

## Responses to Referee #2

### **General comments:**

*This manuscript deals with a detailed organic aerosol characterization/speciation study at a high mountain site in Central East China, and contains a valuable aerosol data set. The data are interpreted in the light of available current knowledge on secondary organic aerosol (SOA) formation processes and tracers, and the recent literature on this topic is fairly well cited. An interesting finding is that SOA formation from the photooxidation of isoprene is an important aerosol process at this high mountain site and is enhanced relative to ground level, and that it is more important than SOA formation from monoterpenes and sesquiterpenes. An issue of concern is the method used for the quantitative determination of the various tracers, as outlined in the specific comments. In the opinion of this reviewer a major revision is needed. The English usage also needs to be improved.*

**Response:** The authors are very grateful to the reviewer for his/her valuable comments on this manuscript. In particular, we have appreciated the general comments concerning the potential value of this study.

A substantial effort has been made to re-calculate the SOA tracers that were formerly quantified using surrogate compounds. The quantitative determination of these SOA tracers were performed using a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5), and a flame ionization detector (FID). It was assumed that the GC-FID responses of the trimethylsilyl derivatives of the compounds and their respective internal standards were equivalent because the ionization efficiencies in GC-FID are roughly proportional with the abundance of carbon atoms in the molecules. This technique has been successfully used in the quantification of isoprene SOA tracers (Claeys et al., 2004; Edney et al., 2005). We have also obtained a new standard of 3-hydroxyglutaric acid recently. In the revised manuscript, all the tables and figures will be modified accordingly. They are posted with the revised manuscript to avoid the redundancy in this response. More detailed methods will be given in the revision.

### **Specific comments:**

*Page 16943 – line 8: It is more correct to write: “All the biogenic SOA tracers did not show clear diurnal variations, suggesting that they are formed during long-range transport or over relatively long time scales.”*

**Response:** The sentence is changed following the reviewer’s suggestion.

*Page 16944 – line 9: I suggest to update this sentence and provide some information on recent global estimates of biogenic SOA: “In addition to monoterpenes and sesquiterpenes, isoprene is currently also believed to be a large biogenic source of SOA mass. Global model bottom-up estimates for biogenic SOA are in the range of 9 – 50 Tg C yr<sup>-1</sup> (Kanakidou et al., 2005), while recent top-down estimates, including isoprene SOA, are as high as 185 Tg C yr<sup>-1</sup> (Hallquist et al., 2009).” Ref.: Hallquist et al., ACP, 9, 5155-5236, 2009.*

**Response:** Thank you. This information has been added in the revised manuscript.

Page 16944 – line 3: I suggest to delete the sentence “They estimated its SOA production to be 2 Tg yr<sup>-1</sup>”, but to add some references containing more recent estimates in the last sentence of the paragraph: “. . . . . predicted SOA formation seriously (Henze and Seinfeld, 2006; Tsigaridis and Kanakidou, 2007).”

**Response:** The sentence has been deleted, and the references have been added in the revised manuscript.

Page 16946 – line 17: It is not clear how the calibrations were done for the quantitative determinations. The authors state on line 27 that the data were not corrected for the recoveries, but how did they account for losses during sample workup? This issue should be clarified.

**Response:** We will add the following information in the revised manuscript. “Quantification was conducted using calibration curves by analyzing aliquots of a stock solution of authentic standards that had been derivatized using the procedure mentioned above.” The sentence of Page 16946-Line 24-27 has been modified as “Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters and analyzed as same as samples (n = 3) were 94 ± 2.6% for *meso*-erythritol, 91 ± 5.5% for 3-hydroxyglutaric acid, 64 ± 5.9% for *cis*-pinonic acid, 93 ± 2.3% for *trans*-norpinic acid, and 79 ± 2.3% for pinic acid”.

Detailed information on sample workup procedure has been mentioned earlier in the submitted manuscript. In addition to these SOA tracers, we have analyzed the recoveries for many polar organic compounds such as sugars compounds (e.g., levoglucosan and glucose) and fatty acids by using the same technique. Recovery for levoglucosan was around 90%, which was comparable to those reported by other groups (Kourtchev et al., 2008). Relative standard deviation of the concentrations based on duplicate sample analysis was generally <10%, which has already been mentioned in the manuscript. Therefore, the uncertainties of sample workup are discussed with enough detail to our opinion.

Page 16947 – lines 15-16: the concentrations for the 2-methyltetrols given here differ from those given in Table 1. Please, check whether this is also the case for other tracer concentrations.

**Response:** The concentrations of 2-methyltetrols given here are the sum of 2-methylthreitol and 2-methylerythritol. In Table 1, we reported these two 2-methyltetrols individually to present their relative abundances.

Page 16947 – line 24: The report on the C5-alkene triols is not so recent anymore and dates already from 2005. I suggest to update this sentence and add a more recent relevant reference: “C5-alkene triols, which are also photooxidation products of isoprene (Wang et al., 2005) and unique isoprene SOA tracers under low-NO<sub>x</sub> conditions (Surratt et al., 2006), were detected.....”.

**Response:** Suggestion is taken.

Page 16950 – line 22: I suggest to rephrase two sentences: “As expected, MBTCA and 3-HG, which are higher-generation photooxidation products of *a/b*-pinene, did not show a peak during this episode. The enhanced concentrations of pinic and pinonic acids, which are lower-generation photooxidation products compared to MBTCA and 3-HG (Szmigielski et al., 2007; Kourtchev et al., 2009), suggest that the

*photooxidation of  $\alpha$ -/b-pinene was not complete.”*

**Response:** These two sentences have been changed in the revised manuscript as suggested.

*Page 16952 – line 9: I suggest to weaken the statement relating to the presence of norpinic acid and MBTCA in cluster 3: “. . . . are also in cluster 3, suggesting that these compounds may have the same source regions as the isoprene oxidation products.” The atmospheric behaviors of the isoprene and  $\alpha$ -/b-pinene SOA tracers are quite different, with the isoprene SOA tracers being much more polar/hydrophilic than  $\alpha$ -/b-pinene SOA tracers.*

**Response:** The statement has been weakened as suggested.

*Page 16954 – line 24: I feel the sentence “The relatively . . . . “ is redundant and suggest to delete it. It is fairly well established that isoprene SOA formation involves OH-initiated reactions (see line 20 just above).*

**Response:** The sentence has been deleted.

*Page 16955 – line 26: I suggest to rephrase this sentence: “Thus, we propose here that the  $R_{iso/mono}$  value can be used to estimate . . . .”; it is hard to consider this ratio as a tracer.*

**Response:** The sentence has been rephrased as suggested.

*Page 16956 – line 20: Comparisons with data available for European sites should also be included, i.e., Finland (Kourtchev et al., 2008a), Hungary (Ion et al., 2005) and Germany (Kourtchev et al., 2008b).*

**Response:** Suggestion is taken. We will add this information in the revised manuscript.

*Page 16957 – line 18: I suggest to delete the first part of this sentence (Due to the tracer-based calculation); I feel it is redundant.*

**Response:** The sentence has been deleted.

*Page 16957 – lines 11-12: Also here, I noted that the values differ from the ones given in Table 1.*

*Table 1: the authors should carefully check whether the values correspond with those reported in the main text.*

**Response:** All the values have been re-calculated in the revised manuscript.

*Technical corrections:*

*The English usage needs to be improved. I suggest that the revised version is copyedited. Below is a list of suggested corrections, but this list is certainly not complete.*

*Page 16943 – line 8: . . . tracers did not show clear . . .*

*Page 16943 – line 24: . . . at high altitudes . . . .*

*Page 16944 – line 4: . . . can have an impact on . . .*

*Page 16944 – line 18: . . . at high altitudes . . .*

*Page 16945 – line 11: . . . simultaneous measurements of ozone . . . and hydroxyl radicals. . .*

*Page 16945 – line 24: . . . the observatory . . .*

Page 16945 – line 26: . . . a high-volume air sampler.

Page 16946 – line 8: The GC instrument . . . . . (GC is the abbreviation for gas chromatography)

Page 16946 – line 12: . . . in the electron ionization (EI) mode . . . (the term “electron ionization” is recommended by IUPAC; the term “electron impact” is deprecated)

Page 16956 – line 13: . . . scanned in the m/z range 50 to 650.

Page 16946 – line 25: . . . onto pre-combusted . . . . .

Page 16948 – line 20: . . . 2 times higher than pinic acid.

Page 16948 – line 26: Two novel alpha-pinene SOA tracers were . . .

Page 16948 – line 29: . . . with UV-radiation . . .

Page 16949 – line 23: . . . . . did not show clear . . . . .

Page 16949 – line 25: . . . showed very similar temporal trends.

Page 16951 – line 6: . . . mainly originated from . . . . .

Page 16951 – line 14: . . . due to adsorption onto preexisting aerosol.

Page 16951 – line 22: . . . likely originate from forest fires in South China, since they enhance emissions of BVOCs.

Page 16952 – line 3: . . . is mainly associated . . .

Page 16952 – line 12: . . . the same pattern as that at daytime.

Page 16953 – line 18: . . . at high altitudes . . .

Page 16954 – line 8: . . . in the aerosol phase.

Page 16954 – line 20: Ozonolysis is a minor . . . . .

Page 16955 – line 6: . . . model study indicating that . . . . .

Page 16955 – line 15 (and other places in this paragraph): . . . at lower latitudes . . . at mid-latitudes, . . . at higher latitudes . . . . .

Page 16957 – line 25: . . . BVOC oxidation . . . . .

Page 16957 – line 6: . . . from aircraft observations that reveal very high OC mass loadings over the Northwest Pacific . . . . .

**Responses:** Thanks. All those points mentioned above have been corrected accordingly in the revised manuscript.

## References

- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P. and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303, 1173-1176, 2004.
- Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W. and Claeys, M.: Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO<sub>x</sub>/SO<sub>2</sub>/air mixtures and their detection in ambient PM<sub>2.5</sub> samples collected in the eastern United States, *Atmos. Environ.*, 39, 5281-5289, 2005.
- Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T. and Claeys, M.: Polar organic marker compounds in PM<sub>2.5</sub> aerosol from a mixed forest site in western Germany, *Chemosphere*, 73, 1308-1314, 2008.