

Response to the Reviewer #1

This paper presents long-term concentration and isotopic ratio measurements of TC and WSOC in ambient PM_{2.5} collected at two sites in Japan between July 2017 and July 2019. The authors show a quite impressive series of measurements aiming to investigate sources of the aerosol fine fraction at a suburban and a rural background site. Using stable isotope analyses represents a novel approach for source characterization, thus, is suitable for this goal. The wet oxidation prior to IRMS is very challenging but opens up the opportunity to much easier separate polar compounds and measure their isotopic ratios.

Unfortunately, the presentation is on a poor level. Therefore, it needs to be substantially improved before publishing.

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. As the reviewer suggested, we discussed sections 3.5.1 and 3.5.2 in greater depth as follow topics.

Topic 1. Source identification at suburban site in annual (section 3.5.1)

WSOC in every season at suburban site was affected by biomass burning using WSOC concentration, EC concentration non-sea-salt potassium (nss-K⁺) concentration. In addition, since the C3 and C4 plants have different metabolic pathways, the $\delta^{13}\text{C}$ values are -32 to -20‰ for C3 plants and -17 to -9‰ for C4 plants, respectively (Smith and Epstein, 1971). The average $\delta^{13}\text{C}_{\text{WSOC}}$ in suburban site was $-25.2 \pm 1.1\text{‰}$, suggesting that biomass burning of C3 plants may be a dominant source. The results were consisted with previous research.

Topic 2. Source identification at rural site from autumn to spring and summer (section 3.5.2)

WSOC during autumn to spring at rural site was affected by biomass burning using WSOC, EC and non-sea-salt potassium (nss-K⁺). In particular, biomass burning of C3 plants seemed to be dominant source of WSOC using isotope. In summer, the formation of secondary organic aerosols from biogenic volatile organic compounds (VOCs) was affected to WSOC using biogenic VOCs and isotope fractionation from gas to particle. From February to April 2019, $\delta^{13}\text{C}_{\text{WSOC}}$ became heavier. The reason seemed to be affected both by biomass burning and aging of OC during long-range transport selectively enriches the ^{13}C content in organic aerosols, leading to heavier $\delta^{13}\text{C}$ values in the remaining aerosol.

Detailed point by point responses are given below.

General comments:

Far too little emphasis is placed on the contribution of the isotope measurements to elucidate aerosol sources or chemical processing during atmospheric transport. The main criticism for this manuscript is that the isotopic discussions are generally kept at a very superficial level. The lines of reasoning are often vague, sometime contrived.

Response:

As the reviewer suggested, we discussed sections 3.5.1 and 3.5.2 in greater depth as above topics. In particular, the discussion about C3, C4 plants and long-range transport were added to be interpreted using isotopes. As a result, the dominant annual source for WSOC was C3 plant burning in Tsukuba. In Yurihonjo, the heavy $\delta^{13}\text{C}_{\text{WSOC}}$ from autumn to spring were a result mainly of biomass burning of rice straw, whereas the light $\delta^{13}\text{C}_{\text{WSOC}}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds. Thus, our $\delta^{13}\text{C}_{\text{WSOC}}$ approach was useful to elucidate the sources and atmospheric processes that contribute to seasonal variations of WSOC concentrations.

We revised the sections 3.5.1 and 3.5.2.

Specific comments:

1) The authors present $\delta^{13}\text{C}$ for WSOC and TC. They compare their observations with isotopic ratios of single tracers such as for levoglucosan or toluene, which is quite senseless. As for the former (Sections 3.5.1 and 3.5.2 as well as in the abstract), even during intense biomass burning activities, levoglucosan contributes with few percent to OC and consequently, with less than 10% to the WSOC. Due to the complexity of the biomass burning sources and processes, it is very unlikely that the levoglucosan source specific $\delta^{13}\text{C}$ (please note here that Sang et al. EST2012 presented $\delta^{13}\text{C}$ of levoglucosan in aerosol formed during the combustion of C3 plants only) will determine alone the WSOC or TC $\delta^{13}\text{C}$.

Response:

As the reviewer pointed out, levoglucosan concentration accounts for only about 3.8% of the WSOC concentration in urban area of Japan (Kumagai et al., 2010). Therefore, we think that the $\delta^{13}\text{C}$ of only levoglucosan cannot prove that the source of WSOC. As described above topics, we interpreted the results not only for $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$, but also carbon component and water-soluble ion concentrations. As a result, the dominant annual source for WSOC was C3 plant burning in Tsukuba. In Yurihonjo, the heavy $\delta^{13}\text{C}_{\text{WSOC}}$ from autumn to spring were a result mainly of biomass burning of rice straw. For $\delta^{13}\text{C}$ of levoglucosan ($-25.86 \pm 0.27\%$ to $-24.26 \pm 0.09\%$ (Sang et al., 2012)), the average $\delta^{13}\text{C}_{\text{WSOC}}$ in Tsukuba was close to the $\delta^{13}\text{C}$ of levoglucosan from burning rice straw. Although $\delta^{13}\text{C}$ of components other than WSOC may exhibit the similar mechanism as levoglucosan, this interpretation was outside the scope of this paper.

The arguments used to interpret the isotopically lighter aerosol in summer are laboured, too. The authors cite here Irei et al., who investigated isotopic ratios of different generation reaction products of toluene oxidation. The depletion by 6 permille is valid only for the mentioned reaction (since KIE epsilon is 5.95 permille) and only for its early stages. For other fossil combustion tracers, oxidation reactions show a large range of KIE (Anderson et al. GRL2004), therefore their products will be very differently depleted at the reaction beginning. Compound specific isotope measurements of single tracers are necessary for detailed studies.

Response:

The $\delta^{13}\text{C}_{\text{WSOC}}$ in summer at Yurihonjo was very light (-27.4%) compared with the average value for the observation period. As described above topic 2, we concluded that the light $\delta^{13}\text{C}_{\text{WSOC}}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic VOCs. As VOCs in the atmosphere are oxidized by photochemical oxidants, the $\delta^{13}\text{C}$ of residual VOCs becomes heavier by isotopic fractionation (Rudolph et al., 2000; Anderson et al., 2004). In other words, secondary production tends lighter $\delta^{13}\text{C}$ of SOA in the atmosphere. Actually, the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of the anthropogenic VOCs emission source for Yurihonjo was calculated as approximately -24.4 to -21.4% by subtracting 3 to 6‰ from the average $\delta^{13}\text{C}_{\text{WSOC}}$ during summer in Yurihonjo (-27.4%). This estimated $\delta^{13}\text{C}$ value of VOCs was heavier than those previously reported for anthropogenic VOCs. Therefore, the anthropogenic VOCs was considered no dominant source of WSOC. We revised the sentences (page 10, lines 296-304).

Yet, the TC and WSOC $\delta^{13}\text{C}$ can be compared with corresponding values (Gensch et al. IJMS2014). The observations agree mainly with TC and WSOC $\delta^{13}\text{C}$ of C3 plant and fossil fuel combustion aerosol.

Response:

As described above topics, we concluded that sources of WSOC affected by C3 plants biomass burning and/or aging of OC during long-range transport. And, $\delta^{13}\text{C}_{\text{WSOC}}$ in summer was a result mainly of the formation of secondary organic aerosols from biogenic volatile organic compounds.

2) As for the TC and WSOC $\delta^{13}\text{C}$ seasonal trend, the authors state in Lines220-224: ' *$\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ at Tsukuba became slightly heavy from February to April 2019, but they showed no other clear seasonal variation (Fig. 2a). In contrast, the $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ at Yurihonjo were heavier in winter and spring than in summer and autumn (Fig. 2b), and they showed a significant seasonal*

variation ($d13CTC$; $p < 0.01$, $d13CWSOC$; $p < 0.01$) compared to those in Tsukuba. At both study sites, $d13CWSOC$ was usually heavier than $d13CTC$, but in summer $d13CWSOC$ was comparable to or lighter than $d13CTC$.

Firstly, most of the differences between TC and WSOC $d13C$ seem to be within the uncertainty range for isotopic measurements. To show the opposite, the authors should present some statistical evidence.

Response:

The average-1SD for $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$ was very small at 0.12‰ (<0.46‰) and 0.09‰ (<0.50‰), respectively, for all samples examined in the present study (page 5, lines 131-132).

We calculated the differences ($\delta^{13}C_{WSOC} - \delta^{13}C_{TC}$) and performed statistical processing. Both sites showed a statistically significant difference in summer (Tsukuba; $p < 0.01$, Yurihonjo: $p < 0.01$). We added the statistical results in the revised manuscript (page 7, lines 214-215).

Secondly, the unlike seasonal variation between the two sites give some additional information, which should be discussed in more detail. In absence of compound specific analyses, there are only qualitative indications, but exactly such discussions (e.g. local sources close by the suburban sampling site, which ‘flatten’ the influence of the long range transport) would enlighten the advantages of using stable isotopes in atmospheric studies. The enrichment by up to 6 permille in winter cannot be explained by chemistry alone, considering the lower oxidant concentration in the cold season. Rather, it looks like significant contribution of heavier sources to the collected aerosol (coal or even C3 plant combustion, see Gensch et al. IJMS2014). This assumption is supported by the similar $d13C$ for TC and WSOC. A back-trajectory analysis would help to elucidate such questions.

Response:

The $\delta^{13}C_{WSOC}$ became heavier at Yurihonjo from February to April 2019. 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). Therefore, we speculate that the heavier $\delta^{13}C_{WSOC}$ from winter to spring 2019 at Yurihonjo is affected both by biomass burning and aging of OC during long-term transport. Using Community Multiscale Air Quality model results, Uranishi et al. (2020) concluded that biomass burning in northeast China was transported in Akita prefecture regions of Japan in February and March 2019. We revised the sentences (page 9, lines 275-285).

3) Line124: remove ‘units, were calculated as follows’. Suggestion: ‘Stable carbon isotope ratios are expressed in terms of δ notation in permil (‰)’ Equation 1 gives only the meaning of $d13C$. In the lab, CO_2 working standards are used (calibrated against IAEA standards). The final $d13C$ values are reported relatively to the international reference VPDB. The calculations behind are described in Brand et al. PureApplChem2010.

Response:

As the reviewer suggested, we revised the sentences as follows (page 4, line 118).

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

We performed the two-point linear calibration to determine $\delta^{13}C$ (Coplen et al., 2006). The calibration method is described in the revised manuscript (page 4-5, lines 122-132).

Editorial revisions:

The authors should consider renouncing to mention the used computer OS (Lines107, 122, 123)

Response:

As the reviewer suggested, we deleted the words (page 5, lines 102, 116, 117).

Generally, the used English is not optimal. I strongly suggest that this manuscript is carefully revised by a native speaker.

Response:

We already had two native speakers check our manuscript before we submitted it.

Some examples of the inadequate language:

1) Unhandy expressions

Lines38-39: '*Although it is possible to estimate the contribution rate using PMF, it is necessary to identify the characterisation of source artificially.*' What is the meaning of 'artificially'? –

Response:

As the reviewer suggested, we deleted the sentences.

Line91: ' Every December to February'

Response:

As the reviewer suggested, we changed “Every December to February” to “Every year from December to February” in the revised manuscript (page 3, line 87).

2) Confusing indications:

Lines157, 159: '*... than the Japan Environmental Standard for the annual average...*' It is surely meant a threshold stipulated in the air quality guidelines of the Japan Environmental...organisation.

Response:

As the reviewer suggested, we changed “the Japan Environmental Standard for the annual average” to “the air quality standard for the annual average of Japan” in the revised manuscript (page 5, lines 151, 153).

3) Wrong wording

Replace 'reasonable' describing the measurements (lines171, 186). Use instead 'good agreement', 'similar to other studies', 'as expected'...

Response:

As the reviewer suggested, we revised the sentences as follows.

“The mass concentration 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).” (page 6, lines 161-163).

“The higher percentage contribution to the PM_{2.5} mass concentration from OC than EC was in agreement with compared to other studies” (page 6, lines 176-178).

Lines226-227: Rephrase: '*d13CWSOC 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.*' The findings of this work should be presented first and then compare them with other studies.

Response:

As the reviewer suggested, we revised the sentences as follows (page 7, lines 217-220).

“No seasonal variation for $\delta^{13}\text{C}_{\text{WSOC}}$ 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 $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ 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).”

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