

1 **Seasonal variation of secondary organic aerosol tracers in Central**
2 **Tibetan Plateau**

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21 **Abstract**

22 Secondary organic aerosol (SOA) affects the earth's radiation balance and global climate.
23 High-elevation areas are sensitive to global climate change. However, at present, SOA origins and
24 seasonal variations are understudied in remote high-elevation areas. In this study, particulate samples
25 were collected from July 2012 to July 2013 at the remote Nam Co (NC) site, Central Tibetan Plateau
26 and analyzed for SOA tracers from biogenic (isoprene, monoterpenes and β -caryophyllene) and
27 anthropogenic (aromatics) precursors. Among these compounds, isoprene SOA (SOA_I) tracers
28 represented the majority ($26.6 \pm 44.2 \text{ ng m}^{-3}$), followed by monoterpene SOA (SOA_M) tracers ($0.97 \pm$
29 0.57 ng m^{-3}), aromatic SOA (SOA_A) tracer (2,3-dihydroxy-4-oxopentanoic acid, DHOPA, 0.25 ± 0.18
30 ng m^{-3}) and β -caryophyllene SOA tracer (β -caryophyllenic acid, $0.09 \pm 0.10 \text{ ng m}^{-3}$). SOA_I tracers
31 exhibited high concentrations in the summer and low levels in the winter. The similar temperature
32 dependence of SOA_I tracers and isoprene emission suggested that the seasonal variation of SOA_I
33 tracers at the NC site was mainly influenced by the isoprene emission. The ratio of high-NO_x to
34 low-NO_x products of SOA_I (2-methylglyceric acid to 2-methyltetrols) was the highest in the winter and
35 the lowest in the summer, due to the influence of temperature and relative humidity. The seasonal
36 variation of SOA_M tracers was impacted by monoterpenes emission and gas-particle partitioning.
37 During the summer to the fall, temperature effect on partitioning was the dominant process influencing
38 SOA_M tracers' variation; while the temperature effect on emission was the dominant process
39 influencing SOA_M tracers' variation during the winter to the spring. SOA_M tracer levels did not elevate
40 with increased temperature in the summer, probably resulting from the counteraction of temperature
41 effects on emission and partitioning. The concentrations of DHOPA were 1-2 orders of magnitude
42 lower than those reported in the urban regions of the world. Due to the transport of air pollutants from
43 the adjacent Bangladesh and the northeastern India, DHOPA presented relatively higher levels in the
44 summer. In the winter when air masses mainly came from the northwestern India, mass fractions of
45 DHOPA in total tracers increased, although its concentrations declined. The SOA-tracer method was
46 applied to estimate secondary organic carbon (SOC) from these four precursors. The annual average of
47 SOC was $0.22 \pm 0.29 \text{ } \mu\text{gC m}^{-3}$, with the biogenic SOC (sum of isoprene, monoterpenes and
48 β -caryophyllene) accounting for 75%. In the summer, isoprene was the major precursor with its SOC
49 contributions of 81%. In the winter when the emission of biogenic precursors largely dropped, the
50 contributions of aromatic SOC increased. Our study implies that anthropogenic pollutants emitted in

51 the Indian subcontinent could transport to the TP and have impact on SOC over the remote NC.

52

53 **Keywords:** Secondary organic aerosol, Tibetan Plateau, Isoprene, Monoterpenes, Aromatics

54

55 1. Introduction

56 Organic aerosol affects the earth's radiation balance and global climate. As a large fraction of
57 organic aerosol, secondary organic aerosol (SOA) is produced by homogenous (Claeys *et al.* 2004) and
58 heterogeneous (Jang *et al.* 2002) reactions of volatile organic compounds (VOCs) as well as aging of
59 organic aerosol (Robinson *et al.* 2007, Donahue *et al.* 2012). The global emission of biogenic VOCs
60 (BVOCs), such as isoprene and monoterpenes (Guenther *et al.* 1995) were estimated to be one order of
61 magnitude higher than those of anthropogenic sources (Piccot *et al.* 1992). Thus, global SOA is
62 believed to be largely from BVOCs.

63 SOA tracers from specific VOCs can provide insight on processes and sources influencing SOA
64 formation and spatiotemporal distribution. The identification of the isoprene SOA (SOA_I) tracers,
65 2-methyltetrols (Claeys *et al.* 2004) revealed the importance of SOA_I in global SOA burden. The
66 further studies in high-NO_x and low-NO_x products of isoprene intermediates (e.g. methacrylic acid
67 epoxide and isoprene epoxydiols) provided more details in the mechanisms of SOA_I formation under
68 the influence of NO_x (Paulot *et al.* 2009, Froyd *et al.* 2010, Surratt *et al.* 2010, Lin *et al.* 2013). The
69 identification of tracers from aromatic SOA (SOA_A) (Offenberg *et al.* 2007) offered a way to directly
70 evaluate the variation of anthropogenic SOA, particularly in urban regions. In addition, specific tracers
71 have been determined in monoterpene SOA (SOA_M) (Jaoui *et al.* 2005, Claeys *et al.* 2007) and
72 β-caryophyllene SOA (SOA_C) (Jaoui *et al.* 2007, van Eijck *et al.* 2013). Based on these SOA tracers,
73 Kleindienst and coworkers further developed an SOA-tracer method to attribute SOA sources in the
74 ambient air. Since it is difficult to directly measure SOA, the SOA-tracer method provides a valuable
75 technique to estimate SOA in the ambient air, and it has been widely used around the world (Hu *et al.*
76 2008, von Schneidmesser *et al.* 2009, Guo *et al.* 2012, Lewandowski *et al.* 2013, Ding *et al.* 2014).

77 High-elevation areas are sensitive to global climate change (Xua *et al.* 2009). Observation of
78 aerosol concentrations and compositions at high elevation sites can provide insight into the influence of
79 natural and anthropogenic aerosols on global climate. The Tibetan Plateau (TP), the largest and highest
80 plateau, is at the juncture of large desert areas and the densely populated Indian subcontinent. Previous

81 study found the northwesterly winds could bring dust from the western deserts to the TP and lead to
82 high levels of geological aerosols at a site on the southeast TP (Zhao *et al.* 2013). Moreover,
83 anthropogenic pollutants (e.g. sulfate, nitrate, potassium, element carbon, and heavy metals) emitted in
84 the developing countries in South Asia could be transported to the TP by the southerly and
85 southwesterly winds, especially during the summer monsoon season (Cong *et al.* 2007, Ming *et al.*
86 2010, Li *et al.* 2013, Zhao *et al.* 2013).

87 The observation at the remote central TP site, Nam Co (NC) discovered that the mean ratio of
88 organic carbon (OC) to element carbon (EC) was 31.9 ± 31.1 during July 2006 to January 2007,
89 implying the significant SOA contribution to OC (Ming *et al.* 2010) in the TP. However, there are only
90 three studies in SOA compositions within the TP. Li *et al.* (2013) reported biogenic SOA (BSOA)
91 tracers during the summer of 2010 at Qinghai Lake in the northeastern part of the TP. Stone *et al.*,
92 (2012) measured BSOA tracers from August to October 2005 on the south slope of Himalayas in the
93 southwestern part of the TP. Due to the limited samples, it was difficult to examine the seasonal
94 variation of these BSOA tracers in the TP. Moreover, due to the lack of anthropogenic SOA tracers, it
95 was not possible to examine anthropogenic SOA in the TP, although above discussions have
96 demonstrated that air pollutants from South Asia could be transported to the TP. Our recent study
97 provided a snapshot of SOA tracers over China (including the NC and Linzhi sites in the TP) during the
98 summer of 2012 (Ding *et al.* 2014). In this study, the observation at the remote NC site extended to one
99 year. Seasonal trends of SOA tracers from isoprene, monoterpene, β -caryophyllene and aromatics were
100 determined in the TP. Furthermore, secondary organic carbon (SOC) was estimated by the SOA-tracer
101 method to check the variations of SOA origins at the NC site. To our knowledge, it is the first time that
102 the seasonal trends of SOA tracers and origins are studied in the remote TP.

103

104 **2. Experiment**

105 **2.1 Field Sampling**

106 Samples were collected at a remote site (4730 meters above sea level) at the southeastern shore of
107 Nam Co Lake in the central TP (Figure 1). Nam Co Lake (90°16' – 91°03' E and 30°30' – 30°55'N) is
108 located in the Nyainqen Tanglha Mountain Range with a total area of 2017 km² (Zhou *et al.* 2013). The
109 major vegetation in the Nam Co Lake Basin is the high cold alpine meadow.

110 Sampling was undertaken from July 2012 to July 2013. An Anderson sampler equipped with

111 9-stage cascade impactors and pre-baked quartz fiber filters (Whatman, baked at 450 °C for 8 h) was
112 used to get size-segregated particle samples at an air flow rate of 28.3 L min⁻¹. The 50% cutoff sizes are
113 <0.4, 0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and ≥9.0 μm, respectively. The
114 flow rate was calibrated before and after each sampling episode using an airflow meter to ensure the
115 sampler operated at the specified flow rate. One set of 9 size-fractionated filters were collected for 72
116 hours every two weeks. Additionally, four sets of field blanks were collected in the same way as the
117 ambient samples for 5 minutes when the sampler was turned off. All samples were wrapped with
118 aluminum foil and stored at -18 °C before analysis.

119

120 2.2 Chemical Analysis

121 Each set of nine filters were combined together as one sample to meet the analysis requirement.
122 Detailed information on the SOA tracer analysis is described elsewhere (Ding *et al.* 2014). Prior to
123 solvent extraction, isotope-labeled standard mixtures were spiked into samples as internal standards.
124 Samples were extracted twice by sonication with the mixed solvent dichloride methane (DCM)/hexane
125 (1:1, v/v), then three times with the mixed solvent DCM/methanol (1:1, v/v). The extracts of each
126 sample were combined, filtered and concentrated to ~2 mL. Then, the concentrated solution was
127 divided into two parts for methylation and silylation, respectively.

128 The samples were analyzed by an a gas chromatography/mass spectrometer detector (GC/MSD,
129 Agilent 7890/5975C) in the selected ion monitoring (SIM) mode with a 30 m HP-5 MS capillary
130 column (i.d. 0.25 mm, 0.25 μm film thickness). Splitless injection of a 2 μL sample was performed.
131 The GC temperature was initiated at 65 °C, held for 2 min, then increased to 290 °C at 5 °C min⁻¹ and
132 held for 20 min. Thirteen SOA tracers were quantified by the GC/MSD coupled with an electron
133 impact (EI) ionization source, including five SOA_M tracers (*cis*-pinonic acid, pinic acid,
134 3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric
135 acid), six SOA_I tracers (2-methylthreitol, 2-methylerythritol, 2-methylglyceric acid,
136 *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene and
137 3-methyl-2,3,4-trihydroxy-1-butene), one SOA_C tracer (β-caryophyllenic acid) and one SOA_A tracer
138 (2,3-dihydroxy-4-oxopentanoic acid, DHOPA). Figure S1 in supplemental information presents the
139 total ion chromatogram (TIC) of these SOA tracers. *cis*-Pinonic acid and pinic acid were quantified by
140 authentic standards. Due to the lack of standards, the SOA_I tracers were quantified using erythritol

141 (Claeys *et al.* 2004, Ding *et al.* 2008). The other SOA_M tracers were quantified using *cis*-pinonic acid.
142 β -Caryophyllenic acid and DHOPA were quantified using octadecanoic acid and azelaic acid,
143 respectively (Ding *et al.* 2012). The EI spectrum of each SOA tracer is shown in Figure S2-S4. The
144 method detection limits (MDLs) for *cis*-pinonic acid, pinic acid, erythritol, octadecanoic acid and
145 azelaic acid were 0.03, 0.05, 0.04, 0.03 and 0.07 ng m⁻³, respectively, at a total volume of 122 m³.

146 **2.3 Quality assurance and quality control**

147 Field and laboratory blanks were analyzed in the same manner as the field samples. These SOA
148 tracers were not detected in the field or laboratory blanks. To evaluate the recoveries of the analytical
149 method, six spiked samples (authentic standards spiked into solvent with pre-baked quartz filters) were
150 analyzed. The recoveries were 101 \pm 3 % for *cis*-pinonic acid, 70 \pm 10 % for pinic acid, 65 \pm 14 % for
151 erythritol, 83 \pm 7 % for octadecanoic acid, and 89 \pm 9 % for azelaic acid. The relative differences for
152 target compounds in samples collected in parallel (n=6) were all below 15%.

153 It should be noted that ketopinic acid was used as the surrogate for the quantification of all SOA
154 tracers by Kleindienst *et al.* (2007); while different surrogates were used to quantify different SOA
155 tracers in this study. The response factors of internal standard calibration for the 5 surrogates ranged
156 from 0.98 (azelaic acid) to 1.78 (pinic acid), with the average of 1.38 and the relative standard
157 deviation (RSD) of 23%. The response factor of ketopinic acid was also calculated in this study. Its
158 value (1.27) was consistent with the average of the five surrogates.

159 **2.4 Estimation of measurement uncertainty**

160 Since there is no commercial standard available for most SOA tracers (except *cis*-pinonic acid and
161 pinic acid), the use of surrogate standards for quantification introduces additional error to measurement.
162 Error in analyte measurement (E_A) is propagated from the standard deviation of the field blank (E_{FB}),
163 error in spike recovery (E_R) and the error from surrogate quantification (E_Q):

$$164 \quad E_A = \sqrt{E_{FB}^2 + E_R^2 + E_Q^2} \quad (1)$$

165 Since SOA tracers were not detected in the field blanks, E_{FB} was 0 in this study. The spike
166 recoveries of surrogate standards were used to estimate the E_R of tracers which ranged from 1%
167 (*cis*-pinonic acid) to 35% (erythritol). Stone *et al.*, (2012) developed an empirical approach to estimate
168 E_Q based on homologous series of atmospherically relevant compounds. The relative error introduced

169 by each carbon atom (E_n) was estimated to be 15 %, each oxygenated functional group (E_f) to be 10%
170 and alkenes (E_d) to be 60%. The errors introduced from surrogate quantification are treated as additive
171 and are calculated as:

$$172 \quad E_Q = E_n \Delta n + E_f \Delta f + E_d \Delta d \quad (2)$$

173 where Δn is the difference in carbon atom number between a surrogate and an analyte, Δf is the
174 difference in oxygen-containing functional group between a surrogate and an analyte, Δd is the
175 difference in alkene functionality between a surrogate and an analyte.

176 Table S1 shows the estimated uncertainties in tracer measurement. The errors from surrogate
177 quantification (E_Q) ranged from 15% (2-methyltetrols) to 155% (β -caryophyllenic acid) in this study.
178 Propagated with the error in recovery, the uncertainties in analyte measurement (E_A) were estimated in
179 the range of 38% to 156%.

180 **2.5 Backward trajectories**

181 The air masses' transport during each sampling episode was investigated using Hybrid Single
182 Particle Lagrangian Integrated Trajectory Model (HYSPPLIT V4.9). Five-day backward trajectories
183 (BTs) were analyzed during each sampling episode with 6-hour step at the height of 500 m above
184 ground level. Then cluster analysis was performed to present the mean trajectory of each cluster, based
185 on all the trajectories during our campaign.

186

187 **3. Results and Discussions**

188 **3.1 Seasonal variations of SOA tracers**

189 Since the NC site is located in the high elevation TP, the annual temperature was only -1.64 °C with
190 the range of -16.1 °C in January to 10.2 °C in July (Table 1). The annual relative humidity (RH) was 58%
191 with the peak in July (84%) and the lowest in January (30%). The sum of all tracers ranged from 0.78
192 to 185 ng m⁻³. Among these compounds, SOA_I tracers (26.6 ± 44.2 ng m⁻³) represented the majority,
193 followed by SOA_M tracers (0.97 ± 0.57 ng m⁻³), DHOPA (0.25 ± 0.18 ng m⁻³) and β -caryophyllenic
194 acid (0.09 ± 0.10 ng m⁻³). During the summer (July-September 2012 and June-July 2013), SOA_I tracers
195 presented the majority (> 95%). The mass fractions of SOA_M tracers in all compounds increased during
196 the cold period (October 2012 to May 2013).

197

198 3.1.1 Isoprene SOA tracers

199 The total concentrations of SOA_I tracers (sum of six tracers) ranged from 0.36 – 184 ng m⁻³. The
200 levels of SOA_I tracers were 1-2 orders of magnitude higher than those over the global oceans and the
201 Arctic (Table 2). Among the SOA_I tracers, 2-methyltetrols (sum of 2-methylthreitol and
202 2-methylerythritol, MTLs) were the major components (72%), with an annual average of 23.8 ± 40.3
203 ng m⁻³ (0.18 to 165 ng m⁻³). The 2-methylglyceric acid (MGA) averaged 1.95 ± 2.92 ng m⁻³ and
204 C₅-alkenetriols (sum of *cis*-2-methyl-1,3,4-trihydroxy-1-butene,
205 *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene) averaged 0.93 ±
206 1.39 ng m⁻³. MTLs are produced through the particle-phase uptake of the epoxydiols that formed in the
207 gas-phase photo-oxidation of isoprene under low-NO_x or NO_x free conditions (Paulot *et al.* 2009,
208 Surratt *et al.* 2010). Since the remote TP is a low-NO_x environment, it is expected that the low-NO_x
209 products, MTLs dominated over other SOA_I tracers. The majority of MTLs at the NC site was
210 consistent with those observed within the TP (Stone *et al.* 2012, Li *et al.* 2013) and over most global
211 oceans (Fu *et al.* 2011, Hu *et al.* 2013), but different from those over the North Pacific Ocean and the
212 Arctic where MGA was the major SOA_I tracer due to the significant influence of Siberian fires (Fu *et*
213 *al.* 2011, Ding *et al.* 2013). The two MTL isomers exhibited a strong correlation with each other
214 throughout the year (R²=0.996, p<0.001) with a slope of 3.7, indicating that the two isomers shared
215 similar formation pathways.

216 Figure 2a presents a typical seasonal trend of SOA_I tracers that high concentrations all existed in
217 the summer. From October 2012 to April 2013, temperature was below zero, the levels of SOA_I tracers
218 dramatically decreased as low as 0.38 ng m⁻³ in January.

219 Isoprene emission rate (E_I) depends on light and temperature (Guenther *et al.* 1993):

$$220 E_I = EF_I \times C_L \times C_T \quad (3)$$

221 where EF_I is the basal emission rate at 30 °C leaf temperature and 1000 μmol m⁻² s⁻¹ PAR. C_L and C_T
222 are the factors representing the influences of light and temperature, respectively. C_T can be estimated
223 as:

$$224 C_T = \frac{\exp\left(\frac{C_{T1}(T-T_s)}{RT_sT}\right)}{1 + \exp\left(\frac{C_{T2}(T-T_m)}{RT_sT}\right)} \quad (4)$$

225 Then the natural logarithm of C_T is calculated as:

226
$$\ln C_T = \frac{C_{T1}}{RT_s} \left(1 - \frac{T_s}{T}\right) - \ln \left[1 + \exp \frac{C_{T2}}{RT_s} \left(1 - \frac{T_m}{T}\right)\right] \quad (5)$$

227 where $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{T1} = 95000 \text{ J mol}^{-1}$, $C_{T2} = 230000 \text{ J mol}^{-1}$, $T_s = 303 \text{ K}$, $T_m = 314 \text{ K}$, and
 228 T is the leaf temperature (Guenther *et al.* 1993). Under the condition of $T < T_m$, the latter part in
 229 Equation (5) is close to zero, and $\ln C_T$ is linearly correlated with $1/T$.

230 Figure 3a presents a negative correlation between the natural logarithm of SOA_I tracer levels and
 231 the reciprocal of temperature in Kelvin ($p < 0.001$). Moreover, the temperature dependence of SOA_I
 232 tracers was similar to that of C_T , and SOA_I tracers exhibited a significant positive correlation with C_T
 233 during our sampling at the NC site (Figure 3b). These results indicated that the seasonal variation of
 234 SOA_I tracers at the NC site was mainly influenced by the isoprene emission. Considering the short
 235 lifetime (several hours) of isoprene in the air, SOA_I should be mainly formed from local precursor. In
 236 summer, high temperature and intense light could enhance isoprene emission and photo-reactions.
 237 Moreover, high temperature in summer could enhance the heterogeneous reactions of isoprene-derived
 238 epoxides on particles which play the key roles in SOA_I formation (Lin *et al.*, 2013; Paulot *et al.*, 2009).
 239 All these interpreted the high levels of SOA_I tracers in the summer at the NC site. In the winter,
 240 isoprene emission significantly dropped due to the extremely low temperature. Thus, the tracers were
 241 only in trace amount at the NC site.

242 It is worth noting that the ratio of MGA to MTLs (MGA/MTLs) was negatively correlated with
 243 temperature (Figure 4a) and RH (Figure 4b). Based on chamber results, the formation mechanisms of
 244 MGA and MTLs are quite different. MGA is produced under high- NO_x conditions; while MTLs are
 245 mainly formed under low- NO_x or NO_x free conditions (Surratt *et al.* 2010). Moreover, low RH (15 –
 246 40 %) could enhance the formation of MGA in the particulate phase but not of MTLs (Zhang *et al.*
 247 2011). In addition, high particle acidity would favor the formation of MTLs instead of MGA (Surratt *et*
 248 *al.* 2007). Although there are few data available in the TP, the aerosols are expected to be neutral at the
 249 remote NC site. Thus, the influence of acidity on MGA/MTLs should be not significant. Isoprene
 250 emission is apparently high in summer due to high temperature and light intensity, which could
 251 enhance the ratio of isoprene to NO_x and favor MTLs formation at the NC site. Moreover, high RH
 252 (~70%) in the summer (Table 1) could not favor MGA formation. Thus, MGA/MTLs exhibited the
 253 lowest values (less than 0.1) in the summer samples (Figure 4). In the winter, both temperature and RH
 254 dropped to the lowest of the whole year. Low temperature reduced isoprene emission and low RH

255 favored MGA formation. Thus, MGA/MTLs increased up to 0.8 in the winter samples (Figure 4).

256

257 3.1.2 Terpene SOA tracers

258 The total concentrations of SOA_M tracers (sum of five tracers) ranged from 0.11 – 2.39 ng m⁻³. The
259 levels of the SOA_M tracers were consistent with those over the global oceans and the Arctic (Table 2).
260 Among these traces, *cis*-pinonic acid was the major compound (54%), with an annual average of 0.49 ±
261 0.38 ng m⁻³, followed by pinic acid (0.22 ± 0.32 ng m⁻³), 3-methyl-1,2,3-butanetricarboxylic acid (0.18
262 ± 0.25 ng m⁻³), 3-hydroxyglutaric acid (0.08 ± 0.06 ng m⁻³) and 3-hydroxy-4,4-dimethylglutaric acid
263 (below MDL in the most samples).

264 The monthly variation of SOA_M tracers did not fully follow that of temperature (Figure 2b). From
265 July to November 2012 (period 1), temperature decreased to -15 °C; while SOA_M tracer levels
266 increased as high as 1.99 ng m⁻³. After that, both temperature and SOA_M tracers dropped to the lowest
267 values in January 2013, and increased concurrently till April 2013 (period 2). During May to July 2013
268 (period 3), SOA_M tracer levels exhibited slight variation, although temperature kept increasing.

269 The seasonal variation of SOA_M tracers could be influenced by monoterpenes emission and
270 gas-particle partitioning. Monoterpenes emission rate (E_M) is often assumed to be solely dependent on
271 temperature (Guenther *et al.* 1993):

$$272 E_M = EF_M \times \gamma_T \quad (6)$$

$$273 \gamma_T = \exp^{\beta(T-T_s)} \quad (7)$$

274 where EF_M is monoterpenes emission rate at a standard temperature T_s (303 K), γ_T is the activity factor
275 by temperature, β is an empirical coefficient usually taken to be 0.09 K⁻¹ (Guenther *et al.* 1993), T is
276 the leaf temperature.

277 SOA yield (Y) of precursors could be expressed using an empirical relationship based on
278 gas-particle partitioning of two semi-volatile products (Odum *et al.*, 1996):

$$279 Y = M_0 \sum_i^2 \frac{\alpha_i K_i}{1 + M_0 K_i} \quad (8)$$

280 where M₀ (μg m⁻³) is the total concentration of absorbing organic material, α_i is the mass stoichiometric
281 coefficients of the product i, K_i (m³ μg⁻¹) is the temperature-dependent partitioning coefficient of the
282 semi-volatile compound i. Assuming a constant activity coefficient and mean molecular weight, the
283 partitioning coefficient, K_i (T) at a certain temperature (T) could be estimated as (Sheehan and

284 Bowman, 2001):

$$285 \quad K_i(T) = K_i^* \frac{T}{T^*} \exp \left[\frac{H_i}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (9)$$

286 where K_i^* is an experimentally determined partitioning coefficient at a reference temperature, T^* . H_i is
287 the vaporization enthalpy, R is the gas constant. To model the temperature-dependent absorptive
288 partitioning, three parameters, α_i , K_i , and H_i , are required for each condensable product.

289 Table S2 lists all the parameters for two-product model of α -pinene SOA which were also used to
290 estimate the temperature effect on SOA partitioning by Sheehan and Bowman (2001). The available
291 data of OC at the NC site were reported in the range of 1.18 to 2.26 $\mu\text{gC m}^{-3}$ during July 2006 to
292 January 2007 with an average of 1.66 $\mu\text{gC m}^{-3}$ (Ming et al., 2010). Thus, M_0 is calculated as 2.32 μg
293 m^{-3} by the average OC multiplying 1.4. Figure S5 shows the temperature dependence of α -pinene
294 emission rate (γ_T) and SOA yield within the temperature range at the NC site (-16.7 to 10.2 $^{\circ}\text{C}$).
295 Obviously, decreasing temperature could reduce the emission but enhance the gas to particle
296 partitioning and SOA yield.

297 From July to November 2012 (period 1), high values of SOA_M tracers and SOA yield existed under
298 low temperature, and SOA_M tracers were positively correlated with SOA yield ($r=0.647$, $p<0.05$, Figure
299 5a). These suggested that the temperature effect on partitioning was the dominant process influencing
300 SOA_M tracers' variation during the period 1. From December 2012 to April 2013 (period 2), high
301 values of SOA_M tracers and activity factor (γ_T) existed under high temperature, and SOA_M tracers were
302 positively correlated with γ_T ($r=0.741$, $p<0.05$, Figure 5b). These suggested that the temperature effect
303 on emission was the dominant process influencing SOA_M tracers' variation during the period 2. The
304 increase of SOA_M tracer concentrations during spring was also observed in the southeastern United
305 States (Ding *et al.* 2008), resulting from the enhancement of monoterpenes emission in spring (Kim
306 2011). From May to July 2013 (period 3), SOA_M tracer concentrations were relative stable, and there
307 was no correlation of SOA_M tracers with γ_T or SOA yield ($p>0.05$). These might result from the
308 counteraction of temperature effects on emission and partitioning during the summer.

309 Previous study proposed that *cis*-pinonic acid and pinic acid (P) were the first-generation products
310 of SOA_M and only formed under low- NO_x conditions (Eddingsaas et al. 2012). The dominance of
311 *cis*-pinonic acid and pinic acid among SOA_M tracers at the remote NC site indicated that SOA_M there
312 was mainly formed under low- NO_x conditions. Moreover, *cis*-pinonic acid and pinic acid could be

313 further photo-degraded to high-generation products, e.g. 3-methyl-1,2,3-butanetricarboxylic acid (M)
314 (Glasius et al. 2000; Jaoui et al. 2005; Szmigielski, et al., 2007). And the ratio of *cis*-pinonic acid plus
315 pinic acid to 3-methyl-1,2,3-butanetricarboxylic acid (P/M) could be applied to trace the aging of
316 SOA_M (Ding et al., 2011; Gómez-González et al., 2012). In the fresh chamber produced α -pinene SOA
317 samples, the ratios of P/M were reported in the range of 1.51 to 3.21 (Offenberg, et al., 2007). In this
318 study, the ratio of P/M averaged 16.7 ± 20.9 . Thus, SOA_M was generally fresh at the NC site and
319 should be mainly formed from local precursors. Figure 6 presents a negative correlation between P/M
320 and temperature ($r=-0.560$, $p=0.008$). Higher P/M ratios were observed in the fall and the winter, and
321 lower P/M ratios occurred in the spring and the summer. Since temperature has positive influence on
322 photo-reaction rates, the higher temperature during the summer could accelerate the photochemistry in
323 the air and result in P to M conversion being more efficient. Thus, SOA_M in the summer was more aged
324 than that in the winter.

325 The levels of SOA_C tracer, β -caryophyllenic acid were in the range of below MDL to 0.40 ng m^{-3} .
326 As Figure 2c shows, the levels elevated from July to November 2012 and dropped to below MDL in
327 December 2012. Then, the concentrations increased from January to March 2013 and decreased from
328 April to June 2013. β -Caryophyllenic acid was positively correlated with SOA_M tracers ($p=0.025$),
329 indicating that the seasonal variation of β -caryophyllenic acid was similar with that of the SOA_M
330 tracers.

331

332 3.1.3 Aromatic SOA tracer

333 The levels of SOA_A tracer, DHOPA were in the range of below MDL to 0.61 ng m^{-3} . This
334 anthropogenic tracer was not detected or reported in global remote areas (Table 2). Due to few human
335 activity at the remote NC site, the highest concentration of DHOPA was 1-2 orders of magnitude lower
336 than those (up to 52 ng m^{-3}) reported in the urban regions of United States (Lewandowski *et al.* 2013)
337 and China (Ding *et al.* 2014). DHOPA exhibited the higher concentrations in the summer and the lower
338 levels in the winter (Figure 2d).

339 Besides urban emissions from solvent and fossil fuel use, biomass burning is an important source of
340 aromatics in many parts of the world (Lewis et al. 2013). The local dung or biomass burning (Duo et al.
341 2015; Xiao et al. 2015) may be potential sources of aromatics in the TP. Hence, DHOPA may come
342 from the processing of biomass burning emission. Figure 7 exhibits the monthly variation of biomass

343 burning tracer, levoglucosan during our sampling. The concentrations of levoglucosan ranged from
344 0.82 ng m^{-3} (October 2012) to 4.55 ng m^{-3} (April 2013) with a mean of $1.87 \pm 1.14 \text{ ng m}^{-3}$. Apparently,
345 the monthly variation trend of levoglucosan was quite different from that of DHOPA. And there was no
346 correlation between DHOPA and levoglucosan ($p > 0.05$) (Figure S6). These indicated that DHOPA was
347 not mainly from the processing of biomass burning emission at the NC site. Since there was few
348 anthropogenic source near the remote NC site, the SOA_A tracer should be not locally formed but
349 mainly transported from upwind regions.

350 To check the potential source areas of anthropogenic emissions, the satellite data of population
351 density (<http://sedac.ciesin.columbia.edu/theme/population>), aerosol optical thickness (AOT,
352 <http://neo.sci.gsfc.nasa.gov/>), tropospheric NO_2 vertical column densities (VCD,
353 <http://avdc.gsfc.nasa.gov/>), and surface CO (<https://www2.acd.ucar.edu/mopitt>) were analysis on the
354 global scale. As shown in Figure S7a, the northern Indian subcontinent was the most populated region
355 of the world, with a population density of more than 1000 persons per km^2 . Moreover, the plots of
356 global AOT, tropospheric NO_2 VCD, and surface CO (Figure S7, b-d) all illustrated that the northern
357 Indian subcontinent, including Bangladesh, Nepal, the northeastern India, and the northwestern India
358 was the global hotspots of these anthropogenic pollutants. Compared with the northern Indian
359 subcontinent, the TP exhibited extremely low population density and low levels of AOT, surface CO,
360 and NO_2 VCD (Figure 8, a-d). Besides these satellite data, a recent study at a site in the northwestern
361 India (Indo-Gangetic plain) witnessed extremely high levels (up to 2065 ng m^{-3}) of polycyclic
362 aromatic hydrocarbons which were mainly formed from anthropogenic combustion processes (Dubey
363 et al., 2015). All these demonstrated that there were high anthropogenic emissions in the northern India
364 subcontinent.

365 The TP features a monsoon climate (Cong *et al.* 2007, Ming *et al.* 2010, Zhao *et al.* 2013). Figure
366 9a presents the average trajectory of each cluster during our sampling in the whole year. The air masses
367 over the NC were primarily from Bangladesh, Nepal and the northeastern India (cluster 1, 32%), the
368 northwestern India (Indo-Gangetic basin) (cluster 3–6, 55%), and the Taklimakan Desert (cluster 2,
369 13%) during the sampling period. In the summer, the prevailing southerly winds (cluster 1, Figure 9b)
370 passed through the heavily polluted areas in the Bangladesh and the northeastern India, and could bring
371 anthropogenic pollutants into the TP. Previous studies in the TP have witnessed the enrichment of
372 anthropogenic metals (Cong *et al.* 2007) and the enhancement of carbonaceous aerosols (Ming *et al.*

373 2010, Zhao *et al.* 2013) under the influence of summer monsoon. Thus, the increase of DHOPA levels
374 at the NC site in the summer was mainly due to the transport of air pollutants from the upwind
375 Bangladesh and the northeastern India.

376 In the winter, the air masses over the NC site were mainly originated from the northwestern India
377 (Indo-Gangetic basin) by the westerly winds (Figure 9b). Compared with the summer samples, the
378 winter samples underwent the longer distance transport. Moreover, extremely low temperature in the
379 winter could reduce DHOPA formation. Therefore, the levels of DHOPA were lower in the winter. It is
380 worth noting that the mass fractions of DHOPA in all tracers significantly elevated in the winter (less
381 than 2% in the summer but up to 10% in January, Figure 2d), although its levels reduced. As described
382 in equation (3) and (6), temperature is an important factor controlling BVOCs emission. The drop of
383 temperature from the summer (up to 10.2 °C) to the winter (low to -16.7 °C) at the NC site would lead
384 to the emission of isoprene and monoterpenes decreasing by 98% and 90%, respectively. The elevated
385 fractions of DHOPA in the winter samples suggested that the SOA contributions from aromatics would
386 increase in the winter when BVOCs emission largely decreased.

387

388 3.2 Source apportionment

389 The SOA-tracer method developed by Kleindienst and co-workers was applied to attribute SOC at
390 the NC site. The researchers performed chamber experiments to obtain the mass fraction of the tracers
391 in SOC (f_{SOC}) for individual precursor:

$$392 \quad f_{\text{SOC}} = \frac{\sum_i [\text{tri}_i]}{[\text{SOC}]} \quad (10)$$

393 where $\sum_i [\text{tri}_i]$ is the total concentrations of the tracers for a certain precursor. [SOC] is the mass
394 concentration of SOC. With these f_{SOC} values and the measured SOA tracers in the ambient air, SOC
395 from different precursors can be estimated in the atmosphere, with the assumption that the f_{SOC} values
396 in the chamber are the same as those in the ambient air. There is some degree of uncertainty in the
397 SOA-tracer method due to the quantification with a single surrogate calibration standard (ketopinic
398 acid) and the simplification of applying SOA tracers and conversion factors to calculate SOC in the
399 ambient samples (Kleindienst *et al.* 2007). However, this method has been widely applied to attribute
400 SOC from different precursors and proven to be able to provide reasonable results in the United States
401 (Kleindienst *et al.* 2007, Stone *et al.* 2009, Lewandowski *et al.* 2013), and China (Hu *et al.* 2008, Guo

402 *et al.* 2012, Peng *et al.* 2013, Ding *et al.* 2014). Lewandowski *et al.* (2008) found that the measured OC
403 in the midwestern United States could be fully explained by primary OC from chemical mass balance
404 (CMB) model plus SOC from the SOA-tracer method, suggesting that the secondary organic tracer
405 technique could be a valuable method for SOC estimation. Kleindienst *et al.* (2010) further compared
406 the estimated SOC by the SOA-tracer method and other four independent methods (multiple
407 regressions, CMB, carbon isotope and EC-tracer) in the southeastern United States, and found that
408 these five methods matched well. Our previous study in the Pearl River Delta found SOC levels
409 estimated by the SOA-tracer method were not only consistent with but also correlated well with those
410 by EC-tracer method in summer, (Ding *et al.*, 2012). The SOC apportionment results were also
411 comparable between the SOA-tracer method and positive matrix factorization (PMF) model in Hong
412 Kong (Hu *et al.* 2010).

413 The f_{SOC} were reported as $0.155 \pm 0.039 \mu\text{g } \mu\text{gC}^{-1}$, $0.023 \pm 0.0046 \mu\text{g } \mu\text{gC}^{-1}$ and 0.00797 ± 0.0026
414 $\mu\text{g } \mu\text{gC}^{-1}$ for isoprene (SOC_I), β -caryophyllene (SOC_C) and aromatics (SOC_A), respectively
415 (Kleindienst *et al.* 2007). In this study, the same set of SOA tracers as reported by Kleindienst *et al.*
416 (2007) were used for SOC estimation, including MGA and MTLs for SOC_I , β -caryophyllenic acid for
417 SOC_C and DHOPA for SOC_A . For monoterpene SOC (SOC_M), nine tracers were involved in the source
418 profile (Kleindienst *et al.* 2007). However, only five of the nine SOA_M tracers were measured in the
419 current study. Wang *et al.* (2013) compared the results from model prediction with field observation in
420 the Pearl River Delta and pointed out that the SOA-tracer method would underestimate SOA_M ,
421 probably due to the mismatch of tracer compositions in the field and the source profile (Ding *et al.*
422 2014). To minimize the uncertainty caused by the mismatch in tracer compositions, the f_{SOC} with the
423 same five SOA_M tracers ($0.059 \mu\text{g } \mu\text{gC}^{-1}$) was computed using the chamber data from another study by
424 the same research group (Offenberg *et al.* 2007). The same f_{SOC} for SOA_M was also applied to estimate
425 SOC_M in our previous study over China (Ding *et al.* 2014).

426 The uncertainty in the SOA-tracer method is induced from the analysis of organic tracers and the
427 determination of the conversion factors. Based on the E_A values in Table S1, the uncertainties in the
428 tracer analyses were within 40% for SOA_I (only MGA and MTLs involved for SOC estimation), 95%
429 for SOA_M , 156% for SOA_C , and 91% for SOA_A . The uncertainties of f_{SOC} were reported to be 25% for
430 isoprene, 48% for monoterpenes, 22% for β -caryophyllene and 33% for aromatics (Kleindienst *et al.*
431 2007, Lewandowski *et al.* 2013). Considering these factors, the uncertainties of SOC apportionment

432 were calculated through error propagation. The RSD were 47% for SOC_I , 106% for SOC_M , 157% for
433 SOC_C , and 96% for SOC_A . On average, the RSD of the reconstructed SOC (sum of the four precursors)
434 was $51 \pm 11\%$.

435 Figure 10 presents the monthly variations of the reconstructed SOC. SOC was high in the summer
436 2012 and declined from October to December. After that, it kept increasing from January to June. The
437 total concentrations of SOC ranged from $0.02 \mu\text{gC m}^{-3}$ to $0.69 \mu\text{gC m}^{-3}$ with an annual average of 0.22
438 $\pm 0.29 \mu\text{gC m}^{-3}$. The available data of OC in total suspended particles at the NC site were reported in
439 the range of 1.18 to $2.26 \mu\text{gC m}^{-3}$ during July 2006 to January 2007 (Ming *et al.* 2010). Since we did
440 not measure OC in our size-segregated samples, the OC data reported by Ming *et al.* (2010) were used
441 to calculate SOC fraction in OC (SOC/OC) from July to January. The calculated SOC/OC was average
442 38% in the summer and up to 58% in September, suggesting that SOC was an important contributor to
443 OC at the NC site during the summer (Ming *et al.* 2010). However, from the fall to winter, the elevated
444 OC and decreased SOC led to SOC/OC declining from 11% (in October) to 1% (in January), indicating
445 that SOA from the four precursors had minor contributions to the elevated OC. Since the air masses
446 during the fall to the winter were mostly originated from the northwestern Indo-Gangetic basin (cluster
447 3-6 in Figure 9), primary pollutants emitted there could transport to the TP and have significant impact
448 on the air at the NC site. In addition, SOA from aqueous-phase reactions and primary OA aging could
449 not be captured by the SOA-tracer method. Thus, the current results might underestimate the total
450 amount of SOC, which partly explained the low OC shares of SOC at the NC site during the fall to the
451 winter.

452 Biogenic SOC (sum of SOC_I , SOC_M , and SOC_C) dominated over SOC_A at the NC site, averagely
453 accounting for 75% of the estimated SOC. In the summer, SOC_I was the major contributor with the
454 SOC shares of 81%. From the fall to the spring, SOC_M became the major contributor, averagely
455 contributing 38% to SOC. Although SOC_A level reduced in the winter, SOC_A contribution elevated as
456 high as 53% in January 2013. The elevated OC and the higher SOC_A contribution in the winter samples
457 (Figure 10) implied that the transport of anthropogenic pollutants from the Indian subcontinent might
458 have significant influence on carbonaceous aerosols over the remote NC during winter.

459

460 **4. Conclusion**

461 Seasonal trends of SOA tracers and origins were studied in the remote TP for the first time. SOA_I

462 tracers represented the majority among these compounds. The significant temperature dependence of
463 SOA_I tracers suggested that the seasonal variation of SOA_I tracers at the NC site was mainly influenced
464 by the isoprene emission. Due to the influence of temperature and relative humidity, the ratio of
465 high-NO_x to low-NO_x products of SOA_I (MGA/MTLs) was the highest in the winter and the lowest in
466 the summer. The seasonal variation of SOA_M tracers was impacted by monoterpenes emission and
467 gas-particle partitioning. Due to the transport of air pollutants from the Indian subcontinent, DHOPA
468 presented relatively higher concentrations in the summer and increased mass fractions in the winter.
469 The SOA-tracer method was applied to estimated SOC from these four precursors. The annual average
470 of SOC was $0.22 \pm 0.29 \mu\text{gC m}^{-3}$, with the biogenic SOC accounting for 75%. In the summer, isoprene
471 was the major precursor with its SOC shares of 81%. In the winter when the emissions of biogenic
472 precursors largely declined, the contributions of SOC_A increased. At present, SOA origins and their
473 seasonal variations are unclear in the remote high-elevation TP. The remote TP is connected to the
474 densely populated Indian subcontinent. Our study implies that anthropogenic pollutants emitted there
475 could transport to the TP and influence SOC over the remote NC.

476

477

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482

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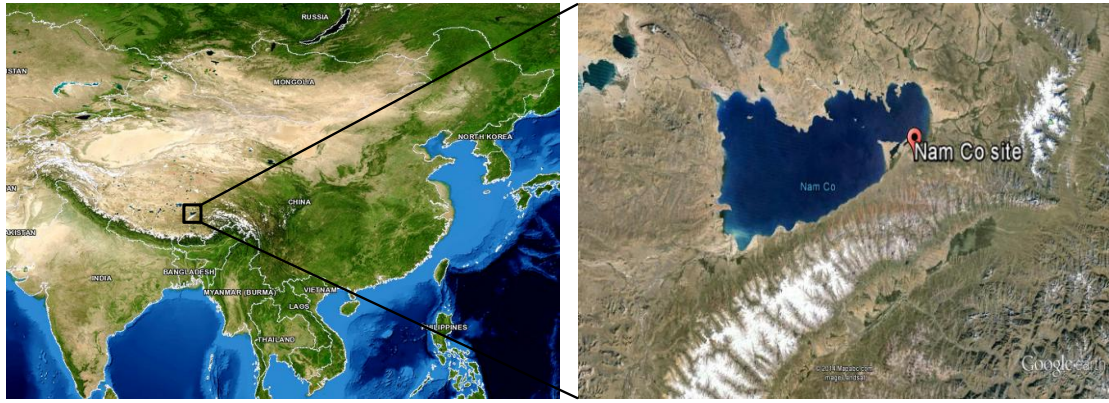
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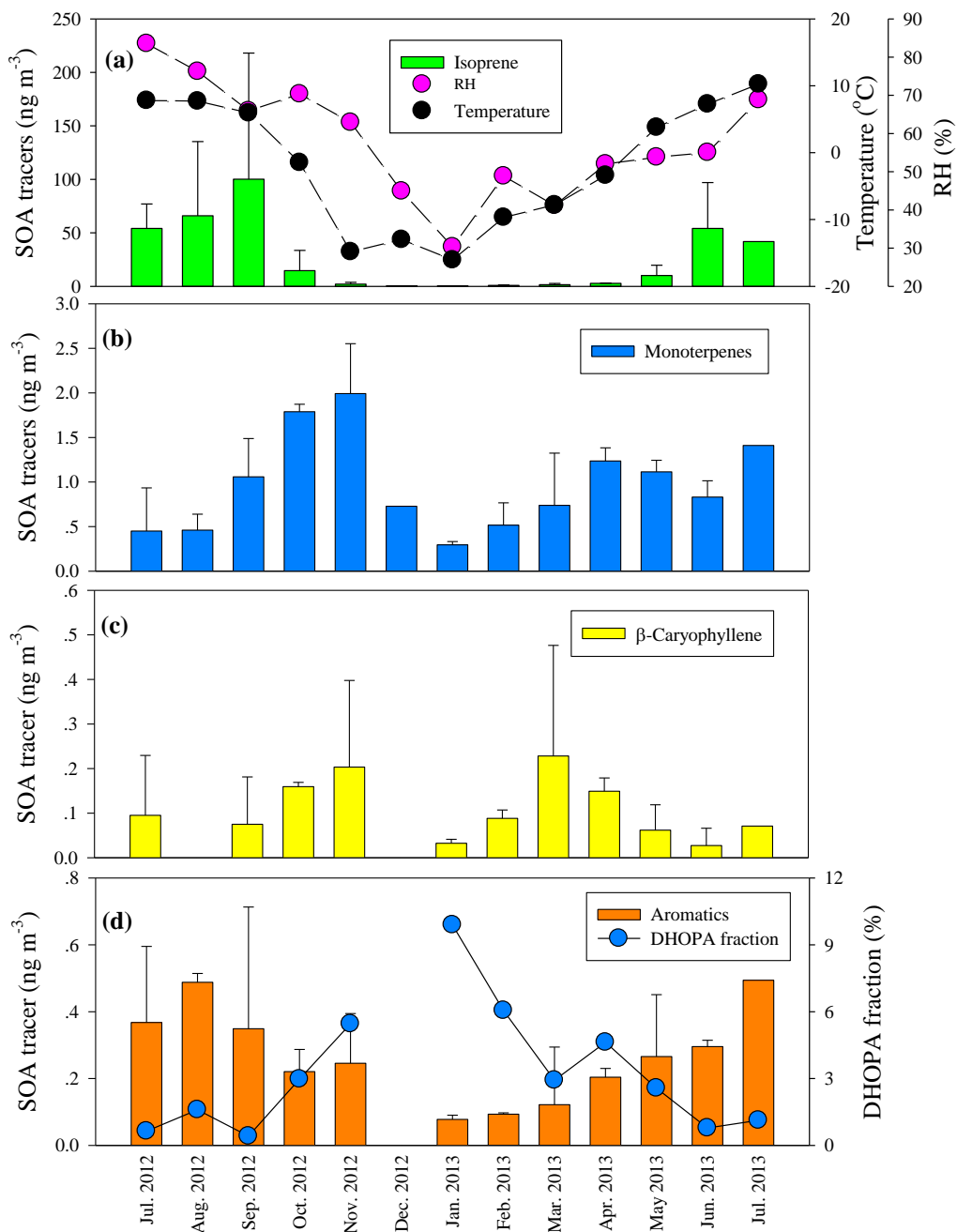
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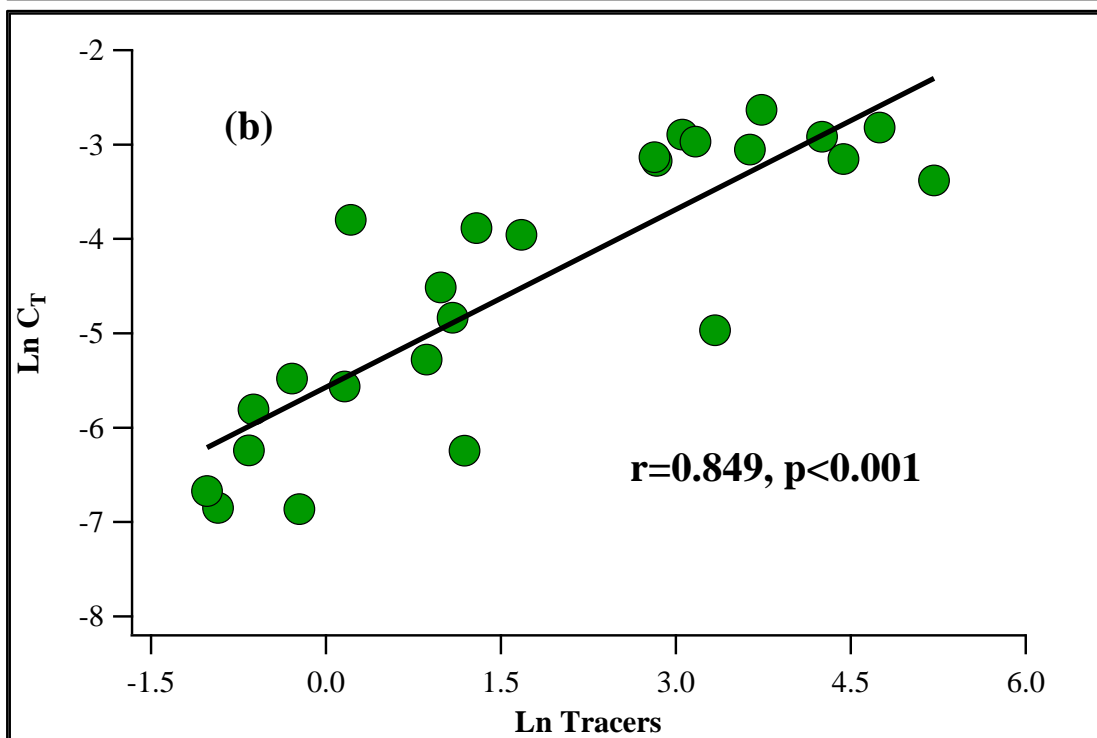
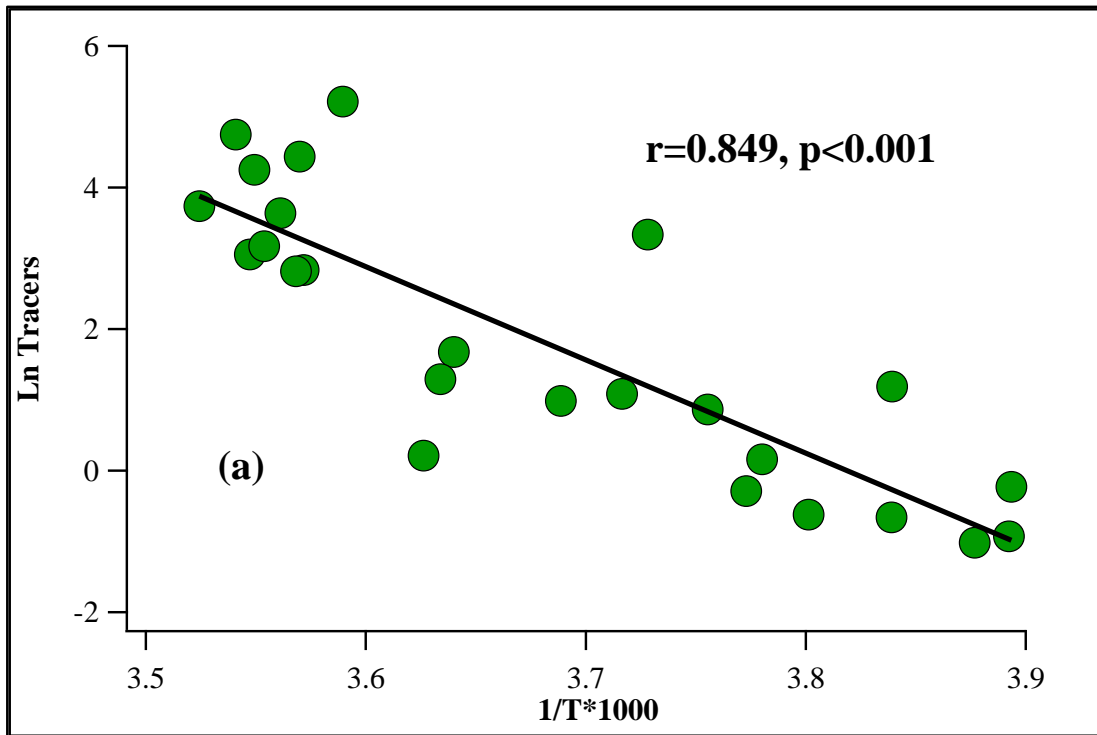
659 Figure 1 Nam Co site in the Tibetan Plateau, China

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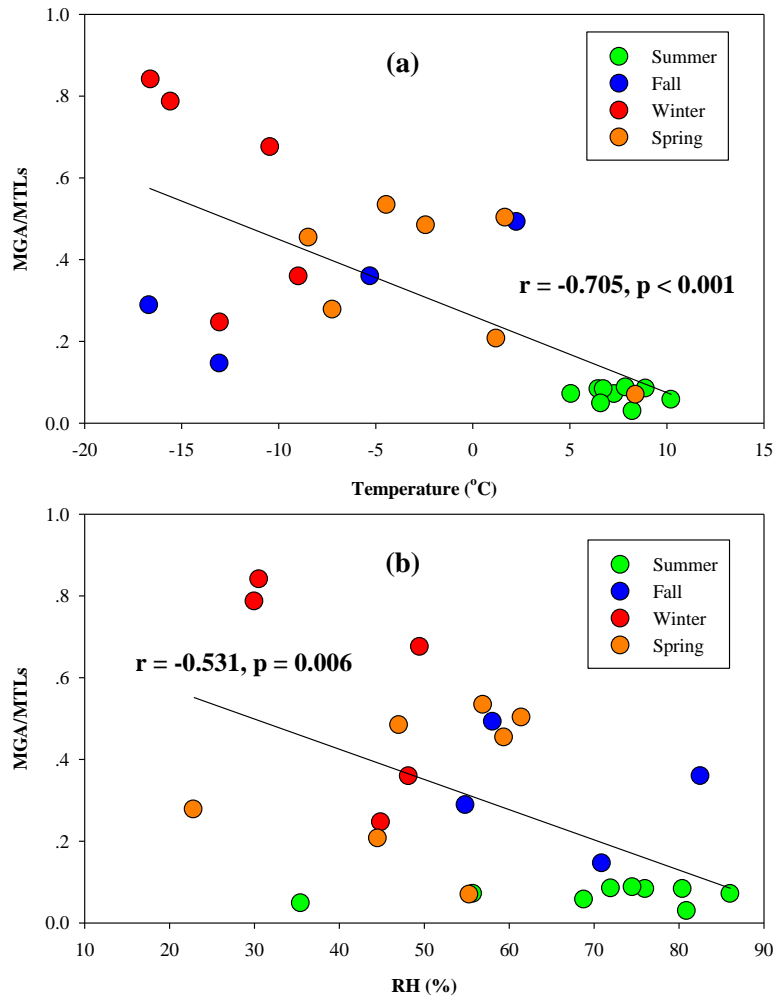
662 Figure 2 Monthly variations of SOA tracers.



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664 Figure 3 Correlations of SOA_I tracers with temperature (a) and C_T (b).

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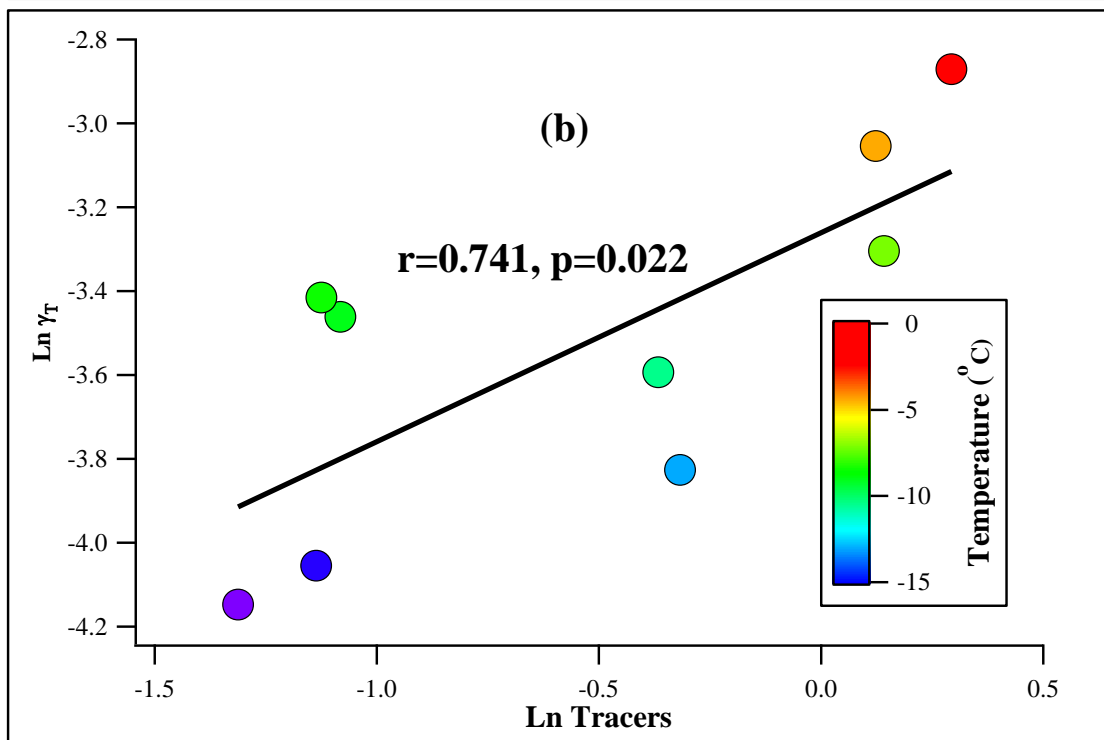
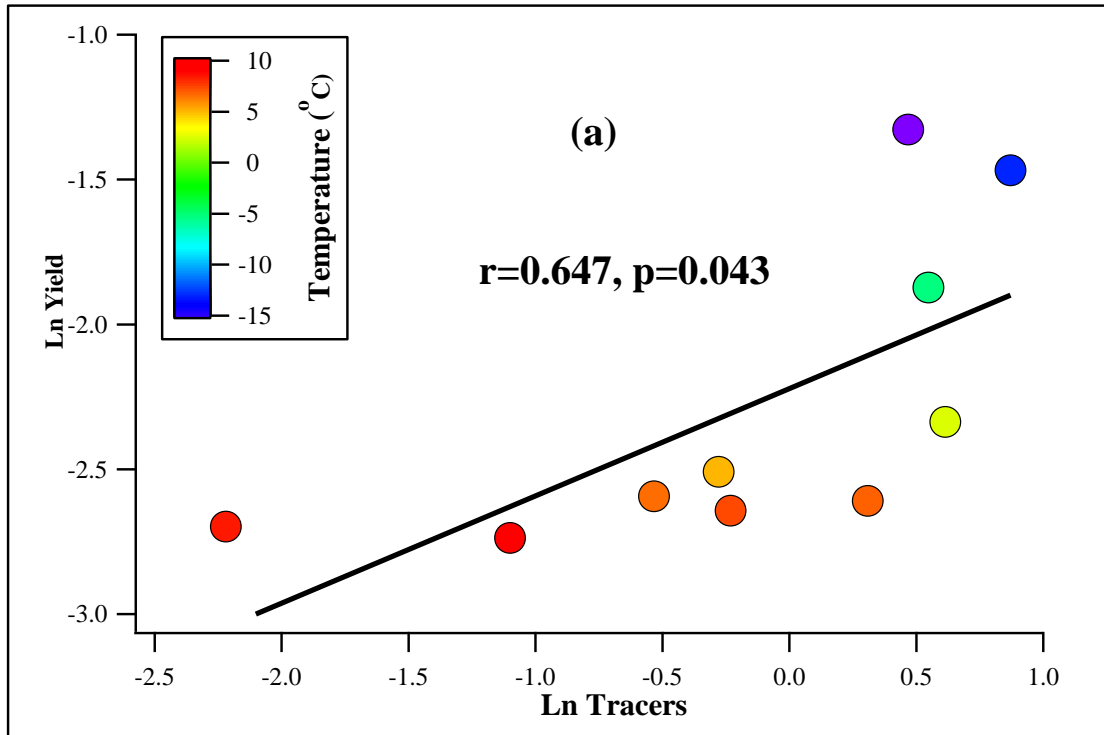
666

667 Figure 4 Correlations of MGA/MTL with temperature (a) and relative humidity (b). Summer is from

668 July to September 2012 and from June to July 2013, fall is from October to November 2012, winter is

669 from December 2012 to February 2013, and spring is from March to May 2013.

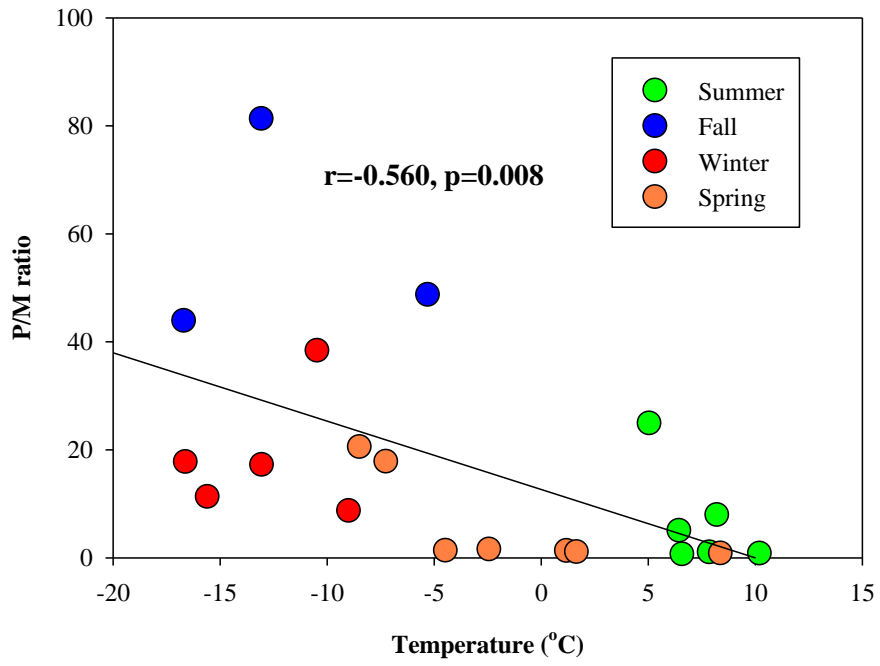
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672 Figure 5 Correlation of SOA_M tracers with SOA yield in period 1 (a) and γ_T in

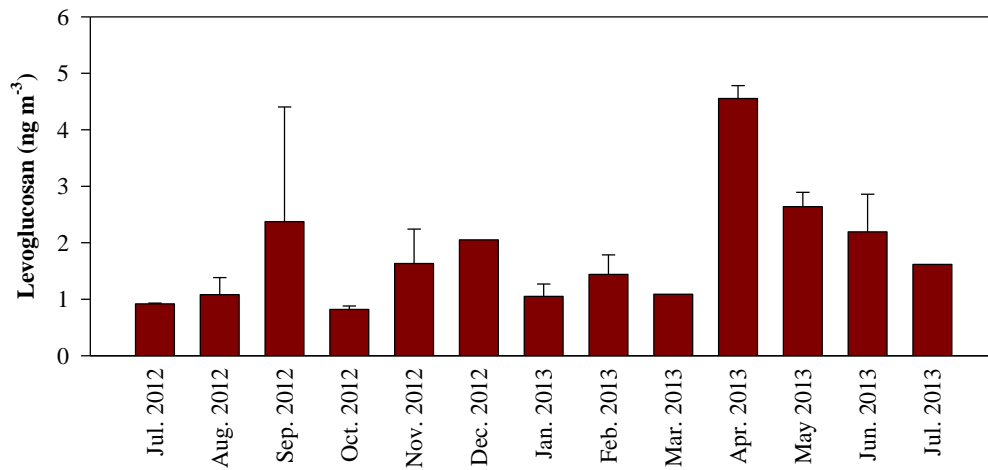
673 period 2 (b)



674

675 Figure 6 Negative correlation between P/M ratio and temperature

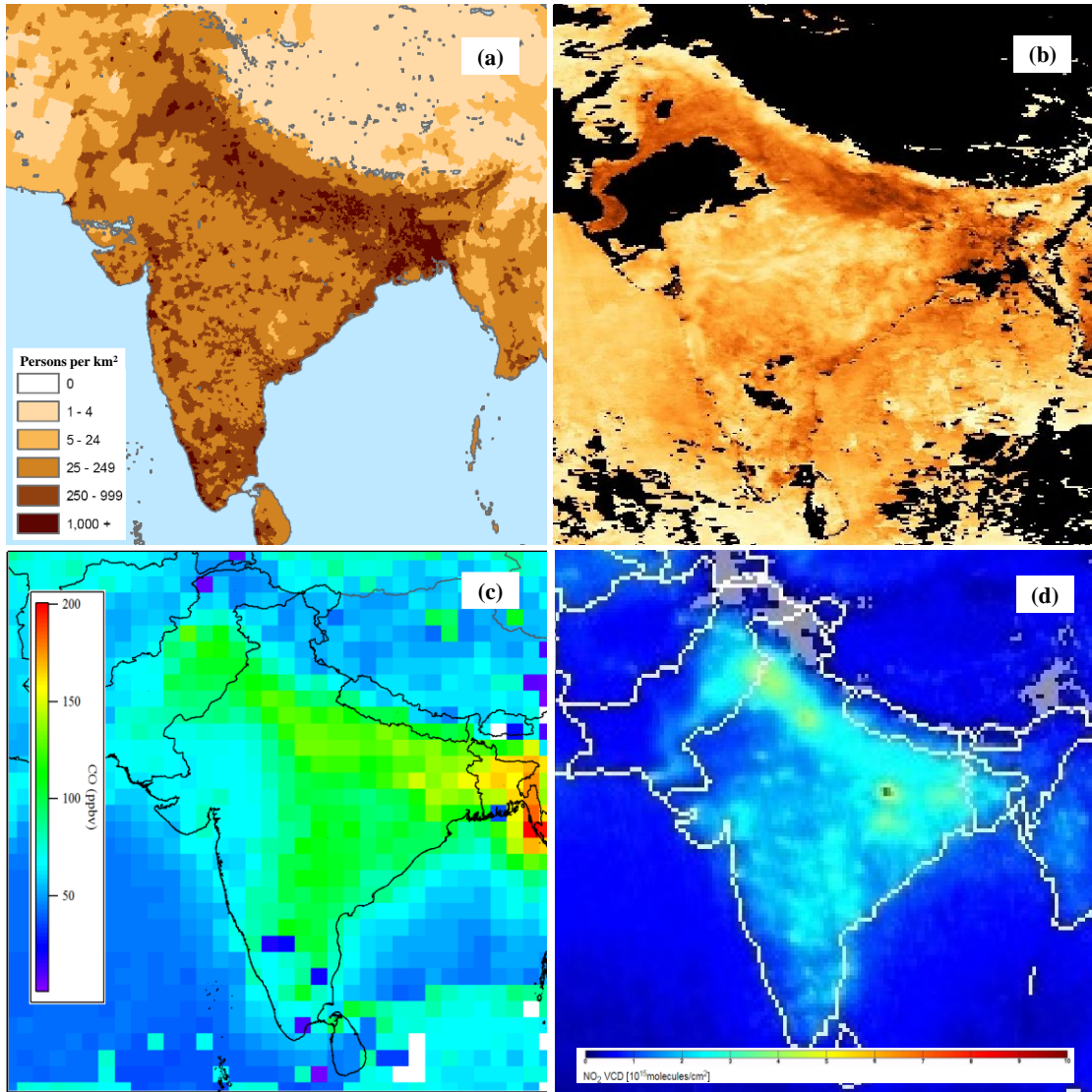
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678 Figure 7 Monthly variation of biomass burning tracer, levoglucosan

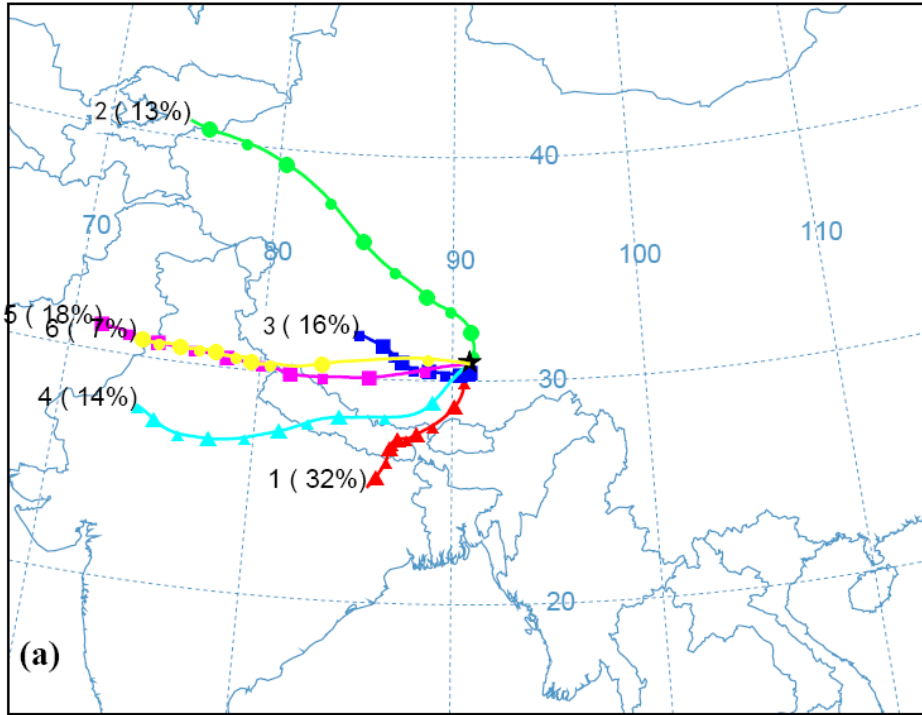
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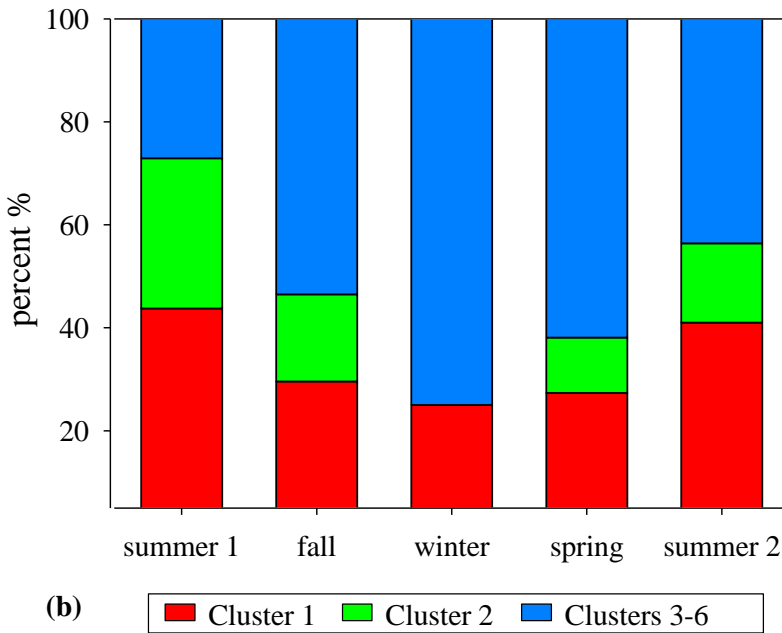
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681 Figure 8 Spatial distribution of population density in 2000 (a), AOT (b), surface CO

682 (c), and NO₂ VCD (d) in May 2013 over the Indian subcontinent and the TP.



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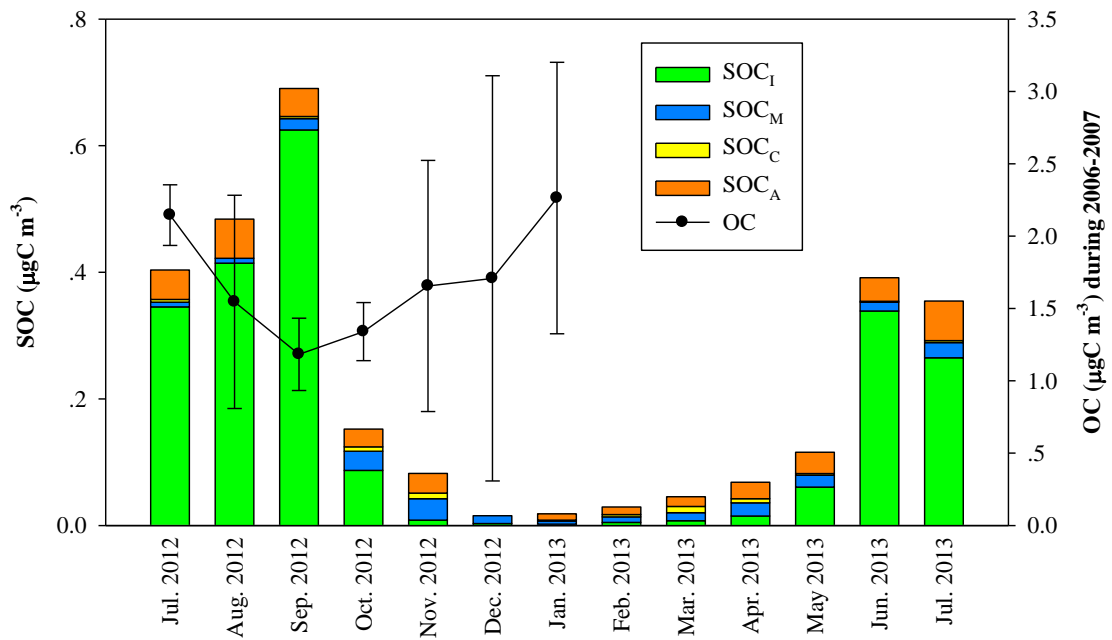


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685 Figure 9 Cluster analyses of air masses at the NC site (a) and seasonal variations of clusters (b), based
 686 on 5-day backward trajectories during the sampling period. Summer 1 is from July to September 2012,
 687 fall is from October to November 2012, winter is from December 2012 to February 2013, spring is
 688 from March to May 2013, summer 2 is from June to July 2013.

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692 Figure 10 Seasonal variations of estimated SOC. OC data at the NC site during July 2006 to January

693 2007 were reported by Ming et al., (2010) and the err bar means one standard deviation in each month.

Table 1 SOA tracers at the NC site (ng m⁻³)

Month	Temp. °C ^a	RH % ^a	SOA tracers				Sum
			Isoprene	Monoterpenes	β-Caryophyllene	Aromatics	
Jul. 2012	7.78	84	54.1±22.9 ^b	0.45±0.48	0.10±0.13	0.37±0.23	55.0±22.5
Aug. 2012	7.70	76	66.0±69.3	0.46±0.18	nd ^c	0.49±0.03	67.0±69.1
Sep. 2012	5.92	66	100±118	1.06±0.43	0.08±0.11	0.35±0.36	102±118
Oct. 2012	-1.50	70	14.7±19.0	1.79±0.08	0.16±0.01	0.22±0.07	16.8±18.9
Nov. 2012	-14.9	63	2.04±1.76	1.99±0.56	0.20±0.19	0.25±0.15	4.48±2.66
Dec. 2012	-13.0	45	0.52	0.73	nd	nd	1.25
Jan. 2013	-16.1	30	0.38±0.02	0.30±0.04	0.03±0.01	0.08±0.01	0.78±0.01
Feb. 2013	-9.69	49	0.86±0.45	0.52±0.25	0.09±0.02	0.09±0.01	1.55±0.22
Mar. 2013	-7.83	41	1.56±1.15	0.74±0.59	0.23±0.25	0.12±0.17	2.65±2.15
Apr. 2013	-3.42	52	2.82±0.20	1.24±0.15	0.15±0.03	0.20±0.03	4.40±0.11
May 2013	3.77	54	10.1±9.70	1.11±0.13	0.06±0.06	0.27±0.19	11.5±9.97
Jun. 2013	7.25	55	54.1±42.9	0.83±0.18	0.03±0.04	0.30±0.02	55.3±42.8
Jul. 2013	10.2	69	41.9	1.41	0.07	0.49	43.9
Annual	-1.64	58	26.6±44.2	0.97±0.57	0.09±0.10	0.25±0.18	28.0±44.2

^aTemperature and RH are monthly averages; ^bone standard deviation; ^c“nd” means not detected.

Table 2 SOA tracers in remote places on the global range (ng m⁻³)

Locations	Seasons	References	SOA tracers				
			Isoprene ^a	Monoterpenes ^a	β -Caryophyllene	Aromatics	
Nam Co Lake	Whole year	This study	26.6(0.36-184) ^b	0.97(0.11-2.39)	0.09(nd-0.40)	0.25(nd-0.61)	
Tibetan Plateau	Qianghai Lake	Summer	(Li <i>et al.</i> 2013)	2.50(0.13-7.15)	2.95(0.30-10.4)	0.87(0.05-2.41)	na ^c
	Himalayas	Summer-autumn	(Stone <i>et al.</i> 2012)	30.7(5.5-105)	13.2(5.6-31.3)	1.6(1.1-2.3)	na
Arctic	Alert	Winter-Summer	(Fu <i>et al.</i> 2009)	0.3(0.08-0.567)	1.6(0.138-5.3)	0.12(0.01-0.372)	na
	Arctic Ocean	Summer	(Fu <i>et al.</i> 2013)	4.0(0.16-31.8)	4.8(0.44-24.1)	0.017(0.005-0.048)	na
Global oceans	Low- to mid-latitude	Fall-Spring	(Fu <i>et al.</i> 2011)	3.6(0.11-22)	2.7(0.02-15)	0.32(0-2.5)	na
	Antarctic to Arctic	Summer	(Hu <i>et al.</i> 2013)	8.5(0.018-36)	3.0(0.05-20)	na	na
	North Pacific and Arctic	Summer	(Ding <i>et al.</i> 2013)	0.62(0.12-1.45)	0.06(0.01-0.25)	0.002(nd-0.03)	nd ^d

^a compositions are different in different studies. ^b data range in brackets. ^c “na” means not available. ^d “nd” means not detected.