Response to the Reviewer #1

Measurement report: Source characteristics of water-soluble organic carbon in PM2.5 at two sites in Japan, as assessed by long-term observation and stable carbon isotope ratio by Suto and Kawashima
The revised manuscript shows that the authors considered only some of the recommendations suggested by the reviewers. Therefore, there are still open points to be reconsidered.

Response:

We thank the reviewer for the insightful comments, which have helped us to significantly improve the paper. We believe through addressing these comments, the quality of the manuscript and its potential impact has been improved. Detailed point by point responses are given below.

The major criticism was unfortunately not reviewed: since only TC isotopic ratios of WSOC and whole aerosol particles were measured, comparison with compound specific d13C are superfluous (to illustrate this, two extremes should be considered, i.e. 3.8% levoglucosan originates from the combustion of corn plant only (d13C=-12 permille) or a C3 wood only (mean d13C=-24 permille). Keeping the rest unchanged, a difference in the bulk d13C of 0.46 permille would result, which is in the uncertainty range of some compound specific analyses). The same is valid for process examination. One of prerequisites to employ mass balance calculations for single mixture components /photo chemical decay is to possess their emissions d13C and the reaction specific KIE. Even then, the complexity of atmospheric processing cannot be solved by just adding up some numbers.

Response:

In our manuscript, the source of WSOC is discussed using $\delta^{13}C_{WSOC}$, carbon components (EC and WSOC concentrations), and water-soluble ion (nss-K^+ concentration) rather than the comparison of compound specific. As the reviewer pointed out, it is not possible to directly compare $\delta^{13}C_{WSOC}$ and $\delta^{13}C$ of levoglucosan due to very low percentages. However, the agreement between the average $\delta^{13}C_{WSOC}$ in Tsukuba (−25.2 ± 1.1‰) and $\delta^{13}C$ of levoglucosan for rice straw (−24.26 ± 0.09‰; Sang et al. (2012)) seemed to be important information. Only $\delta^{13}C$ of levoglucosan has been reported at present, it should be considered to investigate the $\delta^{13}C$ of individual components not only levoglucosan in the future research.

We revised the discussion in section 3.5.1 as follows (page 9, lines 264-271).

"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."

Yet, there are numerous ambient studies on WSOC/TC isotope ratios (see Gensch et al. IJMS2014 and references therein), describing ranges for these compound classes. A sound comparison gives first information on sources. The authors claim that: *'When C3 plants are burned in the laboratory, there is no significant δ13C difference between the produced particles and original C3 plants'*. Still, isn't sounder to compare the measurements with WSOC/TC d13C in combustion aerosol particles and not in plant tissues (whose δ13C values are −34 to −24‰ for C3 plants and −19 to −6‰ for C4 plants, respectively (Smith and Epstein, 1971) and not −32 to −20‰ for C3 plants and −17 to −9‰ for C4 plants, as given in the present manuscript), since this information already exists?

Response:

As the reviewer suggested, we added $\delta^{13}C$ values from C3 plants and C4 plants burning (Kawashima and Haneishi, 2012; Garbaras et al., 2015; Guo et al., 2016). And, we revised the $\delta^{13}C$ of original C3 and C4 plants in the reference (Smith and Epstein, 1971) .

We revised the discussion in section 3.5.1 as follows (page 8-9, lines 250-257).

"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."

1) To get some additional information from this impressive dataset, I recommend to the authors to use the existing isotopic tools, such as combining isotope ratios with concentration data (remote sources for Yurihonjo, higher contribution of local/regional emissions to the samples for Tsukuba?). The authors claim in Lines 275-279: *'From February to April 2019, d13CWSOC became heavier with increasing WSOC concentrations (Fig. 1b and Fig. 2b). Although C4 plants such as corn and grass showed heavy d13C, there was no evidence of burning of C4 plants around during this period. The heavy d13CWSOC during this period cannot be explained only by the effect of biomass burning. Aerosol photochemical aging during long-range transport selectively enriches the 13C content in organic aerosols, leading to heavier d13C values in the remaining aerosol'*. A simultaneous increase in concentration and d13C is rather an indication for heavy sources than aging... especially during periods of low photo chemical activity.

Response:

As the reviewers pointed out, $\delta^{13}C_{WSOC}$ in Yurihonjo was the heaviest with increasing WSOC concentrations (average, 1.5 ± 0.7 μg m^{-3}; −21.3 ± 1.9‰) from February to April 2019 (Fig. 1b and Fig. 2b). 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. We investigated the fire spots using Fire Information for Resource Management System (FIRMS) (NASA, 2017) and air mass backward trajectories using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2013). According to the fire spots data, the number of fire spots were observed during this period in Northeast China (Fig. 1 in this Response file / Fig. S2 in the Supplement). 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). The air mass backward trajectories showed that air masses during this period at Yurihonjo were mainly derived from areas located northeast China (Fig. 2 in this Response file / Fig. S3 in the Supplement). 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., 2013a; Bosch et al., 2014; Dasari et al., 2019; Zhang et al., 2019). Since it could not be denied that aging effect would not occur from February to April 2019 in Yurihonjo, we speculate that the heavier $\delta^{13}C_{WSOC}$ might be affected by C4 plant burning and/or aging during long-term transport.

We revised the discussion in section 3.5.2 as follows (page 9-10, lines 281-297).

"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., 2013a; 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., 2013b). 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."

2) To either prove or reject this hypothesis, the authors should at least roughly (HYSPLIT?) determine the origin of the air masses. In the lines 282-284 the authors state: *'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'*. Noticeably here, China's north-eastern part is belonging to the so called 'corn belt'. As a result of this farming type, it is expected that local heating with corn briquettes and traditional cooking using corn cobs strongly contribute to the aerosol burden. Subsequently, due to long-range transport, this would contribute to the investigated samples, leading to an increase in d13C.

Response:

As the described above, we investigated the fire spots using Fire Information for Resource Management System (FIRMS) (NASA, 2017) and air mass backward trajectories using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2013). According to the fire spots data, the number of fire spots were observed during this period in Northeast China (Fig. 1 in this Response file / Fig. S2 in the Supplement). 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). The air mass backward trajectories showed that air masses during this period at Yurihonjo were mainly derived from areas located northeast China (Fig. 2 in this Response file / Fig. S3 in the Supplement).

We added the figures of fire spots (Fig. S2 in the Supplement) and backward trajectories (Fig. S3 in the Supplement), and revised the discussion in section 3.5.2 as above (page 9-10, lines 281-297).

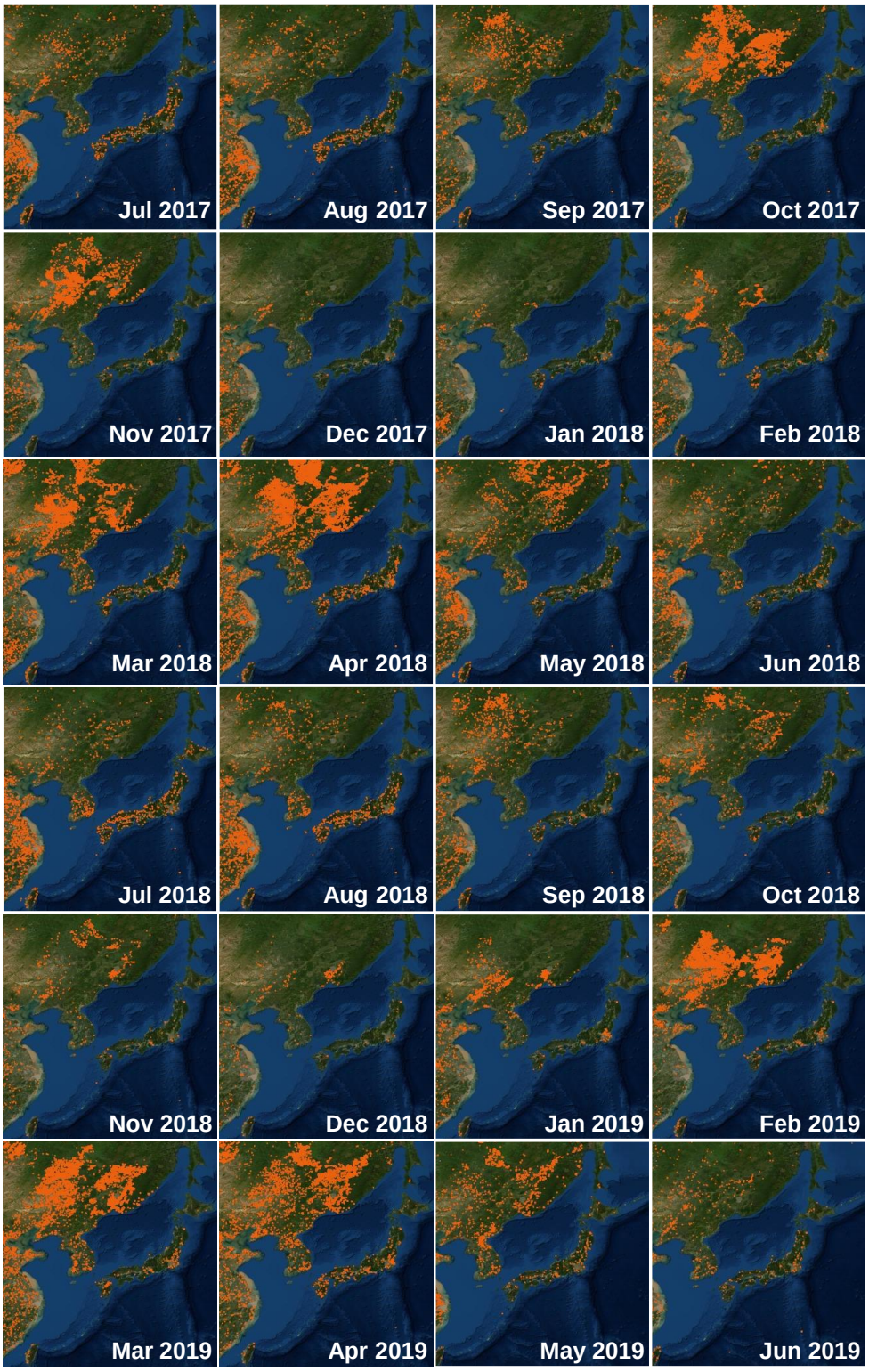

Figure. 1 Monthly fire spots from July 2017 to June 2019 as determined by MODIS in Fire Information for Resource Management System (FIRMS) (NASA, 2017).

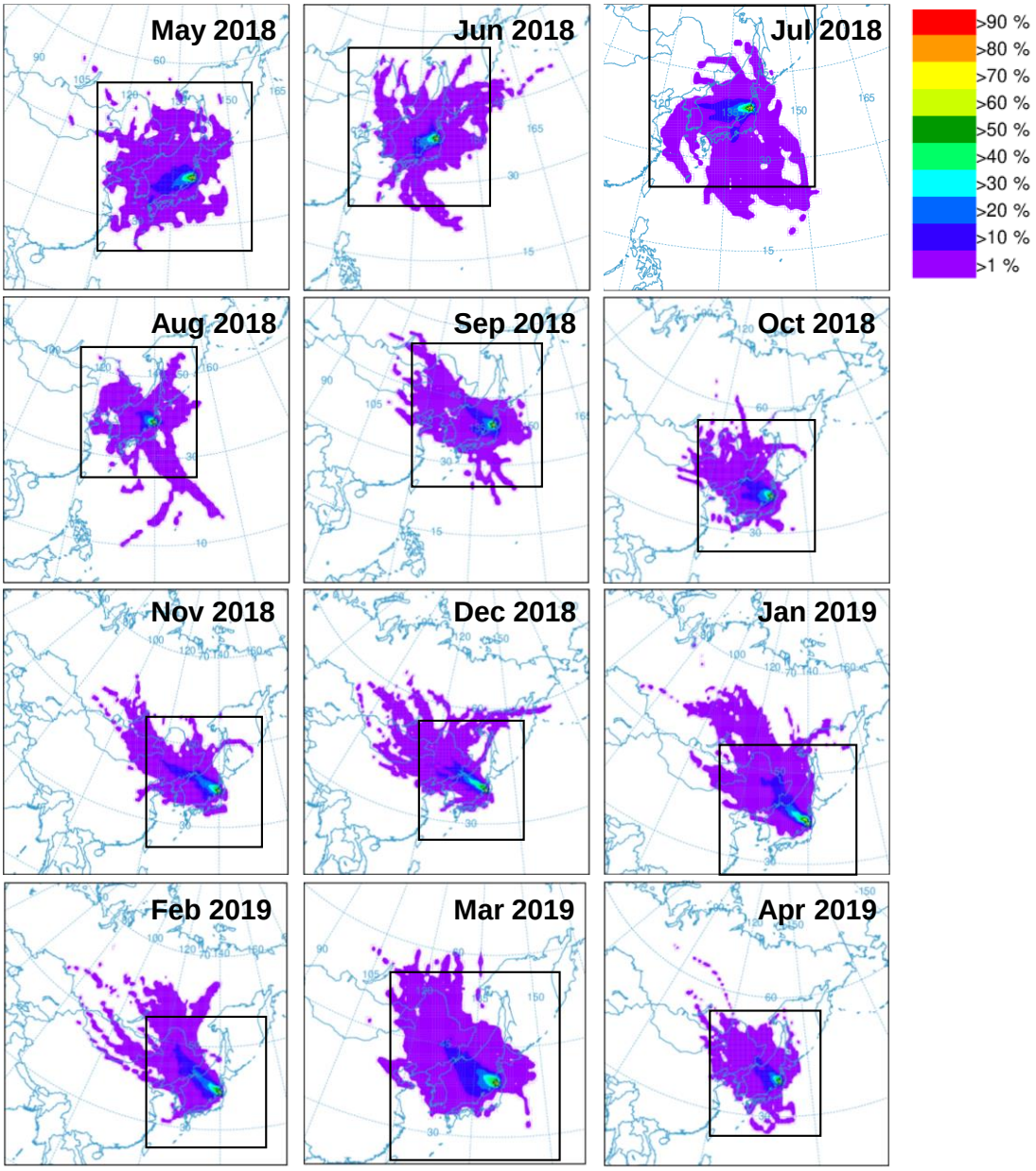

Figure. 2 Monthly air masses backward trajectories frequency at Yurihonjo from May 2018 to April 2019 (Draxler and Rolph, 2013).

Response to the Reviewer #2

The manuscript has been improved. I still have few minor remarks.

Response:

We thank the reviewer for the insightful comments, which have helped us to significantly improve the paper. We believe through addressing these comments, the quality of the manuscript and its potential impact has been improved. Detailed point by point responses are given below.

In Introduction section: *"The wet oxidation/IRMS method described above ... the total analysis time is markedly reduced compared with the combustion method"*. I do not agree with the statement that analysis time for wet oxidation method is shorted compared to the combustion method. Authors detailed described two methods in Section 2.2 Stable carbon isotope analysis, and we see that chemical extraction consumed time for each sample to prepare in wet oxidation method, while for TC combustion analysis time is shorter for one sample.

Response:

This sentence (page 3, lines 70-72) compares the analysis time, including pretreatment time, for the wet oxidation method and combustion method for measuring $\delta^{13}C_{WSOC}$. For the wet oxidation/IRMS method, the sample filter is extracted for 15 min and the extract is measured directly using LC/IRMS (Suto and Kawashima, 2018). On the other hand, the combustion method requires a complex pretreatment process, such as freeze-drying of the aerosol extract under vacuum for 16 hours (Kirillova et al., 2010).

As the reviewer suggested, we added the sentences to clarify as follows (page 3, lines 69-70).

"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 sentence *"In addition, this newer approach is highly sensitive, so only small amounts of sample are needed"*. In my opinion, this sentence is misleading, because for wet oxidation method, 14.13cm^2 of filter was used, comparing to I guess 1 cm^2 for d13C TC. Also, what is mean small amounts? I suggest to use the words "small amount comparing to (another analysis type)". Bear in mind, that here Authors use Hi-Vol sampler of 10 days sampling for one filter with flow rate 1000 l/min, which make high amount of aerosol to accumulate on filter despite sampling location.

Response:

The detection limit of the combustion method for measuring $\delta^{13}C_{WSOC}$ was 120-150 μg of WSOC (Kirillova et al., 2014a; Kirillova et al., 2014b), but the detection limit of the wet oxidation/IRMS method was improved to 1 μgC (Suto and Kawashima, 2018) with high sensitivity. The establishment of the highly sensitive $\delta^{13}C_{WSOC}$ method has made it possible to measure $\delta^{13}C_{WSOC}$ even at sampling sites where the WSOC concentration is relatively low, such as in this study. In addition, $\delta^{13}C_{WSOC}$ measurement with higher time resolution is possible at sampling sites with high WSOC concentration.

As the reviewer suggested, we revised the sentences to clarify as follows (page 3, lines 72-73).

"In addition, this newer approach is highly sensitive, so only small amounts of sample are needed compared to the combustion method."

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