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Measurement report: Source characteristics of water-soluble organic carbon in $PM_{2.5}$ at two sites in Japan, as assessed by long-term observation and stable carbon isotope ratio

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Abstract. The sources and seasonal trends of water-soluble organic carbon (WSOC) in carbonaceous aerosols are of significant interest. From July 2017 to July 2019, we collected samples of $PM_{2.5}$ (particulate matter, aerodynamic diameter < 2.5 μm) from one suburban and one rural site in Japan. The average $\delta^{13}C_{WSOC}$ was −25.2 ± 1.1‰ and −24.6 ± 2.4‰ at the suburban site and rural site, respectively. At the suburban site, the $\delta^{13}C_{WSOC}$ was consistent with the $\delta^{13}C$ of levoglucosan, a tracer of biomass burning, and a high correlation was found between WSOC concentration and non-sea-salt potassium concentration, another tracer of biomass burning, suggesting that the main source of WSOC was biomass from burning of rice straw. At the rural site, the $\delta^{13}C_{WSOC}$ was significantly heavier in winter (−22.6 ± 1.3‰) than in summer (−27.4 ± 0.7‰; $p < 0.01$). The heavy $\delta^{13}C_{WSOC}$ in winter was a result mainly of biomass burning and the aging of OC during long-term transport, whereas the light $\delta^{13}C_{WSOC}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds. Thus, our $\delta^{13}C_{WSOC}$ approach was useful to elucidate the sources and atmospheric processes that contribute to seasonal variations of WSOC concentrations.

Keywords. Water-soluble organic carbon, Stable carbon isotope ratio, $PM_{2.5}$, Seasonal variation, Biomass burning

1 Introduction

Particulate matter (PM) has deleterious effects on human health and contributes to climate change (Pope et al., 1995; Lohmann and Feichter, 2005). A major component of $PM_{2.5}$ (particulate matter, aerodynamic diameter < 2.5 μm) is carbonaceous aerosol, which comprises organic carbon (OC) and elemental carbon (EC) (Chow et al., 1993; Malm et al., 2004; Pöschl, 2005). The OC in carbonaceous aerosol can be further classified as either water-insoluble organic carbon (WIOC) or water-soluble organic carbon (WSOC) (Sullivan and Weber, 2006). WIOC is produced mainly by the combustion of fossil fuels and contains compounds such as alkanes (Pöschl, 2005). WSOC is emitted primarily from combustion processes, industrial process, and natural sources. It can also be formed through secondary processes such as homogeneous gas-phase or heterogeneous aerosol-phase oxidation (Claeys et al., 2004; Koch et al., 2007; Schichtel et al., 2008). WSOC accounts for 10%–80% of the total OC in carbonaceous aerosol depending on the location and season (Decesari et al., 2001; Sullivan et al.,

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2004; Duarte et al., 2007; Duarte et al., 2015; Zappoli et al., 1999). In addition, an average of 74% of all WSOC is contained in fine particles (Yu et al., 2004). WSOC is hygroscopic and therefore it enhances the capability of aerosols to act as cloud condensation nuclei, which affects climate change (Padró et al., 2010; Asa-Awuku et al., 2011). Therefore, source contributions of WSOC have been of significant interest for decades.

A common approach for estimating the source contributions of WSOC is the use of a positive matrix factorization (PMF) model. Using this approach, the annual contributions of biomass burning and secondary processes to WSOC in Beijing, China, were estimated to be 40% and 54%, respectively (Du et al., 2014). Similarly, in Helsinki, Finland, the contribution of secondary organic aerosol (SOA) to WSOC is reported to be high in summer (78%) but low in winter (28%) (Saarikoski et al., 2008). Although it is possible to estimate the contribution rate using PMF, it is necessary to identify the characterisation of source artificially.

WSOC is known to contain various oxygenated compounds, including dicarboxylic acids, ketocarboxylic acids, aliphatic aldehydes, alcohols, saccharides, saccharide anhydrides, aromatic acids, phenols, amines, amino acids, organic nitrates, and organic sulfates (Duarte et al., 2007; Pietrogrande et al., 2013; Timonen et al., 2013; Chalbot et al., 2014; Duarte et al., 2015). However, the precise molecular composition of WSOC is poorly understood because of the large number of compounds involved and the difficulties involved in identifying the individual components.

The stable carbon isotope ratio ($\delta^{13}C$) of carbonaceous aerosols can provide useful information about a sample of particulate matter (Bosch et al., 2014; Gensch et al., 2014; Kirillova et al., 2014b). Elemental carbon (EC) is unreactive, so its $\delta^{13}C$ ($\delta^{13}C_{EC}$) provides information on the primary source of particulate matter (Kawashima and Haneishi, 2012; Zhao et al., 2018). In contrast, OC and WSOC react in the atmosphere, so their $\delta^{13}C$ ($\delta^{13}C_{OC}$ and $\delta^{13}C_{WSOC}$, respectively) provide information not only on the source of the particulate matter but also on any atmospheric processing it has undergone (Kirillova et al., 2013; Ni et al., 2018).

Kirillova et al. (2010) was the first to develop a combustion method for the analysis of $\delta^{13}C_{WSOC}$ in ambient aerosol. In this method, samples of particulate matter are extracted, dehydrated with a freeze drier, dried, and then examined by elemental analyzer/isotope ratio mass spectrometry (EA/IRMS). This combustion method remains a widely used approach, and it has been used to determine the $\delta^{13}C_{WSOC}$ of various particle size collected at various times of the year in Asia (Pavuluri and Kawamura, 2017; Dasari et al., 2019; Han et al., 2020; Yan et al., 2017; Bosch et al., 2014; Kirillova et al., 2014a; Kirillova et al., 2014b; Kirillova et al., 2013), the United States (Wozniak et al., 2012a; Wozniak et al., 2012b), and Sweden (Kirillova et al., 2010) (Table S1 in the Supplement). For example, the $\delta^{13}C$ of total carbon ($\delta^{13}C_{TC}$) and $\delta^{13}C_{WSOC}$ of total suspended particles (TSP) was observed from September 2009 to October 2010 in Hokkaido, Japan (Pavuluri and Kawamura, 2017). Both $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ were heavier in winter than in summer, demonstrating seasonal variation. The authors concluded that the reason why $\delta^{13}C_{WSOC}$ was heavy in winter was because of the greater release of ^{13}C by fossil fuel combustion and biomass burning. Similarly, Kirillova et al. (2013) collected TSP samples from January 2008 to April 2009 in Sinhagad, India, and Hanimaadhoo Island, Maldives. The average $\delta^{13}C_{WSOC}$ was -20.4 ± 0.5‰ in Sinhagad and -18.4 ± 0.5‰ in Hanimaadhoo Island, which are heavier than values reported in other studies. In addition, aerosols reaching Hanimaadhoo Island after long-

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range, over-ocean transport were enriched by 3‰–4‰ in $\delta^{13}C_{WSOC}$ relative to the aerosols collected in Sinhagad. Based on these findings, Kirillova et al. reported for the first time that this enrichment of $\delta^{13}C$ was an effect related to the aging of OC during long-range transport of aerosol. Recent studies have confirmed the aging effect in Bhola, Bangladesh (Dasari et al., 2019).

In the past few years, several new analytical methods for $\delta^{13}C_{WSOC}$ have been developed, such as wet oxidation/IRMS (Suto and Kawashima, 2018), GasBench/IRMS (Zhang et al., 2019), and total organic carbon analyzer/IRMS (Han et al., 2020). These methods do not require a drying stage during sample preparation; therefore, the total analysis time is markedly reduced compared with the EA/IRMS approach. In addition, these newer approaches are highly sensitive, so only small amounts of sample are needed. However, despite these improved approaches and the significant interest in the seasonal trends and source apportionment of WSOC, no studies have examined the change of $\delta^{13}C_{WSOC}$ in $PM_{2.5}$ over a long period of time to understand seasonal variability. As mentioned above, the small particle size $PM_{2.5}$ contains large number of WSOC, further investigations are needed.

Here, we investigated the seasonal trends of WSOC at one suburban site and one rural site in Japan. Samples of $PM_{2.5}$ were collected from July 2017 to July 2019 at both sites, and $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ values, as well as carbon component and water-soluble ion concentrations, were determined. We then characterized the source of WSOC and any atmospheric processes it had undergone using isotope-based approaches. We believe that this is the first report of the use of the wet oxidation/IRMS method (Suto and Kawashima, 2018) for long-term observation of $\delta^{13}C_{WSOC}$.

2 Materials and experimental methods

2.1 Sampling sites and sample collection

Samples of $PM_{2.5}$ were collected at one suburban site and one rural site in Japan (Fig. S1).

The suburban site (Tsukuba, 36°4'N, 140°4'E) was on the rooftop of a 25-m-high building at the Japan Automobile Research Institute in Tsukuba City, Ibaraki Prefecture, Japan. Tsukuba is a suburban city located in the inland Kanto plain approximately 60 km northeast of the Tokyo metropolitan area. This site is surrounded by residential areas and forests, and there is a road in front of the building. $PM_{2.5}$ samples were collected approximately every 10 days from 19 July 2017 to 12 July 2019.

The rural site (Yurihonjo, 39°23'N, 140°4'E) was on the campus of Akita Prefectural University in Yurihonjo City, Akita Prefecture, Japan. Yurihonjo is located 370 km northwest of Tsukuba and about 5 km away from the coast. The sampling site had no local pollutant sources such as large factories. Every December to February, the site is covered with several centimeters of snow (Japan Meteorological Agency, 2020). $PM_{2.5}$ samples were collected approximately every 14 days from 11 August 2017 to 5 July 2019.

At both sites, the $PM_{2.5}$ samples were collected with high-volume samplers (HV-1000F, Sibata Scientific Technology, Saitama, Japan) equipped with a $PM_{2.5}$ impactor (HV-1000-$PM_{2.5}$, Sibata Scientific Technology) at a flow rate of

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approximately 1000 L min^{-1}. The samples were collected on quartz fiber filters (20.3 × 25.4 cm, 2500QAT-UP, Pallflex, Putnam, USA) that had been prebaked at 550 °C for 4 h before use. After sampling, the filters were kept in a freezer at −30 °C. A total of 107 $PM_{2.5}$ samples (62 samples from Tsukuba and 45 samples from Yurihonjo) were collected. $PM_{2.5}$ mass concentration was analyzed gravimetrically by using an electronic balance before and after sampling.

2.2 Stable carbon isotope ratio analysis

Determination of $\delta^{13}C_{TC}$ was performed at the Japan Automobile Research Institute using EA/IRMS (EA IsoLink, Thermo Fisher Scientific, Bremen, Germany; Delta V Advantage, Thermo Fisher Scientific, respectively). Portions of quartz filter (5–10 mg) were packed into a tin cup. The samples were combusted instantaneously in the EA, and the carbon was converted to CO_2 via an oxidation catalyst in the reduction tube of the EA. The oxidation catalyst and reduction tubes were maintained at 1020 °C. The flow rate of ultra-high-purity helium during the analysis was 180 mL min^{-1}. The CO_2 from the EA was ionized, and the $\delta^{13}C$ value was determined by means of IRMS; data acquisition was performed with Isodat software (ver. 3.0, Thermo Fisher Scientific) installed on a PC running Microsoft Windows 7.

Determination of $\delta^{13}C_{WSOC}$ was performed at Akita Prefectural University using the wet oxidation/IRMS method (Suto and Kawashima, 2018). A portion of each quartz fiber filter (14.13 cm^2) was extracted in 5 mL of Milli-Q water under ultrasonic agitation for 30 min. The extract was filtered through a syringe filter (Chromatodisc Type A 0.45 μm, GL Sciences, Japan) to remove insoluble material. The $PM_{2.5}$ samples were not decarbonated before $\delta^{13}C_{WSOC}$ analysis because the difference between the $\delta^{13}C_{WSOC}$ with and without hydrochloric acid pretreatment was within 0.2‰.

A high-performance liquid chromatography (HPLC) system (Shimadzu Co.) was coupled to the IRMS instrument (Isoprime, Elementar UK, Manchester, UK) via a LiquiFace interface (Elementar UK). The HPLC system consisted of a column pump (LC-10ADvp), oxidation pump (LC-10ADvp), post-column pump (LC-10ADvp), autosampler (SIL-10ADvp), degasser (DGU-14A), and UV detector (SPD-10ADvp). The injection volume was 100 μL. The HPLC flow rate (without column), the sodium peroxodisulfate flow rate, and the post-column flow rate were 0.5, 0.4, and 0.3 mL min^{-1}, respectively. Sodium peroxodisulfate (0.5 M) and phosphoric acid (0.2 M) were mixed and then degassed in an ultrasonic bath for 1 h.

One run took about 6 min. The trap current was set at 300 μA. The limits of detection (precision, <±0.3‰; accuracy, <±0.3‰) for levoglucosan and oxalic acid were 1111 and 1133 ngC, respectively.

The IRMS instrument and the data acquisition system were controlled by IonVantage NT software (ver. 1.5.4.0., Isoprime) installed on a PC running Microsoft Windows XP Professional. The HPLC system was controlled by LCsolution software (ver. 1.25, Shimadzu Co.) installed on a PC running Windows 7 Ultimate.

Stable carbon isotope ratios, expressed in δ notation in permil (‰) units, were calculated as follows:

$$\delta^{13}C\ [‰] = \left(\frac{R(^{13}C/^{12}C)_{sample}}{R(^{13}C/^{12}C)_{std}} - 1\right) \quad (1)$$

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where $R(^{13}C/^{12}C)_{sample}$ and $R(^{13}C/^{12}C)_{std}$ (= 0.0111802) are the $^{13}C/^{12}C$ ratios for the sample and the standard (Vienna Pee Dee Belemnite), respectively. For all samples, the EA/IRMS and wet oxidation/IRMS data were measured in triplicate.

A two-point linear calibration was carried out for $\delta^{13}C$. For EA/IRMS, $\delta^{13}C_{TC}$ values and three internal laboratory standards were calculated by using the following international isotopic standards: IAEA-CH-3 (cellulose, $\delta^{13}C = -24.724‰$), IAEA-600 (caffeine, $\delta^{13}C = -27.771‰$), and USGS24 (graphite, $\delta^{13}C = -16.049‰$). These standards were obtained from the International Atomic Energy Agency (Vienna, Austria). As a check of instrumental stability, an isotope working standard (L-alanine, SI Science Co., Tokyo, Japan; $\delta^{13}C = -19.9‰$) was analyzed after every nine samples.

For wet oxidation/IRMS, $\delta^{13}C$ values were calculated by means of a two-point linear calibration method from international isotope standards of sucrose (IAEA-CH-6, $\delta^{13}C = -10.449‰$), and three internal laboratory standards for D-(+)-arabitol ($\delta^{13}C = –23.6‰$), levoglucosan ($\delta^{13}C = –25.8‰$), and oxalic acid ($\delta^{13}C = –28.7‰$) obtained from EA/IRMS. Ultrapure water was prepared with a Milli-Q system (18.2 MΩ.cm; Millipore, Bedford, MA). To check instrumental stability, the laboratory standard of levoglucosan was analyzed after every nine samples. The average-1SD for $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ was 0.12‰ (<0.46‰) and 0.09‰ (<0.50‰), respectively, for all samples examined in the present study.

2.3 Chemical analysis

For determination of OC and EC concentrations, a portion of each quartz fiber filter (0.53 cm^2) was examined using a thermal-optical carbon analyzer (Model 2001, Desert Research Institute), and the samples were processed according to the IMPROVE Thermal Desorption/Optical Reflectance method with a 550 °C, split for OC and EC (Chow et al., 2001). The limits of detection for OC and EC were determined as three times the standard deviation of a blank filter, and they were 0.02 μg m^{-3} and 0.02 μg m^{-3}, respectively. These limits of detection were sufficiently low (Yamagami et al., 2019).

For determination of WSOC concentrations, a portion of each quartz fiber filter (1.58 cm^2) was extracted with 8 mL of ultrapure water for 30 min at room temperature. The water extracts were passed through a polyvinylidene difluoride filter (pore size 0.20 μm, GE Healthcare, USA) to remove insoluble materials, and then the filtrate was analyzed using a total organic carbon analyzer (TOC-L, Shimadzu, Kyoto, Japan). The limit of detection was determined as three times the standard deviation of a blank filter, and it was 0.03 μg m^{-3}, which was sufficiently low (Du et al., 2014).

Quantification of the major water-soluble ions anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) was achieved by ion chromatography (Integrion RFIC; Thermo Fisher Scientific Inc., Sunnyvale, CA, USA). Details of water-soluble ion analysis method are described in Supplement S1.

3 Results and Discussion

3.1 Mass concentrations of $PM_{2.5}$ at the study sites

The average mass concentrations of $PM_{2.5}$ during the observation period were 19.7 ± 8.2 μg m^{-3} (range, 7.1–46.6 μg m^{-3}) in Tsukuba and 11.2 ± 4.7 μg m^{-3} (5.7–23.4 μg m^{-3}) in Yurihonjo (Table 1). The average mass concentration of $PM_{2.5}$ in

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Tsukuba was higher than the Japan Environmental Standard for the annual average (15 μg m^{-3}) by the Ministry of the Environment and that at other residential sites across Japan (annual average in 2018, 11.2 μg m^{-3}) (Japan Ministry of the Environment, 2019). In Yurihonjo, the average mass concentration of $PM_{2.5}$ was lower than the Japan Environmental Standard for the annual average, and it was comparable with that at other residential sites across Japan.

A previous study reviewed the annual $PM_{2.5}$ concentrations in 45 global megacities in 2013 (Cheng et al., 2016). The five most-polluted megacities were Delhi, India; Cairo, Egypt; and Xi'an, Tianjin, and Chengdu, China ($PM_{2.5}$ annual average concentration, 89–143 μg m^{-3}). The five least-polluted megacities were Toronto, Canada; Miami, Philadelphia, and New York, United States; and Madrid, Spain ($PM_{2.5}$ annual average concentration, 7–10 μg m^{-3}). The mass concentration of $PM_{2.5}$ at both sites in the present study was much closer to that determined for the least-polluted megacities than that determined for the most-polluted megacities.

The mass concentration of $PM_{2.5}$ in Tsukuba was significantly higher in winter and spring than in summer and autumn ($p < 0.01$), whereas that in Yurihonjo was significantly higher in spring than in the other seasons ($p < 0.01$). The mass concentration of $PM_{2.5}$ in winter in Yurihonjo was low because the area is covered with several centimeters of snow from December to February. The seasonal trend observed in Yurihonjo was similar to that reported for Niigata, Japan (Li et al., 2018). Thus, the present $PM_{2.5}$ results seemed to be very reasonable compared to existing papers.

3.2 Concentrations of EC, OC, and WSOC, and OC/EC and WSOC/OC ratios

The concentrations of EC, OC, and WSOC, and the OC/EC and WSOC/OC ratios, at the study sites are summarized in Table 1. The concentrations of the carbon components (EC, WIOC, and WSOC) by season are shown in Fig. 1.

The sum of EC and organic matter (1.6 × OC concentration) (Turpin and Lim, 2001) accounted for an average of 32% of the $PM_{2.5}$ mass concentration in Tsukuba and 25% in Yurihonjo. Thus, the contribution was slightly higher at Tsukuba than at Yurihonjo. The average EC concentration during the observation period was 0.9 ± 0.4 μg m^{-3} (0.4–2.4 μg m^{-3}) in Tsukuba and 0.3 ± 0.1 μg m^{-3} (0.2–0.6 μg m^{-3}) in Yurihonjo. These values are comparable to those reported for Nagoya (1.1 μg m^{-3}) (Yamagami et al., 2019) and Niigata (0.5 μg m^{-3}) (Li et al., 2018), Japan, and lower than that reported for Xi'an, China (7.6 μg m^{-3}) (Zhao et al., 2018). The EC concentration contributed an average of 5% to the $PM_{2.5}$ mass concentration in Tsukuba and 3% in Yurihonjo. Currently, EC concentrations in Japan are decreasing as a result of Japanese government regulations on emissions from diesel vehicles (Yamagami et al., 2019).

The average OC concentration during the observation period was 3.2 ± 1.4 μg m^{-3} (1.0–6.6 μg m^{-3}) in Tsukuba and 1.5 ± 0.8 μg m^{-3} (0.6–4.2 μg m^{-3}) in Yurihonjo. The OC concentration contributed an average of 28% to the $PM_{2.5}$ mass concentration in Tsukuba and 22% in Yurihonjo. The higher percentage contribution to the $PM_{2.5}$ mass concentration from OC than EC was reasonable compared to other studies (Contribution of OC and EC concentration in $PM_{2.5}$ concentration: 20% and 6% in Korea) (Park and Cho, 2011; Yamagami et al., 2019).

The OC/EC ratio is an indicator of the source of carbonaceous particles (Chow et al., 1996). The average OC/EC ratio was 3.8 ± 1.4 in Tsukuba and 5.1 ± 1.9 in Yurihonjo. The higher OC/EC ratio at the rural site (Yurihonjo) than at the suburban

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site (Tsukuba) was comparable with the results of other studies (Ho et al., 2006; Zhang et al., 2008). This was likely because primary emissions, such as EC, are low at rural sites, meaning that the OC is larger in comparison. The high OC/EC ratio is due to the formation of secondary organic aerosols and biomass burning (Chow et al., 1996).

The average WSOC concentration during the observation period was 1.2 ± 0.4 μg m^{-3} (0.4–2.4 μg m^{-3}) in Tsukuba and 0.8 ± 0.5 μg m^{-3} (0.3–2.6 μg m^{-3}) in Yurihonjo. These values were similar to those reported for Sapporo (1.0 μg m^{-3}) (Pavuluri and Kawamura, 2017) and Maebashi (2.3 μg m^{-3}) (Kumagai et al., 2009), Japan, but lower than those reported for Beijing, China (7.2 μg m^{-3}) (Du et al., 2014), and Gwangju, South Korea (3.7 μg m^{-3}) (Park and Cho, 2011). The WSOC concentration at Tsukuba was significantly higher in autumn and winter than in spring and summer ($p < 0.01$), whereas that in Yurihonjo was significantly higher in spring than in the other seasons ($p < 0.05$).

The average WSOC/OC ratio was 0.4 ± 0.1 in Tsukuba and 0.5 ± 0.1 in Yurihonjo. This is consistent with previous studies that showed that the average WSOC/OC ratio was higher at rural sites than at urban sites (Kumagai et al., 2009; Ram and Sarin, 2010). This is also the same as the trend we found for OC/EC ratio in the present study.

3.3 $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$

To our knowledge, this is the first report of a two-year-long observation of $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ in $PM_{2.5}$ at two sites simultaneously. $\delta^{13}C_{WSOC}$ values reported from previous studies conducted at various sampling sites and examining various particle sizes are summarized in Table S1.

In the present study, the average $\delta^{13}C_{TC}$ was −25.7 ± 0.7‰ (−26.9 to −24.0‰) in Tsukuba and −24.7 ± 1.6‰ (−27.3 to −20.4‰) in Yurihonjo (Table 1 and Fig. 2). Previous studies have reported the average $\delta^{13}C_{TC}$ of TSP in Sapporo, Japan (−24.8‰ ± 0.68‰) (Pavuluri and Kawamura, 2017), and of $PM_{2.5}$ in Sanjiang Plain, China (−24.2‰) (Cao et al., 2016), and these values are comparable to our present values.

In the present study, the average $\delta^{13}C_{WSOC}$ was −25.2 ± 1.1‰ (−26.7 to −21.8‰) in Tsukuba and −24.6 ± 2.4‰ (−28.4 to −19.8‰) in Yurihonjo (Table 1 and Fig. 2). The $\delta^{13}C_{WSOC}$ of $PM_{2.5}$, which was the particle size examined in the present study, was −25.4‰ ± 1.0‰ in Delhi, India (Dasari et al., 2019), and −24.2‰ ± 0.6‰ in Bhola, Bangladesh (Dasari et al., 2019), which are very close to our $\delta^{13}C_{WSOC}$ values. The $\delta^{13}C_{WSOC}$ of TSP was −24.2‰ ± 1.59‰ in Sapporo, Japan (Pavuluri and Kawamura, 2017), −24.0‰ ± 1.5‰ in Seoul, South Korea (Han et al., 2020), −25.2‰ ± 0.2‰ in Millbrook, USA (Wozniak et al., 2012a), and similar values were obtained for particles of different sizes. In these previous studies, most of the average $\delta^{13}C_{WSOC}$ values were in the range of −25‰ to −24‰ regardless of particle size, although there were some heavy values such as those for Hanimaadhoo Island, Maldives (−18.4‰ ± 0.5‰), and Sinhagad, India (−20.4‰ ± 0.5‰) (Kirillova et al., 2013).

3.4 Seasonal variations in $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ in $PM_{2.5}$

$\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at Tsukuba became slightly heavy from February to April 2019, but they showed no other clear seasonal variation (Fig. 2a). In contrast, the $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at Yurihonjo were heaver in winter and spring than in summer

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and autumn (Fig. 2b), and they showed a significant seasonal variation ($\delta^{13}C_{TC}$; $p < 0.01$, $\delta^{13}C_{WSOC}$; $p < 0.01$) compared to those in Tsukuba. At both study sites, $\delta^{13}C_{WSOC}$ was usually heavier than $\delta^{13}C_{TC}$, but in summer $\delta^{13}C_{WSOC}$ was comparable to or lighter than $\delta^{13}C_{TC}$.

The seasonal trends of $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ observed in the present study were compared with those reported from previous long-term observations. $\delta^{13}C_{WSOC}$ in TSP in Seoul, South Korea, from March 2015 to January 2016 showed no seasonal variation (Han et al., 2020), which is comparable with our present findings for the suburban site, Tsukuba. Similarly, $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ in TSP reported for Sapporo, Japan, from September 2009 to October 2010 were clearly heavier in winter than in summer (Pavuluri and Kawamura, 2017), which is comparable with our present findings for the rural site, Yurihonjo. In both Yurihonjo and Sapporo, it was observed that $\delta^{13}C_{WSOC}$ is usually heavier than $\delta^{13}C_{TC}$ and that this tendency is reversed in summer. Together, these findings imply that $\delta^{13}C_{WSOC}$ shows a weak seasonal trend in suburban or urban sites such as Tsukuba and Seoul, but a clear seasonal trend in rural sites such as Yurihonjo and Sapporo.

The variations (difference between maximum and minimum value) of $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ were 2.9‰ and 4.9‰ in Tsukuba and 7.0‰ and 8.6‰ in Yurihonjo, respectively. The variation of $\delta^{13}C_{WSOC}$ was larger than that of $\delta^{13}C_{TC}$ at both sites, with both variations larger in Yurihonjo. In previous studies, the variation of $\delta^{13}C_{TC}$ was reported as 2.5‰ in Sapporo (Pavuluri and Kawamura, 2017), and that of $\delta^{13}C_{WSOC}$ was reported as 5.5‰ in Sapporo (Pavuluri and Kawamura, 2017), and 6.5‰ in Seoul (Han et al., 2020). The variation of $\delta^{13}C_{EC}$ of $PM_{2.5}$ was only 1.6‰ in Japan (Kawashima and Haneishi, 2012) and 3.7‰ in China (Ni et al., 2018; Zhao et al., 2018). In the present study and these previous studies, the variation of $\delta^{13}C_{WSOC}$ was larger than that of $\delta^{13}C_{EC}$, regardless of sampling site. The reason for this is likely that $\delta^{13}C_{WSOC}$ is affected not only by the source characteristics but also by atmospheric processing. The reasons underlying the seasonal trend observed for $\delta^{13}C_{WSOC}$ are further discussed in Sections 3.5.1 and 3.5.2.

3.5 Determination of seasonal trends and sources of WSOC using $\delta^{13}C_{WSOC}$

3.5.1 Seasonal trends and sources of WSOC in Tsukuba

The WSOC concentration in Tsukuba was significantly higher in autumn and winter than in spring and summer ($p < 0.01$), and EC concentration showed a similar seasonal trend ($p < 0.01$) (Table 1).

Correlation coefficients between WSOC concentration and $\delta^{13}C_{WSOC}$, EC concentration, and non-sea-salt potassium (nss-K^+) concentration by season are shown in Table 2. A weak correlation ($r = 0.18$) was found between WSOC concentration and $\delta^{13}C_{WSOC}$. In contrast, the correlation coefficient between WSOC concentrations and EC concentrations, which is a tracer of combustion (Bond et al., 2007), was high in all seasons (annual average, $r = 0.71$), suggesting that WSOC was affected by combustion at this suburban study site. The nss-K^+ is a tracer of biomass burning that is calculated by using the equation nss-$K^+ = [K^+] - 0.0335 \times [Na^+]$, which excludes K^+ originating from seawater (Lai et al., 2007). Strong correlations were observed between WSOC concentration and nss-K^+ in every season (autumn, $r = 0.96$; winter, $r = 0.83$; spring, $r = 0.85$; summer $r = 0.77$; $p < 0.01$), which again suggests that WSOC was affected by biomass burning.

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In the Kanto Region of Japan, which is where Tsukuba is located, large aerosol emissions due to biomass burning occur in autumn and winter (Kumagai et al., 2010). The most productive crop in Japan is rice, followed by barley and wheat (Japan Ministry of Agriculture Forestry and Fisheries, 2020). In Ibaraki Prefecture, the crop acreage of rice was 68,400 ha, and the harvest was 358,400 tons in 2018, the largest in the Kanto Region. In Japan, the harvest season for rice is from September to October.

The main chemical component generated by the breakdown of cellulose by burning rice straw is levoglucosan, which can be used as a tracer of biomass burning (Simoneit et al., 1999). The $\delta^{13}C$ of levoglucosan emitted from burning rice straw by open combustion in a field is reported to be in the range of −25.86 ± 0.27‰ to −24.26 ± 0.09‰ (Sang et al., 2012). The average $\delta^{13}C_{WSOC}$ at Tsukuba was −25.2 ± 1.1‰, which is very close to the reported $\delta^{13}C$ of levoglucosan. Therefore, together with the high correlation between WSOC concentration and nss-K^+ concentration, we speculate that the main source of WSOC in Tsukuba is the burning of rice straw. This is consistent with other studies that have reported very high concentrations of levoglucosan in Japan in autumn and winter (257 ng m^{-3}) (Kumagai et al., 2010; Sasaka et al., 2017). Using radiocarbon analysis, which can distinguish between biogenic and anthropogenic sources, a higher proportion of OC in $PM_{2.5}$ observed in Tokyo, Japan in 2014 was reported to be biogenic from autumn to winter than in summer (Hoshi and Saito, 2020).

3.5.2 Seasonal trends and sources of WSOC in Yurihonjo

The $\delta^{13}C_{WSOC}$ values at Yurihonjo were heavier in winter and spring than in summer and autumn. We suggest two possible reasons for this seasonality of $\delta^{13}C_{WSOC}$: (1) changes in combustion source together with aging of OC during long-range transportation in the winter, and (2) increased photochemical reactivity of biogenic volatile organic compounds (VOCs) in the summer.

The correlation between WSOC concentrations and EC concentrations was highest in winter (r = 0.87, p < 0.01), followed by autumn (r = 0.83, p < 0.01) and spring (r = 0.64, p < 0.05), and lowest in summer (r = 0.24) (Table 2). In addition, the correlation between nss-K^+ concentration and WSOC concentration was very high in autumn (r = 0.93), winter (r = 0.99), and spring (r = 0.80; all p < 0.01) but not in summer (r = 0.40). These strong correlations suggest that the WSOC concentration from autumn to spring at Yurihonjo was mainly related to combustion sources such as biomass burning.

As described in Section 3.5.1, the $\delta^{13}C$ of levoglucosan emitted from burning rice straw by open combustion in a field is in the range of −25.86 ± 0.27‰ to −24.26 ± 0.09‰ (Sang et al., 2012). In Akita Prefecture, an area of Japan famous for its rice production, the crop acreage of rice was 87,700 ha, and the harvest was 491,100 tons in 2018 (Japan Ministry of Agriculture Forestry and Fisheries, 2020). However, the average $\delta^{13}C_{WSOC}$ in winter was −22.6‰, which was much heavier than the $\delta^{13}C$ of levoglucosan. Therefore, the heavy $\delta^{13}C_{WSOC}$ in winter cannot be explained only by the effect of biomass burning.

Recent studies have reported that the $\delta^{13}C_{WSOC}$, $\delta^{13}C_{OC}$, and $\delta^{13}C$ of levoglucosan in aerosols are enriched due to photochemical aging of OC during long-range transport (Kirillova et al., 2013; Bosch et al., 2014; Gensch et al., 2018; Dasari et al., 2019). In general, aerosol photochemical aging selectively enriches the ^{13}C content in organic aerosols, leading to heavier

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$\delta^{13}C$ values in the remaining aerosol (Pavuluri and Kawamura, 2012). In a field study, the isotope fractionation values for $\delta^{13}C_{WSOC}$ were estimated to be enriched by 3‰–4‰ because of aging during transport (Kirillova et al., 2013). Therefore, the heavier $\delta^{13}C$ in winter was considered to be a result not only of increased combustion but also of the aging of OC. Indeed, long-range transport of contaminants from Northeast Asia has been observed in Niigata, which is located on the coast of the Sea of Japan (Li et al., 2018). Therefore, we speculate that the heavier $\delta^{13}C_{WSOC}$ in winter at Yurihonjo is affected both by biomass burning and aging of OC during long-term transport.

The $\delta^{13}C_{WSOC}$ in summer was very light (−27.4‰) compared with the average value for the observation period. The weak correlation between WSOC concentration and EC concentration in summer (r = 0.24; Table 2) suggests that WSOC concentration is affected by some non-combustion source. In general, the formation of WSOC involves atmospheric reactions such as the formation of SOA. Indeed, SOA formed by oxidation of biogenic and anthropogenic VOCs is an important source of WSOC (Miyazaki et al., 2009). These biogenic VOCs include isoprene, monoterpenes, and sesquiterpenes released from vegetation, with isoprene producing the most SOA (Atkinson and Arey, 1998). The oxidation product of isoprene is 2-methyltetrol, which is widely used as an organic tracer to evaluate the production of SOA from isoprene (Claeys et al., 2004). That is, because isoprene has high photochemical reactivity, it is difficult to directly measure the $\delta^{13}C$ of isoprene, so the $\delta^{13}C$ of 2-methyltetrol is measured instead (Li et al., 2010). The average $\delta^{13}C$ of 2-methyltetrol was −27.36‰ (−28.23 to −26.46‰) in four forests in Sichuan Province, China (Li et al., 2019). The $\delta^{13}C$ of 2-methyltetrol is close to the $\delta^{13}C_{WSOC}$ detected in summer in Yurihonjo, suggesting that the components produced by secondary reaction of biogenic VOCs have a strong influence during summer in Yurihonjo.

Aliphatic hydrocarbons (e.g., alkanes and alkenes) and aromatics (e.g., benzene, toluene, ethylbenzene, and xylene) emitted from solvent evaporation and vehicle emissions are important anthropogenic VOCs precursors of SOA (Chen et al., 2010). The $\delta^{13}C$ values for alkanes in tunnel, gas station, underground garage, and refinery samples were reported to range from −28.6 ± 1.8‰ to −27.3 ± 2.1‰ (Rudolph et al., 2002). Toluene and xylene are the aliphatic hydrocarbons with the highest annual emissions in Japan (Japan Ministry of Economy Trade and Industry, 2020). The $\delta^{13}C$ of toluene and xylene are reported to range from −27.4‰ to −27.1‰ and −27.7‰ to −27.4‰ in gas station, −26.1‰ to −24.8‰ in cold-start vehicle emissions, and −24.9‰ to −23.8‰ in hot-start vehicle emissions, respectively (Kawashima and Murakami, 2014; Rudolph et al., 2002). Irei et al. (2006) reported from a laboratory-based experiment that the $\delta^{13}C$ of SOA particles formed by OH-radical-induced reaction of toluene was on average 5.8‰ lighter than that of the parent toluene. Assuming this isotope fractionation for toluene applies also to all other potential components, the $\delta^{13}C$ of the VOCs emission source for Yurihonjo was calculated as approximately −21.6‰ by subtracting 5.8‰ from the average $\delta^{13}C_{WSOC}$ during summer in Yurihonjo (−27.4‰). This estimated $\delta^{13}C$ value of VOCs was heavier than those previously reported for anthropogenic VOCs, as described above; therefore, the effect of anthropogenic VOCs on WSOC was considered to be smaller than that of biogenic VOCs. Indeed, at the global scale, biogenic VOCs emissions are more than an order of magnitude higher than those of anthropogenic VOCs (Farina et al., 2010).

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4 Conclusion

The WSOC concentration, $\delta^{13}C_{TC}$ and the $\delta^{13}C_{WSOC}$ of $PM_{2.5}$ were observed at one rural and one suburban, in Japan over a two-year period. The average WSOC concentration during the observation period was 1.2 ± 0.4 μg m^{-3} (0.4–2.4 μg m^{-3}) in suburban site and 0.8 ± 0.5 μg m^{-3} (0.3–2.6 μg m^{-3}) in rural site. The $\delta^{13}C_{WSOC}$ was −25.2 ± 1.1‰ (−26.7 to −21.8‰) in suburban site and −24.6 ± 2.4‰ (−28.4 to −19.8‰) in rural site. The $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at suburban site became slightly heavy from February to April 2019, but they showed no other clear seasonal variation. In contrast, the $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at rural site were heaver in winter and spring than in summer and autumn, and they showed a significant seasonal variation ($\delta^{13}C_{TC}$; $p < 0.01$, $\delta^{13}C_{WSOC}$; $p < 0.01$). By $\delta^{13}C_{WSOC}$, carbon components and water-soluble ions, at the suburban site, at the suburban site, the main source of WSOC during autumn and winter was estimated biomass burning of rice straw. At the rural site, the heavy $\delta^{13}C_{WSOC}$ in winter was a result mainly of biomass burning and the aging of OC during long-term transport, whereas the light $\delta^{13}C_{WSOC}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds. Thus, we were able to use a $\delta^{13}C_{WSOC}$ based approach to understand the source characteristics of WSOC and the atmospheric processes that contribute to the WSOC concentrations at the two study sites.

Data availability. Data are available from the corresponding author on request (nsuto@jari.or.jp).

Author contribution. NS and HK were involved in research planning and experimental design. NS performed the sampling and measurements of $\delta^{13}C_{TC}$, carbon components and water-soluble ions. HK performed the sampling and measurements of $\delta^{13}C_{wsoc}$. All authors clarified the experimental data and contributed to the witing of the paper.

Competing interests. The authors declare that they have no conflict of interest.

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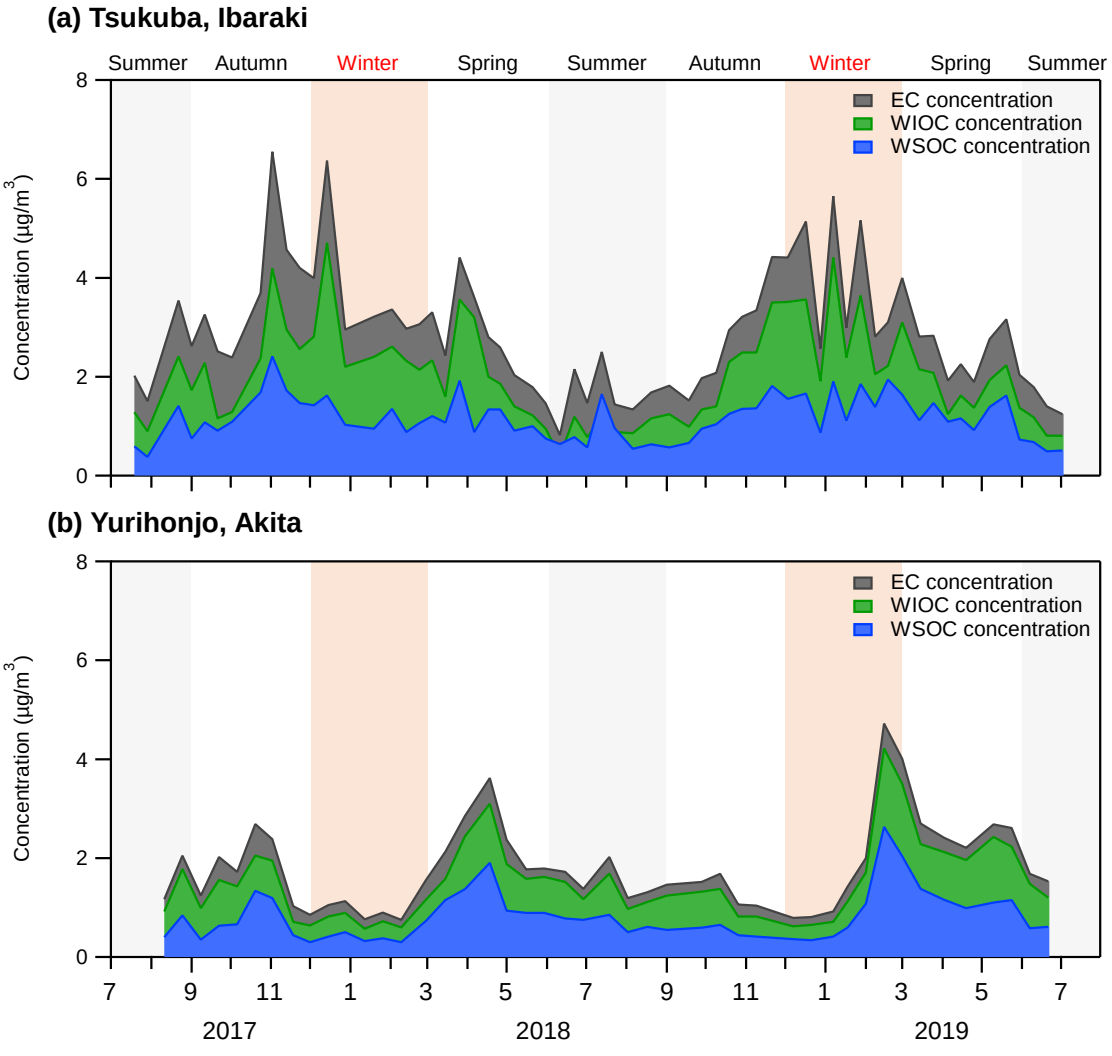

Figure 1: Concentrations of EC, WIOC, and WSOC of $PM_{2.5}$ from July 2017 to July 2019 in (a) Tsukuba, Ibaraki, and (b) Yurihonjo, Akita, Japan.

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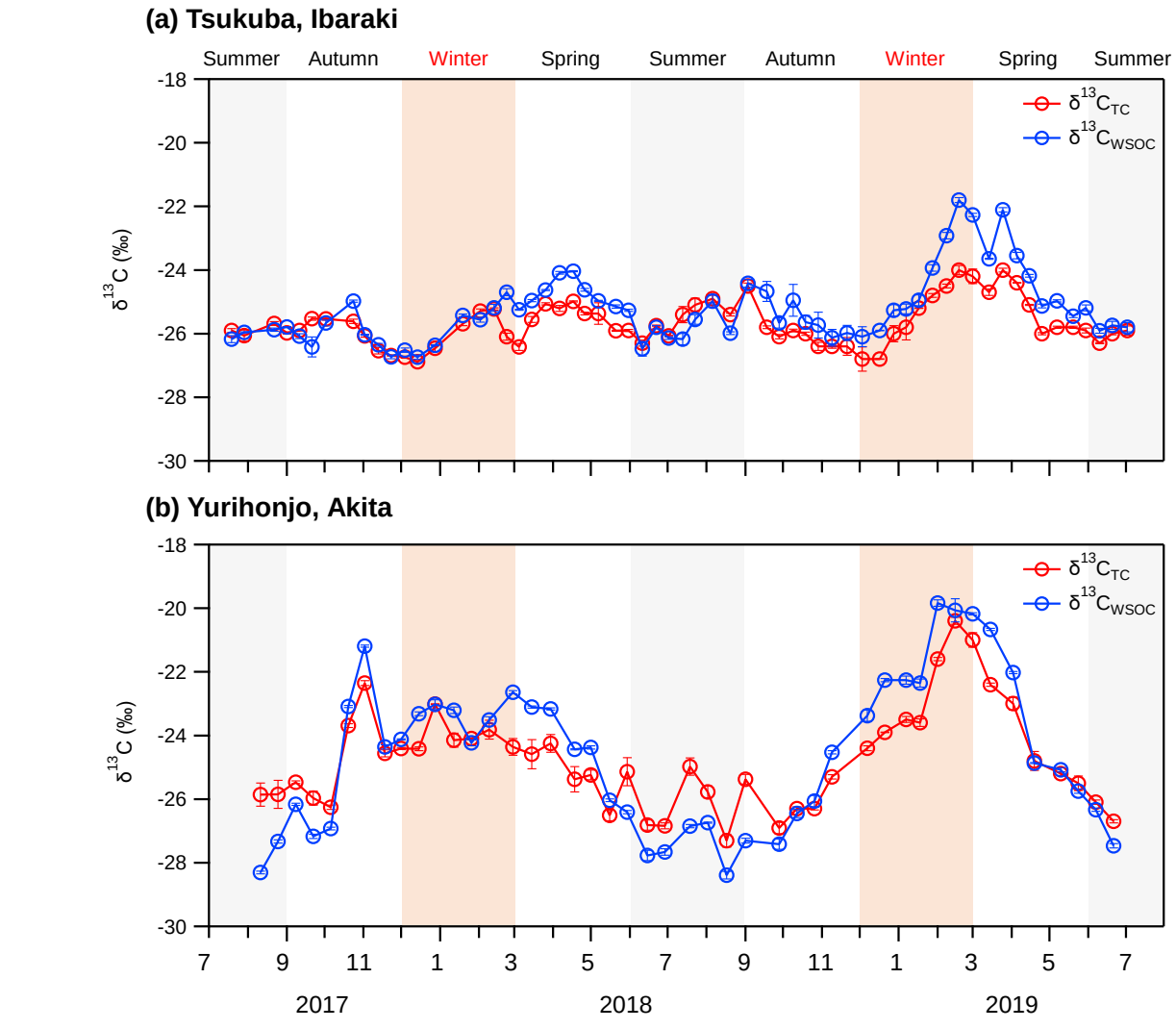

Figure 2: $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ of $PM_{2.5}$ from July 2017 to July 2019 in (a) Tsukuba, Ibaraki, and (b) Yurihonjo, Akita, Japan.

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Table 1. Seasonal average concentrations of $PM_{2.5}$, EC, OC, and WSOC; OC/EC and WSOC/OC ratios; and $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ values for $PM_{2.5}$, in Tsukuba and Yurihonjo, Japan.

Tsukuba

Compound	Season (average ± SD)				Average (n = 62)
	Spring (n = 18)	Summer (n = 13)	Autumn (n = 16)	Winter (n = 15)	
$PM_{2.5}$ (μg m^{-3})	23.5 ± 7.7	14.4 ± 4.1	16.5 ± 7.2	23.0 ± 8.9	19.7 ± 8.2
EC (μg m^{-3})	0.7 ± 0.2	0.7 ± 0.3	1.1 ± 0.5	1.0 ± 0.4	0.9 ± 0.4
OC (μg m^{-3})	3.2 ± 1.0	1.8 ± 0.8	3.4 ± 1.4	4.2 ± 1.2	3.2 ± 1.4
WSOC (μg m^{-3})	1.2 ± 0.3	0.8 ± 0.4	1.3 ± 0.5	1.4 ± 0.4	1.2 ± 0.4
OC/EC	4.5 ± 1.6	2.7 ± 0.6	3.5 ± 1.2	4.4 ± 0.8	3.8 ± 1.4
WSOC/OC	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.0	0.3 ± 0.1	0.4 ± 0.1
$\delta^{13}C_{TC}$ (‰)	−25.3 ± 0.7	−25.8 ± 0.4	−26.0 ± 0.5	−25.7 ± 0.9	−25.7 ± 0.7
$\delta^{13}C_{WSOC}$ (‰)	−24.4 ± 1.0	−25.9 ± 0.4	−25.7 ± 0.6	−25.1 ± 1.4	−25.2 ± 1.1

Yurihonjo

Compound	Season (average ± SD)				Average (n = 45)
	Spring (n = 12)	Summer (n = 9)	Autumn (n = 11)	Winter (n = 13)	
$PM_{2.5}$ (μg m^{-3})	15.8 ± 4.2	8.6 ± 2.4	8.1 ± 1.2	11.4 ± 5.1	11.2 ± 4.7
EC (μg m^{-3})	0.4 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
OC (μg m^{-3})	2.2 ± 0.6	1.3 ± 0.3	1.3 ± 0.5	1.1 ± 1.0	1.5 ± 0.8
WSOC (μg m^{-3})	1.2 ± 0.4	0.7 ± 0.2	0.7 ± 0.3	0.6 ± 0.6	0.8 ± 0.5
OC/EC	6.6 ± 2.1	5.5 ± 1.5	4.2 ± 1.2	4.1 ± 1.5	5.1 ± 1.9
WSOC/OC	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.5 ± 0.1
$\delta^{13}C_{TC}$ (‰)	−24.4 ± 1.6	−26.2 ± 0.7	−25.3 ± 1.3	−23.5 ± 1.2	−24.7 ± 1.6
$\delta^{13}C_{WSOC}$ (‰)	−23.8 ± 2.0	−27.4 ± 0.7	−25.5 ± 2.0	−22.6 ± 1.3	−24.6 ± 2.4

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Table 2. Correlation (*r*) between WSOC concentration and the stated parameters.

	Tsukuba			Yurihonjo		
Season	$\delta^{13}C_{WSOC}$	EC	nss-K^+	$\delta^{13}C_{WSOC}$	EC	nss-K^+
Spring	0.36	0.73	0.85	0.63	0.64	0.80
Summer	−0.14	0.84	0.77	0.17	0.24	0.40
Autumn	−0.45	0.75	0.96	0.65	0.83	0.93
Winter	0.29	0.68	0.83	0.77	0.87	0.99
Annual	0.18	0.71	0.88	0.44	0.72	0.87