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Atmospheric Chemistry and Physics Discussions

Interactive comment on "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* Nana Suto and Hiroto Kawashima

Anonymous Referee #1

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This paper presents long-term concentration and isotopic ratio measurements of TC and WSOC in ambient PM2.5 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.

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

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.

Specific comments:

1) The authors present d13C 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 then 10% to the WSOC. Due to the complexity of the biomass burning sources and processes, it is very unlikely that the levoglucosan source specific d13C (please note here that Sang et al. EST2012 presented d13C0 of levoglucosan in aerosol formed during the combustion of C3 plants only) will determine alone the WSOC or TC d13C. 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. Yet, the TC and WSOC d13C can be compared with corresponding values (Gensch et al. IJMS2014). The observations agree mainly with TC and WSOC d13C of C3 plant and fossil fuel combustion aerosol.

2) As for the TC and WSOC d13C seasonal trend, the authors state in Lines220-224: 'd13CTC and d13CWSOC at Tsukuba became slightly heavy from February to April 2019, but they showed no other clear seasonal variation (Fig. 2a). In contrast, the d13CTC and d13CWSOC at Yurihonjo were heaver 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. 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.

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, CO2 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.

Editorial revisions:

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

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122, 123)

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

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'? - Line91: ' Every December to February' 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. 3) Wrong wording - Replace 'reasonable' describing the measurements (lines171, 186). Use instead 'good agreement', 'similar to other studies', 'as expected'... - 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.

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