Aircraft Measurement of Organic Aerosols over China

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Lower to middle (0.5–3.0 km altitude) tropospheric aerosols (PM$_{2.5}$) collected by aircraft over inland and east coastal China were, for the first time, characterized for organic molecular compositions to understand anthropogenic, natural, and photochemical contribution to the air quality. n-Alkanes, fatty acids, sugars, polyacids are detected as major compound classes, whereas lignin and resin products, sterols, polycyclic aromatic hydrocarbons, and phthalic acids are minor species. Average concentrations of all the identified compounds excluding malic acid correspond to 40–50% of those reported on the ground sites. Relative abundances of secondary organic aerosol (SOA) components such as malic acid are much higher in the aircraft samples, suggesting an enhanced photochemical production over China. Organic carbon (OC) concentrations in summer (average, 24.3 µg m$^{-3}$) were equivalent to those reported on the ground sites. Higher OC/EC (elemental carbon) ratios in the summer aircraft samples also support a significant production of SOA over China. High loadings of organic aerosols in the Chinese troposphere may be responsible to an intercontinental transport of the pollutants and potential impact on the regional and global climate changes.

1. Introduction
Air quality in China is getting worse following the economic expansion, which has continued to increase in the past decades. Emissions of particles, volatile organic compounds, and nitrogen oxides have sharply increased in urban areas of this country (1). The rapid growth in the fossil fuel consumption in East Asia including China has resulted in the excess emissions of nitrogen oxides compared to those from Europe and North America (2, 3). Menon et al. (4) reported that anthropogenic aerosols (e.g., black carbon) in China have led to the increase of summer floods in the south and drought in the north in the past decades by altering the local and regional atmospheric circulation. Around 20–30% of carbonaceous aerosols in the global atmosphere are generated in China (5). These aerosols, together with the soil dusts originated from the deserts in the north/west regions, are occasionally transported to the western United States across the North Pacific Ocean (6). Thus, atmospheric particles over China have potential impacts on air quality, human health, and climate on a global scale.

Chinese inorganic aerosols have been seriously studied because the desert areas in the country are considered as the source of Asian dust storms (7), and the $\mathrm{SO}_2$ emissions from its coal burning are thought as the origins of acid rain in East Asia (2, 8, 9). However, organic aerosols have not been seriously studied in the country and only a few of measurements have been documented so far (10, 11). To our knowledge, the Chinese tropospheric aerosols collected by aircraft have never been reported for organics on a molecular level, although aviation measurement of the inorganic aerosols was conducted (12). There are few measurements reporting on organic carbon (OC)/elemental carbon (EC) and molecular composition of organic aerosols over the Yellow Sea and East China Sea (13–15), an outflow region of Chinese aerosols. In this study, we conducted aircraft campaigns to understand the spatial and vertical distributions of organic aerosols over inland China. Along with the results reported for ground surface (11), i.e., observation for organic aerosols from 14 Chinese megacities, we discuss the seasonal and spatial distributions of molecular compositions of the Chinese tropospheric aerosols.

2. Experimental Section

2.1. Aerosol Collection. Aircraft campaigns were carried out over China in winter (12/25/2002–01/06/2003), summer (08/08–09/13, 2003), and spring (05/19–06/10/2004) using Yun-12 and Yun-5 airplanes. PM$_{2.5}$ aerosols were collected on precombusted quartz fiber filter (Φ 90 mm) using a medium-volume air sampler (made by Beijing Geological Instrument Factory, China) under a flow rate of 78 L min$^{-1}$ at the altitudes of 0.5–3 km. The sample was not denuded in this study. Although some volatile organics could be in part adsorbed on the quartz fiber, we feel that positive artifacts should be minimal and not seriously affect the results (16). Flight tracks and other detailed sampling information are shown in the Supporting Information section Figure S1. During the campaigns, we collected 18 winter samples over the east coast and 15 summer and 14 spring samples over the inland. Collection efficiency of PM$_{2.5}$ particles was more than 90% for the aircraft sampling system, which was tested using the methods reported by Pui et al. (17) and Muyschondt et al. (18). Concentrations of the organic compounds reported here at ambient temperature and pressure were averaged based on the round flights between two flight stops or on the local flights (Figure S1).

2.2. Extraction and Derivatization. Details of the sample extraction and derivatization are presented elsewhere (11, 19). Briefly, aliquots of the sample and blank filters were extracted three times with a mixture of dichloromethane and methanol (2:1 v/v) each for 10 min under ultrasonication. The extracts were then reacted with 50 µL of N,O-bis-(trimethylsilyl) trifluoroacetamide with 1% trimethylsilyl chloride and 10 µL of pyridine at 70 °C for 3 h, and diluted with 40 µL of n-hexane containing C$_{13}$ n-alanine (1.43 ng µL$^{-1}$, internal standard) prior to GC–MS injection.

2.3. Gas Chromatography–Mass Spectrometry. Gas chromatography–mass spectrometry (GC–MS) determination of the derivatized fraction was conducted using a
Hewlett-Packard 6890 GC interfaced to a Hewlett-Packard 5973 MSD. The GC separation was performed on a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., 0.5 μm film thickness) with the GC oven temperatures programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ and then to 300 °C at 5 °C min⁻¹ with final isotherm held at 300 °C for 16 min. The sample was injected on a splitless mode at the injector temperature of 280 °C. The mass spectrometer was operated on an electron impact mode (EI) at 70 eV and scanned from 50 to 650 daltons. GC-MS response factors were determined using authentic standards. More details of the method including recoveries are described elsewhere (11, 19).

A field blank was mounted onto the sampler for seconds without drawing air during campaign. Each blank or sample filter was placed in a clean glass jar sealed with a Teflon-lined cap, transported to the laboratory, and stored at −20 °C prior to analysis. The field blank filters were also analyzed by the procedure described above; their results showed no significant contamination except for some fatty acids (i.e., C₁₄:₀, C₁₅:₀, C₁₆:₀, C₁₇:₀, and C₁₈:₀), whose data were not used here. Data reported here were all corrected for the blanks.

3. Results and Discussion

Figure 1 presents the seasonal and spatial distributions of various compound classes in the Chinese aerosols. Eight classes of organic compounds were detected in the samples, of which n-alkanes, fatty acids, sugars, polyacids are major compound classes, while lignin and resin products, sterols, polycyclic aromatic hydrocarbons (PAHs), and phthalic acids are minor species (see Table 1 and for more details see Table S1). Over the east coastal China malic acid was the most abundant single compound detected in the winter aerosols (Table S1), followed by levoglucosan, glucose, C₁₉/C₂₀ n-alkanes, and cholesterol. In the inland summer and spring samples, C₂₁/C₂₂ n-alkanes was most abundant, followed by levoglucosan, malic acid and unsaturated fatty acids (C₁₆:₁ and C₁₈:₁). Such spatial distributions in the aircraft samples are different from those on the ground surface, where levoglucosan was one of the most abundant compounds whereas malic acid was rather minor (11). Total concentration of organic compounds quantified in the coastal aircraft PM$_{2.5}$ aerosols was 474 ± 174 ng m⁻³ during the winter, while in the inland aerosols, the total amount was 410 ± 180 ng m⁻³.

FIGURE 1. Spatial and seasonal distributions of organic aerosols in the lower/middle Chinese troposphere. The winter columns represent the average values of organic aerosols collected between two flight stops. Similarly, the second and fourth summer and spring columns also represent the averages between two flight stops, but other summer and spring columns represent the averages from the local flights (flight numbers and tracks shown in Figure S1).
in the summer and 337 ± 245 ng m\(^{-3}\) in the spring (Table 1).

### 3.1. Major Organic Compound Class \(n\)-Alkanes

Homologues of normal alkanes (C\(_{16}\)–C\(_{34}\)) were detected in the aircraft samples with a maximum in a range of C\(_{19}\)–C\(_{22}\) (Figure 2a). Concentrations of total \(n\)-alkanes in winter over coastal China were 44–316 ng m\(^{-3}\) (average 157 ng m\(^{-3}\)) whereas those over inland China were 62–349 ng m\(^{-3}\) (205 ng m\(^{-3}\)) in summer and 57–615 ng m\(^{-3}\) (199 ng m\(^{-3}\)) in spring (Table 1). There was no significant difference between spring and summer over inland China (Figure 1a) due to the reason mentioned below. The spring campaign was made on May 19 to June 10, 2004; this period is actually beginning of a summer rather than a typical spring. Therefore, there is no significant seasonal difference in concentrations of the organic aerosols between the 2003 summer and 2004 spring samples.

In general, fossil fuel combustions emit more lower molecular weight (LMW) \(n\)-alkanes with no odd/even carbon number preference, whereas vegetations emit more higher molecular weight (HMW) \(n\)-alkanes with a strong odd/even carbon number preference (20). The \(n\)-alkanes peaked at C\(_{18}\)/C\(_{19}\) in winter, and the peak shifted to C\(_{21}\)/C\(_{22}\) in summer and spring (Figure 2a). Carbon preference index (CPI, concentration ratios of odd-to-even carbon number \(n\)-alkanes) (21) in the winter, spring and summer are 1.09 ± 0.03.

### TABLE 1. Concentrations (ng m\(^{-3}\)) of Organic Compounds in Chinese PM\(_{2.5}\) Aerosols Collected by Aircraft (0.5–3.0 km Altitude, 2003–2004)

<table>
<thead>
<tr>
<th>compounds</th>
<th>east coast</th>
<th></th>
<th></th>
<th>inland</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>winter (n = 18)</td>
<td></td>
<td></td>
<td>winter (n = 15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>max</td>
<td>mean</td>
<td>std</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>(n)-alkanes</td>
<td>44</td>
<td>316</td>
<td>157</td>
<td>69</td>
<td>62</td>
<td>349</td>
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<tr>
<td>fatty acids(^a)</td>
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<td>68</td>
<td>35</td>
<td>30</td>
<td>223</td>
</tr>
<tr>
<td>sugars</td>
<td>39</td>
<td>384</td>
<td>109</td>
<td>83</td>
<td>6</td>
<td>123</td>
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<tr>
<td>polyacids</td>
<td>21</td>
<td>120</td>
<td>61</td>
<td>27</td>
<td>5</td>
<td>65</td>
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<tr>
<td>lignin and resin products</td>
<td>4</td>
<td>13</td>
<td>9</td>
<td>3</td>
<td>6</td>
<td>42</td>
</tr>
<tr>
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<td>65</td>
<td>28</td>
<td>16</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>PAHs</td>
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<td>54</td>
<td>24</td>
<td>15</td>
<td>4</td>
<td>42</td>
</tr>
<tr>
<td>phthalic acids</td>
<td>4</td>
<td>76</td>
<td>18</td>
<td>18</td>
<td>4</td>
<td>42</td>
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<td>860</td>
<td>474</td>
<td>174</td>
<td>145</td>
<td>689</td>
</tr>
<tr>
<td>OC, (\mu g) m(^{-3})</td>
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<td>na(^c)</td>
<td>na(^c)</td>
<td>na(^c)</td>
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</tr>
<tr>
<td>EC, (\mu g) m(^{-3})</td>
<td>na(^a)</td>
<td>na(^c)</td>
<td>na(^c)</td>
<td>na(^c)</td>
<td>1.0</td>
<td>5.0</td>
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<tr>
<td>OC/EC</td>
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<td>na(^c)</td>
<td>na(^c)</td>
<td>na(^c)</td>
<td>7.3</td>
<td>23.0</td>
</tr>
</tbody>
</table>

\(^a\) Fatty acids excluding C\(_{14:0}\)–C\(_{18:0}\). \(^b\) nd is not detectable \(^c\) na is not available.
n-alkanes in the aerosol particles are mainly derived from fossil fuel combustion, especially in winter due to coal burning for house heating (19, 22). The CPI values in the aircraft samples were similar to those on the ground surface (CPI: 1.17 ± 0.14 in winter versus 1.16 ± 0.12 in summer) (11), but were slightly lower than those over the northwestern Pacific (average, 1.3) (15), further supporting that n-alkanes in the Chinese tropospheric aerosols were more influenced by fossil fuel combustion.

Over the coastal areas the wintertime concentrations of n-alkanes in the aircraft samples were approximately 50% of those reported on the ground surface (average, 320 ng m⁻³) (Figure 3a), whereas over the inland areas the summertime concentrations in the aircraft samples were slightly lower than those on the ground surface (236 ng m⁻³) (Figure 3b), although concentrations of n-alkanes did not show a vertical trend in the altitudes of 0.5–3 km. We found that the concentrations of n-alkanes obtained by aviation over China (spring average, 199 ng m⁻³) are several times higher than those reported over the northwestern Pacific (29 ng m⁻³) by aircraft measurements (15), demonstrating a high loading of organic aerosols in the lower/middle troposphere over China.

3.2. Fatty Acids. A homologous series of fatty acids (C₁₀₀ to C₂₄₀) was detected in the aerosols as a major compound class. Unfortunately, data of C₁₆₀–C₁₈₀ fatty acids could not be used here because of their significant occurrence in the blanks, and thus are not taken into consideration for the comparison of both aircraft and ground surface samples. The wintertime concentrations (68 ± 35 ng m⁻³) of fatty acids excluding C₁₄₀–C₁₆₀ in the aircraft samples collected over the coastal area are 3 times lower than those (286 ± 55 ng m⁻³) reported for the ground surface aerosols (Figure 3a), while over the inland regions, the summertime concentrations (97 ± 55 ng m⁻³) in the aircraft samples were about one-sixth of those (595 ng m⁻³) reported on the ground (11) (Figure 3b). This summertime concentration was found to be higher than that in the spring samples (27 ± 29 ng m⁻³) (Table 1). Fatty acids in the aircraft samples over China are 1–2 orders of magnitude more abundant than those collected over the northwestern Pacific (average, 5.4 ng m⁻³) (15).

FIGURE 3. Comparison of organic aerosols observed by aircraft and on ground surface (The ground surface concentrations in winter are the averages from five east coastal Chinese cities, i.e., Hangzhou, Shanghai, Qingdao, Tianjin, and Beijing, and the ground surface concentrations in summer are averaged values from three continental cities in mid China, i.e., Wuhan, Chongqing and Xi’an. Data calculated from Wang et al., (17)).

Wintertime concentration of unsaturated fatty acids (sum of C₁₆₁, C₁₈₁, and C₂₂₁) in the aircraft samples collected over the coastal region was 18.6 ng m⁻³ (on average, Table S1), whereas over the inland area springtime and summertime concentrations of the unsaturated fatty acids in the aircraft samples were 2.0 and 37.5 ng m⁻³. The reason why the seasonal difference was so big is still unknown and this needs more study. Concentrations of the unsaturated fatty acids in the 0.3–5 km altitude of atmosphere are around 5–10 times less than those (186 ng m⁻³ in winter versus 125 ng m⁻³ in summer) reported on the ground surface (11), indicating an enhanced photochemical oxidation of double bonds occurring in the lower/middle troposphere.

3.3. Sugars and Polyacids. Eight saccharides were detected in the aircraft samples with concentrations of 109 ± 83 ng m⁻³ in winter, 31 ± 25 ng m⁻³ in summer, and 52 ± 63 ng m⁻³ in spring (Table 1). Summer and spring aircraft samples over inland China showed a predominance of levoglucosan among sugar species (Figure 2b). However, winter samples from the coastal area are dominated by not only levoglucosan but also fructose, glucose, and sucrose, indicating the different sugar sources between the inland and coastal regions. Concentrations of sugars in the aircraft samples are much less than those reported for the ground sites (262 ng m⁻³ during winter in the coastal cities, 329 ng m⁻³ during summer in the inland cities) (Figure 3), but are much higher than those over the northwestern Pacific (4.1–22.5 ng m⁻³) (15). Interestingly, levoglucosan showed a sharp decrease in the concentrations with an increase in the altitude in winter (Figure 4a).

Levoglucosan is a specific marker produced by burning cellulose materials, whereas primary saccharides such as fructose, glucose, sucrose, and trehalose are major fraction of soil organic matter (23, 24). Reduced sugars (e.g., arabitol and mannitol) are products of fungal metabolism (24, 25). Thus, this study suggests that emissions from biomass burning and suspended soil dusts are two important sources for the organic aerosols in the lower troposphere over China. In the coastal aircraft samples, sugars are less abundant in the south than in the north (Figure 1c), probably due to more suspended soil dust in north China by wind erosion process.
are detected in the aircraft samples with a predominance of dehydroabiatic acid. Those compounds are produced by pyrolysis of lignin and pine resin. Their total concentrations are 9 ± 3 ng m⁻³ in winter over coastal China, and 20 ± 10 ng m⁻³ in summer and 0.8 ± 0.4 ng m⁻³ in spring over inland China (Table 1). They are lower than those reported for the ground surface samples (26 ng m⁻³ in the coast and 24 ng m⁻³ in the inland) (Figure 3) (11), although the molecular distributions are similar. Their occurrences in the aircraft samples further suggest an important contribution of biofuel combustion and/or biomass burning to the lower/middle tropospheric aerosols over China.

Two sterols (cholesterol and β-sitosterol) are quantified in the aerosols with wintertime concentrations of 28 ± 16 ng m⁻³ over the coastal region and summertime and springtime concentrations of 9 ± 6 and 6 ± 4 ng m⁻³ over the inland area (Table 1). Concentrations of sterols in the aircraft samples were 2–4 times lower than those (88 ng m⁻³ in winter versus 37 ng m⁻³ in summer) reported on the ground surface (Figure 3) (11). Cholesterol is much more abundant than β-sitosterol and detectable in all the samples, whereas β-sitosterol is detected only in a few winter samples (Table S1). β-sitosterol can be emitted to the atmosphere by burning plant leaves (21), and cholesterol is a tracer for meat cooking (27). Occurrence of cholesterol in the samples indicates that Chinese cooking activities are also important sources of organic aerosols.

3.4.2. PAHs and Phthalic Acids. PAHs (28 species) were detected only in the winter samples collected over coastal China with total concentration of 24 ± 15 ng m⁻³ (Table 1), which is 4 times lower than those obtained on the ground surface (11). The PAHs with 2 rings (2-methylnaphthalene is dominant) (Figure 2c) are detectable in the aircraft samples rather than in ground surface aerosols (11), probably due to the decreased volatility under the lower ambient temperature conditions in the middle troposphere. Among the 3- to 7-ring PAHs, benzo(b)fluoranthene (BbF) is the most abundant species, being consistent with the results of ground-surface aerosols (11) and the aircraft samples from East China Sea (15). Concentrations of total PAHs in the aircraft samples over the coastal area are about 2 orders of magnitude higher than those reported over East China Sea (0.27 ng m⁻³) (15). PAHs in the Chinese aerosols are mainly derived from household coal combustion, where BbF has been reported as the dominant solid-phase PAH (11). Abundant 3–7 ring PAHs with a predominance of BbF in the winter aerosols further demonstrate the importance of coal burning as a source of PAHs in the country.

A clear decrease in the PAH concentrations as a function of altitude was found for the HMW species (sum of 4-, 5-, and 6-ring) (Figure 4b), probably due to the more photochemical degradation in the upper troposphere. Benzo(a)pyrene (BaP) is photochemically more labile than its isomer benzo(e)pyrene (BeP). The average ratio of BaP/BeP for the aircraft samples was 0.38 ± 0.44, which is lower than those (0.86 ± 0.34) reported in winter for the ground level aerosols (11). Photochemical degradation of PAHs may be important in the lower/middle troposphere over China, in which radiation is stronger than on the ground surface.

Three phthalic acids (α-, m-, and p- isomers) are detected in the aircraft samples with total concentrations of 18 ± 18, 17 ± 13, and 21 ± 23 ng m⁻³ in winter, summer, and spring, respectively (Table 1), which are 10 times more abundant than those (average, 1.5 ng m⁻³) reported over the northwestern Pacific (15). Their molecular distributions are characterized by a predominance of α-phthalic acid, being consistent with those reported by the aerial observation over East China Sea (15). Their concentrations generally well correlated each other (0.90 ≥ R² ≥ 0.70, p = 0.01), suggesting a common source for these compounds and/or similar fates.
in photooxidation and transport processes in the atmosphere. In the spring samples, m- and p- phthalic acids also showed a strong linear correlation ($r^2 = 0.91, p = 0.01$), but o-phthalic acid did not correlate with two others, indicating its different origin and/or different atmospheric lifetime. Interestingly, concentrations of p-phthalic acid in the three seasons clearly decreased with an increase in the altitude (Figures 4c, 4d, and 4e).

OC in summer gave a very high concentration (24.3 ± 15.1 μg m⁻³), being consistent with that on the ground surface (24.3 ± 12.9 μg m⁻³) (Figure 3b) (11). In contrast, EC concentrations (1.8 ± 1.1 μg m⁻³) in the summer aircraft samples are much lower than those (7.2 ± 5.5 μg m⁻³) on ground surface (11), making OC/EC ratio much higher (14.0 ± 4.6) in the aircraft samples than that (4.0 ± 1.2) on ground sites (11) (Figure 3b). The aircraft measured OC and EC were more abundant than those (4.5 ± 1.4 μg m⁻³ for OC and 1.2 ± 0.7 μg m⁻³ for EC) (14) in the free troposphere over the North Pacific. The abundant OC in the Chinese aircraft samples is consistent with ACE-Asia data reported by Heald et al. (28), indicating a large, sustained source of secondary organic aerosols in the free troposphere over East Asia from oxidation of long-lived volatile organic precursors and its potential impact on radiative forcing of climate.

In summary, concentrations of total organic components detected in the 0.5–3.0 km tropospheric aerosols correspond to 22–92% (42 ± 24%) of those reported for ground surface aerosols in the east coast during winter and 9–87% (45 ± 34%) of those for the inland during the summer (11). Although around 95% of organic aerosols are not characterized in this study, they may include dicarboxylic acids, amino acids, humic like substances, protein, and others.

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Supporting Information Available
A table showing the concentrations of single organic compounds of PM2.5 aerosols and a figure detailing the flight tracks of the collection campaigns. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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