

Response to the Reviewer #2

The manuscript entitled “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” by N. Suto and H. Kawashima represents investigation of aerosol particles through the prism of carbon stable isotopes, EC, OC and ion analysis. The sample collection was performed during two years, which allowed for the authors to catch the seasonal changes in some aerosol parameters.

In general, the manuscript is a bit chaotic, sometimes pointing at not relevant issues. Also, I think Authors have not exploited the benefits of long time samples collection and analysis.

I would like to address the issues that I am concerned on:

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.

Lines 25-30 In the introduction part, the most recent reference is from the year 2011.

Response:

As the reviewer suggested, we added the latest references (Du et al., 2014; Zhang et al., 2019) (page 1-2, lines 28-30).

Line 35. Why authors mention about PMF? They are not using PMF in this manuscript? What it means “it is necessary to identify the characterisation of source artificially”?

Response:

We don't use PMF models. As the reviewer suggested, we deleted the sentences.

Line 45. In general, the isotope ratio literature review part is too narrow in this manuscript. I propose to make overview on most recent references, which deals with aerosols and stable isotopes in different areas, which are relevant for this manuscript: transportation, natural terrestrial and marine (also oceanic) sources, fires etc. Suggestions: Zhang W. et al., 2019, ACP 19, 11071-11087 ($\delta^{13}\text{C}$ of WSOC in China); Fisseha R. et al 2006, Atmos. Env. 43 431-437 ($\delta^{13}\text{C}$ values in the different aerosol fractions in Zurich, Switzerland); Kirillova E.N. et al. 2010 Anal. Chem. 82 7973-7978; Lang S.Q. et al. 2012 Rapid Commun Mass Sp. 26 9-16; Suto N. and Kawashima H. Rapid Commun Mass Sp. 32 1668-1674 (In this manuscript the same Authors present the own developed method for $\delta^{13}\text{C}$ in WSOC). The last citation is used later, but I propose to cite it here also, as it is relevant to this part.

Response:

As the reviewer suggested, we revised the isotope part of the introduction follows (page 2, lines 42-57).

“The stable carbon isotope ratio ($\delta^{13}\text{C}$) 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 $\delta^{13}\text{C}_{\text{EC}}$ in their aerosols directly (e.g., Kawashima and Haneishi, 2012; Zhao et al., 2018). In contrast, OC reacts in the atmosphere, so their $\delta^{13}\text{C}_{\text{OC}}$ 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 $\delta^{13}\text{C}_{\text{WSOC}}$ in PM has been actively carried out in recent years (e.g., Kirillova et al., 2010; Kirillova et al., 2013; Suto and Kawashima, 2018; Zhang et al., 2019). The analysis of $\delta^{13}\text{C}_{\text{WSOC}}$ 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 $\delta^{13}\text{C}_{\text{WSOC}}$ 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 $\delta^{13}\text{C}_{\text{WSOC}}$ 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., 2013; 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).”

Section 2.1. I see that present study two sampling points were separated by a distance of 370 km . Both Tsukuba and Yurihonjo has a Humid continental climate, with different annual mean temperature of about 2°C. Tsukuba is close to Ocean, while Yurihonjo is close to Sea of Japan. I assume that air mass back trajectories are important when comparing two sampling points in this case. I assume that can be problematic to compare suburban or rural places, as they can be influenced by totally different atmosphere (and aerosol sources) conditions. In the rest of the text I'm missing marine source evaluation (except nss-K+).

Response:

We considered that we need to compare the two sampling sites (suburban site and rural site). The suburban site is 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. In contrast, the rural site faces the Sea of Japan, and had no local pollutant sources such as large factories. In particular, reports of $\delta^{13}\text{C}_{\text{WSOC}}$ in rural site are limited, so we believe that this study will be a very important result.

Line 95. I did not understand how long sampling for one filter was performed, does all filters were loaded periodically? Maybe worth to add as supplementary filter data (time, weight of loaded aerosol). How Authors ensured that the filter not lost mass itself, as quartz filters break easily, and making gravimetric measurements can be complicated. Does Authors used equilibration for the unexposed and exposed filter to account for humidity?

Response:

PM_{2.5} samples were collected approximately every 10 days in Tsukuba and 14 days in Yurihonjo (page 3, lines 84, 88) in order to obtain enough carbon amount in samples for isotope analysis. We confirmed that the PM_{2.5} mass concentration calculated from the filter weight was in agreement with the result of the automatic measuring instrument near the sampling site (Ministry of the Environment, 2021). The slope of the scatter plot was 1.27 for Tsukuba and 0.95 for Yurihonjo. Thus, we think the filter weight is reasonable.

Section 2.2 can be improved. I miss a clear step-by-step description of analytical procedures: Line 105: “. . .the carbon was converted to CO₂ via an oxidation catalyst in the reduction tube of EA” - I think is incorrect and must be clarified. Does oxygen was added? Does nitrogen was seperated from CO₂? What

about blank measurements, does it gave any signal? In this section, is no clear separation, which part of the section corresponds to total carbon measurements, which part to WSOC?

Response:

The analytical methods for $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{13}\text{C}_{\text{WSOC}}$ were described lines 96-102 and lines 103-115, respectively.

As the reviewer suggested, we revised the part of the measurement for $\delta^{13}\text{C}_{\text{TC}}$ using EA/IRMS (page 4, lines 96-102). No filter blank was detected.

Line 170. Authors state that snow is responsible for low PM_{2.5} concentration in Yurihonjo. My question, does land in winter emits significant amount of aerosol, even not covered by snow? What about heating activities, long range transport etc. I want to say that Authors must to think generally what they want to deliver to the reader, and maybe skip parts which are not relevant to the main purpose of the article (for example about most polluted megacities, as here megacities are not investigated). Yurihonjo can't be compared to a megacity, as by definition it is an urban site (last line in 165).

Response:

As the reviewer pointed out, we couldn't find any evidence that snow is the reason for low PM_{2.5} concentration. Therefore, we deleted this sentence. As described topic 2, we revised the section 3.5.2.

We think that information on PM_{2.5} concentrations in global megacities is necessary for this manuscript. This part shows that PM_{2.5} concentration in this study is low enough compared to the polluted megacities (page 5-6, lines 155-160).

Line 260-265. The assumption that rice residues burning is the main source of WSOC in Tsukuma is nice assumption, but I was not convinced by this statement. Usually, in urban sites weak seasonal trend in carbon delta values is due to transportation influence. Here, Authors did not evaluate the $\delta^{13}\text{C}$ of fossil fuel emissions. In addition, assuming that crop combustion is the main source of WSOC, we must to see correlation with delta values. No correlation between WSOC concentrations and delta values means that does not exist one dominating aerosol source. In other words, if in Tsukuma main source would be crop burning, we must observe correlation between WSOC and delta values. Or, delta values are affected by atmospheric processing, but then air mass back trajectory analysis (even with Solar intensity) must be performed to understand the resident time of the aerosol.

Response:

The WSOC have both primary and secondary sources that can be biogenic or anthropogenic. Also biomass burning is another important source of WSOC (Sullivan and Weber, 2006). As described topic 1, the $\delta^{13}\text{C}_{\text{WSOC}}$ was consistent with the $\delta^{13}\text{C}$ of C3 plant, and a high correlation was found between WSOC concentration and non-sea-salt potassium concentration in Tsukuba. These results suggested that the main source of WSOC was biomass burning of rice straw. In fact, the season of biomass burning for rice straw is from September to October in Tsukuba (Tomiyama et al., 2017).

As the reviewer pointed out, a weak correlation ($r = 0.18$) was found between $\delta^{13}\text{C}_{\text{WSOC}}$ and WSOC concentrations. If the value of $\delta^{13}\text{C}$ is constant, the correlation between $\delta^{13}\text{C}$ and concentration will be low.

Line 290. Speculations about long-range transport must be verified by air mass trajectory analysis. Also, Authors can use other delta signatures (various crops, land and forest fires, transportation and fuel burning emissions, shipping emissions etc.), not only rice burning.

Response:

The result of seasonal back trajectory analysis at Yurihonjo has been described in Kawashima and Haneishi (2012). The seasonal variations of air masses show similar trends every year. The air masses came mainly from northeastern China and Siberia during autumn and spring, while they came from the Pacific Ocean in summer.

Since there are no $\delta^{13}\text{C}_{\text{WSOC}}$ data from the various sources (e.g., fossil fuel, transportation, and fuel burning) pointed out by the reviewers, we could not be compared in this study.

Line 310. Kawashima and Murakami 2014 report that in roadside samples VOC ranged from -29.6 to 23.5 permill (the same range for ambient samples). It makes difficulty interpreting vehicular emissions from a stable isotopes perspective. I'm not sure if only Toluene and Xylene are responsible for WSOC in Yurihonjo, so 5.8 permill subtraction must be made carefully (Authors note themselves that anthropogenic emissions of VOC are smaller than that biogenic).

Response:

As the reviewer suggested, it is difficult to estimate the effects of anthropogenic VOCs and biogenic VOCs of as sources of WSOC. In particular, WSOC are formed by oxidation of VOCs and involve isotope fractionation. This study considered the effects of anthropogenic VOCs using the isotope fractionation from VOCs to SOA. As a result, the anthropogenic VOCs was considered no dominant source of WSOC. Therefore, we speculated that the light $\delta^{13}\text{C}_{\text{WSOC}}$ in summer was a result mainly of the formation of SOA from biogenic VOCs.

We revised the sentences to section 3.5.2 (page 10, lines 286-304).

Figure 2. I not found in the manuscript explanation, what causes enriched delta values in the winter in season 2018/2019 compared to 2017/2018 at both locations?

Response:

The $\delta^{13}\text{C}_{\text{WSOC}}$ from February to April 2019 was heavy at both sampling sites. The reason is affected both by biomass burning and aging of OC during long-term transport in Yurihonjo. In contrast, the reason for the heavy $\delta^{13}\text{C}_{\text{WSOC}}$ in Tsukuba remains unclear.

We added the sentences to section 3.5.2 (page 9, lines 275-285).

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