Response to reviewers' comments

We appreciate the comments and suggestions from three reviewers. We have carefully considered these comments and revise the manuscript accordingly. Our point-to-point responses are presented below. Note that the comments are in black, our response in blue, and revise in the manuscript in red.

ACPD manuscript: **10.5194/acp-2018-693**
Authors: **Yanqing An, Jianzhong Xu, Lin Feng, Xinghua Zhang, Yanmei Liu, Shichang Kang, Bin Jiang, Yuhong Liao**

Reviewer #1

This study analyzed the molecular chemical composition of water soluble organic matter (WSOM) from two fine particulate filter samples collected at a high altitude station(Qomolangma Station, QOMS, 4276 m a.s.l.) in the northern Himalayas using positive mode electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI(+)-FTICR-MS). The molecular compositions of WSOM mainly comprised CHO and CHON compounds with equal important contribution. Detailed molecular information in the common formula of these two filters was explored. The authors found that water-soluble organic compounds were mainly from biomass burning and biogenic emissions. All compounds had relatively high DBE values suggesting potential high light absorption feature and have important application in atmospheric radiative forcing and biogeochemical effects in the remote region. As the analysis of molecular chemical compositions of WSOM using ultra-high resolution mass spectrometry in such a high altitude regions is rare and important, the data set provided by this work is thus very valuable. The authors also performed a comprehensive analysis on this dataset, and the findings, conclusions are well supported by such analyses. Overall, the paper is within the scope of ACP and generally well written and documented. I recommend publication of this paper in ACP after some revisions.

Specific comments:
1. Line 19, the weighted double bond equivalent (DBEw) was used here and in Table 1, however, the calculation method for DBEw was not given in Sect. 2.3 besides that for DBE, please added.

The equation for calculating DBEw and other weighted indexes is added in the method section as follows.

"The wighted DBE (DBEw), O/C (O/Cw), and H/C (H/Cw) were calculated using equation 2,

$$X_w = \sum(w_i * X_i) / \sum w_i \qquad (2)$$

where X_i and wi are the parameters above and the relative intensity (RI) for each individual formula, i."

2. Line 69-76, the advantages of FTICR-MS method compared with the previous measurements in HTP as well as the wide usage of FTICR-MS worldwide need to be more emphasized in the introduction, whereas the current version were relatively simple.

We have enriched this part in the updated manuscript as follows.

“Fourier transform-ion cyclotron resonance mass spectrometry (FTICR-MS) coupled with soft ionization source, such as electrospray ionization (ESI), can be used to identify the individual molecular formula of extremely complex mixture because of its ultra-high resolution and mass accuracy (Mazzoleni et al., 2010). Similar methods have been used for identification of components in aqueous secondary OA (SOA) and in ambient samples, and allow the identification and separation of thousands of compounds in a sample (e.g., Mazzoleni et al., 2010; Altieri et al., 2012; Mead et al., 2013). Kinds of methods such as double bond equivalents (DBE), elemental ratios, Kendrick mass defects (KMD) can be applied to deduce the chemical characterization of obtained molecular.”

3. Line 82-93, the logic in these sentences about the description of sampling site and instruments are confused, namely the sentence of "and the instruments used in this study...BC mass concentration" need to be moved before "A low-volume (16.7 L min-1)...". Overall, the description of sampling site and weather first following by the instrument. Besides, the instruments used in this study included a HR-ToF-AMS, PAX, and PQ-200, rather than just HR-ToF-AMS and PAX but description PQ-200 alone in the following part.

The logic of this paragraph has been updated as suggested by the reviewer.

4. Line 163, "However, most of WSOM in PM2.5 is in accumulation size mode (less than 1μm) which could be detected by HR-ToF-AMS.", please provide reference.

One related literature is added in the updated manuscript.

“Zhang, Q., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., Jimenez, J.L., 2005. Time- and size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes. J. Geophys. Res., 110, D07S09, 10.1029/2004JD004649.”

5. Line 190-191, please rephrase this sentence and make it easy to understand.

Revised as follows.

“Note that individual species in the ESI-FTICR MS mass spectra could have many different isomeric structures, then the percentages reflect only the number of unique molecular formulas in each category.”

6. Line 197, the common ions are selected from the two samples in Fig. 3 and Table, however, how to calculate the RI for these common ions? From F43? please verify.

The RI for the common ions was calculated from the average of RI in two spectra and then normalized to the highest peak. We added this information in the 3.2 section as follows.

“Note that the mass spectrum of common ions was calculated from the average RI of the individual common ion from two mass spectra and normalized to the highest peak.”

7. Line 202, "suggesting a relative higher oxidation and saturation degree" is different from that in Line 20 in abstract of " suggesting their medium oxidation and saturation degrees."

We have revised these two sentences to be consistent as follows.

“…suggesting higher oxidation and saturation degrees for P1.”

8. Line 205, EI is first mentioned here in the manuscript, please add the full description.

Revised as the reviewer suggested.

9. Line 207-208, the statement of "The CHO compounds had relatively higher O/Cw ratio than that of CHON compounds in these two samples" is inappropriate for F43 in Table 1, please check.

The sentence has been removed.

10. Line 218-221, the author compared the DBR values (7.73-8.62 from Table 2) in this study with those in previous studies, however, the comparisons were not clear as the author declared that the DBE values is relatively lower than 5 –9.5 (Song et al., 2018), but close to 9.4 – 10.7 (Dzepina et al., 2015), please rephrase.

We made a mistake here and the sentence has been revised as follows.

“Comparing with other studies, the DBE values in our filter are relative close to the results from biomass burning aerosol and aerosol samples from remote sites (Table 2).”

11. Line 225-226, "The AImod, ..., was correspondingly higher in F43 which contained 49.1% aliphatic (60.4% in F30), 45.9% olefinic (36.8% in F30), and 5.1% aromatic compounds (2.9% in F30)." What was correspondingly higher in F43? The total number of the following three compounds? Consideration the higher number in F30 for aliphatic, the current expression is ambiguous.

Agree. This sentence has been revised as follows.

“…was correspondingly higher in P2 as illustrated by its higher contribution of olefinic (75.0% vs. 73.9% for P2 and P1) and aromatic compounds (10.3% vs. 7.7% for P2 and P1) (Table 1).”

12. Line 237-279, a total of 4554 and 5192 molecular formulas was identified for F30 and F43 and existed 3700 common molecular formulas, however, the unique molecular formulas were just 619 and 1142 for the two filter rather than the rest 4554-3700 and 5192-3700, please modify or add specific values to Table 1.

We have made the number consistently in the updated manuscript.

13. Line 258, "A threshold DBE/C value of 0.7 usually serves as a criterion to identify species with condensed aromatic ring structures", please added references.

Done.

14. Line 269-270, the RI values mentioned here are in this study rather than in the reference, please declare.

Agree. The RI values are all listed in Table 3.

15. Line 313, there is no information about the 1N and 2N compounds in the Table 1.

We made a mistake here and revised accordingly.

16. Line 372, the 7.6% contribution of nitrogencontaining compounds to PM1 is from Zhang et al. (2018) for the entire long period rather than the two filter period (9% in Fig. 1), please added the reference to give a clear description.

Revised as the reviewer suggested.

“Due to the relative higher mass concentration and higher contribution of nitrogen-containing compounds (9% of PM_1) during these two periods based on HR-ToF-AMS results (Zhang et al., 2018), it is believed that aerosol transported to the Himalayas have important application in atmospheric radiative forcing.”

Minor comments:
Line 18, change "are" to "were"
Line 22, change “significant” to “significantly”
Line 25, change “diagnose” to “diagnostic”
Line 26, change “highly” to “high”
Line 29, change "biomass mass burning" to "biomass burning"
Line 31, remove "are"
Line 53, change "could" to "can"
Line 57, remove "of", change "elevation" to "elevated"
Line 84, change "includes" to "included"
Line 92, change "with an average temperature..." to "and an average temperature..."
Line 101, 219, change "relative" to "relatively"
Line 218, change "than than of F30" to "than that for F30"
Line 260, change "were" to "have"
Line 366, change "particular" to "particulate"

All the minor issues above have been revised accordingly.

Reviewer #2

The authors of this paper reported sampled water-soluble organic matter (WSOM) at a high elevation site of Himalayas. They identified CHO and CHON compounds to be primary molecular compositions of WSOM. The paper provided important information on organic aerosols which could contribute to climate change and atmospheric oxidation over the Tibetan Plateau. The article should be published in ACPD. At this stage, I have only several minor comments as outlined below.

1. The authors attributed the sources of WSOM to biogenic volatile organic compounds and biomass mass burning. Given the lower temperature (∼5.7◦C), BVOCs might not be readily formed and unlikely transported from distance sources as well. Or there is a high level of solar radiation/photosynthetically active radiation (PAR) in the Himalayas which favors the BVOC formation? Authors perhaps need to make a comment on this point.

In the manuscript, we emphasize that the oxidation products of biogenic volatile organic compounds (BVOCs) could be emitted and/or formed in low elevation regions in the south Asia. Oxidation products of BVOCs was found in inland of India (Fu et al., 2010) and in low elevation of Himalayas (Stone et al., 2012) during monsoon and post monsoon seasons. Aerosol in low elevation of south Asia could be transported to Himalayas and the inland of Tibetan Plateau through favorable large-scale atmospheric circulation (Zhang et al., 2017a) and regional/local meteorological conditions. Biogenic aerosol was also identified in aerosol collected in Namco Station which is far away from south Asia and has higher elevation than our sampling site (Ding et al., 2014). Actually, BVOCs were also observed in the mountain area of southern Himalayas at high elevation area (5050 m) (Ciccioli et al., 1993). In our results, products from ozonolysis of α-pinene were found with high relative intensity. Therefore, we believed that these signals were real, and these oxidation products could be transported to our sampling site. To clarify this point, we add a few sentences and references to support this conclusion (line 282 – 288).

2. I don’t think that the measurement site of this study was located in the free troposphere (Table 2ïïjˇ Nand perhaps the sampling sites in other studies listed in Table 2). The free troposphere means the troposphere above the boundary-layer. Although the elevation of the sampling site is 4275 m, it is on the ground surface and hence within the boundary layer.

Agree. The sampling site is in the boundary-layer which was frequently impacted by long-range transport air mass from low elevation regions. We change them to remote sites in Table 2.

Please check the language carefully.
There are quite a lot of grammar and spelling errors. For example,
Line 51 ‘is’ should be ‘are’;
Line 53, ‘could from’;
Line 57, ‘in the southern of’;
Line 158 and 164, ‘were’ should be ‘was’,
Line 171, ‘person correlation efficiency’;
Line 181, ‘transport’ should be ‘transported’;
Line 698 (Fig. 2 captions), ‘ground level of 1000m’, you mean 1000 m above the ground level?

All the language issues have been revised and we have carefully checked the language throughout the manuscript.

Reviewer #3

The manuscript presented by Y. An et al. presents the detailed molecular chemistry of two samples collected from the Qomolangma Station in the Himalayas. The detailed molecular chemistry was derived from ultra-high resolution FT-ICR mass spectrometry measurements following electrospray ionization to generate positive ions. The authors discuss the molecular composition of the two samples and compare them carefully to previously published studies using similar approaches. Specifically, they found an increased degree of unsaturation of the prominent species in their study. As the authors suggest, these molecules may contribute to aerosol absorption. The manuscript is well prepared and the methodology is technically sound. However, I recommend the authors consider revisions to the manuscript to address method limitations pertaining to the ionization (potential artifacts, differences between + and -, anticipated functional groups, etc.) and discuss more specifically the significance of the results (both with respect to the implications and the limitations).

The limitation of our study only using ESI(+) are presented in the updated manuscript in method section and implication section. The response to potential artifacts and differences between ESI+ and ESI- is presented in specific question below. In the implication section, we also emphasize the significance of our results of the molecular compounds for the radiative forcing in the Himalayas and remove the content of biogeochemical effects.

Specific major comments without any predetermined order:

1. It appears that many assumptions about the ionization method were made in the data interpretation. Those assumptions are not explicitly stated and may be incorrect. (i) For example, NH4+ is a common cation that readily adducts to molecular to assist in forming positive ions (similar to Na+). Please explicitly state your assumptions regarding this possible artifact. (ii) CHON compounds observed in ESI are expected to vary with the ionization mode. For example, reduced N (e.g., amino functional groups) are not expected to be observed in the negative ion mode. Likewise, oxidized N (e.g., nitrate functional groups) are not expected to be observed in the positive ion mode. Please explicitly state your assumptions regarding the ionization method and possible differences between ESI positive ions and ESI negative ions.

Thank you for your point this out. We state our assumptions regarding the potential compounds ionized in ESI positive mode in the updated manuscript (line 134-141). For the adduct of NH_4^+, we cannot exclude the possibility that some of compounds many form $[M + NH_4]^+$, however, the possibility of this formation was low by comparing with formation of Na^+ adducts because the binding strength of oxygen containing organic molecules with Na^+ ion is expected to be stronger than that of NH_4^+ ion. Highly oxygenated molecules that contain multiple peroxide functionalities were found to be readily cationized by the attachment of Na+ during electrospray ionization operated in the positive ion mode (Zhang et al., 2017b). In addition, the concentration of ammonium was low and we control the concentration of SPE effluent WSOM to be ~0.2 mg/mL which was not too concentrated for artifact adducts. The degree of ionization of nitro-phenolic compounds at low acidic condition could be high and the pH of our mobile phase was between 2 and 3 which was thought to favor for nitro-phenolic compounds ionization.

2. Due to differences in the ESI ionization process (positive vs negative), the direct comparison of the data can be difficult. Please be sure to check the ionization mode of referenced datasets and discuss the method limitations associated with the datasets and the resulting limitations on the conclusions.

Agree. The ESI mode in each reference has been listed in Table 2. The direct comparison of molecular composition between different data in the manuscript was mainly based on the same ESI mode.

3. How were the molecular formulas and their homologous series formed from biogenic VOCs and biomass burning identified?

We remove the content of homologous series formed from biogenic VOCs and biomass burning emissions in the abstract and only emphasize the marker of these aerosol sources. The homologous series identified in KMD vs. KM plot were only focused on the potentially predominated compounds.

4. The phrase “important implications” (line 32) is an empty phrase. Please be more specific with the inferred implications and impacts associated with the studied molecular classes.

This sentence has been revised as follows.

“The high DBE and high fraction of nitrogen containing aerosol can potentially impact aerosol light absorption in this remote region.”

5. What do your sample names indicate or represent? Consider changing the samples names to be more descriptive.

The names of samples are now denoted as P1 (period 1) and P2 (period 2), respectively, and consistent throughout the manuscript.

6. What is meant by “pristine region”?

This has been changed to “remote region”.

7. The literature review describing the significance of light absorbing aerosol is severely out of date.

We have enriched this part and updated the references as follows.

“Brown carbon can originate from primary emission and/or secondary process, and have an increasing contribution (up to ~20%) to the light absorption in recent years (Laskin et al., 2015, and reference therein). Due to the light absorption of brown carbon is strongly depended on their molecular structure, light absorbing compounds at molecular level were explored during recent years and found that nitrogen-containing compositions are important brown carbon compounds (Lin et al., 2016; Lin et al., 2017)."

8. The phrase "Many studies" requires more than just one example reference.

We added one more literature here.

9. The goal of the paper is what exactly?

We add one sentence to mention the purpose of this study as follows.

"In this study, we focus on the molecule composition of water soluble organic compound in fine particle aerosol in the Himalayas using positive mode ESI-FTICR MS and evaluate the sources, chemical processing, and potential impact of aerosol in this region."

10. What is the relevance of discussing the tourist season?

This sentence has been removed.

11. Ultrasonic baths can introduce reactive oxygen species. What care was taken to avoid extraction artifacts?

We added ice during ultrasonic extraction and kept the sample immersing in the mixture of ice and water. This information is updated in the manuscript as follows.

"The sample tubes were immersed in the mixture of ice-water during ultrasonic extraction to prevent potential chemical reaction."

12. Please discuss the SPE recovery.

We did not measure the SPE recovery for this study. Based on the previous studies, water soluble organic carbon recoveries ranged between 20% and 65% for the different SPE sorbents (Dittmar et al., 2008; Green et al., 2014; Raeke et al., 2016). PPL usually has higher recovery than C18 or HLB for subsequent FT-ICR MS analysis (Green et al., 2014). In addition, the FT-ICR mass spectra of the original sample and the SPE extracts did not differ significantly in their molecular weight distribution, but they showed sorbent specific differences in the degree of oxygenation and saturation; The selective enrichment of freshwater WSOM by SPE is less critical for subsequent FT-ICR MS analysis, because those fractions that are not sufficiently recovered have comparatively small effects on the mass spectra (Raeke et al., 2016). We add one sentence to support the usage of PPL cartridge in the updated manuscript as follows.

"PPL cartridge generally has the best properties for WSOM enrichment for subsequent FT-ICR MS analysis (Raeke et al., 2016)."

13. Please discuss the steps that were taken to avoid ESI artifacts?

The possible artifacts of positive ESI method is the formation of adducts such as sodium, ammonium and so on which could complex mass spectrum. These artifacts could try to be avoided by removing the inorganic salt by SPE before measurement. In our study, we apply SPE concentration to eliminate the inorganic salts as more as possible, although we cannot exclude the possibility that some of compounds may form from these artifacts. In addition, we control the concentration of SPE effluent WSOM to be ~0.2 mg/mL which was not too concentrated for artifact adducts. We revised the sentence in the updated manuscript to mention this as follows.

“Prior to FTICR MS analysis, the extraction was concentrated and purification using PPL (Agilent Bond Elut-PPL cartridges, 500 mg, 6 mL) solid phase extraction (SPE) cartridges for water soluble organic matter (WSOM) to avoid possible ESI artifacts. PPL cartridge generally has the best properties for WSOM enrichment for subsequent FTICR MS analysis (Raeke et al., 2016). In addition, we control the concentration of SPE effluent to be ~0.2 mg/mL which was not too concentrated for artifact adducts.”

14. The parameters associated with your “custom software” need to be more thoroughly described. How did you eliminate ambiguous formula assignments?

The formula assignment is controlled by the mass accuracy up to ±1.5 ppm as well as a number of criteria including the isotope pattern and elemental ratios, such as H/C, O/C, N/C, S/C, and DBE/C in the ranges of 0.3-3.0, 0-3, 0-0.5, 0-0.2, and 0-1. We add this information in the updated manuscript as follows.

“The ions detected in filter blank were subtracted and molecular formulas in the samples were assigned to all ions with signal-to-noise ratios of greater than 10 with a mass tolerance of ±1.5 ppm using custom software. Molecular formulas with their maximum numbers of atoms were defined as: 30 ^{12}C, 60 ^{1}H, 20 ^{16}O, 3 ^{14}N, 1 ^{32}S, 1 ^{13}C, 1 ^{18}O and 1 ^{34}S. Identified formulas with H/C, O/C, N/C, S/C, and DBE/C ranged in 0.3 – 3.0, 0 – 3, 0 – 0.5, 0 – 0.2, and 0 – 1, were selected, and formulas containing isotopomers (i.e., ^{13}C, ^{18}O or ^{34}S) were not considered.”

15. What is meant by the “processing error” mentioned in line 161? How did you ensure that the error did not affect the molecular composition?

We are sorry for your confusion by this sentence. Actually, we made a mistake during the weighting of the samples which was not related with chemical measurement. The processing error was that we did not balance the filters at the same conditions as that before sampling. So that the gravimetrically data of the filters were not correct.

16. What is the procedure for identifying the NOA compounds with HR-ToF-AMS?

The NOA compounds identified in HR-ToF-AMS is based on positive matrix factorization (PMF) analysis which was included in details in our previous paper (Zhang et al., 2018). Basically, the identification of NOA factor was based on its special mass spectrum, diurnal pattern, and correlation with other tracers. We mention this information in the updated manuscript as follows.

“The OA was comprised by biomass burning emitted OA (BBOA), nitrogen-contained OA (NOA), and more-oxidized oxygenated OA (MO-OOA) decomposed by positive matrix factorization (PMF) analysis (Fig. 1). The details on PMF analysis can be found in Zhang et al. (2018).”

17. How was the influence of potential fresh OA inferred?

The fresh OA here mean less oxidized OA which was inferred based on the short trajectory distance and higher contribution of BBOA in P2 than P1. In order to clarify this, we revise this sentence as follows.

“The air mass during P2 was partly (13%) transported with low wind speed and short distance (less than 100 km) which could contain some fresh OA as illustrated with higher fraction of BBOA.”

18. In the discussion of common ions, the authors assume that the two samples have a similar aerosol source? What if instead, the common compounds are simply not marker compounds. Complex mixtures are expected to have many ions in common.

We agree that complex organic mixture has many ions in common. The two samples in this study collected during one long-range transport event at different stages. Although, the chemical characteristics between these two samples were kind of different, the aerosol sources for them could be similar based on trajectory analysis and AMS-PMF results. In addition, the mass spectra and ion composition from FTICR MS between them were also very similar. Therefore, for more confident on our analysis, we extract the common formula for further discussion.

19. What is the balance of source contribution vs. aerosol aging in these samples.

It is hard to know the exactly ratio between source contribution and aerosol aging. We analyzed the potential aging processes including photo reaction, aqueous reaction and dark reaction during the transport in Zhang et al., (2018), and found these reactions could be important for aerosol aging.

20. I’m surprised that the long-range transported aerosol reported in Dzepina et al. is similar to the samples reported here. How is that observation justified with respect to the transport pathways?

We agree that this sentence is confused and therefore delete it in the updated manuscript.

21. The “distinct group of CHON aromatic compounds” in the lower left of the VK diagram may be incorrect assignments. What are the limits for the DBE range?

We set the limit of DBE/C of 0-1 and this group CHON is in this range. Consider the extremely high carbon number (>40), we remove this group.

22. What is the significance of the difference in the max abundance between H+ and Na+ type ions?

The $[M + Na]^+$ compounds could be carboxylic acid groups that readily form $[M + Na]^+$ ions in the positive electrospray ionization mode. Since we delete the high abundance group of $[M + Na]^+$, the sentence related with $[M + Na]^+$ has been removed.

23. The detailed description given over lines 279-298 is quite tedious. Perhaps some of these formulas can be better presented in a figure or table?

A new table (Table 3) is added in the updated manuscript to present all the formula mentioned in the text.

24. What is the significance of 1N vs 2N?

We compare the compounds of 1N and 2N to get the information of structure and chemical formation of nitrogen-containing compounds. As shown in the manuscript, the elemental ratios (O/C, H/C, O/N, and DBE) were different for 1N and 2N compounds, and the potential formation for 1N and 2N compounds are discussed in the manuscript.

25. How do you observe acidic N in the positive ion mode?

We remove the citation of amino acids here. The CHON compounds observed in our positive ESI mode could contain reduced N functional groups (e.g., amines), which are preferentially ionized in ESI+ mode. Similar results which observed CHON compounds in positive ESI mode was also found in previous study in biomass burning influenced aerosol (Lin et al., 2012; Wang et al., 2017). In addition be nitro-phenolic compounds are also likely ionized in ESI+ mode in the acidic mobile phase. We have made the CHON compounds more clear in the updated manuscript.

26. The statement in lines 330-333 is not convincing. Please rephrase and add more evidence or description.

Agree. We have added a few sentences here as follows.

“Lin et al. (2017) found aged biomass burning aerosol in the present urban oxidants (such as NO_x) could result in higher fraction of CHON compounds comparing to the fresh biomass burning aerosol. Considering the high influence of biomass burning emission in the Himalayas (Zhang et al., 2018b), the CHON compounds in our study were probably related with biomass burning emissions. Recent studies have proven that burning of mixed biomass fuels in Nepal could emit amount of nitrogen species such as NH_3, NO_x, HCN, benzene, and organics, and the emission factors for these species are higher than that of wood (Stockwell et al., 2016; Jayarathne et al., 2018). In addition, it is likely that smoldering burning of bio-fuels in high elevation area is also responsible for the presence of many nitrogen-containing compounds in BBOA (Chen et al., 2010).”

27. Lines 351- 353: How does the sample matrix effect the observation of ions in ESI?

This explanation was deleted.

28. Where are the major products of BVOC as mentioned in lines 359-363?

These formulas were monoterpene products with NO_3 radical and these information is listed in Table 3.

29. The discussion of the research implications can be enhanced with a deeper discussion of the molecular composition and method limitations. What other observations of absorbing species have been made in the Himalayas?

So far there is not molecular based light absorption measurement. We have improved the discussion on the implications which include the molecular composition and method limitations as follows.

"More comprehensive methods are needed in the future for identifying BrC in the Himalayas due to the chemical complexity of BrC. For example, the BrC extraction is highly dependent on the used solvent and water insoluble OA can contribute higher light absorption than water soluble OA (Chen and Bond, 2010). In addition, Budisulistiorini et al. (2017) found that a number of compounds can dominate the light absorption of BrC, although they have a minor contribution to the aerosol mass. Therefore, it is important to know the exactly chromophores of BrC which can be obtained by combining with high performance liquid chromatography, light absorption measurement with a photodiode (PDA) detector, and chemical composition with high resolution mass spectrometer (HPLC-PDA-HRMS system) (Lin et al., 2016). For mass spectrometry analysis, different ionization sources are also favorable for different compounds, such as ESI only detect a part of polar compounds; non-polar compounds which could dominated the contributing of BrC, can be measured using atmospheric pressure photo ionization (APPI) (Lin et al., 2018). Recent study indicate that over 40% of the solvent-extractable BrC light absorption is attributed to water insoluble, non-polar to semi-polar compounds such as PAHs and their derivative (Lin et al., 2018). In contrast, the polar, water-soluble BrC compounds, which are detected in ESI, account for less than 30% of light absorption by BrC (Lin et al., 2018)."

30. The implications regarding nutrients and biogeochemical cycling are beyond the scope of the current research and seem to be a bit too ambitious. Please revise.

Agree. This information has been removed.

31. Related to the previous comment, did you study deposition?

Yes. We collected precipitation samples during this field study and the project we involved cover several direction including biogeochemical cycling. But we agree that the biogeochemical cycling is out of the range of this study and remove this information in the updated manuscript.

32. Again, what type of N did you study with your analytical method. Please be clear with the limitations and assumptions that are necessary.

The nitrogen compounds in our study were likely reduced nitrogen and nitro-aromatic compounds. To make more clarify this point, a few sentences are added in 3.3.2 section.

33. How are the measurement sites defined? The listed free troposphere sites do not consistently sample free tropospheric air. In each case, seasonal factors may play a strong role in the height of the boundary layer.

Agree. Free troposphere sites should above boundary layer height and have less influence from it. Our site and some other sites in Table2 were strongly influenced by the air from boundary layer. We have revised these sites in Table 2 to remote sites.

34. Figure 3 appears to contain several high intensity regularly spaced peaks that are not associated with the sample. Please remove or flag these peaks as contaminants.

This high intensity group has been removed.

35. Please add the specific details regarding your treatment of blank samples to the methods section.

Agree. The description for the treatment of blank sample is added in the method section.

“One procedure blank was also adopted in this study as like that of aerosol samples to subtract the potential background.”

“The ions detected in filter blank were subtracted and molecular formulas in the samples were assigned to all ions with signal-to-noise ratios of greater than 10 with a mass tolerance of ±1.5 ppm using custom software.”

36. How are the FT-ICR MS ions related to the fragment ions from HR-ToF-AMS (as shown in figure 4)?

The connection between FT-ICR MS ions and HR-ToF-AMS frags is through the index of carbon oxidation state (OSc) (Kroll et al., 2011). The shaded ovals indicate locations of different ambient organic aerosol classes as determined from factor analysis of HR-ToF-AMS data, which the nC is estimated from volatility measurements (Kroll et al., 2011).

Additional minor comments:
Line 19: DBE = double bond equivalents; DBE is plural not singular

Revised as suggested by reviewer.

Line 31: “high nitrogen containing of aerosol” is unclear. Please rephrase.

Revised to “high fraction of nitrogen containing of aerosol”.

Line 32: “important implications” (use plural)
This sentence has been changed accordingly.

“The high DBE and high fraction of nitrogen containing aerosol can potentially impact aerosol light absorption in this remote region.”

Line 32: “and the biogeochemical cycle” (insert article)

The biogeochemical cycle content has been removed.

Line 42: “Accompany” is awkward. Please rephrase.

Revised to “Under favorable atmospheric circulation”.

Line 43: “to the Himalayas” (insert article)

Done and check throughout the manuscript.

Line 46: “essential” is awkward. Please rephrase

Change to negative.

Line 172: What is the IA method?

For AMS study, there is an improved method to calculate the elemental ratios in recent year. The full name of IA method and reference are shown in the manuscript.

Line 181: “transported" (verb tense)

Done.

Line 185: Fix typo.

Done.

Lines 247 & 249: “molecular weight” not "molecule weight"

Revised and throughout the manuscript.

Lines 256 & 258: Typo? Did you mean to use Cw or C in these two sentences?

Change to C.

Line 261: “carbon oxidation state” (lower case “C”)

Revised as suggested by the reviewer.

Line 307: “average O atoms contained in” (plural and verb tense)

Revised as suggested by the reviewer.

Line 368: “two compounds” or “two compound groups"

Change to two compound groups.

Line 373: “believed” (verb tense)

Done.

Table 1 (and Figure 3): Are the values shown for F30 and F43 for all ions or only unique ions?

The values shown in Table 1 and Figure 3 are for all ions. The captions of Table 1 and Figure 3 have been improved.

Figure 1: What is the purpose of the blue shading behind the pie chart?

The blue shading has been removed.

Figure 1 (and elsewhere): Please remember to define all of the acronyms used in the figure within the figure caption.

Agree. All the acronyms used in the figures have been shown with the full name.

Figure 2: Please include the vertical profile for the back trajectories

The vertical profile has been colored on each cluster using air pressure data.

References

Altieri, K. E., Hastings, M. G., Peters, A. J., and Sigman, D. M.: Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry, Atmos. Chem. Phys., 12, 3557-3571, 2012.

Ciccioli, P., Brancaleoni, E., Cecinato, A., Sparapani, R., and Frattoni, M.: Identification and determination of biogenic and anthropogenic volatile organic compounds in forest areas of Northern and Southern Europe and a remote site of the Himalaya region by high-resolution gas chromatography—mass spectrometry, Journal of Chromatography A, 643, 55-69, https://doi.org/10.1016/0021-9673(93)80541-F, 1993.

Ding, X., He, Q.-F., Shen, R.-Q., Yu, Q.-Q., and Wang, X.-M.: Spatial distributions of secondary organic aerosols from isoprene, monoterpenes, β-caryophyllene, and aromatics over China during summer, J. Geophys. Res., 119, 11,877-811,891, doi:10.1002/2014JD021748, 2014.

Dittmar, T., Koch, B., Hertkorn, N., and Kattner, G.: A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater, Limnology and Oceanography: Methods, 6, 230-235, doi:10.4319/lom.2008.6.230, 2008.

Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T., and Chen, J.: Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation, Atmos. Chem. Phys., 10, 2663-2689, 10.5194/acp-10-2663-2010, 2010.

Green, N. W., Perdue, E. M., Aiken, G. R., Butler, K. D., Chen, H., Dittmar, T., Niggemann, J., and Stubbins, A.: An intercomparison of three methods for the large-scale isolation of oceanic dissolved organic matter, Marine Chemistry, 161, 14-19, https://doi.org/10.1016/j.marchem.2014.01.012, 2014.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nat Chem, 3, 133-139, http://www.nature.com/nchem/journal/v3/n2/abs/nchem.948.html#supplementary-information, 2011.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, Chem. Rev., 4335-4382, 10.1021/cr5006167, 2015.

Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, Environ. Sci. Technol., 46, 7454-7462, 10.1021/es300285d, 2012.

Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, Environ. Sci. Technol., 50, 11815-11824, 10.1021/acs.est.6b03024, 2016.

Lin, P., Bluvshtein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event, Environ. Sci. Technol., 51, 11561-11570, 10.1021/acs.est.7b02276, 2017.

Mazzoleni, L. R., Ehrmann, B. M., Shen, X., Marshall, A. G., and Collett, J. L.: Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Environ. Sci. Technol., 44, 3690-3697, 10.1021/es903409k, 2010.

Mead, R. N., Mullaugh, K. M., Brooks Avery, G., Kieber, R. J., Willey, J. D., and Podgorski, D. C.: Insights into dissolved organic matter complexity in rainwater from continental and coastal storms by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry, Atmos. Chem. Phys., 13, 4829-4838, 10.5194/acp-13-4829-2013, 2013.

Raeke, J., Lechtenfeld, O. J., Wagner, M., Herzsprung, P., and Reemtsma, T.: Selectivity of solid phase extraction of freshwater dissolved organic matter and its effect on ultrahigh resolution mass spectra, Environ Sci Process Impacts, 18, 918-927, 10.1039/c6em00200e, 2016.

Stone, E. A., Nguyen, T. T., Pradhan, B. B., and Man Dangol, P.: Assessment of biogenic secondary organic aerosol in the Himalayas, Environ. Chem., 9, 263-272, 10.1071/EN12002, 2012.

Wang, Y., Hu, M., Lin, P., Guo, Q., Wu, Z., Li, M., Zeng, L., Song, Y., Zeng, L., Wu, Y., Guo, S., Huang, X., and He, L.: Molecular Characterization of Nitrogen-Containing Organic

Compounds in Humic-like Substances Emitted from Straw Residue Burning, Environ. Sci. Technol., 51, 5951-5961, 10.1021/acs.est.7b00248, 2017.

Zhang, R., Wang, Y., He, Q., Chen, L., Zhang, Y., Qu, H., Smeltzer, C., Li, J., Alvarado, L. M. A., Vrekoussis, M., Richter, A., Wittrock, F., and Burrows, J. P.: Enhanced trans-Himalaya pollution transport to the Tibetan Plateau by cut-off low systems, Atmos. Chem. Phys., 17, 3083-3095, 10.5194/acp-17-3083-2017, 2017a.

Zhang, X., Lambe, A. T., Upshur, M. A., Brooks, W. A., Gray Bé, A., Thomson, R. J., Geiger, F. M., Surratt, J. D., Zhang, Z., Gold, A., Graf, S., Cubison, M. J., Groessl, M., Jayne, J. T., Worsnop, D. R., and Canagaratna, M. R.: Highly Oxygenated Multifunctional Compounds in α-Pinene Secondary Organic Aerosol, Environ. Sci. Technol., 51, 5932-5940, 10.1021/acs.est.6b06588, 2017b.

Zhang, X., Xu, J., Kang, S., Liu, Y., and Zhang, Q.: Chemical characterization of long-range transport biomass burning emissions to the Himalayas: insights from high-resolution aerosol mass spectrometry, Atmos. Chem. Phys., 18, 4617-4638, 10.5194/acp-18-4617-2018, 2018.

Molecular characterization of organic aerosol in Himalayas: insight from ultra-high resolution mass spectrometry

Yanqing An[1], Jianzhong Xu[1], Lin Feng[1, ~~2~~3], Xinghua Zhang[1, ~~2~~3], Yanmei Liu[1, ~~2~~3], Shichang Kang[1], ~~[2]~~
Bin Jiang[2], Yuhong Liao[2]

[1]State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

~~[2]University~~[2]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[3]University of Chinese Academy of Sciences (UCAS), Beijing 100049, China

Corresponding Author: Jianzhong Xu, jzxu@lzb.ac.cn

Abstract

An ~~increasing~~increased trend in aerosol concentration has been observed in the Himalayas in recent years, but the understanding of the chemical composition and sources of aerosol remains ~~poor.~~poorly understood. In this study, molecular chemical composition of water soluble organic matter (WSOM) from two filter samples ~~(denoted as F30 and F43)~~ collected during two high aerosol loading periods (denoted as P1 and P2) at a high~~-~~-altitude station (Qomolangma Station, QOMS, 4276 m a.s.l.) in the northern Himalayas were identified ~~by positive~~using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR~~-~~ MS). More than ~~4500~~4000 molecular formulas were identified in each filter sample which were classified into two compound groups (CHO and CHON) based on their elemental composition with both accounting for nearly equal contributions in number (45% – 55%). The relative abundance weighted mole ratio of O/C$_w$ for ~~F30~~P1 and ~~F43 are~~P2 were 0.43 and 0.~~38~~39, respectively, and the weighted double bond ~~equivalent~~equivalents (DBE$_w$), an index for the saturation of organic molecules, were ~~6.26~~7.12 and ~~6.92~~7.87, respectively~~, suggesting their medium oxidation and saturation degrees.~~. Although the O/C$_w$ mole ratio was comparable for CHO and CHON compounds, the DBE$_w$ was ~~significant~~significantly higher in CHON compounds than CHO compounds. More than 50% molecular formulas in Van Krevelen (VK) diagram (H/C vs. O/C) located in 1 – 1.5 (H/C) and 0.2 – 0.6 (O/C) regions, suggesting potential lignin-like compounds. The distributions of CHO and CHON compounds in VK diagram, DBE vs. number of C atoms, and other ~~diagnose~~diagnostic diagrams showed ~~highly~~high similarities between each other suggesting their similar source and/or atmospheric processes. ~~Detailed molecular information in the common formula of these two filters was explored.~~ Many formulas ~~with their homologous series of compounds~~ formed from biogenic volatile organic compounds (e.g., ozonolysis of α-pinene products) and biomass ~~mass~~ burning emitted compounds (e.g., phenolic compounds) were found in the WSOM ~~with high relative abundance~~ suggesting the important contribution of these two sources in the Himalayas. The high DBE and high fraction of nitrogen containing ~~of~~ aerosol ~~would have important implication for~~can potentially impact aerosol light absorption ~~and biogeochemical cycle~~ in this remote region. Further comprehensive study is needed due to the complexity of organic aerosol and limited molecular number identified in this study.

1. Introduction

~~Elevated pollutant concentrations has~~Relatively high aerosol concentration events have been frequently observed over the Himalayas during pre-monsoon period (March to June) (Bonasoni et al., 2010). The ~~high~~ aerosol ~~loading~~ plume are originated from the southern regions of the Himalayas such as northwestern India and/or Indian Gangetic region based on air mass back trajectory analysis and satellite observation (Liu et al., 2008; Lu et al., 2012; Lüthi et al., 2015). ~~In recent decades, due~~Due to increased consumption on fuels (including biofuels and fossil fuels) by industry and residents in recent decades, air pollution has been a serious issue in South Asia (Gustafsson et al., 2009). ~~Accompany with~~Under favorable atmospheric circulation, air pollutants emitted or formed in these regions can be fast transported to the Himalayas and Tibetan Plateau (HTP) (Xia et al., 2011).

~~Elevated~~Enhanced aerosol concentration for the ~~pristine~~remote region of the HTP is thought to have ~~essential~~many negative climate and environment effects. For example, the transported aerosol could heat the air at the higher layer of troposphere over the HTP and impact on the monsoon system of south Asia and accelerate the melting of glacier in the Himalayas (Lau et al., 2006; Ramanathan et al., 2007). This heating effect is predominantly from the light absorbing particular aerosol (LAPA) such as black carbon (BC) and brown carbon which ~~is~~are part of organic aerosol (OA) (Ram et al., 2010; Zhang et al., 2015; Zhang et al., 2017). BC ~~come~~is from incomplete combustion and dominates the absorption of LAPA; Brown carbon ~~could~~can originate from ~~many processes such as~~ primary emission and/or secondary process, and have an increasing contribution (up to ~20%) to the light absorption in recent years ~~(Laskin et al., 2015).~~(Laskin et al., 2015, and reference therein). Due to the light absorption of brown carbon is strongly depended on their molecular structure, light absorbing compounds at molecular level were explored during recent years and found that nitrogen-containing compositions are important brown carbon compounds (Lin et al., 2016; Lin et al., 2017). Many studies show that ~~open~~ biomass burning is an important source of ~~BC and brown carbon (e. g., Saleh et al., 2014)~~brown carbon (e. g., Saleh et al., 2014; Washenfelder et al., 2015), which is very popular in developing regions in the southern ~~of~~ Himalayas. ~~However~~Comparison with other regions, high elevation and mixed biomass fuels in

~~these regions~~the southern Himalayas could make the evolution ~~of~~and chemical composition of OA from biomass burning emission ~~-~~more complicated ~~and the chemical information of OA remains poorly characterized so far (Fleming et al., 2018)~~(Stockwell et al., 2016; Fleming et al., 2018; Jayarathne et al., 2018).

The details on the molecular composition of OA are important for understanding the sources and chemical evolution of OA ~~(Laskin et al., 2018)~~(Laskin et al., 2018). Previous studies conducted in the HTP have focused on a limited number of molecular markers such as organic acids which are closely related with biomass burning emission (Cong et al., 2015), and some toxicology species such as polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) which are related with anthropogenic activities (Wang et al., 2015; Wang et al., 2016). In addition, online measurement using Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) had provided more details on the OA chemistry and sources with high time resolution (Xu et al., 2018). However, different instrument has its limitations on OA detection and ultra-high mass resolution of mass spectrometry which can identify ~~a large number of~~many molecular formulas is lacking.

~~Electrospray ionization (ESI) with ultrahigh resolution~~ Fourier transform-ion cyclotron resonance mass spectrometry (FTICR~~-MS)~~ MS) coupled with soft ionization source, such as electrospray ionization (ESI), can be used to identify the individual molecular formula of extremely complex mixture because of its ~~extremely~~ ultra-high resolution and mass accuracy (Mazzoleni et al., 2010)~~.~~. Similar methods have been used for identification of components in aqueous secondary OA (SOA) and in ambient samples, and allow the identification and separation of thousands of compounds in a sample (e.g., Mazzoleni et al., 2010; Altieri et al., 2012; Mead et al., 2013). Kinds of methods such as double bond equivalents (DBE), elemental ratios, Kendrick mass defects (KMD) can be applied to deduce the chemical characterization of obtained molecular. In this study, we focus on the ~~comprehensive characterization of the molecule~~molecular composition of water soluble organic compound in fine particle aerosol ~~collected~~ in the ~~northern slope of central~~ Himalayas using ~~positive mode~~ ESI-FTICR~~-~~ MS and evaluate the sources, chemical processing, and potential impact of aerosol in this region.

2. Methodology

2.1. Aerosol sampling

Field study was conducted at the Qomolangma Station (QOMS, 28.36° N, 86.95° E, 4276 m a.s.l.) located at the toe of Mt. Qomolangma from Apr. 12 to May 12, 2016 using a suit of online instruments (Zhang et al., 2018b), ~~and the instruments used in this study includes~~including a HR-ToF-AMS (Aerodyne Research Inc., Billerica, MA, USA) for 5-min size-resolved chemical compositions (organics, sulfate, nitrate, ammonium, and chloride) of non-refractory submicron particulate matter (NR-PM$_1$) and a photoacoustic extinctionmeter (PAX, DMT Inc., Boulder, CO, USA) for BC mass concentration. ~~The QOMS observatory locates at a remote site with sparse local residents and anthropogenic activities around it, except for a high way for the tourism to the west about 500 m. The tourists are normally increased from June each year due to the warmer weather during summer. The weather at the QOMS during the field study was dominated by westerlies with the prevailed wind from west and southwest with an average air temperature of 5.7 ± 5.0 °C. A~~In addition, a low-volume (16.7 L min^{-1}) particular matter (PM) sampler (BGI, USA, model PQ 200) with an aerodyne diameter cutoff of 2.5 μm at the inlet was used to collect PM$_{2.5}$ filter samples on pre-baked quartz fiber filters (47 mm, Pall Life Science, NY, USA). Due to the low aerosol loading at this remote region, two days sampling strategy was adapted for each filter collection starting from 8:00 am to 7:45 am at the day after tomorrow (local time). A total of 18 filter samples were collected during the field study with three procedure blanks which were used to assess potential contamination during sampling and transportation. The sampling air volume ranged from 35.1 to 48.1 m^3 at ambient conditions. -Two ~~filter~~ samples collected during Apr. 25 – 27 (~~F30~~P1) and Apr. 29 – May 1 (~~F43)~~P2), respectively, were ~~chosen~~used in this study due to the ~~relative~~relatively higher aerosol loading based on HR-ToF-AMS results (section 3.1) and distinct particulate matter on the filter. ~~In addition, the temporal variations of aerosol concentration recorded by HR-ToF-AMS during these two filter periods shown a smoothly increase indicating a regional transportation which could be typical long-range transport events at this region~~One procedure blank was also adopted in this study as like that of aerosol samples to subtract the potential background.

2.2. Chemical analysis

For FTICR~~-~~ MS analysis, ~~these two filters~~filter samples were ~~firstly~~ extracted in 20 mL Milli-Q water in an ultrasonic bath for 30 min and filtered using 0.45 µm pore-size Acrodisc syringe filters to remove water insoluble matter (Pall Science, USA). ~~Prior to FTICR~~ The sample tubes were immersed in the mixture of ice-water during ultrasonic extraction to prevent potential chemical reaction. Prior to FTICR MS analysis, the extraction was concentrated and purification using PPL (Agilent Bond Elut-PPL cartridges, 500 mg, 6 mL) solid phase extraction (SPE) cartridges for water soluble organic matter (WSOM~~).~~) to avoid possible ESI artifacts. PPL cartridge generally has the best properties for WSOM enrichment for subsequent FTICR MS analysis (Raeke et al., 2016). In addition, we control the concentration of SPE effluent to be ~0.2 mg/mL which was not too concentrated for artifact adducts. Note that through SPE cartridge, the most hydrophilic compounds such as inorganic ions, and low-molecular-weight organic molecules such as organic acids and sugars were removed, whereas the relatively hydrophobic fraction was retained. The details on the SPE method using PPL cartridges and analysis by ~~FTICR~~ FT-ICR MS can be found in our previous paper (Feng et al., 2016). Briefly, the mass spectrometry analyses of these samples were performed using a SolariX XR ~~FT-ICR~~ FTICR MS (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and a Paracell analyzer cell. The samples were ionized in positive ion modes using the ESI ion source (Bruker Daltonik GmbH, Bremen, Germany). A typical mass-resolving power of >400 000 was achieved at m/z 400 with an absolute mass error of <0.5 ppm. ~~Molecular formulas~~The ions detected in filter blank were subtracted and molecular formulas in the samples were assigned to all ions with signal-to-noise ratios of greater than 10 with a mass tolerance of ±1.5 ppm using custom software. Molecular formulas with their maximum numbers of atoms were defined as: 30 ^{12}C, 60 ^{1}H, 20 ^{16}O, 3 ^{14}N, 1 ^{32}S, 1 ^{13}C, 1 ^{18}O and 1 ^{34}S. ~~Identified~~Identified formulas with H/C, O/C, N/C, S/C, and DBE/C ranged in 0.3 – 3.0, 0 – 3, 0 – 0.5, 0 – 0.2, and 0 – 1, were selected, and formulas containing isotopomers (i.e., ^{13}C, ^{18}O or ^{34}S) were not considered. Compounds were detected as either sodium adducts, [M + Na]$^{+}$, or protonated species, [M + H~~]$^{+}$. We report all detected compounds as neutral species, unless stated otherwise.~~]$^{+}$. Although ammonium could also readily be adduct to assist in forming positive ions, this possibility in our sample was because of the low concentration of ammonium (Fig. 1). We report all detected compounds as neutral species, unless stated otherwise. Note that the ESI+ mode is more easily to detect basic functional group compounds and the reported organic molecules here is only part of organic aerosol which are biased ionized in ESI+ mode. In addition, highly functionalized compounds could be detected in both positive and negative modes (Lin et al., 2012).

2.3. Data processing

The assigned molecular formulas were examined using the van Krevelen diagram (Wu et al., 2004), ~~double-bond equivalents (DBEs), Kendrick mass defects (KMD)~~DBE, KMD series, and aromatic indices (AI_{mod}). The O/C and H/C ratios were calculated by dividing the number of O and H atoms, respectively, by the number of C atoms in a formula. DBE analysis was used to determine the number of rings and double bonds in a molecule. The DBE was calculated using equation (1~~,~~),

$$\mathrm{DBE} = 1 + c - h/2 + n/2, \qquad (1)$$

where c, h, and n are the numbers of C, H, and N atoms, respectively, in the formula.

The wighted DBE (DBE_w), O/C (O/C_w), and H/C (H/C_w) were calculated using equation (2),

$$X_w = \sum(w_i * X_i) / \sum w_i, \qquad (2)$$

where X_i and w_i are the parameters above and the relative intensity (RI) for each individual formula, i.

The Kendrick mass (KM) and KMD ~~can be~~for CH_2 series, used to search for potential oligomeric units (Hughey et al., 2001)~~. The Kendrick mass (KM) and KMD for CH_2 series~~, were calculated using equations ~~2 and ~~(3~~,~~) and (4),

$$\mathrm{KM} = \text{observed mass} \times 14/14.01565,$$ (~~2~~3)

$$\mathrm{KMD} = \mathrm{NM} - \mathrm{KM},$$ (~~3~~4)

where 14 is the nominal mass (NM) of CH_2, 14.01565 is the exact mass of CH_2, and NM is KM rounded to the nearest integer.~~ A homologous series of compounds differing only by the number of base units form a horizontal line in a plot of KMD against KM.~~

~~$\mathrm{AI_{mod}}$ is a measure of the probable aromaticity of a molecule assuming that half the O atoms are double bonded and half have only σ bonds (Koch and Dittmar, 2006). $\mathrm{AI_{mod}}$ was calculated using equation 4,~~

Furthermore, a two-order mass defect analysis using the base units of CH_2 and H_2 was applied following the method described in Roach et al. (2011) which could greatly simplifies visualization of complex mass spectra.

$\mathrm{AI_{mod}}$ is a measure of the probable aromaticity of a molecule assuming that half the O atoms are double bonded and half have only σ bonds (Koch and Dittmar, 2006). $\mathrm{AI_{mod}}$ was calculated using equation (5),

$\mathrm{AI_{mod}} = (1 + c - 0.5o - 0.5h - 0.5n) / (c - 0.5o - n)$, (~~4~~5)

where c, o, and h are the number of C, O, H, and N atoms in the formula. $\mathrm{AI_{mod}}$ ranges from 0 for a purely aliphatic compound to higher values being found for compounds with more double bonds and that are more aromatic.

3. Results and discussions

3.1. Chemical characterization of PM_1 during ~~F30~~P1 and ~~F43~~P2 measured by HR-ToF-AMS

The average mass concentration and chemical composition measured by HR-ToF-AMS during ~~F30~~P1 and ~~F43~~P2 periods ~~were~~was shown in Fig. 1. The mass concentration of PM_1 were 9.2 and 10.6 μg m^{-3}, respectively, which were at the high range of all filters (1.3 – 10.6 μg m^{-3}) because of a continuous long-range transport event at the QOMS (Zhang et al., 2018b). Due to our sample processing error, the mass concentration of filter measured gravimetrically could not be used and thus the fractions of PM_1 to $PM_{2.5}$ are not available. ~~However, most of WSOM in $PM_{2.5}$ is in accumulation size mode (less than 1μm) which could be detected by HR-ToF-AMS. The chemical composition of PM_1 during F30 and F43 were~~However, most of WSOM in $PM_{2.5}$ is in accumulation size mode (less than 1μm) which could be detected by HR-ToF-AMS (Zhang et al., 2005). The chemical composition of PM_1 during P1 and P2 was all dominated by OA (55% and 57%), followed by BC (26% and 22%), sulfate (7% and 8%), nitrate (5% and 6%), and ammonium (5% and 6%). The OA was comprised by biomass burning emitted OA (BBOA), nitrogen-contained OA (NOA), and more-oxidized oxygenated OA (MO-OOA) decomposed by positive matrix factorization (PMF) analysis (Fig. 1). ~~The mass contribution of BBOA was higher during F43 than F30 (32% vs. 22%), whereas the contribution of MO-OOA was higher during F30 than F43 (24% vs. 16%). The mass spectra of OA for these two filter periods were closely similar with a person~~The details on PMF analysis can be found in Zhang et al. (2018b). The mass contribution of BBOA was higher during P2 than P1 (32% vs. 22%), whereas the contribution of MO-OOA was higher during P1 (24% vs. 16%). The mass spectra of OA for these two filter periods were closely similar with a Poisson correlation efficiency (*r*) being 0.9. The elemental ratios of oxygen (O) to carbon (C) of OA were 1.04 and 0.97 for ~~F30~~P1 and ~~F43~~P2 periods ~~(IA method, Canagaratna et al., 2015)~~(Improved Ambient method, Canagaratna et al., 2015), respectively, and accordingly the ratios of hydrogen (H) to C were 1.26 and 1.32. These suggest that the OA during ~~F43~~P2 was relatively less oxidized than that during ~~F30~~P1 (*t*-test, $p<0.05$). The six category ions ($C_xH_y^+$, $C_xH_yO_2^+$, $C_xH_yO_1^+$, $C_xH_yN^+$, $C_xH_yO_zN^+$, and HO^+) detected by HR-ToF-AMS for these two filter periods were all dominated by $C_xH_yO_2^+$, following by $C_xH_y^+$, $C_xH_yO_1^+$, $C_xH_yN^+$, $C_xH_yO_zN^+$, and HO^+. The air mass trajectory analyses using the hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model for ~~F35~~P1 and ~~F43~~P2 periods show air mass mainly originated from west and southwest of the QOMS across north and northwest India where there were many fire spots during these two periods (Fig. 2). The air mass during ~~F43~~P2 was partly (13%) ~~transport~~transported with low wind speed and short distance (less than 100 km) ~~indicating~~which could contain some ~~potential~~ fresh OA as illustrated with higher fraction of BBOA.

3.2. The chemical characteristics of WSOM from ESI-FTICR-MS

A total of ~~4554~~4295 and ~~5192~~4770 molecular formulas ~~was~~were identified by ESI~~(+) -~~FTICT-MS over the mass range of 100-700 Da for ~~F30~~P1 and ~~F43~~P2, respectively. The identified molecular formulas were grouped into two subgroups based on their elemental composition, i.e., CHO and CHON, all of which had equal important contribution (45% – 55%) in number (Fig. 3). Note that individual species in the ESI-FTICR-MS mass spectra could have many different isomeric structures, then the percentages reflect only the number of unique molecular formulas ~~and do not reflect the number of unique molecular formulas in each category. Although there exists the difference on ionization sensitivity of ESI(+) between different studies, the contribution of CHON in our study is higher than the results before (10% – 30%) (Laskin et al., 2009; Dzepina et~~

~~al., 2015). The distinct contribution of CHON compounds in ESI-FTICR-MS mass spectra is consistent with the results of HR-ToF-AMS which identified a separate NOA factor in PMF analysis. The mass spectra of these two samples were highly similar in the distributions of molecular relative intensity (RI) (Fig. 3). The most abundant peaks were a series of CHO compounds cationized by Na^+ (RI>20%, $C_{19}H_{28}O_3(C_2H_4O)_{n=0-6}Na^+$). These compounds were most likely to contain carboxylic acid groups that readily form $[M + Na]^+$ ions in the positive mode electrospray ionization (Smith et al., 2009). The average weighted element ratios of F30 and F45 were 0.43 vs. 0.38 for O/C_w, 1.38 vs. 1.33 for H/C_w, and 1.72 vs. 1.67 for OM/OC_w (Table 1), suggesting a medium oxidation and saturation degree for F30 than F43. These trends are similar with those of HR-ToF-AMS results~~in each category. The mass spectra of these two samples were highly similar in the distributions of molecular (Fig. 3). The average weighted element ratios of P1 and P2 were 0.43 vs. 0.39 for O/C_w, 1.36 vs. 1.31 for H/C_w, and 1.72 vs. 1.68 for OM/OC_w (Table 1), suggesting a relatively higher oxidation and saturation degree for P1 than P2. These trends are consistent with the results of HR-ToF-AMS, although the elemental ratios are different between them which is due to the difference on the detection range of m/z and the ionization efficiency of different mass spectrometry (ESI vs. ~~EI~~electron impact) (Yu et al., 2016). The elemental ratios of WSOM from ESI-FTICR~~-~~ MS in our study are similar with those results observed in aerosol samples in remote site using ESI-FTICR~~-~~ MS (e.g., 0.35 – 0.53 for O/C) (Table 2).~~ The CHO compounds had relatively higher O/C_w ratio than that of CHON compounds in these two samples and CHO compounds were more saturated with a higher H/C_w ratio than CHON (Table 1).~~ The O/C and H/C in Van Krevelen diagrams (Wu et al., 2004) for these two filters and the subgroup molecular show similar distributions and all concentrate in 1.2~~-~~ – 1.8 for H/C and 0.3~~-~~ – 0.7 for O/C (Fig. 3) suggesting their similar aerosol sources and atmospheric processes. The similar distributions for these two filters are also observed in ~~KMD vs. KM plots and located in a narrow and uniform distribution, which are similar with highly processed aerosol found at the Pico Mountain Observatory (Dzepina et al., 2015).~~plots of KMD vs. KM and DBE vs. C (Fig. 3).

Structural information for the assigned molecular formulas is inferred from the DBE_w value which was higher for ~~F43~~P2 than that of ~~F30 (6.92~~P1 (7.87 vs. ~~6.26~~7.12) (Table 1). Comparing with other studies, the ~~DBE~~DBE_w values in our filter ~~is~~are relative ~~lower than those in fresh emitted aerosol~~

~~from fuel combustion (5 – 9.5) (Song et al., 2018), but~~ close to the results from biomass burning aerosol and aerosol samples from remote sites (Table 2) (Dzepina et al., 2015). The DBE$_w$ values for each ~~molecule~~molecular subgroup were higher for CHON than that of CHO (Table 1), especially for ~~F43 (7.46~~P2 (8.32 vs. ~~6.69~~7.38) suggesting more rings and double bonds in CHON molecular. The AI$_{mod}$, reflecting the minimum number of carbon-carbon double bonds and rings ~~(Koch and Dittmar, 2006)~~(Koch and Dittmar, 2006), was correspondingly higher in ~~F43 which contained 49.1% aliphatic (60.4% in F30), 45.9%~~ P2 as illustrated by its higher contribution of olefinic (~~36.8% in F30),~~75.0% vs. 73.9% for P2 and P1) and ~~5.1%~~ aromatic compounds (~~2.9% in F30).~~ 10.3% vs. 7.7% for P2 and P1) (Table 1). For aromatic compounds (AI$_{mod}$ >=0.5) in ~~F43, ~60~~P2, 52% of them were CHON formulas (~~39% for F30) (Table 1). A distinct group of CHON aromatic compounds is shown in lower left corner in Van Krevelen diagram for F43 but not~~45% for ~~F30 (Fig. 3~~P1). Higher DBE and AI$_{mod}$ values in CHON compounds suggest more unsaturated compounds with them which could contain a certain number of chromophores. The distribution of DBE vs. carbon number of two filters showed a systematic increase in a concentrated region and a highly similarity with each other. This similarity further suggests the consistent source and chemical processes for the aerosol of these two filters.

There were ~~3700~~3955 common molecular formulas between these two filters with the number contribution of CHO by ~~47~~50.7% and CHON by ~~53~~49.3%. These common molecular formulas accounted for ~~81% (F30~~92.1% (P1) and ~~71% (F43~~82.9% (P2) of two filters, respectively. There were ~~619~~340 unique molecular formulas in ~~F30~~P1 with ~~91~~73% being CHO compounds; whereas there were ~~1142~~815 unique molecular formulas in ~~F43~~P2 with ~~62~~65.3% being CHON compounds. For more confidence on molecule assignment, we focus on the common molecular formulas detected in these two samples in the section below. Note that the mass spectrum of common ions was calculated from the average RI from two mass spectra and normalized to the highest peak.

3.3. The potential sources and formation processes

3.3.1. CHO compounds

CHO compounds have been frequently detected in ambient aerosol samples (Altieri et al., ~~2009a~~2009b; Mazzoleni et al., 2010; Lin et al., 2012; Fleming et al., 2018), which could comprise of high ~~molecule~~molecular weight humic-like substances (HULIS) or oligomers, and from primary emission or secondary formation of different aerosol sources (Mazzoleni et al., 2012; Wozniak et al., 2014; Lin et al., 2016; Cook et al., 2017). In our samples, the weighted ~~molecule~~molecular weight of CHO compounds was ~~363.7~~361.9 with an average C atom of 19.~~1~~3 ± 5.3 per molecule; the most abundant O atoms located in 5~~-~~–10 with an average value of 7.~~6~~8 ± 2.9 per molecule (Fig. 4a and b). ~~Among~~The oxygen distribution is also evidenced by the ~~1744 common CHO formulas, 388 of them (22%) are observed as [M + Na$^+$] ions with the majority of detected as protonated species. The most abundant sodiated molecules~~longest homologous series in two-order mass defect analysis (CH_2-H_2) which were all O_5-O_{10} compounds (Fig. 4d).~~the ESI/MS ranged in m/z 350-550, whereas the most abundant protonated species ranged in m/z 200-350.~~ The DBE of CHO increased with the carbon number with the DBE_w ~~being 5.96~~value of 6.75 (Fig. 3); the carbon-normalized ~~DBE_w (~~DBE~~/C_w~~ (DBE/C) was 0.~~33 (Table 1).~~39 ± 0.14. These two values were close to the results from biomass burning aerosol samples in other studies and at the high range of published data (Table 2) (Lin et al., 2012; Mazzoleni et al., 2012)~~. A threshold DBE/C value of 0.7 usually serves as a criterion to identify species with condensed aromatic ring structures and therefore the CHO compounds~~, suggesting relatively high aromaticity in our samples~~ were relative low aromaticity likely due to the relative long oxygenation time during long-range transport.~~. The ~~Carbon~~carbon oxidation state (~~OSc~~OS_C) values (Kroll et al., 2011), a useful metric for the degree of oxidation of organic species in the atmosphere, exhibited between ~~-~~–1 and 0 with 25 or less carbon atoms, suggesting that they are semi- and low-volatile organic compounds corresponding to “fresh” (BBOA) and “aged” (LV-OOA) SOA by multistep oxidation reactions (Fig. 4c).

There are several possible sources and chemical formation pathways for high oxygen-containing CHO compounds. Ozonolysis of α-pinene has been found to form highly oxygenated molecules~~, and one of the~~ with some important products ~~is~~such as $C_{17}H_{26}O_8$ (m/z 358) ~~(RI = 9.2%)~~ and $C_{19}H_{28}O_7$ (m/z 368) ~~(RI = 3.2%)~~ which is a possible esterification product of cis-pinic ($C_9H_{14}O_4$, m/z 186~~, RI = 7.2%)~~) and diaterpenylic acid ($C_8H_{14}O_5$, m/z 190) (Kristensen et al., 2013). The first three ~~compounds~~formulas were all found in ~~the~~our common CHO molecules with high relative abundance ~~and ionized by Na$^+$.~~(Table 3). The appearance of these formulas together with high relative abundance gave our more confidence on the products of ozonolysis of α-pinene. Ozone concentration in the Himalayas during pre-monsoon was the highest based on the on-line measurement at the Nepal Climate Observatory at Pyramid (NCO-P) during 2006-2008 (61 ± 9 ppbv) (Cristofanelli et al., 2010). ~~High biogenic~~Biogenic volatile organic ~~compound emissions~~compounds could ~~occur due to high density of forest~~be transported from the low elevation regions in the ~~southern Himalayas~~subtropical India and biogenic secondary organic aerosol has been found to be important source in the Himalayas (Stone et al., 2012). A number of previously reported other monoterpene oxidation ~~products were also observed in our study, such as $C_6H_{10}O_5Na^+$ (RI = 1.3%), $C_8H_{10}O_5Na^+$ (RI = 3.9%), $C_8H_{12}O_5H^+$ (RI = 6.7%), $C_9H_{14}O_5H^+$ (RI = 5.4%), $C_{10}H_{14}O_6Na^+$ (RI = 7.7%), $C_{10}H_{14}O_7Na^+$ (RI = 8.4%), $C_9H_{12}O_6Na^+$ (RI = 3.4%), $C_7H_{10}O_5Na^+$ (RI = 2.9%), $C_{10}H_{16}O_3H^+$ (RI = 3.8%), $C_7H_{10}O_5Na^+$ (RI = 1.8%), $C_7H_{12}O_5Na^+$ (RI = 2.0%), $C_8H_{12}O_6Na^+$ (RI = 6.7%)~~product formulas were also observed in our study (Table 3) (Claeys et al., 2007; Kleindienst et al., 2007; Zhang et al., 2018a). ~~We also observed formulas that could be lignin pyrolysis products such as vanillic acid ($C_8H_8O_4H^+$, RI = 1.1%), syringaldehyde ($C_9H_{10}O_4H^+$; RI = 2.1%), and syringic acid ($C_9H_{10}O_5H^+$; RI = 2.7%). In addition,~~In addition, some biomass burning aerosol markers were also found in CHO compounds. Sun et al. (2010) and Yu et al. (2014; 2016) observed that aqueous-phase oxidation of lignin produces phenol (C_6H_6O), guaiacol ($C_7H_8O_2$) and syringol ($C_8H_{10}O_3$) yields a substantial fraction of dimers and higher oligomers with key dimer markers identified as $C_{16}H_{18}O_6$ and $C_{14}H_{14}O_4$. The dimer markers ~~$C_{16}H_{18}O_6H^+$~~$C_{16}H_{18}O_6$ and ~~$C_{14}H_{14}O_4H^+$~~$C_{14}H_{14}O_4$ were also present in our sample with high RI (~~7.6~~5.5% and ~~7.8%) and $C_{16}H_{18}O_6Na^+$ was also observed (RI = 1.5%).~~27.5%). The high relative intensity of these compounds ~~indicate~~indicates that fog and cloud processing of phenolic species (biomass burning aerosol) could be an important mechanism for the production of low-volatility SOA in the Himalayas. ~~Some other biomass burning emission compounds were also found, such as dicarboxylic acid series $C_6H_{10}O_4(CH_2)_nH^+$ and dihydroxycarboxylic acids $C_9H_{18}O_4(CH_2)_nH^+$; A series of saturated $C_{16}H_{12}O_8(CH_2)_nH^+$ ketones were also observed in the sample (Fig. 4d).~~ Compounds ~~($C_9H_{10}O_3H^+$, $C_{10}H_{10}O_3H^+$, $C_{11}H_{10}O_3H^+$, $C_{11}H_{12}O_3H^+$, $C_{12}H_{12}O_2H^+$, $C_{13}H_{12}O_3H^+$, $C_{13}H_{14}O_3H^+$, $C_{13}H_{14}O_4H^+$, $C_{14}H_{16}O_4H^+$, $C_{14}H_{16}O_3H^+$)~~ observed in biomass burning emission (cow dung and brush wood) ~~sampling~~ during residential cooking in Nepal were also found in our samples (Fleming et al., 2018)~~ were also found in our samples.~~.

3.3.2 CHON compounds

The frequency distribution for n_o and n_c in CHON formulas were shown in Fig. 5a which show peaks between 6~~-~~ – 10 and 15~~-~~ – 20, respectively. The DBE of CHON formulas ranged into 4 – 10 with $\mathrm{DBE_w}$ being ~~6~~7.79 (Fig. 5b and Table 1). In the CHON~~$^{+}$~~ class, compounds contained one or two nitrogen (1N or 2N) atoms with 1N compounds accounting for 70.5% and 2N for 29.5%, respectively. Most (~~98~~93.6%) of 1N compounds contained more than 3 oxygen atoms and could up to 13 oxygen atoms, whereas about 62.5% of 2N compounds contained more than 6 oxygen atoms (Fig. 6a). The average O ~~atom containing~~atoms contained in each molecular formula ~~was~~were therefore higher for 1N compounds than 2N compounds (8.1 ± 2.9 vs. 6.3 ± 2.3). ~~The high O atom containing in CHON formula suggest that nitrogen was in the form of organic nitrate or nitro groups with excess oxygen forming additional oxygenated groups.~~ The ratios of $\mathrm{O/C_w}$ and ~~$\mathrm{OSc_w}$~~$\mathrm{OS_{Cw}}$ for 1N compounds were accordingly higher than that of 2N compounds (0.42 vs. 0.37 for $\mathrm{O/C_w}$~~;~~ and −0.48 vs. −0.54 for ~~$\mathrm{OSc_w}$~~$\mathrm{OS_{Cw}}$, respectively), suggesting higher oxidation state for 1N compounds (Fig. 5c). In contrast, the $\mathrm{DBE_w}$ and $\mathrm{AI_{mod}}$ values for 2N compounds were higher than that of 1N compounds (Table 1). With higher $\mathrm{H/C_w}$ for 2N compounds (~~Table 1~~Fig. 5d), it suggests that 2N compounds could contain ~~amount of~~many aromatic N-heterocyclic compounds. For 1N compounds, longer and higher relative intensity $\mathrm{CH_2}$ homologous series compounds were found based on the Kendrick mass defect plot (Fig. 6b); 1073 of the ~~1378~~1373 detected 1N compounds can be grouped into 145 homologous. The abundant long $\mathrm{CH_2}$ homologous series in 1N compounds contained 7~~-~~ – 10 O atoms, while 5~~-~~ – 8 O atoms for 2N compounds (Fig. 6).

~~There are many potential sources for~~Many CHON compounds could be identified in ESI+ mode, such as ~~amino acids,~~ reduced N functional compounds~~,~~ and nitro-aromatic compounds~~, and organic nitrate~~ (Altieri et al., ~~2009b~~2009a; Laskin et al., 2009; Lin et al., 2012; O'Brien et al., 2013; Wang et al., 2017)~~. Biomass burning has been found to be an important source for nitrogen-containing compounds in atmosphere (Hoffmann et al., 2007).~~. Laskin et al. (2009) identified amount of N-heterocyclic alkaloid compounds from kinds of fresh biomass burning aerosol. ~~Fleming et al. (2018) conducted study in Nepal by collecting fresh emitted aerosol from dung and brushwood burning household cookstoves and identified amount of nitrogen-containing aerosol.~~Lin et al., (2012) and Wang et al., (2017) also identified many CHON compounds in fresh and aged biomass burning aerosol. Oxygenated organic nitrogen compounds in ambient aerosol (Dzepina et al., 2015), rain water ~~(Altieri et al., 2009b), and fog water (Mazzoleni et al., 2010)~~(Altieri et al., 2009a), and fog water (Mazzoleni et al., 2010) from biomass burning emission influenced regions were also observed. ~~Although the dominated CHN compounds in fresh aerosol in Laskin et al. (2009) and Fleming et al. (2018) were not found in our study which was likely due to the highly oxygenated OA in our samples, biomass burning emissions could be an important source for CHON compounds in our study. Recent studies have proven that burning of dung-fuel in Nepal can~~Lin et al. (2017) found aged biomass burning aerosol in the present urban oxidants (such as NO_x) could result in higher fraction of CHON compounds comparing to the fresh biomass burning aerosol. Considering the high influence of biomass burning emission in the Himalayas (Zhang et al., 2018b), the CHON compounds in our study were probably related with biomass burning emissions. Recent studies have proven that burning of mixed biomass fuels in Nepal could emit amount of nitrogen species such as NH_3, NO_x, HCN, benzene, and organics, and the emission factors for these species are higher than that of wood (Stockwell et al., 2016; Jayarathne et al., 2018). In addition, it is likely that smoldering burning of bio-fuels in high elevation area is also responsible for the presence of ~~a large number of nitrogen-containing compounds in BBOA.~~many nitrogen-containing compounds in BBOA (Chen et al., 2010). Nitroaromatic compounds such as Methyl-Nitrocatechols ($C_7H_7NO_4$) are introduced to be tracer for biomass burning secondary organic aerosols (Iinuma et al., 2010). Although $C_7H_7NO_4$ formula is not found in our measurement, $C_{14}H_{14}N_2O_8$ were found in our measurement, of which is probably its dimer formula. In addition, the homologous series compounds which $C_7H_7NO_4$ serve as the core molecule was also found in our samples. Some ~~medium~~high relative abundance CHON molecular formulas identified in a recent paper ~~in~~from biomass burning aerosol were also found in our measurement ~~such as $C_{15}H_{19}N_1O_8H^+$ (RI = 6.7%), $C_{16}H_{21}N_1O_8H^+$ (RI = 6.6%), $C_{17}H_{23}N_1O_8H^+$ (RI = 5.9%), $C_{14}H_{13}N_1O_3H^+$ (RI = 2.9%), $C_{15}H_{15}N_1O_3H^+$ (RI = 2.6%), $C_{13}H_{17}N_1O_3H^+$ (RI = 4.2%)~~(Table 3) (Song et al., 2018).

Besides primary emission and/or secondary formation from biomass burning emission, nitrogen-containing OA could also be formed through other chemical processes. For example, biogenic volatile organic compounds (BVOC) can react with NO_3 radical or RO_2+NO into organic nitrate

(Ng et al., 2017). Although organic nitrate is not favored to be ionized in positive ESI-MS (Wan and Yu, 2006), organic nitrate formed from BVOC could be highly functionalized (Lee et al., 2016) and ionized in positive MS through other alkaline functional groups. Recent studies have shown that BVOC, including isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$), dominate the organic nitrate formation in the southeastern United States under the condition of the mixed anthropogenic NO_x and BVOC (Xu et al., 2014; Lee et al., 2016; Zhang et al., 2018a). Several molecular formulas formed from monoterpene and NO_3 radical were found in our study (~~$C_9H_{13}NO_6$, $C_9H_{15}NO_6$, $C_{10}H_{17}NO_4$, $C_{10}H_{15}NO_5$, $C_{10}H_{17}NO_5$, $C_{10}H_{19}NO_5$, $C_{10}H_{15}NO_6$, $C_{10}H_{17}NO_6$, $C_{10}H_{19}NO_6$,)~~Table 3) (Lee et al., 2016; Zhang et al., 2018a)~~. Additionally, some alkaloids, such as imidazole, imidazole-2-carboxaldehyde and 1N-glyoxal-substitutted imidazole, are also reported to be major products of BVOC reaction with ammonium ions or primary amines on SOA (De Haan et al., 2009; Galloway et al., 2009; Updyke et al., 2012). Imidazole signal was found in our HR-ToF-AMS measurement.~~.

4. Implications and limitations

This study analyzed the WSOM using ESI(+)-FTICR~~-~~ MS in fine ~~particular~~particulate aerosol from the Himalayas and found that the molecular compositions of WSOM were mainly comprised by two group compounds (CHO and CHON~~ compounds~~) with equal important contribution. The two ~~compounds~~compound groups could be originated from biomass burning emission and BVOC oxidation ~~of which~~products because many markers for these two sources were found in these molecular compounds. All our compounds had relatively high DBE values suggesting potential high light absorption feature. Due to ~~their~~the relative ~~high~~higher mass concentration and ~~high~~higher contribution of nitrogen-containing compounds (~~7.6~~9% of PM_1) during these two periods based on HR-ToF-AMS results~~,~~ (Zhang et al., 2018), it is ~~believe~~believed that ~~the~~ aerosol transported to the Himalayas have important application in atmospheric radiative forcing~~ and biogeochemical effects~~.

Ramanathan and Carmichael (2008) found distinct warming effect of light absorbing aerosol over the Himalayas through estimating aerosol radiative forcing by BC. However, ~~light-absorbing OA (~~brown carbon~~)~~ have not been considered before which could also be ~~another~~ important light absorbing aerosol due to their ~~large fraction of atmospheric aerosol~~high mass loading (Laskin et al., 2015). Zhang et al. (2017) estimated the light absorption contribution of brown carbon from inland of the TP which was up to ~13% of that of BC. The high DBE and nitrogen-containing OA in our study suggested aerosol in the Himalayas could also contain amount of light-absorbing organic matter because light absorption properties of organic molecules are closely related with the number of double bonds and rings in the molecule and nitrogen atoms. Many studies had found that the dominated chemical molecules in the brown carbon were related with nitrogen-containing aerosol (e.g., Lin et al., 2016). This kind of aerosol combined with BC could have higher radiative forcing than before in this area.

~~In addition, nitrogen is an important nutrient for plant and microbial in terrestrial and aquatic systems especially for arid and semi-arid areas (Andreae and Crutzen, 1997). Chen et al. (2013) evaluated the potential biogeochemical cycle in the TP under the current rapidly climate change and suggested that nitrogen availability plays a critical role in controlling ecological production because nitrogen is a limited nutrient in many ecosystems. To our knowledge, there was no study focusing on the organic nitrogen deposition in this remote region, but only on inorganic nitrogen species (Liu et al., 2015). Organic nitrogen is an important source of nitrogen (Neff et al., 2002), and should be taken account in the future study.~~ More comprehensive methods are needed in the future for identifying BrC in the Himalayas due to the chemical complexity of BrC. For example, the BrC extraction is highly dependent on the used solvent and water insoluble OA can contribute higher light absorption than water soluble OA (Chen and Bond, 2010). In addition, Budisulistiorini et al. (2017) found that a number of compounds can dominate the light absorption of BrC, although they have a minor contribution to the aerosol mass. Therefore, it is important to know the exactly chromophores of BrC which can be obtained by combining with high performance liquid chromatography, light absorption measurement with a photodiode (PDA) detector, and chemical composition with high resolution mass spectrometer (HPLC-PDA-HRMS system) (Lin et al., 2016). For mass spectrometry analysis, different ionization sources are also favorable for different compounds, such as ESI only detect a part of polar compounds; non-polar compounds which could dominated the contributing of BrC, can be measured using atmospheric pressure photo ionization (APPI) (Lin et al., 2018). Recent study indicate that over 40% of the solvent-extractable BrC light absorption is attributed to water insoluble, non-polar to semi-polar compounds such as PAHs and their derivative (Lin et al., 2018). In contrast, the polar, water-soluble BrC compounds, which are detected in ESI, account for less than 30% of light absorption by BrC (Lin et al., 2018).

Acknowledgements

This research was supported by grants from the National Natural Science Foundation of China (41771079, 41421061), the Key Laboratory of Cryospheric Sciences Scientific Research Foundation (SKLCS-ZZ-2018), and the Chinese Academy of Sciences Hundred Talents Program. The authors thank the QOMS for logistic support.

References

Altieri, K. E., Turpin, B. J., and Seitzinger, S. P.: Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry, Environ. Sci. Technol., 43, 6950-6955, 10.1021/es9007849, 2009a.

Altieri, K. E., Turpin, B. J., and Seitzinger, S. P.: Oligomers, organosulfates, and nitrooxy organosulfates in rainwater identified by ultra-high resolution electrospray ionization FT-ICR mass spectrometry, Atmos. Chem. Phys., 9, 2533-2542, 10.5194/acp-9-2533-2009, ~~2009a~~2009b.

~~Altieri, K.~~Altieri, K. E., Hastings, M. G., Peters, A. J., and Sigman, D. M.: Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry, Atmos. Chem. Phys., 12, 3557-3571, 2012.

~~E., Turpin, B. J., and Seitzinger, S. P.: Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry, Environ. Sci. Technol., 43, 6950-6955, 10.1021/es9007849, 2009b.~~

~~Andreae, M. O., and Crutzen, P. J.: Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry, Science, 276, 1052-1058, 10.1126/science.276.5315.1052, 1997.~~

Bonasoni, P., Laj, P., Marinoni, A., Sprenger, M., Angelini, F., Arduini, J., Bonafè, U., Calzolari, F., Colombo, T., Decesari, S., Di Biagio, C., di Sarra, A. G., Evangelisti, F., Duchi, R., Facchini, M. C., Fuzzi, S., Gobbi, G. P., Maione, M., Panday, A., Roccato, F., Sellegri, K., Venzac, H., Verza, G. P., Villani, P., Vuillermoz, E., and Cristofanelli, P.: Atmospheric Brown Clouds in the Himalayas: first two years of continuous observations at the Nepal Climate Observatory-Pyramid (5079 m), Atmos. Chem. Phys., 10, 7515-7531, 10.5194/acp-10-7515-2010, 2010.

Budisulistiorini, S. H., Riva, M., Williams, M., Chen, J., Itoh, M., Surratt, J. D., and Kuwata, M.: Light-Absorbing Brown Carbon Aerosol Constituents from Combustion of Indonesian Peat and Biomass, Environmental Science & Technology, 51, 4415-4423, 10.1021/acs.est.7b00397, 2017.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Chen, ~~H., Zhu, Q., Peng, C., Wu, N., Wang, Y., Fang, X., Gao, Y., Zhu, D., Yang, G., Tian, J., Kang, X., Piao, S., Ouyang, H., Xiang, W., Luo, Z., Jiang, H., Song, X., Zhang, Y., Yu, G., Zhao, X., Gong, P., Yao, T., and Wu, J.: The impacts of climate change and human activities on biogeochemical cycles on the Qinghai-Tibetan Plateau, Global Change Biol., 19, 2940-2955, 10.1111/gcb.12277, 2013~~L. W. A., Verburg, P., Shackelford, A., Zhu, D., Susfalk, R., Chow, J. C., and Watson, J. G.: Moisture effects on carbon and nitrogen emission from burning of wildland biomass, Atmos. Chem. Phys., 10, 6617-6625, 10.5194/acp-10-6617-2010, 2010.

Chen, Y., and Bond, T. C.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773-1787, 10.5194/acp-10-1773-2010, 2010.

Choi, J. H., Ryu, J., Jeon, S., Seo, J., Yang, Y. H., Pack, S. P., Choung, S., and Jang, K. S.: In-depth compositional analysis of water-soluble and -insoluble organic substances in fine (PM2.5) airborne particles using ultra-high-resolution 15T FT-ICR MS and GCxGC-TOFMS, Environmental Pollution, 225, 329-337, 10.1016/j.envpol.2017.02.058, 2017.

Claeys, M., Szmigielski, R., Kourtchev, I., Van der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Hydroxydicarboxylic Acids: Markers for Secondary Organic Aerosol from the Photooxidation of α-Pinene, Environ. Sci. Technol., 41, 1628-1634, 10.1021/es0620181, 2007.

Cong, Z., Kawamura, K., Kang, S., and Fu, P.: Penetration of biomass-burning emissions from South Asia through the Himalayas: new insights from atmospheric organic acids, Sci. Rep., 5, 9580, 10.1038/srep09580, 2015.

Cook, R. D., Lin, Y. H., Peng, Z., Boone, E., Chu, R. K., Dukett, J. E., Gunsch, M. J., Zhang, W., Tolic, N., Laskin, A., and Pratt, K. A.: Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water, Atmos. Chem. Phys., 17, 15167-15180, 10.5194/acp-17-15167-2017, 2017.

Cristofanelli, P., Bracci, A., Sprenger, M., Marinoni, A., Bonafè, U., Calzolari, F., Duchi, R., Laj, P., Pichon, J. M., Roccato, F., Venzac, H., Vuillermoz, E., and Bonasoni, P.: Tropospheric ozone variations at the Nepal Climate Observatory-Pyramid (Himalayas, 5079 m a.s.l.) and influence of deep stratospheric intrusion events, Atmos. Chem. Phys., 10, 6537-6549, 10.5194/acp-10-6537-2010, 2010.

~~De Haan, D. O., Corrigan, A. L., Tolbert, M. A., Jimenez, J. L., Wood, S. E., and Turley, J. J.: Secondary Organic Aerosol Formation by Self-Reactions of Methylglyoxal and Glyoxal in Evaporating Droplets, Environ. Sci. Technol., 43, 8184-8190, 10.1021/es902152t, 2009.~~

Draxler, R. R., and Hess, G. D.: An overview of the hysplit-4 modeling system for trajectories, Aust. Meteorol. Mag., 47, 295-308, 1998.

Dzepina, K., Mazzoleni, C., Fialho, P., China, S., Zhang, B., Owen, R. C., Helmig, D., Hueber, J., Kumar, S., Perlinger, J. A., Kramer, L. J., Dziobak, M. P., Ampadu, M. T., Olsen, S., Wuebbles, D. J., and Mazzoleni, L. R.: Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: a case study with a long-range transported biomass burning plume, Atmos. Chem. Phys., 15, 5047-5068, 10.5194/acp-15-5047-2015, 2015.

Feng, L., Xu, J., Kang, S., Li, X., Li, Y., Jiang, B., and Shi, Q.: Chemical Composition of Microbe-Derived Dissolved Organic Matter in Cryoconite in Tibetan Plateau Glaciers: Insights from Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Analysis, Environ Sci Technol, 50, 13215-13223, 10.1021/acs.est.6b03971, 2016.

Fleming, L. T., Lin, P., Laskin, A., Laskin, J., Weltman, R., Edwards, R. D., Arora, N. K., Yadav, A., Meinardi, S., Blake, D. R., Pillarisetti, A., Smith, K. R., and Nizkorodov, S. A.: Molecular composition of particulate matter emissions from dung and brushwood burning household cookstoves in Haryana, India, Atmos. Chem. Phys., 18, 2461-2480, 10.5194/acp-18-2461-2018, 2018.

~~Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331-3345, 10.5194/acp-9-3331-2009, 2009.~~

Gustafsson, Ö., Kruså, M., Zencak, Z., Sheesley, R. J., Granat, L., Engström, E., Praveen, P. S., Rao, P. S. P., Leck, C., and Rodhe, H.: Brown Clouds over South Asia: Biomass or Fossil Fuel Combustion?, Science, 323, 495-498, 10.1126/science.1164857, 2009.

~~Hoffmann, D., Iinuma, Y., and Herrmann, H.: Development of a method for fast analysis of phenolic molecular markers in biomass burning particles using high performance liquid chromatography/atmospheric pressure chemical ionisation mass spectrometry, J. Chromatogr. A, 1143, 168-175, 10.1016/j.chroma.2007.01.035, 2007.~~

Hughey, C. A., Hendrickson, C. L., Rodgers, R. P., Marshall, A. G., and Qian, K.: Kendrick Mass Defect Spectrum: A Compact Visual Analysis for Ultrahigh-Resolution Broadband Mass Spectra, Anal. Chem., 73, 4676-4681, 10.1021/ac010560w, 2001.

Iinuma, Y., Böge, O., Gräfe, R., and Herrmann, H.: Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols, Environ. Sci. Technol., 44, 8453-8459, 10.1021/es102938a, 2010.

Jayarathne, T., Stockwell, C. E., Bhave, P. V., Praveen, P. S., Rathnayake, C. M., Islam, M. R., Panday, A. K., Adhikari, S., Maharjan, R., Goetz, J. D., DeCarlo, P. F., Saikawa, E., Yokelson, R. J., and Stone, E. A.: Nepal Ambient Monitoring and Source Testing Experiment (NAMaSTE): emissions of particulate matter from wood- and dung-fueled cooking fires, garbage and crop residue burning, brick kilns, and other sources, Atmos. Chem. Phys., 18, 2259-2286, 10.5194/acp-18-2259-2018, 2018.

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location, Atmos. Environ., 41, 8288-8300, 10.1016/j.atmosenv.2007.06.045, 2007.

Koch, B. P., and Dittmar, T.: From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter, Rapid Commun. Mass~~. Sp,~~ Spect., 20, 926-932, 10.1002/rcm.2386, 2006.

Kristensen, K., Enggrob, K. L., King, S. M., Worton, D. R., Platt, S. M., Mortensen, R., Rosenoern, T., Surratt, J. D., Bilde, M., Goldstein, A. H., and Glasius, M.: Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols, Atmos. Chem. Phys., 13, 3763-3776, 10.5194/acp-13-3763-2013, 2013.

Laskin, A., Smith, J. S., and Laskin, J.: Molecular Characterization of Nitrogen-Containing Organic Compounds in Biomass Burning Aerosols Using High-Resolution Mass Spectrometry, Environ. Sci. Technol., 43, 3764-3771, 10.1021/es803456n, 2009.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, Chem. Rev., 4335-4382, 10.1021/cr5006167, 2015.

Laskin, J., Laskin, A., and Nizkorodov, S. A.: Mass Spectrometry Analysis in Atmospheric Chemistry, Anal. Chem., 90, 166-189, 10.1021/acs.analchem.7b04249, 2018.

Lau, K. M., Kim, M. K., and Kim, K. M.: Asian summer monsoon anomalies induced by aerosol direct forcing: the role of the Tibetan Plateau, Clim. Dynam., 26, 855-864, 10.1007/s00382-006-0114-z, 2006.

Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurtén, T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Xu, L., Ng, N. L., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., de Gouw, J., Olson, K., Goldstein, A. H., Seco, R., Kim, S., McAvey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., D'Ambro, E. L., and Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, Proc. Natl. Acad. Sci. USA.,, 113, 1516-1521, 10.1073/pnas.1508108113, 2016.

Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, Environ. Sci. Technol., 46, 7454-7462, 10.1021/es300285d, 2012.

Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, Environ. Sci. Technol., 50, 11815-11824, 10.1021/acs.est.6b03024, 2016.

~~Liu, Y. W., Xu, R., Wang, Y. S., Pan, Y. P., and Piao, S. L.: Wet deposition of atmospheric inorganic nitrogen at five remote sites in the Tibetan Plateau, Atmos. Chem. Phys., 15, 11683-11700, 10.5194/acp-15-11683-2015, 2015.~~

Lin, P., Bluvshtein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event, Environ. Sci. Technol., 51, 11561-11570, 10.1021/acs.est.7b02276, 2017.

Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization, Analytical Chemistry, 10.1021/acs.analchem.8b02177, 2018.

Liu, Z., Liu, D., Huang, J., Vaughan, M., Uno, I., Sugimoto, N., Kittaka, C., Trepte, C., Wang, Z., Hostetler, C., and Winker, D.: Airborne dust distributions over the Tibetan Plateau and surrounding areas derived from the first year of CALIPSO lidar observations, Atmos. Chem. Phys., 8, 5045-5060, 10.5194/acp-8-5045-2008, 2008.

Lu, Z., Streets, D. G., Zhang, Q., and Wang, S.: A novel back-trajectory analysis of the origin of black carbon transported to the Himalayas and Tibetan Plateau during 1996–2010, Geophys. Res. Lett., 39, L01809, 10.1029/2011gl049903, 2012.

Lüthi, Z. L., Škerlak, B., Kim, S. W., Lauer, A., Mues, A., Rupakheti, M., and Kang, S.: Atmospheric brown clouds reach the Tibetan Plateau by crossing the Himalayas, Atmos. Chem. Phys., 15, 6007-6021, 10.5194/acp-15-6007-2015, 2015.

Mazzoleni, L. R., Ehrmann, B. M., Shen, X., Marshall, A. G., and Collett, J. L.: Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Environ. Sci. Technol., 44, 3690-3697, 10.1021/es903409k, 2010.

Mazzoleni, L. R., Saranjampour, P., Dalbec, M. M., Samburova, V., Hallar, A. G., Zielinska, B., Lowenthal, D. H., and Kohl, S.: Identification of water-soluble organic carbon in non-urban aerosols using ultrahigh-resolution FT-ICR mass spectrometry: organic anions, Environ. Chem., 9, 285, 10.1071/en11167, 2012.

~~Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H., and Russell, K. M.: The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?, Biogeochemistry, 57, 99-136, 10.1023/a:1015791622742, 2002.~~

Mead, R. N., Mullaugh, K. M., Brooks Avery, G., Kieber, R. J., Willey, J. D., and Podgorski, D. C.: Insights into dissolved organic matter complexity in rainwater from continental and coastal storms by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry, Atmos. Chem. Phys., 13, 4829-4838, 10.5194/acp-13-4829-2013, 2013.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, Atmos. Chem. Phys., 17, 2103-2162, 10.5194/acp-17-2103-2017, 2017.

O'Brien, R. E., Laskin, A., Laskin, J., Liu, S., Weber, R., Russell, L. M., and Goldstein, A. H.: Molecular characterization of organic aerosol using nanospray desorption/electrospray ionization mass spectrometry: CalNex 2010 field study, Atmos. Environ., 68, 265-272, 10.1016/j.atmosenv.2012.11.056, 2013.

Raeke, J., Lechtenfeld, O. J., Wagner, M., Herzsprung, P., and Reemtsma, T.: Selectivity of solid phase extraction of freshwater dissolved organic matter and its effect on ultrahigh resolution mass spectra, Environ Sci Process Impacts, 18, 918-927, 10.1039/c6em00200e, 2016.

Ram, K., Sarin, M. M., and Hegde, P.: Long-term record of aerosol optical properties and chemical composition from a high-altitude site (Manora Peak) in Central Himalaya, Atmos. Chem. Phys., 10, 11791-11803, 10.5194/acp-10-11791-2010, 2010.

Ramanathan, V., Ramana, M. V., Roberts, G., Kim, D., Corrigan, C., Chung, C., and Winker, D.: Warming trends in Asia amplified by brown cloud solar absorption, Nature, 448, 575-578, 10.1038/nature06019, 2007.

Ramanathan, V., and Carmichael, G.: Global and regional climate changes due to black carbon, Nature Geos., 1, 221-227, 10.1038/ngeo156, 2008.

Roach, P. J., Laskin, J., and Laskin, A.: Higher-Order Mass Defect Analysis for Mass Spectra of Complex Organic Mixtures, Anal. Chem., 83, 4924-4929, 10.1021/ac200654j, 2011.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Presto, A. A., Dubey, M. K., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, Nature Geos., 7, 647-650, 10.1038/ngeo2220, 2014.

Schmitt-Kopplin, P., Liger-Belair, G., Koch, B. P., Flerus, R., Kattner, G., Harir, M., Kanawati, B., Lucio, M., Tziotis, D., Hertkorn, N., and Gebefügi, I.: Dissolved organic matter in sea spray: a transfer study from marine surface water to aerosols, Biogeosciences, 9, 1571-1582, 10.5194/bg-9-1571-2012, 2012.

~~Smith, J. S., Laskin, A., and Laskin, J.: Molecular Characterization of Biomass Burning Aerosols Using High-Resolution Mass Spectrometry, Anal. Chem., 81, 1512-1521, 10.1021/ac8020664, 2009.~~

Song, J., Li, M., Jiang, B., Wei, S., Fan, X., and Peng, P. a.: Molecular Characterization of Water-Soluble Humic like Substances in Smoke Particles Emitted from Combustion of Biomass Materials and Coal Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Environ. Sci. Technol., 52, 2575-2585, 10.1021/acs.est.7b06126, 2018.

Stockwell, C. E., Christian, T. J., Goetz, J. D., Jayarathne, T., Bhave, P. V., Praveen, P. S., Adhikari, S., Maharjan, R., DeCarlo, P. F., Stone, E. A., Saikawa, E., Blake, D. R., Simpson, I. J., Yokelson, R. J., and Panday, A. K.: Nepal Ambient Monitoring and Source Testing Experiment (NAMaSTE): emissions of trace gases and light-absorbing carbon from wood and dung cooking fires, garbage and crop residue burning, brick kilns, and other sources, Atmos. Chem. Phys., 16, 11043-11081, 10.5194/acp-16-11043-2016, 2016.

Stone, E. A., Nguyen, T. T., Pradhan, B. B., and Man Dangol, P.: Assessment of biogenic secondary organic aerosol in the Himalayas, Environ. Chem., 9, 263-272, 10.1071/EN12002, 2012.

Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, Atmos. Chem. Phys., 10, 4809-4822, 10.5194/acp-10-4809-2010, 2010.

~~Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, Atmos. Environ., 63, 22-31, 10.1016/j.atmosenv.2012.09.012, 2012.~~

Wan, E. C. H., and Yu, J. Z.: Determination of sugar compounds in atmospheric aerosols by liquid chromatography combined with positive electrospray ionization mass spectrometry, J. Chromatogr. A, 1107, 175-181, 10.1016/j.chroma.2005.12.062, 2006.

Wang, X., Gong, P., Sheng, J., Joswiak, D. R., and Yao, T.: Long-range atmospheric transport of particulate Polycyclic Aromatic Hydrocarbons and the incursion of aerosols to the southeast Tibetan Plateau, Atmos. Environ., 115, 124-131, 10.1016/j.atmosenv.2015.04.050, 2015.

Wang, X., Ren, J., Gong, P., Wang, C., Xue, Y., Yao, T., and Lohmann, R.: Spatial distribution of the persistent organic pollutants across the Tibetan Plateau and its linkage with the climate systems: a 5-year air monitoring study, Atmos. Chem. Phys., 16, 6901-6911, 10.5194/acp-16-6901-2016, 2016.

Wang, Y., Hu, M., Lin, P., Guo, Q., Wu, Z., Li, M., Zeng, L., Song, Y., Zeng, L., Wu, Y., Guo, S., Huang, X., and He, L.: Molecular Characterization of Nitrogen-Containing Organic

Compounds in Humic-like Substances Emitted from Straw Residue Burning, Environ. Sci. Technol., 51, 5951-5961, 10.1021/acs.est.7b00248, 2017.

Washenfelder, R. A., Attwood, A. R., Brock, C. A., Guo, H., Xu, L., Weber, R. J., Ng, N. L., Allen, H. M., Ayres, B. R., Baumann, K., Cohen, R. C., Draper, D. C., Duffey, K. C., Edgerton, E., Fry, J. L., Hu, W. W., Jimenez, J. L., Palm, B. B., Romer, P., Stone, E. A., Wooldridge, P. J., and Brown, S. S.: Biomass burning dominates brown carbon absorption in the rural southeastern United States, Geophys. Res. Lett., 42, 653-664, 10.1002/2014GL062444, 2015.

Wozniak, A. S., Bauer, J. E., Sleighter, R. L., Dickhut, R. M., and Hatcher, P. G.: Technical Note: Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Atmos. Chem. Phys., 8, 5099-5111, 10.5194/acp-8-5099-2008, 2008.

Wozniak, A. S., Willoughby, A. S., Gurganus, S. C., and Hatcher, P. G.: Distinguishing molecular characteristics of aerosol water soluble organic matter from the 2011 trans-North Atlantic US GEOTRACES cruise, Atmos. Chem. Phys., 14, 8419-8434, 10.5194/acp-14-8419-2014, 2014.

Wu, Z., Rodgers, R. P., and Marshall, A. G.: Two- and three-dimensional van krevelen diagrams: a graphical analysis complementary to the kendrick mass plot for sorting elemental compositions of complex organic mixtures based on ultrahigh-resolution broadband fourier transform ion cyclotron resonance, Anal. Chem., 76, 2511-2516, 10.1021/ac0355449, 2004.

Xia, X., Zong, X., Cong, Z., Chen, H., Kang, S., and Wang, P.: Baseline continental aerosol over the central Tibetan plateau and a case study of aerosol transport from South Asia, Atmos. Environ., 45, 7370-7378, 10.1016/j.atmosenv.2011.07.067, 2011.

Xu, J., Zhang, Q., Shi, J., Ge, X., Xie, C., Wang, J., Kang, S., Zhang, R., and Wang, Y.: Chemical characteristics of submicron particles at the central Tibetan Plateau: insights from aerosol mass spectrometry, Atmos. Chem. Phys., 18, 427-443, 10.5194/acp-18-427-2018, 2018.

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.-H., 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. USA., 10.1073/pnas.1417609112, 2014.

Yu, L., Smith, J., Laskin, A., Anastasio, C., Laskin, J., and Zhang, Q.: Chemical characterization of SOA formed from aqueous-phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical, Atmos. Chem. Phys., 14, 13801-13816, 10.5194/acp-14-13801-2014, 2014.

Yu, L., Smith, J., Laskin, A., George, K. M., Anastasio, C., Laskin, J., Dillner, A. M., and Zhang, Q.: Molecular transformations of phenolic SOA during photochemical aging in the aqueous phase: competition among oligomerization, functionalization, and fragmentation, Atmos. Chem. Phys., 16, 4511-4527, 10.5194/acp-16-4511-2016, 2016.

Zhang, H., Yee, L. D., Lee, B. H., Curtis, M. P., Worton, D. R., Isaacman-VanWertz, G., Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Beaver, M. R., Holder, A. L., Lonneman, W. A., Docherty, K. S., Jaoui, M., Pye, H. O. T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Guo, H., Weber, R. J., de Gouw, J., Koss, A. R., Edgerton, E. S., Brune, W., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Kreisberg, N. M., Spielman, S. R., Hering, S. V., Wilson, K. R., Thornton, J. A., and Goldstein, A. H.: Monoterpenes are the largest source of summertime organic aerosol in the southeastern United States, Proc. Natl. Acad. Sci. USA~~.,, 115, 2038-2043,~~., 10.1073/pnas.1717513115, 2018a.

Zhang, Q., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Time- and size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes, J. Geophys. Res., 110, 10.1029/2004jd004649, 2005.

Zhang, R., Wang, H., Qian, Y., Rasch, P. J., Easter, R. C., Ma, P. L., Singh, B., Huang, J., and Fu, Q.: Quantifying sources, transport, deposition, and radiative forcing of black carbon over the Himalayas and Tibetan Plateau, Atmos. Chem. Phys., 15, 6205-6223, 10.5194/acp-15-6205-2015, 2015.

Zhang, X., Xu, J., Kang, S., Liu, Y., and Zhang, Q.: Chemical characterization of long-range transport biomass burning emissions to the Himalayas: insights from high-resolution aerosol mass spectrometry, Atmos. Chem. Phys., 18, 4617-4638, 10.5194/acp-18-4617-2018, 2018b.

Zhang, Y., Xu, J., Shi, J., Xie, C., Ge, X., Wang, J., Kang, S., and Zhang, Q.: Light absorption by water-soluble organic carbon in atmospheric fine particles in the central Tibetan Plateau, Environ. Sci. Pollut. Res., 24, 21386-21397, 10.1007/s11356-017-9688-8, 2017.

Zhao, Y., Hallar, A. G., and Mazzoleni, L. R.: Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry, Atmos. Chem. Phys., 13, 12343-12362, 10.5194/acp-13-12343-2013, 2013.

Tables 1. Chemical characterization of ~~the~~all molecular assignments detected in WSOM for ~~F30, F43~~P1, P2, and common ions. Relative intensity weighted (w) each data subset (O/C, H/C, OM/OC, DBE, and DBE/C) are given.

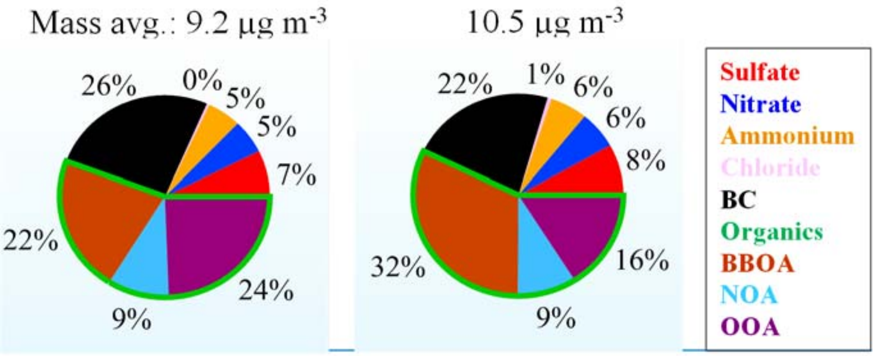
		All	CHO	CHON
~~F30~~P1	O / C_w	0.43	0.~~43~~44	0.42
	H / C_w	1.~~38~~36	1.~~40~~37	1.~~35~~34
	OM / OC_w	1.72	1.~~69~~70	1.~~77~~76
	DBE_w	~~6.26~~7.12	6.~~00~~74	~~6.69~~7.79
	DBE / C_w	0.~~34~~39	0.~~32~~37	0.~~36~~43
	~~Number~~Percentage (%) of Aliphatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ = 0)	~~2602~~18.4	~~1514~~9.4	~~1088~~9.0
	Olefinic (0.5 > ~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >0)	~~1584~~73.9	~~708~~39.7	~~876~~34.2
	Aromatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >= 0.5)	~~123~~7.7	~~75~~4.1	~~48~~3.5
~~F43~~P2	O / C_w	0.~~38~~39	0.~~38~~39	0.39
	H / C_w	1.~~33~~31	1.~~35~~32	1.31
	OM / OC_w	1.~~67~~68	1.~~62~~63	1.~~72~~73
	DBE_w	~~6.92~~7.87	~~6.36~~7.38	~~7.46~~8.32
	DBE / C_w	0.~~36~~42	0.~~34~~40	0.~~38~~44
	~~Number~~Percentage (%) of Aliphatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ = 0)	~~2413~~14.7	~~1200~~6.0	~~1213~~8.7
	Olefinic (0.5 > ~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >0)	~~2256~~75.0	~~870~~34.3	~~1306~~40.7
	Aromatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >= 0.5)	~~249~~10.3	~~103~~4.9	~~146~~5.4
Common ions	O / C_w	0.~~41~~42	0.43	0.~~40~~42
	H / C_w	1.~~36~~35	1.~~34~~36	1.~~37~~33
	OM / OC_w	1.~~70~~72	1.~~65~~69	1.76
	DBE_w	~~6.33~~7.18	~~5.96~~6.75	~~6~~7.79
	DBE / C_w	0.~~34~~40	0.~~33~~38	0.~~37~~43
	~~Number~~Percentage (%) of Aliphatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ = 0)	~~2067~~15.6	~~1019~~6.7	~~1048~~8.9
	Olefinic (0.5 > ~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >0)	~~1518~~76.5	~~653~~39.7	~~865~~36.8
	Aromatic (~~AI~~$\mathrm{AI}_{\mathrm{mod}}$ >= 0.5)	~~112~~7.8	~~71~~4.3	~~41~~3.6

Table 2. Chemical characterization of the molecular assignments detected in aerosol samples from selected studies (adapted and modified from Table 3 in Dzepina et al. (2015)). Note that all values are presented as arithmetic ~~mean~~means which are convenience for comparison. The data for our study are the arithmetic means for P1 and P2.

Sample type	Measurement site	Instrument	O / C	H / C	OM / OC	DBE	DBE / C	Reference
Aerosol	~~Free troposphere~~Remote	ESI(+)-FTICR-MS	0.~~38~~39–0.42	1.~~27~~30–1.~~31~~34	1.~~66~~68–1.~~71~~72	7.~~73~~71–8.~~62~~38	0.~~36~~41–0.~~37~~42	This study
Aerosol	Free troposphere	ESI(−)-FTICR-MS	0.42–0.46	1.17–1.28	1.67–1.73	9.4–10.7	0.42–0.47	Dzepina et al. (2015)
Aerosol	~~Free troposphere~~Remote	ESI(−)-FTICR-MS	0.53 ± 0.2	1.48 ± 0.3	1.91 ± 0.3	6.18 ± 3.0	/	Mazzoleni et al. (2012)
Aerosol	Rural	ESI(−)-FTICR-MS	0.28–0.32	1.37–1.46	1.54–1.60	6.30–7.45	0.33–0.38	Wozniak et al. (2008)
Aerosol	Suburban	ESI(−)-FTICR-MS	0.46	1.34	1.85	5.3	0.45	Lin et al. (2012)
Aerosol	Urban	ESI(+)-FTICR-MS	0.31	1.34	/	8.68	0.41	Choi et al. (2017)
Aerosol	Marin boundary layer	ESI(−)-FTICR-MS	0.35	1.59	1.67	4.37	0.28	Schmitt-Kopplin et al. (2012)
Aerosol	Marine boundary layer	ESI(−)-FTICR-MS	0.36 –0.42	1.49–1.56	1.70–1.74	5.88–6.76	0.28–0.32	Wozniak et al. (2014)
Cloud water	~~Free troposphere~~Remote	ESI(−)-FTICR-MS	0.61–0.62	1.46	2.06–2.08	6.29–6.30	0.38	Zhao et al. (2013)
Cloud water	Rural	ESI(−)-FTICR-MS	0.51	1.47	/	6.03	/	Cook et al. (2017)
Fog water	Rural	ESI(−)-FTICR-MS	0.43	1.39	1.77	5.6	0.40	Mazzoleni et al. (2010)

Table 3. List of identified BVOC products and biomass burning emission related compounds in this study.

Mass (m/z)	Molecular formula	Relative intensity	Compound type	References
358.1622	$C_{17}H_{26}O_8$	33.1%	α-pinene products	Kristensen et al., 2013
368.1829	$C_{19}H_{28}O_7$	11.5%		
186.0887	$C_9H_{14}O_4$	26.0%		
168.0417	$C_8H_8O_4$	4.75%	Monoterpene products	Claeys et al., 2007; Kleindienst et al., 2007; Zhang et al., 2018a
182.0574	$C_9H_{10}O_4$	8.12%		
198.0523	$C_9H_{10}O_5$	11.6%		
231.0737	$C_9H_{13}NO_6$	12.7%	BVOC oxidant products	Lee et al., 2016; Zhang et al., 2018a
233.0894	$C_9H_{15}NO_6$	14.0%		
215.1152	$C_{10}H_{17}NO_4$	10.6%		
229.0945	$C_{10}H_{15}NO_5$	16.5%		
231.1101	$C_{10}H_{17}NO_5$	16.8%		
233.1257	$C_{10}H_{19}NO_5$	9.5%		
245.0894	$C_{10}H_{15}NO_6$	26.4%		
247.1050	$C_{10}H_{17}NO_6$	16.5%		
249.1207	$C_{10}H_{19}NO_6$	9.6%		
306.1099	$C_{16}H_{18}O_6$	5.5%	Aqueous-phase oxidation of biomass burning aerosol	Yu et al., 2014 and 2016; Sun et al., 2010
246.0886	$C_{14}H_{14}O_4$	27.5%		
166.0624	$C_9H_{10}O_3$	4.9%	Cow dung and brush wood burning	Fleming et al., 2018
178.0624	$C_{10}H_{10}O_3$	5.7%		
190.0624	$C_{11}H_{10}O_3$	7.7%		
192.0781	$C_{11}H_{12}O_3$	7.0%		
188.0832	$C_{12}H_{12}O_2$	4.3%		
216.0781	$C_{13}H_{12}O_3$	12.5%		
218.0937	$C_{13}H_{14}O_3$	16.7%		
198.0866	$C_{13}H_{14}O_4$	30.5%		
248.1043	$C_{14}H_{16}O_4$	32.2%		
232.1094	$C_{14}H_{16}O_3$	21.6%		
338.0745	$C_{14}H_{14}N_2O_8$	5.7%	Biomass burning aerosol	Song et al., 2018
341.1105	$C_{15}H_{19}N_1O_8$	27.2%		
355.1261	$C_{16}H_{21}N_1O_8$	29.4%		
369.1418	$C_{17}H_{23}N_1O_8$	24.0%		
243.0890	$C_{14}H_{13}N_1O_3$	9.3%		
257.1046	$C_{15}H_{15}N_1O_3$	9.5%		
235.1203	$C_{13}H_{17}N_1O_3$	17.0%		



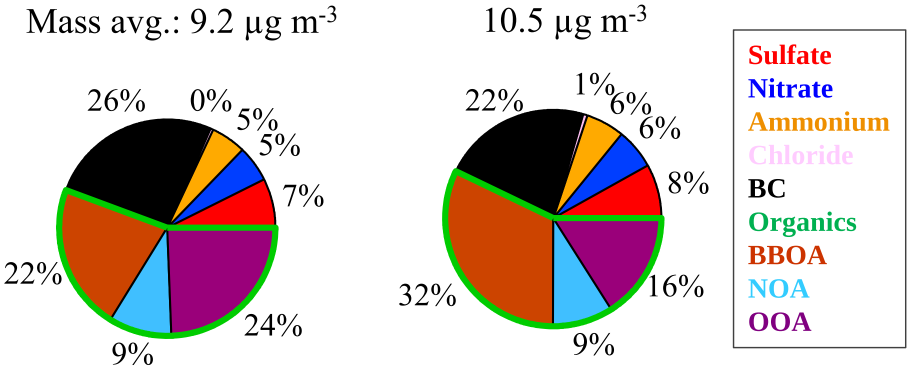


Fig. 1. The average mass concentration (mass avg.) and chemical composition of PM_1 during ~~F30~~P1 (left) and ~~F43~~P2 (right) periods, respectively, measured by HR-ToF-AMS and PAX. Note that the compounds of PM_1 include sulfate, nitrate, ammonium, chloride, BC (black carbon), organics, BBOA (biomass burning emitted OA), NOA (nitrogen-contained OA), and OOA (oxidized oxygenated OA).

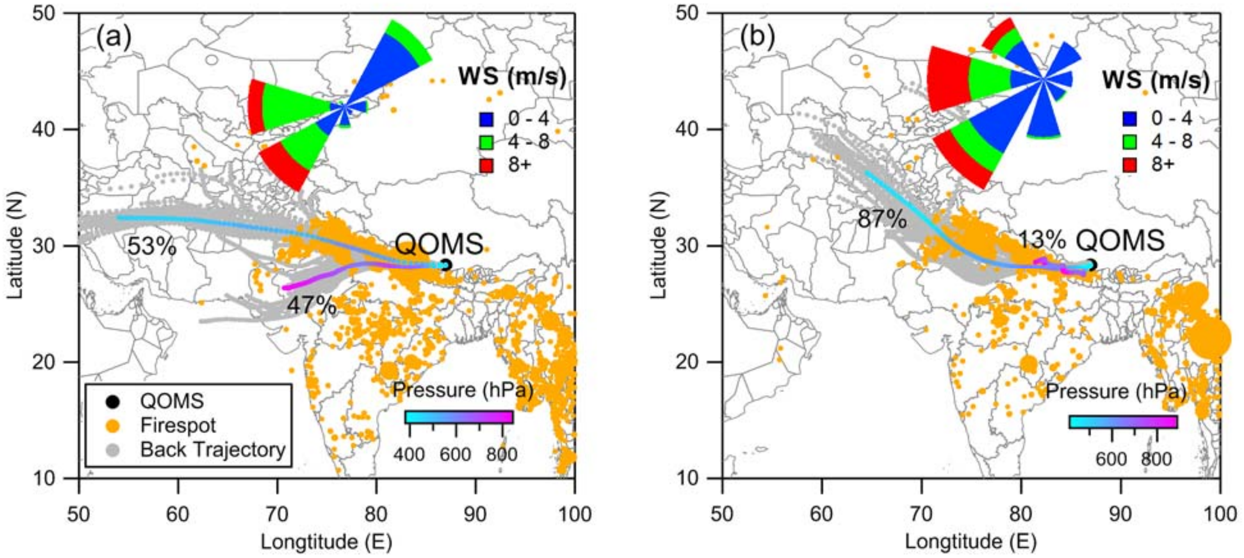
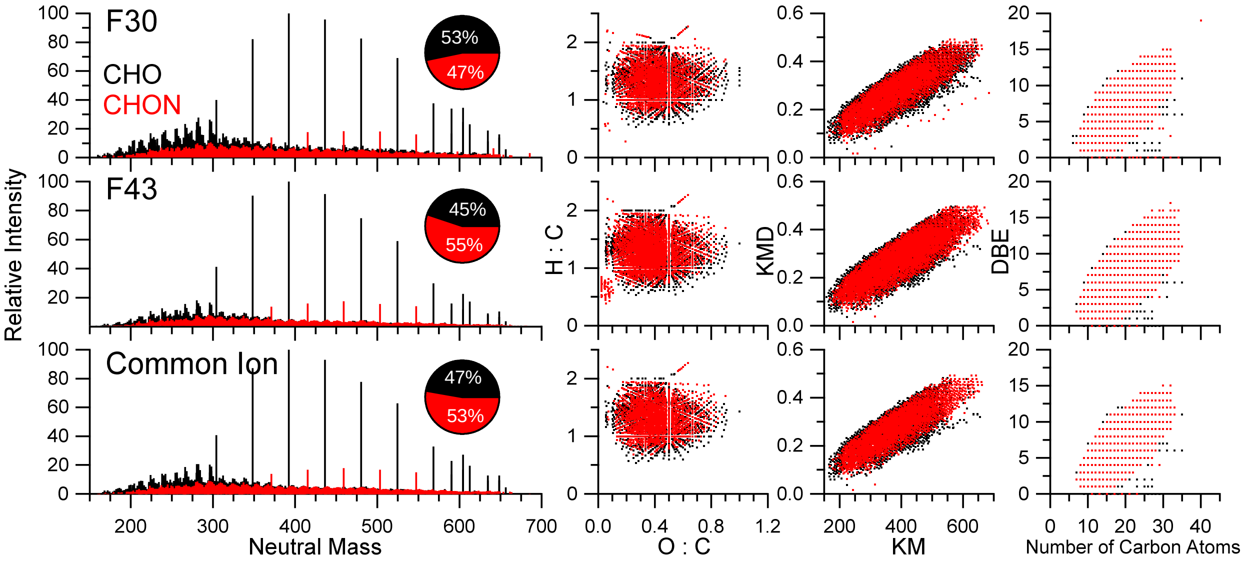


Fig. 2. The air mass back trajectory analysis using HYSPLIT model (Draxler and Hess, 1998) during (a) ~~F30~~P1 and (b) ~~F43~~P2. The air mass trajectories were recovered back to 72 h at 1 h interval from the sampling site (QOMS) at 1000 m above the ground level~~ of 1000 m~~ using 1° resolution Global Data Assimilation System (GDAS) dataset (https://ready.arl.noaa.gov/gdas1.php). The cluster analysis for these trajectories was completed based on the directions of the trajectories (angle distance) and colored according to air pressure~~.~~ (vertical profile). The fire spot observed from MODIS (https://firms.modaps.eosdis.nasa.gov) and the average wind rose plot colored by wind speed (WS) for during each filter sampling period were also shown. The fire spot is sized by fire radiative power (FRP).



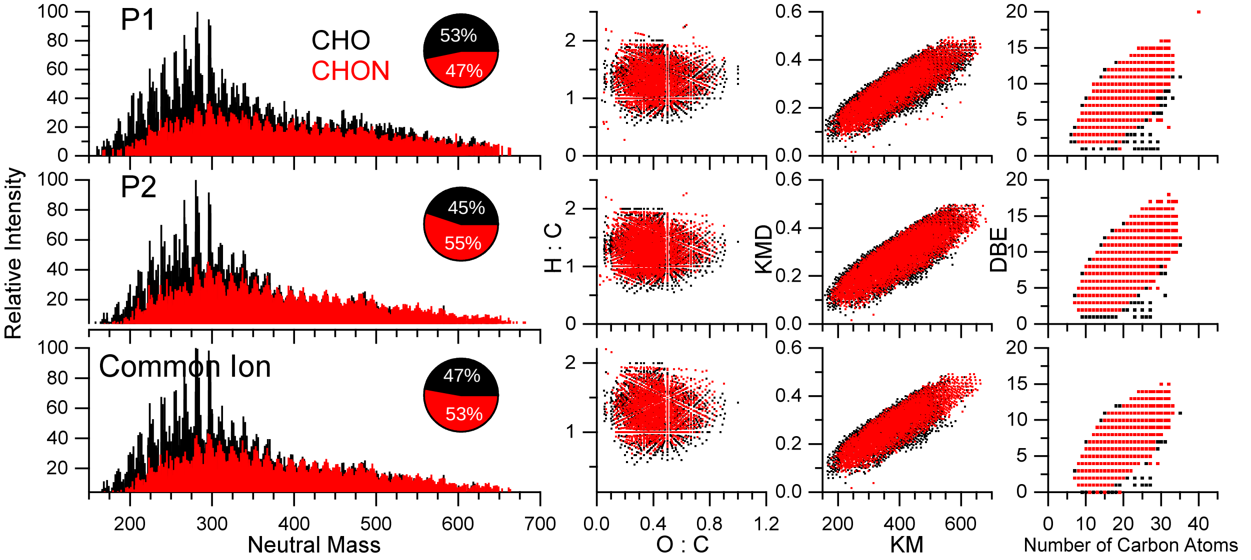
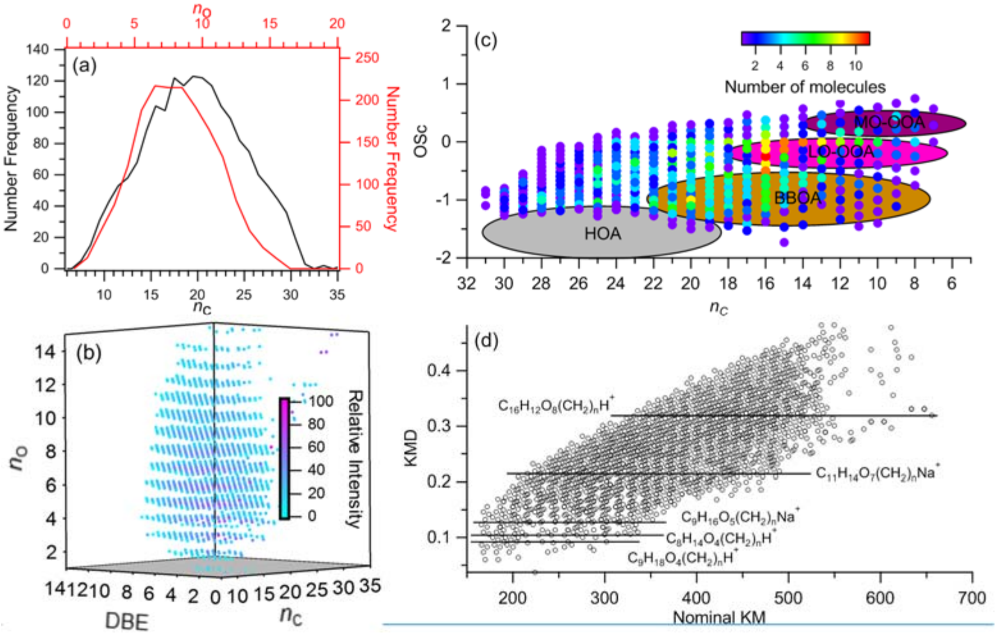


Fig. 3. The combo plot for ~~F30, F43~~all molecular of P1, P2, and ~~Common Ion~~common ion including high-resolution mass spectrum, Van Krevelen diagram, Kendrick mass defects (KMD) vs. Kendrick mass (KM~~,~~), and double bond equivalents (DBE) vs. number of carbon atoms.


(a)
Number Frequency
Number Frequency
n_O
n_C
0
5
10
15
20
140
120
100
80
60
40
20
0
250
200
150
100
50
0
10
15
20
25
30
35
(b)
n_O
14
12
10
8
6
4
2
DBE
14 12 10 8 6 4 2 0
n_C
10 15 20 25 30 35
Relative Intensity
100
80
60
40
20
0
(c)
Number of molecules
2
4
6
8
10
OSc
2
1
0
-1
-2
MO-OOA
LO-OOA
BBOA
HOA
32
30
28
26
24
22
20
18
16
14
12
10
8
6
n_C
(d)
KMD
0.4
0.3
0.2
0.1
$C_{16}H_{12}O_8(CH_2)_nH^+$
$C_{11}H_{14}O_7(CH_2)_nNa^+$
$C_9H_{16}O_5(CH_2)_nNa^+$
$C_8H_{14}O_4(CH_2)_nH^+$
$C_9H_{18}O_4(CH_2)_nH^+$
200
300
400
500
600
700
Nominal KM

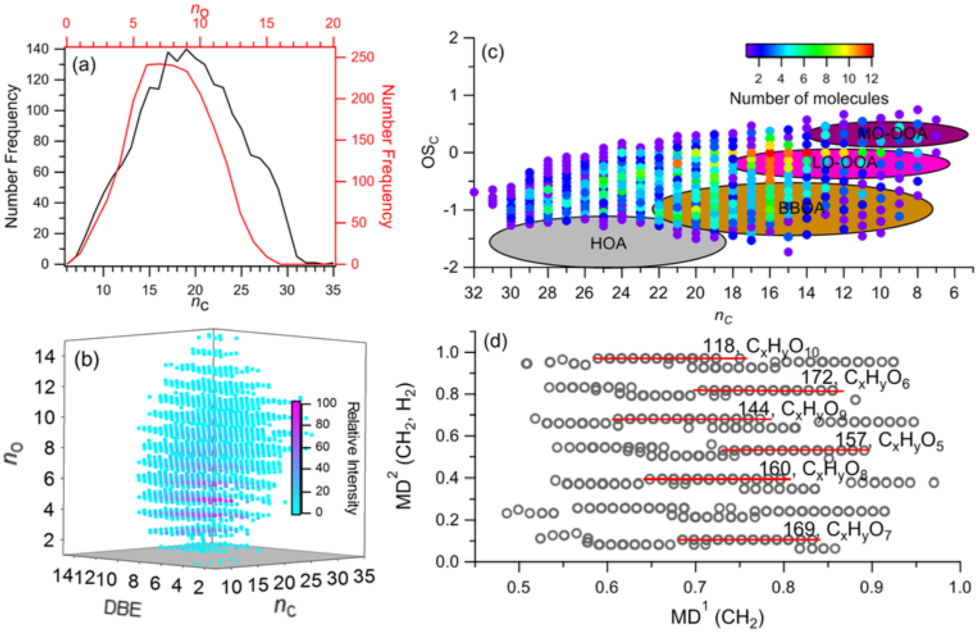
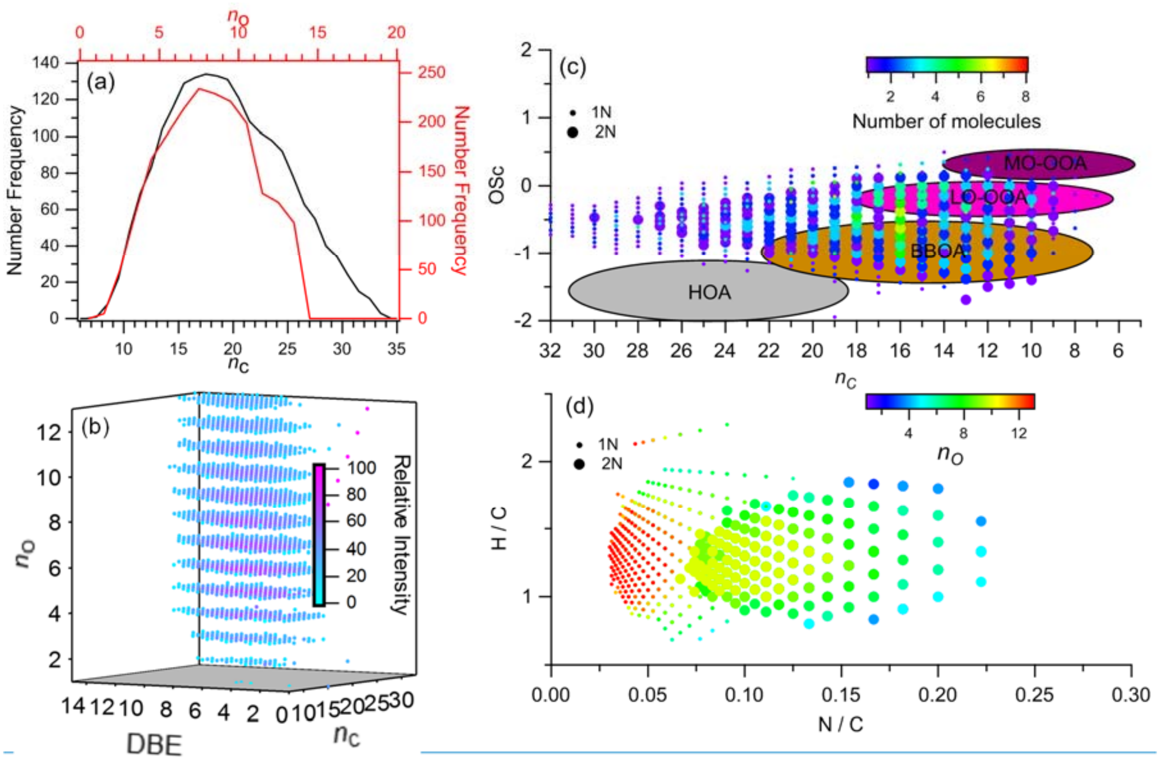


Fig. 4. The molecular information for common CHO compounds~~ of two filters~~. (a) The number frequency distribution of carbon (n_c) and oxygen (n_o); (b) The 3-D plot for n_o, n_c, and double bond equivalents (DBE) colored by their relative intensity; (c)~~-~~ Scatter plot of carbon based oxidation state (OSc) vs. n_c colored by the distribution of number of molecules; (d) The ~~Van Kerevelen diagram by H/C vs. N/C colored by no. The size of dot marker in (c) and (d) represent the 1N and 2N compounds~~two-order mass defect analysis (MD^2 (CH$_2$, H$_2$) vs. MD^1 (CH$_2$)) using the base of CH$_2$ and H$_2$. The longest homologous series were marked with the group number and formula type.


(a)
Number Frequency
Number Frequency
n_O
n_C
(b)
n_O
DBE
n_C
Relative Intensity
(c)
1N
2N
Number of molecules
OSc
MO-OOA
LO-OOA
BBOA
HOA
n_C
(d)
1N
2N
n_O
H / C
N / C

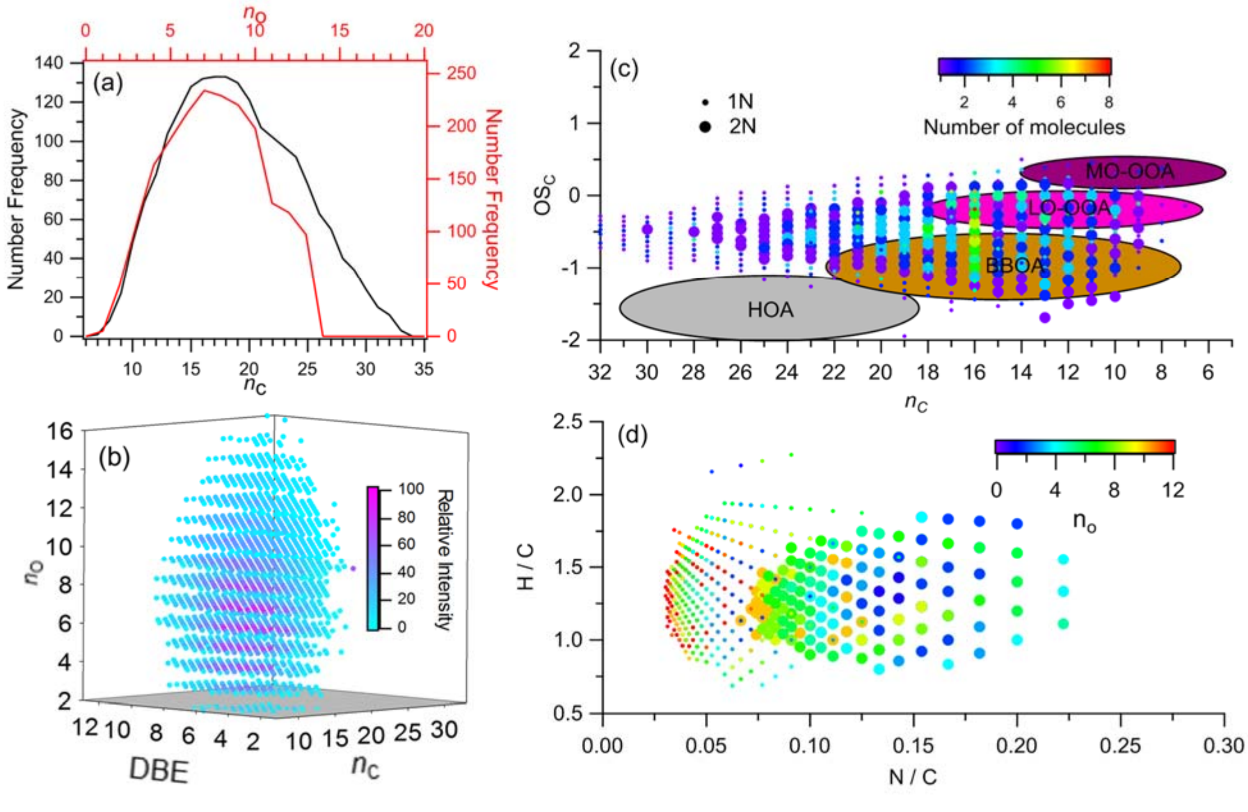

(a)
Number Frequency
Number Frequency
n_O
n_C
(b)
n_O
DBE
n_C
Relative Intensity
(c)
1N
2N
Number of molecules
OS_C
MO-OOA
LO-OOA
BBOA
HOA
n_C
(d)
n_o
H / C
N / C

Fig. 5. The molecular information for common CHON compounds~~ of two filters~~. (a) The number frequency distribution of carbon (n_c) and oxygen (n_o). (b) The 3-D plot for n_o, n_c, and double bond equivalents (DBE) colored by their relative intensity. (c)~~-~~ Scatter plot of carbon based oxidation state (OSc) vs. n_c colored by the distribution of number of molecules. (d) The Van Kerevelen diagram by H/C vs. N/C colored by ~~no.~~number of oxygen (n_o). The size of dot marker in (c) and (d) represent the 1N and 2N compounds.

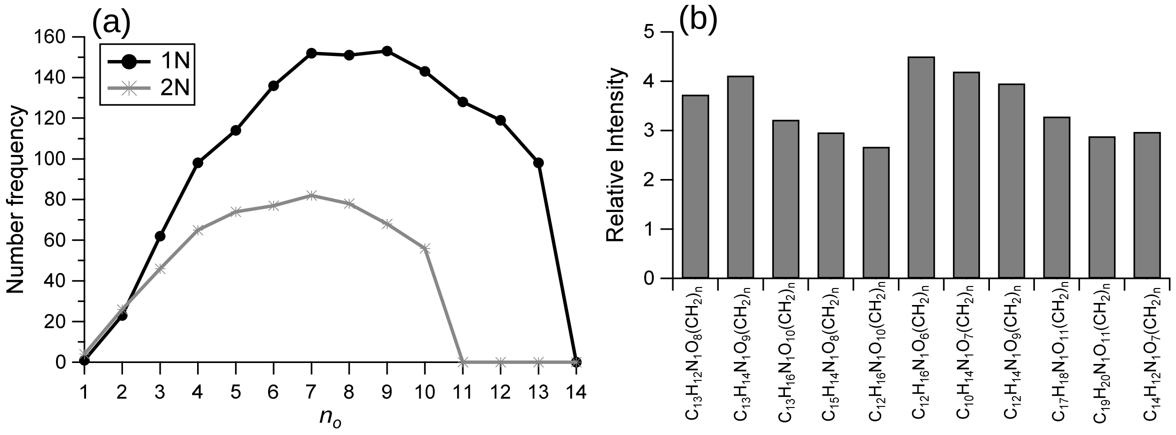


Fig. 6. (a) The number frequency distribution of n_o for 1N and 2N compounds and (b) the longest ten CH_2 homologous series compounds in 1N compounds.