Wintertime Organic Aerosols in Christchurch and Auckland, New Zealand: Contributions of Residential Wood and Coal Burning and Petroleum Utilization

HAOBO WANG,¹* KIMITAKA KAWAMURA,¹ AND DAVID SHOOTER¹
Institute of Low-Temperature Science, Hokkaido University, Sapporo 060-0819, Japan, and School of Geography and Environmental Science, Tamaki Campus, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Wintertime PM₁₀ samples from two New Zealand cities (Christchurch and Auckland) have been characterized using gas chromatography—mass spectrometry for biomass burning tracers, hopanes, n-alkanes, fatty acids, n-alkanols and sugars. The aerosol samples of Christchurch, which were heavily influenced by residential wood and coal burning, showed substantially higher ambient concentrations for most of the organic compounds than those of Auckland, where major sources of aerosols were vehicular emissions and sea-salt. Mass ratios between the biomass burning tracers studied were found to be significantly different (e.g., β-sitosterol to nssK⁺ ratios were more than three times higher in Christchurch than in Auckland), although levoglucosan to nssK⁺ ratios were similar at both sites. We also estimated, for the first time using stereochemical configurations of hopanes, that 60% of fossil fuel emissions came from petroleum utilization with the remaining 40% being from coal burning in Christchurch. In contrast, contribution of coal burning was negligible in Auckland. Moreover, contributions of most biomass burning tracers to organic carbon (OC) were significantly higher in Christchurch than in Auckland. On the other hand, saccharides (excluding levoglucosan) and hopanes accounted for larger fractions of OC in Auckland. This study demonstrates that intensive wood and coal burning can significantly affect organic aerosol composition in an urban environment.

Introduction

Organic aerosols in the atmosphere have relevance to radiative forcing of climate (1), pollution transport (2), health effects (3, 4), and pollution source apportionment (5–8). Extensive studies on organic aerosols in relation to biomass burning have been reported (7). Organic compounds emitted from residential wood burning have also been characterized (9–12). However, research on organic aerosol composition has been limited in an urban environment that is significantly influenced by domestic wood and coal burning. Residential wood and coal burning, which significantly emits particulate matter to the atmosphere, is still widely used as an energy source for home heating and cooking in many urban and rural areas throughout the globe (7, 13).

In this study, daily PM₁₀ (particles with a diameter <10 μm) samples were collected in the winter of 2004 from two New Zealand cities: Christchurch and Auckland, which have quite different relative strengths of major emission sources for air pollutants. Christchurch (population ca. 0.4 million) has been experiencing a serious air pollution problem in winter for many years, where domestic wood and coal burning is the dominant emission source (14, 15). In contrast, previous research has found that the major sources of PM₁₀ in Auckland (the largest New Zealand city with a population of ca. 1.3 million) are vehicular emissions and sea-salt with a relatively small contribution from home heating (16, 17). The main objective of this research is to better understand the influence of domestic wood and coal burning on the molecular characteristics of organic aerosols in an urban environment.

This article reports atmospheric concentrations of 69 organic compounds in the New Zealand aerosol samples. Possible sources and source strengths for the urban organic aerosols are studied based on their molecular characteristics. Contributions of individual compound classes to total organic carbon (TOC), water-soluble organic carbon (WSOC), and water-insoluble organic carbon (WIOC) are also discussed.

Experimental Section

Aerosol Sampling. Atmospheric PM₁₀ aerosols were collected on preheated (450 °C, >3 h) Whatman quartz fiber filters (20 × 25 cm²) using high volume samplers (Graseby Anderson/GMW, equipped with a Thermo Anderson PM₁₀ sampler head/10 μm inlet) at a flow rate of ca. 1.1 m³ min⁻¹. The samplers were fixed on the ground with the sampling heads being ca. 2 m above the ground level. Each filter had a sampling duration of ca. 24 h. Field blank filters were also collected in the same way except for a zero flow rate. The exposed filters were stored in a freezer at −20 °C prior to analysis.

In Christchurch, samples were collected at Coles Place starting from 9 am every day from 17 June to 7 July 2004. This site was located within a purely residential area and well away from major road systems. In Auckland, sampling was conducted at the Tamaki Campus, the University of Auckland starting from around 1 pm every day (17 June to 8 July 2004).

Extraction and Derivatization. An aliquot (ca. 1/20) of each filter was extracted three times with a mixture of dichloromethane and methanol (2:1, v/v) under sonication for 10-min. each. The extracts were filtered through a Pasteur pipet packed with quartz wool, concentrated by a rotary evaporator and then to dryness under blow-down with pure nitrogen gas. To convert carboxylic acids, alcohols and sugars to their trimethylsilyl derivatives, the extracts were reacted with 50 μL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h (18). After the reaction, the derivatized extracts were diluted with an appropriate volume of n-hexane containing 1.43 ng μL⁻¹ of the internal standard (C₁₃n-alkane).

Gas Chromatography—Mass Spectrometry Analyses. Gas chromatography—mass spectrometry (GC—MS) analyses of the derivatized extracts were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 MSD. The separation was achieved on a HP-5 fused silica capillary column (25 m × 0.25 mm i.d., 0.5 μm film thickness). The GC conditions and MS data analysis protocol are the
same as those reported by Wang and Kawamura (19). Field and laboratory blank filters were processed and analyzed in the same way as the samples. Only a few compounds (C16:0 and C18:0 fatty acids, glycerol, and levoglucosan) were detected at a noticeable level in the blanks, with their signals for blank filters being less than 5% of those for real samples. Concentrations of the quantified organics reported here have been corrected for the field blanks. Recoveries of the quantified organic compounds were generally better than 80%. The recoveries were studied by spiking certain amounts

FIGURE 1. Salient features of the GC—MS data for total extracts of aerosol samples from Christchurch (June 28–29, 2004) and Auckland (June 22–23, 2004). The Christchurch sample was heavily influenced by wood and coal burning, while the main sources for the Auckland sample were vehicular exhausts and sea-salt with a minor contribution from wood and coal burning.
of authentic standards on to blank filters that were then analyzed in a same way as the samples, but labeled standards were not used.

Detailed procedures for the measurements of carbonaceous components and inorganic ions can be found in the Supporting Information (SI). Their atmospheric concentrations in the samples have been reported elsewhere (20).

Results and Discussion

General Description of GC–MS Traces and Concentrations.

Detailed atmospheric concentrations of the quantified organic compounds in the samples can be found in the SI (Table S1). Carbon preference index (CPI) for n-alkanes and n-alkanoic acids, and average chain length (ACL, concentration-weighted mean carbon chain length) (21) for n-alkanes, n-alkanoic acids and n-alkanols are also given in this table. Most of the compounds show substantially higher concentrations in Christchurch than in Auckland, with median total concentrations of individual compound classes being at least three times higher in Christchurch. In both cities, levoglucosan is the most abundant species, and fatty acids concentrations of individual compound classes being at least three times higher in Christchurch. In both cities, levoglucosan is the most abundant species, and fatty acids are the most abundant compound class among aliphatic lipids. Figure 1 presents typical GC–MS traces at total ion current (TIC), m/z 85 for n-alkanes, m/z 117 for n-alkanoic acids, m/z 75 for n-alkanols, and m/z 191 for hopanes (18) for a Christchurch sample (heavily influenced by wood and coal burning) and an Auckland sample (vehicular exhausts and sea-salt as the major sources). Different patterns in the traces can be readily observed between two cities. For example, relative responses of biomass burning tracers (levoglucosan, vanillic, and dehydroabietic acids) are significantly weaker in Auckland than in Christchurch and molecular distributions (relative abundances) of n-alkanes, n-alkanoic acids, n-alkanols, and hopanes are quite different between the two cities.

Biomass Burning Tracers. Biomass burning injects numerous organic compounds into the atmosphere (7). Levoglucosan has been proposed as a major marker of biomass burning, which is produced in large quantities during pyrolysis of cellulose (22, 23). As seen in Table S1, median concentration of levoglucosan in Christchurch (772 ng m⁻³) is ca. 5 times higher than that in Auckland. Indeed, its concentrations are comparable to NO₃⁻ and SO₄²⁻ in the Christchurch samples, but significantly lower than these two major inorganic ions in Auckland (20). This confirms that wood burning for home heating was an important emission source in Christchurch in the winter.

β-Sitosterol can also be used as a general biomass burning tracer, which is present in all vegetations (7). On the other hand, dehydroabietic acid is a key marker for the smoke from conifer wood (a soft wood) burning (24). Burning of lignin in wood yields phenolic tracers in the smoke. The major markers for lignin burning include syringic acid being indicative of hardwood, and vanillic acid being indicative of mainly softwood but also hardwood (25, 26). Although all the marker compounds were detected in the samples, their median concentrations were more than 15 times higher in Christchurch than in Auckland (Table S1). It should be noted that the population size in Christchurch is less than one-third of that in Auckland and that wind speeds during the sampling were found to be quite similar in the two cities (overall means were around 2.2 m s⁻¹). The significantly higher concentrations of biomass burning tracers found in Christchurch most likely reflect the much more intensive domestic wood burning occurring in the city. Other factors, however, may have also contributed to the significant concentration differences. For example, thermal inversion layers often form in Christchurch winter (14). In contrast, the Auckland air generally has a better dispersion since Auckland is situated in an isthmus.

Compared to the wintertime concentrations of the biomass burning markers at other urban sites, concentrations of levoglucosan in Christchurch are higher than those reported for Gent, Belgium (PM₁₀) (27) and Nanjing, China (PM₁₂) (19), but lower than those in Bakersfield and Fresno, USA (PM₁₀) (11). However, concentrations of β-sitosterol and vanillic acid in Christchurch are higher than those in Bakersfield, Fresno and Nanjing. In contrast, concentrations of the biomass tracers in Auckland are lower than those at all the above-mentioned sites.

Concentrations of all the biomass burning tracers discussed above, including nonsea-salt K⁺ (nssK⁺) (28), were found to be highly variable but to correlate strongly with each other (in Christchurch, R (correlation coefficient) > 0.90 and p (significance) < 0.01; in Auckland, R > 0.84 and p < 0.01 except for the correlation between dehydroabietic acid and β-sitosterol where R = 0.76). This suggests that these compounds are produced from common sources and/or similar meteorological processes govern their concentrations. Figure 2 presents median mass ratios for various biomass burning tracers. Interestingly, median ratios of levoglucosan to nssK⁺ (Levo/nssK⁺) in the two cities are similar (ca. 3).
Further studies are required to test whether this is a common ratio for wood burning emissions. In contrast, median ratio of $\beta$-sitosterol to nssK$^+$ (Sitost/nssK$^+$) is significantly lower in Auckland (0.03) than in Christchurch (0.1). One reason for this might be that $\beta$-sitosterol can also be injected into the atmosphere directly from vegetation by wind ablation (29), a production process different from that of nssK$^+$. Moreover, Christchurch has higher median ratios of syringic to dehydroabietic acids (Syr/Dhey) and vanillic to dehydroabietic acids (Van/Dhey) than Auckland, suggesting that more hard wood was burned relative to soft wood in Christchurch than in Auckland. Cholesterol has multiple sources including meat cooking (30, 31) and marine algae (29). A significantly lower median ratio (0.09) of cholesterol to $\beta$-sitosterol (Chol/Sitost) was found in Christchurch than that (0.46) in Auckland.

**Hopanoid Hydrocarbons.** Hopanoid hydrocarbons (hopanes) are specific biomarkers of petroleum (8, 32, 33) and coal (13). The stereochemical configurations at $C_{27}$ and $C_{28}$ positions of hopanes are often used to determine the maturity of a geological sample, where hopanes with configurations of 17$\beta$(H), 21$\beta$(H) ($\beta\beta$) are immature, 17$\beta$(H), 21$\alpha$(H) ($\beta\alpha$) are moderately mature and 17$\alpha$(H), 21$\beta$(H) ($\alpha\beta$) are fully mature (13). Their thermodynamic stability increases in the same order (8, 13). Trace levels of 11 hopanes ($C_{27}$ to $C_{38}$, but no $C_{26}$, see Table S1) were detected in the samples. $C_{29}\alpha\beta$ (sum of S and R configurations) was the most abundant, followed by $C_{30}\alpha\beta$ and $C_{30}\beta\beta$, except for about half of the Auckland samples in which $C_{30}\beta\beta$ was more abundant than $C_{30}\alpha\beta$. The $\alpha\beta$ configurations were detected at significantly higher concentrations than their corresponding $\beta\alpha$ configurations, indicating that highly matured petroleum is used in both cities.

In typical petroleum, the extended 17$\alpha$(H), 21$\beta$(H) hopane homologues $\geq C_{31}$ have the $C_{29}$ epimers at an equilibrium $S/(S+R)$ ratio of ca. 0.6 (34). However, in coal burning emissions the ratio is much smaller and increases with coal rank (13). As seen in Figure 3, the median ratios of $S/(S+R)$ for both $C_{31}\alpha\beta$ and $C_{30}\beta\beta$ in Auckland are close to those in vehicular exhausts (34), suggesting that contribution of coal burning to PM$_{10}$ was negligible in Auckland in the winter. In contrast, the $S/(S+R)$ ratios in the Christchurch samples are between those of petroleum and coal burning emissions. A survey found that of the coal produced in New Zealand in 1996, 47% was bituminous (more mature), 46% sub-bituminous, and 7% lignite (less matured) (35, 36). If we assume that the local coals were used in Christchurch winter, the mean ratio of $S/(S+R)$ for $C_{31}\alpha\beta$ would be 0.27 (0.37 $\times 47% + 0.2 \times 46% + 0.05 \times 7%$) for the coal burning emissions. Using the following equation, we can estimate the relative contributions of petroleum utilization and coal burning to PM$_{10}$ in Christchurch:

$$0.6x + 0.27(1-x) = z$$  

where $x$ is the fraction of petroleum utilization in fossil fuel contribution in a sample, and $z$ is the ratio of $S/(S+R)$ for $C_{31}\alpha\beta$ hopane determined in the sample. The results are shown in Figure 4. On average, about 60% of the fossil fuel emissions was contributed by petroleum utilization with the remaining 40% being from coal burning in Christchurch in the season.

**n-Alkanes.** Although $n$-alkanes ($C_{29}$--$C_{38}$) are more abundant in Christchurch than in Auckland (Table S1), a larger fraction (median: 17.3%) of the alkanes may be apportioned to plant wax (37) for the Auckland samples than that (median: 11.5%) of Christchurch samples. This is consistent with higher CPI (median: 1.32 vs 1.22) and ACL (median: 27.4 vs 25.9) found in Auckland since higher plant wax contains longer chain $n$-alkanes with strong odd carbon number preference but a CPI close to 1 can be generally found for $n$-alkanes in fossil fuels (13, 38). Moreover, many Christchurch samples showed carbon number maxima ($C_{\text{max}}$) at $C_{25}$. In contrast, nearly half of the Auckland samples gave $C_{\text{max}}$ at $C_{29}$ or $C_{31}$. Except for a few Auckland samples, the CPI

### TABLE 1. Contribution of Individual Organic Compound Classes to TOC, WSOC and WIOC in Aerosols (%)

<table>
<thead>
<tr>
<th>compound class</th>
<th>range</th>
<th>mean/median</th>
<th>SD</th>
<th>range</th>
<th>mean/median</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Christchurch (n = 18)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>0.28–0.58</td>
<td>0.40/0.42</td>
<td>0.08</td>
<td>0.20–1.0</td>
<td>0.46/0.45</td>
<td>0.22</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>0.83–2.4</td>
<td>1.2/1.1</td>
<td>0.36</td>
<td>0.91–4.3</td>
<td>1.7/1.5</td>
<td>0.84</td>
</tr>
<tr>
<td>dehydroabietic acid</td>
<td>1.5–3.7</td>
<td>2.4/2.2</td>
<td>0.66</td>
<td>0.23–4.0</td>
<td>1.2/1.0</td>
<td>0.78</td>
</tr>
<tr>
<td>n-Alkanols</td>
<td>0.24–0.47</td>
<td>0.35/0.34</td>
<td>0.07</td>
<td>0.19–1.6</td>
<td>0.48/0.36</td>
<td>0.34</td>
</tr>
<tr>
<td>Steroids</td>
<td>0.11–0.55</td>
<td>0.23/0.20</td>
<td>0.11</td>
<td>0.05–0.37</td>
<td>0.10/0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Saccharides</td>
<td>0.02–0.23</td>
<td>0.11/0.10</td>
<td>0.05</td>
<td>0.001–1.5</td>
<td>0.33/0.21</td>
<td>0.40</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>1.4–4.4</td>
<td>3.0/2.8</td>
<td>0.72</td>
<td>0.03–4.9</td>
<td>2.4/2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Lignin products</td>
<td>0.09–0.35</td>
<td>0.22/0.21</td>
<td>0.07</td>
<td>0.002–0.16</td>
<td>0.06/0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Hopanes</td>
<td>0.02–0.05</td>
<td>0.03/0.03</td>
<td>0.01</td>
<td>0.03–0.11</td>
<td>0.05/0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Total quantified</td>
<td>5.2–11</td>
<td>7.9/7.8</td>
<td>1.7</td>
<td>3.5–10</td>
<td>6.8/7.1</td>
<td>2.1</td>
</tr>
<tr>
<td><strong>Auckland (n = 19)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>0.04–0.37</td>
<td>0.21/0.19</td>
<td>0.08</td>
<td>0.001–3.0</td>
<td>0.73/0.52</td>
<td>0.86</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>3.1–8.0</td>
<td>5.7/5.5</td>
<td>1.3</td>
<td>0.12–9.8</td>
<td>5.2/6.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Dehydroabietic acid</td>
<td>0.006–0.04</td>
<td>0.02/0.02</td>
<td>0.007</td>
<td>BDL–0.10</td>
<td>0.03/0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Vanillic acidb</td>
<td>0.13–0.58</td>
<td>0.32/0.28</td>
<td>0.12</td>
<td>BDL–0.19</td>
<td>0.08/0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Total soluble</td>
<td>3.4–8.8</td>
<td>6.3/6.0</td>
<td>1.4</td>
<td>0.24–11</td>
<td>6.1/7.7</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>To WSOC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>0.51–1.2</td>
<td>0.86/0.83</td>
<td>0.22</td>
<td>0.34–1.8</td>
<td>0.81/0.84</td>
<td>0.34</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>1.6–5.1</td>
<td>2.6/2.4</td>
<td>0.84</td>
<td>1.3–10</td>
<td>3.1/2.7</td>
<td>0.20</td>
</tr>
<tr>
<td>Dehydroabietic acid</td>
<td>2.7–8.2</td>
<td>5.0/4.6</td>
<td>1.5</td>
<td>0.32–7.6</td>
<td>2.2/2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>n-Alkanols</td>
<td>0.44–1.2</td>
<td>0.75/0.75</td>
<td>0.22</td>
<td>0.37–2.2</td>
<td>0.85/0.65</td>
<td>0.50</td>
</tr>
<tr>
<td>Steroids</td>
<td>0.28–1.2</td>
<td>0.48/0.41</td>
<td>0.21</td>
<td>0.08–0.63</td>
<td>0.19/0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>0.04–0.20</td>
<td>0.12/0.12</td>
<td>0.05</td>
<td>0.003–0.14</td>
<td>0.04/0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Hopanes</td>
<td>0.04–0.10</td>
<td>0.07/0.06</td>
<td>0.02</td>
<td>0.05–0.20</td>
<td>0.10/0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Total insoluble</td>
<td>6.2–14</td>
<td>9.9/9.5</td>
<td>2.5</td>
<td>4.7–15</td>
<td>7.3/7.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*$^a$ TOC, total organic carbon; WSOC, water-soluble organic carbon; WIOC, water-insoluble organic carbon; SD, standard deviation; BDL, below detection limit. $^b$ Vanillic acid is slightly soluble in water.
in the urban samples are significantly lower than those (2.1–8.5) found at a remote site in New Zealand (39, 40). This is quite reasonable because influence of local fossil fuel emissions is more important in the cities.

**Fatty Acids.** Total concentrations of n-alkanoic acids (C14–C30) in the aerosols are significantly higher than those of n-alkanes or n-alkanols by a factor of 3–4 (Table S1). Fatty acids show strong even carbon number predominance (CPIn) quite reasonable because influence of local fossil fuel combustion especially for the Christchurch aerosols, given that levoglucosan at C24 can be generated from terrestrial higher plants and marine microbial components (18, 41). It is worth noting that although concentrations of C20 are substantially lower than that of C28 or C26 alkanoic acids) in eight samples from Christchurch. This suggests that although most of the organic aerosols are aged, fresh biogenic materials may have often contributed to organic aerosols in Christchurch.

**n-Alkanols.** The n-alkanols range from C16 to C28, with very strong even carbon number predominance (essentially no odd numbered alkanols detected) and Cmax mostly at C26 or C28 (Table S1). Their ACL values are slightly higher in Auckland than in Christchurch (median: 23.5 vs 22.8). Fatty alcohols are believed to derive from higher plants. It should be pointed out that biomass burning can also produce a large amount of n-alkanols and n-alkanoic acids (7, 43). A significant fraction of n-alkanols and n-alkanoic acids detected in the samples may have been generated by wood burning especially for the Christchurch aerosols, given that their concentrations in the cities are much higher than those in the remote New Zealand site (39, 40) and biomass burning tracers are abundantly present in the Christchurch aerosols. On the other hand, higher ACL values found for n-alkanes and n-alkanols in the Auckland aerosol samples may also be explained by the hypothesis that plants in tropical regions need longer chain lipids to maintain the integrity of their epicuticular waxes. (44) (Auckland is a more tropical city than Christchurch).

**Sugar Compounds.** Primary saccharides consisting of glucose, fructose, inositol, sucrose, and mycose (trehalose), as well as some saccharide polysols including glycerol, arabinol, and mannitol were detected in the samples at relatively low concentrations (median total concentration was 30 ng m⁻³ in Christchurch and 8.3 ng m⁻³ in Auckland), with glucose and glycerol being the most abundant (Table S1). These sugar compounds are completely water-soluble and thus contribute to WSOC in aerosols. They have been proposed as tracers for resuspension of surface soil and unpaved road dust (45). Other water-soluble organic compounds in the samples, mainly low molecular weight dicarboxylic acids, will be determined using a more specific method (dibutyl esterification) (46) and will not be discussed here.

**Contribution to Organic Carbon.** To better understand organic chemical composition of the aerosols, contributions of each compound class to TOC, WSOC, and WIOC in the samples were studied (Table 1). Although levoglucosan at both sites comprises a similar fraction in TOC (median: 2.8% vs 2.5%) and also in WSOC (median: 5.5% vs 6.3%), contributions of other biomass burning tracers, that is hydroxyacids, steroids (mainly δ-sitosterol) and lignin products, to TOC and WIOC are more than twice higher in Christchurch than in Auckland. This indicates that intensive wood burning can significantly affect chemical composition of organic aerosols.

It is interesting to note that contributions of aliphatic lipid components (n-alkanes, fatty acids, and n-alkanols) to TOC and WIOC are quite similar at both sites, although fatty acids make a larger contribution than the other two compound classes. On the other hand, saccharides (excluding levoglucosan) and hopanes comprise larger fractions of TOC and WSOC or WIOC in Auckland than in Christchurch. However, the sum of all the organic compounds determined account for only 5.2–11% (median: 7.8%) of TOC in Christchurch and 3.5–10% (median: 7.1%) of TOC in Auckland, indicating that a major portion of organic aerosols studied is still unknown in terms of chemical structure. Similar findings have been reported for the aerosols collected in the ACE–Asia campaign (18).

**Acknowledgments**

We thank Environment Canterbury and Mr. Vincent Lane for aerosol sampling. This study was in part supported by the Japanese Ministry of Education, Science, and Culture through Grant-in-Aid no. 01470041. Financial support to H.W. by the Japan Society for the Promotion of Science is also acknowledged.

**Supporting Information Available**

Detailed procedures for the measurements of carbonaceous and inorganic ions and detailed atmospheric concentrations of the quantified organic compounds in the samples. This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**

(12) Sheesley, R. J.; Schauer, J. J.; Chowdhury, Z.; Cass, G. R.; Simoneit, B. R. T. Characterization of organic aerosols emitted from the


Received for review December 17, 2005. Revised manuscript received June 8, 2006. Accepted July 6, 2006.