SOURCE AND REACTION PATHWAYS OF DICARBOXYLIC ACIDS, KETOACIDS AND DICARBONYLS IN ARCTIC AEROSOLS: ONE YEAR OF OBSERVATIONS*

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Abstract—Normal saturated (C2-C11) and unsaturated (C4-C5, C6) dicarboxylic acids were measured in arctic aerosol samples collected weekly at Alert, Canada in 1987-1988. In all seasons, oxalic (C2) acid was usually the dominant diacid species (1.8-70 ng m⁻³, av. 14 ± 12 ng m⁻³) followed by malonic (C3; 0.05-19 ng m⁻³, av. 2.5 ± 3.3 ng m⁻³) and succinic (C4; 0.51-18 ng m⁻³, av. 3.8 ± 3.5 ng m⁻³) acids. The total concentrations of dicarboxylic acids showed a seasonal variation (4.3-97 ng m⁻³, av. 25 ± 20 ng m⁻³), with two maxima in September to October and in March to April. The autumn peak is characterized by high concentrations of oxalic acid and azelaic (C9) acids, which were probably caused by enhanced contributions from anthropogenic and biogenic sources, respectively, followed by photochemical reactions. This is consistent with higher concentrations of n-alkanes from terrestrial plant waxes and of soil-derived aluminum in the autumn aerosol samples. On the other hand, during "Arctic Sunrise" in March to April, oxalic, malonic and succinic acids as well as some other (C5-C6) diacids were 5 to 20 times more abundant than in the preceding dark winter months, suggesting that diacids are produced in situ by secondary photochemical oxidation of organic pollutants carried to the Arctic. α,ω-Oxocarboxylic acids (C2-C6, C8), pyruvic acid and x-dicarbonyls (methylglyoxal and glyoxal) were also detected in the arctic aerosols. Their concentration also showed spring maxima; however, they were observed a few weeks earlier than the spring peak of diacids. The α,ω-oxoacids are likely intermediates to the production of α,ω-dicarboxylic acids at the polar sunrise.

Key word index: Water soluble organic compounds, diacids, ketoacids, dicarbonyls, arctic aerosols, oxalic acid, malonic acid, succinic acid.

INTRODUCTION

Studies of low molecular weight dicarboxylic acids in urban and suburban aerosols demonstrated that the smallest diacid, oxalic acid, is the most abundant dicarboxylic acid in the range of C2-C10 (Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994). The amounts of these diacids were found to account for up to 1% of total aerosol mass and 2% of the total carbon content of urban aerosols. Concentrations of aerosol dicarbonylic acids in the Tokyo atmosphere showed a summer maximum and a positive correlation with oxidants. These results suggested that, for the most part, the small dicarboxylic acids are produced by photochemically induced reactions of anthropogenic organic pollutants in the urban atmosphere (Kawamura and Ikushima, 1993). Laboratory experiments have shown that some diacids such as adipic (C6) acid are produced by photochemical oxidation of cyclic alkenes (Grosjean et al., 1978; Grosjean and Friedlander, 1980; Hatakeyama et al., 1985, 1987), which are present in the atmosphere as a result of atmospheric emissions from internal combustion engines (Grosjean and Fung, 1984).

Long-term observations of arctic aerosols (more than five years) have demonstrated the long-range atmospheric transport of pollutants such as sulfate from mid-latitudes to the Arctic maximized in winter to spring seasons (Barrie and Hoff, 1985; Barrie, 1986; Barrie and Barrie, 1990). Ozonodestruction and photochemical reactions have been proposed to occur at

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polar sunrise in the lower arctic troposphere (Barrie et al., 1988). However, arctic aerosol chemical observations have been mostly focused on inorganic species while organic compounds were rarely studied. Kawamura et al. (1995) briefly examined one year of particulate observations taken at Alert, Canada in 1987/88 for dicarboxylic acids and found a correlation with springtime particulate Br associated with tropospheric ozone depletion at polar sunrise (Barrie et al., 1988).

In this paper, that Alert data set dicarboxylic acids is discussed in more detail together with \( \omega \)-oxocarboxylic acids and \( \alpha \)-dicarboxyls detected in the arctic aerosols with an emphasis on reaction pathway. Based on the seasonal variation of their molecular distribution, we explore the photochemical production of dicarboxylic acids and the long-range atmospheric transport of anthropogenic and biogenic organic compounds which are their precursors.

**EXPERIMENTAL**

The aerosol samples were collected on Whatmann 41 filters (20 x 25 cm) at Alert (82.5°N, 62.3°W) from July 1987 to June 1988 using a high-volume air sampler. The sampling period was generally 7 days (Barrie and Hoff, 1985). Over the year, weekly mean ambient temperature ranged from \(-38\) to \(5°C\). The sample filters collected during summer showed a white or very faint dark color whereas those collected in the rest of the year were light grey to black. The filters were blackest from December to February, suggesting an enhanced long-range transport of fossil fuel combustion products such as black carbon to the Arctic atmosphere from industrialized areas including Europe (Barrie and Bottenheim, 1991). Some autumn samples showed a yellowish dark color, suggesting a possible contribution from soil particles. This is consistent with a peak in aerosol Al concentrations in September/October at Alert (Barrie and Barrie, 1990).

Filter samples were analyzed by the method of Kawamura and Ikushima (1993). Briefly, aliquots of filters (c. 12 or 25 cm\(^2\) ) were extracted with pure water, which was prepared in an all glass apparatus by distillation of Milli-Q water after oxidizing organic impurities with potassium permanganate. The water extracts containing dicarboxylic acids were concentrated to c. 1 ml by rotary evaporation under vacuum, and then passed through a Pasteur pipet column packed with quartz wool to remove particles. The water soluble fraction was concentrated to nearly dryness and esterified with 14% BF3/n-butanol (0.25 ml) at 100°C for 30 min. The dicarboxylic acid dibutyl esters were extracted with n-hexane after adding pure water and a small amount (0.2 ml) of acetonitrile, and then dissolved in 50 \(\mu\)l n-hexane. The aldehyde group in \(\omega\)-oxocarboxylic acids and dicarboxyls were derivatized to dibutoxy acetal. The derivatives were separated in the same fraction of diacid esters by extraction with n-hexane (Kawamura, 1993).

Dibutyl esters and other derivatives were determined with a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a split/splitless injector, fused silica capillary column (HP-5, 0.3 mm ID x 25 m long x 0.52 \(\mu\)m film thickness) and an FID detector. The GC peak areas were calculated with Shimadzu C-R7A integrator. Identification of the compounds were performed by comparing GC retention times with those of authentic standards. The compounds were further analyzed by a Finnigan-MAT ITS 40 GC-mass spectrometer for mass spectral identification using authentic standards. Mass spectra (m/z 45–500) were obtained every 1 s and processed with the ITS 40 systems with INCOS mass spectral data library.

Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 71% for oxalic acid and better than 90% for malonic, succinic and adipic acids (Kawamura and Ikushima, 1993). Duplicate analyses of some sample filters showed an error of less than 15% for major diacids. The gas chromatograms of blank filters showed peaks of phthalic, oxalic, succinic, and other acids. However, their concentration levels were generally less than 10% of those for sample filters, except for phthalic acid (up to c. 50%). The concentrations reported in this paper are corrected for the blanks but not for recoveries. Actual recoveries on samples are expected to be higher than for spiked filters because of metal ions in aerosols.

**RESULTS AND DISCUSSION**

**Molecular distributions and origin of dicarboxylic acids, ketocarboxylic acids and \(\alpha\)-dicarboxyls**

Figure 1 shows a typical gas chromatogram of dicarboxylic acid dibutyl esters and related polar compounds isolated from the arctic aerosol samples (4–11 April 1988). Three types of organic compounds were detected in the water soluble fraction of the aerosols: (1) an homologous series of dicarboxylic acids including aliphatic \(\alpha\)-\(\omega\)-dicarboxylic acids (C\(_2\)-C\(_{11}\)) and aromatic (phthalic) acid, (2) ketocarboxylic acids including 8-oxocarboxylic acids (C\(_2\)-C\(_8\)) and pyruvic acid, (3) \(\alpha\)-dicarboxyls (glyoxal and methylglyoxal) (see Fig. 2 for chemical structures).

Table 1 summarizes the polar organic compounds measured, their mean concentrations, concentration ranges and the month when their maximum concentration was observed.

**Homologous series of \(\alpha\)-\(\omega\)-dicarboxylic acids (C\(_2\)-C\(_{11}\)).** Throughout all the samples, oxalic acid (C\(_2\)) was found as the most abundant diacid species. The second most abundant diacid was malonic (C\(_3\)) or succinic (C\(_4\)) acid. The C\(_2\)-C\(_4\) diacids accounted for more than 80% of total diacids (4.3–97 ng m\(^{-3}\)) in the arctic aerosols studied. Longer chain normal diacids were less abundant and their concentrations generally decreased with increasing carbon number. The exception was C\(_6\) diacid which was more abundant than C\(_8\) species. Branched chain saturated dicarboxylic acids were also detected in the Alert aerosols, including methylmalonic (iC\(_2\)), methylsuccinic (iC\(_3\)) and 2-methylglutaric (iC\(_4\)) acids. They are less abundant than corresponding straight-chain dicarboxylic acids. In addition to saturated \(\alpha\)-\(\omega\)-dicarboxylic acids, unsaturated diacids were detected in the arctic aerosols, including maleic, fumaric and methylmaleic acids. The abundance of the unsaturated diacids are lower than those of corresponding saturated species, although maleic acid was relatively abundant in winter samples. Aromatic acid (phthalic) was detected as the fourth most abundant dicarboxylic acid.

\(\alpha\)-\(\omega\)-Dicarboxylic acids with an additional functional group were also detected in the arctic aerosols. They include ketomalonic acid (kC\(_3\)), 4-oxopimelic
Dicarboxylic acids in arctic aerosols

Fig. 1. Capillary gas chromatogram of dicarboxylic acid dibutyl esters and related polar compounds isolated from the arctic aerosol sample (4–11 April 1988).

Fig. 2. Chemical structures of dicarboxylic acids (a–n), ketoacids (o–q) and α-dicarbonyls (r–s) detected in the Alert aerosols.

Low molecular weight dicarboxylic acids with oxalic acid being the predominant, have been reported in aerosols collected in urban Los Angeles (Kawamura and Kaplan, 1987) and in Tokyo.

Acid (kC7) and hydroxysuccinic (malic) acid (hC4). However, these tri-functional compounds were found as relatively minor components compared to bifunctional C2–C4 diacids.
Table 1. Dicarboxylic acids (ng m\(^{-3}\)) in the Arctic aerosol samples collected from Alert in July 1987–June 1988

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Conc. range</th>
<th>Mean conc. (\pm) st. dev.</th>
<th>Month (max conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dicarboxylic acids</strong></td>
<td></td>
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</tr>
<tr>
<td><strong>Normal saturated diacids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic</td>
<td>C(_2)</td>
<td>1.8–70</td>
<td>13.6 (\pm) 12.1</td>
</tr>
<tr>
<td>Malonic</td>
<td>C(_3)</td>
<td>0.048–19</td>
<td>2.46 (\pm) 3.3</td>
</tr>
<tr>
<td>Succinic</td>
<td>C(_4)</td>
<td>0.51–18</td>
<td>3.73 (\pm) 3.55</td>
</tr>
<tr>
<td>Glutaric</td>
<td>C(_5)</td>
<td>0.16–4.3</td>
<td>0.90 (\pm) 0.91</td>
</tr>
<tr>
<td>Adipic</td>
<td>C(_6)</td>
<td>&lt; 0.003–9.5</td>
<td>0.82 (\pm) 1.43</td>
</tr>
<tr>
<td>Pimelic</td>
<td>C(_7)</td>
<td>0.001–1.8</td>
<td>0.13 (\pm) 0.26</td>
</tr>
<tr>
<td>Suberic</td>
<td>C(_8)</td>
<td>0.015–1.8</td>
<td>0.15 (\pm) 0.26</td>
</tr>
<tr>
<td>Azelaic</td>
<td>C(_9)</td>
<td>0.036–2.0</td>
<td>0.26 (\pm) 0.32</td>
</tr>
<tr>
<td>Sebacic</td>
<td>C(_10)</td>
<td>&lt; 0.003–1.7</td>
<td>Not calc.</td>
</tr>
<tr>
<td>Undecanedioic</td>
<td>C(_11)</td>
<td>&lt; 0.003–1.1</td>
<td>0.064 (\pm) 0.15</td>
</tr>
<tr>
<td><strong>Branched saturated diacids</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Methylmalonic</td>
<td>iC(_4)</td>
<td>&lt; 0.003–0.64</td>
<td>0.13 (\pm) 0.12</td>
</tr>
<tr>
<td>Methylsuccinic</td>
<td>iC(_5)</td>
<td>&lt; 0.003–1.8</td>
<td>0.36 (\pm) 0.37</td>
</tr>
<tr>
<td>2-Methylglutaric</td>
<td>iC(_6)</td>
<td>&lt; 0.003–0.21</td>
<td>0.016 (\pm) 0.038</td>
</tr>
<tr>
<td><strong>Unsaturated diacids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic</td>
<td>C(_4), M</td>
<td>0.016–0.61</td>
<td>0.19 (\pm) 0.14</td>
</tr>
<tr>
<td>Fumaric</td>
<td>C(_4), F</td>
<td>0.017–1.1</td>
<td>0.14 (\pm) 0.19</td>
</tr>
<tr>
<td>Methylmaleic</td>
<td>C(_5), mM</td>
<td>&lt; 0.003–0.22</td>
<td>0.034 (\pm) 0.056</td>
</tr>
<tr>
<td>Phthalic</td>
<td>C(_8), Ph</td>
<td>&lt; 0.005–5.8</td>
<td>1.5 (\pm) 1.5</td>
</tr>
<tr>
<td><strong>Ketodiacids</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ketomalonic</td>
<td>kC(_3)</td>
<td>0.026–2.1</td>
<td>0.31 (\pm) 0.38</td>
</tr>
<tr>
<td>4-Ketopimelic</td>
<td>kC(_7)</td>
<td>0.18–0.62</td>
<td>0.20 (\pm) 0.17</td>
</tr>
<tr>
<td><strong>Hydroxylated diacid</strong></td>
<td></td>
<td></td>
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<tr>
<td>Malic</td>
<td>hC(_4)</td>
<td>&lt; 0.003–0.14</td>
<td>0.026 (\pm) 0.038</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>4.3–97</td>
</tr>
<tr>
<td><strong>(\omega)-Oxocarboxylic acids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxylic</td>
<td>(\omega)C(_2)</td>
<td>&lt; 0.003–10.1</td>
<td>1.7 (\pm) 2.4</td>
</tr>
<tr>
<td>3-Oxopropanoic</td>
<td>(\omega)C(_3)</td>
<td>0.012–0.20</td>
<td>0.07 (\pm) 0.05</td>
</tr>
<tr>
<td>4-Oxobutanoic</td>
<td>(\omega)C(_4)</td>
<td>&lt; 0.003–0.94</td>
<td>0.35 (\pm) 0.24</td>
</tr>
<tr>
<td>5-Oxopentanoic</td>
<td>(\omega)C(_5)</td>
<td>&lt; 0.003–0.10</td>
<td>0.02 (\pm) 0.02</td>
</tr>
<tr>
<td>9-Oxononanoic</td>
<td>(\omega)C(_9)</td>
<td>&lt; 0.003–0.11</td>
<td>0.01 (\pm) 0.02</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>0.18–10.8</td>
</tr>
<tr>
<td><strong>(\alpha)-Ketocarboxylic acid</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyruvic</td>
<td>C(_3), Pyr</td>
<td>&lt; 0.003–0.52</td>
<td>0.13 (\pm) 0.13</td>
</tr>
<tr>
<td><strong>Dicarbonyls</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxal</td>
<td>C(_2), Gly</td>
<td>&lt; 0.003–2.29</td>
<td>0.54 (\pm) 0.56</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>C(_1), MeGly</td>
<td>&lt; 0.003–0.59</td>
<td>0.16 (\pm) 0.14</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>&lt; 0.003–2.66</td>
</tr>
</tbody>
</table>

(Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994). The predominance of oxalic acid was also recognized in the molecular distribution of diacids in remote marine aerosols from the North Pacific (Kawamura and Usukura, 1993). Oxalic acid has been detected in Alaska aerosol samples by Li and Winchester (1993), using ion chromatography. Other diacids were not measured. Diacids with oxalic acid being relatively less abundant were reported in aerosols from Takasáki, central Japan using methyl ester derivatization followed by GC determination (Satsumabayashi et al., 1990), which results in a serious underestimation of oxalic and malonic acids (Kawamura and Ikushima, 1993). The atmospheric chemical sources and sinks of dicarboxylic acids are not quantitatively well known. However, there is a growing body of knowledge that allows a qualitative picture to be painted, as illustrated in Fig. 3. Laboratory experiments have shown that they are produced in the ozone and cycloalkene reaction (Hatakeyama et al., 1987). In addition, evidence suggests that they are produced in the atmosphere as a result of secondary photochemical reaction of anthropogenic aromatic hydrocarbons such as benzene and toluene and their oxidation intermediates such as glyoxal and methylglyoxal (Norton et al., 1983; Kawamura and Ikushima, 1993). The abundant presence of cis configuration (maleic acid
Dicarboxylic acids in arctic aerosols

Fig. 3. Possible photochemical production of oxalic (C₂), malonic (C₃), succinic (C₄) and azelaic (C₉) acids in the atmosphere. For abbreviations and chemical structures, see Table 1 and Fig. 2.

and methylmaleic acid) in the urban atmosphere supports an oxidation of these aromatic hydrocarbons as a precursor of oxalic acid. In automobile exhausts, oxalic acid was predominant followed by succinic acid and, to a lesser extent, malonic acid (Kawamura and Kaplan, 1987).

In contrast, malonic acid which is hardly produced by the oxidation of aromatic structures having conjugated double bonds, is likely produced by the photochemical oxidation of succinic acid with malic acid as an intermediate (Kawamura and Ikushima, 1993). In turn succinic acid and longer chain diacids are likely oxidation products of gaseous aliphatic monocarboxylic acids, which are in part produced by photo-induced oxidations of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987) and other precursors such as n-alkanes, aldehydes and mid-chain ketocarboxylic acids (see Fig. 3). A one-year observational study of low molecular weight dicarboxylic acids in urban aerosols of Tokyo suggested that photochemical reactions which peak in summer result in production of LMW diacids and in summer contribute more to the particulate diacids than direct emissions from anthropogenic and natural sources (Kawamura and Ikushima, 1993).

ω-Oxocarboxylic acids and ketoacid. The homologous series of aldehydic acids were detected in the range of C₂–C₁₀ in the arctic aerosols. Although the presence of C₂–C₅ and C₁₀ ω-oxoacids was confirmed by mass chromatography techniques using characteristic mass fragment ions (e.g. m/z M-73, Kawamura, 1993), their concentrations were not measured due to the small and, sometimes, non-detectable peaks on the GC-FID chromatograms, thus not reported in Table 1. Interestingly, glyoxylic acid (ωC₂), the smallest ω-oxoacid, was generally the most abundant species in winter to spring seasons. In contrast, ω-oxobutanoic acid (ωC₄) overwhelmed the ωC₂ in the summer aerosols, although the concentrations were lower than in other seasons. Total concentrations of ω-oxoacids (ωC₂ to ωC₅ and ωC₉) ranged from 0.18 to 10.8 ng m⁻³ and largely fluctuated with seasons. Their concentrations (av. 2.2 ng m⁻³) were lower than those of ω,ω-dicarboxylic acids (av. 25 ng m⁻³) throughout four seasons. The ketoacid, pyruvic acid, was also detected in the aerosols. However, concentrations (av. 0.13 ng m⁻³) were much lower than glyoxylic acid (ωC₂, av. 1.7 ng m⁻³).

The predominance of glyoxylic acid in the ω-oxocarboxylic acids has been reported in the urban atmosphere (Kawamura, 1993). Glyoxylic acid may be produced by atmospheric oxidation of glyoxal (Kawamura, 1993). Pyruvic acid was also reported in urban aerosols and rainwaters (Kawamura, 1993; Sempere and Kawamura, 1994), remote continental rain and aerosols from Amazon (Talbot et al., 1990) and remote marine atmosphere (Kawamura and Usukura, 1993; Zhou and Mopper, 1990). These ketoacids may be intermediate in the photochemical oxidation of anthropogenic and natural organic compounds to the production of oxalic acid.

ω-Dicarbonyls. Glyoxal and methylglyoxal were detected in Alert aerosols. Glyoxal atmospheric concentrations were highest in the winter-spring. The dicarbonyls were detected at much lower concentrations < 0.003 to 2.66 ng m⁻³ than the dicarboxylic acids (4.3–97 ng m⁻³) and ω-oxocarboxylic acids (0.18–10.8 ng m⁻³). This is likely because dicarbonyls are largely present in the gas phase.
The α-dicarbonyls have been reported in the urban (Kawamura, 1993) and marine atmosphere (Zhou and Mopper, 1990). Laboratory studies show that glyoxal and methylglyoxal are produced as photochemical oxidation products of aromatic hydrocarbons such as benzene and toluene (Bandow and Washida, 1985; Bandow et al., 1985).

Seasonal variations of polar compounds: long-range transport and photochemical production

One year of observations of arctic aerosols showed strong variations in the concentrations. Figure 4 presents overall seasonal variations in the total concentrations of dicarboxylic acids, ω-oxocarboxylic acids, and α-dicarbonyls in the arctic aerosol samples collected in 1987–1988. Total dicarboxylic acids showed two major peaks in autumn and spring. In contrast, concentrations of ω-oxoacids and α-dicarbonyls showed a maximum in the spring and no significant peaks in autumn. However, individual species fluctuated in a different manner, as follows.

Saturated diacids (C$_2$–C$_9$). Figure 5 gives seasonal variations of individual ω,ω-dicarboxylic acids in the Alert aerosols. The most abundant diacid (oxalic acid) showed two major peaks in September to October and March to April. The highest concentration (ca. 70 ng m$^{-3}$) was obtained in the aerosol sample collected on 14–21 September 1987. In late October to January, the concentrations stayed at rather low levels with a relatively small fluctuation (2–20 ng m$^{-3}$). Its concentration started to increase significantly in March and peaked in early April (Fig. 5a). The C$_2$ concentration at the April peak was ca. 3 times more abundant than that of the preceding dark winter months. The April peak of oxalic acid appeared at the time of arctic sunrise, suggesting that oxalic acid is significantly produced in the arctic atmosphere by photo-induced reactions. During arctic sunrise, much chemical activity involving Cl and Br atoms reacting with hydrocarbons takes place (Barrie et al., 1994b; Jobson et al., 1994), resulting in oxidants such as ozone, hydrogen peroxide and hydroxyl radicals. The oxidants may react with various organic compounds which are transported and accumulated in the Arctic during dark winter to produce oxalic acid. After the spring peak, oxalic acid concentration decreased in the summer to a level similar to that observed in the winter months. Lower concentrations in the summer are due to scavenging of the particulate diacids by more frequently occurring precipitation, coupled with a weakened transport of polluted air parcels from mid-latitudes (Barrie, 1986).

Similar seasonal variations were observed for C$_2$–C$_9$ α,ω-dicarboxylic acids (Figs 5b–d), except that autumn peaks are relatively weaker and amplitudes of the spring peaks are larger (10 to 20 times) than that of oxalic acid (3 times). Their concentrations started to increase at the beginning of March, peaked in April and returned to the background levels in late June. These results again suggest in situ photochemical production of these diacids in the arctic atmosphere. However, the peak shapes are slightly different from each other. Thus C$_3$ and C$_5$ diacids showed maxima in the 4–11 April sample whereas C$_4$ diacid peaked three weeks later. Such a variation may be associated with different source inputs and/or different production mechanisms. The C$_6$ diacid showed a seasonal distribution similar to that of C$_3$–C$_5$ diacids, however, the amplitude of the April peak was much greater than that of C$_3$–C$_5$ acids (Fig. 5e).

On the other hand, longer chain diacids (C$_7$–C$_{11}$) showed seasonal variations different from those of shorter chain diacids (C$_2$–C$_6$), i.e. they showed a large peak in early October, and no significant peak in early spring. Except for the autumn peak, their concentrations stayed low in dark winter months and become only slightly higher in summer, although higher concentrations were observed in early April (Fig. 5). It is important to note that, in the early October samples, C$_7$, C$_8$, C$_9$, C$_{10}$ and C$_{11}$ diacids were found as...
Dicarboxylic acids in arctic aerosols

Fig. 5. Seasonal distribution of individual normal saturated α,ω-dicarboxylic acid in the arctic aerosol samples collected from Alert, 1987–1988. For abbreviations, see Table 1 and Fig. 3.

abundant as C₂ to C₆ diacids (Fig. 5). Furthermore, longer chain dicarboxylic acids (C₁₂ to C₁₆) were also detected in the early October sample (5–11 October 1987; for the gas chromatogram, see Fig. 6). The characteristic molecular distribution in the late September to October samples is very different from the rest of the samples, suggesting a different source. Because long chain normal alkanes with odd carbon number predominance (C₂₇, C₂₉, C₃₁, C₃₃) were abundantly detected in the 5–11 October sample (Kawamura et al., unpublished results), the aerosols are heavily influenced by terrestrial organic matter associated with higher plant waxes and soil dust particles. Aluminum concentration in the October aerosols was significantly higher (1500 ng m⁻³) compared to the background level of c. 100 ng m⁻³ observed in winter (Barrie et al., 1994a). This is likely a sample affected by local wind blown dust.

The seasonal variation of branched chain dicarboxylic acids (iso C₄–C₆) seems to be similar to those
of straight chain C3-C5 diacids (Figs 7a-c). Their concentrations were low in the dark winter, started to increase in February and peaked in April at concentrations 5-10 times greater than those of the preceding dark winter months. The amplitude in the April peak is a factor of c. 5-10 higher than background, being similar to that of the corresponding straight chain diacids. However, peak shapes are different. The iso C4 and C5 diacids showed a maximum in late April similar to that of succinic acid. In contrast, iso C6 diacid showed a maximum three weeks earlier than the iso C4 and C5 peaks. The iso C6 diacid may be in situ produced by atmospheric oxidation of 2-methyl cyclohexene which is of anthropogenic origin whereas other branched diacids may be derived from different precursors. The difference in the peak timing suggests that the molecular distribution of precursor cyclic alkenes has shifted in the arctic atmosphere probably due to changes in the origin of air mass.

**Unsaturated diacids.** Maleic (cis configuration) acid showed a unique seasonal distribution pattern with a maximum in winter (Fig. 7e), being different from those of saturated diacids. Its concentration began to increase between summer and autumn and peaked in December. During dark winter, it remained high and then began to steadily decrease in February to a summer minimum. Such a distribution suggests that maleic acid is not produced in situ in the arctic atmosphere, but rather, is transported from mid-latitudes where it is produced by the atmospheric photochemical oxidation of aromatic hydrocarbons. High concentration of maleic acid has been measured in the urban atmosphere of Tokyo (Kawamura and Ikuushima, 1993). In contrast, fumaric acid, the trans positional isomer of maleic acid, showed a distribution pattern different from the cis configuration (Fig. 7f). It was highest in summer and lowest in the winter season. In addition a secondary spring maximum was apparent. This acid may be produced in situ by photochemically induced isomerization of maleic acid in the Arctic during arctic sunrise and afterwards. The summer peak of fumaric acid suggests the presence of a non-anthropogenic precursor. Phenolic compounds may be a likely candidate, which have been reported to originate from macroalgae and enriched in the sea surface slicks (Carlson, 1982).

**Keto dicarboxylic acids.** Oxomalonic acid, which was detected as the predominant ketodicarboxylic acid in the Alert aerosol samples, showed a concentration maximum in the early spring (Fig. 7g). Its seasonal variation is almost the same as that of malonic acid (Fig. 5b), but its concentration is much lower. Their carbon skeletons are the same (see Figs 2b and I). This parallel seasonal distribution and chemical consideration suggest that ketomalonic acid is likely produced by the atmospheric oxidation of malonic acid. 4-Oxopimelic acid also gave the April maximum; however, its concentrations were high during the summer season (Fig. 7h). A parallel distribution was not recognized between the seasonal variations of 4-oxopimelic acid (KC7) and pimelic acid (C7).

**Oxocarboxylic acids.** αC2 which is the smallest but most abundant ketoacid species in the arctic aerosols, showed a gradual increase in late winter season and maximum concentration in late March (Fig. 8a). After the March maximum, its concentration decreased steadily through summer to an autumn/winter minimum. The March peak is more than 50 times higher than the background concentrations in the summer and early winter months. This seasonal pattern was similar to that of C3 and C4 diacids (Figs 5b, c); however, the concentration of αC2 started to increase two months earlier (December) than those of C3 and
Fig. 7. Seasonal distribution of individual branched-chain saturated and unsaturated $\omega,\omega$-dicarboxylic acid as well as $\omega,\omega$-dicarboxylic acid with keto functional group detected in the arctic aerosol samples collected from Alert, 1987–1988. For abbreviations, see Table 1 and Fig. 3.

$C_4$ diacids did (February). Furthermore, $\omega C_2$ peaked one or two weeks earlier (Fig. 8a) than the $C_3$–$C_5$ diacids (Figs 5b–d) and $C_3$ ketodiacid did (Fig. 7g). This suggests that glyoxylic acid is produced in winter under weak solar radiation probably during the south-to-north transport of polluted air mass which originate in mid-latitudes and then transported and accumulated in the dark Arctic. As described earlier, glyoxylic acid may be extensively produced at polar sunrise by in situ photo-oxidation of accumulated organic pollutants and then serve as a precursor of oxalic acid, which peaked one or two weeks later.

On the other hand, concentrations of $\omega C_3$ which were much lower than those of $\omega C_2$ and peaked in early April, although the concentrations largely scattered (Fig. 8b). The time lag between peaks of these two acids suggests that the $\omega C_3$ is produced from the precursor differently than $\omega C_2$. The seasonal
distribution of \( \omega \text{C}_4 \) showed lower concentrations in winter and higher values in spring and summer months (Fig. 8c). \( \omega \text{C}_5 \) was also detected in the aerosol samples; however, its concentration levels were roughly one-tenth of the concentration of \( \omega \text{C}_4 \). The seasonal distribution of the \( \omega \text{C}_5 \) species showed two peaks in October and April (Fig. 8d). \( \omega \text{C}_6 \) has been proposed as the photochemically-induced oxidation product of biogenic unsaturated fatty acids, which contain a double bond predominantly at C-9 position (Kawamura and Gagosian, 1987). This compound was detected in the samples as a relatively minor compound in the \( \omega \)-oxocarboxylic series.

The seasonal variation of pyruvic acid concentration peaked in February to April, although higher concentrations were sporadically observed in October, November, January, May (see Fig. 8f).

\( \alpha \)-Dicarbonyls. Glyoxal and methylglyoxal showed a seasonal variation similar to that of \( \omega \text{C}_2 \) (Figs 8g and h), although concentration levels of these...
dicarboxylic acids in arctic aerosols

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Fig. 9. Seasonal changes in the relative abundance (%) of selected dicarboxylic acid in the total diacid concentrations. For abbreviations, see Table 1 and Fig. 3.

Relative abundance of dicarboxylic acids and \( \omega \)-oxoacids: preferential production

Spring peaks of the major dicarboxylic acids and related polar compounds suggested photochemically induced reactions produce small diacids, which are end products and intermediates of the chain reactions occurring on the organic molecules transported to the Arctic. An increase in the diacid at the polar sunrise is consistent with the spring maximum of sulfate, which is in significant part produced in the arctic atmosphere by the photochemical oxidation of sulfur dioxide (Barrie and Barrie, 1990; Barrie et al., 1994a). An in situ production is supported by the presence of a strong linear correlation between shorter chain diacids \((C_2-C_5)\) and particulate Br in the arctic tropospheric aerosols at Alert (February–June, 1988) (Kawamura et al., 1995). Particulate Br is produced during the depletion of ozone in the Arctic boundary layer (Barrie et al., 1988, 1994). Bromine may be involved with the initiation of oxidative chain reactions on the organic molecules under strong solar radiation. In contrast, enhanced transport of small diacids in spring is not likely because of an absence of a strong peak of primary anthropogenic particulate matter such as vanadium (Barrie et al., 1994a) or lead (Barrie and Barrie, 1990).

During in situ production of the diacids in the arctic troposphere, molecular distributions are likely shifted in time probably by preferential production of certain diacids. Figure 9 presents seasonal changes in the relative abundance of individual diacids \((C_2-C_4, C_9, M, kC_7)\) in the total diacid mixture in arctic aerosols. \( C_2 \) showed higher relative abundance in dark winter (Fig. 9a). This is consistent with the higher...
percentages of maleic acid (M) (Fig. 9e), which is a photo-oxidation product of aromatic hydrocarbons and transported from mid-latitudes to the Arctic. The relative abundance of oxalic acid began to decrease towards the spring season as a result of preferential production and enrichment of other diacids. Especially, production of malonic acid (C3) is remarkable, that is, its relative abundance in the total diacids jumped from less than 10% to c. 20% at the polar sunrise (Fig. 9b). Selective enrichment of C3 diacid has been reported in the mid-latitudinal urban atmosphere during the seasons of summer to autumn as a result of enhanced photochemical oxidation of longer chain compounds such as succinic acid (Kawamura and Ikushima, 1993).

After polar sunrise, the relative abundance of malonic acid significantly decreased towards the summer season. In contrast to this, succinic acid (C4) peaked in late May (Fig. 9e), probably due to enhanced atmospheric transport of soil particles from China and other arid areas (Barrie and Barrie, 1990; Welch et al., 1991; Franzen et al., 1994). Except for a few summer samples, the relative abundance of succinic acid seems to be higher in summer season than winter. This may suggest that the precursor of succinic acid supplied in summer season originate from biogenic sources rather than anthropogenic sources. Sucinic acid could be produced by photochemical oxidation of > C4 carboxylic acids, including ωC4 (Fig. 3) and carboxylic acids containing an additional keto group at C-4 position, which were not measured in this study. The former acid is detected in the arctic aerosol samples and its concentration increased from winter to summer seasons (Fig. 8c). Further, its relative abundance in the total ω-oxoacids also showed an increase in summer season (Fig. 10c), being in contrast to C2 ω-oxoacid (Fig. 10a). On the other hand, 4-oxo-carboxylic acids have been detected among the mid-chain aliphatic ketocarboxylic acids (C7–C13) in the remote marine aerosols (Kawamura and Gagosian, 1988) and in the present arctic aerosols (Kawamura et al., unpublished results). These ketoacids could serve as precursors of succinic acid.

Figure 11 presents behaviors of M, ωC2 and C2 in winter to summer seasons, whose concentrations are normalized by the highest one and plotted by 5 point running means. M showed a maximum in December and decreased toward spring and summer. In contrast, ωC2 and C2 showed maximum in late March, however, the former acid seemed to peak slightly earlier than the latter. Such a shift of the concentration peaks from M (intermediate) in winter to C2 (end product) in spring suggests that chain reactions occur in the anthropogenic organic compounds transported to the Arctic predominantly in winter.

Interestingly, the relative abundance of azelaic acid (C9 diacid) largely increased after May and showed higher values in summer to autumn (Fig. 9d). Because azelaic acid is a photo-oxidation product of biogenic unsaturated fatty acids emitted to the atmosphere on
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Malonic acid may be further oxidized to ketomalonic acid and oxalic acid (Fig. 3). Such a chain reaction may also control the molecular distribution of dicarboxylic acids.

4. After the polar sunrise, concentrations of low molecular weight diacids decreased toward summer. However, azelaic acid (C9), a unique photochemical oxidation product of biogenic unsaturated fatty acids containing a double bond predominantly at the C-9 position, showed a peak in summer likely due to enhanced sea-to-air emission of marine derived organic matter to the Arctic due to the warming and retreat of sea ice in the polar ocean.

5. In September to October, concentrations of azelaic acid in the Arctic aerosols largely increased, probably due to local soil peaking in this time (Barrie and Barrie, 1990).

Finally, this study demonstrates that the Arctic is an excellent natural laboratory for the study of photochemical transformation of anthropogenic and natural organic matter in the troposphere, and is useful for understanding the complex chemistry of dicarboxylic acids and related organic compounds. More laboratory studies of the reaction mechanisms of these compounds are needed.

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SUMMARY AND CONCLUSIONS

To understand the molecular distributions and seasonal changes of water soluble organic compounds including dicarboxylic acids, ketocarboxylic acids and dicarboxyls, a capillary gas chromatographic and mass spectroscopic analysis of 47 arctic aerosol samples collected weekly from Alert, Canada was conducted. Major results and conclusions are as follows.

1. Oxalic (C2) acid was the most abundant diacid species followed by malonic (C3) and succinic (C4) acids. These small diacids comprised more than 80% of the total diacid concentrations (4–97 ng m−3).

2. During polar sunrise (late March to early April), concentrations of major diacids (C2–C5) became 3–20 times higher than those in the preceding winter months. The large increase in diacid concentrations was explained as a result of enhanced photochemical oxidation of organic pollutants such as unsaturated hydrocarbons, which were transported and accumulated in the Arctic atmosphere during dark winter. C2-Oxocarboxylic acids and C2-dicarboxyls which are a likely intermediate to the production of dicarboxylic acids also showed a concentration maximum about two weeks earlier than the peak of diacids.

3. Selective production of malonic acid was observed during polar sunrise: its relative abundance in the total diacids jumped from c. 7–8% in the winter season to 18% just after the polar sunrise. Malonic acid was suggested to be produced by the photochemical oxidation of succinic acid through intermediates such as hydroxysuccinic (malic) acid (Fig. 3).

4. Malonic acid may be further oxidized to ketomalonic acid and oxalic acid (Fig. 3). Such a chain reaction may also control the molecular distribution of dicarboxylic acids.

5. After the polar sunrise, concentrations of low molecular weight diacids decreased toward summer. However, azelaic acid (C9), a unique photochemical oxidation product of biogenic unsaturated fatty acids containing a double bond predominantly at the C-9 position, showed a peak in summer likely due to enhanced sea-to-air emission of marine derived organic matter to the Arctic due to the warming and retreat of sea ice in the polar ocean.

6. In September to October, concentrations of azelaic acid in the Arctic aerosols largely increased, probably due to local soil peaking in this time (Barrie and Barrie, 1990).

Finally, this study demonstrates that the Arctic is an excellent natural laboratory for the study of photochemical transformation of anthropogenic and natural organic matter in the troposphere, and is useful for understanding the complex chemistry of dicarboxylic acids and related organic compounds. More laboratory studies of the reaction mechanisms of these compounds are needed.

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