

We appreciate the referee's valuable comments and thoughts on our paper. We have carefully revised the manuscript by taking account of the comments. Our responses to the specific comments are given below.

Responses to the comments of Referee#2:

Comment 1: Sampling Size: I would argue that this sampling period is rather limited. Do the authors worry at all that this is providing a very narrow window into what occurs at this site? How do you know this time is optimal for studying this chemistry at this site? It is unclear why this period was selected. This seems to be a major weakness of this study.

Reply 1:

Our previous study on the annual measurements of biogenic VOC fluxes showed that the fluxes were largest in July and August at the same study site (Mochizuki et al., 2014). On the basis of that study, we made the flux and VOC measurements as well as aerosol samplings during the period of 8 days in the current study. We have selected these specific 5 days for the ambient measurements, because some contrast of biogenic VOC emissions and subsequent SOA formation were expected to be observed in terms of photochemical activity and anthropogenic influence. Taking account of the referee's comments, we have mentioned the sampling period in the revised manuscript (section 2.1): *"Our previous study reported the annual measurements of biogenic VOC fluxes at the same site, which showed that the fluxes were largest in July and August (Mochizuki et al., 2014). The specific 5 days were selected for the ambient measurements, because some contrast of BVOC emissions and subsequent SOA formation were expected to be observed in terms of photochemical activity and anthropogenic influence. Although the measurements focused on the events over a 5-day period, the data were obtained under typical meteorological conditions at this study site in summer."* (Page 4, Lines 15-21)

Comment 2: Experimental Section: There clearly needs to be a subsection within the experimental section and likely corresponding SI section that provides the details of your PMF analyses. There is no way for the reader to know how well you conducted your PMF and why you ended up selecting 3 factors. Why not 4 or 5 or more? This absolutely needs to be included in a revised submission. How do we know if this PMF means anything, considering this is a statistical solution?

Reply 2:

According to the comment, we have now added a subsection 2.5 that provides the details of our PMF analyses.

“To investigate factors controlling the formation of biogenic SOA at the study site, we conducted a positive matrix factorization (PMF) (Paatero and Tapper, 1994). The PMF analysis was performed using the concentration values for the measured 17 gas/aerosol species including VOCs and organic tracer compounds as well as inorganic species in aerosols. The sum of the analytical uncertainty and one third of the detection limit values as the overall uncertainty to each input parameter. To find the number of sources, we have tested different number of sources (three to five) and found the optimal one with the most physically reasonable results. In this study, the number of sources was determined to be three to discuss factors controlling the formation of 2-MTLs and 3-MBTCA. These factors are discussed in section 3.4.” (Page 7, Line 26 - Page 8, Line 6)

Along with this, we have deleted the following sentences at the beginning of section 3.4.

“To investigate the factors controlling biogenic SOA formation at the study site, we conducted a positive matrix factorization (PMF) (Paatero and Tapper, 1994). The PMF analysis was performed for the collected samples including VOCs and tracer compounds as well as inorganic species in aerosols. The PMF analysis resulted in the deduction of three interpretable factors.”

Comment 3: SOA tracer analyses: How were the isoprene- and alpha-pinene-derived SOA tracers quantified? Ideally, authentic standards are preferable, as is starting to be done by other groups (Surratt, Claeys, Keutsch or Geiger groups). If ketopinic acid was used based on the Kleindienst et al. (2007, Atmos. Environ.), I don't think this is a good standard to use for all compounds and could affect the quantification reported here. The authors need to clarify. In a revised manuscript details of identification, quantification and how this was done is absolutely needed.

Reply 3:

According to the comment, we have made additional statement on the details of identification and quantification of the tracer compounds as follows.

“Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data. For the quantification of pinonic, pinic, and 3-hydroxyglutalic acids, their GC-MS response factors were determined using authentic standards. The standards were purchased from Sigma Aldrich and Wako Wako Pure Chemical. 2-Methylglyceric acid and 2-methyltetrols were quantified using the response factor of meso-erythritol, whereas 3-methyl-1,2,3- butanetricarboxylic and 3-hydroxyglutaric acids were estimated using the response factors of pimelic and malic acids, respectively.” (Page 6, Line 27 - Page 7, Line 2)

Comment 4: Aerosol Sampling:

I have several questions about the aerosol sampling:

a.) TSP is not ideal, especially in terms of size cuts. Most of the BSOA will be in the fine mode, so it isn't clear to me why TSP sampling was selected here?

Reply 4-a:

Our previous study showed that that a nonnegligible fraction of the BSOA mass resided in the coarse mode ($D_p > 2.5 \mu\text{m}$) in some cases observed at the forest site (e.g., pinonic acid, 2-MTLs) (Miyazaki et al., 2014). In order to collect the total mass of BSOA tracers discussed in the manuscript, we have sampled the TSP. Taking account of the referee's comment, we have added the following sentences in section 2.3.

“Our previous study showed that some of the BSOA mass resided in the coarse mode observed at the forest site (e.g., pinonic acid, 2-methyltetrols (2-MTLs)) (Miyazaki et al., 2014). In order to collect the total mass of the BSOA tracers, we sampled the TSP in the current study.” (Page 6, Lines 4-7)

b.) Precombustion of filters at 450°C for 6 hours may not be long enough. Why did the authors not consider higher temps (550°C) for 12 hours or longer? In addition, with TSP sampling, are the authors worried about any potential artifacts from gas-phase absorption or evaporation of semivolatiles? This issue needs to be addressed here. Why wasn't PM_{2.5} considered?

Reply 4-b:

We have analyzed our field blank filters for quality assurance. In fact, target organic compounds discussed in this study were not detected in the blanks. This supports that the time for the precombustion of filters at 450°C (6 hours) is long enough to avoid any contamination of filters on the target compounds under our analytical condition.

As the referee pointed out, the quartz fiber filters may adsorb gas phase compounds, causing positive artifacts. On the other hand, semi-volatile compounds collected on the filter may evaporate, which may result in negative artifacts. These artifacts are possible for any filter-based measurements. With regard to these possible artifacts, we have added the following sentences in section 2.3.

“It is noted that the quartz fiber filters may adsorb gas-phase compounds, which may cause an overestimate of the mass of the target compound (positive artifacts). On the other hand, it is possible that semi-volatile compounds collected on the filter may evaporate, which may underestimate the mass of the target compound (negative artifacts). However, it is difficult to quantify these effects for ambient conditions in the current

study.” (Page 6, Lines 13-17)

“Additionally, field blank filters were analyzed for quality assurance. The target organic compounds discussed in this paper were not detected in the blanks.” (Page 7, Line 2-4)

Comment 5: Discussion of known mechanism of SOA formation and how this relates to acidity and NO_x is lacking:

I’m surprised there was no mention of the likely importance of isoprene epoxydiols (IEPOX) formed under HO₂-dominant conditions (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T; Lin et al., 2014, ES&T; Nguyen et al., 2014, PNAS; Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters). It has been shown that the presence of wet acidic sulfate seed aerosol controls the uptake of IEPOX in forming SOA, including the 2-MTs. I’m curious to know why the authors didn’t consider calculating aerosol acidity using their inorganic aerosol data and met data using one of the available thermodynamic models, such as ISOROPPIA II (Guo et al., 2014, ACP) from Thanos Nenes group at GA Tech. You could explore how acidity correlates to these compounds. In addition, how do these compounds correlate to sulfate levels?

Reply 5:

According to the referee’s comment, we have added the following sentences in section 3.4.

“Recent studies have suggested that 2-MTLs can be formed via reactions of reactive intermediates, isoprene epoxydiols (IEPOX) (e. g., Surratt et al., 2010, Lin et al., 2014). It has been shown that isoprene SOA is enhanced in the presence of acidified sulfate seed aerosol, where acid-catalyzed particle-phase reactions increase the uptake of IEPOX (e. g., Surratt et al., 2010, Lin et al., 2014). In order to examine the effects of aerosol acidity on the formation of 2-MTLs, we measured pH in the water-extracted samples (section 2.3) which offers insights into the aerosol acidity. The resulting pH of the water-extracted samples ranged from about 4.2 to 6.4, indicating that the observed aerosols were generally acidic. The 2-MTLs concentrations showed a negative correlation with pH ($r^2 = 0.45$) and a positive correlation with the SO_4^{2-} concentrations ($r^2 = 0.31$). This relation between 2-MTLs and indicators of the acidity supports that the aerosol acidity likely contributed to the formation of 2-MTLs at the forest site.” (Page 14, Lines 5-16)

In this context, the following sentences have been also added to the text: ***“The quartz fiber filters were also used to determine pH in the water-extracted aerosol samples. A portion of the filter was extracted with 30-ml ultrapure water. The pH of the water extracts was measured with a Horiba D-21 pH meter using an electrode (Miyazaki et al., 2014).”*** (Page 7, Lines 11-13)

Comment 6: Discussion of relevant new pathways related to alpha-pinene SOA:

I suspect ozone chemistry might explain your higher levels of alpha-pinene SOA. If so, how do your results fit into the context of recent work on ELVOC chemistry (Ehn et al., 2014, Nature)? It is now thought that ELVOC chemistry explains most of the SOA mass from alpha-pinene + O₃.

Related to this, based on your ozone measurements at the site, do you expect the lifetime of alpha-pinene to be shorter with O₃ than with OH? You should consider at least doing a back-of-the-envelope calculation.

Reply 6:

Recent studies showed that ELVOC and 3-MBTCA are formed via different reaction pathways originating from α -pinene. Because the ELVOC are shown to form at significant mass yield, the formation of 3-MBTCA via OH and O₃ reactions with α -pinene is likely linked with the formation of ELVOC via reactions of α -pinene with O₃. Although we have not discussed the total amount of SOA in this paper, the observed increase in the 3-MBTCA and O₃ levels on 10 and 17 July indicates that the formation of ELVOC and their contribution to the total SOA mass were likely significant.

Taking account of the referee's comment, we have added sentences in section 3.4.

“More recently, Ehn et al. (2012, 2014) and Schobesberger et al. (2013) have observed highly oxidized multifunctional organic compounds (i.e., extremely low-volatility organic compounds (ELVOCs)) based on laboratory experiments and ambient measurements at a boreal forest site. ELVOCs can be formed by the ozonolysis of α -pinene. Because the ELVOCs are shown to form at significant mass yield, the formation of 3-MBTCA via OH and O₃ reactions with α -pinene is likely linked with the formation of ELVOCs. Although we have not discussed the total amount of SOA in this study, the observed increase in the 3-MBTCA and O₃ levels on 10 and 17 July indicates that the formation of ELVOC and their contribution to the total SOA mass were expected to be significant.” (Page 15, Lines 1-10)

The lifetime of α -pinene with OH is estimated to be ~3.4 h at 25°C assuming the OH concentration of 1.5×10^6 molecules cm⁻³. Meanwhile, the lifetime of α -pinene with O₃ is ~4.6 h based on our O₃ measurement data (~30 ppb). Description on this simple estimation has been also added to the text. (Page 12, Lines 16-18)

We have added the following papers to the reference list.

Reference

Lin, Y. H., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K. E., and Surratt, J. D.: Light-absorbing oligomer formation in secondary organic aerosol from reactive uptake of isoprene epoxydiols, *Environ. Sci. Technol.*, 48, 12012-12021, 2014. (Page 20, Line 8-11)

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *PNAS*, 107(15), 6640-6645, 2010. (Page 22, Line 7-9)

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel T. M.: A large source of low-volatility secondary organic aerosol, *Nature*, 506, 476-479, 2014, doi:10.1038/nature13032. (Page 17, Line 10-16)

Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Maso, M. D., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, Th. F.: Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, *Atmos. Chem. Phys.*, 12, 5113-5127, 2012. (Page 17, Line 6-9)

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M., and Worsno, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, *PNAS*, 110(43), 17223-17228, 2013. (Page 21, Line 21-29)