

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 appreciate all the comments and suggestions from the referees and editor. They are valuable in helping us improve our manuscript. Our point-by-point response is provided below and marked in blue text. Note the line numbers quoted in this response document correspond to the changes-tracked revised manuscript, which also show the revised text in blue.

Responses to comments from Referee #1:

- 1) The authors responded properly to the comments raised by the reviewers and corresponding modifications were made to the manuscript. Though the revised manuscript was more clearly presented than the original version, I still have one more comment on the statement of more SOA contribution during the local episodes. It can be found from Table 2 that the average SOM/POM ratio was 4.0, 5.1, 3.9 and 3.8 during the local episodes, mixed-influence episodes, transport episodes and non-episodic periods respectively, it would thus be misleading to say " Episodes primarily influenced by local air masses were characterized with higher proportions and mass increments of secondary OA". Comparing with POM, SOM contribution during the local episodes was not significantly higher, but the contribution of inorganic ions significantly lower. I would suggest the authors to verify the concern and make corresponding modification to the manuscript.

Response: The statement "more SOA contribution during the local episodes" is meant to describe "more SOA contributions to PM_{2.5}", which is 26.5% during the local episode, higher than the other types of episodes (See Table 2). We'd like to clarify that it is meant to indicate that more SOM relative to POM (i.e., SOM/POM ratio) as understood by the reviewer. We now revise the statement to the following to improve the clarity:

Line 17:

"Episodes primarily influenced by local air masses were characterized with higher proportions in PM_{2.5} and mass increments of both primary and secondary OA".

In the main content when we discuss the variations of major components in PM_{2.5} during different episodic events (Line 216-220), we have also mentioned that "Indeed, primary species (e.g., POM, EC, potassium, chloride, geological material matters and other trace elements) also showed noticeable increases with summed contributions up to 29% during local episodes, while their percent contributions during the transport and mixed-influence episodes were in the range of 8-14%. The higher proportions of primary species together with significantly higher values of NO/NO₂ and T/B ratios indicate that local PM_{2.5} episodes in Shanghai were largely influenced by freshly emitted primary pollutants in the local areas".

Responses to comments from Referee #3:

- 1) During the last round of review, I asked the authors to add some key experimental details to the manuscript. It is important to let readers know the full details of the experiments without spending much effort to check the authors' previous papers. But only a few details were added in the revised paper. I think it is not sufficient.

Response: In the revised manuscript (Line 79-93), we have added more information related to the operational procedure of the TAG system. Additionally, we have also given more descriptions for other instruments employed in this study in the revised supporting material (Text S1, Line 32-71).

Line 79-94

"The measurement principle and operational procedure of the TAG system have been detailed in previous studies (He et al., 2020; Kreisberg et al., 2009; Wang et al., 2020; Williams et al., 2006; S. Zhu et al., 2021). In brief, the TAG system was operated with a time resolution of 2 hours. During the first hour, aerosol was collected at a flow of 10 L/min, and during the second hour, GC-MS analysis was performed. After sampling at room temperature and subsequent addition of 5 µL internal standard (IS) mixtures, the thermal desorption cell (CTD) was held at 45 °C for

2 min, then increased to 330 °C in 6 min, and held at 330 °C for 12 min. During this thermal desorption step, polar organic compound in PM_{2.5} deposit on the CTD underwent in-situ derivatization under a helium stream saturated with derivatization agent N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA). Subsequently, the organic compounds were re-concentrated onto a focusing trap (FT) cooled by a fan. Afterwards, the CTD was purged with pure helium to vent the excess MSTFA and the FT was heated to 330°C to transfer the organic compounds into the valve-less injection (VLI) system, which employs a restrictive capillary tube to connect with the inlet of the gas chromatograph (GC). Then the GC/MS analysis started and concurrently, the next ambient sample was collected via the above-mentioned steps. In this study, a total of 98 polar and nonpolar organic compounds were identified and quantified (Text S1) and the full list is provided in Table S1. The detailed quality control measures and results for the TAG measurements have also been reported in S. Zhu et al. (2021) and given in section 2.2.1.”

Text S1, line 32-71

“An Aerosol Mass Spectrometer (AMS) was deployed to quantify major components in PM₁ during the campaign. The AMS was operated alternately between V & pToF combined mode and W mode for 150 s each. Filtered ambient air was sampled and analyzed before and after the campaign for 30 min with a HEPA-filter placed in front of the inlet, defined as the filter periods. The gas-phase CO₂ contribution to the CO₂⁺ signal was corrected by the data during the filter periods and the detection limits of species are defined as three times the standard deviation of the measured species concentrations in the filter periods, which were 0.19, 0.033, 0.067, 0.182, and 0.032 µg/m³ for organic, sulfate, nitrate, ammonium, and chloride, respectively. The PMF2 algorithm with a toolkit (version 3.04A) based on Igor Pro software was applied to perform PMF analysis of AMS mass spectra. More detail descriptions of AMS-PMF analysis during this measurement period have been reported by Huang et al (2021) and the PMF analysis results are given in Figure S1.

For volatile organic compounds, two on-line gas chromatograph with flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC C2-C6 #5250308 and airmoVOC C6-C12 #2260308, Chromatotec, Bordeaux, France) were employed to provide their mass concentrations continuously with 30 min time resolution. The C₂ - C₆ VOCs were collected through a preconcentration trap containing porous substances (Carbotrap C, Carboxen) and Carbopack B. The trap was cooled by a cell with Peltier effect during the sampling period. After sampling, it was heated to 220 °C to thermally desorb trapped C₂ - C₆ VOCs. For the C₆ - C₁₂ VOCs, they were collected with a trap filled with Carbotrap B, which was also cooled during the sampling period while heated to 380 °C during the thermal desorption step. The desorbed C₂ - C₆ and C₆ - C₁₂ VOC compounds were then separated on ultimet column and quantified by flame ionization detector (FID). Calibrations were conducted automatically once a day with three internal permeation tubes containing standard compounds during the campaign. Additionally, manual calibrations by standard gas (Spectra, USA) were also performed before and after the campaign.

Major components and trace elements in PM_{2.5} were measured in this study with hourly time-resolution. Among them, water-soluble inorganic ions, including Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺, were measured by a commercial instrument for online monitoring of aerosols and gases (MARGA, model ADI 2080, Applikon Analytical B.V.). In this instrument, aerosol samples were first drawn through a wet rotating annular denuder (WRD) where water-soluble gases diffused to the absorption solution (0.0035% H₂O₂), then particles were collected in a stream-jet aerosol collector (SJAC). After sampling, the absorption solutions were drawn from the WRD and the SJAC to syringes and subsequently injected to ion chromatographs with an internal standard (LiBr) for quantifications.

OC and EC in PM_{2.5} were monitored using a semicontinuous OC/EC analyzer (model RT-4, Sunset Laboratory Inc.) equipped with a PM_{2.5} cyclone and an upstream parallel-plate organic denuder (Sunset Laboratory Inc.). Ambient PM_{2.5} was sampled on a quartz filter in the oven at a flow rate of 8.0 L/min. Then the sample was analyzed by the thermal-optical transmittance method (TOT) using a two-stage thermal procedure that consisted of 600 - 840 °C in a helium atmosphere and 550 - 650 - 870 °C in an oxidizing atmosphere (2% oxygen in helium).

A total of 15 trace elements (K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Ba, Pb, Si, and S) in PM_{2.5} were measured at the site using an online non-destructive X-ray fluorescence spectrometer (XRF, model Xact 625, Cooper Environmental), which employs a reel-to-reel method to sample and analyze elements. PM_{2.5} samples were pumped through a section of Teflon filter tape at a flow rate of 16.7 L/min. Then the section of filter tape was analyzed by non-destructive X-Ray Fluorescence. The sampling and analysis processes occurred simultaneously, producing hourly data for the monitored trace elements.”