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Dicarboxylic acids in the arctic aerosols and snowpacks collected during ALERT2000

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Abstract

Saturated (C_2-C_{11}) and unsaturated (C_4-C_5, C_8) dicarboxylic acids were measured in arctic aerosol and surface snowpack samples collected during dark winter (February) and light spring (April-May) using a gas chromatography and gas chromatography/mass spectrometry. Their molecular distributions were characterized by a predominance of oxalic acid (C_2), except for few spring snowpack samples that showed the predominance of succinic acid (C_4). Concentrations of short chain saturated diacids (C_3-C_5) and 4-ketopimelic acid in the aerosol samples increased by a factor of ~5 from winter to spring. In contrast, those of saturated C_6-C_{11} diacids and unsaturated (maleic, methylmaleic and phthalic) acids decreased by a factor of ~4 from winter to spring aerosol samples. Snowpack samples also showed a similar trend. These results of the aerosol samples suggested that the diacids are largely produced in spring by photochemical oxidation of hydrocarbons and other precursors that are transported long distances from the mid- and low-latitudes to the Arctic, but the production of oxalic acid is in part counteracted by photo-induced degradation possibly associated with bromine chemistry.

Keywords:
oxalic acid, malonic acid, succinic acid, photooxidation, bromine chemistry

1. Introduction

Dicarboxylic acids have been reported to be major organic constituents of the aerosols collected from urban, remote continental and marine atmosphere (*e.g.* Grosjean *et al.*, 1978; Kawamura and Kaplan, 1987; Kawamura and Sakaguchi, 1999; Limbeck *et al.*, 2001). Because their vapor pressures are low and their water solubilities are high, the diacids have an influence on the chemical and physical properties of aerosols (Lightstone *et al.*, 2000). Consequently, they may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation, which counteracts the global warming caused by the increase of greenhouse gases. In addition, diacids may play a role in reactions occurring in the aqueous phase of aerosol particle, *e.g.* reduction of Fe(Ⅲ) to Fe(Ⅱ) (Zuo and Hoigné, 1992) and Br_2 to Br^- (Behnke *et al.*, 1999).

The atmospheric concentrations of diacids are influenced by primary source such as motor exhausts (Kawamura and Kaplan, 1987) and biomass burning (Narukawa *et al.*, 1999). Secondary sources such as production from photooxidation of hydrocarbons are expected to be important, because diacids have been reported to be the oxidation products of aromatic hydrocarbons and alkanes in the laboratory studies (Behnke *et al.*, 1999; Kleindienst *et al.*, 1999; Edney *et al.*, 2000; Kalberer *et al.*, 2000). In the Arctic, concentrations of diacids in aerosols have been found to increase during polar sunrise (Kawamura *et al.*, 1995). In March to May, concentrations of oxalic (C_2), malonic (C_3) and succinic (C_4) acids as well as some other (C_5, C_6) diacids were 5-20 times more abundant than those in the preceding dark winter months. This increase has been attributed to enhanced photochemical oxidation of organic pollutants, which were transported and accumulated in the arctic atmosphere during dark winter.

Diacids (C_2-C_{10}) have also been detected in Greenland ice core (Kawamura and Yasui, 1991; Kawamura *et al.*, 1999, 2001). Historical trends of the diacids were explained in terms of the past changes in the sea-to-air emissions of marine organic matter, which is subsequently subjected to photochemical oxidation in the atmosphere during long-range transport toward the Greenland ice sheet. Diacids in the ice core have been proposed as a potential proxy for the reconstruction of atmospheric oxidizing capacity in the past. However, source, sink and formation pathways of diacids in the arctic aerosols and snowpacks are not well understood.

In this study, we report on aerosol and surface snowpack samples collected in the dark winter (February) and light spring (April-May) periods during the ALERT2000 experiment. The samples were analyzed for diacids using a capillary gas chromatography (GC) and GC/mass spectrometry (GC/MS). In addition, aerosol and snowpack samples were also analyzed for major anions. We describe the molecular composition and concentrations of diacids in the aerosol and snowpack samples and discuss the source, sink and formation pathway of diacids in the arctic aerosols and snowpack. We also discuss the implication of diacids for ice core studies.

2. Methodology

2.1. Sample Collection

Aerosol and surface snowpack samples were collected during dark winter (14-22 February) and light spring (17 April – 6 May), 2000, at Alert, Nunavut, Canada (82°30’ N, 62°21’ W) as part of the ALERT2000 field study. Aerosol samples were collected near the Special Study Trailer (SST) (175 m a.s.l.), which is located approximately 6 km south-southwest of the base at Alert. Aerosol samples were collected on pre-combusted (450 °C, 3 hours) quartz fiber filters (Pallflex, 2500QAT) using a high-volume air sampler, which has no inlet line and no cut-off, and were stored in a glass jar with a Teflon lined cap. Filters were exposed for periods of 48 h at flow rates of ca. 1.5 m^3 min^{-1}. Surface snowpack samples (ca. 1 cm in depth) were also collected near the SST and an ice camp on the sea ice, which was located about 7 km northwest from the base. Snowpack samples were collected generally once a week and stored in clean 5 L Teflon bottles. In total, 4 aerosol and 4 snowpack samples were collected during the winter period, and 5 aerosol and 5 snowpack samples during the spring period. The aerosol filter and snowpack samples were transported to our laboratory in Sapporo under freezing condition and stored in darkness at –20 °C until analysis.

2.2. Chemical Analysis

The analytical procedure of diacids was modified from Kawamura and

Ikushima (1993). One eighth of the aerosol filter was cut in pieces and extracted with Milli Q water under ultrasonication for water-soluble organic compounds. The extracts were passed through a glass column (Pasteur pipette) packed with quartz wool to remove particles such as black carbon and filter debris. Less water-soluble organic compounds such as long chain organic acids were extracted with ethyl acetate from the residue of the filter samples and the extracts were passed through the glass column as described above. Both extracts were combined and concentrated to almost dryness by a rotary evaporator under vacuum, to which 14% borontrifluoride in n-butanol (ca. 0.2 mL, Alltech Associates, Inc.) was added. The extracts and reagent were mixed under ultrasonication and then heated at 100 °C for 1 hour to derive carboxylic acid butyl esters. The esters were extracted with 10 mL n-hexane after adding 10 mL Milli Q water and 0.2 mL acetonitrile, the latter improves the excess n-butanol transfer into the aqueous phase. The n-hexane layer was washed with pure water (10 mL × 4). The esters were dried by using a rotary evaporator and nitrogen blow-down system and then dissolved in 200 μL of n-hexane.

Snowpack samples were melted at room temperature and the melt water was immediately filtrated by glass fiber filter (Whatman GF/F) and then stored at 4 °C in a pre-cleaned brown glass bottle with a Teflon-lined screw cap prior to analysis. An aliquot of the filtered water samples was poisoned with mercuric chloride for organic analysis to prevent microbial degradation of organic compounds. The water samples were concentrated with a rotary evaporator and analyzed for diacids as described above.

The butyl esters were determined with a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m × 0.2 mm i.d. × 0.5 μm film thickness) and an FID detector. The identification of the compounds was performed with a GC/MS (ThermoQuest, Trace GC2000 and Trace MS) equipped with an on-column injector and fused-silica capillary column (DB-5MS, 60 m × 0.32 mm i.d. × 0.25 μm film thickness) by using authentic standards.

Recoveries of authentic standards spiked onto a precombusted quartz fiber filter were 70 % for oxalic (C_2) acid, and better than 90 % for succinic (C_4) and adipic

(C_6) acids. Procedural blanks showed small peaks of oxalic, succinic, adipic, and phthalic acids in the GC chromatograms. However, their blank levels were almost constant and generally less than 10% of those for the aerosol and snowpack samples. The concentrations of the diacids reported here are corrected for the procedural blanks. The relative standard deviation of the diacid measurements based on duplicate analysis of the aerosol and snowpack samples was generally less than 10%.

For anion analysis, one eighth of filter samples was cut in pieces and ultrasonically extracted with Milli Q water. The extracts were filtrated with preparation filter (GL Sciences, Chromatodisk 13AI). Major anions (Cl^-, Br^-, NO_3^-, and SO_4^{2-}) in the aerosol and snowpack samples were determined by ion chromatograph (Dionex, DX-500) using Dionex-AS12A columns, 4.05 mM Na_2CO_3/ 0.45 mM $NaHCO_3$ eluent and auto-suppressor ASRS-1. The injection loop volume was 500 μL. Procedural blanks showed small peaks of Cl^-, NO_3^-, SO_4^{2-} in the IC chromatograms. However, they were less than 5% of those for the aerosol and snowpack samples. The concentrations of the anions reported here are corrected for the procedural blanks. Although cations were also determined for the samples, we do not report here because of the relatively high procedural blanks.

3. Results and Discussion

3.1. Difference in the molecular distribution of dicarboxylic acids between winter and spring

Fig. 1 shows a typical total ion chromatogram of dicarboxylic acids as butyl esters isolated from the arctic aerosol samples. Homologous series of normal saturated diacids (C_2-C_{11}) were detected in both aerosol and snowpack samples. Oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3), succinic (C_4) or glutaric (C_5) acid, except for few spring snowpack samples that showed a predominance of C_4 diacid. Longer chain normal diacids were less abundant, except for azelaic acid (C_9), which was more abundant than suberic acid (C_8). Branched chain saturated diacids were also detected in the samples, including methylmalonic (iC_4), methylsuccinic (iC_5) and 2-methylglutaric (iC_6) acids, but they were less abundant than the corresponding straight-chain diacids. Also 4-ketopimelic acid (kC_7) was detected. In addition to the saturated species, aliphatic unsaturated and aromatic diacids were detected, including maleic (M), fumaric (F), methylmaleic (mM), methylfumaric (mF), and phthalic (Ph) acids. mF was detected for the first time in environmental samples both in aerosols and snowpacks. Compositions of diacids in the aerosol samples are similar to those previously reported in arctic aerosols (Kawamura *et al.* 1995, 1996).

Table 1 presents concentration range and median of diacids detected in the aerosol and snowpack samples, together with their chemical formula. C_2 diacid concentrations are similar to those of the previous studies (see Table 2 for comparison). C_3, C_4 and C_5 diacids also showed similar concentrations to those in Alert (Kawamura *et al.*, 1995), but one order of magnitude lower than those reported in Finland far south of our sampling location (Kerminen *et al.*, 1999; Fridlind *et al.*, 2000). Concentrations of C_2 diacid in the surface snowpack samples are consistent with those reported in the snowpack samples from Barrow, Alaska in March-April 1989 (Li and Winchester, 1993).

No significant change was found in the aerosol concentrations of C_2 diacid between the winter and spring samples. Previous study of the arctic aerosols showed that the C_2 diacid peaked in late March to early April (Kawamura *et al.*, 1996). This difference may be due to a lack of sample collection of aerosols in these periods in the present study. However, concentrations of C_3-C_5 saturated diacids and kC_7 diacid increased by a factor of ~5 from the winter to spring aerosol samples (Fig. 2a). By contrast, concentrations of C_6-C_{11} saturated diacids and M, mM and Ph decreased by a factor of ~4 from the winter to spring samples. No significant change in the molecular composition of diacids was observed between the ice camp and SST snowpack samples. However, their concentrations were quite variable from one sample to another (Table 1). Interestingly, concentrations of C_3-C_5 saturated and kC_7 diacids in the snowpack samples increased from the winter to spring, being similar to the increase seen in aerosols (Fig. 2b).

To better evaluate the difference in diacid composition, the data sets of dicarboxylic acids in aerosol and snowpack samples were subjected to a principal component analysis (PCA) with varimax rotation. Table 3 and 4 gives the results with component loadings for aerosol and snowpack samples, respectively. Two components account for 91% and 88% of the variance in the data sets of the aerosol and snowpack samples, respectively. These statistical analyses suggest that changes of diacid distributions from winter and spring can be explained by two groups, that is, one is C_3-C_5 saturated and kC_7 diacids group and another is C_6-C_{11} and unsaturated diacids group. These groups seem to be associated with different sources and/or different chemical reaction processes in the arctic.

3.2. Photochemical production of dicarboxylic acids in the arctic spring

An increase in the concentrations of C_3-C_5 diacids from the winter to spring samples suggest that these diacids are produced in the arctic atmosphere by photochemical oxidation of anthropogenic hydrocarbons and other organic precursors (Kawamura *et al.*, 1996). In late winter, pollutants originating from mid latitudes are transported and accumulated in the arctic atmosphere (Barrie and Barrie, 1990). However, concentration of unsaturated diacids (M, mM and Ph) and longer chain saturated diacids ($\geqq C_6$) rather decreased from winter to spring (Fig. 2a). This apparent discrepancy suggests that (1) the transport of precursor of the unsaturated diacids to the Arctic is depressed in spring, and/or (2) the unsaturated diacids are further decomposed immediately after their photochemical production under a strong solar radiation in spring. Our previous study on the arctic aerosols showed that concentrations of maleic acid were higher in February than April and May (Kawamura *et al.*, 1996), suggesting that the unsaturated diacids are further decomposed probably to oxalic acid in spring. This, together with the evidence that M isomerizes to F under light, lends some support to the secondary process in the atmosphere.

Although *cis* configurations of unsaturated diacids, i.e., M and mM showed a decrease in their concentrations from the winter to spring aerosol samples, their *trans* configurations, i.e., F and mF, did not show any significant decrease. Both M and mM have been reported to be formed by photochemical degradation of aromatic hydrocarbons (Kleindienst *et al.*, 1999; Edney *et al.*, 2000). M isomerizes to F under light irradiation or due to heating to its melting point (>130 °C), thus in the ambient atmosphere isomerization can only be due to solar radiation. F to M ratios (F/M) increased from 0.42±0.14 in winter to 0.91±0.11 in spring. mF diacid may be formed by isomerization of mM diacid, being similar to the case of M and F diacids. Their ratios (mF/mM) were 0.10±0.04 in dark winter and 0.50±0.19 in light spring. These results suggest that *cis* to *trans* conversion of unsaturated diacids occurred in the arctic atmosphere under the strong sunlight conditions in spring.

During the light sampling period (late April to early May), several ozone depletion events occurred. Previous studies, during ozone depletion in the arctic boundary layer, reported an increase in the concentrations of formaldehyde (de Serves, 1994) and acetone (Yokouchi, 1994), which are likely products of photochemical oxidation of VOCs. Similar decrease was also reported for alkanes (Jobson *et al.*, 1994). They considered that the decomposition of these compounds are closely linked to halogen atom chemistry. In this study, the diacids concentrations were expected to be higher in the spring aerosol samples than the winter samples, because diacids are oxidation products of aliphatic and aromatic hydrocarbons, as described above. Although C_2 diacid peaked in late March to early April (Kawamura et al. 1995, 1996), we did not observe any increase in the C_2 diacid concentration in aerosols from the winter to spring samples. In contrast, concentrations of saturated diacids (C_3-C_5) in the aerosol samples became ~5 times higher than those collected during winter (Fig. 2a). These results suggest a selective degradation of C_2 diacid relative to C_3-C_5 diacids in the arctic spring.

The apparent depletion of C_2 diacid relative to C_3-C_5 diacids in spring (Fig. 2a) may be associated with Br chemistry in the sea salt particles that may be linked to ozone depletion events. Based on a laboratory study, Behnke *et al.* (1999) reported that oxalic acid (C_2) is decomposed by Br_2 in aqueous phase. Consequently, a release of Br_2 from the aqueous phase should be inhibited by the presence with C_2 diacid. Because Br^- in the aerosol samples is more abundant in spring (21.7±19.7 ng m^{-3}) than winter (3.2±1.9 ng m^{-3}), the reaction of C_2 diacid with Br_2 (the latter is produced in sea salt particles during ozone depletion, Barrie *et al.*, 1988) is possible in the particles. C_2 diacid could be preferentially decomposed by Br_2, although this acid is photochemically produced in the arctic atmosphere. Fig. 3 shows a relationship between concentration ratios of C_2 to C_4 diacids and concentration of Br^- in the arctic aerosols. A relatively strong negative correlation (r=-0.81) was obtained, with higher Br^- concentration in spring samples. This negative correlation shows further evidence that C_2 diacid can be decomposed in the sea salt particles as a result of photochemical processes involved with Br atom chemistry.

3.3. Transfer of dicarboxylic acids from the air to snow: implication for ice core studies

Fig. 4 shows the relative abundance (%) of individual diacids (C_2-C_5) compared to the total amount of diacids (C_2-C_{11}) in the aerosol and snowpack samples collected in dark winter and light spring. No significant change was found in the relative abundance of diacids between the aerosol and snowpack samples in dark winter (Fig. 4a). Interestingly, the relative abundance of C_2 diacid in the spring samples (ca. 40%) became lower than that of the winter samples (ca. 60%) (Fig. 4b). Conversely, the relative abundance of C_3-C_5 diacid in both the aerosol and snowpack samples increased from winter to spring. These changes again suggest photochemical formation and decomposition of diacids in the arctic atmosphere under solar radiation. A distinguishing feature was found in the relative abundance of diacids between the aerosol and snowpack samples collected in spring. The relative abundance of C_2 and C_3 diacids decreased from 44% to 37% and from 20% to 9% from the atmospheric particulate samples to snowpack samples, respectively. In contrast, C_4 and C_5 diacids showed an increase from 23% to 31% and 3% to 8%, respectively.

The different distribution of diacids between aerosol and snowpack samples in spring may be caused by several possible reasons, including their evaporation, deposition, different particle size distribution, source differences, and snow chemistry. Because diacids are low volatility and highly polar compounds, their evaporation from snow surface are not likely. Diacids exist partly in gas phase (Baboukas *et al.*, 2000). Gaseous C_2 and C_3 diacids should be adsorbed on snowpack surface more than C_4 and C_5 acids due to their polarity. However, our results showed that the snowpacks were depleted with C_2 and C_3 diacids in spring, suggesting that the above process is unlikely.

Deposition velocities of individual diacids should be the same, because C_2-C_5 diacids in fine particles have been reported to have the same size distribution (Kerminen *et al.*, 1999). Apparent discrepancy of the molecular distribution of diacids between aerosol and snowpack samples may be caused by the differences of their sources and/or snow chemistry. Because aerosol samples were collected only when ozone depletion event occurred, the diacids in snowpacks collected before ozone depletion events may be derived from the sources different from the aerosols. Alternatively, C_2 and C_3 diacids may be preferentially decomposed and/or C_4 and C_5 diacids may be selectively formed in the snow surface under solar radiation in spring.

C_2 and other diacids have been measured in the Greenland ice cores (Legrand *et al.*, 1992; Legrand *et al.*, 1995; Tison *et al.*, 1998; Kawamura *et al.*, 2001). Concentration of C_4 diacid in Greenland ice core was nearly equal to that of C_2 diacid (Kawamura *et al.*, 1991, 2001). In the present study, similar molecular composition was found in the spring snowpack samples, but this was not seen in the spring aerosol samples and winter samples (Fig. 2). This could suggest that distributions of diacids in ice core may be influenced by changes of their sources and/or photochemical processes in the snow surface as well as in the atmosphere. Further studies are required to determine the chemical processes of diacids in the air/snow interface and to understand the distribution of diacids in ice core.

4. Summary and Conclusions

Normal (C_2-C_{11}) and unsaturated (C_4-C_5, C_8) diacids were detected in the aerosol and surface snowpack samples collected at Alert, Nunavut, Canada during dark winter (February) and light spring (April-May). For aerosol and snowpack samples, concentration of C_2 diacid did not show any significant change between the seasons, whereas concentration of C_3-C_5 saturated diacids and kC_7 diacid increased by a factor of ~5 from winter to spring. Compositions of diacids in the aerosol samples are similar to those previously reported in the Arctic.

Comparison of molecular distribution of diacids with the concentration of Br^- ion in the aerosol samples suggested that the production and decomposition of C_2 diacid is related to Br chemistry in the arctic sea salt particles.

The diacids showed a difference in the molecular distribution between aerosol and snowpack samples in spring, suggesting an increase of C_4 and C_5 diacids, relative to C_2 and C_3 diacids, in surface snow under solar radiation.

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Figure Captions

Fig. 1. Total ion chromatogram (mass range: m/z 40-580) of dicarboxylic acid butyl esters isolated from the arctic aerosol sample collected at Alert (26-28 April 2000). For abbreviation, see Table 1.

Fig. 2. Mean concentrations of (a) C_2-C_5 diacids and Ph, and other dicarboxylic acids in the aerosol samples, and (b) C_2-C_5 diacids and Ph, and other dicarboxylic acids in the snowpack samples collected during winter (February) and spring (April-May) at Alert, 2000. Vertical bars indicate standard deviation.

Fig. 3. Relationship between the concentrations of Br^- and ratios of C_2 to C_4 diacids in the winter and spring aerosol samples. One sample data (4/26-28) is not included, because it was collected under irregular weather (snowstorm) and the concentration of Br^- was abnormally high (57 ng m^{-3}).

Fig. 4. Relative abundance (%) of individual diacids (C_2-C_5) in the total diacids (C_2-C_{11}) in the aerosol and snowpack samples collected at Alert, 2000 during (a) dark winter and (b) light spring. Vertical bars indicate standard deviation.

Table 1

Concentrations of dicarboxylic acids in the aerosol and snowpack samples collected in the Arctic, 2000

Dicarboxylic acids (abbr.)	Chemical Formula	Aerosols (ng m^{-3})[a]				Snowpacks (μ g l^{-1})			
		Winter (2/14—2/22)		Spring (4/26—5/6)		Winter (2/16—2/21)		Spring (4/17—5/5)	
		Range	Median	Range	Median	Range	Median	Range	Median
Normal saturated									
Oxalic (C_2)	$HOOC-COOH$	13.2 - 23.5	21.8	13.3 - 40.9	19.0	8.2 - 15.9	9.27	5.9 - 13.5	9.51
Malonic (C_3)	$HOOC-CH_2-COOH$	3.19 - 5.03	4.14	7.3 - 11.6	9.42	0.61 - 1.00	0.80	0.65 - 5.44	2.53
Succinic (C_4)	$HOOC-(CH_2)_2-COOH$	2.25 - 3.21	2.61	7.8 - 15.4	12.3	0.91 - 1.33	1.13	3.6 - 14.6	9.64
Glutaric (C_5)	$HOOC-(CH_2)_3-COOH$	0.84 - 1.21	1.05	0.78 - 2.16	2.07	0.15 - 0.67	0.57	0.30 - 6.81	3.40
Adipic (C_6)	$HOOC-(CH_2)_4-COOH$	0.47 - 0.54	0.49	0.17 - 0.55	0.36	0.22 - 1.86	0.43	0.03 - 1.12	0.58
Pimelic (C_7)	$HOOC-(CH_2)_5-COOH$	0.07 - 0.09	0.07	0.01 - 0.06	0.02	0.02 - 0.07	0.07	<0.01 - 0.15	0.06
Suberic (C_8)	$HOOC-(CH_2)_6-COOH$	0.08 - 0.12	0.09	0.01 - 0.10	0.03	0.03 - 0.14	0.09	<0.01 - 0.09	0.06
Azelaic (C_9)	$HOOC-(CH_2)_7-COOH$	0.32 - 0.61	0.41	0.03 - 0.44	0.10	0.11 - 0.47	0.35	0.02 - 0.37	0.11
Sebacic (C_{10})	$HOOC-(CH_2)_8-COOH$	0.03 - 0.05	0.04	<0.01 - 0.03	0.03	<0.01 - 0.03	0.03	<0.01	—
Undecanedioic (C_{11})	$HOOC-(CH_2)_9-COOH$	<0.01 - 0.04	0.04	<0.01 - 0.02	0.02	<0.01 - 0.02	0.02	<0.01	—
Branched saturated									
Methylmalonic (iC_4)	$HOOC-CHCH_3-COOH$	0.11 - 0.15	0.13	0.45 - 0.68	0.63	0.02 - 0.07	0.04	0.04 - 0.49	0.21
Methylsuccinic (iC_5)	$HOOC-CHCH_3CH_2-COOH$	0.28 - 0.41	0.35	0.57 - 1.53	1.17	0.10 - 0.36	0.23	0.27 - 3.71	2.03
2-Methylglutaric (iC_6)	$HOOC-CHCH_3(CH_2)_2-COOH$	0.09 - 0.15	0.13	0.03 - 0.10	0.09	0.03 - 0.13	0.12	0.03 - 1.05	0.42
Keto									
4-Ketopimelic (kC_7)	$HOOC-(CH_2)_2-CO-(CH_2)_2-COOH$	0.12 - 0.18	0.15	0.27 - 0.66	0.63	<0.01 - 0.05	0.04	0.04 - 1.23	0.26
Unsaturated									
Maleic (M)	$HOOC-CH=CH-COOH$ (*cis*)	0.31 - 0.66	0.51	0.12 - 0.26	0.16	0.09 - 0.43	0.17	<0.01 - 0.34	0.22
Fumaric (F)	$HOOC-CH=CH-COOH$ (*trans*)	0.12 - 0.27	0.20	0.12 - 0.23	0.13	0.03 - 0.15	0.11	0.05 - 0.60	0.23
Methylmaleic (mM)	$HOOC-CCH_3=CH-COOH$ (*cis*)	0.33 - 0.36	0.35	0.05 - 0.11	0.08	0.07 - 0.38	0.11	<0.01 - 0.29	0.20
Methylfumaric (mF)	$HOOC-CCH_3=CH-COOH$ (*trans*)	0.02 - 0.05	0.04	0.03 - 0.04	0.04	<0.01	—	<0.01 - 0.03	0.03
Phthalic (Ph)	$HOOC-C_6H_4-COOH$ (*o*-)	2.18 - 3.13	3.04	0.52 - 1.00	0.79	0.46 - 3.18	1.10	0.02 - 1.79	0.90

[a] Concentrations of diacids in the aerosol samples are reported at 0℃ and 1013hPa.

Table 2

Mean concentration (ng m^{-3}) of dicarboxylic acids measured in the Arctic aerosol

Location	Date	Sampling Method	Oxalic	Malonic	Succinic	Glutaric	Reference
Alert, Canada	July 1987—June 1988	Hi-Volume filter	14	2	4	1	Kawamura *et al.* (1996)
Arctic troposphere (>60°N)	July—August 1988	Middle-Volume filter unit	21[a], 17[b]				Talbot *et al.* (1992)
Barrow, Alaska	March—April 1989	Low-Volume filter unit	26				Li and Winchester (1993)
Sevettijarvi, Finland	July 1996	Low pressure impactor	21	16	23	6	Kerminen *et al.* (1999)
Sevettijarvi, Finland	July 1997	Low pressure impactor	63		45	16	Fridlind *et al.* (2000)
Alert, Canada	February, April—May 2000	Hi-Volume filter	22[c], 19[d]	4[c], 9[d]	3[c], 12[d]	1[c], 2[d]	This work

[a] Boundary layer.

[b] Free troposphere.

[c] Dark winter samples.

[d] Light spring samples.

Table 3
Varimax-rotated principal component loadings of the data of dicarboxylic acids in the arctic aerosols

Diacids	Abbreviation	Component 1	Component 2
Oxalic	C2	-0.52	0.76
Malonic	C3	-0.98	-0.11
Succinic	C4	-0.95	-0.26
Glutaric	C5	-0.89	0.24
Adipic	C6	0.10	0.97
Azelaic	C9	0.33	0.90
Phthalic	Ph	0.74	0.55
Variance		0.52	0.39

Table 4
Varimax-rotated principal component loadings of the data of dicarboxylic acids in the arctic snowpacks

Diacids	Abbreviation	Component 1	Component 2
Oxalic	C2	0.68	-0.35
Malonic	C3	0.20	-0.96
Succinic	C4	-0.03	-0.98
Glutaric	C5	0.19	-0.98
Adipic	C6	0.89	-0.20
Azelaic	C9	0.94	0.13
Phthalic	Ph	0.96	-0.12
Variance		0.45	0.43