Composition and Photochemical Transformation of Organic Aerosols from the Arctic

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ABSTRACT
Pollutants emitted to the atmosphere from the northern hemisphere mainly the Eurasian and North American continents are transported long distances over the Arctic. Their transport is maximized in winter. In late March after the dark winter, sun light comes back to the Arctic and induces photochemical reactions of organic and inorganic chemicals. The combination of atmospheric transport of the pollutants and photochemical reactions is known to cause so-called arctic haze. Continuous irradiation of sun light at and after polar sunrise under relatively stable atmospheric conditions in the Arctic provides a natural laboratory for the studies of photochemical processes. However, previous studies on arctic aerosols have been conducted for inorganic species such as sulfate, nitrate and metals, and have rarely focused on organic aerosols. Ten years ago, we started organic chemical analyses of arctic aerosols at molecular levels. Here, I review recent progress in the organic geochemistry of arctic aerosols with a focus on photochemical production of water soluble dicarboxylic acids and photochemical degradation of polynuclear aromatic hydrocarbons.

Key words : organic aerosols, dicarboxylic acids, photochemical transformation, arctic, polynuclear aromatic hydrocarbons

1. INTRODUCTION

Atmospheric particles play an important role in the global radiation balance because they directly reflect sun light back to space and/or adsorb solar energy. Hence, they may potentially have a cooling or warming effect on the earth's climate. Evaluation of their effect on climate forcing is an important issue of global environment science. However, the indirect effect of aerosols on radiation through cloud formation is poorly understood and the uncertainty in the estimation is large (IPCC, 1996), because characterization of aerosols has been insufficient : their effect depends significantly on chemical composition. Chemical characterization of inorganic species in tropospheric aerosols has often been studied on regional and global scales. In contrast, organic aerosols have rarely been studied in remote sites, even though organic compounds are ubiquitous in the atmosphere and play an important role in the atmospheric chemistry of aerosols. Recently, organic aerosols have received much attention because they have been recognized as important cloud condensation nuclei (Novakov and Penner, 1993).

Polar regions have been recognized important in the study of global climate change since the discovery of the stratospheric ozone hole over Antarctica. Antarctica is surrounded by southern oceans and its tropospheric chemistry is less affected by human activity. In contrast, the Arctic is surrounded by the Eurasian and North American continents and anthropogenic chemicals are transported long distances from the mid-latitudes over the Arctic (Barrie, 1986). Due to the cold temperatures in December to February, low-to-high latitudinal transport of air masses containing both gases and particles emitted from anthropogenic sources is maximized in the arctic winter (Barrie, 1986). Some of them are photochemically oxidized during transport in the atmosphere, in which a gas-to-particle conversion of sulfur dioxide and volatile hydrocarbons is important. These particles are the source of arctic haze, which peaks in late March to early April when the polar sunrise occurs (Barrie and Barrie, 1990). The major component of arctic haze is sulfate which is in situ produced in the arctic atmosphere by photochemical oxidation of SO_2.

In the course of organic geochemical study of arctic aerosols, we detected a homologous series of low molecular weight dicarboxylic acids and related polar compounds, as well as hydrocarbons, fatty acids, and other lipid class compounds. During polar sunrise from late March to early April, oxalic acid and other small dicarboxylic acids greatly increased in the arctic atmosphere (Kawamura et al., 1995a, 1995b, 1996a) while polynuclear aromatic hydrocarbons decreased at polar sunrise and afterwards (Yanase et al., 1995). With a detailed molecular analysis of the aerosols, we are able to get an insight into photochemical chain reactions occurring in the arctic atmosphere. This paper reviews progress of recent studies on photochemical production and transformation of organic aerosols in the Arctic.
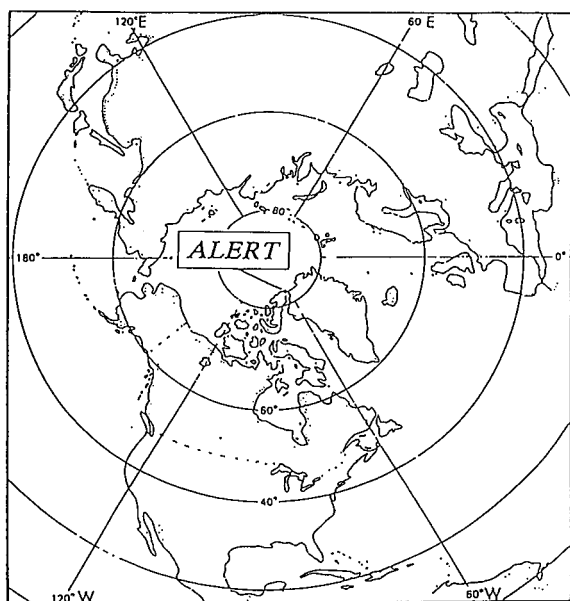
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Fig. 1 Sampling location (Alert) and map of the Arctic.

butanol to derive dibutyl esters for dicarboxylic acids and dibutoxy acetal butyl esters for ω-oxocarboxylic acids. Dicarbonyls were also derivatized to dibutoxy acetals. These derivatives were determined using capillary gas chromatography(GC) and GC/MS (Kawamura and Ikushima, 1993 ; Kawamura, 1993). Lipid class compounds were also extracted from the quartz filters with organic solvents and divided, using silica gel column chromatography, into compounds classes(aliphatic hydrocarbons, aromatic hydrocarbons, ketones, alcohols, fatty acids, etc.). The lipid class compounds were determined with a capillary GC and GC/MS(Kawamura, 1995).

To determine total carbon and nitrogen contents, aerosol samples were subjected to an elemental analyzer. Water soluble organic carbon was also determined using a carbon analyzer employing a high temperature combustion technique after extracting the filters with pure water(Sempere and Kawamura, 1994).

Details of analytical procedures are described in the literature cited above.

2. SAMPLE COLLECTION OF ARCTIC AEROSOLS AND ANALYTICAL METHODS

The arctic aerosol samples were collected with a high volume air sampler at Alert on Ellesmere Is., Canadian Arctic(82.5° N, 62.3° N, see Fig.1)using cellulose or quartz fiber filters(Barrie, 1986). For the measurement of water soluble organic compounds, filters were extracted with organic-free pure water and the water extracts were concentrated to nearly dryness. The extracts were reacted with BF_3 in n-

3. AEROSOL MASS CONCENTRATION, TOTAL CARBON, TOTAL NITROGEN, AND WATER SOLUBLE ORGANIC CARBON

Table 1 summarizes the results of the arctic aerosol samples collected in February to June, 1991 (Kawamura et al., 1995a). Aerosol mass concentrations generally decreased from winter to summer, however, they increased in late March to early April. The increase may involve photochemical production of sulfuric acid and organic aerosols during polar sunrise. The relative abundance of sulfate in the

Table 1 Concentrations of aerosol total Carbon(TC), total nitrogen(TN), water soluble organic carbon (WSOC), and dicarboxylic acids, and α-dicarbonyls in the atmosphere of the Canadian Arctic, Alert, from February to June, 1991.

Components	Conc. Range	Mean Conc.
Aerosols	2.5 - 9.1 μgm^{-3}	5.2 μgm^{-3}
Total Carbon (TC)	88 - 639 ngm^{-3}	359 μgm^{-3}
Total Nitrognen (TN)	16 -154 ngm^{-3}	86 μgm^{-3}
C/N Weight Ratio	2.4 - 7.1	4.5
TC/Aero.	2.4 - 11.1 %	6.8%
TN/Aero.	0.48 - 2.4 %	1.6%
Water Soluble Organic Carbon (WSOC)	40.7 - 300 ngm^{-3}	186 μgm^{-3}
WSOC/TC	30 - 72 %	53%
WSOC/Aero.	1.2 - 5.5 %	3.4%
Diacids (C_2-C_{11})	7.4 - 84.5 ngm^{-3}	36.6 μgm^{-3}
Ketoacids (C_2-C_6)	0.76 - 8.9 ngm^{-3}	3.7 μgm^{-3}
α-Dicarbonyls (C_2-C_3)	0.05 - 2.8 ngm^{-3}	0.88 μgm^{-3}
Diacid-C/TC	1.5 -9.1 %	3.8%
Ketoacid-C/TC	0.18 - 0.78 %	0.34%
α-Dicarbonyl-C/TC	0.019 - 0.17 %	0.073%

aerosol mass was high(5-36%) in the arctic samples and maximized in late March to early April (Suzuki *et al.*, 1995). Concentrations of total carbon (TC) and nitrogen (TN) were 88-639 ngm^{-3} and 16-154 ngm^{-3}, respectively. Their relative abundances in the aerosol mass were 2-11% (av. 6.8%) and 0.5-2.4% (av. 1.6%), respectively. TC and TN concentrations are roughly two orders of magnitudes lower than those of urban Tokyo aerosols (Kawamura and Ikushima, 1993).

Concentrations of water soluble organic carbon (WSOC) ranged from 41 ngm^{-3} to 300 ngm^{-3}. The WSOC concentrations are 10 to 500 times lower than those reported from Tokyo (Sempere and Kawamura, 1994). WSOC comprises 1.2-5.5% of total aerosol mass in the Arctic. Although aerosol mass concentrations decreased toward the summer, WSOC increased in the period of polar sunrise. WSOC is composed of water soluble monocarboxylic acids, dicarboxylic acids, ketocarboxylic acids and aldehydes, as well as unidentified organic compounds including carbohydrates, amino acids, humic acids, etc. Interestingly, relative abundances of WSOC in TC were high (30-72 %) and maximized in April to May.

On the other hand, concentrations of total diacids (C_2-C_{10}) were in a range of 7-85ngm^{-3}, which comprises 0.2-1.4% of aerosol mass and is much less than that of sulfate. The diacid concentrations in the arctic aerosols are roughly 10 times lower than those of Tokyo aerosols (Kawamura and Ikushima, 1993). They were found to account for 1.5-9.1% of aerosol carbon and 3-13 % of water soluble organic carbon. It is important to note that the relative abundance of the diacids in TC was much higher than those (0.06-4.6%) reported from Tokyo aerosols (Kawamura and Ikushima, 1993 ; Sempere and Kawamura, 1994). These values increased from March to April, suggesting that the organic aerosols produced during polar sunrise are water soluble and rich in carboxyl groups. Interestingly, the diacid concentrations largely increased from winter to spring and maximized at polar sunrise (April). The increase is caused by photochemical production of diacids, a point to be discussed later.

4. SEASONAL DISTIBUTIONS OF WATER SOLUBLE ORGANIC COMPOUNDS

Figure 2 shows a gas chromatogram of dicarboxylic acids and related polar compounds isolated from the Arctic aerosol sample. Three types of organic compounds were detected in the water soluble fraction of the aerosols : (1) an homologous series of dicarboxylic acids including aliphatic α,ω-dicarboxylic acids (C_2-C_{11}) and aromatic (phthalic) acid, (2) ketocarboxylic acids including ω-oxocarboxylic acids (C_2-C_9) and pyruvic acid, (3) α-dicarbonyls (glyoxal and methylglyoxal). Figure 3 gives chemical structures for these polar organic compounds.

4.1. Molecular distributions of low molecular weight carboxylic acids

Throughout the samples studied, oxalic acid (C_2) was found to be the most abundant diacid species. The second most abundant diacids were malonic (C_3) and succinic (C_4) acid. The C_2-C_4 diacids accounted for more than 80% of total diacids (4.3-97 ngm^{-3}) in the arctic aerosols studied. Longer chain normal diacids were less abundant and their concentrations generally decreased with increasing carbon number. The exception was the C_9 diacid which was more abundant than the C_8 species. Branched chain saturated dicarboxylic acids were also detected in the Alert aerosols, including methylmalonic (iC_4), methylsuccinic (iC_5) and 2-methylglutaric (iC_6) acids. They were less abundant than corresponding straight-chain dicarboxylic acids. In addition to saturated α, ω-dicarboxylic acids, unsaturated diacids were detected in arctic aerosols, including maleic, fumaric and methylmaleic acids. The abundance of unsaturated diacids was lower than that of corresponding saturated species, although maleic acid was relatively abundant in winter samples. Aromatic acid (phthalic) was detected as the fourth most abundant dicarboxylic acid.

α, ω-Dicarboxylic acids with an additional functional group were also detected in the arctic aerosols. They included ketomalonic acid (kC_3), 4-oxopimelic
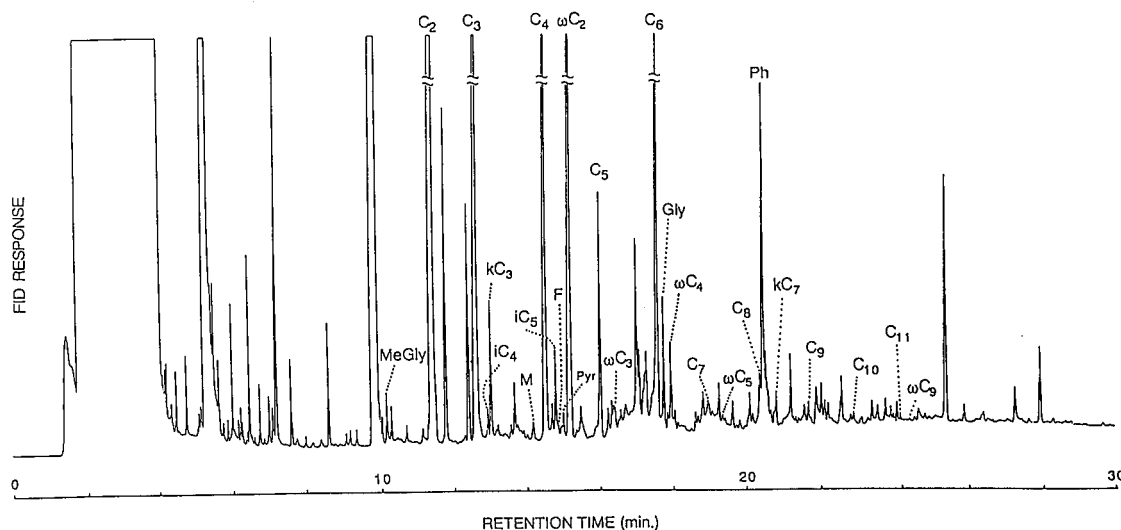

Fig. 2 Capillary gas chromatogram of dicarboxylic acid dibutyl esters and related polar compounds isolated from the arctic aerosol sample (April 4-11, 1988).
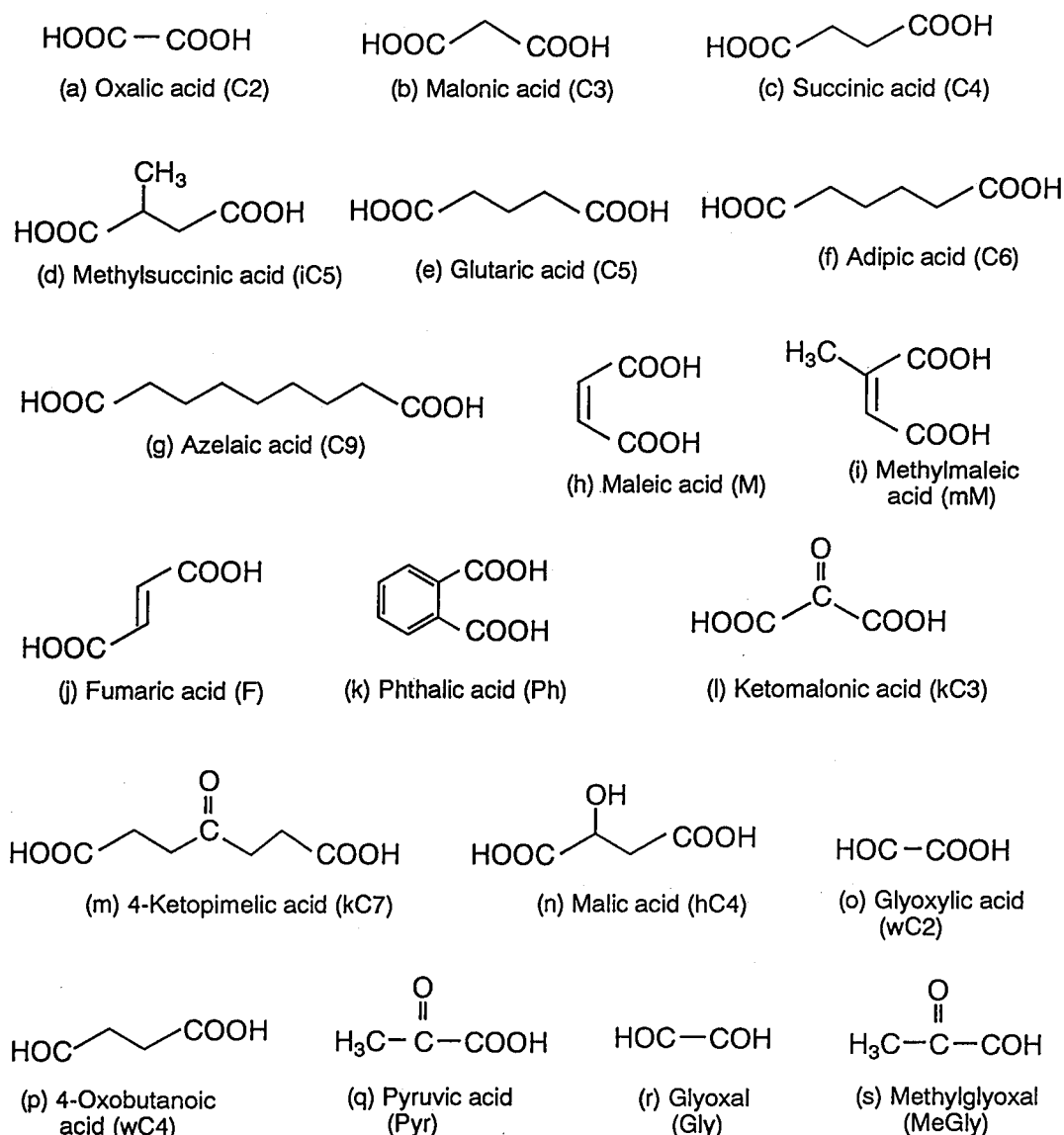
HOOC — COOH

(a) Oxalic acid (C2)

HOOC COOH

(b) Malonic acid (C3)

HOOC COOH

(c) Succinic acid (C4)

CH_3

HOOC COOH

(d) Methylsuccinic acid (iC5)

HOOC COOH

(e) Glutaric acid (C5)

HOOC COOH

(f) Adipic acid (C6)

HOOC COOH

(g) Azelaic acid (C9)

COOH
COOH

(h) Maleic acid (M)

H_3C COOH
COOH

(i) Methylmaleic acid (mM)

COOH
HOOC

(j) Fumaric acid (F)

COOH
COOH

(k) Phthalic acid (Ph)

O
‖
C
HOOC COOH

(l) Ketomalonic acid (kC3)

O
‖
C
HOOC COOH

(m) 4-Ketopimelic acid (kC7)

OH
HOOC COOH

(n) Malic acid (hC4)

HOC — COOH

(o) Glyoxylic acid (wC2)

HOC COOH

(p) 4-Oxobutanoic acid (wC4)

O
‖
H_3C— C—COOH

(q) Pyruvic acid (Pyr)

HOC — COH

(r) Glyoxal (Gly)

O
‖
H_3C—C—COH

(s) Methylglyoxal (MeGly)

Fig. 3   Chemical structures of dicarboxylic acids (a-n), ketoacids (o-q) and α-dicarbonyls (r-s) detected in the Alert aerosols.

acid (kC$_7$) and hydroxysuccinic (malic) acid (hC$_4$). However, these tri-functional compounds were found to be relatively minor components compared to bifunctional C$_2$-C$_4$ diacids.

Low molecular weight dicarboxylic acids, with oxalic acid being tpredominant, have been reported in aerosols collected in urban Los Angeles (Kawamura and Kaplan, 1987) and in Tokyo (Kawamura and Ikushima, 1993 ; Sempere and Kawamura, 1994). The predominance of oxalic acid was also recognized in the molecular distribution of diacids in remote marine aerosols from the North Pacific (Kawamura and Usukura, 1993). Oxalic acid has been detected in Alaskan aerosol samples by Li and Winchester (1993), using ion chromatography.

The atmospheric chemical sources and sinks of dicarboxylic acids are not quantitatively well known. However, there is a growing body of knowledge that allows a qualitative picture to be painted, as illustrated in Fig 4. Laboratory experiments have shown that they are produced in ozone and cycloalkene reactions (Hatakeyama et al., 1987). In addition evi-

dence suggests that they are produced in the atmosphere as a result of secondary photochemical reactions of anthropogenic aromatic hydrocarbons such as benzene and toluene and their oxidation intermediates
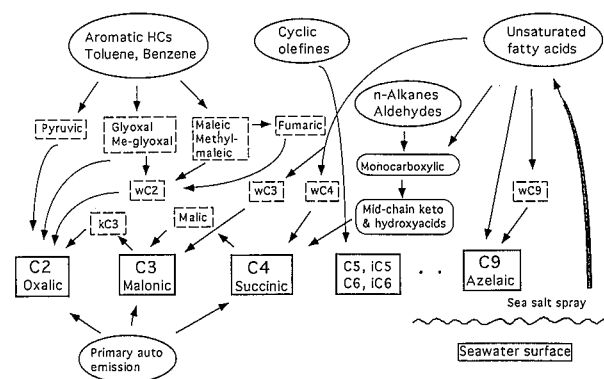
Fig. 4   Possible photochemical production of oxalic (C$_2$), malonic (C$_3$), succinic (C$_4$) and azelaic (C$_4$) acids in the atmosphere (Kawamura et al., 1996 a). For abbreviations and chemical structures, see Fig. 3.

such as glyoxal and methylglyoxal(Norton *et al.*, 1983 ; Kawamura and Ikushima, 1993). The abundant presence of cis configuration(maleic acid and methylmaleic acid)in the urban atmosphere supports the theory of oxidation of these aromatic hydrocarbons as precursors of oxalic acid. In automobile exhaust, oxalic acid was predominant followed by succinic acid and, to a lesser extent, malonic acid(Kawamura and Kaplan, 1987).

In contrast, malonic acid which is hard to produce by the oxidation of aromatic structures having conjugated double bonds, is more likely to be produced by the photochemical oxidation of succinic acid with malic acid as an intermediate(Kawamura and Ikushima, 1993). In turn succinic acid and longer chain diacids are likely oxidation products of gaseous aliphatic monocarboxylic acids, which are in part produced by photo-induced oxidation of biogenic unsaturated fatty acids(Kawamura and Gagosian, 1987)and other precursors such as n-alkanes, aldehydes and mid-chain ketocarboxylic acids(see Fig. 4). A one year observational study of low molecular weight dicarboxylic acids in urban aerosols of Tokyo suggested that photochemical reactions which peak in summer result in production of LMW diacids and contribute more to the particulate diacids in summer than direct emissions from anthropogenic and natural sources(Kawamura and Ikushima, 1993).

4.2. Molecular distributions of aldehydic acids, ketoacids and dicarbonyls

A homologous series of aldehydic acids were detected in the range of C_2-C_{10} in arctic aerosols. Interestingly, glyoxylic acid (ωC_2), the smallest ω-oxoacid, was generally the most abundant species in winter to spring. In contrast, ω-oxobutanoic acid (ωC_4)overwhelmed ωC_2 in the summer aerosols, although the concentrations were lower than in other seasons. Total concentrations of ω-oxoacids(ωC_2 to ωC_5 andωC_9)ranged from 0.18 ngm^{-3} to 10.8 ngm^{-3} and greatly fluctuated with seasons. Their concentrations (av. 2.2 ngm^{-3}) were lower than those of α,ω-dicarboxylic acids(av. 25 ngm^{-3}) throughout the four seasons. The ketoacid, pyruvic acid, was also detected in the aerosols. However, concentrations (av. 0.13 ngm^{-3})were much lower than those of glyoxylic acid (ωC_2, av. 1.7 ngm^{-3}).

The predominance of glyoxylic acid in the ω-oxocarboxylic acids has been reported in urban atmospheres(Kawamura, 1993). Glyoxylic acid may be produced by atmospheric oxidation of glyoxal (Kawamura, 1993). Pyruvic acid was also reported in urban aerosols and rainwaters(Kawamura, 1993 ; Sempere and Kawamura, 1994), remote continental rain and aerosols from the Amazon(Talbot *et al.*, 1990)and remote marine atmospheres(Kawamura and Usukura, 1993 ; Zhou and Mopper, 1990). These ketoacids may be intermediate in the photochemical oxidation of anthropogenic and natural organic compounds to the production of oxalic acid.

α-Dicarbonyls such as glyoxal and methylglyoxal were detected in Alert aerosols. Glyoxal atmospheric concentrations were highest in the winter to spring.

Dicarbonyls were detected at much lower concentrations <0.003 to 2.66 ngm^{-3} than dicarboxylic acids(4.3-97 ngm^{-3})and ω-oxocarboxylic acids(0.18-10.8 ngm^{-3}). This is likely because dicarbonyls are largely present in the gas phase.

α-Dicarbonyls have been reported in urban (Kawamura, 1993)and marine atmospheres(Zhou and Mopper, 1990). Laboratory studies show that glyoxal and methylglyoxal are produced as photochemical oxidation products of aromatic hydrocarbons such as benzene and toluene(Bandow and Washida, 1985 ; Bandow *et al.*, 1985).

4.3. Seasonal variations and photochemical production of water soluble organic species

One year of observations of arctic aerosols showed strong variations in concentrations. Figure 5 presents overall seasonal variations in total concentrations of dicarboxylic acids, ω-oxocarboxylic acids, and α-dicarbonyls in arctic aerosol samples collected in 1987
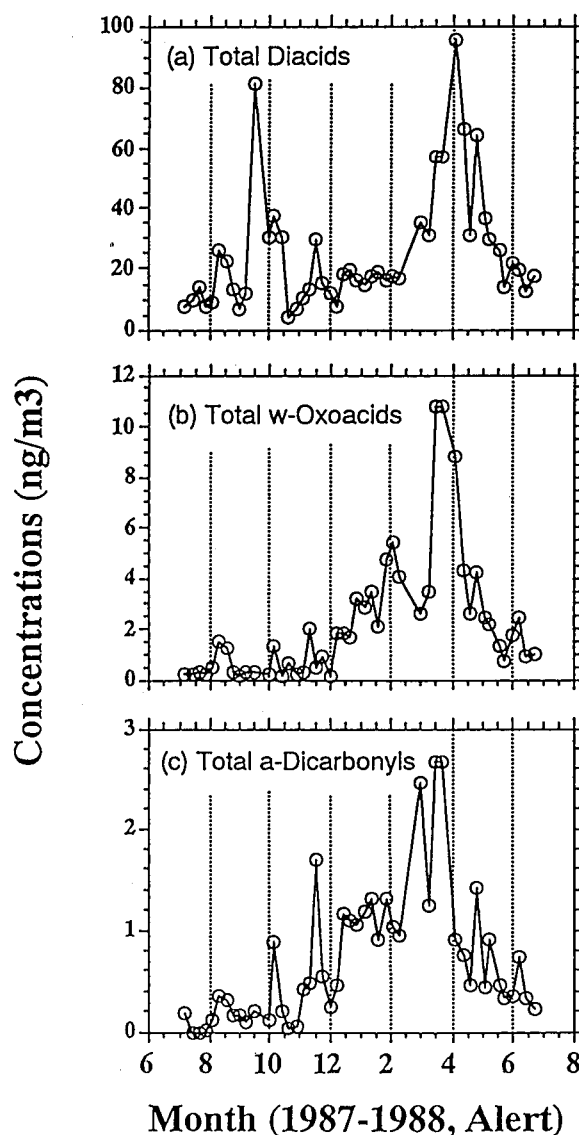
Fig. 5 Seasonal variations of total concentrations of (a) dicarboxylic acids (C_2-C_{11}), (b) ω-oxocarboxylic acids (C_2-C_5, C_9), and (c) α-dicarbonyls (C_2-C_3) in the Alert aerosols, 1987-1988 (Kawamura et al., 1996 a). Aldehydic acids are included in ω-oxocarboxylic acids.

-1988. Total dicarboxylic acids showed two major peaks, one in autumn and one in spring. In contrast, concentrations of ω-oxoacids and α-dicarbonyls showed a maximum in the spring and no significant peaks in autumn. However, individual species fluctuated in a different manner, as follows.

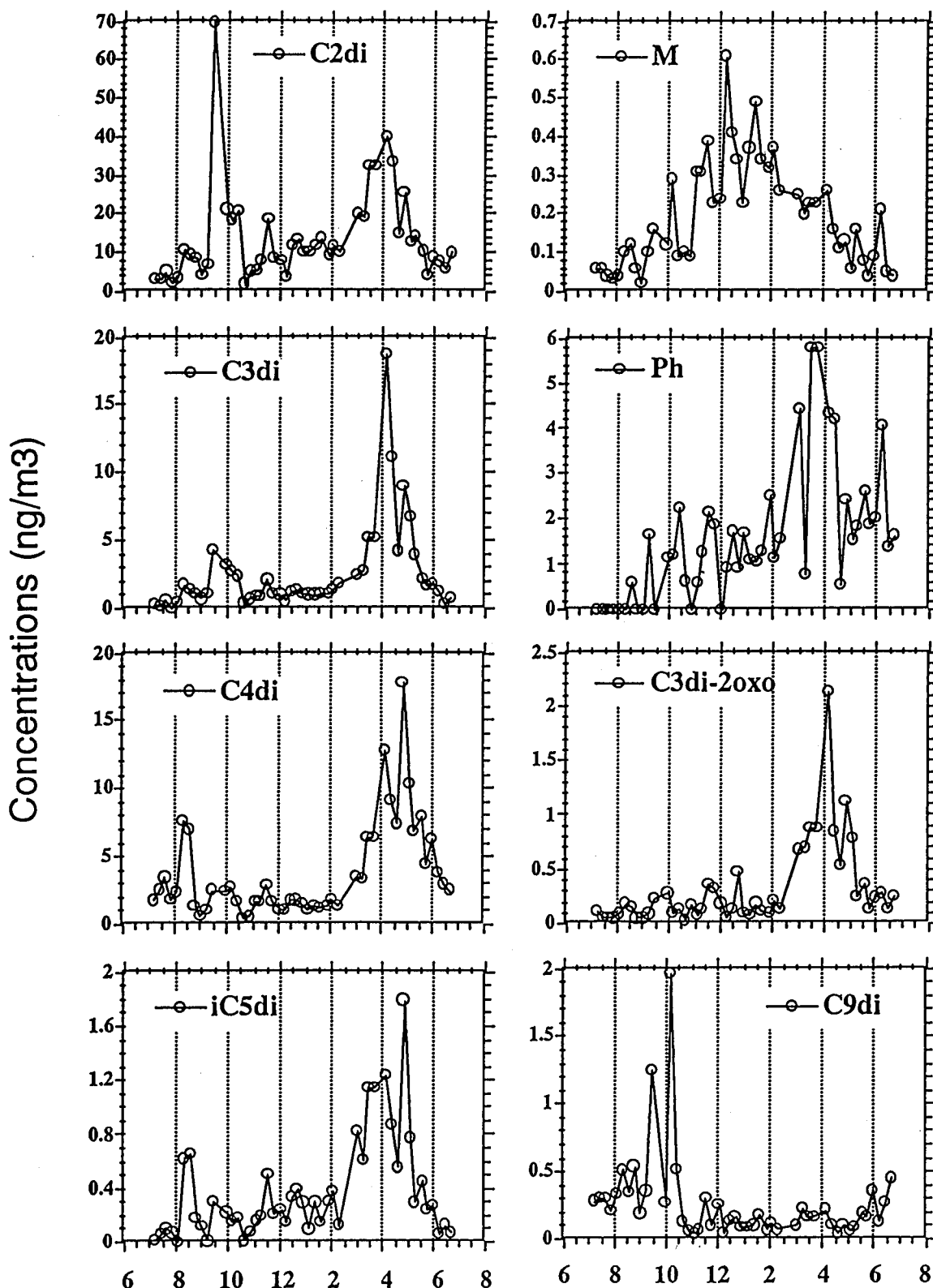Figure 6 gives seasonal variations of individual α, ω-dicarboxylic acids. The most abundant diacid (oxalic

Fig. 6 Seasonal distribution of individual normal saturated α, ω-dicarboxylic acid in the arctic aerosol samples collected from Alert, 1987-1988. For abbreviations, see Fig. 3.

acid) showed two major peaks in September to October and March to April. The highest concentration (ca. 70 ngm^{-3}) was obtained in the aerosol sample collected September 14-21, 1987. In late October to January, concentrations stayed at rather low levels with relatively small fluctuation (2-20 ngm^{-3}). The concentration of oxalic acid started to increase significantly in March and peaked in early April. The C_2 concentration at the April peak was ca. 3 times more abundant than that of the preceding dark winter months. The April peak of oxalic acid appeared at the time of arctic sunrise, suggesting that oxalic acid is significantly produced in the arctic atmosphere by photo-induced reactions. During arctic sunrise, much chemical activity involving Cl and Br atoms reacting with hydrocarbons takes place (Barrie et al., 1994b ; Jobson et al., 1994), resulting in oxidants such as ozone, hydrogen peroxide and hydroxyl radicals. The oxidants may react with various organic compounds which are transported and accumulated in the Arctic during the dark winter to produce oxalic acid. After the spring peak, the oxalic acid concentration decreased in the summer to a level similar to that observed in the winter months. Lower concentrations in the summer are due to scavenging of particulate diacids by more frequently occurring precipitation, coupled with weakened transport of polluted air parcels from mid-latitudes (Barrie, 1986).

Similar seasonal variations were observed for C_3-C_5 α,ω - dicarboxylic acids (Figure 6), except that autumn peaks were relatively weaker and amplitudes of the spring peaks were larger (10 to 20 times) than that of oxalic acid (3 times). Their concentrations started to increase at the beginning of March, peaked in April and returned to background levels in late June. These results again suggest in situ photochemical production of these diacids in the arctic atmosphere. However, the peak shapes are slightly different from each other. Thus C_3 and C_5 diacids showed maxima in the April 4-11 sample whereas C_4 diacid peaked three weeks later. Such a variation may be associated with different source inputs and/or different production mechanisms. C_6 diacid showed a seasonal distribution similar to that of C_3-C_5 diacids, but, the amplitude of the April peak was much greater than that of C_3-C_5 acids (Figure 6). Seasonal variation of branched chain dicarboxylic acids (iso C_4-C_6) was similar to that of straight chain C_3-C_5 diacids.

Maleic (cis configuration) acid showed a unique seasonal distribution pattern with a maximum in winter, being different from those of saturated diacids (see Fig. 6). Its concentration began to increase between summer and autumn and peaked in December. During the dark winter, it remained high and then began steadily to decrease in February to a summer minimum. Such a distribution suggests that maleic acid is not produced in situ in the arctic atmosphere, but rather, is transported from mid-latitudes where it is produced by atmospheric photochemical oxidation of aromatic hydrocarbons. High concentrations of maleic acid have been measured in the urban atmosphere of Tokyo (Kawamura and Ikushima, 1993). In

contrast, fumaric acid, the trans positional isomer of maleic acid, showed a distribution pattern different from the cis configuration. It was highest in summer and lowest in the winter season. In addition a secondary spring maximum was apparent. This acid may be produced in situ by photochemically induced isomerization of maleic acid in the Arctic during arctic sunrise and afterwards. The summer peak of fumaric acid suggests the presence of a non-anthropogenic precursor.

Oxomalonic acid, which was detected as the predominant ketodicarboxylic acid in the Alert aerosol samples, showed a concentration maximum in the early spring. Its seasonal variation is almost the same as that of malonic acid, but its concentration is much lower. Their carbon skeletons are the same (see Fig. 3). This parallel seasonal distribution and chemical consideration suggest that ketomalonic acid is likely produced by atmospheric oxidation of malonic acid. 4-Oxopimelic acid also gave an April maximum, but, its concentration was also high during summer. A parallel distribution was not recognized between the seasonal variations of 4-oxopimelic acid (kC$_7$) and pimelic acid (C$_7$).

This production route of dicarboxylic acids is further supported by the following evidence (Kawamura et al., 1995). First, there is a strong linear correlation with particulate Br and certain lower carbon number dicarboxylic acid end-products and precursors (Fig. 7). The correlation coefficient (r) for the period (February to June, n=16) when the Arctic is most polluted by transport from mid-latitudinal sources was as follows : methylsuccinic (0.91), methylmalonic (0.89),
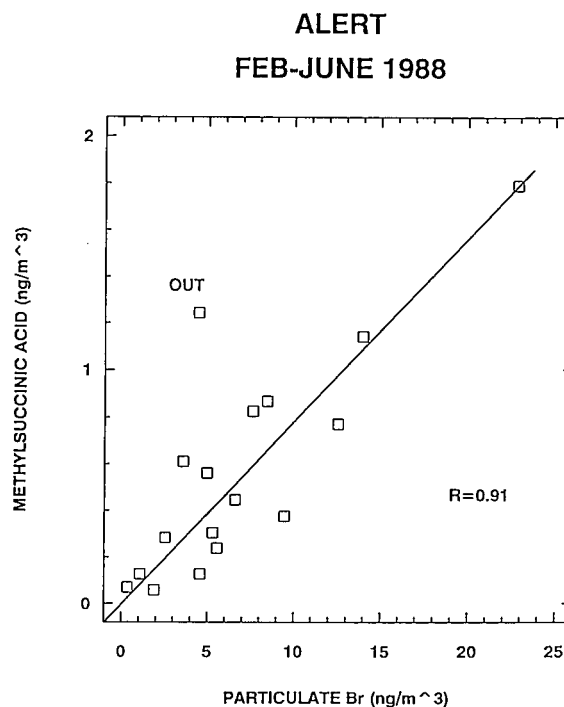
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Fig. 7 The relationship between concentrations (ngm^{-3}) of methylsuccinic acid and particulate Br in the arctic tropospheric aerosol at Alert (February to June, 1988). "Out" represents an outlier not included in the regression (Kawamura et al., 1995 b).

ketomalonic (0.77), succinic (0.77), glutaric (0.71), malonic (0.70), and oxalic (0.61). No significant correlation was observed for any of the other diacids detected. At polar sunrise, particulate Br is associated with depletion of ozone in the Arctic boundary layer (Barrie *et al.*, 1988, 1994) as well as depletion of non-methane hydrocarbons (Jobson *et al.*, 1994), trichloroethylene (Yokouchi *et al.*, 1994) and the production of acetone (Yokouchi *et al.*, 1994) and formaldehyde (de Serves, 1994). Cl and Br atoms play an important role in this chemistry occurring at a relatively low solar zenith angle (Jobson *et al.*, 1994). Fumaric acid showed a significant non-linear correlation with particulate Br similar to that of particulate I reported by Barrie *et al.* (1994). When fumaric acid is plotted against particulate iodine, a significant linear correlation (r = 0.69) appears. Although the case of this linearity is not well understood at this time, production of fumaric acid, iodine and bromine aerosols may be linked by common photochemistry in the ozone depleted arctic atmospheric boundary layer at polar sunrise.

Second, in situ arctic production of diacids is supported by selective enrichment of malonic acid (C3) in the dicarboxylic acid mixture at polar sunrise.
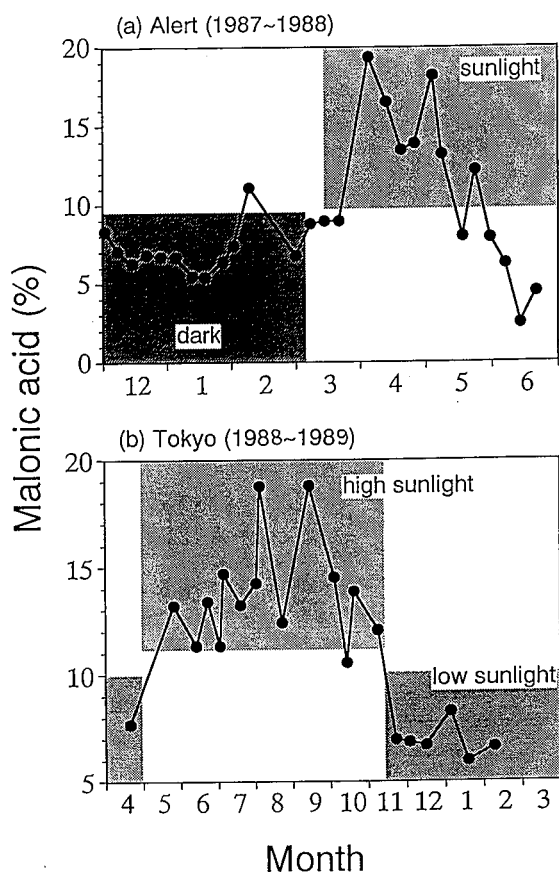
Its relative contribution to total diacids jumped from ca. 7-8% in the dark winter season to 18% just after polar sunrise (Fig. 8a). The observed shift is similar to the observed, photochemically-induced shift in urban aerosols (Kawamura and Ikushima, 1993) between the relatively high solar intensity period of summer and the rest of the year (Fig. 8). The selective enrichment of C_3 acid in the mid-latitudinal urban atmosphere during the seasons of summer to autumn is probably the result of enhanced photochemical oxidation of longer chain compounds such as succinic acid (Kawamura and Ikushima, 1993). The latter also peaks in the Arctic at polar sunrise. C_3 is further oxidized to kC_3 and C_2, both of which showed an increase at polar sunrise and a correlation with particulate Br (r = 0.77 and 0.61, respectively). These observations assist in understanding how organic pollutants containing polymethylene chains are oxidized in the atmosphere to result in shorter chain diacids and also why smaller diacids are relatively more abundant in the arctic aerosols at polar sunrise.

5. DEGRADATION OF POLYNUCLEAR AROMATIC HYDROCARBONS AT POLAR SUNRISE

Polynuclear aromatic hydrocarbons (PAHs) are produced during internal combustion of fossil fuels and emitted to the atmosphere. PAHs can be used as tracers of combustion-derived pollutants (Daisey *et al.*, 1981). Because of the presence of conjugated double bonds in their structures, PAHs are photochemically decomposed. Here, we report the results of PAH analysis conducted for Alert aerosol samples (Yanase *et al.*, 1995).

Figure 9 presents a capillary gas chromatogram of a PAH fraction isolated from arctic aerosols. Among the identified 28 PAHs, major species are phenanthrene, fluoranthene, pyrene, chrysene, benzo (k) fluoranthene, benzo (e) pyrene, benzo (a) pyrene, benzo (ghi) perylene. Compositions of PAHs in arctic aerosols are similar to those reported in urban atmospheres and motor exhaust (Schuetzle, 1983 ; Simoneit *et al.*, 1991 ; Simoneit *et al.*, 1993). However, PAHs in the Arctic are dominated by 3-ring or 4-ring structures such as phenanthrene, fluoranthene and pyrene. This is in contrast to aerosols from mid-latitudes, where PAHs containing 5-rings are more abundant (e.g., benzo (k) fluoranthene). This is mainly due to the cold temperature (-35°C to 0°C) during sample collection in the Arctic, in which 3- and 4-ring PAHs are largely present as particles.

Figure 10 gives seasonal changes in PAH concentrations. PAH concentrations exponentially decreased from February to March and stayed low in March to June. This drastic decrease in March may be explained by (1) a decrease in the amounts of PAHs transported over the Arctic, and/or (2) photochemical degradation of PAHs at and after polar sunrise. To better understand the atmospheric transport of combustion derived materials, vanadium concentrations (measured by Barrie *et al.*,) are co-plotted in Figure
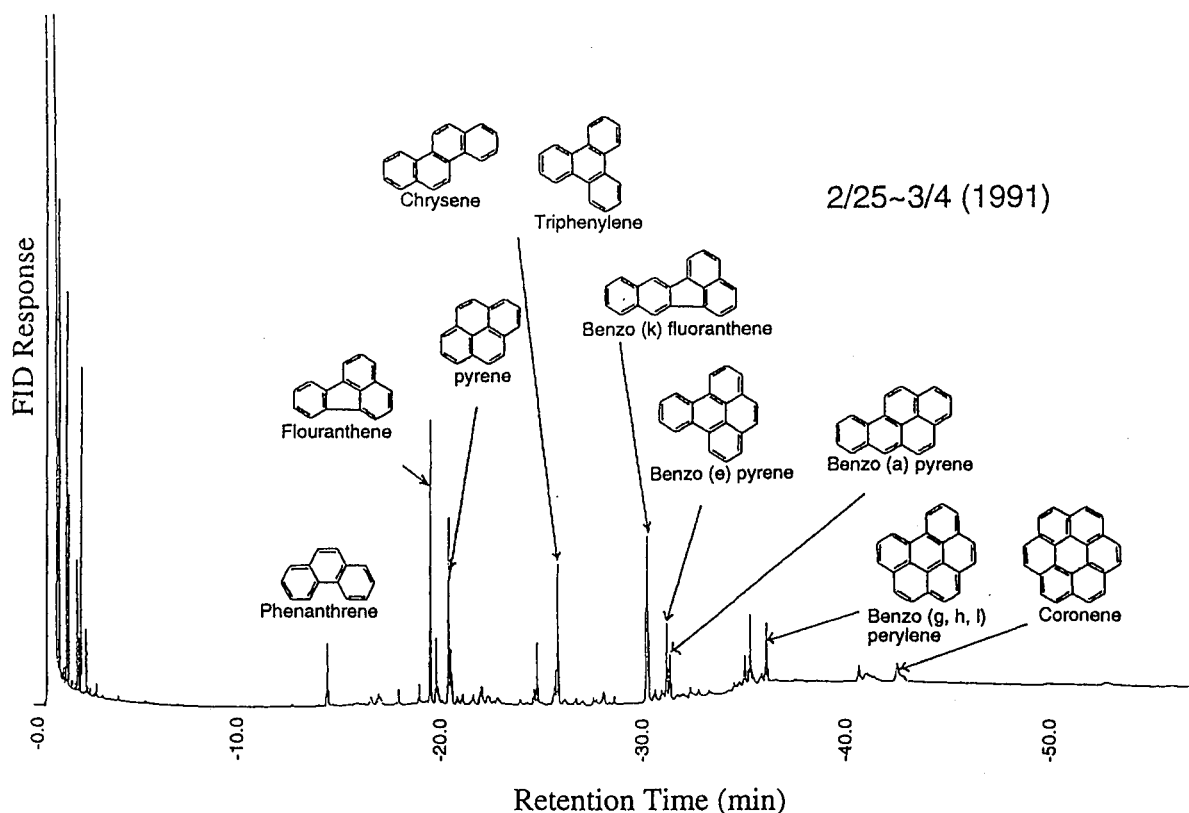

Fig. 8 The change in relative abundance (%) of malonic acid (C₃) in the total dicarboxylic acids (C₂-C₁₁) in arctic aerosol samples at polar sunrise (a) compared to similar observed differences in urban Tokyo (Kawamura and Ikushima, 1993) between light solar intensity in summer and lower solar intensity for the remainder of the year (b) (Kawamura *et al.*, 1995 b).

Fig. 9 Capillary gas chromatogram of polynuclear aromatic hydrocarbons separated from the arctic aerosol sample (Alert, February 25-March 4, 1991). The peak of benzo (k) fluoranthene may contain two other positional isomers : benzo (b) fluoranthene and benzo (j) fluoranthene (Yanase et al., 1995).
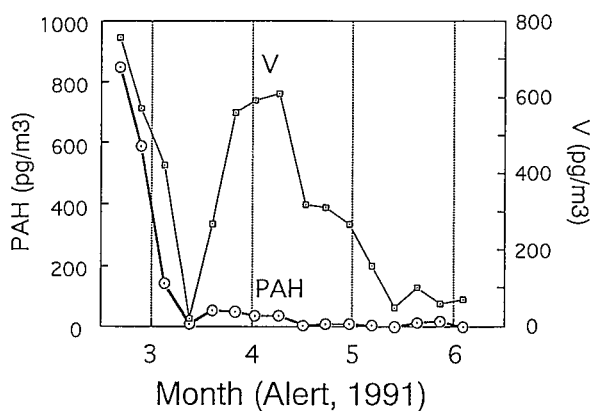

Fig. 10 Seasonal changes in the concentrations (pgm⁻³) of polynuclear aromatic hydrocarbons in the arctic aerosol samples collected from the Canadian Arctic, Alert, as well as concentrations of vanadium (Yanase et al., 1995). The V data are from Barrie et al. (unpublished results).

10. Vanadium is present widely in crude oils and coals, and emitted to the atmosphere during combustion of fossil fuels. The decrease of PAHs in February to March is consistent with the decrease in V concentration, indicating wreaked atmospheric transport of PAHs rather than their photochemical degradation in the period. From late March to early April, however, concentrations of V largely increased whereas PAH concentrations increased only slightly. These results indicate that the transport of PAHs toward the Arctic probably intensified in late March to early April, but,

they are largely decomposed in the atmosphere during long-range transport on the way to the Arctic and/or in the Arctic at polar sunrise. This period is consistent with the period when small dicarboxylic acids are largely produced in the Arctic.

Photochemical degradation of PAHs is further supported by detailed analysis of molecular compositions of PAHs. In motor exhaust benzo(a)pyrene (BaP) is as abundant as its structural isomer, i.e., benzo(e)pyrene(BeP). Thus, the BaP/BeP ratio is close to 1(Simoneit *et al.*, 1993). However, in atmospheric conditions with solar radiation, the former PAH is more unstable than the latter. During photochemical transformation of aerosols, the BaP/BeP ratios decrease. Arctic aerosols showed that the ratios are about 0.6 before polar sunrise and decreased to less than 0.2 during polar sunrise and afterwards. Such a drop of the BaP/BeP ratio is consistent with the results obtained in urban Tokyo, where the ratio decreases from 1.0 in winter to 0.6 in summer. However, the ratios are much lower in arctic aerosols than those of aerosols from Tokyo. This suggests that photochemical degradation of PAHs in the Arctic is more significant than in urban atmospheres in the mid -latitude and photochemical modification of organic aerosols is more intensified in the arctic atmosphere.

6. CONCLUDING REMARKS

Organic geochemical study of arctic aerosols demonstrates that the Arctic is an excellent natural laboratory for the study of photochemical transformation

of anthropogenic and natural organic matter in the troposphere, and is useful for understanding the complex chemistry of dicarboxylic acids and related polar organic compounds. There is ample evidence to suggest that dicarboxylic acids consisting mainly of low carbon number species (C_2-C_4) form an important part of the organic fraction of arctic aerosols. Furthermore, they are produced in situ in the lower arctic troposphere at polar sunrise by photo-induced chemical reactions involving mainly anthropogenic reactants. Production may occur simultaneously with chemical reactions that produce particulate Br whose precursors are involved in ozone depletion. During the photochemical production of diacids, photo-degradation of PAHa was also observed in the arctic atmosphere. Organic geochemistry of the Arctic region has also been studied to learn about atmospheric transport of soil-derived organic matter over the Arctic (Kawamura et al., 1996b) and polynuclear aromatic hydrocarbons and dicarboxylic acids in Greenland's snow and ice (Kawamura et al., 1994 ; Kawamura et al., 1996c).

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