Reviewer 1

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

This manuscript reports the results from a field study conducted in a forested mountain region at Whistler, BC, in summer 2010. A main focus of this study was to investigate biogenic SOA formation in a coniferous forest and the discussions are primarily based on the measurement data acquired with an HR-ToF-AMS and a PTR-ToF-MS. The manuscript provides new information on SOA formation pathways in biogenic emissions and the discussions are thoughtful. Overall, this work fits well within the scope of ACP and I recommend it to be accepted for publication after the authors address the following comments.

PTR-ToF-MS can measure a large number of VOC species but only 8 are reported in Table S1. It would be useful to provide information about additional VOC species, e.g., BTEX for anthropogenic emissions and acetonitrile for biomass burning emissions. For example, showing the time series of BTEX in Fig. 1 could provide additional support for the classification of periods into anthropogenic, biogenic, or mixed.

Response: 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 in 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. The biogenic period is referred as Period 1. The above information has been added to the first paragraph of Section 3 in the revised manuscript.

Given that most HR-ToF-AMS studies so far reported O/C and H/C values using the Aiken's method, in order to understand how the values reported here compare to those from other locations, it would be useful that the authors provide some information about how the elemental ratios of OA determined from the Aiken and the Canagaratna methods compare for this study. Maybe providing in the supplemental material scatter plots of the O/C and H/C values from the two methods.

Response: Thanks for the reviewer's suggestion. We agree that it would be useful to compare the results between Aiken's and improved-methods. Comparison of the two methods is shown in Figure S5 of the revised supplementary information.

There was very little information on how PMF was performed and how the solution was selected and validated. Given that this study relies heavily on the mass spectra and the time trends of the PMF OA factors to infer BSOA properties and formation pathways, it is necessary that more technical details are provided about the PMF work in this study.

Response: Additional information and Figures S9-12 have been added to the revised manuscript and supplementary information, respectively, to better describe the PMF analysis performed in this study. The following paragraph has been added to Section 2.2.

"Positive matrix factorization (PMF) was performed to analyze the high resolution AMS organic measurement for identification of the forms of organic aerosol in this study. The bilinear model was solved using the PMF2 algorithm in robust mode (Paatero and Tapper, 1994) and the final solution was selected using the PMF Evaluation Tool (PET) version 2.06 (Ulbrich et al., 2009). A three-factor solution was selected as the optimum solution based on examination of the PMF quality of fit parameter (Q/Qexpected) as a function of the number of PMF factors up to seven factors (Figure S9). Further increasing the number of factors from three to four factors only splits a factor representing background organic aerosol, and thus more than three factors was not considered in this study. Time series and mass spectra of two-, three- and four-factor PMF solutions are shown in Figure S10, S11 and S12 respectively."

Line 8, page 28012, the chemical formula for hexafluoropropene is wrong

Response: Thanks for pointing out the error. The formula has been corrected to C_3F_6.

Line 1, page 28014, methanol has both primary and secondary sources. What is the relative importance of the two sources for methanol during this study?

Response: We cannot differentiate the relative contribution 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 describe the correlations between VOCs and organic aerosol mass in Section 3.1.

Line 28 2013, Fig. 4 shows the correlations of OA with methanol, acetone, and acetic acid. However, the term "SOA" is used at here. I think it is necessary that the authors justify first the assumption that all OA mass was secondary in this study.

Response: We agree that it is inappropriate to use the term SOA here. "Total OA mass" is used in the revised version.

Line 24, 28014, change "values" to "value".

Response: Done

Same page, the volatility of an OA does not necessarily correlate with its O/C. Unless volatility measurements (e.g., using a thermodenuder) were available during this study, it is not appropriate to claim the volatility order for the 3 OA factors.

Response: Thanks for pointing out this error. We have removed the argument regarding the volatility order for the 3 OA factors.

Line 6, page 28017, define LT and its relationship to UTC.

Response: LT = local time, UTC -8 hours. This information has been added to the manuscript.

Line 15, page 28017, what are the f82 values in different OA factors? Give the ion formula at m/z 82 for isoprene SOA.

Response: According to previous studies, the ion formula at m/z 82 for isoprene SOA is $C_5H_6O^+$ (Robinson et al., 2011, Hu et al., 2015). The f82 values of background OA, BSOA-1 and BSOA-2 are 0.003, 0.007 and 0.006, respectively, which match previous AMS measurements from studies strongly influenced by monoterpene emissions (Hu et al., 2015). The discussion has been moved to Section 3.2 of the revised manuscript.

References:
Hu, W. W., Campuzano-Jost, P., Palm, B. B., Day, D. A., Ortega, A. M., Hayes, P. L., Krechmer, J. E., Chen, Q., Kuwata, M., Liu, Y. J., de Sá, S. S., McKinney, K., Martin, S. T., Hu, M., Budisulistiorini, S. H., Riva, M., Surratt, J. D., St. Clair, J. M., Isaacman-Van Wertz, G., Yee, L. D., Goldstein, A. H., Carbone, S., Brito, J., Artaxo, P., de Gouw, J. A., Koss, A., Wisthaler, A., Mikoviny, T., Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K. S., Alexander, M. L., Robinson, N. H., Coe, H., Allan, J. D., Canagaratna, M. R., Paulot, F., and Jimenez, J. L.: Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, Atmos. Chem. Phys., 15, 11807-11833, 2015.

Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, Atmos. Chem. Phys., 11, 1039–1050, 2011.

Section 3.5, I would like to ask the authors to elaborate a bit more on f91 and its utility as an indicator of BSOA. It could be useful to show f91 values in the mass spectra of the other OA types, such as urban/anthropogenic SOA, BBOA, HOA, and COA. What compound(s) or classes of compounds in BSOA that could produce C7H7+ in the AMS?

Response: Thanks for the reviewer's suggestions. As discussed in the original manuscript, f91 is unlikely a unique tracer for BSOA but it can be potentially used to evaluate formation pathways of BSOA in this unpolluted, forest environment (e.g., evaluate relative importance of BSOA formation pathways and precursors). Therefore, to avoid potential confusion, we decide not to make an in-depth comparison of f91 values in the mass spectra of different organic aerosols. The following paragraph has been added to Section 3.5 for discussing potential sources of $C_7H_7^+$ fragment.

"Although major contributors of $C_7H_7^+$ observed in this study are not well characterized, it is well known that formation of tropylium ion ($C_7H_7^+$) by electron impact ionization of benzyl compounds can attribute to this organic fragment (McLafferty and Turecek, 1993). While combustion processes are major sources of aromatic compounds, Gratien et al. (2011) observed formation of p-cymene via oxidation of a-pinene in laboratory experiments, suggesting possible biogenic origins of aromatic compounds. Other terpenes perhaps undergo similar chemistry but their atmospheric significance remains unclear."

References:

McLafferty, L. W. and Turecek, F.: Interpretation of Mass Spectra; University Science Books: Mill Valley, CA, 1993

Gratien, A., Johnson, S. N., Ezell, M. J., Dawson, M. L., Bennett, R. and Finlayson-Pitts, B. J.: Surprising Formation of p-Cymene in the Oxidation of alpha-Pinene in Air by the Atmospheric Oxidants OH, O-3, and NO3, Environ. Sci. Technol., 45, 2755-2760, 2011.

Showing the ion-speciated mass spectra of different OA factors in Fig. 3 is more informative. For example, it is interesting that the mass spectra of BSOA-1 and BSOA-2 look quite different but their O/C ratios are very similar. Do the m/z 43 peaks in the three factors have the same composition or do they have different ratios of C3H7+ to C2H3O+? I would like to see the relative contributions of CxHy ions and oxygen-containing ions at each m/z.

Response: We have modified Figure 3 a-c to show the ion-speciated mass spectra of different PMF factors. It is clear that m/z 43 peaks in the three factors are primarily due to presence of $C_2H_3O^+$. This observation may explain the similar O:C ratio observed in BSOA-1 and BSOA-2. This information has been added to Section 3.2 of the revised manuscript.

It may be helpful to scale the y axis of Fig. 3d to allow the H/C differences among data points more clearly seen.

Response: The scale of y-axis of Figure 3d has been changed.

Fig. S5 was not discussed. It was only mentioned in the figure caption of Fig. 3 and the purpose of showing it is not clear. In fact, how were the "biogenic" data points selected?

Response: The purpose of this figure is to illustrate the distributions of O:C and H:C ratios observed in the biogenic period and the whole sampling period. Since this information can be obtained from the Van-Krevelen diagram, Figure S5 has been removed in the revised manuscript.

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°) to upslope (~250°) 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.

Substantial secondary organic aerosol formation in a coniferous forest: Observations of both day and night time chemistry

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Abstract

Substantial biogenic secondary organic aerosol (BSOA) formation was investigated in a coniferous forest mountain region at Whistler, British Columbia. A largely biogenic aerosol growth episode was observed, providing a unique opportunity to investigate BSOA formation chemistry in a forested environment with limited influence from anthropogenic emissions. Positive matrix factorization of aerosol mass spectrometry (AMS) measurement identified two types of BSOA (BSOA-1 and BSOA-2), which were primarily generated by gas-phase oxidation of monoterpenes and perhaps sesquiterpenes. The temporal variations of BSOA-1 and BSOA-2 can be explained by gas-particle partitioning in response to ambient temperature and the relative importance of different oxidation mechanisms between day and night. While BSOA-1 arises from gas-phase ozonolysis and nitrate radical chemistry at night, BSOA-2 is likely less volatile than BSOA-1 and consists of products formed via gas-phase oxidation by OH radical and ozone during the day. Organic nitrates produced through nitrate radical chemistry can account for 22-33% of BSOA-1 mass at night. The mass spectra of BSOA-1 and BSOA-2 have higher values of the mass fraction of m/z 91 (f91) compared to the background organic aerosol. Using f91 to evaluate BSOA formation pathways in this unpolluted, forested region, heterogeneous oxidation of BSOA-1 is a minor production pathway of BSOA-2.

1 Introduction

Biogenic secondary organic aerosol (BSOA) generated by gas-phase oxidation of biogenic volatile organic compounds (BVOCs, such as isoprene, monoterpenes, and sesquiterpenes) emitted from vegetation is one of the major contributors to the global SOA budget (Hallquist et al., 2009). As a result of the atmospheric importance of BSOA, many laboratory studies have focused on determining the mass yields and chemical characteristics of BSOA from oxidation of different gas-phase precursors (e.g., Chhabra et al., 2010, Lee et al., 2006ab). However, chamber SOA is usually less oxidized than ambient SOA (e.g., Aiken et al., 2008, Ng et al., 2011), indicating that the current understanding of BSOA formation remains incomplete. Furthermore, the SOA yield parameters for atmospheric models and the degree of oxygenation of chamber SOA largely depends on the experimental conditions such as organic aerosol mass loading and seed particle surface area (Ehn et al., 2012, Shilling et al., 2009, Zhang et al., 2014).

Forested environments such as the boreal forest and Amazon rainforest can be considered giant chemical reactors for BSOA production (e.g., Chen et al., 2009, Ehn et al., 2012, Kanakidou et al., 2005, Slowik et al., 2010). Elevated temperature and/or solar radiation over forests can enhance their BVOC emissions from the forest (Rinne et al., 2002, Leaitch et al., 2011), meanwhile BSOA can be produced efficiently due to active photochemistry during the day. Despite the fact that many field studies have been performed near or in forested areas to investigate BSOA formation, anthropogenic influence was frequently observed during those studies, further complicating the SOA formation chemistry (e.g., Han et al., 2014, Setyan et al., 2012). In particular, it has been hypothesized that the interactions of BVOCs with anthropogenic pollutants contributed to high aerosol loadings in the southeastern United States (Goldstein et al., 2009). Shilling et al. (2013) observed that the enhancement of SOA formation from isoprene was strongly related to the NO_x concentrations in Sacramento, California. Xu et al. (2015) recently reported that isoprene-derived SOA was directly mediated by sulfate, and NO_x was shown to enhance night time SOA formation via nitrate radical oxidation of monoterpenes in the southeastern United States.

In addition to the uncertainties of anthropogenic-biogenic interactions on BSOA formation, there is growing evidence of uncaptured BSOA formation chemistry in smog chamber experiments. For example, Ehn et al. (2014) recently showed that the wall effects of smog chambers can result in a substantial loss of highly oxygenated organic compounds with vapor pressures orders of magnitude lower than previously identified gas-phase oxidation products of BVOCs (i.e. referred to as extremely low volatility organic compound, ELVOC). Furthermore, Zhang et al. (2014) illustrated that the formation yields of toluene-derived SOA depend on the seed-to-chamber surface area ratio predominantly due to the loss of SOA-forming vapour to the chamber wall. The observed yield suppression likely extends to BSOA formation systems. Mueller et al. (2012) reported that cis-pinonic acid, one of the first generation products from α-pinene ozonolysis, experienced a significant wall loss in smog chambers. Such wall losses have not been adequately taken into consideration when aerosols yields were reported from earlier chamber studies. As a result, conducting a field measurement in a forested environment without significant influence of anthropogenic emissions and without the constraints of smog chamber walls is an attractive approach that can be used to re-evaluate our current knowledge of BSOA formation.

In this study, we deployed an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to characterize ambient aerosol in a coniferous forest mountain region at Whistler, British Columbia from June 15 to July 28, 2010. Simultaneous measurements of gas-phase VOCs were made with a high resolution proton-transfer reaction mass spectrometer (PTR-ToF-MS). The measurement was part of the Whistler Aerosol and Cloud Study (WACS) 2010 campaign. The study duration covered a period when the forested region in Whistler experienced persistently high levels of nearly pure BSOA up to about 5 μg/m^3, providing a unique opportunity to investigate BSOA formation in a coniferous forest. This amount of SOA formation is considerably larger than that observed in pure isoprene-emission-dominated forests, such as in the Amazon (Martin et al., 2010). Rather, it matches the very high levels of BSOA observed in the summertime in another northern location in central Canada (Slowik et al., 2010). Positive matrix factorization (PMF) analysis was performed to understand the types of organic aerosol that contributed to the total organic aerosol mass during this time. The relative importance of different oxidation chemistry (i.e. ozonolysis, OH radical and nitrate radical oxidation) on BSOA formation between day and night are evaluated. Compared to previous laboratory studies, the mass spectral characteristics of the BSOA factors identified in the current study provide insight into the BSOA formation mechanisms.

2 Experiment

2.1 Sampling location and period

The Whistler Aerosol and Cloud Study (WACS) was a large-scale field campaign conducted at Whistler, British Columbia from June 15 to July 28, 2010. One of the two sampling sites on Whistler Mountain (Raven's Nest, see Figure S1) sits within a coniferous forest mountain area at an elevation of 1320 m-asl. In this paper, we focus on the observations at Raven's Nest from July 1 to 19, 2010, covering a large BSOA event that lasted approximately 5 days (July 6-10) and contrast them with those from a period with mixed biogenic and regional background influence (July 13-18) (Figures 1 and S2, and see Section 3 for discussion). Key measurements used in this analysis are briefly described in the following sections.

2.2 Aerosol measurements

An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) and scanning mobility particle sizer (SMPS; TSI Inc., model 3936L75) were deployed to measure real-time non-refractory particulate matter (NR-PM, i.e., ammonium, nitrate, sulfate and organic) and particle number size distributions (16-685 nm), respectively. The ambient air was drawn through a stainless steel sampling line by the HR-ToF-AMS, SMPS and other collocated particle instruments. The working principle of the HR-ToF-AMS has been reported in detail previously (DeCarlo et al., 2006). In brief, an aerodynamically focused particle beam impacts a tungsten vaporizer that was maintained at ~600^{o}C to vaporize the NR-PM, and the resulting vapors are ionized with electron impact ionization. The ions are then detected by a high-resolution time-of-flight mass spectrometer, which was operated in V-mode (5 minutes, mass resolving power ~2000 with a higher sensitivity) and W-mode (5 minutes, mass resolving power ~ 4000 with a lower sensitivity) alternatively. Ionization efficiency (IE) calibrations were performed on-site using monodisperse ammonium nitrate particles. The default relative IE (RIE) of nitrate, sulfate, ammonium, chloride and organic were used (Jimenez et al., 2003).

The data were processed using the AMS data analysis software (Squirrel, version 1.51H for unit mass resolution (UMR) data and Pika, version 1.10H for high resolution peak fitting, http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html) with the corrected air fragment column of the standard fragmentation table (Allan et al., 2004, DeCarlo et al., 2006). The data reported here are obtained from the high-resolution mass spectral fitting of W-mode data. Elemental analysis (oxygen- and hydrogen-to-carbon ratios, O:C and H:C) is based on the improved-method proposed by Canagaratna et al., (2015). Given that most HR-ToF-AMS studies reported O:C and H:C values using Aiken's method (Aiken et al., 2008), comparison between Aiken's and improved-method is shown in Figure S5. Positive matrix factorization (PMF) was performed to analyze the high resolution AMS organic measurement for identification of the forms of organic aerosol in this study. The bilinear model was solved using the PMF2 algorithm in robust mode (Paatero and Tapper, 1994) and the final solution was selected using the PMF Evaluation Tool (PET) version 2.06 (Ulbrich et al., 2009). A three-factor solution was selected as the optimum solution based on examination of the PMF quality of fit parameter ($Q/Q_{expected}$) as a function of the number of PMF factors up to seven factors (Figure S9). Further increasing the number of factors from three to four factors only splits a factor representing background organic aerosol, and thus more than three factors was not considered in this study. Time series and mass spectra of two-, three- and four-factor PMF solutions are shown in Figure S10, S11 and S12 respectively.

2.3 VOC measurements

Measurements of volatile organic compounds (VOCs) were performed using a high-resolution proton transfer time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH). The ambient air was drawn through a 5 meter-long Perfluoroalkoxy (PFA) sampling line by a diaphragm pump at a rate of 5 slpm. A 200 sccm sample was drawn into the instrument through a heated inlet from the sampling line. Five-minute backgrounds were collected hourly through a platinum wool catalyst heated to 350^{o}C. The time resolution of measurement was 1 minute. The E/N (E = electric field strength and N = buffer gas density) in the drift tube is kept at about 135 Townsend (Td). The raw PTR-ToF-MS data were acquired by the TofDaq software (Tofwerk AG, Switzerland) and post processed by PTR-MS ToF Viewer (Ionicon Analytik GmbH). Operations of proton transfer reaction mass spectrometer (PTR-MS) with a quadrupole mass spectrometer have been presented in great detail (Blake et al., 2009, de Gouw and Warneke, 2007). Briefly a PTR-MS is a soft ionization technique that allows for detection of VOCs that have a greater proton affinity than water. While the ionization process is the same in the PTR-ToF-MS as the PTR-MS, the high-resolution time-of-flight mass spectrometer used in the PTR-ToF-MS captures the entire mass spectrum from 12 to a high mass number (usually about 400) at high time resolutions (e.g., 1 second). The high mass resolution of the mass detector (approximately 4000-5000) allows isobars to be resolved. A list of mass-to-charge (m/z) ratios of some selected VOCs is shown in Table S1.

Periodic calibrations of the PTR-ToF-MS were performed on-site for α-pinene, isoprene, methanol, acetone, methyl vinyl ketone (MVK), and 2-methyl-3-buten-2-ol (MBO). Post-campaign calibration of formic acid was obtained utilizing heated permeation tubes. The sensitivity of formic acid was then ratioed to the acetone sensitivity measured both during and after the campaign, and the ratio together with the acetone field calibration was used to retrieve formic acid from the field measurements. The sensitivities and limits of detection (LOD) of calibrated VOCs are shown in Table S1. Three one-hour integrated VOCs samples were also collected each day in 3L stainless steel canisters. Analysis for both polar and non-polar compounds was carried out off-site by gas chromatography. It should be noted that the PTR-ToF-MS isoprene signal at m/z 69.070 can be influenced significantly by MBO fragments so that a correction factor based on the linear correlation between the isoprene concentrations determined by PTR-ToF-MS and canister samples (i.e., canister isoprene = 0.7*PTR-ToF-MS isoprene, $R^2 = 0.79$) was used to correct the real-time isoprene concentration measured by the PTR-ToF-MS for the MBO interference.

2.4 Ozone and OH radical measurements

Ozone was measured by a UV absorption monitor (Model TECO 49C, Thermo Environmental Instruments Inc.). During the last 10 days of the campaign (July 19-28), hydroxyl (OH) radicals were measured using the well-established technique of chemical ionization mass spectrometry (OH-CIMS) (Tanner et al., 1997). The measurement was used to estimate the diurnal pattern of OH radical concentration from July 13 to 18 for evaluating BSOA formation chemistry. The instrument has been previously described (Berresheim et al., 2000, Sjostedt et al., 2007, Tanner et al., 1997). Briefly, hydroxyl radicals are measured by titration with isotopically labelled $^{34}SO_2$ to produce $H^{34}SO_4$. The isotopically labelled sulfuric acid molecules were then ionized by charge transfer with nitrate ions (NO_3^-), produced by passing a flow of nitrogen containing HNO_3 through a ^{210}Po ion source. In order to minimize wall losses of OH radicals, a flow of 2400 slpm is drawn through an inlet with 7.6 cm inner diameter and about 2 feet in length. The instrument background was determined periodically by adding hexafluoropropene (C_3F_6) through the front injectors to scavenge the ambient OH radicals. Calibrations were performed in situ by photolyzing water vapor with a mercury pen ray lamp in the sampling inlet. The detection limit for a 5 minute integration of OH radical was $5x10^4$ molecules/cm^3.

3 Results and Discussion

Figure 1 shows the time series of various measurements from July 1 to 19, which can be divided into three periods based on the meteorological conditions previously reported (Ahlm et al., 2013, Pierce et al., 2012). The first period (July 1-5) was humid and cloudy with low temperature. A relatively high concentration of secondary sulfate indicates that this period was strongly influenced by aged/transported air masses. The second period (July 6-10) started with increasing ambient temperature and was accompanied by rapidly increasing levels of biogenic volatile organic compounds (BVOCs, e.g., monoterpenes and isoprene) which were followed by increasing total organic aerosol mass (Figure 1a, d and f). This period is referred to as the "biogenic period (or Period 1)" hereafter and will be the focus of Sections 3.1 and 3.2. The aerosol sulfate concentration was low during the biogenic period. The third period (July 13-19) was cooler than the biogenic period. Although the diurnal cycles of different measurements indicate that the third period had both biogenic and regional background influence (referred to as Period 2 hereafter), the observations provide insights into the pathways of biogenic secondary organic aerosol (BSOA) formation during the biogenic period (Section 3.3). 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 within July 1-19, indicating limited influence by local anthropogenic emissions and biomass burning. The significance of night time nitrate radical chemistry will be discussed in Section 3.4. Lastly, a comparison between previous laboratory studies and these field observations will be discussed in Section 3.5.

3.1 Biogenic period

Enhancement of BVOC (monoterpenes and isoprene) emissions from the forest due to high temperature and/or solar radiation was observed throughout the campaign (Figure 1a and d). Specifically, significant positive correlations of daily average temperature and monoterpenes (R^2 = 0.91) and isoprene (R^2 = 0.84) mixing ratios were obtained (Figure S3). The forested area in Whistler is dominated by conifers. Therefore, monoterpenes, rather than isoprene, are the dominant BVOCs emitted into air. For example, for the biogenic period, monoterpenes observed at the site were about a factor of three higher than isoprene. Considering the low SOA formation yield from gas-phase isoprene photo-oxidation chemistry determined in smog chamber experiments, monoterpenes likely play a more critical role than isoprene in BSOA formation in Whistler (Lee et al., 2006ab). Note that sesquiterpenes could not be determined by the PTR-ToF-MS; thus their contributions to BSOA formation cannot be evaluated.

The uniform air mass within the biogenic period led to the accumulation of organic aerosol (Figure 1f) (Pierce et al., 2012). The organic aerosols formed during the pristine event were almost entirely biogenic in origin as determined by the FTIR analysis of filter samples during this period (Ahlm et al., 2013). Inorganic constituents generally accounted for less than 5% of the total NR-PM by mass. Even though the sulfate concentration was slightly enhanced during the strong new particle formation events on July 5 and 6 (i.e., particle number rapidly increased in the 20-30 nm size range), the particle growth to diameters larger than 100 nm was primarily due to condensation of BSOA materials on the nucleation mode particles (Figure 1f and h) (Pierce et al., 2012). There are strong correlations among methanol, acetone, and total OA mass throughout the study (Figures 2 and S4), suggesting that they are likely from the similar origin. The methanol-to-acetone ratio determined in this study is 3.61 ($R^2 = 0.94$) as shown in Figure 2. The correlation between total organic aerosol mass and formic acid ($R^2 = 0.77$) is also presented in Figure S4. Note that methanol sources can be dominated by terrestrial vegetation in forest areas.Overall, the biogenic episode provides a unique opportunity to investigate the properties and formation mechanisms of BSOA in a forested area dominated by terpene emissions.

3.2 Chemical characteristics of BSOA

Positive matrix factorization (PMF) was performed to understand the chemical characteristics of BSOA. The PMF analysis separates the total organic aerosol into three factors: background organic aerosol (background OA), biogenic SOA-1 (BSOA-1), and biogenic SOA-2 (BSOA-2). The organic speciated mass spectra and time series of these factors are shown in Figures 3a-c and 1g, respectively. The background OA represents aged organic aerosol with an intense signal of CO_2^+ fragments (i.e., a tracer of organic acid) and a high degree of oxygenation (O:C = 0.87), and largely correlates with secondary sulfate (see Section 3.3). The BSOA-1 and BSOA-2 factors represent two different types of fresh BSOA based on their mass spectral features and temporal profiles (see Section 3.3). Elemental analysis shows that the degree of oxygenation of BSOA-2 (O:C = 0.58) and BSOA-1 (O:C = 0.56) is similar even though they have very different m/z 44-to-m/z 43 ratios (a parameter for evaluating the degree of aging of oxygenated OA (OOA) from unit mass resolution AMS spectra) (Ng et al., 2010). This observation can be due to the fact that CH_2O^+ and $C_2H_3O^+$ fragments are the primary contributors of organic m/z 30 and 43, respectively, for both BSOA. Note that the isoprene SOA signature (i.e. a high mass fraction of m/z 82 ($C_5H_6O^+$) to total organic mass, f82) was not observed in the mass spectrum of BSOA-1 and BSOA-2 (Robinson et al., 2011, Slowik et al., 2012, Hu et al., 2015). The f82 values of background OA, BSOA-1 and BSOA-2 are 0.003, 0.007 and 0.006, respectively, which match previous AMS measurements from studies strongly influenced by monoterpene emissions (Hu et al., 2015).

The Van-Krevelen diagram in Figure 3d shows that the ambient data (orange dots for the biogenic period only) can be a linear combination of the three PMF factors. Comparison between Aiken's and the improved-method for elemental composition characterization is shown in Figure S5. The linear fit of ambient data from the whole campaign (slope = -0.35 and y-intercept = 1.67) is shown in Figure 3d. The y-intercept is close to the theoretical H:C of most BVOCs such as isoprene (C_5H_8), α-pinene ($C_{10}H_{16}$), limonene ($C_{10}H_{16}$), and β-caryophyllene ($C_{15}H_{24}$). Furthermore, some major products of α-pinene ozonoylsis including cis-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) fall along the linear fit of the ambient data, consistent with the VOC measurements that terpenes are likely one of the major BSOA precursors in the Whistler forest (see Section 3.1). Cis-pinonic and pinic acids are α-pinene first generation oxidation products with the average saturation vapor concentrations (C*) categorized as intermediate-VOCs (IVOCs, C* = 10^3-10^6 μg/m^{-3}) and semi-VOCs (SVOCs, C* = 10^2-10^0 μg/m^{-3}), respectively (Donahue et al., 2012). MBTCA is a low volatility (C* = 10^{-1}-10^{-3} μg/m^{-3}), later generation product of α-pinene SOA and a tracer of terpene SOA. It is important to note that the observed growth for small particles (< 50 nm) at the early stage of the biogenic period in Whistler must have an average C* less than 10^{-2} μg/m^{-3} based on the modeling results from Pierce et al. (2012). This implies that at least small amounts of organic materials with volatility much lower than BSOA-1 and 2 (e.g., ELVOC observed by Ehn et al., (2014)) were required to permit the observed initial growth.

3.3 Understanding BSOA formation from its diurnal character

At the beginning of the biogenic period when there was significant nucleation, BSOA-1 was more prevalent than BSOA-2. BSOA-2, however, sustained the particle growth at the elevated temperature after the new particle formation event on July 7, likely because of its low volatility. BSOA-1 started to decline from July 8 and the total organic mass was dominated by BSOA-2 during the rest of the biogenic period. The temporal profile of the BSOA-1-to-BSOA-2 ratio is shown in Figure S6 to illustrate the relative contribution of these BSOA factors within the biogenic period. These observations imply different formation chemistry of the two BSOA materials within the biogenic period (see later discussion).

The clear diurnal patterns of both gas- and particle-phase species within the period with a mix of biogenic and regional background influence (Period 2) permit evaluation of both the influence of photochemistry and meteorological conditions on the formation of BSOA-1 and BSOA-2. Figure 4b illustrates the morning increase in OH radical concentrations and ozone mixing ratios due to increases in solar radiation (i.e., indicated by the elevated ambient temperature), suggesting more active photo-oxidative chemistry during the daytime and less deposition in the case of ozone. The reaction rate constants of monoterpenes with ozone and OH radical are on the order of 10^{-15}-10^{-17} and 10^{-10}-10^{-11} $cm^3 molecule^{-1} s^{-1}$, respectively, and both oxidation processes give comparable SOA formation yields for monoterpenes (Lee et al., 2006ab). Given that the concentrations of ozone and OH radical during the daytime are on the order of 10^{11} and 10^5-10^6 molecules/cm^3, respectively (Figure 4b), the overall contributions of ozonolysis and OH oxidation of monterpenes to daytime BSOA formation in Whistler can be comparable to each other, even though ozonolysis may play a larger role than OH oxidation in late afternoon and night time.

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).

Other BVOCs and their oxidation products such as acetone, isoprene and probably MVK/methacrolein (MACR; PTR-ToF-MS cannot separate MVK and MACR, and other isoprene oxidation products may contribute to this mass-to-charge ratio signal) increased in connection with ozone, providing further evidence of active photochemistry during the day. The similar diurnal cycles of these VOCs were also clearly observed during the later period of the biogenic episode (i.e. July 9-10, Figure 1). Different diurnal cycles of isoprene and monoterpene mixing ratios were observed previously in forest (Harrison et al., 2001). Note that isoprene emission flux is sensitive to both solar radiation and temperature (Rinne et al., 2002).

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).

The BSOA-2 diurnal profile matches the variation of ozone plus OH radical levels during the daytime, suggesting that oxidation of monoterpenes and its oxidation products is likely one of the major BSOA-2 formation pathways. BSOA-1 has a diurnal pattern clearly distinct from BSOA-2, with a night time peak. BSOA-1 is likely more volatile than BSOA-2 based on their relative fCO_2^+ values (Huffman et al., 2009). The low temperature at night may favour partitioning of BSOA-1 materials to the particle phase, resulting in a higher concentration of BSOA-1 at night. In addition to the gas-particle partitioning of BSOA-1 materials, BSOA-1 formation via ozonolysis of monoterpenes at night is possible because of the large abundance of monoterpenes and presence of ozone. Nocturnal nitrate radical chemistry can also contribute to BSOA-1 production significantly (see Section 3.4). Lastly, BSOA-2 was composed of a higher fraction of organic acids (i.e., fCO_2^+) compared to BSOA-1. Additional information is required to evaluate the possibility of heterogeneous conversion of BSOA-1 to BSOA-2 during the daytime (see Section 3.5).

3.4 Nitrate radical chemistry at night

Nitrate radical ($NO_3\bullet$) is a product of ozone and NO_x and is a well-known nocturnal oxidant. Xu et al. (2015) recently reported that $NO_3\bullet$ chemistry could play a key role in producing BSOA at night in southeast United States. The average ozone and NO_x mixing ratios at night during WACS 2010 were about 20-30 ppbv (Figures 1b and 4) and 0.34 ppbv (Figure 5a) throughout the entire study, respectively, which are comparable to the levels reported by Xu et al. (2015) (i.e. O_3 = 21 ppbv and NO_x = 0.54 ppbv). Laboratory studies have shown that organic nitrates can be produced from the reaction between $NO_3\bullet$ and BVOCs (Ng et al., 2008, Fry et al., 2009). Fragmentation of organic nitrates produces NO^+ and NO_2^+ signals in AMS measurement with the NO^+/NO_2^+ ratio much higher than that of inorganic nitrate (e.g. Farmer et al., 2010). The NO^+/NO_2^+ ratio of ammonium nitrate determined in our calibration was approximately 3.38. In contrast, the average NO^+/NO_2^+ ratio observed in the AMS measurement was 11.4 and it was relatively constant throughout the whole sampling period (Figure 5a). The diurnal cycle of ambient NO^+/NO_2^+ ratio observed in Period 2 is shown in Figure 5c. 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 (e.g. Farmer et al., 2010, Xu et al., 2015).

No diurnal cycles of NO^+ and NO_2^+ AMS fragments were observed (Figure S7) to confirm significant $NO_3\bullet$ chemistry at night, possibly due to the upslope mixing of anthropogenic/aged aerosol particles mentioned in the previous sections. There was some covariance in the temporal variations of sulfate and nitrate (Figure S8). To evaluate the possibility of night time NO_3• chemistry in this study, the AMS nitrate mass is normalized by sulfate mass to eliminate the potential effects of upslope mixing on nitrate aerosol concentrations. The NO_3^-/SO_4^{2-} ratio correlates extremely well with the BSOA-1 (R^2 = 0.71) for the whole sampling period (Figure 5b). Furthermore, the diurnal pattern of this ratio during Period 2 (July 13-18) was almost identical to that of BSOA-1 (Figure 5d), indicating the formation of organic nitrates at night. The formation of organic nitrates during the biogenic episode under relatively high temperature and low RH conditions further suggests that the diurnal cycle of the NO_3^-/SO_4^{2-} ratio cannot be fully explained by gas-particle partitioning of nitric acid which would occur preferentially at lower temperatures.

Assuming the NO^+/SO_4^{2-} and NO_2^+/SO_4^{2-} mass ratios were constant in the air mass carried by upslope winds and are approximately equal to 0.088 and 0.009 respectively (i.e. the minimum values observed during the upslope wind condition), the NO^+ and NO_2^+ mass originating from the upslope wind air masses can be subtracted from their total mass loadings. After that, 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 μg/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.

3.5 Comparison to previous laboratory studies

Potential formation pathways of BSOA can be evaluated through examination of specific mass fragments. Organic fragments at m/z 91 have been observed in laboratory-generated and ambient BSOA, and the BSOA-1 and BSOA-2 factors have a distinct peak at m/z 91 mostly due to the presence of the $C_7H_7^+$ fragment (Figure 3). Although major contributors of $C_7H_7^+$ observed in this study are not well characterized, it is well known that formation of tropylium ion ($C_7H_7^+$) by electron impact ionization of benzyl compounds can attribute to this organic fragment (McLafferty and Turecek, 1993). While combustion processes are major sources of aromatic compounds, Gratien et al. (2011) observed formation of p-cymene via oxidation of α-pinene in laboratory experiments, suggesting possible biogenic origins of aromatic compounds. Other terpenes perhaps undergo similar chemistry but their atmospheric significance remains unclear.

Even though the mass fraction of m/z 91 to total organic (f91) is not a unique tracer for BSOA (Ng et al., 2011), f91 can be potentially used to evaluate formation pathways of BSOA in this unpolluted, biogenic-rich environment (e.g., evaluate relative importance of BSOA formation pathways and precursors). The f91 values of both raw data and PMF results are shown in Figure 6a along with f91 values from previously published laboratory and field studies. Recent inter-comparison of Aerodyne aerosol chemical speciation monitors (ACMS) highlighted a significant variability of mass fraction of specific m/z to total organic between instruments (Fröhlich et al, 2015), and hence the comparisons of f91 values between studies are only semi-quantitative. Nevertheless, Chen et al. (2015) reported that the f91 value of α-pinene SOA generated in smog chamber experiments at low NO_x condition is much lower than β-caryophyllene SOA generated in the same study. Previous plant chamber experiments (i.e. oxidation of a mixture of BVOCs) further suggest that the value of f91 likely depends on the relative contribution of sesquiterpenes to total BVOCs; the average value of f91 of SOA generated by the oxidation of different plant emissions is reported here (Kiendler-Scharr et al., 2009). The above observations indicate that sesquiterpenes may play an important role to the production of m/z 91 (or $C_7H_7^+$ fragments) observed in Whistler and other forest region such as a boreal forest in Finland (Finessi et al., 2012).

Laboratory studies have also shown that some of the first generation products of α-pinene ozonolysis can have a relatively high level of f91 in their AMS spectra including cis-pinonic acid droplets generated by atomization (Lee et al., 2012) and pinonaldehyde uptake to sulfuric acid particles (Liggio and Li, 2006). Although cis-pinonic acid and pinonaldehyde are rather volatile, they may experience significant wall loss in smog chambers during the SOA formation experiments previously reported (Mueller et al., 2012, Zhang et al., 2015). The wall effect can suppress subsequent gas-phase reactions of intermediate products that may produce less volatile, SOA-forming organic acids with the same f91 signature. Since the surface characteristics of the land and vegetation in the remote forested region can be very different to the wall surface of smog chambers, α-pinene is possibly an important precursor of $C_7H_7^+$ fragments in the real atmosphere.

The difference in the f91 values between BSOA-1 and BSOA-2 can be further used to evaluate the relationship between these two PMF factors. In the same campaign at Whistler, Slowik et al. (2012) performed a set of in-situ heterogeneous OH oxidation experiments using a flow tube reactor to age BSOA sampled during the biogenic period. They clearly observed that the f91 value declined with heterogeneous oxidation and the mass spectra of reaction products determined by PMF analysis did not contain a high value of f91. Because BSOA-2 has a higher level of f91 than BSOA-1 (Figure 6), we conclude that there is little heterogeneous oxidative conversion of BSOA-1 to BSOA-2.

4 Conclusions and atmospheric implications

The strong biogenic episode observed in this study provides a unique opportunity to improve current understanding of BSOA formation chemistry in a coniferous forest. The high levels of SOA formation are comparable to those previously observed in the summertime in another Canadian forested location also dominated by terpene emissions (Slowik et al., 2010). Given the considerable emphasis placed on isoprene SOA in the past few years and given the high SOA levels observed in this study, there is merit to addressing the formation of SOA in these coniferous forested regions. Indeed, with pronounced high latitude warming it is very important to better understand SOA formation in such regions to know how they will respond to changing climate conditions (Leaitch et al., 2011).

The BSOA observed during the biogenic episode was primarily due to ozonolysis and OH oxidation of BVOCs (i.e., monoterpenes and perhaps sesquiterpenes) during the day. We also provide evidence that nitrate radical chemistry with BVOCs at night can be significant. PMF analysis identified two types of BSOA, namely BSOA-1 and BSOA-2, and separated them from the background organic aerosol. BSOA-1 represents gas-phase ozonolysis and nitrate radical oxidation products, and is likely semi-volatile in nature, resulting in higher concentrations at low ambient temperature during the night. BSOA-2 has a much stronger CO_2^+ signal than BSOA-1, and consists of products from gas-phase oxidation by OH radical and ozone during the day. Hence, the temporal variations of BSOA-1 and BSOA-2 observed here are due to their gas-particle partitioning in response to ambient temperature, the relative importance of different oxidation chemistry between day and night, and the gradual oxidation of early generation gas-phase oxidation products. The calculation in Section 3.4 suggests that BSOA-1 can be largely contributed by organic nitrates at night (22-33% by mass) due to nitrate radical chemistry.

This study evaluates the values of f91 obtained from the AMS measurements as a tracer to investigate the BSOA-2 potential formation pathways. We demonstrated that heterogeneous oxidation of BSOA-1 is expected to be a minor production pathway of BSOA-2. Nevertheless, we cannot rule out the possibility that some BSOA-1 material repartitions to the gas phase due to elevated temperature during the daytime and then undergoes gas-phase oxidation to produce BSOA-2 materials. This may partly explain the decay of BSOA-1 and a higher level of BSOA-2 observed in the later period of biogenic episode. 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. Moreover, recently chamber experiments suggested that high signals at $C_7H_7^+$ in ambient aerosol mass spectrum can be potentially used to indicate the presence of SOA products generated from β-pinene and nitrate radical reactions (Boyd et al., 2015).

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Figures:

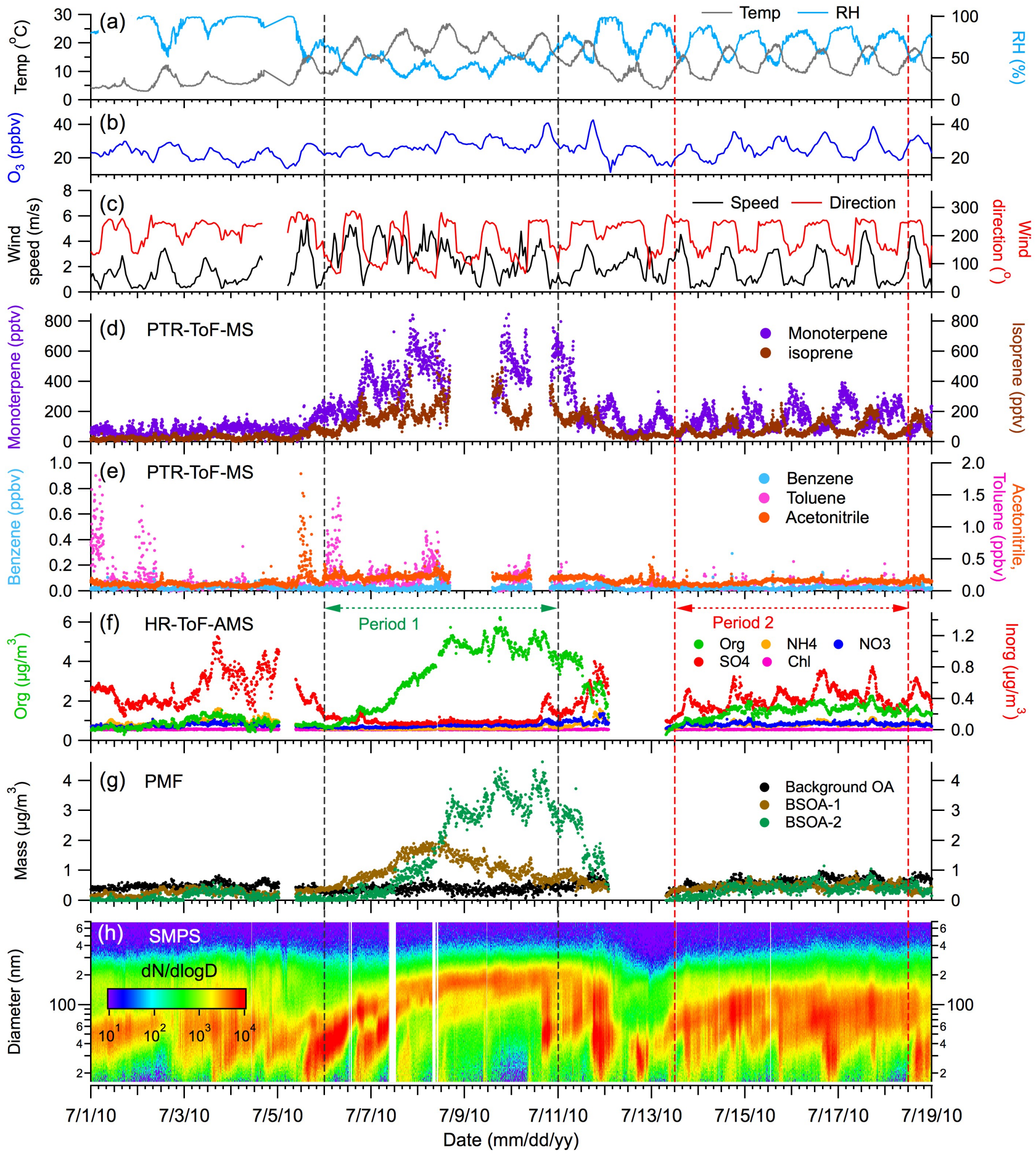

Figure 1: Time series (PST) profiles of (a) Temperature and relative humidity, (b) ozone, (c) wind speed and direction, (d) monoterpene and isoprene measured by PTR-ToF-MS, (e) benzene toluene and acetonitrile measured by PTR-ToF-MS, (f) Organic, nitrate, sulfate, ammonium, and chloride measured by HR-ToF-AMS, (g) background OA, BSOA-1, and BSOA-2 determined by PMF analysis, (h) particle number size distribution measured SMPS. The gray and red dashed lines represent the boundaries of period 1 (July 6-10) and period 2 (July 13-18), respectively. Figure S2 enlarges the time series during (a) July 6-10 and (b) July 13-18.

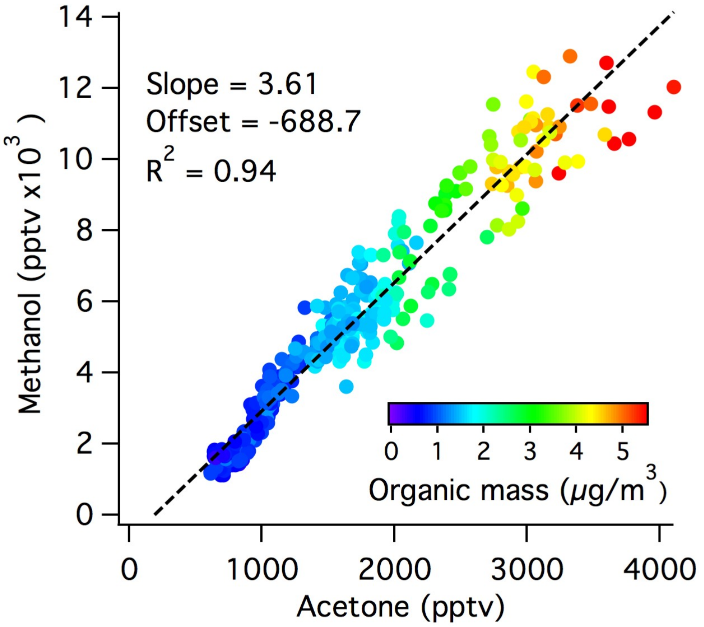

Figure 2: Correlation of methanol and acetone measured by PTR-ToF-MS. The color scales represent the total organic mass measured by HR-ToF-AMS.

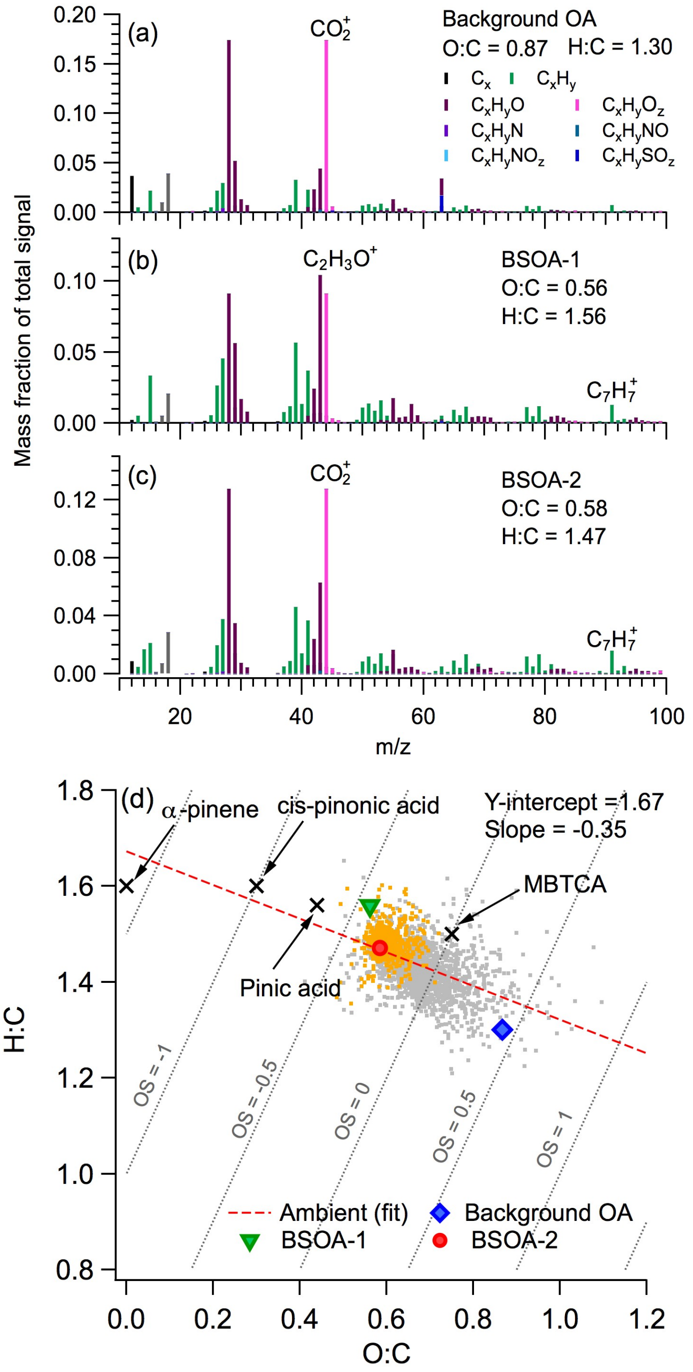

Figure 3: Normalized unit mass resolution mass spectra of PMF factors (a) background OA, (b) BSOA-1, and (c) BSOA-2. (d) Van-Krevelen diagram: orange and gray dots represent observations from the regional biogenic period (July 6-10) and the whole study period, respectively. The cross symbols represent the O:C and H:C ratios of α-pinene and its major oxidation products (cis-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid

(MBTCA)). Comparison between Aiken's and improved-method for elemental composition analysis is shown in Figure S5.

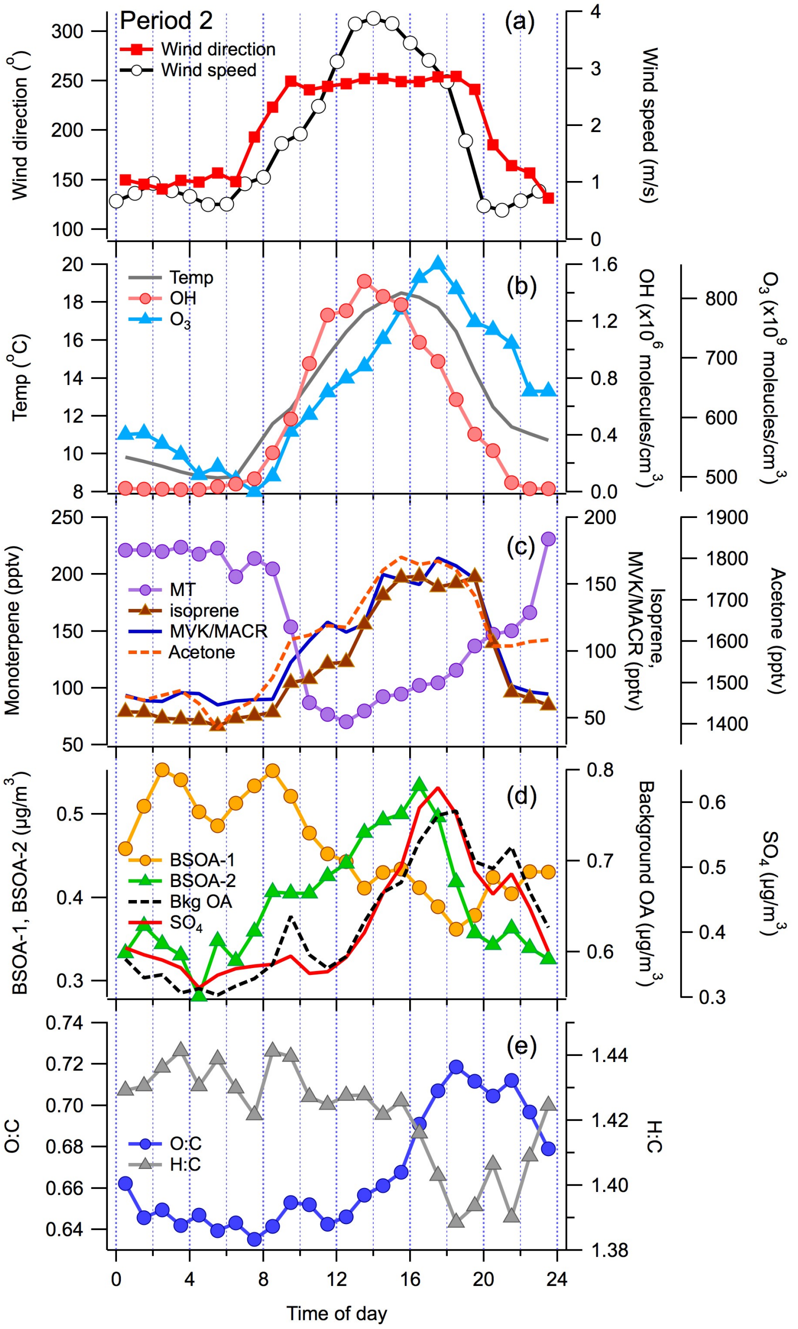

Figure 4: Diurnal cycles of (a) temperature, OH radical and ozone (b) monoterpene (MT), isoprene, methyl vinyl ketone (MVK)/ methacrolein (MACR), and acetone, (c) background OA, BSOA-1, BSOA-2 and SO_4, and (d) elemental compositions of total organics (O:C and H:C) observed during July 13-18 (Period 2). Note that the OH radical concentration is the average value measured after July 19.

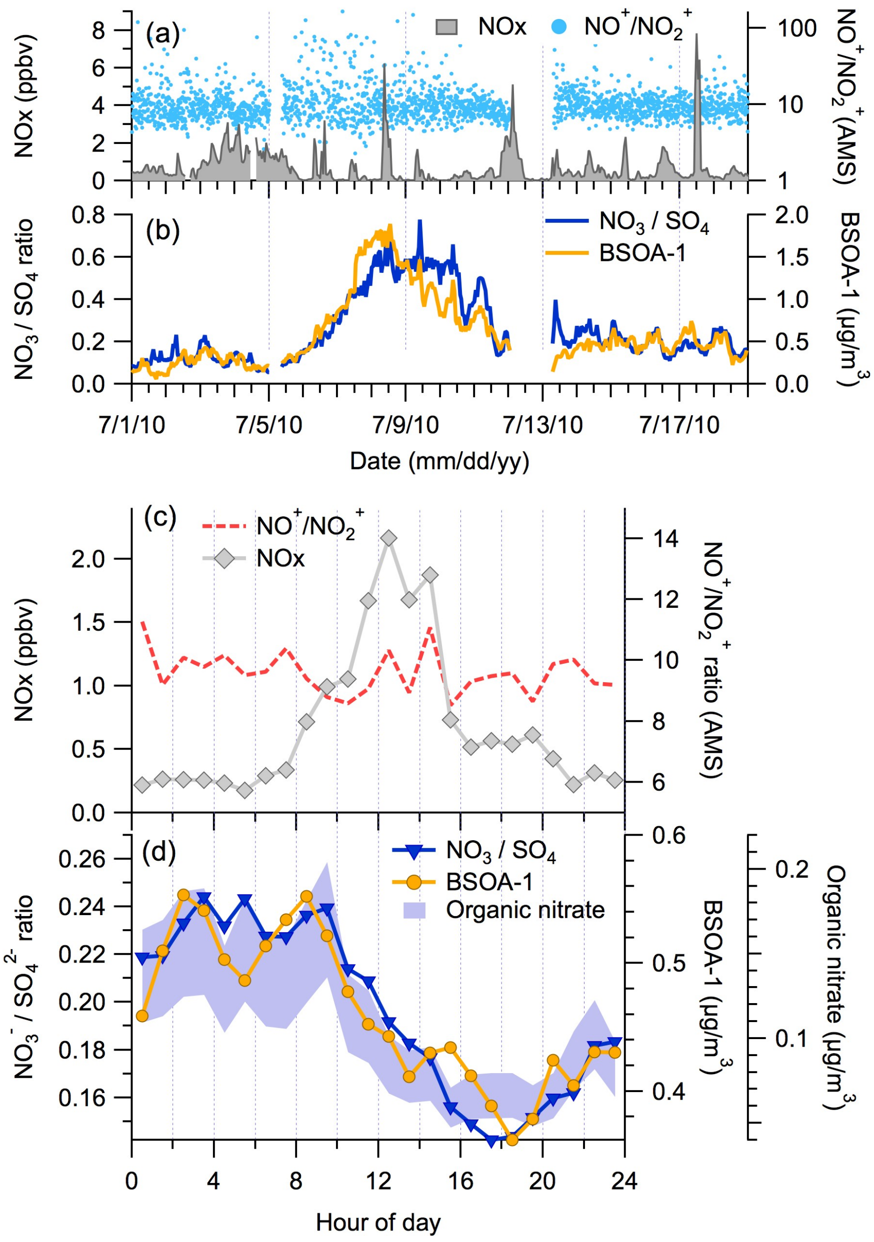

Figure 5: Time series (PST) profiles of (a) NOx mixing ratio and NO^+/NO_2^+ ratio measured by HR-ToF-AMS and (b) NO_3^-/SO_4^{2-} ratio and mass loading of BSOA-1. Diurnal cycles of (c) NOx mixing ratio and NO^+/NO_2^+ ratio measured by HR-ToF-AMS and (d) NO_3^-/SO_4^{2-} ratio and mass loadings of BSOA-1 and organic nitrates in Period 2.

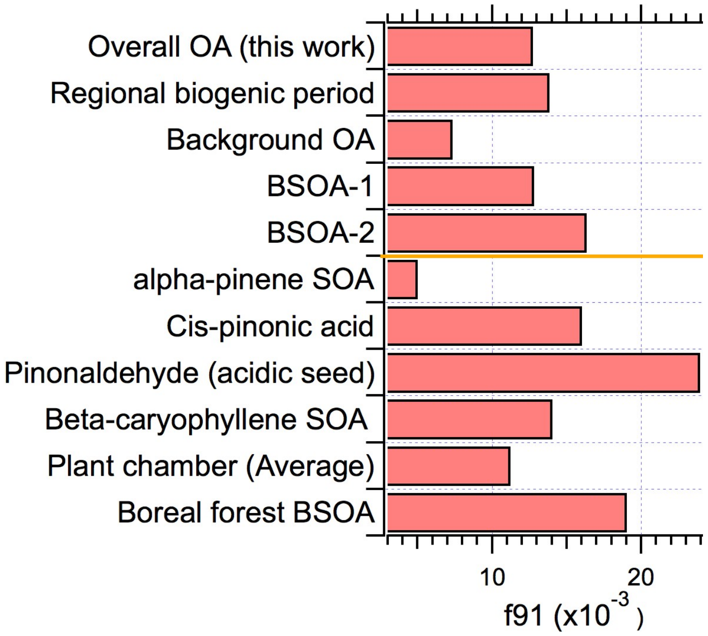

Figure 6: The mass fraction of m/z 91 (f91) observed in this study (overall OA, regional biogenic period, background OA, BSOA-1 and BSOA-2), α-pinene and β-caryophyllene SOA generated by chamber experiments (Chen et al., 2015), pinonaldehyde uptake on sulphuric acid seeds (Liggio and Li 2006), plant chamber SOA (Kiendler-Scharr et al., 2009), cis-pinonic acid (Lee et al., 2012), and BSOA observed in boreal forest in Finland (Finessi et al., 2012).