

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

Anonymous Referee #2

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This paper is a summary of gaseous sulfuric acid (GSA) measurements made by a chemical ionization mass spectrometry technique in Beijing, China during the 2008 CAREBeijing project. The material is of interest to ACP readers. The writing is clear, however, the analysis is brief and not detailed. The analysis is largely based on examining hourly averaged data over a 2 and half-month period (7 July to 25 September). As discussed below, I wonder if changes occurring on shorter scales, such as week long synoptic weather patterns and policy motivated short-term emission control strategies, are not coming out in the analysis. For example, Fig. 3 shows measure GSA before, during, and after different emission control scenarios with peak GSA levels increasing during the full control period, but the analysis of sulfate production is done by averaging over all data. Also, there is no discussion of the sulfate budget in general or the relative contribution from GSA.

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Comments:

1) Introduction. GSA is a function of SO₂ levels (p 5021 R1, R2, and R3), however, there is little discussion of SO₂ sources in the Beijing area. An annual emission of SO₂ is given, but not divided into sources. Page 5022 lines 20-30 specifically mention air quality control measures removing automobiles from roadways during the measurement period. However, the relative contribution to the annual SO₂ emissions from automobiles and power plants is not given. Are automobiles an important enough source of SO₂ to affect GSA production, is the affect on OH from automobile NO_x significant, or is primary emission of particles from automobiles the force driving the observations from the air quality control periods, i.e. less surface aerosol surface area leads to higher GSA? The introduction could better set-up the rest of the paper.

2) p. 5023-5024, Section 2.1 GSA Measurements. The authors claim that GSA is difficult to measure because of its low vapor pressure. However, they also claim to have a custom made, adjustable, GSA primary source. More detail about the calibration source should be given including the uncertainty of the source generation. Twice a week calibrations does not seem frequent enough for a CIMS measurement. Was the whole inlet calibrated? If not, is it known that the inlet wall loss (line 25) was minimized. Were these standard additions onto ambient air with ambient aerosol loadings? What is the sensitivity in Hz per molecule cm⁻³? How was instrument background determined/

3) p. 5025-5026, Section 3.1 Instrument performance and meteorological effect. I am puzzled by the inclusion of this section. I fail to see how it adequately addresses the first sentence, “Accurate measurements of GSA represent a great challenge because of its low concentration”. The NSD analysis doesn’t address whether or not there are significant inlet losses or if there is inlet effects due to ambient conditions, such as relative humidity. It may be comforting that the signal coming through the inlet exhibits no systematic bias but how is that related to the true ambient conditions. I feeling that showing a time series of GSA signal through calibration, background, and ambient measurement sequence would characterize and define the instrument performance

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through parameters such as signal to noise ratio and time response. These parameters have better physical meaning than the NSD.

4) p. 5027 line 12. Is the mean velocity referring to dry deposition velocity or something else? Please clarify.

5) p. 5027 line 26. Is the 1-sigma error bar the standard deviation of the average or truly the error of the measurement?

6) p. 5027 Equation 3. No NO₂ measurement is mentioned in Section 2.2. What NO₂ data was used in calculating OH? What is the uncertainty in this calculated OH?

7) p.5028 lines 15-19. I find it hard to follow the one week periodicity in peak GSA values in Figure 3, especially early in the project. I would think there should be meteorological data to support the hypothesis that large-scale weather patterns are causing the periodicity. Expand and briefly discuss the supporting data.

8) p 5029 lines 1-5. The increase in GSA is attributed to the pollution control periods due to a decrease in aerosol surface area, i.e., a decrease in the loss term of equation 2. Did the pollution control measures not affect the production term? What had a larger affect on the loss term, pollution control measures or the periodicity of the large-scale weather patterns? It seems that there could be a few factors influencing GSA levels and there is no attempt to distinguish what is really controlling the GSA.

9) p. 5029 Section 3.3. I understand that the nucleation events and the MSM analysis are discussed in detail elsewhere. However, without some introduction or summary conclusion details I do not understand what Table 1 is conveying. How are nucleation events defined, especially, in light of conventional instrumentation limitations discussed on p. 5021 line 9? How are GSA and RH related to the calculated formation rate?

10) p. 5029 – 5030 Section 3.4 and Figure 5. The sulfate production from is very small, peaking at 0.014 and 0.05 $\mu\text{g m}^{-3} \text{ hr}^{-1}$ for Aitken and accumulation modes, respectively. It would take over a day at the peak sulfate production from GSA rate to

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account for the observed sulfate increases. This seems too slow to be a significant contributor to the total sulfate mass. The increases in measured sulfate seem to be visually enhanced by the range of the axis chosen. For example. In 5a, the production rate increases by a factor of 6 from 0800 to the peak at 1300, while the measured sulfate only increases by ~20% in the same time period. Obviously, there is much more sulfate measured than can be accounted for by GSA production. Where is that coming from? The manuscript should be strengthened by discussing the contribution of GSA to the sulfate budget. I also wonder if analyzing hourly average diurnal profiles over ~ 80 days is the best way to look at the data. The observations span multiple emission control periods and large-scale weather events. Has the effect of sulfate production from GSA been averaged out over the different periods? Fig. 3 shows that absolute GSA levels differ during the different periods. Does sulfate production differ, too?

11) p. 5030 lines 21-23. This sentence is confusing. Since biomass burning and automobile exhaust contribute to fine particles why does it follow that secondary sources can, too?

12) p. 5040 Figure 3. The arrows do a poor job of separating the different control measure regimes. I suggest light background shading for the different time periods.

13) p. 5041 Figure 4. What are the estimated uncertainties in the OH calculation and the simulated GSA curves?

14) p. 5042 Figure 5. The traces in Fig. 5 are lighter than in Fig. 4 and the symbols are open not filled in making it harder to read.

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