

Editor and Reviewer comments:

Response: We thank the editor and reviewers for good comments and suggestions. We have addressed each comment in the following point by point. In addition, we have adjusted our reference list according to the ACP guideline.

RC1: ['Comment on acp-2022-220'](#), Anonymous Referee #1, 04 Apr 2022

The work by Honga et al. investigated distribution of several organic tracer compounds, water-soluble inorganic ions in PM_{2.5} and gas phase HCl, HONO, HNO₃, NH₃ species in coastal areas of South-eastern China. The authors employed well established analytical techniques for identification and quantification of tracer compounds (e.g. TMS derivatisation). The obtained results are interesting and can be useful for researchers dealing with tracer compounds. I recommend this work for publication under *Measurements Reports* after considering my comments below:

Response: Thank you very much for all the valuable comments and suggestions. We have addressed each comment in the following point by point and have revised the manuscript accordingly.

Materials and methods:

The authors use **a single** internal standard (IS) to cover **fifteen** organic tracer compounds: Lines 152-153 state "At last, 140 µL of internal standard solution (13 C n-alkane solution, 1.507 ng µ L⁻¹) was added into the samples". The majority of considered tracer compounds are of highly polar nature (containing hydroxylic groups). What was the rationale for selecting a non-polar ¹³C n-alkane as an IS for polar compounds? One of the requirements for IS that it should structurally resemble the analyte of interest (structural analogue or stable label) such that it behaves similarly during sample preparation and analysis (Lowes et al., 2011). The IS that is added to each sample compensates for unavoidable assay variance due to, for example, extraction efficiency, ionisation effects and transfer losses, and thus I am concerned about the discussion of correlation of various tracers in this work if the observed variability or absence of correlation could be due to other than environmental variability factors.

Response: Thank you for your kindly comments and good suggestions. We have described it clearly in the revised manuscript. In this study, four surrogate standards (structurally resemble the analytes of interest) was used to compensate for unavoidable assay variance in each sample during the pretreatment process, then internal standard (IS) was added after this process and before the instrument analysis.

Then, relative response factors (RRFs) of surrogate and internal standard were calculated to quantify the targeted organic compound in each sample, including SOA_I, SOA_M, SOA_C and SOA_A tracer.

These sentences have been rewritten, as follows:

Due to the lack of authentic standards, surrogate standards (including erythritol, malic acid, PA and citramalic acid) were used to compensate for unavoidable assay variance of SOA_I, SOA_M, SOA_C and SOA_A tracer in each sample during the pretreatment process, respectively (Fu et al., 2009; Lowes et al., 2011).

Then, relative response factors (RRFs) of surrogate and internal standard were calculated to quantify the targeted organic tracers in each sample. Details of SOA tracer's calculated concentrations based on RRFs were presented in our previous studies (Hong et al., 2019; Liu et al., 2020).

Lowes, S., Jersey, J., Shoup, R., Garofolo, F., Savoie, N., Mortz, E., Needham, S., Caturla, M. C., Steffen, R., Sheldon, C., Hayes, R., Samuels, T., Di Donato, L., Kamerud, J., Michael, S., Lin, Z. P., Hillier, J., Moussallie, M., Teixeira, L. D., Rocci, M., Buonarati, M., Truog, J., Hussain, S., Lundberg, R., Breau, A., Zhang, T. Y., Jonker, J., Berger, N., Gagnon-Carignan, S., Nehls, C., Nicholson, R., Hilhorst, M., Karnik, S., de Boer, T., Houghton, R., Smith, K., Cojocar, L., Allen, M., Harter, T., Fatmi, S., Sayyarpour, F., Vija, J., Malone, M., and Heller, D.: Recommendations on: internal standard criteria, stability, incurred sample reanalysis and recent 483s by the Global CRO Council for Bioanalysis, *Bioanalysis*, 3, 1323-1332, 10.4155/Bio.11.135, 2011.

Results and discussion:

The authors give a fair description of isoprene oxidation products; however, I can't say the same about the other discussed tracers. For example, I realise that levoglucosan is commonly used as a marker compound for biomass burning; however, nothing is stated about stability of this compound. It has been shown that the oxidation of levoglucosan in atmospheric deliquescent particles is at least as fast as that of the other atmospherically relevant organic compounds and levoglucosan may not be as stable in the atmosphere, especially under high relative humidity conditions (Hoffmann et al., 2010). Can this be one of the reasons for absence of correlation with other tracers? Could you elaborate why are you expecting a correlation of CPA with levoglucoasan (lines 357-358)? This is not clear to me. As I understand, the applied derivatisation technique allows separation of other biomass burning markers e.g. mannosan and galactosan, which often accompany levoglucosan. Have the authors observed these isomers along with levoglucosan? The relative ratios of levoglucosan to mannosan have been used for source reconstruction of combustion derived byproducts in atmospheric aerosols (e.g. Iinuma et al., 2007, 2009, Engling et al., 2009) and can be useful to support some of the conclusions made in this work.

Response: Thank you for your good comments and suggestions. Indeed, as you mentioned, levoglucosan is commonly used as a marker compound for biomass burning, and may not be as stable in the atmosphere, especially under high relative humidity conditions. In this study, maybe, it's hard to reflect the real concentration of levoglucosan, and we do not try demonstrate the variations and sources of levoglucosan during the monitoring period. So, we didn't talk about the stability of this compound. But, the seasonal and diurnal trend of levoglucosan could be referred. A correlation of CPA with levoglucosan was carried out to discuss the impacts of biomass burning on the distribution of SOA tracers through local or long-range transport. CPA, the typical tracer of sesquiterpenes, is formed by the photooxidation of β -caryophyllene. Some of them originated from the emission of biomass burning.

Due to the lack of authentic standards, mannosan and galactosan were not measured. The reviewer raised a good point. In the future, we will pay more attention to the characteristics of biomass burning markers including levoglucosan, mannosan and galactosan when our researches focus on the effects of biomass burning on chemical compositions of aerosol particles.

In addition, DHOPA, an anthropogenic SOA tracer, was used to reflect the influence of anthropogenic activities emissions. Aromatic hydrocarbons (AHs) are typical AVOCs and a major class of ASOA precursors. In this study, the correlation between CPA and DHOPA was analyzed (Fig.S2) in order to discuss the influence of anthropogenic emissions on the source of CPA. We didn't comprehensively elaborate the variations and sources of DHOPA during the monitoring period.

These sentences have been added in the manuscript, as follows:

Levoglucosan (LEV), a typical tracer of biomass burning, similar seasonal and diurnal trend to other tracers was observed. However, LEV may not be as stable in the atmosphere, especially under high relative humidity conditions (Hoffmann et al., 2010). In this study, maybe, it's hard to reflect the real concentration of LEV. A correlation of CPA with LEV was carried out (Fig.S2), just to discuss the impacts of biomass burning on the distribution of CPA tracers through local or long-range transport.

Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric Stability of Levoglucosan: A Detailed Laboratory and Modeling Study, *Environmental Science & Technology*, 44, 694-699, 10.1021/es902476f, 2010.

Conclusion section:

At least the way how it is formulated in the text I find it rather difficult to see how the presented work led to the conclusion that there is an impact from anthropogenic–biogenic interaction.

Response: Thank you for your suggestions. We have changed the description of “anthropogenic–biogenic interaction” in the revised manuscript.

The sentence has been rewritten, as follows:

However, in winter, the formation of BSOA tracers were attributed to the impacts of anthropogenic emissions and atmospheric stagnant conditions.

Minor comment:

Line 27 (page 23) The authors state "These results also proved the obvious effects of anthropogenic emissions on secondary formation of aerosol particles under atmospheric relatively stability conditions during the winter." I think the use of correlations is indeed helpful to support some specific trends; however, I believe such data processing techniques are not sufficient to provide a definite answer on the specific emission source and therefore the words such as “obvious” should be avoided (at least in this context), or supported by other than correlation data.

Response: Thank you for your suggestions. We have deleted the word “obvious” in the revised manuscript.

These sentences have been rewritten, as follows:

In coastal cities of southeastern China, with the development of rapid urbanization, air pollution caused by motor vehicles and industrial emissions is becoming more frequent in winter (Wu et al., 2020). The Xiamen port is one of the top 10 ports in China, resulting the impacts of ship emissions and port activities on ambient air quality (Xu et al., 2018), and the numbers of motor vehicles increased sharply in recent years. We also found that the 90th percentile of maximum daily average 8h (MDA8) O₃ concentrations in Xiamen was significantly increased from 2015 to 2020 (Fig. S3). During the past several years, the elevated secondary inorganic components, including NO₃⁻, SO₄²⁻ and NH₄⁺, accounted for 40-50% of the total PM_{2.5}, and OM ranged from 30% to 40% (Wu et al., 2019; Hong et al., 2021). These results also implied the effects of anthropogenic emissions and enhanced atmospheric oxidation capacity on secondary formation of aerosol particles under atmospheric stagnant conditions.

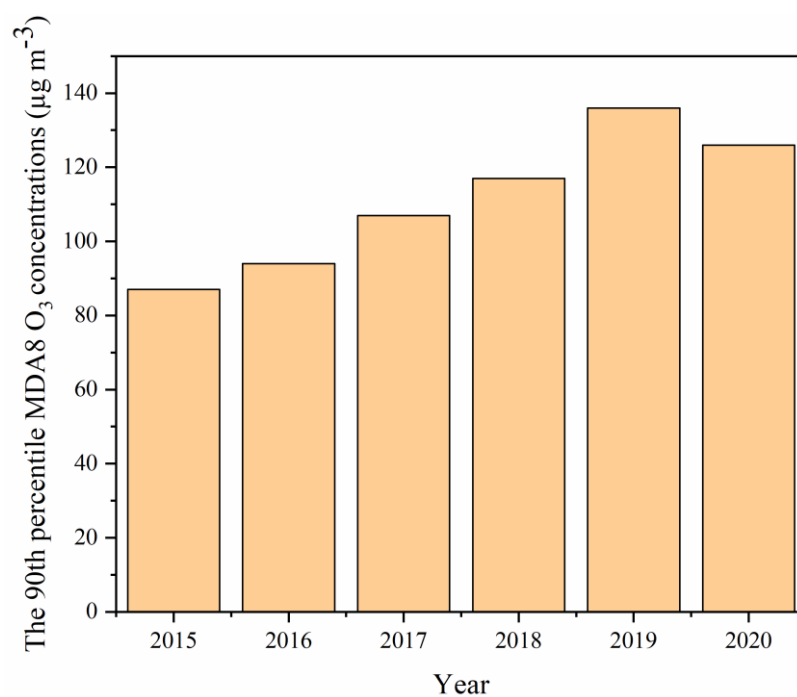


Fig.S3 Annual trends of the 90th percentile MDA8 O₃ concentrations in Xiamen

Xu, L., Jiao, L., Hong, Z., Zhang, Y., Du, W., Wu, X., Chen, Y., Deng, J., Hong, Y., and Chen, J.: Source identification of PM_{2.5} at a port and an adjacent urban site in a coastal city of China: Impact of ship emissions and port activities, *Science of the Total Environment*, 634, 1205-1213, [10.1016/j.scitotenv.2018.04.087](https://doi.org/10.1016/j.scitotenv.2018.04.087), 2018.