

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  $\alpha$ -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-PM<sub>1</sub>) 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<sup>-1</sup>) particular matter (PM) sampler (BGI, USA, model PQ 200) with an

100 aerodyne diameter cutoff of 2.5  $\mu\text{m}$  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  $\text{m}^3$  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  $\mu\text{m}$  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  $\sim 0.2$  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  $\pm 1.5$  ppm using custom  
134 software. Molecular formulas with their maximum numbers of atoms were defined as: 30  $^{12}\text{C}$ , 60  
135  $^1\text{H}$ , 20  $^{16}\text{O}$ , 3  $^{14}\text{N}$ , 1  $^{32}\text{S}$ , 1  $^{13}\text{C}$ , 1  $^{18}\text{O}$  and 1  $^{34}\text{S}$ . 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.,  $^{13}\text{C}$ ,  $^{18}\text{O}$  or  $^{34}\text{S}$ ) 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 ( $\text{AI}_{\text{mod}}$ ). 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 ( $\text{DBE}_w$ ), O/C ( $\text{O/C}_w$ ), and H/C ( $\text{H/C}_w$ ) 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 CH<sub>2</sub> 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 CH<sub>2</sub>, 14.01565 is the exact mass of CH<sub>2</sub>, and NM is KM  
165 rounded to the nearest integer.

166  
167 Furthermore, a two-order mass defect analysis using the base units of CH<sub>2</sub> and H<sub>2</sub> was applied  
168 following the method described in Roach et al. (2011) which could greatly simplify  
169 visualization of complex mass spectra.

170  
171  $\text{AI}_{\text{mod}}$  is a measure of the probable aromaticity of a molecule assuming that half the O atoms are  
172 double bonded and half have only  $\sigma$  bonds (Koch and Dittmar, 2006).  $\text{AI}_{\text{mod}}$  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.  $\text{AI}_{\text{mod}}$  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 PM<sub>1</sub> 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 PM<sub>1</sub> were 9.2 and 10.6  $\mu\text{g m}^{-3}$   
183 <sup>3</sup>, 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 PM<sub>1</sub> to PM<sub>2.5</sub> are not available. However, most of WSOM in PM<sub>2.5</sub> is in  
187 accumulation size mode (less than 1 $\mu\text{m}$ ) which could be detected by HR-ToF-AMS (Zhang et  
188 al., 2005). The chemical composition of PM<sub>1</sub> 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  $19.3 \pm 5.3$  per molecule; the most abundant O  
263 atoms located in 5 – 10 with an average value of  $7.8 \pm 2.9$  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  $\text{DBE}_w$  value of 6.75 (Fig. 3); the carbon-normalized DBE ( $\text{DBE}/\text{C}$ )  
267 was  $0.39 \pm 0.14$ . 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 ( $\text{OS}_\text{C}$ ) 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  $\alpha$ -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  $\alpha$ -  
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 ( $61 \pm 9$  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 ( $8.1 \pm 2.9$  vs.  $6.3 \pm 2.3$ ). 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 NO<sub>3</sub> radical or RO<sub>2</sub>+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 (C<sub>5</sub>H<sub>8</sub>) and monoterpenes (C<sub>10</sub>H<sub>16</sub>), dominate the organic  
351 nitrate formation in the southeastern United States under the condition of the mixed  
352 anthropogenic NO<sub>x</sub> and BVOC (Xu et al., 2014; Lee et al., 2016; Zhang et al., 2018a). Several  
353 molecular formulas formed from monoterpene and NO<sub>3</sub> 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 PM<sub>1</sub>) 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 <sub>w</sub>	0.43	0.44	0.42	
	H / C <sub>w</sub>	1.36	1.37	1.34	
	OM / OC <sub>w</sub>	1.72	1.70	1.76	
	DBE <sub>w</sub>	7.12	6.74	7.79	
	DBE / C <sub>w</sub>	0.39	0.37	0.43	
	Percentage (%) of				
	Aliphatic (AI <sub>mod</sub> = 0)		18.4	9.4	9.0
	Olefinic (0.5 > AI <sub>mod</sub> > 0)		73.9	39.7	34.2
	Aromatic (AI <sub>mod</sub> >= 0.5)		7.7	4.1	3.5
	P2	O / C <sub>w</sub>	0.39	0.39	0.39
H / C <sub>w</sub>		1.31	1.32	1.31	
OM / OC <sub>w</sub>		1.68	1.63	1.73	
DBE <sub>w</sub>		7.87	7.38	8.32	
DBE / C <sub>w</sub>		0.42	0.40	0.44	
Percentage (%) of					
Aliphatic (AI <sub>mod</sub> = 0)		14.7	6.0	8.7	
Olefinic (0.5 > AI <sub>mod</sub> > 0)		75.0	34.3	40.7	
Aromatic (AI <sub>mod</sub> >= 0.5)		10.3	4.9	5.4	
Common ions		O / C <sub>w</sub>	0.42	0.43	0.42
	H / C <sub>w</sub>	1.35	1.36	1.33	
	OM / OC <sub>w</sub>	1.72	1.69	1.76	
	DBE <sub>w</sub>	7.18	6.75	7.79	
	DBE / C <sub>w</sub>	0.40	0.38	0.43	
	Percentage (%) of				
	Aliphatic (AI <sub>mod</sub> = 0)		15.6	6.7	8.9
	Olefinic (0.5 > AI <sub>mod</sub> > 0)		76.5	39.7	36.8
	Aromatic (AI <sub>mod</sub> >= 0.5)		7.8	4.3	3.6

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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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699

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 <sub>17</sub> H <sub>26</sub> O <sub>8</sub>	33.1%	α-pinene	Kristensen et al., 2013
368.1829	C <sub>19</sub> H <sub>28</sub> O <sub>7</sub>	11.5%	products	
186.0887	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	26.0%		
168.0417	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	4.75%	Monoterpene	Claeys et al., 2007;
182.0574	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	8.12%	products	Kleindienst et al., 2007;
198.0523	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	11.6%		Zhang et al., 2018a
231.0737	C <sub>9</sub> H <sub>13</sub> NO <sub>6</sub>	12.7%	BVOC	Lee et al., 2016; Zhang et al., 2018a
233.0894	C <sub>9</sub> H <sub>15</sub> NO <sub>6</sub>	14.0%	oxidant	
215.1152	C <sub>10</sub> H <sub>17</sub> NO <sub>4</sub>	10.6%	products	
229.0945	C <sub>10</sub> H <sub>15</sub> NO <sub>5</sub>	16.5%		
231.1101	C <sub>10</sub> H <sub>17</sub> NO <sub>5</sub>	16.8%		
233.1257	C <sub>10</sub> H <sub>19</sub> NO <sub>5</sub>	9.5%		
245.0894	C <sub>10</sub> H <sub>15</sub> NO <sub>6</sub>	26.4%		
247.1050	C <sub>10</sub> H <sub>17</sub> NO <sub>6</sub>	16.5%		
249.1207	C <sub>10</sub> H <sub>19</sub> NO <sub>6</sub>	9.6%		
306.1099	C <sub>16</sub> H <sub>18</sub> O <sub>6</sub>	5.5%	Aqueous-phase	Yu et al., 2014 and
246.0886	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub>	27.5%	oxidation of biomass burning aerosol	2016; Sun et al., 2010
166.0624	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	4.9%	Cow dung	Fleming et al., 2018
178.0624	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	5.7%	and brush	
190.0624	C <sub>11</sub> H <sub>10</sub> O <sub>3</sub>	7.7%	wood	
192.0781	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	7.0%	burning	
188.0832	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	4.3%		
216.0781	C <sub>13</sub> H <sub>12</sub> O <sub>3</sub>	12.5%		
218.0937	C <sub>13</sub> H <sub>14</sub> O <sub>3</sub>	16.7%		
198.0866	C <sub>13</sub> H <sub>14</sub> O <sub>4</sub>	30.5%		
248.1043	C <sub>14</sub> H <sub>16</sub> O <sub>4</sub>	32.2%		
232.1094	C <sub>14</sub> H <sub>16</sub> O <sub>3</sub>	21.6%		
338.0745	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>8</sub>	5.7%	Biomass	Song et al., 2018
341.1105	C <sub>15</sub> H <sub>19</sub> N <sub>1</sub> O <sub>8</sub>	27.2%	burning	
355.1261	C <sub>16</sub> H <sub>21</sub> N <sub>1</sub> O <sub>8</sub>	29.4%	aerosol	
369.1418	C <sub>17</sub> H <sub>23</sub> N <sub>1</sub> O <sub>8</sub>	24.0%		
243.0890	C <sub>14</sub> H <sub>13</sub> N <sub>1</sub> O <sub>3</sub>	9.3%		
257.1046	C <sub>15</sub> H <sub>15</sub> N <sub>1</sub> O <sub>3</sub>	9.5%		
235.1203	C <sub>13</sub> H <sub>17</sub> N <sub>1</sub> O <sub>3</sub>	17.0%		

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

708  
709 Fig. 2. The air mass back trajectory analysis using HYSPLIT model (Draxler and Hess, 1998)  
710 during (a) P1 and (b) P2. The air mass trajectories were recovered back to 72 h at 1 h interval  
711 from the sampling site (QOMS) at 1000 m above the ground level using 1° resolution Global  
712 Data Assimilation System (GDAS) dataset (<https://ready.arl.noaa.gov/gdas1.php>). The cluster  
713 analysis for these trajectories was completed based on the directions of the trajectories (angle  
714 distance) and colored according to air pressure (vertical profile). The fire spot observed from  
715 MODIS (<https://firms.modaps.eosdis.nasa.gov>) and the average wind rose plot colored by wind  
716 speed (WS) for during each filter sampling period were also shown. The fire spot is sized by fire  
717 radiative power (FRP).

718  
719 Fig. 3. The combo plot for all molecular of P1, P2, and common ion including high-resolution  
720 mass spectrum, Van Krevelen diagram, Kendrick mass defects (KMD) vs. Kendrick mass (KM),  
721 and double bond equivalents (DBE) vs. number of carbon atoms.

722  
723 Fig. 4. The molecular information for common CHO compounds. (a) The number frequency  
724 distribution of carbon ( $n_c$ ) and oxygen ( $n_o$ ); (b) The 3-D plot for  $n_o$ ,  $n_c$ , and double bond  
725 equivalents (DBE) colored by their relative intensity; (c) Scatter plot of carbon based oxidation  
726 state (OSc) vs.  $n_c$  colored by the distribution of number of molecules; (d) The two-order mass  
727 defect analysis (MD<sup>2</sup> (CH<sub>2</sub>, H<sub>2</sub>) vs. MD<sup>1</sup> (CH<sub>2</sub>)) using the base of CH<sub>2</sub> and H<sub>2</sub>. The longest  
728 homologous series were marked with the group number and formula type.

729  
730 Fig. 5. The molecular information for common CHON compounds. (a) The number frequency  
731 distribution of carbon ( $n_c$ ) and oxygen ( $n_o$ ). (b) The 3-D plot for  $n_o$ ,  $n_c$ , and double bond  
732 equivalents (DBE) colored by their relative intensity. (c) Scatter plot of carbon based oxidation

733 state (OSc) vs.  $n_c$  colored by the distribution of number of molecules. (d) The Van Kerevelen  
734 diagram by H/C vs. N/C colored by number of oxygen ( $n_o$ ). The size of dot marker in (c) and (d)  
735 represent the 1N and 2N compounds.

736

737 Fig. 6. (a) The number frequency distribution of  $n_o$  for 1N and 2N compounds and (b) the longest  
738 ten CH<sub>2</sub> homologous series compounds in 1N compounds.

739