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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.

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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 derivatiza-

tion (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. 1. 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.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C7640/2013/acpd-13-C7640-2013-supplement.zip

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

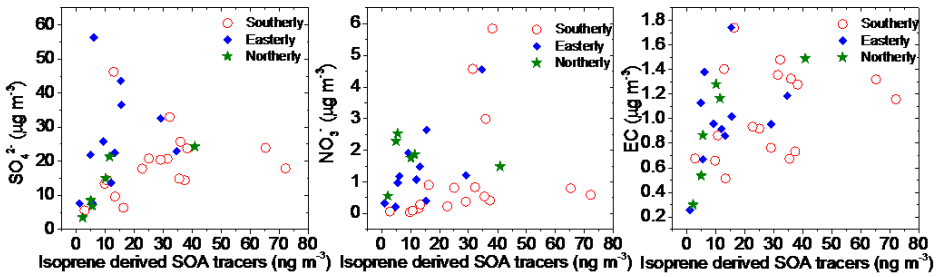

Fig. 1. Relationships between BSOA tracers and anthropogenic pollutants