[acp-2013-357]  
Observation of Biogenic Secondary Organic Aerosols in the Atmosphere of a Mountain Site in Central China: Temperature and Relative Humidity Effects

Dear ACP editor

After carefully reading the comments from the two reviewers, we have revised our manuscript. Our responses to the comments are itemized below.

Anything about our paper, please feel free to contact me at [wanggh@ieecas.cn](mailto:wanggh@ieecas.cn)

Best regards!

Sincerely yours

Gehui Wang

Oct. 2, 2013

**Anonymous Referee #1**

**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 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 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, pH*IS*) in the aqueous phase and liquid water content (LWC) of particles. However, direct measurements of pH*IS* have not been realized yet. Aerosol Inorganic Model (AIM) has been proved to be one of the best ways to indirectly calculate the pH*IS* and LWC at present (Xue et al, 2011; Budisulistiorini et al., 2013). However, all the four versions of AIM (I-IV) model have no 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.

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 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, -pinene, and -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, pH*IS* 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?

**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.

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. Chem. Phys., 11, 6411-6424, 2011.**Anonymous Referee #2**

**Overall Comment and Suggestion:**

Biogenic secondary organic aerosol (BSOA) formation is currently an active area of research within the atmospheric chemistry community. Understanding the environmental parameters and anthropogenic influences on BSOA remain unclear and certainly warrants further investigation. The authors of the present manuscript set out to measure known BSOA tracers from isoprene, monoterpenes, and sesquiterpenes using gas chromatography interfaced to mass spectrometry (GC/MS) with prior derivatization (i.e., trimethylsilylation) in order to determine their presence and abundance at Mt. Hua, which is a high altitude site within in China. With the quantitative chemical composition data they obtain using GC/MS applied to PM10 samples, they then set out to understand the effects of temperature and relative humidity (RH) on their formation. Furthermore, they investigate what size fractions these BSOA tracers are found in. Except for cis-pinonic acid, all of the measured BSOA tracers are found in the fine aerosol mode, which is not too surprising. The authors properly use the GC/MS method and I applaud them for using surrogate standards that closely resemble the compounds under investigation. Many of the compounds being measured lack commercially available authentic standards, and thus, this is the best they can do in order to quantify these compounds (I’m not complaining about this, but pointing out to the Editor that their selection of surrogate standards is quite appropriate). If I’m to evaluate this paper based on the goals the authors set out to achieve, I think they have done that. However, I must agree with Reviewer 1 that detailed statistics is lacking, especially when looking at the effects of RH. BSOA tracer data is certainly lacking in China, and thus, I think this paper could be publishable in Atmospheric Chemistry and Physics once the authors address my specific comments below, as well as Reviewer 1’s comments. I have additional comments that I would like to raise that were not raised by Reviewer 1. In order to be concise, I don’t want to repeat the same comments by Reviewer 1. I will state here that I completely agree with Reviewer 1’s assessment of this paper and I think the authors need to clearly address Reviewer 1’s concerns. By using the data set they already have here, I think the authors could restructure this manuscript to focus on a more scientifically interesting topic; specifically, what are the potential anthropogenic influences on BSOA formation? The authors certainly address this question in the current manuscript by looking at the correlations with in-situ aerosol acidity. Due to my concerns and Reviewer 1’s concerns, I must suggest that this manuscript be "accepted with major revisions noted."

**Response:** Many thanks for the reviewer’s comments, which is very helpful for improving our paper quality. As suggested by the reviewer, we revised the manuscript and itemized our response to the comments as follows.

**Specific comments:**

1.) Page 17650, Lines 1-3: The authors state: "Furthermore, the higher concentration of sulfate and nitrate can also enhance BSOA formation by an acid-catalyzed reaction"

This statement in the manuscript made me think of my point raised in the overall comment above about possibly restructuring this paper to focus on the influences of anthropogenic emissions on BSOA formation. Why didn’t the authors consider examining correlations of BSOA tracers with sulfate and nitrate data they obtained using IC? Also, do the authors have NOx and SO2 data at their site? If so, did they consider looking how these anthropogenic pollutants correlate with BSOA tracers? You also have EC data, so it would be interesting to know how that correlates with your BSOA data. In general, what can be learned from comparing these data to anthropogenic emission tracers?

**Response:** According to the Reviewer 1’s comments, t-tests comparing the mean values from different air masses were conducted and the results showed that nearly all of the anthropogenic products (e.g. EC, SO42-, NO3-, NH4+, phthalic acids and levoglucosan) presented statistically insignificant differences in the air masses from the south and east directions. In addition, we have already tried to look for the correlations between BSOA tracers and anthropogenic pollutants. However, no significant correlation between these compounds was found (see figures below). We do not have the data of NOx and SO2 data in the Mt. Hua atmosphere during the sampling period, which may impel us to conduct a more comprehensive observation in the future.



Fig. R1 Relationships between BSOA tracers and anthropogenic pollutants

2.) Experimental Section - Missing some isoprene SOA tracers:

Besides measuring the 2-methyltetrols and 2-methylglyceric acid, why didn’t the authors measure or report the C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols? I understand why the authors only quantified the 2-methyltetrols and 2-methylglyceric acid for purposes of using the Kleindienst et al. (2007, Atmos. Environ.) method. However, the C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols have been shown to be quite abundant in the S.E. USA region, especially the C5-alkene triols (Lin et al., 2013, ACP). The C5-alkene triols measured by GC/MS have been measured to be of similar abundance to the 2-methyltetrols in the S.E. USA region.

**Response:** Suggestion taken. We added detailed information about C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols in the PM10 and size-resolved samples. We also found that C5-alkene triols are of similar abundance to the 2-methyltetrols in the Mt. Hua region. Please see Table 2, Table 4, and section 3.1.

3.) Recoveries:

Why did the authors not use the recoveries measured from spiking filters with known amounts of the surrogate standards in the data they presented in this paper? This was unclear to me.

**Response:** Recovery experiment was done with succinic acid, glutraric acid, suberic acid, malic acid, phthalic acids, levoglucosan and arabitol. Averaged recoveries of the target compounds were better than 70%. Recovery experiment is a method for QA and QC. However, compounds used in a recovery experiment are usually pure agent while those in real samples are a mixture with other organic and inorganic components, which means that the recovery experiment could not entirely reflect the conditions of target compounds in the atmosphere. Thus, many documents report the data without a correction by recovery. For example, US ASTM method D 6209-98 for atmospheric PAH, the section 16.4.2 at page 12 notes that “Typically, measured PAH analyte concentrations are not corrected for surrogate recovery”. Therefore, in this paper the data reported were not corrected by the recoveries.

4.) Application of the Kleindienst et al. (2007, Atmos. Environ) SOA Tracer Method: Even though the authors use the Kleindienst et al. tracer method, this method has a lot of uncertainties associated with it. The authors need to acknowledge the fact that this tracer method was only developed under very limited experimental conditions of NOx, aerosol acidity, and RH. Thus, its application could result in major underestimates of the true BSOA contributions to total OC mass. For example, isoprene-derived epoxides (IEPOX and MAE) (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2013) produced from isoprene oxidation have been demonstrated to lead to SOA but depend on the level of aerosol acidity (and thus composition of pre-existing aerosol) and liquid water content (LWC).

**Response:** We agree with the review’s comment. We added a sentence “However, the tracer-based method (Kleindienst et al., 2007) was developed under very limited experimental conditions of NOx, aerosol acidity, and relative humidity. Thus, the estimated isoprene, α-/β-pinene and β-caryophyllene derived SOC might be underestimated in the current study” into text to noted the defect of the tracer method. See page 7, Line 163-166.

5.) Aerosol acidity estimates:

I agree with Reviewer 1’s concern about not considering the Mg2+ and Ca2+ in the aerosol acidity calculation. I’m surprised to see that the AIM-2 model was able to model aerosol acidity for all 34 samples. A lot of recent studies have had trouble being able to run this model due to low RHs or complete neutralization of the aerosol samples (e.g., Lin et al., 2013, ACP). Also, aerosol acidity is a difficult parameter to predict well, especially without considering the organic interaction. Recent work from Smith et al., (2012, ACP) showed that efflorescence and deliquescence RHs were affected by the miscibility of isoprene SOA material with ammonium sulfate particles. Of course, the models are still being developed to better account for interactions like this. Thus, the AIM-2 model (or even isopropia) really represent the best we can do at this time.

**Response:** We also believe that the AIM-2 model is one of the best ways to calculate aerosol in-situ acidy and LWC at present. The AIM model worked very well in the current study. All of the 34 data points can be input into AIM model and in-situ pH and LWC were successfully calculated, because the Mt. Hua aerosols are not neutralized, which are acidic ([H+]free=39-524 nmol m-3), and RH of the mountain air was high (45−99%) during the sampling period. In addition, we added the detailed information of four other cations including Na+, K+, Mg2+ and Ca2+ into the manuscript (Table 2 and Table 4), which is helpful for readers to understand the potential influence of these cations on aerosol in-situ acidity and LWC.

**Minor Comments:**

1.) Section 3.1.3:

The authors may want to note in this section recent work by Lin et al. (2013, ACP) and Ding et al. (2008, ES&T), especially since they found that the 2-methyltetrol contribution to OM and OC was 5% and 6%, respectively, in the S.E. USA region. The contributions of 2-methyltetrols are much more abundant in the S.E. USA region than found here in the current study.

**Response:** We thank the reviewer’s comments. We cited the work by Lin et al. (2013, ACP) and Ding et al. (2008, ES&T) in the manuscript (Page 9, Line 204-208 and Table 3). We noted that isoprene products are so abundant in the S.E. USA region.

2.) Page 17653, Line 11:

Change "tion, in contrast," to "tion. In contrast,"

**Response:** Suggestion taken. Please see Page 12, Line 273.

3.) Page 17653, Line 18:

Change "low NOx condition," to "low-NOx conditions,"

**Response:** Suggestion taken. Please see Page 12, Line 280.

4.) Page 17654, Line 4:

Change "researches" to "studies"

**Response:** Suggestion taken. Please see Page 13, Line 293.

5.) Page 17654, Lines 11-22:

When you are talking about RH improving BSOA yields and affecting composition, you should be more specific and state isoprene SOA. The RH effects on monoterpene and sesquiterpene SOA have not been fully analyzed in the laboratory.

**Response:** Suggestion taken. Please see Page 13, Line 300-301.

6.) Page 17654, Line 21:

Change "to conduct for understanding" to "in order to understand".

**Response:** Suggestion taken. Please see Page 13, Line 309.