Seasonal variation of secondary organic aerosol tracers in Central Tibetan Plateau

R.-Q. Shen¹,³, X. Ding¹, Q.-F. He¹,³, Z.-Y. Cong², Q.-Q. Yu¹,³, and X.-M. Wang¹

¹State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
²Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085, China
³University of Chinese Academy of Sciences, Beijing, 100049, China

Correspondence to: X. Ding (xiangd@gig.ac.cn)

Received: 13 January 2015 – Published in Atmos. Chem. Phys. Discuss.: 10 March 2015
Revised: 8 July 2015 – Accepted: 1 August 2015 – Published: 10 August 2015

Abstract. Secondary organic aerosol (SOA) affects the earth’s radiation balance and global climate. High-elevation areas are sensitive to global climate change. However, at present, SOA origins and seasonal variations are understudied in remote high-elevation areas. In this study, particulate samples were collected from July 2012 to July 2013 at the remote Nam Co (NC) site, Central Tibetan Plateau and analyzed for SOA tracers from biogenic (isoprene, monoterpenes and β-caryophyllene) and anthropogenic (aromatics) precursors. Among these compounds, isoprene SOA (SOAI) tracers represented the majority (26.6 ± 44.2 ng m⁻³), followed by monoterpane SOA (SOAM) tracers (0.97 ± 0.57 ng m⁻³), aromatic SOA (SOA₄) tracer (2,3-dihydroxy-4-oxopentanoic acid, DHOPA, 0.25 ± 0.18 ng m⁻³) and β-caryophyllene SOA tracer (β-caryophyllenic acid, 0.09 ± 0.10 ng m⁻³). SOAI tracers exhibited high concentrations in the summer and low levels in the winter. The similar temperature dependence of SOAI tracers and isoprene emission suggested that the seasonal variation of SOAI tracers at the NC site was mainly influenced by the isoprene emission. The ratio of high-NOx to low-NOx products of SOAI (2-methylglyceric acid to 2-methyltetrols) was highest in the winter and lowest in the summer, due to the influence of temperature and relative humidity. The seasonal variation of SOAM tracers was impacted by monoterpenes emission and gas-particle partitioning. During the summer to the fall, temperature effect on partitioning was the dominant process influencing SOAM tracers’ variation; while the temperature effect on emission was the dominant process influencing SOAM tracers’ variation during the winter to the spring. SOAM tracer levels did not elevate with increased temperature in the summer, probably resulting from the counteraction of temperature effects on emission and partitioning. The concentrations of DHOPA were 1–2 orders of magnitude lower than those reported in the urban regions of the world. Due to the transport of air pollutants from the adjacent Bangladesh and northeastern India, DHOPA presented relatively higher levels in the summer. In the winter when air masses mainly came from northwestern India, mass fractions of DHOPA in total tracers increased, although its concentrations declined. The SOA-tracer method was applied to estimate secondary organic carbon (SOC) from these four precursors. The annual average of SOC was 0.22 ± 0.29 µgC m⁻³, with the biogenic SOC (sum of isoprene, monoterpenes and β-caryophyllene) accounting for 75 %. In the summer, isoprene was the major precursor with its SOC contributions of 81 %. In the winter when the emission of biogenic precursors largely dropped, the contributions of aromatic SOC increased. Our study implies that anthropogenic pollutants emitted in the Indian subcontinent could be transported to the TP and have an impact on SOC over the remote NC.
1 Introduction

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

SOA tracers from specific VOCs can provide an insight into processes and sources influencing SOA formation and spatiotemporal distribution. The identification of the isoprene SOA (SOA$_I$) tracers, 2-methyltetrols (Claeys et al., 2004) revealed the importance of SOA$_I$ in global SOA burden. Further studies in high-NO$_x$ and low-NO$_x$ products of isoprene intermediates (e.g. methacrylic acid epoxide and isoprene epoxidiols) provided more details in the mechanisms of SOA$_I$ formation under the influence of NO$_x$ (Paulot et al., 2009; Froyd et al., 2010; Surratt et al., 2010; Lin et al., 2013). The identification of tracers from aromatic SOA (SOA$_A$) (Offenberg et al., 2007) offered a way to directly evaluate the variation of anthropogenic SOA, particularly in urban regions. In addition, specific tracers have been determined in monoterpane SOA (SOA$_M$) (Jaoui et al., 2005; Claeys et al., 2007) and β-caryophyllene SOA (SOA$_C$) (Jaoui et al., 2007; van Eijck et al., 2013). Based on these SOA tracers, Kleindienst and coworkers further developed an SOA tracer method to attribute SOA sources in the ambient air. Since it is difficult to directly measure SOA, the SOA-tracer method provides a valuable technique to estimate SOA in the ambient air, and it has been widely used around the world (Hu et al., 2008; von Schneidemesser et al., 2009; Guo et al., 2012; Lewandowski et al., 2013; Ding et al., 2014).

High-elevation areas are sensitive to global climate change (Xua et al., 2009). Observation of aerosol concentrations and compositions at high-elevation sites can provide insight into the influence of natural and anthropogenic aerosols on global climate. The Tibetan Plateau (TP), the largest and highest plateau, is at the juncture of large desert areas and the densely populated Indian subcontinent. Subsequent studies found the northwesterly winds could bring dust from the western deserts to the TP and lead to high levels of geological aerosols at a site on the southeast TP (Zhao et al., 2013). Moreover, anthropogenic pollutants (e.g. sulfate, nitrate, potassium, element carbon, and heavy metals) emitted in the developing countries in South Asia could be transported to the TP by the southerly and southwesterly winds, especially during the summer monsoon season (Cong et al., 2007; Ming et al., 2010; Li et al., 2013; Zhao et al., 2013).

The observation at the remote central TP site, Nam Co (NC) discovered that the mean ratio of organic carbon (OC) to element carbon (EC) was 31.9 ± 31.1 during July 2006 to January 2007, implying the significant SOA contribution to OC (Ming et al., 2010) in the TP. However, there are only three studies in SOA compositions within the TP. Li et al. (2013) reported biogenic SOA (BSOA) tracers during the summer of 2010 at Qinghai Lake in the northeastern part of the TP. Stone et al. (2012) measured BSOA tracers from August to October 2005 on the south slope of Himalayas in the southwestern part of the TP. Due to the limited samples, it was difficult to examine the seasonal variation of these BSOA tracers in the TP. Moreover, due to the lack of anthropogenic SOA tracers, it was not possible to examine anthropogenic SOA in the TP, although above discussions have demonstrated that air pollutants from South Asia could be transported to the TP. Our recent study provided a snapshot of SOA tracers over China (including the NC and Linzhi sites in the TP) during the summer of 2012 (Ding et al., 2014). In this study, the observation at the remote NC site extended to 1 year. Seasonal trends of SOA tracers from isoprene, monoterpene, β-caryophyllene and aromatics were determined in the TP. Furthermore, secondary organic carbon (SOC) was estimated by the SOA-tracer method to check the variations of SOA origins at the NC site. To our knowledge, it is the first time that the seasonal trends of SOA tracers and origins are studied in the remote TP.

2 Experiment

2.1 Field sampling

Samples were collected at a remote site (4730 m above sea level) at the southeastern shore of Nam Co Lake in the central TP (Fig. 1). Nam Co Lake (90°16' to 91°03'E and 30°30' to 30°55'N) is located in the Nyainqen Tanglha Mountain Range with a total area of 2017 km$^2$ (Zhou et al., 2013). The major vegetation in the Nam Co Lake Basin is the high cold alpine meadow.

Sampling was undertaken from July 2012 to July 2013. An Anderson sampler equipped with nine-stage cascade impactors and pre-baked quartz fiber filters (Whatman, baked at 450 °C for 8 h) was used to get size-segregated particle samples at an air flow rate of 28.3 L min$^{-1}$. The 50 % cutoff sizes are < 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 flow rate was calibrated before and after each sampling episode using an airflow meter to ensure the sampler operated at the specified flow rate. One set of nine size-fractionated filters were collected for 72 h every 2 weeks. Additionally, four sets of field blanks were collected in the same way as the ambient samples for 5 min when the sampler was turned off. All samples were wrapped with aluminum foil and stored at −18 °C before analysis.
2.2 Chemical analysis

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

The samples were analyzed by a gas chromatography/mass spectrometer detector (GC/MSD, Agilent 7890/5975C) in the selected ion monitoring (SIM) mode with a 30 m HP-5 MS capillary column (i.d. 0.25 mm, 0.25 µm film thickness). Splitless injection of a 2 µL sample was performed. The GC temperature was initiated at 65 °C, held for 2 min, then increased to 290 °C at 5 °C min⁻¹ and held for 20 min. Thirteen SOA tracers were quantified by the GC/MSD coupled with an electron impact (EI) ionization source, including five SOAM tracers (cis-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid), six SOAI tracers (2-methylthreitol, 2-methylerythritol, 2-methylglyceric acid, cis-2-methyl-1,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-1,3,4-trihydroxy-1-butene), one SOAC tracer (β-caryophyllenic acid) and one SOAA tracer (2,3-dihydroxy-4-oxopentanoic acid, DHOPA). Figure S1 in the Supplement presents the total ion chromatogram (TIC) of these SOA tracers. cis-Pinonic acid and pinic acid were quantified by authentic standards. Due to the lack of standards, the SOAI tracers were quantified using erythritol (Claeys et al., 2004; Ding et al., 2008). The other SOAM tracers were quantified using cis-pinonic acid. β-Caryophyllenic acid and DHOPA were quantified using octadecanoic acid and azelaic acid, respectively (Ding et al., 2012). The EI spectrum of each SOA tracer is shown in Figs. S2–S4. The method detection limits (MDLs) for cis-pinonic acid, pinic acid, erythritol, octadecanoic acid and 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.

2.3 Quality assurance and quality control

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

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

2.4 Estimation of measurement uncertainty

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

\[
E_A = \sqrt{E_{FB}^2 + E_R^2 + E_Q^2}.
\]

(1)

Since SOA tracers were not detected in the field blanks, \(E_{FB}\) was 0 in this study. The spike recoveries of surrogate standards were used to estimate the \(E_R\) of tracers which ranged from 1% (cis-pinonic acid) to 35% (erythritol). Stone et al. (2012) developed an empirical approach to estimate \(E_Q\) based on homologous series of atmospherically relevant compounds. The relative error introduced by each carbon atom \((E_n)\) was estimated to be 15%, each oxygenated functional group \((E_f)\) to be 10% and alkenes \((E_d)\) to be 60%. The errors introduced from surrogate quantification are treated as additive and are calculated as

\[
E_Q = E_n \Delta n + E_f \Delta f + E_d \Delta d,
\]

(2)

where \(\Delta n\) is the difference in carbon atom number between a surrogate and an analyte, \(\Delta f\) is the difference in oxygen-containing functional group between a surrogate and an analyte, \(\Delta d\) is the difference in alkene functionality between a surrogate and an analyte.

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

2.5 Backward trajectories

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

3 Results and discussions

3.1 Seasonal variations of SOA tracers

Since the NC site is located in the high-elevation TP, the annual temperature was only \(-1.64^\circ\text{C}\) with the range of \(-16.1^\circ\text{C}\) in January to 10.2\(^\circ\text{C}\) in July (Table 1). The annual relative humidity (RH) was 58% with the peak in July (84%) and the lowest in January (30%). The sum of all tracers ranged from 0.78 to 185 ng m\(^{-3}\). Among these compounds, SOA\(_1\) tracers (26.6 ± 44.2 ng m\(^{-3}\)) represented the majority, followed by SOA\(_M\) tracers (0.97 ± 0.57 ng m\(^{-3}\)), DHOPA (0.25 ± 0.18 ng m\(^{-3}\)) and \(\beta\)-caryophyllenic acid (0.09 ± 0.10 ng m\(^{-3}\)). During the summer (July–September 2012 and June–July 2013), SOA\(_1\) tracers presented the majority (>95%). The mass fractions of SOA\(_M\) tracers in all compounds increased during the cold period (October 2012 to May 2013).

3.1.1 Isoprene SOA tracers

The total concentrations of SOA\(_1\) tracers (sum of six tracers) ranged from 0.36–184 ng m\(^{-3}\). The levels of SOA\(_1\) tracers were 1–2 orders of magnitude higher than those over the global oceans and the Arctic (Table 2). Among the SOA\(_1\) tracers, 2-methyltetrols (sum of 2-methylthreitol and 2-methylyxthreitol, MTLs) were the major components (72%), with an annual average of 23.8 ± 40.3 ng m\(^{-3}\) (0.18 to 165 ng m\(^{-3}\)). The 2-methylglyceric acid (MGA) averaged 1.95 ± 2.92 ng m\(^{-3}\) and \(\beta\)-alkenetriols (sum of cis-2-methyl-1,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene) averaged 0.93 ± 1.39 ng m\(^{-3}\). MTLs are produced through the particle-phase uptake of the epoxydiols that formed in the gas-phase photo-oxidation of isoprene under low-NO\(_X\) or NO\(_X\) free conditions (Paulot et al., 2009; Surratt et al., 2010). Since the remote TP is a low-NO\(_X\) environment, it is expected that the low-NO\(_X\) products, MTLs dominated over other SOA\(_1\) tracers. The majority of MTLs at the NC site was consistent with those observed within the TP (Stone et al., 2012; Li et al., 2013) and over most global oceans (Fu et al., 2011; Hu et al., 2013), but different from those over the North Pacific Ocean and the Arctic where MGA was the major SOA\(_1\) tracer due to the significant influence of Siberian fires (Fu et al., 2011; Ding et al., 2013). The two MTL isomers exhibited a strong correlation with each other throughout the year \((R^2 = 0.996, p < 0.001)\) with a slope of 3.7, indicating that the two isomers shared similar formation pathways.

Figure 2a presents a typical seasonal trend of SOA\(_1\) tracers that high concentrations all existed in the summer. From October 2012 to April 2013, temperature was below zero, the levels of SOA\(_1\) tracers dramatically decreased as low as 0.38 ng m\(^{-3}\) in January.

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

\[
E_I = E_{F1} \times C_L \times C_T,
\]

(3)

where \(E_{F1}\) is the basal emission rate at 30\(^\circ\text{C}\) leaf temperature and 1000\(\mu\text{mol m}^{-2} \text{s}^{-1}\) PAR, \(C_L\) and \(C_T\) are the factors representing the influences of light and temperature, respectively. \(C_T\) can be estimated as

\[
C_T = \frac{\exp\left(\frac{CT_1(T-T_1)}{RT_1}\right)}{1 + \exp\left(\frac{CT_1}{RT}\right)}.
\]

(4)

Then the natural logarithm of \(C_T\) is calculated as

\[
\ln C_T = \frac{CT_1}{RT_1} \left(1 - \frac{T}{T_1}\right) - \ln[1 + \exp\left(\frac{CT_1}{RT}\right)].
\]

(5)
Table 1. SOA tracers at the NC site (ng m\(^{-3}\)).

<table>
<thead>
<tr>
<th>Month</th>
<th>Temp.</th>
<th>RH</th>
<th>Isoprene</th>
<th>Monoterpenes</th>
<th>(\beta)-Caryophyllene</th>
<th>Aromatics</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul 2012</td>
<td>7.78</td>
<td>84</td>
<td>54.1 ± 22.9(^b)</td>
<td>0.45 ± 0.48</td>
<td>0.10 ± 0.13</td>
<td>0.37 ± 0.23</td>
<td>55.0 ± 22.5</td>
</tr>
<tr>
<td>Aug 2012</td>
<td>7.70</td>
<td>76</td>
<td>66.0 ± 69.3</td>
<td>0.46 ± 0.18</td>
<td>0.10 ± 0.11</td>
<td>0.35 ± 0.36</td>
<td>67.0 ± 69.1</td>
</tr>
<tr>
<td>Sep 2012</td>
<td>5.92</td>
<td>66</td>
<td>100 ± 118</td>
<td>1.06 ± 0.43</td>
<td>0.08 ± 0.11</td>
<td>0.22 ± 0.07</td>
<td>102 ± 118</td>
</tr>
<tr>
<td>Oct. 2012</td>
<td>−1.50</td>
<td>70</td>
<td>14.7 ± 19.0</td>
<td>1.79 ± 0.08</td>
<td>0.16 ± 0.01</td>
<td>0.15 ± 0.03</td>
<td>16.8 ± 18.9</td>
</tr>
<tr>
<td>Nov 2012</td>
<td>−14.9</td>
<td>63</td>
<td>2.04 ± 1.76</td>
<td>1.99 ± 0.56</td>
<td>0.20 ± 0.19</td>
<td>0.25 ± 0.15</td>
<td>4.48 ± 2.66</td>
</tr>
<tr>
<td>Dec 2012</td>
<td>−13.0</td>
<td>45</td>
<td>0.52 ± 0.73</td>
<td>nd</td>
<td>nd</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>Jan 2013</td>
<td>−16.1</td>
<td>30</td>
<td>0.38 ± 0.02</td>
<td>0.30 ± 0.04</td>
<td>0.03 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>0.78 ± 0.01</td>
</tr>
<tr>
<td>Feb 2013</td>
<td>−9.69</td>
<td>49</td>
<td>0.86 ± 0.45</td>
<td>0.52 ± 0.25</td>
<td>0.09 ± 0.02</td>
<td>0.09 ± 0.01</td>
<td>1.55 ± 0.22</td>
</tr>
<tr>
<td>Mar 2013</td>
<td>−7.83</td>
<td>41</td>
<td>1.56 ± 1.15</td>
<td>0.74 ± 0.59</td>
<td>0.23 ± 0.25</td>
<td>0.12 ± 0.17</td>
<td>2.65 ± 2.15</td>
</tr>
<tr>
<td>Apr 2013</td>
<td>−3.42</td>
<td>52</td>
<td>2.82 ± 0.20</td>
<td>1.24 ± 0.15</td>
<td>0.15 ± 0.03</td>
<td>0.20 ± 0.03</td>
<td>4.40 ± 0.11</td>
</tr>
<tr>
<td>May 2013</td>
<td>3.77</td>
<td>54</td>
<td>10.1 ± 9.70</td>
<td>1.11 ± 0.13</td>
<td>0.06 ± 0.06</td>
<td>0.27 ± 0.19</td>
<td>11.5 ± 9.97</td>
</tr>
<tr>
<td>Jun 2013</td>
<td>7.25</td>
<td>55</td>
<td>54.1 ± 42.9</td>
<td>0.83 ± 0.18</td>
<td>0.03 ± 0.04</td>
<td>0.30 ± 0.02</td>
<td>55.3 ± 42.8</td>
</tr>
<tr>
<td>Jul 2013</td>
<td>10.2</td>
<td>69</td>
<td>41.9 ± 4.1</td>
<td>1.41</td>
<td>0.07</td>
<td>0.49</td>
<td>43.9</td>
</tr>
<tr>
<td>Annual</td>
<td>−1.64</td>
<td>58</td>
<td>26.6 ± 44.2</td>
<td>0.97 ± 0.57</td>
<td>0.09 ± 0.10</td>
<td>0.25 ± 0.18</td>
<td>28.0 ± 44.2</td>
</tr>
</tbody>
</table>

\(^a\) Temperature and RH are monthly averages; \(^b\) one standard deviation; \(^c\) “nd” means not detected.

Table 2. SOA tracers in remote places on the global range (ng m\(^{-3}\)).

<table>
<thead>
<tr>
<th>Locations</th>
<th>Seasons</th>
<th>References</th>
<th>Isoprene(^a)</th>
<th>Monoterpenes(^a)</th>
<th>SOA tracers</th>
<th>(\beta)-Caryophyllene</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tibetan Plateau</td>
<td>Whole year</td>
<td>This study</td>
<td>26.0(3.6–184)(^b)</td>
<td>0.97(0.11–2.39)</td>
<td>0.09(nd–0.40)</td>
<td>0.25(nd–0.61)</td>
<td></td>
</tr>
<tr>
<td>Nam Co Lake</td>
<td>Summer</td>
<td>Li et al. (2013)</td>
<td>2.50(0.13–7.15)</td>
<td>2.95(0.30–10.4)</td>
<td>0.87(0.05–2.41)</td>
<td>NA(^c)</td>
<td></td>
</tr>
<tr>
<td>Qianghai Lake</td>
<td>Summer</td>
<td>Stone et al. (2012)</td>
<td>30.75(55–100)</td>
<td>13.25(56–31.3)</td>
<td>1.61(1.3–2.3)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Himalayas</td>
<td>Summer–autumn</td>
<td>Ding et al. (2013)</td>
<td>3.08(0.08–5.57)</td>
<td>1.60(1.35–5.5)</td>
<td>0.12(0.01–0.37)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Arctic Alert</td>
<td>Winter–Summer</td>
<td>Fu et al. (2009)</td>
<td>0.13(0.01–2.39)</td>
<td>0.09(0.02–1.5)</td>
<td>0.03(0.04–0.01)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Arctic Ocean</td>
<td>Summer</td>
<td>Fu et al. (2013)</td>
<td>4.00(0.16–31.8)</td>
<td>4.80(4.4–24.1)</td>
<td>0.017(0.005–0.048)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Low- to mid-latitude</td>
<td>Summer</td>
<td>Fu et al. (2011)</td>
<td>3.6(0.11–22)</td>
<td>2.7(0.02–15)</td>
<td>0.32(0.25)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Antarctic to Arctic</td>
<td>Summer</td>
<td>Hu et al. (2013)</td>
<td>8.5(0.018–36)</td>
<td>3.0(0.05–20)</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>North Pacific and Arctic</td>
<td>Summer</td>
<td>Ding et al. (2013)</td>
<td>0.62(0.12–1.45)</td>
<td>0.06(0.01–0.25)</td>
<td>0.002(nd–0.03)</td>
<td>nd(^d)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Compositions are different in different studies. \(^b\) data range in brackets. \(^c\) “NA” means not available. \(^d\) “nd” means not detected.

The ratio of MGA to MTLs (MGA/MTLs) was negatively correlated with temperature (Fig. 3a). Based on chamber results, the formation mechanisms of MGA and MTLs are quite different. MGA is produced under high-NO\(_x\) conditions, while MTLs are mainly formed under low-NO\(_x\)-free conditions (Surratt et al., 2010). Moreover, low RH (15–40 %) could enhance the formation of MGA in the particulate phase but not of MTLs (Zhang et al., 2011). In addition, high particle acidity would favor the formation of MTLs instead of MGA (Surratt et al., 2007). Although there are few data available in the TP, the aerosols are expected to be neutral at the remote NC site. Thus, the tracers were only in trace amount at the NC site.
MGA/MTLs exhibited the lowest values (less than 0.1) in the summer samples (Fig. 4). In the winter, both temperature and RH dropped to the lowest of the whole year. Low temperature reduced isoprene emission and low RH favored MGA formation. Thus, MGA/MTLs increased up to 0.8 in the winter samples (Fig. 4).

3.1.2 Terpene SOA tracers

The total concentrations of SOA\textsubscript{M} tracers (sum of five tracers) ranged from 0.11–2.39 ng m\textsuperscript{−3}. The levels of the SOA\textsubscript{M} tracers were consistent with those over the global oceans and the Arctic (Table 2). Among these traces, cis-pinonic acid was the major compound (54 %), with an annual average of 0.49 ± 0.38 ng m\textsuperscript{−3}, followed by pinic acid (0.22 ± 0.32 ng m\textsuperscript{−3}), 3-methyl-1,2,3-butanetricarboxylic acid (0.18 ± 0.25 ng m\textsuperscript{−3}), 3-hydroxyglutaric acid (0.08 ± 0.06 ng m\textsuperscript{−3}) and 3-hydroxy-4,4-dimethylglutaric acid (below MDL in the most samples). The monthly variation of SOA\textsubscript{M} tracers did not fully follow that of temperature (Fig. 2b). From July to November 2012 (period 1), temperature decreased to −15 °C; while SOA\textsubscript{M} tracer levels increased as high as 1.99 ng m\textsuperscript{−3}. After that, both temperature and SOA\textsubscript{M} tracers dropped to the lowest values in January 2013, and increased concurrently until April 2013 (period 2). During May to July 2013 (period 3), SOA\textsubscript{M} tracer levels exhibited slight variation, although the temperature kept increasing.

The seasonal variation of SOA\textsubscript{M} tracers could be influenced by monoterpenes emission and gas-particle partitioning. Monoterpenes emission rate (E\textsubscript{M}) is often assumed to be solely dependent on temperature (Guenther et al., 1993):

\[
E_M = E_{M} \times \gamma_T
\]

\[
\gamma_T = \exp(\beta(T - T_s))
\]

where \(E_M\) is monoterpenes emission rate at a standard temperature \(T_s\) (303 K), \(\gamma_T\) is the activity factor by temperature, \(\beta\) is an empirical coefficient usually taken to be 0.09 K\textsuperscript{−1} (Guenther et al., 1993), \(T\) is the leaf temperature.

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

\[
Y = M_0 \sum_{i} \frac{\alpha_i K_i}{1 + M_0 K_i}
\]

where \(M_0\) (µg m\textsuperscript{−3}) is the total concentration of absorbing organic material, \(\alpha_i\) is the mass stoichiometric coefficients of the product \(i\), \(K_i\) (m\textsuperscript{3} µg\textsuperscript{−1}) is the temperature-dependent partitioning coefficient of the semi-volatile compound \(i\). Assuming a constant activity coefficient and mean molecular...
weight, the partitioning coefficient, $K_i(T)$ at a certain temperature ($T$) could be estimated as (Sheehan and Bowman, 2001)

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

(9)

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

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

From July to November 2012 (period 1), high values of SOA$M$ tracers and SOA yield existed under low temperature, and SOA$M$ tracers were positively correlated with SOA yield ($r = 0.647$, $p < 0.05$, Fig. 5a). These suggested that the temperature effect on partitioning was the dominant process influencing SOA$M$ tracers’ variation during the period 1. From December 2012 to April 2013 (period 2), high values of SOA$M$ tracers and activity factor ($\gamma_T$) existed under high temperature, and SOA$M$ tracers were positively correlated with $\gamma_T$ ($r = 0.741$, $p < 0.05$, Fig. 5b). These suggested that the temperature effect on emission was the dominant process influencing SOA$M$ tracers’ variation during the period 2. The increase of SOA$M$ tracer concentrations during spring was also observed in the southeastern United States (Ding et al., 2008), resulting from the enhancement of monoterpenes emission in spring (Kim, 2001). From May to July 2013 (period 3), SOA$M$ tracer concentrations were relative stable, and there was no correlation of SOA$M$ tracers with $\gamma_T$ or SOA yield ($p > 0.05$). These might result from the counteraction of temperature effects on emission and partitioning during the summer.

Previous study proposed that cis-pinonic acid and pinic acid (P) were the first-generation products of SOA$M$ and only formed under low-NO$_x$ conditions (Eddingsaas et al.,
The dominance of cis-pinonic acid and pinic acid among SOA$_M$ tracers at the remote NC site indicated that SOA$_M$ was mainly formed under low-NOx conditions. Moreover, cis-pinonic acid and pinic acid could be further photo-degraded to high-generation products, e.g., 3-methyl-1,2,3-butanetricarboxylic acid (M) (Glasius et al., 2000; Jaoui et al., 2005; Szmigielski et al., 2007). And the ratio of cis-pinonic acid plus pinic acid to 3-methyl-1,2,3-butanetricarboxylic acid (P/M) could be applied to trace the aging of SOA$_M$ (Ding et al., 2011; Gómez-González et al., 2012). In the fresh chamber-produced $\alpha$-pinene SOA samples, the ratios of P/M were reported in the range of 1.51 to 3.21 (Offenberg et al., 2007). In this study, the ratio of P/M averaged 16.7 ± 20.9. Thus, SOA$_M$ was generally fresh at the NC site and should be mainly formed from local precursors. Figure 6 presents a negative correlation between P/M and temperature ($r = -0.560$, $p = 0.008$). Higher P/M ratios were observed in the fall and the winter, and lower P/M ratios occurred in the spring and the summer. Since temperature has a positive influence on photo-reaction rates, the higher temperature during the summer could accelerate the photo-chemistry in the air and result in P to M conversion becoming more efficient. Thus, SOA$_M$ in the summer was more aged than that in the winter.

The levels of SOA$_A$ tracer, $\beta$-caryophyllenic acid were in the range of below MDL to 0.61 ng m$^{-3}$. This anthropogenic tracer was not detected or reported in global remote areas (Table 2). Due to little human activity at the remote NC site, the highest concentration of DHOPA was 1–2 orders of magnitude lower than those (up to 52 ng m$^{-3}$) reported in the urban regions of the United States (Lewandowski et al., 2013) and China (Ding et al., 2014). DHOPA exhibited the higher concentrations in the summer and the lower levels in the winter (Fig. 2d).

Besides urban emissions from solvent and fossil fuel use, biomass burning is an important source of aromatics in many parts of the world (Lewis et al., 2013). The local dung or biomass burning (Duo et al., 2015; Xiao et al., 2015) may be potential sources of aromatics in the TP. Hence, DHOPA may come from the processing of biomass burning emission. Figure 7 exhibits the monthly variation of biomass burning tracer, levoglucosan during our sampling. The concentrations of levoglucosan ranged from 0.82 ng m$^{-3}$ (October 2012) to 4.55 ng m$^{-3}$ (April 2013) with a mean of 1.87 ± 1.14 ng m$^{-3}$. Apparently, the monthly variation trend of levoglucosan was quite different from that of DHOPA. And there was no correlation between DHOPA and levoglucosan ($p > 0.05$) (Fig. S6). These indicated that DHOPA at the NC site was not mainly from the processing of biomass burning emission. Since there were few anthropogenic sources near the remote NC site, the SOA$_A$ tracer should be not locally formed but mainly transported from upwind regions.

To check the potential source areas of anthropogenic emissions, the satellite data of population density (http://sedac.ciesin.columbia.edu/theme/population), aerosol optical thickness (AOT, http://neo.sci.gsfc.nasa.gov/), tropospheric NO$_2$ vertical column densities (VCD, http://avdc.gsfc.nasa.gov/), and surface CO (https://www2.acd.ucar.edu/mopitt) were analysis on the global scale. As shown in Fig. S7a, the northern Indian subcontinent was the most populated region of the world, with a population density of more than 1000 persons per km$^2$. Moreover, the plots of global
AOT, tropospheric NO$_2$ VCD, and surface CO (Fig. S7b–d) all illustrated that the northern Indian subcontinent, including Bangladesh, Nepal, northeastern India, and northwestern India were the global hotspots of these anthropogenic pollutants. Compared with the northern Indian subcontinent, the TP exhibited extremely low population density and low levels of AOT, surface CO, and NO$_2$ VCD (Fig. 8a–d). Besides these satellite data, a recent study at a site in northwestern India (Indo-Gangetic plain) witnessed extremely high levels (up to 2065 ng m$^{-3}$) of polycyclic aromatic hydrocarbons which were mainly formed from anthropogenic combustion processes (Dubey et al., 2015). All of these demonstrated that there were high anthropogenic emissions in the northern Indian subcontinent.

The TP features a monsoon climate (Cong et al., 2007; Ming et al., 2010; Zhao et al., 2013). Figure 9a presents the average trajectory of each cluster during our sampling in the whole year. The air masses over the NC were primarily from Bangladesh, Nepal and northeastern India (cluster 1, 32 %), northwestern India (Indo-Gangetic basin) (clusters 3–6, 55 %), and the Taklimakan Desert (cluster 2, 13 %) during the sampling period. In the summer, the prevailing southerly winds (cluster 1, Fig. 9b) passed through the heavily polluted areas in Bangladesh and northeastern India, and could bring anthropogenic pollutants into the TP. Previous studies in the TP have witnessed the enrichment of anthropogenic metals (Cong et al., 2007) and the enhancement of carbonaceous aerosols (Ming et al., 2010; Zhao et al., 2013) under the influence of summer monsoon. Thus, the increase of DHOPA levels at the NC site in the summer was mainly due to the transport of air pollutants from the upwind Bangladesh and northeastern India.

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

3.2 Source apportionment

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

$$f_{SOC} = \frac{\sum_i [\text{tri}]}{[\text{SOC}]}$$

where $\sum_i [\text{tri}]$ is the total concentrations of the tracers for a certain precursor. $[\text{SOC}]$ is the mass concentration of SOC. With these $f_{SOC}$ values and the measured SOA tracers in the ambient air, SOC from different precursors can be estimated in the atmosphere, with the assumption that the $f_{SOC}$ values in the chamber are the same as those in the ambient air. There is some degree of uncertainty in the SOA-tracer method due to the quantification with a single surrogate calibration standard (ketopinic acid) and the simplification of applying SOA tracers and conversion factors to calculate SOC in the ambient samples (Kleindienst et al., 2007). However, this method has been widely applied to attribute SOC from different precursors and proven to be able to provide reasonable results in the United States (Kleindienst et al., 2007; Stone et al., 2009; Lewandowski et al., 2013) and China (Hu et al., 2008; Guo et al., 2012; Peng et al., 2013; Ding et al., 2014). Lewandowski et al. (2008) found that the measured OC in the midwestern United States could be fully explained by primary OC from the chemical mass balance (CMB) model plus SOC from the SOA-tracer method, suggesting that the secondary organic tracer technique could be a valuable method for SOC estimation. Kleindienst et al. (2010) further compared the estimated SOC by the SOA-tracer method and other four independent methods (multiple regressions, CMB, carbon isotope and EC-tracer) in the southeastern United States, and found that these five methods matched well. Our previous study in the Pearl River Delta found SOC levels estimated by the SOA-tracer method were not only consistent with but also correlated well with those by EC-tracer method in summer (Ding et al., 2012). The SOC apportionment results were also comparable between the SOA-tracer method and the positive matrix factorization (PMF) model in Hong Kong (Hu et al., 2010).

The $f_{SOC}$ were reported as 0.155 ± 0.039, 0.023 ± 0.0046 and 0.00797 ± 0.0026 µg µgC−1 for isoprene (SOC$_I$), β-caryophyllene (SOC$_C$) and aromatics (SOC$_A$), respectively (Kleindienst et al., 2007). In this study, the same set of SOA tracers as reported by Kleindienst et al. (2007) were used for SOC estimation, including MGA and MTLs for SOC$_I$, β-caryophyllene acid for SOC$_C$ and DHOPA for SOC$_A$. For monoterpane SOC (SOC$_M$), nine tracers were involved in the source profile (Kleindienst et al., 2007). However, only five of the nine SOC$_M$ tracers were measured in the current study. Wang et al. (2013) compared the results from model prediction with field observation in the Pearl River Delta and pointed out that the SOA-tracer method would underestimate SOA$_M$, probably due to the mismatch of tracer compositions in the field and the source profile (Ding et al., 2014). To minimize the uncertainty caused by the mismatch in tracer compositions, the $f_{SOC}$ with the same five SOC$_M$ tracers (0.059 µg µgC−1) was computed using the chamber data from another study by the same research group (Offenberg et al., 2007). The same $f_{SOC}$ for SOC$_M$ was also applied to estimate SOC$_M$ in our previous study over China (Ding et al., 2014).

The uncertainty in the SOA-tracer method is induced from the analysis of organic tracers and the determination of the conversion factors. Based on the $E_A$ values in Table S1, the uncertainties in the tracer analyses were within 40 % for SOA$_I$ (only MGA and MTLs involved for SOC estimation), 95 % for SOC$_M$, 156 % for SOA$_C$, and 91 % for SOC$_A$. The uncertainties of $f_{SOC}$ were reported to be 25 % for isoprene, 48 % for monoterpenes, 22 % for β-caryophyllene and 33 % for aromatics (Kleindienst et al., 2007; Lewandowski et al., 2013). Considering these factors, the uncertainties of SOC apportionment were calculated through error propagation. The RSD were 47 % for SOC$_I$, 106 % for SOC$_M$, 157 % for SOC$_C$, and 96 % for SOC$_A$. On average, the RSD of the reconstructed SOC (sum of the four precursors) was 51 ± 11 %.

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

Biogenic SOC (sum of SOC$_I$, SOC$_M$, and SOC$_C$) dominated over SOC$_A$ at the NC site, on average accounting for 75 % of the estimated SOC. In the summer, SOC$_I$ was the major contributor with the SOC shares of 81 %. From the fall to the spring, SOC$_M$ became the major contributor, on average contributing 38 % to SOC. Although SOC$_A$ levels reduced in the winter, SOC$_A$ contributions elevated as high as 53 % in January 2013. The elevated OC and the higher SOC$_A$ contributions in the winter samples (Fig. 10) implied that the transport of anthropogenic pollutants from the Indian subcontinent might have a significant influence on carbonaceous aerosols over the remote NC during winter.

4 Conclusion

Seasonal trends of SOA tracers and origins were studied in the remote TP for the first time. SOA$_I$ tracers represented the majority among these compounds. The significant temperature dependence of SOA$_I$ tracers suggested that the seasonal variation of SOA$_I$ tracers at the NC site was mainly influenced by the isoprene emission. Due to the influence of temperature and relative humidity, the ratio of high-NO$_x$ to low-NO$_x$ products of SOA$_I$ (MGA/MTLs) was the highest in the winter and the lowest in the summer. The seasonal variation of SOA$_M$ tracers was impacted by monoterpenes emission and gas-particle partitioning. Due to the transport of air pollutants from the Indian subcontinent, DHOPA presented relatively higher concentrations in the summer and increased mass fractions in the winter. The SOA-tracer method was applied to estimated SOC from these four precursors. The annual average of SOC was $0.22 \pm 0.29 \mu gC m^{-3}$, with the biogenic SOC accounting for 75 %. In the summer, isoprene was the major precursor with its SOC shares of 81 %. In the winter when the emissions of biogenic precursors largely declined, the contributions of SOC$_A$ increased. At present, SOA origins and their seasonal variations are unclear in the remote high-elevation TP. The remote TP is connected to the densely populated Indian subcontinent. Our study implies that anthropogenic pollutants emitted there could be transported to the TP and influence SOC over the remote NC.

The Supplement related to this article is available online at doi:10.5194/acp-15-8781-2015-supplement.

Acknowledgements. This research was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (CAS) (XDA05100104/XDB05010200/XDA05100105), the National Science Foundation of China (41273116/41473099), and Youth Innovation Promotion Association, CAS.

Edited by: X. Xu

References


