

Secondary formation of water-soluble organic acids and α -dicarbonyls and their contributions to total carbon and water-soluble organic carbon: Photochemical aging of organic aerosols in the Arctic spring

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[1] Water-soluble dicarboxylic acids (C_2 - C_{12}), ketocarboxylic acids (C_2 - C_6 , C_9), and α -dicarbonyls (glyoxal and methylglyoxal) were determined in the Arctic aerosols collected in winter to early summer, as well as aerosol total carbon (TC) and water-soluble organic carbon (WSOC). Concentrations of TC and WSOC gradually decreased from late February to early June with a peak in spring, indicating a photochemical formation of water-soluble organic aerosols at a polar sunrise. We found that total (C_2 - C_{11}) diacids (7 – 84 $ng\ m^{-3}$) increased at polar sunrise by a factor of 4 and then decreased toward summer. Their contributions to TC (average 4.0%) peaked in early April and mid-May. The contribution of total diacids to WSOC was on average 7.1%. It gradually increased from February (5%) to a maximum in April (12.7%) with a second peak in mid-May (10.4%). Although oxalic acid (C_2) is the dominant diacid until April, its predominance was replaced by succinic acid (C_4) after polar sunrise. This may indicate that photochemical production of C_2 was overwhelmed by its degradation when solar radiation was intensified and the atmospheric transport of its precursors from midlatitudes to the Arctic was ended in May. Interestingly, the contributions of azelaic (C_9) and ω -oxobutanoic acids to WSOC increased in early summer possibly due to an enhanced emission of biogenic unsaturated fatty acids from the ocean followed by photochemical oxidation in the atmosphere. An enhanced contribution of diacids to TC and WSOC at polar sunrise may significantly alter the hygroscopic properties of organic aerosols in the Arctic.

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1. Introduction

[2] Low molecular weight carboxylic acids are water-soluble and thus their presence in aerosols enhances the hygroscopic properties of atmospheric particles. The presence of these compounds in atmospheric particles may enhance their ability to act as cloud condensation nuclei (CCN) or ice nuclei (IN). In the Canadian High Arctic, a homologous series (C_2 - C_{10}) of low molecular weight dicarboxylic acids have been detected in ground level aerosols collected at Alert [Kawamura *et al.*, 1996a]. Their con-

centrations significantly increased at polar sunrise by a factor of 5–20 depending on the organic species. These studies clearly demonstrated that highly water-soluble dicarboxylic acids are photochemically produced in the Arctic air at polar sunrise via gas-to-particle conversion and heterogeneous reactions on aerosol particles [Kawamura *et al.*, 2005]. The secondary organic aerosols could significantly contribute to total aerosol carbon (TC) in the Arctic. However, such a hypothesis has not been evaluated in previous field experiments [Kawamura *et al.*, 1996a] partly due to the use of nitrocellulose filters as a particle collection medium. Nitrocellulose filters are not available for the measurements of TC or organic carbon (OC) because the filter materials are burnt during the analytical procedure.

[3] There have been few studies of TC or OC in the Arctic aerosols [e.g., Kawamura *et al.*, 1996a; Narukawa *et al.*, 2003a, 2003b, 2008] but there is no data of water-soluble organic carbon (WSOC), in contrast to many studies of inorganic species [Barrie and Hoff, 1985; Barrie, 1986; Barrie *et al.*, 1988, 1989, 1994a; McConnell *et al.*, 1992; Li *et al.*, 1994; Kerminen *et al.*, 1999; Sirois and Barrie, 1999;

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Norman et al., 1999; Quinn et al., 2009]. Consequently, contributions of dicarboxylic acids and related polar organics to aerosol TC and WSOC are not well understood in the Arctic. Measurements of TC and diacids have been simultaneously conducted in atmospheric aerosols from Antarctica, in which the contribution of dicarboxylic acids to aerosol TC increased up to 3.2% when solar radiation peaks in summer [Kawamura et al., 1996b]. Contributions of low molecular weight dicarboxylic acids to TC have been observed to increase up to 2% in the urban atmosphere from Tokyo during summer [Kawamura and Ikushima, 1993], and to significantly increase up to 16% in the remote marine aerosols from the central Pacific [Kawamura and Sakaguchi, 1999]. Such an increase has been interpreted as due to secondary production of diacids in the atmosphere either by gas-phase and/or aerosol-phase oxidation.

[4] In this study, we have collected Arctic aerosol samples at Alert in the High Canadian Arctic using quartz fiber filters from February to June in 1991 during a period that spans polar sunrise season. The samples were analyzed for the first time for water-soluble dicarboxylic acids, ketocarboxylic acid and α -dicarbonyls and for TC and WSOC. Here, we report seasonal changes in the distributions of water-soluble dicarboxylic acids and related compounds in the Arctic haze and discuss an enhanced contribution of water-soluble organic compounds to TC and WSOC during the polar sunrise. These results are compared with the data of trace metals and inorganic ions to better understand the source, long-range transport and formation pathways in the Arctic.

2. Samples and Methods

[5] Arctic aerosol samples (total suspended particles) were collected for a week at Alert (82.5°N; 62.3°W) outdoors near the Special Study Trailer Laboratory (175 m above sea level) from 19 February to 10 June 1991 using a high-volume air sampler without a denuder and a quartz fiber filter (Pallflex 2500 QAT-UP, 20 × 25 cm), which was precombusted at 450°C for 3 h to remove potential organic contaminants. Sampling periods were in general seven days. Field blank filters were taken once a month. Averaged ambient temperature during sample collection ranged from -34.9°C in February to -1.9°C in June. Polar sunrise starts 5 March and the Sun completely rises on the horizon on 1 April. Filter samples were stored in a precleaned glass jar (150 mL) with a Teflon-lined screw cap before and after sampling. After the sampling, filter samples were transported to Tokyo in a cooler at temperature below 0°C and stored in darkness at -20°C until the analyses. Details of sampling site and sampling method are given elsewhere [Barrie et al., 1994a; Kawamura et al., 1996a]. A high-volume aerosol sampling using Whatman 41 filters was simultaneously conducted at the site for the determination of metals by INAA [Barrie et al., 1994a, 1994b]. Because sampling period (a week) is long, a positive artifact by the adsorption of gaseous organic acids on the quartz filter would be negligible and not affect their concentrations.

[6] Water-soluble organic species including low molecular weight dicarboxylic acids, ketoacids, and α -dicarbonyls were determined using a capillary gas chromatography (GC) [Kawamura et al., 1996a]. Briefly, an aliquot of a frozen filter sample was extracted with organic-free pure water and

the extracts were concentrated nearly to dryness using a rotary evaporator under vacuum and a nitrogen gas blow down. Dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls were derivatized with 14% BF₃/n-butanol to dibutyl esters, dibutoxy acetal butyl esters and dibutoxy acetals, respectively [Kawamura and Ikushima, 1993; Kawamura et al., 1996a]. The derivatives were determined using a capillary gas chromatography (GC) equipped with a split/splitless injector, an HP-5 fused silica capillary column and an FID detector. Identification of organic compounds was confirmed by comparing the GC retention times with those of authentic standards and the mass spectra obtained by GC/mass spectrometer. Both field and laboratory blanks showed small peaks of oxalic and phthalic acids. However, their amounts were less than 10% of those of the actual samples. Concentrations of diacids and related compounds were corrected for the blanks. Spiked experiments of authentic dicarboxylic acids to the quartz filter showed that recoveries were 73% for oxalic acid, 88% for malonic and maleic acids and 100% for succinic and adipic acids. Recoveries of glyoxylic acid, pyruvic acid and methylglyoxal were 88%, 72% and 47%, respectively [Kawamura and Yasui, 2005]. Spiked experiment of diacid standards to a real filter sample showed higher recoveries of oxalic (86%), malonic (94%) and succinic (100%) acids [Kawamura and Yasui, 2005]. Concentrations were not corrected for the recoveries.

[7] For the WSOC measurement, another aliquot of filter sample was extracted with organic-free pure water. The water extracts were filtrated and then acidified with 1 M HCl solution. Dissolved inorganic carbon was purged by bubbling with a pure nitrogen gas and the liquid sample (100 μ L) was injected to Shimadzu TOC-500 carbon analyzer, in which a high-temperature (680°C) catalytic conversion column was installed with platinum coated aluminum granules [Sempéré and Kawamura, 1994]. The derived CO₂ was determined with a NDIR detector. The analytical precision of repeated WSOC measurement was 2%.

[8] Aliquots of filter samples (3.14 cm²) were used for the measurements of total carbon (TC) and total nitrogen (TN) using a Carlo Erba elemental analyzer (NA 1500) and a Sn cup at a combustion temperature of > 1400°C [Kawamura et al., 2004]. Carbon and nitrogen were converted to CO₂ and NO₂, respectively. The latter was reduced to N₂ in the reduction column. The N₂ and CO₂ were isolated on a packed GC column and then determined with a thermal conductivity detector. Analytical errors in the duplicate measurements of TC and TN were within 2%.

[9] The data presented here are all corrected for the field blanks. The analyses of filter samples for molecular composition of diacids and WSOC were conducted at Tokyo Metropolitan University by 1994. One filter sample (QFF 298) was reanalyzed for diacids in 2010. We confirmed that concentrations of major diacids were equivalent to those obtained in 1994 within the analytical errors. On the other hand, TC and TN measurements were conducted in 2009. TC and TN values were also confirmed to be equivalent to those obtained in 1994 using a Yanagimoto MT-2 CHN analyzer. Inorganic ions were measured by ion chromatography [Suzuki et al., 1995].

[10] Air mass trajectories were calculated for 10 days at 500 m height every 12 h using the METEX program of Center for Global Environmental Research, National Insti-

Table 1. Temperatures and Concentrations of Major Components in the Arctic Aerosols Studied

Components	Minimum	Maximum	Average	Median
Ambient temperature, °C	-35.0	-2.0	-19.6	-24.0
Aerosol mass, ng m ⁻³	2540	9130	5250	5520
TC, ng m ⁻³	68.9	634	342	347
TN, ng m ⁻³	11.0	157	78.9	83.8
TC/Aerosol mass, %	2.06	10.1	6.27	6.38
TN/Aerosol mass, %	0.33	2.08	1.41	1.49
C/N weight ratios	3.19	6.30	4.61	4.45
WSOC, ngC m ⁻³	41	300	186	214
WSOC/TC ratios, %	39.3	69.1	55.7	54.7
WSOC/aerosol mass ratios, %	1.21	5.51	3.41	3.41
Major ions, ^a ng m ⁻³				
Na	11.5	448	128	70.8
NH ₄	33.2	185	113	126
K	1.4	39.7	11.4	8.3
Mg	0.7	136	33.0	18.0
Ca	6.9	103	38.9	32.6
Cl	1.9	719	95.5	16.3
NO ₃	0.6	82.9	26.8	16.8
SO ₄	161	2010	1120	1160
nssSO ₄	158	1990	1090	1080
MSA	0.0	10.6	3.8	3.0

^aIon data are from Suzuki *et al.* [1995].

tute of Environmental Studies in Tsukuba, Japan (<http://db.cger.nies.go.jp/metex/trajectory.html>). The trajectory analyses showed that the air masses mainly originate from North Europe, North America and the Arctic Ocean as well as the northwestern Atlantic during sampling period. In late May, the air masses mainly originated from the Arctic Ocean and North Greenland, while in early June they mainly came from the North American Continent and the North Atlantic as well as the Arctic Ocean.

3. Results and Discussion

3.1. TC, TN, and WSOC

[11] Table 1 summarizes concentration ranges and mean concentrations of total aerosol mass, TC, total nitrogen (TN), and WSOC in the Arctic aerosols as well as their relative abundances in aerosol mass and those of WSOC in TC. Although no data have been reported on these parameters in the Arctic, there are several data sets reported in midlatitudes that can be compared with the present Arctic data. Ranges of TC concentrations were 88–639 ng m⁻³ (average 359 ng m⁻³) in the Arctic. These TC values are approximately 60 times lower than those reported from Tokyo (e.g., 10,200–44,100 ng m⁻³, average 22,300 ng m⁻³) [Kawamura and Ikushima, 1993], the North Pacific between Tokyo and Honolulu (480–11,000 ng m⁻³) [Uematsu *et al.*, 1995], and Christchurch (3500–63,000 ng m⁻³, average 20,500 ng m⁻³) [Wang and Kawamura, 2005], but equivalent or a little lower than those (69–5270 ng m⁻³, average 380 ng m⁻³) from the western north to central Pacific including tropics [Kawamura and Sakaguchi, 1999]. Lower concentrations were reported in the remote marine aerosols from the Southern Hemisphere at Samoa (70–140 ng m⁻³), off the coast of Peru (60–270 ng m⁻³) and Amsterdam Island (150 ng m⁻³) [Cachier *et al.*, 1986]. On the other hand, higher carbon concentrations were reported in the tropical aerosols from west Africa (1600–46,400 ng m⁻³) [Cachier *et al.*, 1985], central Africa (14,000–

55,000 ng m⁻³) [Ruellan *et al.*, 1999], and Amazonia (19,500–86,400 ng m⁻³) [Kundu *et al.*, 2010].

[12] Aerosol TN contents ranged from 16 ng m⁻³ to 154 ng m⁻³ (average 86 ng m⁻³) in the Arctic samples. They are much lower (~70 times) than those reported from urban Tokyo (e.g., 1100–21,200 ng m⁻³, average 6000 ng m⁻³) [Kawamura and Ikushima, 1993], but are little higher than those (440–1020 ng m⁻³, average 750 ng m⁻³) observed at the Japanese Syowa station, Antarctica [Kawamura *et al.*, 1996b]. C/N weight ratios ranged from 2.4 to 7.1 (average 4.5), which are similar to those (e.g., 2.1–10.9, average 4.8) reported from urban Tokyo [Kawamura and Ikushima, 1993] and those (0.7–8.3, average 2.8) from the Pacific [Kawamura and Sakaguchi, 1999], but lower than those (6–89, average 36) from Antarctica [Kawamura *et al.*, 1996b]. TC/aerosol mass and TN/aerosol mass ratios ranged from 2.4 to 11.1% (average 6.8%) and from 0.48 to 2.4% (average 1.6%), respectively, in the Arctic samples. These values are generally lower than those (e.g., 9.2–38% and 1.9–15%) reported in urban aerosols from Tokyo [Kawamura and Ikushima, 1993], but higher than those (0.14–4.8% and 0.05–1.3%) from the western north to central Pacific Ocean including tropics [Kawamura and Sakaguchi, 1999].

[13] WSOC concentrations in the Arctic aerosols ranged from 40.7 to 300 ng m⁻³ (average 186 ng m⁻³). These values are 2 orders of magnitude lower than those reported in urban aerosols from Hachioji, Tokyo (e.g., 3200–23,200 ng m⁻³) [Sempéré and Kawamura, 1994] and in the tropical aerosols from Amazonia (18,400–51,000 ng m⁻³) [Kundu *et al.*, 2010]. However, relative abundances of WSOC in TC in the Arctic aerosols are very high (39–69%, average 56%). These values are higher than those reported in urban aerosols from Tokyo (28–55%, average 37%) [Sempéré and Kawamura, 1994] and those in the marine aerosols from the western Pacific (29–53%, average 40%) [Sempéré and Kawamura, 2003], but equivalent to or lower than those reported in the tropical aerosols (average 77% in daytime and 57% in nighttime) [Kundu *et al.*, 2010]. These comparisons indicate that a significant portion of carbonaceous aerosols from the Arctic is water-soluble. WSOC/aerosol mass ratios were 1.2–5.5% (average 3.4%) in the Arctic aerosol samples, which are within the range (1.8–10.7%, average 5.0%) reported for the urban aerosols from Tokyo [Sempéré and Kawamura, 1994].

[14] As shown in Figure 1a, TC showed a decreasing trend from February to June, with peaks in late March to early April and late May. The TC peak in early spring is probably due to in situ production of particulate organic carbon by photochemical oxidation of volatile organic compounds because this period corresponds to polar sunrise season in the Arctic. Unfortunately, ozone was not measured during this campaign; hence we cannot discuss the seasonal changes of organics in relation to oxidants. However, enhanced transport of anthropogenic organic aerosols and their precursors should also contribute to this peak because V (a tracer of fossil fuel combustion), Ca and Al (tracers of soil dusts) increased in late March (Figure 2). In contrast, the second peak observed in late May could not be explained by an enhanced transport of polluted organic aerosols and their precursors (VOCs) because no significant increase was observed for SO₄²⁻, V, Mn or Na (Figure 2). This peak is likely

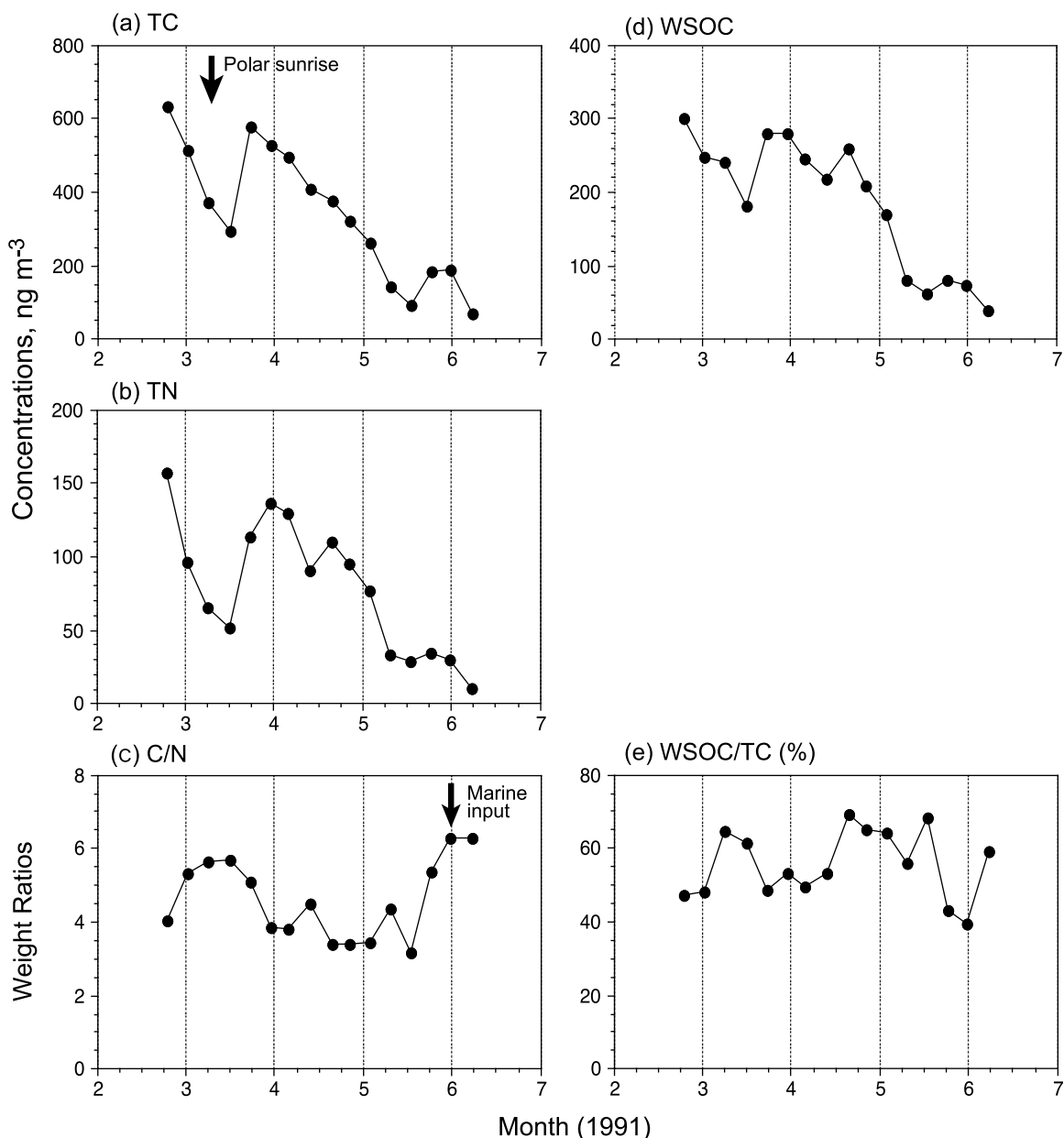


Figure 1. Temporal variations of (a) total carbon (TC), (b) total nitrogen (TN), (c) C/N weight ratios, (d) water-soluble organic carbon (WSOC), and (e) WSOC/TC (%) in the Arctic aerosol samples collected at Alert.

caused by the emission of marine organic matter because concentrations of methanesulfonic acid (MSA) increased toward early summer (Figure 2i).

[15] MSA is produced by the atmospheric oxidation of dimethylsulfide, which is released as a gas from marine microbial processes and thus can be used as a tracer of secondary organic aerosols of marine biological origin [Miyazaki *et al.*, 2010]. Interestingly, Quinn *et al.* [2009] reported a decadal increase of MSA and nss SO₄ at Barrow, Alaska in summer due to a changing climate in the Arctic (e.g., warmer sea surface temperature and reduced sea ice extent). Fu *et al.* [2009b] suggested that, based on the analyses of isoprene oxidation products in the same aerosol samples, secondary production of organic aerosols was

enhanced in late May to early June possibly due to enhanced emission of organic precursors from the open oceans as a result of spring bloom. Narukawa *et al.* [2008] also indicated an enhanced emission of marine organic carbon in early summer to the Arctic atmosphere based on a strong correlation between Na/TC ratios and stable carbon isotopic ratios of TC.

[16] The general decrease of TC from winter to summer may be caused by the scavenging of particulate matter due to more frequent occurrence of precipitation in the High Arctic, coupled with a weakened transport of polluted air parcels from midlatitudes [Barrie *et al.*, 1994a]. TN also showed a temporal variation similar to TC (Figure 1b), but C/N weight ratios (range: 3.2–6.3) peaked in mid-March

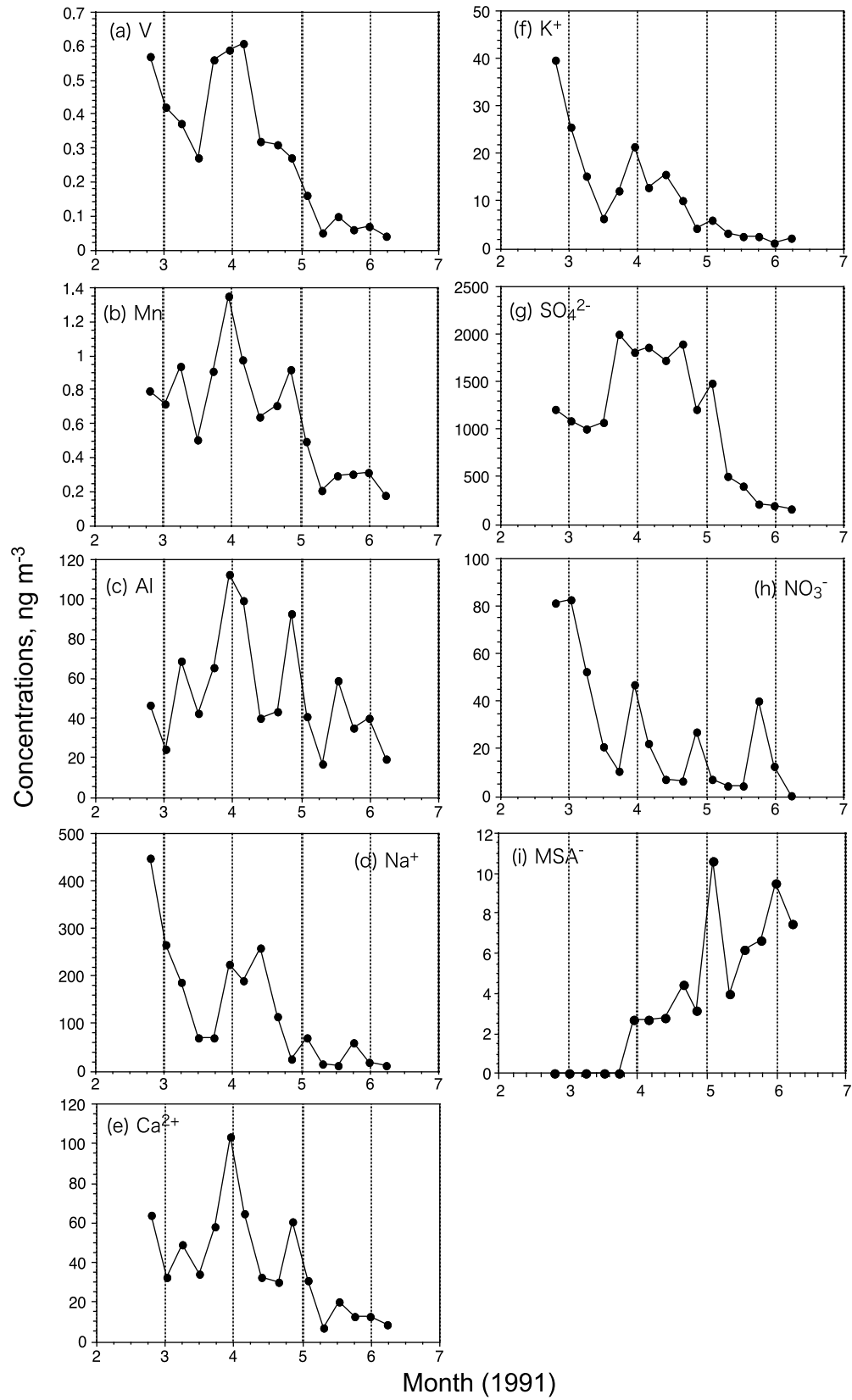


Figure 2. Temporal variations of (a) vanadium (V), (b) manganese (Mn), (c) aluminum (Al), (d) sodium (Na), (e) calcium (Ca), (f) potassium (K), (g) sulfate, (h) nitrate, and (i) methanesulfonate (MSA^-).

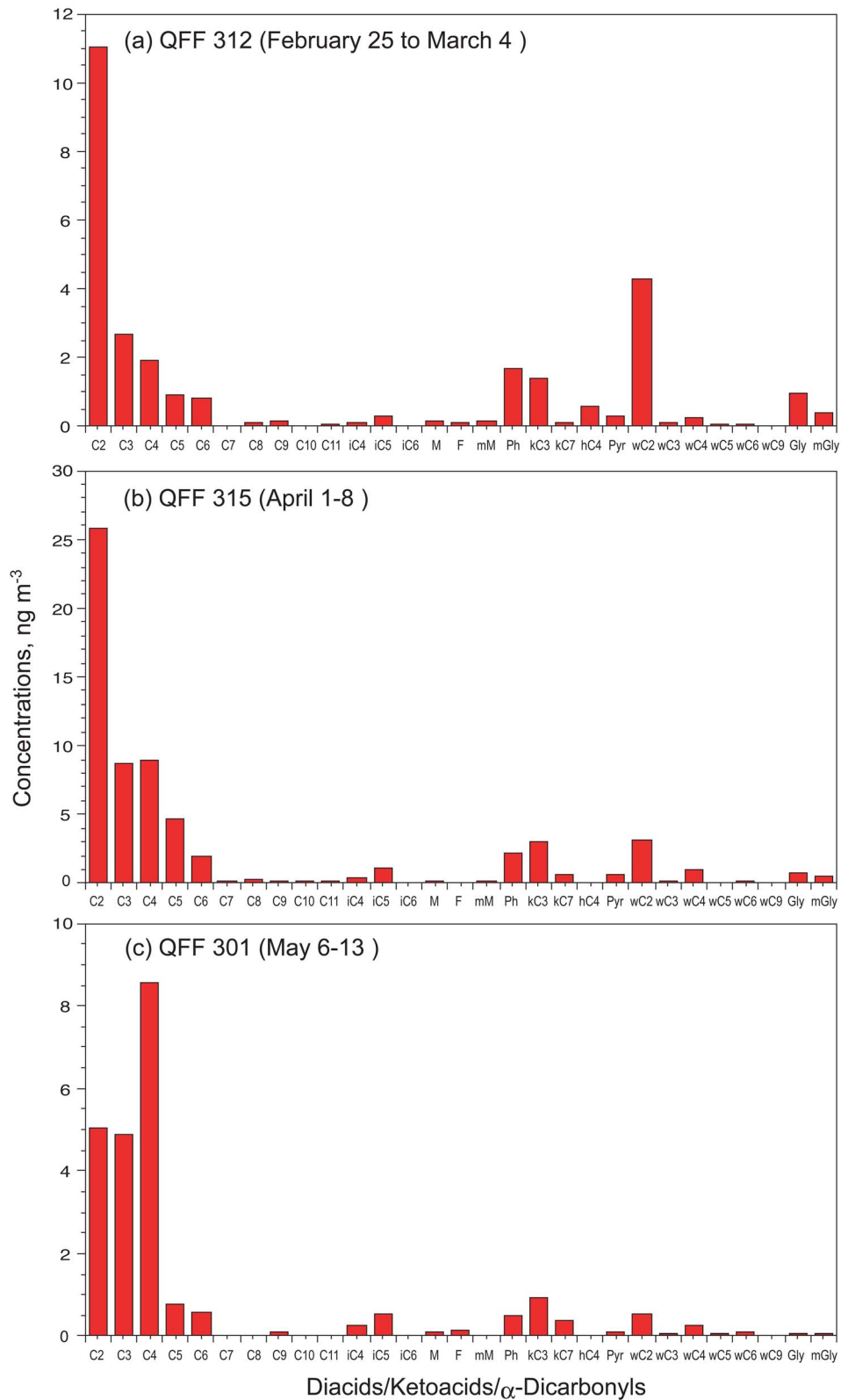


Figure 3. Bar charts of atmospheric concentrations of dicarboxylic acids, ketocarboxylic acids, and related compounds in the Arctic aerosols from Alert for various quartz fiber filter (QFF) weekly samples: (a) QFF312 (25 February to 4 March), (b) QFF305 (16–22 April), and (c) QFF301 (6–13 May).

Table 2. Concentrations (ng m^{-3}) of Dicarboxylic Acids and Related Compounds in the Arctic Aerosols ($n = 16$)

Compounds	Minimum	Maximum	Average	Median
Saturated straight chain diacids				
Oxalic, C ₂	3.08	52.7	16.8	12.4
Malonic, C ₃	1.45	9.15	4.85	3.79
Succinic, C ₄	1.35	12.9	5.69	5.91
Glutaric, C ₅	0.22	5.93	2.04	1.60
Adipic, C ₆	0.21	2.94	1.43	1.24
Pimelic, C ₇	0.01	0.48	0.12	0.08
Suberic, C ₈	0.02	0.29	0.11	0.08
Azelaic, C ₉	0.04	0.19	0.11	0.10
Sebacic, C ₁₀	0.00	0.16	0.03	0.02
Undecanoic, C ₁₁	0.01	0.14	0.06	0.05
Unsaturated diacids				
Fumaric, F	0.08	0.34	0.17	0.15
Maleic, M	0.04	0.83	0.23	0.18
Methylmaleic, mM	0.01	0.38	0.11	0.11
Phthalic, Ph	0.16	3.25	1.59	1.56
Branched chain diacids				
Methylmalonic, iC ₄	0.08	0.43	0.22	0.19
Methylsuccinic, iC ₅	0.05	1.68	0.59	0.49
2-methylglutaric, iC ₆	0.01	0.17	0.05	0.05
Keto or hydroxy diacids				
Ketomalonic, C _{3di,oxo}	0.22	4.60	1.29	0.92
4-ketopimelic, C _{7di,4oxo}	0.11	0.75	0.38	0.32
Hydroxysuccinic, Malic, hC ₄	0.02	3.57	0.79	0.06
Total dicarboxylic acids	7.42	84.5	36.7	34.0
Ketoacids				
Glyoxylic, ω C ₂	0.20	7.68	2.46	1.53
3-oxopropanoic, ω C ₃	0.02	0.24	0.12	0.14
4-oxobutanoic, ω C ₄	0.18	1.29	0.57	0.49
6-oxopentanoic, ω C ₅	0.01	0.13	0.07	0.07
7-oxohexanoic, ω C ₆	0.00	0.35	0.10	0.08
8-oxononanoic, ω C ₉	0.00	0.09	0.04	0.03
Pyruvic, Pyr	0.06	0.60	0.30	0.30
Total ketoacids	0.76	8.93	3.65	2.71
α -dicarbonyls				
Glyoxal, Gly	0.01	2.00	0.55	0.42
Methylglyoxal, MeGly	0.04	0.82	0.32	0.25
Total α -dicarbonyls	0.05	2.82	0.88	0.68
Total diacid-C/TC, %	1.52	7.00	3.95	3.61
Total diacid-C/WSOC, %	3.13	12.7	7.08	6.53

(5.7) and late May to early June (6.3) (Figure 1c), suggesting a change in the source region and/or sources. Because seasonal pattern of TN is similar to that of V, TN should mostly be transported from continental pollution sources. Ammonium showed similar pattern to TN (data are not shown as a figure), suggesting that NH_3 is reacted with H_2SO_4 produced at polar sunrise to contribute to TN. The C/N peak in late May to early June may be explained by the sea-to-air emission of marine organic matter and/or gas-to-particle formation of organic aerosols as discussed above. The C/N ratios in the early summer are similar to that (6.6) calculated from the Redfield ratio, that is, an averaged elemental composition of marine phytoplankton [Libes, 1992], suggesting that emissions of marine organic matter became significant in early summer, when sea ice melts and lead expands in the Arctic Ocean.

[17] Figure 1d shows a temporal variation of WSOC in the Arctic aerosols. Concentrations of WSOC decreased from February to mid-March and then increased in late March and mid-April. WSOC significantly decreased toward early summer. The peak in late March may be mainly caused by an enhanced transport of anthropogenic aerosols because a peak of anthropogenic aerosol V was observed in the same

period (Figure 2a). However, photochemical production of water-soluble organic species could also be important during polar sunrise. The peak in mid-April is most likely associated with the secondary production of water-soluble organic compounds after polar sunrise as discussed later in more detail in relation to diacids and related water-soluble organic species. A significant decrease of WSOC from late April to May can be explained by more frequent scavenging of the particles and the weaker long-range transport of pollutants (precursor organic compounds) from lower latitudes as discussed above. Such a decrease of pollutants is consistent with the decreased concentrations of anthropogenic vanadium and sulfate in the Arctic aerosols (Figure 2).

[18] High values of TC and WSOC in February (Figures 1a and 1c) may be caused by an enhanced transport of anthropogenic organic matter in winter because the highest concentrations of anthropogenic polycyclic aromatic hydrocarbons (PAHs) were obtained in February [Fu *et al.*, 2009a]. Although Shaw *et al.* [2010] proposed that organics from frost flowers account for significant wintertime organic aerosols (OA), we consider this contribution is not important at Alert in February. This seems to be supported by relatively low $\delta^{13}\text{C}$ ratios of TC (ca. -26%) in February to March (P. Fu *et al.*, unpublished data, 2009). WSOC/TC ratios peak in mid-April to mid-May (see Figure 1e) as solar radiation intensified following polar sunrise on 5 March. This is likely related to the enhanced photochemical production of water-soluble organics in aerosol particles as discussed later. The increase in WSOC/TC ratios from April to May (Figure 1e) suggest that Arctic organic aerosols are indeed photochemically more processed after polar sunrise than before sunrise. In contrast, much higher WSOC/OC ratios ($85 \pm 15\%$) were reported for airborne aerosols collected over central Africa [Ruellan *et al.*, 1999], which are 2–3 times higher than the ground surface aerosols. Hagler *et al.* [2007] also reported high WSOC/OC ratios (81% on average) for the aerosols collected at Summit, Greenland, which may be due to either the oxidation of primary OC during transport and/or gas-to-particle formation of secondary WSOC.

3.2. Water-Soluble Dicarboxylic Acids, Ketoacids, and α -Dicarbonyls

[19] A homologous series of dicarboxylic acids (C₂–C₁₁), ketoacids (C₂–C₉) and α -dicarbonyls (C₂–C₃) were detected in the Arctic aerosol samples. Table 2 summarizes their concentrations as well as their contributions to TC and WSOC. Concentration ranges of total diacids, ketoacids and α -dicarbonyls are 7.4–84.5 ng m^{-3} , 0.76–8.9 ng m^{-3} , and 0.05–2.8 ng m^{-3} , respectively. Molecular distributions of diacids are generally characterized by a predominance of oxalic acid (C₂), followed by succinic (C₄) or malonic (C₃) acid (Figure 3a). Short-chain species (C₂–C₄) account for >75% of the total diacids. The predominance of oxalic acid has been observed in the aerosol samples collected from different regions in the low to high latitudes including urban Tokyo [Kawamura and Ikushima, 1993], Chinese megacities [Ho *et al.*, 2007], Hong Kong [Yao *et al.*, 2004], southern India [Pavuluri *et al.*, 2010], the North and Central Pacific [Kawamura and Sakaguchi, 1999], New Zealand [Wang and Shooter, 2004], South African savanna [Limbeck *et al.*, 2001], Amazonia with biomass burning influence [Kundu

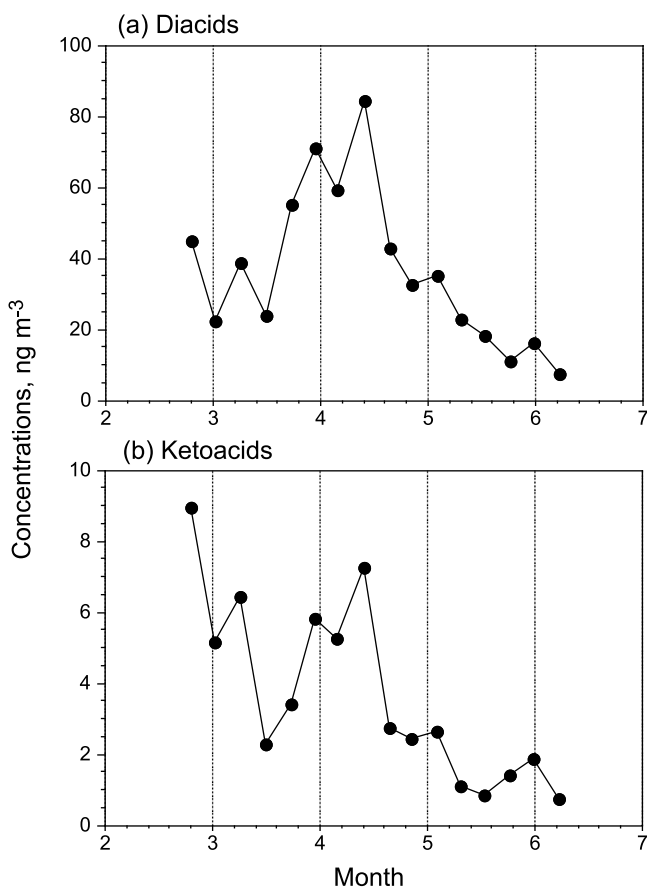


Figure 4. Seasonal changes in the concentrations of total (a) dicarboxylic acids and (b) ketocarboxylic acids in the Arctic aerosols at Alert.

et al., 2010], Europe [Legrand *et al.*, 2007], and the Arctic [Kerminen *et al.*, 1999].

[20] However, molecular distributions of diacids significantly changed in the course of polar sunrise. We found that the peak of C₂ was weakened relative to C₃ and C₄ in late April to May (Figure 3b) and was overwhelmed by C₄ in two of May samples. In particular, C₄ diacid became the most abundant diacid in mid-May (Figure 3c). In late May to June, the predominance of C₂ was recovered although the concentration levels of diacids are low. Similar depletion of C₂ was observed in the Arctic samples from Alert collected in 1988, although this phenomena has not been discussed before [Kawamura *et al.*, 1996a]. The predominance of succinic acid has often been detected in the ice core samples from Greenland [Kawamura *et al.*, 2001]. Interestingly, similar distribution pattern has been reported in the Antarctic aerosols collected at Syowa Station in summer [Kawamura *et al.*, 1996b]. The apparent decrease of C₂ in mid-May may be caused by either an enhanced production of C₃ and C₄ diacids or preferential degradation of C₂ after polar sunrise as discussed later in more detail.

[21] Figure 4 gives seasonal variation of the concentrations of total diacids and ketoacids in the Arctic aerosols. Total dicarboxylic acids peaked in early April and decreased toward summer. Total ketoacids also showed a peak in early April although the highest concentration was obtained in February (Figure 4b). These seasonal variations are different

than those of TC and WSOC (Figures 1a and 1e). A similar springtime maximum has been observed in the Arctic atmosphere during earlier polar sunrise experiments in 1988 and 1992 [Kawamura *et al.*, 1996a, 2005]. The spring peak of diacids at polar sunrise indicates that they are produced in situ in the Arctic atmosphere by photochemical oxidation of gaseous anthropogenic unsaturated hydrocarbons and other organic precursors, which are abundantly transported to the Arctic from the midlatitude during winter to early spring. Heterogeneous reactions on aerosol particles may also be important to produce diacids [Kawamura *et al.*, 2005]. Alternatively, photochemical formation of diacids on the sea ice surface followed by the wind blown emissions to the air cannot be excluded.

[22] Figure 5 presents seasonal variations in the concentrations of individual dicarboxylic acids. Oxalic acid, C₄-C₆ and iC₅ diacids and unsaturated (M, F, mM) diacids showed maxima in mid-April (Figures 5c–5e, 5j–5l and 5o), suggesting that photochemical breakdown of precursor organic compounds might result in the increases of these diacids. Although many diacid species including C₂ showed a peak at polar sunrise, malonic acid showed a drop in mid-April (Figure 5a and 5b). In order to confirm that this point is not experimental anomaly, the sample analysis was repeated and we obtained the same results. This suggests that a significant decomposition of malonic acid happened in mid-April when the Sun was above the horizon all day and exposure to solar radiation was accordingly intensified. Because malonic acid (C₃) contains only one methylene chain adjacent to two carbonyl groups, hydrogen atoms bonded to the methylene chain should be activated and easily attached by OH radicals. They are likely subjected to the hydrogen abstraction reaction by OH radicals and further decomposed to oxalic acid under the conditions of strong solar radiation in April.

[23] Interestingly, oxomalonic acid whose structure is similar to malonic acid except for keto group also showed a decrease in the concentrations in mid-April (Figure 5p) when malonic acid dropped significantly. Because this acid does not contain hydrogen atoms to be subtracted by OH radicals, it may be stable against OH attack. Instead, oxomalonic acid may be subjected to photolysis at C = O position adjacent to two carboxyl groups, which may activate the carbonyl group. Although we did not observe any anomalies of chemical compositions including halogen (Br, I, Cl) species and Cl/Na ratios in this April sample, unknown processes that we cannot specify at this moment may have occurred in the Arctic atmosphere in mid-April.

[24] After polar sunrise, concentrations of diacid species mostly decreased in May and June due to declining strength of atmospheric transport of anthropogenic pollutants (precursors) from midlatitudes [Barrie, 1986] and increasing removal of aerosols by wet deposition indicated by declining primary pollutants in aerosols [Barrie and Bottenheim, 1991]. The decreased concentrations of diacids are consistent with the decreases of V and sulfate in early summer (Figures 1a and 1g). However, the concentrations of azelaic acid (Figure 6h), fumaric acid (Figure 5j) and 4-oxopimelic acid (Figure 5q) increased in late spring to early summer. Azelaic acid is an oxidation product of unsaturated fatty acids such as oleic and linoleic acids [Kawamura and Gagosian, 1987; Yokouchi and Ambe, 1986; Stephanou

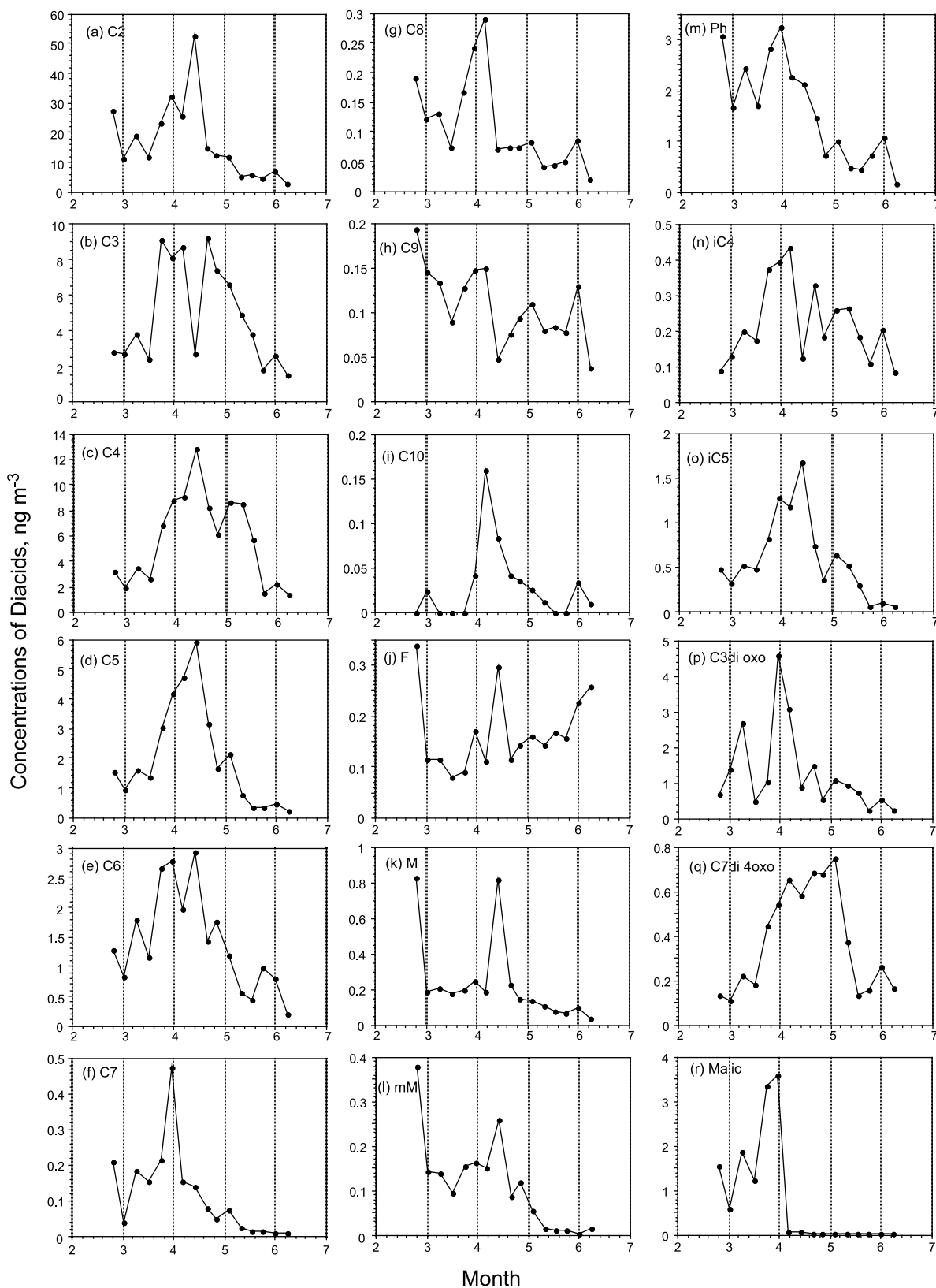


Figure 5. Seasonal variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) glutaric acid (C_5), (e) adipic acid (C_6), (f) pimelic acid (C_7), (g) suberic acid (C_8), (h) azelaic acid (C_9), (i) sebacic acid (C_{10}), (j) fumaric acid (F), (k) maleic acid (M), (l) methylmaleic acid (mM), (m) phthalic acid (Ph), (n) methylmalonic acid (iC_4), (o) methylsuccinic acid (iC_5), (p) ketomalonic acid ($C_{3di,oxo}$), (q) 4-ketopimelic acid ($C_{7di,4-oxo}$), and (r) malic acid (hC_4) in the Arctic aerosols from Alert.

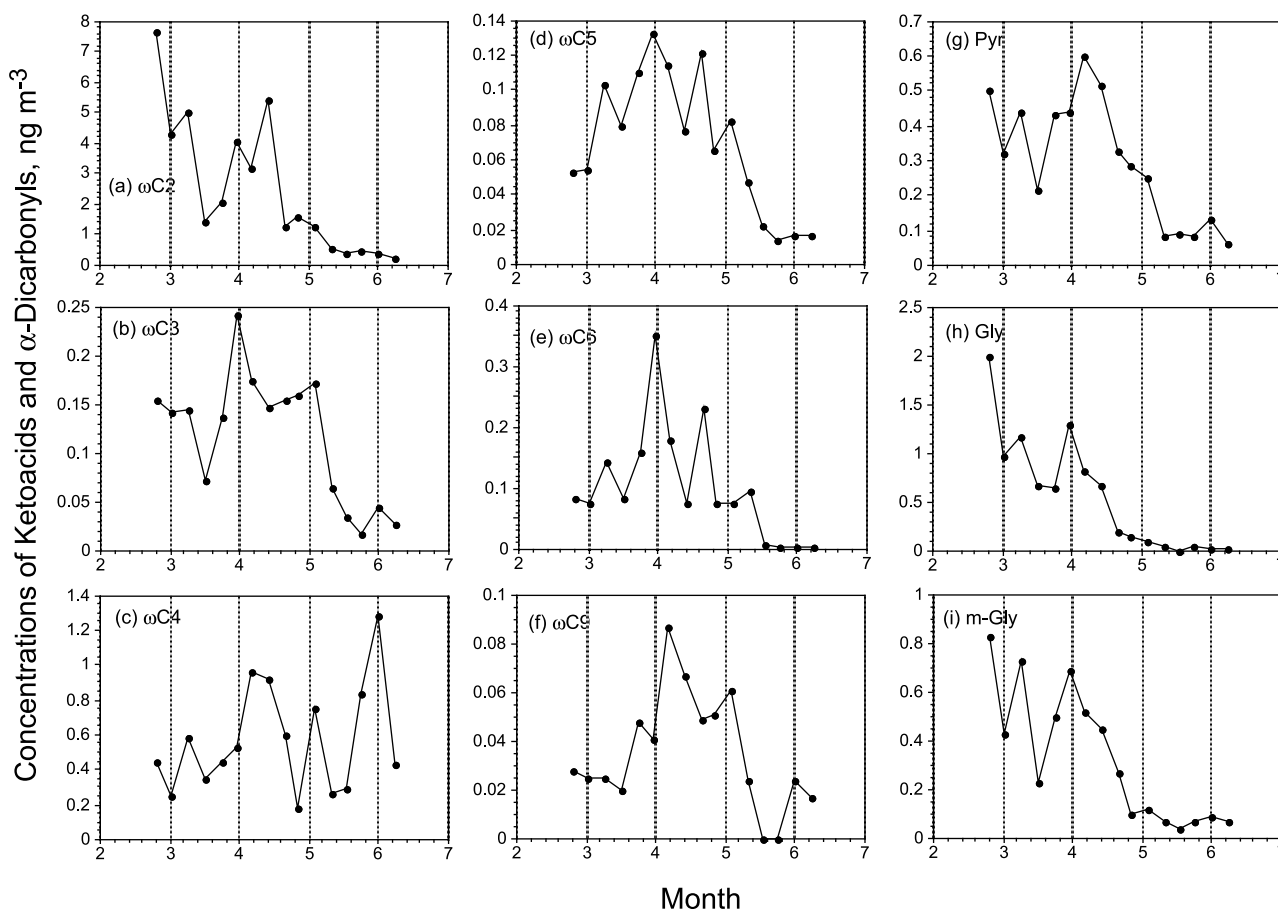


Figure 6. Seasonal variations of (a) glyoxylic acid (ωC_2), (b) 3-oxopropanoic acid (ωC_3), (c) 4-oxobutanoic acid (ωC_4), (d) 5-oxopentanoic acid (ωC_5), (e) 6-oxohexanoic acid (ωC_6), (f) 9-oxononanoic acid (ωC_9), (g) pyruvic acid (Pyr), (h) glyoxal (Gly), and (i) methylglyoxal (MeGly) in the Arctic aerosols from Alert.

and Stratigakis, 1993], which are likely emitted from the Arctic Ocean when sea ice starts to retreat and lead expands in late spring. Thus biological activity may have been enhanced in the ocean to result in an increased sea-to-air emission of unsaturated fatty acids that are produced by marine biota (phytoplankton) and accumulate in the microlayer of ocean surface. Similar results have been obtained in the Arctic experiment of 1988 [Kawamura *et al.*, 1996a]. The increase of fumaric acid can be explained by cis to trans isomerization of maleic acid under strong solar radiation. The 4-oxopimelic acid may be produced by the oxidation of pimelic acid.

[25] The ω -ketocarboxylic acids (C_2 – C_6 , C_9) and pyruvic acid (C_3) were also detected in the water-soluble fraction of the aerosols as well as α -dicarbonyls (glyoxal and methylglyoxal). The seasonal distributions are presented in Figure 6. Generally, glyoxylic acid (ωC_2) was the most abundant ketoacid in the Arctic aerosols. The ωC_2 has been proposed as one of the precursors of oxalic acid [Kawamura *et al.*, 1996a; Warneck, 2003; Lim *et al.*, 2005]. Its concentrations showed a maximum in late February, decreased toward mid-March and then increased during polar sunrise showing a peak in mid-April (Figure 6a). After the peak, its concentrations decreased toward summer. During the period of late February to early March just before polar sunrise, ωC_2 was the second most

abundant organic species following oxalic acid (Figure 3a), but it became less abundant than C_3 or C_4 diacid after polar sunrise (Figures 3b and 3c). This supports the hypothesis that glyoxylic acid is an intermediate in the oxidative reactions of VOCs to the formation of oxalic acid [Kawamura *et al.*, 1996a].

[26] Although glyoxylic acid (ωC_2) was in general the most abundant ketoacid followed by 4-oxobutanoic acid (ωC_4), ωC_4 became more abundant than ωC_2 in early summer (after late May) (see Figures 6a and 6c). This suggests that a transition of organic precursors occurs in the Arctic from anthropogenic VOCs, which are long-range transported in winter, to other source precursors including biogenic VOCs and other organics derived from the ocean in spring to early summer. This is likely because sea ice starts to melt in spring resulting in emissions of biogenic organic matter from the ocean surface, being consistent with the seasonal trend of MSA (Figure 2i). Similar phenomenon of ωC_4 has been reported in the Arctic aerosols collected in early summer of 1988 [Kawamura *et al.*, 1996a]. This again suggests that marine biological productivity in the Arctic Ocean controls the organic aerosol composition in early summer. Although C_3 – C_9 ω -ketoacids and pyruvic acid are minor species, they showed concentration maxima in early April (Figures 6b–6g). This result suggests that homologous series of ω -ketoacids

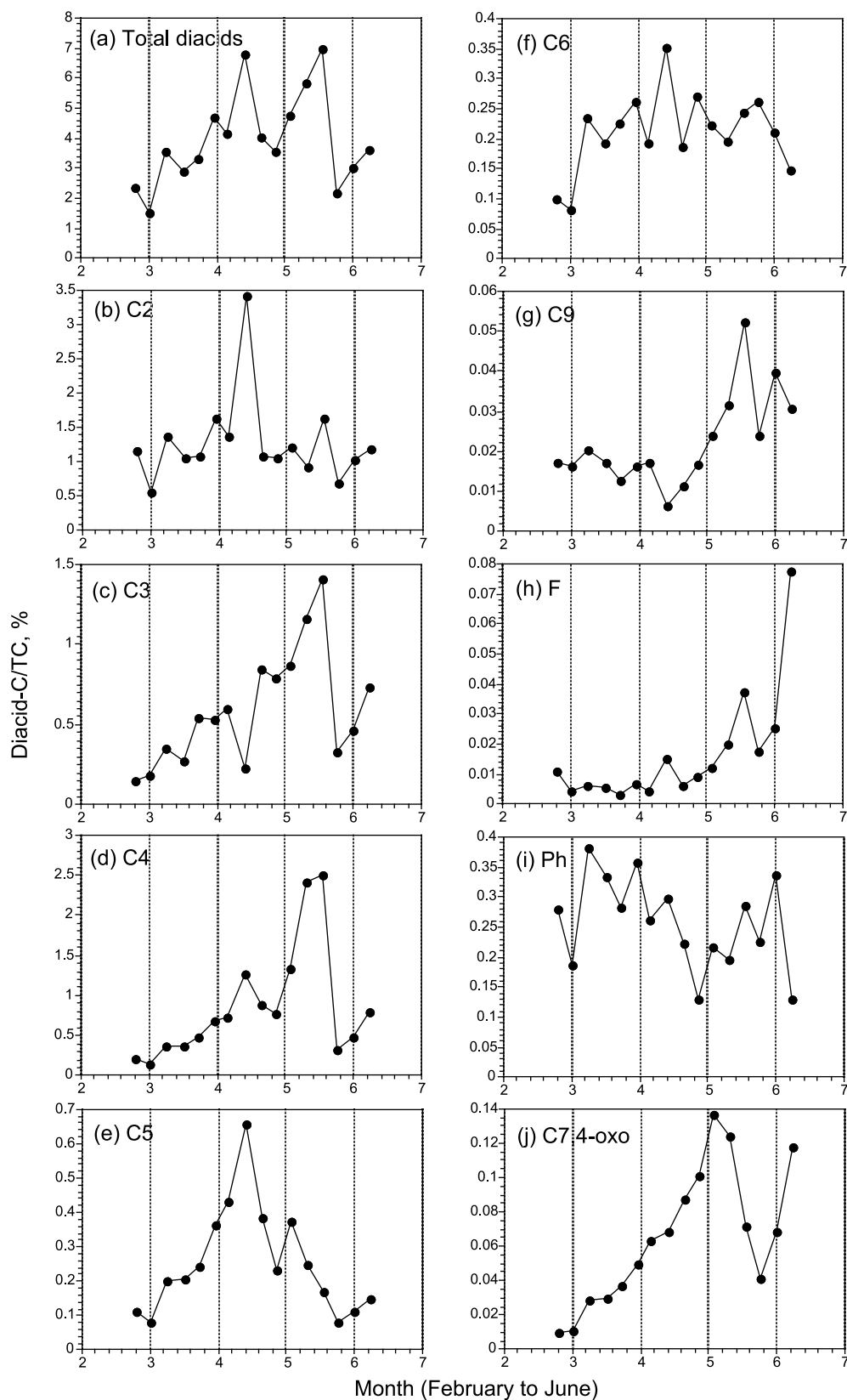


Figure 7. Seasonal variations in the contributions of dicarboxylic acid carbon (diacid-C) to total carbon (TC) in the Arctic aerosols from Alert: (a) total diacids, (b) oxalic acid (C_2), (c) malonic acid (C_3), (d) succinic acid (C_4), (e) glutaric acid (C_5), (f) adipic acid (C_6), (g) azelaic acid (C_9), (h) fumaric acid (F), (i) phthalic acid (Ph), and (j) 4-oxopimelic acid (C_7 , 4-oxo).

and pyruvic acid are photochemically produced in the Arctic atmosphere during the polar sunrise season.

[27] Glyoxal and methylglyoxal, which can also serve as precursors of oxalic acid and glyoxylic acid [Kawamura *et al.*, 1996a; Warneck, 2003], showed a seasonal variation with a peak in early April, being similar to glyoxylic acid (Figures 6a, 6h and 6i). These α -dicarbonyls are also produced in the Arctic atmosphere during polar sunrise event and can contribute as possible precursors of oxalic acid.

3.3. Contribution of Diacids, Ketoacids, and α -Dicarbonyls to TC

[28] Figure 7 presents contributions (%) of total diacids and selected diacid species to aerosol total carbon (TC). Total diacid-C/TC ratios range from 1.5 to 9.0% with an average of 4.0% (Figure 7a). These values are much higher than those (0.18–1.8%, average 0.95%) reported from urban Tokyo [Kawamura and Ikushima, 1993], but equivalent to or lower than those (1.1–15.8%, average 8.8%) from the western north and central Pacific in which photochemical processing of OA significantly occurs [Kawamura and Sakaguchi, 1999]. Although diacids were not determined, Hagler *et al.* [2007] reported high WSOC/OC ratios (up to 80%) in the aerosols at Summit, Greenland, possibly due to photochemical processing during long-range transport. These comparisons suggest that the Arctic organic aerosols are enriched with water-soluble dicarboxylic acids compared to near-source aerosols probably due to photochemical processing during long-range atmospheric transport and strong radiation during polar sunrise. As seen in Figure 7a, total diacid-C/TC ratios are low (\sim 2%) in dark winter (late February) but increased toward light spring showing two peaks (\sim 7%) in mid-April and mid-May. The ratios then decreased to lower values (\sim 2–3%) in early summer. The first peak is consistent with a large increase in the concentrations of oxalic (C_2) acid (Figure 7b) and glutaric (C_5) acid (Figure 7e). In contrast, the second peak (Figure 7a) is caused by the increase of malonic (C_3) and succinic (C_4) acids (Figures 7c and 7d) and, to a lesser extent, azelaic (C_9) acid (Figure 7g). These increases again suggest a preferential production of C_3 , C_4 and C_9 by the oxidation of precursor organics including unsaturated fatty acids.

[29] It is of interest to note that the contributions of C_3 and C_4 to TC gradually increase from late February to mid-May, although their contributions declined in mid to late April (Figures 7c and 7d). On the other hand, relative contributions of fumaric acid to TC continuously increase to early summer most likely due to the photochemical *cis* to *trans* isomerization reaction of maleic acid to fumaric acid under a strong solar radiation [Kawamura and Ikushima, 1993]. Phthalic acid showed higher relative abundances in March and late May (Figure 7i). The former peak may be associated with the enhanced transport of naphthalene and other PAHs that are precursors of phthalic acid [Kawamura and Ikushima, 1993]. A substantial increase was found in the contribution of 4-oxopimelic acid to TC from late February to early May (Figure 7j). After the drop in late May, this oxoacid again increased toward early summer. Although pimelic acid could serve as one of the precursors of 4-oxopimelic acid, its relative abundance to TC did not show an increase; rather it decreased toward early June after the peak at the end of March (data not shown as a figure). The source and formation

pathway of 4-oxopimelic acid are still unknown. However, Sakaguchi and Kawamura [1994] reported that this ketoacid might be produced by the oxidation of monocarboxylic acids containing additional keto group at C-4 position. Homologous 4-ketocarboxylic acids (C_7 – C_{13}) have been reported in the marine atmosphere from the Pacific [Kawamura and Gagosian, 1990].

[30] Total ketoacids were found to comprise 0.2–0.6% of TC, which showed three peaks in early March, mid-April and early June (Figure 8a). Glyoxylic acid mainly contributed to the first and second peaks whereas 4-oxobutanoic acid (ωC_4) dominantly contributed to the third peak in early June (Figures 8b and 8d). The ωC_3 , ωC_5 , ωC_6 and ωC_9 contribute to less than 0.03% of TC (Figures 8c and 8e–8g). However, it is of interest to note that both ωC_4 and ωC_9 show an increase in the contributions to TC from winter to early summer, except for a drop of ωC_9 in May (Figures 8d and 8g). The ωC_9 is a typical oxidation product of unsaturated fatty acids such as oleic and linoleic acids that contain a double bond at C-9 position [Kawamura and Gagosian, 1987], suggesting an increased contribution of biogenic sources probably from seawater surfaces toward summer season.

3.4. Contribution of Diacids, Ketoacids, and α -Dicarbonyls to WSOC

[31] The contributions of total diacid carbon to WSOC were found to be relatively high (3–13%) with two maxima in mid-April and mid-May as shown in Figure 9a. The peak in mid-April is largely caused by the increase of C_2 and C_5 whereas that in mid-May is by C_3 and C_4 . A similar pattern is evident for the contributions of diacids to TC (Figure 7). Seasonal variations of diacid-C/WSOC showed that C_2 – C_6 diacids, except for C_3 , peaked in mid-April (8 to 16 April). After this peak (6.5% for C_2 only), the contributions of C_2 to WSOC significantly dropped and stayed rather low around at 2%, whereas C_3 and C_4 diacids showed a continuous increase with a maximum in mid-May, when C_3 and C_4 diacids comprised \sim 2.1% and 4.3% of WSOC, respectively. The latter peak is twice higher than that (\sim 2%) of C_2 in the same period.

[32] A sharp drop of the contribution of C_2 to WSOC in late April (Figure 9b) may be associated with photochemical decomposition of oxalic acid. Oxalic acid is in general stable against OH attack because this shortest diacid does not contain methylene chain and the associated hydrogen atom that can react with OH radicals. However, this bifunctional organic acid can form a complex with Fe (III) (iron (III)-oxalato complex), which can photolyze under an irradiation of UV-A into visible region to result in CO_2 and Fe (II) [Zuo and Hoigné, 1992; Deguillaume *et al.*, 2005]. A significant decrease of oxalic acid relative to WSOC in late April (Figure 9b) suggests that photolysis of oxalic acid-iron (III) complex in aerosols may have occurred as discussed above and overwhelmed its production in the Arctic atmosphere when the Sun completely rose on the horizon. If iron complexes are responsible for enhanced degradation of oxalic acid after April it can have two causes: enhanced sunlight and more iron from soil dust. As suggested from the seasonal variation of Al [Sirois and Barrie, 1999], soil dust input was enhanced in mid-April at Alert. This suggests that enhanced

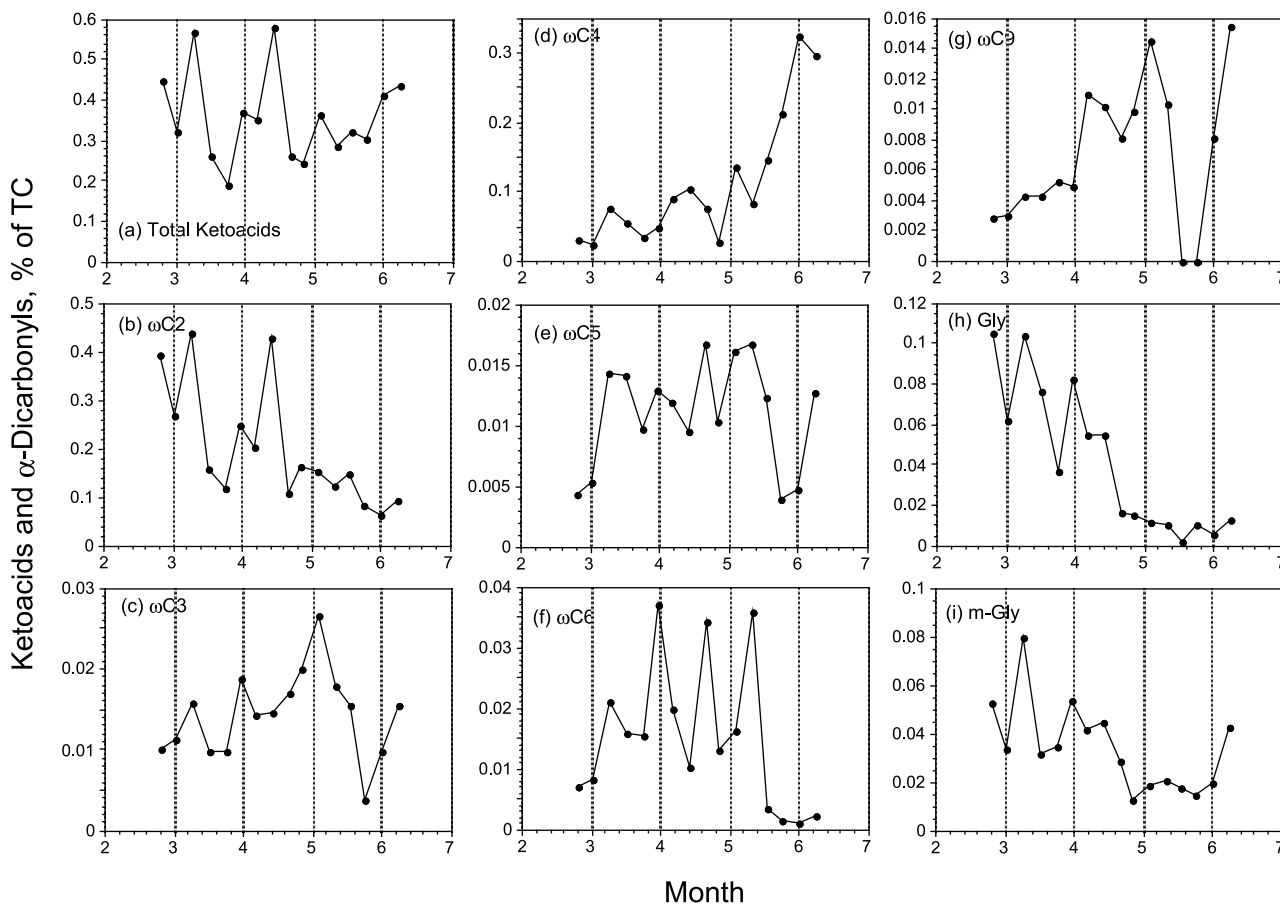


Figure 8. Seasonal variations in the contributions of ketocarboxylic acids and α -dicarbonyls to total carbon (TC) in the Arctic aerosols from Alert: (a) total ketoacids, (b) glyoxylic acid (ωC_2), (c) 3-oxopropionic acid (ωC_3), (d) 4-oxobutanoic acid (ωC_4), (e) 5-oxopentanoic acid (ωC_5), (f) 6-oxohexanoic acid (ωC_6), (g) 9-oxononanoic acid (ωC_9), (h) glyoxal (Gly), and (i) methylglyoxal (MeGly).

sunlight and soil dust are both important to control the degradation of oxalic acid.

[33] The seasonal contributions of C_9 and other diacids to WSOC showed different patterns each other (Figures 9g–9j). Azelaic acid (C_9) did not show a peak in mid-April, but increased toward summer showing a peak in early June (Figure 9g). This increase may be caused by the emission of biogenic precursors (unsaturated fatty acids) from the ocean followed by photochemical oxidation as stated above. Although fumaric acid also gave a similar trend (Figure 9f), it should be explained by enhanced cis-to-trans conversion of maleic acid, which can be produced by the oxidation of aromatic structures. Phthalic acid-C/WSOC ratios showed two peaks in late March (0.7%) and early June (0.8%). The first peak is consistent with the peak of V (Figure 2a), suggesting an enhanced contribution and long-range transport from anthropogenic emissions. However, the second peak does not match the V peak, rather it is consistent with the peak of C_9 (Figure 9g). This result may suggest that phthalic acid is derived from natural sources in early summer. Kawamura and Sakaguchi [1999] suggested, based on the marine aerosol study, that Ph can be produced by the oxidation of phenolic compounds that are enriched in sea surface slicks [Carlson, 1982] and may be emitted to the atmosphere. It is interesting to note that Bahadur *et al.* [2010] detected phenol

compounds in the marine aerosols from the northeastern Atlantic using a FTIR spectroscopy and reported that they are associated with seawater-derived emissions. The 4-oxopimelic acid-C/WSOC showed a seasonal trend similar to that of TC-normalized ratios (Figure 7j).

[34] Total ketoacid-C/WSOC ratios (range 0.4–1.5%) showed three peaks in late February, mid-April and early June (Figure 10a). The first and second peaks are mainly derived by the high abundances of glyoxylic acid (Figure 10b) whereas the third peak is caused by the increase of ωC_4 acid (Figure 10d). Although ωC_3 , ωC_5 , ωC_6 and ωC_9 are rather minor contributors to WSOC, they showed several peaks at early April, early May and mid-May. Interestingly, ω -oxononanoic acid (ωC_9) showed a gradual increase from late February to early summer with a drop in May. This increase suggests an enhanced emission of biogenic unsaturated fatty acids from the ocean surface when sea ice starts to melt. The α -dicarbonyls account for 0.02–0.35% of WSOC. Both glyoxal and methylglyoxal generally show a decrease from winter to summer (Figures 10h and 10i), but methylglyoxal increased in late April to early June. It may be produced by the atmospheric oxidation of VOCs including isoprene emitted from the ocean after the retreat of sea ice. Methylglyoxal is known as the oxidation product of isoprene [Brasseur *et al.*, 1999; Matsunaga *et al.*, 2004; Lim *et al.*,

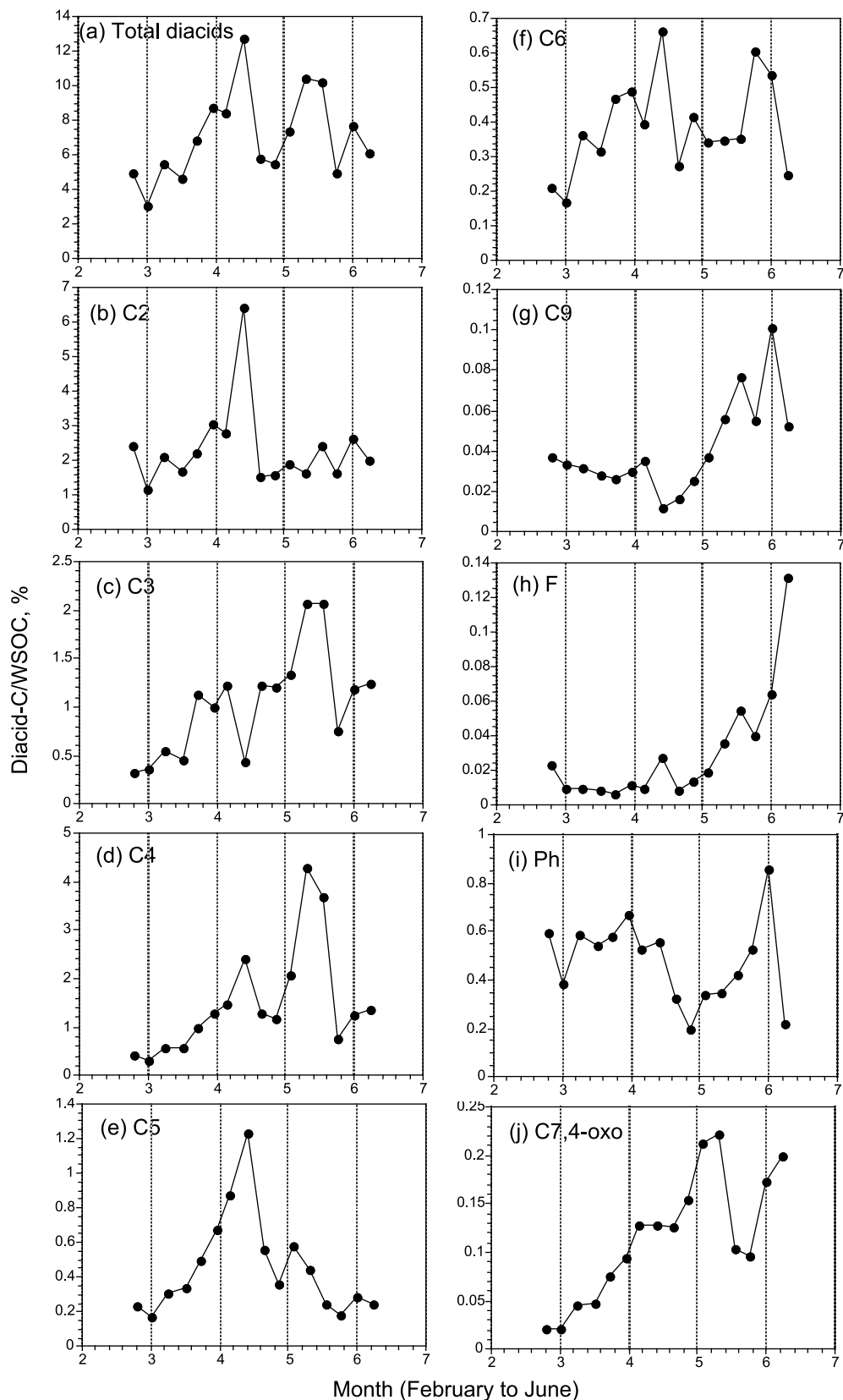


Figure 9. Seasonal variations in the contributions of dicarboxylic acid carbon to water-soluble organic carbon (diacid-C/WSOC) in the Arctic aerosols from Alert: (a) total diacids, (b) oxalic acid (C₂), (c) malonic acid (C₃), (d) succinic acid (C₄), (e) glutaric acid (C₅), (f) adipic acid (C₆), (g) azelaic acid (C₉), (h) fumaric acid (F), (i) phthalic acid (Ph), and (j) 4-oxopimelic acid (C₇, 4-oxo).

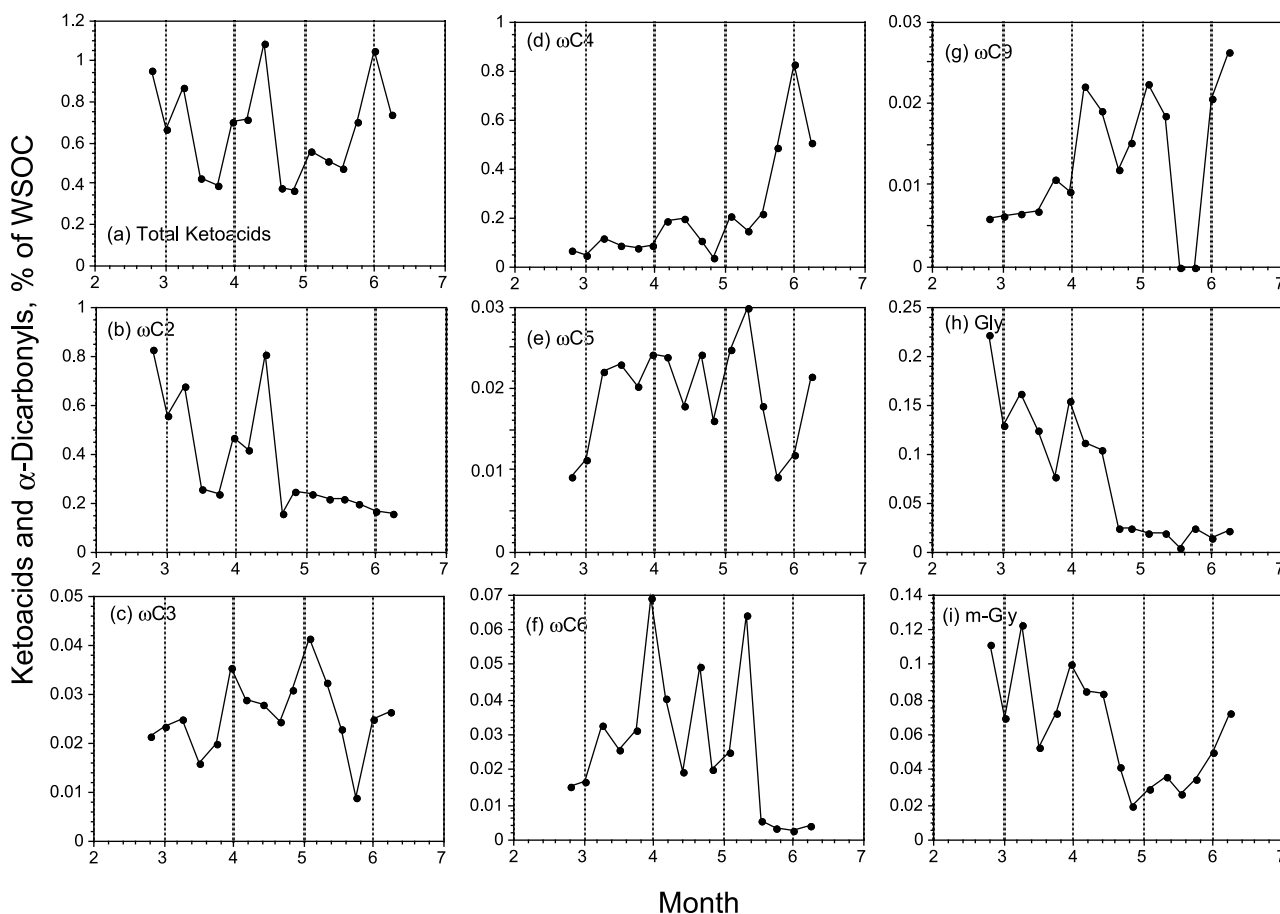


Figure 10. Seasonal variations in the contributions of ketoacids and α -dicarbonyls to water-soluble organic carbon (WSOC) in the Arctic aerosols from Alert: (a) total ketoacids, (b) glyoxylic acid (ωC_2), (c) 3-oxopropanoic acid (ωC_3), (d) 4-oxobutanoic acid (ωC_4), (e) 5-oxopentanoic acid (ωC_5), (f) 6-oxohexanoic acid (ωC_6), (g) 9-oxononanoic acid (ωC_9), (h) glyoxal (Gly), and (i) methylglyoxal (MeGly).

2005; Ieda *et al.*, 2006]. Interestingly, Fu *et al.* [2009b] reported an increased concentration of isoprene oxidation products such as 2-methyltetrols in the same Arctic aerosols in early June.

[35] Although the contributions of diacids, ketoacids and α -dicarbonyls to TC and WSOC are significant, major portion of WSOC is composed of unidentified organic species, which may include monocarboxylic acids, carbohydrates, amino acids, and humic-like polymers. Fu *et al.* [2009a] detected various organic compounds in the Arctic aerosols, which are derived from different sources including higher plant waxes, microbial/marine sources, biomass burning products, fossil fuel combustion, soil resuspension, plastics and secondary oxidation products. Based on FTIR spectroscopy of organic aerosols, Russell *et al.* [2010] suggest that majority of organics in Arctic marine regions are often carbohydrate-like materials emitted as primary particles during wave breaking.

4. Summary and Conclusions

[36] Water-soluble organic acids and α -dicarbonyls were measured in Arctic aerosol samples collected at Alert during

winter to early summer in 1991. Samples were also analyzed for total carbon (TC) and nitrogen (TN) as well as water-soluble organic carbon (WSOC). Dicarboxylic acids and ketoacids are major organic species that contribute significantly to WSOC (up to 13%) in particular at polar sunrise. The concentrations of diacids, as well as diacid-C/WSOC, increased at polar sunrise, demonstrating that water-soluble organic acids are photochemically produced in the Arctic atmosphere in spring. Detailed analyses of organic chemical composition also demonstrate that secondary production and loss of diacids and ketoacids occurs at and after polar sunrise, thus contributing to photochemical aging in the polar atmosphere. In particular, there was a significant depletion of oxalic acid in late April to early May right after polar sunrise. The molecular distributions with depletion of oxalic acid and a predominance of succinic acid are similar to those found in the Antarctic aerosol sample [Kawamura *et al.*, 1996b] and the ice core samples from Greenland [Kawamura *et al.*, 2001]. This suggests that oxalic acid can be selectively decomposed under strong solar radiation in the presence of Fe (III), although the degradation pathway is not fully understood at present. In the high Arctic during spring and summer, photochemical processes as well as biological

emissions from the ocean when sea ice melts largely control the molecular composition of water-soluble organic aerosols. Because of the recent global warming and subsequently enhanced retreat of sea ice in the Arctic Ocean, the influence of biological emissions from the ocean surface on the formation of primary and secondary organic aerosols in the Arctic should have been more significant during spring to early summer in the early 21st century compared to two decades ago.

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References

- Bahadur, R., T. Uplinger, L. M. Russell, B. C. Sive, S. S. Cliff, D. B. Millet, A. Goldstein, and T. S. Bates (2010), Phenol groups in northeastern U. S. submicrometer aerosol particles produced from seawater sources, *Environ. Sci. Technol.*, *44*, 2542–2548, doi:10.1021/es9032277.
- Barrie, L. A. (1986), Arctic air pollution: An overview of current knowledge, *Atmos. Environ.*, *20*, 643–663, doi:10.1016/0004-6981(86)90180-0.
- Barrie, L. A., and J. W. Bottenheim (1991), Sulphur and nitrogen pollution in the Arctic atmosphere, in *Pollution of the Arctic Atmosphere*, edited by W. T. Sturges, pp. 155–183, Elsevier, New York.
- Barrie, L. A., and R. M. Hoff (1985), Five years of air chemistry observations in the Canadian Arctic, *Atmos. Environ.*, *19*, 1995–2010, doi:10.1016/0004-6981(85)90108-8.
- Barrie, L. A., J. W. Bottenheim, R. C. Schnell, P. J. Crutzen, and R. J. Rasmussen (1988), Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic troposphere, *Nature*, *334*, 138–141, doi:10.1038/334138a0.
- Barrie, L. A., G. den Hartog, J. W. Bottenheim, and S. Landsberger (1989), Anthropogenic aerosols and gases in the lower troposphere at Alert Canada in April 1986, *J. Atmos. Chem.*, *9*, 101–127, doi:10.1007/BF00052827.
- Barrie, L. A., S.-M. Li, D. L. Toom, S. Landsberger, and W. Sturges (1994a), Lower tropospheric measurements of halogens, nitrates, and sulphur oxides during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, *99*, 25,453–25,467, doi:10.1029/94JD01533.
- Barrie, L. A., R. Staebler, D. Toom, B. Georgi, and G. den Hartog (1994b), Arctic aerosol size-segregated chemical observations in relation to ozone depletion during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, *99*, 25,439–25,451, doi:10.1029/94JD01514.
- Brasseur, G. P., J. J. Orlando, and G. S. Tyndall (1999), *Atmospheric Chemistry and Global Change*, 654 pp., Oxford Univ. Press, New York.
- Cachier, H., P. Buat-Ménard, and M. Frontugne (1985), Source terms and source strength of the carbonaceous aerosol in the tropics, *J. Atmos. Chem.*, *3*, 469–489, doi:10.1007/BF00053872.
- Cachier, H., P. Buat-Ménard, M. Fontugne, and R. Chesselet (1986), Long-range transport of continentally derived particulate carbon in the marine atmosphere: Evidence from stable carbon isotope studies, *Tellus, Ser. B*, *38*, 161–177, doi:10.1111/j.1600-0889.1986.tb00184.x.
- Carlson, D. J. (1982), Surface microlayer phenolic enrichments indicate sea surface slicks, *Nature*, *296*, 426–429, doi:10.1038/296426a0.
- Deguillaume, L., M. Leriche, K. Desboeufs, G. Mailhot, C. George, and N. Chaumerliac (2005), Transition metals in atmospheric liquid phases: Source, reactivity, and sensitive parameters, *Chem. Rev.*, *105*, 3388–3431, doi:10.1021/cr040649c.
- Fu, P., K. Kawamura, and L. A. Barrie (2009a), Photochemical and other sources of organic compounds in the Canadian high arctic aerosol pollution during winter-spring, *Environ. Sci. Technol.*, *43*, 286–292, doi:10.1021/es803046q.
- Fu, P., K. Kawamura, J. Chen, and L. A. Barrie (2009b), Isoprene, monoterpene, and sesquiterpene oxidation products in the High Arctic aerosols during late winter to early summer, *Environ. Sci. Technol.*, *43*, 4022–4028, doi:10.1021/es803669a.
- Hagler, G. S. W., M. H. Bergin, E. A. Smith, and J. E. Dibb (2007), A summer time series of particulate carbon in the air and snow at Summit, Greenland, *J. Geophys. Res.*, *112*, D21309, doi:10.1029/2007JD008993.
- Ho, K. F., J. J. Cao, S. C. Lee, K. Kawamura, R. J. Zhang, J. C. Chow, and J. G. Watson (2007), Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, *112*, D22S27, doi:10.1029/2006JD008011.
- Ieda, T., Y. Kitamori, M. Mochida, R. Hirata, T. Hirano, K. Inukai, Y. Fujinuma, and K. Kawamura (2006), Diurnal variations and vertical gradients of biogenic volatile and semi-volatile organic compounds at the Tomakomai larch forest station in Japan, *Tellus, Ser. B*, *58*, 177–186, doi:10.1111/j.1600-0889.2006.00179.x.
- Kawamura, K., and R. B. Gagosian (1987), Implications of ω -oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, *325*, 330–332, doi:10.1038/325330a0.
- Kawamura, K., and R. B. Gagosian (1990), Mid-chain ketocarboxylic acids in the remote marine atmosphere: Distribution patterns and possible formation mechanisms, *J. Atmos. Chem.*, *11*, 107–122, doi:10.1007/BF00053670.
- Kawamura, K., and K. Ikushima (1993), Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, *27*, 2227–2235, doi:10.1021/es00047a033.
- Kawamura, K., and F. Sakaguchi (1999), Molecular distribution of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, *104*, 3501–3509, doi:10.1029/1998JD100041.
- Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, *39*, 1945–1960, doi:10.1016/j.atmosenv.2004.12.014.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (1996a), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, *30*, 1709–1722, doi:10.1016/1352-2310(95)00395-9.
- Kawamura, K., R. Sempéré, Y. Imai, M. Hayashi, and Y. Fujii (1996b), Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols, *J. Geophys. Res.*, *101*, 18,721–18,728, doi:10.1029/96JD01541.
- Kawamura, K., K. Yokoyama, Y. Fujii, and O. Watanabe (2001), A Greenland ice core record of low molecular weight dicarboxylic acids, oxocarboxylic acids and a-dicarbonyls: A trend from Little Ice Age to the present (1540 to 1989 A.D.), *J. Geophys. Res.*, *106*, 1331–1345, doi:10.1029/2000JD900465.
- Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan, Geochem. Soc. Publ. Ser.*, vol. 9, edited by R. J. Hill et al., pp. 243–265, Elsevier, New York.
- Kawamura, K., Y. Imai, and L. A. Barrie (2005), Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events, *Atmos. Environ.*, *39*, 599–614, doi:10.1016/j.atmosenv.2004.10.020.
- Kerminen, V.-M., K. Teinilä, R. Hillamo, and T. Mäkelä (1999), Size-segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, *33*, 2089–2100, doi:10.1016/S1352-2310(98)00350-1.
- Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae (2010), Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil, *J. Aerosol Sci.*, *41*, 118–133, doi:10.1016/j.jaerosci.2009.08.006.
- Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, S. Kasper-Goebel, and P. Laj (2007), Origin of C₂–C₅ dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.*, *112*, D23S07, doi:10.1029/2006JD008019.
- Li, S.-M., Y. Yokouchi, L. A. Barrie, K. Muthuramu, P. B. Shepson, J. W. Bottenheim, W. T. Sturges, and S. Landsberger (1994), Organic and inorganic bromine compounds and their composition in the Arctic troposphere during polar sunrise, *J. Geophys. Res.*, *99*, 25,415–25,428, doi:10.1029/93JD03343.
- Libes, S. M. (1992), *An Introduction to Marine Biogeochemistry*, 734 pp., John Wiley, Hoboken, N. J.
- Lim, H. J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, *39*, 4441–4446, doi:10.1021/es048039h.

- Limbeck, A., H. Puxbaum, L. Otter, and M. C. Scholes (2001), Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, *35*, 1853–1862, doi:10.1016/S1352-2310(00)00497-0.
- Matsunaga, S., M. Mochida, and K. Kawamura (2004), Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan, *J. Geophys. Res.*, *109*, D04302, doi:10.1029/2003JD004100.
- McConnell, J. C., G. S. Henderson, L. Barrie, J. Bottenheim, H. Niki, C. H. Langford, and E. M. J. Templeton (1992), Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature*, *355*, 150–153, doi:10.1038/355150a0.
- Miyazaki, Y., K. Kawamura, and M. Sawano (2010), Size distributions of organic nitrogen and carbon in remote marine aerosols: Evidence of marine biological origin based on their isotopic ratios, *Geophys. Res. Lett.*, *37*, L06803, doi:10.1029/2010GL042483.
- Narukawa, M., K. Kawamura, K. G. Anlauf, and L. A. Barrie (2003a), Fine and coarse modes of dicarboxylic acids in the arctic aerosols collected during the Polar Sunrise Experiment 1997, *J. Geophys. Res.*, *108*(D18), 4575, doi:10.1029/2003JD003646.
- Narukawa, M., K. Kawamura, H. Hatsushika, K. Yamazaki, S.-M. Li, J. W. Bottenheim, and K. G. Anlauf (2003b), Measurement of halogenated dicarboxylic acids in the spring arctic aerosols, *J. Atmos. Chem.*, *44*, 323–335, doi:10.1023/A:1022948103518.
- Narukawa, M., K. Kawamura, S.-M. Li, and J. W. Bottenheim (2008), Stable carbon isotopic composition of the high Arctic aerosols: An increase in $\delta^{13}\text{C}$ values from winter to spring, *J. Geophys. Res.*, *113*, D02312, doi:10.1029/2007JD008755.
- Norman, A. L., L. A. Barrie, D. Toom-Saunty, A. Sirois, H. R. Krouse, S. M. Li, and S. Sharma (1999), Sources of aerosol sulphate at Alert: Apportionment using stable isotopes, *J. Geophys. Res.*, *104*, 11,619–11,631, doi:10.1029/1999JD900078.
- Pavuluri, C. M., K. Kawamura, and T. Swaminathan (2010), Water-soluble organic carbon, dicarboxylic acids, ketoacids and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.*, *115*, D11302, doi:10.1029/2009JD012661.
- Quinn, P. K., T. S. Bates, K. Schulz, and G. E. Shaw (2009), Decadal trends in aerosol chemical composition at Barrow, Alaska: 1976–2008, *Atmos. Chem. Phys.*, *9*, 8883–8888, doi:10.5194/acp-9-8883-2009.
- Ruellan, S., H. Cachier, A. Gaudichet, P. Masclat, and J. P. Lacaux (1999), Airborne aerosols over central Africa during the Experiment for regional sources and sinks of oxidants (EXPRESSO), *J. Geophys. Res.*, *104*, 30,673–30,690, doi:10.1029/1999JD900804.
- Russell, L. M., L. N. Hawkins, A. A. Frossard, P. K. Quinn, and T. S. Bates (2010), Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, *Proc. Natl. Acad. Sci. U. S. A.*, *107*, 6652–6657, doi:10.1073/pnas.0908905107.
- Sakaguchi, F., and K. Kawamura (1994), Identification of 4-oxoheptanedioic acid in the marine atmosphere by a capillary gas chromatography-mass spectrometry, *J. Chromatogr. A*, *687*, 315–321, doi:10.1016/0021-9673(94)00925-2.
- Sempéré, R., and K. Kawamura (1994), Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, *Atmos. Environ.*, *28*, 449–459, doi:10.1016/1352-2310(94)90123-6.
- Sempéré, R., and K. Kawamura (2003), Trans-hemispheric contribution of $\text{C}_2\text{--C}_{10}$ α , ω -dicarboxylic acids and related polar compounds to water soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cycles*, *17*(2), 1069, doi:10.1029/2002GB001980.
- Shaw, P. M., L. M. Russell, A. Jefferson, and P. K. Quinn (2010), Arctic organic aerosol measurements show particles from mixed combustion in spring haze and from frost flowers in winter, *Geophys. Res. Lett.*, *37*, L10803, doi:10.1029/2010GL042831.
- Sirois, A., and L. A. Barrie (1999), Arctic lower tropospheric aerosol trends and composition at Alert, Canada: 1980–1995, *J. Geophys. Res.*, *104*, 11,599–11,618, doi:10.1029/1999JD900077.
- Stephanou, E. G., and N. Stratigakis (1993), Oxocarboxylic and α , ω -dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols, *Environ. Sci. Technol.*, *27*, 1403–1407, doi:10.1021/es00044a016.
- Suzuki, K., K. Kawamura, H. Kasukabe, A. Yanase, and L. A. Barrie (1995), Concentration changes of MSA and major ions in arctic aerosols during polar sunrise, *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, *9*, 163–171.
- Uematsu, M., K. Kawamura, T. Ibusuki, and T. Kimoto (1995), Chemical composition of marine aerosols over the central North Pacific, in *Biogeochemical Processes of Ocean Flux in the Western Pacific*, edited by H. Sakai and Y. Nozaki, pp. 3–14, Terra Sci., Tokyo.
- Wang, G. H., and K. Kawamura (2005), Molecular characteristics of urban organic aerosols from Nanjing: A case study of a mega-city in China, *Environ. Sci. Technol.*, *39*, 7430–7438, doi:10.1021/es051055+.
- Wang, H., and D. Shooter (2004), Low molecular weight dicarboxylic acids in PM_{10} in a city with intensive solid fuel burning, *Chemosphere*, *56*, 725–733, doi:10.1016/j.chemosphere.2004.04.030.
- Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, *37*, 2423–2427, doi:10.1016/S1352-2310(03)00136-5.
- Yao, X., M. Fang, C. K. Chan, K. F. Ho, and S. C. Lee (2004), Characterization of dicarboxylic acids in $\text{PM}_{2.5}$ in Hong Kong, *Atmos. Environ.*, *38*, 963–970, doi:10.1016/j.atmosenv.2003.10.048.
- Yokouchi, Y., and Y. Ambe (1986), Characterization of polar organics in airborne particulate matter, *Atmos. Environ.*, *20*, 1727–1734, doi:10.1016/0004-6981(86)90121-6.
- Zuo, U., and J. Hoigné (1992), Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes, *Environ. Sci. Technol.*, *26*, 1014–1022, doi:10.1021/es00029a022.

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