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Fine and coarse modes of dicarboxylic acids in the Arctic aerosols collected during the Polar Sunrise Experiment 1997

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Abstract

Fine (<1 μm) and coarse (>1 μm) aerosol particles were collected at Alert, Canada (82°27’N, 62°30’W) during the Arctic spring as part of the Polar Sunrise Experiment 1997 and were analyzed for low molecular weight dicarboxylic acids (C_2-C_{11}) using gas chromatography with flame ionization detector (GC-FID) and GC/mass spectrometry (GC/MS). More than 80 % of total diacids were detected in the fine fraction, suggesting the production by gas-to-particle conversion in the Arctic. In both fractions, oxalic acid was the dominant diacid species followed by succinic and malonic acids. Shorter chain diacids (C_2-C_5) showed the concentration maximum on April 5-7, however, longer chain diacids ($\geqq C_6$) did not show a clear peak in the same periods. A significant depletion of ozone was observed during the experiment, where an anti-correlation was observed between the concentrations of ozone and shorter chain diacids (C_2-C_5) in both fine and coarse aerosols. During this event, we also observed the enhanced concentration of filterable bromine in both modes. Peaks of dicarboxylic acids in both coarse and fine aerosols during ozone depletion events indicate that heterogeneous reactions are occurring on coarse particle and possibly on fine particles. Dicarboxylic acids may be produced by the oxidation of precursor compounds such as glyoxal and glyoxylic and other ω-oxocarboxylic acids that contain aldehyde (hydrated form) group, being involved with ozone and halogen chemistry in the Arctic marine boundary layer.

1. Introduction

Homologous series of low molecular weight (LMW) dicarboxylic acids are ubiquitous aerosol composition in many regions of the world including the urban [e.g., *Grosjean et al*., 1978; *Kawamura and Ikushima*, 1993; *Wang et al*., 2002], marine [*Kawamura and Sakaguchi*, 1999; *Mochida et al*., 2003, *Sempéré and Kawamura*, 2003] and polar atmosphere [*Kawamura et al*., 1996a, 1996b, *Hara et al*., 2002]. LMW diacids are produced by fossil fuel combustion [*Kawamura and Kaplan*, 1987] and biomass burning processes [*Narukawa et al*., 1999] as well as photochemical oxidations of both anthropogenic and biogenic organic precursors [*Grosjean et al*., 1978; *Kawamura and Ikushima*, 1993]. They are now considered as important constitutes of water-soluble organic aerosols [*Saxena and Hildemann*, 1996] and also recognized to act as cloud condensation nuclei and to affect on the earth radiative forcing directly and indirectly [*Saxena et al*., 1995]. During a polar sunrise, concentrations of small diacids have been reported to increase drastically by a factor of 5-20 times [*Kawamura et al*., 1995]. Such an increase was interpreted as a photochemical production of diacids via an oxidation of anthropogenic organic precursors that are transported from mid and high latitudes. If volatile organic compounds are the major precursors, gas-to-particle conversion should play an important role, producing diacids in submicron aerosols. Alternatively, heterogeneous reactions may result in the production of diacids on super micron sizes as well. However, there is no reported data on the size distributions of diacids in the Arctic atmosphere at a polar sunrise.

The Arctic is surrounded with industrialized countries, from which gaseous and particulate pollutants are emitted. During winter, the Arctic air is isolated from the seawater in the Arctic Ocean by sea ice. In this cold and dark winter environment, sunlight-induced chemical reactions in the atmosphere as well as removal of aerosols from the Arctic air are more depressed than those farther south. Thus, reactive gas and aerosols accumulate in the Arctic atmosphere prior to polar sunrise. At polar sunrise in late March to early April, the Arctic troposphere act as a unique chemical reactor with an influence from human activity in the mid to high latitudes as well as the natural sources from the Arctic Ocean [*Barrie et al*., 1994]. Observation of unusually low O_3 mixing ratios in the Arctic marine boundary layer at the time of polar sunrise has been first reported in the mid 1980s [*Oltmans and Komhyr,* 1986; *Bottenheim et al.*, 1986]. Linkage of the O_3 data with concurrent filterable bromine measurements thereafter led to the hypothesis that O_3 is consumed via a chain reaction involving Br and BrO [*Barrie et al.*, 1988]. However, important details of the overall process are still poorly understood in part due to the lack of the information on size distributions of the particulate chemical composition at polar sunrise.

Organic compounds also participate in the surface ozone depletion events together with halogen compounds. *Jobson et al.* [1994] showed a decrease in the concentrations of nonmethane hydrocarbons (NMHCs) and their distribution changes during low-ozone episodes in the Arctic spring. Further, particulate LMW dicarboxylic acids have been reported to largely generate by enhanced photochemical processes as stated above. The photochemical production of diacids may be linked with halogen chemistry because a strong positive correlation was found between the concentrations of particulate Br and LMW dicarboxylic acids in the bulk aerosols from Alert [*Kawamura et al.*, 1995]. To improve our understanding on the formation mechanism of dicarboxylic acids at Arctic polar sunrise, we have collected daily aerosol samples that were segregated to fine and coarse modes during the Polar Sunrise Experiment 1997 (PSE97). The samples were analyzed for molecular distribution of LMW dicarboxylic acids and the results were discussed in terms of the photochemical processes together with the results of inorganic species including bromine.

2. Experiment

Aerosol samples were collected during Arctic polar sunrise at Alert (82°30’N, 62°21’W) as part of PSE97 (see Figure 1 for a map of the Arctic). The sampling site is located near the Special Study Trailer (SST) site (175 m a.s.l.), approximately 6 km south-southeast of the main military base at Alert. Daily aerosol samples that were segregated into coarse ($D_p > 1$ μm) and fine ($D_p < 1$ μm) fractions were collected using a high-volume virtual impactor on the pre-combusted (450 °C, 3 hrs) quartz fiber filters (Pallflex, 2500QAT) from March 29 to April 14 (day of year 88-104), 1997. During the campaign, ambient temperature ranged from

–34.5 °C to –18 °C at the sampling site. Filters were stored in a cleaned glass jar with a Teflon-lined cap. The aerosol filter samples were frozen and transported to our laboratory in Sapporo, Japan and stored in darkness at –20 °C until analysis.

A part of the aerosol filter was cut in pieces and extracted with Milli Q water under ultrasonication for water-soluble organic compounds. The extracts were passed through a glass column (Pasteur pipette) packed with quartz wool to remove particles such as black carbon and filter debris. The extracts were concentrated to almost dryness by a rotary evaporator under vacuum, to which 14 % borontrifluoride in n-butanol (ca. 0.2 ml, Alltech Associates, Inc.) was added. The extracts and reagent were mixed under ultrasonication and then heated at 100 °C for 1 hour to generate carboxylic acid butyl esters. The esters were extracted with 10 ml n-hexane after adding 10 ml Milli Q water and 0.2 ml acetonitrile, the latter improving transfer of the excess n-butanol into the aqueous phase. The n-hexane layer was washed with pure water (10 ml x 4). The esters were concentrated by a rotary evaporator and further dried under a nitrogen stream, and the residue was dissolved in 50 μl of n-hexane.

The dicarboxylic acid dibutyl esters were determined using a GC-FID (Hewlett Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m x 0.2 mm i.d. x 0.52 μm film thickness). The identification of the compounds was performed with a GC/MS instrument (ThermoQuest, Voyager) equipped with an on-column injector and fused silica capillary column (DB-5MS, 60 m x 0.32 mm i.d. x 0.25 μm film thickness) by using authentic standards.

Recoveries of authentic standards spiked onto a precombusted quartz fiber filter were 70 % for oxalic (C_2) acid, 85% for malonic (C_3) acid, and better than 90 % for succinic (C_4) and adipic (C_6) acids. Procedural blanks showed small peaks of oxalic, succinic, adipic, and phthalic acids in the GC chromatograms. However, their blank levels were almost constant and generally <10 % of those for the aerosol samples. The concentrations of the diacids reported here are corrected for the procedural blanks. The relative standard deviation of the diacid measurements based on duplicate analysis of the aerosol samples was generally 10 %. More details of the analytical procedure are described elsewhere [*Kawamura and Ikushima*, 1993].

For ion analysis, an aliquot of the aerosol filter samples was cut in pieces and ultrasonically extracted with Milli Q water. The extracts were filtered with a filter pack (GL Sciences, Chromatodisk 13AI). Major anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were determined by ion chromatography (Dionex, DX-500). For anion analysis, Dionex-AS12A columns, 4.05 mM Na_2CO_3/ 0.45 mM $NaHCO_3$ eluent and an auto-suppressor ASRS-1 were used. For cation analysis, Dionex-CS12A columns, 20.5 mM methanesulfonic acid eluent and auto-suppressor CSRS-ULTRA were used. The injection loop volume was 500 μl. Procedural blanks showed small peaks of Cl^-, SO_4^{2-} and Ca^{2+} in the ion chromatograms. However, they were less than 5 % of those for the aerosol samples. The concentrations of the ions reported here are corrected for the procedural blanks. This analytical procedure has already been used in our previous study [*Narukawa et al.*, 2002].

3. Results and Discussion

3.1. Composition and concentrations of dicarboxylic acids and inorganic ions in fine and coarse particles

A homologous series of normal saturated LMW dicarboxylic acids (C_2-C_{11}) were detected as well as branched (C_4-C_7), unsaturated (C_4-C_5), and aromatic (C_8) diacids. Dicarboxylic acids with keto group (C_3 and C_7) were also detected. Figure 2 presents a typical molecular distribution of dicarboxylic acids in the arctic aerosols (April 6-7, Day 97). Oxalic acid (C_2) was found as the most abundant diacid species followed by succinic (C_4) acid and then malonic (C_3) acids in both fine and coarse aerosol samples. The longer chain diacids are less abundant. Diacids are more abundant in fine mode than in coarse mode. Similar distributions were also observed in other samples. The molecular distributions detected in this study were consistent with those reported previously for the bulk aerosol samples from Alert [*Kawamura et al.*, 1996a; *Narukawa et al.*, 2002]. Table 1 presents mean concentrations and ranges of diacids determined in the fine and coarse aerosol samples. Concentration ranges of diacids are also consistent with those reported for the bulk aerosol samples collected weekly at Alert in 1988 [*Kawamura et al.*, 1996a]. Although ω-oxocarboxylic acids such as glyoxylic acid and α-dicarbonys (e.g., glyoxal) are abundantly present in the Arctic aerosols [*Kawamura et al*., 1996a], their concentrations are not available for the samples in this study because they were not determined unfortunately.

As seen from Figure 3, shorter chain diacids (C_2-C_5) largely present as fine aerosols (on average 85-87 %). A correction was not made for the part of fine size fraction that may end up in the coarse size fraction. Enrichment of diacids in submicron aerosols was also obtained for another sets of size-segregated aerosols collected by Micro-Orifice Uniform Deposit Impactor at Alert [*Narukawa et al.,* in preparation]. These results suggest that such diacids are, for the most part, formed by gas-to-particle conversion and accumulate in fine aerosol mode (< 1 μm). A major portion of the longer chain diacids (C_6-C_9) was also found in the fine mode (on average, 83-95 %, Figure 3). Even azelaic acid (C_9), an oxidation product of biogenic unsaturated fatty acids containing a double bond predominantly at C-9 position [*Kawamura and Gagosian*, 1987; *Stephanou and Stratigakis*, 1993], was mostly associated with the fine particles (average, 83 %), although this acid was increased on Day 98 in the coarse particles together with Na^+. These results suggest that the longer chain diacids are not significantly produced in the Arctic spring or they are scavenged by dry deposition as coarse particles. Longer chain diacids are likely emitted from soils (mid-latitude) or produced in the marine atmosphere on the way to the Arctic [*Kawamura et al.*, 1996c], and have been reported in an ice core from Greenland [*Kawamura et al.*, 2001]. In winter to spring wet precipitation is limited in the Arctic, hence dry deposition processes likely scavenge coarse mode aerosols.

However, on Days 98-99, concentrations of C_8 and C_9 diacids in coarse particles increased together with Na^+ and Br^-, suggesting a contribution of marine organic matter as well as sea salt spray followed by heterogeneous reactions on the coarse aerosols. During the same period, concentrations of shorter chain saturated diacids (C_2, C_3, C_4, and C_5) and unsaturated diacids (maleic and fumaric acids) on coarse mode also increased relative to those of fine mode. This phenomenon seems to be involved with the O_3 depletion and bromine chemistry, a topic to be discussed later.

Table 2 presents mean concentrations and ranges of inorganic ions detected in the fine and coarse aerosol samples from the Arctic. SO_4^{2-} is the most abundant anion in both fractions, followed by NO_3^- and Br^- in the fine fraction and by Cl^- and NO_3^- in coarse fraction. SO_4^{2-} is roughly ten times more abundant than organic anions (diacids) in the fine aerosols. Concentration levels of NO_3^- are similar to those of oxalic acid. Interestingly, Br^- is more abundant than Cl^- in fine aerosols although opposite trend was found in coarse fraction. On the other hand, NH_4^+ is the most abundant cation in the fine aerosols whereas Na^+ is the dominant in the coarse fraction.

Size distributions of inorganic ions showed different trends than dicarboxylic acids. Figure 4 presents the averaged relative abundances of inorganic species in fine and coarse aerosols. Cl^- in coarse aerosols accounted for 94 % of the total concentrations. By contrast, Br^- ion in fine aerosols accounted for 63 % of the total. Similarly, SO_4^{2-} and NH_4^+ in fine mode comprised more than 80 % of the total concentrations. Enrichment of SO_4^{2-} and NH_4^+ on fine mode is consistent with the case of dicarboxylic acids (Figure 3). K^+ in fine aerosols comprised 62 % of the total, whereas fine mode NO_3^-, Na^+, Mg^+, Ca^{2+} accounted for about 50 % of total concentrations. These results suggest that SO_4^{2-} is produced by gas-to-particle conversion and that Cl^- is associated with fine aerosols and more importantly with coarse aerosols. Cl^- may be lost as HCl gas from the sea-salt particles to the atmosphere through the following reaction.

$$2NaCl_{(p)} + H_2SO_{4(p)} \rightarrow 2HCl_{(gas)} + Na_2SO_{4(p)}$$

This process may occur on the surface of aged marine aerosols on coarse mode in the air [*Graedel and Keene*, 1995]. Our calculation showed that more than 84 % (average 97 %) of chlorine, which was originally derived from sea salts, was depleted in the fine aerosols. The chlorine loss was also observed for coarse particles, but the depletion (8-89 %, average 52 %) was less than the fine particles. Chlorine depletion has been reported for the bulk aerosols from the Arctic [Suzuki et al., 1995].

3.2. Correlations of dicarboxylic acids with different chemical components

To further understand the variation of the aerosol composition and to extract information of the source and reaction mechanisms, the data sets of dicarboxylic acids and inorganic ions in fine and coarse aerosol samples as well as ozone were subjected to a factor analysis with varimax rotation. Table 3 gives the results with factor loadings for fine aerosol samples. Four factors were found to account for 91% of the variance (sum of variances ≥ 0.1) in the data set. Factor 1 seems to be related mostly to sea salt aerosols, where K^+, Ca^{2+}, Mg^{2+}, NO_3^- and Cl^- are positively correlated each other. Factor 2 relates to atmospheric chemistry involved with O_3 in marine boundary layer. In this factor, C_2-C_5 diacids are inversely correlated with O_3, but positively correlated with Br^-. These results suggest that the small diacids detected in the fine aerosols are heterogeneously generated with a consumption of ozone in the presence of bromine. Factor 3 shows a positive correlation among adipic acid, SO_4^{2-} and NH_4^+, indicating anthropogenic sources. Adipic acid (C_6) has been reported as an oxidation product of cyclohexene [Grosjean et al., 1978; Hatakeyama et al., 1987], which has been reported in urban air [Grosjean and Fung, 1984]. This result also suggests that C_6 acid is produced by gas-to-particle conversion, being similar with sulfate. Ammonia (NH_3) gas was likely adsorbed on the SO_4^{2-} rich particles whose sizes are small. Factor 4 shows a correlation between Na^+ and Cl^-, although the correlation coefficient is not high due to an evaporation of chloride. These statistical analyses on the fine aerosol composition suggest that the production of dicarboxylic acids in fine aerosols is involved with ozone and bromine chemistry in the Arctic spring.

Table 4 presents the results of factor analysis for coarse mode aerosols. The results indicate that three factors account for 88% of the variance in the data set. Factor 1 is related to sea salt and continental aerosols, showing a positive correlation among Cl^-, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+}. Gaseous nitric acid may be adsorbed on the coarse mode particles enriched with sea salt and calcium carbonate. Factor 2 is related to the photochemical production of diacids, although the correlation with Br^- is not strong as the case of fine mode particles. This again suggests that the production of small diacids are involved with the depletion of ozone and the increase of bromine. Factor 3 shows a correlation among O_3, SO_4^{2-} and NH_4^+, although there is no relationship with small diacids. Gaseous NH_3 may be adsorbed on sulfate aerosols that are also present in the coarse mode. The results for coarse aerosols are generally consistent with those of fine particles, suggesting that the dicarboxylic acids are also produced on the coarse aerosols by photochemical reactions, but with less influence from bromine chemistry.

3.3. Temporal variation of dicarboxylic acids and inorganic ions

Concentrations of shorter chained diacids (C_2-C_5) in fine and coarse aerosols showed a maximum on Day 97 and Days 97-98 during the beginning of sunny (but still cold) period and a decrease thereafter (Figure 5). Maximum concentrations of the shorter chain diacids were 3-5 times higher than the concentrations for the beginning of sampling period. These diacids have been considered to generate by secondary photochemical reactions induced by solar radiation at the Arctic sunrise [*Kawamura et al.*, 1995]. A laboratory study using a smog-chamber reported that oxalic acid was produced in the presence of O_3, alkanes and NaCl [*Behnke et al.*, 1999]. The small diacids might be formed from the NMHCs ($<C_6$) that exist in the Arctic marine boundary layer [*Jobson et al.*, 1994]. In contrast, concentrations of longer chain diacids ($>C_7$) did not show a clear peak on Days 97-98 (Figure 5). The difference in the concentrations between shorter and longer chained diacids may result from the difference in their sources and/or source regions. Since longer chained volatile hydrocarbons ($\geqq C_6$) are less abundant [*Jobson et al.*, 1994], they cannot serve as important precursors for longer diacids in the Arctic troposphere. Thus, longer diacids are likely associated with the precursors that already exist on preexisting aerosols or transported from the source regions.

Concentrations of SO_4^{2-} and NH_4^+ ions did not show any significant peaks during sampling period although they are more abundant on Day 95-96 (Figure 6). Inorganic ions derived from sea salts (Na^+, Cl^-, Mg^{2+}) showed two maxima on Days 97-98 and 102-104. However, the peaks of Cl^- on fine mode were not clearly observed. During Days 96-98, concentrations of Mg^{2+} on both modes showed a peak, but the peak on coarse mode preceded that of fine mode. Concentrations of NO_3^- also showed higher values on these days, where the peaks of coarse mode preceded that of fine mode. Throughout the campaign, concentrations of Br^- ion in both fine and coarse modes indicated a strong peak on Days 97-98. The peak of Br^- is very consistent with oxalic and other small diacids whose peaks also appeared on the same days.

3.4. Formation mechanism of dicarboxylic acids at the Arctic polar sunrise

During the sampling period between March 29 (Day 88) and April 14 (Day 104), we observed two episodes of ozone depletion (Figure 7). One minor ozone loss occurred on Days 89-90 whereas major ozone depletion appeared on Days 96-99 when ozone levels became below the detection limit (≈ 1 ppbv). During the major ozone depletion, we observed a peak of oxalic acid and other small diacids with higher concentrations in fine aerosols (Figures 7 and 5). A peak of Br_2 was also reported at the beginning of and during the ozone depletion event in the same campaign [*Impey et al.*, 1999]. In PSE1992, *Jobson et al.* [1994] reported the variations of NMHCs that correlated with ozone. Concentration changes of alkanes were explained by the reaction with Cl atom. Formaldehyde and acetone in gas phase were also reported to increase during the ozone depletion event [*de Serves*, 1994; *Yokouchi et al*., 1994]. These results and discussion lead to a conclusion that the production of shorter chain diacids at polar sunrise is involved with the oxidative reaction of NMHCs and halogen chemistry in the Arctic marine boundary layer.

This study also demonstrated that the production of small diacids is characterized by anti-correlation with ozone and positive correlation with bromine present in both gas phase [Impey et al., 1999] and particles. Although the highest concentrations of C_2-C_5 diacids were observed on Days 96-98 in both fine and coarse aerosols (Figure 5), the peaks of fine mode were larger and seemed to precede the peaks of coarse mode by one day or two days. These results suggest that gas-to-particle conversion have resulted in the production of diacids mostly in the fine mode and then the fine particles containing those diacids are grown to coarse particles. Heterogeneous bromine chemistry, however, may also be involved with the production of dicarboxylic acids on the surface of both fine and coarse particles. This process seemed to be enhanced during the episode of major ozone depletion (Days 96-99), when bromine concentrations significantly increased on both fine and coarse mode (see Figure 6h, the concentration of Br^- on coarse mode overwhelmed that of the fine mode). At the same period, the relative abundance of diacids in coarse aerosols also increased (Figures 8 and 5). In fact, relative abundance of coarse mode oxalic acid increases from 12 % (see Figure 2 for Day 97 at the maximum of ozone depletion) to 30 % on Day 99 (see Figure 8 for Day 99, two days after the ozone depletion). These results suggest that a heterogeneous production of diacids is also important on the aerosol surface during O_3 depletion.

Behnke et al. [1999] reported that oxalic acid reduces Br_2 and this reaction may be responsible for the inhibition of chain reactions in gas phase involving bromine chemistry. However, during the major ozone depletion, concentrations of Br_2 [Impey et al., 1999] and shorter chain diacids including oxalic acid (Figure 7) both increased significantly. The mechanism for the production of diacids accompanied with halogen chemistry is still unidentified. However, our study suggests that photochemical production of halogen may be involved with the oxidation of possible precursors of diacids, including glyoxal, glyoxylic acid and other ω-oxocarboxylic acids that are abundantly present in the Arctic air at polar sunrise [*Kawamura et al.,* 1996a]. Aldehyde group that is hydrated with water in aerosol particles [*Warneck*, 2003] may be reacted with halogen atoms via abstraction of hydrogen as shown in Scheme I. The organic radical generated may further react with O_2 to result in the production of carboxylic acid [*Graedel and Weschler,* 1981]. Heterogeneous chemistry of oxygen-containing organic compounds in the presence of sea salt and sunlight needs to be further investigated for understanding formation mechanisms of diacids at the polar sunrise.

4. Summary and Conclusions

A homologous series of LMW diacids (C_2-C_{11}) were detected in both fine and coarse aerosols collected during PSE97 on a daily basis. Shorter chain diacids (C_2-C_5) in both fine and coarse aerosols showed the maximum concentrations on Days 96-98. Their concentration peaks were higher in fine mode than coarse mode, suggesting the production of small diacids by gas-to-particle conversion. In contrast, the longer chain acids ($\geqq C_6$) did not show a clear peak for that period. The diacids in fine aerosols accounted for more than 80 % of total fine and coarse diacids. These results suggest that the longer chain acids were transported long distances to the Arctic, but were not significantly produced during the polar sunrise period. During ozone depletion events, shorter chain diacids showed the concentration peaks together with filterable bromine. These results, together with factor analysis, further suggests that C_2-C_5 diacids were produced by heterogeneous reactions on the aerosol surfaces associated with halogen chemistry in the Arctic marine boundary layer. Likely precursors of these diacids may be semi-volatile oxygenated organic compounds including glyoxal, glyoxylic acid and other ω-oxocarboxylic acids, which are oxidation products of NMHCs. Both coarse and fine particulate dicarboxylic acids showed maximum concentrations during ozone depletion episodes, indicating that heterogeneous reactions are occurring on at least coarse particle and possibly on fine particles.

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Figure and Scheme Caption

Figure 1. Map for the Arctic region with a sampling site of Alert (82°30'N, 62°21'W).

Figure 2. Molecular distributions of dicarboxylic acids detected in fine and coarse fractions of the Arctic aerosol sample (6-7 April, 1997, Day 97). For abbreviation, see Table 1.

Figure 3. Averaged fine and coarse fraction (%) of individual normal saturated dicarboxylic acids (C_2-C_9) in the aerosol particles collected at Alert in 1997. Correction was not made for the part of the fine size fraction that may end up in the coarse size fraction.

Figure 4. Averaged fine and coarse fraction (%) of individual inorganic ions in the aerosol particles collected at Alert in 1997.

Figure 5. Daily changes in the concentrations (ng m^{-3}) of dicarboxylic acids in fine and coarse aerosols at Alert in 1997.

Figure 6. Daily changes in the concentrations (ng m^{-3}) of inorganic ions in fine and coarse aerosols at Alert in 1997.

Figure 7. Daily changes in the concentrations of ozone (ppbv) and oxalic acid (ng m^{-3}) in fine aerosols at Alert in 1997.

Figure 8. Molecular distributions of dicarboxylic acids in fine and coarse fractions of the arctic aerosols (April 8-9, Day 99) collected at Alert. For abbreviations, see Table 1.

Scheme I. Proposed mechanism of halogen chemistry for the production of dicarboxylic acids from the precursors containing aldehyde functional group (glyoxal, glyoxylic acids and other ω-oxocarboxylic acids).

Fig. 1 (Narukawa et al.)

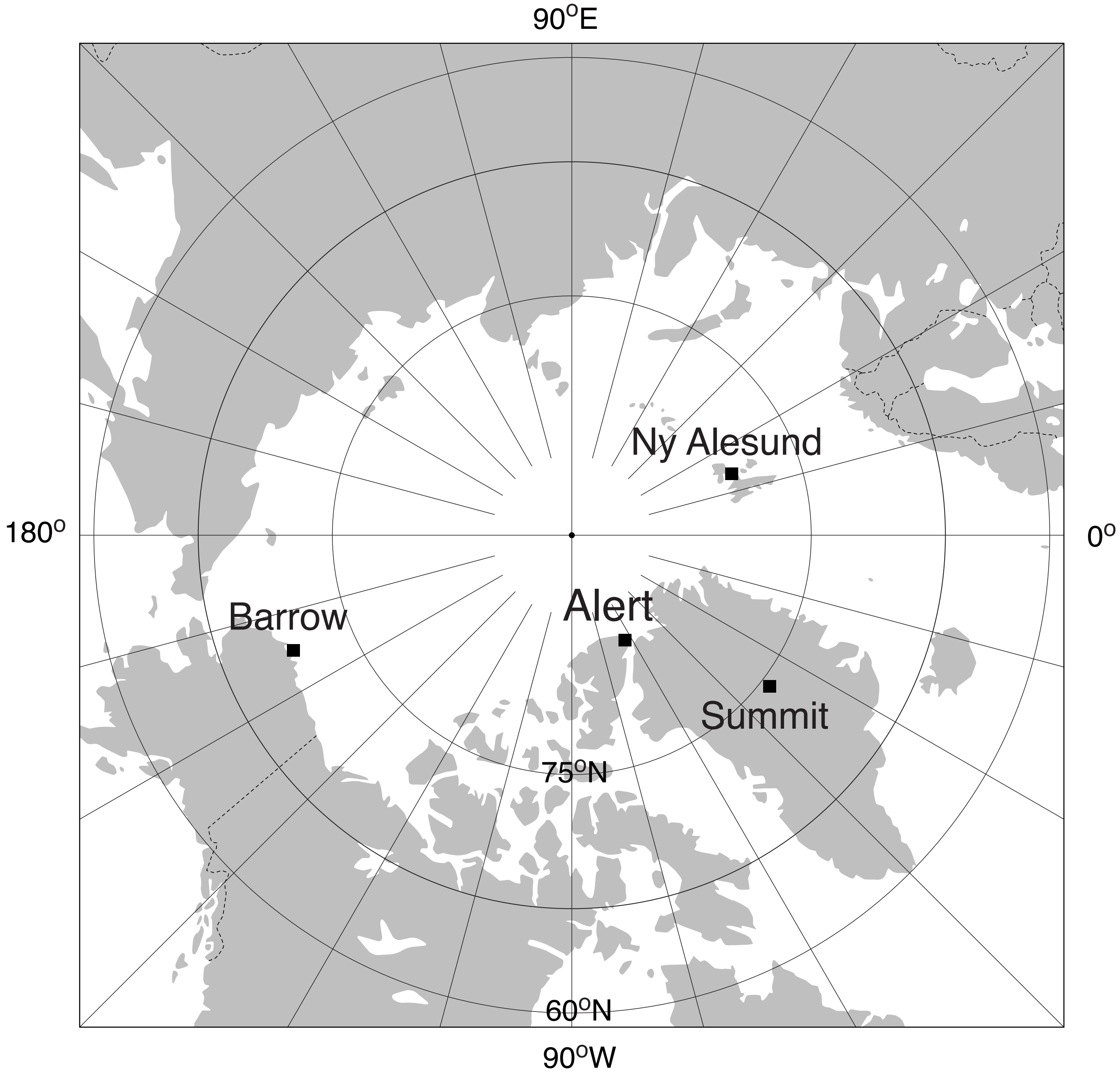


Figure 2 (Narukawa et al.)

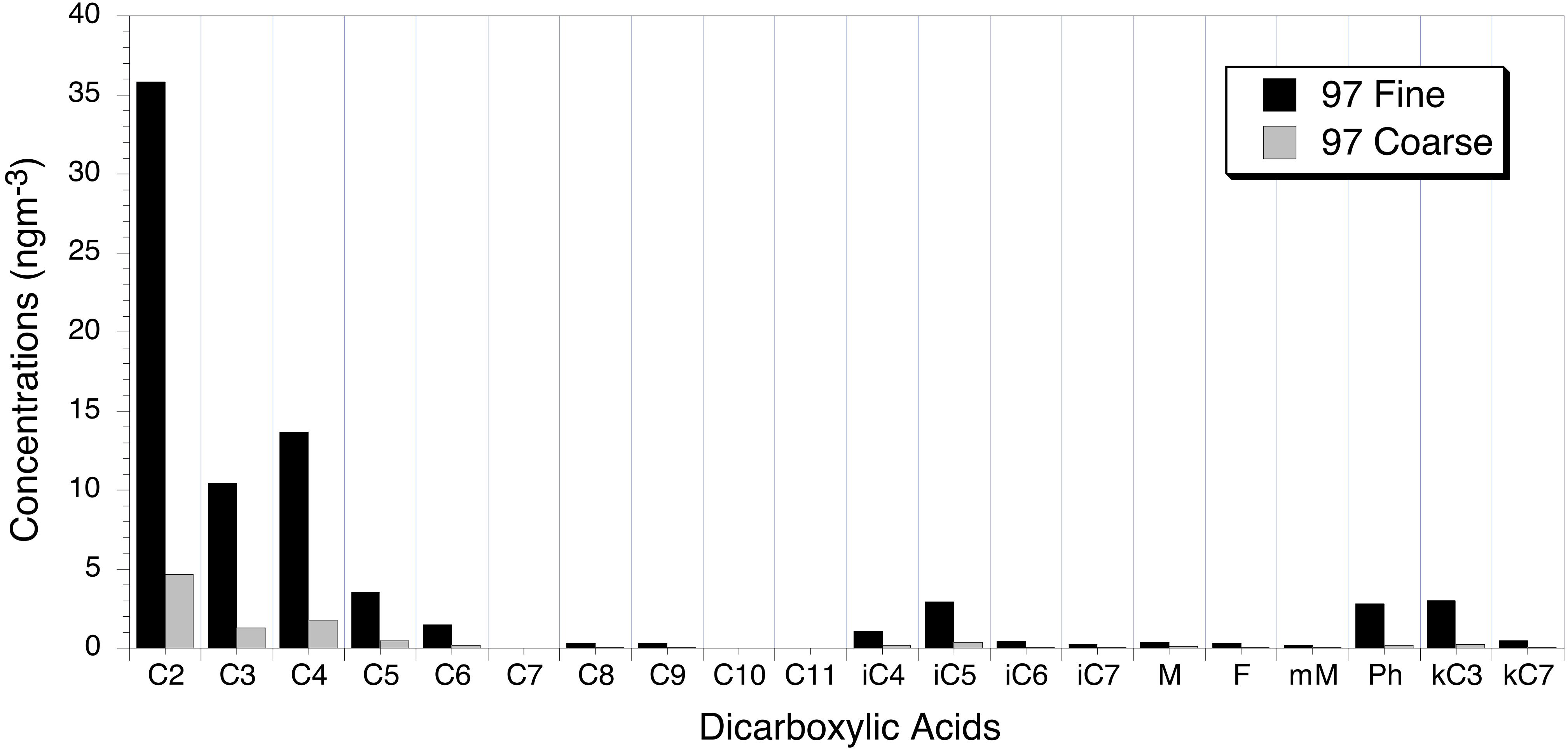


Figure 3. Narukawa et al.

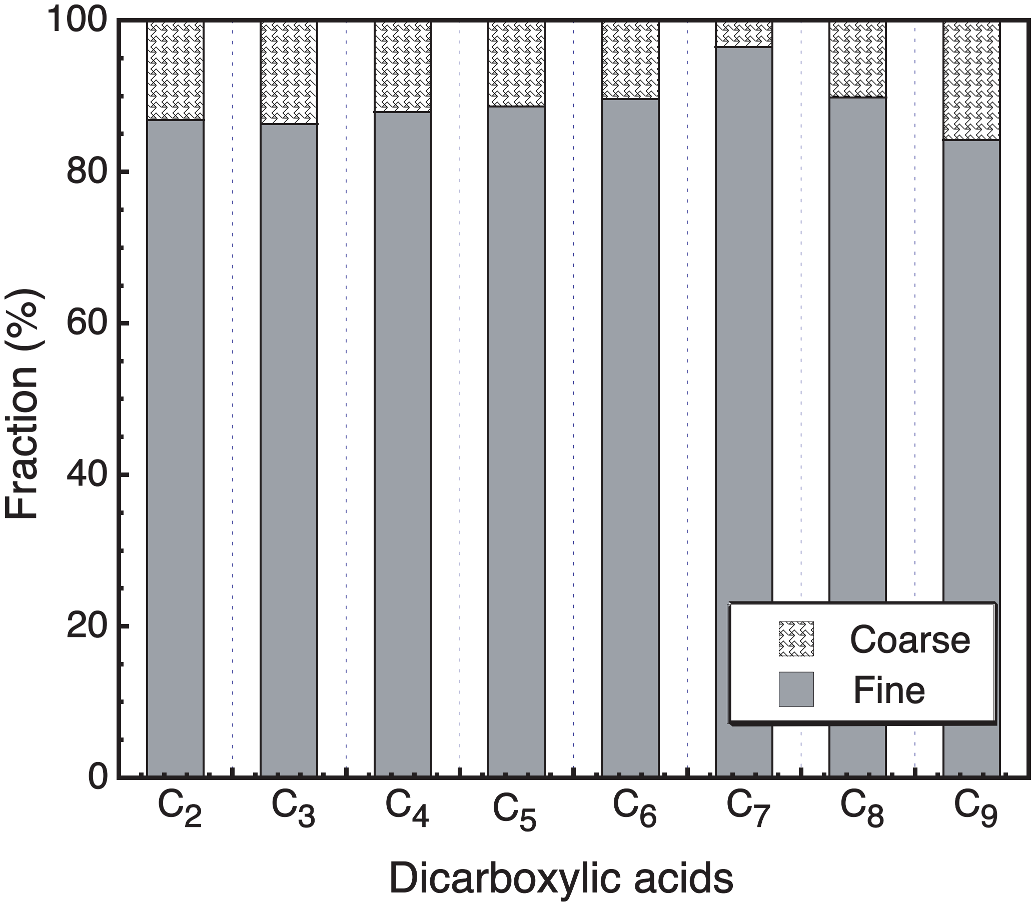


Fig. 4 (Narukawa et al.)

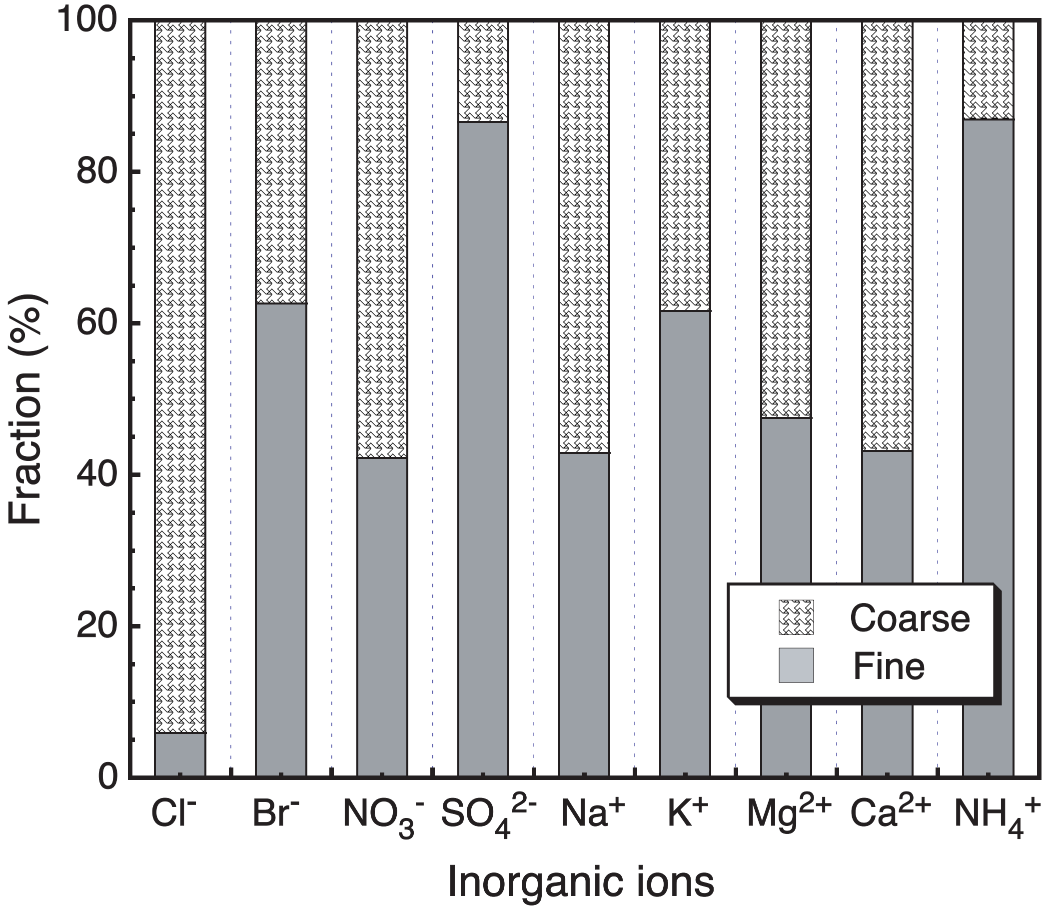


Figure 5. Narukawa et al.

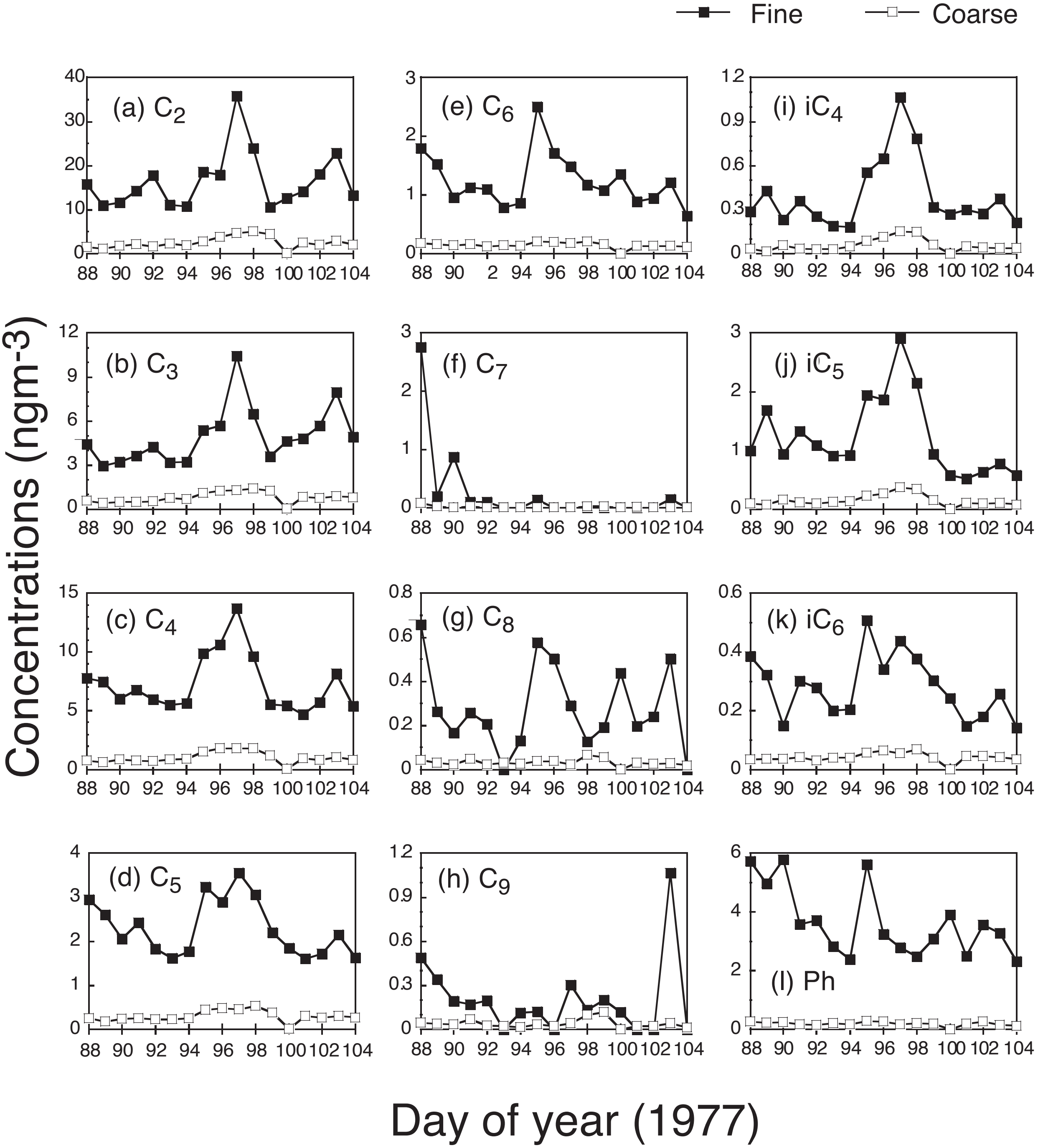


Figure 6. Narukawa et al.

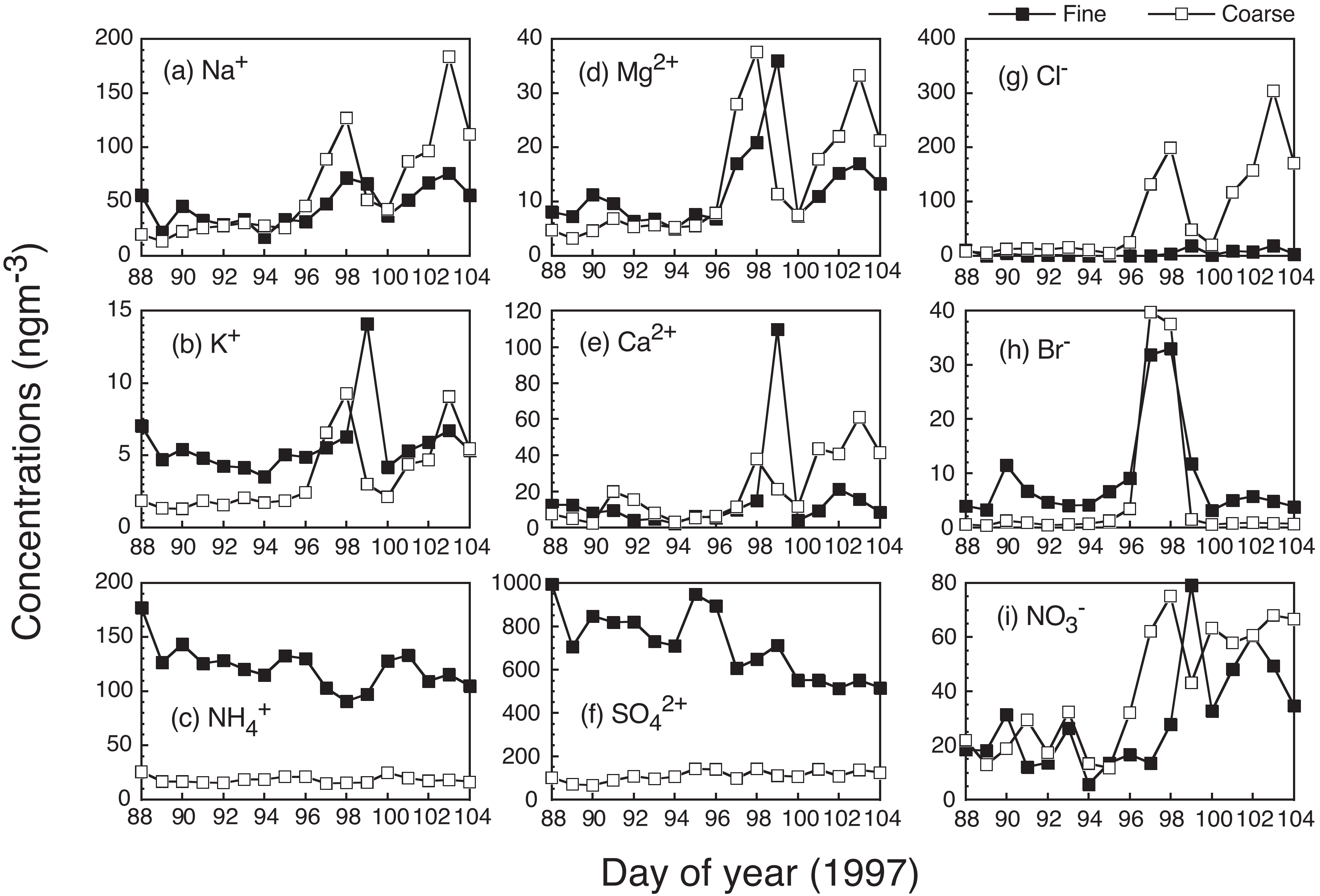


Figure 7. Narukawa et al.

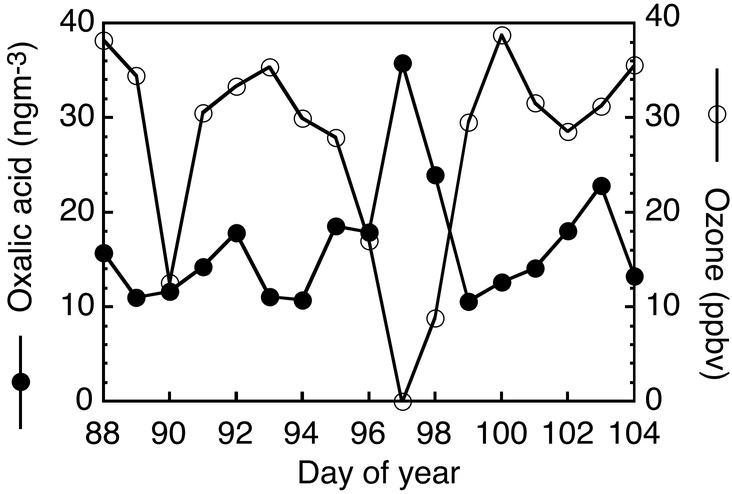
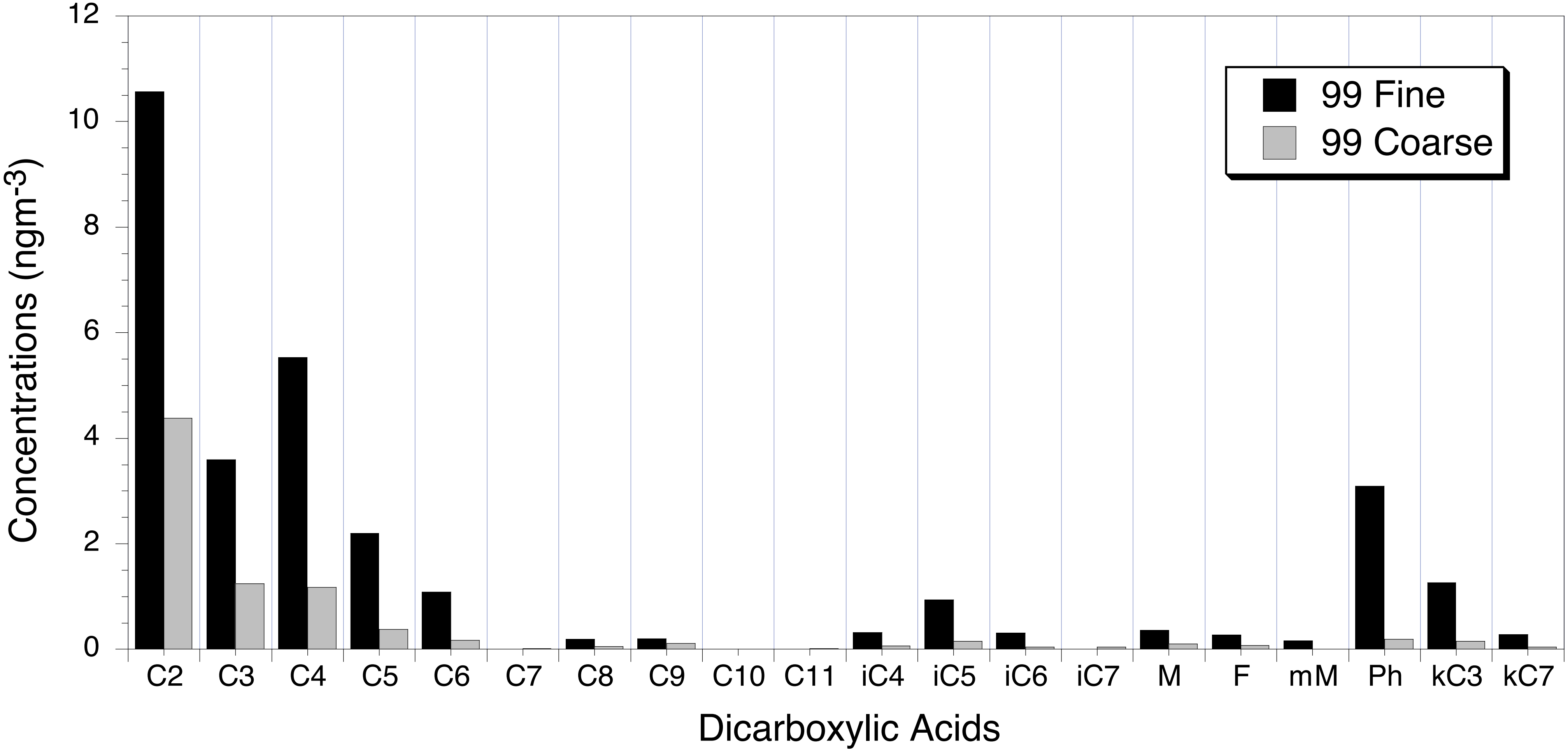
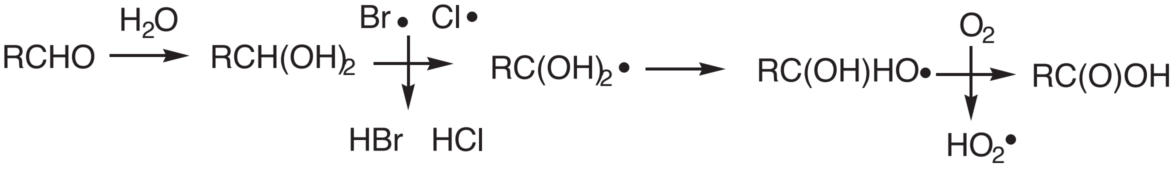


Fig. 8 (Narukawa et al.)



Scheme I (Narukawa et al.)



$$\mathrm{RCHO} \xrightarrow{\mathrm{H_2O}} \mathrm{RCH(OH)_2} \xrightarrow[\mathrm{HBr}\quad \mathrm{HCl}]{\mathrm{Br}\bullet\quad \mathrm{Cl}\bullet} \mathrm{RC(OH)_2}\bullet \longrightarrow \mathrm{RC(OH)HO}\bullet \xrightarrow[\mathrm{HO_2}\bullet]{\mathrm{O_2}} \mathrm{RC(O)OH}$$

Table 1. Concentrations (ng m^{-3}) of Dicarboxylic Acids in the Fine and Coarse Aerosol Samples Collected in the Spring Arctic, 1997

Dicarboxylic acids (abbr.)	Fine (D_p<1 μm)		Coarse (D_p>1 μm)	
	Range	Mean conc. ± st. dev.	Range	Mean conc. ± st. dev.
Normal saturated				
Oxalic (C_2)	10.8-35.8	16.5±6.46	0.04-5.09	2.50±1.33
Malonic (C_3)	2.96-10.4	4.97±1.94	0.03-1.40	0.79±0.37
Succinic (C_4)	4.68-13.7	7.29±2.42	0.02-1.79	1.00±0.47
Glutaric (C_5)	1.60-3.55	2.30±0.64	0.01-0.52	0.30±0.13
Adipic (C_6)	0.64-2.51	1.25±0.46	<0.01-0.21	0.14±0.05
Pimelic (C_7)	<0.01-2.76	0.25±0.68	<0.01-0.08	0.01±0.02
Suberic (C_8)	<0.01-0.66	0.28±0.19	<0.01-0.07	0.03±0.02
Azelaic (C_9)	<0.01-1.06	0.20±0.26	<0.01-0.12	0.04±0.03
Sebacic (C_{10})	<0.01-1.44	0.20±0.42	<0.01-0.04	0.01±0.01
Undecanedioic (C_{11})	<0.01	-	<0.01-0.01	-
Branched saturated				
Methylmalonic (iC_4)	0.18-1.06	0.40±0.24	<0.01-0.15	0.06±0.04
Methylsuccinic (iC_5)	0.52-2.91	1.22±0.67	<0.01-0.37	0.15±0.10
2-Methylglutaric (iC_6)	0.14-0.51	0.28±0.11	<0.01-0.07	0.04±0.02
2-Methyladipic (iC_7)	<0.01-0.48	0.25±0.13	<0.01-0.11	0.04±0.02
Unsaturated				
Maleic (M)	0.25-0.60	0.40±0.08	<0.01-0.11	0.07±0.03
Fumaric (F)	0.18-0.80	0.32±0.15	<0.01-0.11	0.05±0.02
Methylmaleic (mM)	0.08-0.30	0.18±0.06	<0.01-0.06	0.03±0.02
Phthalic (Ph)	2.31-5.79	3.63±1.19	<0.01-0.28	0.19±0.08
Keto				
Ketomalonic (kC_3)	0.19-2.98	1.24±0.71	<0.01-0.26	0.12±0.07
4-Ketopimelic (kC_7)	0.21-0.67	0.35±0.12	<0.01-0.05	0.03±0.01

Table 2. Concentrations (ng m^{-3}) of Inorganic Ions in the Fine and Coarse Aerosol Samples Collected in the Spring Arctic, 1997

Inorganic ion	Fine (D_p<1 μm)		Coarse (D_p>1 μm)	
	Range	Mean conc. ± st. dev.	Range	Mean conc. ± st. dev.
Anions				
Cl^-	<0.1-18.8	4.6±6.3	4.9-305	73.9±89.8
Br^-	3.2-33.0	9.0±9.2	0.4-39.7	5.4±12.5
NO_3^-	5.7-79.1	29.5±19.8	11.7-75.0	40.4±22.7
SO_4^{2-}	513-995	713±154	65.8-141	111±23.6
Cations				
Na^+	17.1-76.2	45.5±17.9	13.5-184	60.5±47.8
K^+	3.5-14.1	5.7±2.4	1.3-9.3	3.6±2.6
Mg^{2+}	4.9-36.0	12.1±7.7	3.2-37.6	13.4±11.1
Ca^{2+}	2.2-110	15.2±24.8	2.3-61.1	20.1±18.0
NH_4^+	90.9-177	123±20.0	15.1-25.7	18.5±3.2

Table 3. Factor Analysis with Varimax-Rotation for the Data Set of Dicarboxylic Acids and Inorganic Ions in the Fine Mode of Arctic Aerosols

Components	Factor 1	Factor 2	Factor 3	Factor 4
ozone	-0.03	0.88	-0.07	0.17
C_2	-0.09	-0.89	-0.02	0.38
C_3	-0.02	-0.81	0.08	0.53
C_4	-0.12	-0.89	-0.38	0.05
C_5	0.03	-0.76	-0.61	-0.07
C_6	-0.09	-0.32	-0.84	0.04
Cl^-	0.76	0.20	0.05	0.55
Br^-	0.19	-0.91	0.14	-0.12
NO_3^-	0.79	0.21	0.36	0.33
SO_4^{2-}	-0.07	0.07	-0.85	-0.38
Na^+	0.64	-0.23	0.22	0.61
NH_4^+	-0.29	0.44	-0.73	0.19
K^+	0.99	-0.03	-0.08	0.01
Mg^{2+}	0.92	-0.30	0.25	0.04
Ca^{2+}	0.96	0.05	0.03	-0.17
Variance	0.30	0.33	0.18	0.10

Table 4. Factor Analysis with Varimax-Rotation for the Data Set of Dicarboxylic Acids and Inorganic Ions in the Coarse Mode of Arctic Aerosols

Components	Factor 1	Factor 2	Factor 3
ozone	-0.08	-0.63	-0.65
C_2	0.31	0.87	0.27
C_3	0.29	0.92	0.09
C_4	0.13	0.97	0.15
C_5	0.17	0.98	0.10
C_6	-0.16	0.86	0.11
Cl^-	0.96	0.14	0.11
Br^-	0.31	0.53	0.62
NO_3^-	0.91	0.00	0.13
SO_4^{2-}	0.56	0.51	-0.58
Na^+	0.97	0.16	0.06
NH_4^+	-0.17	-0.17	-0.73
K^+	0.91	0.31	0.21
Mg^{2+}	0.90	0.31	0.27
Ca^{2+}	0.93	-0.03	-0.11
Variance	0.39	0.36	0.13