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:

horizonal 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.~~43~~4 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:

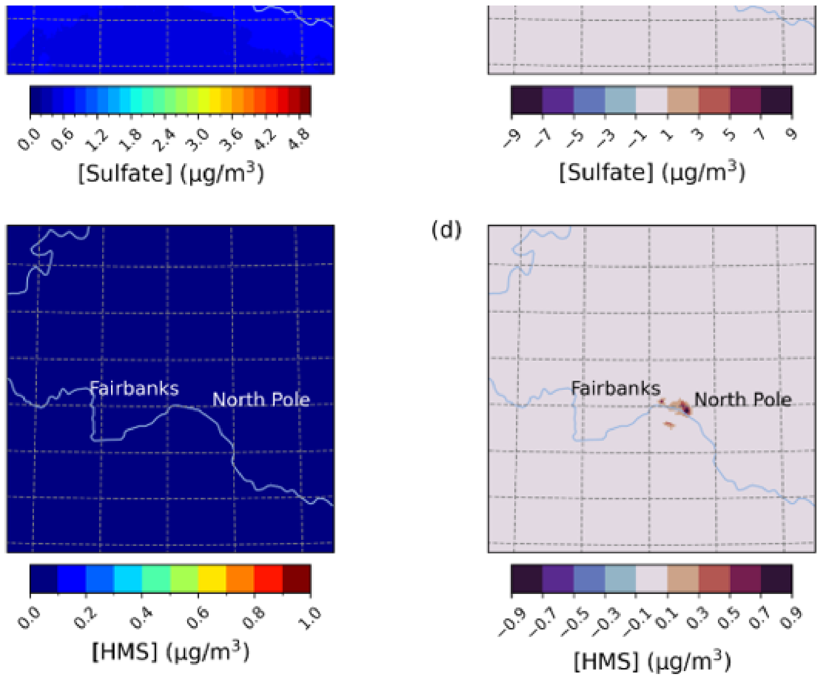
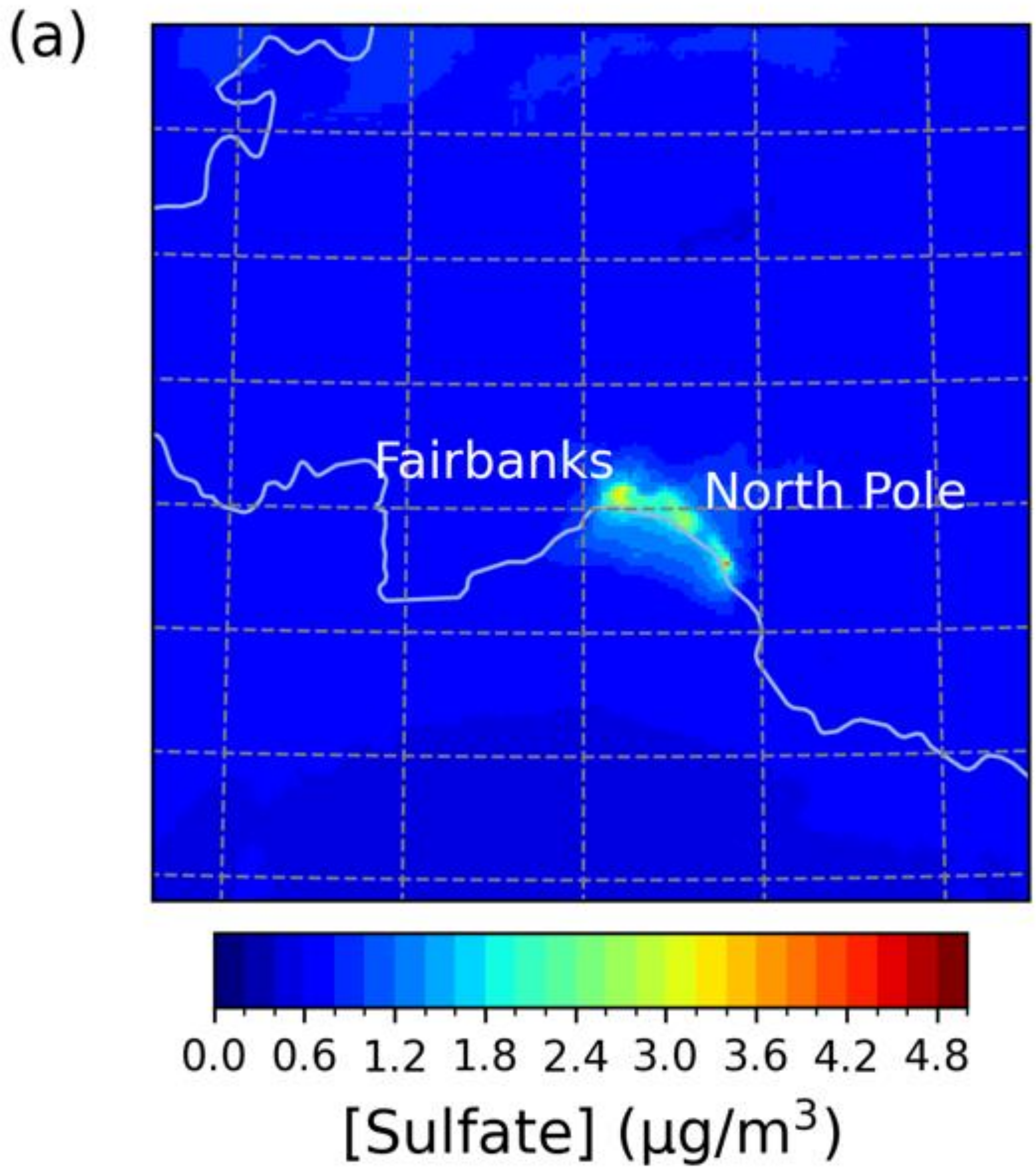


Figure 1: Episode average sulfate (a), and HMS (c) concentrations in the Base simulation along with daily max differences in sulfate (b), and HMS (d) concentrations between the Base_Het and Base CMAQ simulations over Fairbanks and North Pole AK for episode 1 (from January 25th, 2008, to February 11th, 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 $\mu g/m^3$ 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 $\mu g/m^3$:



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:

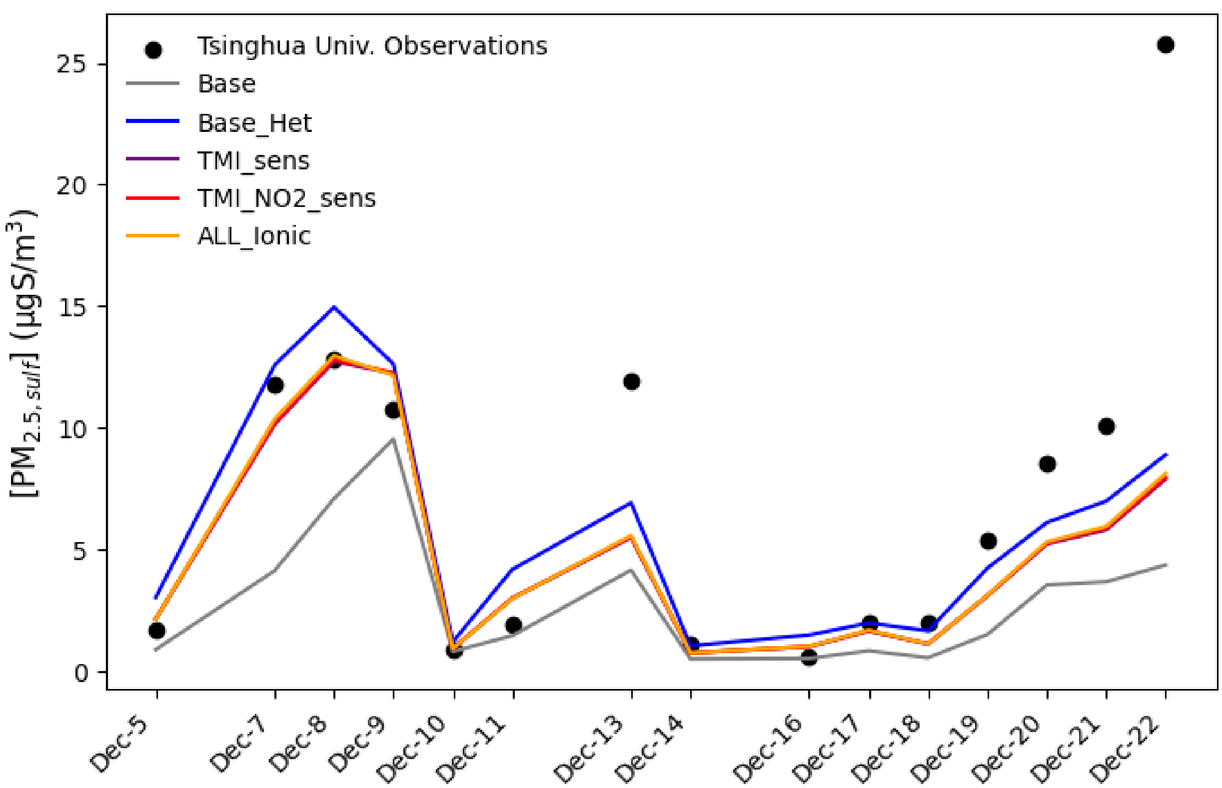
Gas-phase chemistry was simulated using the CB6r3 mechanism (Luecken et al., 2019) and aerosol dynamics were simulated using the aero7 module. Boundary conditions for the Fairbanks domain were sourced from the EPA's Air QUAlity TimE Series Project (EQUATES) (USEPA, 2021). The sulfur tracking method (STM) (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.

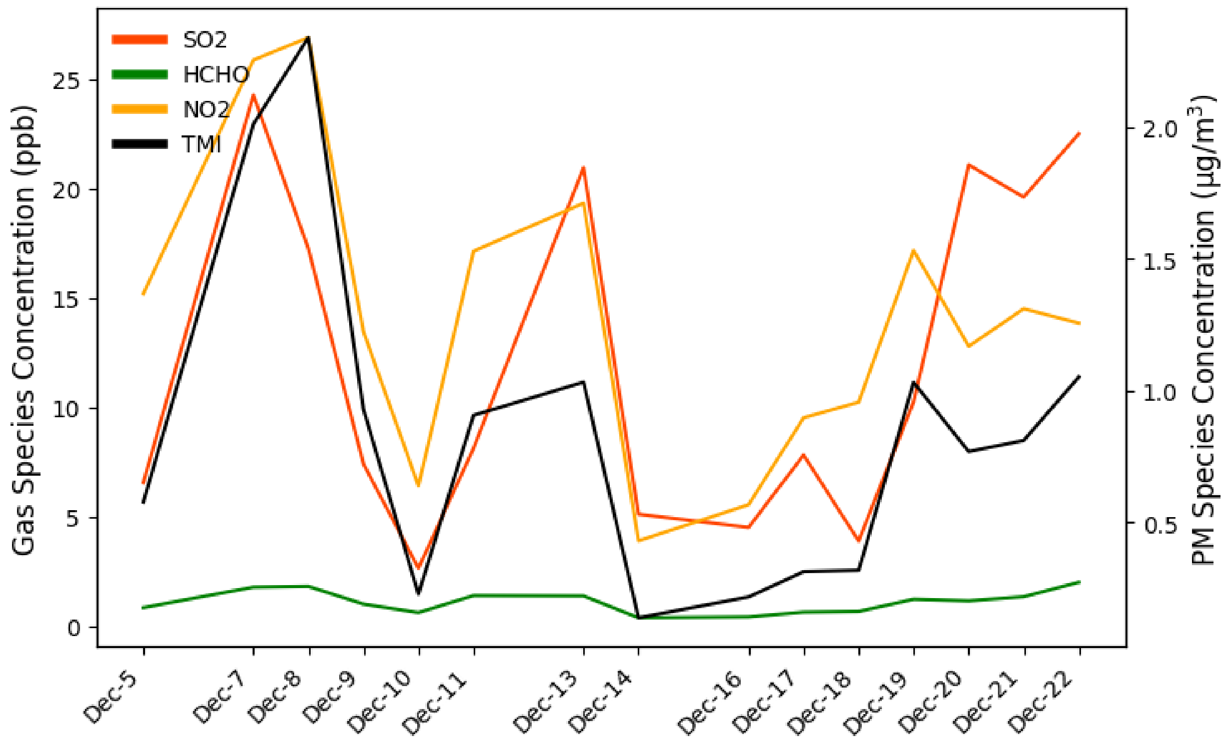
7. In Figure 7, is there any explanation for the major differences on Dec 13 and 27? I think this should be discussed due to the large discrepancy between model and measurements.

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 2.97 µgS/m³ (model mean bias with Base was -4.25 µgS/m³ and mean bias with Base_Het was -1.38 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.

Addressing Review Comment 2

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The discrepancy between field-observed sulfate concentrations during haze episodes and the values simulated by air quality models has garnered significant attention over the past two decades. Many scientists believe the traditional mechanism for S(IV) reaction in cloud chemistry is inadequate. Therefore, the multiphase and heterogeneous chemistry of S(IV) compounds has been a particularly intriguing topic in atmospheric chemistry. However, there is a lack of models that incorporate the dominant mechanisms into air quality models for comparison, and very few simulations specifically focus on the impact of ionic strength on reaction rates. The key methodological contribution of this paper is the implementation of a model developed by the authors using CMAQ to simulate the conversion of SO_2 to sulfate and HMS, yielding accurate results in Alaska. I had a few minor reservations in my reading, but I still highly recommend this article for publication in Atmospheric Chemistry and Physics.

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

Here are my suggestions.

1. Line 18: The definition of "heterogeneous" needs clarification. In my understanding, Heterogeneous processes can be categorized as surface chemistry, while multiphase chemistry generally refers to reactions occurring in the liquid phase. (DOI:10.1126/science.276.5315.1058, DOI: 10.5194/acp-23-9765-2023)

Thank you for attaching the above articles. We use the heterogeneous reactive uptake parameterization outlined in Hanson et al., (1994) to parameterize the multistep process of diffusion of a reactant towards a particle, dissolution in the particle, and reaction in the particle. Based on the rate of reaction vs diffusion of the precursor in the particle, the uptake may scale with surface area (fast reaction relative to particle diffusion) or volume (slow reaction relative to particle diffusion). The abstract has been reworded to indicate we model the process as heterogeneous reactive uptake:

Abstract. A portion of Alaska's Fairbanks North Star Borough was designated as nonattainment for the 2006 24-hour $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) in 2009. $PM_{2.5}$ NAAQS exceedances in Fairbanks mainly occur during the dark and cold winters, when temperature inversions form and trap high emissions at the surface. Sulfate (SO_4^{2-}), often the second largest contributor to $PM_{2.5}$ mass during these wintertime PM episodes, is underpredicted by atmospheric chemical transport models (CTMs). Most CTMs account for primary SO_4^{2-}, and secondary SO_4^{2-} formed via gas-phase oxidation of sulfur dioxide (SO_2) and in-cloud aqueous oxidation of dissolved S(IV). Dissolution and reaction of SO_2 in aqueous aerosols~~,~~ is generally not ~~often~~ included in CTMs~~,~~ but can be represented as heterogeneous reactive uptake and may help better represent the high SO_4^{2-} concentrations observed during Fairbanks winters. In addition, hydroxymethanesulfonate (HMS), a particulate sulfur species sometimes misidentified as SO_4^{2-}, is known to form during Fairbanks winters. Heterogeneous formation of SO_4^{2-} and HMS in aerosol liquid water (ALW) was implemented in the Community Multiscale Air Quality (CMAQ) modeling

And then also included this at the end of the introduction:

In this paper we describe the implementation of heterogenous sulfur chemistry in ALW in the Community Multiscale Air Quality (CMAQv5.3.2) modeling system (USEPA, 2020), leading to additional SO_4^{2-} and HMS formation. We refer to this chemistry as heterogeneous given the use of the heterogeneous framework (Hanson et al., 1994). Heterogeneous sulfur chemistry pathways implemented include the oxidation of dissolved S(IV) species by H_2O_2, O_3, PAA, MHP, TMI-O_2, NO_2, and the in-aerosol aqueous formation of HMS. In addition to heterogeneous chemistry updates, ionic strength effects were added to condensed-phase rate expressions and Henry's law coefficients of some species. The updated model was applied for several time periods and for different domains and horizonal resolutions. Two historical wintertime PM episodes were

2. Line 39: Please give the meaning of "2006 24-hour PM2.5 NAAQS".

We have included a footnote to define this:

suggested that secondary SO_4^{2-} may be efficiently produced in aerosol liquid water (ALW) (Cheng et al., 2016; Fan et al., 2020; Liu et al., 2020). Hygroscopic $PM_{2.5}$ (both inorganic and organic) can increase ALW content (Nguyen et al., 2014; Petters and Kreidenweis, 2007; Pye et al., 2017), which can facilitate secondary SO_4^{2-} formation (Zhang et al., 2021a), enhancing SO_4^{2-} concentrations in a positive feedback loop – which is particularly important during high relative humidity haze events (Cheng et al., 2016; Song et al., 2021b; Wang et al., 2016; Wang et al., 2014).

[1] The United States Clean Air Act requires EPA to set National Ambient Air Quality Standards (NAAQS) for six pollutants including fine particulate matter (PM2.5) and to periodically review those standards. In 2006, EPA updated the NAAQS for PM2.5 concentrations averaged over a 24-hour time period. This updated standard requires the calculation of the 98^{th} percentile of daily (24-hour) PM2.5 concentrations for three years, and that the average of those three 98^{th} percentile concentrations be at or below a threshold of 35 ug/m3. For simplicity, we refer to this as the 2006 24-hour PM2.5 NAAQS.

3. Line 109: The introduction provides detailed information on specific reaction mechanisms in the gas phase and clouds. This paper suggests presenting the new mechanisms introduced here in detail and reconfirming the roles of heterogeneous and multiphase processes. It is recommended that the specific mechanisms introduced in this paper be listed in detail in this section and that the issues related to heterogeneous and multiphase processes be reconfirmed.

We have included the specific heterogeneous pathways in the last paragraph of the introduction

In this paper we describe the implementation of heterogenous sulfur chemistry in ALW in the Community Multiscale Air Quality (CMAQv5.3.2) modeling system (USEPA, 2020), leading to additional SO_4^{2-} and HMS formation. We refer to this chemistry as heterogeneous given the use of the heterogeneous framework (Hanson et al., 1994). Heterogeneous sulfur chemistry pathways implemented include the oxidation of dissolved S(IV) species by H_2O_2, O_3, PAA, MHP, TMI-O_2, NO_2, and the in-aerosol aqueous formation of HMS. -In addition to heterogeneous chemistry updates, ionic strength effects were added to condensed-phase rate expressions and Henry's law coefficients of some species. The updated model was applied for several time periods and for different domains and horizonal 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

4. Line 130: How should the boundary problem of ionic strength (I) in aerosol water be addressed? Although this is mentioned later, the I values used here are based on maximum boundaries tested in laboratory tests. However, in actual aerosol during haze events, I can often reach several tens of M, which is significantly higher than the few M observed in laboratory conditions. Considering the potential exponential growth of the enhancement factor (EF) with increasing ionic strength (I), the intensity of aerosol ions may significantly impact the reaction rate. Of course, these are merely my thoughts and discussions. The authors do not need to address this issue directly, but they could consider it further in their outlook or future work.

This is a good and an important topic for future modeling work! In representing reactions that can occur in dark, cold, haze conditions, we would be eager to see the ionic strength experimental bounds extended for the NO_2 and TMI-catalyzed O_2 aqueous oxidation pathways. We looked into incorporating the higher ionic strength bounds published in Liu et al., (2020) for secondary sulfate formation via H_2O_2, however, this pathway was not a dominant sulfate formation pathway in the episodes and contexts in Alaska with minimal photochemistry (Liu et al., 2020). Nonetheless, this can be investigated in the future.

5. Lines 320-324: It is recommended that HMS use a different color bar range than sulfate. Using a maximum value of 5, for instance, results in nearly zero HMS concentration, and the spatial distribution of HMS is not effectively captured in Figure 1c. The same issue is observed for the figures 3, 6, 8, and 10.

Yes. The reason why the concentrations appear nearly zero in these plots is because they are zero. HMS is not an included species in Base CMAQ (neither formed in ALW nor in cloud liquid water). To evade confusion, we included this information in the figure caption for all of the aforementioned figures:

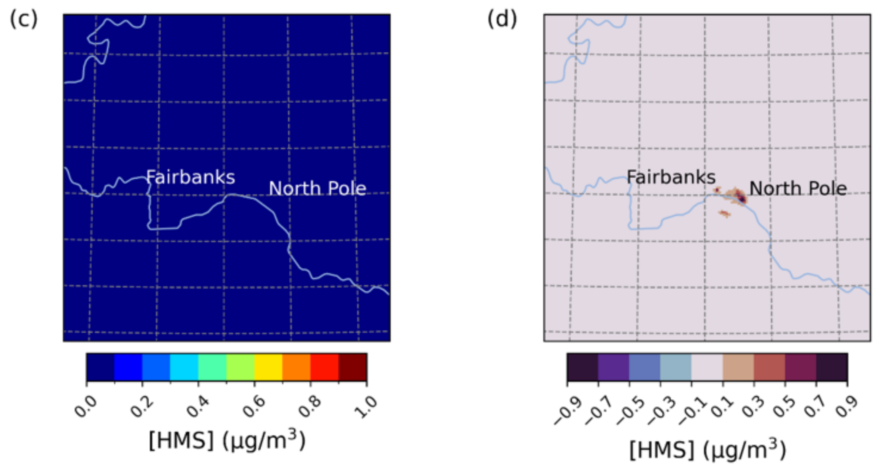

Figure 1: Episode average sulfate (a), and HMS (c) concentrations in the Base simulation along with daily max differences in sulfate (b), and HMS (d) concentrations between the Base_Het and Base CMAQ simulations over Fairbanks and North Pole AK for episode 1 (from January 25th, 2008, to February 11th, 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.

Nonetheless, to pair better with the counter difference plot, we have constrained the color bars and made all discrete instead of continuous for all of these figures and Fig 12.

6. Lines 331-332: What does atmospheric acidity, particularly aerosol pH, look like in this context? It is suggested that the authors consider incorporating pH into the exploration of dominant pathways to help explain why TMI is dominant in Alaska.

To clarify, the pH referred to in this line is the episode-averaged modelled aerosol pH. The overall heterogeneous production rate for the TMI-O_2 pathway in the Base_Het is pH dependent in that the effective Henry's law coefficient for SO2 is pH dependent, however, its k_{chem} is actually pH independent (Table 1) (Martin and Good, 1991). We have made the following modifications:

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 (aerosol 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] = 6 μg/m^3, and Temp = 243K) (Fig. S2) and is ~ 1 order of magnitude higher than that for HMS formation in ALW. Despite the NO_2 k_{chem} being higher, however, the TMI-catalyzed O_2 heterogeneous rate of sulfate formations rate limiting stepis dependent upon is SO_2 partitioning into the particle, as Fe and Mn are both aerosol species, and simulated dark conditions reduce the conversion of Fe^{3+} to Fe^{2+} from daytime photochemical reactions (Alexander et al., 2009; Rao and Collett, 1998; Shao et al., 2019). The effective Henry's law coefficient for SO_2 increases with pH, while the Henry's law coefficient for NO_2 remains low across the pH spectrum. This and a higher mass accommodation coefficient (by ~2 orders of magnitude) for SO_2 compared to NO_2 Another potential reasoncontribute to thethe TMI-catalyzed O_2 pathway outcompetinges the NO_2 pathways for this model configuration. is due to its mass accommodation coefficient (α, Eq. 2) being higher than that for the NO_2 pathway by ~2 orders of magnitude. The TMI-catalyzed O_2 heterogeneous reactive uptake pathway also outcompetes the H_2O_2 and O_3 heterogeneous reactive uptake pathways due to low photochemical activity with the dark conditions of this domain and episode.

We incorporate a pH and temperature dependent (Ibusuki and Takeuchi, 1987) in our sensitivity runs (TMI_sens, TMI_NO2_sens, and ALL_IONIC) to explore the effects of acidity and temperature on the k_{chem} of this pathway and the entire sulfate and HMS formation system. We find that this formation pathway no longer dominates, however, it is difficult to say whether this is aerosol pH or temperature driven.

Using a back-of-the-envelope excel calculation, when decreasing aerosol pH from 4 to 3, the k_{chem} for the TMI pathway decreases by ~81%, however, when decreasing the temperature from 243K to 233K (a decrease in temperature that is within range for Fairbanks winters), the k_{chem} for the TMI pathway decreases by ~77%. Therefore, this particular formation pathway is sensitive to both temperature and pH. We made this change to better clarify this takeaway in the discussion:

4.3 $PM_{2.5,sulf}$ formation pathways of interest during cold and dark episodes

In addition to the inclusion of both heterogeneous SO_4^{2-} and HMS formation in CMAQ, we determined which $PM_{2.5,sulf}$ formation pathways are the most important given ionic strength, pH, and temperature regimes characteristic of dark and cold conditions. Across both the Fairbanks and CONUS domains in the Base_Het during the wintertime, the most prevailing

heterogeneous SO_4^{2-} formation pathway was the TMI-catalyzed O_2 pathway (Fig. 2, 4, S11). In the TMI_sens E1 in Fairbanks, however, this formation pathway was the third most important behind HMS formation and the NO_2 pathway (Fig. S3). Although the modelled pH for the TMI_sens ranged between 3-6 for Fairbanks and North Pole and for both episodes (Fig. S4) which included the optimal pH for this pathway (pH=4.2; (Ibusuki and Takeuchi, 1987)), the dampening of this pathway can also~~mostly~~ be attributed to the extremely cold temperatures (modelled average -30° C or 243° K)~~, which drastically lower the k_{chem}~~.

It is also noted, however, that aerosol pH may be overestimated in the TMI_sens given the methods used to calculate it only consider inorganic aerosol species and $PM_{2.5,sulf}$ concentrations are largely HMS:

TMI_sens modelled aerosol pH was seen to be least acidic in comparison to all of the other model simulations, especially in North Pole (Fig. S4). As noted before, HMS was the largest contributor to secondary $PM_{2.5,sulf}$ formation at North Pole, the formation (and loss) rates of which increase with increasing pH (Ervens et al., 2003; Kok et al., 1986) (Fig. 2). Aerosol pH and ALW calculations in ISORROPIA II only consider inorganic species. Organic species (e.g., organic acids) may also increase aerosol acidity (Zuend et al., 2011; Zuend and Seinfeld, 2012), and therefore the predicted aerosol pH in the TMI_sens might represent an overprediction. Aerosol pH for the Base_Het, TMI_NO2_sens, and All_Ionic model simulations were similar at both North Pole and Fairbanks with both sensitivity simulations predicting slightly higher pH than the Base_Het simulation during E1 and slightly lower pH during E2.

7. Lines 306 and 381: The title 'Time' is not recommended. If you want to highlight the similarities between sections 3.1.1 and 3.1.2, consider combining the discussions. If the goal is to emphasize the differences, please choose a title that reflects the unique feature of each section.

The goal is to emphasize the differences and therefore we changed the sub-headings to reflect this:

3 Results

3.1 Modelled particulate sulfur enhancement during dark and cold PM episodes in Fairbanks and North Pole, AK

3.1.1 Aerosol sulfur enhancements during a wintertime haze event (E~~E~~pisode 1 (E1)~~)) January 25 – February 11, 2008~~

The Base simulation average E1 sulfate concentrations around Fairbanks and North Pole, AK are ~ 2 - 3.5 mg/m^3 (Fig. 1a and c). Compared to the Base, the Base_Het simulation leads to increased $PM_{2.5,sulf}$ predictions concentrated around the cities of Fairbanks and North Pole as well as the region south of the Tanana River (Figure 1b, d). The additional heterogeneous chemistry in the Base_Het simulation contributes up to an additional 11 μg/m^3 of maximum daily $PM_{2.5,sulf}$ compared to the

3.1.2 Aerosol sulfur enhancements with liquid cloud events (e~~E~~pisode 2 (E2)~~)) November 4 – 17, 2008~~

Sulfate and HMS are known to form efficiently in cloud and fog droplets (Altwicker and Nass, 1983; Boyce and Hoffmann, 1984; Calvert et al., 1978; Clifton et al., 1988; Ibusuki and Takeuchi, 1987; Lee and Schwartz, 1983a; Martin and Good, 1991; McArdle and Hoffmann, 1983). In E1, there was minimal cloud or fog liquid water simulated; however, during E2 (November 4 – November 11, 2008), there were some periods where cloud/fog chemistry impacts on $PM_{2.5,sulf}$ formation were evident.

Compared to E1, $PM_{2.5,sulf}$ concentration enhancements were lower overall during E2. Differences between Base_Het and Base simulations, however, are appreciable during this episode with $PM_{2.5,sulf}$ increasing up to 4.6 μg/m^3 across the entire domain (daily maximum difference) (Fig. 3). Enhancements in $PM_{2.5,sulf}$ are mainly driven by increased SO_4^{2-} formation in and around Fairbanks and North Pole; however, simulated HMS concentrations reached up to 4.4 μg/m^3 south of the Tanana River (daily

8. Line 649: I was very excited to see the HMS simulation. I'm eager to know whether the modeling of HMS and the multiphase chemistry of sulfate (including the effects of ionic strength) will be included in a future official version of CMAQ.

We plan to incorporate the updates from this work in CMAQv6.0 which as a 2026 target date for release. 😊

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

Ibusuki, T., and Takeuchi, K. (1987). Sulfur dioxide oxidation by oxygen catalyzed by mixtures of manganese(II) and iron(III) in aqueous solutions at environmental reaction conditions. *Atmospheric Environment (1967), 21*(7), 1555-1560. doi:https://doi.org/10.1016/0004-6981(87)90317-9

Liu, T., Clegg, S. L., and Abbatt, J. P. D. (2020). Fast oxidation of sulfur dioxide by hydrogen peroxide in deliquesced aerosol particles. *Proceedings of the National Academy of Sciences, 117*(3), 1354. doi:10.1073/pnas.1916401117

Martin, L. R., and Good, T. W. (1991). Catalyzed oxidation of sulfur dioxide in solution: The iron-manganese synergism. *Atmospheric Environment. Part A. General Topics, 25*(10), 2395-2399. doi:https://doi.org/10.1016/0960-1686(91)90113-L

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