

Responses to the comments of Referee#1

General comments:

Manuscript entitled “Origin of secondary fatty alcohols in atmospheric aerosols in a cool-temperate forest based on their mass size distributions” to investigate the origin and formation of secondary fatty alcohols (SFAs) based on their mass size distribution in aerosol samples obtained from a deciduous forest site. This manuscript gives us a clearer understanding of the five SFAs and their mass size distributions in the forest environment for the first time. The author concluded that the mass concentrations of SFAs were the highest in spring and the mass size distributions were highly correlated with bulk WIOC. Furthermore, SFAs were induced that mainly originated from plant wax from the results of the aerosol and leaf samples. This study provides new insights into possible source of primary biological aerosol particles (PBAPs) and their effects on the ice nucleation activity of aerosol based on seasonal changes in particles. Finally, these results demonstrated that the different growth stages of plants can result in differences in the size distributions of PBAPs. The Reviewer supports this manuscript for publication in *Biogeosciences* if the authors could carefully address the following comments.

Reply: We appreciate the referee’s valuable comments on our work. Our responses to the specific comments and details of the changes made to the manuscript are given below.

Specific comments:

1. Why did the authors analyze only spring, summer, and autumn atmospheric samples, but not winter samples? In my opinion, the winter sample can be used as a blank comparative analysis, excluding the interference of other environmental factors. Please explain it in detail.

Reply 1: Our previous study on source apportionment of organic aerosols at the same forest site suggested that majority of aerosols originated from the local forest in spring, summer, and autumn (Miyazaki et al., 2012). On the other hand, the observed aerosols in winter were significantly affected by marine and

anthropogenic sources rather than showing blank or background levels at this forest site (Miyazaki et al., 2012). Because we focused on effects of forest vegetation on SFAs in aerosols, we have not shown the data in winter in this study. To clearly mention this, we made additional statement as follows:

P.2 L. 30: *“Indeed, the source apportionment study suggested that majority of aerosols originated from the local forest in spring, summer, and autumn, whereas the observed aerosols in winter were significantly affected by marine and anthropogenic sources (Miyazaki et al., 2012). Because we focus on effects of forest vegetation on SFAs in aerosols, the data obtained in spring, summer, and autumn are shown and discussed in this study.”*

2. Page 2 Lines 32-33: Why is the particle size only analyzed to 10 μm ? This is very confusing, 10 μm is represent the maximum particle size or larger than 10 μm ? How is the particle size measured? If it is based on the sampler, you may be able to try more levels of impactors.

Reply 2: The top stage of the impactor collected particles with diameter larger than 10 μm ($D_p > 10 \mu\text{m}$) as we described in the original text. The particle size cut was based on theoretical calculation which was reflected to the structure of impactor. In general, atmospheric residence time of larger particles with diameters of tens of micrometer is very short (e.g., an order of mins to tens of mins), which may not have significant impact on atmospheric chemical field. We believe that the data shown in our study can be a useful reference for further studies on aerosol SFAs.

3. Humidity can influence the particle size distribution. Did the authors consider environmental factors (such as humidity) in the analysis.

Reply 3: First of all, the sampling was made without temperature or humidity control in this study. We agree that relative humidity can influence the particle size distribution. However, SFAs are water-insoluble fractions of organic aerosol which might be less hygroscopic, and their size distributions may be less affected by relative humidity. Indeed, in our study, the size distributions of SFAs did not necessarily show the peak in the larger size ranges in summer, when relative humidity is highest in all the seasons at the site. Rather, our data suggested that

the mass concentrations and their maximum size range was more influenced by the plant activities or age as we discussed in the manuscript. As the referee pointed out, the following description has been added in the revised manuscript:

P.11 L. 36: “*It is noted that relative humidity can influence particle size distribution. However, SFAs are water-insoluble fractions of organic aerosol (Fig.4) which might be less hygroscopic, and their size distributions may be less affected by relative humidity. Indeed, the size distributions of SFAs observed in this study exhibited peaks in the larger size ranges in spring, despite the highest relative humidity was observed in summer at the site, suggesting insignificant effects of relative humidity on the size distributions in this study.*”

4. Page 2 Line 34-36: For the analysis of SFAs, the authors choose the sampling time of 1 week and at a flow rate of 120 L min^{-1} , this indicating that the concentration of SFAs is lower. So please explain the atmospheric significance of analyzing SFAs and its seasonal variations.

Reply 4: As we described in the *introduction* section, the seasonal variations in the mass concentration and size distributions of SFA provide important clues for understanding its origin. Because SFAs were measured as “molecular tracers” of origin of aerosols, the low concentration does not mean that it is not important. Rather, SFAs reflect the changes of the activity of local vegetation in different seasons as shown in this study. Our study suggested that SFAs originated from plant waxes, the emission strength of which is likely controlled by the seasonal difference of plant growth. The significance of analyzing SFAs is that such new tracers of PBAPs provides new insight into biogenic sources of organic aerosols and their impact on ice nuclei activity.

5. Page 3 Lines 16-17: “a quarter of each sample filter with an area of 10.18 cm^2 was extracted using a mixture of dichloromethane and methanol (2:1, V:V)”. Why did the author choose the mixture of dichloromethane and methanol (2:1) as the extracted solution?

Reply 5: The method using mixture of dichloromethane and methanol has been already established as an optimal solvent for the extraction of organic compounds in aerosol samples. We adopted the optimal extraction method used in many of

previous studies (Fu et al. (2009) and many of other relevant studies). Furthermore, Miyazaki. (2019) successfully extracted and measured five compounds of SFAs in aerosol samples obtained at forest sites. Therefore, we also used this optimal method in this study.

6. Page 7 Figure 3: Why is the error bar so large for the spring and summer samples in Figure 3?

Reply 6: Three sets of samples were used for the calculation of average values in each season. In spring and summer, concentrations in one sample set were significantly different from those in the other two sample sets, which resulted in the large error bars despite the similar size distributions among the three sets. One possible explanation is that precipitation that occurs in summer and spring (Miyazaki et al., 2012) caused decrease in the concentrations of aerosols. Because the shape of size distributions of aerosol SFAs was similar in each season, we believe that this does not significantly affect our conclusions. To clarify the statement, we have added the sentence as follows:

P.6 L. 10: *“The large standard deviation shown in Fig. 3 can be partly explained by the effect of precipitation that occurred in spring and summer (Miyazaki et al., 2012), which might cause a decrease in the concentrations of SFAs in aerosols.”*

7. Page 9 Figure 7: In the seasonal variation shown in Figure 7, the mass size distribution does not change significantly compared with Figure 11.

Reply 7: Figure 7 shows the seasonal changes in the size distributions of two molecular tracers of PBAPs in color, which are different from those of *n*-nonacosan-10-ol summarized in Figure 11. The difference and similarity in the size distributions between Figure 7 and Figure 11 are discussed in the section 3.3 as well as shown in the original Figure 10.

8. Page 12 Figure 10: It is suggested that the author place Figure 10 into the supplementary material.

Reply 8: As the referee suggested, Figure 10 has been moved to the supplementary material in the revised manuscript.

References

- Fu, P., Kawamura, K., Chen, J., and Barrie, L.: Isoprene, monoterpene, and sesquiterpene oxidation products in the high Arctic aerosols during late winter to early summer, *Environ. Sci. Technol.*, 43, 4022–4028, 2009.
- Miyazaki, Y., Fu, P., Kawamura, K., Mizoguchi, Y., and Yamanoi, K.: Seasonal variations of stable carbon isotopic composition and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, *Atmos. Chem. Phys.*, 12, 1367-1376, doi:10.5194/acp-12-1367-2012, 2012.
- Miyazaki, Y., Gowda, D., Tachibana, E., Takahashi, Y., and Hiura, T.: Identification of secondary fatty alcohols in atmospheric aerosols in temperate forests, *Biogeosciences*, 16, 2181-2188, <https://doi.org/10.5194/bg-16-2181-2019>, 2019.