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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects" *by* J. J. Li et al.

Anonymous Referee #1

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Overview – This manuscript presents field measurements of SOA tracers at Mt. Hua, a remote mountain location in China in summertime PM10 samples and across 9 PM size fractions. Measurements are used to evaluate the sources and sinks of SOA in this region, including atmospheric transport. Similar measurements have been reported in other nearby locations (Table 3) and the conclusions are not particularly novel. There are notable deficiencies in the manuscript in its present form: 1) statistical analysis is needed to appropriately evaluate the significance of the correlations presented, 2) further consideration of mineral ions in PM10 aerosol acidity is needed, 3) alternative explanations for their observations need to be considered. Particularly, the trend of

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increasing relative humidity and decreasing biogenic SOA tracers could alternatively be explained by scavenging of PM by precipitation. Additional details of the method and approach are requested in specific comments below. Thorough grammatical editing is needed prior to publication.

Major comments

1. Thorough grammatical editing is needed prior to publication.

2. The description of the flora surrounding the sampling site (section 2.1) should draw upon primary, peer-reviewed scientific literature, not a secondary source like Wikipedia.

3. There appears to be a significant amount of missing data in July 2009, as presented in Figure 3. The description of sample collection (section 2.1) should briefly address the reason for the missing data.

4. Table 2 should be reorganized so that compounds are grouped together in a meaningful way (i.e. isoprene tracers, monoterpene tracers, anthropogenic tracers, etc.). In addition, references should be added as supporting evidence for the "possible sources" of the designated tracers.

5. The discussion of results in section 3.1.1. and presentation of data in Table 2 require clear explanation of the meaning of numbers and errors. For example, are the values arithmetic means for each period? Are the errors analytical uncertainties or standard deviations?

6. It is unclear how an increased boundary layer height would cause an increase sulfate and nitrate concentrations (as suggested on page 17648, lines 11-12). Rather, an increased boundary layer would lead to more vertical mixing and thus decrease PM concentrations.

7. Are the differences in sulfate, nitrate, and o-phthalic acid concentrations in southerly and easterly air masses when compared to northerly air masses statistically significant? Or can the observed variation be ascribed to random variations in the data?

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A t-test comparing the two mean values is needed to determine whether the trend is significant, or not. In addition, are other tracers of anthropogenic activity (e.g. nitrate, EC, acidity) statistically different in air masses from different directions?

8. The author's use of isoprene tracer-to-OC ratios to evaluate isoprene emissions is erroneous (in section 3.1.3, page 17650, line 11-14). The ratio of tracer-to-OC is comprised of 1) the numerator – or isoprene tracer concentrations, which are a function of isoprene emissions, aerosol acidity, and availability of oxidants, meteorology (solar flux and relative humidity) and 2) the denominator – total OC concentrations, which depends on all primary, secondary, natural, and anthropogenic sources of organic aerosol in the atmosphere. Thus, the ratio of the isoprene tracers-to-OC is useful to evaluate the impact of isoprene-derived SOA relative to other OC sources, but does not provide direct insight to isoprene emissions.

9. Why do the authors choose the version of the AIM-II model to estimate aerosol acidity (page 17651, line 23-25), which only includes sulfate, nitrate, ammonium, and protons. As noted on page 17655, line 28, "coarse particles are generally basic, because they are in most cases enriched with mineral species". Excluding calcium and magnesium ions from the ion balance equation will certainly lead to an overestimation of acidity.

10. It appears that the authors have measured calcium and magnesium, as they indicate that these mineral ions were observed at high levels (page 17652, line 4). The authors should use these data to develop an improved estimate of aerosol acidity and estimate the magnitude of the bias introduced when excluding mineral ions from the aerosol acidity estimation.

11. The important role of mineral ions in the PM10 ion balance equation also needs to be considered when comparing PM10 data in this study to PM2.5 data from other locations (page 17652, first paragraph).

12. If the authors wish to evaluate their hypothesis that "mountain aerosols are more

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hygroscopic" (page 17652, line 9) they should utilize the measurements data collected at Mt. Hua when air masses were coming from different directions, rather than comparing to PM2.5 measurements from Hong Kong, which is a very different and geographically separate location.

13. The authors should provide their rationale for breaking the data into three groups when evaluating the effects of temperature on biogenic SOA formation (page 17652, line 15).

14. The author's discussion of the effects of relative humidity on biogenic SOA formation is based on the premise that they have measured (and understand) biogenic SOA formation. However, they have actually measured ambient biogenic SOA concentrations and have estimated biogenic SOA yields. The ambient SOA tracer concentrations are a function of its sources (SOA formation and transport) and its sinks (wet/dry deposition, aqueous phase processing, partitioning to the gas phase). Thus, the discussion should be framed around temperature and RH effects on biogenic SOA concentrations, instead of SOA formation.

15. The apparent trend in biogenic SOA tracer concentrations decreasing with relative humidity is largely explained by the author's observation that "sharp declines [of biogenic SOA tracers] during rainy days suggest a significant scavenging effect of wet deposition" (page 17652, line 11-12). The lengthy discussion about RH effects on LWC, pH, and acid-catalyzed SOA formation mechanisms is unnecessary and is not well supported by the data.

16. The authors state that "isoprene, a/b-pinene, and b-caryophyllene showed a significant negative linear correlations with relative humidity." However, they do not provide any evidence of the statistical significance of the correlation. Several critical calculations are currently missing; these include 1) a t-test for the significance of the slope at the 95% confidence interval and 2) the fraction of the variance that is explained by the variable of interest (relative humidity). As it is known that biogenic SOA concentrations

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are influenced by many factors, i.e. acidity, RH, and temperature, the authors should further consider multiple variables simultaneously using analysis of variance (ANOVA) techniques.

17. In the discussion of correlations among measured and modeled variables, the authors use both R (figure 4, page 17654 paragraph 3) and R2 (page 17653, paragraph 3). The authors should be consistent throughout the manuscript, using one or the other.

18. The authors need to clearly state what values were used for temperature and RH in Figure 4. Are these daily average, minimum, maximum concentrations?

Minor comments

19. Page 17645, line 6-7: The opening sentence of the second paragraph reads as an unsupported opinion. Please revise to: "China is a large and diverse source of aerosols and trace gases to the atmosphere."

20. The number of field blanks collected (section 2.1) should be clearly stated for the PM10 sampler and the Anderson 9-stage sampler.

21. The sentence describing how SOA tracers were quantified using surrogate standards (page 17647, line 15-19) should utilize "respectively" in the appropriate place so that it is clear which standard was used for each tracer.

22. Also, in section 2.2 the authors need to clarify their quantification approach for the analysis of SOA tracers. Was quantitation based on peak area or height? Was quantitation based on response of individual ions or the total in count (TIC)?

23. Typo at page 17647, line 28, "liquid water content (LWC)."

24. Table 2, footnote b – should be expanded to include pH and a brief statement of how pH and LWC were estimated (as was done for SOC mass concentrations).

25. Reference needed on page 17648, lines 15-17 supporting the designation of methyltetrols and 2-MGA as isoprene tracers.

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26. Please be more specific in the use of arabitol as a tracer for biological emissions on page 17649, line 10. In what type of biogenic emissions is arabitol found?

27. The authors need to be more specific in acknowledging the “AIM Model group” by stating this group’s affiliation and location.

28. Figure 2 is not referred to in the text and should be incorporated into section 2.2.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17643, 2013.