of your manuscript the modified 'Code and Data Availability' section, the DOI of the code (and another DOI for the dataset if necessary).

Also, in the GitHub repository it says that the code is "open-source"; however, there is no license listed. If you do not include a license, despite what you state in the README file, the code is not "open-source", it continues to be your property. Therefore, when uploading the model's code to Zenodo, you could want to choose a free software/open-source (FLOSS) license. We recommend the GPLv3. You only need to include the file 'https://www.gnu.org/licenses/gpl-3.0.txt' as LICENSE.txt with your code. Also, you can choose other options that Zenodo provides: GPLv2, Apache License, MIT License, etc.

Juan A. Anel

Geosc. Mod. Dev. Exec. Editor

Reply:

We appreciate your notice on our statement for Code and Data availability. We reviewed the policy of this journal, and fully revised the code availability statement as follows.

Code availability

The CMAQ version 5.2 are available from
https://doi.org/10.5281/zenodo.1167892 (United States Environmental Protection
Agency, 2017).

We also added the appropriate reference as follows.
Reference:

United States Environmental Protection Agency: CMAQ (Version 5.2) [Software],

Zenodo, https://doi.org/10.5281/zenodo.1167892, 2017.

We believe that these statements can comply the data policy of the journal of
Geoscientific Model Development.