Addressing Review Comment 1

Reviewer comments are reproduced in black. Responses are in blue. Updates to the manuscript are shown with underline (addition) or strikeout (removal).

Many models are not able to reproduce high sulfate concentrations, and do not consider heterogeneous chemistry in aerosol droplets. This paper examines sulfate and HMS formation in aerosol droplets as a possible cause for model underestimation. This is interesting work which I recommend for publications upon completion of some minor revisions.

Thank you for the time it took to review our paper, your kind words, and suggestions!

1. Sentence starting on line 41 is hard to read due to length and many parentheses. I suggest splitting it into two or more sentences.

The following change has been made:

Sulfate (SO_4^{2-}), often a major component of $PM_{2.5}$ in Fairbanks and North Pole (ADEC, 2017) as well as globally (Snider et al., 2016), can be emitted directly (primary) or formed secondarily via atmospheric ~~via gas-phase~~ oxidation of sulfur dioxide (SO_2). Known secondary SO_4^{2-} formation processes include but are not limited to gas phase oxidation of SO_2 (Calvert et al., 1978), particle surface oxidation of SO_2 (Clements et al., 2013; Wang et al., 2021), and aqueous-phase oxidation of inorganic sulfur species with oxidation number 4 ($S(IV) = SO_2{\cdot}H_2O + HSO_3 + SO_3$) (secondary) (Hoffmann and Calvert, 1985; Ibusuki and Takeuchi, 1987; Lagrange et al., 1994; Lee and Schwartz, 1983a; Maahs, 1983; Maaß et al., 1999; Martin and Good, 1991; McArdle and Hoffmann, 1983). Aside from contributing directly to $PM_{2.5}$ mass, SO_4^{2-} can facilitate the formation of other $PM_{2.5}$ species as a reactant (Brüggemann et al., 2020; Huang et al., 2019; Huang et al., 2020; Surratt et al., 2010), by increasing aerosol water uptake (Kim et al., 1994; Nguyen et al., 2014), and by altering aerosol acidity (Li et al., 2022; Pye et al., 2020).

2. Line 100: write out CONUS

The following change has been made:

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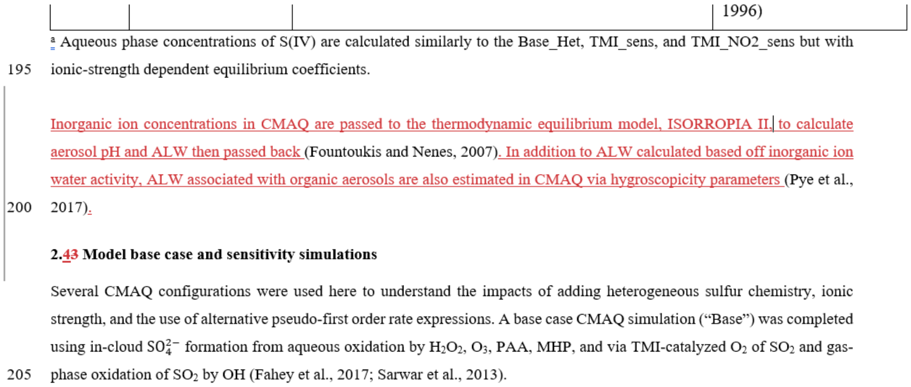
horizontal resolutions. Two historical wintertime PM episodes were simulated for a finely resolved (1.33 km) domain centered over Fairbanks, Alaska, winter, and summer periods over the contiguous United States (CONUS) (12 km) during 2016, and the 2015-2016 winter season over the N. hemisphere (108 km) to investigate the impacts of these updates for different chemical regimes, domains, and seasons. Changes to SO_4^{2-}, HMS, and SO_4^{2-} + HMS ($PM_{2.5,sulf}$) predictions were tracked with each update (i.e., for (1) adding heterogeneous sulfur reactions and (2) adding ionic strength effects), and model performance was evaluated with available observations. This study aims to better understand the impacts that heterogeneous sulfur chemistry parameterizations may have on predicted $PM_{2.5,sulf}$ concentrations and whether the additional chemistry can resolve SO_4^{2-} underpredictions in cold and dark conditions.

3. Methods: It's unclear how ALW and pH were calculated. Please state explicitly where these numbers (for example the pH and ALW in line 331) come from.

The thermodynamic equilibrium model, ISOROPPIA (Fountoukis and Nenes, 2007) was used to calculate aerosol pH and ALW. In response to this suggestion, we've included a small paragraph stating this in section 2.3:



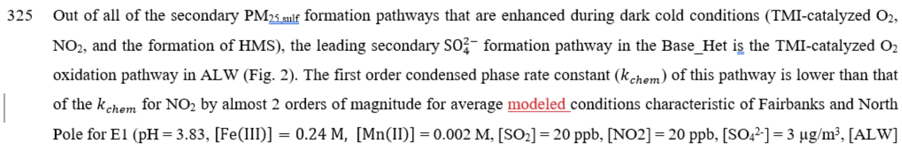
			1996)

[a] Aqueous phase concentrations of S(IV) are calculated similarly to the Base_Het, TMI_sens, and TMI_NO2_sens but with ionic-strength dependent equilibrium coefficients.

Inorganic ion concentrations in CMAQ are passed to the thermodynamic equilibrium model, ISORROPIA II, to calculate aerosol pH and ALW then passed back (Fountoukis and Nenes, 2007). In addition to ALW calculated based off inorganic ion water activity, ALW associated with organic aerosols are also estimated in CMAQ via hygroscopicity parameters (Pye et al., 2017).

2.4~~3~~ Model base case and sensitivity simulations

Several CMAQ configurations were used here to understand the impacts of adding heterogeneous sulfur chemistry, ionic strength, and the use of alternative pseudo-first order rate expressions. A base case CMAQ simulation ("Base") was completed using in-cloud SO_4^{2-} formation from aqueous oxidation by H_2O_2, O_3, PAA, MHP, and via TMI-catalyzed O_2 of SO_2 and gas-phase oxidation of SO_2 by OH (Fahey et al., 2017; Sarwar et al., 2013).



Out of all of the secondary $PM_{25,sulf}$ formation pathways that are enhanced during dark cold conditions (TMI-catalyzed O_2, NO_2, and the formation of HMS), the leading secondary SO_4^{2-} formation pathway in the Base_Het is the TMI-catalyzed O_2 oxidation pathway in ALW (Fig. 2). The first order condensed phase rate constant (k_{chem}) of this pathway is lower than that of the k_{chem} for NO_2 by almost 2 orders of magnitude for average modeled conditions characteristic of Fairbanks and North Pole for E1 (pH = 3.83, [Fe(III)] = 0.24 M, [Mn(II)] = 0.002 M, [SO_2] = 20 ppb, [NO2] = 20 ppb, [SO_4^{2-}] = 3 µg/m^3, [ALW]

4. In figures 1 and 3, the concentrations of the species are hard to see because the text partially covers it. Stating the domain size would also be helpful here.

We shifted the labels a little outside of the area of interest and made the font size smaller so that concentrations can be better seen and included the domain size as well in the caption:

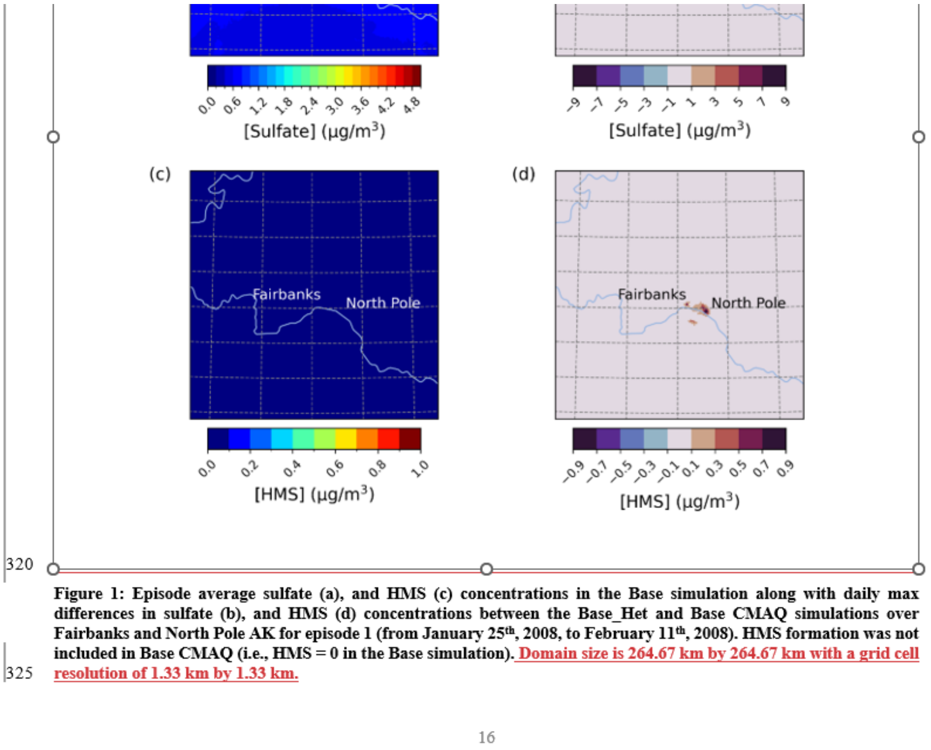
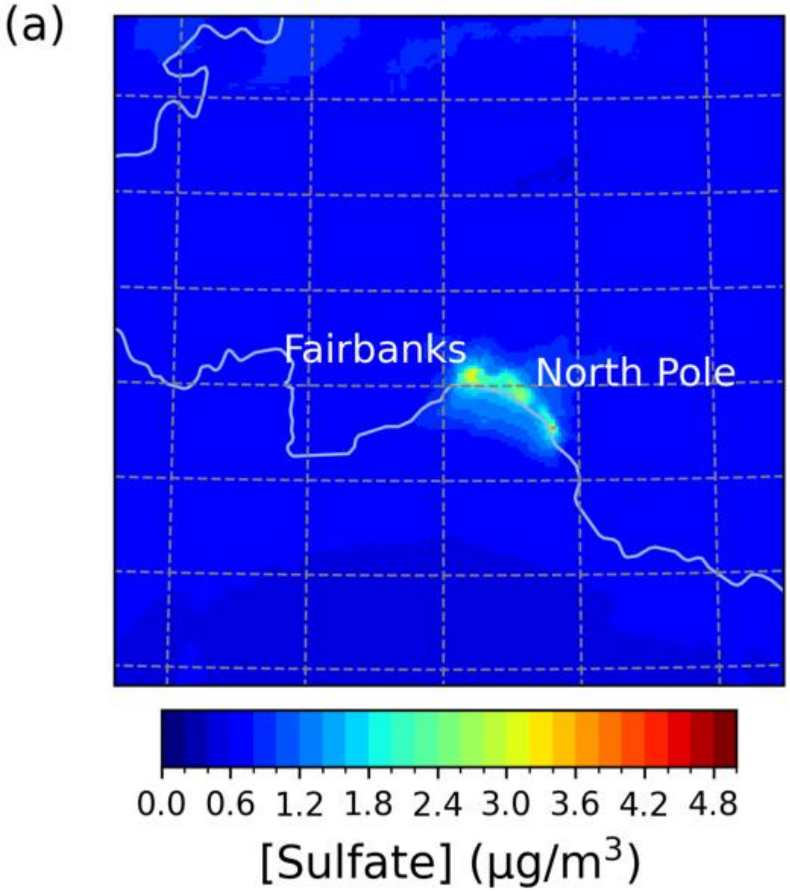


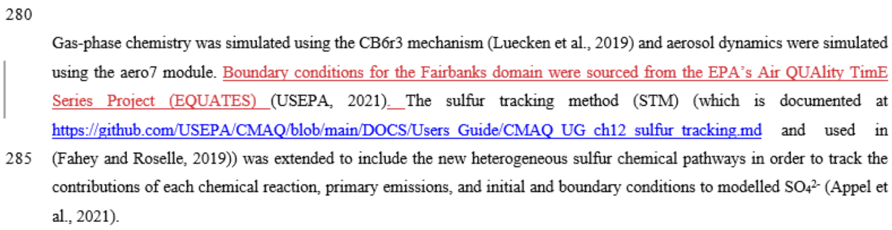
Figure 1: Episode average sulfate (a), and HMS (c) concentrations in the Base simulation along with daily max differences in sulfate (b), and HMS (d) concentrations between the Base_Het and Base CMAQ simulations over Fairbanks and North Pole AK for episode 1 (from January 25th, 2008, to February 11th, 2008). HMS formation was not included in Base CMAQ (i.e., HMS = 0 in the Base simulation). Domain size is 264.67 km by 264.67 km with a grid cell resolution of 1.33 km by 1.33 km.

5. In Figure 1a, it seems there's a high (~1 ug/m3) background of sulfate surrounding the Fairbanks and North Pole area, which seems strange. I would expect near-zero sulfate concentrations in these areas because there is very little anthropogenic activity.

Thank you for pointing this out. These concentrations are attributed to background conditions. While the background concentrations are not 0, they are not quite ~1 μg/m^3 and this is easier to see with a discrete color bar. We made this change to the plots and the background sulfate concentration for our base run is ~0.6 μg/m^3:



While most boundary conditions in modeling studies are seasonal averages, we used hourly-resolved boundary conditions for 2008 from the EQUATES project (USEPA, 2021). We have included a sentence in section 2.4 detailing this:



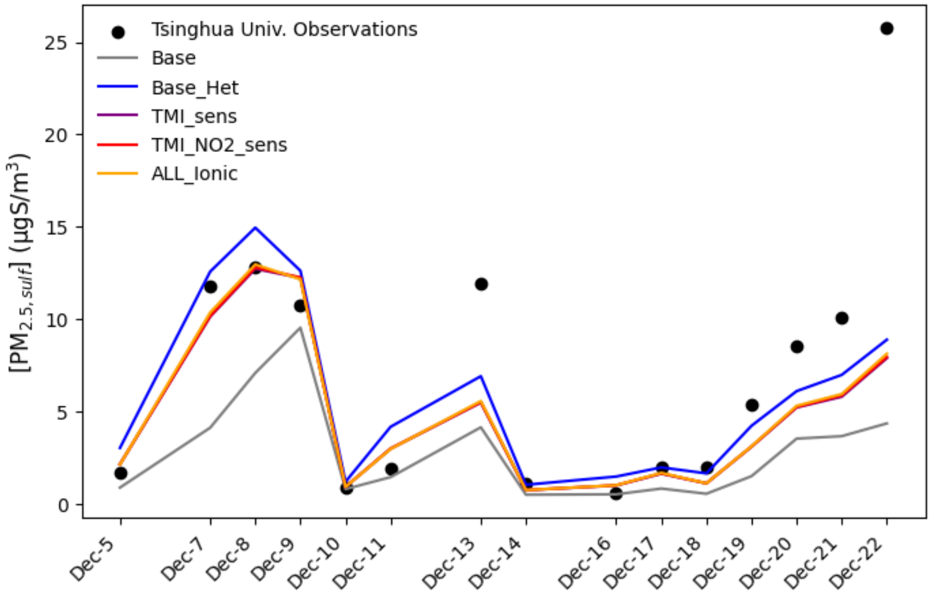
Gas-phase chemistry was simulated using the CB6r3 mechanism (Luecken et al., 2019) and aerosol dynamics were simulated using the aero7 module. Boundary conditions for the Fairbanks domain were sourced from the EPA's Air QUAlity TimE Series Project (EQUATES) (USEPA, 2021). The sulfur tracking method (STM) (which is documented at https://github.com/USEPA/CMAQ/blob/main/DOCS/Users_Guide/CMAQ_UG_ch12_sulfur_tracking.md and used in (Fahey and Roselle, 2019)) was extended to include the new heterogeneous sulfur chemical pathways in order to track the contributions of each chemical reaction, primary emissions, and initial and boundary conditions to modelled SO_4^{2-} (Appel et al., 2021).

6. Line 358: HSO3 and SO3 should have their charges written out like sulfate (SO_4^{2-}). Check for other mentions of HSO3 and SO3 in the paper.

These typo's have been addressed in this line and throughout the paper.

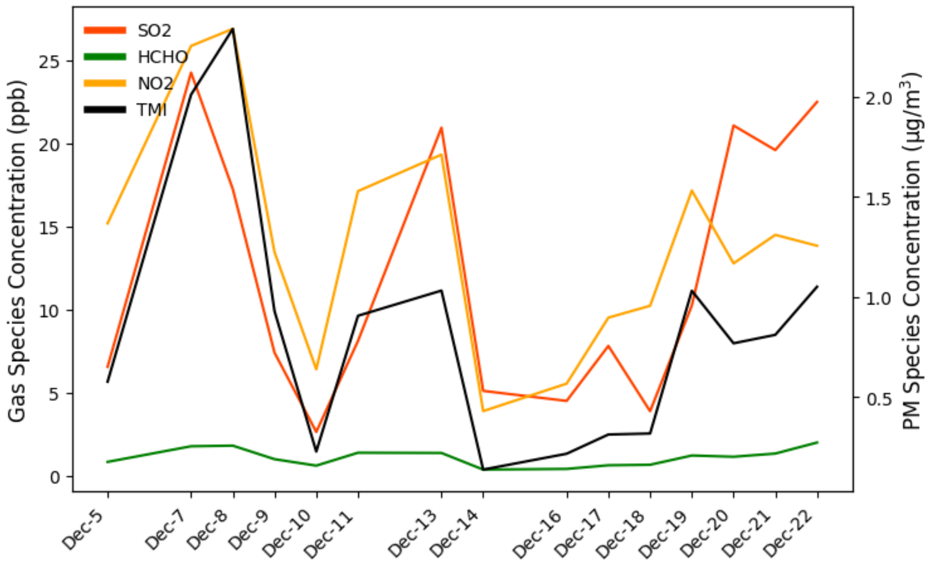
7. In Figure 7, is there any explanation for the major differences on Dec 13 and 27? I think this should be discussed due to the large discrepancy between model and measurements.

When looking into the cause for these differences, we realized that we had accidentally mis-matched model and observed time points by 1 day. We have resolved this and now this is what Fig. 7 should look like:

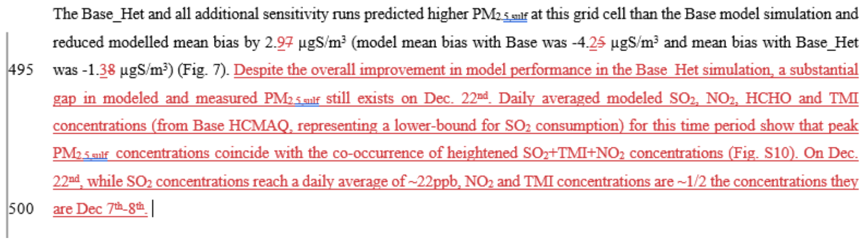


We have replaced this figure in the paper and the model-measurement gap for Dec. 13th is resolved slightly. We have also updated the model performance metrics in the text.

There still remains a large discrepancy between model output and observations for Dec. 22nd. Our hemispheric simulations (while our heterogeneous chemistry updates were included) did not include the sulfur tracking method tags for our new pathways and therefore contributions from each pathway were not tracked. The contribution of each pathway can be potentially inferred with looking at precursor oxidant concentrations. In this newly created figure (Fig. S10), the dominant the $PM_{2.5,sulf}$ peak modeled concentrations trend with peak coincidental SO_2, NO_2, and TMI concentrations:



I have included discussion of the Dec 22nd discrepancy as well:



The Base_Het and all additional sensitivity runs predicted higher $PM_{2.5,sulf}$ at this grid cell than the Base model simulation and reduced modelled mean bias by 2.9~~7~~ μgS/m³ (model mean bias with Base was -4.2~~5~~ μgS/m³ and mean bias with Base_Het was -1.3~~8~~ μgS/m³) (Fig. 7). Despite the overall improvement in model performance in the Base_Het simulation, a substantial gap in modeled and measured $PM_{2.5,sulf}$ still exists on Dec. 22nd. Daily averaged modeled SO_2, NO_2, HCHO and TMI concentrations (from Base HCMAQ, representing a lower-bound for SO_2 consumption) for this time period show that peak $PM_{2.5,sulf}$ concentrations coincide with the co-occurrence of heightened SO_2+TMI+NO_2 concentrations (Fig. S10). On Dec. 22nd, while SO_2 concentrations reach a daily average of ~22ppb, NO_2 and TMI concentrations are ~1/2 the concentrations they are Dec 7th-8th.

8. Line 716: ALPACA should be Alaska Layered Pollution And Chemical Analysis. You may want to cite this paper as well https://doi.org/10.1021/acsestair.3c00076

Thank you for this suggestion, we have included this citation.

Fountoukis, C., and Nenes, A. (2007). ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺–Ca²⁺–Mg²⁺–NH₄⁺–Na⁺–SO₄^{2−}–NO₃^{−}–Cl^{−}–H₂O aerosols. *Atmos. Chem. Phys., 7*(17), 4639-4659. doi:10.5194/acp-7-4639-2007

USEPA. (2021). *EQUATESv1.0: Emissions, WRF/MCIP, CMAQv5.3.2 Data -- 2002-2019 US_12km and NHEMI_108km*. Retrieved from: https://doi.org/10.15139/S3/F2KJSK