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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

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.

J. J. Li et al.

wanggh@ieecas.cn

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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 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. Response: We thank the reviewer's comments, which is very helpful for us to improve the paper quality. As suggested by the reviewer, we added more detailed information according to the specific comments. We have checked the text for grammar mistakes. Because the above comments also present below, we will answer all the questions one by one.

Major comments

1. Thorough grammatical editing is needed prior to publication.

Response: Suggestion taken. We have already checked the whole manuscript for grammar.

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.

Response: Suggestion taken. A published paper was cited in the section 2.1. See page 4, line 82-84.

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.

Response: Suggestion taken. "The samples of July 22∼25 and July 27-29 were not collected because of the power interruption". See page 4, Line 86-87).

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

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addition, references should be added as supporting evidence for the “possible sources” of the designated tracers.

Response: I think the reviewer was talking about Table 1, not Table 2, and the suggestion was taken. Table 1 was reorganized and the references are also added. See Table 1 on page 21-22.

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?

Response: Suggestion taken. The values are arithmetic means and the errors means standard deviations. Detailed information was added in the text and the title of Table 2. See page 6, line 140-141, and page 23, Table 2 title.

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.

Response: We agree the reviewer’s comment. We revised the related discussion (Page 7, Line 144-148)

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? 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?

Response: Suggestion taken. T-tests comparing the mean values were conducted by SPSS soft. Based the statistic results, we found that nearly all of the anthropogenic

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products (e.g. EC, SO42-, NO3-, NH4+, phthalic acids and levoglucosan) presented a p-value larger than 0.05, which statistically means there is no significant difference for these components between the three directions. Related discussion was revised. See page 8, Line 186-192.

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.

Response: We agree on the reviewer's comments and the related discussion was revised (Page9, Line 200-213).

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.

Response: Chemical reactions in aerosol phase or gas-particle distributions in aerosol surface are much linked to the actual pH (i.e., in-situ pH, pHIS) in the aqueous phase and liquid water content (LWC) of particles. However, direct measurements of pHIS have not been realized yet. Aerosol Inorganic Model (AIM) has been proved to be one of the best ways to indirectly calculate the pHIS and LWC at present (Xue et al, 2011; Budisulistiorini et al., 2013). However, all the four versions of AIM (I-IV) model have no

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regard for calcium and magnesium ions. Thus, we currently cannot estimate the exact effect of calcium and magnesium ions on in-situ acidity of aerosols.

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.

Response: We added the detailed information of four other cations including Na+, K+, Ca2+ and Mg2+ in the manuscript. The concentrations of the four cations in PM10 are about 1.0 μg m-3, and much lower than ammonium (4.3 μg m-3) (Table 2). It seems that the effect of mineral ions to aerosol acidity estimation was not so significant. However, as mentioned above, the model currently cannot estimate the effect of mineral ions such as Ca2+ and Mg2+.

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).

Response: We agree the reviewer's comment. The AIM model probably overestimated the aerosol acidity, because it excludes mineral ions, although the total concentration of Na+, K+, Ca2+ and Mg2+in the Mt. Hua PM10 samples are much less than that of NH4+. The related statements were modified. See page 11, line 244-247.

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

Response: Suggestion taken. See page 11, line 247-250.

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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).

Response: Suggestion taken. We re-wrote the sentence to make the rationale more clear. See page 11, line 256-258.

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.

Response: We agree on the comments above and have changed the subtitle see page 11, line 251, the subtitle of section 3.3 and page 12, line 268, the subtitle of section 3.4. We did not directly measure the BSOA formation process. Instead, we measured their concentrations and size distributions and estimated the effects of temperature and relative humidity on the BSOA yields to discuss their sources and formation mechanisms.

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.

Response: Certainly, rain has a scavenging effect and thus can decrease the BSOA concentrations. However, we found the suppressing effect of RH on BSOC yields does exist, because we found the negative linear correlation of BSOA concentration with

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RH become more significant when the samples collected on rainy days are excluded (see Figure 4r). Acidity of aerosol is dependent on RH, and acid-catalysis takes an important role during BSOA formation process. Such a suppressing effect of RH on BSOA formation was also reported by other researchers such as Zhang et al, 2011 and Budisulistiorini et al (2013). Our data do support our conclusion of the RH effects. See the section 3.4, page 12-13, line 289-299.

16. The authors state that "isoprene, ïĄąïĂŕïĄć-pinene, and ïĄć-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 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.

Response: Suggestion taken. A t-test was performed and the detailed statistic results of the correlations are shown in Table S1. We agree with the reviewer that BSOA concentrations are influenced by many factors. That is the reason why we use AIM mode to discuss the effects of RH and acidity of particles on BSOA yields. In fact, pHIS and LWC values calculated by considering multiple variables including T, RH and inorganic ions, so we didn't do a further multivariate statistics.

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.

Response: Suggestion taken. All R2 were changed into R.

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?

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Response: Suggestion taken. These values are daily average concentrations. Detailed information was added to the caption of Fig. 4.

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."

Response: Suggestion taken. Please see Page 3, Line 56.

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

Response: Suggestion taken. . Please see Page 5, Line 95-97.

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.

Response: Suggestion taken. Please see Page 6, Line 118-125.

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)?

Response: Suggestion taken. Quantification was based on peak area of individual ions. Please see page 5, line 115-116.

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

Response: Suggestion taken. Please see Page 6, Line 133.

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).

Response: Suggestion taken. Please see Page 23, Table 2.

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

Response: Suggestion taken. We added two references. See page 7, line 155.

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?

Response: Suggestion taken. Please see Page 8, Line 173-176.

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

Response: Suggestion taken. Please see page 16, Acknowledgements.

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

Response: We corrected the mistake. The figure was referred in the revised manuscript. Please see Page 5, Line 114-115.

Reference:

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K. and co-authors 2013. Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor. Environ. Sci. Technol. 47, 5686-5694.

Xue, J., Lau, A. K. H. and Yu, J. Z. 2011. A study of acidity on PM2.5 in Hong Kong using online ionic chemical composition measurements. Atmos. Environ. 45, 7081-7088.

Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, Atmos.

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Chem. Phys., 11, 6411-6424, 2011.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C7630/2013/acpd-13-C7630-2013-supplement.zip

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