

## VERTICAL DISTRIBUTIONS OF LOW MOLECULAR WEIGHT DICARBOXYLIC ACIDS IN THE GREENLAND ICE CORE

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**Abstract:** Forty three ice sections taken from the Greenland ice core (Site-J, 206 m long, *ca.* 450 yrs old) have been studied for low molecular weight dicarboxylic acids using capillary gas chromatography and mass spectrometry. A homologous series of  $\alpha,\omega$ -dicarboxylic acids ( $C_2$ – $C_{10}$ ) and phthalic acid were detected in the ice core samples. Their molecular distributions show a predominance of succinic acid ( $C_4$ ) followed by oxalic acid ( $C_2$ ), malonic acid ( $C_3$ ), glutaric acid ( $C_5$ ), and azelaic acid ( $C_9$ ). The distribution patterns suggest that the dicarboxylic acids are photochemical oxidation products of biogenic compounds such as marine-derived unsaturated fatty acids rather than anthropogenic organic matter. Among the diacids, azelaic acid ( $C_9$ ) showed the most drastic changes: its concentrations were low before the 1890s, but abruptly increased after that period to recent years showing a maximum in the 1940s. Because  $C_9$  diacid is a specific photochemical oxidation product of unsaturated fatty acids, its historical trend suggests that sea ice coverage around Greenland was significantly enhanced before the 1890s and retreated in the 20th century. The maximum concentration of  $C_9$  diacid observed in the 1940s is consistent with a reported maximum of sea surface temperature (SST) in the Arctic and a reported decrease of drift ice around Iceland.

### 1. Introduction

In a preliminary study of snow and ice core samples collected from Site-J, Greenland (KAWAMURA and YASUI, 1991), we detected a homologous series of low molecular weight  $\alpha,\omega$ -dicarboxylic acids ( $C_2$ – $C_{10}$ ) and aromatic diacid (phthalic acid). Their molecular distributions were characterized by the predominance of succinic acid ( $C_4$ ) followed by oxalic acid ( $C_2$ ). This feature was found to be in contrast to aerosol samples collected from mid-latitudes (KAWAMURA and IKUSHIMA, 1993; KAWAMURA and USUKURA, 1993) and the Arctic (KAWAMURA *et al.*, 1995), which always showed a predominance of oxalic acid ( $C_2$ ). The preliminary results suggest that the major portion of dicarboxylic acids in the Greenland ice core are not derived from anthropogenic hydrocarbons such as benzene and toluene, which are photooxidized in the atmosphere to produce oxalic acid (KAWAMURA and IKUSHIMA, 1993). The ice core dicarboxylic acids may be rather derived from bio-

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genic sources coupled with photochemical reactions, which suggest their potential usefulness as chemical tracers to understand past changes both in the atmospheric transport of biological materials and in the atmospheric circulation.

In this study, we obtain the detailed information from the Greenland ice core divided into 43 ice sections. Here, we report historical trends of total and individual dicarboxylic acids in the ice core and discuss their biogeochemical implications for the climatic changes of lands and oceans over the last 450 years.

## 2. Samples and Methods

The ice core samples (205 m long) were collected from Site-J, Greenland ( $66^{\circ}51.9'N$ ,  $46^{\circ}15.9'W$ , altitude: 2030 m, see Fig. 1) in 1989 with a mechanical shallow drill by the Japanese Arctic Glaciological Expedition 1989 (WATANABE and FUJII, 1990). The ice layer chronology was determined by electrical conductivity and volcanic eruption records:

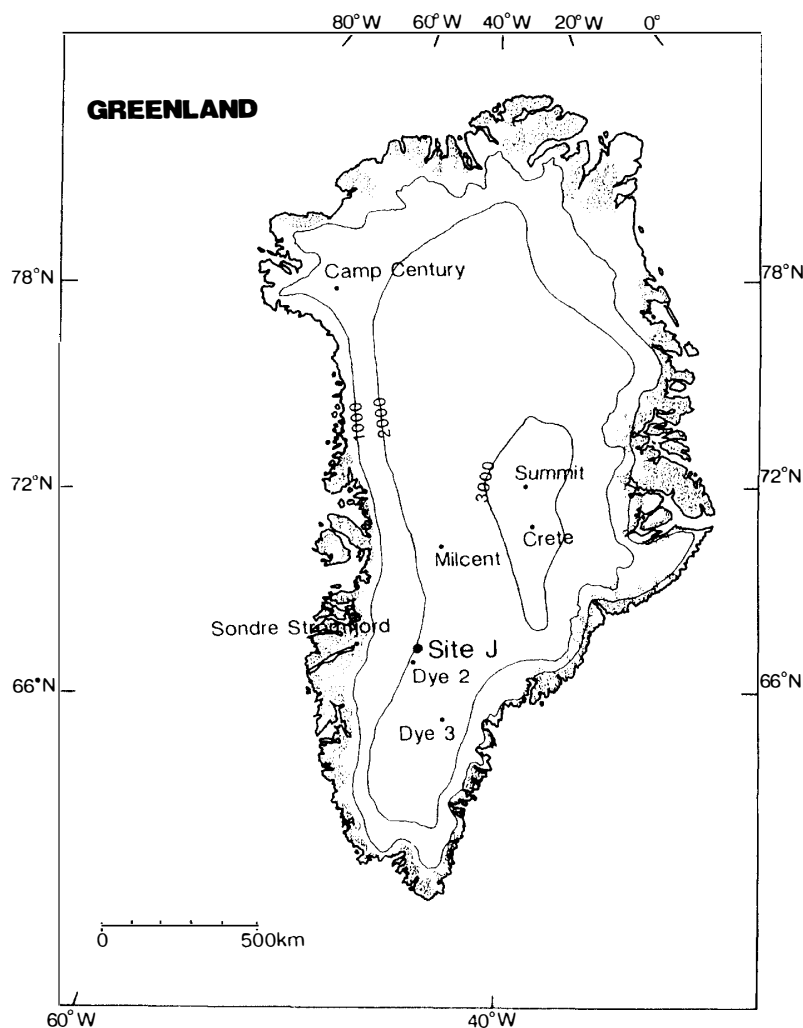


Fig. 1. A sampling site (Site-J) for the Greenland ice core analyzed in this study.

the 205 m layer was estimated to be 1546 AD (SHOJI *et al.*, 1991). The ages of the surface layers were confirmed by the detection of a tritium signal from nuclear bomb tests (IZUMI, 1991, unpublished result). Forty three sections were collected from the ice core and handled as described in KAWAMURA and YASUI (1991). The length of each section was 0.2–1.5 m, which corresponds to less than one half year to 4 years. Most of the ice sections were less than the average annual accumulation rate (42 cm of ice or 38 cm of water, SHOJI *et al.*, 1991).

The ice samples were melted in a clean room and concentrated using a rotary evaporator under a vacuum. The dicarboxylic acids in the samples were dried under a nitrogen stream and then reacted with 14% borontrifluoride in n-butanol to derive corresponding dibutyl esters. The derivatives (diacid dibutyl esters) were determined with a Hewlett Packard gas chromatograph (HP 5890) equipped with a split/splitless injector, fused silica capillary column (UP-2, 0.3 mm × 25 m), and an FID detector. The diacids were identified by a comparison of GC retention times with those of authentic standards and confirmed by mass spectral analysis using a Finnigan MAT ITS-40 GC/MS system. Details of analytical procedure are described in KAWAMURA and YASUI (1991) and KAWAMURA and IKUSHIMA (1993).

### 3. Results and Discussion

Figure 2 presents a capillary gas chromatogram of dicarboxylic acid dibutyl esters isolated from the ice core sample from Greenland. Molecular distribution of the diacids

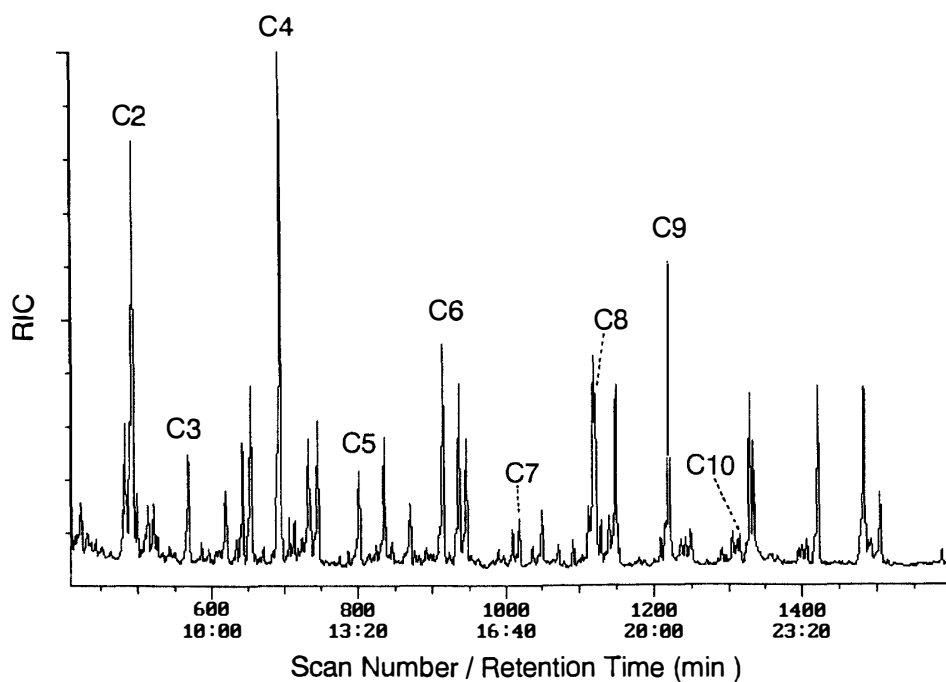


Fig. 2. Reconstructed ion chromatogram (RIC) of dicarboxylic acid dibutyl esters isolated from the ice core from Site-J, Greenland (Section # 58, 26.4 m in depth, 1949 AD). C<sub>2</sub>: oxalic, C<sub>3</sub>: malonic, C<sub>4</sub>: succinic, C<sub>5</sub>: glutaric, C<sub>6</sub>: adipic, C<sub>7</sub>: pimelic, C<sub>8</sub>: suberic, C<sub>9</sub>: azelaic, C<sub>10</sub>: sebacic acid.

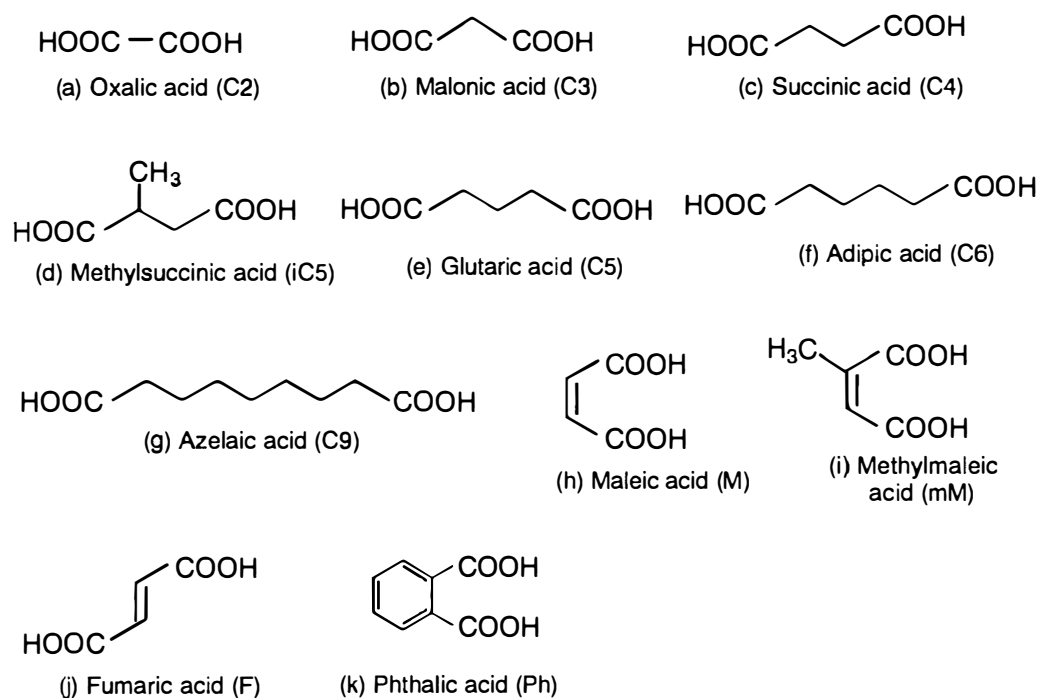


Fig. 3. Chemical structures of some low molecular weight dicarboxylic acids detected in the Greenland ice core.

is generally characterized by a predominance of succinic acid (C<sub>4</sub>) followed by oxalic acid (C<sub>2</sub>) throughout the ice core. Malonic (C<sub>3</sub>), glutaric (C<sub>5</sub>), adipic (C<sub>6</sub>), phthalic (C<sub>8</sub>) and azelaic (C<sub>9</sub>) acids were also detected as relatively abundant diacid species. Some of the chemical structures are given in Fig. 3. Although these dicarboxylic acids have been reported in marine and continental aerosols and wet precipitation (KAWAMURA and USUKURA, 1993; KAWAMURA and IKUSHIMA, 1993; SEMPÉRÉ and KAWAMURA, 1994), their molecular distributions are different from those of previously reported atmospheric samples. In particular, succinic acid has never been reported as the dominant diacid species in mid-latitude and arctic aerosols, in which oxalic acid is always dominant (KAWAMURA and IKUSHIMA, 1993; KAWAMURA *et al.*, 1995), except for previously analyzed aerosol samples using a BF<sub>3</sub>/methanol derivatization prior to GC injection (GROSJEAN *et al.*, 1978; SATSUMABAYASHI *et al.*, 1990). The BF<sub>3</sub>/methanol derivatization has been pointed out to cause a significant underestimation for the determination of oxalic and malonic acids (KAWAMURA and IKUSHIMA, 1993).

Their characteristic molecular distribution in the ice core suggests that the major portion of the diacids is not derived from photochemical oxidation of anthropogenic aromatic hydrocarbons which produce oxalic acid predominantly (KAWAMURA and IKUSHIMA, 1993); rather, they originate from photooxidation of biologically-derived aliphatic structures. Biogenic origin of the ice core diacids is supported by the abundant presence of azelaic acid (C<sub>9</sub>), which is a specific photo-oxidation product of unsaturated fatty acids containing a double bond predominantly at the C<sub>9</sub> position (KAWAMURA and KAPLAN, 1983; YOKOUCHI and AMBE, 1986; KAWAMURA and GAGOSIAN, 1987). The biogenic origin of the diacids is also supported from their vertical profile in the ice core. As

shown in Fig. 4a, the ice core profile of total dicarboxylic acids did not show an increase in the 20th century. This is in contrast to the vertical profile of fossil fuel-combustion derived polynuclear aromatic hydrocarbons in the ice core, which showed a large increase after 1900 AD (KAWAMURA *et al.*, 1994).

Concentration range of total dicarboxylic acids ( $C_2$ – $C_{10}$ ) in the Greenland ice core was 3–33 ng/g-ice with a mean concentration of 11.1 ng/g (Fig. 4a). These values are an order of magnitude lower than those (12–540 ng/g-water) reported in continental rain and snow samples collected from mid-latitudes (SEMPÉRÉ and KAWAMURA, 1994). Although other diacids have not been determined, LEGRAND *et al.* (1992) reported the background concentrations of oxalic acid in the Summit-Greenland ice core (330 to 2500 years BP) to be *ca.* 1–2 ng/g-ice. Our results showed that the concentration range of ice core oxalic acid at Site-J is 0.38–10.7 ng/g-ice with a mean concentration of 2.1 ng/g-ice. The background concentration of oxalic acid at Site-J is *ca.* 1 ng/g-ice, being similar to that reported in Summit ice core for pre-industrial periods (LEGRAND *et al.*, 1992). These considerations again suggest that the major portion of dicarboxylic acids in the upper layers of the Greenland ice core is not of anthropogenic origin. However, diacid species with carbon numbers more than  $C_3$  have not been reported in the previously studied ice cores from Greenland and elsewhere because conventional ion chromatography technique fails to detect longer chain diacids.

As shown in Fig. 4a, concentrations of total diacids fluctuated by a factor of ten. Based on three-point running means, total diacid concentrations show a historical trend with higher values in the 1600s–1640s, 1760s–1810s, 1920s–1940s, and 1980s, and lower values in the 1540s–1590s, 1650s–1730s, 1820s–1870s, and 1960s–1970s. Concentration of oxalic acid (0.36–10.7 ng/g-ice, av. 2.1 ng/g-ice) shows a historical trend similar to that of total diacids; however, its trend seems much smoother (Fig. 4b). Although major diacids showed similar ice core records, some diacids showed different trends than that of total diacids as follows.

Concentrations of malonic acid ( $C_3$ ) (0.13–5.11 ng/g-ice, av. 0.77 ng/g-ice) are generally less than those of  $C_2$  diacid; however,  $C_3$  is more abundant than the  $C_2$  diacid in the middle 1600s (2.7 ng/g-ice vs. 2.6 ng/g-ice for the #C286 section: 1631 year; 0.69 ng/g-ice vs. 0.47 ng/g-ice for the #A-277 section: 1649 year) and in the late 1900s (1.19 ng/g-ice vs. 0.71 ng/g-ice for the #21 section: 1972, 5.11 ng/g-ice vs. 4.05 ng/g-ice for the #10 section: 1980 year) (Fig. 4c). The predominance of malonic acid over oxalic acid has not been detected in the aerosol samples collected from the polluted Canadian Arctic, Alert (KAWAMURA *et al.*, 1995), continental mid-latitudes (KAWAMURA and IKUSHIMA, 1993; SEMPÉRÉ and KAWAMURA, 1994) and the North Pacific (KAWAMURA and USUKURA, 1993). Interestingly, the ice core  $C_3$  diacid showed relatively large peaks in the early 1600s and 1970s, but a smaller peak in the early 1900s.

Succinic acid ( $C_4$ ) shows a historical profile similar to malonic acid (Figs. 4c and 4d); however, its concentrations (1.3–13.4 ng/g-ice, av. 4.8 ng/g-ice) are generally much greater than those of  $C_3$  and even  $C_2$  diacid. The predominance of  $C_4$  diacid has never been observed in the previously studied atmospheric samples from mid-latitudes; however, Antarctic summer aerosols collected at Syowa Station located near the coast show a predominance of  $C_4$  diacid with its relative abundance of 69% in the total diacids (KAWAMURA *et al.*, 1996a).

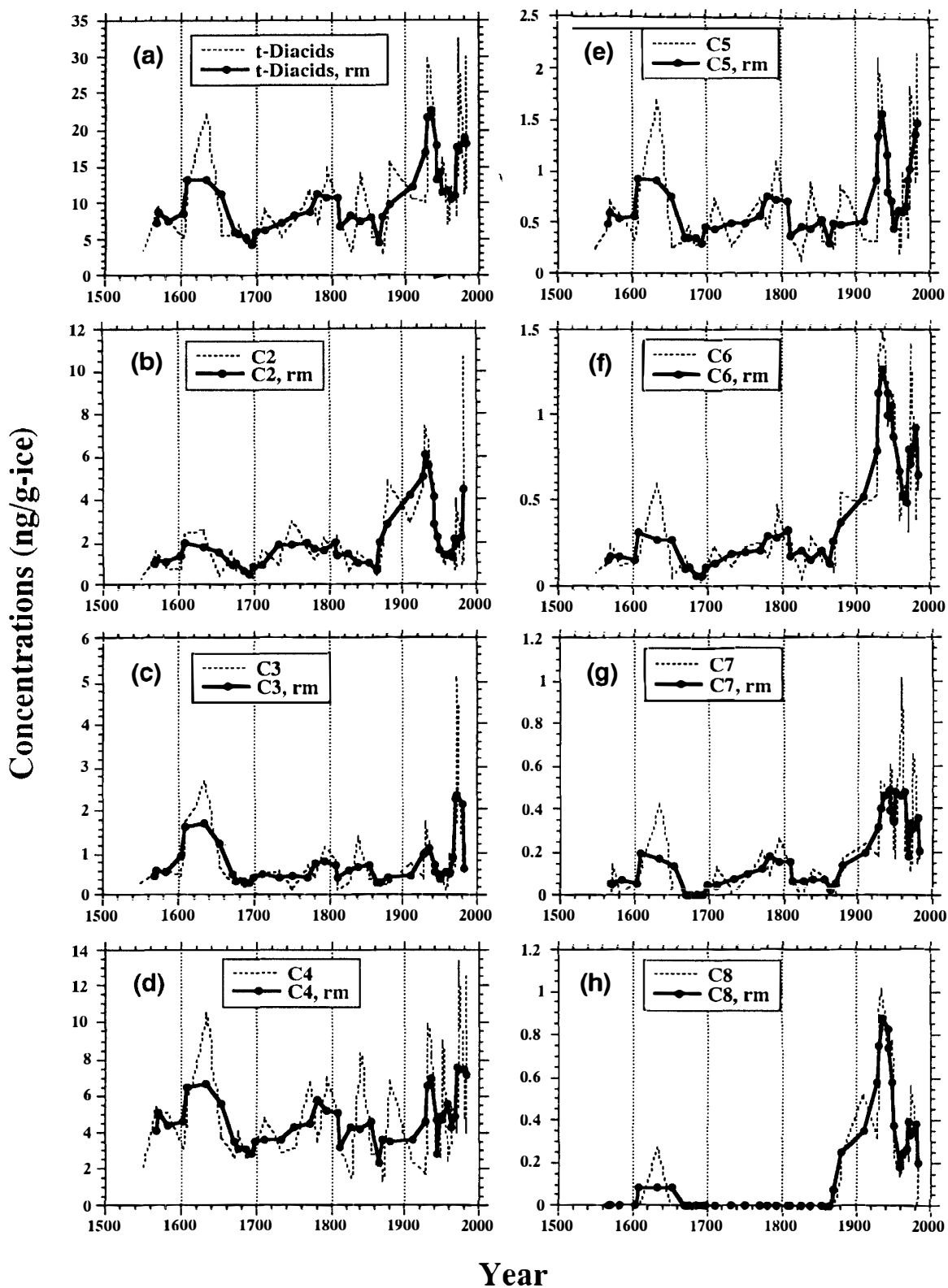


Fig. 4. Historical changes in the concentrations of (a) total ( $C_2$ - $C_{10}$ ) and (b-p) individual dicarboxylic acids in the ice core from Site-J, Greenland. For abbreviations, see Figs. 2 and 3. The abbreviation "rm" indicates 3-point running means.

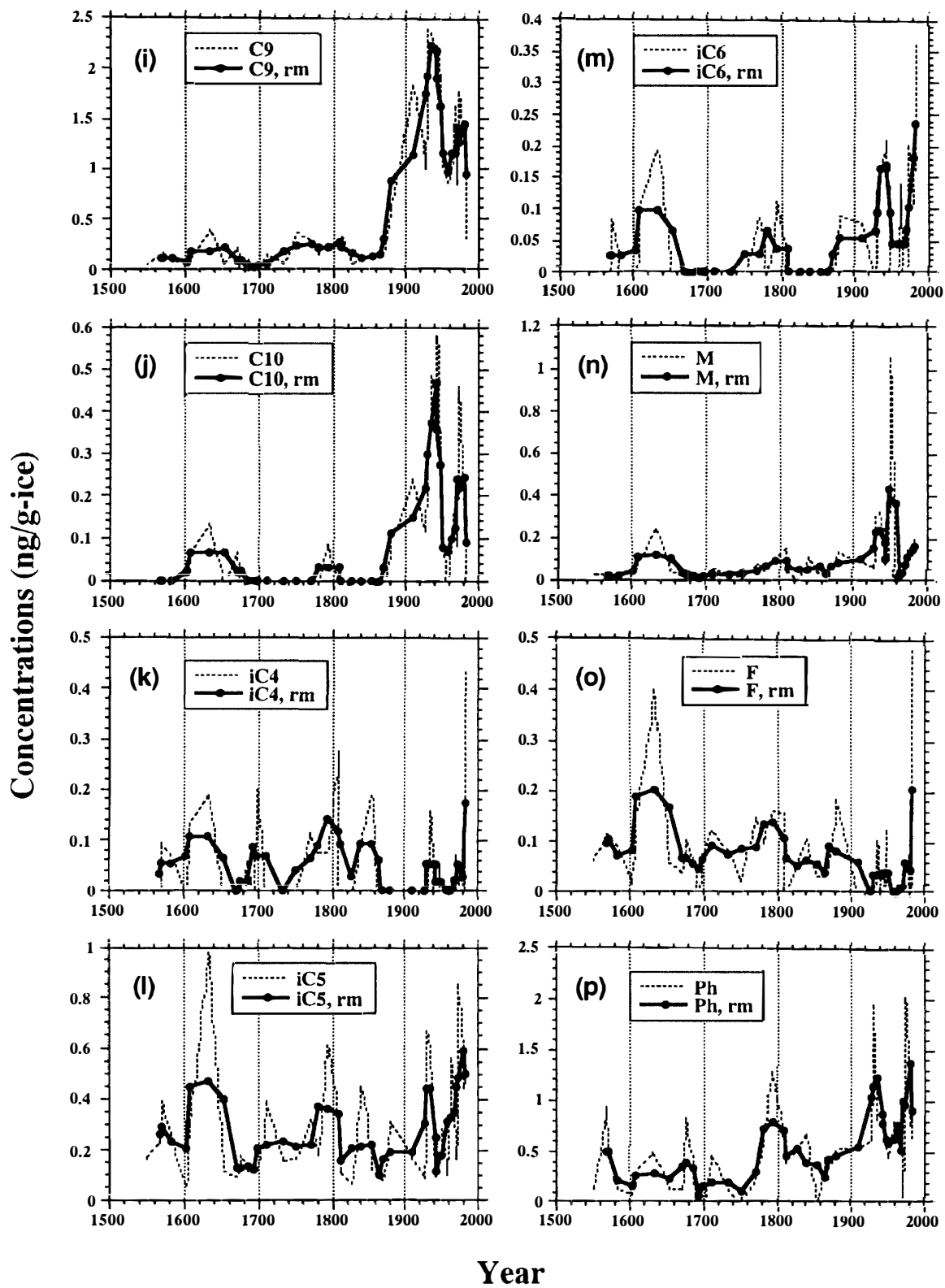


Fig. 4. (Continued)

Longer chain dicarboxylic acids ( $\geq C_5$ ) are less abundant than short chain diacids ( $C_2$ ,  $C_3$  and  $C_4$ ). Their concentrations fluctuated significantly, showing several peaks in certain periods. The ice core trends of glutaric ( $C_5$ ) and adipic ( $C_6$ ) acids are similar to that of  $C_4$  diacid (Figs. 4e and 4f), except that peaks in the 1930s–1950s and the 1980s are relatively much higher. Enhanced peaks in the same periods were also observed in the profiles of suberic ( $C_8$ ), azelaic ( $C_9$ ) and sebacic ( $C_{10}$ ) acids (Figs. 4h–4j). Interestingly,  $C_9$  diacid, whose concentrations ranged from  $< 0.01$  ng/g-ice to 2.38 ng/g-ice (av. 0.64 ng/g-ice), was a minor species in the 1500s–1700s, but, suddenly became the third most abundant diacid species after the late 1800s and maximized in the 1930s–1940s. After the large peak in the early 1900s,  $C_9$  diacid concentrations showed a sharp drop toward the 1960s–1970s and again increased in the 1980s.

Branched chain  $C_4$ ,  $C_5$  and  $C_6$  diacids are less abundant than the corresponding straight chain diacids (Figs. 4h–4m). Methylsuccinic acid (iso  $C_5$ ) is the dominant branched diacid, which showed a concentration range of 0.0061–0.98 ng/g-ice (av. 0.28 ng/g-ice) and peaked in the early 1600s, 1800s, 1930s and 1980s. Its historical trend seems to be similar to that of the corresponding straight chain diacid (glutaric acid,  $C_5$ ).

Unsaturated dicarboxylic acids are less abundant than the saturated ones (Figs. 4n–4p). Concentration range of maleic acid (*cis* configuration) was  $< 0.01$ –1.06 ng/g-ice (av. 0.10 ng/g-ice) whereas that of *trans* isomer (fumaric acid) was  $< 0.01$ –0.48 ng/g-ice (av. 0.06 ng/g-ice). Maleic acid was abundantly detected in the early 1600s, early 1800s, and mid 1900s. After the peak in 1956, maleic acid concentration showed a sharp drop in the 1960s–1970s, and then gradually increased toward the 1980s. The trend of fumaric acid was similar to that of maleic acid, except that the concentrations were relatively low in the 1950s. Aromatic (phthalic) diacid fluctuated with a concentration range of  $< 0.01$ –2.02 ng/g-ice (av. 0.56 ng/g-ice). Its concentrations showed peaks in the 1800s, 1920s–1940s and 1980s.

As stated above, the diacids detected in the ice core are most likely derived from atmospheric oxidation of biologically-derived organic compounds. 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 and other precursors such as n-alkanes, aldehydes and mid-chain ketocarboxylic acids (KAWAMURA *et al.*, 1996b). Unsaturated fatty acids are produced by marine organisms and enriched in microlayers of surface seawater (MARTY *et al.*, 1979), and injected to the atmosphere by bubble bursting mechanisms caused by winds. They are also constituents of cell walls of terrestrial higher plants (HITCHCOCK and NICHOLS, 1971). Thus, the ice core record of dicarboxylic acids should be related to (1) changes in sea-to-air and/or land-to-air flux of the precursor compounds, (2) their atmospheric transport over Greenland (Site-J) which is associated with changes in atmospheric circulation patterns, and (3) changes in the capability for photochemical reactions in the atmosphere and on snow surfaces in the past.

Azelaic acid ( $C_9$ ) is one of the well-known photochemical tracers: it is a specific photochemical reaction product of biogenic unsaturated fatty acids (*e.g.*, KAWAMURA and GAGOSIAN, 1987). Interestingly, the ice core record of this acid showed the most drastic changes among the dicarboxylic acids (Fig. 4i). During the 1500s to middle 1800s, concentrations of  $C_9$  are significantly low compared to more recent times, although they



showed a minimum around 1700 and maximum between 1750 and 1820. The low concentrations at those times suggest that atmospheric inputs and subsequent oxidation of biogenic fatty acids to azelaic acid were suppressed by a certain mechanism, a point to be discussed below. On the other hand, higher concentrations of azelaic acid in the late 1800s to 1940s mean enhanced atmospheric inputs of the unsaturated fatty acids, coupled with their photochemical oxidation in the atmosphere during a long-range transport and on snow surfaces after deposition. These historical changes in the concentrations of azelaic acid may have been associated with climatic changes in the past.

Because unsaturated fatty acids are enriched in the microlayers of seawater surfaces (MARTY *et al.*, 1979), their sea-to-air emissions may depend on the areas of open ocean around Greenland from which unsaturated fatty acids are emitted to the air. From the 1890s to the 1940s when C<sub>9</sub> diacid concentrations were high (Fig. 4i), it may have happened that sea ice coverage around Greenland shrank and the surrounding open ocean area was enhanced. Although there were no direct observations of sea ice activity during these periods, BERGTHORSSON (1969) reported a decreased incidence of Iceland drift ice in the 1920s to 1950s. The drift ice records are consistent with our Greenland ice core records of C<sub>9</sub> diacid, supporting our idea that sea ice activity around Greenland was depressed in the 1890s and the 20th century. Interestingly, the historical trend of C<sub>9</sub> diacid is seemingly in good agreement with sea surface temperature (SST) of the Arctic, which increased in the 1920s to 1940s and then decreased toward the 1970s (JONES and KELLY, 1983), and with the SST of the Northern Hemisphere (FOLLAND and PARKER, 1990).

Further, the ice core peak of C<sub>9</sub> diacid in the 1940s is also consistent with a marked increase in the annual air temperature in the Icelandic coastal area over the same periods (STEFANSSON, 1969) and with higher air temperatures in North America reconstructed from tree ring data (JACOBY and D'ARRIGO, 1989). The distributions of C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub> and C<sub>10</sub> diacids in the ice core also showed historical trends similar to that of C<sub>9</sub> diacid: higher concentrations in the late 1890s to the 20th century. These diacids have also been reported in the marine atmosphere and are considered to be produced by the photooxidation of unsaturated fatty acids with a double bond at position different from C-9 (KAWAMURA and GAGOSIAN, 1987). These apparent agreements between the ice core records of dicarboxylic acids and climatic changes over the last 100 years suggest that organic compounds stored in the Greenland ice core have imprinted information of changes in sea/air interactions caused by climate change in the Northern Hemisphere.

In contrast, azelaic acid concentrations were low from the 1550s to the 1860s, with a minimum around 1700 (Fig. 4i). This result suggests that sea-to-air emissions of the precursor compounds (unsaturated fatty acids) of C<sub>9</sub> diacid were depressed at those times probably due to the more developed sea ice coverage around Greenland. We do not have any record of sea ice activities in northern high latitudes oceans at those times. However, it is interesting to note that the above ages fall in the period of the so-called Little Ice Age, which occurred on a global scale in the 1500s to the 1800s after the Medieval Warm Epoch (800 AD to 1200 AD) (BRADLEY and JONES, 1992). During the Little Ice Age, it is likely that sea ice coverage over the high latitude oceans around Greenland developed much more and sea-to-air emissions of marine derived organic materials were significantly depressed. These biogeochemical processes in high latitudes seem to be preserved in the vertical distributions of dicarboxylic acids in the Greenland ice core.

#### 4. Concluding Remarks

Although we cannot at present explain all the ice core records of dicarboxylic acids, it is clear now that they are associated with atmospheric inputs of biogenic organic compounds of marine origin, such as unsaturated fatty acids, which are subsequently subjected to photochemical chain reactions in the atmosphere during long-range transport and on snow surfaces after deposition. Sea-to-air emission of the diacid precursors in high latitudes is primarily controlled by sea ice coverage in the oceans around Greenland. This study suggests that organic compounds preserved in the Greenland ice core can be used as new tracers to understand past changes of biogeochemical cycles of marine-derived organic materials at the sea/air interface and in marine boundary layers. Ice core records of dicarboxylic acids are most likely connected to global cooling and warming in the Northern Hemisphere.

#### Acknowledgments

We thank the Japanese Arctic Glaciological Expedition (JAGE) 1989 members for their collaboration in the ice core drilling and their permission to use the samples in this study. We also thank Prof. T. MIKAMI and Dr. K. SUZUKI of Tokyo Metropolitan University for valuable comments and discussion. This study was supported in part by the Tokyo Metropolitan University Special Research Fund (1990) and the Ministry of Education, Science, Sports and Culture through Grant-in-Aid No. 06453009.

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*(Received January 10, 1996; Revised manuscript accepted March 1, 1996)*