

Interactive comment on “A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing” by Yiqun Lu et al.

Anonymous Referee #1

Received and published: 20 December 2018

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.

Major comments: 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

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measurement? How do these uncertainties compare to the model predicted amounts?

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 $1.1 \times 10^{10} \text{ cm}^{-3}$ 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.

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 pre-existing 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.

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.

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.

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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?

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.

Minor comments:

P1 Line 28: desirable for the atmospheric. . .

P1 36-27 change one of the "using"

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).

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

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

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

P3 Line 68: NO₃- and ligands.

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.

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

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worth taking a look at.

P3 line 83: has been proven

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

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

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

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

P5 119: OH radicals

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

P5 line 128: Criegee should be capitalized

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

P6 line 154: Is this a custom-built inlet? If so, could the authors provide a diagram and write in the dimensions?

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

P6 line 164: should it be ToFTools?

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

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

P 8 paragraph starting on line 228: This was a difficult paragraph to understand. Can the authors better phrase it to explain the differences in parameters?

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P 8 line 242: a matlab software. A custom-made one? Or just a function in matlab?

P 9: 1-2 orders of magnitude. Maybe change to 10-100 times higher to be more clear.

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

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?

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

P10 300: molecules cm^{-3} is normally written as just cm^{-3} .

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?

P11 line 324: “unlike assumed in Eq. (3)” wording seems incorrect

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?

Page 12 line 356: “Only occasionally slightly higher” too many adverbs. Rephrase

Page 12 line 356: The authors refer to a previous study to justify linearity of NO_2 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.

Page 12 line 376: authors should specify that this covers sulfuric acid concentrations for this location. 10^6 cm^{-3} does not cover sulfuric acid concentrations around the world.

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

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the wording “for the best proxy accuracy” or consider rewording this section to make it a bit less confusing/

Page 14 line 439: I do not understand how this work has shown the importance of heterogeneous 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.

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

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

Figure 4: As mentioned above, it would be useful to show the time lines for the other measured concentrations (CS, OH, NO_2 , etc.) that the proxy model uses.

Works cited for this review: Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J. and McMurry, P. H.: Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, *Proc. Natl. Acad. Sci.*, 109, 18713–18718, doi:10.1073/pnas.1210285109, 2012. Gopalakrishnan, R. and Hogan Jr., C. J.: Determination of the Transition Regime Collision Kernel from Mean First Passage Times, *Aerosol Sci. Technol.*, 45(12), 1499–1509, doi:10.1080/02786826.2011.601775, 2011. Jen, C. N., McMurry, P. H. and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *J. Geophys. Res. Atmospheres*, 119, 2014JD021592, doi:10.1002/2014JD021592, 2014. Kuang, C., Chen, M., Zhao, J., Smith, J., McMurry, P. H. and Wang, J.: Size and time-resolved growth rate measurements of 1 to 5 nm freshly formed atmospheric nuclei, *Atmos Chem Phys*, 12, 3573–3589, doi:10.5194/acp-12-3573-2012, 2012. Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma,

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J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R. and Curtius, J.: Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric conditions, *Proc. Natl. Acad. Sci.*, doi:10.1073/pnas.1404853111, 2014.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-1132>, 2018.