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Time-resolved variations in the distributions of inorganic ions, carbonaceous components, dicarboxylic acids and related compounds in atmospheric aerosols from Sapporo, northern Japan during summertime

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Abstract

To better understand time-resolved variations of water-soluble organic aerosols in the atmosphere, we collected atmospheric particles (TSP) every 3 h during summertime (8-10 August, 2005) in Sapporo, northern Japan. We measured inorganic ions, carbonaceous components, dicarboxylic acids, ketoacids and α-dicarbonyls in TSP. SO_4^{2-} was found as the most abundant ionic species (57 ± 9% of total ions determined) followed by NH_4^+ and NO_3^-. However, none of the ionic species showed any diurnal trend throughout the campaign. Organic carbon (OC) ranged from 2.1 to 12.1 μg m^{-3} whereas elemental carbon (EC) was negligible in most of the samples (0.31 ± 0.56 μg m^{-3}). Oxalic (C_2) acid was the most abundant diacid species, followed by malonic (C_3) and succinic (C_4) acids. Water-soluble OC (WSOC), water-insoluble OC (WIOC) and OC as well as dominant diacids (C_2-C_4), total diacids, ketoacids and α-dicarbonyls did not show diurnal trend on 8 August, but they showed clear diurnal distributions during 9-10 August following the changes in ambient temperature (and radiation). Detailed analyses of time-resolved aerosols demonstrate that diurnal variations of organic aerosol compositions are caused by local in situ photochemical production, but are significantly superimposed by long-range atmospheric transport of aerosols, particularly when the air masses are enriched with emissions from higher plants and/or biomass burning, and their photochemical processing during the transport.

Keywords: Inorganic ions; Organic carbon; WSOC; Dicarboxylic acids; Ketoacids; α-Dicarbonyls; Time-resolved variation; Long-range transport

1. Introduction

Atmospheric aerosols have serious impact on Earth's radiative balance and hydrological cycle (Ackerman et al., 2000; Ramanathan et al., 2001), and have adverse effects on human health (Nel, 2005). The impacts of aerosols largely depend on their abundance and chemical composition. Organic carbon (OC) and SO_4^{2-} are highly reflective against solar light and thus cause cooling effect on the Earth surface (Hay-wood and Ramaswamy, 1998). Water-soluble OC (WSOC) and in particular dicarboxylic acids, ketoacids and α-dicarbonyls alter the chemical and physical properties of aerosols and enhance their cloud condensation nuclei (CCN) activity (Giebl et al., 2002; Kawamura and Usukura, 1993) and thus regulate the indirect radiative effect and hydrological cycle (Albrecht, 1989; Twomey, 1977). Atmospheric aerosols are directly emitted from fossil fuel combustion, biomass burning, soil dust and biosphere and are secondarily formed by photo-oxidation of gas phase precursors in the atmosphere. Organic aerosols (OA), which represent a large fraction (up to 90%) of fine particles (Kanakidou et al., 2005), consist of secondary organic aerosol (SOA) as dominant fraction (60-90%) in various environments (Zhang et al., 2007). SOA is produced by ozone or radical-initiated oxidations of hydrocarbon precursors, resulting in low-volativity products which can form new particles or adsorb on pre-existing particles (Kavouras et al., 1998). On the other hand, in-cloud processing (aqueous chemistry) has been considered as a major formation pathway of SOA (Ervens et al., 2004; Lim et al., 2010 and references therein).

Photochemical production of dicarboxylic acids and related compounds under controlled laboratory conditions has been reported (Hatakeyama et al. 1985; Tedetti et al., 2007). Based on field experiments, Kawamura and Ikushima (1993) reported enhanced concentrations of C_2-C_6 diacids in urban aerosols in summer. Kawamura et al. (1996) found a drastic increase in the concentrations of diacids in the Arctic atmosphere by a factor of 5-20 from the dark winter to light spring, supporting the photochemical production of diacids in the atmosphere. Recently, Kawamura and Yasui (2005) reported diurnal changes in the distributions of diacids, ketoacids and α-dicarbonyls in atmospheric aerosols collected every 3 h during summer and winter from Tokyo. They interpreted the diurnal distributions by photochemical production. On the other hand, Fu and Kawamura (2011) found a strong diurnal variation in the distributions of isoprene oxidation products in forest aerosols collected every 4 h during summer in Hokkaido, Japan but no such trends were detected in the oxidation products of α/β-pinene and β-caryophyllene. Warneke et al. (2004) reported diurnal variations in mixing ratios of isoprene, monoterpenes, and aromatics in the marine atmosphere along the coast of New England and interpreted the results as their emissions and the abundance of the oxidants. These results indicate that the type (origin) of precursors should influence the diurnal variations of SOA, due to differences in their reactivity and the type of oxidants.

On the other hand, diurnal variations of OA may also be variable if the aerosols are transported from distant sources and are subjected to atmospheric processing during the transport and/or mixed with primary emissions along the transport pathway. Aggarwal and Kawamura (2008) reported no systematic diurnal trend on a day/night basis in the distributions of diacids as well as their mass fractions in total carbon (TC) in Sapporo aerosols, which were considered as aged aerosols. In contrast, Pavuluri et al. (2010) reported a weak daytime maximum in diacid-C/TC in tropical Indian aerosols, which might be influenced by mixing of primary emissions along the transport pathway. In order to better understand the day- and night-time chemistry of atmospheric aerosols, time-resolved studies on both inorganic and organic aerosols are needed, however, such studies are very limited (Kawamura and Yasui, 2005; Fu and Kawamura, 2011). In particular, the plausible influence of different sources on diurnal distributions of OA is not yet understood at molecular levels.

Here we report time-resolved variations in the distributions of inorganic ions, carbonaceous components, diacids, ketoacids and α-dicarbonyls in atmospheric aerosols (TSP) collected every 3 h for 3-day period during summer in Sapporo, northern Japan. Interestingly, the backward air mass trajectories that arrived in Sapporo during the campaign originated from three different regions, providing a unique opportunity to examine the importance of long-range transport of pollutants from different source regions (origins) that may significantly influence the compositions of organic aerosols. We discuss the analytical results in terms of local photochemical processing and long-range atmospheric transport of OA.

2. Experimental

2.1. Aerosol sampling and analyses

Aerosol (TSP) sampling was performed for 3-day period from 8-10 August, 2005 on the rooftop of the 3-story building of Institute of Low Temperature Science, Hokkaido University, Sapporo, northern Japan (43.07°N, 141.36°E). University campus is surrounded mainly by residential area, and the sampling point is at least ca. 500 m away from the main streets. Aerosol samples were collected with 3 h interval with sampling hours: 1-4, 4-7, 7-10, 10-13, 13-16, 16-19, 19-22, and 22-1 h on local time using a high volume air sampler (Kimoto AS-810B) and pre-combusted (450°C, 4 h) quartz fiber filters (Pallflex 2500QAT-UP, 20 × 25 cm). The sample filter was placed in a pre-heated glass jar with a Teflon-lined screw cap and stored in darkness at -20°C prior to analysis. Field blank was collected at the end of the sampling by setting the filter in the cartridge of the air sampler without sucking the air.

TSP mass was gravimetrically measured by the mass difference of each filter before and after sampling. The filters were conditioned in a desiccator for ca. 48 h before and after sampling.

Inorganic ions (anions: Cl^-, NO_3^- and SO_4^{2-}; cations: Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured as described in Wang et al. (2005). Briefly, an aliquot of filter (ca. one-twentieth) was extracted with 20 ml Milli-Q water under ultra sonication for 20 min. The extracts were then filtered using a syringe filter (Millex-GV, 0.22 μm, Millipore) and inorganic ions were determined using ion chromatograph (Dionex-500). For each sequence of sample analysis, a calibration curve was evaluated by the analysis of a set of authentic standards. Analytical error in duplicate analysis of filter sample was within 4% for all the ions.

OC and EC were determined using OC/EC Analyzer (Sunset Laboratory Inc., USA) following Interagency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol and assuming carbonate carbon to be negligible. Briefly, a filter disc (1.5 cm^2) was placed in a quartz sample boat inside the thermal desorption chamber of the analyzer and then stepwise heating was applied (Wang et al. 2005). The evolved CO_2 at each temperature step was measured directly by a non-dispersive infrared (NDIR) detector system. A He-Ne laser was used for setting up OC/EC split point and thereby OC correction. The sum of OC and EC was considered as TC. Analytical errors in duplicate analysis were within 8%.

An aliquot of filter (2 discs with 3 cm in diameter) was extracted with organic-free Milli-Q water (5 ml × 3) under ultra sonication for 5 min. The extracts were then combined and filtered using a syringe filter (Millex-GV, 0.22 μm, Millipore) and then the water-soluble organic carbon (WSOC) was measured using TOC analyzer (Shimadzu 5000A) (Wang et al., 2005). The difference between OC and WSOC was considered as water-insoluble OC (WIOC). Analytical error in duplicate analysis was within 8%.

Dicarboxylic acids, ketoacids and α-dicarbonyls were determined by the method reported elsewhere (Kawamura, 1993; Kawamura and Ikushima, 1993). Briefly, one fifth of the filter was extracted with organic-free Milli-Q water (10 mL × 3) under ultra sonication for 10 min. The extracts were concentrated to near dryness and then derivatized to dibutyl esters and/or dibutoxy acetals with 14% BF_3/n-butanol at 100°C. The derivatives were extracted with *n*-hexane and then quantified using a capillary GC-FID (HP 6890). Identification of the compounds was performed by GC retention times and mass spectral examination using a GC-MS (Thermo Trace MS) system. Field blanks showed small peaks for oxalic, phthalic and glyoxylic acids but their amounts are less than 2% of the actual samples. The error in replicate injection for GC-FID was within 4% and the analytical error in duplicate analysis of filter sample for major diacid species was within 12%.

Concentrations of inorganic ions, carbonaceous components and diacids and related compounds reported here are corrected for the field blank.

2.2. Meteorology and air mass trajectories

Hourly meteorological data, which were obtained at a meteorological station located ca. 2 km away from the sampling point, were supplied by Japan meteorological agency, Japan (http://www.data.jma.go.jp) for the period of sampling. Figure 1 shows the variations of 3 h averages of ambient temperature, solar radiation, relative humidity (RH) and wind speed and direction. No rainfall was observed during the campaign.

Ten-day backward trajectories of air masses that arrive in Sapporo at an altitude of 500 m during the campaign were computed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2012). In order to obtain the representative air mass trajectory for each and every sample, the flow pattern was updated every 3 h by setting the ending time of each sample collection as the time of trajectory arrival in Sapporo.

3. Results and Discussion

3.1. Compositions and time-resolved variations

Concentrations of aerosol mass and inorganic ions, carbonaceous components, dicarboxylic acids, ketoacids and α-dicarbonyls in TSP are given in Table 1. Carbonaceous components, diacids, ketoacids and α-dicarbonyls mass ratios in OC and their correlation coefficients with WSOC are also provided in Table 1. Time-resolved variations of TSP, inorganic ions, and carbonaceous components, diacids and related compounds are shown in Figures S1 and S2, respectively. TSP masses did not show any clear trend on 8 August but showed diurnal pattern during 9-10 August (see Fig. S1).

3.1.1. Inorganic ions

SO_4^{2-} was found as the most abundant ionic species (57 ± 9% of total ions determined) followed by NH_4^+ (25 ± 2%) and NO_3^- (10 ± 4%). Average concentrations of SO_4^{2-} (6.0 μg m^{-3}) and NH_4^+ (2.4 μg m^{-3}) were comparable to those (5.2 μg m^{-3} and 2.5 μg m^{-3}, respectively) reported in Sapporo aerosols collected from the same sampling site during May to July 2005 whereas concentrations of other ions (Cl^-, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+}) were lower by a factor of 1.4-8.5 (Table 1) (Aggarwal and Kawamura, 2009). The comparability of SO_4^{2-} and NH_4^+ indicate that the secondary aerosol formation in August is similar to that in previous months (May-July). In contrast, the lower concentrations of other ions in August are likely due to a decreased contribution of Asian dusts, which are enriched with pollutants from China in spring (March-May).

Time-resolved variations of all ions did not show any clear diurnal pattern, except for NO_3^-, SO_4^{2-} and NH_4^+, which showed a diurnal trend on 10 August (see Fig. S1). The concentrations of NO_3^-, SO_4^{2-} and NH_4^+ minimized at 13-16 h on 8 August and then NO_3^- suddenly increased to maximize at 19-22 h on the same day. On the other hand, SO_4^{2-} and NH_4^+ gradually increased showing a peak in the afternoon (13-16 h) on 9 August (see Fig. S1). In contrast, meteorological parameters such as temperature, radiation and RH showed a clear diurnal trend during whole period of the campaign (Fig. 1). In addition, the trends of K^+, a tracer of biomass burning, and NH_4^+, which is significantly derived from biomass burning, were comparable on 8 August but is not comparable in the rest of the campaign. On the other hand, NO_3^- that is mainly derived from anthropogenic sources was much more abundant on 9 August than on 8 and 10 August. Such a different day-to-day trend of ionic species suggest that the Sapporo aerosols are seriously affected by long-range atmospheric transport of air masses originated from different source regions and by their atmospheric processing during long-range transport rather than local photochemistry.

3.1.2. Carbonaceous components

Average concentration of OC (6.7 μg m^{-3}) is comparable to that (7.4 μg m^{-3}) reported in May-July, 2005 whereas that of EC is three times lower (Table 1) (Aggarwal and Kawamura, 2009). It is also of noteworthy that the average concentration of WSOC (3.2 μg m^{-3}) is comparable to that (3.1 μg m^{-3}) reported in May-July (Table 1) (Aggarwal and Kawamura, 2009). In fact, EC was found to be below the detection limit in most of the samples and did not show any trend (see Fig. S1). These results indicate that contribution of SOA formation to OC in August is similar to that in May-July, however, the contribution of primary aerosols may not be similar probably due to the difference in source regions between two seasons.

Time-resolved variations of OC, WSOC and WIOC did not show any trend on 8 August but they showed some diurnal distributions on 9 August. Their concentrations started to increase from early (1-4 h) to morning hours (7-10 h) and stayed relatively constant until evening hours (16-19 h) on 9 August. In contrast, on 10 August they showed a clear diurnal trend with a maximum at 13-16 h (see Fig. S1), following clear diurnal variations of temperature, radiation and RH (Fig. 1). Further, the concentrations of WSOC were higher than WIOC on 8 August, except for two samples, whereas WSOC became more abundant than WIOC on 9 August only in the morning to late afternoon hours (7-16 h) (see Fig. S1). In contrast, the concentrations of WIOC were higher than WSOC on 10 August, except for noontime (13-16 h) sample (see Fig. S1). These results demonstrate that the sources of WSOC and WIOC and their formation pathways were different from day-to-day during the campaign. Such a difference may be caused by long-range transport of air masses originated from different regions rather than local source and photochemistry. The higher levels of WSOC than WIOC, especially on 8 August, (see Fig. S1) further suggest that the secondary production of OA is significant during long-range atmospheric transport.

3.1.3. Dicarboxylic acids, ketoacids and α-dicarbonyls

A homologous series of normal (C_2-C_{12}) and branched (iso C_4-C_6) saturated α,ω-diacids, unsaturated aliphatic (maleic, fumaric and methylmaleic) and aromatic (phthalic, isophthalic and terephthalic) diacids and the diacids with an additional functional group (malic, ketomalonic and 4-ketopimelic) were detected in aerosols, together with ω-ketoacids (C_2-C_4 and C_9), α-ketoacid (pyruvic) and α-dicarbonyls (glyoxal and methylglyoxal) (Table 1). In all the samples, oxalic (C_2) acid was found as the most abundant species followed by malonic (C_3) and succinic (C_4) acids (Table 1). Their relative abundances in total diacids were 42%, 21% and 16%, respectively. Interestingly, phthalic (Ph) acid was the fourth most abundant species and glutaric (C_5), oxopimelic (kC_7) and oxomalonic (kC_3) acids were found to be higher than azelaic (C_9) acid (Table 1), which is a specific oxidation product of unsaturated fatty acids (Kawamura et al., 1996) and is relatively abundant in aerosols. The branched C_4-C_6 diacids were much lower than the corresponding normal structures (Table 1). Glyoxylic (ωC_2) acid was the most abundant ketoacid species followed by pyruvic (Pyr) acid whereas methylglyoxal (mGly) was abundant than glyoxal (Gly) (Table 1). Although molecular distributions of diacids and related compounds in this study are quite similar to those reported in May-July, concentrations of C_3, C_4, Ph, isophthalic (*i*-Ph), terephthalic (*t*-Ph), kC_3 and kC_7 acids and mGly were significantly higher than those reported in May-July (Aggarwal and Kawamura, 2008).

Being similar to WSOC and OC (see Fig. S1), none of the diacid, ketoacid and α-dicarbonyl species showed any clear diurnal trend on 8 August but most of them (C_2-C_7, iC_4-iC_6, Ph, *i*Ph, *t*Ph, ωC_2, ωC_4, Pyr, Gly and mGly) showed a diurnal distribution on 9 and 10 August (see Fig. S2). Although all the other species (C_8, C_9, M, mM, F, hC_4, kC_3, kC_7, ωC_3 and ωC_9) did not show a clear diurnal distribution, their concentrations were relatively lower in nighttime than in daytime (see Fig. S2). It is also important to note that the peak of every species, except for C_8 diacid, at 10-13 h on 8 August (see Fig S2) was consistent with that of WSOC (see Fig. S2). Interestingly, individual species of diacids (except for kC_7), ketoacids and α-dicarbonyls as well as total diacids, ketoacids and α-dicarbonyls showed a positive correlation (p=0.01 or 0.05) with WSOC (Table 1). Further, the time-resolved variations of total diacids, ketoacids and α-dicarbonyls were highly consistent with those of WSOC and OC (see Fig. S3). These results suggest that secondary processes may control concentrations of diacids and related compounds and in turn their formation pathways should have been different from day-to-day during the campaign.

3.2. Relative abundance of WSOC, diacids, ketoacids and α-dicarbonyls in OC

Figure 2 shows time-resolved changes in the contributions of WSOC as well as total diacids, ketoacids and α-dicarbonyls to OC. The contributions of WSOC, diacids, ketoacids and α-dicarbonyls did not show any clear trend on 8 August although their changes are similar each other on that day (Fig. 2). This suggests that the contributions of photochemically produced WSOC, diacids and related compounds during long-range atmospheric transport may be significant in addition to local in situ photochemical production. On 9 and 10 August, the contributions of both WSOC and diacids to OC showed a different diurnal trend each other (Fig. 2a, b). On 10 August WSOC/OC gradually increased from early morning to late afternoon followed by a decrease in the evening. The diacid-C/OC ratios increased from morning hours toward midnight (Fig. 2a, b). The relative abundances of C_2-C_4 and C_9 diacids in OC showed a diurnal variation with a maximum at 19-22 or 22-1 h on 9 and 10 August (Fig. 3). However, other diacids did not show such a diurnal variation (not shown as a figure). The abundances of ketoacids and α-dicarbonyls relative to OC stayed almost constant (Fig. 2c, d).

The higher WSOC/OC ratios in daytime can be explained by enhanced photochemical production of WSOC from biogenic and/or anthropogenic gaseous precursors. Grieshop et al. (2009) found a substantial increase in OA by a factor of 1.5 to 2.8 after several hours of exposure of wood burning emissions under plume-like conditions to OH radicals with concentrations typical to summer. Several studies reported a good correlation between oxygenated organic aerosol (OOA) and other aerosol species such as SO_4^{2-} and NO_3^-, suggesting a significant contribution of anthropogenic water-soluble SOA (Zhang et al., 2007). The continuous increase in the abundances of C_2-C_4 and C_9 diacids relative to OC can be explained by the production even in darkness if the oxidant (e.g., NO_3, an important oxidant at night; Finlayson-Pitts and Pitts, 2000) and levels of organic precursors are significant. In addition, the secondary production of these diacids, especially C_2-C_4 diacids, possibly overwhelms their degradation and/or deposition. Kawamura and Yasui (2005) also found a continuous increase in diacid-C/TC mainly due to the production of C_2-C_4 diacids in urban aerosols in the afternoon with the peak at 11-14 h during summer (June).

The differences in diurnal variations of C_2-C_4 and C_9 diacids and other species including ketoacids and α-dicarbonyls may be due to a difference in their precursors, formation pathways and/or atmospheric scavenging either by decomposition or deposition. C_2-C_4 diacids are produced from common precursors including unsaturated and saturated hydrocarbons, monocarboxylic acids, aldehydes, ketoacids, etc. whereas C_9 diacid is specifically produced by the oxidation of unsaturated fatty acids (Kawamura et al., 1996). Unsaturated and branched-chain diacids have been considered to generate via photochemical oxidation of more specific precursors such as aromatic hydrocarbons (Kawamura et al., 1996; Fisseha et al., 2004) and cycloalkenes (Grosjean and Fung, 1984) by OH radicals rather than O_3 (Finlayson-Pitts and Pitts, 2000). α-Dicarbonyls are produced by photochemical oxidation of biogenic (isoprene) and anthropogenic (aromatic) hydrocarbons and are further oxidized to keotacids and then to oxalic acid (Lim et al., 2005; Warneck, 2003).

The lower amplitudes in diurnal variations of relative abundances of diacid species (not shown as a figure) other than C_2-C_4 and C_9 (Fig. 3), total ketoacids (Fig. 2c) and α-dicarbonyls (Fig. 2d) are most likely due to large contributions of aged aerosols rather than local emissions and/or photochemical production. Interestingly, diurnal distributions of the relative abundances of diacids, ketoacids and α-dicarbonyls in OC in Sapporo aerosols (Fig. 2) are not comparable to those in TC in winter- and summer-time aerosols from Tokyo where local anthropogenic emissions are more important than long-range transport of organic pollutants, which showed a maximum at 8-11 h or 11-14 h (Kawamura and Yasui, 2005). On the other hand, the unclear trend of diacid-C/TC ratios on 8 August is similar to that reported for Sapporo aerosols collected on day/night basis during May-July (Aggarwal and Kawamura, 2008), in which the contribution of long-range transport of aged aerosols was considered to be more significant. These comparisons further support an importance of aerosols originated from distant sources and their photochemical processing during long-range transport in the atmosphere of Sapporo.

3.3. Source regions (origins) of aerosols

As plotted in Figure 4, 10-day backward air mass trajectories arriving in Sapporo at 500 m above the ground level during the campaign showed three distinct source regions and transport pathways. The air masses that arrived in Sapporo at 4 JST on 8 to 10 JST on 9 August originated from Siberia (Region #1) whereas those at 13 h on 9 to 1 h on 10 August originated from northeastern China and/or the East China Sea passing over and near the Asian continent (region #2). During 4 h on 10 to 1 h on 11 August, the air masses mostly originated from the western North Pacific (Region #3). Although we cannot preclude the mixing of emissions from different sources along the transport pathway, the air masses coming from regions #1, #2 and #3 should have more involved with (1) biogenic emissions and biomass burning, (2) anthropogenic emissions, and (3) marine emissions, respectively. Unfortunately, we do not have any data of molecular tracer or isotopic signature to estimate the extent of such source contributions.

However, we examine the source types in each region, following the mass concentration ratios of nss-K^+, NO_3^- and WSOC to OC. It is well established that K^+ and NO_3^- are mostly derived from biomass burning (Andreae, 1983) and anthropogenic emissions, respectively. WSOC is more enriched in atmospheric aerosols influenced by higher plant and biomass burning emissions (Kiss et al., 2002; Miyazaki et al., 2012) whereas WIOC is more enriched in aerosols influenced by anthropogenic (Favez et al., 2008) and marine (Facchini et al., 2008) emissions. As shown in Fig. 5, nss-K^+/OC ratios in cat #1 and #2 were higher than those in cat #3 whereas NO_3^-/OC ratio in cat #2 was higher than those in cat #1 and #3, suggesting that the anthropogenic emissions are significantly higher in region #2 whereas biomass burning emissions may be more significant in both regions #1 and #2. Interestingly, WSOC/OC ratio was higher in cat #1 than in cat #2 followed by cat #3 (Fig. 5). In fact, the fraction of WSOC in OC (56.3 ± 19.6%) in cat #1 is comparable to that (66%) in fine ($D_p \leq$ 1.5 μm) aerosols that were collected from a forest-clearing site on the Great Hungarian Plain (Kiss et al., 2002). The fraction of WSOC in OC (38.1 ± 7.7%) in cat #3 is consistent to that (WIOC/OC = 77 ± 5%) in marine aerosols collected during periods of high ocean biological activity in the North Atlantic (Facchini et al., 2008). These results suggest that the emissions from biological source and biomass burning (region #1), anthropogenic (#2) and marine (#3) sources are major source origins, respectively.

Hence, we classify the samples collected at 1-4 h on 8 August to 7-10 h on 9 August (n=11), 10-13 h to 22-1 h on 9 August (n=5), and 1-4 h to 22-1 h on 10 August (n=8) into three categories: cat #1, cat #2 and cat #3, following their source regions #1, #2 and #3, respectively, to examine the influence of source regions on time-resolved variations of OA.

3.4. Influence of long-range transport on diurnal variations of organic aerosols

Emissions of biogenic volatile organic compound (BVOC) increase with an increase in temperature (Peñuelas and Llusià, 2001; Ruuskanen et al., 2007; Tambunan et al., 2006). Emissions from mobile sources that significantly contribute to anthropogenic VOCs are generally larger during the day than night (Niemeier, 2003). The VOCs are immediately oxidized in gas phase to result in less volatile species that form new particles and/or adsorb on pre-existing particles (Kavouras et al., 1998; 1999 and references therein), causing a clear diurnal distributions of their oxidation products. However, the occurrence of such trend depends on not only the VOC emissions but also the concentrations of the oxidants such as OH, NO_3 and O_3. For example, biogenic VOCs such as isoprene and α/β-pinene rapidly react with both OH and NO_3 whereas anthropogenic VOCs such as alkanes, alkenes and aromatics react only with OH or react very slowly with NO_3, and the O_3 initiated oxidation plays a relatively minor role in both cases (Warneke et al., 2004). OH initiated oxidation is the main pathway during daytime whereas the reactions with NO_3 become more significant during nighttime when the photolytic source of OH becomes very small and the NO_3 mixing ratios increase significantly.

Because the formation and destruction of oxidants are associated with temperature (and radiation), the relations of organics with these parameters demonstrate their day- and night-time chemistry and thus the importance of formation pathways. As shown in Figure 6, OC, WSOC, total diacids, ketoacids and α-dicarbonyls do not give any significant relation to ambient temperature in cat #1. However, they show good correlations in cat #2 and cat #3, except for diacids in cat #3. They further present similar relations ($r = 0.61\sim0.91$) with radiation, except for diacids ($r = -0.19$) and ketoacids ($r = 0.39$) in cat #3 samples (not shown as a figure). In addition, the relations of OC to temperature (and radiation) are comparable to those of WSOC, diacids, ketoacids and α-dicarbonyls (Fig. 6), suggesting that a major fraction of OA is secondarily produced in the atmosphere during the campaign. As discussed in the previous section, long-range transport of organic aerosols was significant in Sapporo during whole period of the campaign. These results suggest that the weak correlations of OC, WSOC, diacids, ketoacids and α-dicarbonyls with temperature (and radiation) in cat #1 should have been associated with long-range atmospheric transport of organic aerosols derived from terrestrial higher plants as well as biomass burning. Strong correlations in cat #2 and cat #3 might be caused by local photochemical oxidation of anthropogenic (fossil fuel combustion) and marine (phytoplankton) organic precursors.

The air masses that originated from Siberia (region #1) and thus cat #1 samples may have been enriched with monoterpene oxidation products because ca. 90% of biogenic VOCs emitted from Siberian larch in summer are monoterpenes, in which sabinene accounts for almost half with other major species of Δ^3-carene and α/β-pinene, followed by sesquiterpenes and isoprene (Ruuskanen et al., 2007). As noted earlier, monoterpenes readily react with OH and NO_3 (see Table S1; Atkinson et al., 1990) and their oxidation products (semi- and non-volatile intermediate compounds) may involve in further oxidation reactions forming next-generation organic species. Such reactions may continue preferably in aqueous phase during long-range atmospheric transport. Hence, it is apparent that the diurnal distributions of SOA produced from monoterpenes may not show any diurnal trend. Recently, Ding et al. (2011) reported a poor correlation between α-pinene SOA tracers and temperature in South China whereas Fu and Kawamura (2011) found no clear trends in the distributions of α/β-pinene- and β-caryophyllene-oxidation products in forest aerosols. These studies further support our results and interpretations.

On the contrary, the air masses that originated from Northeast Asia (region #2) should be enriched with anthropogenic VOCs such as alkenes, aromatics and oxygenated compounds, which react mostly with OH radicals (see Table S1; Atkinson, 1984; 1994). Hence, it is obvious that the distributions of their oxidation products should show a diurnal trend especially if the local emissions are significant. Kawamura and Yasui (2005) also reported clear diurnal distributions of diacids and related compounds in the Tokyo atmosphere where anthropogenic emissions are dominated. Although the long-range transported aerosols are significant in Sapporo, diurnal variations in the distributions of OA and their positive relations with temperature and (and radiation) are likely because the short-chain oxygenated (intermediate) compounds such as acetone and acetaldehyde produced from precursors preferably react with OH rather than NO_3 (see Table S1).

Similarly, the air masses originated from the western North Pacific (region #3) may be enriched with non-methane hydrocarbons (NMHCs) because of larger emission of NMHCs from phytoplankton in summer, in which alkenes such as ethene, propene, butene and isoprene are predominant (Broadgate et al., 1997; Matsunaga et al., 2002). In addition, the contribution of isoprene from higher plants should have also been significant as the air masses passed over Okinawa Island, Japan where isoprene emissions from the plants are significant (Tambunan et al., 2006). Except for isoprene whose rate constant with OH and NO_3 at 298 K is 101×10^{-12} and 0.68×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively (Atkinson, 1984; 1994), all other alkenes react mostly with OH radicals (see Table S1). Further the oxidation products of isoprene, such as methacrolein and methyl vinyl ketone, also react mostly with OH radicals (see Table S1; Atkinson, 1984; 1994). Fu and Kawamura (2011) found a strong diurnal variation of the isoprene oxidation products in forest aerosols. Hence, clear diurnal variations in the distributions of OA and good relations with temperature (and radiation) in Sapporo aerosols are very likely on 9 and 10 August.

4. Summary and Conclusions

This study presents time-resolved variations of inorganic ions, carbonaceous components, diacids, ketoacids and α-dicarbonyls in atmospheric aerosols collected from Sapporo, northern Japan for 3 consecutive days in summer. Despite clear diurnal variations of meteorological parameters (temperature, radiation and RH), all inorganic ions did not show any diurnal trend, suggesting that their variations depend mainly on other factors such as the sources and atmospheric processing during long-range atmospheric transport. Time-resolved concentrations of OC, WSOC, total diacids, ketoacids and α-dicarbonyls did not show any temporal trend on 8 August but showed a clear diurnal variation on 9 and 10 August. The latter results suggest a significant contribution of secondary organic aerosol formation in

Sapporo. The contributions of WSOC and total diacids to OC showed a diurnal trend on 9 and 10 August, although their trends were not similar. In contrast, total ketoacid and dicarbonyl-C/OC stayed almost constant, indicating that the aged aerosols were transported from distant source regions during the campaign. Positive correlations of OC, WSOC, total diacids, ketoacids and α-dicarbonyls with temperature (and radiation) were obtained in categories #2 (from East Asia) and #3 (from the oceans). This study implies that long-range transport and local photochemical ageing depending on origins of precursors significantly influence temporal variations of organic aerosols in Sapporo, northern Japan.

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Figure captions

Fig. 1. Diurnal variations of ambient temperature, solar radiation, relative humidity (RH) and wind speed and direction during 8-10 August 2005 in Sapporo, northern Japan.

Fig. 2. Time-resolved variations of relative abundances of (a) water-soluble organic carbon (WSOC), (b) total dicarboxylic acids, (c) total ketoacids and (d) total α-dicarbonyls in organic carbon (OC) in aerosols (TSP) collected from Sapporo, northern Japan every 3 h during 8-10 August 2005.

Fig. 3. Time-resolved variations of relative abundances of (a) oxalic (C_2), (b) malonic (C_3), (c) succinic (C_4) and (d) azelaic (C_9) acids in organic carbon (OC) in aerosols (TSP) collected from Sapporo, northern Japan every 3 h during 8-10 August 2005.

Fig. 4. Plots of 10-day backward air mass trajectories arriving at an altitude of 500 m above Sapporo during 8-10 August 2005 showing three distinct pathways reflecting three different source regions: Siberia (Region #1), Northeastern China (Region #2) and Western North Pacific (Region #3).

Fig. 5. Mass concentration ratios of nss-K^+, NO_3^- and water-soluble organic carbon (WSOC) to organic (OC) in aerosols (TSP) collected every 3 h and temperature during 8-10 August 2005 at Sapporo, northern Japan. Cat #1, #2 and #3 represent the samples collected at 1-4 h on 8 August to 7-10 h on 9 August (n=11), 10-13 h to 22-1 h on 9 August (n=5), and 1-4 h to 22-1 h on 10 August (n=8), respectively.

Fig. 6. Scatter plots between organic carbon (OC), water-soluble OC (WSOC), total dicarboxylic acids, total ketoacids and total α-dicarbonyls in aerosols (TSP) collected every 3 h and temperature during 8-10 August 2005 at Sapporo, northern Japan. Cat #1, #2 and #3 represent the samples collected at 1-4 h on 8 August to 7-10 h on 9 August (n=11), 10-13 h to 22-1 h on 9 August (n=5), and 1-4 h to 22-1 h on 10 August (n=8), respectively.

Table 1. Concentrations of aerosol (TSP) mass and inorganic ions, carbonaceous components, dicarboxylic acids, ketoacids and α-dicarbonyls as well as mass fractions (%) of carbonaceous components and diacids and related compounds in OC and their correlation coefficients with WSOC in TSP collected from Sapporo, northern Japan every 3 h during 8-10 August, 2005[a].

	Concentration Ave. (Range)	Ave. % in OC	'r' with WSOC
TSP (µg m^{-3})			
	77.7 (46.1–121)		
Inorganic ions (µg m^{-3})			
Cl^-	0.13 (0.01–0.41)		
NO_3^-	0.90 (0.22–1.65)		
SO_4^{2-}	6.01 (0.79–12.0)		
NH_4^+	2.40 (0.53–3.9)		
Na^+	0.13 (BDL–0.43)		
K^+	0.14 (0.02–0.35)		
Mg^{2+}	0.04 (0.01–0.09)		
Ca^{2+}	0.33 (0.10–0.73)		
Carbonaceous components (µg m^{-3})			
EC	0.31 (BDL–1.92)	4.68	
OC	6.72 (2.13–12.1)		0.71
WSOC	3.16 (1.17–5.88)	48.8	
WIOC	3.54 (0.32–8.78)	51.2	0.21
Dicarboxylic acids (ng m^{-3})			
Oxalic (C_2)	196 (86.3–281)	0.87	0.55
Malonic (C_3)	102 (37.0–157)	0.58	0.67
Succinic (C_4)	74.4 (33.6–109)	0.50	0.67
Glutaric (C_5)	13.9 (5.40–22.9)	0.10	0.75
Adipic (C_6)	5.46 (2.18–10.3)	0.044	0.71
Pimelic (C_7)	1.07 (0.23–2.59)	0.009	0.68
Suberic (C_8)	1.19 (0.47–2.23)	0.010	0.73
Azelaic (C_9)	5.91 (3.25–11.7)	0.057	0.20
Sebacic (C_{10})	1.13 (BDL–13.2)	0.009	0.37
Undecanedioic (C_{11})	0.22 (BDL–2.95)	0.002	0.08
Dodecanedioic (C_{12})	0.07 (BDL–0.31)	0.001	0.27
Methylmalonic (iC_4)	2.24 (BDL–4.45)	0.016	0.42
Methylsuccinic (iC_5)	3.20 (0.94–7.86)	0.023	0.81
2-Methylglutaric (iC_6)	1.48 (0.38–3.60)	0.011	0.80
Maleic (M)	5.39 (3.01–12.9)	0.037	0.39
Fumaric (F)	1.72 (0.67–3.44)	0.011	0.63
Methylmaleic (*m*M)	3.60 (1.86–8.05)	0.027	0.58
Phthalic (Ph)	26.2 (14.6–44.6)	0.25	0.67
Isophthalic (*i*-Ph)	2.68 (0.14–5.88)	0.026	0.74
Terephthalic (*t*-Ph)	4.30 (1.37–8.61)	0.044	0.81
Malic (hC_4)	1.86 (0.46–3.20)	0.010	0.76
Oxomalonic (kC_3)	7.49 (2.66–15.1)	0.037	0.34
4-Oxopimelic (kC_7)	11.4 (2.21–71.9)	0.093	-0.02
Subtotal	473 (218–696)	2.77	0.67
Ketoacids (ng m^{-3})			
Glyoxalic (ωC_2)	27.3 (16.4–45.5)	0.14	0.85
3-Oxopropanoic (ωC_3)	0.26 (BDL–0.89)	0.001	0.45
4-Oxobutanoic (ωC_4)	7.27 (3.37–13.9)	0.053	0.81
9-Oxononanoic (ωC_9)	2.52 (0.75–6.24)	0.026	0.55
Pyruvic (Pyr)	9.37 (1.90–16.8)	0.059	0.79
Subtotal	46.7 (24.8–78.4)	0.28	0.88
Dicarbonyls (ng m^{-3})			
Glyoxal (Gly)	5.43 (2.39–11.1)	0.035	0.83
Methylglyoxal (*m*Gly)	9.13 (4.09–20.7)	0.073	0.79
Subtotal	14.6 (6.49–31.8)	0.11	0.82

[a] Ave. Average; BDL = Below Detection Limit.

Figure 1.

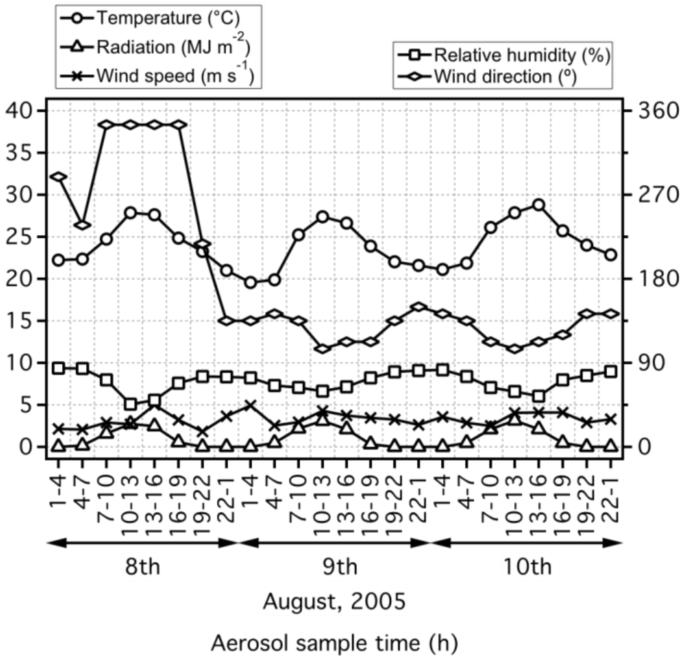

Temperature (°C)
Radiation (MJ m-2)
Wind speed (m s-1)
Relative humidity (%)
Wind direction (º)
40
35
30
25
20
15
10
5
0
360
270
180
90
0
1-4
4-7
7-10
10-13
13-16
16-19
19-22
22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Figure 2.

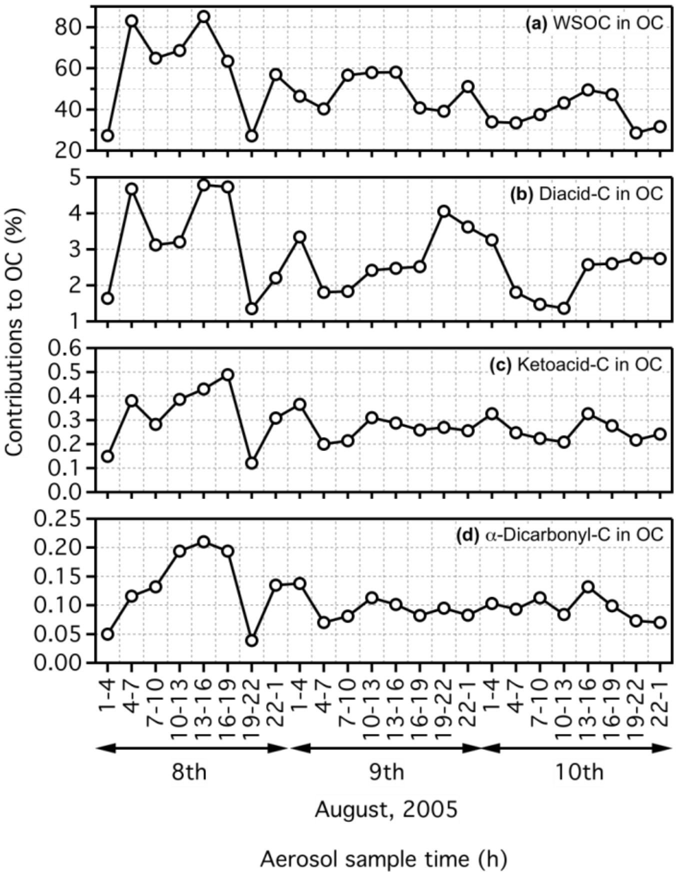

(a) WSOC in OC
80
60
40
20
(b) Diacid-C in OC
5
4
3
2
1
(c) Ketoacid-C in OC
0.6
0.5
0.4
0.3
0.2
0.1
0.0
(d) α-Dicarbonyl-C in OC
0.25
0.20
0.15
0.10
0.05
0.00
Contributions to OC (%)
1-4
4-7
7-10
10-13
13-16
16-19
19-22
22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Figure 3.

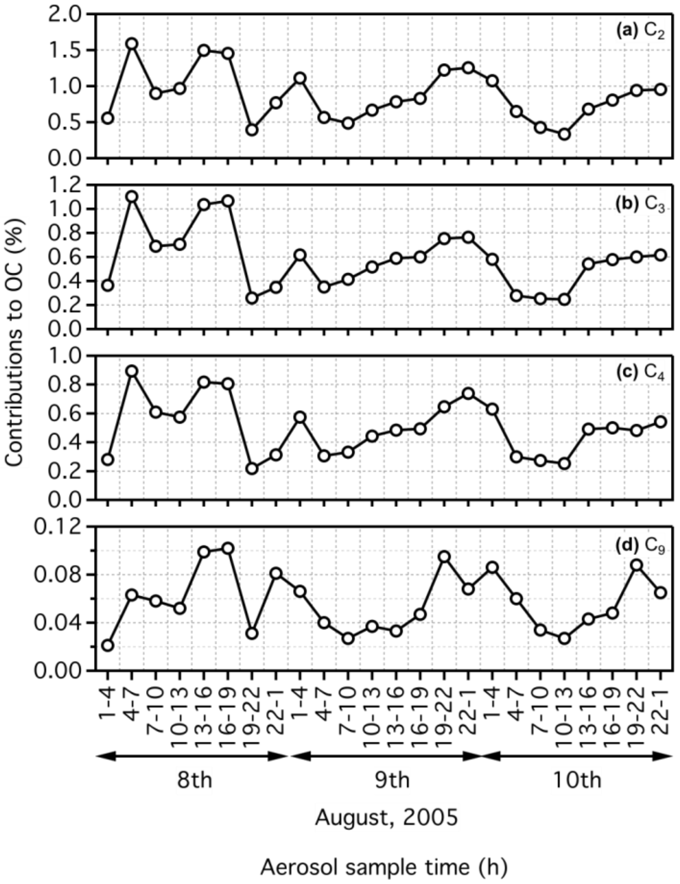

(a) C_2
(b) C_3
(c) C_4
(d) C_9
Contributions to OC (%)
2.0
1.5
1.0
0.5
0.0
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1.0
0.8
0.6
0.4
0.2
0.0
0.12
0.08
0.04
0.00
1-4
4-7
7-10
10-13
13-16
16-19
19-22
22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Figure 4.

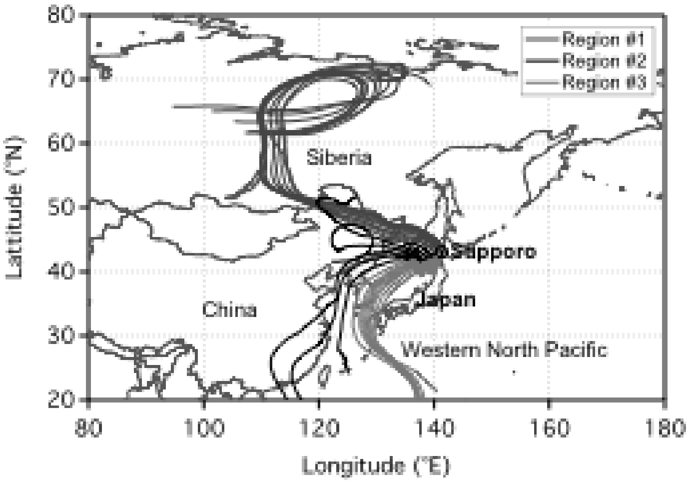

Region #1
Region #2
Region #3
Siberia
Sapporo
Japan
China
Western North Pacific
80
70
60
50
40
30
20
Latitude (°N)
80
100
120
140
160
180
Longitude (°E)

Figure 5.

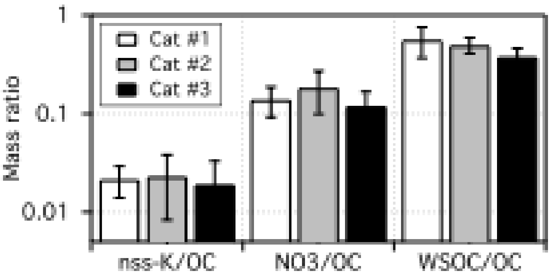
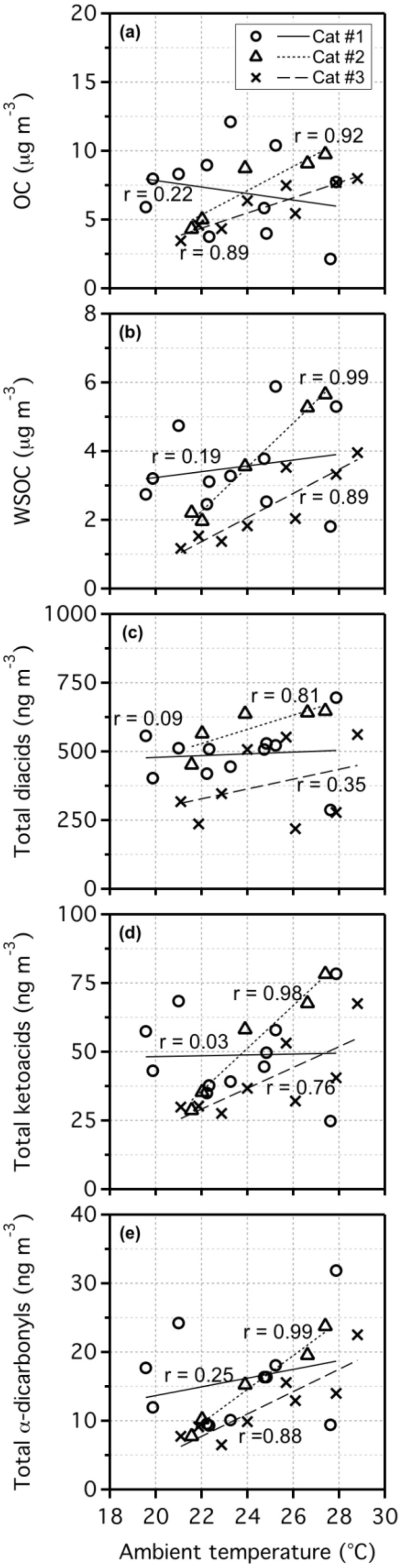


Figure 6.


(a)
OC (μg m^{-3})
Cat #1
Cat #2
Cat #3
r = 0.92
r = 0.22
r = 0.89
(b)
WSOC (μg m^{-3})
r = 0.99
r = 0.19
r = 0.89
(c)
Total diacids (ng m^{-3})
r = 0.81
r = 0.09
r = 0.35
(d)
Total ketoacids (ng m^{-3})
r = 0.98
r = 0.03
r = 0.76
(e)
Total α-dicarbonyls (ng m^{-3})
r = 0.99
r = 0.25
r =0.88
18 20 22 24 26 28 30
Ambient temperature (°C)

Supplement

Figure captions

Fig. S1. Time-resolved variations of concentrations of aerosol (TSP) mass and inorganic ions such as Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} and carbonaceous components such as organic carbon (OC), elemental carbon (EC), water-soluble OC (WSOC) and water-insoluble OC (WIOC) in TSP collected from Sapporo, northern Japan every 3 h during 8-10 August 2005.

Fig. S2. Time-resolved variations of concentrations of dicarboxylic acids, ketoacids and α-dicarbonyls in aerosols (TSP) collected from Sapporo, northern Japan every 3 h during 8-10 August 2005.

Fig. S3. Time-resolved variations of concentrations of total dicarboxylic acids, ketoacids and α-dicarbonyls in aerosols (TSP) collected from Sapporo, northern Japan every 3 h during 8-10 August 2005.

Figure S1.

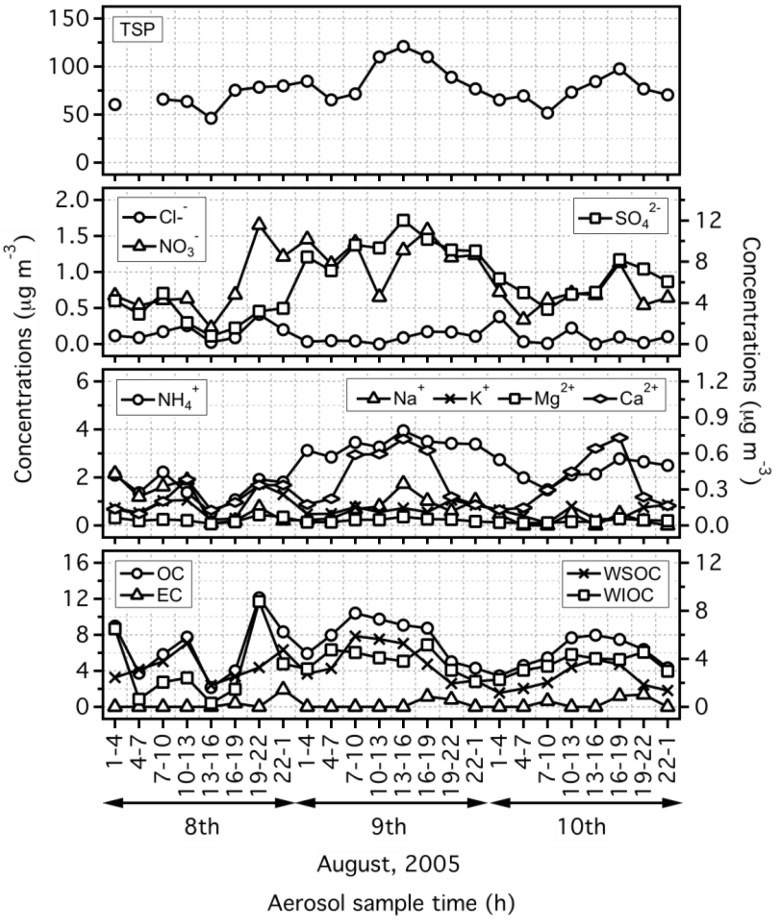
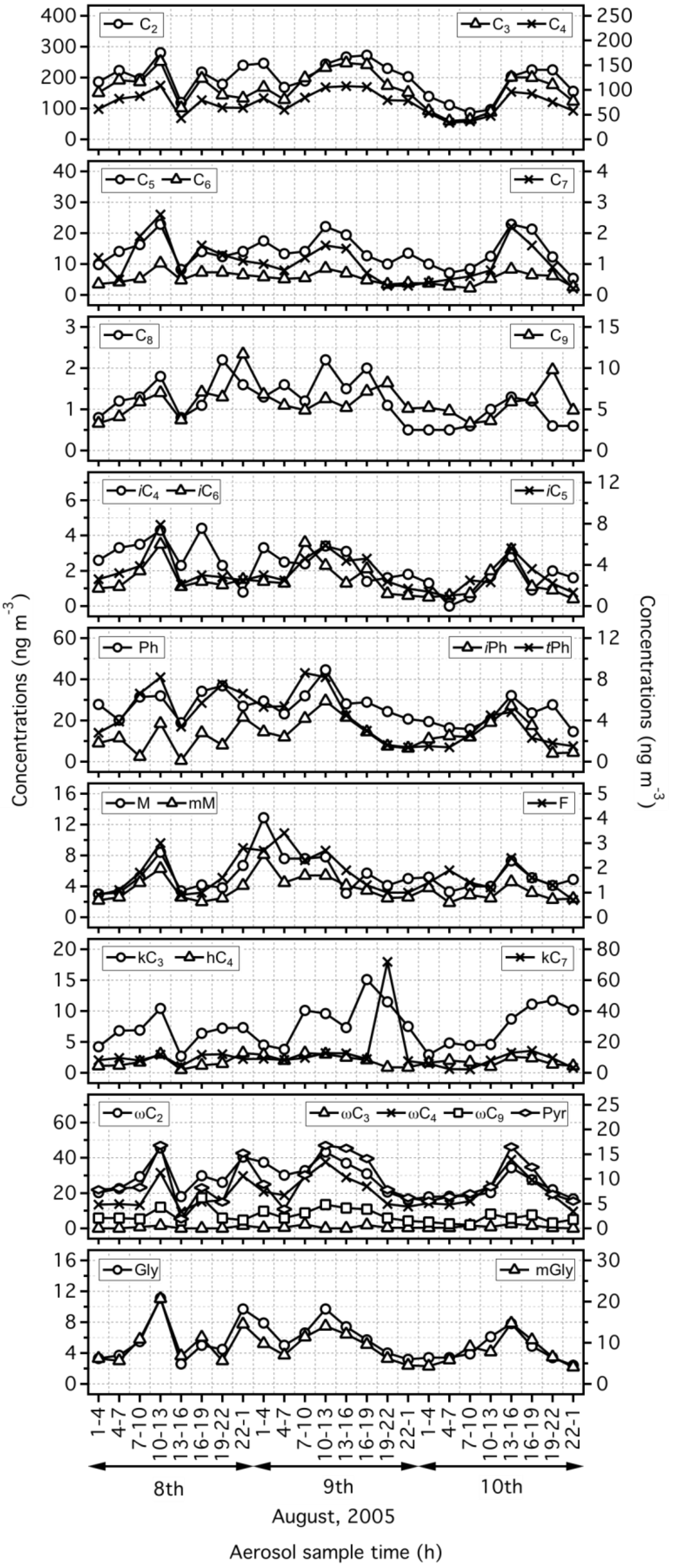

TSP
150
100
50
0
Cl-
NO_3^-
SO_4^{2-}
2.0
1.5
1.0
0.5
0.0
12
8
4
0
NH_4^+
Na^+
K^+
Mg^{2+}
Ca^{2+}
6
4
2
0
1.2
0.9
0.6
0.3
0.0
OC
EC
WSOC
WIOC
16
12
8
4
0
12
8
4
0
Concentrations (µg m^{-3})
Concentrations (µg m^{-3})
1-4
4-7
7-10
10-13
13-16
16-19
19-22
22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Figure S2.



C₂
C₃ C₄
C₅ C₆
C₇
C₈
C₉
iC₄ iC₆
iC₅
Ph
iPh tPh
M mM
F
kC₃ hC₄
kC₇
ωC₂
ωC₃ ωC₄ ωC₉ Pyr
Gly
mGly
0 100 200 300 400
0 50 100 150 200 250
0 10 20 30 40
0 1 2 3 4
0 1 2 3
0 5 10 15
0 2 4 6
0 4 8 12
0 20 40 60
0 4 8 12
0 4 8 12 16
0 1 2 3 4 5
0 5 10 15 20
0 20 40 60 80
0 20 40 60
0 5 10 15 20 25
0 4 8 12 16
0 10 20 30
Concentrations (ng m-3)
Concentrations (ng m-3)
1-4 4-7 7-10 10-13 13-16 16-19 19-22 22-1 1-4 4-7 7-10 10-13 13-16 16-19 19-22 22-1 1-4 4-7 7-10 10-13 13-16 16-19 19-22 22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Figure S3.

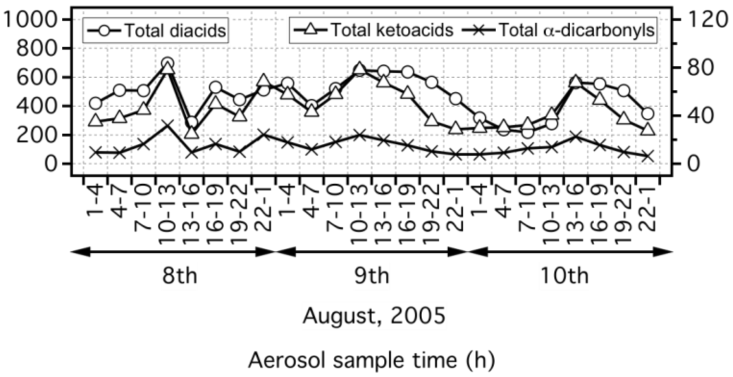

Total diacids
Total ketoacids
Total α-dicarbonyls
1000
800
600
400
200
0
120
80
40
0
1-4
4-7
7-10
10-13
13-16
16-19
19-22
22-1
8th
9th
10th
August, 2005
Aerosol sample time (h)

Table S1. Rate constants of selected compounds at 298 K[a].

Compound	k_{OH}	k_{NO3}
	$\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}	
Sabinen	117	10.1
Δ^3-carene	87.8	10.1
α-pinene	53.7	5.79
β-pinene	78.9	2.36
Ethene	8.52	0.00021
Propene	26.3	0.009
Benzene	1.23	<0.00006
Acetone	0.22	<0.00003
Acetaldehyde	15.8	0.0027
Methacrolein	33.0	0.33
Methyl vinyl ketone	19.0	0.06

[a] Rate constants are taken from Atkinson, 1994; Atkinson et al., 1990; Atkinson et al., 1984**.**