

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 SO₂ 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 (SO₄²⁻), 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 SO₄²⁻, and secondary SO₄²⁻ formed via gas-phase oxidation of sulfur dioxide (SO₂) and in-cloud aqueous oxidation of dissolved S(IV). Dissolution and reaction of SO₂ 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 SO₄²⁻ concentrations observed during Fairbanks winters. In addition, hydroxymethanesulfonate (HMS), a particulate sulfur species sometimes misidentified as SO₄²⁻, is known to form during Fairbanks winters. Heterogeneous formation of SO₄²⁻ 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 heterogeneous 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 horizontal resolutions. Two historical wintertime PM episodes were

2. Line 39: Please give the meaning of "2006 24-hour PM_{2.5} 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 (PM_{2.5}) and to periodically review those standards. In 2006, EPA updated the NAAQS for PM_{2.5} concentrations averaged over a 24-hour time period. This updated standard requires the calculation of the 98th percentile of daily (24-hour) PM_{2.5} concentrations for three years, and that the average of those three 98th percentile concentrations be at or below a threshold of 35 ug/m³. For simplicity, we refer to this as the 2006 24-hour PM_{2.5} 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 heterogeneous 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 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

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:

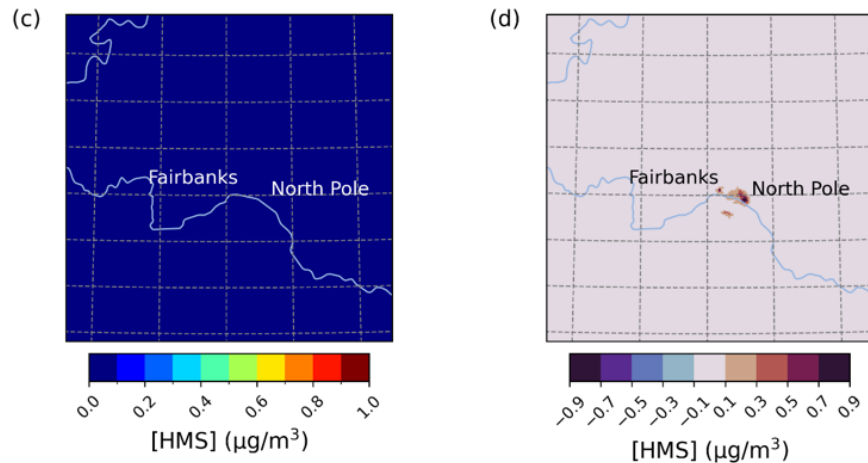


Figure 1: Episode average sulfate (a), and HMS (c) concentrations in the Base simulation along with daily max differences in sulfate (b), and HMS (d) concentrations between the Base_Het and Base CMAQ simulations over Fairbanks and North Pole AK for episode 1 (from January 25th, 2008, to February 11th, 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-O₂ 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 $\text{PM}_{2.5\text{ sulf}}$ 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, $[\text{Fe(III)}] = 0.24 \text{ M}$, $[\text{Mn(II)}] = 0.002 \text{ M}$, $[\text{SO}_2] = 20 \text{ ppb}$, $[\text{NO}_2] = 20 \text{ ppb}$, $[\text{SO}_4^{2-}] = 3 \text{ }\mu\text{g/m}^3$, $[\text{ALW}] = 6 \text{ }\mu\text{g/m}^3$, 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 step is dependent upon 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 reason contribute to the TMI-catalyzed O_2 pathway outcompeting 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 SO₄²⁻ 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

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heterogeneous SO₄²⁻ formation pathway was the TMI-catalyzed O₂ 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 NO₂ 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 ~~alsomostly~~ 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 (Episode 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/m³ (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/m³ of maximum daily PM_{2.5,sulf} compared to the

3.1.2 Aerosol sulfur enhancements with liquid cloud events (Episode 2 (E2)) November 4–17, 2008

Sulfate and HMS are known to form efficiently in cloud and fog droplets (Altwickler 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/m³ across the entire domain (daily maximum difference) (Fig. 3). Enhancements in PM_{2.5,sulf} are mainly driven by increased SO₄²⁻ formation in and around Fairbanks and North Pole; however, simulated HMS concentrations reached up to 4.4 µg/m³ 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. 😊

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- 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](https://doi.org/10.1016/0960-1686(91)90113-L)
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(2015). Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. *Atmos. Chem. Phys.*, 15(4), 2031-2049. doi:10.5194/acp-15-2031-2015