Review of “Ammonium nitrate promotes sulfate formation through uptake kinetic regime “ by Yongchun Liu et al. (2021)

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 SO_2 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.

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.

(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.

(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 $10\% \leq RH \leq 30\%$, 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. http://dx.doi.org/10.1080/02786826.2016.1263384.

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.

Page2 line 28: Define SOR.

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

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

Page2 line 29: Remove "kinetics".

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).

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.

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.

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.

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.

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

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

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 H_2O_2 and Particulate Sulfate in the Winter North China Plain, Environ. Sci. Technol. https://doi.org/10.1021/acs.est.1c00561.

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.

Page4 line 79: Insert “the” after “pathways to”.

Page4 line 82: “an observe based” should be “observation-based”

Page5 line 83: Delete “simulation”.

Page5 line 83: Add “Gas-phase” before “Oxidation”.

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

Page5 line 85: “simulations”

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

H_2O_2 and Particulate Sulfate in the Winter North China Plain, Environ. Sci. Technol. https://doi.org/10.1021/acs.est.1c00561

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.

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."

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

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.

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

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

Page6 line 120: "Particle-phase"

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

Page7 line 133: Define "IE".

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

Page7 line 146: "gas-phase"

Page8 line 153: "gas-phase"

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

Page9 line 183: "we aimed to understand"

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.

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.

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

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

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.

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

Page12 line 238: Remove “well”.

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

Page12 line 240: “than in Beijing”.

Page12 Fig1: The legend is not well placed.

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!

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

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

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.

Page14 line 276: “gas-phase”

Page14 line 276: “multiphase”

Page14 line 282-283: “PM2.5 mass concentration well kept pace with the high sulfate concentration” sounds bad.

Page14 line 288: “a similar”.

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.

Page18 line 352: “gas-phase”.

Page19 line 368: “the uptake”.

Page19 line 369: “a quick”.

Page19 line 373: “metals”.

Page19 line 373: “metals”.

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

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

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

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.

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?

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.

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.

Page28 line 560: “gas-phase”.

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.

Page29 line 588: “liquid-phase”.

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