Determination of Dicarboxylic Acids and Levoglucosan in Fine Particles in the Kanto Plain, Japan, for Source Apportionment of Organic Aerosols

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ABSTRACT

Fine particles were collected at a suburban site in the inland Kanto plain, Japan, in the spring and winter of 2007, and the summer of 2008. Organic carbon (OC), water-soluble organic carbon (WSOC), elemental carbon (EC), inorganic ions, and water-soluble organic compounds (dicarboxylic acids and levoglucosan) were analyzed. The WSOC/OC ratio was the highest in summer, followed by in spring, suggesting that organic aerosols were influenced by aging. The concentrations of total diacids (C_2–C_9) in spring and summer were higher than in winter. In each season, WSOC showed a strong positive correlation with the total diacids. Levoglucosan, which is recognized as a biomass burning tracer, was observed in a considerably higher concentration in winter than in spring or summer. In winter, WSOC also showed a strong positive correlation with levoglucosan. These results indicate that secondary formation is important as a source of WSOC and OC especially in the warm seasons, although emissions from biomass burning also contribute to WSOC in winter. By using the combination of source profile for biomass burning emission and EC tracer method, OC derived from biomass combustion in winter was calculated to be 47% of OC and OC derived from secondary formation in summer was calculated to be 75% of OC.

Keywords: Organic carbon; Water-soluble organic carbon; Secondary formation; Biomass burning.

INTRODUCTION

Atmospheric particulate matter is a major air pollutant in Japan (Sakamoto *et al.*, 1994, 1998; Minoura *et al.*, 2006; Takahashi *et al.*, 2008; Bao *et al.*, 2009a). Organic matter is a large and important fraction of atmospheric fine particles (Turpin *et al.*, 2000). Nevertheless, the chemical properties, environmental behavior, and potential sources of organic matter have not been sufficiently elucidated because of analytical difficulties and the existence of a large variety of organic compounds.

The organic matter contained in atmospheric particles is not only directly emitted from potential sources (primary) but also produced by photochemical reactions of volatile organic compounds in the atmosphere (secondary) (Turpin *et al.*, 2000). In general, secondary organic aerosols are water-soluble because they have polar functional groups (e.g., hydroxyl, carbonyl, and carboxyl) produced by oxidation reactions (Saxena and Hildemann, 1996). Water-soluble organic carbon (WSOC) is closely correlated to the formation of secondary organic aerosols (Miyazaki *et al.*, 2006). As an individual species, dicarboxylic acids are an important water-soluble group of atmospheric aerosols (Kawamura *et al.*, 1996). Dicarboxylic acids are produced by the secondary photochemical oxidation of organic pollutants (Hatakeyama *et al.*, 1987; Kawamura and Ikushima, 1993; Bao *et al.*, 2009b).

Water-soluble organic compounds can also be derived from primary sources such as biomass burning (Mayol-Bracero *et al.*, 2002). However, the source contribution of biomass burning to organic aerosol is not well understood. Levoglucosan (1,6-anhydro-β-D-glucopyranose), which is

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formed by pyrolysis of cellulose, is a primarily generated water-soluble sugar compound and is recognized as a unique tracer of biomass burning (Simoneit *et al.*, 1999; Lee *et al.*, 2008). It is possible to assess the contribution of biomass burning by determining the concentration of levoglucosan in aerosols (Gelencsér *et al.*, 2007; Puxbaum *et al.*, 2007; Kourtchev *et al.*, 2008; Zhang *et al.*, 2008).

In our previous study, we investigated WSOC in fine (aerodynamic diameter (d_p) < 2.1 μm) and coarse (d_p = 2.1–11 μm) particles collected at suburban site in the inland Kanto plain, Japan, from April 2005 to March 2006 (Kumagai *et al.*, 2009). This region is affected by air pollutants transported from the coastal metropolitan areas of Tokyo (Wakamatsu, 2001). We found that WSOC was abundantly present in fine particles and accounted for much of the organic carbon (OC). The WSOC/OC ratio was higher in summer but the seasonal variations were not large. The WSOC concentration was significantly positively correlated with the concentrations of SO_4^{2-}, elemental carbon (EC), and K^+, suggesting occurrences of photochemical reactions and fuel/biomass combustion (Kumagai *et al.*, 2009). Therefore, the identification of the origin of water-soluble organic compounds is necessary in order to gain a better understanding of the atmospheric behavior of OC.

In this paper, we focus on dicarboxylic acids and levoglucosan, tracer species of WSOC, contained in fine particles collected at Maebashi in the inland Kanto plain, Japan, in 2007 and 2008. We discuss seasonal differences in the chemical characteristics of water-soluble organic compounds and source contributions of organic aerosols.

METHODS

Sample Collection

Particulate matter samples were collected at Maebashi (36.4°N, 139.1°E) in Gunma Prefecture, Japan (Fig. 1). The Maebashi site is located in a suburban city (population; 0.3 million) situated in the inland Kanto plain and is approximately 100 km northwest of the Tokyo metropolitan area. The monitoring site is surrounded by residential areas and agricultural fields, and it is 100 m away from a road with moderate traffic. There is a small manufacturing area 2 km away from this site, but there is no significant large emission source. The sampling

equipment was installed on a building rooftop, about 20 m above the ground. A strong prevailing southeast wind caused by sea breezes develops in spring and summer in this area. This wind can bring polluted air from the Tokyo metropolitan area, which is the largest source of air pollution in Japan. A typical example is the high levels of photochemical oxidants (above 100 ppb) than are frequently observed during the presence of sea breezes in these seasons. In contrast, the northwesterly dry winds are dominant in winter. Sample collections were carried out in spring (May 14–25, 2007), summer (July 28–August 10, 2008), and winter (December 17–27, 2007). The average temperature during the sampling period was 19.5, 27.9, and 4.7°C in spring, summer, and winter, respectively; the average amount of solar radiation during the sampling period in these seasons was 20.7, 18.2, and 8.7 MJ/m^3/day, respectively.

Ambient particles were collected on quartz fiber filters (φ80 mm, 2500QAT-UP, Pallflex, Putnam, USA) with an Andersen low-volume air sampler (AN-200, Tokyo Dylec, Tokyo, Japan). The particles were classified by d_p < 2.1 μm. The air flow rate was 28.3 L/min, and the sampling period was 24 h (48 h on August 2 and 9, 2008), starting at 10 a.m. Japan Standard Time (JST). We obtained the particulate mass by the gravity method. To control the weight of moisture, we conditioned the filters in a constant temperature and humidity chamber (20 ± 0.5°C and 50 ± 3% RH) for 24 h prior to weighing their mass (BP211D, Sartorius, Goettingen, Germany).

Chemical Analyses

EC, OC, WSOC, inorganic ions, and water-soluble organic compounds were determined in the collected fine particles. Detailed analytical procedures for EC, OC, WSOC, and inorganic ions are described elsewhere (Kumagai *et al.*, 2009). Half of each filter was cut into small pieces and extracted with 20 mL of ultrapure water to measure the water-soluble compounds, WSOC, and ionic species. The samples were ultrasonically extracted for 15 min, and the extracts were filtered. The concentration of WSOC was determined using a total carbon analyzer (TOC-V, Shimadzu, Kyoto, Japan) (Yang *et al.*, 2003). The inorganic ions (Cl$^-$, NO_3^-, SO_4^{2-}, Na$^+$, NH_4^+, K$^+$, Mg^{2+}, and Ca^{2+}) and oxalic acid (C$_2$) were measured with an ion chromatograph (DX-500, Dionex, CA, USA). OC and EC
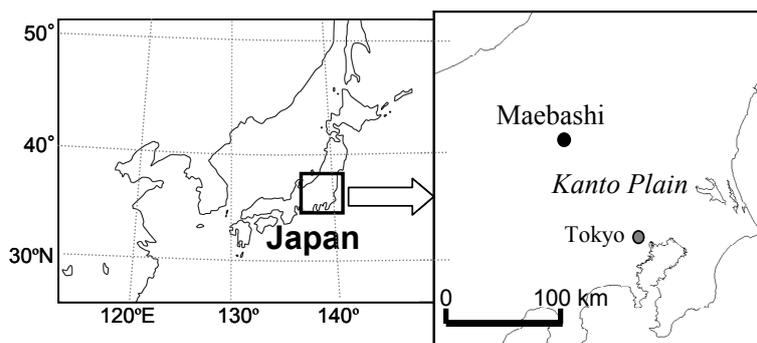

Fig. 1. Location of the monitoring site.

were determined using a thermal/optical carbon analyzer (DRI Model 2001, Atmoslytic Inc., CA, USA) by following the IMPROVE thermal/optical reflectance protocol (Chow *et al.*, 2001). A portion of each sample filter (φ8 mm of the total) was used to determine OC and EC. Blank filters were analyzed for all components, and blank values were subtracted for some detected components.

Dicarboxylic acids (malonic acid: C_3; succinic: C_4; glutaric: C_5; adipic: C_6; pimelic: C_7; suberic: C_8; azelaic: C_9) and levoglucosan were determined by a derivatization GC/MS method (Hagino *et al.*, 2006; Bi *et al.*, 2007). A quarter of each filter was cut into small pieces and extracted with a dichloromethane and methanol mixture (2:1, *v/v*) by ultrasonic agitation for 15 min. All organic solvents used in our study were pesticide-residue grade. In the extraction step, 10 μL of a 1 mg/mL solution of cis-ketopinic acid was spiked into the extract as an internal recovery standard. The extracts were filtered and dried by a nitrogen stream in a silylation vial. For the derivatization, 50 μL of the trimethylsilylation mixture containing the reagent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane as a catalyst was added to the dried samples. They were reconstituted to 200 μL with a dichloromethane and hexane (1:1, *v/v*) solution and the reaction was carried out at 70°C for 2.5 h by using a dry bath. After the reaction, the derivatives were determined with a GC/MS (Agilent 6890GC/5973MS, Agilent

Technologies, CA, USA) equipped with a split/splitless injector and a fused silica capillary column (DB5MS, 60 m × I.D. 0.25 mm × 0.25 μm film thickness, Agilent Technologies, CA, USA). A sample volume of 1.0 μL was injected in the splitless mode at a temperature of 270°C. The carrier gas was helium (1 mL/min). The temperature program started with an initial temperature of 60°C for 1 min and was subsequently increased to 200°C at 10 °C/min; then a gradient of 5 °C/min was used up to 300°C and the final temperature was held for 10 min. The electron ionization source was operated at 70 eV and 230°C. The target compounds were identified by comparing the GC retention times with mass chromatograms of authentic standards and the mass spectral library of the GC/MS data system. The chromatograph was calibrated with standard solutions prepared with the target compound reagents. A procedural blank was run in parallel with the aerosol samples, and it showed no significant background interference.

RESULTS AND DISCUSSION

Mass Concentration of Particulate Matter and Major Components

The mass concentrations of the fine particles (< 2.1 μm) and their major components are shown in Table 1. The mean mass concentrations were 21.4 (9.2–37.8), 24.3 (7.5–37.9), and NH_4^+, as shown in Table 1. Cl^- was also a major ion in

Table 1. Concentrations of particulate mass, major components, and water-soluble organic compounds (diacids and levoglucosan) in fine particles collected at Maebashi.

	Spring (*n* = 10)			Summer (*n* = 11)			Winter (*n* = 8)		
	Mean	(Max. —	Min.)	Mean	(Max. —	Min.)	Mean	(Max. —	Min.)
Mass and major components				Concentrations [μg/m³]					
Mass	21.4	(37.8 —	9.2)	24.3	(37.9 —	7.5)	23.1	(43.4 —	9.0)
Cl^-	0.10	(0.37 —	0.02)	0.06	(0.30 —	0.01)	0.91	(1.83 —	0.10)
SO_4^{2-}	5.38	(8.68 —	2.08)	7.57	(13.8 —	3.22)	3.24	(4.83 —	0.93)
NO_3^-	2.32	(7.04 —	0.52)	1.34	(3.59 —	0.29)	3.85	(11.1 —	0.85)
NH_4^+	2.50	(5.05 —	0.83)	3.13	(5.65 —	1.00)	2.54	(5.40 —	0.87)
K^+	0.17	(0.28 —	0.07)	0.18	(0.47 —	0.07)	0.25	(0.49 —	0.11)
Total inorganic ions	10.7	(21.6 —	3.7)	12.4	(21.8 —	4.8)	11.0	(23.9 —	3.9)
EC	2.10	(2.57 —	1.11)	1.99	(2.72 —	1.04)	2.78	(4.72 —	1.41)
OC	4.32	(7.21 —	2.07)	5.33	(8.91 —	3.21)	6.12	(10.7 —	2.91)
WSOC	2.69	(4.25 —	1.12)	4.35	(7.98 —	2.58)	2.92	(6.05 —	1.06)
Water-soluble organic compounds				Concentrations [ng/m³]					
Oxalic (C_2)	435.4	(735.0 —	146.3)	472.1	(749.5 —	171.7)	175.7	(332.1 —	86.2)
Malonic (C_3)	26.2	(62.0 —	3.0)	85.4	(137.3 —	39.1)	6.6	(26.8 —	N.D.)
Succinic (C_4)	27.8	(55.7 —	14.4)	39.0	(74.0 —	23.0)	22.5	(43.8 —	10.0)
Glutaric (C_5)	1.1	(5.2 —	N.D.)	9.5	(14.4 —	4.3)	1.3	(7.7 —	N.D.)
Adipic (C_6)	15.2	(42.1 —	3.1)	23.9	(39.3 —	12.3)	28.5	(62.4 —	6.6)
Pimelic (C_7)	3.4	(8.2 —	N.D.)	N.D.	(N.D. —	N.D.)	4.0	(10.2 —	N.D.)
Suberic (C_8)	18.7	(31.3 —	N.D.)	20.7	(37.1 —	13.1)	28.5	(54.0 —	N.D.)
Azelaic (C_9)	14.6	(24.8 —	8.3)	5.2	(7.8 —	2.9)	22.3	(40.2 —	7.4)
Total diacids	542.5	(916.4 —	178.2)	655.8	(917.8 —	275.1)	289.6	(577.3 —	121.0)
Levoglucosan	54.8	(98.4 —	27.0)	37.4	(76.1 —	14.2)	257.5	(436.0 —	54.5)

winter, in addition to SO_4^{2-}, NO_3^-, and NH_4^+. These four and 23.1 (9.0–43.4) μg/m^3 in spring, summer, and winter, respectively. The major inorganic ions were SO_4^{2-}, NO_3^-, components accounted for most of the inorganic ions (96 ± 1% of the total inorganic ion mass). The inorganic ions accounted for 49 ± 8% of the fine particulate mass. The mean concentrations of OC were 4.32, 5.33, and 6.12 μg/m^3 in spring, summer, and winter, respectively; the mean concentrations of EC in these seasons were 2.10, 1.99, and 2.78 μg/m^3, respectively. The total carbon accounted for 35 ± 12% of the fine particulate mass.

Characteristics of seasonal and daily changes were found in the chemical composition of the particles. In spring and summer, the concentrations of SO_4^{2-} and OC were relatively high. In spring, the concentration of NO_3^- occasionally increased to the same levels as those of SO_4^{2-} and OC. In winter, OC and NO_3^- were the major species, followed by SO_4^{2-} or EC. An increase in the SO_4^{2-}, NO_3^-, and OC concentrations resulted in a higher concentration of the fine particle mass. The EC concentrations stayed within a relatively narrow range in spring and summer.

Carbonaceous Component

Fig. 2 shows the variation of the OC, WSOC, and EC concentrations and the WSOC/OC and OC/EC ratios. The OC concentration varied from day to day, in contrast to the small EC variation in spring and summer. The OC/EC ratio ranged from 0.9 to 2.9 in spring and from 2.0 to 3.5 in summer. Relatively high concentrations of OC were observed when photochemical oxidants were present in a high concentration (maximum >100 ppb, e.g., May 22–24, 2007; August 7–8, 2008). The OC/EC ratios were also relatively high. During the sampling periods in spring and

summer, the predominant wind direction was southeast. Lower OC/EC ratios were observed on rainy days such as May 17 and 25, 2007. They might have been affected by the decrease in photochemical reactions, precipitation, and the change in the particle size distribution. On the other hand, in winter, the concentrations of EC and OC showed similar daily changes. The OC/EC ratio in winter ranged from 1.9 to 2.5, exhibiting fluctuations smaller than those in the other seasons. The daily minimum temperatures approximately reached the freezing point and northwesterly moderate winds were dominant. The elevated EC concentrations in winter were thought to be due to meteorological conditions in the low mixing layer, because the concentrations of other pollutants such as nitrogen oxides increased simultaneously, and/or an enhanced primary emission. It might have been a result of local pollution, which originates from sources such as vehicles and biomass burning.

The average seasonal WSOC concentrations were 2.69, 4.35, and 2.92 μg/m^3 in spring, summer, and winter, respectively (Table 1). The largest WSOC/OC ratio was found in summer (average value; 0.82), followed by in spring (0.62) and winter (0.46). The seasonal characteristic of the WSOC/OC ratio was similar to that observed in our previous measurements at Maebashi, and the ratio in summer was higher than that found previously (Kumagai *et al.*, 2009). These results indicate that the contribution of secondary formation to organic aerosols is more important in summer. Miyazaki *et al.* (2006) reported a value of 0.35 for the WSOC/OC ratio of fine particles in summer/late fall in Tokyo. Bao *et al.* (2009a) reported a value of 0.67 at a suburban site in summer in Saitama, located between Tokyo and Maebashi. Both these figures are lower than
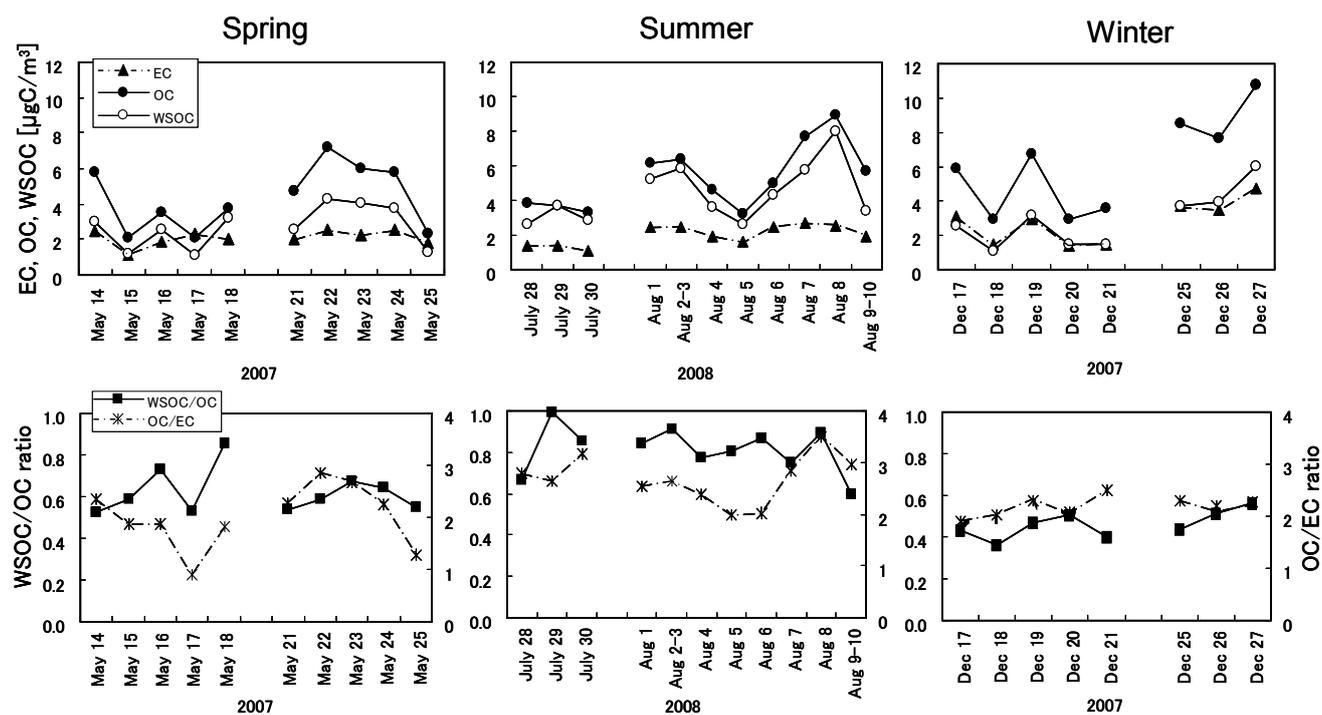

Fig. 2. Variations of EC, OC, and WSOC concentrations and WSOC/OC, OC/EC ratios in fine particles.

that obtained for summer in this study. The WSOC fraction in OC is considerably influenced by aerosol aging (Aggarwal and Kawamura, 2009). The oxidative transformation of organic aerosols during atmospheric transport from the coastal Tokyo region toward the inland area could be an important factor in the increase in the WSOC fraction in summer.

Seasonal Variation of Dicarboxylic Acids

The concentration ranges of dicarboxylic acids and levoglucosan in fine particles at Maebashi are given in Table 1. The average concentrations of total dicarboxylic acids (C_2–C_9) were 542.5, 655.8, and 289.6 ng/m³ in spring, summer, and winter, respectively. Higher concentrations were observed in spring and summer than in winter. In all the samples, the most abundant species was oxalic acid (C_2). In spring and summer, the second most abundant species was either malonic (C_3) or succinic (C_4) acid, whereas in winter, the concentrations of succinic (C_4), adipic (C_6), sebacic (C_8), and azelaic (C_9) acids were approximately the same as the concentration of the second most abundant species. Fig. 3 shows the relative abundance of dicarboxylic acid in the total diacids in each season. Oxalic acid accounted for 80 ± 5% of the total diacids concentration in spring; this figure was 71 ± 6% in summer and 61 ± 8% in winter. C_2–C_4 diacids accounted for more than 80% of the total diacids in spring and summer. The low-molecular diacids are produced by photochemical reactions of anthropogenic organic pollutants. The production of C_6 diacid in laboratory studies of cyclohexene-ozone reactions has been reported (Hatakeyama *et al.*, 1987). C_9 diacid is a product of the oxidation of biogenic unsaturated fatty acids (Kawamura
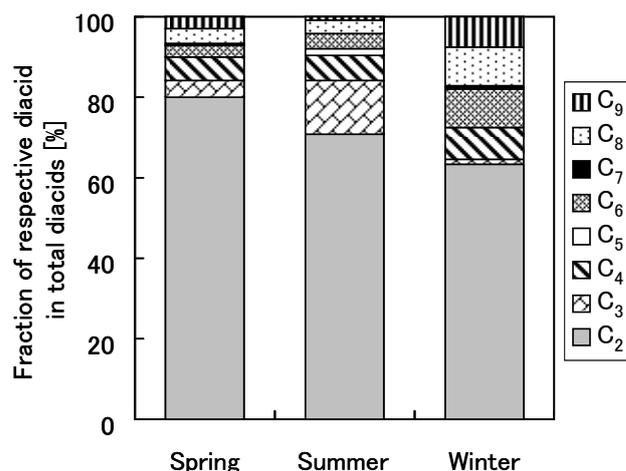
Fig. 3. Seasonal average of relative abundance of C_2–C_9 dicarboxylic acid in the total diacids concentrations in fine particles.

and Ikushima, 1993). Kawamura and Ikushima (1993) have demonstrated that the low-molecular-weight diacids that are present in the urban aerosols are most likely to be generated by photochemical reactions. Since long-chain diacids can be oxidized to short-chain diacids by photochemical reactions, the high abundance of short-chain diacids such as C_2 and C_3 diacids observed in the warmer seasons is a piece of evidence indicating the sampling periods were under photochemically activated conditions.

Figs. 4(a) and (b) show the temporal variations in the concentrations of ambient oxidants and dicarboxylic acids. It was observed that the concentrations of the total diacids
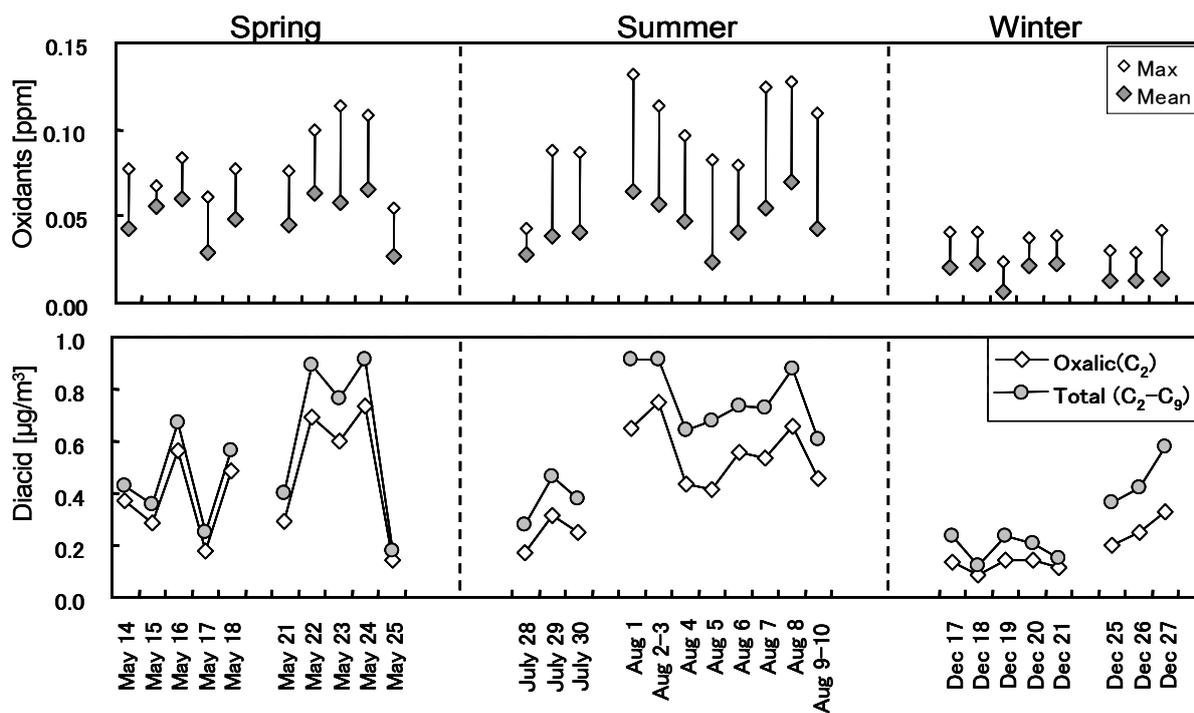
Fig. 4. Variations of concentrations of (a) oxidants and (b) dicarboxylic acids.

and oxalic acid increased when the concentration of oxidants was high. Concurrently, the southeasterly winds constantly blew from morning to night or midnight every day in spring and summer. Therefore, the air mass transported from the metropolitan area may be involved in secondary formation. We examined the relationship between the concentration of oxalic acid and the mean concentration of ambient oxidants. We observed a high correlation between them ($r = 0.83$, $p < 0.001$). A similar relationship was obtained between the concentration of total diacids and the oxidants ($r = 0.76$, $p < 0.001$). In spring and summer, oxalic acid was also positively correlated with sulfate, which is known to be a secondary product formed by photochemical oxidation ($r = 0.83$, $n = 10$, $p < 0.005$ in spring; $r = 0.81$, $n = 11$, $p < 0.005$ in summer); however, in winter, although positive correlation was observed, the correlation was not significant ($r = 0.59$, $n = 8$, $p > 0.05$).

Seasonal Variation of Levoglucosan

The average concentration of levoglucosan was observed to be significantly higher in winter (257.5 ng/m^3) than in spring (54.8 ng/m^3) or summer (37.4 ng/m^3) (Table 1). Levoglucosan is a specific biomass burning marker (Simoneit *et al.*, 1999; Lee *et al.*, 2008). Thus, these results indicate that there were aerosols derived from biomass burning in fine particles at Maebashi. Fig. 5 shows temporal variations of the concentrations of levoglucosan. The concentration of levoglucosan during spring and summer was lower than the reported background value in Beijing (92 ng/m^3, Zhang *et al.*, 2008) and higher than the concentration during spring in Sapporo in northern Japan (16 ng/m^3, Aggarwal and Kawamura, 2009). The highest concentration of levoglucosan observed in winter (December 25–27, 2007) was approximately ten times greater than those observed in the other seasons, as shown Fig. 5. In winter, the emission amount from biomass burning was thought to be quite different from that in the other seasons at Maebashi. Open burning of agricultural biomass and dry vegetation might be the dominant sources of biomass-derived aerosols. We found that the concentration of levoglucosan was strongly correlated with

the concentration of EC in winter ($r = 0.96$, $p < 0.001$); this suggests that in winter, EC was emitted not only from vehicles but also from burning biomass.

Relationship between Water-soluble Organic Compounds and WSOC

Fig. 6(a) shows the relationship between the concentrations of WSOC and oxalic acid. We observed strong significant correlations: $r = 0.89$, $n = 10$, $p < 0.001$ in spring; $r = 0.80$, $n = 11$, $p < 0.005$ in summer; and $r = 0.95$, $n = 8$, $p < 0.001$ in winter. The slopes of the regression lines in spring and summer were larger than that in winter, indicating that the WSOC observed in the warmer seasons was to a large extent derived from the secondary formation of organic compounds in the atmosphere. The slope for summer was slightly smaller than that for spring (Fig. 6(a)). Since oxalic acid is semivolatile, some portions of particulate oxalic acid might be volatilized due to high temperature in summer. The total diacids were also strongly correlated with WSOC. The total diacids–C accounted for 2.7–8.3% (with an average of 6.2% in spring, 4.9% in summer, and 3.6% in winter) of WSOC and 1.2–6.7% (averaging 3.9%, 3.9%, and 1.7%) of OC.

As for levoglucosan, its concentration was strongly positively correlated with the concentration of WSOC in winter ($r = 0.93$, $p < 0.001$) (Fig. 6(b)). In contrast, no significant correlations between the concentrations of levoglucosan and WSOC were found in spring and summer ($p > 0.05$). These results suggest that emissions from biomass burning contributed to WSOC in winter. We examined the relationship between the concentrations of WSOC and K$^+$ because K$^+$ is also recognized as a tracer for biomass burning. A significant positive correlation was found in winter ($r = 0.96$, $p < 0.001$). A smaller positive correlation was found in spring ($r = 0.72$, $p < 0.05$). In winter, levoglucosan–C accounted for 2.3–4.9% (average 3.7%) of WSOC and 0.8–2.4% (average 1.7%) of OC. These values were roughly the same as those determined at the other suburban site in the inland Kanto plain (Hagino *et al.*, 2006).
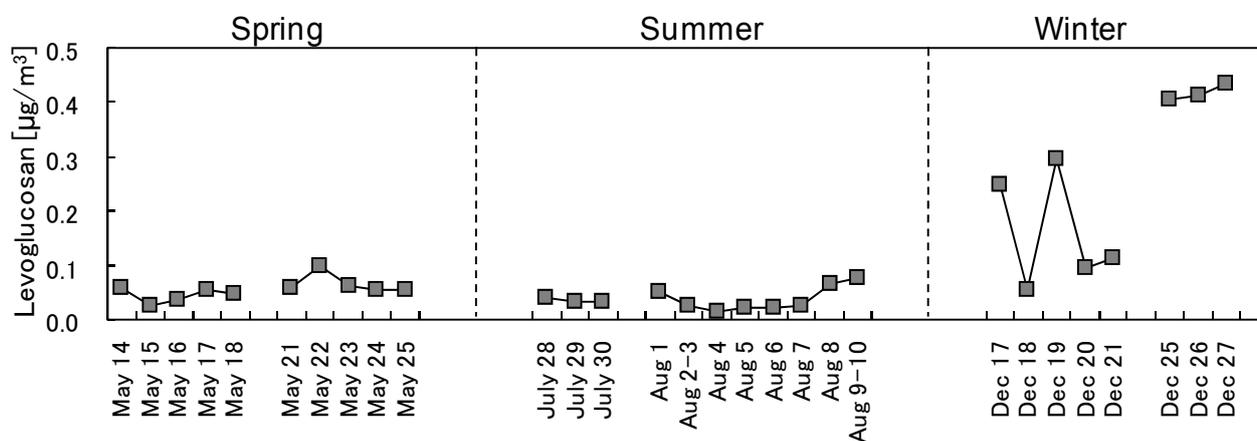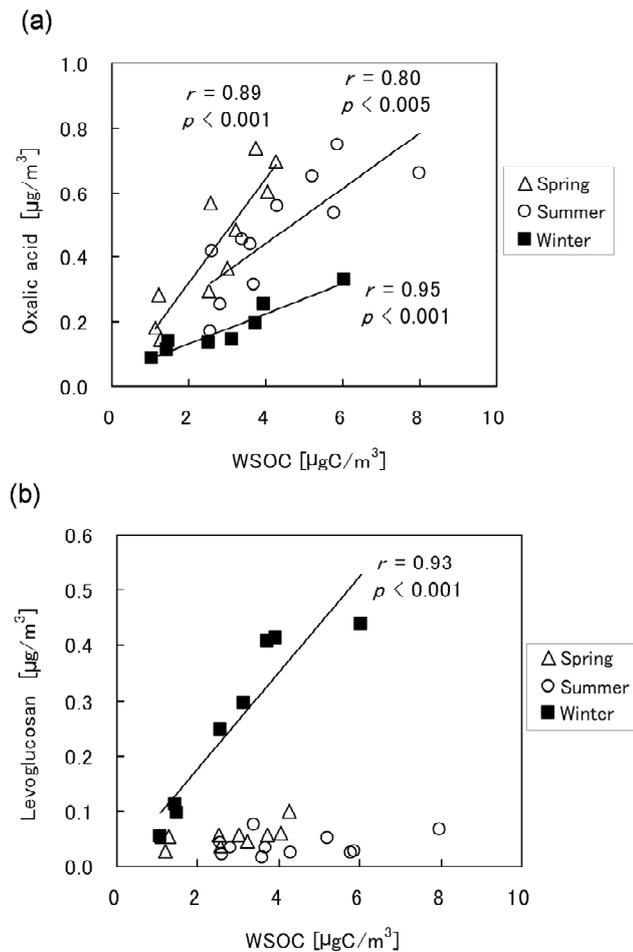

Fig. 5. Variation of concentration of levoglucosan.

(a)

(b)

Fig. 6. Relationship between the concentrations of WSOC and (a) oxalic acid, (b) levoglucosan.

Estimation of Biomass Burning and Secondary Organic Aerosol Contributions

Since the chemical properties of biomass-burning-derived aerosol vary depending on the type of original biomass (wood, vegetation, agricultural waste) and the combustion conditions, there are several reports on the source profiles of organic compounds emitted by biomass combustion (Hays *et al.*, 2005; Zhang *et al.*, 2007; Fabbri *et al.*, 2008; Medeiros and Simoneit, 2008; Schmidl *et al.*, 2008). For example, Schmidl *et al.* (2008) found the mass content of levoglucosan and OC to be 9.3% and 52%, respectively, in wood smoke. Zhang *et al.* (2007) found that the percentages of OC, EC, and levoglucosan were 54.6 ± 6.0%, 7.1 ± 2.9%, and 4.5 ± 1.4%, respectively, in $PM_{2.5}$ emitted from cereal straw combustion. Wood fuel is rarely used for residential heating and cooking in Japan. In our observation area, since rice and wheat are cultivated, the burning of agricultural residue such as cereal straws may be considered. We roughly estimated the contribution of biomass burning to OC using the source profile of cereal straw burning (54.6% of OC, 7.1% of EC, and 4.5% of levoglucosan) (Zhang *et al.*, 2007; Zhang *et al.*, 2008). The OC derived from biomass burning (OC_{bio}) was determined by multiplying the observed concentration of

levoglucosan by the OC/levoglucosan ratio for the source profile. EC derived from biomass burning (EC_{bio}) was calculated in a similar manner using the EC/levoglucosan ratio.

Fig. 7 shows the contributions of OC_{bio} and EC_{bio} to observed OC and EC at Maebashi. In winter, the average percentage of OC_{bio} was found to be 47% (maximum 66%) of the OC in fine particles. Therefore, in winter, biomass combustion is an important source of organic aerosols. On the other hand, the percentages of OC_{bio} in spring and summer were lower, averaging 17% and 9%, respectively. The average percentage of EC_{bio} was found to be 14% in winter, 4% in spring, and 3% in summer (Fig. 7), and these percentages were relatively lower than those of OC_{bio}. The dominant source of EC was thought to be emission from fuel fossil combustion, e.g., vehicle emission. However, particularly in winter, EC emission from biomass burning should not be neglected.

The EC tracer method (Turpin and Huntzicker, 1991) is a simple approach for the determination of primary or secondary OC. In this concept, the primary OC/EC ratio is assumed to be mostly constant. However, we found significant seasonal differences in the contribution of biomass burning to the concentration of carbonaceous components. This also indicates that the primary OC/EC ratio differs depending on the season. We calculated the fractions of OC and EC that were not derived from biomass burning ($OC_{non\text{-}bio}$ and $EC_{non\text{-}bio}$, respectively) by subtracting OC_{bio} and EC_{bio} from the observed OC and EC, respectively. We used the EC tracer method along with the $OC_{non\text{-}bio}/EC_{non\text{-}bio}$ ratios in order to estimate the contribution of secondary organic aerosols. A similar source apportionment approach has been reported by Gelencsér *et al.* (2007). In this case, $OC_{non\text{-}bio}$ comprises secondarily generated OC (OC_{sec}) and primarily generated OC (OC_{pri}), excluding the OC derived from biomass burning. On the other hand, for $EC_{non\text{-}bio}$, many kinds of combustion sources such as vehicles and oil combustion should be taken into consideration. However, there is no significant oil combustion source in the vicinity of our sampling site. In fact, our previous study (Iijima *et al.*, 2008) demonstrated that the contribution of oil combustion to particulate matter was significantly lower than that of
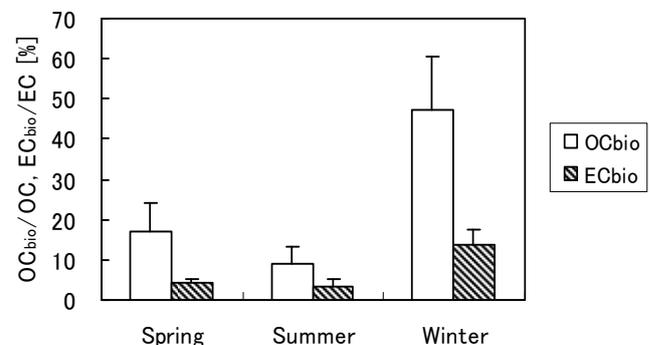
Fig. 7. Estimated contribution of biomass burning to OC and EC (mean ± S.D.). OC_{bio} and EC_{bio} indicate carbonaceous components derived from biomass burning.

vehicles, through chemical mass balance analysis. Therefore, we simply assumed $EC_{non\text{-}bio}$ to be vehicle-derived EC. The fraction of OC_{sec} was calculated by the following equations:

$$OC_{pri} = EC_{non\text{-}bio} \times (OC/EC)_{pri},$$

$$OC_{sec} = OC_{non\text{-}bio} - OC_{pri},$$

where $(OC/EC)_{pri}$ is the primary OC/EC ratio. Since the EC/TC ratios at roadsides in Tokyo have been reported to be 0.6–0.7 (Hasegawa *et al.*, 2006; Takahashi *et al.*, 2008), we used an $(OC/EC)_{pri}$ ratio of 0.43 (Hasegawa *et al.*, 2006) for the calculation.

Fig. 8 shows the relationship between the calculated OC_{sec} and the observed concentration of total diacids–C. A positive correlation was found between the two ($r = 0.79$, $p < 0.001$), suggesting that our apportionment is reasonable. Fig. 9 shows the calculated concentrations of the primary and secondary OC. An important factor that contributed to the increase in the OC concentration was the enhancement of secondary formation in warm seasons. On the other hand, biomass burning was the dominant source of OC in winter. The seasonal average contributions of OC_{sec} to OC were 60, 75, and 36% in spring, summer, and winter, respectively. The maximum contribution of OC_{sec} was 81% in summer, and this value was roughly equal to the WSOC/OC ratio, as shown in Fig. 2. Therefore, WSOC in summer can be regarded as secondary organic aerosol. On the other hand, even if OC_{sec} was completely water soluble, the OC_{sec} contribution in winter was approximately equivalent to three-quarters of the observed WSOC/OC ratio (0.46) (see Fig. 2). Although these evaluations are rough estimates, it can be concluded that biomass burning is another important source of WSOC in winter. The concentration of OC derived from vehicle emission showed no seasonal differences, unlike in the case of OC_{sec} or OC_{bio} (Fig. 9), probably because the emission from vehicles was approximately constant.
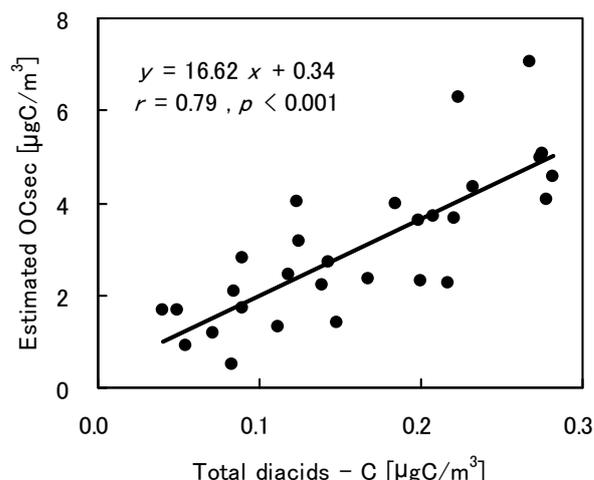

Fig. 8. Comparison of the estimated secondary organic carbon (OC_{sec}) with the observed concentration of total diacids–C.

When the ratio of organic mass to OC was considered to be 1.6 (Turpin and Lim, 2001), which may vary depending on the season (Bae *et al.*, 2006), the contribution of secondary organic aerosols was estimated to account for 29% (maximum: 59%) of the fine particle mass in summer. Similarly, organic aerosols from biomass combustion in winter were estimated to account for 20% of the fine particle mass. These simple estimations clearly indicate that secondary formation and biomass burning are important sources of OC in summer and winter, respectively.

CONCLUSIONS

Fine particulate matter was collected at a suburban site in the inland Kanto plain, Japan, in the spring and winter of 2007 and in the summer of 2008. Its chemical composition was analyzed; the analysis considered OC, WSOC, EC, inorganic ions, and water-soluble organic
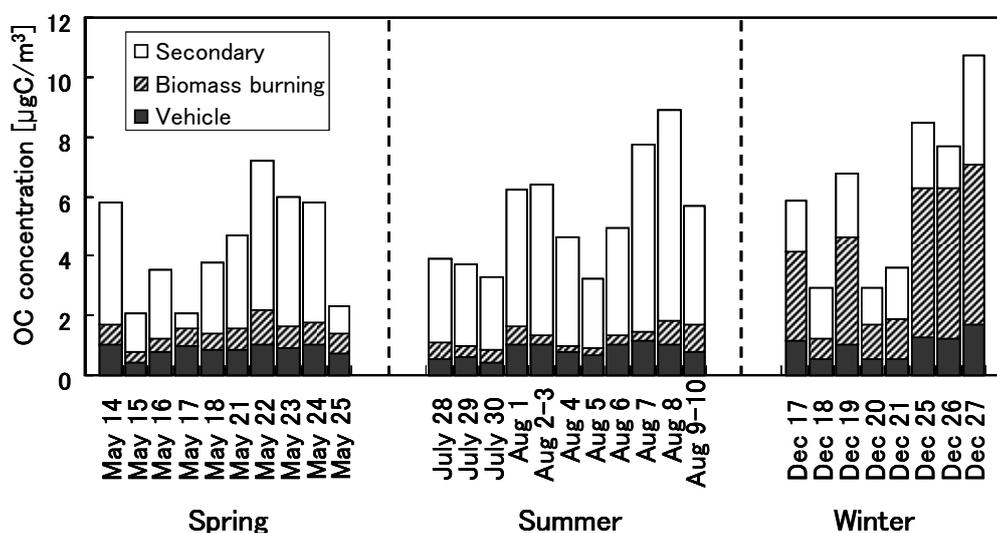
Fig. 9. Source apportionment for OC in fine particles.

compounds. The SO_4^{2-} and OC concentrations were relatively high in spring and summer, whereas OC and NO_3^- were major species in winter. The WSOC concentration was higher in summer than in spring or winter. The WSOC fraction in the OC was highest in summer and lowest in winter, suggesting that the organic aerosols are influenced by aging.

Oxalic acid (C_2), which is a product of photochemical reactions, was the most abundant dicarboxylic acid in all the samples. The concentration of oxalic acid was correlated with the concentrations of ambient oxidants and SO_4^{2-}. Total diacids (C_2–C_9) accounted for (on average) 6.2%, 4.9%, and 3.6% of WSOC in spring, summer, and winter, respectively. Levoglucosan, a biomass burning tracer, was observed in a considerably higher concentration in winter. In each season, WSOC was positively correlated with oxalic acid and the total diacids. However, in winter, WSOC also showed a strong positive correlation with levoglucosan and K^+. These results indicate that secondary formation is important as a source of WSOC and OC, especially in the warm seasons, and that emissions from biomass burning also contribute to WSOC in winter. By using the source profile of biomass burning emissions, the OC derived from biomass combustion in winter was estimated to be on average 47% of OC and 20% of the fine particle mass. Further, we estimated the contribution of secondary formation on the basis of the results obtained using the combination of the EC tracer method and the above-mentioned source profile and found that secondary formation is responsible for 75% of OC and 29% of the fine particle mass in summer. Although these evaluations have uncertainties because of their dependence on profile data, the results clearly indicate that secondary formation is the dominant source of organic aerosols, particularly in warm seasons, and that biomass burning is another important source of organic aerosols in winter.

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