## RE: A point-to-point response to reviewers' comments

"A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing" (acp-2018-1132) by Yiqun Lu, Chao Yan, Yueyun Fu, Yan Chen, Yiliang Liu, Gan Yang, Yuwei Wang, Federico Bianchi, Biwu Chu, Ying Zhou, Rujing Yin, Rima Baalbaki, Olga Garmash, Chenjuan Deng, Weigang Wang, Yongchun Liu, Tuukka Petäjä, Veli-Matti Kerminen, Jingkun Jiang, Markku Kulmala, Lin Wang

We are grateful to the helpful comments from this anonymous referee, and have carefully revised our manuscript accordingly. A point-to-point response to the comments, which are repeated in italic, is given below.

In addition to the reviewers' comments, we have noticed and corrected a key typo from our previous version of manuscript. "The [$NO_2$] concentration" in our manuscript is in fact "the [$NO_x$] concentration". Correction of this term does not lead to changes in our conclusions.

### Reviewer #1's comments:

*This study examines the relationship of [SO2] to [H2SO4] as a function of light intensity, particle concentration, and other gas phase reactants in Beijing. As the authors point out, this relationship is likely different in Beijing than in European and US cities. Overall, this study is straight forward and generally useful for research conducted in megacities. However, several issues should be address before this study can be considered for publication in ACP.*

Reply: We are very grateful to the positive viewing of our manuscript by Reviewer #1, and have now revised our manuscript accordingly.

## Major comments:

1. *P5 147: Sulfuric acid concentration was measured using nitrate LToF-CIMS. It would be useful for the reader to know more details on how the sulfuric acid concentration was determined from the signals of the instrument. Does this measurement include sulfuric acid in molecular clusters (i.e. is fragmentation contributing to the sulfuric acid signal?) What are the estimated uncertainties of the sulfuric acid measurement? How do these uncertainties compare to the model predicted amounts?*

Reply: We measured signals of charged sulfuric acid as $HSO_4^-$ , $HSO_4^- \cdot HNO_3$, and $HSO_4^- \cdot (HNO_3)_2$, and charged clusters of $HSO_4^- \cdot H_2SO_4$. The clusters of $HSO_4^- \cdot H_2SO_4$ come from ion-induced clustering of neutral sulfuric acid and bisulfate ions within the LTOF-CIMS ion reaction zone, and also from the evaporation of dimethylamine (DMA) and the replacement of one molecule of $H_2SO_4$ with one bisulfate ion, $HSO_4^-$, during the $NO_3^-$ reagent ion charging of a stabilized neutral sulfuric acid dimer in the real atmosphere in presence of DMA or a molecule that works in the same way as DMA. Although the total signals of $HSO_4^-$, $HSO_4^- \cdot HNO_3$, and $HSO_4^- \cdot (HNO_3)_2$ were normally orders higher than that of $HSO_4^- \cdot H_2SO_4$, the sum of $HSO_4^-$, $HSO_4^- \cdot HNO_3$, $HSO_4^- \cdot (HNO_3)_2$ and $HSO_4^- \cdot H_2SO_4$ has been used to derive the gaseous sulfuric acid concentration.

The uncertainty in measured concentrations of sulfuric acid is estimated to vary between 21% and 51%, which is comparable with that in Kürten *et al.* (2012).

The uncertainties of proxies came from both those of CIMS and those of proxy methods. We have elaborated how the sulfuric acid concentration was determined in our revised manuscript, which reads (L164-L183), "For example, the atmospheric $H_2SO_4$ molecules would be charged by nitrate reagent ion $NO_3^-(HNO_3)_{0\text{-}2}$ and mainly produce $HSO_4^-$ ions (m/z = 96.9601 Th), $HSO_4^- \cdot HNO_3$ ions (m/z = 159.9557 Th), and $HSO_4^- \cdot (HNO_3)_2$ ions (m/z = 222.9514 Th). In addition, $HSO_4^- \cdot H_2SO_4$ ions (m/z = 194.9275 Th) were formed from ion-induced clustering of neutral sulfuric acid and bisulfate ions within the LToF-CIMS ion reaction zone, and also from the evaporation of dimethylamine (DMA) and the replacement of one molecule of $H_2SO_4$ with one bisulfate ion, $HSO_4^-$, during the $NO_3^-$ reagent ion charging of a stabilized neutral sulfuric acid dimer in the real atmosphere in presence of DMA or a molecule that works in the same way as DMA. During the campaign, the sample flow rate was kept at 8.8 slpm, since mass flow controllers fixed the sheath flow rate and the excess flow rate, and the flow into the mass spectrometer (around 0.8 slpm) was fixed by the size of a pinhole between the ionization source and the mass spectrometer. The concentration of gaseous sulfuric acid was then determined by Eq. (2).

$$[H_2SO_4] = \frac{HSO_4^- \cdot (HNO_3)_{0-2} + HSO_4^- \cdot H_2SO_4}{NO_3^-(HNO_3)_{0-2}} \cdot C \qquad (2)$$

where C is the calibration coefficient, and $NO_3^-(HNO_3)_{0\text{-}2}$, $HSO_4^- \cdot (HNO_3)_{0\text{-}2}$ and $HSO_4^- \cdot H_2SO_4$ represent the signals of corresponding ions and are in unites of counts per second (cps). The unit of resulting $[H_2SO_4]$ is molecule $cm^{-3}$ …".

2. *P6 162: Along these same lines, the authors comment that the calibration coefficient takes into account diffusion losses in the sampling line. Was this loss measured? It is a bit surprising that the calibration coefficient that Kurten et al. (2012) determined was 1.1 x10^10 cm-3 is the same in this study. I would have thought differences in instrument and sampling line losses (1.6 m is quite long) would have impacted this number. The authors should more clearly lay out how the sulfuric acid concentration was determined since it is an integral measurement for this paper.*

Reply: The loss rate was calculated assuming a diffusion loss of sulfuric acid in a circular tube under a laminar flow condition (Gormley and Kennedy, 1949). The identical values for the effective calibration coefficient are just by coincidence. Our calibration coefficient is $3.79 \times 10^9$ molecule $cm^{-3}$ in absence of the diffusion loss correction. We have elaborated our discussion on the calibration coefficient, which reads (L186-L190), "We obtain a calibration coefficient of $3.79 \times 10^9$ molecule $cm^{-3}$ for our instrument and use $1.1 \times 10^{10}$ molecule $cm^{-3}$ as the effective calibration coefficient, after taking into account the diffusion losses in the stainless-steel tube and the nitrate chemical ionization source".

3. *P6 L 176: The Fuchs-Sutugin transition kernel is used. There is associated error with using this kernel in the transition regime where sulfuric acid condenses on preexisting particles. Can the authors comment on this error? How sensitive is the fitting parameters to changes in the collision kernel? It may be helpful for the authors to use the empirically-derived collision kernel for the full regime from (Gopalakrishnan and Hogan Jr., 2011) to help limit the uncertainties from this parameter.*

Reply: We have calculated $H(Kn_D)$ from the nondimensionalized form of Fuchs-Sutugin and the First passage regression (Gopalakrishnan and Hogan Jr., 2011) in our $Kn_D$ range. The difference between the calculated $H(Kn_D)$ from two methods is within 8 %. Hence, we don't think calculation of the collision kernels in this study will lead to a significant uncertainty. Nevertheless, we have added this citation to give a more comprehensive discussion on the transition-regime correction factor, which reads (L211-L213), "$\beta_m$ represents a transition-regime correction factor dependent on the Knudsen number (Fuchs and Sutugin, 1971; Gopalakrishnan and Hogan Jr., 2011)".

4. *P5 134: The authors state that two months of measurements were conducted. It is not clear from the paper if all two months of measurements were used to determine the proxy relationship. Have the authors examined how the proxy relationship changes from day to day? Or week to week? The authors correctly state that the proxy relationship likely depends on location but does it also depend on time? It is possible that other processes that affect sulfuric acid concentrations (like Criegee intermediates) are not captured in the proxy relationship may play a larger role during some times of day than others.*

Reply: The intensive campaign was carried out from 9 February to 14 March, 2018 (L172), which lasts a bit more than a month. The performance of proxies could be different more or less on different days as the proxies are derived from a statistical analysis of the entire data set in this study. We have expanded the discussion about the applicability of the proxies, which reads (L491-L496) "Furthermore, the proxies might be site-specific and season-specific. Since we derived the proxies in winter in urban Beijing, the exponents of factors in the proxy for other cities or other seasons could have different values. Thus, the proxies in this study should be further tested before their application to other Chinese megacities or other seasons".

Criegee intermediates are not intended to be included in the proxy because Criegee intermediates seem not to play an important role in the daytime formation of sulfuric acid (L135-L139) (Boy et al., 2013; Mauldin et al., 2012).

5. *P13 line 389: If two months of measurements were taken, why was only one day used to compare measured to predicted sulfuric acid concentrations? How does the comparison for the other days look? It's not necessary to add graphs of these comparison, but a few lines stating the comparison for other days is necessary for the reader to determine how useful this proxy relationship is.*

Reply: The measurements lasted a bit more than a month as mentioned above. Figure 3 (now updated to a new version) presents a statistical comparison between measured and predicted sulfuric acid concentrations in all the measurement days. Relevant discussions can be found in section 4.4.

6. *P13 line 396: Authors state that the proxy relationship developed for the boreal forest and applied to Beijing is a factor of 20 too low due to differences in CS. Why didn't the authors use the Beijing CS values when applying Petäjä et al.'s proxy relationship? Would the differences between measured and predicted from Petäjä then be smaller?*

Reply: We actually used atmospheric variables including CS values from our measurements when applying Petäjä *et al.*'s proxy relationship. The reason for the poor performance of Petäjä *et al.*'s proxy relationship on Beijing data could be the much higher CS values in Beijing with a much more complex atmosphere.

7. *Figure 4: It would be useful for the reader to see timelines of all the measured concentrations that go into the proxy relationships as well.*

Reply: Here we present results from a comprehensive campaign with participation from multiple universities and institutions. As a result, this manuscript will only focus on the development of the statistical analysis of the sulfuric acid proxy, and other manuscripts in preparation will discuss the variations of atmospheric variables.

## Minor comments:

1. *P1 Line 28: desirable for the atmospheric. . .*

Reply: We have revised our manuscript accordingly, which reads (L28) "…highly desirable for the atmospheric chemistry community".

2. *P1 36-27 change one of the "using"*

Reply: We have revised our manuscript accordingly, which reads (L37-L39) "A proxy for atmospheric daytime gaseous sulfuric acid concentration was derived through a statistical analysis method by using the UVB intensity, [$SO_2$], condensation sink (CS), [$O_3$], and [HONO] (or [$NO_x$]) as the predictor variables".

3. *P3 Line 57: sulfuric acid DMA system. The citation for Petäjä et al. (2011) might not be the best. Several studies have pointed out potential experimental issues with this study (Jen et al., 2014; Kürten et al., 2014).*

Reply: We have updated the citations, which reads (L59-L61) "…$H_2SO_4$-DMA-$H_2O$ ternary nucleation (Almeida et al., 2013; Jen et al., 2014; Kürten et al., 2014; Petäjä et al., 2011; Yao et al., 2018)".

4. *P3 line 57: demand participation is a strange phrase. Maybe necessitates participations?*

Reply: We have revised our manuscript, which reads (L61) "…involve the participation of gaseous sulfuric acid molecules".

5. *P3 line 59: Would be worth reading and citing (Kuang et al., 2012) for sulfuric acid growth rates.*

Reply: We have added this citation, which reads (L61-L63) "In addition, the condensation of gaseous sulfuric acid onto newly-formed particles contributes to their initial growth (Kuang et al., 2012; Kulmala et al., 2013)".

6. *P3 line 62: Knowing sulfuric acid concentrations prior to a nucleation event is also important.*

Reply: We have revised our manuscript, which reads (L63-L67)"Quantitative assessments of the contribution of gaseous sulfuric acid to both the new particle formation rates and the particle growth rates require real-time measurements of gaseous sulfuric acid concentrations prior to and during the NPF events (Nieminen et al., 2010; Paasonen et al., 2010) ".

7. *P3 Line 68: NO3- and ligands.*

Reply: We have revised our manuscript, which reads (L72) "…with $NO_3^-$ and its ligands as reagent ions".

8. *P3 line 68: CIMS is actually a pretty broad class of instruments. The low detection limit for sulfuric acid is because the instrument ionizes and samples at atmospheric pressure, which is different than the traditional CIMS.*

Reply: We have revised the sentence accordingly, which reads (L72-L73) "because nitrate CIMS with an atmospheric pressure interface (API) has a low detection limit …".

9. *P3 line 80: (Chen et al., 2012) shows a nice figure of sulfuric acid concentrations measured at numerous locations around the world. Not critical to add the citation but worth taking a look at.*

Reply: We appreciate that this reviewer points out a very important paper presenting the measurements of sulfuric acid in different locations. We would like to add the citation, which reads (L84-L88) "Thereafter, measurements of sulfuric acid using CIMS have been performed around the world (e.g., Berresheim et al., 2000; Bianchi et al., 2016; Chen et al., 2012; Jokinen et al., 2012; Kuang et al., 2008; Kürten et al., 2014; Kurtén et al., 2011; Petäjä et al., 2009; Weber et al., 1997; Zheng et al., 2011) …".

10. *P3 line 83: has been proven*

Reply: We have revised our manuscript accordingly, which reads (L88) "CIMS has been proven to be a robust tool ...".

11. *P4 line 105: After reading this, the reader will naturally wonder why is there a positive correlation between CS and sulfuric acid concentration?*

Reply: We have revised our manuscript accordingly, which reads (L108-L111) "In several proxies developed by Mikkonen et al. (2011), the correlation between the gaseous sulfuric acid concentration and CS is positive, which is against what one would expect because a larger CS normally leads to a faster loss for gaseous sulfuric acid". In addition, we put the detailed discussion of this issue in section 4.2 and 4.3.

12. *P4 line 108: locations that characterize with an. . . one or two of those words are not correct.*

Reply: We have revised our manuscript, which reads (L114-L115) "…in locations with atmospheric environments different from those in the six sites of that study".

13. *P4 line 110: Please state the range of CS in addition to how much higher it is compared to other locations.*

Reply: We have stated the range of CS, which reads (L116-L117) "Beijing is a location with typical values of CS (*e.g.*, 0.01-0.24 $s^{-1}$ in the 5-95% percentiles in this study) being 10-100 times higher …".

14. *P4 line 113: For north America: how do these numbers compare to Mexico City?*

Reply: The level of $SO_2$ in Beijing has decreased significantly in recent years as we have presented in L488-L489. Nevertheless, the $SO_2$ concentration in Mexico City in 2003 is comparable with our measured $SO_2$ in Beijing. We have added one citation regarding the $SO_2$ measurements and two citations regarding the sulfuric acid concentration in Mexico City, which reads (L118-L123) "…typical $SO_2$ concentrations being 1-10 times higher (Wang et al., 2011a; Wu et al., 2017) than those in Europe and North America (Dunn et al., 2004; Mikkonen et al., 2011), yet measured gaseous sulfuric acid concentrations are relatively similar in these environments (Chen et al., 2012; Smith et al., 2008; Wang et al., 2011b; Zheng et al., 2011)."

15. *P5 119: OH radicals*

Reply: We have revised our manuscript, which reads (L126) "… a potentially important source of OH radicals in the atmosphere".

16. *P5 119: remove the not only and but also. It is harder to read with them there.*

Reply: We have removed the two expressions.

17. *P5 line 128: Criegee should be capitalized*

Reply: We have capitalized “C”.

18. *P6 line 153: was guided through. . . strange phrasing*

Reply: We have revised our manuscript, which reads (L160) “…was introduced into a PhotoIonizer …”.

19. *P6 line 154: Is this a custom-built inlet? If so, could the authors provide a diagram and*

*write in the dimensions?*

Reply: The inlet is a commercial product from Aerodyne Research, Inc.

20. *P6 line 160: CIMS was calibrated. How? It would be useful to describe this procedure in brief.*

Reply: We have added a brief introduction of the calibration process, which reads (L183-L186) “The CIMS was calibrated during the campaign with a home-made calibration box that can produce adjustable concentrations of gaseous sulfuric acid from $SO_2$ and OH radicals following the protocols in previous literatures (Kürten et al., 2012; Zheng et al., 2015).”

21. *P6 line 164: should it be ToFTools?*

Reply: The code maker just named it as tofTools.

22. *P6 line 166: 1 nm. Is this mobility diameter?*

Reply: Yes, it is mobility diameter.

23. *P7 line 213: Authors should better justify pseudo-steady state assumption*

Reply: The Mikkonen et al. (2011) study has indicated that the pseudo-steady state assumption holds well for typical atmospheric conditions. Furthermore, the errors for nonlinear proxies derived from the pseudo-steady state assumption in Mikkonen et al. study are in a range of 40-42 %, whereas ours are in a range of 17.6-19.2 % when evaluating the performances of the proxies with the “error” metric in Mikkonen et al. study. Therefore, we think that the pseudo-steady state assumption can be applied to our proxies.

24. *P8 paragraph starting on line 228: This was a difficult paragraph to understand. Can the authors better phrase it to explain the differences in parameters?*

Reply: We have revised the paragraph, which reads (L272-L283) “In practice, the exponents for variables in nonlinear fitting procedures are rarely equal to 1 (Mikkonen et al., 2011), so we replaced the factors $x_i$ with $x_i^{w_i}$ in the proxy, where $x_i$ can be an atmospheric variable and $w_i$ defines $x_i$’ exponent in the proxy. Since $k$ is a temperature-dependent reaction constant and varies within a

10 % range in the atmosphere temperature range of 267.6 - 292.6 K, *i.e.*, the actual atmospheric temperature variation in this study, we approximately regard $k$ as a constant and use a new scaling factor $k_0$. This methodology has been used previously in the proxies of gaseous sulfuric acid in Hyytiälä, Southern Finland (Petäjä et al., 2009). As a result, the general proxy equation can be written as Eq. (7), with the UVB intensity, [$SO_2$], condensation sink (CS), [$O_3$], and [HONO] (or [$NO_x$]) as predictor variables:".

25. *P8 line 242: a matlab software. A custom-made one? Or just a function in matlab?*

Reply: The nonlinear curve-fitting procedures are performed by a custom-made MATLAB software. We have revised our manuscript, which reads (L287-L289) "The nonlinear curve-fitting procedures using iterative least square estimation for the proxies of gaseous sulfuric acid concentration based on Eq. (7) were performed by a custom-made MATLAB software."

26. *P9: 1-2 orders of magnitude. Maybe change to 10-100 times higher to be more clear.*

Reply: We have revised our manuscript, which reads (L303-L304) "which is about 10-100 times higher …".

27. *P9 line 261: 60% RH does not seem dry.*

Reply: The mean RH in this campaign is 28%. We have revised our manuscript, which reads (L312-L313) "In addition, Beijing is dry in winter with a mean ambient relative humidity of 28% during the campaign".

28. *P9 272: I do not understand how the correlation coefficient numbers are consistent with accepted formation pathways? Does the formation pathways have powers that are less than 1?*

Reply: We have rephrased the sentence, which reads (L324-L326) "…which indicate that [$SO_2$] and UVB have important influences on the formation of atmospheric gaseous sulfuric acid".

29. *P9 line 276: Authors should explain potential reasons why sulfuric acid positively correlates with CS.*

Reply: We discussed in P18 Line 108 that "In several proxies developed by Mikkonen et al. (2011), the correlation between the gaseous sulfuric acid concentration and CS is positive, which is against what one would expect because a larger CS normally leads to a faster loss for gaseous sulfuric acid". In this campaign, CS correlates well with [$SO_2$] ($r$ = 0.83), which suggests that a high CS value could serve as an indicator of atmospheric particulate pollution, and be accompanied with a high concentration of $SO_2$ that is propitious for the formation of gaseous sulfuric acid. Please also refer to our discussion of this issue in section 4.3.

30. *P10 300: molecules cm-3 is normally written as just cm-3.*

Reply: the unit of molecule $cm^{-3}$ has been extensively used in the literature and we decide to keep this unit.

31. *P10 line 316: Authors mention that proxy relationship is location specific. Why then did the authors use the justification for not including RH based upon conclusions drawn from a different location?*

Reply: We made a test by introducing RH into the proxy N1 (containing CS terms) and resulted in a RH-corrected CS term ($CS \cdot RH$) instead of CS as what Mikkonen *et al*. have done (2011). The performance of proxy has not significantly improved (REs changed from 20.04 % to 19.83 %, see our reply to comments #6 and #14 from Reviewer #2 for REs) and the exponent of CS was still close-to-zero (from 0.03 to -0.02). We have rephrased our discussion on RH, which reads (L371-L374) "…because a test by introducing RH into the proxies do not result in a significantly better performance, which is consistent with those conclusions in the Mikkonen et al. study (2011)."

32. *P11 line 324: "unlike assumed in Eq. (3)" wording seems incorrect*

Reply: We have revised the sentence, which reads (L379-L380) "…unlike the assumption in Eq. (6) …".

33. *P11 line 324: The naming convention between the equations in table 3 and the equations in the paper is confusing. Which equation 3 does this line refer to?*

Reply: We have used the term "function" in Table 3 to avoid confusion.

34. *Page 12 line 356: "Only occasionally slightly higher" too many adverbs. Rephrase*

Reply: We have revised the sentence, which reads (L412-L413) "Occasionally, higher [HONO]/[$NO_x$] ratios could be seen in the morning".

35. *Page 12 line 356: The authors refer to a previous study to justify linearity of NO2 and HONO. Where was the location of this study? This paragraph is general is difficult to discern results from previous studies and results from this study. Please make this more clear.*

Reply: We have revised this paragraph to focus on the measurements in Beijing, which reads (L406-L420) "Although so far the proxy N5 had the best fitting quality, it is impractical to explicitly include [HONO] because HONO measurements are very challenging. As shown in Fig. 2, [HONO] and [$NO_x$] tend to correlate linearly with each other in the daytime during this campaign, with a linearly fitted [HONO]/[$NO_x$] ratio of around 0.03 and a relative error of 0.42. Occasionally, higher [HONO]/[$NO_x$] ratios could be seen in the morning, which might be due to the fact that HONO concentration could have an accumulation process during the nighttime and lead to a deviation from the steady state. Therefore, due to the good correlation, the proxy N7 replaces [HONO] by [$NO_x$], a more easily measured variable, and performs equally well with the proxy N5."

36. *Page 12 line 376: authors should specific that this cover sulfuric acid concentrations for this location. 10^6 cm-3 does not cover sulfuric acid concentrations around the world.*

Reply: We have revised the sentence, which reads (L425-L427) "…in the sulfuric acid concentration range of $(2.2-10)\times10^6$ cm$^{-3}$, which covers the 5-95% percentiles of sulfuric acid concentrations in this study."

37. *Page 13 line 416: It is a bit confusing that the authors mention that proxy N5 is the most accurate when they spend most of the paper justifying the use of N7. Maybe change the wording "for the best proxy accuracy" or consider rewording this section to make it a bit less confusing/*

Reply: We have revised the sentence, which reads (L463) "For a comprehensive consideration of the formation pathways of OH radicals…".

38. *Page 14 line 439: I do not understand how this work has shown the importance of heterogenous chemistry as a potential source of OH. Was this mentioned somewhere else in the main paper? The authors should better justify this point if they want to include in the summary.*

Reply: We have removed this statement.

39. *Figure 1-2: What day were these measurements done?*

Reply: Figure 1-2 show all the measured data points during the campaign from 9 February to 14 March, 2018. We have included the duration of measurements in the revised figure caption.

40. *Figure 2: Can the authors explain why there seems to be clear break up group of points during the early morning that do not follow the linear trend?*

Reply: We have expanded the discussion, which reads (L412-L415) "Occasionally, higher [HONO]/[NO$_x$] ratios could be seen in the morning, which might be due to the fact that HONO concentration could have an accumulation process during the nighttime and lead to a deviation from the steady state."

41. *Figure 4: As mentioned above, it would be useful to show the time lines for the other measured concentrations (CS, OH, NO2, etc.) that the proxy model uses.*

Reply: Here we present results from a comprehensive campaign with participation from multiple universities and institutions. As a result, this manuscript will only focus on the development of the statistical analysis of the sulfuric acid proxy, and other manuscripts in preparation will discuss the variations of atmospheric variables.

Reference

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H. and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502(7471), 359–363, doi:10.1038/nature12663, 2013.

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# A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing

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**Abstract**. Gaseous sulfuric acid is known as one of the key precursors for atmospheric new particle formation processes, but its measurement remains a difficulty.~~but its measurement remains a major challenge.~~ A proxy method that is able to derive gaseous sulfuric acid concentrations from parameters that can be measured relatively easily and accurately is therefore highly desirable for the atmospheric chemistry community~~highly desirable among the atmospheric chemistry community~~. Although such methods are available for clean atmospheric environments, a proxy that works well in a polluted atmosphere, such as those in Chinese megacities, is yet to be developed. In this study, the gaseous sulfuric acid concentration was measured in February-March, 2018, in urban Beijing by a nitrate based - Long Time-of-Flight Chemical Ionization Mass Spectrometer (LToF-CIMS). A number of atmospheric parameters were recorded concurrently including the ultraviolet radiation B (UVB) intensity, concentrations of $O_3$, $NO_x$ (sum of NO and $NO_2$), $SO_2$ and HONO, and aerosol particle number size

distributions. A proxy for atmospheric daytime gaseous sulfuric acid concentration was derived ~~using~~ through a statistical analysis method by using the UVB intensity, [$SO_2$], condensation sink (CS), [$O_3$], and [HONO] (or [$NO_x$]) as the predictor variables. In this proxy method, we considered the formation of gaseous sulfuric acid from reactions of $SO_2$ and OH radicals during the daytime, and loss of gaseous sulfuric acid due to its condensation onto the pre-existing particles. In addition, we explored formation of OH radicals from the conventional gas-phase photochemistry using ozone as a proxy and from the photolysis of ~~heterogeneously formed~~ HONO using HONO (and subsequently $NO_x$) as a proxy. Our results showed that the UVB intensity and [$SO_2$] are dominant factors for the production of gaseous sulfuric acid, and that the simplest proxy could be constructed with the UVB intensity and [$SO_2$] alone. When the OH radical production from both homogenously- and heterogeneously-formed precursors were considered, the relative errors were reduced up to 20 %.~~, resulting in up to 29% relative deviations when sulfuric acid concentrations were larger than 2.0 × $10^6$ molecules $cm^{-3}$. When the OH radical production from both homogenously- and heterogeneously-formed precursors were considered, the relative deviations were lower than 24%.~~

## 1 Introduction

Gaseous sulfuric acid ($H_2SO_4$) is a key precursor for atmospheric new particle formation (NPF) processes (Kerminen, 2018; Kirkby et al., 2011; Kuang et al., 2008; Kulmala and Kerminen, 2008; Sipilä et al., 2010). A number of atmospheric nucleation mechanisms including $H_2SO_4$-$H_2O$ binary nucleation (Benson et al., 2008; Duplissy et al., 2016; Kirkby et al., 2011), $H_2SO_4$-$NH_3$-$H_2O$ ternary nucleation (Kirkby et al., 2011; Korhonen et al., 1999; Kürten et al., 2015), and $H_2SO_4$-DMA-$H_2O$ ternary nucleation (Almeida et al., 2013; Jen et al., 2014; Kürten et al., 2014; Petäjä et al., 2011; Yao et al., 2018) involve~~demand~~ the participation of gaseous sulfuric acid molecules. In addition, the condensation of gaseous sulfuric acid onto newly-formed particles contributes to their initial growth (Kuang et al., 2012; Kulmala et al., 2013). Quantitative assessments of the contribution of gaseous sulfuric acid to both the new particle formation rates and the particle growth rates require real-time measurements of gaseous sulfuric acid concentrations prior to and during the NPF events (Nieminen et al., 2010; Paasonen et al., 2010).

Measurements of gaseous sulfuric acid in the lower troposphere are challenging because its ambient concentration is typically quite low ($10^6$-$10^7$ molecule $cm^{-3}$) (Kerminen et al., 2010; Mikkonen et al., 2011). Reported real-time measurements of gaseous sulfuric acid are currently based on Chemical Ionization Mass Spectrometry with $NO_3^-$ and its ligands as reagent ions (nitrate CIMS) because nitrate CIMS with an atmospheric pressure interface (API)~~CIMS~~ has a low detection limit for the atmospheric concentration range of gaseous sulfuric acid (Jokinen et al., 2012), and a constant fraction of sulfuric acid present in the air sample will be ionized by excessive nitrate ions in CIMS under constant instrumental conditions (Kürten et al., 2012; Zheng et al., 2010), which makes the quantification of gaseous sulfuric acid feasible.

Arnold and Fabian (1980) measured the negative ions in the stratosphere ~~using a passive CIMS~~ and derived the concentration of stratospheric gaseous sulfuric acid from the fractional abundances of a series of stratospheric negative ions as well as the ~~associated equilibrium or~~ rate constants. Later, real-time measurement of sulfuric acid in the lower troposphere was performed using nitrate CIMS (Eisele and Tanner, 1993), with laboratory calibrations by production of known concentrations of OH radicals that ~~will be~~are titrated into gaseous sulfuric acid. Thereafter, measurements of sulfuric acid using CIMS have been performed around the world (e.g., Berresheim et al., 2000; Bianchi et al., 2016; Chen et al., 2012; Jokinen et al., 2012; Kuang et al., 2008; Kürten et al., 2014; Kurtén et al., 2011; Petäjä et al., 2009; Weber et al., 1997; Zheng et al., 2011), and CIMS has been proven~~d~~ to be a robust tool for gaseous sulfuric acid detection. However, sulfuric acid measurements are still rather sparse because of the high cost of the CIMS instrument and the extensive demand of specialized expertise on the instrument calibration, maintenance, and data processing, etc. Therefore, a proxy for gaseous sulfuric acid concentration is highly desirable.

Proxies for the estimation of atmospheric gaseous sulfuric acid concentrations were previously developed to approximate measurement results of sulfuric acid in Hyytiälä, Southern Finland (Petäjä et al., 2009), assum~~suppos~~ing that gaseous sulfuric acid is formed from reactions between $SO_2$ and OH radicals, and lost due to its condensation onto pre-existing particles. The derived simplest proxy can be written as Eq. (1) below, and the authors recognized that the proxies might be site-specific and should be verified prior to utilization in other environments.

$$[\boldsymbol{H_2SO_4}] = \boldsymbol{k} \cdot \frac{[\boldsymbol{SO_2}] \cdot (\boldsymbol{UVB\ \ or\ \ Global\ \ radiation})}{\boldsymbol{CS}} \qquad (\mathbf{1})$$

Mikkonen et al. (2011) later developed a couple of statistical proxies based on measurements of sulfuric acid in six European and North American sites, including urban, rural and forest areas. Their results showed that the radiation intensity and $[SO_2]$ are the most important factors to determine the concentration of sulfuric acid, and that the impact of condensation sink (CS)~~, a proxy for condensational sink~~ for gaseous sulfuric acid, is generally negligible. In several proxies developed by Mikkonen et al. (2011), the correlation between the gaseous sulfuric acid concentration and CS is positive, which is against what one would expect because a larger CS normally leads to a faster loss for gaseous sulfuric acid. In addition, the performance of a proxy equation is site-specific because of varying atmospheric conditions from one site to another, which implies that the proxy suggested by Mikkonen et al. (2011) might not work well in locations ~~that characterized~~ with~~ an~~ atmospheric environments different from those in the six sites of that study.

Beijing is a location with typical values of CS (e.g., 0.01-0.24 $s^{-1}$ in the 5-95% percentiles in this study) being 10-100 times higher (Herrmann et al., 2014; Wu et al., 2007; Xiao et al., 2015; Yue et al., 2009; Zhang et al., 2011) and typical $SO_2$ concentrations being 1-10 times higher (Wang et al., 2011a; Wu et al., 2017) than those in Europe and North America (Dunn et al., 2004; Mikkonen et al., 2011), yet measured gaseous sulfuric acid concentrations are relatively similar ~~between~~ in these environments (Chen et al., 2012; Smith et al., 2008; Wang et al., 2011b; Zheng et al., 2011). Whether previous proxies developed for European and North American sites work in Beijing remains to be tested. Furthermore, in addition to the gas phase reaction between O($^1$D) and water molecules (Crutzen and Zimmermann, 1991; Logan et al., 1981), photolysis of HONO could be a potentially important source of OH radicals in the atmosphere ~~not only~~ in the early morning (Alicke et al., 2002, 2003; Elshorbany et al., 2009; Li et al., 2012) and ~~but also~~ during the daytime (Acker et al., 2005; Aumont et al., 2003; Kleffmann, 2007). An experimental study measuring HONO near the surface layer estimated that HONO was a main contributor to OH production in Beijing, with HONO's contribution being larger than 70 % at around 12:00-13:00, except for summer when the contribution of $O_3$ dominated (Hendrick et al., 2014). Given the distinct characteristics of these two OH radical formation pathways, they both should be included and evaluated separately when a proxy for atmospheric gaseous sulfuric acid concentration is being built. The reactions between $SO_2$ and C~~c~~riegee intermediates formed from the ozonolysis of atmospheric alkenes could be a potential source of sulfuric acid only in the absence of solar radiation (Boy et al., 2013; Mauldin et al., 2012), so these reactions are expected to provide a minor contribution to the formation of gaseous sulfuric acid during the daytime in urban Beijing.

In this study, gaseous sulfuric acid concentration was measured by a Long Time-of-Flight Chemical Ionization Mass Spectrometer (LToF-CIMS) in February - March, 2018, in urban Beijing. A number of atmospheric parameters were recorded concurrently, including the ultraviolet radiation B (UVB) intensity, concentrations of $O_3$, $NO_x$, $SO_2$ and HONO, and particle number size distributions. The objective of this study is to develop a robust daytime gaseous sulfuric acid concentration proxy for Beijing, a representative Chinese megacity with urban atmospheric environments.

## 2 Ambient measurements

An intensive campaign was carried out from 9 February to 14 March, 2018 on the fifth floor of a teaching building in the west campus of Beijing University of Chemical Technology ($39^{\circ}94^{\prime}\ N, 116^{\circ}30^{\prime}\ E$). This monitoring site is 2 km to the west of the West 3rd Ring Road and surrounded by commercial properties and residential dwellings. Hence, this station can be regarded as a representative urban site.

The sulfuric acid concentration was measured by a LToF-CIMS (Aerodyne Research, Inc.) equipped with a nitrate chemical ionization source. Ambient air was drawn into the ionization source through a stainless-steel tube with a length of 1.6 m and a diameter of 3/4 inch. A mixture of a 3 standard cubic centimeter per minute (sccm) ultrahigh purity nitrogen flow containing nitric acid and a 20 standard liter per minute (slpm) pure air flow supplied by a zero-air generator (Aadco 737, USA), together as a sheath flow, was introduced into~~guided through~~ a PhotoIonizer (Model L9491, Hamamatsu, Japan) to produce nitrate reagent ions. This sheath flow was then introduced into a co-axial laminar flow reactor concentric to the sample flow. Nitrate ions were pushed to the middle of the sample flow under an electric field and subsequently charged sample molecules. For example, the atmospheric $H_2SO_4$ molecules would be charged by nitrate reagent ion $NO_3^-(HNO_3)_{0-2}$ and mainly produce $HSO_4^-$ ions (m/z = 96.9601 Th), $HSO_4^- \cdot HNO_3$ ions (m/z = 159.9557 Th), and $HSO_4^- \cdot (HNO_3)_2$ ions (m/z = 222.9514 Th). In addition, $HSO_4^- \cdot H_2SO_4$ ions (m/z = 194.9275 Th) were formed from ion-induced clustering of neutral sulfuric acid and bisulfate ions within the LToF-CIMS ion reaction zone, and also from the evaporation of dimethylamine (DMA) and the replacement of one molecule of $H_2SO_4$ with one bisulfate ion, $HSO_4^-$, during the $NO_3^-$ reagent ion charging of a stabilized neutral sulfuric acid dimer in the real atmosphere in presence of DMA or a molecule that works in the same way as DMA. During the campaign, the sample flow rate was kept at 8.8 slpm, since mass flow controllers fixed the sheath flow rate and the excess flow rate, and the flow into the mass spectrometer (around 0.8 slpm) was fixed by the size of a pinhole between the ionization source and the mass spectrometer. The concentration of gaseous sulfuric acid was then determined by Eq. (2).

$$[H_2SO_4] = \frac{HSO_4^- \cdot (HNO_3)_{0-2} + HSO_4^- \cdot H_2SO_4}{NO_3^-(HNO_3)_{0-2}} \cdot C \qquad (2)$$

where C is the calibration coefficient, and $NO_3^-(HNO_3)_{0-2}$, $HSO_4^- \cdot (HNO_3)_{0-2}$ and $HSO_4^- \cdot H_2SO_4$ represent the signals of corresponding ions and are in units of counts per second (cps). The unit of resulting $[H_2SO_4]$ is molecule cm$^{-3}$. The CIMS was calibrated during the campaign with a home-made calibration box that can produce adjustable concentrations of gaseous sulfuric acid from $SO_2$ and OH radicals following the protocols in previous literatures (Kürten et al., 2012; Zheng et al., 2015). We obtain a calibration coefficient of $3.79 \times 10^9$ molecule cm$^{-3}$ for our instrument and use $1.1 \times$

$10^{10}$ molecule cm$^{-3}$ as the effective calibration coefficient, after taking into account the diffusion losses in the stainless-steel tube and the nitrate chemical ionization source.~~During the campaign, the sample flow rate was kept at 8.4 slpm, since mass flow controllers fixed the sheath flow rate and the excess flow rate and the flow into the mass spectrometer (around 0.4 slpm) was fixed by the size of a pinhole between the ionization source and the mass spectrometer. The CIMS was calibrated twice during the campaign following the protocols in previous literatures (Kürten et al., 2012; Zheng et al., 2015). Here we use 1.1 × $10^{10}$ molecule cm$^{-3}$ as the calibration coefficient, after taking into account diffusion losses in the stainless-steel tube and the nitrate chemical ionization source.~~ The obtained mass spectra were analyzed with a tofTools package based on the MATLAB software (Junninen et al., 2010).

Ambient particle number size distributions down to about 1 nm were measured using a combination of a scanning mobility particle sizer spectrometer (SMPS) equipped with a diethylene glycol-based condensation particle counter (DEG-CPC, ~1-10 nm) and a conventional particle size distribution system (PSD, ~3 nm - 10 µm~~3-700 nm~~) consisting of a pair of aerosol mobility spectrometers developed by Tsinghua University (Cai et al., 2017; Jiang et al., 2011; Liu et al., 2016). The values of CS were calculated following Eq. (3) (Dal Maso et al., 2002):

$$CS = 2\pi D \int_0^\infty D_p \beta_m(D_p) n(D_p) dD_p = 2\pi D \sum_i \beta_i D_{pi} N_i \qquad (3)$$

where $D_{pi}$ is the geometric mean diameter of particles in the size bin $i$ and $N_i$ is the particle number concentration in the corresponding size bin. $D$ is the diffusion coefficient of gaseous sulfuric acid, and $\beta_m$ represents a transition-regime correction factor dependent on~~that could be defined as a function of~~ the Knudsen number (Fuchs and Sutugin, 1971; Gopalakrishnan and Hogan Jr., 2011).

$SO_2$, $O_3$ and $NO_x$ concentrations were measured using a $SO_2$ analyzer (Model 43i, Thermo, USA), a $O_3$ analyzer (Model 49i, Thermo, USA) and a $NO_x$ analyzer (Model 42i, Thermo, USA) with the detection limits of 0.1 ppbv, 0.5 ppbv and 0.4 ppbv, respectively. The above instruments were pre-calibrated before the campaign. The UVB (280 - 315 nm) intensity (UV-S-B-T, KIPP&ZONEN, The Netherlands) was measured on the rooftop of the building. Atmospheric HONO concentrations were measured by a home-made HONO analyzer with a detection limit of 0.01 ppbv (Tong et al., 2016).

Particle number size distributions and concentrations of gaseous sulfuric acid, $SO_2$, $O_3$, $NO_x$~~$_2$~~ and HONO were recorded with a time resolution of 5 min, and the UVB intensity with time resolution of 1 min. A linear interpolation method was used for deriving the variables with the same time intervals, *i.e.*, 5 min. Only data between local sunrise and sunset were used in the subsequent analysis.

## 3 Development of a proxy for atmospheric gaseous sulfuric acid

We derived the gaseous sulfuric acid concentration proxy on the basis of currently accepted formation pathways of sulfuric acid in the atmosphere (R1-R3) (Finlayson-Pitts and Pitts, 2000; Stockwell and Calvert, 1983):

$$\boldsymbol{OH + SO_2 \rightarrow HSO_3} \qquad \boldsymbol{(R1)}$$

$$\boldsymbol{HSO_3 + O_2 \rightarrow SO_3 + HO_2} \qquad \boldsymbol{(R2)}$$

$$\boldsymbol{SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O} \qquad \boldsymbol{(R3)}$$

The reaction (R1) is the rate-limiting step of this formation pathway (Finlayson-Pitts and Pitts, 2000), so our proxy will consider the two major processes that determine the abundance of gaseous sulfuric acid: the formation of gaseous sulfuric acid from reactions between $SO_2$ and OH radicals, and the loss of gaseous sulfuric acid due to its condensation onto pre-existing particles (Dal Maso et al., 2002; Kulmala et al., 2012; Pirjola et al., 1999).

The rate of change of sulfuric acid concentration can be written as Eq. (4) (Mikkonen et al., 2011):

$$\boldsymbol{d[H_2SO_4]/dt = k \cdot [OH] \cdot [SO_2] - [H_2SO_4] \cdot CS} \qquad \boldsymbol{(4)}$$

where $k$ is a temperature-dependent reaction constant given by Eq. (5) (DeMore et al., 1997; Mikkonen et al., 2011).

$$\boldsymbol{k = \frac{A \cdot k_3}{(A + k_3)} \cdot exp\left\{k_5 \cdot \left[1 + log_{10}\left(\frac{A}{k_3}\right)^2\right]^{-1}\right\} \quad cm^3(molecule \cdot s)^{-1}} \qquad \boldsymbol{(5)}$$

where $A = k_1 \cdot [M] \cdot (\frac{300}{T})^{k_2}$, $[M]$ represents the density of the air in molecule cm$^{-3}$

as calculated by $0.101 \cdot (1.381 \cdot 10^{-23} \cdot T)^{-1}$, $k_1 = 4 \cdot 10^{-31}$, $k_2 = 3.3$, $k_3 = 2 \cdot 10^{-12}$ and $k_5 = -0.8$.~~where $k$ is a temperature-dependent reaction constant (DeMore et al., 1997).~~

To simplify the calculation, the production and loss of sulfuric acid can be assumed to be at pseudo steady-state (Mikkonen et al., 2011; Petäjä et al., 2009). Then the sulfuric acid concentration can be written as Eq. (6).

$$[H_2SO_4] = k \cdot [OH] \cdot [SO_2] \cdot CS^{-1} \qquad (6)$$

Atmospheric OH radical measurements represent a major challenge as well. Since previous studies suggest that the OH radical concentration is strongly correlated with the intensity of UVB, [OH] could be replaced with UVB intensity in the proxy equation (Petäjä et al., 2009; Rohrer and Berresheim, 2006). Although photolysis of $O_3$ ($\lambda < 320\ nm$) and subsequent reactions with $H_2O$ are considered to be the dominant source of OH radicals in the atmosphere (Logan et al., 1981), recent studies argue that photolysis of HONO ($\lambda < 400$ nm) is a potentially important OH radical formation pathway (Hendrick et al., 2014; Kleffmann, 2007; Su et al., 2011; Villena et al., 2011). Thus, we attempt to introduce both $O_3$ and HONO into the proxy equation and evaluate their effects on the concentration of OH radicals.

In practice, the exponents for variables~~values of the exponential factors~~ in nonlinear fitting procedures are rarely equal to 1 (Mikkonen et al., 2011), so we replaced the factors $x_i$ with $x_i^{w_i}$ in the proxy, where $x_i$ can be an atmospheric variable such as UVB and $[SO_2]$, and $w_i$ defines $x_i$' weight in the proxy. Since $k$ is a temperature-dependent reaction constant and varies within a 10 % range ~~(~~in the atmosphere temperature range of 267.6 - 292.6 K~~)~~, *i.e.*, the actual atmospheric temperature variation in this study, we approximately regard $k$ as a constant and use a new scaling factor $k_0$. This methodology has been used previously in the proxies of gaseous sulfuric acid~~we further replaced $k$ with a scaling factor $k_0$ that is also used in the proxy methods built~~ in Hyytiälä, Southern Finland (Petäjä et al., 2009). As a result, the general proxy equation can be written as Eq. (7), with the UVB intensity, $[SO_2]$, condensation sink (CS), $[O_3]$, and [HONO] (or $[NO_x]$) as predictor variables:

$$[H_2SO_4] = f\left(k_0, x_i^{\omega_i}\right), \qquad x_i = UVB, [SO_2], CS, [O_3], [HONO] \ldots \qquad (7)$$

The nonlinear curve-fitting procedures using iterative least square estimation for the proxies of gaseous sulfuric acid concentration based on Eq. (7) were performed by a custom-made MATLAB software. In addition to the correlation coefficient (R), relative error (RE) is used to evaluate the performance of proxies in the statistical analysis and can be written as Eq. (8).

$$\boldsymbol{RE = \frac{1}{n} \cdot \sum_{i=1}^{n} \frac{|[H_2SO_4]_{proxy,i} - [H_2SO_4]_{meas.,i}|}{[H_2SO_4]_{meas.,i}}} \qquad \mathbf{(8)}$$

## 4 Results and discussion

### 4.1 General Characteristics of daytime sulfuric acid and atmospheric parameters

Table 1 summarizes the mean, median and 5-95 % percentiles of gaseous sulfuric acid concentrations and other variables measured during the daytime of the campaign. The 5-95 % percentile ranges of the UVB intensity, [$SO_2$], [NO$_x$~~$_2$~~] and [$O_3$] were 0-0.45 W m$^{-2}$, 0.9-11.4 ppbv, 3.3-61.4 ppbv and 3.5-23.3 ppbv, respectively. Compared with the sites in the study by Mikkonen et al. (2011), Beijing was characterized with a factor of 1.4-13.1 higher mean [$SO_2$] but a factor of 3.4-5.4 lower mean [$O_3$]. The 5-95 % percentile range of CS in Beijing was 0.01-0.24 s$^{-1}$, which is about 10-100 times higher~~ 1-2 orders of magnitude larger~~ than corresponding value ranges in Europe and North America. The concentration of gaseous sulfuric acid during this campaign was $(2.2-10.0) \times 10^6$ molecule cm$^{-3}$ ~~was~~ in the~~a~~ 5-95 % percentile range~~ of~~, relatively similar to observed elsewhere around the world. A diurnal mean concentration of 0.74 ppbv for HONO was observed in this campaign, consistent with previous long-term HONO measurements of about 0.48-1.8 ppbv (averaged values) in winter in Beijing (Hendrick et al., 2014; Spataro et al., 2013; Wang et al., 2017), which is a factor of 4-10 higher than HONO concentrations measured in Europe (Alicke et al., 2002, 2003). In addition, Beijing is dry in winter with a mean ambient relative humidity of 28 % during the campaign.~~an ambient relative humidity generally lower than 60%.~~

### 4.2 Correlations between [$H_2SO_4$] and atmospheric variables

Table 2 summarizes the correlation coefficients between [$H_2SO_4$] and atmospheric variables using a Spearman-type correlation analysis. ~~Note that only correlations with p-values smaller than 0.01 were included to ensure a statistical significance.~~ Clearly, the UVB intensity is an isolated variable that is independent of all the other variables but that imposes a positive influence on $O_3$ because of photochemical formation of ozone, and a negative influence on HONO because of HONO's photochemical degradation. The sulfuric acid concentration shows positive correlations with all the other variables. The correlation coefficients between [$H_2SO_4$] and [$SO_2$] and between [$H_2SO_4$] and UVB intensity are 0.74 and 0.46, respectively, which indicate that [$SO_2$] and UVB have important influences on the formation of atmospheric gaseous sulfuric acid.~~consistent with the accepted formation pathway of gaseous sulfuric acid from the reaction between $SO_2$ and OH radicals.~~ Accordingly, [$O_3$] and [HONO] show positive correlations with [$H_2SO_4$] because both $O_3$ and HONO could be precursors of OH radicals. Surprisingly, a high positive correlation coefficient (0.6) was found between [$H_2SO_4$] and CS, which is in contrast to the conventional thought that CS describes the loss of gaseous sulfuric acid molecules onto pre-existing particles and thus should show a negative correlation. CS correlates well with [$SO_2$] ($r = 0.83$) and [NO$_x$~~$_2$~~] ($r = 0.77$): a high CS value, as an indicator of ~~an~~ atmospheric particle ~~-~~pollution, is thus usually accompanied with a high concentration of both $SO_2$ and NO$_x$~~$_2$~~ in urban China, indicating co-emissions. A strong correlation between [HONO] and [NO$_x$~~$_2$~~] ($r = 0.88$) in our measurement is supported by the fact that HONO can be either heterogeneously formed by reactions of $NO_2$ on various surfaces (Calvert et al., 1994) or homogeneously formed by the gas phase NO + OH reaction, between which the former likely dominate for the daytime HONO production in urban Beijing (Liu et al., 2014).~~.~~

Since the UVB intensity and [$SO_2$] have been reported as the dominating factors for the formation of sulfuric acid (Mikkonen et al., 2011; Petäjä et al., 2009), we further explored the relationship of the measured sulfuric acid concentrations with the UVB intensity and [$SO_2$] using the nonlinear curve-fitting method with a single variable. Figure 1a presents a scatter plot of [$H_2SO_4$] against the UVB intensity, color-coded by [$SO_2$]. A good correlation layering with~~with a clear lamination by~~ [$SO_2$] is evident, indicating that the UVB intensity and [$SO_2$] together play an important role in the formation of sulfuric acid. A similar scatter plot (Figure 1b) of [$H_2SO_4$] against [$SO_2$], color-coded by the UVB intensity, leads to a similar conclusion.

### 4.3 Proxy construction

Similar to the non-linear proxies suggested by Mikkonen et al. (2011), we tested a number of proxies for gaseous sulfuric acid, listed in Table 3 with their respective fitting parameters and performance summarized in Table 4. The scatter plots of observed

[$H_2SO_4$] *versus* predicted values given by proxies are presented in Fig. S1. In these proxies, the concentration of a gaseous species is in the unit of molecule cm$^{-3}$, the unit of the UVB intensity is W m$^{-2}$, the unit of CS is s$^{-1}$, and $k_0$ is a scaling factor.

The proxy N1 was built by using the UVB intensity and [$SO_2$] as the source terms and CS as the sink term, which follows the conventional idea of the $H_2SO_4$ formation and loss in the atmosphere. CS was then removed from this proxy to examine the performance of the proxy N2 that has~~ve~~ the UVB intensity and [$SO_2$] as the only predictor variables. Since the formation of OH radicals in the atmosphere depends on precursors in addition to UVB, we further attempted to introduce the OH precursor term into the $H_2SO_4$ proxy. The proxies N3 and N4 were built by introducing $O_3$ as the only OH precursor to evaluate its influence on the formation of sulfuric acid. Furthermore, we added HONO as another potential precursor for OH radicals, resulting in the proxies N5 and N6. Lastly, the proxy N7 was built by replacing [HONO] with [NO$_x$~~$_2$~~] because firstly, HONO is not regularly measured, and secondly, a good linear correlation between [HONO] and [NO$_x$~~$_2$~~] was generally observed in the daytime during this campaign, although higher [HONO]/[NO$_x$~~$_2$~~] ratios were observed in the morning due to the accumulation of HONO during the night (Figure 2). RH was not considered in the current study because a test by introducing RH into the proxies do not result in a significantly better performance, which is consistent with those conclusions~~the introduction of RH into the proxy did not yield significantly better results~~ in the Mikkonen et al. study (2011).

As shown in Table 4, the correlation coefficients are in the range of 0.83-0.86 and R~~MA~~Es are in the range of 19.1-20.0 %~~ (0.94 – 1.03) × 10$^6$ molecule cm$^{-3}$~~. The exponents for the UVB intensity range from 0.13 to 0.16, and those for [$SO_2$] generally range from 0.38 to 0.41, except in case of the proxy N6 (b=0.33). The obtained exponent *b* for [$SO_2$] is significantly smaller than 1 unlike the assumption~~ed~~ in Eq. (6~~3~~), mainly because [$SO_2$] is also an indicator of air pollution that usually influences the sinks of both OH radicals and sulfuric acid. The exponent for [$SO_2$] ranged from 0.5 to 1.04 in the previous proxy study for European and North American sites (Mikkonen et al., 2011), including values from 0.48 to 0.69 in Atlanta, GA, USA, which was probably quite a polluted site because the measurements were conducted only 9 km away from a coal-fired power plant. The obtained value range of the exponent *b* for [$SO_2$] in our study is probably related to the urban nature of Beijing. The value of exponent c for CS in the proxy N1 is as low as 0.03, which either might be due to the covariance of CS and certain $H_2SO_4$ sources that cancels the dependence on CS, or it might indicate that CS is actually insufficient in regulating the $H_2SO_4$ concentration, as recently suggested by Kulmala et al. (2017). By comparing the proxies N1 and N2, we can see that CS plays a minor role because the exponents of [$SO_2$] and UVB, the overall correlation coefficient and the R~~MA~~Es are almost identical with and without CS. We can see the negligible role of CS also when comparing the results of the proxies N3 and N4 where $O_3$ is considered. However, the role of CS becomes evident between the proxies N5 and N6 when HONO is introduced: the exponents of [$SO_2$], [$O_3$], and [HONO] significantly increased when taking into account the CS, suggesting that the covariance between HONO and CS can explain, at least partially, the close-to-zero exponent of CS in the proxies N1-N4. In addition, when [$O_3$] is introduced as the only precursor for OH radicals, minor improvements in the correlation coefficient and R~~MA~~E were obtained, as suggested by comparing the proxies N3 and N1. When both [$O_3$] and [HONO] were introduced as OH precursors in the proxies N5-N7, REs have noticeable improvements, and correlation coefficients improved slightly.~~MAE and correlation coefficient significantly improved.~~ Altogether, these observations suggest that it is crucial to introduce HONO into the proxy, both in our study and also likely for the previous work where the exponent of CS is close-to-zero (Mikkonen et al., 2011).

Although so far the proxy N5 had the best fitting quality, it is impractical to explicitly include [HONO] because HONO measurements are very challenging. As shown in Fig. 2, [HONO] and [NO$_x$~~$_2$~~] ~~are~~ tended to correlate linearly with each other in the daytime during this campaign, with a linearly fitted [HONO]/[NO$_x$~~$_2$~~] ratio of around 0.03 and a relative error of 0.42~~mean absolute error (MAE) of 0.3 ppbv~~. ~~Similar, strong linearity was observed in a previous study by Hao et al. (2006) who attributed this observation to the heterogeneous conversion of $NO_2$ to HONO. Only o~~Occasionally ~~slightly~~ higher [HONO]/[NO$_x$~~$_2$~~] ratios ~~in the morning~~ could be seen in the morning, which might be due to the fact that HONO concentration could have an accumulation process during the nighttime and lead to a deviation from the steady state. ~~deviation from the steady state. Bernard et al. (2016) reported that [$NO_2$] has a similar diurnal behavior to that of [HONO] and hence the ratio of [HONO]/[$NO_2$] varies slightly during the diurnal cycle.~~ Therefore, due to the good correlation, the proxy N7 replaces [HONO] by [NO$_x$~~$_2$~~], a more easily measured variable, and performs equally well with the proxy N5.

Clearly, the proxy N2 provides the simplest parameterization, but the proxies N5 and N7 result in the best fitting quality because of the introduction of [HONO]. Figure 3 presents the RE values for the proxies N2 and N7, respectively, as a function of linear bins of measured sulfuric acid concentrations. The performance of the proxy N7 is considerably better than that of the proxy N2 in the sulfuric acid concentration range of $(2.2 - 10) \times 10^6$ molecule cm$^{-3}$, which covers the 5-95% percentiles of sulfuric acid concentration in this study. In the worst scenario, RE of proxy N2 is 1.2 times as high as that of proxy N7, *e.g.*, REs are 16.75 % and 13.99 %, respectively, in the sulfuric acid concentration bin of $(4 - 5) \times 10^6$ molecule cm$^{-3}$, and 16.71 % and 14.42 %, respectively, in the bin of $(7 - 8) \times 10^6$ molecule cm$^{-3}$.

### 4.4 Comparison of measured and predicted [$H_2SO_4$]

A comparison between measured and predicted [$H_2SO_4$] was performed. Figure 4 includes calculated results from the proxies N2 and N7 as well as from a proxy constructed according to measurement in a boreal forest site, Finland, *i.e.*, Eq (1) (Petäjä et al., 2009). The measured daytime [$H_2SO_4$] on 10 March, 2018, was above $4 \times 10^6$ molecules cm$^{-3}$ when averaged to~~with~~ a time resolution of 5 min. The predicted [$H_2SO_4$] using the proxies N2 and N7 both track the measured [$H_2SO_4$] pretty well, even when an unexpected dip in the sulfuric acid concentration was observed at around 10:00-11:00. The performance of the proxy N7 is better than that of proxy N2 during the entire day, consistent with our results in Fig. 3. The proxy by Petäjä et al. (2009) underestimated the concentrations of sulfuric acid by a factor of 20 or so, which can be attributed to the very different values of CS between Beijing and the boreal forest. The fact that $[H_2SO_4]_{\text{Petäjä } et\ al.}$ does not track the measured [$H_2SO_4$] even after including a scaling factor indicates that proxies are site-specific and do not necessarily work well in locations other than where they have originally been developed for. In addition, the direct performance comparison between the proxy N2 and the proxy by Petäjä et al. (2009) indicates the importance of assigning exponential weights to variables in the nonlinear fitting procedures, which is consistent with results by Mikkonen et al. (2011).

### 5 Summary and conclusions

Sulfuric acid is a key precursor for atmospheric new particle formation. In this study, we constructed a number of proxies for gaseous sulfuric acid concentration according to our measurements in urban Beijing during the winter. According to the obtained proxies and their performance, the UVB intensity and [$SO_2$] were the dominant influencing factors. Hence, the simplest proxy (Proxy N2) only involves UVB intensity and [$SO_2$] as shown by Eq. (9). The units of [$H_2SO_4$] and [$SO_2$] are molecule cm$^{-3}$, and the unit of UVB is W m$^{-2}$.

$$[H_2SO_4] = 280.05 \cdot UVB^{0.14} \cdot [SO_2]^{0.40} \qquad (9)$$

~~This proxy resulted in a relative deviation of up to 29 %.~~

For a comprehensive consideration of the formation pathways of OH radicals,~~For the best proxy accuracy,~~ [$O_3$] and [HONO] as well as CS should be included (Proxy N5), as shown by Eq. (10). The units of [$H_2SO_4$], [$SO_2$], [$O_3$] and [HONO] are molecule cm$^{-3}$, the unit of UVB is W m$^{-2}$, and the unit of CS is s$^{-1}$.~~:~~

$$[H_2SO_4] = 0.0072 \cdot UVB^{0.15} \cdot [SO_2]^{0.41} \cdot CS^{-0.17} \cdot ([O_3]^{0.36} + [HONO]^{0.38}) \qquad (10)$$

Since HONO measurements are not a regular practice, we can further replace [HONO] with [NO$_x$~~$_2$~~], shown in Eq. (11), which can be justified by the strong linear correlation between [HONO] and [NO$_x$~~$_2$~~] observed in this study. The units of [$H_2SO_4$], [$SO_2$], [$O_3$] and [$NO_x$] are molecule cm$^{-3}$, the unit of UVB is W m$^{-2}$, and the unit of CS is s$^{-1}$.~~:~~

$$[H_2SO_4] = 0.0013 \cdot UVB^{0.13} \cdot [SO_2]^{0.40} \cdot CS^{-0.17} \cdot ([O_3]^{0.44} + [NO_{x\cancel{2}}]^{0.41}) \qquad (11)$$

We consider this last proxy more reasonable than the others due to the following reasons: first, it makes the equation physically meaningful as the CS starts to be involved as a sink term, and second, the ~~absolute and relative fitting error~~RE was~~ere~~ reduced considerably compared with the other proxies. Overall, this suggests that the photolysis of $O_3$ and HONO are both important OH sources in urban Beijing.

As a summary, we recommend using the simplest proxy (proxy N2 as shown in Eq. (9)) and a more accurate proxy (Proxy N7 as shown in Eq. (11)) for calculating daytime gaseous sulfuric acid concentrations in the urban Beijing atmosphere. It is clear that the current proxies are based on only a month-long campaign of sulfuric acid measurements in urban Beijing during winter. Given the dramatic reduction in the concentration of $SO_2$ in recent years (Wang et al., 2018) and the strong dependence of calculated [$H_2SO_4$] on [$SO_2$], the performance of the proxies in the past and future years remain to be evaluated. Furthermore, the proxies might be site-specific and season-specific. Since the proxies were derived with atmospheric parameters in winter, in urban Beijing, the exponents for atmospheric variables in the proxy could have different values for other cities or other seasons. Thus, the proxies in this study should be further tested before their application to other Chinese megacities or other seasons.~~Nevertheless, our work here shows the importance of heterogeneous chemistry as a potential source of OH radicals in an urban air; however, the proxies might be site-specific and should be further tested before their application to other Chinese megacities.~~

## Author contributions

LW designed this study. YL (Yiqun Lu), CY, YF, YC, YL (Yiliang Liu), GY, YW, YZ, RY, RB and CD conducted the field campaign. YL (Yiqun Lu) analyzed data with contributions from LW and all the other co-authors. YL (Yiqun Lu) and LW wrote the manuscript with contributions from all the other co-authors.

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Table 1 Mean, median, 5-95 % percentiles of key atmospheric variables and $[H_2SO_4]$ in the daytime.

| | UVB (W $m^{-2}$) | $[SO_2]$ (ppbv) | CS ($s^{-1}$) | $[O_3]$ (ppbv) | [HONO] (ppbv) | $[NO_{x\cancel{2}}]$ (ppbv) | $[H_2SO_4]$ ($\times 10^6$ molecule $cm^{-3}$) | RH (%) |
|---|---|---|---|---|---|---|---|---|
| mean | 0.17 | 4.6 | 0.11 | 10.5 | 0.74 | 25.3 | 5.4 | 28 |
| median | 0.14 | 3.7 | 0.11 | 9.0 | 0.51 | 23.0 | 4.9 | 26 |
| 5-95% percentiles | 0.00-0.45 | 0.9-11.4 | 0.01-0.24 | 3.5-23.3 | 0.09-2.65 | 3.3-61.4 | 2.2-10.0 | 9-59 |

Table 2 Correlation coefficients (Spearman type) between [$H_2SO_4$] and atmospheric variables in the daytime.~~ Only correlation coefficients with p-values less than 0.01 are included to ensure a statistical significance.~~

| | UVB | [$SO_2$] | CS | [$O_3$] | [HONO] | [$NO_2$] | [$H_2SO_4$] |
|---|---|---|---|---|---|---|---|
| UVB | 1 | 0.01~~/~~ | -0.02~~/~~ | 0.14 | -0.23 | -0.04~~/~~ | 0.46 |
| [$SO_2$] | | 1 | 0.83 | 0.25 | 0.64 | 0.70 | 0.74 |
| CS | | | 1 | 0.36 | 0.75 | 0.77 | 0.60 |
| [$O_3$] | | | | 1 | -0.02~~/~~ | -0.04~~/~~ | 0.29 |
| [HONO] | | | | | 1 | 0.88 | 0.39 |
| [$NO_2$] | | | | | | 1 | 0.53 |
| [$H_2SO_4$] | | | | | | | 1 |

Table 3 Proxy functions for the nonlinear fitting procedure.

| Proxy | Function~~Equation~~[#] |
|---|---|
| N1 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot CS^c$ |
| N2 | $k_0 \cdot UVB^a \cdot [SO_2]^b$ |
| N3 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot CS^c \cdot [O_3]^d$ |
| N4 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot [O_3]^d$ |
| N5 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot CS^c \cdot ([O_3]^d + [HONO]^e)$ |
| N6 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot ([O_3]^d + [HONO]^e)$ |
| N7 | $k_0 \cdot UVB^a \cdot [SO_2]^b \cdot CS^c \cdot ([O_3]^d + [NO_x$~~$_2$~~$]^f)$ |

[#] UVB is the intensity of ultraviolet radiation b in W cm$^{-3}$; [SO$_2$] is the concentration of sulfur dioxide in molecule cm$^{-3}$; CS is the condensation sink in s$^{-1}$; [O$_3$] is the concentration of ozone in molecule cm$^{-3}$; [HONO] is the concentration of nitrous acid in molecule cm$^{-3}$; [NO$_x$~~$_2$~~] is the concentration of nitrogen dioxide in molecule cm$^{-3}$; $k_0$ is a scaling factor.

Table 4 Results of the nonlinear fitting procedure for different proxy functions, together with correlation coefficient (R, Pearson type) and relative error (RE).~~mean absolute error ($MAE$).~~

| Proxy | $k_0$ | $a$ | $b$ | $c$ | $d$ | $e$ | $f$ | $R$ | $R$~~$MA$~~$E$ (~~$\times 1$~~ |
|---|---|---|---|---|---|---|---|---|---|
| N1 | 515.74 | 0.14 | 0.38 | 0.03 | | | | 0.83 | 20.04~~1.03~~ |
| N2 | 280.05 | 0.14 | 0.40 | | | | | 0.83 | ~~1.03~~20.00 |
| N3 | 9.95 | 0.13 | 0.39 | -0.01 | 0.14 | | | 0.85 | ~~1.00~~19.95 |
| N4 | 14.38 | 0.13 | 0.38 | | 0.14 | | | 0.85 | ~~1.00~~19.95 |
| N5 | 0.0072 | 0.15 | 0.41 | -0.17 | 0.36 | 0.38 | | 0.86 | ~~0.94~~19.11 |
| N6 | 2.38 | 0.14 | 0.33 | | 0.24 | 0.24 | | 0.85 | ~~0.98~~19.66 |
| N7 | 0.0013 | 0.13 | 0.40 | -0.17 | 0.44 | | 0.41 | 0.86 | ~~0.95~~19.34 |

## Figure Captions

**Figure 1.** Correlations (a) between [$H_2SO_4$] and UVB intensity, and (b) between [$H_2SO_4$] and [$SO_2$] during the campaign from 9 February to 14 March, 2018.. $k_m$ is a constant term.

**Figure 2.** Correlation between [HONO] and [NO$_x$~~$_2$~~] during the campaign from 9 February to 14 March, 2018. The black line represents a linear fitting with a zero intercept.

**Figure 3.** Performance assessments of proxy N2 and proxy N7. The REs are used to evaluate the performances of proxy N2 and N7, respectively as a function of linear bins of measured sulfuric acid concentrations. ~~The averaged deviation and the relative deviation in the plots are defined by Eq. (6) and Eq. (7) and used to evaluate the performance of proxy N2 and N7, respectively. "Overlap" refers to the smaller values between proxy N2 and proxy N7, and the larger ones are indicated by the color code of proxies N2 and N7.~~

**Figure 4.** Comparison of measured [$H_2SO_4$], $[\mathrm{H_2SO_4}]_{\mathrm{N2}}$ , $[\mathrm{H_2SO_4}]_{\mathrm{N7}}$ and $[\mathrm{H_2SO_4}]_{\mathrm{Petäjä}\ et\ al.}$ on 10 March, 2018 with a time resolution of 5 min.

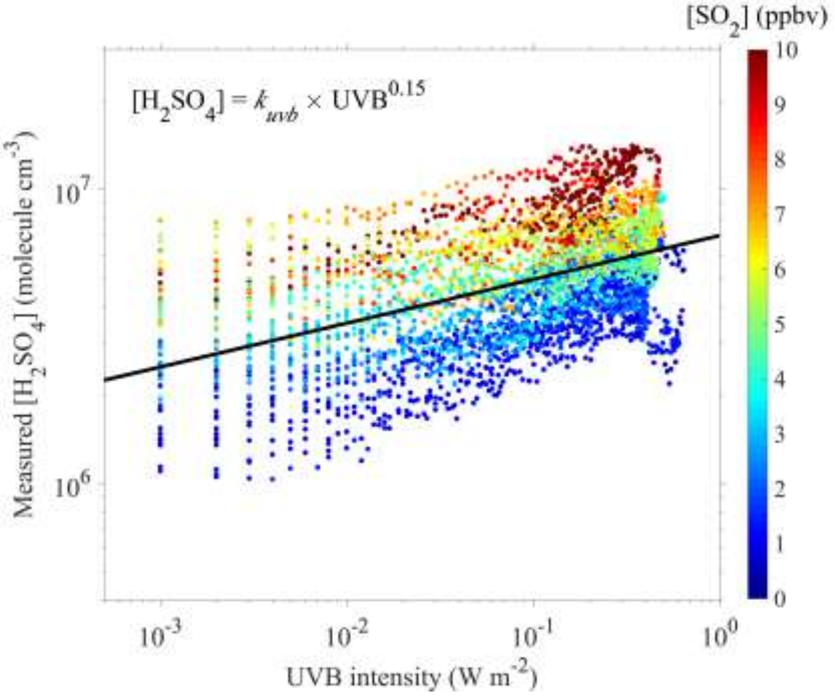


**Figure 1a**

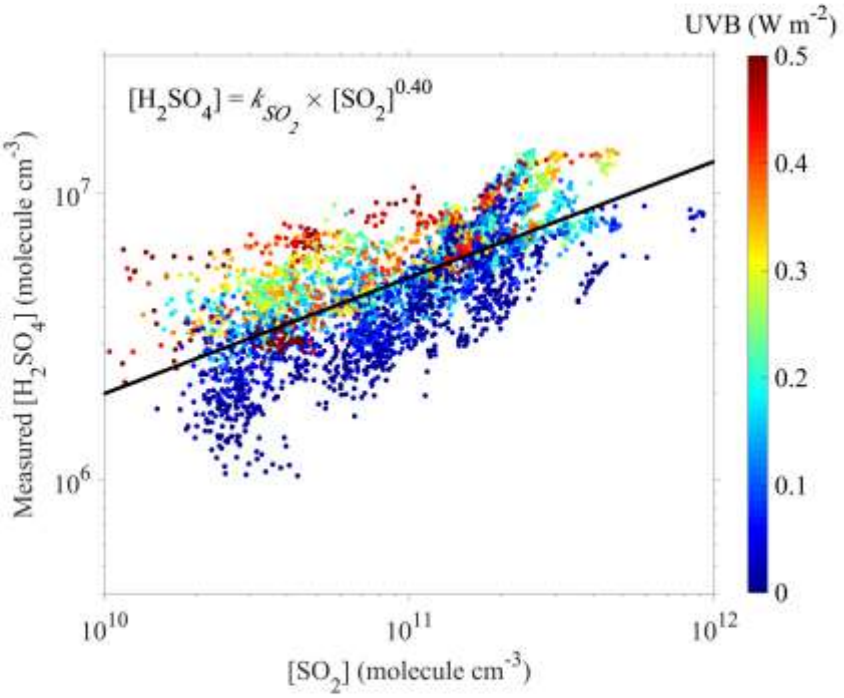


**Figure 1b**

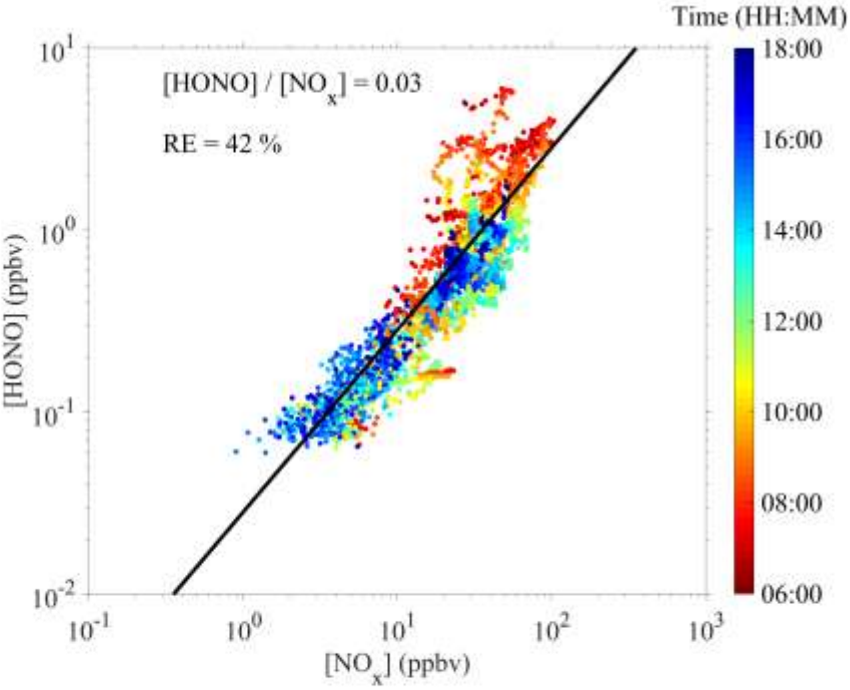

Time (HH:MM)
18:00
16:00
14:00
12:00
10:00
08:00
06:00
[HONO] / [NO$_x$] = 0.03
RE = 42 %
[HONO] (ppbv)
[NO$_x$] (ppbv)
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
$10^{-1}$
$10^0$
$10^1$
$10^2$
$10^3$

**Figure 2**

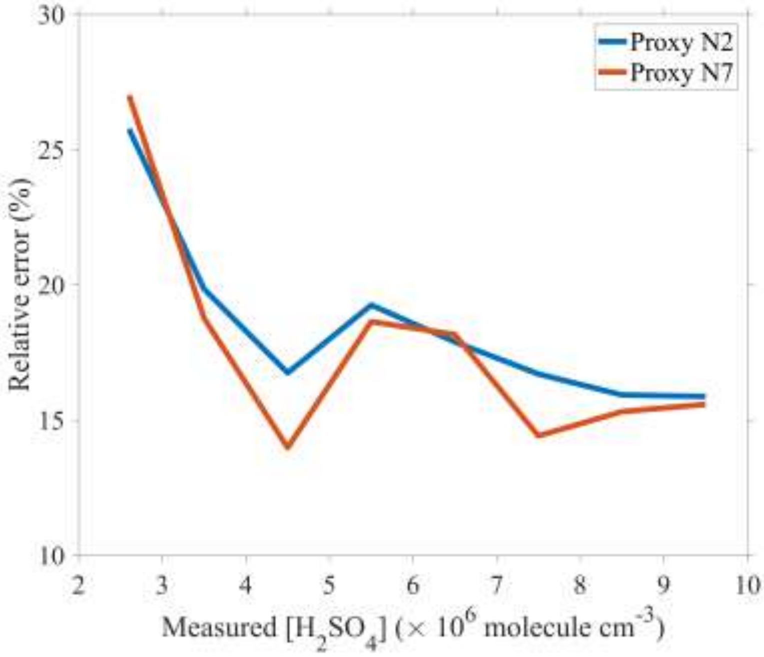
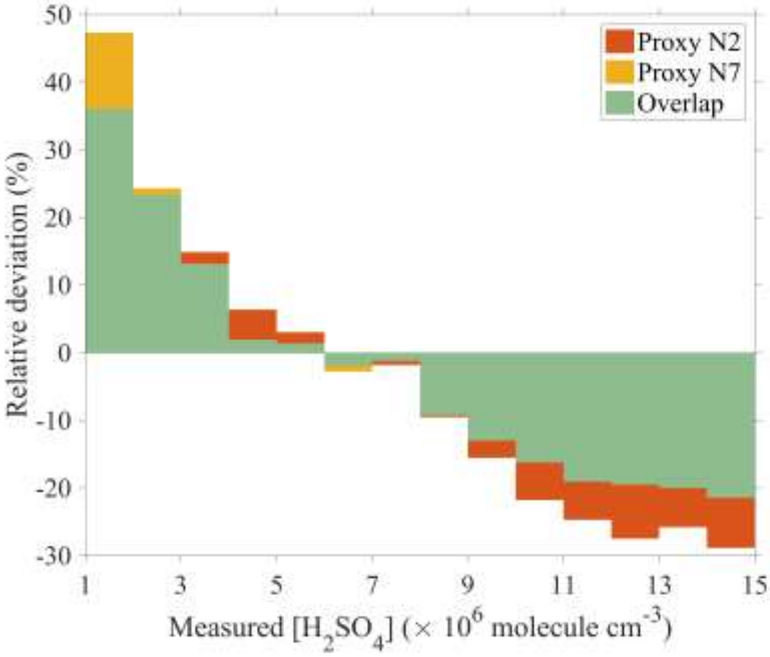


**Figure 3~~a~~**



~~**Figure 3b**~~

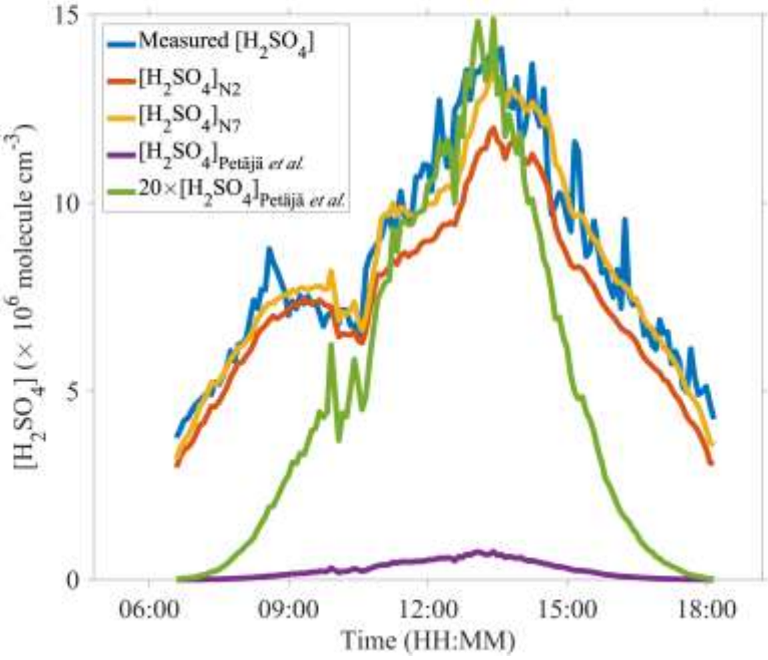

Measured $[H_2SO_4]$
$[H_2SO_4]_{N2}$
$[H_2SO_4]_{N7}$
$[H_2SO_4]_{\text{Petäjä et al.}}$
$20\times[H_2SO_4]_{\text{Petäjä et al.}}$
$[H_2SO_4]$ ($\times 10^6$ molecule cm$^{-3}$)
0
5
10
15
06:00
09:00
12:00
15:00
18:00
Time (HH:MM)

**Figure 4**