

SEASONAL CHANGES OF LOW MOLECULAR WEIGHT DICARBOXYLIC ACIDS IN SNOW SAMPLES FROM DOME FUJI STATION, ANTARCTICA

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Abstract: Fresh snow samples were collected at Dome Fuji Station, Antarctica, from October 1995 to November 1996, and were analyzed for dicarboxylic acids by capillary gas chromatography and mass spectrometry. Concentrations of oxalic acid (C₂, the most abundant diacid) ranged from 2.07 to 17.4 μg/kg-snow. C₂-C₈ dicarboxylic acids showed clear seasonal changes with higher concentration in summer than in winter. This suggested that low molecular weight dicarboxylic acids were produced by photochemical reactions. Concentrations of dicarboxylic acids at Dome Fuji Station were about 20 times higher than the snow samples collected on the route from Syowa Station to Dome Fuji Station. The concentrations of maleic acid and phthalic acid (derived from photochemical oxidation of anthropogenic aromatic hydrocarbons) at Dome Fuji Station was about 40 times higher than the route samples. In contrast, the concentrations of C₈ and C₉ diacids (derived from photochemical oxidation of biogenic unsaturated fatty acids) at Dome Fuji Station were only 3-5 times higher than the route samples. This comparison suggests that surface snow samples at Dome Fuji Station contained photooxidation products of anthropogenic organic matter, suggesting that the diacids are emitted from incomplete combustion of fossil fuel used at the Station and/or produced in the atmosphere by photooxidation of exhaust gases. On the other hand, concentration ratios of fumaric acid (*trans*-C₄ unsaturated diacid) to maleic acid (*cis*-C₄ unsaturated diacid) showed higher values in summer than in winter, suggesting that *cis* to *trans* isomerization occurs photochemically in the atmosphere and possibly in the snow surface. Although the atmosphere over Dome Fuji Station is contaminated by diesel exhaust from the station, seasonal distribution of dicarboxylic acids in fresh snow samples provide useful information on photochemical reactions occurring in the polar atmosphere.

1. Introduction

Water soluble organic matter such as low molecular weight dicarboxylic acids (LMW diacids) is likely to act as cloud condensation nuclei (CCN) in the atmosphere, and have a large effect on regional and global scale cooling. LMW diacids account for 1-20% of the organic fraction in aerosols (KAWAMURA and IKUSHIMA, 1993; KAWAMURA *et al.*, 1996a). They are not only directly emitted from combustion sources to the

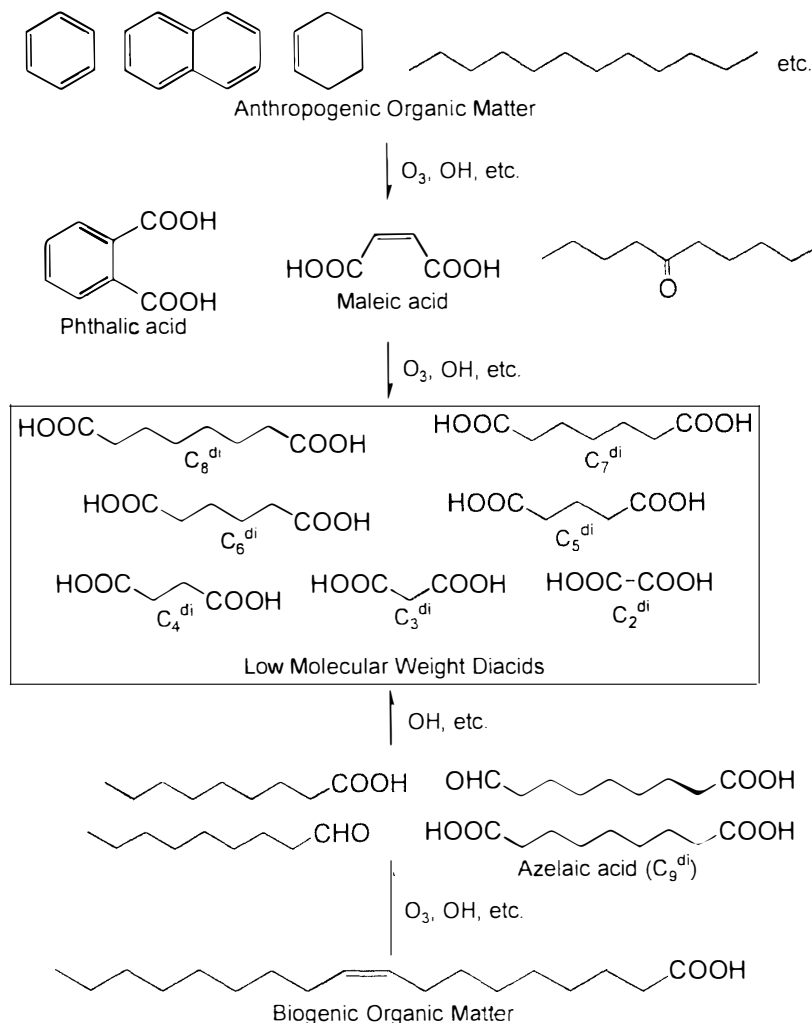


Fig. 1. Proposed pathway for the production of LMW diacids from anthropogenic and biogenic organic matter initiated by ozone and OH (KAWAMURA and IKUSHIMA, 1993).

atmosphere (GROSJEAN *et al.*, 1978; HATAKEYAMA *et al.*, 1987; KAWAMURA and KAPLAN, 1987) but are also secondarily produced in the atmosphere by photochemical reactions of reactive organic molecules such as unsaturated hydrocarbons and unsaturated fatty acids (YOKOUCHI and AMBE, 1986; KAWAMURA and GAGOSIAN, 1987; STEPHANOU and STRATIGAKIS, 1993). Figure 1 shows the source and photochemical reaction process of LMW diacids (KAWAMURA and IKUSHIMA, 1993). Both anthropogenic and biological matter can serve as diacid sources.

Polar regions are an ideal natural laboratory for the study of photochemical reactions of organic matter in the atmosphere, because sun light is continuously irradiated to the atmospheric compounds after the polar sunrise. Polar sunrise experiments conducted at Alert have provided fruitful information on the natural and anthropogenic sources and reaction processes of LMW diacids (KAWAMURA *et al.*, 1995). The organic compounds produced by photochemical reactions are scavenged

from the air by wet (snow) and/or dry deposition over the ice sheet. By analyzing fresh snow samples in the polar regions, we can obtain information on both source and photochemical reactions occurring in the atmosphere.

To understand photochemical reactions of organic matter in the polar atmosphere, we collected fresh snow samples at Dome Fuji Station, Antarctica, and analyzed the samples for the distribution of LMW diacids. Here, we discuss the photochemical processes of anthropogenic and biogenic organic matter over Dome Fuji Station.

2. Samples and Analytical Procedures

Nine fresh snow samples were collected at Dome Fuji Station, Antarctica (Fig. 2)

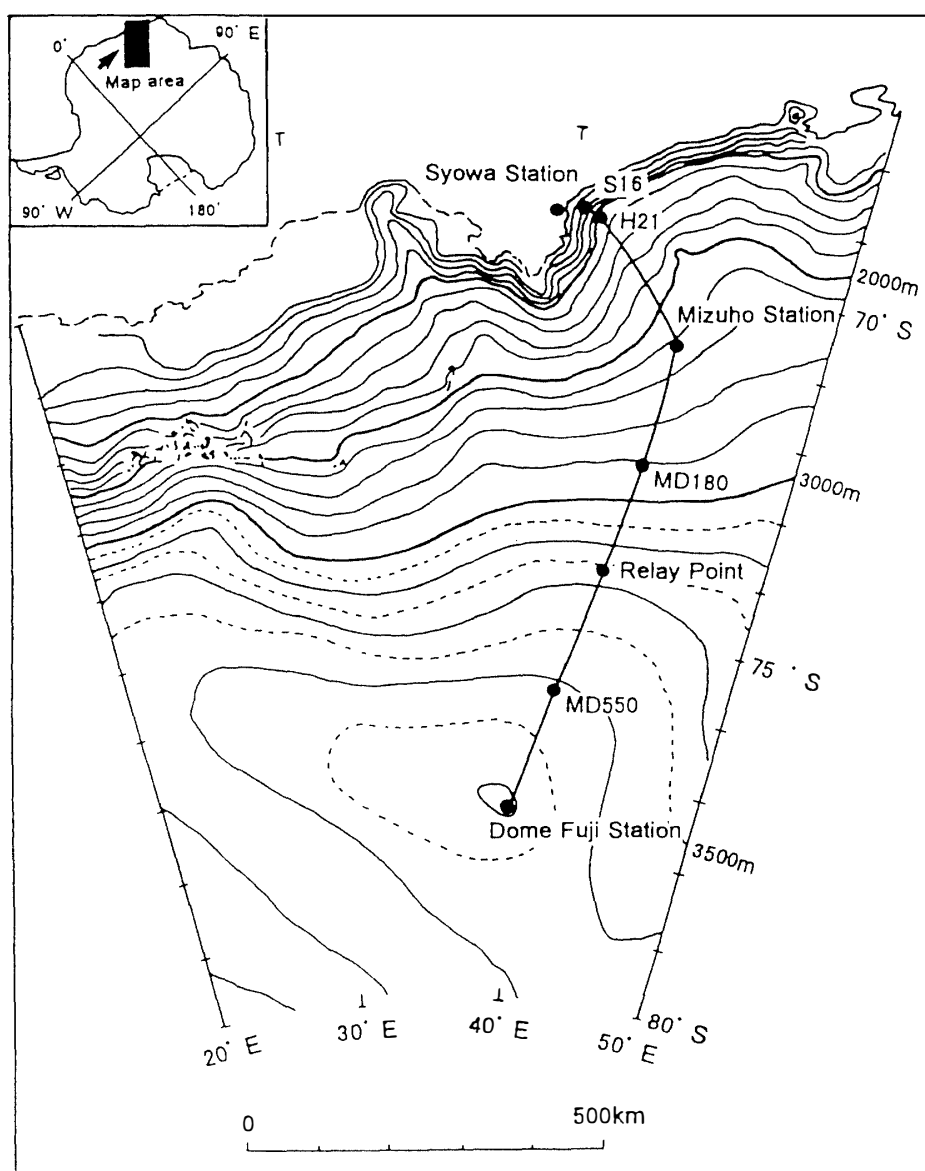


Fig. 2. Location of Dome Fuji Station and the route from the coast of Antarctica to Dome Fuji Station.

from October 1995 to November 1996. The snowfall samples that were taken in a 10 L glass bottle with a Teflon-lined cap were transported to the laboratory at a temperature below -15°C and stored at -20°C prior to analysis. In order to avoid microbial degradation during melting at room temperature, snow samples were poisoned with HgCl_2 before melting. The melt water (148–162 ml) was immediately analyzed. A melt water sample was concentrated with a rotary evaporator under vacuum, and butylated with 14% BF_3 in butanol. The butyl esters were extracted with *n*-hexane, washed with pure water and were concentrated (KAWAMURA and IKUSHIMA, 1993). Each analytical step was conducted in a clean room. The esters were analyzed by Hewlett Packard HP-6890 gas chromatograph (GC) equipped with a split/splitless injector (250°C), fused silica HP-5 capillary column ($0.25\text{ mm} \times 25\text{ m}$, $0.5\text{ }\mu\text{m}$) and an FID detector (310°C). The GC peak was identified by comparing the retention times with those of authentic standards. Recoveries of dicarboxylic acids (C_2 , C_3 , C_4 and C_6) in this analytical procedure were 70, 88, 98 and 100%, respectively. The detection limit was 4.5 ng/kg-snow for C_4 dicarboxylic acid.

3. Results and Discussion

3.1. Molecular distribution of LMW diacids in fresh snow samples at Dome Fuji Station

A homologous series of saturated α , ω -dicarboxylic acids were detected in the snow samples as well as unsaturated dicarboxylic acids such as phthalic, maleic and fumaric acids. Generally, oxalic acid is the most abundant diacid species, followed by succinic acid or malonic acid. Similar molecular distribution has been reported in Antarctic aerosols from Syowa Station (KAWAMURA *et al.*, 1996a) and aerosols from the urban atmosphere (KAWAMURA and IKUSHIMA, 1993). Table 1 shows concentrations of LMW

Table 1. Concentrations ($\mu\text{g}/\text{kg-snow}$) of LMW diacids in fresh snow at Dome Fuji Station.

Diacids	Sampling dates (YYMMDD)								
	951016	960118	960319	960417	960528	960709	960825	960920	961110
C_2^{di}	2.16	17.4	11.3	5.01	2.80	2.06	2.25	3.46	15.2
C_3^{di}	4.32	15.1	5.56	1.58	0.760	0.710	0.625	0.900	5.80
C_4^{di}	9.04	12.3	5.98	2.63	1.35	1.36	1.30	2.69	12.3
C_5^{di}	0.910	3.66	2.29	0.820	0.387	0.560	0.234	0.342	1.89
C_6^{di}	0.322	1.20	1.15	0.719	0.234	0.337	0.193	0.166	0.614
C_7^{di}	0.061	0.458	0.278	0.045	0.124	0.027	0.019	0.022	0.260
C_8^{di}	0.055	0.222	0.095	0.055	0.075	0.038	0.028	0.024	0.079
C_9^{di}	0.108	0.165	0.202	0.065	0.136	0.127	0.058	0.059	0.145
$\text{C}_{10}^{\text{di}}$	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.035
$\text{C}_{11}^{\text{di}}$	BDL	0.175	0.078	0.111	0.034	0.078	0.010	BDL	0.050
Maleic	0.762	1.367	1.738	0.596	0.315	0.530	0.339	0.363	0.677
Fumaric	0.183	0.709	0.821	0.353	0.127	0.106	0.063	0.114	0.407
Phthalic	6.06	2.20	2.64	1.44	0.485	1.02	1.07	2.32	2.26
Total	24.0	55.1	32.2	13.4	6.83	6.97	6.19	10.5	39.8

BDL: Below detection limit. Detection limit = 4.5 ng/kg-snow.

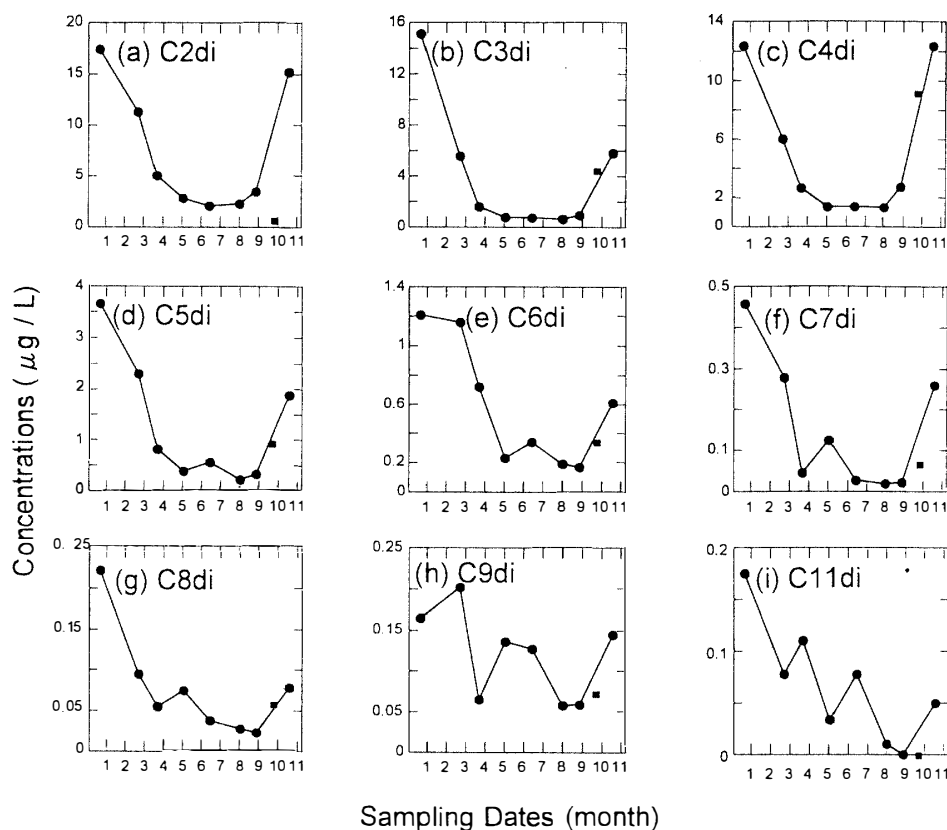


Fig. 3. Seasonal changes in the concentrations of LMW diacids in surface snow samples at Dome Fuji Station. The square points are the datum on 16 October 1995.

diacids in the snow samples. The concentration range ($6.2\text{--}55\mu\text{g/kg-snow}$) of total diacids is higher than that of ice core samples ($<1\text{--}10\mu\text{g/kg-ice}$) from H-15, coastal Antarctica (KASUKABE and KAWAMURA, unpublished results). Further, the concentration at Dome Fuji Station is 3–5 times higher than those of snow samples collected on the route from Syowa Station to Dome Fuji Station (MATSUNAGA *et al.*, 1998, unpublished results). However, the concentrations are 5–20 times lower than those of rain and snow samples from Los Angeles (KAWAMURA *et al.*, 1996b).

Concentrations of LMW diacids in the snow samples at Dome Fuji Station were higher in summer than in winter. Their seasonal variation agrees well with the change in solar radiation (see Fig. 3 and Fig. 4). Averaged concentrations of LMW diacids during summer at Dome Fuji Station are about 20 times higher than those of the route samples. Snow samples collected in summer season at Dome Fuji Station were used for this comparison, because the route samples were collected only in summer. Especially, Dome Fuji Station snow samples showed that concentrations of maleic acid and phthalic acid (derived from anthropogenic organic matter) were about 40 times higher than those of the route, samples, suggesting that the snow samples at Dome Fuji Station are heavily contaminated from pollution sources possibly from the diesel exhausts from the station. In contrast, concentrations of C_8 and C_9 diacids (derived from biogenic

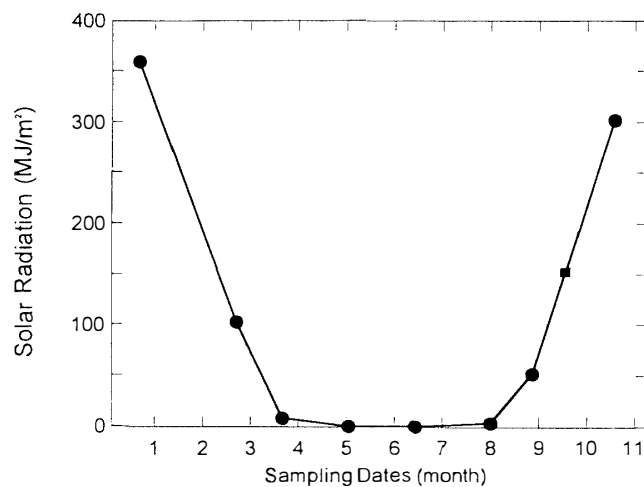


Fig. 4. Seasonal change in solar radiation at Dome Fuji Station. The square point is the datum on 16 October 1995.

organic matter) were only 3–5 times higher than the route samples. We consider two reasons for the differences in concentrations of C₈ and C₉ diacids between Dome Fuji Station and the route samples. First, LMW diacids in the Dome Fuji Station snow samples are more concentrated, because of the lesser snowfall amount at Dome Fuji Station. Second, C₈ and C₉ diacids are produced from *n*-alkanes emitted from incomplete combustion of fossil fuel at the station by photochemical reactions.

The concentration of azelaic acid (C₉ diacid) was generally higher than those of C₈ and C₁₀ diacid in urban and marine aerosols. Azelaic acid is produced from oleic acid (C_{18:1 ω 9}) by ozone oxidation at the C=C double bond. Suberic acid (C₈ diacid) may be produced from azelaic acid by α -oxidation with OH radical (KAWAMURA and GAGOSIAN, 1987). But diacids, larger than azelaic acid, are not produced from azelaic acid. It is reasonable that the concentration of suberic acid is lower than that of azelaic acid and higher than that of sebacic acid (C₁₀ diacid) which is sometimes below the detection limit. On the other hand, oleic acid is thought to be concentrated in the sea surface microlayer (BARGER and GARRETT, 1970). Thus, the predominance of azelaic acid suggests that surface snow at Dome Fuji Station partly contains biogenic organic matter derived from the coastal ocean near Antarctica, and from the Southern Ocean. Undecanedioic acid (C₁₁ diacid) was also detected. This may be produced by photooxidation of C_{18:1 ω 7} monocarboxylic acid (vaccenic acid), that is also concentrated in the sea surface microlayer.

These results and discussion lead us to conclude that much of the LMW diacids in surface snow samples at Dome Fuji Station are originated from anthropogenic organic matter, specifically from fossil fuel combustion at the station. However, the samples also contained LMW diacids that are derived from photooxidation of biogenic unsaturated fatty acids such as oleic acid.

3.2. Photochemical production of LMW diacids in the atmosphere and snow surface

Figure 5 presents amounts of fossil fuel consumed at Dome Fuji Station from October 1995 to November 1996. The fossil fuels used at Dome Fuji Station, were

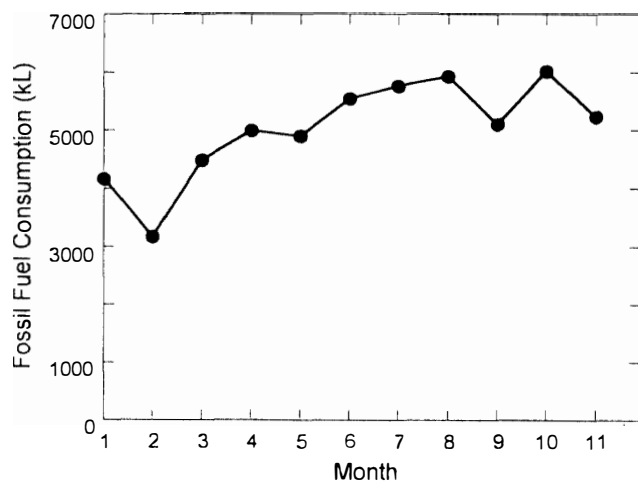
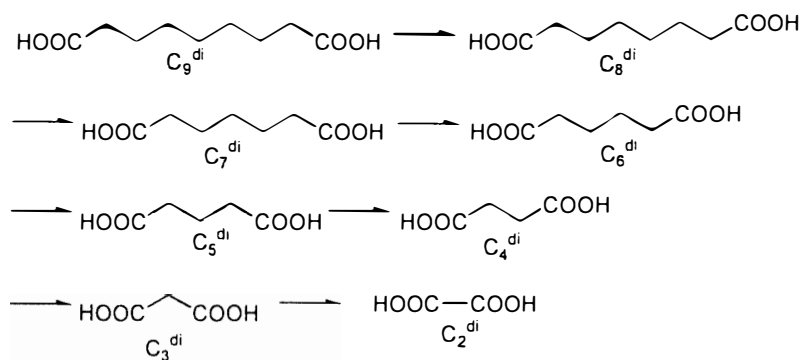
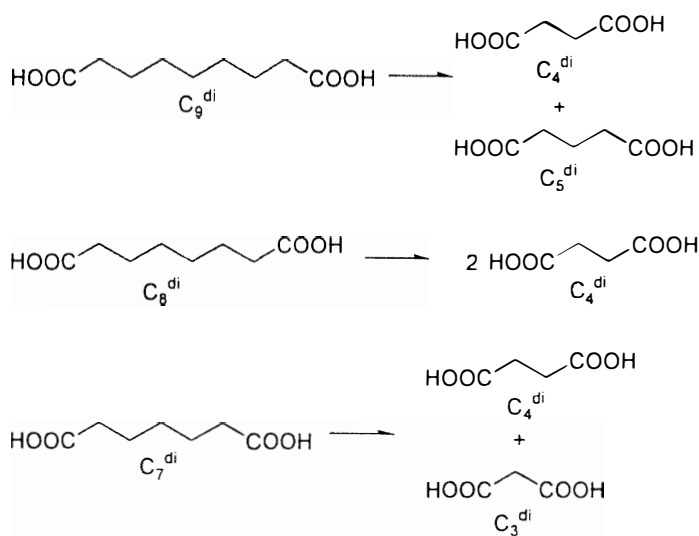


Fig. 5. Consumption amounts of fossil fuel (total of diesel oil and kerosene) at Dome Fuji Station in 1996. (Fuel consumption data are presented from Office of Antarctic Observations, Japan Meteorological Agency.)



(a)



(b)

Fig. 6. Proposed pathways for the production of LMW diacids from longer chain diacids through α -oxidation and oxidation at mid-chain carbon.

mostly diesel oil for the generator and kerosene for heating. The amounts of fossil fuels consumed increased in winter and decreased in summer. However, the pattern of consumption was clearly different from the concentrations of LMW diacids at Dome Fuji Station. This indicates that majority of the diacids are not directly emitted from the combustion processes, rather, they are secondarily produced in the atmosphere. In fact, seasonal changes in the concentrations of LMW diacids follow the changes in solar radiation (see Fig. 3 and Fig. 5). This suggests that LMW diacids in the snow samples are mostly produced by photochemical oxidation of anthropogenic organic matter derived from fossil fuel combustion at Dome Fuji Station.

Figure 6 presents two proposed pathways of photochemical reaction for the production of LMW diacids. They are thought to be produced by α -oxidation (Fig. 6a) and oxidation at mid-chain carbon (Fig. 6b) with OH radical. LMW diacid (C_n) produces smaller diacid (C_{n-1}) by α -oxidation. Figure 7 presents concentration ratios of C_n diacids over C_{n-1} diacid. Some combinations show an increase in summer and decrease in winter (Fig. 7). These results suggest that C_5 , C_7 and C_8 diacids are produced by α -oxidation with atmospheric oxidants such as OH radical in summer when photochemical oxidants are more abundant. On the other hand, the concentration ratios (Fig. 7) did not show an increase in summer, rather, they increased in winter. This suggests that C_2 and/or C_3 diacids have other sources in winter season, or they may photodissociate in the atmosphere.

Figure 8 presents concentration ratios of C_n diacids over C_{m+n} diacid. These ratios show an increase in summer and a decrease in winter. These comparisons suggest that C_8 and C_9 diacids were oxidized at mid-chain carbon with atmospheric oxidants such as OH radical and converted to lower molecular weight diacids.

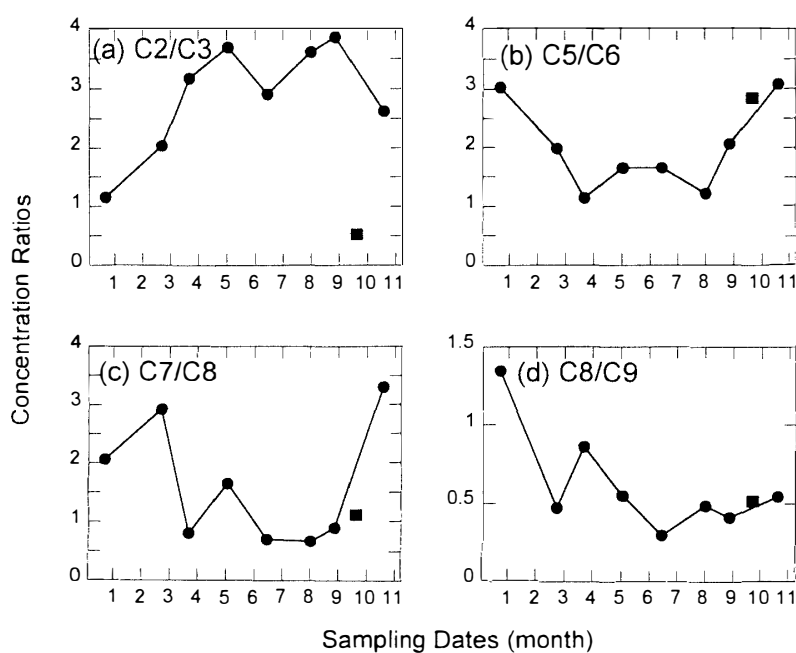


Fig. 7. Seasonal changes in the concentration ratios of C_n diacids to C_{n+1} diacids. The square points are the datum on 16 October 1995.

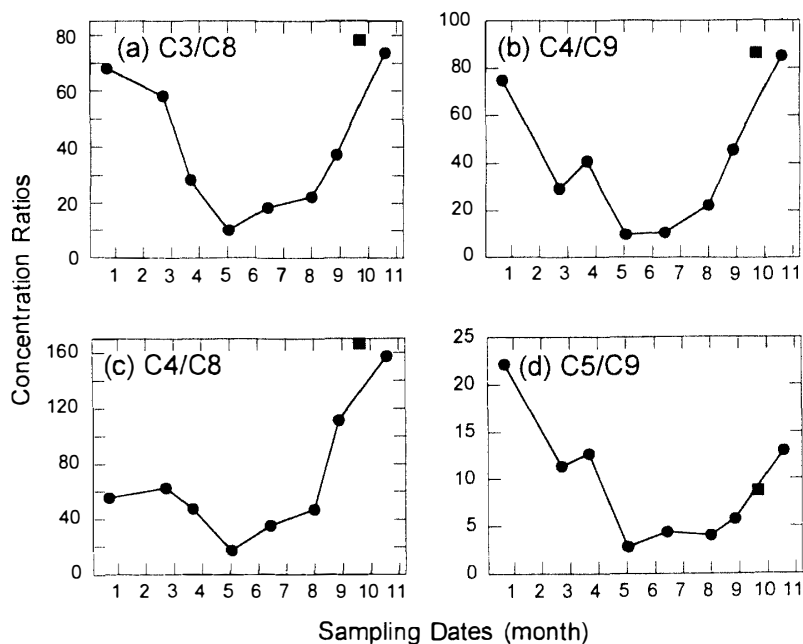


Fig. 8. Seasonal changes in the concentration ratios of C_n diacids to C_{m+n} diacids. The square points are the datum on 16 October 1995.

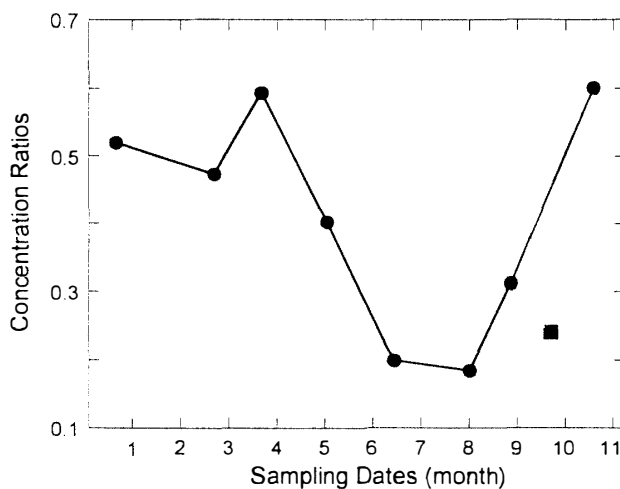


Fig. 9. Seasonal changes in the concentration ratios of fumaric acid to maleic acid. The square point is the datum on 16 October 1995.

3.3. Isomerization reaction by solar radiation

Maleic acid (*cis*- C_4 unsaturated diacid) is selectively produced by photooxidation of aromatic hydrocarbons. In contrast, fumaric acid (*trans*- C_4 unsaturated diacid) is produced by photochemically induced isomerization of maleic acid. Thus, the concentration ratio of fumaric acid to maleic acid (F/M ratios) should be low without solar radiation, and increase with solar radiation. This ratio can be used to evaluate the photochemical transformation of atmospheric organic matter (KAWAMURA and IKUSHIMA, 1993). The F/M ratios show a seasonal change with higher values in summer, being consistent with the change of solar radiation at Dome Fuji Station (Fig.

9). Although *trans*-configuration is more stable than *cis*-configuration, the F/M ratios are at most 0.6. This is in constant to the remote marine aerosols from Pacific Ocean where the F/M ratios are much higher (average 4.0) (KAWAMURA and SAKAGUCHI, 1999). These results may suggest that solar radiation is not strong enough to transform organic matter over Dome Fuji Station.

4. Summary and Conclusion

Fresh snow samples which were collected around Dome Fuji Station, Antarctica, were analyzed for LMW diacids by using GC and GC/MS. It is clear that much of these LMW diacids were produced by photochemical reactions of the anthropogenic organic matter emitted from fossil fuel combustion at Dome Fuji Station. The ratios of LMW diacids to their total concentrations suggest that LMW diacids were produced by α -oxidation and oxidation at mid-chain carbon. These results are consistent with previously proposed mechanisms for LMW diacids production.

The concentration ratios of fumaric acid to maleic acid showed a seasonal change with higher values in summer, which agreed with seasonal change of solar radiation. However, the ratios have never reached more than unity, suggesting that much of the precursor of LMW diacids in snow samples were not transported long distances from another source region. Although the LMW diacids detected in the Dome Fuji Station snow samples are mostly originated from a local pollution source, their seasonal changes provided information on the photochemical conversion process of combustion-derived organic matter to water soluble dicarboxylic acids.

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References

- BARGER, W.R. and GARRETT, W.D. (1970): Surface active organic material in the marine atmosphere. *J. Geophys. Res.*, **75**, 4561–4566.
- GROSJEAN, D., CAUWENBERGUE, K.V., SCHMID, J.P., KELLY, P.E. and PITTS, J.N., Jr. (1978): Identification of C₃-C₁₀ aliphatic dicarboxylic acids in airborne particulate matter. *Environ. Sci. Technol.*, **12**, 313–317.
- HATAKEYAMA, S., OHNO, M., WENG, J., TAKAGI, H. and AKIMOTO, H. (1987): Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air. *Environ. Sci. Technol.*, **21**, 52–57.
- KAWAMURA, K. and GAGOSIAN, R.B. (1987): Implications of ω -oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. *Nature*, **325**, 330–332.
- KAWAMURA, K. and IKUSHIMA, K. (1993): Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.*, **27**, 2227–2235.
- KAWAMURA, K. and KAPLAN, I.R. (1987): Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. *Environ. Sci. Technol.*, **21**, 105–110.

- KAWAMURA, K. and SAKAGUCHI, F. (1999): Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. *J. Geophys. Res.*, **104**, 3501–3509.
- KAWAMURA, K., KASUKABE, H., YASUI, O. and BARRIE, L.A. (1995): Production of dicarboxylic acids in the arctic atmosphere at polar sunrise. *Geophys. Res. Lett.*, **22**, 1253–1256.
- KAWAMURA, K., SEMPERE, R., IMAI, Y. and HAYASHI, M. (1996a): Water soluble dicarboxylic acids and related compounds in Antarctic aerosols. *J. Geophys. Res.*, **101**, 18721–18728.
- KAWAMURA, K., STEINBERG, S. and KAPLAN, I.R. (1996b): Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in Southern California wet precipitations: Comparison of urban and nurban samples and compositional changes during scavenging. *Atmos. Environ.*, **30**, 1035–1052.
- STEPHANOU, E.G. and STRATIGAKIS, N. (1993): Oxocarboxylic and α , ω -dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environ. Sci. Technol.*, **27**, 1403–1407.
- YOKOUCHI, Y. and AMBE, Y. (1986): Characterization of polar organics in airborne particulate matter. *Atmos. Environ.*, **20**, 1727–1734.

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