

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 (DBE_w) was used here and in Table 1, however, the calculation method for DBE_w was not given in Sect. 2.3 besides that for DBE, please added.

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

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

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

where X_i and w_i 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 PM_{2.5} is in accumulation size mode (less than 1 μm) 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 Almod, ..., 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 PM₁) 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 ($\sim 5.7^{\circ}\text{C}$), 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 2) 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, NH_4^+ 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 $[\text{M} + \text{NH}_4]^+$, 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 ^1H , 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 NH₃, 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 NO₃ 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.

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

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11 **Abstract**

12 An increased trend in aerosol concentration has been observed in the Himalayas in recent years,
13 but the understanding of the chemical composition and sources of aerosol remains poorly
14 understood. In this study, molecular chemical composition of water soluble organic matter
15 (WSOM) from two filter samples collected during two high aerosol loading periods (denoted as
16 P1 and P2) at a high-altitude station (Qomolangma Station, QOMS, 4276 m a.s.l.) in the northern
17 Himalayas were identified using electrospray ionization Fourier transform ion cyclotron
18 resonance mass spectrometry (ESI-FTICR MS). More than 4000 molecular formulas were
19 identified in each filter sample which were classified into two compound groups (CHO and
20 CHON) based on their elemental composition with both accounting for nearly equal
21 contributions in number (45% – 55%). The relative abundance weighted mole ratio of O/C_w for
22 P1 and P2 were 0.43 and 0.39, respectively, and the weighted double bond equivalents (DBE_w),
23 an index for the saturation of organic molecules, were 7.12 and 7.87, respectively. Although the
24 O/C_w mole ratio was comparable for CHO and CHON compounds, the DBE_w was significantly
25 higher in CHON compounds than CHO compounds. More than 50% molecular formulas in Van
26 Krevelen (VK) diagram (H/C vs. O/C) located in 1 – 1.5 (H/C) and 0.2 – 0.6 (O/C) regions,
27 suggesting potential lignin-like compounds. The distributions of CHO and CHON compounds in
28 VK diagram, DBE vs. number of C atoms, and other diagnostic diagrams showed high
29 similarities between each other suggesting their similar source and/or atmospheric processes.
30 Many formulas formed from biogenic volatile organic compounds (e.g., ozonolysis of α -pinene
31 products) and biomass burning emitted compounds (e.g., phenolic compounds) were found in the
32 WSOM suggesting the important contribution of these two sources in the Himalayas. The high
33 DBE and high fraction of nitrogen containing aerosol can potentially impact aerosol light
34 absorption in this remote region. Further comprehensive study is needed due to the complexity of
35 organic aerosol and limited molecular number identified in this study.

36

37 **1. Introduction**

38 Relatively high aerosol concentration events have been frequently observed over the Himalayas
39 during pre-monsoon period (March to June) (Bonasoni et al., 2010). The aerosol plume are

40 originated from the southern regions of the Himalayas such as northwestern India and/or Indian
41 Gangetic region based on air mass back trajectory analysis and satellite observation (Liu et al.,
42 2008; Lu et al., 2012; Lüthi et al., 2015). Due to increased consumption on fuels (including
43 biofuels and fossil fuels) by industry and residents in recent decades, air pollution has been a
44 serious issue in South Asia (Gustafsson et al., 2009). Under favorable atmospheric circulation,
45 air pollutants emitted or formed in these regions can be fast transported to the Himalayas and
46 Tibetan Plateau (HTP) (Xia et al., 2011).

47
48 Enhanced aerosol concentration for the remote region of the HTP is thought to have many
49 negative climate and environment effects. For example, the transported aerosol could heat the air
50 at the higher layer of troposphere over the HTP and impact on the monsoon system of south Asia
51 and accelerate the melting of glacier in the Himalayas (Lau et al., 2006; Ramanathan et al.,
52 2007). This heating effect is predominantly from the light absorbing particular aerosol (LAPA)
53 such as black carbon (BC) and brown carbon which are part of organic aerosol (OA) (Ram et al.,
54 2010; Zhang et al., 2015; Zhang et al., 2017). BC is from incomplete combustion and dominates
55 the absorption of LAPA; Brown carbon can originate from primary emission and/or secondary
56 process, and have an increasing contribution (up to ~20%) to the light absorption in recent years
57 (Laskin et al., 2015, and reference therein). Due to the light absorption of brown carbon is
58 strongly depended on their molecular structure, light absorbing compounds at molecular level
59 were explored during recent years and found that nitrogen-containing compositions are important
60 brown carbon compounds (Lin et al., 2016; Lin et al., 2017). Many studies show that biomass
61 burning is an important source of brown carbon (e. g., Saleh et al., 2014; Washenfelder et al.,
62 2015), which is very popular in developing regions in the southern Himalayas. Comparison with
63 other regions, high elevation and mixed biomass fuels in the southern Himalayas could make the
64 evolution and chemical composition of OA from biomass burning emission more complicated
65 (Stockwell et al., 2016; Fleming et al., 2018; Jayarathne et al., 2018).

66
67 The details on the molecular composition of OA are important for understanding the sources and
68 chemical evolution of OA (Laskin et al., 2018). Previous studies conducted in the HTP have
69 focused on a limited number of molecular markers such as organic acids which are closely

70 related with biomass burning emission (Cong et al., 2015), and some toxicology species such as
71 polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) which are
72 related with anthropogenic activities (Wang et al., 2015; Wang et al., 2016). In addition, online
73 measurement using Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-
74 ToF-AMS) had provided more details on the OA chemistry and sources with high time
75 resolution (Xu et al., 2018). However, different instrument has its limitations on OA detection
76 and ultra-high mass resolution of mass spectrometry which can identify many molecular
77 formulas is lacking.

78
79 Fourier transform-ion cyclotron resonance mass spectrometry (FTICR MS) coupled with soft
80 ionization source, such as electrospray ionization (ESI), can be used to identify the individual
81 molecular formula of extremely complex mixture because of its ultra-high resolution and mass
82 accuracy (Mazzoleni et al., 2010). Similar methods have been used for identification of
83 components in aqueous secondary OA (SOA) and in ambient samples, and allow the
84 identification and separation of thousands of compounds in a sample (e.g., Mazzoleni et al.,
85 2010; Altieri et al., 2012; Mead et al., 2013). Kinds of methods such as double bond equivalents
86 (DBE), elemental ratios, Kendrick mass defects (KMD) can be applied to deduce the chemical
87 characterization of obtained molecular. In this study, we focus on the molecular composition of
88 water soluble organic compound in fine particle aerosol in the Himalayas using ESI-FTICR MS
89 and evaluate the sources, chemical processing, and potential impact of aerosol in this region.

90

91 **2. Methodology**

92 **2.1. Aerosol sampling**

93 Field study was conducted at the Qomolangma Station (QOMS, 28.36° N, 86.95° E, 4276 m
94 a.s.l.) located at the toe of Mt. Qomolangma from Apr. 12 to May 12, 2016 using a suit of online
95 instruments (Zhang et al., 2018b), including a HR-ToF-AMS (Aerodyne Research Inc., Billerica,
96 MA, USA) for 5-min size-resolved chemical compositions (organics, sulfate, nitrate, ammonium,
97 and chloride) of non-refractory submicron particulate matter (NR-PM₁) and a photoacoustic
98 extinctionmeter (PAX, DMT Inc., Boulder, CO, USA) for BC mass concentration. In addition, a
99 low-volume (16.7 L min⁻¹) particulate matter (PM) sampler (BGI, USA, model PQ 200) with an

100 aerodyne diameter cutoff of 2.5 μm at the inlet was used to collect $\text{PM}_{2.5}$ filter samples on pre-
101 baked quartz fiber filters (47 mm, Pall Life Science, NY, USA). Due to the low aerosol loading
102 at this remote region, two days sampling strategy was adapted for each filter collection starting
103 from 8:00 am to 7:45 am at the day after tomorrow (local time). A total of 18 filter samples were
104 collected during the field study with three procedure blanks which were used to assess potential
105 contamination during sampling and transportation. The sampling air volume ranged from 35.1 to
106 48.1 m^3 at ambient conditions. Two samples collected during Apr. 25 – 27 (P1) and Apr. 29 –
107 May 1 (P2), respectively, were used in this study due to the relatively higher aerosol loading
108 based on HR-ToF-AMS results (section 3.1) and distinct particulate matter on the filter. One
109 procedure blank was also adopted in this study as like that of aerosol samples to subtract the
110 potential background.

111

112 **2.2. Chemical analysis**

113 For FTICR MS analysis, filter samples were extracted in 20 mL Milli-Q water in an ultrasonic
114 bath for 30 min and filtered using 0.45 μm pore-size Acrodisc syringe filters to remove water
115 insoluble matter (Pall Science, USA). The sample tubes were immersed in the mixture of ice-
116 water during ultrasonic extraction to prevent potential chemical reaction. Prior to FTICR MS
117 analysis, the extraction was concentrated and purification using PPL (Agilent Bond Elut-PPL
118 cartridges, 500 mg, 6 mL) solid phase extraction (SPE) cartridges for water soluble organic
119 matter (WSOM) to avoid possible ESI artifacts. PPL cartridge generally has the best properties
120 for WSOM enrichment for subsequent FTICR MS analysis (Raeke et al., 2016). In addition, we
121 control the concentration of SPE effluent to be ~ 0.2 mg/mL which was not too concentrated for
122 artifact adducts. Note that through SPE cartridge, the most hydrophilic compounds such as
123 inorganic ions, and low-molecular-weight organic molecules such as organic acids and sugars
124 were removed, whereas the relatively hydrophobic fraction was retained. The details on the SPE
125 method using PPL cartridges and analysis by FT-ICR MS can be found in our previous paper
126 (Feng et al., 2016). Briefly, the mass spectrometry analyses of these samples were performed
127 using a SolariX XR FTICR MS (Bruker Daltonik GmbH, Bremen, Germany) equipped with a
128 9.4 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg,
129 France) and a Paracell analyzer cell. The samples were ionized in positive ion modes using the

130 ESI ion source (Bruker Daltonik GmbH, Bremen, Germany). A typical mass-resolving power of
131 >400 000 was achieved at m/z 400 with an absolute mass error of <0.5 ppm. The ions detected in
132 filter blank were subtracted and molecular formulas in the samples were assigned to all ions with
133 signal-to-noise ratios of greater than 10 with a mass tolerance of ± 1.5 ppm using custom
134 software. Molecular formulas with their maximum numbers of atoms were defined as: 30 ^{12}C , 60
135 ^1H , 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
136 DBE/C ranged in 0.3 – 3.0, 0 – 3, 0 – 0.5, 0 – 0.2, and 0 – 1, were selected, and formulas
137 containing isotopomers (i.e., ^{13}C , ^{18}O or ^{34}S) were not considered. Compounds were detected as
138 either sodium adducts, $[\text{M} + \text{Na}]^+$, or protonated species, $[\text{M} + \text{H}]^+$. Although ammonium could
139 also readily be adduct to assist in forming positive ions, this possibility in our sample was
140 because of the low concentration of ammonium (Fig. 1). We report all detected compounds as
141 neutral species, unless stated otherwise. Note that the ESI+ mode is more easily to detect basic
142 functional group compounds and the reported organic molecules here is only part of organic
143 aerosol which are biased ionized in ESI+ mode. In addition, highly functionalized compounds
144 could be detected in both positive and negative modes (Lin et al., 2012).

145

146 **2.3. Data processing**

147 The assigned molecular formulas were examined using the van Krevelen diagram (Wu et al.,
148 2004), DBE, KMD series, and aromatic indices (AI_{mod}). The O/C and H/C ratios were calculated
149 by dividing the number of O and H atoms, respectively, by the number of C atoms in a formula.
150 DBE analysis was used to determine the number of rings and double bonds in a molecule. The
151 DBE was calculated using equation (1),

$$152 \text{DBE} = 1 + c - h/2 + n/2, \quad (1)$$

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

154

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

$$156 X_w = \sum(w_i * X_i) / \sum w_i, \quad (2)$$

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

159

160 The Kendrick mass (KM) and KMD for CH₂ series, used to search for potential oligomeric units
161 (Hughey et al., 2001), were calculated using equations (3) and (4),

$$162 \text{ KM} = \text{observed mass} \times 14/14.01565, \quad (3)$$

$$163 \text{ KMD} = \text{NM} - \text{KM}, \quad (4)$$

164 where 14 is the nominal mass (NM) of CH₂, 14.01565 is the exact mass of CH₂, and NM is KM
165 rounded to the nearest integer.

166
167 Furthermore, a two-order mass defect analysis using the base units of CH₂ and H₂ was applied
168 following the method described in Roach et al. (2011) which could greatly simplifies
169 visualization of complex mass spectra.

170
171 AI_{mod} is a measure of the probable aromaticity of a molecule assuming that half the O atoms are
172 double bonded and half have only σ bonds (Koch and Dittmar, 2006). AI_{mod} was calculated using
173 equation (5),

$$174 \text{ AI}_{\text{mod}} = (1 + c - 0.5o - 0.5h - 0.5n) / (c - 0.5o - n), \quad (5)$$

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

178

179 **3. Results and discussions**

180 **3.1. Chemical characterization of PM₁ during P1 and P2 measured by HR-ToF-AMS**

181 The average mass concentration and chemical composition measured by HR-ToF-AMS during
182 P1 and P2 periods was shown in Fig. 1. The mass concentration of PM₁ were 9.2 and 10.6 $\mu\text{g m}^{-3}$
183 ³, respectively, which were at the high range of all filters (1.3 – 10.6 $\mu\text{g m}^{-3}$) because of a
184 continuous long-range transport event at the QOMS (Zhang et al., 2018b). Due to our sample
185 processing error, the mass concentration of filter measured gravimetrically could not be used and
186 thus the fractions of PM₁ to PM_{2.5} are not available. However, most of WSOM in PM_{2.5} is in
187 accumulation size mode (less than 1 μm) which could be detected by HR-ToF-AMS (Zhang et
188 al., 2005). The chemical composition of PM₁ during P1 and P2 was all dominated by OA (55%
189 and 57%), followed by BC (26% and 22%), sulfate (7% and 8%), nitrate (5% and 6%), and

190 ammonium (5% and 6%). The OA was comprised by biomass burning emitted OA (BBOA),
191 nitrogen-contained OA (NOA), and more-oxidized oxygenated OA (MO-OOA) decomposed by
192 positive matrix factorization (PMF) analysis (Fig. 1). The details on PMF analysis can be found
193 in Zhang et al. (2018b). The mass contribution of BBOA was higher during P2 than P1 (32% vs.
194 22%), whereas the contribution of MO-OOA was higher during P1 (24% vs. 16%). The mass
195 spectra of OA for these two filter periods were closely similar with a Poisson correlation
196 efficiency (r) being 0.9. The elemental ratios of oxygen (O) to carbon (C) of OA were 1.04 and
197 0.97 for P1 and P2 periods (Improved Ambient method, Canagaratna et al., 2015), respectively,
198 and accordingly the ratios of hydrogen (H) to C were 1.26 and 1.32. These suggest that the OA
199 during P2 was relatively less oxidized than that during P1 (t -test, $p < 0.05$). The six category ions
200 ($C_xH_y^+$, $C_xH_yO_2^+$, $C_xH_yO_1^+$, $C_xH_yN^+$, $C_xH_yO_zN^+$, and HO^+) detected by HR-ToF-AMS for these
201 two filter periods were all dominated by $C_xH_yO_2^+$, following by $C_xH_y^+$, $C_xH_yO_1^+$, $C_xH_yN^+$,
202 $C_xH_yO_zN^+$, and HO^+ . The air mass trajectory analyses using the hybrid single particle Lagrangian
203 integrated trajectory (HYSPLIT) model for P1 and P2 periods show air mass mainly originated
204 from west and southwest of the QOMS across north and northwest India where there were many
205 fire spots during these two periods (Fig. 2). The air mass during P2 was partly (13%) transported
206 with low wind speed and short distance (less than 100 km) which could contain some fresh OA
207 as illustrated with higher fraction of BBOA.

208

209 **3.2. The chemical characteristics of WSOM from ESI-FTICR MS**

210 A total of 4295 and 4770 molecular formulas were identified by ESI-FTICT MS over the mass
211 range of 100-700 Da for P1 and P2, respectively. The identified molecular formulas were
212 grouped into two subgroups based on their elemental composition, i.e., CHO and CHON, all of
213 which had equal important contribution (45% – 55%) in number (Fig. 3). Note that individual
214 species in the ESI-FTICR MS mass spectra could have many different isomeric structures, then
215 the percentages reflect only the number of unique molecular formulas in each category. The
216 mass spectra of these two samples were highly similar in the distributions of molecular (Fig. 3).
217 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
218 H/C_w , and 1.72 vs. 1.68 for OM/OC_w (Table 1), suggesting a relatively higher oxidation and
219 saturation degree for P1 than P2. These trends are consistent with the results of HR-ToF-AMS,

220 although the elemental ratios are different between them which is due to the difference on the
221 detection range of m/z and the ionization efficiency of different mass spectrometry (ESI vs.
222 electron impact) (Yu et al., 2016). The elemental ratios of WSOM from ESI-FTICR MS in our
223 study are similar with those results observed in aerosol samples in remote site using ESI-FTICR
224 MS (e.g., 0.35 – 0.53 for O/C) (Table 2). The O/C and H/C in Van Krevelen diagrams (Wu et al.,
225 2004) for these two filters and the subgroup molecular show similar distributions and all
226 concentrate in 1.2 – 1.8 for H/C and 0.3 – 0.7 for O/C (Fig. 3) suggesting their similar aerosol
227 sources and atmospheric processes. The similar distributions for these two filters are also
228 observed in plots of KMD vs. KM and DBE vs. C (Fig. 3).

229
230 Structural information for the assigned molecular formulas is inferred from the DBE_w value
231 which was higher for P2 than that of P1 (7.87 vs. 7.12) (Table 1). Comparing with other studies,
232 the DBE_w values in our filter are relative close to the results from biomass burning aerosol and
233 aerosol samples from remote sites (Table 2) (Dzepina et al., 2015). The DBE_w values for each
234 molecular subgroup were higher for CHON than that of CHO (Table 1), especially for P2 (8.32
235 vs. 7.38) suggesting more rings and double bonds in CHON molecular. The AI_{mod} , reflecting the
236 minimum number of carbon-carbon double bonds and rings (Koch and Dittmar, 2006), was
237 correspondingly higher in P2 as illustrated by its higher contribution of olefinic (75.0% vs.
238 73.9% for P2 and P1) and aromatic compounds (10.3% vs. 7.7% for P2 and P1) (Table 1). For
239 aromatic compounds ($AI_{mod} \geq 0.5$) in P2, 52% of them were CHON formulas (45% for P1).
240 Higher DBE and AI_{mod} values in CHON compounds suggest more unsaturated compounds with
241 them which could contain a certain number of chromophores. The distribution of DBE vs. carbon
242 number of two filters showed a systematic increase in a concentrated region and a highly
243 similarity with each other. This similarity further suggests the consistent source and chemical
244 processes for the aerosol of these two filters.

245
246 There were 3955 common molecular formulas between these two filters with the number
247 contribution of CHO by 50.7% and CHON by 49.3%. These common molecular formulas
248 accounted for 92.1% (P1) and 82.9% (P2) of two filters, respectively. There were 340 unique
249 molecular formulas in P1 with 73% being CHO compounds; whereas there were 815 unique

250 molecular formulas in P2 with 65.3% being CHON compounds. For more confidence on
251 molecule assignment, we focus on the common molecular formulas detected in these two
252 samples in the section below. Note that the mass spectrum of common ions was calculated from
253 the average RI from two mass spectra and normalized to the highest peak.

254

255 **3.3. The potential sources and formation processes**

256 **3.3.1. CHO compounds**

257 CHO compounds have been frequently detected in ambient aerosol samples (Altieri et al., 2009b;
258 Mazzoleni et al., 2010; Lin et al., 2012; Fleming et al., 2018), which could comprise of high
259 molecular weight humic-like substances (HULIS) or oligomers, and from primary emission or
260 secondary formation of different aerosol sources (Mazzoleni et al., 2012; Wozniak et al., 2014;
261 Lin et al., 2016; Cook et al., 2017). In our samples, the weighted molecular weight of CHO
262 compounds was 361.9 with an average C atom of 19.3 ± 5.3 per molecule; the most abundant O
263 atoms located in 5 – 10 with an average value of 7.8 ± 2.9 per molecule (Fig. 4a and b). The
264 oxygen distribution is also evidenced by the longest homologous series in two-order mass defect
265 analysis ($\text{CH}_2\text{-H}_2$) which were all $\text{O}_5\text{-O}_{10}$ compounds (Fig. 4d). The DBE of CHO increased with
266 the carbon number with the DBE_w value of 6.75 (Fig. 3); the carbon-normalized DBE (DBE/C)
267 was 0.39 ± 0.14 . These two values were close to the results from biomass burning aerosol
268 samples in other studies and at the high range of published data (Table 2) (Lin et al., 2012;
269 Mazzoleni et al., 2012), suggesting relatively high aromaticity in our samples. The carbon
270 oxidation state (OS_C) values (Kroll et al., 2011), a useful metric for the degree of oxidation of
271 organic species in the atmosphere, exhibited between -1 and 0 with 25 or less carbon atoms,
272 suggesting that they are semi- and low-volatile organic compounds corresponding to “fresh”
273 (BBOA) and “aged” (LV-OOA) SOA by multistep oxidation reactions (Fig. 4c).

274

275 There are several possible sources and chemical formation pathways for high oxygen-containing
276 CHO compounds. Ozonolysis of α -pinene has been found to form highly oxygenated molecules
277 with some important products such as $\text{C}_{17}\text{H}_{26}\text{O}_8$ (m/z 358) and $\text{C}_{19}\text{H}_{28}\text{O}_7$ (m/z 368) which is a
278 possible esterification product of cis-pinic ($\text{C}_9\text{H}_{14}\text{O}_4$, m/z 186) and diaterpenylic acid ($\text{C}_8\text{H}_{14}\text{O}_5$,
279 m/z 190) (Kristensen et al., 2013). The first three formulas were all found in our common CHO

280 molecules with high relative abundance (Table 3). The appearance of these formulas together
281 with high relative abundance gave our more confidence on the products of ozonolysis of α -
282 pinene. Ozone concentration in the Himalayas during pre-monsoon was the highest based on the
283 on-line measurement at the Nepal Climate Observatory at Pyramid (NCO-P) during 2006-2008
284 (61 ± 9 ppbv) (Cristofanelli et al., 2010). Biogenic volatile organic compounds could be
285 transported from the low elevation regions in the subtropical India and biogenic secondary
286 organic aerosol has been found to be important source in the Himalayas (Stone et al., 2012). A
287 number of previously reported other monoterpene oxidation product formulas were also
288 observed in our study (Table 3) (Claeys et al., 2007; Kleindienst et al., 2007; Zhang et al., 2018a).
289 In addition, some biomass burning aerosol markers were also found in CHO compounds. Sun et
290 al. (2010) and Yu et al. (2014; 2016) observed that aqueous-phase oxidation of lignin produces
291 phenol (C_6H_6O), guaiacol ($C_7H_8O_2$) and syringol ($C_8H_{10}O_3$) yields a substantial fraction of
292 dimers and higher oligomers with key dimer markers identified as $C_{16}H_{18}O_6$ and $C_{14}H_{14}O_4$. The
293 dimer markers $C_{16}H_{18}O_6$ and $C_{14}H_{14}O_4$ were also present in our sample with high RI (5.5% and
294 27.5%). The high relative intensity of these compounds indicates that fog and cloud processing
295 of phenolic species (biomass burning aerosol) could be an important mechanism for the
296 production of low-volatility SOA in the Himalayas. Compounds observed in biomass burning
297 emission (cow dung and brush wood) during residential cooking in Nepal were also found in our
298 samples (Fleming et al., 2018).

299

300 **3.3.2 CHON compounds**

301 The frequency distribution for n_o and n_c in CHON formulas were shown in Fig. 5a which show
302 peaks between 6 – 10 and 15 – 20, respectively. The DBE of CHON formulas ranged into 4 – 10
303 with DBE_w being 7.79 (Fig. 5b and Table 1). In the CHON class, compounds contained one or
304 two nitrogen (1N or 2N) atoms with 1N compounds accounting for 70.5% and 2N for 29.5%,
305 respectively. Most (93.6%) of 1N compounds contained more than 3 oxygen atoms and could up
306 to 13 oxygen atoms, whereas about 62.5% of 2N compounds contained more than 6 oxygen
307 atoms (Fig. 6a). The average O atoms contained in each molecular formula were therefore higher
308 for 1N compounds than 2N compounds (8.1 ± 2.9 vs. 6.3 ± 2.3). The ratios of O/C_w and OS_{C_w}
309 for 1N compounds were accordingly higher than that of 2N compounds (0.42 vs. 0.37 for O/C_w

310 and -0.48 vs. -0.54 for OS_{C_w} , respectively), suggesting higher oxidation state for 1N compounds
311 (Fig. 5c). In contrast, the DBE_w and AI_{mod} values for 2N compounds were higher than that of 1N
312 compounds (Table 1). With higher H/C_w for 2N compounds (Fig. 5d), it suggests that 2N
313 compounds could contain many aromatic N-heterocyclic compounds. For 1N compounds, longer
314 and higher relative intensity CH_2 homologous series compounds were found based on the
315 Kendrick mass defect plot (Fig. 6b); 1073 of the 1373 detected 1N compounds can be grouped
316 into 145 homologous. The abundant long CH_2 homologous series in 1N compounds contained 7
317 – 10 O atoms, while 5 – 8 O atoms for 2N compounds (Fig. 6).

318
319 Many CHON compounds could be identified in ESI+ mode, such as reduced N functional
320 compounds and nitro-aromatic compounds (Altieri et al., 2009a; Laskin et al., 2009; Lin et al.,
321 2012; O'Brien et al., 2013; Wang et al., 2017). Laskin et al. (2009) identified amount of N-
322 heterocyclic alkaloid compounds from kinds of fresh biomass burning aerosol. Lin et al., (2012)
323 and Wang et al., (2017) also identified many CHON compounds in fresh and aged biomass
324 burning aerosol. Oxygenated organic nitrogen compounds in ambient aerosol (Dzepina et al.,
325 2015), rain water (Altieri et al., 2009a), and fog water (Mazzoleni et al., 2010) from biomass
326 burning emission influenced regions were also observed. Lin et al. (2017) found aged biomass
327 burning aerosol in the present urban oxidants (such as NO_x) could result in higher fraction of
328 CHON compounds comparing to the fresh biomass burning aerosol. Considering the high
329 influence of biomass burning emission in the Himalayas (Zhang et al., 2018b), the CHON
330 compounds in our study were probably related with biomass burning emissions. Recent studies
331 have proven that burning of mixed biomass fuels in Nepal could emit amount of nitrogen species
332 such as NH_3 , NO_x , HCN, benzene, and organics, and the emission factors for these species are
333 higher than that of wood (Stockwell et al., 2016; Jayarathne et al., 2018). In addition, it is likely
334 that smoldering burning of bio-fuels in high elevation area is also responsible for the presence of
335 many nitrogen-containing compounds in BBOA (Chen et al., 2010). Nitroaromatic compounds
336 such as Methyl-Nitrocatechols ($C_7H_7NO_4$) are introduced to be tracer for biomass burning
337 secondary organic aerosols (Iinuma et al., 2010). Although $C_7H_7NO_4$ formula is not found in our
338 measurement, $C_{14}H_{14}N_2O_8$ were found in our measurement, of which is probably its dimer
339 formula. In addition, the homologous series compounds which $C_7H_7NO_4$ serve as the core

340 molecule was also found in our samples. Some high relative abundance CHON molecular
341 formulas identified in a recent paper from biomass burning aerosol were also found in our
342 measurement (Table 3) (Song et al., 2018).

343
344 Besides primary emission and/or secondary formation from biomass burning emission, nitrogen-
345 containing OA could also be formed through other chemical processes. For example, biogenic
346 volatile organic compounds (BVOC) can react with NO₃ radical or RO₂+NO into organic nitrate
347 (Ng et al., 2017). Although organic nitrate is not favored to be ionized in positive ESI-MS (Wan
348 and Yu, 2006), organic nitrate formed from BVOC could be highly functionalized (Lee et al.,
349 2016) and ionized in positive MS through other alkaline functional groups. Recent studies have
350 shown that BVOC, including isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆), dominate the organic
351 nitrate formation in the southeastern United States under the condition of the mixed
352 anthropogenic NO_x and BVOC (Xu et al., 2014; Lee et al., 2016; Zhang et al., 2018a). Several
353 molecular formulas formed from monoterpene and NO₃ radical were found in our study (Table 3)
354 (Lee et al., 2016; Zhang et al., 2018a).

355

356 **4. Implications and limitations**

357 This study analyzed the WSOM using ESI(+)-FTICR MS in fine particulate aerosol from the
358 Himalayas and found that the molecular compositions of WSOM were mainly comprised by two
359 group compounds (CHO and CHON) with equal important contribution. The two compound
360 groups could be originated from biomass burning emission and BVOC oxidation products
361 because many markers for these two sources were found in these molecular compounds. All our
362 compounds had relatively high DBE values suggesting potential high light absorption feature.
363 Due to the relative higher mass concentration and higher contribution of nitrogen-containing
364 compounds (9% of PM₁) during these two periods based on HR-ToF-AMS results (Zhang et al.,
365 2018), it is believed that aerosol transported to the Himalayas have important application in
366 atmospheric radiative forcing.

367

368 Ramanathan and Carmichael (2008) found distinct warming effect of light absorbing aerosol
369 over the Himalayas through estimating aerosol radiative forcing by BC. However, brown carbon

370 have not been considered before which could also be important light absorbing aerosol due to
371 their high mass loading (Laskin et al., 2015). Zhang et al. (2017) estimated the light absorption
372 contribution of brown carbon from inland of the TP which was up to ~13% of that of BC. The
373 high DBE and nitrogen-containing OA in our study suggested aerosol in the Himalayas could
374 also contain amount of light-absorbing organic matter because light absorption properties of
375 organic molecules are closely related with the number of double bonds and rings in the molecule
376 and nitrogen atoms. Many studies had found that the dominated chemical molecules in the brown
377 carbon were related with nitrogen-containing aerosol (e.g., Lin et al., 2016). This kind of aerosol
378 combined with BC could have higher radiative forcing than before in this area.

379
380 More comprehensive methods are needed in the future for identifying BrC in the Himalayas due
381 to the chemical complexity of BrC. For example, the BrC extraction is highly dependent on the
382 used solvent and water insoluble OA can contribute higher light absorption than water soluble
383 OA (Chen and Bond, 2010). In addition, Budisulistiorini et al. (2017) found that a number of
384 compounds can dominate the light absorption of BrC, although they have a minor contribution to
385 the aerosol mass. Therefore, it is important to know the exactly chromophores of BrC which can
386 be obtained by combining with high performance liquid chromatography, light absorption
387 measurement with a photodiode (PDA) detector, and chemical composition with high resolution
388 mass spectrometer (HPLC-PDA-HRMS system) (Lin et al., 2016). For mass spectrometry
389 analysis, different ionization sources are also favorable for different compounds, such as ESI
390 only detect a part of polar compounds; non-polar compounds which could dominated the
391 contributing of BrC, can be measured using atmospheric pressure photo ionization (APPI) (Lin et
392 al., 2018). Recent study indicate that over 40% of the solvent-extractable BrC light absorption is
393 attributed to water insoluble, non-polar to semi-polar compounds such as PAHs and their
394 derivative (Lin et al., 2018). In contrast, the polar, water-soluble BrC compounds, which are
395 detected in ESI, account for less than 30% of light absorption by BrC (Lin et al., 2018).

396

397

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

		All	CHO	CHON	
P1	O / C _w	0.43	0.44	0.42	
	H / C _w	1.36	1.37	1.34	
	OM / OC _w	1.72	1.70	1.76	
	DBE _w	7.12	6.74	7.79	
	DBE / C _w	0.39	0.37	0.43	
	Percentage (%) of				
	Aliphatic (AI _{mod} = 0)		18.4	9.4	9.0
	Olefinic (0.5 > AI _{mod} > 0)		73.9	39.7	34.2
	Aromatic (AI _{mod} >= 0.5)		7.7	4.1	3.5
P2	O / C _w	0.39	0.39	0.39	
	H / C _w	1.31	1.32	1.31	
	OM / OC _w	1.68	1.63	1.73	
	DBE _w	7.87	7.38	8.32	
	DBE / C _w	0.42	0.40	0.44	
	Percentage (%) of				
	Aliphatic (AI _{mod} = 0)		14.7	6.0	8.7
	Olefinic (0.5 > AI _{mod} > 0)		75.0	34.3	40.7
	Aromatic (AI _{mod} >= 0.5)		10.3	4.9	5.4
Common ions	O / C _w	0.42	0.43	0.42	
	H / C _w	1.35	1.36	1.33	
	OM / OC _w	1.72	1.69	1.76	
	DBE _w	7.18	6.75	7.79	
	DBE / C _w	0.40	0.38	0.43	
	Percentage (%) of				
	Aliphatic (AI _{mod} = 0)		15.6	6.7	8.9
	Olefinic (0.5 > AI _{mod} > 0)		76.5	39.7	36.8
	Aromatic (AI _{mod} >= 0.5)		7.8	4.3	3.6

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693

694 Table 2. Chemical characterization of the molecular assignments detected in aerosol samples
 695 from selected studies (adapted and modified from Table 3 in Dzepina et al. (2015)). Note that all
 696 values are presented as arithmetic means which are convenience for comparison. The data for
 697 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	Remote	ESI(+)-FTICR MS	0.39– 0.42	1.30– 1.34	1.68– 1.72	7.71– 8.38	0.41– 0.42	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	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	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)

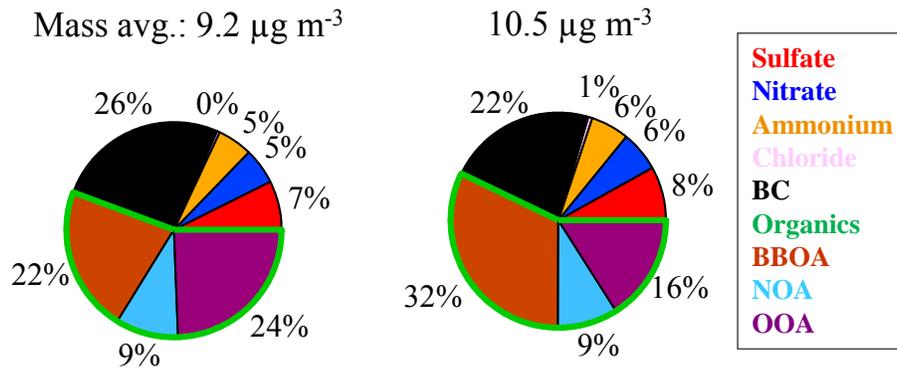
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700 Table 3. List of identified BVOC products and biomass burning emission related compounds in
 701 this study.

Mass (m/z)	Molecular formula	Relative intensity	Compound type	References
358.1622	C ₁₇ H ₂₆ O ₈	33.1%	α-pinene	Kristensen et al., 2013
368.1829	C ₁₉ H ₂₈ O ₇	11.5%	products	
186.0887	C ₉ H ₁₄ O ₄	26.0%	Monoterpene products	Claeys et al., 2007; Kleindienst et al., 2007; Zhang et al., 2018a
168.0417	C ₈ H ₈ O ₄	4.75%		
182.0574	C ₉ H ₁₀ O ₄	8.12%		
198.0523	C ₉ H ₁₀ O ₅	11.6%		
231.0737	C ₉ H ₁₃ NO ₆	12.7%	BVOC oxidant products	Lee et al., 2016; Zhang et al., 2018a
233.0894	C ₉ H 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%		
246.0886	C ₁₄ H ₁₄ O ₄	27.5%		
166.0624	C ₉ H 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 ₂ O ₈	5.7%	Biomass burning aerosol	Song et al., 2018
341.1105	C ₁₅ H ₁₉ N ₁ O ₈	27.2%		
355.1261	C ₁₆ H ₂₁ N ₁ O ₈	29.4%		
369.1418	C ₁₇ H ₂₃ N ₁ O ₈	24.0%		
243.0890	C ₁₄ H ₁₃ N ₁ O ₃	9.3%		
257.1046	C ₁₅ H ₁₅ N ₁ O ₃	9.5%		
235.1203	C ₁₃ H ₁₇ N ₁ O ₃	17.0%		

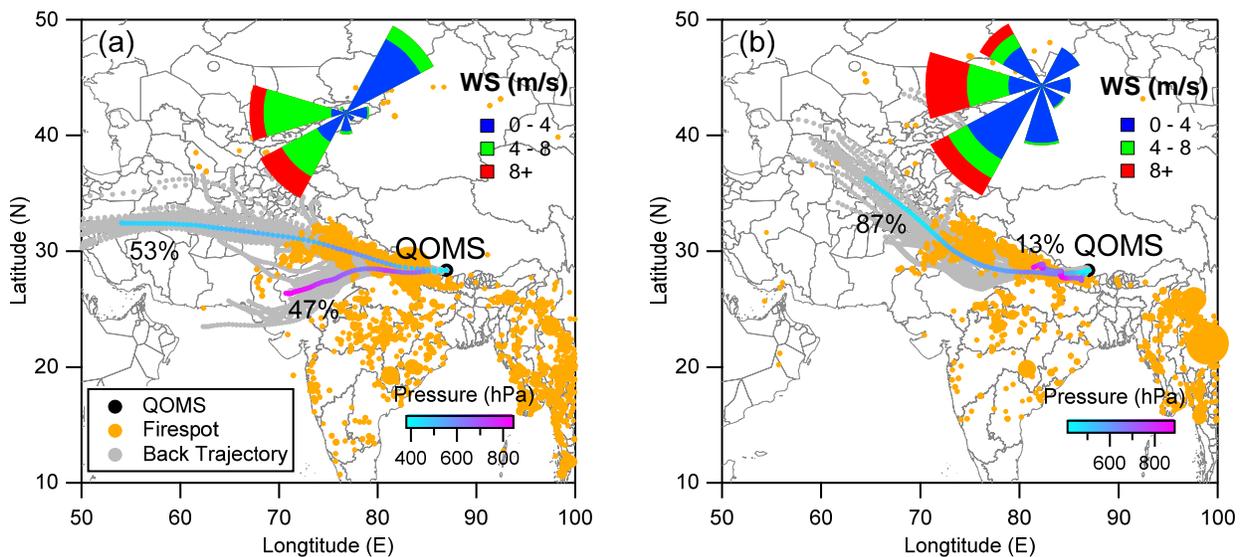
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705 Fig. 1. The average mass concentration (mass avg.) and chemical composition of PM₁ during P1
706 (left) and P2 (right) periods, respectively, measured by HR-ToF-AMS and PAX. Note that the
707 compounds of PM₁ include sulfate, nitrate, ammonium, chloride, BC (black carbon), organics,
708 BBOA (biomass burning emitted OA), NOA (nitrogen-contained OA), and OOA (oxidized
709 oxygenated OA).

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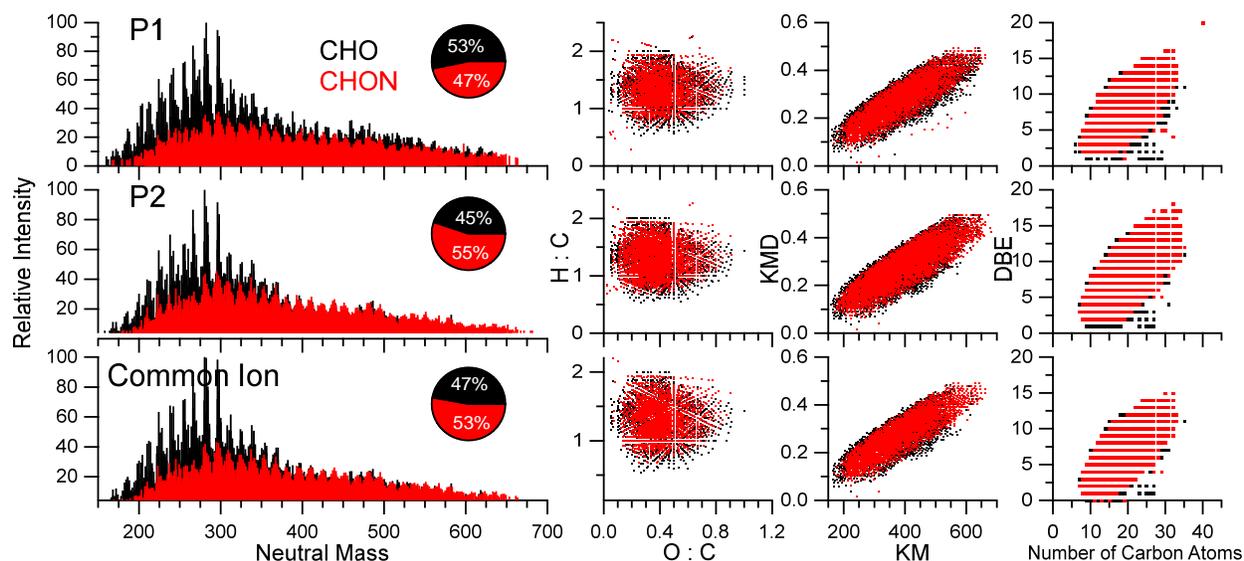


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712 Fig. 2. The air mass back trajectory analysis using HYSPLIT model (Draxler and Hess, 1998)
713 during (a) P1 and (b) P2. The air mass trajectories were recovered back to 72 h at 1 h interval
714 from the sampling site (QOMS) at 1000 m above the ground level using 1° resolution Global
715 Data Assimilation System (GDAS) dataset (<https://ready.arl.noaa.gov/gdas1.php>). The cluster
716 analysis for these trajectories was completed based on the directions of the trajectories (angle

717 distance) and colored according to air pressure (vertical profile). The fire spot observed from
718 MODIS (<https://firms.modaps.eosdis.nasa.gov>) and the average wind rose plot colored by wind
719 speed (WS) for during each filter sampling period were also shown. The fire spot is sized by fire
720 radiative power (FRP).

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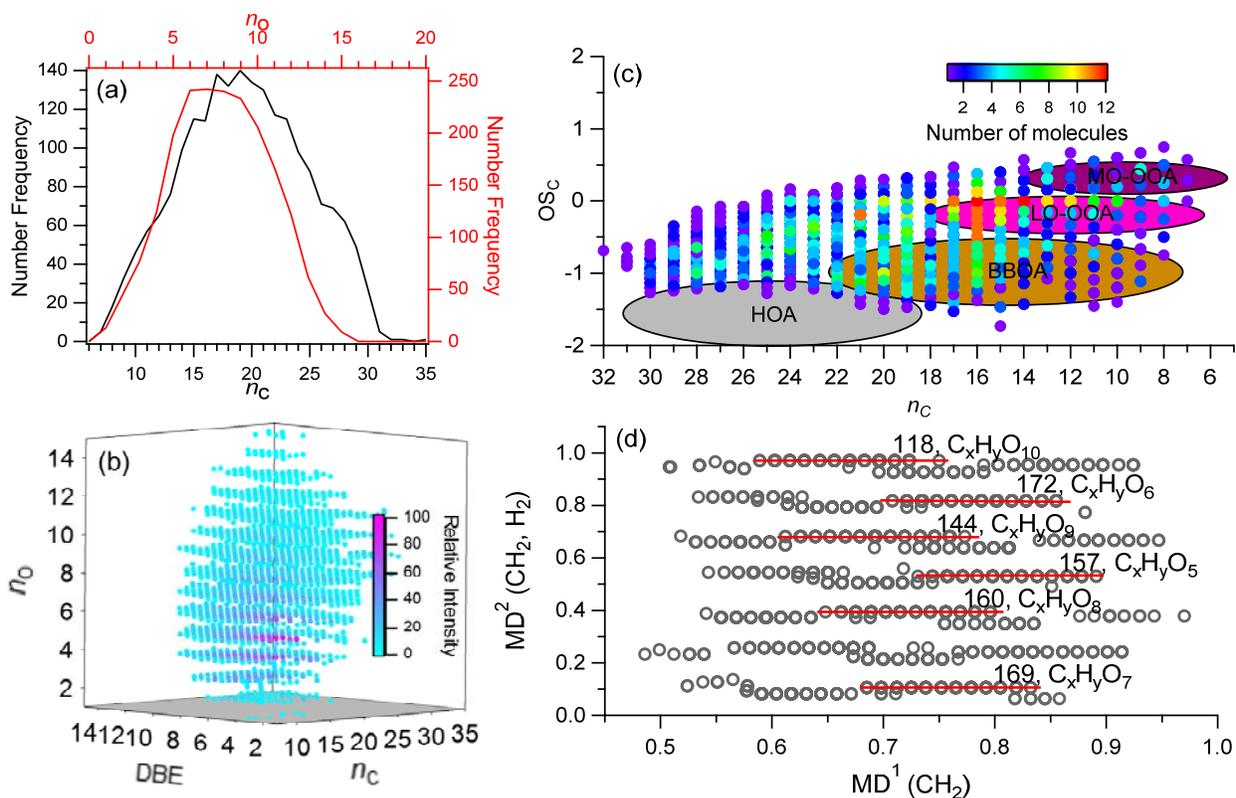


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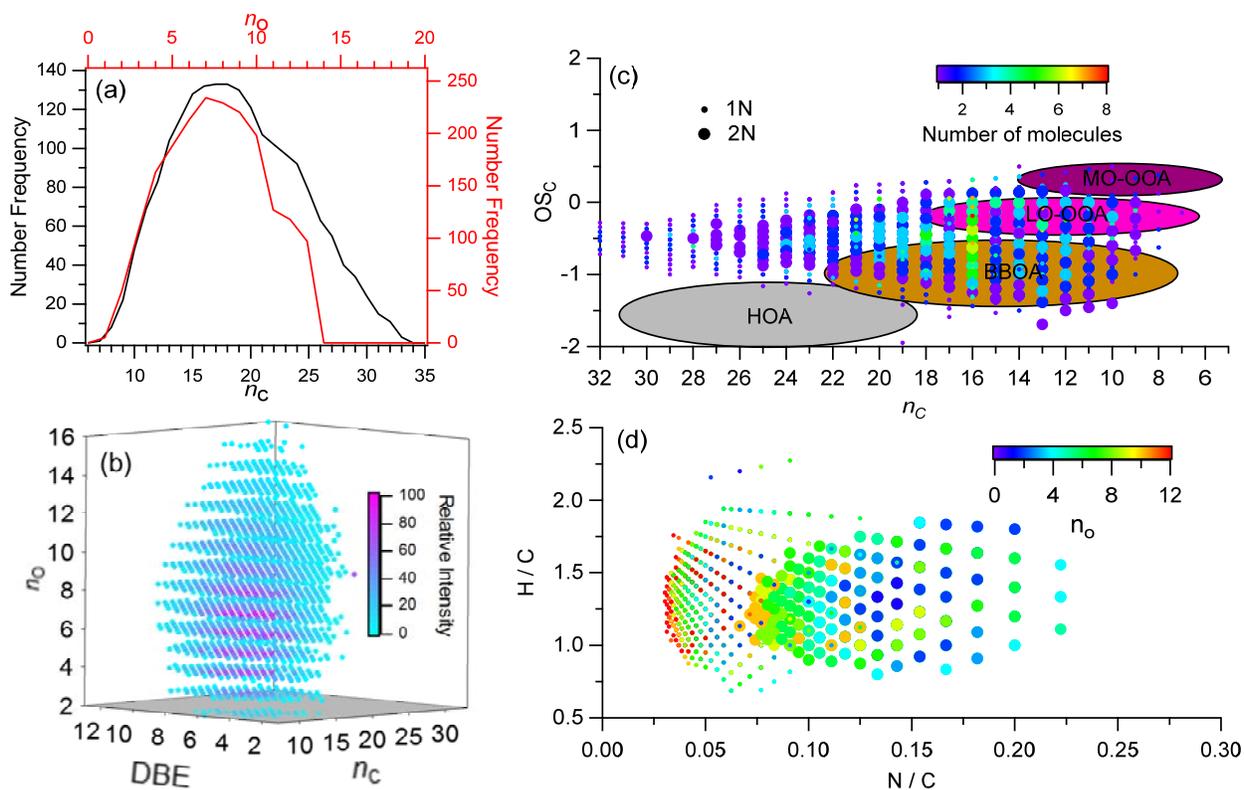
723 Fig. 3. The combo plot for all molecular of P1, P2, and common ion including high-resolution
724 mass spectrum, Van Krevelen diagram, Kendrick mass defects (KMD) vs. Kendrick mass (KM),
725 and double bond equivalents (DBE) vs. number of carbon atoms.

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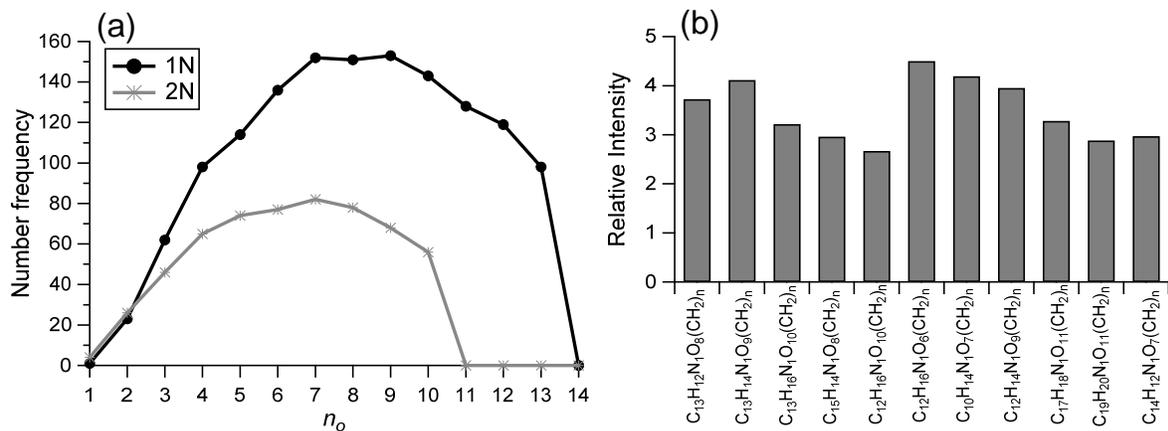


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 729 Fig. 4. The molecular information for common CHO compounds. (a) The number frequency
 730 distribution of carbon (n_c) and oxygen (n_o); (b) The 3-D plot for n_o , n_c , and double bond
 731 equivalents (DBE) colored by their relative intensity; (c) Scatter plot of carbon based oxidation
 732 state (OSc) vs. n_c colored by the distribution of number of molecules; (d) The two-order mass
 733 defect analysis ($MD^2(\text{CH}_2, \text{H}_2)$ vs. $MD^1(\text{CH}_2)$) using the base of CH_2 and H_2 . The longest
 734 homologous series were marked with the group number and formula type.
 735



736
 737 Fig. 5. The molecular information for common CHON compounds. (a) The number frequency
 738 distribution of carbon (n_c) and oxygen (n_o). (b) The 3-D plot for n_o , n_c , and double bond
 739 equivalents (DBE) colored by their relative intensity. (c) Scatter plot of carbon based oxidation
 740 state (OSc) vs. n_c colored by the distribution of number of molecules. (d) The Van Krevelen
 741 diagram by H/C vs. N/C colored by number of oxygen (n_o). The size of dot marker in (c) and (d)
 742 represent the 1N and 2N compounds.

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 746 Fig. 6. (a) The number frequency distribution of n_o for 1N and 2N compounds and (b) the longest
 747 ten CH_2 homologous series compounds in 1N compounds.
 748