

Interactive comment on “Measurements of gaseous H₂SO₄ by AP-ID-CIMS during CAREBeijing 2008 Campaign” by J. Zheng et al.

Anonymous Referee #1

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This paper is a well-written summary of the first measurement of gaseous sulfuric acid made in China using a state-of-the-art mass spectrometer. The material is of interest to ACP readers, although the topic is rather narrowly focused. While the methodology is for the most part clear, there are some aspects that need clarification. More importantly, the analysis is especially brief and does not discuss some of the obvious questions regarding the source of the large quantities of particulate sulfate found in the Beijing atmosphere. Notably, the authors argue that sulfuric acid in Beijing controls the Aitken-mode particulate sulfate, when in fact the little evidence to that effect is largely an artifact of graph scaling. To be of broader interest, the manuscript needs revision to try to place these observations of gas-phase sulfuric acid in Beijing into the broader context of the overall sulfate budget.

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Major comments:

- 1) p. 5024, lines 5-11. I would like to see more discussion of the calibration methodology. Was the apparatus described by Zheng et al. (Anal. Chem., 2010) used? If so, would you please summarize in 2-3 sentences the methodology?
- 2) p. 5025, line 12. The SO₂ analyzer is probably an Ecotech EC9850 model.
- 3) p. 5025, line 13. Was there measurement of NO₂? If not, how was Eqn. 3, in which OH is calculated, solved? Was O₃ measured at the site?
- 4) p. 5026, lines 13-20. I am puzzled by the discussion of diffusion and turbulence here and also in the Zheng et al. (2010) paper. If the flow is laminar, wall losses by molecular diffusion will not be a function of tube diameter, since for a given flowrate the residence time will increase proportionally to the diffusion time if diameter is changed. However, the flow here is surely turbulent, with Reynolds numbers exceeding 16 000. Thus a spiral flow mixer for calibration (Zheng et al.) is probably not needed. Similarly, turbulence generated by wind shifts is probably not a factor in molecular losses in this turbulent inlet.
- 5) p. 5028, line 19. The authors state that cleaner conditions lead to higher gaseous sulfuric acid (GSA) concentrations due to the reduction of aerosol surface. But is there also not a substantial decrease in SO₂ from the clean air direction? This would be a good location to look independently at the production and loss terms and see which is driving the increase in GSA abundance in cleaner conditions.
- 6) p. 5029, lines 1-5. The authors attribute the increase in GSA concentrations during the pollution control period to those mitigation efforts. However, since GSA is heavily controlled by OH production, might seasonal variations in actinic flux (due to cloudiness, for example), or changes in meteorology (more flow from the northwest) or humidity be equally likely to cause these changes? This is another opportunity to look at the elements in the production and loss terms to see what is really controlling GSA

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concentrations in this time period relative to the before- and after-control period.

7) In figures 4 and 5, some of the plotted parameters are not scaled to zero, but are expanded to zoom in on the variability. I believe this is misleading, as it emphasizes very small perturbations that may not really be associated with GSA. For example, in Fig. 5, sulfate production rates from GSA are scaled from 0 to 0.014 $\mu\text{g}/\text{m}^3/\text{hr}$. The co-plotted Aitken-mode sulfate scale goes from 1.6 to 2.1 $\mu\text{g}/\text{m}^3$. The change in Aitken mode sulfate mass that is purported to be associated with the GSA diurnal cycle is about 0.35 $\mu\text{g}/\text{m}^3$, or about 20% of the total Aitken sulfate mass. If this axis were plotted from 0 to 2.1 $\mu\text{g}/\text{m}^3$, it would be evident that the GSA maximum is largely uncorrelated with Aitken mode sulfate mass. The zoomed-in axis artificially emphasizes a very small perturbation to the sulfate budget. Furthermore, it would take more than 2 days of peak production of GSA to account for this $\sim 20\%$ perturbation to the Aitken mode sulfate budget. It is evident that parameters other than instantaneous production of GSA control the sulfate mass. This lack of quantitative correspondence is not discussed, and is in fact masked by the chosen scale of the ordinate. This graph scaling, and the lack of discussion of the relevance of the observed GSA to the sulfate budget, must be corrected in a revised manuscript.

8) p. 5030, lines 19-20. Continuing on point (7) above, it is extremely unlikely that intermodal coagulation can explain the very large amount of sulfate in the accumulation mode. The measured in-situ GSA production rates for both the Aitken and accumulation modes are far too small to source this much sulfate over reasonable time frames. The only logical explanations are a) that GSA production rates are much higher in the source regions, which are primarily industrial areas upwind of Beijing, where SO_2 is more concentrated, and/or b) other production mechanisms such as in-cloud oxidation contribute the bulk of the particulate sulfate production. It is likely that the GSA concentrations measured in Beijing have no real correspondence to particulate sulfate concentrations, which are the time-integrated product of oxidation processes occurring over many days since the time of emission. Measurements in the plumes of coal-fired

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industries indicate conversion of SO_2 to sulfate by OH oxidation over e-folding time scales of 2-3 days, giving plenty of time for production of the sulfate observed in Beijing.

9) p. 5030, lines 21-23. I don't understand the logic of this sentence. Why does it follow that other sources of particle mass lead to fine-mode sulfate production in Beijing?

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