Dear Reviewer,

We appreciate your careful consideration of our manuscript. We have carefully responded to all of your point-by-point comments and issues and have revised the manuscript accordingly. These revisions are described in detail below.

Review 2#

Very high particulate matter (PM) concentration levels are still a serious air quality and health issue in the North China Plain (NCP) that is strongly connected to formation of secondary inorganic (SIA) components such as sulfate. The formation pathway responsible for particulate sulfate in China are still highly uncertain and under debate. In the submitted manuscript, the authors present (i) a statistical analysis of long-term field observation data of two sites in the North China Plain investigating the formation mechanism of particulate sulfate and (ii) results from conducted flow tube experiments on the reactive uptake of SO2 which supported the field data analyses. The analysis focuses on the impact of (1) the aerosol liquid water content (ALWC), (2) the particle composition and (3) other factors such as the concentration of important oxidants for the sulfate formation. In my opinion, the paper under discussion is well structured, contains interesting information on an important topic of atmospheric chemistry and provides crucial implications on the formation particulate sulfate under polluted conditions in China. However, the paper in its present forms need major revision. After addressing my comments/questions/suggestions given below, this paper might be suitable for publication in ACP.

Response: Thank you for your positive comments.

General comments:

(1) Although the paper includes already a comprehensive analysis of important factors influencing the sulfate formation, aerosol acidity as one of the driving parameters for the sulfate formation and the partitioning of semi-volatile gases is hardly discussed in the paper. The paper mentions the importance of the pH only in a few places. However,

the study has applied two thermodynamic models (ISOROPIA II and E-AIM) that calculate acidity. Therefore, I'm puzzled why this provided information was not used in the statistical analysis. The authors should discuss the role of acidity in an additional subsection in the revised manuscript. This would substantially improve the manuscript and the interpretation of the field data.

Response: Thank you for your good suggestion. Aerosol acidity has complicated influences on sulfate formation. As shown in Fig. R1, when aerosol pH is lower than 4.5, the oxidation rate of S(IV) in aerosol liquid phase decreases as a function of pH because oxidation of S(IV) by transition metals is the dominant path, which is negatively dependent on aerosol pH. However, it increases as a function of aerosol pH when the pH is higher than 4.5 because the solubility and effective Henry's law constant of SO_2 are positively dependent on pH (Cheng et al., 2016;Liu et al., 2021;Liu et al., 2020). We added a short paragraph "Aerosol acidity is one of important factors affecting the sulfate formation and the partitioning of semi-volatile gases in the atmosphere (Liu et al., 2021). As shown in Fig. S11, when aerosol pH is lower than 4.5, the oxidation rate of S(IV) in aerosol liquid phase decreases as a function of pH because the oxidation of S(IV) by transition metals is the dominant path and is negatively dependent on aerosol pH. However, the oxidation rate of S(IV) increases when the aerosol pH is higher than 4.5. This can be explained by the fact that the solubility and effective Henry's law constant of SO_2 are positively dependent on pH (Cheng et al., 2016;Liu et al., 2021;Liu et al., 2020), which is consistent with the promotion effect of sulfate formation by NH_3" in lines 642-650 in the revised manuscript.

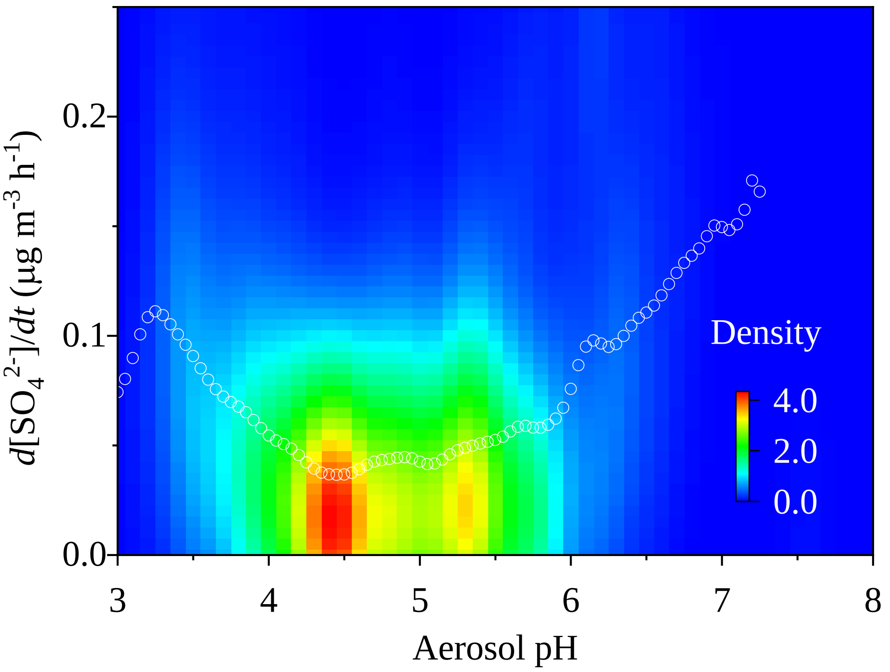

Fig. R1. The dependence of the oxidation rate of S(IV) in aerosol liquid phase on aerosol pH in Shijiazhuang. The white circles are the probability weighted values.

(2) My second major concern is about drying procedure of the dust and ammonium nitrate (NH_4NO_3) mixture (line 166 -170). Have the authors checked, e.g. by an IC analysis, that there is still NH_4NO_3 left after their drying procedure? It is well-known that NH_4NO_3 is semi-volatile and its volatilization strongly depends on the temperature (see e.g., Schaap et al. (2004) and references therein). At higher temperatures, NH_4NO_3 evaporates. So, my concern is that no NH_4NO_3 left after drying at 393K (120°C). If this is the case, then the interpretation of the uptake experiments needs to be fully revised. Please provide some information on how much NH_4NO_3 is left after drying.

Schaap, M., et al. (2004). Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL Atmos. Environ., 38, 6487-6496, https://doi.org/10.1016/j.atmosenv.2004.08.026.

Response: Thank you so much for your good comment. Yes, we checked the composition of the mixture of dust and NH_4NO_3 with an IC. 49.7 % of NH_4NO_3 was still remained in the mixture.

On the other hand, we compared the γ_{SO2} on different samples in the presence of

NO_2 and NH_3 at 80% RH. As shown in Table R1, the γ_{SO2} on the mixture of dust and NH_4NO_3 is comparable with that on the mixture of dust and $NaNO_3$. In addition, the γ_{SO2} on the mixture samples containing nitrate is significantly higher than that on the pure dust sample, which is comparable with that on α-Fe_2O_3 and γ-Al_2O_3 reported in our previous work (Yang et al., 2019). This further supported the IC results.

Table R1. The uptake coefficient of SO_2 on different samples at RH 80%

Samples	Atmosphere	γ_{SO2} (10^{-5})
Dust	$SO_2 + NO_2 + NH_3$	0.030 ± 0.004
Dust+$NaNO_3$	$SO_2 + NO_2 + NH_3$	1.23 ± 0.15
Dust+NH_4NO_3	$SO_2 + NO_2 + NH_3$	1.12 ± 0.13

We added a sentence "NH_4NO_3 in the mixture was further confirmed using an Ion Chromatograph (Ω Metrohm 940, Applikon Analytical B.V., Netherlands). Around 50 % of NH_4NO_3 remained in the mixture due to evaporation." in lines 186-189 in the revised manuscript.

(3) In Section 3.3, the influence of the particle composition on the ALWC and sulfate formation is discussed. The fractions of the major salts were calculated by E-AIM and the deliquescence RH (DRH) of different salts are considered for the discussion. I was surprised to see no contribution of ammonium-hydrogensulfate, $(NH_4)HSO_4$ at lower RH conditions in Figure 5 and no discussion of it in the text. $(NH_4)HSO_4$ is characterized by a much lower DRH (see Li et al. (2017) and references therein) than NH_4NO_3. Considering this information will surely change the discussion in this section. Comparing Figure 5A and 5B, I don't understand why there is almost 100% mass fraction of $(NH_4)_2SO_4$ at 10%≤RH≤30%, but Figure 5A shows concentrations of both NH_4NO_3 and $(NH_4)_2SO_4$ (surprisingly no $(NH_4)HSO_4$ here!). Based on my concerns, I expect that section 3.3. and its conclusions need to be strongly revised.

Y.-J. Li, et al. (2017) Rebounding hygroscopic inorganic aerosol particles: Liquids, gels, and hydrates, Aerosol Science and Technology, 51:3, 388-396

Response: Thank you for your good comment. We agree with you that $(NH_4)HSO_4$ has a lower DRH than NH_4NO_3. However, NH_3 is abundant in North China to neutralize sulfuric and nitrous acids in $PM_{2.5}$. For example, the annual mean concentration of NH_3 was 34.5±18.0 ppb in Shijiazhuang. Figure R2 shows the molar ratio of NH_4^+/SO_4^{2-} ($R_{NH4+/SO42-}$) in Shijiazhuang. 98.4 % of the dataset showed the $R_{NH4+/SO42-}$ higher than 2.0, which means the corresponding NH_4HSO_4 concentration values were zero. For the rest data with the $R_{NH4+/SO42-}$ less than 2.0, NH_4HSO_4 concentrations were very low (with mean and median values of 0.12 and 0.007 μg m^{-3}). This is the reason why we cannot see the contribution of NH_4HSO_4 to $PM_{2.5}$ in Fig. 5A and B. As shown in Fig. 5D, NH_4HSO_4 is observable but the absolute concentration is too low to be seen in Fig. 5C.

In the revised manuscript, we added a new short paragraph "It should be noted that $(NH_4)HSO_4$ has a lower DRH than NH_4NO_3 (Li et al., 2017b). However, 98.4% of the data points showed the $R_{NH4+/SO42-}$ higher than 2.0 in Shijiazhuang. This means that the contribution of $(NH_4)HSO_4$ to $PM_{2.5}$ should be negligible because of the abundance of atmospheric NH_3 in North China" in lines 517-521 in the revised manuscript.

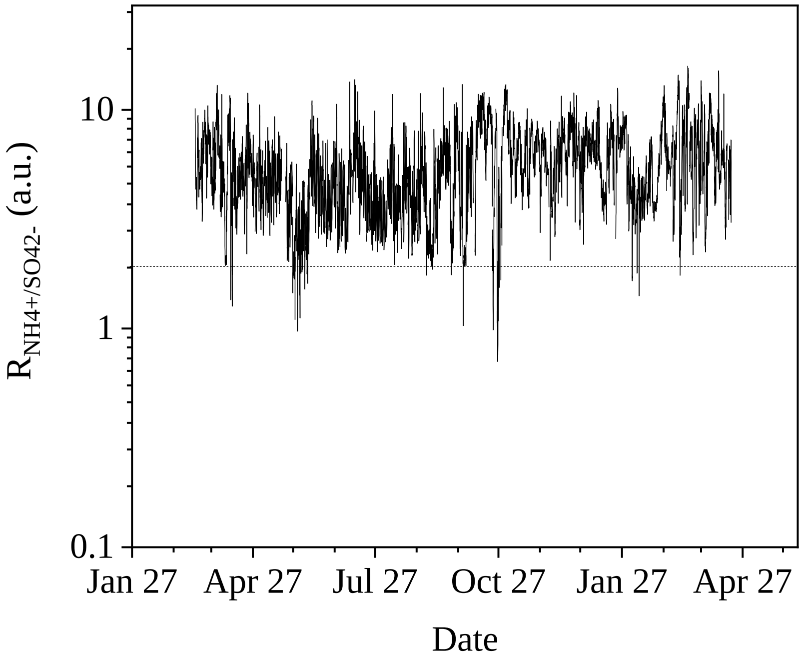

Fig. R2. Variation of the NH_4^+/SO_4^{2-} ratio in Shijiazhuang

Further Comments/Questions/Suggestions:

Page2 line 24-25: "This implies an enhanced formation rate of SO_4^{2-} in the ambient air". However, the smaller decrease in particulate sulfate can also be caused by a changed oxidation budget (increasing ozone budget) and/or because the sulfate formation in China is not a SO_2-limited process but rather an uptake or oxidant-limited process.

Response: Thank you. We agree with you that increases in oxidation budget or oxidation-limited process and uptake process can lead to the observed smaller decrease rate of SO_4^{2-} than SO_2 in China. We think this is not conflict with our statement "This implies an enhanced formation rate of SO_4^{2-} in the ambient air, and the mechanism is still under debate".

Page2 line 28: Define SOR.

Response: Thank you. It has been defined "sulfur oxidation ratio (SOR)" in line 28 in the revised manuscript.

Page2 line 33: Replace "in particle-phase" by "in the particle phase".

Response: Thank you. It has been corrected in line 33 in the revised manuscript.

Page2 line 29: "…transition of particle phase" means "change of phase state"?

Response: Thank you. It has been corrected in lines 34-35 in the revised manuscript.

Page2 line 29: Remove "kinetics".

Response: Thank you. We revised it to "Our results" in line 32 in the revised manuscript.

Page3 line 42: "(WHO, 2013;Lelieveld et al., 2015)" Please revise your citation style here and throughout the manuscript, and insert a space between the different references (after the semicolon).

Response: Thank you. It has been corrected in line 49 and other places throughout the manuscript.

Page3 line 52: The abbreviation "SNA" is quite unusual to me. Instead, I would recommend to use the abbreviation "SIA (Secondary inorganic aerosol)" that is more commonly used or remove SNA as its only used three times in the manuscript.

Response: Thank you. It has been replaced with "Secondary inorganic aerosol (SIA)" in lines 51 and 54 in the revised manuscript.

Page3 line 58-60: "However, the decrease rate of particulate SO_4^{2-} concentration (Lang et al., 2017;Li et al., 2017) is much smaller than SO_2 (Lang et al., 2017;Zhang et al., 2020)." The statement is vague, so, please provide some numbers.

Response: Thank you for your suggestion. We added a new sentence here "For example, the annual mean concentration of SO_4^{2-} decreased by 0.1 μg m^{-3} $year^{-1}$ from 2000 to 2013, followed by 1.9 μg m^{-3} $year^{-1}$ from 2013 to 2015 in Beijing, while it decreased by 3.8 μg m^{-3} $year^{-1}$ for SO_2 (Lang et al., 2017)" in lines 60-63 in the revised manuscript.

Page4 line 58-60: Please include the more recent reference of Liu et al. (2021).

Liu, T., A. W. H. Chan, and J. P. D. Abbatt (2021), Multiphase Oxidation of Sulfur Dioxide in Aerosol Particles: Implications for Sulfate Formation in Polluted Environments, Environ. Sci. Technol., 55(8), 4227-4242. https://doi.org/10.1021/acs.est.0c06496.

Response: Thank you so much. It has been included in line 60 in the revised manuscript.

Page4 line 66: Add "in the gas phase and subsequent uptake onto particles." at the end of the sentence. Here, it should be also mentioned that the OH pathway is the dominant gas-phase oxidation pathway.

Response: Thank you so much. This sentence has been revised "Particulate SO_4^{2-} can be formed through homogeneous oxidation of SO_2 by hydroxyl radicals (OH) and Stabilized Criegee Intermediates (SCIs) in the gas phase and subsequent uptake onto particles, while the OH pathway is the dominant gas-phase oxidation pathway" in lines

68-71 in the revised manuscript.

Page4 line 66: "~54.2 %" Please, provide only relevant decimal places.

Response: Thank you. It has been corrected in line 72 in the revised manuscript.

Page4 line 71 and 75: Why is the NO_2 oxidation pathway mentioned twice?

Response: Thank you. We moved that in line 76 to line 80 in the revised manuscript.

Page4 line 71: Please include the recent references of Liu et al. (2021) and Ye et al. (2021) for the H_2O_2 oxidation pathway.

Liu, T., et al. (2021), Multiphase Oxidation of Sulfur Dioxide in Aerosol Particles: Implications for Sulfate Formation in Polluted Environments, Environ. Sci. Technol., 55(8), 4227-4242. https://doi.org/10.1021/acs.est.0c06496.

Ye, C., et al. (2021), Particle-Phase Photoreactions of HULIS and TMIs Establish a Strong Source of H2O2 and Particulate Sulfate in the Winter North China Plain, Environ. Sci. Technol. https://doi.org/10.1021/acs.est.1c00561.

Response: Thank you so much. It has been included in line 77 in the revised manuscript.

Page4 line 75: Please include the work of Spindler et al. (2003) as this showed much lower rate constants compared to Clifton et al. (1988) and Lee and Schwartz (1983).

Spindler, G., et al. (2003), Wet annular denuder measurements of nitrous acid: laboratory study of the artefact reaction of NO_2 with S(IV) in aqueous solution and comparison with field measurements, Atmos. Environ., 37(19), 2643-2662, https://doi.org/10.1016/S1352-2310(03)00209-7.

Clifton, C. L., et al. (1988), Rate constant for the reaction of nitrogen dioxide with sulfur(IV) over the pH range 5.3-13, Environ. Sci. Technol., 22(5), 586-589. https://doi.org/10.1021/es00170a018.

Lee, Y.-N., and S. E. Schwartz (1983), Kinetics of Oxidation of Aqueous Sulfur(IV) by Nitrogen Dioxide, in Precipitation Scavenging, Dry Deposition, and Resuspension.

Volume 1: Precipitation Scavenging, edited by H. R. Pruppacher, R. G. Semonin and W. G. Slinn, pp. 453-470, Elsevier, New York, Amsterdam, Oxford.

Response: Thank you so much. It has been included in line 81 in the revised manuscript.

Page4 line 79: Insert "the" after "pathways to".

Response: Thank you. It has been corrected in line 85 in the revised manuscript.

Page4 line 82: "an observe based" should be "observation-based"

Response: Thank you. It has been corrected in line 88 in the revised manuscript.

Page5 line 83: Delete "simulation".

Response: Thank you. It has been corrected in line 88 in the revised manuscript.

Page5 line 83: Add "Gas-phase" before "Oxidation".

Response: Thank you. It has been corrected in line 89 in the revised manuscript.

Page5 line 84: Replace "BTH" by "the Beijing-Tianjin-Hebei province". The abbreviation is only used here once.

Response: Thank you. It has been corrected in lines 89-90 in the revised manuscript.

Page5 line 85: "simulations"

Response: Thank you. It has been corrected in line 91 in the revised manuscript.

Page5 line 87: Cite also Ye et al. (2021) here.

Ye, C., et al. (2021), Particle-Phase Photoreactions of HULIS and TMIs Establish a Strong Source of H2O2 and Particulate Sulfate in the Winter North China Plain, Environ. Sci. Technol. https://doi.org/10.1021/acs.est.1c00561

Response: Thank you. It has been cited in line 93 in the revised manuscript.

Page5 line 86-89: In this discussion, it would be appropriate to include results from isotope measurements and their interpretations on the key oxidation pathways. The results of conducted isotope measurements should also be included at other places in the manuscript. They can support the findings of the current study.

Response: Thank you for your good suggestion. We added a short paragraph "However, the relative importance of these oxidation paths varied greatly among different researches. For instance, TMI-catalyzed oxidation could explain ~69 % of aqueous sulfate formation in NCP based on isotopic measurements and modeling (Shao et al., 2019), while oxidation by NO_2 or O_2 was the dominant oxidation path (66-73%) based on isotopic measurements in another study (He et al., 2018)" in lines 96-100 in the revised manuscript. We also added a sentence "This might be the reason why these oxidation paths showed inconsistent relative importance of among different studies even using the same method, such as isotopic measurements (Shao et al., 2019; He et al., 2018)" in lines 414-416 in the revised manuscript.

Page5 line 94: "what the control factors are from gas-phase SO_2 to particle-phase sulfate" does not sound good. Maybe better: "what are the controlling factors of the S(IV)-to-S(VI) conversion in the gas phase."

Response: Thank you. It has been corrected as you suggested "…what are the controlling factors of the S(IV)-to-S(VI) conversion from the gas phase to the particle phase" in lines 105-106 in the revised manuscript.

Page5 line 95-97: These two sentences here do not fit, or a transition sentence is missing.

Response: Thank you. We added a new sentence between these two sentences "This will modify its physical properties, such as morphology, phase-state and so on" in lines 108-109 in the revised manuscript.

Page5 line 100: "… statistically investigated to identify the controlling factors." Subsequently, the different sensitivity investigations should be briefly mentioned. The uptake investigations are missing in this paragraph.

Response: Thank you for your suggestion. We revised this sentence "…statistically investigated to identify the controlling factors. The role of mass transfer of SO_2 and the oxidation of S(IV) in particle-phase have been discussed based on flow tube experiments and box model simulations" in lines 113-115 in the revised manuscript.

Page5 line 101: Replace "mainly" by "strongly".

Response: Thank you. It has been corrected in line 117 in the revised manuscript.

Page6 line 106: Remove "Lat." and "Lon.". Instead, add "N" and "E" behind the numbers, respectively.

Response: Thank you. It has been corrected in lines 121 and 122 in the revised manuscript.

Page6 line 120: "Particle-phase"

Response: Thank you. It has been corrected in lines 135-136 in the revised manuscript.

Page6 line 120: Measured Fe and Mn concentrations are total metal concentrations or water-soluble concentrations?

Response: Thank you. They are total metal concentrations. This sentence has been revised "Particle-phase total concentrations of Fe and Mn were measured…" in lines 135-136 in the revised manuscript.

Page7 line 133: Define "IE".

Response: Thank you. It has been defined "The ionization efficiency (IE)…" in line 148 in the revised manuscript.

Page7 line 143: "influence of RH" and "the uptake coefficient (γ_{SO2})"

Response: Thank you. It has been corrected in line 158 in the revised manuscript.

Page7 line 146: “gas-phase”

Response: Thank you. It has been corrected in line 161 in the revised manuscript.

Page8 line 153: “gas-phase”

Response: Thank you. It has been corrected in line 168 in the revised manuscript.

Page8 line 155: “BET” must already be defined here for the first time, and not only in line 188.

Response: Thank you so much. It has been corrected in line 170 in the revised manuscript.

Page9 line 183: “we aimed to understand”

Response: Thank you. It has been corrected in line 200 in the revised manuscript.

Page10 line 203-205: Why haven’t the authors applied more simple approaches to calculate or estimate the pH. Please see Pye et al. (2020) and proxy approaches therein. Pye, H. O. T., et al. (2020), The acidity of atmospheric particles and clouds, Atmos. Chem. Phys., 20(8), 4809-4888. https://doi.org/10.5194/acp-20-4809-2020.

Response: Thank you. Actually, the calculation method for pH in this work is the same as that used in the literature (Pye et al., 2020). Because the unit of H^+ is μg m^{-3} in the output file of ISORROPIA II model, we need to convert it to molality. We revised equation 1 “$\mathrm{pH} = -\log_{10}(\gamma_{H^+} m_{H^+}) = -\log_{10}\frac{1000\gamma_{H^+} c_{H^+}}{AWC}$ (1)

where γ_{H+} is the activity coefficient of H^+ and m_{H+} is the molality of H^+” in lines 221-222 in the revised manuscript.

Page10 line 207-212: Please, provide the references for all kinetic rate expressions given. Furthermore, the authors should look at two reviews published recently that have evaluated kinetic data on sulfur oxidation (Liu et al. (2021); Tilgner et al. (2021, under review in ACPD)). Are the applied kinetic data in agreement with their recommended values?

Liu, T., et al. (2021), Multiphase Oxidation of Sulfur Dioxide in Aerosol Particles: Implications for Sulfate Formation in Polluted Environments, Environ. Sci. Technol., 55(8), 4227-4242. https://doi.org/10.1021/acs.est.0c06496 .

Tilgner, A., et al. (2021), Acidity and the multiphase chemistry of atmospheric aqueous particles and clouds, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-58, in review, 2021.

Response: Thank you for your suggestion. The citations have been added in lines 231-232 in the revised manuscript. The kinetic data in this work are agreement with their recommended values (Liu et al., 2021;Tilgner et al., 2021). These references have also been added in line 241 in the revised manuscript.

Page11 line 215: “8:7” should be “8.7”

Response: Thank you. It has been corrected in line 239 in the revised manuscript.

Page11 line 219: Please, cite the references for all Henry’s law constants.

Response: Thank you. It has been cited “1.1×10^{-2}, 1.0×10^{5} and 1.0×10^{-2} M atm^{-1} at 298 K for O_3, H_2O_2 and NO_2 (Seinfeld and Pandis, 2006), respectively” lines 243-244 in the revised manuscript.

Page11 line 219-221: Where can I find the derived H_2O_2 concentrations? Do they fit to measurements in the NCP, see e.g. Ye et al. (2018)?

Ye, C., et al. (2018), 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. Tech. Let., 5(12), 757-763, https://doi.org/10.1021/acs.estlett.8b00579.

Response: Thank you so much for your comment. Fig. R3A shows the derived H_2O_2 concentrations. Fig. R3B shows the diurnal curves of H_2O_2 in winter. The black line and the grey shadow are the mean values and the error bars reported by Ye et al. (Ye et al., 2018) and the red line with error bars is the derived H_2O_2 concentrations in winter in this work. Overall, the H_2O_2 concentrations derived in this work are comparable with those reported by Ye et al.(Ye et al., 2018). In the revised manuscript, we added this figure in the SI. We also added a short paragraph "Fig. S2 shows the derived H_2O_2 concentrations and the diurnal curves of H_2O_2 in winter in Shijiazhuang. The H_2O_2 concentrations varied from 0.05 to 3.7 ppbv, with a mean value of 0.62±0.52 ppbv. Overall, the wintertime H_2O_2 concentrations derived in this work are comparable with those reported in the literature (Ye et al., 2018)" in lines 245-249 in the revised manuscript.

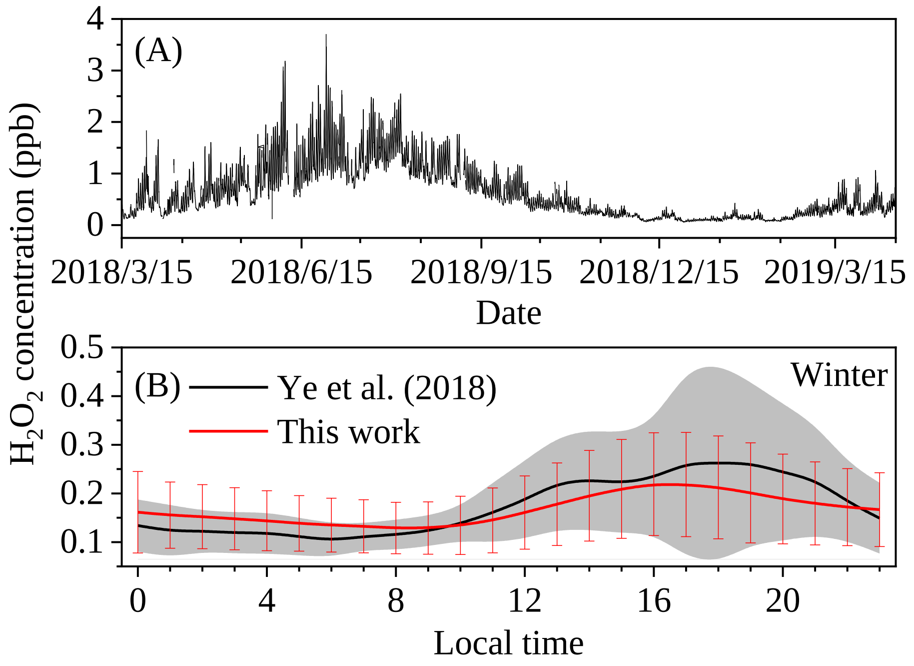

Fig. R3. (A) the derived H_2O_2 concentrations and (B) the diurnal variations of H_2O_2 in winter in Shijiazhuang.

Page11 line 235-236: Please, provide only relevant decimal places.

Response: Thank you. It has been corrected in line 264 in the revised manuscript.

Page12 line 238: Remove "well".

Response: Thank you. It has been corrected in line 266 in the revised manuscript.

Page12 line 238: "larger population of heavy industries" sounds bad. Do you mean "larger density of heavy industries"?

Response: Thank you. It has been replaced with "larger density of heavy industries" in line 267 in the revised manuscript.

Page12 line 240: "than in Beijing".

Response: Thank you. It has been corrected in line 268 in the revised manuscript.

Page12 Fig1: The legend is not well placed.

Response: Thank you. This problem has been fixed in Fig. 1 in the revised manuscript.

Page13 line 261: Another consequence of "the increased traffic emissions in Beijing", i.e. higher NOx emissions, is that the concentrations of ozone are elevated in Beijing. This should be mentioned!

Response: Thank you. Figure R4 shows the daily mean concentrations of SO_2, NO_2 and O_3 in Beijing from 2014 to 2020. The concentrations of SO_2 decreased obviously, while the concentrations of NO_2 showed a slight decrease and the concentrations of O_3 are relatively stable in the same season. So, we revised the sentence "This can be ascribed to the effective reduction of SO_2 emissions, but less effective reduction of traffic emissions in Beijing" in lines 288-289 in the revised manuscript.

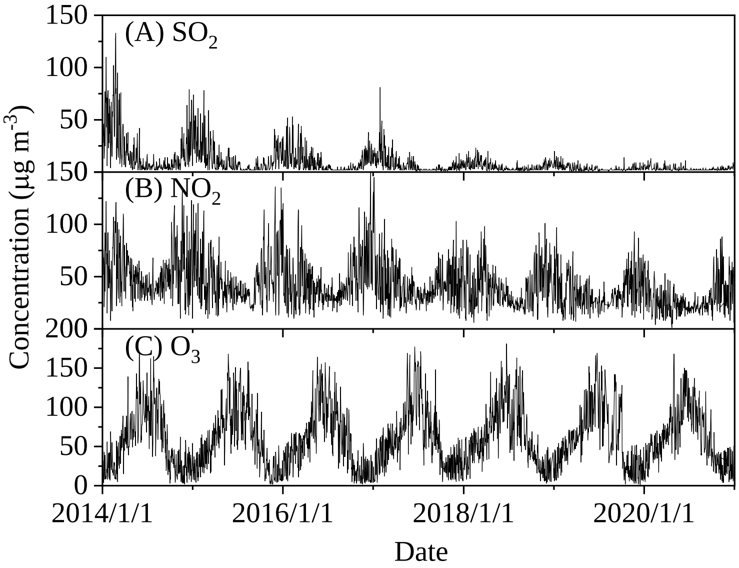

Fig. R4. Variations of daily mean concentrations of (A) SO_2, (B) NO_2 and (C) O_3 in Beijing from 2014 to 2020.

Page13 line 272: Better say that the Shijiazhuang site is more influenced by primary emissions.

Response: Thank you for your suggestion. We revised this sentence as "The high primary emissions of SO_2 in Shijiazhuang should lead to a lower SOR than that in Beijing" in lines 298-299 in the revised manuscript.

Page13 line 274: Please clarify "significantly higher". 55 ppb and 51 ppb are not significantly different!

Response: Thank you. Although the difference is not so big, it is significant with a *P* value of 9×10^{-96} based on T-test. This means the difference is significant at 95% significance level.

Page14 line 275-279: I do not agree with the conclusion drawn here, because of the higher primary emissions in Shijiazhuang affecting the SOR. Perhaps other parameters are required to reach this conclusion.

Response: Thank you so much for your good comment. We rewrote this paragraph as "The high primary emissions of SO_2 in Shijiazhuang should lead to a lower SOR than that in Beijing. On the other hand, secondary transform of SO_2 to sulfate should also have influence on the SOR. The O_x ($O_x = NO_2+O_3$) concentration in Shijiazhuang was usually higher than that in Beijing (Fig. 1F). The annual mean O_x concentration in Shijiazhuang was 55.2 ± 22.3 ppb, which was significantly higher than that in Beijing (50.7 ± 21.5 ppb) at 0.05 level. This is inconsistent with the observed higher SOR in Beijing if gas-phase oxidation mainly contributed to sulfate formation. These results suggest that heterogeneous and/or multiphase reactions may also play important roles in particulate sulfate formation during transport (Zheng et al., 2015; Martin and Good, 1991; Wu et al., 2019)" in lines 288-307 in the revised manuscript.

Page14 line 276: "gas-phase"

Response: Thank you. It has been corrected in line 304 in the revised manuscript.

Page14 line 276: "multiphase"

Response: Thank you. It has been corrected in line 305 in the revised manuscript.

Page14 line 282-283: "$PM_{2.5}$ mass concentration well kept pace with the high sulfate concentration" sounds bad.

Response: Thank you. We changed this sentence as "…$PM_{2.5}$ mass concentration coincided with the high sulfate concentration, the fraction of sulfate and the SOR" in lines 310-311 in the revised manuscript.

Page14 line 288: "a similar".

Response: Thank you. It has been corrected in line 316 in the revised manuscript.

Page15 line 288: "As shown in Fig. 2D, the high concentration of sulfate positively correlated with high RH in most cases". I'm not convinced here and it's hard to see from the Figure! Please provide a correlation coefficient.

Response: Thank you for your comments. Figure R5 shows the 2D Kernel density graph between the sulfate concentration and the RH. Overall, we can see a positive correlation between sulfate concentration and RH. The correlation coefficient is 0.92 between the probability weighted concentration and RH.

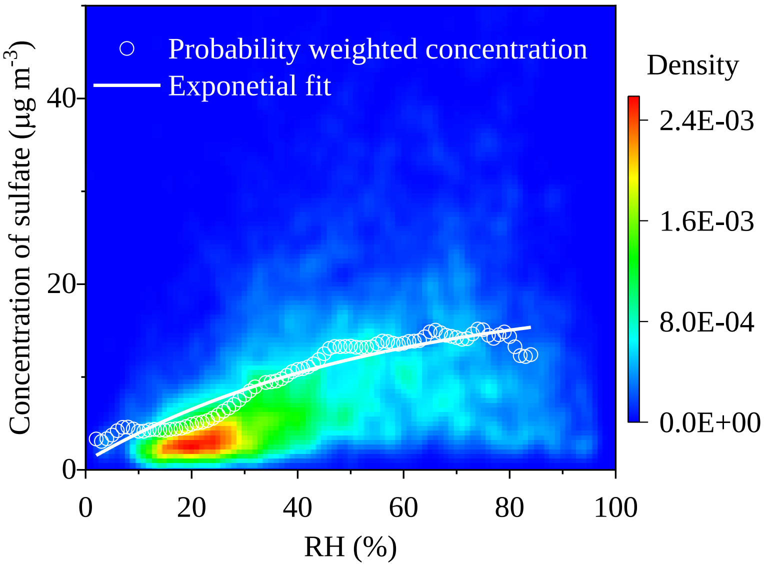

Fig. R5. The 2D Kernel density graph between the sulfate concentration and the RH.

Page18 line 352: "gas-phase".

Response: Thank you. It has been corrected in line 380 in the revised manuscript.

Page19 line 368: "the uptake".

Response: Thank you. It has been corrected in line 396 in the revised manuscript.

Page19 line 369: "a quick".

Response: Thank you. It has been corrected in line 397 in the revised manuscript.

Page19 line 373: "metals".

Response: Thank you. It has been corrected in line 403 in the revised manuscript.

Page19 line 381: I think Fig.S5 contains important information and should be therefore part of the main manuscript.

Response: Thank you for your suggestion. We added it in Fig. R6A and Fig. 4A.

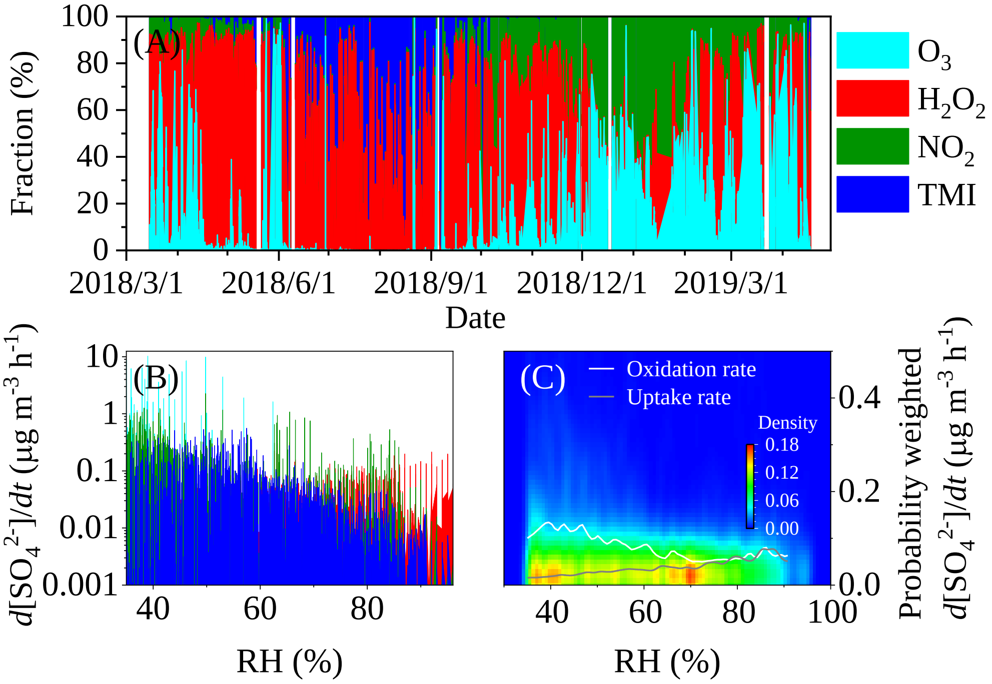

Fig. R6. (A) The relative importance of oxidation paths of S(IV) in aqueous phase, the dependence of (B) sulfate formation rates and (C) the probability weighted sulfate formation rates on RH in Shijiazhuang.

Page23 line 451: Replace “with” by “as a function of”.

Response: Thank you. It has been corrected in line 497 in the revised manuscript.

Page23 line 457-458: Please revise the Figure caption and describe in more detail what is shown in the different items.

Response: Thank you. We revised the caption “Variations of (A) the mass concentrations and (B) the mass fractions of molecular composition in $PM_{2.5}$, (C) the estimated AWC attributed to different composition and (D) the corresponding AWC fraction as a function of RH in Shijiazhuang” in lines 503-505 in the revised manuscript.

Page23 line 459-461: Please see e.g. Li et al. (2017) for more recent DRH values incl. other salts. Why $(NH_4)HSO_4$ is not listed here which has a lower DRH than $(NH_4)NO_3$? Therefore, the following conclusion (“…ammonium nitrate should the major contributor to the AWC compared with sulfate and chloride…") can be wrong and the subsequent discussion should be revised.

Li, Y. J., et al. (2016), Rebounding hygroscopic inorganic aerosol particles: Liquids, gels, and hydrates, Aerosol Sci. Technol., 51(3), 388-396. https://doi.org/10.1080/02786826.2016.1263384.

Response: Thank you for your good suggestion. We agree with you that $(NH_4)HSO_4$ has a lower DRH than NH_4NO_3. However, NH_3 is abundant in North China. For example, the annual mean concentration of NH_3 was 34.5±18.0 ppb in Shijiazhuang. Figure R2 shows the $R_{NH4+/SO42-}$ in Shijiazhuang. Only 1.6% of the data points showed the $R_{NH4+/SO42-}$ lower than 2.0. The concentrations of NH_4HSO_4 for 98.4% of the dataset were zero. As shown in Figure 5C, NH_4NO_3 and $(NH_4)_2SO_4$ are the major contributors to the AWC. Especially, NH_4NO_3 dominated the AWC when the RH ranged from 60 % to 80 %. In the revised manuscript, we deleted the sentence "…ammonium nitrate should the major contributor to the AWC compared with sulfate and chloride…" We also added a new short paragraph "It should be noted that $(NH_4)HSO_4$ has a lower DRH than NH_4NO_3 (Li et al., 2017b). However, 98.4% of the data points showed the $R_{NH4+/SO42-}$ higher than 2.0 in Shijiazhuang. This means that the contribution of $(NH_4)HSO_4$ to $PM_{2.5}$ should be negligible because of the abundance of atmospheric NH_3 in North China" in lines 517-521 in the revised manuscript.

Page23 line 465: Here, the E-AIM model is mentioned for the first time. Why not in Section 2? Would it be possible to use only E-AIM or ISOROPIA in the present study?

Response: Thank you so much. We moved the sentence "The deliquescence curves of inorganic salts were calculated at 298.5 K using the E-AIM model (Clegg et al., 1998). Then, the AWC attributed to individual salt was calculated with the mass of the salt and the mass-based growth factor at the corresponding RH" to Section 2 (lines 222-225) in the revised manuscript. ISOROPIA is a widely used model for AWC and aerosol pH calculations (Ding et al., 2019). However, the AWC attributed to different molecular component is unavailable in the outputs of the ISOROPIA model. Thus, we calculated it using the mass-based growth factor and the mass concentration of individual salt. Thus, the E-AIM was used to calculate the growth factor. It is also a widely used model to calculate the growth factor of salts.

Page26 line 524-535: A recently submitted review by Tilgner et al. (2021, under review in ACPD) has outlined that the reaction rate constant of the NO_2 reaction with dissolved S(IV) by Clifton et al. (1988) is far too high and that studies by Spindler et al. (2003) showed much lower values. This fact should be also reflected in the discussion here.

Clifton, C. L., et al. (1988), Rate constant for the reaction of nitrogen dioxide with sulfur(IV) over the pH range 5.3-13, Environ. Sci. Technol., 22(5), 586-589. https://doi.org/10.1021/es00170a018.

Spindler, G., et al. (2003), Wet annular denuder measurements of nitrous acid: laboratory study of the artefact reaction of NO_2 with S(IV) in aqueous solution and comparison with field measurements, Atmos. Environ., 37(19), 2643-2662, https://doi.org/10.1016/S1352-2310(03)00209-7.

Tilgner, A., et al. (2021), Acidity and the multiphase chemistry of atmospheric aqueous particles and clouds, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-58, in review, 2021.

Response: Thank you so much for your good suggestion. We added the point "3) The previous calculations were conducted using a high reaction rate constant of the NO_2 reaction with dissolved S(IV) (Clifton et al., 1988; Cheng et al., 2016), while a small value was reported in the more recent study (Spindler et al., 2003; Tilgner et al., 2021)" in lines 581-584 in the revised manuscript.

Page28 line Fig.6: In this Figure, it would be better to use O_3 instead of O_x, because NO_2 is also considered separately.

Response: Thank you for your good suggestion. We replaced O_x with O_3 in Fig. 6 and Fig. S10 in the revised manuscript. We also updated the corresponding text (from lines 621 to 623).

Page28 line 560: “gas-phase”.

Response: Thank you. Thank you. It has been corrected in line 589 in the revised manuscript. We also fixed the same problems throughout the paper, such as in lines 70, 89, 161, 168, 380, 479, 620 in the revised manuscript.

Page29 line 577-579: Here, it should be mentioned that the effective solubility of SO_2 can be enhanced due the increase of the aerosol pH. Furthermore, a lower acidity also promotes other oxidation processes and enables therefore higher S(VI) formation rates.

Response: Thank you so much. We revised it as “These results further confirm that NH_3 can promote the uptake of SO_2 at high RH, possible through enhancing the solubility of SO_2 in water (Chen et al., 2019;Cheng et al., 2016;Wang et al., 2016) because the effective solubility of SO_2 can be enhanced due to the increase of the aerosol pH” in lines 637-641 in the revised manuscript. The effect of aerosol pH on oxidation rate of S(IV) was also discussed in a new paragraph “Aerosol acidity is one of important factors affecting the sulfate formation and the partitioning of semi-volatile gases in the atmosphere (Liu et al., 2021). As shown in Fig. S11, when aerosol pH is lower than 4.5, the oxidation rate of S(IV) in aerosol liquid phase decreases as a function of pH because the oxidation of S(IV) by transition metals is the dominant path and is negatively dependent on aerosol pH. However, the oxidation rate of S(IV) increases when the aerosol pH is higher than 4.5. This can be explained by the fact that the solubility and effective Henry’s law constant of SO_2 are positively dependent on pH (Cheng et al., 2016; Liu et al., 2021; Liu et al., 2020a), which is consistent with the promotion effect of sulfate formation by NH_3” in lines 642-650 in the revised manuscript.

Page29 line 588: “liquid-phase”.

Response: Thank you. It has been corrected through the paper, such as lines 659, 687 and 459 in the revised manuscript.

Page32 line 643 ff: Please check again all references. The reference style is not uniform, for example the doi style.

Response: Thank you so much. We fixed all the references including the doi style.

Supporting Information (SI): The Figure captions in the SI are in parts rather brief. I strongly recommend to extend the captions, especially for complex Figures with multiple items.

Response: Thank you for your suggestion. We extended the captions in SI. For example, the caption of Fig. S7 was revised "Correlation of the ionic charge between inorganic anions (NO_3^-, SO_4^{2-}, Cl^-) and cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) and (B) the relative contribution of cations to the total positive charges in soluble $PM_{2.5}$". The caption of Fig. S9 was also revised "(A) The time series of AWC calculated under different episodes and (B) the relative change of AWC due to reduction of ammonium nitrate (AN) and ammonium sulfate (AS) in $PM_{2.5}$".

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