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 C3 plant burning, and a high correlation was found between WSOC concentration and non-sea-salt potassium concentration. These results suggested that the main source of WSOC was biomass burning of rice straw. At the rural site, the average $\delta^{13}C_{WSOC}$ was significantly heavier from autumn to spring (−23.9 ± 2.1‰) than in summer (−27.4 ± 0.7‰) ($p < 0.01$). The $\delta^{13}C_{WSOC}$ from autumn to spring were a result mainly of biomass burning of rice straw, whereas the $\delta^{13}C_{WSOC}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds. In particular, the reason for the heaviest $\delta^{13}C_{WSOC}$ (−21.3 ± 1.9‰) from February to April 2019 might be affected by long-range transport of C4 plant burning such as corn from overseas. Thus, our $\delta^{13}C_{WSOC}$ approach was useful to elucidate the sources and atmospheric processes that contribute to seasonal variations of WSOC concentrations.

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 water-insoluble organic carbon (WIOC) and 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 20%–80% of the total OC in carbonaceous aerosol depending on the location and season (Decesari et al., 2001; Sullivan et al., 2004; Du et al.,

2014; Duarte et al., 2015; Zhang et al., 2019). 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). 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 PM (e.g., Widory et al., 2004; Fisseha et al., 2009; Cao et al., 2011; Gensch et al., 2014). Since EC is unreactive, it is possible to identify the source from $\delta^{13}C_{EC}$ in their aerosols directly (e.g., Kawashima and Haneishi, 2012; Zhao et al., 2018). In contrast, OC reacts in the atmosphere, so their $\delta^{13}C_{OC}$ provide information not only on the source of the PM but also on any atmospheric processing it has undergone (e.g., Cao et al., 2011; Ni et al., 2018). The measurement of $\delta^{13}C_{WSOC}$ in PM has been actively carried out in recent years (e.g., Kirillova et al., 2010; Kirillova et al., 2013b; Suto and Kawashima, 2018; Zhang et al., 2019). The analysis of $\delta^{13}C_{WSOC}$ in ambient aerosol has been performed by wet oxidation method using GasBench/isotope ratio mass spectrometry (IRMS) (Fisseha et al., 2006) and combustion method using elemental analyzer/IRMS (EA/IRMS) (Kirillova et al., 2010). In the past few years, a highly sensitive analytical methods for $\delta^{13}C_{WSOC}$ based on wet oxidation using liquid chromatography/IRMS (LC/IRMS) (Suto and Kawashima, 2018) and GasBench/IRMS (Zhang et al., 2019), and total organic carbon analyzer/IRMS (Han et al., 2020) have been developed. The combustion method is the most widely used approach today. The $\delta^{13}C_{WSOC}$ of various particle size collected has been reported at various times in East Asia (Miyazaki et al., 2012; Kirillova et al., 2014a; Pavuluri and Kawamura, 2017; Yan et al., 2017; Suto and Kawashima, 2018; Zhang et al., 2019; Han et al., 2020), South Asia (Kirillova et al., 2013b; Bosch et al., 2014; Kirillova et al., 2014b; Dasari et al., 2019), Europe (Fisseha et al., 2006; Fisseha et al., 2009; Kirillova et al., 2010), and the United States (Wozniak et al., 2012a; Wozniak et al., 2012b) (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. (2013a) 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-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 study reported that the enrichment of $\delta^{13}C_{WSOC}$ between source site (Delhi, India) and receptor site (Hanimaadhoo Island, Maldives) is caused by aging effect during long-range transport (Dasari et al., 2019).

The combustion method, which is widely used at present, requires more pretreatment time because samples of PM are extracted, dehydrated with a freeze drier, dried, and then measured by EA/IRMS. The wet oxidation/IRMS method described above do not require a drying stage during sample preparation; therefore, the total analysis time is markedly reduced compared with the combustion method. In addition, this newer approach is highly sensitive, so only small amounts of sample are needed compared to the combustion method. 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 in the Supplement). 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 year from December to February, the site is covered with several centimeters of snow (Japan Meteorological, 2019). $PM_{2.5}$ 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 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 with oxygen in the EA, and the carbon was converted to CO_2 via an oxidation/reduction tube of the EA. The oxidation/reduction tube and the packed column were maintained at 1020 °C and 60 °C, respectively. 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).

Determination of $\delta^{13}C_{WSOC}$ was performed at Akita Prefectural University using the wet oxidation/IRMS method (Kawashima et al., 2018; 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). The HPLC system was controlled by LCsolution software (ver. 1.25, Shimadzu Co.).

Stable carbon isotope ratios are expressed in δ notation in permil (‰)

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

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 $\delta^{13}C$ (Coplen et al., 2006). 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 Tsukuba was higher than the air quality standard for the annual average of Japan (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}) (Ministry of the Environment,

2019). In Yurihonjo, the average mass concentration of $PM_{2.5}$ was lower than the air quality standard for the annual average of Japan, 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 concentrations of $PM_{2.5}$ in Tsukuba and Yurihonjo were significantly higher in winter and spring than in summer and autumn ($p < 0.01$). The mass concentrations of $PM_{2.5}$ were consistent with the seasonal variation for nearby sites of Atmospheric Environmental Regional Observation System (AEROS) provided by the Ministry of the Environment (Ministry of the Environment, 2021).

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 in agreement with compared to other studies (Contribution of OC and EC concentration in $PM_{2.5}$ concentration: 20% and 6% in Korea) (Park and Cho, 2011).

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 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., 2013a).

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 showed no other clear seasonal variation, but they became slightly heavy from February to April 2019 (Fig. 2a). In contrast, the $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at Yurihonjo were heaver from autumn to spring than in summer (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. In addition, $\delta^{13}C_{WSOC}$ became heavier from February to April 2019 as 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 $\delta^{13}C_{TC}$ (Tsukuba; $p < 0.01$, Yurihonjo; $p < 0.01$).

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. No seasonal variation for $\delta^{13}C_{WSOC}$ in the suburban site, Tsukuba is comparable with that in

TSP in Seoul, South Korea, from March 2015 to January 2016 (Han et al., 2020). Similarly, clearly trend for heavier in winter than in summer for $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ in the rural site, Yurihonjo is comparable with that in TSP reported for Sapporo, Japan, from September 2009 to October 2010 (Pavuluri and Kawamura, 2017). 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 (e.g., fossil fuel and/or biomass burning) at this suburban 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 suggests that WSOC was affected by biomass burning. The dominant annual source for WSOC was consistent with that reported in Seoul by Han et al. (2020).

The average $\delta^{13}C_{WSOC}$ was −25.2 ± 1.1‰ in Tsukuba. Since the C3 and C4 plants have different metabolic pathways, the $\delta^{13}C$ values are −34 to −24‰ for C3 plants and −19 to −6‰ for C4 plants, respectively (Smith and Epstein, 1971). When C3 plants are burned in the laboratory, there is no significant $\delta^{13}C$ difference between the produced particles and original C3 plants (Turekian et al., 1998; Das et al., 2010). In contrast, the particles produced by burning the C4 plants were 3.5‰ lighter

than the original C4 plants (Turekian et al., 1998). Therefore, the $\delta^{13}C$ of C4 plants was estimated to be −22.5 to −9.5‰. In fact, the $\delta^{13}C$ from C3 plants and C4 plants burning were −34.7 to −25.1‰ and −19.3 to −16.1‰, respectively (Kawashima and Haneishi, 2012; Garbaras et al., 2015; Guo et al., 2016). Thus, the average $\delta^{13}C_{WSOC}$ at Tsukuba suggested that biomass burning of C3 plants might be a dominant source. The most productive crop in Japan is rice, followed by barley and wheat (Ministry of Agriculture Forestry and Fisheries, 2018). In Ibaraki Prefecture, where Tsukuba city is located, the crop acreage of rice was 68,400 ha, and the harvest was 358,400 tons in 2018, the largest in the Kanto Region (Ministry of Agriculture Forestry and Fisheries, 2018). According to a field investigation, Tomiyama et al. (2017) reported that the biomass burning type and season in Tsukuba were rice straw and rice hulls, and from September to October, respectively. 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).

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, peanut stalk, mulberry stalk, China fir, Chinese red pine, chinese guger tree, Chestnut such as C3 plants ranged from −26.05 to −22.60‰, especially from rice straw, which was −24.26 ± 0.09‰ (Sang et al., 2012). The average $\delta^{13}C_{WSOC}$ in Tsukuba was very close to the $\delta^{13}C$ of levoglucosan from burning rice straw. However levoglucosan concentration accounts for only about 3.8% of the WSOC concentration in urban area of Japan (Kumagai et al., 2010), and was very low percentages. Thus, it is difficult to compare the source directly using only the $\delta^{13}C$ of levoglucosan. In the future research, it should be considered to investigate the $\delta^{13}C$ of individual components not only levoglucosan.

3.5.2 Seasonal trends and sources of WSOC in Yurihonjo

The correlation in Yurihonjo 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). This suggests that WSOC was affected by combustion at this rural site during autumn and spring. 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. The average $\delta^{13}C_{WSOC}$ at Yurihonjo was −23.9 ± 2.1‰ during autumn and spring, suggesting that biomass burning of C3 plants such as rice straw and rice hulls may be a dominant source as in Tsukuba. 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 (Ministry of Agriculture Forestry and Fisheries, 2018). From February to April 2019, $\delta^{13}C_{WSOC}$ was the heaviest with increasing WSOC concentrations (average, 1.5 ± 0.7 μg m^{-3}; −21.3 ± 1.9‰) (Fig. 1b and Fig. 2b). The moderate correlation between $\delta^{13}C_{WSOC}$ and WSOC concentration was observed (r = 0.54, p = 0.27 > 0.1). This $\delta^{13}C_{WSOC}$ value might be related to heavy $\delta^{13}C$ source such as C4 plants (e.g., corn and grass). Around the sampling site at Yurihonjo, there was no evidence of burning of C4 plants during this period. Northeast China is the largest producer of corn in China (MWCACP, 2019), and biomass burning is actively used for heating in winter (Chen et al., 2017).

In Figure S2 in the Supplement, the number of fire spots were observed from February to April 2019 (NASA, 2017). The air mass backward trajectories showed that air masses during this period at Yurihonjo were mainly derived from areas located northeast China (Fig. S3 in the Supplement). For other air model, Uranishi et al. (2020) concluded that biomass burning in northeast China was transported in Akita prefecture regions of Japan in February and March 2019 from Community Multiscale Air Quality model results. For water-soluble ion data, the correlation between Na^+ and Cl^- concentration was highest from winter to spring 2019 (r = 0.98, p < 0.01), suggesting the influence of sea salt. Recently, aerosol photochemical aging during long-range transport selectively enriches the ^{13}C content in organic aerosols, leading to heavier $\delta^{13}C$ values in the remaining aerosol (Kirillova et al., 2013b; Bosch et al., 2014; Dasari et al., 2019; Zhang et al., 2019). 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., 2013a). We speculate that the heavier $\delta^{13}C_{WSOC}$ from February to April 2019 at Yurihonjo might be affected by C4 plant burning and/or aging 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. SOA is formed by oxidation of anthropogenic and biogenic VOCs (Heo et al., 2013). For anthropogenic VOCs, 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 for gas station and vehicle emissions are reported to range from −27.7‰ to −23.8‰ (Rudolph et al., 2002; Kawashima and Murakami, 2014). For example, as VOCs in the atmosphere are oxidized by photochemical oxidants, the $\delta^{13}C$ of residual VOCs becomes heavier by isotopic fractionation (Rudolph et al., 2000; Anderson et al., 2004). In other words, secondary production tends lighter $\delta^{13}C$ of SOA in the atmosphere. Actually, the $\delta^{13}C$ of SOA particles formed by photooxidation of toluene was 3 to 6‰ lighter in laboratory-based experiment than that of the precursor toluene, varying systematically with the extent of the oxidation reaction (Irei et al., 2006; Irei et al., 2011). 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 −24.4 to −21.4‰ by subtracting 3 to 6‰ 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. Therefore, the anthropogenic VOCs was considered no dominant source of WSOC.

For biogenic VOCs, the 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). The average $\delta^{13}C$ of 2-methyltetrol in aerosols 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. In field study, Miyazaki et al. (2012) reported that the lightest values of $\delta^{13}C_{WSOC}$ (average −25.6 ± 0.7‰) was observed in forests of northern Japan from June to September. They have concluded from the PMF results that biogenic SOA production (isoprene SOA and α-/β-pinene) were the dominant source of WSOC in summer, which was consistent with the conclusions of this study. At the global scale, biogenic VOCs emissions are more than an order of magnitude higher than those of anthropogenic VOCs (Farina et al., 2010).

4 Conclusion

The WSOC concentration, $\delta^{13}C_{TC}$ and the $\delta^{13}C_{WSOC}$ of $PM_{2.5}$ were observed at one suburban and one rural, 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 showed no other clear seasonal variation, but they became slightly heavy from February to April 2019. In contrast, the $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ at rural site were heaver from autumn to spring than in summer, 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, the main source of WSOC was estimated biomass burning of rice straw. At the rural site, the $\delta^{13}C_{WSOC}$ from autumn to spring were a result mainly of biomass burning of rice straw, whereas the $\delta^{13}C_{WSOC}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds. In particular, the reason for the heaviest $\delta^{13}C_{WSOC}$ (−21.3 ± 1.9‰) from February to April 2019 might be affected by long-range transport of C4 plant burning such as corn from overseas. 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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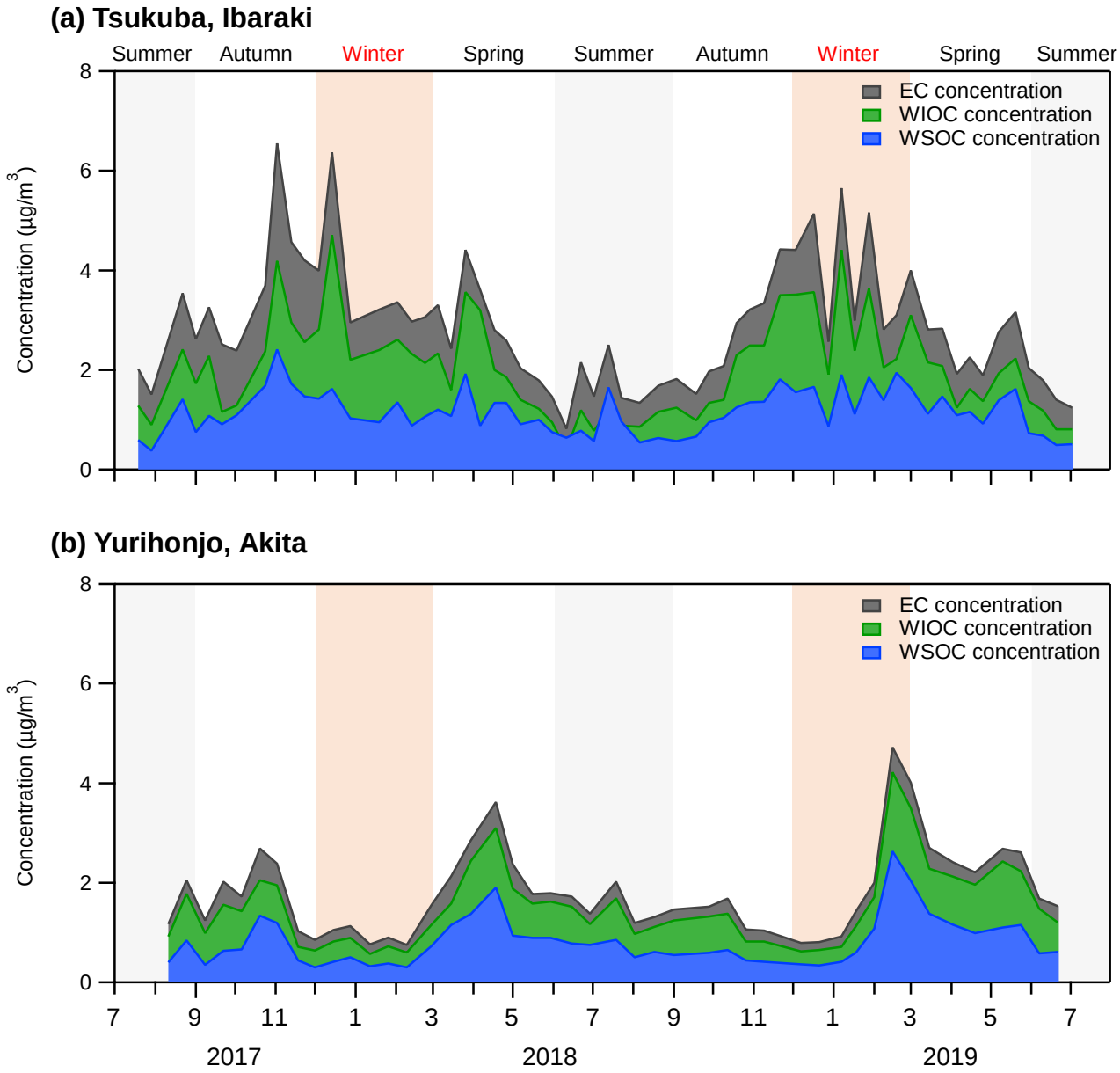

Figure 1: Concentrations of EC, WIOC, and WSOC of $PM_{2.5}$ from July 2017 to July 2019 in (a) Tsukuba, Ibaraki, and (b) Yurihonjo, Akita, Japan.

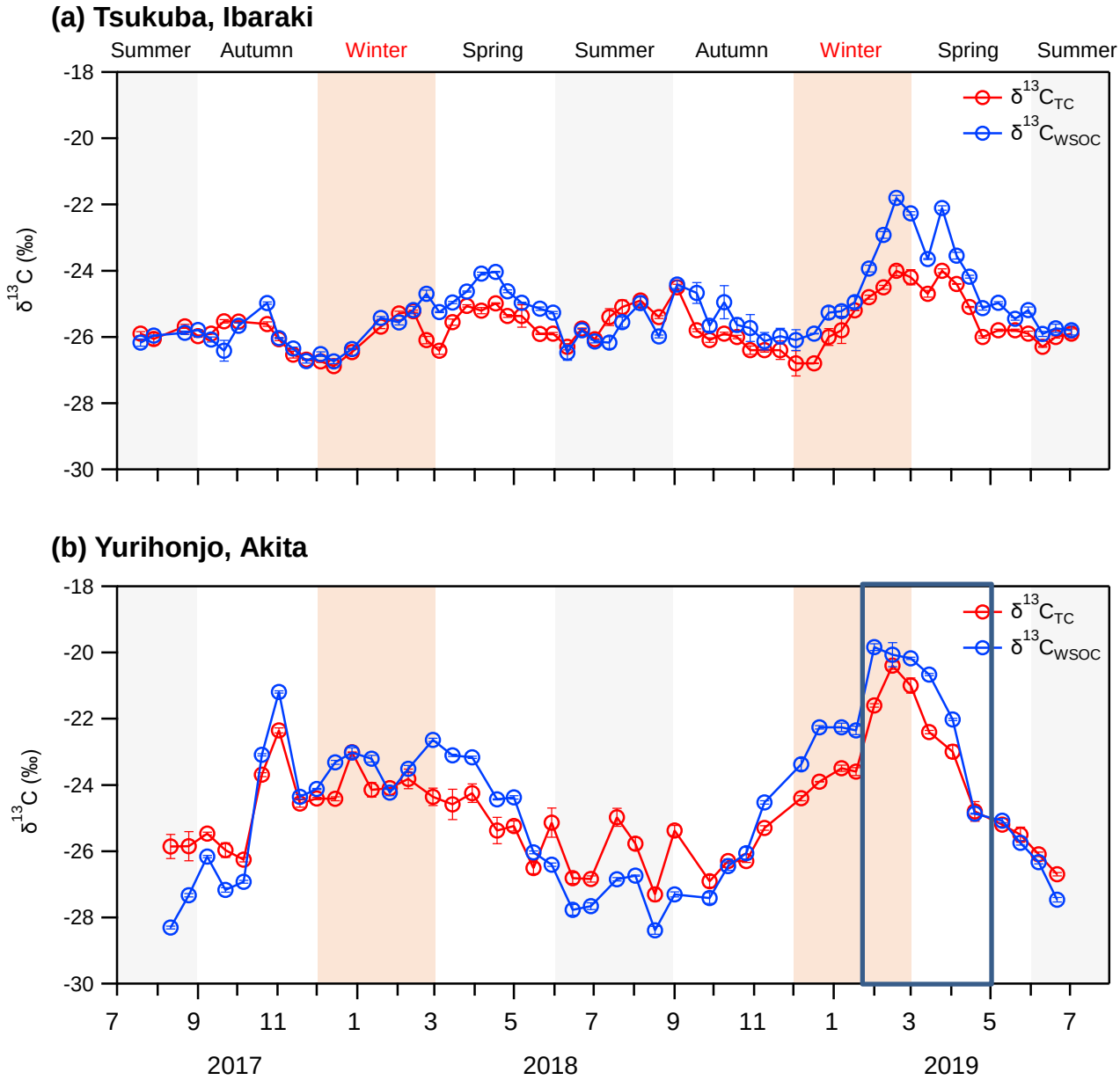

Figure 2: $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ of $PM_{2.5}$ from July 2017 to July 2019 in (a) Tsukuba, Ibaraki, and (b) Yurihonjo, Akita, Japan.

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

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