

Manuscript title: Evolution and chemical characteristics of organic aerosols during wintertime PM_{2.5} episodes in Shanghai, China: Insights gained from online measurements of organic molecular markers

Point-by-point response to comments

We sincerely thank the referee for the comments concerning our manuscript. They are valuable in helping us improve our manuscript. Our point-by-point response is provided below and marked in blue text.

- 1) The authors should discuss more HOMs compounds as well as their analytical analysis. Is this analytical method appropriate for their analysis? Recently offline techniques were reported to characterize several HOMs compounds in field samples including work from this group.

Response: In general, highly oxygenated organic molecules (HOMs) refers to a group of organic compounds which are formed in the atmosphere via autoxidation involving peroxy radicals and their chemical structures contain six or more oxygen atoms, many of which are incorporated as hydroperoxide (-OOH) functional group (Ehn et al., 2014, 2017; Bianchi et al., 2019). The -OOH functional group renders HOMs thermally liable, thus not amenable for analysis by gas chromatography (GC) techniques.

Here in our study, majority of the organic compounds reported (e.g., DCAs, hDCAs, α PinT) contain less than six oxygen atoms. Two exceptions are 3-MBTCA (3-methyl-1,2,3-butanetricarboxylic acid, C₈H₁₂O₆) and mannitol (C₆H₁₄O₆), both containing six oxygen atoms. However, they are not regarded as HOMs since neither of them is formed via autoxidation or contain hydroperoxide functional group. Given that the organic compounds reported in this study are not HOMs and the TAG instrument, incorporating GC as part of its instrument component to achieve separation of organic mixture, is not designed for analyzing HOMs, we feel it is outside the scope of this work to discuss more about HOMs.

The reviewer mentioned that offline techniques have been developed by our group to quantify HOMs in field samples. We guess the reviewer may be referring to the papers by Nie et al. (2022) and Lu et al. (2023), which adopted CIMS and chemical-ionization orbitrap mass spectrometry to measure oxygenated organic molecules (OOMs) including several HOMs compounds. However, these instruments were not deployed during this campaign.

- 2) Winter pollution is associated with nitrogen-containing compounds (mainly nitrates). The authors should discuss if nitrates were observed. Are they detected using the TAG method?

Response: We agree with the reviewer regarding the importance of organic nitrates. Organic nitrates can play an important role in PM_{2.5} pollution, especially in urban areas with high NO_x emissions. However, the TAG method, which thermally desorbs the organic compounds in particle samples, is not suitable for analyzing organic nitrates due to the inherent instability of their chemical structures (the -ONO₂ function group). For example, peroxy nitrates (RO₂NO₂) will dissociate when temperature raises to ~150°C and alkyl nitrates (ANs, RONO₂) are found to dissociate around 200~250 °C (Hao et al., 1994; Keehan et al., 2020). Among the nitrogen-containing compounds, only four nitro-substituted aromatic compounds (i.e., 4-nitrophenol, 4-nitrocatechol, 3-methyl-5-nitrocatechol, and 4-methyl-5-nitrocatechol) were quantified during this field campaign, as these compounds have sufficient thermal stability, with higher dissociation temperature (> 350 °C) (Hao et al., 1994; Jaoui et al., 2018).

- 3) The authors report aging process occurs during these episodes based on the structure of the markers observed by the authors. The authors should discuss how they distinguished between aging OA and non-aging OA (specify the representative chemicals responsible for aging for example)? The interpretation of the markers based on the structure (more oxygenated) is presented and is a bit tedious but is important for the authors to clarify this issue.

Response: The unambiguous molecular information offered by the TAG system enables us to interpret OA aging processes through specific SOA tracers and their formation chemistry established in controlled chamber experiments. For example, a number of chamber studies have confirmed that pinic acid and pinonic acid are early generation SOA products of α -pinene ozonolysis while 3-MBTCA is a later generation product (kristensen et al., 2014; Ma et al., 2008; Szmigielski et al., 2007). Several studies have also shown that L_DCAs and L_hDCAs are aging SOA tracers, the formation of which require multiple oxidation steps (Ervens et al., 2004; Yang et al., 2008). Also, as shown in Figure

S2, DHOPA and pinic acid showed stronger correlations with LO-OOA derived from AMS measurements while L_DCAs and L_hDCAs showed stronger correlations with MO-OOA. This further supports our interpretations of aging and non-aging SOA. Better clarification will be provided in the revised manuscript.

- 4) The authors should clarify how the AMS and TAG DATA were used and interconnected in this study. Mainly for differentiating between the 3 categories/groups of episodes, the aging process, and SOA vs POA. They are areas in the manuscript where these processes need to be carefully and explicitly discussed and more cautious about the reconciliation between the two methods AMS and TAG (PM₁ and PM_{2.5} analyzed by AMS and TAG respectively).

Response: The measurement data from TAG were generally consistent with those from AMS. As shown in Figure S2, the TAG-measured SOA tracers produced in early generations (e.g., DHOPA, phthalic acid, pinic acid) correlated well with LO-OOA derived from AMS while those associated with later generation products (e.g., C₃₋₅ DCAs, C₃₋₅ hDCAs) had stronger correlations with MO-OOA. After further investigating OA compositions in PM₁ during different episodes, we also find that local episodes were characterized by higher mass proportions of POA and less aged SOA (LO-OOA) while mix-influenced and transport episodes were associated with higher mass proportions of more aged SOA (MO-OOA), which is consistent with the observations from TAG. We will add a figure in the revised manuscript to present OA compositions in PM₁ during different episodes to clarify how the AMS and TAG DATA were used and interconnected for differentiating episodic events.

- 5) There are instances where I feel confused when the authors refer to SOA and POA to link to sources of OA in the different episodes reported in this study (for example the role of O₃).

Response: Our data indicate O₃ oxidation played a relatively limited role in SOA formation during local episodes. We'd like to make a few points related to this. First, the high NO_x concentrations as well as the high mass ratios of NO/NO₂ during local episodes likely have kept O₃ low and thus suppressed O₃ oxidation pathway (Table 2). Consequently, we observed more significant increases in mass concentrations of SOA markers formed via OH oxidation pathway compared with those formed via O₃ oxidation pathway. For example, DHOPA, which is a typical SOA product of monoaromatics with OH radicals, showed drastic increase in the mass concentration by 777%, in reference to non-episodic periods. In comparison, C₉ acids, which are typical oxidation products of fatty acids with O₃, their mass concentrations increased by 326% during local episodes in reference to non-episodic periods. And the mass concentrations of αPinT and βCaryT, which are oxidation products of biogenic VOCs with O₃, increased by 393% and 276% during local episodes in reference to non-episodic periods, respectively. Such contrasts between SOA products from OH-initiated vs O₃-initiated oxidation pathways appear to suggest that SOA formed during local episodes were more influenced by pathways other than ozonolysis (e.g., OH oxidation). We will add these explanations in the manuscript to further clarify SOA formation during different episodes.

- 6) Lines 16-20: Please clarify if secondary and primary are dominating the OA. It seems to me that (line 17): secondary sources were important and in the next few lines the authors report that primary also are important sources!

Response: The claim in Line 17 that local episodes were significantly influenced by SOA is deduced from the mass variations of major chemical components in PM_{2.5}. That is, SOA overall had higher percentage proportions in PM_{2.5} during local episodes compared with mix-influenced and transport episodes, while the latter two were characterized by significant higher mass incrementations in secondary inorganic ions (e.g., nitrate) in PM_{2.5}. When we further investigated OA compositions with the measurement data obtained from the TAG system, we find that SOA enhancements during local episodes were associated with sources from vehicle and cooking emissions. In other words, abundant precursors from local vehicle and cooking emissions greatly contributed to the formation of local SOA. Therefore, it is not odd that we also observed mass incrementations in hopanes, alkanes, and fatty acids during local episodes, which are typical POA markers for vehicle and cooking emissions. In this case, the claims in Lines 16-20 do not contradict each other.

- 7) Is sampling done every 2 hours (see abstract) or every one hour as mentioned in the text (Table 1/line 63 etc.)? Please clarify.

Response: The time resolution of TAG system is 2-hour. We will correct related information in Table 1.

- 8) Line 17: suggests replacing "elevation" with "increase" or clarifying the sentence!

Response: We will rephrase the sentence.

9) Line 35. Please correct the references (e.g., “L. Chen et al., 2017” should be “Chen et al. 2017”). Please check this throughout the manuscript.

Response: We will correct the references.

10) Line 54: Add reference(s) to Recent studies....end of the sentence.

Response: We will add references to support the statement.

11) Table 1. Please clarify which parameters were measured in the gas or particle phase and for how long?

Response: All parameters listed in Table 1 were measured from 25th November 2019 to 23rd January 2020 as stated in Line 75. In the column “parameter” of Table 1, we have stated that organic molecular markers, inorganic water-soluble ions, OC, EC, and 15 trace elements were measured in PM_{2.5}, and organics were measured in PM₁. In other words, these parameters were measured in the particle phase. For the parameter “C₂ - C₁₂ VOCs”, they were measured in the gas phase and we will clarify this in the revised manuscript.

12) Line 94: Table S1...to the end of the sentence. It seems to me that IS were also measured. The quantification of the 98 cpds was done using IS!

Response: We apologize that our wording was unclear. Below is a detailed explanation of how we quantify the 98 compounds and the role of internal standards (IS). We added a series of deuterated ISs in each sample introduced to the TAG system to compensate the matrix effects and other injection-to-injection variations (Gosetti et al., 2010; Wang et al., 2020). In our study, calibration curves were first established before using the TAG system to measure ambient samples. To be specific, 5 µL of ISs was mixed with 0-5 loops (5 µL/loop) of external standards and co-injected into CTD cell for GC-MS quantification. This yielded a five-point calibration curve for each analyte. Calibration curves were established by fitting the normalized peak areas of external standards to their corresponding IS with respective concentrations. During the ambient measurements, we also introduced 1 loop (5 µL) of IS in each aerosol sample. Then we calculated peak area ratios of target organic compounds against their corresponding IS (listed in Table S1) for each ambient sample and used the above-mentioned calibration curves to quantify their masses in real aerosol samples. The detail descriptions of the TAG calibration and quantification method have been given in several of our previously published papers (He et al., 2020; Wang et al., 2020).

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