

DISTRIBUTIONS AND HISTORICAL RECORDS OF ALIPHATIC CARBOXYLIC ACIDS IN THE H15 ICE CORE FROM ANTARCTICA

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Abstract: An ice core collected from Antarctica (site H15) has been studied for molecular distributions of fatty acids and dicarboxylic acids using capillary gas chromatography and mass spectrometry. Molecular distributions of normal saturated fatty acids (C₈-C₃₀) showed an even carbon number predominance with a maximum at C₁₆ or C₁₈, suggesting that they were mainly derived from marine phytoplankton. The ice core fatty acids have been emitted to the atmosphere from the sea surface microlayers in the Southern Ocean through a bubble bursting process and subsequently transported long distances over the Antarctic ice sheet. Their concentrations fluctuated in the ice core with a range of 1-4110 ng/kg-ice, showing lower values between the 1630s and 1840s and higher values after the 1850s. The lower concentrations may suggest depressed emission of marine-derived fatty acids to the atmosphere due to enhanced sea ice coverage whereas the higher concentrations after the 1850s may be caused from enhanced emissions from the ocean due to the retreat of sea ice. The former is probably associated with the Little Ice Age, the latter with global warming. Unsaturated fatty acids (C_{16:1}, C_{18:1} and C_{18:2}) were also detected in the ice core together with their unique photochemical oxidation product: C₉ α,ω -dicarboxylic acid (azelaic acid). Interestingly, concentration ratios of azelaic acid to unsaturated fatty acids in the ice core showed a rapid increase after the 1970s, suggesting that photochemical transformation of organic aerosols in the Antarctic atmosphere and/or in the surface of the ice sheet was enhanced after the 1970s. An enhanced oxidizing capability suggested in the Antarctic troposphere may be involved with ozone depletion in the stratosphere, which has been observed over Antarctica for the last two decades.

1. Introduction

Polar ice cores contain atmospheric trace gases and aerosol constituents from the past atmosphere; thus, their chemical analyses provide data sets to reconstruct past changes in climate and the environment (DELMAS, 1992). Previous ice core analyses of chemical species have been focused on inorganic species (*e.g.*, BARNOLA *et al.*, 1987; LEGRAND *et al.*, 1988; DELMAS, 1992). Although many natural organic compounds are present in the

atmospheric environment, they have rarely been studied in polar snow and ice (LEGRAND and SAIGNE, 1988; KAWAMURA *et al.*, 1995). In aerosols from the present atmosphere, specific lipid class compounds have been detected and successfully used as chemical tracers to evaluate marine and terrestrial source inputs to the remote marine atmosphere (SIMONEIT *et al.*, 1977; GAGOSIAN *et al.*, 1981; STEPHANOU, 1992a) and photochemical transformation of organic aerosols (KAWAMURA and GAGOSIAN, 1987, 1990a, b; SATSUMABAYASHI *et al.*, 1990; STEPHANOU, 1992b).

In a previous study, we analyzed the Antarctic aerosols collected from Syowa Station and detected a homologous series of fatty acids, α,ω -dicarboxylic acids, and some oxocarboxylic acids (NISHIKIORI *et al.*, 1996; KAWAMURA *et al.*, 1996). Their molecular distributions indicated that the organic constituents in Antarctic aerosols mainly originate from marine organisms and their photochemical transformation is intensified in summer. These results suggest that the ice core analyses for organic compounds could provide unique information on past changes in the sea-to-air flux of the marine organic matter and photochemical transformation of organic aerosols.

In this study, we analyzed an ice core sample taken from site H15, Antarctica. Here, we report the molecular distributions of fatty acids and dicarboxylic acids and their historical trends in the ice core. The results will be discussed in terms of past changes in the atmospheric transport of marine-derived organic materials over the Antarctic ice sheet and their photochemical transformation in the atmospheric environments.

2. Samples and Analytical Procedures

A 120 m long ice core (core diameter; 70 mm) was collected in 1991 at site H15, Antarctica (69°04'46"S, 40°46'54"E, 1057 m a.s.l) using an electromechanical drill with no fluid during the 32nd Japanese Antarctic Research Expedition. The ice core chronology was determined based on annual accumulation rate of 26 g/cm², which was estimated from a signal peak of ECM corresponding to volcanic eruption events such as Tambora in 1815 (MACHIDA *et al.*, 1995). The 120 m layer was estimated to be *ca.* 350 years old. Thirty six sections were cut off from the ice core for the analysis of lipid class compounds. In order to avoid potential contamination, the sample surfaces were removed. Each section was then melted in a pre-cleaned Teflon container in a clean room. The melt water was poisoned with mercuric chloride to prevent microbial degradation of organic compounds. The samples were stored at 4°C in a pre-cleaned brown glass bottle with a Teflon-lined screw cap prior to analysis.

A melt water sample (160–638 ml) was extracted with a methylene chloride/ethyl acetate (2 : 1) mixture (70+40+40 ml) after acidification with 6 M HCl (5–8 ml) to pH=1. Extracts were combined and concentrated down to 2 ml and then saponified with a 0.2 M KOH/methanol solution (50 ml) containing 10% water. After neutral components were removed by extraction with an n-hexane/methylene chloride (10 : 1) mixture, the saponified fraction was acidified (pH=1) with 6 M HCl and extracted with a methylene chloride/ethyl acetate (9 : 1) mixture to isolate carboxylic acids. The carboxylic acids were methylated with 14% BF₃ in methanol and the methyl ester derivatives were divided into three fractions on a silica gel (Bio-Sil A, 200–400 mesh) column by eluting with an n-hexane/methylene chloride (1 : 2) mixture (A-1: monocarboxylic acid methyl esters),

methylene chloride/ethyl acetate (98 : 2) mixture (A-2: dicarboxylic acid dimethyl esters) and methylene chloride/methanol (95 : 5) mixture (A-3: hydroxyacid methyl esters).

The A-1 and A-2 fractions were concentrated and analyzed with a Fisons MEGA 2 gas chromatograph (GC) equipped with a Grob-type cold on-column injector, fused silica DB-5 capillary column (0.32 mm × 30 m × 0.25 μm) and an FID detector. The GC peak was identified by comparing the retention times with those of authentic standards. Identification of the compounds was confirmed using GC/mass spectrometry (Finnigan-MAT ITS 40). Recoveries of monocarboxylic (C₁₆ and C₂₄) and dicarboxylic (C₁₁ and C₁₆) acids in the analytical procedures were 75 and 85%, respectively. Duplicate analyses of a few samples showed the analytical error was to be less than 21% for the compounds reported here. Concentrations of compounds are corrected for the procedural blanks.

All the organic solvents used were re-distilled in the laboratory prior to use. Reagents were used after appropriate treatment with organic solvents to remove potential contamination.

3. Results and Discussion

In the ice core samples, monocarboxylic acids (fatty acids), dicarboxylic acids and oxocarboxylic acids have been detected. Table 1 presents their total concentrations in each section.

3.1. Distributions of monocarboxylic acids

Figure 1 presents a typical gas chromatogram of A-1 fraction isolated from the H15 ice core. A homologous series of normal saturated fatty acids were detected in the range of C₈–C₃₀. Their distribution showed a strong even carbon number predominance with a maximum at C₁₆ or C₁₈, except for C₉, which was more abundant than C₈ and C₁₀. The C₁₆ and C₁₈ acids are dominant fatty acid species of marine algae and terrestrial higher plants whereas C₉ fatty acid is a photochemical reaction product of unsaturated fatty acids such as oleic acid (C_{18:1}) (KAWAMURA and GAGOSIAN, 1987). Unsaturated fatty acids (C_{16:1}, C_{18:1} and C_{18:2}) were also detected in the ice core (see Fig. 1). They are dominant species in marine algae and are abundantly present in the sea surface microlayers.

Lower molecular weight (C₁₂–C₁₉) fatty acids are much more abundant than higher molecular weight (C₂₀–C₃₀) fatty acids, which are characteristic of terrestrial higher plants and soil dust particles (GAGOSIAN, 1986; PELTZER and GAGOSIAN, 1989). Chain length distributions of normal saturated fatty acids are similar to those detected in sea surface water samples collected from the Antarctic Ocean (NISHIKIORI and KAWAMURA, unpublished data), suggesting that they originate from marine organisms through sea-to-air emissions and subsequent atmospheric transport over Antarctica. The ice core distributions are similar to those obtained for the marine aerosol samples from the Antarctic Ocean (KAWAMURA and NIWAI, unpublished data) and the Antarctic aerosols from Syowa Station (NISHIKIORI *et al.*, 1996). These comparisons suggest that fatty acids in the ice core originate from marine aerosols by long distance atmospheric transport and subsequent dry and wet deposition over the Antarctic ice sheet.

Total concentrations of both the saturated and unsaturated fatty acids fluctuated considerably in the ice core (Fig. 2) with a range of 1–4110 ng/kg-ice (av. 660 ng/kg-ice)

Table 1. Concentrations (ng/kg-ice) of fatty acids, dicarboxylic acids and oxocarboxylic acids in the H15 ice core from Antarctica.

Ice section	Year AD	Fatty acids		Dicarboxylic acids (C ₆ -C ₁₃)	Oxocarboxylic acids (C ₈ , C ₉)
		Saturated (C ₈ -C ₃₀)	Unsaturated (C ₁₆ , C ₁₈)		
290/291	1633	214	215	8	BDL
278	1652	424	367	63	BDL
270/271	1664	40	69	BDL	BDL
263	1676	108	126	31	BDL
251	1692	197	320	84	BDL
238	1709	132	63	9	BDL
232	1719	102	76	19	BDL
220/221	1733	64	37	BDL	BDL
209-# 2	1747	1	57	BDL	BDL
209-# 1	1748	18	40	9	BDL
198	1759	21	37	12	BDL
185/186-# 2	1777	10	123	7	18
185/186-# 1	1778	55	22	6	BB
176	1791	75	99	9	BB
166	1805	52	61	33	BB
160/161	1812	106	27	4	BB
151	1825	48	18	16	26
145	1833	BB	37	18	BB
137	1844	29	1	52	BB
125/126	1857	1190	1050	274	65
117	1868	2010	3610	987	80
108	1880	396	398	302	19
95/96	1895	430	277	211	14
86/87	1904	310	271	322	13
75/76	1916	827	501	216	26
67	1926	804	291	412	45
59	1934	4100	1950	2410	117
53	1941	722	446	486	16
45/46	1949	1590	1360	2610	74
40/41	1955	713	553	585	26
31/32	1964	458	332	422	13
22/23	1974	1240	1720	1300	56
16/17	1980	663	515	1290	42
8/9	1986	1460	222	1790	72
3	1990	1030	337	1740	57
1/2	1991	4110	529	2140	228

BB: Below blank.

BDL: Below detection limit (<1 ng/kg-ice).

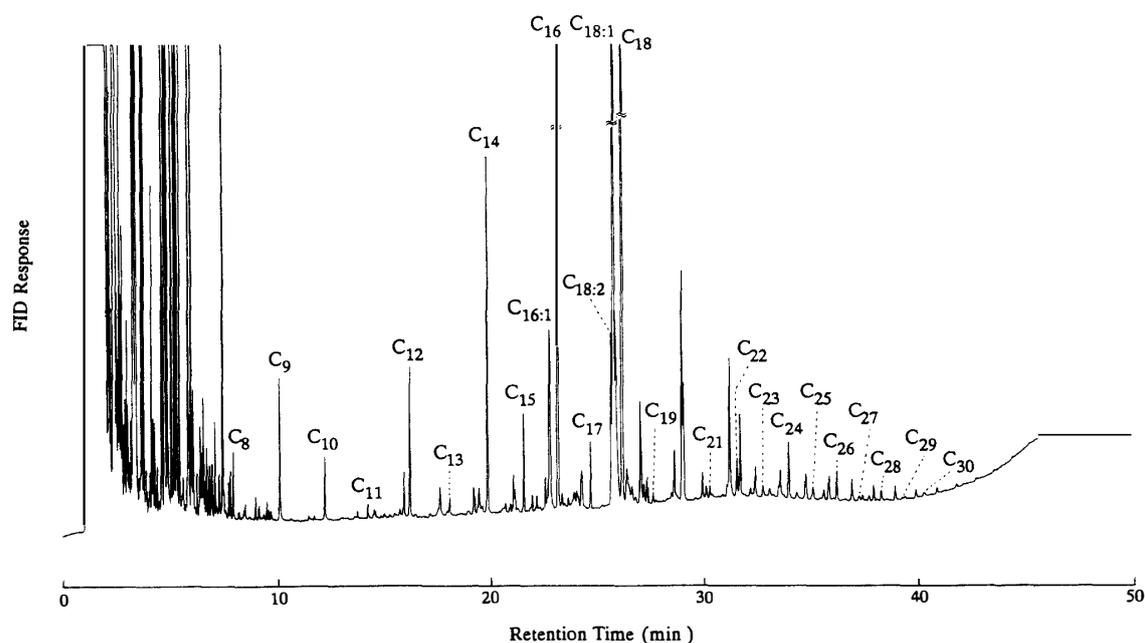


Fig. 1. Capillary gas chromatogram of monocarboxylic acid methyl ester fraction isolated from the H15 ice core sample (No. 16/17, 6.78 m in depth, 1980AD).
 $C_{n:m}$ means unsaturated fatty acid with n carbon numbers and m double bonds.

and 1–3610 ng/kg-ice (av. 450 ng/kg-ice), respectively. They are more than 10 times lower than the concentrations in the Greenland Site-J ice core (KAWAMURA *et al.*, 1995). This may suggest that fluxes of fatty acids at site H15 are much smaller than those at Site-J, although total organic carbon content in the H15 ice core (0.29–4.9 ppm, av. 2.0 ppm, KAWAMURA *et al.*, unpublished data) was comparable to those in the Site-J ice core (0.7–5.7 ppm, av. 1.7 ppm, KAWAMURA *et al.*, 1992).

Figure 2a gives a historical record of total normal saturated fatty acids in the H15 ice core. Their concentrations slowly decreased from the 1630s to 1750s and stayed very low (less than *ca.* 100 ng/kg-ice) for the following hundred years. After the 1850s, the concentrations started to increase significantly and showed two maxima, in the 1870s (*ca.* 2000 ng/kg-ice) and 1930s (*ca.* 4100 ng/kg-ice). They then decreased in the 1960s (*ca.* 460 ng/kg-ice) and increased again toward the 1990s (*ca.* 4100 ng/kg-ice). These fluctuations in the ice core suggest that the atmospheric transport of organic materials over the Antarctic ice sheet was weakened in the 1630s to 1840s, and significantly enhanced after the 1850s. The concentration levels in the 1900s (*ca.* 500 ng/kg-ice or more) are more than 5 times higher than those (*ca.* 100 ng/kg-ice) in the 1700s to 1840s. In addition, the amplitude of the fluctuations in the 1900s is about 10 times more than those in the 1700s to 1800s. Such a large fluctuation cannot be explained by the changes (within 34%) in snow accumulation rate in the sampling area (KOHNO *et al.*, 1996), suggesting that the air-to-snow flux of the fatty acids has significantly increased in the 20th century.

Figure 2b gives an ice core record of unsaturated fatty acids. Their concentrations decreased from the 1630s to early 1700s and stayed very low (less than *ca.* 100 ng/kg-ice) between the 1710s and 1840s. They then increased between the 1850s and 1990s, being

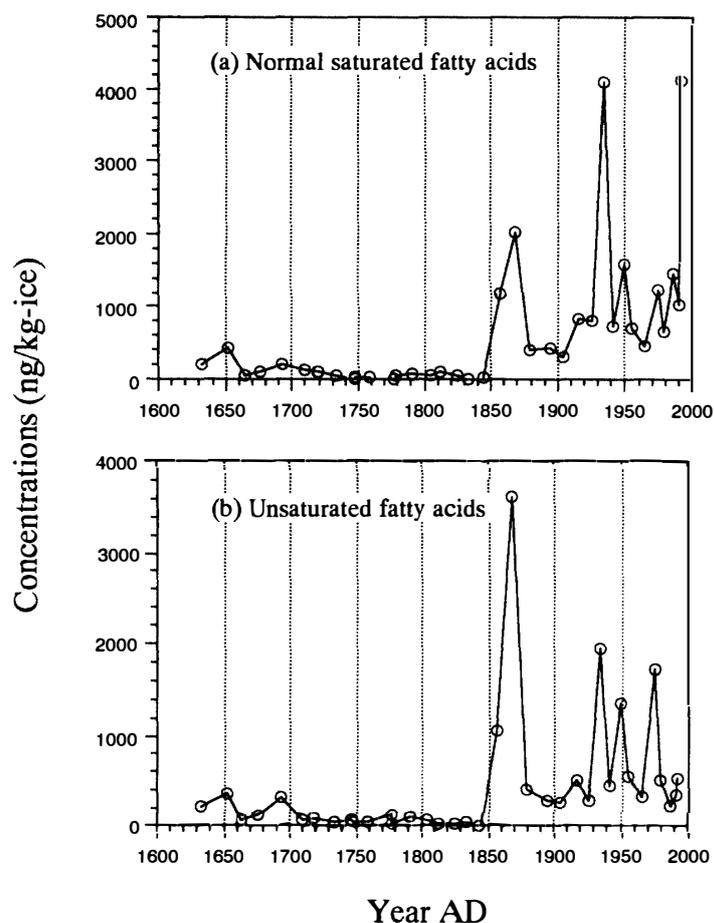


Fig. 2. Historical records of concentrations of (a) normal saturated fatty acids (C_8 - C_{30}) and (b) unsaturated fatty acids (C_{16} and C_{18}) in the H15 ice core from Antarctica.

similar to the fluctuation of normal saturated fatty acids. However, in the 1970s to 1990s, unsaturated fatty acids fluctuated in a way different from normal saturated fatty acids (see Fig. 2a). Unsaturated fatty acids are major lipid components of marine algae and are abundantly present in sea surface microlayers. They are emitted to the atmosphere through a bubble bursting mechanism at the sea/air interface, together with saturated fatty acids. Because unsaturated fatty acids are unstable, they should be subjected to rapid oxidation in the atmosphere during long distance transport (KAWAMURA and GAGOSIAN, 1987). In contrast, saturated fatty acids are more stable than unsaturated ones in the atmosphere. Unsaturated fatty acids are potentially further degraded in the snow surface after deposition. Therefore, it is reasonable to consider that the unsaturated fatty acids behave differently from saturated fatty acids in the Southern Ocean and Antarctic atmosphere.

The period from the 17th to 19th century in which fatty acids showed very low ice core concentrations is known as the so-called "Little Ice Age" (BRADLEY and JONES, 1992). The low concentrations in that period suggest a decreased air-to-snow flux, which may have been caused by decreased atmospheric transport of organic aerosols over the Antarctic ice sheet. Such a change should be coupled with a decrease in their sea-to-air flux associated

with an expansion of sea ice area in the Southern Ocean. In contrast, relatively high concentrations of the fatty acids in the 1850s to 1990s may be associated with enhanced atmospheric transport of marine derived organic matter over Antarctica, which could be caused by the retreat of sea ice and expansion of open ocean in the Southern Ocean. Although there is no direct evidence of sea ice retreat and/or advance in the Southern Ocean, the increased concentrations of fatty acids in the 1850s to 1990s could be associated with global warming which started in the late 19th century (FOLLAND and PARKER, 1990).

3.2. Distributions of dicarboxylic acids and oxocarboxylic acids

A homologous series of α,ω -dicarboxylic acids (C_6 - C_{13}) were detected in the A-2 fraction isolated from the H15 ice core (Fig. 3). In addition to α,ω -dicarboxylic acids, 4-oxooctanoic acid, 4-oxononanoic acid, 9-oxononanoic acid, phthalic acid and isophthalic acid were also detected in the same fraction. Azelaic acid (C_9) was detected as the dominant α,ω -dicarboxylic acid in the H15 ice core. This acid is known as a photochemical oxidation product of biogenic Δ^9 unsaturated fatty acids whose double bond is present at the C-9 position (KAWAMURA and GAGOSIAN, 1987). The predominance of azelaic acid has been found in the aerosols collected from the Antarctic (NISHIKIORI *et al.*, 1996), mid-latitude urban areas (KAWAMURA, unpublished data) and the North Pacific Ocean (KAWAMURA and GAGOSIAN, 1987, 1990a). Photochemical precursors of azelaic acid, that is, Δ^9 unsaturated fatty acids (C_{16} and C_{18}), have also been detected in the A-1 fraction.

On the other hand, long-chain dicarboxylic acids ($>C_{20}$) which have been proposed as indicators of atmospheric transport of soil dust particles (KAWAMURA and GAGOSIAN, 1990a) were not detected in the H15 ice core, although they are found in the Greenland

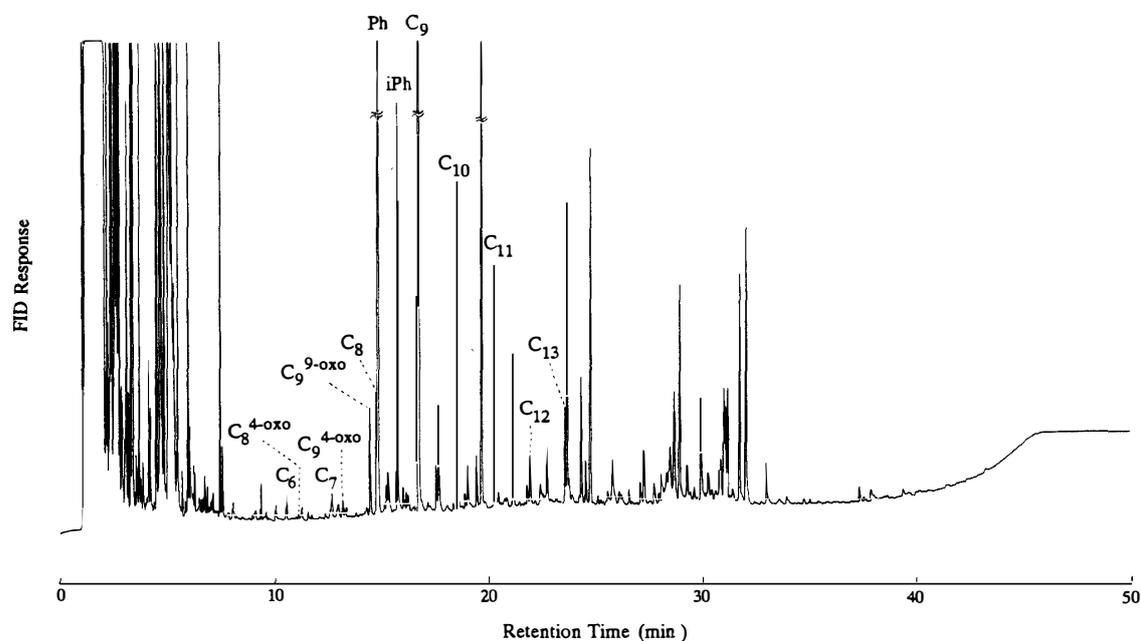


Fig. 3. Capillary gas chromatogram of dicarboxylic acid dimethyl ester fraction isolated from the H15 ice core sample (No. 16/17, 6.78 m in depth, 1980AD). $C_9^{4\text{-oxo}}$ means mid-chain oxocarboxylic acid with 9 carbon numbers and oxo functional group at the C-4 position. Ph: phthalic acid, iPh: isophthalic acid.

Site-J ice core (KAWAMURA, unpublished data). This indicates that atmospheric transport of soil-derived particles over Antarctica is less significant than that over Greenland. This is consistent with the molecular distribution of fatty acids in the ice core, that is, concentrations of C_{20} - C_{30} fatty acids were low in comparison to C_{12} - C_{18} fatty acids.

Figure 4 shows a historical record of azelaic acid in the ice core. Concentrations of azelaic acid stayed very low (less than 100 ng/kg-ice) until the 1840s and then started to increase significantly. They showed two maxima in the 1870s (*ca.* 700 ng/kg-ice) and 1930s to 1950s (1900 ng/kg-ice) and decreased in the 1960s. After the minimum in the 1960s (*ca.* 400 ng/kg-ice), they increased considerably toward the 1990s (*ca.* 1500 ng/kg-ice). The azelaic acid concentrations in the 1990s are almost 5 times more than those in the 1960s. However, the precursor compounds (Δ^9 unsaturated fatty acids) of azelaic acid did not increase toward the 1990s; rather their concentrations decreased after the 1960s (see Fig. 2b). The difference in the historical trends of azelaic acid (product) and Δ^9 unsaturated fatty acids (precursors) in the late 1900s suggests that the atmospheric oxidation of unsaturated fatty acids was enhanced in the Southern Ocean and Antarctica during the last 70 years.

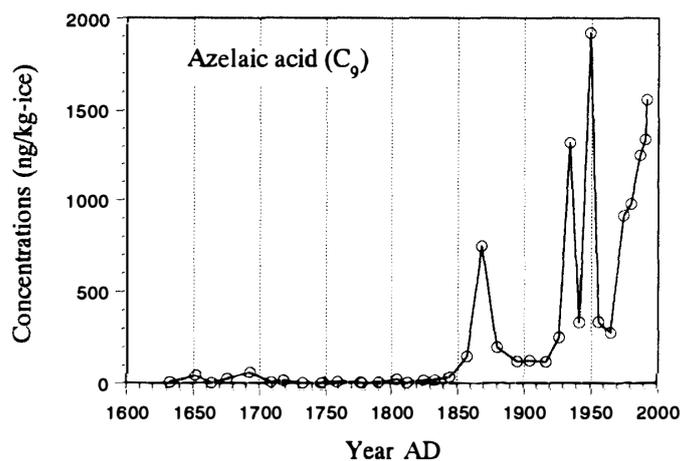


Fig. 4. Historical records of azelaic acid (C_9 dicarboxylic acid) concentrations in the H15 ice core from Antarctica.

Figure 5 gives historical trends of concentration ratios of azelaic acid to Δ^9 unsaturated fatty acids in the ice core. The ratios were relatively constant in the 1600s and 1700s. In the 1800s to 1970s, they seemed to show a gradual increase with some fluctuation. However, the ratios showed a rapid increase after the 1970s. The rapid increase in the product/precursor ratios should be caused by a significant change in the degree of photochemical oxidation reaction on unsaturated fatty acids. The increase in the ratios suggests that the oxidizing capability of the atmosphere has increased in the Antarctic atmosphere and Southern Ocean. The photochemical enhancement of the Antarctic atmosphere may be associated with the continued decline of total ozone observed in the atmosphere over Antarctica (FARMAN *et al.*, 1985; JONES and SHANKLIN, 1995). The stratospheric ozone destruction mainly caused by increased atmospheric emission of anthropogenic chlorofluorocarbons should have caused a significant increase of ultraviolet

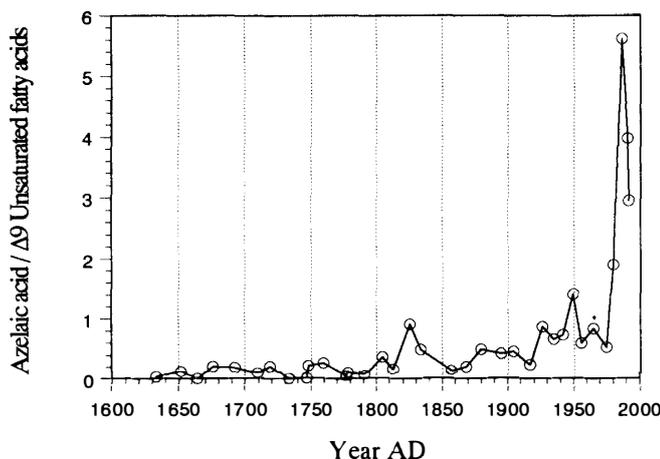


Fig. 5. Historical trends of the concentration ratios of azelaic acid to $\Delta 9$ unsaturated fatty acids in the H15 ice core from Antarctica.

radiation in the troposphere, resulting in an increase in the oxidizing capability of the Antarctic atmosphere.

4. Concluding Remarks

Molecular distributions of normal saturated fatty acids in the H15 ice core indicate that major sources of organic materials are originated from marine microorganisms through sea-to-air emissions by bubble bursting processes in the sea surface microlayer. They are transported long distances over the Antarctic ice sheet. Their transport and subsequent air-to-snow flux in Antarctica were most likely depressed during the Little Ice Age, but enhanced after the 1850s. The increased concentrations of fatty acids are consistent with global warming which started in the late 19th century. These considerations suggest that the ice core fatty acid concentrations may be linked with the advance and retreat of sea ice. Azelaic acid, which is a photochemical oxidation product of biogenic unsaturated fatty acids, was found as the dominant α,ω -dicarboxylic acid throughout the ice core. The concentration ratios of azelaic acid to unsaturated fatty acids in the ice core showed a rapid increase after the 1970s, indicating that photochemical oxidation in the troposphere over the Antarctic may have been intensified after the 1970s, probably due to stratospheric ozone depletion.

Acknowledgments

We thank the 32nd Japanese Antarctic Research Expedition for their cooperation in collecting the H15 ice core. We also appreciate the useful comments of reviewers. This study was in part supported by the Ministry of Education, Science and Culture through Grant-in-Aid 06453009.

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(Received January 30, 1997; Revised manuscript accepted April 2, 1997)