



# Comparison of Plant-derived Carbonaceous Components (Organic Molecular Markers and $^{14}\text{C}$ carbon) in $\text{PM}_{2.5}$ in Summer and Autumn at Kazo, Japan

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## ABSTRACT

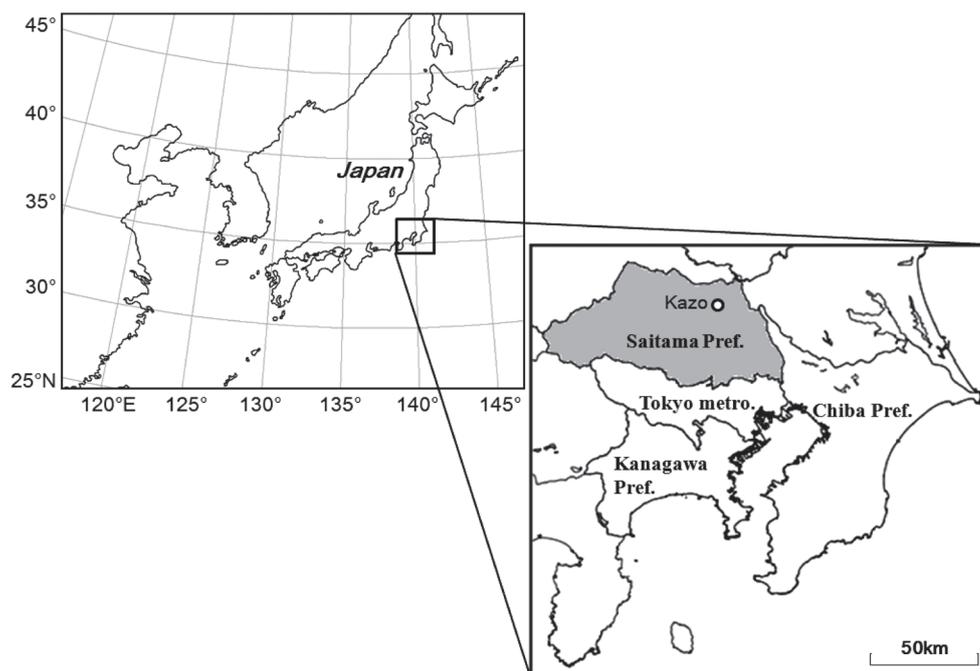
In Japan, the primary carbonaceous particles emitted from motor vehicles and waste incinerators have been reduced due to strict regulations against exhaust gas. However, the relative contribution of carbonaceous particles derived from plants and biomass has been increasing. Accordingly, compositional analysis of carbonaceous particles has become increasingly important to determine the sources and types of particles produced. To reveal the sources of the organic particles contained in particulate matter with diameters of  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) and the processes involved in their generation, we analyzed molecular marker compounds (2-methyltetrols, *cis*-pinonic acid, and levoglucosan) derived from the plants and biomass in the  $\text{PM}_{2.5}$  collected during daytime- and nighttime-sampling periods in summer (July and August) and autumn (November) in Kazo, which is in the northern area of Saitama prefecture, Japan. We also measured  $^{14}\text{C}$  carbonaceous concentrations in the same  $\text{PM}_{2.5}$  samples. The concentrations of 2-methyltetrols were higher in the summer than in the autumn. Because the deciduous period overlaps with this decrease in the levels of 2-methyltetrols, we considered the emission source to broad-leaved trees. In contrast, the emission source of the *cis*-pinonic acid precursor was considered to be conifers, because its concentration remained almost constant throughout the year. The concentration of levoglucosan was considerably increased in the autumn due to frequent biomass open burning. The ratio of plant-derived carbon to total carbon, obtained by measuring of  $^{14}\text{C}$ , in summer  $\text{PM}_{2.5}$  sample was higher in the nighttime, and could be influenced by anthropogenic sources during the daytime.

**Key words:** Biomass burning, Carbon isotopic analysis, Fossil fuels, Molecular marker, Secondary formation

## 1. INTRODUCTION

In Japan, long-term vehicle emission regulations and the strengthening of soot and dust emission standards from waste incinerators as countermeasures against dioxin have achieved the desired effect of improving air quality (Takahashi *et al.*, 2008). In addition, in September 2009, the Japanese Ministry of Environment (MOEJ) established the environmental quality standards for particulate matter with diameters of  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) based on their mass concentration (MOEJ, 2009). However, this improvement trend has dulled in recent years. In the MOEJ report for the 2014 fiscal year (MOEJ, 2016), the  $\text{PM}_{2.5}$  environmental quality standards were met at only 37.8% (254/672) of ambient air pollution monitoring stations (APMSs) and 25.8% (51/198) of roadside APMSs. However, the difference in the mass concentration and the difference in chemical composition of  $\text{PM}_{2.5}$  at roadside APMSs compared with that at other APMSs, has reduced over time. Consequently, the relative contribution of carbonaceous particles derived from plants and biomass has been increasing throughout the year (Minoura *et al.*, 2012; Takahashi *et al.*, 2007).

Carbonaceous particles contribute considerably (20%-90%) to the  $\text{PM}_{2.5}$  mass (Kanakidou *et al.*, 2005), and comprise many organic components. They are classified into primary particles emitted directly from the source and secondary particles that are formed by the photochemical conversion of volatile organic compounds (VOCs) in the atmosphere (Turpin *et al.*, 2000).



**Fig. 1.** Location of the observation site (Kazo).

However, the source and behavior of carbonaceous particles, especially secondary particles, are still not well understood. VOC emissions from plants, as with aromatic hydrocarbons from anthropogenic sources, have long been recognized as important precursors of carbonaceous particles (Kalberer *et al.*, 2004; Anderson-Sköld and Simpson, 2001; Odum *et al.*, 1997; Went, 1960).

In the United States (Wang *et al.*, 2012; Kleindienst *et al.*, 2007) and China (Hu *et al.*, 2010, 2008), molecular marker compounds of secondary organic particles from biogenic VOCs (BVOCs), such as isoprene and terpenes released from terrestrial plants, have been identified. Conjecture regarding the contributions of BVOCs to  $PM_{2.5}$  has also been put forward. Yet, the behavior of BVOCs and their contribution to  $PM_{2.5}$  formation in Japan remain poorly understood. Therefore, compositional analyses of the organic particles have become increasingly important to determine the sources and types of particles produced (Sakamoto, 2013).

We analyzed carbonaceous particles derived from plants and biomass by using gas chromatography-mass spectrometry (GC-MS), and investigated their composition. To fully understand the contribution of plant-derived carbon components, we need to know not only the concentration of each molecular marker compound but also the ratio of the biogenic or anthropogenic carbon components to the total carbon component. In this

paper, we focus on molecular marker compounds (2-methyltetrols, *cis*-pinonic acid, and levoglucosan) derived from plants and biomass, and carbon isotope ( $^{14}C$ ) found in  $PM_{2.5}$ . We discuss the differences in the sources of the carbonaceous particles in  $PM_{2.5}$  and the contributions of plant-derived carbon to  $PM_{2.5}$  in summer and autumn.

## 2. METHODOLOGY

### 2.1 Sampling Site and Duration

$PM_{2.5}$  samples were collected on the campus of the Center for Environmental Science in Saitama at Kazo ( $36^{\circ}05'10''N$ ,  $139^{\circ}33'37''E$ ) in Saitama Prefecture, Japan (Fig. 1). Kazo is the inland Kanto plain and is approximately 40 km north-northwest of the Tokyo metropolitan area. The sampling site is surrounded by a paddy field; there are no specific emission sources such as large-scale factories or traffic-laden roads nearby (Yonemochi *et al.*, 2011). The sampling instrument was installed on a building rooftop, about 6 m above the ground. During summer, the country's highest temperature is often recorded at the Kumagaya Local Meteorological Observatory (Kumagaya, Saitama Prefecture, Japan), which is located about 15 km northwest of the sampling site. In summer, anthropogenic pollutants, mostly emitted from the surrounded Tokyo bay area, are transported to this area by sea

**Table 1.** Analytical conditions used for the GC/MS analysis.

GC/MS Instrument	ISQ LT GC-MS (Thermo Fisher Scientific)
Column	Fused silica capillary Rtx-5ms (0.25 mm i.d. × 60 m × 0.25 μm, RESTEK)
Oven	Column, 60°C (hold for 1 min) to 200°C at 10°C/min then to 300°C at 5°C/min (hold for 5 min)
Inlet temperature	270°C
Injection	1 μL Splitless
Carrier gas	He, 1.0 mL/min
Ionization voltage	70 eV
Ion source temperature	230°C
MS mode	SIM

breezes and undergo various photochemical reactions during their transportation. Open burning of biomass such as withered grass is carried out near the sampling site after the autumn harvest (Yonemochi *et al.*, 2011, 2007).

Sample collections were carried out in summer (July 26-August 6, 2014), and autumn (October 29-November 13, 2014). The average temperature during the sampling period was 28.2°C in summer and 13.8°C in autumn; the average amounts of solar radiation during the sampling periods in summer and autumn were 24.5 and 8.1 MJ/m<sup>2</sup>/day, respectively. We obtained meteorological data for the sampling site from the local monitoring network, which is managed by the Saitama Prefectural Government. In addition, for the concentration of PM<sub>2.5</sub>, we used the monitoring data from the PM<sub>2.5</sub>/PM<sub>10-2.5</sub>/PM<sub>10</sub>/OBC Dichotomous Monitor (PM-712, Kimoto Electric Co., Ltd., Osaka, Japan) located at this site.

## 2.2 Sampling and Analysis

PM<sub>2.5</sub> samples were collected on quartz fiber filters (20 cm × 25 cm, Pallflex 2500QAT-UP, Pall Corp., Putnam, USA) with a high-volume air sampler (HV-1000R, Sibata Scientific Technology Ltd., Soka, Japan) attached to an impactor type PM<sub>2.5</sub> classifier (HVI-2.5, Tokyo Dylec Corp., Tokyo, Japan) (Kaneyasu, 2010). A glass fiber filter (φ 130 mm, HV-F, Tokyo Dylec Corp.) was used as trapping material on the collision collecting plate in the classifier. The sampling period was 9:00-17:00 (daytime) and 21:00-5:00 (nighttime), and the airflow rate was 740 L/min. All filters were baked at 600°C for 6 h before use to remove organic contaminants. In the US Environmental Protection Agency (EPA) WINS impactor and similar PM<sub>2.5</sub> sampling devices authenticated by the US EPA, such trapping material filters are impregnated with oil to prevent blow off of the separated coarse particles. However, in this research, we used an untreated trapping

material filter in an effort to avoid subsequent analytical obstacles. All samples were stored at -30°C until analyzed.

Molecular marker compounds were assessed by using a derivatization-GC/MS method (Hu *et al.*, 2008; Kleindienst *et al.*, 2007; Hagino *et al.*, 2006; Simoneit *et al.*, 2004). The analytical target compounds were 2-methyltetrols (2-methylthreitol and 2-methylerythritol), *cis*-pinonic acid, and levoglucosan. 2-Methyltetrols and *cis*-pinonic acid are secondary molecular marker compounds derived from isoprene and α-pinene emitted from many plant species, respectively (Liang *et al.*, 2012; Wagener *et al.*, 2012; Fu and Kawamura, 2011; Fu *et al.*, 2009; Bhat and Fraser, 2007; Kleindienst *et al.*, 2007; Claeys *et al.*, 2004). Levoglucosan is a primary molecular marker compound produced by biomass burning (Wagener *et al.*, 2012; Offenberg *et al.*, 2011; Kumagai *et al.*, 2010; Lee *et al.*, 2008; Bhat and Fraser, 2007; Hagino *et al.*, 2006; Simoneit *et al.*, 1999). Thirty punches of rounded pieces (φ 10 mm) were analyzed. Prior to extraction, the sample pieces were spiked with an internal recovery standard mixture (S-(+)-ketopinic acid and levoglucosan-*d*<sub>7</sub>, for each μg of equivalency). They were ultrasonically extracted for 20 min each in 10 mL of a dichloromethane and methanol mixture (2 : 1, *v/v*). The extracts were then filtered and dried by a gentle stream of ultrapure nitrogen in a reaction vial. For the derivatization, 50 μL of the reagent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, including trimethylchlorosilane as a catalyst) was added to the dried samples. The samples were then reconstituted to 200 μL with a dichloromethane and hexane solution (1 : 1, *v/v*) and the reaction was carried out at 70°C for 2.5 h by using a dry bath. After the reaction, the resulting trimethylsilyl derivatives were evaluated by means of GC/MS (ISQ LT GC-MS, Thermo Fisher Scientific Inc., Waltham, USA). The analytical conditions of the GC/MS analysis are summarized in Table 1. Reference compounds

**Table 2.** Atmospheric concentrations of molecular marker compounds (unit: ng/m<sup>3</sup>).

	Summer samples		Autumn samples	
	Daytime ( <i>n</i> = 12)	Nighttime ( <i>n</i> = 12)	Daytime ( <i>n</i> = 16)	Nighttime ( <i>n</i> = 16)
2-Methyltetrols*	42.2 ± 11.1	16.3 ± 7.8	4.7 ± 3.2	2.4 ± 1.6
<i>cis</i> -Pinonic acid	16.7 ± 1.9	6.5 ± 1.5	10.6 ± 3.2	5.3 ± 1.4
Levoglucozan	64.5 ± 38.1	43.4 ± 21.1	805.9 ± 423.7	400.6 ± 224.2

\*The concentration of the 2-methyltetrols is the sum of the concentrations of 2-methylthreitol and 2-methylerythritol. (95% CI)

were available for the target compounds, compounds were identified by comparing the GC retention times with the mass chromatograms of the pure reference compounds. Alternatively, they were identified by comparing their mass spectra with previously reported data (Hu *et al.*, 2008; Claeys *et al.*, 2007; Kleindienst *et al.*, 2007; Jaoui *et al.*, 2004) and by examining their retention times relative to those of other known compounds in GC chromatograms. A procedural blank was analyzed for each PM<sub>2.5</sub> filter sample, and the concentration estimate was adjusted accordingly.

Carbon component analysis was conducted using a thermal/optical carbon analyzer (DRI model 2001A, Atmoslytic Inc., Calabasas, CA, USA) with the IMPROVE Thermal-Optical-Reflectance Analysis method (Chow *et al.*, 2001, 1993). A punch of a round piece (φ 8 mm) from each filter, sample was used to determine the carbon components. Blank filters were analyzed for all components, and blank values were subtracted from each detected component. We applied the definition of char-EC and soot-EC previously used by Han *et al.* (2007) to our results. The components of organic carbon (OC) and elemental carbon (EC), were classified as OC1, OC2, OC3, OC4, pyrolytic OC (PyOC), char-EC (= EC1-PyOC), soot-EC (= EC2) and EC3, and their behaviors were compared. Total carbon (TC) was defined as the sum of OC and EC.

Carbon isotopic analysis was carried out at the Paleo Labo Co. Ltd., Japan, using a compact 500 kV Accelerator Mass Spectrometer (1.5SDH, National Electrostatics Corp., Middleton, USA). To measure <sup>14</sup>C by using an Accelerator Mass Spectrometer, 1 mg or more of carbon per sample is required. Therefore, the amount of carbon per filter was determined from the OC and EC concentrations of the PM<sub>2.5</sub> samples collected in summer. Consequently, eleven summer samples (seven daytime samples and four nighttime samples) that contained sufficient TC components were selected, and 1/4 to 1/2 sheets were analyzed. The percent modern carbon (pMC), an index of plant origin, was estimated based on the <sup>14</sup>C concentration (pMC = 100%, Δ<sup>14</sup>C = 0‰) in 1950 as the reference value. Sample activity was corrected for isotopic fractionation to δ<sup>13</sup>C = -25.0‰.

### 3. RESULTS AND DISCUSSION

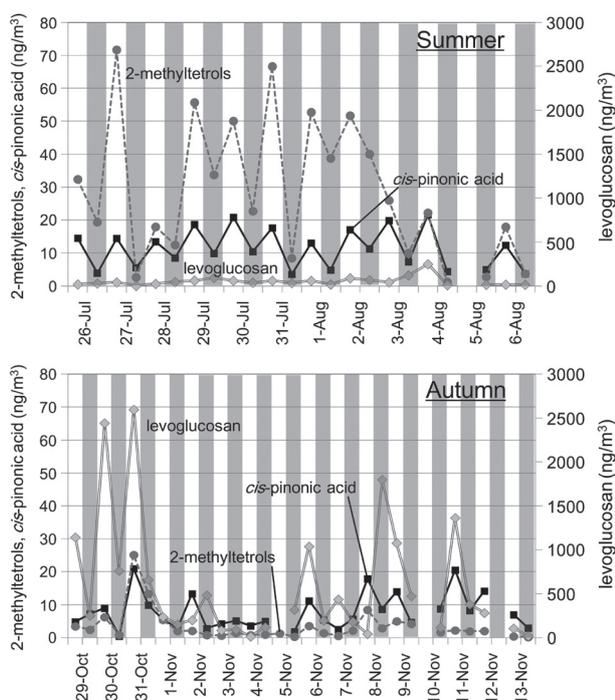
#### 3.1 Changes Overtime in the Concentrations of Molecular Marker Compounds in PM<sub>2.5</sub> during the Summer and Autumn

The atmospheric concentrations of the molecular marker compounds (2-methyltetrols, *cis*-pinonic acid, and levoglucozan) are shown in Table 2. The concentration of the 2-methyltetrols, derived from isoprene, was higher in the summer than in the autumn (November). Because the deciduous period overlaps with this decrease in the levels of the 2-methyltetrols, we considered the emission source to be broad-leaved tree. In contrast, the concentration of *cis*-pinonic acid, derived from α-pinene, remained almost constant throughout the summer and autumn. Therefore, we considered its emission source to be conifers, which undergo less defoliation. The concentration of levoglucozan was considerably increased in the autumn due to frequent biomass open burning. It is well known that the concentration of levoglucozan increases during harvest season because of the outdoor burning of rice husks and straw, and our results support this conventional wisdom.

The change over time in the atmospheric concentrations of the molecular marker compounds during the summer and autumn are shown in Fig. 2. In summer, the concentrations of the 2-methyltetrols and *cis*-pinonic acid increased during the daytime, but decreased during the nighttime. Similar, but weaker, trends were found in the autumn, suggesting weak secondary production.

#### 3.2 Behavior of the Carbon Component

The change over time in the concentrations of total carbon (TC), elemental carbon (EC = char-EC + soot-EC + EC3), and organic carbon (OC = OC1 + OC2 + OC3 + OC4 + PyOC) during the summer and autumn are shown in Fig. 3. In summer, the weather was almost always fine, except for at the beginning of sample collection on the night of August 1. In contrast, it occasionally rained during the autumn sampling period (Oct. 31-Nov. 1, 6, 9, and 11-12), and high concentrations were observed in the intervals between the rain.



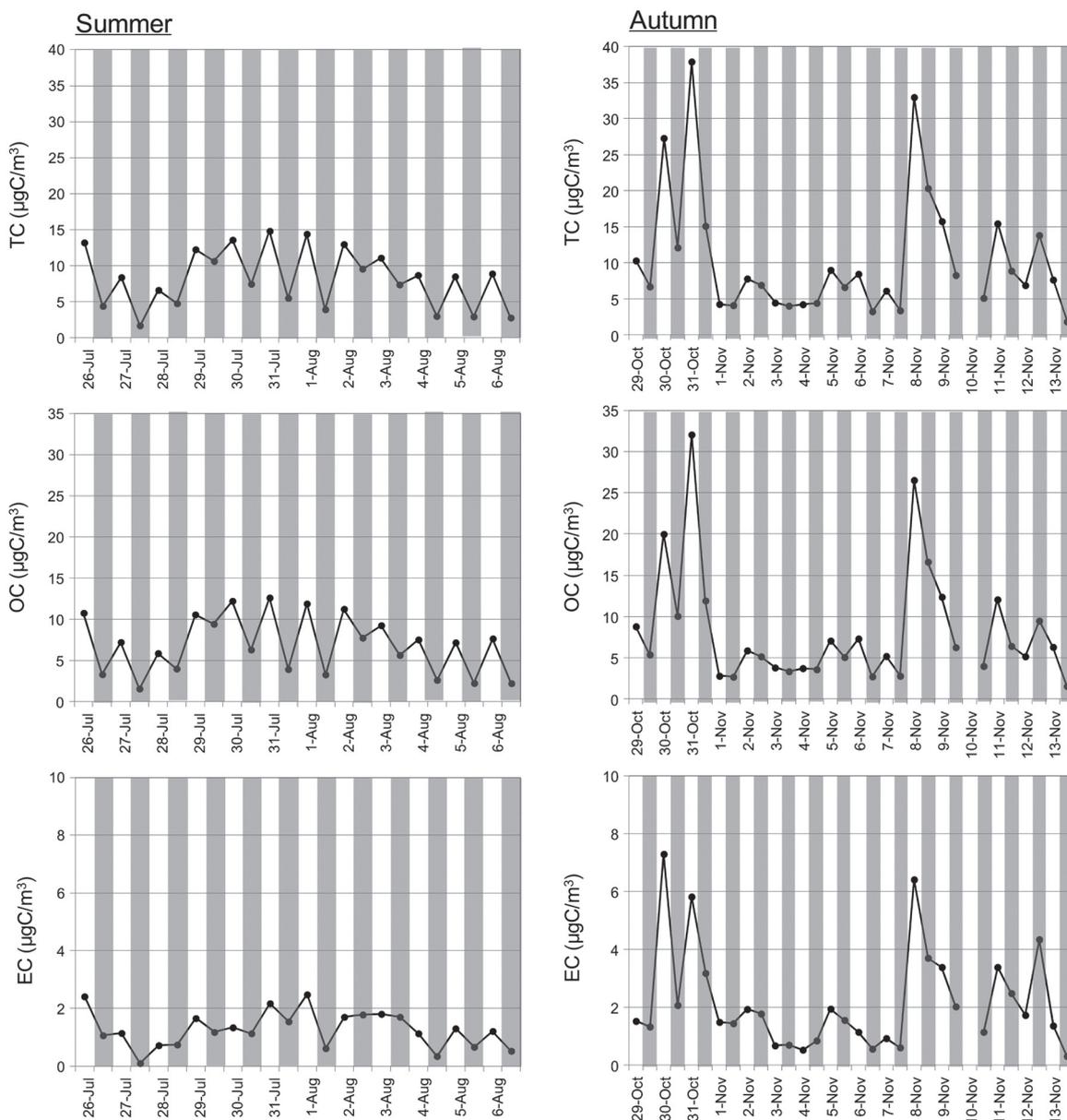
**Fig. 2.** Changes over time in the concentrations of molecular marker compounds in  $PM_{2.5}$  during summer and autumn. The concentration of the 2-methyltetrols is the sum of the concentrations of 2-methylthreitol and 2-methylerythritol. The white background indicates daytime, and the gray background indicates nighttime.

Although the concentrations of the carbon components in the autumn may be slightly underestimated due to rainfall, they were higher than those in the summer and higher in the daytime than in the nighttime. In addition, on days when the concentrations of the carbonaceous components were high, the concentration of levoglucosan was also high. This increase in the concentrations of the carbon components may also be the result of biomass burning in autumn. Moreover, the high concentrations on days with no rainfall may also reflect a situation as outdoor burning.

The changes over time in the concentrations of the carbon fractions during summer and autumn are shown in Fig. 4 and Fig. 5, respectively. In summer, the components of the carbon fraction were, in order of daytime concentration (highest to lowest), OC2 [ $3.2 \pm 0.4 \mu\text{gC}/\text{m}^3$  (daytime),  $1.4 \pm 0.3 \mu\text{gC}/\text{m}^3$  (nighttime)], OC3 [ $2.7 \pm 0.4 \mu\text{gC}/\text{m}^3$  (daytime),  $1.5 \pm 0.5 \mu\text{gC}/\text{m}^3$  (nighttime)], char-EC [ $2.3 \pm 0.6 \mu\text{gC}/\text{m}^3$  (daytime),  $1.1 \pm 0.4 \mu\text{gC}/\text{m}^3$  (nighttime)], and PyOC [ $1.9 \pm 0.4 \mu\text{gC}/\text{m}^3$  (daytime),  $0.8 \pm 0.3 \mu\text{gC}/\text{m}^3$  (nighttime)]. In contrast, in autumn, the order became OC3 [ $3.5 \pm 1.4 \mu\text{gC}/\text{m}^3$  (daytime),  $2.0 \pm 0.7 \mu\text{gC}/\text{m}^3$  (nighttime)], char-EC [ $3.4 \pm 1.6 \mu\text{gC}/\text{m}^3$  (daytime),  $1.9 \pm 0.8 \mu\text{gC}/\text{m}^3$  (nighttime)],

OC2 [ $2.5 \pm 1.0 \mu\text{gC}/\text{m}^3$  (daytime),  $1.7 \pm 0.5 \mu\text{gC}/\text{m}^3$  (nighttime)], and PyOC [ $2.1 \pm 1.0 \mu\text{gC}/\text{m}^3$  (daytime),  $1.0 \pm 0.4 \mu\text{gC}/\text{m}^3$  (nighttime)]. With the exception of OC1 and OC3, the fraction concentrations showed a significant correlation with the average concentration of  $PM_{2.5}$  during the daytime in summer [ $r=0.60-0.90$  ( $n=12$ ,  $p < 0.05$ )]. This trend was almost the same for the maximum concentration of photochemical oxidant [ $r=0.63-0.78$  ( $n=12$ ,  $p < 0.05$ )], suggesting the influence of photochemical secondary production. In the nighttime, the correlation was weaker as a whole, but the concentrations of OC2, PyOC, and soot-EC each showed a significant correlation with the average concentration of  $PM_{2.5}$  [ $r=0.55-0.65$  ( $n=12$ ,  $p < 0.05$ )]. In contrast, during autumn, there was a significant strong correlation between all fractions and the average concentration of  $PM_{2.5}$  during both the daytime [ $r=0.52-0.97$  ( $n=15$ ,  $p < 0.05$ )] and nighttime [ $r=0.70-0.97$  ( $n=16$ ,  $p < 0.01$ )]. However, the highest concentration of photochemical oxidant showed a moderate correlation with only the PyOC concentration [ $r=0.61$  ( $n=16$ ,  $p < 0.05$ )] in the daytime, and the influence of photochemical secondary production was considered to be small.

The changes over time in the ratio of the char-EC concentration to the soot-EC concentration are shown in Fig. 6. The ratio was  $2.0 \pm 0.4$  (daytime) and  $1.6 \pm 0.4$  (nighttime) in summer, and  $2.8 \pm 0.8$  (daytime) and  $2.6 \pm 1.0$  (nighttime) in autumn. During rainfall, when the influence of outdoor burning would be considered small, the soot-EC, which was likely derived from automobiles, would be expected to be dominant, and this ratio was around 1 in some cases. On the other hand, when high concentrations of carbon components are observed in autumn, the ratio is significantly higher (5 and above). The one exception to this finding, on Oct. 30 when the ratio was low despite the high concentration of levoglucosan, does not negate the impact of biomass burning. This low ratio is due to a considerably high concentration of soot-EC. Consequently, we consider that one of the emission source was car exhaust gas. Although other emission sources are not clear, soot-EC may be formed by outdoor burning of plastic products (e.g., agricultural materials, domestic waste). Han *et al.* (2007) define char-EC as derived from low-temperature incomplete combustion, and soot-EC as particleized after gasification by high-temperature incomplete combustion. In other words, the higher ratio of char-EC concentration to soot-EC concentration means that the contribution of low-temperature incomplete combustion (e.g., biomass burning), is greater than that of high-temperature incomplete combustion (e.g., discharge from an internal combustion engine), so the value of this ratio can be considered an



**Fig. 3.** Changes over time in the concentrations of the carbonaceous components (total carbon: TC, elemental carbon: EC, and organic carbon; OC) of  $PM_{2.5}$ . The white background indicates daytime, and the gray background indicates nighttime.

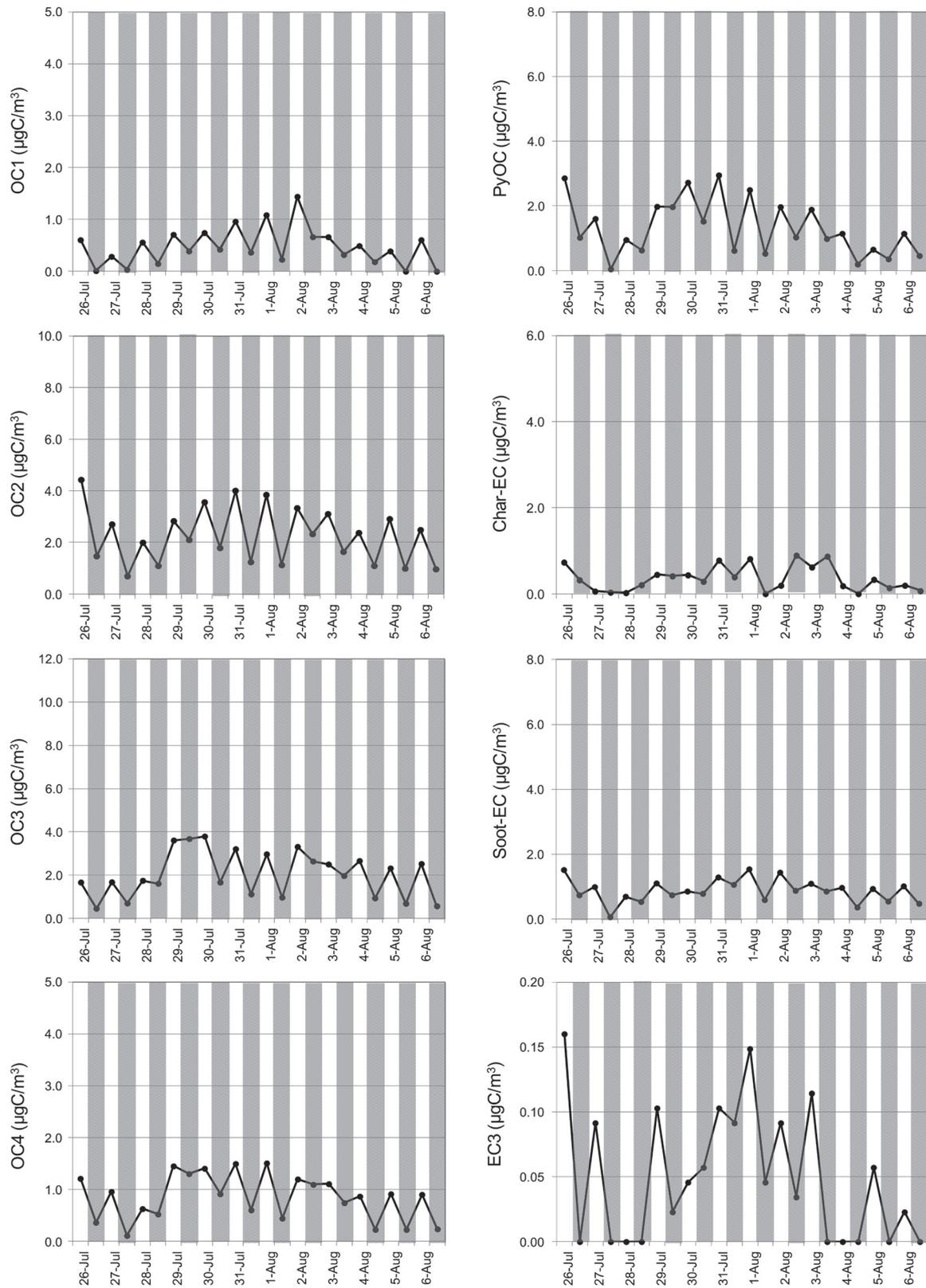
indicator of outdoor open burning.

### 3.3 The Proportion of Plant-derived Carbon for TC in $PM_{2.5}$ Samples of Summer

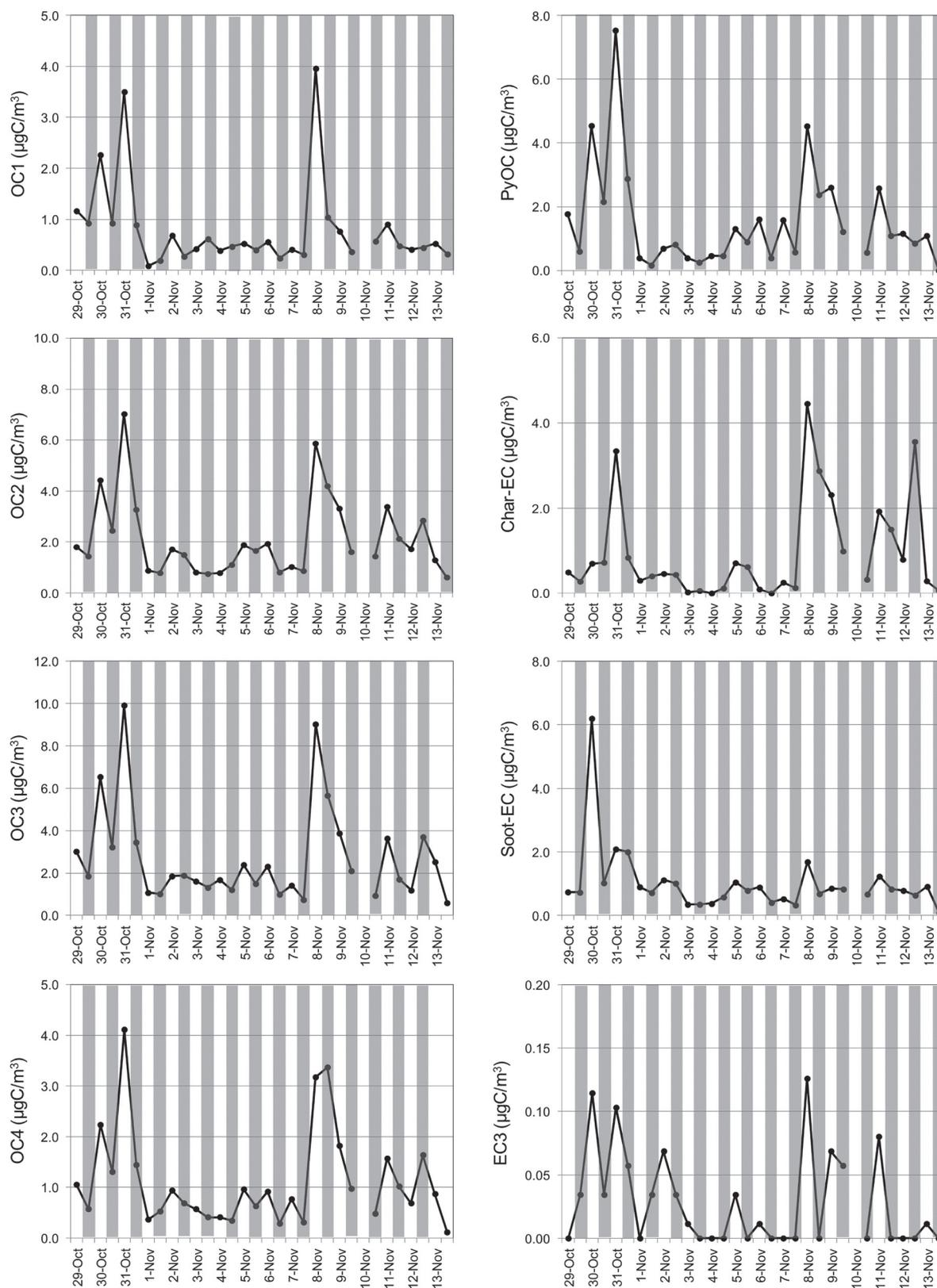
The  $^{14}C$  analysis revealed that the pMC for TC in the  $PM_{2.5}$  collected in summer ranged from 50.7% to 74.4% in the daytime (average, 62%), and from 60.3% to 92.9% in the nighttime (average, 77%). In other words, the ratio of plant-derived carbon to TC in the  $PM_{2.5}$  was higher than that of fossil fuel-derived carbon during

the daytime and nighttime, indicating that the plant-derived carbon contributes greatly to  $PM_{2.5}$ . The difference between the daytime and the nighttime values was likely due to anthropogenic sources from social activities during the daytime. A similar trend was seen in a summer survey in Maebashi, Japan (Fushimi *et al.*, 2011).

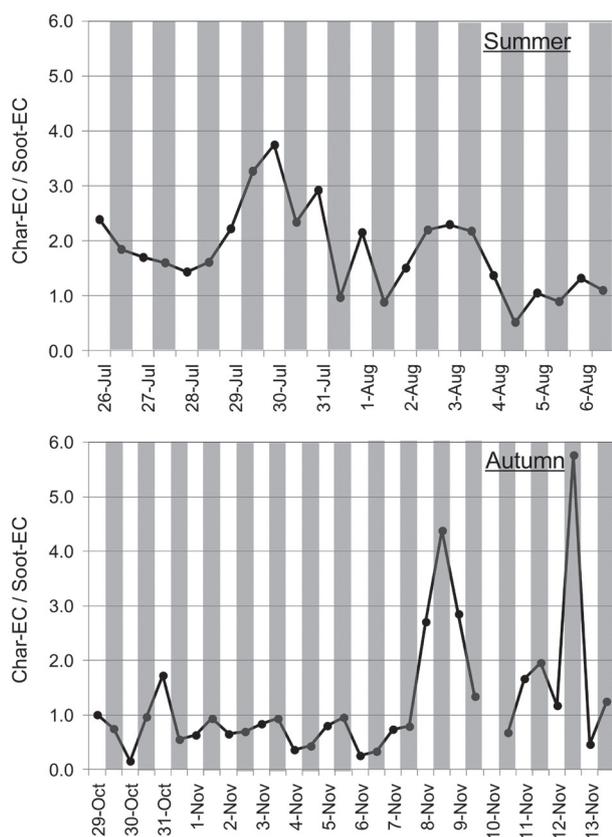
Diurnal changes in the carbonaceous concentrations derived from fossil fuel ( $C_{FF}$ ) and non-fossil fuel ( $C_{NFF}$ ) in summer  $PM_{2.5}$  samples are shown in Fig. 7. The  $C_{FF}$



**Fig. 4.** Changes in the concentrations of the carbonaceous fractions during the summer. The white background indicates daytime, and the grey background indicates nighttime.



**Fig. 5.** Changes in the concentrations of the carbonaceous fractions during the autumn. The white background indicates daytime, and the gray background indicates nighttime.

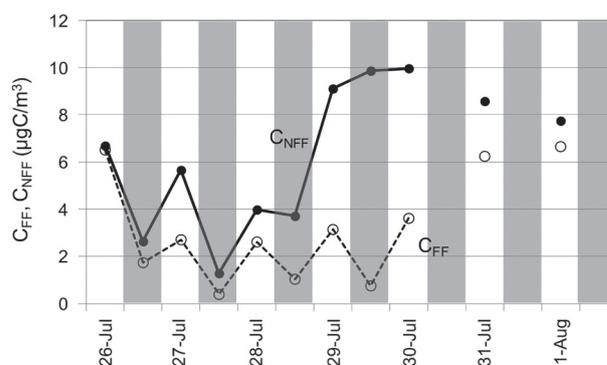


**Fig. 6.** Changes over time in the ratios of the char-EC concentration to the soot-EC concentration during the summer and autumn. The white background indicates daytime, and the gray background indicates nighttime.

and  $C_{\text{NFF}}$  increased during the daytime, but decreased during the nighttime. This variation in  $C_{\text{FF}}$  demonstrates the influence of anthropogenic sources from social activities during the daytime. The variation in  $C_{\text{NFF}}$  was in good agreement with the changes in the atmospheric concentrations of the 2-methyltetrols and *cis*-pinonic acid in summer (Fig. 2). There was one exception to this finding:  $C_{\text{NFF}}$  during the nighttime on July 29 was higher than that during the daytime. This was consistent with the changes in the ratios of the char-EC concentration to the soot-EC concentration (Fig. 6) but was not very consistent with the change in the concentration of levoglucosan. Since the cause is unclear, it should be investigated further by extending the analysis to new samples.

#### 4. CONCLUSION

PM<sub>2.5</sub> sample evaluation was conducted in Kazo in Saitama Prefecture, the inland Kanto plain, during the



**Fig. 7.** Diurnal changes of the carbonaceous concentrations derived from fossil fuel ( $C_{\text{FF}}$ ) and non-fossil fuel ( $C_{\text{NFF}}$ ) in summer PM<sub>2.5</sub> samples. The white background indicates daytime, and the gray background indicates nighttime.

daytime and nighttime in the summer and autumn of 2014. The characteristics of the carbonaceous aerosol were obtained by using carbon profile analysis and GC-MS analysis of molecular marker compounds (2-methyltetrols, *cis*-pinonic acid, and levoglucosan), including source information such as fossil fuel emission origin, plant origin, biomass open burning products, and photochemical reaction products. In addition, the <sup>14</sup>C carbonaceous concentrations in the same PM<sub>2.5</sub> samples were measured.

1) The change over time in concentration of the 2-methyltetrols and *cis*-pinonic acid showed that their emission sources were deciduous trees and conifers, respectively. In summer, the concentrations of these compounds increased during the daytime, and reduced during the nighttime. Similar, albeit weaker, trends were found in autumn suggesting weak secondary production. The concentration of levoglucosan increased considerably during after the autumn harvest due to frequent biomass open burning.

2) The concentrations of the carbonaceous components were higher in the autumn than in the summer, and higher in the daytime than in the nighttime. Most of the fractions showed a significant correlation with the maximum concentration of photochemical oxidant during the daytime in summer, suggesting the influence of photochemical secondary production. In autumn, the ratio of the char-EC concentration to the soot-EC concentration was significantly higher due to the increase in the concentrations of the carbon components as a result of biomass open burning, accordingly, this ratio could be used as an indicator of outdoor open burning.

3) The proportion of plant-derived carbon for TC in the PM<sub>2.5</sub> was higher than that of fossil fuel-derived carbon during the daytime and nighttime, indicating

that the plant-derived carbon greatly contributes to  $PM_{2.5}$ . The difference between the daytime and the nighttime likely stemmed from anthropogenic sources due to social activities during the daytime. The carbonaceous concentrations derived from fossil fuel and non-fossil fuel increased during the daytime, but decreased during the nighttime. The variations in carbonaceous concentrations derived from non-fossil fuel were in good agreement with the changes in the atmospheric concentrations of 2-methyltetrols and *cis*-pinonic acid in summer. Exceptionally, the high  $C_{NFF}$  at night was consistent with the changes in the ratios of the char-EC concentration to the soot-EC concentration but was not very consistent with the change in the concentration of levoglucosan. This suggests that the carbonaceous component derived from non-fossil fuel at night is mainly due to biomass open burning, and this should be investigated further by extending the analysis to new samples.

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