Dear Dr. Harris,

Please find below our itemized responses to the reviewers' comments and a marked-up manuscript. We have addressed all the comments raised by both reviewers and incorporated them in the revised manuscript.

Sincerely,
Jingyuan Shao et al.

Reviewer #1

The study of Shao et al. Implemented four heterogeneous sulfate formation mechanism into GEOS-Chem model with a focus of the low biases of modeled sulfate production rates in China. The four paths are via H2O2, O3, NO2, and TMI on aerosols. In addition, TMI-catalyzed oxidation in clouds were also considered. To reduce the uncertainties, the oxygen isotopes observations were used for comparison as it's highly sensitive to the relative importance of different sulfate production mechanism. To investigate the dependence on aerosol PH, sensitivity studies with prescribed values of aerosol PH were also conducted. The design of the experiments are comprehensive and the results are convincing. Overall, the results with the four added heterogeneous reactions significantly reduced the low biases of sulfate and also oxygen isotopes, which show better agreement with the observations. The publication is very well written, clearly structured, and the analyses are comprehensive and convincing. In particular, the authors present a thorough analysis of the heterogeneous oxidation paths, substituting the bulk first-order uptake of SO2 (reaction probability /uptake coefficients) by a more specific calculation approach. The paper has a good chance to become an important reference for future studies on the sulfate heterogeneous reaction mechanism in China. It also has regional/global impacts. I support publication of this manuscript and have only a few small comments that may require minor revision.

Response: We thank the reviewer for the valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized response below.

Comment: 1. P5 L45 Can you add some more details of the methodology of the in-cloud TMI- catalyzed aqueous-phase S(IV) oxidation? As it seemed this in-cloud TMI-relevant path is very important in polluted events.

Response: Thanks for pointing it out. Metal-catalyzed S(IV) oxidation by O_2 (TMI) in cloud droplets was considered to be one of the most important sulfate formation pathways during the winter in the North Hemisphere (Huang et al., 2014; Harris et al., 2013; Alexander et al., 2009; Sofen et al., 2011), and we also found that the pathway accounted for over 20% of total sulfate formation during HPP at Beijing (P11L355). We now state in the text (P5L145) "In the model simulation Run_TMI, we implemented the in-cloud TMI-catalyzed aqueous-phase S(IV) oxidation

by O_2 into the model, which is thought to be one of the most important sulfate formation pathways during the North Hemisphere winter (Huang et al., 2014; Harris et al., 2013; Alexander et al., 2009; Sofen et al., 2011). The parameterization of TMI-catalyzed S(IV) oxidation in cloud for GEOS-Chem follows Alexander et al. (2009).”

We have also added more details on the methodology of the in-cloud TMI-catalyzed aqueous-phase S(IV) oxidation in the Supplement (Text S3; Figure S4; Table S2; Table S3). This also addresses Comment #2 below. We now state in the text (P5L155) “After modification, the average aqueous-phase concentration of Fe(III) in cloud water during our studying period is 2.9 µM and Mn(II) is 1.3 µM in the model, which is consistent with previous work (He et al., 2018; Shen et al., 2012; Guo et al., 2012) (see Text S3 in the Supplement for more details).”

Text S3 in the Supplement is as follows:

The parameterization of TMI-catalyzed S(IV) oxidation in clouds in GEOS-Chem is described in Alexander et al., (2009). The natural source of Fe ($[Fe]_{nat}$) and Mn ($[Mn]_{nat}$) from mineral dust are scaled to total dust mass. $[Fe]_{nat}$ is 3.5% of total dust mass and $[Mn]_{nat}$ is a factor of 50 lower than $[Fe]_{nat}$ (Alexander et al., 2009). The anthropogenic source of Fe ($[Fe]_{ant}$) and Mn ($[Mn]_{ant}$) from coal combustion are scaled to the abundance of primary anthropogenic sulfate due to their common source and atmospheric lifetime $[Mn]_{ant}$ is 1/300 of primary sulfate concentration and $[Fe]_{ant}$ is 10 times that of $[Mn]_{ant}$ as described in Alexander et al. (2009). Figure S4 show the distribution of simulated $[Fe]_{nat}$ and $[Fe]_{ant}$ during the entire model simulation period. Table S2 compares autumn-winter mean modeled Mn and Fe with the observations at several sites in east Asia, including 3 sites in the North China Plain (NCP) region (Beijing, Tianjin and Shijiazhuang), 2 sites in the Sichuan Basin (Chengdu and Chongqing), and Lanzhou and Seoul which are the upwind and downwind of Beijing, respectively. The model tends to underestimate both Fe and Mn at the NCP sites by a factor of 0.25-0.72. Model comparison with observations in the Sichuan Basin shows good agreement on Mn concentration (within 20% for both Chongqing and Chengdu), with model calculations overestimating the observations of Fe concentrations. For sites in Lanzhou (northwest of Beijing, upwind) and Seoul (southeast of Beijing, downwind), model comparison with observations indicates good agreement on Fe (within 5%), and underestimates Mn by 60%. The model underestimates Fe and Mn in the NCP region and overestimates in Sichuan Basin. These discrepancies highlight the limitations of our approach applying a global-scale factor of $[SO4]_{primary}/[Mn]_{ant}$ and $[dust]/[Fe]_{nat}$, as regionally varying emissions control technologies and mass fraction of Fe in dust may impact the relative emission rates.

However, sulfate formation by the TMI-catalyzed oxidation pathway is influenced by soluble Fe^{3+} and Mn^{2+} concentrations, as opposed to total Fe and Mn. Previous studies suggest that the solubility of Fe and Mn ranges from 0.03 to 54% and 1.2 to 97%, respectively. The solubility of metals is influenced by several factors such as the natural versus anthropogenic origin of samples (A.R. Baker et al., 2006; K.V. Desboeufs et al., 2005; K.V. Desboeufs et al., 2001; Spokes et al., 1994; A. Ito1 and Y. Feng, 2010; P.Y. Chuang et al., 2005; Solmon et al., 2009), acidity, and sunlight. In

this study, we assume a solubility of 10% for $[Fe]_{ant}$, 0.45% for $[Fe]_{nat}$, 50% for $[Mn]_{ant}$, and 5% for $[Mn]_{nat}$ in cloud water. The modeled soluble Fe^{3+} and Mn^{2+} concentration is shown in Table S3. After modification, the average modeled concentration of soluble Fe(III) in cloud water during our study period is 2.9±1.8 μM and Mn(II) is 1.3±0.7 μM, which is consistent with estimates (He et al., 2018) and observations (Shen et al., 2012; Guo et al., 2012). A sensitivity study is performed based on Run_TMI but with the higher solubility of Fe and Mn as Alexander et al. (2009): the solubility of 1% of $[Fe]_{nat}$ and 50% for $[Mn]_{nat}$ in cloud water. The modeled soluble Fe(III) and Mn(II) concentration reaches 20μM and 10 μM during HPP, up to a factor of 5 higher than the observations. The simulated sulfate concentration is also overestimated the observation by around 100% during HPP in Beijing.

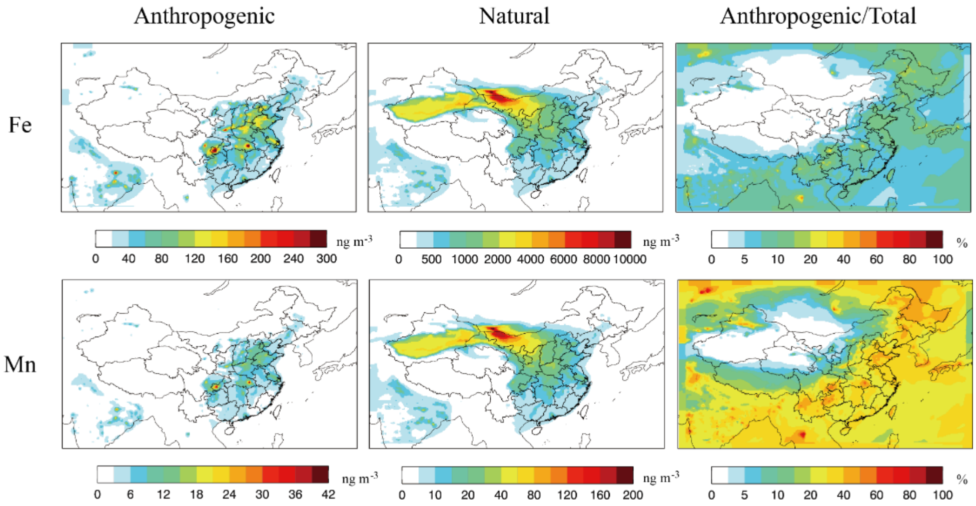


Figure S4. Modeled anthropogenic and natural Fe and Mn (ng m^{-3}) at the surface, along with the anthropogenic/total Fe and Mn concentration percentages.

Table S2. Comparison of observed and modeled autumn and winter mean Mn and Fe concentrations (ng m^{-3}) from several East Asian locations.

Location	Fe (Mn) observation (ng m^{-3})	Fe (Mn) model (ng m^{-3})	Fe (Mn) Model/observation	Reference
Beijing	1800 (90)	835 (22.7)	0.46 (0.25)	Zhao et al. (2013)
Tianjin	1980 (120)	1239 (36.2)	0.72 (0.30)	
Shijiazhuang	2250 (150)	1615 (44.3)	0.63 (0.30)	
Chengdu	875 (38)	1245.7 (34.1)	1.42 (0.90)	Wang et al. (2018)
Chongqing	502.5 (36.5)	1226.0 (39.7)	2.4 (1.09)	
Lanzhou	1534 (59)	1456.9 (33.0)	0.95 (0.56)	Wang et al. (2016)
Seoul	227 (21)	219.8 (6.1)	0.97 (0.30)	Park et al. (2018)

Table S3. Comparison of observed and modeled soluble Mn(II) and Fe(III) concentrations (μM).

	This study Range (monthly mean)	Beijing (He et al., 2018)	Mt. Tai[a] (Shen et al., 2012)	Mt. Tai (Guo et al., 2012)
Fe(III)	0.4-11.2 (2.9±2.7)	0.6-6.1 (2.6±1.8)	0.8-7.4	2.6
Mn(II)	0.4-4.8 (1.3±0.9)	1	0.4-1.7	1.2

[a]Mt. Tai is located in central Shandong province at the eastern edge of the NCP region.

Comment: 2. P5 L45 The TMI-catalyzed oxidation path are important both in-cloud (aqueous) and on-aerosol (heterogeneous). Is there any possibility to verify the assumption of Fe and Mn treatments in the model, from the natural dust and anthropogenic emissions, solubility, ionic strength of cloud liquid water, etc.? Or if not, is it necessary to add some discussions about the uncertainty of those assumptions and the possibility of the impacts on the analysis?

Response: Thanks for pointing it out. We now state in the text (P5L155): "After modification, the average modeled concentration of Fe(III) in cloud water during our study period is 2.9 μM and that of Mn(II) is 1.3 μM, which are consistent with previous work (He et al., 2018; Shen et al., 2012; Guo et al., 2012) (see Text S3 in the Supplement for more details)." Natural and anthropogenic dust emissions are now shown in Figure S7. The influence of ionic strength on the in-cloud, TMI-catalyzed S(IV) oxidation pathway is negligible, but is significant in aerosol water (heterogeneous pathway). Please refer to the response for Comment #1 and Text S3 in the Supplement for the discussions on Fe and Mn treatments and associated uncertainties.

In addition, we deleted the sentence on P5L155 to avoid misunderstanding. We also rewrite the sentence on P6L165 "In addition, we considered the impacts of acidity and ionic strength on TMI-catalyzed reaction rates following Cheng et al. (2016) (Table S2 in the SI of Cheng et al., 2016), since the ionic strength of aerosol liquid water can reach 20 M during polluted periods (He et al., 2018; Herrmann et al., 2015)."

Comment: 3. P7 L110 The 2010_MEIC emission is used in the study, however the anthropogenic SO2 emissions has been reduced largely since 2009 thus the SO2 overestimation might be expected for Beijing. Is there any impacts/uncertainty induced by this issue?

In the Run_Het results, the TMI-relevant reactions are the most important among the four heterogeneous paths during both clean and polluted events. "In the model, the heterogeneous sulfate production rate from the TMI-catalyzed reaction is calculated as first-order uptake in SO2". Is that relevant with the SO2 overestimation in the model?

Response: Thanks for pointing this out. Unfortunately, the updated MEIC emission inventory was not released at the time when we ran our model simulations. We now state in the text (P13L388) "Anthropogenic SO_2 emissions in China have been reduced sharply since 2009 due to the stringent pollution control measures implemented (Zheng et al., 2018; Van der A et al., 2017; Krotkov et al.,

2016). Compared with 2010, anthropogenic SO_2 emissions reduced by about 50% in 2015 (Krotkov et al., 2016; Zheng et al., 2018; Van der A et al., 2017). NH_3 and non-methane volatile organic compounds (NMVOC) emissions in China remained stable during 2010–2017 due to the absence of effective mitigation measures in current policies (Zheng et al., 2018). The emission changes may affect the abundances of species that influence cloud and aerosol pH, and further influence sulfate production rates and the contribution of each sulfate formation pathway. However, other studies using observations between 2014-2016 (Liu et al., 2017; Song et al., 2018a) found a similar pH range as calculated here, suggesting that a modeled low bias in aerosol pH is not likely to be the source of the modeled discrepancy in $\Delta^{17}O(SO_4^{2-})$."

We believe that the SO_2 overestimation in the model will not change the dominance of TMI-relevant pathway in the model because SO_2 concentrations influence all four heterogeneous sulfate formation pathways. As shown in Figure S1, heterogeneous sulfate production rates parameterized as first-order in SO_2 or first-order in the oxidant result in similar values when aerosol pH < 6, the only difference is when production rates are limited by the mass transport across the air-water interface at higher pH values. SO_2 concentration influence the sulfate formation by gas-phase oxidation by OH and aqueous-phase oxidation by H_2O_2, O_3 and O_2 catalyzed oxidation by TMI. Anthropogenic sulfate emission also scales to anthropogenic SO_2 emission in the model. Therefore, the SO_2 overestimation would not change the main conclusion of this study regarding the fractional contribution of each sulfate formation pathway to total sulfate abundance in Beijing.

Comments: 4. P7 L120 The mass accommodation coefficients for O3 and NO2 are much lower that for SO2. Is this the reason that TMI-relevant reactions are much important in the analysis? How those parameters were determined? Any assumption? Is it necessary to put Text S2 in the manuscript? As the analysis is done for the October-November period, is it possible to apply to other seasons? any sensitivity/uncertainties to regions/seasons etc?

Response: Thanks for suggestions. The mass accommodation coefficients would influence heterogeneous sulfate production rates when aerosol pH >6, but the aerosol pH seldom reaches these values in the model. Even if aerosol pH reaches 6 in the model, Fe^{3+} and Mn^{2+} concentrations are very low due to low solubility at high pH (Cheng et al., 2016), thus less sulfate would be produced by this pathway under this condition. Therefore, the mass accommodation coefficients are not the reason that TMI-relevant reactions are so important among the four heterogeneous pathways. The mass accommodation coefficients for O_3, NO_2, H_2O_2 and SO_2 are from laboratory calculations and widely used (Jacob, 2000). Considering the importance of Table S2, we now move it to the manuscript.

The importance of heterogeneous sulfate formation for the global sulfur budget and in different seasons is the focus of our next paper, and is beyond the scope of this manuscript.

Comments: 5. P11 L345 It seemed the sulfate bias is reduced while the PM2.5 bias is still there. I'm just wondering is there any observational data of nitrate or ammonia available for comparison? It might give some indication of the partitioning of sulfate-nitrate. If the nitrate are well simulated or not impacted by the competition from sulfate formation, larger improvements of PM2.5 are expected?

Response:

Thanks for the comment. Both the sulfate and $PM_{2.5}$ low biases still exist, even after implementing the four heterogeneous sulfate production pathways, as discussed in the manuscript. We have discussed in the text the potential influence of HMS in reconciling the remaining low bias in sulfate. This paper focuses on sulfate production mechanisms. Investigation of model biases in nitrate and ammonia are outside the scope of this paper, although we do have a separate paper in preparation focusing on a comparison of modeled and observed nitrate in Beijing. In the figure below, we compare modeled and observed nitrate and ammonia concentrations, which shows that the enhancements in sulfate abundance in Run_Het result in a small increase in ammonia, but have a negligible effect on nitrate concentrations. As noted in previous work (Wang et al., 2013), the model tends to overestimate nitrate concentrations.

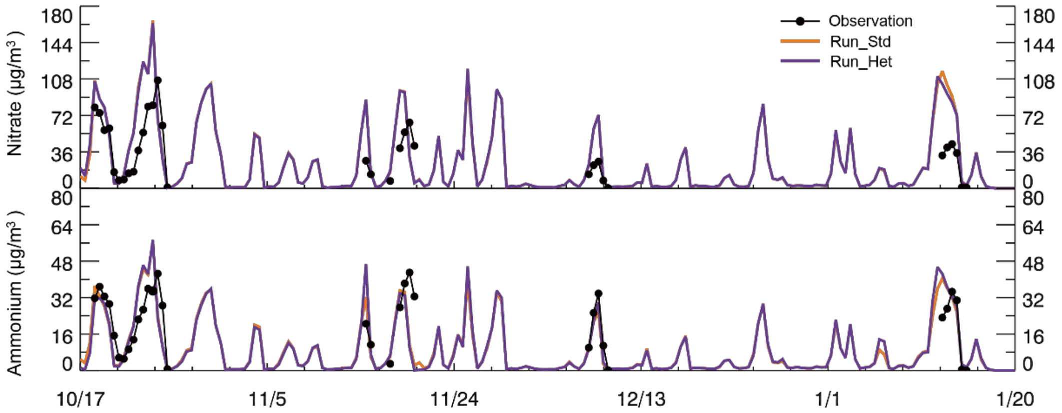


Figure. Time series of nitrate and ammonium at the surface in Beijing during the study period of 17 October 2014 – 20 January 2015. 12-hour average nitrate and ammonium observations (black line) are compared with model results from Run_Std (orange line) and Run_Het (purple line).

Comments: 6. P11 L349 The largest sulfate enhancements due to heterogeneous sulfate formation occur in megacities in eastern China and Sichuan Basin. For Sichuan region, is that also due to the high cloud liquid water path/RH?

Response: Thanks for pointing this out. We now state in the text (P10L320): "The largest enhancement in sulfate abundance after adding the in-cloud TMI pathway occurs in Sichuan basin (around 6.5 µg m^{-3}), where simulated anthropogenic Fe and Mn from coal fly ash (Figure S4) and SO_2 are high (Zhang et al., 2009) in part due to high SO_2 emissions combined with stagnant air and high relative humidity all year (Huang et al., 2014)." We have also compared the observed and modeled Fe and Mn concentrations in the Sichuan region as shown in Table S2.

Comments: 7. In Run_HET, the simulated oxygen isotopes are improved in average but the median are largely underestimated. In addition to the assumption of O3 oxidation underestimation, is there any possibility of other missing paths that not taken into account? Any discussions necessary?

Response: Ozone is the only oxidant with a $\Delta^{17}O$ value high enough to explain the majority of the discrepancy. The ozone oxidation pathway is mainly limited by the fraction of S(IV) that exists as SO_3^{2-}, which increases with increasing aerosol pH. In the manuscript, we have suggested that sulfate formed via oxidation of SO_2 by ozone on alkaline dust could explain at least part of the discrepancy, as this reaction is not included in the model (P14L440).

An underestimate of H_2O_2 could also explain part of the discrepancy. We now state in the text "The average modeled H_2O_2 concentrations during HPP and CP (Figure S3) underestimates the observations (Ye et al., 2018) by up to an order of magnitude (Figure S3). Mao et al. (2013) proposed a HO_2−Cu−Fe catalytic mechanism for H_2O_2 production in the aerosol phase. In their mechanism, the uptake of HO_2 and subsequent heterogeneous reactions with Cu and Fe will lead to production of H_2O_2 when the molar ratio of dissolved Cu to Fe was >0.1. Ye et al. (2018) found that the molar ratio of dissolved Cu to Fe could be >0.1 during moderately polluted days, suggesting the uptake of HO_2 radicals on particles might be an important source of H_2O_2 during the winter in Beijing. We note however that an underestimate of modeled H_2O_2 cannot explain all of the discrepancy in $\Delta^{17}O(SO_4^{2-})$, as sulfate formed from H_2O_2 oxidation (0.7 ‰) is lower than the observed mean $\Delta^{17}O(SO_4^{2-})$ of 0.9 ‰. All other oxidation pathways yield $\Delta^{17}O(SO_4^{2-})$ = 0 ‰ and cannot explain the model's low bias in $\Delta^{17}O(SO_4^{2-})$."

Reviewer #2

It has been a long question regarding the origin(s) of the non-zero Δ17O (but also Δ33S and Δ36S values) observed in tropospheric aerosols. This study implements the four majors SO2 oxidation pathways into the GEOS-Chem model in clouds and on aerosols and compared with the sulfates measured in China (coupled with the O- isotopes). This study also discussed the contribution of the different oxidation path- ways by estimating the pH in urban aerosols. While current models underestimate the sulfate formation in aerosols, results in this study significantly reduced the difference between observed and modeled in both sulfates concentrations and oxygen isotopes. However uncertainties remain but it has been identified that O2+TMI oxidation pathway is dominant when pH < 5. Another oxidation pathways on alkaline dust has also been hypothetized (very speculative) to explain the high Δ 17O-values.

Response: We thank the reviewer for the valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized response below.

Comments: 1. Input of stratospheric sulfates and sulfates resulting from Criegee radicals oxidation pathway are nowadays largely discussed when taking into account the S-isotopes. It is suggested that those processes are responsible for high Δ33S-values which cannot be explained yet by current knowledge. How would those processes affect the results? Is it possible to determine their contribution? I suggest these processes being discussed.

Response: Thanks for pointing this out. Based on the theoretical mechanism of sulfate production from the gas-phase oxidation of SO_2 by stabilized Criegee Intermediats (sCI) described in Taatjes et al. (2014), the $\Delta^{17}O$ value of sulfate formed through this mechanism will be equal to 0 permil as it is the central oxygen atom of ozone is transferred to the sulfate product. Additionally, it is expected that sCIs are not important for sulfate formation in wintertime in Beijing (Pierce et al., 2013). We have reiterated in the discussion (P14L439) that all sulfate formation pathways other than ozone and H_2O_2 cannot explain the modeled low bias in $\Delta^{17}O(SO_4^{2-})$ as they produce sulfate with $\Delta^{17}O(SO_4^{2-})$ = 0‰. Given that the HPP periods occur during time periods of stable conditions and a stagnant boundary layer with little vertical mixing, the stratospheric contribution at the surface is likely minor.

Taatjes, C. A., Shallcross, D. E., and Percival, C. J.: Research frontiers in the chemistry of Criegee intermediates and tropospheric ozonolysis, Phys Chem Chem Phys, 16, 1704-1718, doi:10.1039/c3cp52842a, 2014.

Pierce, J. R., Evans, M. J., Scott, C. E., Andrea, S. D. D', Farmer, D. K., Swietlicki, E., and Spracklen, D. V.: Weak global sensitivity of cloud condensation nuclei and the aerosol indirect effect to Criegee + SO_2; chemistry, Atmos. Chem. Phys., 13, 3163-3176, doi:10.5194/acp-13-3163-2013, 2013.

Comments: 2. The std_run model can account for the seasonality observed in the aerosols. Does the implementation of the four oxidation pathways change the results? Is it more accurate? If not, what would be the drivers?

Response: Thanks for this suggestion. The importance of four heterogeneous sulfate formation for global and seasonal variation is the focus of our next paper, and is beyond the scope of the current manuscript. In the current manuscript, we focus on autumn and winter in Beijing when $PM_{2.5}$ concentrations are highest and $\Delta^{17}O(SO_4^{2-})$ observations are available at relatively high time resolution.

Comments: 3. The RHs seem to be an important factor when it comes to understand the sulfate formation. However, as described in the paper, why would the Sichuan province be the only one to exhibit the largest enhancement of sulfate formation? Many places in China might be characterized by high humidity and air stagnation?

Response: Thanks for pointing this out. We now state in the text (P10L320): "The largest enhancement in sulfate abundance after adding the in-cloud TMI pathway occurs in Sichuan basin (around 6.5 µg m^{-3}), where simulated anthropogenic Fe and Mn from coal fly ash (Figure S4) and SO_2 are high largely due to high SO_2 emissions (Zhang et al., 2009) combined with stagnant air and high relative humidity all year (Huang et al., 2014)."

Comments: 4. The model supposes a constant contribution of primary aerosols emitted by the human. However the contribution of each sources might change depending of the seasons which should also affect the O-isotopes (towards 0 %o). Thus how would this sources variations change the results?

Response: Thanks for this comment. The importance of four heterogeneous sulfate formation for sulfate seasonal variation is the focus of our next paper, and is beyond the scope of the current manuscript.

Comments: 5. Recent studies suggested that dust particles would be responsible for pollution in China during winter, this certaintly due to photooxidation by mineral dust. Does the new models takes into account input of dust mineral from desert etc? It has also been shown that others reactions occurred on the dust particles besides NO2 and ozone (OH for example). How would it affect the O-isotopes? What would be the contribution of this oxidation pathway during the winter? Would it change the contribution value (9%)? I suggested this being discussed.

Response: Thanks for this suggestion. Run_Het does account for desert dust. We now state in the text (P13L425) "Modeled anthropogenic dust accounts for 28% of total dust in Beijing (Figure S7), and natural dust mostly originates from the Gobi Desert in southwestern Mongolia and the Badain Jaran Desert in northern China (Zhang et al., 2003; Zhang et al., 2016). The anthropogenic dust is not abundant enough to explain the difference between the results of Uno et al. (2017) and amount of sulfate production on alkaline dust required to explain the observed $\Delta^{17}O(SO_4^{2-})$." We now present the natural and anthropogenic dust distributions in China in Figure S7.

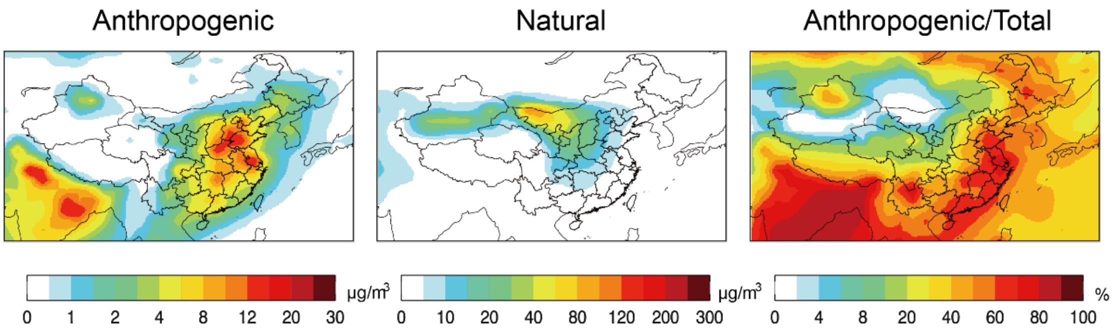


Figure S7. Modeled anthropogenic and natural dust (µg m^{-3}) at the surface, along with the percentage contribution of anthropogenic dust to total dust concentration.

Comments: 6. Although this study is very interesting and promising, results show that many uncertainties remain when it comes to understand the different oxidation pathways undertaken by SO2. I suggest that the conclusion should be more contrasted as O2+TMI cannot alone account for all the O-isotopes signatures.

Response: We agree that there are many remaining uncertainties, and that the TMI pathway is particularly uncertain due to limitations in the ability to model soluble Fe(III) and Mn(II). A discussion of this limitation is in Section Text S3. In the conclusions, we now emphasize that these results are a model prediction that is highly uncertain (P15L470): "The model predicts that TMI-catalyzed oxidation dominates heterogeneous sulfate production under calculated aerosol pH of

≤5; however, this reaction is highly uncertain due to limitations in our ability to assess modeled dissolved Fe(III) and Mn(II) concentrations.”

Comments: 7. With all the pollution in China, none of the models predict high pollution in Beijing which is surprising. How could it be explained?

Response: This paper aims to investigate the potential role of different heterogeneous sulfate production mechanisms to explain this discrepancy. We have added to the introduction (P2L55) “Previous simulations have shown that most models fail to predict severe haze pollution in Beijing at least in part because of sulfate underestimation (Jiang et al., 2013; Park et al., 2014; Pozzer et al., 2012).”

Comments: 8. In Figure 1, why the SOR is not correlated to SO4 during the 11/5 ?

Response: Thanks for pointing this out. Beijing held the Asia-Pacific Economic Cooperation (APEC) Summit on 11/5-11, 2014. Stringent emission control measures were applied in Beijing and its surrounding regions to improve air quality (Zhang et al., 2016). We now state in the text P4L105 “During and before APEC, SO_2 emissions in Beijing and its surrounding regions decrease due to strict emission controls to improve air quality (Zhang et al., 2016; Liu et al., 2015b).” The increase in SOR (to ~30%) and stable sulfate concentrations during APEC likely suggest more efficient SO_2 oxidation.

Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: Air quality model assessment using observations of sulfate oxygen isotopes in Beijing

Jingyuan Shao[1,2], Qianjie Chen[2,3], Yuxuan Wang[4], Xiao Lu[1], Pengzhen He[5], Yele Sun[6], Viral Shah[2,7], Randall V. Martin[8], Sajeev Philip[9], Shaojie Song[7], Yue Zhao[10], Zhouqing Xie[5], Lin Zhang[1], and Becky Alexander[2]

[1]Laboratory for Climate and Ocean-Atmosphere Studies, Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing 100871, China

[2]Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, USA

[3]Department of Chemistry, University of Michigan, MI 48109, USA

[4]Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204, USA

[5]Anhui Province Key Laboratory of Polar Environment and Global Change, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China

[6]State Key Laboratory of Atmospheric Boundary Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[7]School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

[8]Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada

[9]NASA postdoctoral program, NASA Ames Research Center, Moffett Field, CA, USA

[10]School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

Correspondence to: Becky Alexander (beckya@uw.edu), Lin Zhang (zhanglg@pku.edu.cn) and Zhouqing Xie (zqxie@ustc.edu.cn)

Abstract

Air quality models have not been able to reproduce the magnitude of the observed concentrations of fine particulate matter ($PM_{2.5}$) during wintertime Chinese haze events. The discrepancy has been at least partly attributed to low biases in modeled sulfate production rates due to the lack of heterogeneous sulfate production on aerosols in the models. In this study, we explicitly implement four heterogeneous sulfate formation mechanisms into a regional chemical transport model, in addition to gas-phase and in-cloud sulfate production. We compare the model results with observations of sulfate concentrations and oxygen isotopes ($\Delta^{17}O(SO_4^{2-})$) in the winter of 2014-2015, the latter of which is highly sensitive to the relative importance of different sulfate production mechanisms. Model results suggest that heterogeneous sulfate production on aerosols accounts for about 20% of sulfate production in clean and polluted conditions, partially reducing the modeled low bias in sulfate concentrations. Model sensitivity studies in comparison with the $\Delta^{17}O(SO_4^{2-})$ observations suggest that heterogeneous sulfate formation is dominated by transition metal ion catalyzed oxidation of SO_2.

1. Introduction

China has experienced rapid urbanization and industrialization in recent years, which has led to significant growth in concentration of $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm) in Chinese megacities, particularly in Beijing (the capital of China) and surrounding areas (Zhang et al., 2016; Wang et al., 2014; Zhang et al., 2015). Extensive studies consistently show high $PM_{2.5}$ levels in winter due to increased coal combustion for heating and a stable atmospheric boundary layer (Sun, et al., 2016; Sun, et al., 2014; Liu et al., 2015a). The frequency and concentration of $PM_{2.5}$ pollution negatively impacts human health and atmospheric visibility and results in economic losses (Gao et al., 2015; Lelieveld, et al., 2015; Zhang et al., 2015). The Chinese government has implemented a series of policies to improve air quality, and as a result the annual average $PM_{2.5}$ concentration in Beijing decreased by ~20% from 2013 to 2017 (Sun et al., 2016; Zheng et al., 2018; Beijing Environment Protection Agency, 2018; Chinese State Council, 2013). Despite these improvements, $PM_{2.5}$ concentrations in Beijing still regularly exceed the Chinese National Ambient Air Quality Standard (CNAAQS, 35 μg m^{-3} annual average) (Sun et al., 2016; Zhang et al., 2016; Beijing Environment Protection Agency, 2018).

Sulfate is one of the most important components of $PM_{2.5}$, representing 10-30% of $PM_{2.5}$ mass in eastern China (Huang et al., 2014; Zhang et al., 2013; Wang et al., 2014; Sun et al., 2016; Shi et al., 2017). Recent observations show that the sulfate mass fraction of $PM_{2.5}$ increases during haze pollution periods, indicating that sulfate is a key driver for severe haze events (Wang et al., 2014; Wang et al., 2016; Cheng et al., 2016; Li et al., 2017). Previous simulations have shown that most models fail to predict severe haze pollution in Beijing at least in part because of sulfate underestimation (Jiang et al., 2013; Park et al., 2014; Pozzer et al., 2012). Globally, sulfate production is dominated by the gas-phase oxidation of SO_2 by OH and aqueous-phase oxidation of S(IV) ($=SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$) by H_2O_2, O_3, and O_2 catalyzed by transition metal ions

(TMI) in cloud droplets (Stockwell and calvert, 1983; Schwartz, 1987; Harris et al., 2013; Alexander et al., 2012; Chen et al., 2018). Heterogeneous sulfate production, which refers to aqueous-phase oxidation of S(IV) ($=SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$) on the surface of and/or within the bulk pre-existing aerosols, is generally thought to be minor due to the low liquid water content of aerosols (< 10^{-9} cm^3 cm^{-3}) compared to clouds (10^{-8} to 10^{-6} cm^3 cm^{-3}) (Jacob, 2000). However, recent studies have shown that traditional gas- and aqueous-phase chemistry in cloud droplets cannot explain rapid sulfate production observed during haze, suggesting missing sulfate formation mechanisms on aerosols in the models (Zheng et al., 2015; Chen et al., 2016; Zhang et al., 2015; Wang et al., 2014; Cheng et al., 2016; Huang et al., 2014). These missing sulfate formation mechanisms on aerosols include heterogeneous oxidation of SO_2 by NO_2 (Cheng et al., 2016; Wang et al., 2016; Wang et al., 2018; Gao et al., 2016; Zhang et al., 2015) and O_2 catalyzed by TMI (Li et al., 2017a; Li et al., 2011) and via a free radical chain mechanism (Huie and Neta, 1984; Hung and Hoffman, 2015). The importance of these heterogeneous reactions remains highly uncertain due in part to uncertainties regarding the aerosol liquid water content, pH, and ionic strength, all of which impact heterogeneous reaction rates (Herrmann et al., 2015; Cheng et al., 2016). In particular, ambient aerosol pH cannot be directly measured, and thus represents a large source of uncertainty (Hennigan et al., 2015).

Previous studies have calculated a large range of aerosol pH values (3.4 – 7.8) in Beijing using a thermodynamic model (ISORROPIA-II) (Fountoukis and Nenes, 2007). He et al. (2018) noted that the large differences in calculated aerosol pH depended on whether they assume aerosols exist in stable (Wang et al., 2016; He et al., 2018) or metastable state (Liu et al., 2017; Guo et al., 2017; He et al., 2018). Stable-state assumption allows for the simultaneous existence of solid and aqueous phases, while the metastable-state assumption allows for the existence of aqueous phase only by assuming salts to be supersaturated in aerosols (Fountoukis and Nenes, 2007). Aerosol pH values simulated assuming stable state are near neutral (pH of 7), much higher than when assuming metastable state (pH of 4-5) during haze events in China (Guo et al., 2017; Liu et al., 2017; He et al., 2018). However, a recent study calculated aerosol pH of around 4.6 during Chinese haze events for both the stable and metastable assumptions in ISORROPIA-II after fixing coding errors that impacted the stable state assumption (Song et al., 2018~~a~~). This casts doubt on the existence of neutral aerosol pH during Chinese haze events and thus the importance of the NO_2 oxidation pathway, which is not important under acidic conditions. Other factors, such as underestimate of NH_3 emissions (Zhang et al., 2017) and Ca^{2+} concentrations in aerosols (Shen et al., 2016) and the lack of consideration of organic acids in aerosol pH calculations (Wang et al., 2018), add additional uncertainties in estimates of aerosol pH and thus sulfate production rates and mechanisms in Chinese haze events.

The oxygen isotopic composition $\Delta^{17}O$ ($\approx \delta^{17}O - 0.52 \times \delta^{18}O$) of secondary sulfate ($\Delta^{17}O(SO_4^{2-})$) reflects the relative importance of different oxidation mechanisms in sulfate production because some of the oxidants transfer unique oxygen isotope signatures to the sulfate oxidation product (Savarino et al., 2000). Sulfate production via S(IV) oxidation by O_3 and H_2O_2 leads to positive $\Delta^{17}O(SO_4^{2-})$ values of 9.8‰ and 0.7‰, respectively, while all other oxidants lead to $\Delta^{17}O(SO_4^{2-})$ at or near 0‰ (Table S1) (Vicars and Savarino, 2014; Savarino and Thiemens, 1999; Lee and Schwartz, 1983; Holt et al., 1981;

Dubey et al., 1997). Primary sulfate, both natural (dust and sea salt) and anthropogenic (coal and oil combustion), also has $\Delta^{17}O(SO_4^{2-})$ values equal to 0‰ (Dominguez et al., 2008; Lee et al., 2001). Once formed, sulfate in the atmosphere does not undergo further isotope exchange. Surface observations around the world show that $\Delta^{17}O(SO_4^{2-})$ ranges from 0 to 6‰ (Alexander et al., 2012; Alexander et al., 2005; Chen et al., 2016; Dominguez et al., 2008; Jenkins and Bao, 2006; Lee et al., 2001; Lee and Thiemens, 2001; McCabe et al., 2006; Patris et al., 2007; He et al., 2018). Due to the large positive enrichment of sulfate formed from O_3 oxidation ($\Delta^{17}O(SO_4^{2-})$ = 9.8 ‰) and the strong pH dependence of this aqueous-phase reaction, $\Delta^{17}O(SO_4^{2-})$ is highly sensitive to pH.

In this work, we implement four heterogeneous reactions for sulfate formation (via H_2O_2, O_3, NO_2, and TMI) into a global chemical transport model (GEOS-Chem) and compare the model results with observations of sulfate and SO_2 concentrations and $\Delta^{17}O(SO_4^{2-})$ in Beijing from October 2014 to January 2015. During this time period, Beijing held the Asia-Pacific Economic Cooperation (APEC) meeting from November 5-11, 2014. During and before APEC, SO_2 emissions in Beijing and its surrounding regions decrease due to strict emission controls to improve air quality (Zhang et al., 2016; Liu et al., 2015b).~~strict emission control measures were applied in Beijing and its surrounding regions to improve air quality (Zhang et al., 2016).~~ This paper is organized as follows. Section 2 describes the model simulations and the observations, and the method used to calculate heterogeneous sulfate production rates. Section 3 discusses model results with and without heterogeneous sulfate production considered in comparison with observed concentration and $\Delta^{17}O(SO_4^{2-})$. Section 4 discusses and explains the differences between our results and observations. Section 5 summarizes the main conclusions.

2 Methodology

2.1 GEOS-Chem model

We use the three-dimensional GEOS-Chem chemical transport model nested-grid version v10-01 (http://www.geos-chem.org/) to investigate sulfate formation mechanisms in Beijing, China between October 18, 2014 and January 17, 2015 (Wang et al., 2004; 2013; 2014; Zhang et al., 2015; 2016). The model has a horizontal resolution of 1/4° latitude by 5/16° longitude over East Asia (70°E - 140°E, 15°N - 55°N) and 47 vertical levels up to 0.01 hPa (≈ 81 km). In the boundary layer where most heterogeneous sulfate production occurs, the vertical layer thickness is 120 - 150 m for the first 12 model layers (below 1700 m altitude). The model is driven by assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-FP), which has a temporal resolution of 3 hours (1 hour for surface quantities and mixing depths).

The model utilizes the global anthropogenic emission inventory EDGAR v4.2 (EC-JRC/PBL, http://edgar.jrc.ec.europa.eu/, 2011), overwritten by regional inventories such as the MIX Asian emission inventory over Asia (Li et al., 2017), EMEP over Europe (http://www.emep.int/index.html), and NEI2011 over the U.S. (https://www.epa.gov/ttn/chief/net/2011inventory.html). In particular, the MIX Asian emission inventory includes emissions of SO_2, NO_x, CO, NH_3 and NMVOC at a spatial resolution of 0.25°×0.25° for the year 2010 (Li et al., 2017; Geng et al., 2017). Mineral dust aerosols are emitted in the model as described in Fairlie et al. (2007) and distributed in four size bins (radius of 0.1-1.0 μm, 1.0-1.8 μm, 1.8-3.0 μm, and 3.0-6.0 μm). In addition to natural dust, our model includes anthropogenic dust (radius of 0.1 - 1.0 μm) released from anthropogenic activities such as road-residential-commercial construction and combustion, following Phillip et al. (2017). Previous studies have suggested that anthropogenic dust accounts for about 25% of the $PM_{2.5}$ mass fraction in Beijing (Zhang et al., 2015; Phillipet al., 2017).

The sulfate-nitrate-ammonium aerosol system is fully coupled to oxidant chemistry (Park et al., 2004), with aerosol pH, ionic strength, and aerosol water content (AWC) calculated from the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) that was implemented into GEOS-Chem by Pye et al. (2009). In the standard model (Run_Std), sulfate is produced from gas-phase oxidation of SO_2 by OH, aqueous-phase oxidation of S(IV) ($=SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$) by H_2O_2 and O_3 in cloud droplets, and heterogeneous oxidation on sea-salt aerosols by O_3 (Alexander et al., 2005). Primary anthropogenic emissions of sulfate constitute 3.1% of total anthropogenic sulfur emissions in China and 1.5% - 3.5% elsewhere. Sulfate is removed from the atmosphere via dry (Zhang et al., 2001) and wet (Liu et al., 2001) deposition, with a global lifetime of about 4 days (Alexander et al., 2005).

We performed three simulations at high horizontal resolution (1/4°×5/16°) and seven sensitivity simulations at low horizontal resolution (4°×5°) to investigate sulfate formation mechanisms in Beijing, as summarized in Table 1. In the model simulation Run_TMI, we implemented the in-cloud TMI-catalyzed aqueous-phase S(IV) oxidation by O_2 chemistry into the model, which is thought to be one of the most important sulfate formation pathways during the North Hemisphere winter (Huang et al., 2014; Harris et al., 2013; Alexander et al., 2009; Sofen et al., 2011). The parameterization of TMI-catalyzed S(IV) oxidation in cloud for GEOS-Chem follows Alexander et al. (2009), ~~following Alexander et al. (2009),~~ but with reduced ~~the~~ solubility of trace metals Fe and Mn derived from natural dust (from 1% to 0.45% for Fe and from 50% to 5% for Mn) to better match observations (Desboeufs et al., 2001; 2005; Chuang et al., 2005). In the model, Fe from natural dust ($[Fe]_{nat}$) is 3.5% of total dust mass and Mn from natural dust ($[Mn]_{nat}$) is a factor of 50 lower than $[Fe]_{nat}$ (Alexander et al., 2009). Anthropogenic Mn ($[Mn]_{ant}$) and Fe ($[Fe]_{ant}$) are scaled to the abundance of primary anthropogenic sulfate due to common sources and atmospheric lifetimes. $[Mn]_{ant}$ is 1/300 of primary sulfate concentration and $[Fe]_{ant}$ is 10 times that of $[Mn]_{ant}$ as described in Alexander et al. (2009). Only soluble Fe and Mn in the oxidation states Fe(III) and Mn(II) catalyze S(IV) oxidation. For Fe, we assume solubility of 10% for $[Fe]_{ant}$ and 0.45% of $[Fe]_{nat}$ in cloud water, respectively, with 10% in the form of Fe(III) during daytime and 90% at night. For Mn, we assume a solubility of 50% for $[Mn]_{ant}$ and 5% for $[Mn]_{nat}$ in cloud water, respectively, with 100% in the form of Mn(II). After modification, the average aqueous-phase concentration of Fe(III) in cloud water during our studying period is 2.9 μM and Mn(II) is 1.3 μM in the model, which is consistent with previous work (Fe(III): 0.6-7.4 μM; Mn(II): 0.4-1.7 μM) (He et al., 2018; Shen et al., 2012; Guo et al., 2012) (see Text S3 in the Supplement for more details).~~In addition, we considered the impacts of acidity and ionic strength on TMI-catalyzed~~

~~reaction rates following Cheng et al. (2016) as described in the SI (Table S2), since the ionic strength of cloud liquid water can reach 0.01M during polluted periods (Herrmann et al., 2015).~~

In the model run Run_Het, we added four heterogeneous sulfate production mechanisms (via H_2O_2, O_3, NO_2, and TMI) on aerosols into the model, in addition to TMI-catalyzed oxidation in clouds. Implementation of these reactions in the model is described in Sect. 2.2. In Run_Het, heterogeneous sulfate production on aerosols only occurs when relative humidity (RH) is greater than 50%, effectively assuming that aerosol water content is too low for sufficient heterogeneous sulfate production at RH < 50%. When RH < 50%, aerosols are assumed to remain crystallized until reaching the deliquescence relative humidity (DRH). This is consistent with observations in previous studies showing that sulfate production rates in Chinese haze are positively correlated with RH (Sun et al., 2013; Zhang et al., 2015; Wang et al., 2016). Ca^{2+} and Mg^{2+} cations from dust (both natural and anthropogenic) are included in the aerosol thermodynamic calculations (aerosol pH, aerosol water content, ionic strength). We assume that Ca^{2+} and Mg^{2+} cations constitute 3.0% and 0.6% of the dust by mass, respectively, based on observations near East Asian dust source regions (Fairlie et al., 2010). In addition, we considered the impacts of acidity and ionic strength on TMI-catalyzed reaction rates following Cheng et al. (2016) (Table 2), since the ionic strength of aerosol liquid water can reach 20 M during polluted periods (He et al., 2018; Herrmann et al., 2015). We performed seven sensitivity studies based on Run_Het but with prescribed values of aerosol pH to examine the dependence of model results on aerosol pH alone (Table 1).

For all model simulations, sulfate produced from each oxidation pathway is labeled as a separate "tracer" in the model with a corresponding $\Delta^{17}O(SO_4^{2-})$ values (9 sulfate tracers in total, Table S1) as originally described in Alexander et al. (2005). Primary anthropogenic sulfate is also included as a separate tracer in the model with $\Delta^{17}O = 0‰$ (Lee et al., 2002). The details for calculating $\Delta^{17}O(SO_4^{2-})$ in the model are described in the supplement (Text S1).

2.2 Heterogeneous sulfate production on aerosols

Heterogeneous S(IV) oxidation in the model occurs on all aerosol types, including sulfate-nitrate-ammonium, dust, black carbon, organic carbon, and sea-salt aerosols. The heterogeneous sulfate production rate on aerosol (P_{het}) is calculated in the model assuming a first-order loss of SO_2 or oxidant (depending on which is the rate limiting step) via uptake by the aerosol (Eq. 1).

$$P_{\text{het}} = k[\text{SO}_2 \text{ or oxidant}] \qquad (1)$$

The first-order loss rate constant (k, s^{-1}) is calculated using the reaction probability formulation in Jacob (2000) (Eq. 2).

$$k = (\frac{r_{\mathrm{a}}}{D_g} + \frac{4}{v\gamma})^{-1} A \qquad (2)$$

where r_{a} is the radius of the specific type of aerosol (cm); A is the total aerosol surface area per unit volume of air for the specific type of aerosol ($\mathrm{cm}^2\ \mathrm{cm}^{-3}$); v is the mean molecular speed of SO_2 or the oxidant ($\mathrm{cm\ s}^{-1}$); D_g represents the gas-phase molecular diffusion coefficient of SO_2 or the oxidant ($\mathrm{cm}^2\ \mathrm{s}^{-1}$) calculated as:

$$D_g = \frac{9.45l10^{17} \times \sqrt{T \times (3.47 \times 10^{-2} + (1/M))}}{\rho_{\mathrm{air}}} \quad (3)$$

where T is air temperature (K), ρ_{air} is air density (molecule m^{-3}), and M represents the molar mass of SO_2 or the oxidant (g mol^{-1}). The reaction probability (γ) is defined as the probability that a molecule impacting the aerosol surface undergoes a chemical reaction (Ravishankara, 1997; Jacob, 2000). Due to limited understanding of sulfate formation on aerosols, chemical transport models typically calculate heterogeneous sulfate production rate on aerosols by assuming the bulk first-order uptake of SO_2 and using a wide range of γ values (10^{-4} - 10^{-1}) (Wang et al., 2014; Zhang et al., 2014). However, the relative contribution of different sulfate production mechanisms, which is important to inform air pollution mitigation efforts, cannot be determined with this simplified approach.

In this study, we use a more specific approach to calculate γ for each heterogeneous sulfate production mechanisms following Jacob (2000) and Ammann et al. (2013) (Eq. 4).

$$\gamma = \left[\frac{1}{\alpha} + \frac{v}{4K^{*}RT\sqrt{D_a k_{chem}}} \cdot \frac{1}{f_{\mathrm{r}}}\right]^{-1} \quad (4)$$

where α is the mass accommodation coefficient (unitless); k_{chem} is the pseudo first-order aqueous-phase chemical rate constant between S(IV) and the oxidant (O_3, H_2O_2, NO_2 or O_2) (s^{-1}) (Table ~~S~~2); D_a is the aqueous-phase molecular diffusion coefficient of SO_2 or the oxidant ($\mathrm{cm}^2\ \mathrm{s}^{-1}$); K^{*} is the effective Henry's law constant of SO_2 or the oxidant (M atm^{-1}); R is the universal gas constant (L atm mol^{-1} K^{-1}), and f_{r} is reacto-diffusive correction term that compares the radius of aerosols (r_{a}) with the reacto-diffusive length scale of the reaction (l):

$$f_r = \coth\frac{r_{\mathrm{a}}}{l} - \frac{l}{r_{\mathrm{a}}} \qquad (5)$$

$$l = \sqrt{\frac{D_a}{k_{chem}}} \qquad (6)$$

In the model, the heterogeneous sulfate production rate from the TMI-catalyzed reaction is calculated as first-order uptake in SO_2. All other heterogeneous sulfate production pathways are calculated as first-order uptake in the oxidant (H_2O_2, O_3, and NO_2). This is based on whether the heterogeneous sulfate production on aerosol is limited by the availability of SO_2 or the oxidant. F~~For example, f~~or aerosol pH values less than 6, heterogeneous sulfate production rates calculated as a first-order loss in SO_2 or the oxidant are similar (Figure S1(b)). For aerosol pH values greater than 6, heterogeneous sulfate production rates calculated as a first-order loss in SO_2 are higher than those calculated as a first-order loss in the oxidants O_3 and NO_2. The reaction rate for S(IV) oxidation by O_3 and NO_2 increases with increasing pH, and at high pH values γ is limited by the mass accommodation coefficient and becomes independent of pH. The mass accommodation coefficients for O_3 (2×10^{-3}) and NO_2 (2×10^{-4}) are much lower than for SO_2 (0.23). The mass accommodation coefficient for H_2O_2 (0.11) is similar to SO_2, and γ for the reaction of S(IV) with H_2O_2 was limited by the oxidant concentration. More details on first-order loss rates are described in Text S2.

In addition to the model simulations described in Table 1, we have also examined heterogeneous oxidation of SO_2 by O_2 on the surface of acidic microdroplets (Hung and Hoffman, 2015) and by HOBr (Chen et al., 2016; 2017). The results are described in the supplementary material (Text S2).

2.3 Observations of sulfate concentrations and oxygen isotopic composition

Between 17 October 2014 and 20 January 2015, $PM_{2.5}$ samples were collected every 12 hours for daytime (08:00-20:00 Beijing Time) and nighttime (20:00-08:00 Beijing Time) conditions at the campus of University of the Chinese Academy of Sciences (40.41°N, 116.68°E, 20 m from the ground) in Beijing, around 60 km northeast of downtown. The oxygen-17 excess of sulfate ($\Delta^{17}O(SO_4^{2-})$) of~~on~~ these $PM_{2.5}$ samples were measured at University of Washington, Seattle. A detailed description of sampling and measurements of $\Delta^{17}O(SO_4^{2-})$ can be found in He et al. (2018). Observations of hourly sulfate concentrations were conducted at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39.99°N, 116.37°E) at ground level (~4 m), an urban site in the north of Beijing, as described by Sun et al. (2016). Sulfate concentrations in submicron aerosols (PM_1) were measured by an Aerodyne High Resolution Aerosol Mass Spectrometer (HR-AMS). The difference of SO_4^{2-} concentration between $PM_{2.5}$ and PM_1 is small because most sulfate exists in fine aerosols (Guo et al., 2014). A comparison of SO_4^{2-} concentration in $PM_{2.5}$ and PM_1 during 22 November – 29 November 2017 is shown in the supplement (Figure S2). Surface $PM_{2.5}$, SO_2, NO_2, and O_3 measurements (Figures 1 and S6~~5~~) are from the China National Environmental Monitoring Center (http://106.37.208.233:20035/) with 12 sites in Beijing, including 8 urban and 4 suburban sites.

3 Results

3.1 Observed $PM_{2.5}$ and sulfate concentrations and $\Delta^{17}O(SO_4^{2-})$

Figure 1 shows the time series of observed concentrations of $PM_{2.5}$ and sulfate from 17 October 2014 to 20 January 2015, along with temperature and relative humidity in Beijing from GEOS-FP. A previous study showed that the GEOS-FP meteorological data for temperature and relative humidity are in good agreement with the ground-based measurements in Beijing ($R^2 > 0.9$) (Zhang et al., 2016). The CNAAQS defines the 24h average air quality levels as excellent ($PM_{2.5}$ = 0-35

μg m^{-3}), good (PM$_{2.5}$ = 35-75 μg m^{-3}), light (PM$_{2.5}$ = 75-115 μg m^{-3}), moderate (PM$_{2.5}$ = 115-150 μg m^{-3}), heavy (PM$_{2.5}$ = 150-250 μg m^{-3}), and severe (PM$_{2.5}$ > 250 μg m^{-3}). Using this metric, 10 time periods are categorized as heavy or severe (>150 μg m^{-3}) during 17 October 2014 – 20 January 2015, and we refer to these as "Heavy Polluted Period" (HPP). Another 10 time periods were in the excellent to good category and we refer to these days as "Clean Period" (CP). The average relative humidity (RH) from GEOS-FP during HPP was 60±11%, much higher than the average RH during CP (42±10%). Higher RH can accelerate the rates of conversion of SO$_2$ and NO$_2$ to SO$_4^{2-}$ and NO$_3^-$, respectively, contributing to increases in PM$_{2.5}$ concentrations (Wang et al., 2016; Hua et al., 2015).

The observed SO$_4^{2-}$ concentrations show a similar variation as PM$_{2.5}$, increasing from 2.1±1.8 μg m^{-3} in CP to 25.9±11.3 μg m^{-3} in HPP with a mean of 11.5±7.3 μg m^{-3} during the entire measurement period. The mass fraction of SO$_4^{2-}$ to PM$_{2.5}$ ranged from 5% to 19%, varying from a mean of 8±2% in CP to 13±2% in HPP. Observed sulfate concentrations shown in Figure 1 are 15% lower on average during HPP than those reported in He et al. (2018) because the SO$_4^{2-}$ concentrations shown here represent PM$_1$ instead of PM$_{2.5}$, which is in good agreement with previous studies (Sun et al., 2013; 2014; 2016) (Fig. S2). Figure 1 also shows the observed sulfur oxidation ratio (SOR), defined as the molar ratio of sulfate over the sum of sulfate and SO$_2$ (SO$_4^{2-}$/(SO$_2$ + SO$_4^{2-}$)) (Colbeck and Harrison, 1984). The observed SOR increases from CP (9±6%) to HPP (32±18%), consistent with increased sulfate production rates during HPP.

Figures 2 and S4 show the Δ^{17}O(SO$_4^{2-}$) observations, 24 measurements represent HPP and 10 represent CP. The Δ^{17}O(SO$_4^{2-}$) values are similar in HPP and CP, 0.9±0.1‰ and 0.9±0.5‰, respectively. A more detailed description of the Δ^{17}O(SO$_4^{2-}$) observations can be found in He et al. (2018).

3.2 Analyses of sulfate formation pathways

3.2.1 Sulfate formation in the standard model

Figure 1 compares the measured and modeled PM$_{2.5}$ and sulfate concentration in Beijing. The standard model (Run_Std) generally captures the temporal variations of PM$_{2.5}$ and SO$_4^{2-}$ observations during the entire sampling period, but underestimates the PM$_{2.5}$ and SO$_4^{2-}$ observations during HPP by 28% and 64%, respectively. Modeled sulfate concentrations increase from 1.5±1.2 μg m^{-3} in CP to 8.9±3.1 μg m-3 in HPP, which is a much smaller enhancement compared to observations (from 2.1±1.8 μg m^{-3} in CP to 25.9±11.3 μg m^{-3} in HPP). The model simulated sulfate mass fractions in PM$_{2.5}$ are 8±2% in CP and 7±2% in HPP. The model fails to reproduce increases in observed sulfate mass fraction from CP (8±2%) to HPP (13±2%). This is consistent with previous modeling studies, suggesting missing sulfate formation pathways (Wang et al., 2014; Zhang et al., 2015). The model also underestimates the sulfur oxidation ratio (SOR) observations during HPP by 53%. This further suggests that the modeled SO$_2$ oxidation rate is too slow.

Figure 2 compares observed and modeled $\Delta^{17}O(SO_4^{2-})$. The modeled hourly $\Delta^{17}O$ (SO_4^{2-}) values were averaged at 12h intervals for comparison with the observations. The simulated $\Delta^{17}O(SO_4^{2-})$ values in Run_Std range from 0.02‰ to 1.5‰ with a mean of 0.5±0.1‰. Unlike the observations, modeled $\Delta^{17}O$ (SO_4^{2-}) values in Run_Std during HPP (0.4±0.1‰) are lower than those during CP (0.6±0.1‰) due to higher fractional contribution of in-cloud H_2O_2 and O_3 oxidation pathways during CP, as discussed below. Run_Std underestimates the $\Delta^{17}O(SO_4^{2-})$ observations (by 44% on average), particularly during HPP (by 53% on average).

Figure 3 shows modeled spatial distribution of sulfate concentrations over China, and the fractional contribution of each sulfate formation pathway to total sulfate abundance in Beijing. The average simulated sulfate concentration in Beijing in Run_Std is around 6.2 $\mu g\ m^{-3}$ (Figure 3a), smaller than the observations (11.5 $\mu g\ m^{-3}$) over the study period. Figure 3 also shows the model calculated average contribution of each sulfate production pathway to total sulfate concentration at the surface in Beijing during HPP and CP. In Run_Std, sulfate produced by gas-phase oxidation of SO_2 by OH dominates the total sulfate abundance (59.7%, 5.3 $\mu g\ m^{-3}$) in HPP. Primary sulfate represents the second most important contributor (33.6%, 3.0 $\mu g\ m^{-3}$) despite the fact that primary sulfate is only 3% of total anthropogenic sulfur emissions. The high fraction of primary anthropogenic sulfate reflects the relatively slow oxidation rate of SO_2 in the model. In-cloud sulfate production contributes only 7% of total sulfate abundance at the surface during HPP. For clean days, primary sulfate dominates surface sulfate concentrations (49.4%, 0.7 $\mu g\ m^{-3}$), suggesting an even slower SO_2 oxidation rate in the model during CP compared to HPP. Gas-phase production via OH oxidation is the second most important contributor (26.1%, 0.4 $\mu g\ m^{-3}$) during CP. Gas-phase oxidation of SO_2 by OH is more important in HPP than in CP because modeled OH concentrations during HPP are much higher than in CP, consistent with observations of high OH during polluted wintertime conditions in Beijing (Tan et al., 2018). Higher modeled OH in HPP compared to CP is due to higher nitrous acid (HONO) levels during HPP (Figure S3) resulting from heterogeneous uptake of NO_2 to produce HNO_3 and HONO in the model. This is consistent with observation-based studies in Beijing showing that OH production from HONO photolysis is 10 times higher than that from O_3 photolysis in winter (Hendrick et al., 2014) and that $NO_2(g)$ dissolution in acidic aerosol water is a source of HONO (Li et al., 2018). In-cloud sulfate production contributes 24.5% of total sulfate abundance during CP, much higher than HPP (6.9%) due to higher modeled H_2O_2 and O_3 in CP.

3.2.2 Transition metal ion catalyzed oxidation of S(IV) in clouds

The in-cloud concentration of soluble Fe^{3+} and Mn^{2+} determines the rate of sulfate formation via the TMI-catalyzed oxidation pathway, but large uncertainties exist in estimates of soluble Fe^{3+} and Mn^{2+} due to lack of observations. Adding aqueous-phase TMI-catalyzed S(IV) oxidation by O_2 in cloud droplets in Run_TMI increases the average sulfate concentration in Beijing during the entire measurement period from 6.2 $\mu g\ m^{-3}$ to 8.3 $\mu g\ m^{-3}$ due to increases in the in-cloud sulfate production rate. However, the model still underestimates observations of $PM_{2.5}$ (-35%), sulfate (-48%), and SOR (-40%) during HPP.

Sulfate from TMI-catalyzed oxidation dominates in-cloud sulfate production and accounts for up to 28.3% of total sulfate abundance during HPP, but only 8.1% during CP in Beijing (Figure 3b). The lower contribution of TMI-catalysis during CP is due to lower concentrations of Fe and Mn in the model during CP. The largest enhancement in sulfate abundance after adding the in-cloud TMI pathway occurs in Sichuan basin (around 6.5 µg m^{-3}), where simulated anthropogenic Fe and Mn from coal fly ash (Figure S4) and SO_2 are high ~~(Zhang et al., 2009)~~ ~~in part~~ due to high SO_2 emissions (Zhang et al., 2009) combined with stagnant air and high relative humidity all year (Huang et al., 2014). After adding the in-cloud TMI oxidation pathway, the average modeled $\Delta^{17}O(SO_4^{2-})$ decreased from 0.5‰ to 0.4‰ in Beijing because the TMI oxidation pathway leads to $\Delta^{17}O(SO_4^{2-})$ = 0‰ (Figure 2), which makes the discrepancy between modeled and observed $\Delta^{17}O(SO_4^{2-})$ (0.9 ‰) even larger.

3.2.3 Heterogeneous sulfate formation on aerosols

Adding four heterogeneous S(IV) oxidation mechanisms by H_2O_2, O_3, NO_2 and TMI-catalyzed O_2 on aerosols in Run_Het increases the average SO_4^{2-} concentrations in Beijing (from 8.3 µg m^{-3} in Run_Std to 9.8 µg m^{-3} in Run_Het) (Figure 1c). Modeled heterogeneous sulfate production represents 21.6% of total surface sulfate concentrations in HPP and 19.8% in CP (Figure 3c). Modeled daily-mean aerosol pH ranged from 3.0 to 5.4 with a mean of 4.3 over the entire time period in Beijing (Figure 4), which is consistent with recent estimates (pH=4.2-4.7) (Guo et al, 2017; Song et al, 2018~~a~~; Liu et al., 2017). Heterogeneous sulfate production on aerosols is dominated by TMI-catalyzed O_2 oxidation in both HPP (69%) and CP (67%) (Figure 3c). S(IV) oxidation by O_3 is the second most important heterogeneous oxidation pathway, accounting for 19% of total heterogeneous sulfate formation in both HPP and CP. S(IV) oxidation by H_2O_2 (6% in both HPP and CP) and NO_2 (6% in HPP and 8% in CP) represent a minor heterogeneous sulfate production pathway. Previous studies suggested that oxidation of SO_2 by NO_2 in aerosol water dominates heterogeneous sulfate formation in Beijing during winter (Wang et al., 2016; Cheng et al., 2016) at neutral aerosol pH. However, subsequent studies showed that these high aerosol pH values were unlikely during wintertime Beijing haze events and they calculated aerosol pH values in the range of 4.2-4.7 (Guo et al, 2017; Song et al, 2018~~a~~; Liu et al., 2017).

After adding the heterogeneous S(IV) oxidation pathways, the average modeled $\Delta^{17}O(SO_4^{2-})$ increased from 0.5±0.5‰ to 0.8±0.7‰ in Beijing due to the increased importance of S(IV) oxidation by O_3. Although the average modeled $\Delta^{17}O(SO_4^{2-})$ in Run_Het is similar to the observations (0.9±0.3‰), the modeled median (0.5‰) largely underestimates the observed median (1.0‰) (Figure 2), and the majority of the modeled data underestimates the observed $\Delta^{17}O(SO_4^{2-})$ (Figure S5~~4~~).

Compared to observations in Beijing, mean model biases decrease from -28% to -26% for $PM_{2.5}$, -45% to -21% for sulfate concentration, from -29% to -11% for SOR, and from -45% to -15% for $\Delta^{17}O(SO_4^{2-})$ for the entire measurement period for Run_Het relative to Run_Std. Model biases during HPP decrease from -38% to -32% for $PM_{2.5}$, -65% to -40% for sulfate concentration, -53% to -28% for SOR, and from -50% to -5% for $\Delta^{17}O(SO_4^{2-})$. The largest sulfate enhancements due to heterogeneous sulfate formation occur in megacities in eastern China and Sichuan basin (Figure 3), where both SO_2 and aerosols abundances are highest. In addition, high anthropogenic emissions of Fe^{3+} and Mg^{2+} favor sulfate production catalyzed by TMIs. In Run_Het, the fractional contribution of each sulfate production mechanism in Beijing during HPP is 34% for gas-phase oxidation of SO_2 by OH, 22% for TMI-catalysis in cloud, 21% for the four heterogeneous oxidation pathways, and 20% for primary sulfate, respectively (Figure 3c). The remaining 3% of sulfate is formed via in-cloud sulfate production from H_2O_2 and O_3. For clean days (CP), primary sulfate still dominates surface sulfate concentrations (39%) in Run_Het, with gas-phase production via OH oxidation the second most important contributor (22%) and the added heterogeneous sulfate formation pathways accounting for 22%.

4. Discussion

The model results demonstrate that implementation of heterogeneous sulfate formation pathways on aerosols reduces modeled low biases in both concentration and oxygen isotopic signature of sulfate ($\Delta^{17}O(SO_4^{2-})$), and suggests that TMI-catalysis dominates heterogeneous sulfate production. However, the model is still biased low in both metrics, indicating that the model is still underestimating sulfate production rates. The modeled underestimate in $\Delta^{17}O(SO_4^{2-})$ reveals an underestimate in the O_3 oxidation pathway. Since the relative contribution of heterogeneous sulfate formation pathways are sensitive to aerosol pH, we investigated the influence of aerosol pH using a series of sensitivity simulations with prescribed aerosol pH values between 2 and 8 (Table 1). Figure 5 shows modeled sulfate concentrations produced from different oxidation pathways and resulting $\Delta^{17}O(SO_4^{2-})$ in Beijing averaged over HPP assuming different aerosol pH values. Heterogeneous sulfate formation represents over 50% of total sulfate formation when pH > 5 and when pH < 4. At aerosol pH < 4, heterogeneous sulfate formation is dominated by the TMI pathway because of the high solubility of Fe and Mn at low pH (Guieu et al. 1994, Mackie, et al. 2005). At aerosol pH > 5, heterogeneous sulfate formation is dominated by the O_3 pathway because the solubility of SO_2 increases with increasing pH and because the S(IV) partitioning shifts to favor SO_3^{2-} at higher pH. The aqueous-phase rate constant for $SO_3^{2-} + O_3$ is almost four orders of magnitude faster than for $HSO_3^- + O_3$ (Table ~~S~~2). Heterogeneous sulfate formation by NO_2 also increases with increasing pH due to the increased solubility of SO_2 at high pH, and represents 15-30% of total heterogeneous sulfate production between pH = 6 – 8. In contrast to our results, previous results (Cheng et al., 2016; Wang et al., 2016) suggested that NO_2 oxidation is more important than O_3 oxidation at high pH values. The difference is due to assumed O_3 concentrations used in the rate calculations. The aforementioned studies assumed an O_3 concentration of 1 ppb relative to an NO_2 concentration of 66 ppb. In our model simulations, average O_3 and NO_2 concentrations are 9 ppb and 85 ppb, respectively. Modeled O_3 concentrations are similar to the observations during the measurement period (Figure S6~~5~~). Heterogeneous sulfate production is lower (20%) when pH = 4 - 5 because of the low solubility of Fe and Mn and low concentrations of SO_3^{2-} in this pH range. We note that while the pH-dependence of S(IV) partitioning is well known, the pH-dependency of metal solubility is more uncertain.

Anthropogenic SO_2 emissions in China have been reduced sharply since 2009 due to the stringent pollution control measures implemented (Zheng et al., 2018; Van der A et al., 2017; Krotkov et al., 2016). Compared with 2010, anthropogenic SO_2 emissions reduced by about 50% in 2015 (Krotkov et al., 2016; Zheng et al., 2018; Van der A et al., 2017). However, NH_3 and non-methane volatile organic compounds (NMVOC) emissions in China remained stable during 2010–2017 due to the absence of effective mitigation measures in current policies (Zheng et al., 2018). The emission changes may affect the abundance of species that influence cloud and aerosol pH, and further influence sulfate production rates and the contribution of each sulfate formation pathway. However, other studies using observations between 2014-2016 (Liu et al., 2017; Song et al., 2018) found a similar pH range as calculated here, suggesting that a modeled low bias in aerosol pH is not likely to be the source of the modeled discrepancy in $\Delta^{17}O(SO_4^{2-})$.

Figure 5 also shows that model results with mean aerosol pH > 5 would result in a high bias in $\Delta^{17}O(SO_4^{2-})$ due to the increasing importance of the O_3 oxidation pathway at higher pH values, effectively providing an observational constraint for typical aerosol pH < 5 in Beijing haze. However, modeled $\Delta^{17}O(SO_4^{2-})$ calculated at the aerosol pH of 4.2-4.7 as estimated by recent studies (Guo et al. 2017; Song et al. 2018~~a~~) represents a low bias relative to the observations. A joint comparison of observations and model results with both sulfate concentrations and $\Delta^{17}O\ (SO_4^{2-})$ suggests an average aerosol pH between 5-6 in Beijing during the study period, which is higher than bulk aerosol pH calculations in our model calculations and in previous studies (Guo et al. 2017; Song et al. 2018~~a~~).

Thermodynamic pH calculations in ISORROPIA II are based on the assumption of internally mixed aerosols and do not directly consider aerosol alkalinity (carbonate). Fresh dust is initially alkaline (calcium carbonates). This alkalinity is partially depleted (carbonate is converted to CO_2) upon uptake of acid gases HNO_3, SO_2, and H_2SO_4 (Fairlie et al, 2010; Usher et al., 2003). Due to the high pH of alkaline dust, uptake of SO_2 would be followed by heterogeneous oxidation by O_3 (Fairlie et al., 2010; Ullerstam et al., 2003) and NO_2 (Zhao et al., 2018) if there is enough aerosol liquid water to promote aqueous-phase oxidation. A recent modeling study by Uno et al. (2017) using a previous version of GEOS-Chem explicitly includes uptake of HNO_3, SO_2, and H_2SO_4 on alkaline dust aerosols as described in Fairlie et al. (2010). Their model calculated that sulfate from uptake of SO_2 and H_2SO_4 on alkaline dust in Beijing during our measurement period represents on average 3% of total sulfate abundance. Most of this sulfate formation on alkaline dust was from uptake of H_2SO_4 (70 – 80%, Fairlie et al., 2010), with the remaining fraction (20 – 30%) from uptake of SO_2 followed by oxidation to sulfate. On average, less than 1% of sulfate in Beijing is formed on alkaline dust via the uptake and oxidation of SO_2 in the model.

At pH values representative of alkaline dust (pH = 7 – 8), sulfate formed via oxidation of SO_2 on alkaline dust would be dominated by O_3 leading to a relatively high $\Delta^{17}O(SO_4^{2-})$ value of 6‰ (Figure 5). In order to account for the difference in the median $\Delta^{17}O(SO_4^{2-})$ observed (1.0‰) and modeled (0.5‰), sulfate formation from the uptake and oxidation of SO_2 on alkaline dust would need to account for an average of 9% of total sulfate abundance during our measurement period. This fraction is higher than that calculated in Uno et al. (2017), which did not include anthropogenic dust. In our model, anthropogenic dust accounts for 28~~12~~% of total dust in Beijing (Figure S7), and natural dust mostly originates from the Gobi Desert in southwestern Mongolia and the Badain Jaran Desert in northern China (Zhang et al., 2003; Zhang et al., 2016). The anthropogenic dust is not abundant enough to explain the difference between the results of Uno et al. (2017) and amount of sulfate production on alkaline dust required to explain the observed $\Delta^{17}O(SO_4^{2-})$.~~ which is not enough to explain the difference.~~ Due to uncertainties in processes such as the RH dependence of the uptake of SO_2 on alkaline dust, the importance of this pathway could be underestimated in Uno et al. (2017). If this process does account for the difference in modeled and observed $\Delta^{17}O(SO_4^{2-})$, then NO_2 oxidation may be slightly more important than indicated in Figure 3. Our calculations (Figure 5) suggest that NO_2 oxidation accounts for 23% of heterogeneous sulfate formation at aerosol pH values between 7 and 8. If sulfate formation on alkaline dust accounts for 9% of total sulfate formation, and NO_2 oxidation accounts for 23% of this sulfate formation pathway, then NO_2 oxidation can account for up to 2% of total heterogeneous sulfate formation in Beijing, which still suggests NO_2 oxidation is a minor pathway during wintertime Beijing haze events.

In addition to a model underestimate of the ozone oxidation pathway, a model underestimate of the H_2O_2 oxidation pathway may explain part of the modeled low bias in $\Delta^{17}O(SO_4^{2-})$. The average modeled H_2O_2 concentrations during HPP and CP underestimates the observations (Ye et al., 2018) by up to an order of magnitude (Figure S3(c)). Mao et al., (2013) proposed a HO_2−Cu−Fe catalytic mechanism for H_2O_2 production in the aerosol phase. In their mechanism, the uptake of HO_2 and subsequent heterogeneous reactions with Cu and Fe will lead to production of H_2O_2 when the molar ratio of dissolved Cu to Fe was >0.1. Ye et al. (2018) found that the molar ratio of dissolved Cu to Fe is >0.1 during moderately polluted days, suggesting the uptake of HO_2 radicals on particles might be an important source of H_2O_2 during the winter in Beijing. We note however that an underestimate of modeled H_2O_2 cannot explain all of the discrepancy in $\Delta^{17}O(SO_4^{2-})$, as sulfate formed from H_2O_2 oxidation (0.7 ‰) is lower than the observed mean $\Delta^{17}O(SO_4^{2-})$ of 0.9 ‰. All other oxidation pathways yield $\Delta^{17}O(SO_4^{2-}) = 0$ ‰ and cannot explain the model's low bias in $\Delta^{17}O(SO_4^{2-})$.

An increase in sulfate abundance of 9% from formation on alkaline dust is not enough to explain the remaining model underestimate in sulfate concentrations (-40%) and SOR (-28%) during HPP. Two recent studies suggested that hydroxymethane sulfonate (HMS) may be present in Chinese haze events and measured as sulfate via ion chromatography and HR-AMS (Moch et al., 2018; Song et al., 2019~~8b~~). HMS is formed via aqueous-phase oxidation via nucleophilic attack of HSO_3^- and SO_3^{2-} on HCHO. Moch et al. (2018) suggested that in-cloud formation of HMS could explain the low model bias in sulfate concentrations, while Song et al. (2019~~8b~~) suggested that heterogeneous formation of HMS on aerosol surfaces can explain up to one-third of the low model bias in their study. In the present study, as the organics were removed from the sample matrix prior to $\Delta^{17}O(SO_4^{2-})$ analysis (Geng et al., 2013), suggesting ~~it is unlikely~~ that measured $\Delta^{17}O(SO_4^{2-})$~~–~~ does not have significant contributions from HMS. This will depend on the efficiency of HMS removal in He et al. (2018); previous work suggests that one of the two organic removal techniques employed (H_2O_2 oxidation) does not remove HMS under atmospheric conditions (Munger et al., 1984; 1986). However, the presence of HMS in the sample matrix, if any, would lower measured $\Delta^{17}O(SO_4^{2-})$, and any correction for this would increase the observed $\Delta^{17}O(SO_4^{2-})$ and further increase the discrepancy between modeled and observed $\Delta^{17}O(SO_4^{2-})$.

5. Conclusion

We have used a combination of observations and modeling of sulfate and SO_2 concentrations and $\Delta^{17}O(SO_4^{2-})$ to quantify sulfate production mechanisms in Beijing. We focus on the period of 17 October 2014 – 20 January 2015, when 10 heavy pollution periods (HPP) were defined with observed $PM_{2.5}$ concentrations >150 μg m^{-3}. The standard model simulation that only includes primary sulfate and sulfate formation from gas-phase oxidation by OH and in-cloud oxidation by H_2O_2 and O_3 underestimates mean sulfate concentration by 65% and $\Delta^{17}O(SO_4^{2-})$ by 50% during heavy pollution periods (HPP). Adding in-cloud oxidation catalyzed by transition metal ions (TMI) and heterogeneous oxidation by H_2O_2, O_3, NO_2, and TMI on aerosols can improve the model simulation of sulfate abundance and $\Delta^{17}O(SO_4^{2-})$, with the model biases decreasing from -65% to -40% for sulfate and from -50% to -5% for $\Delta^{17}O(SO_4^{2-})$ during HPP. Modeled heterogeneous sulfate production accounts for around 20% of total sulfate production. The model predicts that t~~T~~he TMI-catalyzed oxidation dominates heterogeneous sulfate production under calculated aerosol pH of ≤5; however, this reaction is highly uncertain due to limitations in our ability to assess modeled dissolved Fe(III) and Mn(II) concentrations. The modeled $\Delta^{17}O(SO_4^{2-})$ is still biased low compared to observations, suggesting an underestimate of sulfate production by O_3 oxidation. ~~however, the modeled $\Delta^{17}O(SO_4^{2-})$ is still biased low compared to observations, suggesting an underestimate of sulfate production by O_3 oxidation.~~ We hypothesize that sulfate aerosol production by O_3 on externally-mixed alkaline dust aerosol can explain at least part of the remaining discrepancy in $\Delta^{17}O(SO_4^{2-})$. The $\Delta^{17}O(SO_4^{2-})$ observations suggest that a fractional sulfate contribution of just 9% originating from SO_2 oxidation on alkaline dust aerosol can explain the model discrepancy in $\Delta^{17}O(SO_4^{2-})$. We calculate that sulfate formation on alkaline dust is dominated by O_3 oxidation (74%) followed by NO_2 oxidation (23%). The $\Delta^{17}O(SO_4^{2-})$ observations combined with our model calculations indicates only a minor (2%) role of heterogeneous sulfate formation via NO_2 oxidation of SO_2. Future studies will examine the impact of these heterogeneous S(IV) oxidation mechanisms on the regional and global sulfur budgets.

Data availability

For the model results please contact Becky Alexander (beckya@uw.edu) and Lin Zhang (zhanglg@pku.edu.cn). For isotope measurements please contact Zhouqing Xie (zqxie@ustc.edu.cn)

Author contribution

BA, LZ, JYS, and YXW designed the study. BA and LZ supervised the project. JYS performed model simulations and conducted analyses with the assistance of QJC, YXW, XL, VS, RVM, SP, SJS and YZ. ZQX and PZH conducted the oxygen isotope measurements; YLS contributed the sulfate measurements. JYS, BA, and LZ wrote the paper. All authors contributed to the interpretation of the results and improvement of the paper.

Acknowledgements

This work is supported by the National Key Research and Development Program of China (2017YFC0210102) and the National Natural Science Foundation of China (41475112). J.Y. Shao acknowledges support from the Chinese Scholarship Council (201606010049). B.A. Acknowledges support from NSF AGS 1644998 and Y. W. acknowledge support from NSF AGS 1645062. Z.Q.Xie acknowledges support from the National Natural Science Foundation of China (91544013). We thank Duncan Fairlie, Itushi Uno, Renyi Zhang, Havala O.T. Pye, Sakiko Ishino, Shohei Hattori, Youfan Chen, Jessica Haskins, Mi Zhou, Yuanhong Zhao for helpful discussions.

References

Alexander, B., R. J. Park, D. J. Jacob, Q. B. Li, R. M. Yantosca, J. Savarino, C. C. W. Lee, and M. H. Thiemens: Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes, J. Geophys. Res., 110, D10307, doi:10.1029/2004jd005659, 2005.

Alexander, B., Park, R. J., Jacob, D. J., and Gong, S.: Transition metal-catalyzed oxidation of atmospheric sulfur: Global implications for the sulfur budget, J. Geophys. Res., 114, D02309, doi:10.1029/2008jd010486, 2009.

~~Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}O$) of atmospheric nitrate, Atmos. Chem. Phys., 9, 5043-5056, doi:10.5194/acp-9-5043-2009, 2009.~~

Alexander, B., Allman, D. J., Amos, H. M., Fairlie, T. D., Dachs, J., Hegg, D. A., and Sletten, R. S.: Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean, J. Geophys. Res., 117, D06304, doi:10.1029/2011jd016773, 2012.

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, doi:10.5194/acp-13-8045-2013, 2013.

Beijing Environment Protection Agency: The report for 2017 air quality in Beijing, 2018 (http://www.bjepb.gov.cn/bjhrb/index/index.html (in Chinese))

Calvert, J. G., and Stockwell, W. R.: Acid generation in the troposphere by gas-phase chemistry, Environ. Sci. Technol., 17, 428A-443A, doi:10.1021/es00115a727, 1983.

Chen, D., Liu, Z., Fast, J., and Ban, J.: Simulations of sulfate–nitrate–ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014, Atmos. Chem. Phys., 16, 10707-10724, doi:10.5194/acp-16-10707-2016, 2016.

Chen, Q., Geng, L., Schmidt, J. A., Xie, Z., Kang, H., Dachs, J., Cole-Dai, J., Schauer, A. J., Camp, M. G., and Alexander, B.: Isotopic constraints on the role of hypohalous acids in sulfate aerosol formation in the remote marine boundary layer, Atmos. Chem. Phys., 16, 11433-11450, doi:10.5194/acp-16-11433-2016, 2016.

Chen, Q., Schmidt, J. A., Shah, V., Jaeglé, L., Sherwen, T., and Alexander, B.: Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets, Geophys. Res. Lett., 44, 7069-7078, doi:10.1002/2017gl073812, 2017.

Chen, Q., Sherwen, T., Evans, M., and Alexander, B.: DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry, Atmos. Chem. Phys., 18, 13617-13637, doi:10.5194/acp-18-13617-2018, 2018.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Poschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Sci. Adv., 2, e1601530, doi:10.1126/sciadv.1601530, 2016.

Chinese State Council. Atmospheric Pollution Prevention and Control Action Plan (http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm (in Chinese)), last access on 12/01/2018)

Chuang, P. Y., Duvall, R. M., Shafer, M. M., and Schauer, J. J.: The origin of water soluble particulate iron in the Asian atmospheric outflow, Geophys. Res. Lett., 32, L07813, doi:10.1029/2004gl021946, 2005.

Clifton, C. L., Altstein, N. and Huie, R. E. : Rate constant for the reaction of nitrogen dioxide with sulfur (IV) over the pH range 5.3-13. Environ. Sci. Technol. 22, 586-589, doi: 10.1021/es00170a018, 1988.

Colbeck, I., and Harrison, R.: Ozone—secondary aerosol—visibility relationships in North-West England, Sci. Total Environ., 34, 87-100, doi:10.1016/0048-9697(84)90043-3, 1984.

Desboeufs, K. V., Losno, R., and Colin, J. L.: Factors influencing aerosol solubility during cloud processes, Atmos. Environ., 35, 3529-3537, doi:10.1016/s1352-2310(00)00472-6, 2001.

Desboeufs, K. V., Sofikitis, A., Losno, R., Colin, J. L., and Ausset, P.: Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter, Chemosphere, 58, 195-203, doi:10.1016/j.chemosphere.2004.02.025, 2005.

Dominguez, G., Jackson, T., Brothers, L., Barnett, B., Nguyen, B., and Thiemens, M. H.: Discovery and measurement of an isotopically distinct source of sulfate in Earth's atmosphere, Proc. Natl. Acad. Sci., 105, 12769-12773, doi:10.1073/pnas.0805255105, 2008.

Dubey, M. K., Mohrschladt, R., Donahue, N. M., and Anderson, J. G.: Isotope Specific Kinetics of Hydroxyl Radical (OH) with Water (H_2O): Testing Models of Reactivity and Atmospheric Fractionation, J. Phys. Chem., 101, 1494-1500, doi:10.1021/jp962332p, 1997.

Fairlie, T. D., Jacob, D. J., and Park, R. J.: The impact of transpacific transport of mineral dust in the United States, Atmos. Environ., 41, 1251-1266, doi:10.1016/j.atmosenv.2006.09.048, 2007.

Fairlie, T. D., Jacob, D. J., Dibb, J. E., Alexander, B., Avery, M. A., van Donkelaar, A., and Zhang, L.: Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes, Atmos. Chem. Phys., 10, 3999-4012, doi:10.5194/acp-10-3999-2010, 2010.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, doi:10.5194/acp-7-4639-2007, 2007.

Gao, M., Guttikunda, S. K., Carmichael, G. R., Wang, Y., Liu, Z., Stanier, C. O., Saide, P. E., and Yu, M.: Health impacts and economic losses assessment of the 2013 severe haze event in Beijing area, Sci. Total Environ., 511, 553-561, doi:10.1016/j.scitotenv.2015.01.005, 2015.

Gao, M., Carmichael, G. R., Saide, P. E., Lu, Z., Yu, M., Streets, D. G., and Wang, Z.: Response of winter fine particulate matter concentrations to emission and meteorology changes in North China, Atmos. Chem. Phys., 16, 11837-11851, doi:10.5194/acp-16-11837-2016, 2016.

Geng, G., Zhang, Q., Martin, R. V., Lin, J., Huo, H., Zheng, B., Wang, S., and He, K.: Impact of spatial proxies on the representation of bottom-up emission inventories: A satellite-based analysis, Atmos. Chem. Phys., 17, 4131-4145, doi:10.5194/acp-17-4131-2017, 2017.

Geng, L., Schauer, A. J., Kunasek, S. A., Sofen, E. D., Erbland, J., Savarino, J., Allman, D. J., Sletten, R. S., and Alexander, B.: Analysis of oxygen-17 excess of nitrate and sulfate at sub-micromole levels using the pyrolysis method, Rapid Commun. Mass Sp., 27, 2411-2419, doi:10.1002/rcm.6703, 2013.

Guieu, C., Duce, R., and Arimoto, R.: Dissolved input of manganese to the ocean: Aerosol source, J. Geophys. Res., 99, 18789-18800, doi:10.1029/94jd01120, 1994.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Rep., 7, 12109, doi:10.1038/s41598-017-11704-0, 2017.

Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett, J. L., Wang, W., and Wang, T.: Characterization of cloud water chemistry at Mount Tai, China: Seasonal variation, anthropogenic impact, and cloud processing, Atmos. Environ., 60, 467-476, doi:10.1016/j.atmosenv.2012.07.016, 2012.

Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L., Molina, M. J., and Zhang, R.: Elucidating severe urban haze formation in China, Proc. Natl. Acad. Sci., 111, 17373-17378, doi:10.1073/pnas.1419604111, 2014.

Harris, E., Sinha, B., van Pinxteren, D., Tilgner, A., Fomba, K. W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of SO_2, Science, 340, 727-730, doi:10.1126/science.1230911, 2013.

He, P., Alexander, B., Geng, L., Chi, X., Fan, S., Zhan, H., Kang, H., Zheng, G., Cheng, Y., Su, H., Liu, C., and Xie, Z.: Isotopic constraints on heterogeneous sulfate production in Beijing haze, Atmos. Chem. Phys., 18, 5515-5528, doi:10.5194/acp-18-5515-2018, 2018.

Hendrick, F., Müller, J. F., Clémer, K., Wang, P., De Mazière, M., Fayt, C., Gielen, C., Hermans, C., Ma, J. Z., Pinardi, G., Stavrakou, T., Vlemmix, T., and Van Roozendael, M.: Four years of ground-based MAX-DOAS observations of HONO and NO_2; in the Beijing area, Atmos. Chem. Phys., 14, 765-781, doi:10.5194/acp-14-765-2014, 2014.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775-2790, doi:10.5194/acp-15-2775-2015, 2015.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, Chem. Rev., 115, 4259-4334, doi:10.1021/cr500447k, 2015.

Hoffmann, M. R. and Calvert, J. G.: Chemical Transformation Modules for Eulerian Acid Deposition Models: Volume II, the Aqueous-phase Chemistry. Atmospheric Sciences Research Laboratory, Office of Research and Development, US Environmental Protection Agency, 1985.

Holt, B. D., Kumar, R., and Cunningham, P. T.: Oxygen-18 study of the aqueous-phase oxidation of sulfur dioxide, Atmos. Environ., 15, 557-566, doi:10.1016/0004-6981(81)90186-4, 1981.

Hua, Y., Cheng, Z., Wang, S., Jiang, J., Chen, D., Cai, S., Fu, X., Fu, Q., Chen, C., Xu, B., and Yu, J.: Characteristics and source apportionment of $PM_{2.5}$ during a fall heavy haze episode in the Yangtze River Delta of China, Atmos. Environ., 123, 380-391, doi:10.1016/j.atmosenv.2015.03.046, 2015.

Huang, X., Song, Y., Zhao, C., Li, M., Zhu, T., Zhang, Q., and Zhang, X.: Pathways of sulfate enhancement by natural and anthropogenic mineral aerosols in China, J. Geophys. Res.: -Atmos., 119, 14,165-114,179, doi:10.1002/2014jd022301, 2014.

Huie, R. E., and Neta, P.: Chemical behavior of SO_3^- and SO_5^- radicals in aqueous solutions, J. Phys. Chem., 88, 5665-5669, doi:10.1021/j150667a042, 1984.

Hung, H. M., and Hoffmann, M. R.: Oxidation of Gas-Phase SO_2 on the Surfaces of Acidic Microdroplets: Implications for Sulfate and Sulfate Radical Anion Formation in the Atmospheric Liquid Phase, Environ. Sci. Technol., 49, 13768-13776, doi:10.1021/acs.est.5b01658, 2015.

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

Ishino, S., Hattori, S., Savarino, J., Jourdain, B., Preunkert, S., Legrand, M., Caillon, N., Barbero, A., Kuribayashi, K., and Yoshida, N.: Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate, and ozone at Dumont d'Urville, coastal Antarctica, Atmos. Chem. Phys., 17, 3713-3727, doi:10.5194/acp-17-3713-2017, 2017.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131-2159, doi:10.1016/s1352-2310(99)00462-8, 2000.

Jenkins, K. A., and Bao, H.: Multiple oxygen and sulfur isotope compositions of atmospheric sulfate in Baton Rouge, Atmos. Environ., 40, 4528-4537, doi:10.1016/j.atmosenv.2006.04.010, 2006.

Jiang, H., Liao, H., Pye, H. O. T., Wu, S., Mickley, L. J., Seinfeld, J. H., and Zhang, X. Y.: Projected effect of 2000–2050 changes in climate and emissions on aerosol levels in China and associated transboundary transport, Atmos. Chem. Phys., 13, 7937-7960, doi:10.5194/acp-13-7937-2013, 2013.

Krotkov, N. A., McLinden, C. A., Li, C., Lamsal, L. N., Celarier, E. A., Marchenko, S. V., Swartz, W. H., Bucsela, E. J., Joiner, J., Duncan, B. N., Boersma, K. F., Veefkind, J. P., Levelt, P. F., Fioletov, V. E., Dickerson, R. R., He, H., Lu, Z., and Streets, D. G.: Aura OMI observations of regional SO_2 and NO_2 pollution changes from 2005 to 2015, Atmos. Chem. Phys., 16, 4605-4629, doi:10.5194/acp-16-4605-2016, 2016.

Lee, C. C. W., and Thiemens, M. H.: The δ17O and δ18O measurements of atmospheric sulfate from a coastal and high alpine region: A mass-independent isotopic anomaly, J. Geophys. Res.:-Atmos., 106, 17359-17373, doi:10.1029/2000jd900805, 2001.

Lee, C. C. W., Savarino, J., and Thiemens, M. H.: Mass independent oxygen isotopic composition of atmospheric sulfate: Origin and implications for the present and past atmosphere of Earth and Mars, Geophys. Res. Lett., 28, 1783-1786, doi:10.1029/2000gl011826, 2001.

Lee, Y. N. and Schwartz, S. E.: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, in: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, Precipitation scavenging, dry Deposition and resuspension, 1, 453–470, 1983.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature, 525, 367-371, doi:10.1038/nature15371, 2015.

Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X., and Molina, L. T.: A possible pathway for rapid growth of sulfate during haze days in China, Atmos. Chem. Phys., 17, 3301-3316, doi:10.5194/acp-17-3301-2017, 2017a.

Li, L., Hoffmann, M. R., and Colussi, A. J.: Role of Nitrogen Dioxide in the Production of Sulfate during Chinese Haze-Aerosol Episodes, Environ. Sci. Technol., 52, 2686-2693, doi:10.1021/acs.est.7b05222, 2018.

Li, M., Zhang, Q., Kurokawa, J.-i., Woo, J.-H., He, K., Lu, Z., Ohara, T., Song, Y., Streets, D. G., Carmichael, G. R., Cheng, Y., Hong, C., Huo, H., Jiang, X., Kang, S., Liu, F., Su, H., and Zheng, B.: MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP, Atmos. Chem. Phys., 17, 935-963, doi:10.5194/acp-17-935-2017, 2017b.

Li, W., Zhou, S., Wang, X., Xu, Z., Yuan, C., Yu, Y., Zhang, Q., and Wang, W.: Integrated evaluation of aerosols from regional brown hazes over northern China in winter: Concentrations, sources, transformation, and mixing states, J. Geophys. Res., 116, D09301, doi:10.1029/2010jd015099, 2011.

Liu, H., Jacob, D. J., Bey, I., and Yantosca, R. M.: Constraints from210Pb and7Be on wet deposition and transport in a global three-dimensional chemical tracer model driven by assimilated meteorological fields, J. Geophys. Res.: -Atmos., 106, 12109-12128, doi:10.1029/2000jd900839, 2001.

Liu, J. G., Xie, P., Wang, Y. S., Wang, Z. F., He, H., Liu, W.: Haze Observation and Control Measure Evaluation in Jing-Jin-Ji (Beijing, Tianjin, Hebei) Area during the Period of the Asia-Pacific Economic Cooperation (APEC) Meeting. Bulletin of the Chinese Academy of Sciences, 30 (3), 368−377, doi: 10.16418/j.issn.1000-3045.2015.03.011, 2015b.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213-5221, doi:10.1002/2017gl073210, 2017.

Liu, Z., Hu, B., Wang, L., Wu, F., Gao, W., and Wang, Y.: Seasonal and diurnal variation in particulate matter (PM_{10} and $PM_{2.5}$) at an urban site of Beijing: analyses from a 9-year study, Environ. Sci. Pollut. Res. Int., 22, 627-642, doi:10.1007/s11356-014-3347-0, 2015.

Ma, Q., Cai, S., Wang, S., Zhao, B., Martin, R. V., Brauer, M., Cohen, A., Jiang, J., Zhou, W., Hao, J., Frostad, J., Forouzanfar, M. H., and Burnett, R. T.: Impacts of coal burning on ambient $PM_{2.5}$ pollution in China, Atmos. Chem. Phys., 17, 4477-4491, doi:10.5194/acp-17-4477-2017, 2017.

Mackie, D. S.: Simulating the cloud processing of iron in Australian dust: pH and dust concentration, Geophys. Res. Lett., 32, L06809, doi:10.1029/2004gl022122, 2005.

Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509-519, doi:10.5194/acp-13-509-2013, 2013.

Martin, L. R. and Hill, M. W.: The iron catalyzed oxidation of sulfur: Reconciliation of the literature rates, Atmos. Environ., 21, 1487-1490, doi:10.1016/0004-6981(67)90100-x, 1967.

Martin, L. R., Hill, M. W., Tai, A. F., and Good, T. W.: The iron catalyzed oxidation of sulfur(IV) in aqueous solution: Differing effects of organics at high and low pH, J. Geophys. Res., 96, 3085, doi:10.1029/90jd02611, 1991.

McArdle, J. V. and Hoffmann, M. R.: Kinetics and mechanism of the oxidation of aquated sulfur dioxide by hydrogen peroxide at low pH, J. Phys. Chem., 87, 5425–5429, doi: 10.1021/j150644a024, 1983.

McCabe, J. R., Savarino, J., Alexander, B., Gong, S., and Thiemens, M. H.: Isotopic constraints on non-photochemical sulfate production in the Arctic winter, Geophys. Res. Lett., 33, L05810, doi:10.1029/2005gl025164, 2006.

Moch, J. M., Dovrou, E., Mickley, L. J., Keutsch, F. N., Cheng, Y., Jacob, D. J., Jiang, J., Li, M., Munger, J. W., Qiao, X., and Zhang, Q.: Contribution of Hydroxymethane Sulfonate to Ambient Particulate Matter: A Potential Explanation for High Particulate Sulfur During Severe Winter Haze in Beijing, Geophys. Res. Lett., 45, 11,969- 11,979, doi:10.1029/2018gl079309, 2018.

Munger, J. W., Jacob, D. J., and Hoffmann, M. R.: The occurrence of bisulfite-aldehyde addition products in fog- and cloud water, J. Atmos. Chem., 1(4), 335–350, doi:10.1007/BF00053799, 1984.

Munger, J. W., Tiller, C., and Hoffmann, M. R.: Identification of hydroxymethanesulfonate in fog water, Science, 231(4735), 247–249, doi:10.1126/science.231.4735.247, 1986.

Park, R. J.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res., 109, D15204, doi:10.1029/2003jd004473, 2004.

Park, R. S., Lee, S., Shin, S. K., and Song, C. H.: Contribution of ammonium nitrate to aerosol optical depth and direct radiative forcing by aerosols over East Asia, Atmos. Chem. Phys., 14, 2185-2201, doi:10.5194/acp-14-2185-2014, 2014.

Patris, N., Cliff, S. S., Quinn, P. K., Kasem, M., and Thiemens, M. H.: Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size, J. Geophys. Res., 112, D23301, doi:10.1029/2005jd006214, 2007.

Philip, S., Martin, R. V., Snider, G., Weagle, C. L., van Donkelaar, A., Brauer, M., Henze, D. K., Klimont, Z., Venkataraman, C., Guttikunda, S. K., and Zhang, Q.: Anthropogenic fugitive, combustion and industrial dust is a significant, underrepresented fine particulate matter source in global atmospheric models, Environ. Res. Lett., 12, 044018, doi:10.1088/1748-9326/aa65a4, 2017.

Pozzer, A., de Meij, A., Pringle, K. J., Tost, H., Doering, U. M., van Aardenne, J., and Lelieveld, J.: Distributions and regional budgets of aerosols and their precursors simulated with the EMAC chemistry-climate model, Atmos. Chem. Phys., 12, 961-987, doi:10.5194/acp-12-961-2012, 2012.

Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J. H.: Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, J. Geophys. Res.:-Atmos., 114, D01205, doi:10.1029/2008jd010701, 2009.

Ravishankara, A. R.: Heterogeneous and Multiphase Chemistry in the Troposphere, Science, 276, 1058-1065, doi:10.1126/science.276.5315.1058, 1997.

Savarino, J., Lee, C. C. W., and Thiemens, M. H.: Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth, ~~Journal~~ J.~~of~~ Geophys~~ica~~.~~l~~ ~~Research~~Res.: ~~-Atmospheres~~Atmos., 105, 29079-29088, doi:10.1029/2000jd900456, 2000.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: From air pollution to climate change. John Wiley & Sons, 2012.

Shen, X. H., Lee, T. Y., Guo, J., Wang, X. F., Li, P. H., Xu, P. J., Wang, Y., Ren, Y., Wang, W., Wang, T., Li, Y., Cam, S. A., and Collett, J. L.: Aqueous phase sulfate production in clouds in eastern China, Atmos. Environ., 62, 502-511, doi:10.1016/j.atmosenv.2012.07.079, 2012.

Shen, Z., Sun, J., Cao, J., Zhang, L., Zhang, Q., Lei, Y., Gao, J., Huang, R.-J., Liu, S., Huang, Y., Zhu, C., Xu, H., Zheng, C., Liu, P., and Xue, Z.: Chemical profiles of urban fugitive dust $PM_{2.5}$ samples in Northern Chinese cities, Sci. Total Environ., 569-570, 619-626, doi:10.1016/j.scitotenv.2016.06.156, 2016.

Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A., and Russell, A. G.: pH of Aerosols in a Polluted Atmosphere: Source Contributions to Highly Acidic Aerosol, Environ. Sci. Technol., 51, 4289-4296, doi:10.1021/acs.est.6b05736, 2017.

Sofen, E. D., Alexander, B., and Kunasek, S. A.: The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core $\Delta^{17}O$ (SO_4^{2-}), Atmos. Chem. Phys., 11, 3565-3578, doi:10.5194/acp-11-3565-2011, 2011.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, doi:10.5194/acp-18-7423-2018, 2018~~a~~.

Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M., Zhou, Z., Cheng, C., Lv, Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger, J. W., Jacob, D. J., and McElroy, M. B.: Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze, Atmos. Chem. Phys., 19, 1357-1371, doi:10.5194/acp-19-1357-2019, 2019.~~Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M., Zhou, Z., Cheng, C., Lv, Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger, J. W., Jacob, D., and McElroy, M. B.: Possible heterogeneous hydroxymethanesulfonate (HMS) chemistry in northern China winter haze and implications for rapid sulfate formation, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1015, in review, 2018b.~~

Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., and Ge, X.: The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China, Atmos. Environ., 77, 927-934, doi:10.1016/j.atmosenv.2013.06.019, 2013.

Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, J. Geophys. Res.: -Atmos., 119, 4380-4398, doi:10.1002/2014jd021641, 2014.

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D. R., and Wang, Z.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, Atmos. Chem. Phys., 16, 8309-8329, doi:10.5194/acp-16-8309-2016, 2016.

Tan, Z., Lu, K., Jiang, M., Su, R., Dong, H., Zeng, L., Xie, S., Tan, Q., and Zhang, Y.: Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O_3-VOC-NOx sensitivity, Sci. Total Environ., 636, 775-786, doi:10.1016/j.scitotenv.2018.04.286, 2018.

Ullerstam, M., Johnson, M. S., Vogt, R., and Ljungström, E.: DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust, Atmos. Chem. Phys., 3, 2043-2051, doi:10.5194/acp-3-2043-2003, 2003.

Uno, I., Osada, K., Yumimoto, K., Wang, Z., Itahashi, S., Pan, X., Hara, Y., Yamamoto, S., and Nishizawa, T.: Importance of Long-Range Nitrate Transport Based on Long-Term Observation and Modeling of Dust and Pollutants over East Asia, Aerosol and Air Quality Research, 17, 3052-3064, doi:10.4209/aaqr.2016.11.0494, 2017.

Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on Mineral Dust, Chem. Rev., 103, 4883-4940, doi:10.1021/cr020657y, 2003.

Van Der A, R. J., Mijling, B., Ding, J., Koukouli, M. E., Liu, F., Li, Q., Mao, H., and Theys, N.: Cleaning up the air: effectiveness of air quality policy for SO_2 and NO_x emissions in China, Atmos. Chem. Phys., 17, 1775-1789, doi:10.5194/acp-17-1775-2017, 2017.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad. Sci., 113, 13630-13635, doi:10.1073/pnas.1616540113, 2016.

Wang, G., Zhang, F., Peng, J., Duan, L., Ji, Y., Marrero-Ortiz, W., Wang, J., Li, J., Wu, C., Cao, C., Wang, Y., Zheng, J., Secrest, J., Li, Y., Wang, Y., Li, H., Li, N., and Zhang, R.: Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts, Atmos. Chem. Phys., 18, 10123-10132, doi:10.5194/acp-18-10123-2018, 2018a.

Wang, G., Zhang, F., Peng, J., Duan, L., Ji, Y., Marrero-Ortiz, W., Wang, J., Li, J., Wu, C., Cao, C., Wang, Y., Zheng, J., Secrest, J., Li, Y., Wang, Y., Li, H., Li, N., and Zhang, R.: Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts, Atmos. Chem. Phys.~~ Discuss.~~, 18~~1-23~~, 10123-10132, doi:10.5194/acp-18-10123-2018~~10.5194/acp-2018-185~~, 2018b.

Wang, Y., Zhang, Q. Q., He, K., Zhang, Q., and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: response to 2000–2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, Atmos. Chem. Phys., 13, 2635-2652, doi:10.5194/acp-13-2635-2013, 2013.

Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, J. Geophys. Res.:-Atmos., 119, 10,425-410,440, doi:10.1002/2013jd021426, 2014.

Wang, Y. X., McElroy, M. B., Jacob, D. J., and Yantosca, R. M.: A nested grid formulation for chemical transport over Asia: Applications to CO, J. Geophys. Res.: -Atmos., 109, D22307, doi:10.1029/2004jd005237, 2004.

Ye, C., Liu, P., Ma, Z., Xue, C., Zhang, C., Zhang, Y., Liu, J., Liu, C., Sun, X., and Mu, Y.: High H_2O_2 Concentrations Observed during Haze Periods during the Winter in Beijing: Importance of H_2O_2 Oxidation in Sulfate Formation, Environ. Sci. Technol. Lett., 5, 757-763, doi:10.1021/acs.estlett8b00579, 2018.

Ying, Q., Wu, L., and Zhang, H.: Local and inter-regional contributions to $PM_{2.5}$ nitrate and sulfate in China, Atmos. Environ., 94, 582-592, doi:10.1016/j.atmosenv.2014.05.078, 2014.

Zhang, L.: A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmos. Environ., 35, 549-560, doi:10.1016/s1352-2310(00)00326-5, 2001.

Zhang, L., Liu, L., Zhao, Y., Gong, S., Zhang, X., Henze, D. K., Capps, S. L., Fu, T.-M., Zhang, Q., and Wang, Y.: Source attribution of particulate matter pollution over North China with the adjoint method, Environ. Res. Lett., 10, 084011, doi:10.1088/1748-9326/10/8/084011, 2015.

Zhang, L., Shao, J., Lu, X., Zhao, Y., Hu, Y., Henze, D. K., Liao, H., Gong, S., and Zhang, Q.: Sources and Processes Affecting Fine Particulate Matter Pollution over North China: An Adjoint Analysis of the Beijing APEC Period, Environ. Sci. Technol., 50, 8731-8740, doi:10.1021/acs.est.6b03010, 2016.

Zhang, L., Chen, Y., Zhao, Y., Henze, D. K., Zhu, L., Song, Y., Paulot, F., Liu, X., Pan, Y., Lin, Y., and Huang, B.: Agricultural ammonia emissions in China: reconciling bottom-up and top-down estimates, Atmos. Chem. Phys., 18, 339-355, doi:10.5194/acp-18-339-2018, 2018.

Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 5131-5153, doi:10.5194/acp-9-5131-2009, 2009.

Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of $PM_{2.5}$; in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, doi:10.5194/acp-13-7053-2013, 2013.

Zhang, X. Y., Gong, S. L., Shen, Z. X., Mei, F. M., Xi, X. X., Liu, L. C., Zhou, Z. J., Wang, D., Wang, Y. Q., and Cheng, Y.: Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 1. Network observations, J. Geophys. Res. -Atmos., 108, 4261-4274, doi:10.1029/2002jd002632, 2003.

Zhao, D., Song, X., Zhu, T., Zhang, Z., Liu, Y., and Shang, J.: Multiphase oxidation of SO_2 by NO_2 on $CaCO_3$ particles, Atmos. Chem. Phys., 18, 2481-2493, doi:10.5194/acp-18-2481-2018, 2018.

Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and Kimoto, T.: 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, 2031-2049, doi:10.5194/acp-15-2031-2015, 2015.

Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions, Atmos. Chem. Phys., 18, 14095-14111, doi:10.5194/acp-18-14095-2018, 2018.

Tables and Figures

Table 1. Description of model simulations.

Model run	TMI-catalysis in clouds	Heterogeneous reactions	Aerosol pH	Horizontal resolution
Run_STD	N	N	ISO[1]	1/4°×5/16° & 4°×5°
Run_TMI	Y	N	ISO	1/4°×5/16° & 4°×5°
Run_Het	Y	Y	ISO	1/4°×5/16° & 4°×5°
Sensitivity simulations based on Run_Het[2]				
Run_pH2	Y	Y	2	4°×5°
Run_pH3	Y	Y	3	4°×5°
Run_pH4	Y	Y	4	4°×5°
Run_pH5	Y	Y	5	4°×5°
Run_pH6	Y	Y	6	4°×5°
Run_pH7	Y	Y	7	4°×5°
Run_pH8	Y	Y	8	4°×5°

[1] ISO means that the aerosol pH was calculated by ISORROPIA II in the model assuming metastable state.

[2] For the sensitivity simulations, aerosol pH was fixed to the stated prescribed value.

Table 2 Aqueous-phase reaction rate expressions, rate constants (k) and influence of ionic strength (I_s) on the first-order aqueous-phase sulfate production in aerosol.

Oxidants	k (s^{-1})	Uptake Gas	References
O_3	$k_1[H_2SO_3]+k_2[HSO_3^-]+k_3[SO_3^{2-}]$ $k_1 = 2.4\times10^4\ M^{-1}\ s^{-1}$ $k_2 = 3.7\times10^5\times\exp(-5530\times(1/T-1/298))\ M^{-1}\ s^{-1}$ $k_3 = 1.5\times10^9\times\exp(-5280\times(1/T-1/298))\ M^{-1}\ s^{-1}$	O_3	Hoffmann and Calvert (1985)
H_2O_2	$k_4[H^+][HSO_3^-]/(1+K[H^+])$ $k_4 = 7.45\times10^7\times\exp(-4430\times(1/T-1/298))\ M^{-1}\ s^{-1}$ $K = 13\ M^{-1}$	H_2O_2	McArdle and Hoffmann (1983)
NO_2	$k_5[S(IV)]$ $k_{5low} = 2\times10^6\ M^{-1}\ s^{-1}$ $k_{5high} = (1.24 - 2.95)\times10^7\ M^{-1}\ s^{-1}$	NO_2	Seinfeld and Pandis (2012) Lee and Schwartz (1983) Clifton, C. L. (1988)
TMI + O_2	$k_6[H^+]^{-0.74}[Mn(II)][Fe(III)]$ ($pH \leqslant 4.2$) $k_6 = 3.72\times10^7\times\exp(-8431.6\times(1/T-1/297))\ M^{-2}\ s^{-1}$ $k_7[H^+]^{0.67}[Mn(II)][Fe(III)]$ ($pH > 4.2$) $k_7 = 2.51\times10^{13}\times\exp(-8431.6\times(1/T-1/297))\ M^{-2}\ s^{-1}$	SO_2	Ibusuki and Takeuchi (1987)
	$\log\left(\frac{k}{k^{I_s=0}}\right) = b_1\sqrt{I_s}/(1+\sqrt{I_s})$ $I_{s,\ max} = 2\ M$ b_1 is in range of -4 to -2		Martin (1991) Martin and Hill (1967)
HOBr	$k_8[HSO_3^-]+k_9[SO_3^{2-}]$ $k_8 = 3.2\times10^9\ M^{-1}s^{-1}$ $k_9 = 5.0\times10^9\ M^{-1}s^{-1}$	HOBr	Chen et al. (2017)
O_2 on acidic microdroplet	1.5×10^6 ($pH \leq 3$)	SO_2	Hung and Hoffmann (2015)

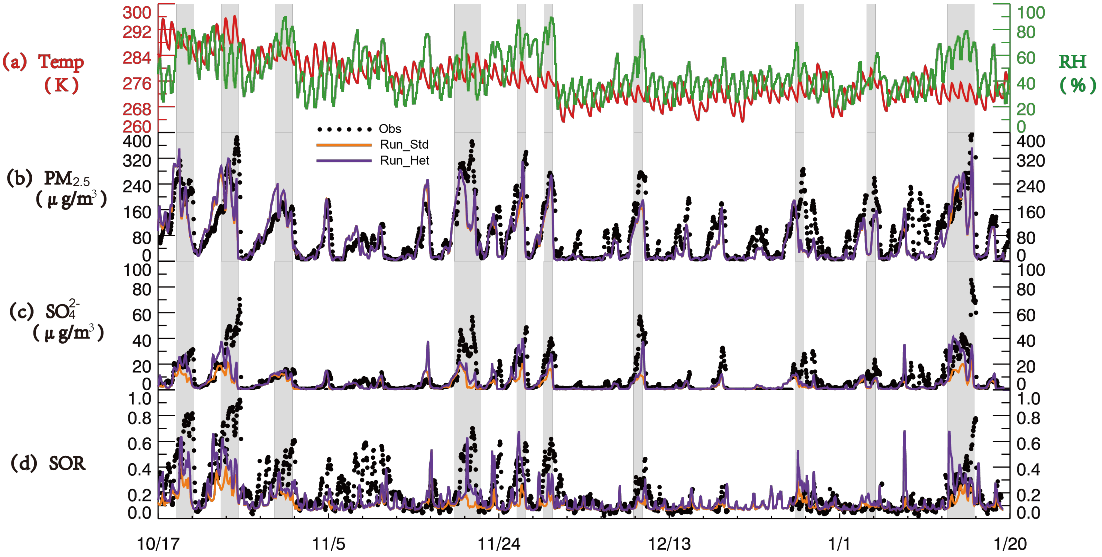


Figure 1. Time series of (a) GEOS-FP temperature (red line) and relative humidity (RH; green line), (b) $PM_{2.5}$ and (c) sulfate concentration, and (d) SOR at the surface in Beijing during the study period of 17 October 2014 – 20 January 2015. Hourly $PM_{2.5}$, sulfate, and SOR observations (black dots) are compared with model results from Run_Std (orange line) and Run_Het (purple line). The gray shaded bars represent 10 heavy pollution periods (HPP) ($PM_{2.5}$>150 $\mu g\ m^{-3}$) as defined in the text.

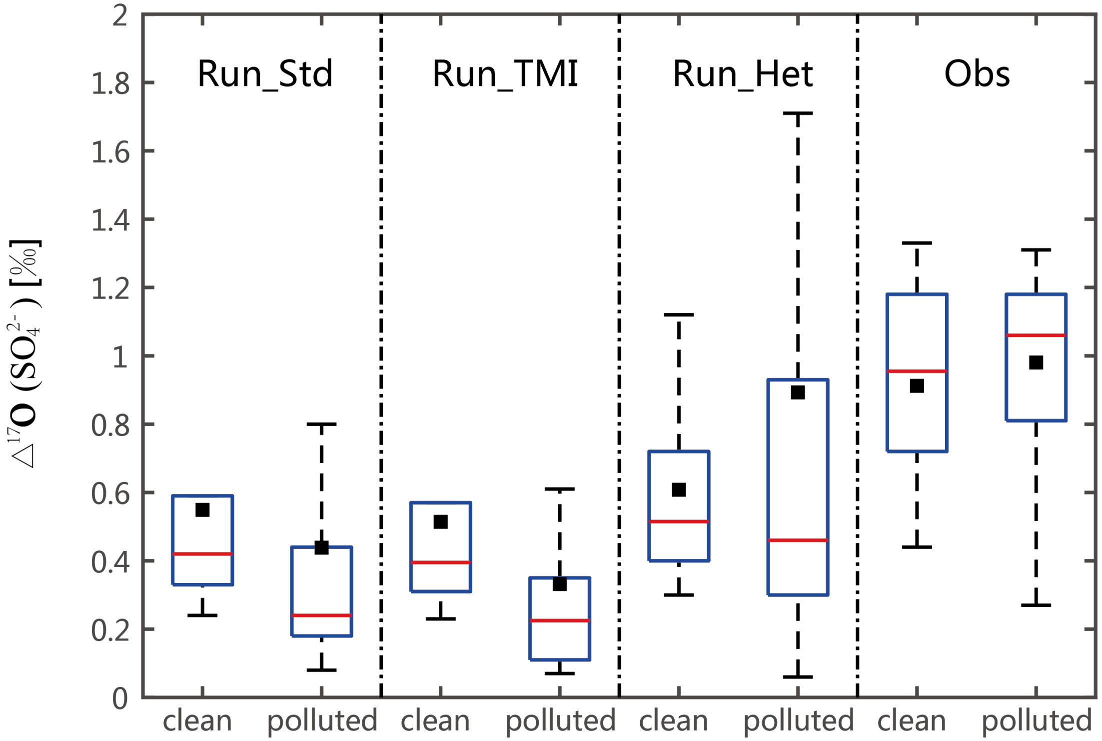


Figure 2. The box charts show observed vs. modeled $\Delta^{17}O(SO_4^{2-})$ in Beijing for each model simulation separated for heavy pollution and clean periods. The box line from bottom to top is respectively percentile of 25%, 50% and 75%, the whisker from bottom to top is respectively the minimum and the maximum, and the black square is mean value. 50

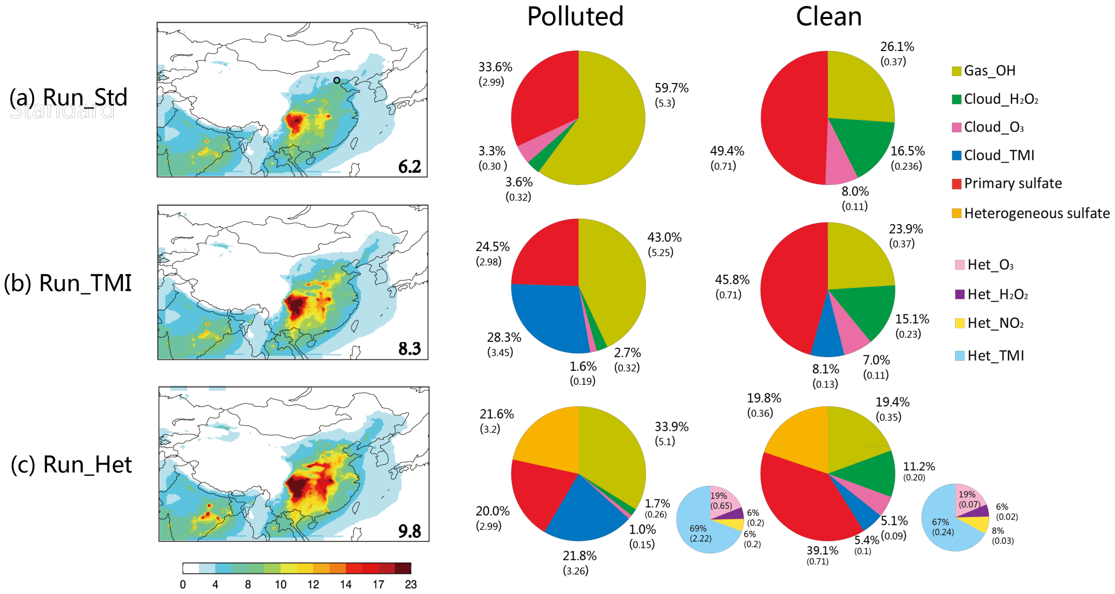


Figure 3. Model simulated sulfate aerosol concentrations (μg m^{-3}) above the ground for (a) Run_Std, (b) Run_TMI, and (c) Run_Het. Panels on the left show the spatial distributions with the numbers in inset representing simulated mean sulfate concentrations in Beijing (black circle in (a)) during the entire measurement period. The middle and right columns show percent contributions of different sulfate formation pathways to sulfate aerosol concentration in Beijing as calculated by the different model runs during polluted (HPP) and clean (CP) periods, respectively. The smaller pie charts in (c) show relative contributions of the four heterogeneous sulfate formation pathways implemented in the model. Numbers are percentage contributions (%) and absolute sulfate concentration (μg m^{-3}) are in parentheses.

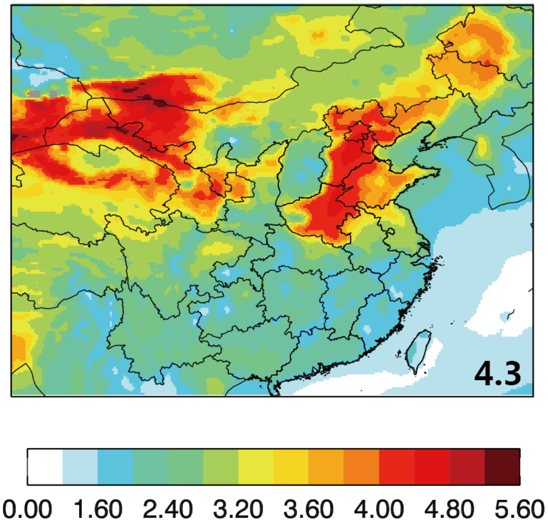
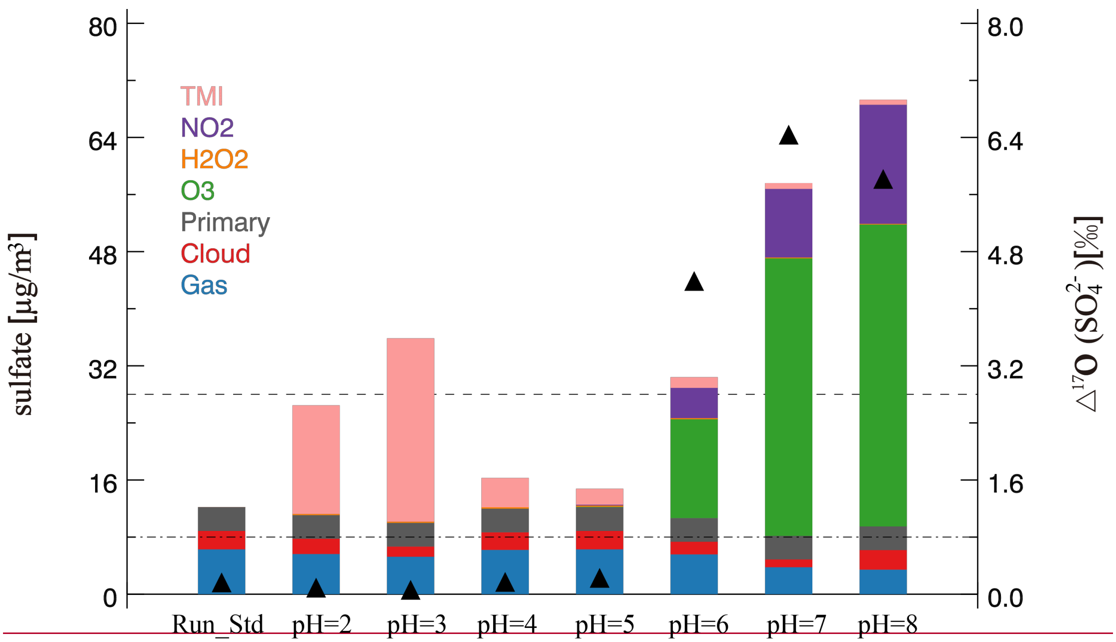


Figure 4. Model simulated mean aerosol pH values at the surface of China from 17 October 2014 to 20 January 2015 from Run_Het. Number in inset represents mean calculated pH values in Beijing.



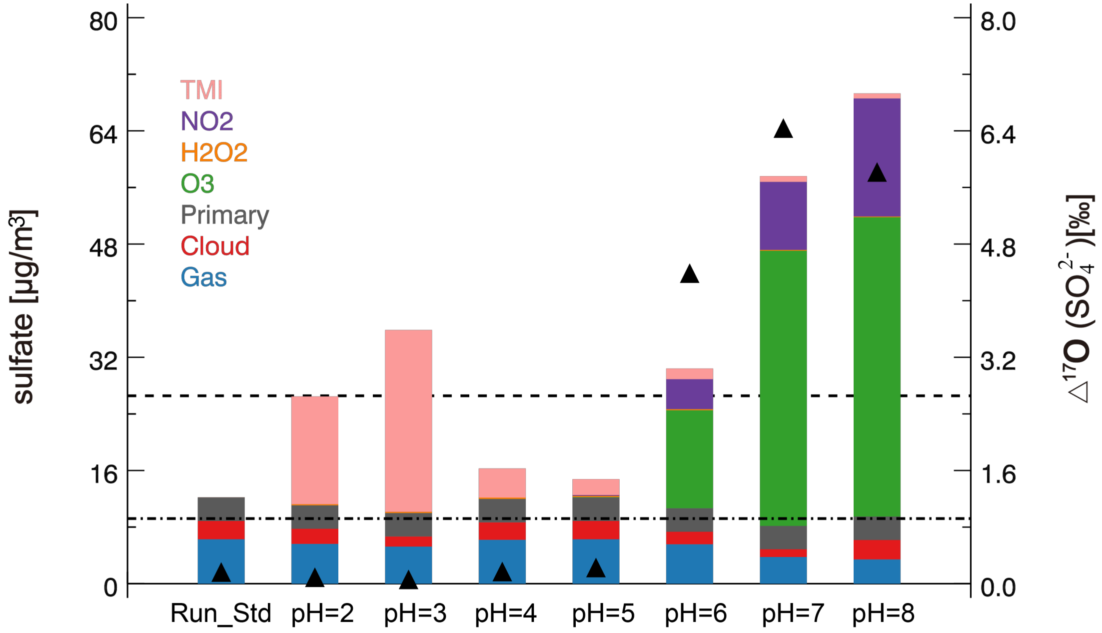


Figure 5. Model simulated mean sulfate concentration in Beijing averaged over heavy pollution periods (HPP as defined in the text). Model results are from the standard simulation (Run_Std) and sensitivity simulations with prescribed aerosol pH ranging 2 to 8. Different colors represent

contributions from different sulfate formation pathways, including four heterogeneous reactions (oxidation by O_2 (TMI), NO_2, H_2O_2, O_3), primary anthropogenic, aqueous-phase oxidation in clouds, and gas-phase oxidation. Also shown are the corresponding modeled $\Delta^{17}O$ (SO_4^{2-}) values in Beijing (black triangles). The dashed line denotes observed mean sulfate concentration (25.9 ug m^{-3}), and the dot-dashed line denotes observed mean $\Delta^{17}O(SO_4^{2-})$ (0.9‰) during HPP in Beijing.