Reviewer 2

We would like to thank for the valuable comments from the reviewer.

Authors present the results obtained during a 20 days field campaign carried out in a coniferous forest mountain region at Whistler (British Columbia, CA). Results presented combine mainly HR-ToF-AMS for NR submicron aerosol composition, PTR-ToF-MS for VOCs mixture composition and OH-CIMS for OH measurements. This dataset is undoubtedly of prime interest for the scientific community.

However, I suggest to complete the data analysis with local meteorological data and in particular wind direction and in a lesser extend wind speed (if any) in order to draw more robust conclusions. As mentioned by the authors "mountains flow (...) contribute to the diurnal variations in chemistry at the site". From my experience, I'd go further. Slope winds alternation can be one of the main drivers of the atmospheric concentrations in such environment. For example, the sharp morning decrease of monoterpenes concentrations is most probably due to a breeze alternation than pure chemical processes. It seems that these dynamic aspects are treated in MacDonald et al (in prep), but without a clearer idea of wind direction influences it is difficult for me to fully validate the conclusions of the paper. Also is there a difference between periods (ie. Biogenic and Biogenic/anthropogenic period) in terms of wind patterns? In other word can the authors add the wind direction diurnal cycle (in fig 4 or 5) and any relevant polar plots in the main text (and/or SI) and add an in-depth discussion of the effect of local meteorology on their observations.

Response: Thanks for the reviewer's comment. We agree that the scientific quality of this manuscript can be significantly improved if wind direction and speed are included in the data analysis. Therefore, time series and diurnal profile of wind direction and speed have been added to Figure 1 and 4, respectively, to complete the data analysis. As shown in Figure 1, diurnal patterns of wind direction are similar between biogenic period (Period 1) and the period with a mix biogenic and regional background influences (Period 2). However, it is worth noting that relatively strong downslope wind was observed when BSOA and BVOCs accumulated in Whistler during the early period of biogenic episode (Figure 1c), which has been highlighted in the revised manuscript. Since regular wind patterns due to the transition of upslope and downslope wind occurred throughout the sampling period, the potential impacts of wind direction to gas- and particle phase species can be clearly observed in Figure 1 and 4, and hence no polar plots are added to the revised manuscript.

Furthermore, we discuss the potential influences of mountain flows (upslope vs. downslope wind) on the observed monoterpene mixing ratios and background OA plus sulfate in Section 3.3 and the related paragraphs have been modified as shown below.

"Monoterpene mixing ratios were highest during the night and then dropped rapidly in the morning (Figure 4c), which can be a combined effect of chemistry and meteorological condition. Firstly, monoterpene emissions generally increase with ambient temperature. This observation indicates that monoterpenes were rapidly oxidized once the concentrations of ozone and OH radicals built up during the daytime. Secondly, the increased mixing depth in the morning and alternation of mountain flows from downslope (~150^{o}) to upslope (~250^{o}) wind at around 7:00-9:00 LT (local time, UTC -8 hours, Figure 4a) might contribute to this observation if the surface layer had relatively low monoterpene mixing ratios. However, additional BVOCs measurement in the valley is required to confirm this argument. Furthermore, monoterpene mixing ratios gradually increased in the afternoon likely in response to the decreasing levels of atmospheric oxidants rather than the transition of upslope to downslope wind in the late afternoon. It is worth noting that a relatively strong downslope wind was observed when BSOA and BVOCs accumulated in Whistler during the early period of biogenic episode (Figure 1c)."

"The diurnal variations of background OA and secondary sulfate that was nearly neutralized by ammonium (Figure S13) are almost identical, and their concentrations peak at around 17:00 LT (Figure 4d). Ozone level also peaks at about the same time. These observations indicate increasing influences of the regional background air mass in Whistler in the late afternoon. Upslope wind likely carried the aged regional aerosol particles to the sampling site and their mass loadings decreased when the transition of upslope to downslope wind occurred. The background OA can be successfully separated from the BSOA components using the PMF analysis. Comparing the total OA, the BSOA components, and the background OA, it is clear that the total organic mass within the biogenic period was not strongly influenced by anthropogenic sources and/or transported air masses (Figure 1g). "

My second main point is related to the f91 discussion and especially the comparison to previous studies. The recent intercomparison exercise of ACSMs (+ToF-AMS) highlighted a significant variability of the fX ratios from one instrument to another (Fröhlich et al, 2015). The discrepancy is much more marked for f44. This section should thus be rewritten/adapted in the light of these recent findings, and the conclusions should probably be smoothed.

Response: Thanks for the reviewer's comments. We have highlighted this recent finding in the revised manuscript and pointed out that the comparisons of f91 values between different studies are only semi-quantitative. In addition, since the discrepancy is much more significant for f44 values, we have removed discussion that was largely based on the comparisons of f44 and f43 values in Section 3.5. Nevertheless, we believe it is reasonable to keep the following two conclusions in the revised version based on the f91 analysis: 1) heterogeneous oxidation of BSOA-1 is a minor production pathway of BSOA-2 in Whistler, and 2) although sesquiterpenes were not measured in this study, they can be potentially important to generate BSOA with distinct peak at m/z 91 (or $C_7H_7^+$ fragments) based on previous laboratory observations.

Specific comments/questions:

Not clear if PMF was performed with HR or UMR AMS data matrix. If UMR was used for the PMF analysis, can the authors explain why? (Particularly important for m/z 43)

Response: Thanks for pointing out this confusion. The PMF was performed with high-resolution AMS data, which has been clearly illustrated in Section 2.2 of the revised manuscript.

P28011 Specify the E/N used for PTR measurements. I'm also surprised that only 6 VOCs (or group of isomers) were quantified within this study. Light aromatics (Benzene, toluene, ..) could have been useful to characterize the anthropogenic influences since no BC is shown in the paper.

Response: The E/N (E = electric field strength and N = buffer gas density) in the drift tube is kept at about 135 Townsend (Td). This information has been added to the revised version.

Table S1 has been updated to report other VOCs measured in this study, including benzene, toluene and acetonitrile. The NO_x (average ± standard deviation = 0.7 ± 0.9 ppbv), benzene (0.02 ± 0.01 ppbv), toluene (0.11± 0.16 ppbv) and acetonitrile (0.08 ± 0.04 ppbv) mixing ratios were generally low throughout the whole study, indicating limited influence by local anthropogenic emissions and biomass burning. However, a relatively high level of secondary sulfate originated from regional background was observed the later period of this study (July 13-19, Period 2) compared to the biogenic period. Therefore, we re-define the later period as "the period with both biogenic and regional background influence" and is referred as Period 2. Biogenic period is referred as Period 1. The above information has been added to the first paragraph of Section 3 in the revised manuscript.

P28012-28013 - What about O3 and OH concentrations differences between the two periods? - Sulfate seems to present a clear diurnal patterns (especially during the second period) and not ammonium. Does it mean that we are in presence of an acidic aerosol or organo sulfates?

Response: Ozone concentrations between the two periods are similar as shown in Figure 1b in the revised manuscript. Compared to Period 2, the diurnal variation of ozone is smaller (i.e. lower day time ozone concentration) during the biogenic period. However, as mentioned in the experimental section, OH radicals were measured during the last 10 days of the campaign, i.e. after period 2. Therefore, the measurement was used to estimate the diurnal pattern of OH radical concentration in Period 2 for evaluating BSOA formation chemistry. The text in Section 2.4 has been revised to clearly clarify this point.

Mass loadings of ammonium measured by the HR-ToF-AMS and predicted by sulfate mass correlates well for the whole period (R^2 = 0.69, Figure S13). The slope of linear fitting is approximately equal to one (0.96), suggesting nearly neutral aerosol particles. It is important to note that organic nitrate dominated the measured nitrate mass as demonstrated in Section 3.4.

P28014 – Remove one "the" (line 1) - First § and fig 2, can we really distinguished the influence of dynamic (mostly accumulation in this case) from chemistry? - Second §, the previous comment regarding the use of the HR data matrix for the PMF analysis, is here particularly important, and may explain why the O/C ratios are not so different between BSOA1 and BSOA2.

Response: Thanks for pointing out the error. The typo has been corrected.

Similar to the comments from Reviewer 1, we cannot differentiate the relative contributions of primary and secondary sources of methanol in this study. However, we believe that the observed methanol was dominated by terrestrial vegetation in forest areas with limited influence of anthropogenic emissions. The wordings have been changed when we described the correlations between VOCs and organic aerosol mass in Section 3.1.

We have modified Figure 3 a-c to report the ion-speciated mass spectra of different PMF factors as suggested by Reviewer 1. It is clear that m/z 43 peaks in the three PMF factors are primarily due to presence of $C_2H_3O^+$. This observation may partly explain the similar O:C ratio observed in BSOA-1 and BSOA-2.

P28018 – line 15 ... between 13 and 18 July - I'm very surprised that no diurnal cycle is observed for the ratio NO+/NO2+. Do you observe any differences in this ratio between the different periods?

Response: Time series of NO^+/NO_2^+ ratio for the whole sampling period has been added to Figure 5a. It can be found that the temporal variations of NO^+/NO_2^+ ratio are small between different periods. The high values and small diurnal variations of NO^+/NO_2^+ ratio indicate low levels of inorganic nitrate and the presence of organic nitrates in the observed BSOA.

P28019 line 16: Xu et al 2015 paper has been corrected. Organo nitrates account now for 20-30% of LO-OOA. Also this estimation of organo nitrates contents (as performed here) suppose that NO+ and NO2+ signal originate solely from organo nitrates (ie. not from inorganic nitrate). This assumption should be discussed.

Response: Thanks for pointing out this error. We have corrected the manuscript accordingly. The assumption has been added to Section 3.4 as below:

"… the mass loading of nitrate functional groups ($-ONO_2$) in organic compounds and thus the organic nitrate mass contributing to the observed BSOA-1 mass can be estimated using the calculation approach used by Xu et al. (2015) (see details in supplementary information) and assuming the subtracted NO^+ and NO_2^+ signal originated solely from organic nitrates and the molecular weight of the organic nitrates to be 200-300 g/mol. The organic nitrate mass accounted for 22-33% of BSOA-1 at night, representing the upper limit, and its diurnal cycle (ranged from 0.05 to 0.2 mg/m^3) is shown in Figure 5d. Results of these calculations suggest that organic nitrates can be a significant contributor to BSOA mass produced via night time NO_3• chemistry. Similarly, Xu et al. (2015) estimated that the organic nitrates accounted for 20-30% of less oxidized OOA (LO-OOA) mass observed during the night time."

Figure 1: Can the authors add to this figure the time series of O3 and OH.

Response: Times series of ozone has been added to Figure 1b. However, as mentioned in the above response, OH radicals were only measured during the last 10 days of the campaign, i.e.

after period 2. Therefore, the measurement was used to estimate the diurnal pattern of OH radical concentration in Period 2 for evaluating BSOA formation chemistry. The text in Section 2.4 has been revised to clearly clarify this point.

Figure 4: add in the legend “biogenic and anthropogenic influenced period”

Response: This period is referred as "period 2" in the revised manuscript. The legend has been added to Figure 4.

Figure 5 a-b: Add the NO+/NO2+ ratio time series

Response: Time series of NO^+/NO_2^+ ratio has been added to Figure 5a.

Figure 5 c-d: Are the diurnal cycles specific of one period or representative of the whole campaign?

Response: Figure 5 c-d shows the diurnal cycles of period 2 (i.e. a period with both biogenic and regional background influence). This information has been added to the figure caption.

Supporting information / Calculation of organic nitrate mass: There is a mistake in the first equation. Coefficients 62/46 and 62/30 are missing. Also explain [NO+] and [NO2+] : ion intensities? Concentration eqNitrates?

Response: $[NO^+]$ and $[NO_2^+]$ are nitrate-equivalent mass concentration of fragment NO^+ and NO_2^+. This has been specified in the supplementary information. The organic nitrate mass contributing to the observed BSOA-1 mass in this study was estimated using the calculation approach proposed by Xu et al. (2015). We have personal communication with the corresponding author of Xu et al. (2015) and confirm that the coefficients of 62/46 and 62/30 can be omitted in the equation if the units of $[NO^+]$ and $[NO_2^+]$ are nitrate-equivalent mass concentration.

References:
Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S., Nenes, A., Weber, R. J. and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proc. Natl. Acad. Sci. U. S. A., 112, 37-42, 2015.