Responses to Referee #3

General comments:

This paper provides the data regarding the biogenic SOA tracers of isoprene, monoterpenes, and β-caryophyllene oxidation products in high mountain regions of Central East China in early summer. In addition, the temporal variations, possible sources, relationship with other species (OH, O_3, NOx) as well as the reasons of enhanced contribution of isoprene oxidation products are further investigated in this study. The study is valuable for more understanding of the contribution of biogenic volatile organic compounds to the secondary organic aerosol (SOA) in high mountain regions. Nevertheless, the main thrust of this paper is to use observation data to draw conclusions on the contribution of SOC derived from biogenic volatile organic compounds to organic carbon (OC). The quantitative determinations and calibration of these biogenic SOA tracers plays a decisive role for the results. In this study, many biogenic tracers were estimated by using the response factors of surrogates due to the lack of authentic standards. It's hard to convince the readers of the results discussed in the paper. Furthermore, this paper also has many controversial discussions, inferences and conclusions, which are not clearly expressed and not supported by substantial evidences (see specific comments). These shortcomings need to revise. In my opinion, the results presented for high mountain region of Central East China is valuable and could be considered for publication after the specific comments below have been carefully addressed, especially for quantitative determinations.

Response: The authors would like to thank for this reviewer for the valuable comments and suggestions on this manuscript. We understand that the main concern is about the usage of the surrogate compounds for quantification in this study, which has also been pointed out by other reviewer. Recently we have purchased a new standard of 3-hydroxyglutaric acid. Now in our study, we improved the quantitative determination of SOA tracers because the concentrations of pinic, pinonic, norpinic and 3-hydroxyglutaric acids have been quantified using authentic standards.

In the revised manuscript, an effort has been made to re-calculate the SOA tracers (e.g., 2-methyltetrols, 2-methylglyceric acid) 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 to the abundances of carbon atoms in the molecules. This technique has been successfully used in the quantification of isoprene SOA tracers such as 2-methyltetrols (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006).

In the revised manuscript, discussions and conclusions are modified accordingly to all the reviewers' comments. Tables and Figures are also changed accordingly and posted with the revised manuscript to avoid the redundancy in this response. We are confident that our manuscript has been greatly improved after revision.

Specific comments:

Page 16944 Lines 10-11: Monoterpenes..., global model estimates about 12-70Tg /yr, Hallquist et al., ACP, 9, 5155-5236, 2009, has updated estimation.

Response: This information is added and the reference is cited in the revised manuscript.

Page 16945 Lines 2-6: The sampling site on Mt. Tai above or under PBL may affect the nighttime results presented in this study. How do the authors distinguish that the sampling site on Mt. Tai is above or under PBL in the nighttime? Could the authors provide which periods the site existed in the free troposphere?

Response: During the MTX2006 campaign, Takigawa et al. (unpublished data) have estimated the diurnal variation of PBL height at Mt. Tai by using a WRF/Chem model. Their results showed that the averaged PBL height during night-time (18:00-6:00, local time) was around 800 m, which is lower than the sampling site at the top of Mt. Tai (1534 m, a.s.l.). This point has been mentioned in the revised manuscript.

Page 16946: With regard to quality assurance of SOC tracer analysis, I suggest the authors should add more statements (e. g. interlab comparison or more quality assurance of SOC tracer analysis) to strengthen the reliability of data.

Response: Suggestion is taken. We add several references and the information of base ion fragments for quantification. The recovery of the newly available standard 3-hydroxyglutaric acid (91±5.5%) is mentioned in the revised manuscript.

Page 16950 Lines 15-28: A suggestion for this paragraph. It would be better to have other measurements of radiation or aging indicators to support the lower degree of photochemical process during 8–10 June.

Response: Suggestion is taken. We find that the temporal variations of the ratio of NO_x/NO_y showed exceptionally high values during 8-10 June, which further suggesting the intrusion of fresh air mass during this period. This information has been added in the revised manuscript.

Page 16951 Lines 4-7: The fair correlation (R^2=0.52) between levoglucosan and β-caryophyllene oxidation products is insufficient to support that β-caryophyllinic acid detected over Mt. Tai was mainly originated from biomass burning process in early summer. Those two compounds may be derived from same source regions and/or have similar atmospheric transport. This statement needs to be made with caution.

Response: We have changed the sentence "…levoglucosan and β-caryophyllinic acid showed a positive correlation (R^2 = 0.52, Figure 2b), indicating that they mainly originated from biomass burning process in early summer." to "levoglucosan and β-caryophyllinic acid showed a positive relation (R^2 = 0.52, Figure 2b), indicating that they mainly originated from biomass burning process in early summer or from the same source regions."

Page 16951 Lines 10-12: It needs some references to support that burning of wheat straws in field or lab experiments releases levoglucosan and sesquiterpenes such as β-caryophyllene to a certain quantity. In addition, it also needs some references to support the statement "Forest fires enhance the emissions of BVOCs" on Page 16951 Line 23.

Response: To the best of our knowledge, there is little documented information on the release of sesquiterpenes from the burning of wheat straws. We have carefully revised the statement as follows: "Although little is known about the specific sesquiterpene emissions of wheat straws, crop species such as corn and potato have been found to emit sesquiterpene species including β-caryophyllene (see Duhl et al. 2009, and references therein). Studies, which examined the temperature-dependency of sesquiterpene emissions, have found that emissions are positively correlated with ambient temperatures (Duhl et al., 2008). Thus, the active field burning activities of wheat straws in the CEC during early summer may release levoglucosan and sesquiterpenes such as β-caryophyllene to a certain quantity through either combustion process or increasing leaf temperature, which is still poorly understood and warrants further study".

Page 16952 Lines 3-4: It would be better to further interpret why 3-HG, a SOA tracer of monoterpene, had good correlation with malic acid and belonged to cluster 1 (emissions from biomass burning).

Response: We have added the following sentences in the revised manuscript. "Although 3-hydroxyglutaric acid can be generated in chamber experiments from the oxidation of α-pinene in the presence of NO_x (Claeys et al., 2007), its formation mechanism is still unclear. Gómez-González et al. (2008) suggested that the isomer of 3-hydroxygluratic acid, 2-hydroxyglutaric acid, may also result from the oxidative decay of unsaturated fatty acids (UFAs), which is similar to malic acid. In this study, the temporal variations 3-hydroxyglutaric acid showed concentration peaks during biomass burning events 1 and 2. Such peaks were also found for malic acid (Fu et al., 2008). However, the active field burning of wheat straws should not enhance the emission of α-pinene, the precursor of 3-hydroxygluraric acid. Alternatively, the significantly high loadings of organic aerosols during E1 and E2 (averaged OC level was about 57 μgC m^{-3}) may influence the gas/particle partitioning of these compounds. In addition, the co-emissions of UFAs and α-pinene from biogenic sources may also be one of the potential reasons to explain the correlation between malic acid and 3-HG observed in this study".

Page 16953 Lines 17-18: Do the authors mean that the isoprene oxidation products are more abundant than "other biogenic SOA precursors" or "other biogenic SOA"?

Response: We have modified the sentence as "This also suggests that the isoprene oxidation products are more abundant than other biogenic SOA in the atmosphere at high altitudes in Central East Asia".

Page 16954 Lines 2-5: The unit of concentration should be mentioned here, is it μg/m3 or μgC/m3?

In addition, authors should more clearly explain why the atmospheric concentrations of isoprene over Mt. Tai about twice higher than those of pinene indicates that both of them (especially isoprene) were not completely oxidized during the transport from their ground sources to the summit of Mt. Tai. Were isoprene and pinene all from the ground sources? Furthermore, why especially for isoprene?

Response: They are mixing ratios. We will add the following discussion in the revised manuscript. "The emissions of biogenic VOCs were mainly from nearby trees or the local biosphere on the mountain slopes, over which the air masses have traveled as the daytime upslope wind. During the MTX2006 campaign, the CO_2 concentrations were measured at the sampling site with a regular daytime drop (nighttime average (21:00–03:00) – daytime average (09:00–15:00) = 3.8 ppb (Komazaki et al., unpublished data, 2006)), suggesting the possibility that the air mass is influenced by the vegetation". The averaged mixing ratios of isoprene and Σmonoterpene at midday over Mt. Tai were 0.28 and 0.19 ppb, respectively. This is mainly influenced by the vegetation type surrounding the sampling site, emission or oxidation rates of BVOCs, etc. We will delete the words "especially isoprene" in the revised manuscript.

Page 16954 Lines 6-11: In addition to the influence of temperature on gas/particle partitioning, some other factors could also affect Riso/mono at daytime and nighttime, such as humidity, and the sampling site above or under PBL. It would be more considerate to taking into all these factors account.

Response: The information of the PBL height during the campaign, as mentioned above, will be added in the text. The factors suggested by the reviewer will be considered.

Page 16954 Lines 14-15 and Fig.5: It is difficult based on Fig.5 to detect that higher Riso/mono values are observed when O3 and NOx concentrations are higher. The correlation coefficients should be mentioned in the text.

Response: We have modified the hour-based mixing ratios of O_3 (or NO_x) to day- and night-based values. There is no linear correlation found between $R_{iso/mono}$ and O_3 because the levels of O_3 were generally high throughout the campaign. However, we still believe it is valuable to keep the temporal trends of O_3 and NO_x in the figure. As suggested by Reviewer #1, the information of [NMHCs]/[NO_x] will be added in the revised manuscript.

Page 16954 Line 27-Page 16955 Line 6: The cloud processing needs to be interpreted. In this paragraph, I cannot find why high NOx supported the enhanced contribution of isoprene oxidation products.

Response: During sampling, brown clouds (polluted clouds) were occasionally observed uplifting from the mountain waist to the mountaintop in the late afternoon to early evening. Ervens et al. (2008) reported an enhanced SOA formation from isoprene in the presence of NOx. They suggested that such a finding might help to explain the observations that particulate OC of mostly biogenic origin correlated with anthropogenic tracers (de Gouw et al., 2005; Weber et al., 2007). This

information will be added in the revised manuscript.

Page 16957 Lines 6-11: Please specify why high levels of pollutants enhance the SOA formation rates. It is not mentioned in the text. In addition, the next conclusions (P16957, L25 - P16958, L3) are also not mentioned or discussed in the text.

Response: As also suggested by Reviewer #1, we deleted these sentences here. Instead, we will briefly mention the limitations (such as a lack of information on organosulfates) and future needs in the Conclusion section.

Page 16958 Lines 3-7: The authors concluded that the high isoprene-derived SOA observed in the high altitudinal aerosols over Mt. Tai is consistent with previous findings from aircraft observation that very high OC values over Northwest Pacific during the ACE-Asia campaign. Did the ACE-Asia campaign also find high isoprene-derived SOA over Mt. Tai?

Response: No. Only high loadings of organic carbon have been reported over East Asia during the ACE-Asia campaign. Our results should be the first to measure the biogenic SOA tracers at high altitudes over this region. We will add the following sentence at the end of the Conclusion section: "However, further field studies such as aircraft measurements of biogenic SOA tracers over China are clearly warranted".

References

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