Significant role of biomass burning in heavy haze formation in a megacity: Molecular-level insights from intensive $PM_{2.5}$ sampling on winter hazy days

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Text S1: The isomeric ratios of anhydrosugars

The isomeric ratios of anhydrosugars are good indicators of biofuels. For instance, the ratio of levoglucosan to mannosan (L/M) tends to be higher for hardwood and crop residues than those for softwood (Engling et al., 2006; Sang et al., 2013; Schmidl et al., 2008; Zhu et al., 2015). Additionally, smoke particles emitted from crop straws, grasses, and biomass briquettes combustion were reported to contain higher amounts of galactosan than mannosan (Fu et al., 2008; Oros et al., 2006; Sheesley et al., 2003). Therefore, the lower L/M and M/G ratios during the first episode ($PM_{2.5}$ > 200 μg m^{-3}) likely indicate mixed contributions from softwood and crop burning to heavy haze formation (Figure S9). In fact, the impact of softwood combustion becomes larger in winter according to the previous report by Cheng (2013). However, the contribution of hardwood burning could not be neglected either, especially in moderate haze events (Figure S8a and Figure S9). This is supported by the rising L/M values with decreasing $PM_{2.5}$ levels as shown in Figure S8b.

Text S2: Chloride in $PM_{2.5}$ samples

Chlorine plays a part in global tropospheric chemistry, affecting the atmospheric oxidation capacity and consequently affecting the formation of $PM_{2.5}$ and O_3, particularly in winter (Wang et al., 2019, 2020; Yi et al., 2023). In this study, the absolute abundance of particulate Cl^- decreased with falling $PM_{2.5}$ levels (1.88-10.2 μg m^{-3}), while its relative contributions to total $PM_{2.5}$ were on the rise (from 3.2% to 8.7%) (Figure 4). An early study concluded that low temperature and high RH facilitate the generation of $PM_{2.5}$-bound Cl^- (Wang et al., 2023), which can account for high Cl^- concentrations in first episode. Based on the backward trajectories of air masses in Figure S1 and S2, roughly three sorts of trajectories were found in Nanjing during the whole sampling period, i.e., continental, marine, and mixed airmasses. Marine sources dominate the global tropospheric chlorine budget mainly through mobilization of chloride from sea-salt aerosols (Wang et al., 2019), as indicated by the obvious correlation between Cl^- and Na^+ ($r = 0.64$, $p < 0.01$). The rising Cl^- proportion with decreasing $PM_{2.5}$ level might be linked to growing influences of sea-salt aerosols via long-range atmospheric transport. In China, however, chlorine is mostly anthropogenic,

including coal combustion, BB, waste incineration, and industrial processes (Fu et al., 2018; Li et al., 2012; Yang et al., 2018). The positive relationship of Cl^- with levoglucosan proves a possible source of BB over this site ($r = 0.50$, $p < 0.05$). The higher mass ratios of Cl^-/Na^+ (about 5.5-15.5) in these samples than sea water (1.81) also indicate a significant contribution of anthropogenic sources to Cl^- in wintertime haze over Nanjing. The concentrations of Cl^- measured in this study (average: 6.38 ± 2.00 μg m^{-3}) are comparable to those observed in winter in Beijing (Wang et al., 2005) but slightly higher than those in a coastal megacity of Shanghai, China (Wang et al., 2006; Ye et al., 2003).

Text S3: Unsaturated diacids

Maleic (cis-isomer) and fumaric (trans-isomer) acid are two principal aliphatic unsaturated diacids found in this study, with concentration ranges of 0.86-41.9 ng m^{-3} and 1.61-27.6 ng m^{-3}, respectively. Significant correlation between fumaric and maleic acid ($r = 0.81$, $p < 0.01$) suggests they may share common sources. In fact, maleic acid, which is a probable product from photochemical oxidation of benzene, could be isomerized photochemically to trans configuration (fumaric acid) in the air with solar radiation, thus M/F ratios depend on the production of maleic acid and the subsequent transformation to fumaric acid. The M/F ratios were higher in second episode with high temperature and low RH (average: 1.38 ± 0.35), but lower in other two episodes (average: 0.71 ± 0.28 and 0.85 ± 0.44, respectively). Higher M/F values may be attributed to the superior photochemical generation of maleic acid over the cis-to-trans isomerization at high ambient temperature and low RH, whereas lower ratios might be in part due to the depressed maleic acid production by low temperature (Kawamura and Ikushima, 1993).

Text S4: Monocarboxylic acids

Two monocarboxylic acids, formic and acetic acid, were determined too. Both formic and acetic acids showed a decreasing temporal trend with decreasing $PM_{2.5}$ values, with the highest concentrations appearing in the heaviest haze events (average: 0.18 ± 0.05 μg m^{-3} for formic acid and 0.22 ± 0.11 μg m^{-3} for acetic acid, respectively). Lower temperature and higher RH in

this episode favor gas to particle conversion leading to high particulate concentrations. A clear relationship between formic and acetic acid existed ($r = 0.88$, $p < 0.01$), suggesting similar sources. Furthermore, formic and acetic acid both correlated significantly with levoglucosan ($r = 0.73$, $p < 0.01$ and $r = 0.61$, $p < 0.01$, respectively), indicating BB is a significant source of these acids. Formic acid was associated with EC as well ($r = 0.67$, $p < 0.01$), demonstrating fossil fuel is another contributor. Actually, secondary sources are also important in the atmospheric budgets of formic and acetic acids (Paulot et al., 2011). The ratio of acetic to formic acid (A/F) can be used to estimate relative importance of primary emissions (> 1) and secondary photochemical transformations (< 1) to carboxylic acids (Wang et al., 2007). The average A/F ratio for three episodes was 1.15 ± 0.32, 1.30 ± 0.52, 1.1 ± 0.30, respectively, suggesting relatively larger contributions from primary sources, such as BB, vegetation, coal burning, vehicular exhausts, and soil emissions in heating season (Khare et al., 1999; Stavrakou et al., 2012; Wang et al., 2007).

Text S5: Other identified chemicals

Methylglyoxal (MeGly) was also detected in these $PM_{2.5}$ aerosols, which are oxidation products from biogenic (e.g., isoprene/monoterpenes) and anthropogenic precursors (e.g., benzene, toluene, and xylenes) (Kampf et al., 2012). Most carbonyls are present in gas phase in the atmosphere. Thus, the high levels of MeGly observed in highest-$PM_{2.5}$ episode (20.4 ± 29.2 ng m^{-3}) might be due to lower temperature that allows more gaseous carbonyls partitioning into aerosol phase (Meng et al., 2018). In addition, fresh plumes from high BB activities during that time may play a role as well (Kampf et al., 2012). The MeGly abundances in other two episodes (10.1 ± 4.93 ng m^{-3} and 6.43 ± 3.04 ng m^{-3}, respectively) were comparable to those from Beijing $PM_{2.5}$ samples (average: 8.3 ± 7.9 ng m^{-3}) (Zhao et al., 2018). A significant correlation between MeGly and ^{14}C-WSOC was obtained in this study ($r = 0.74$, $p < 0.01$), suggesting non-fossil sources such as BB may contribute to atmospheric MeGly.

Methanesulfonic acid (MSA) is an oxidation product of dimethylsulfide (DMS) mainly released by marine phytoplankton. Thus MSA has long been regarded as a useful tracer for marine biogenic sulfur production (Chen et al., 2012; Legrand and Pasteur, 1998). Surprisingly, relatively abundant MSA was detected in this study, with higher levels occurring in the most

polluted episode (0.09 ± 0.02 μg m^{-3}) compared with other two episodes (0.04 ± 0.01 μg m^{-3} and 0.02 ± 0.01 μg m^{-3}, respectively). These values are similar to those reported from $PM_{2.5}$ aerosol in Beijing (Wang et al., 2005). Yuan et al. (2004) pointed out that anthropogenic sources, such as industrial emissions, could be additional sources for MSA in urban atmosphere. The ratio of MSA/nss-SO_4^{2-} (non-sea-salt sulfate) can be used to evaluate the relative contribution of marine sulfur emissions to total sulfur budget in the atmosphere (Legrand and Pasteur, 1998). On average, MSA/nss-SO_4^{2-} ratios for three episodes are 0.003 ± 0.001, 0.002 ± 0.00, 0.002 ± 0.001, respectively. Such low values indicate the influences of marine biogenic sources from coastal and oceanic areas on urban haze formation are rather weak. The significant relationships between MSA and levoglucosan ($r = 0.75$, $p < 0.01$) imply BB could be an important source of MSA in addition to industrial emissions, which is also supported by the significant relationship of non-fossil WSOC with MSA ($r = 0.79$, $p < 0.01$).

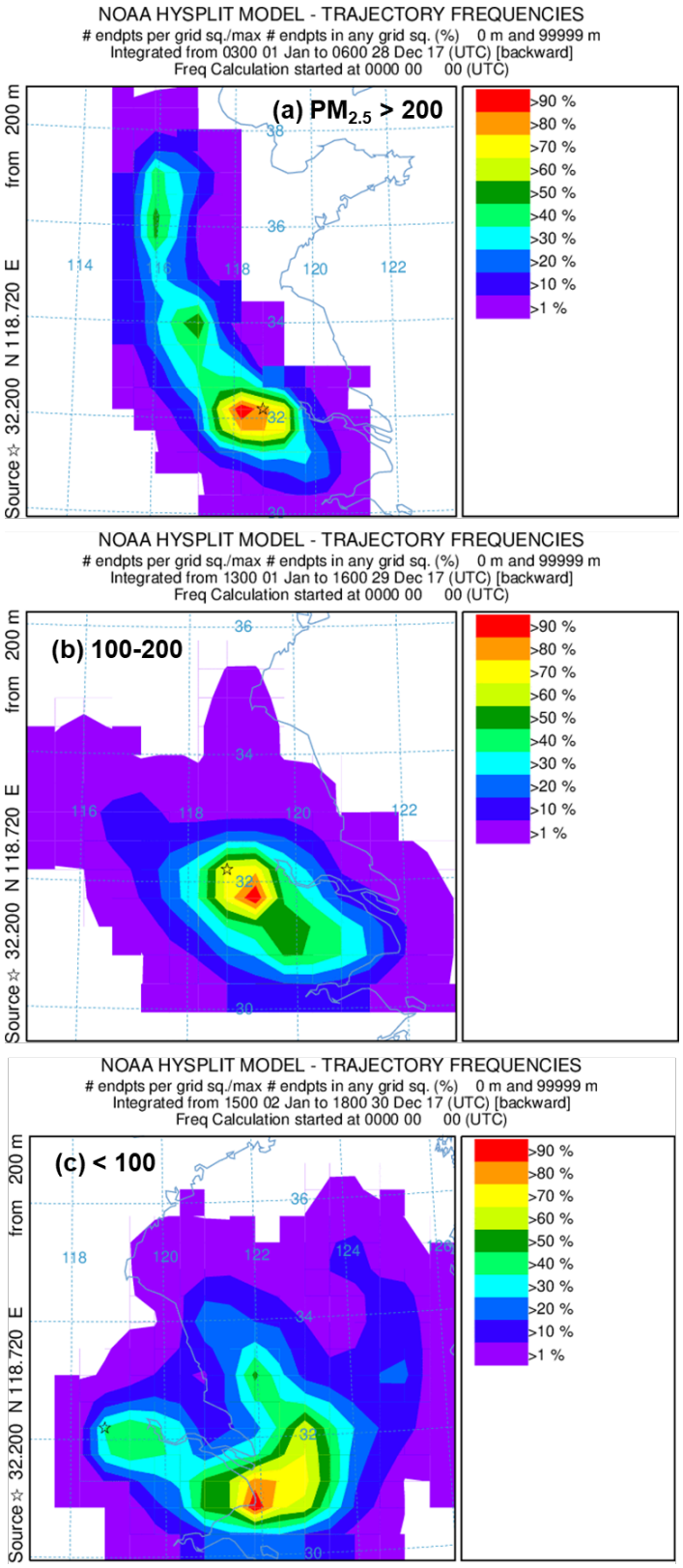

Figure S1. HYSPLIT back trajectories initiated over Nanjing with the altitude of these trajectories remaining below 200 m in the 48 h of the runs in three episodes according to $PM_{2.5}$ concentrations. The black star indicates the sampling site.

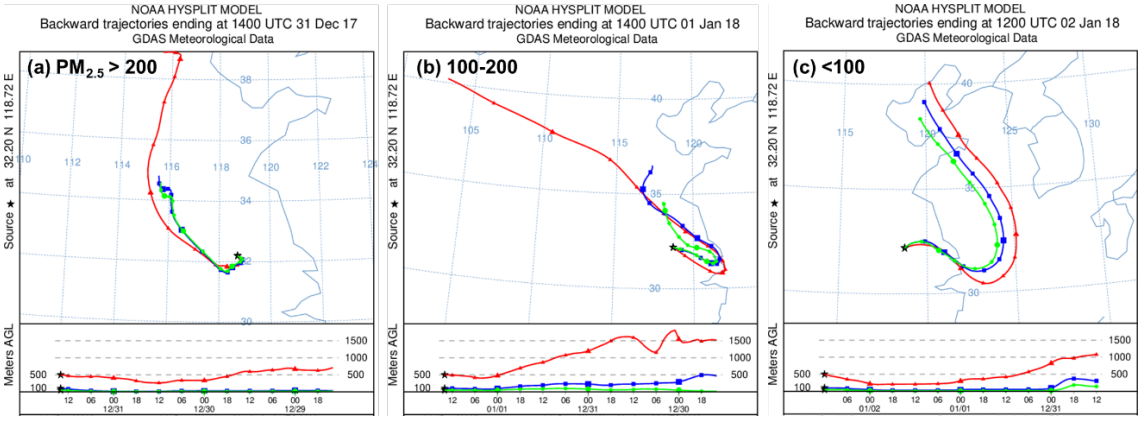

Figure S2. Three-day HYSPLIT back trajectories initiated over Nanjing with the altitude of these trajectories remaining below 500 m in the 72 h of the runs on the more polluted days in three episodes according to $PM_{2.5}$ concentrations. The black star indicates the sampling site.

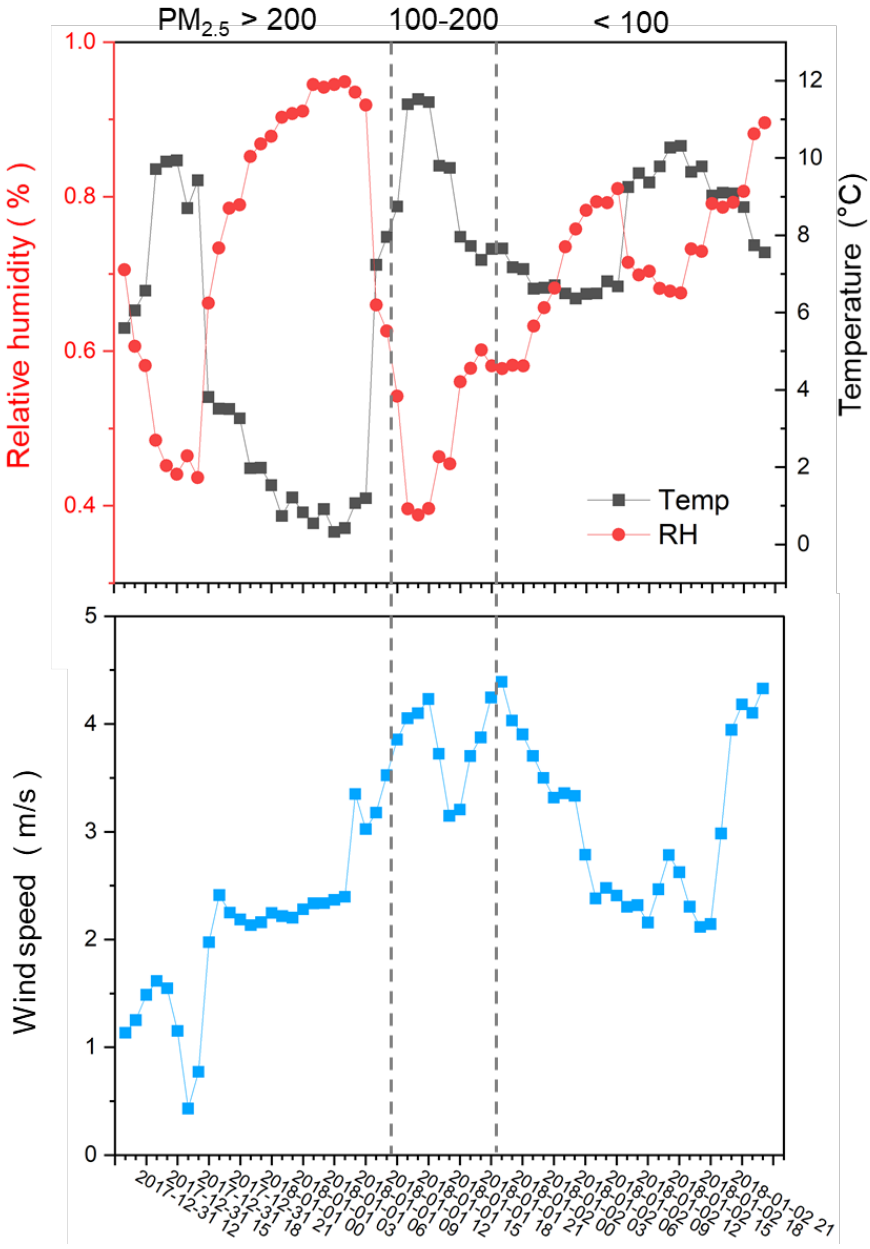

Figure S3. Time series of meteorological parameters (i.e., relative humidity, temperature, and wind speed) during sampling period in urban Nanjing.

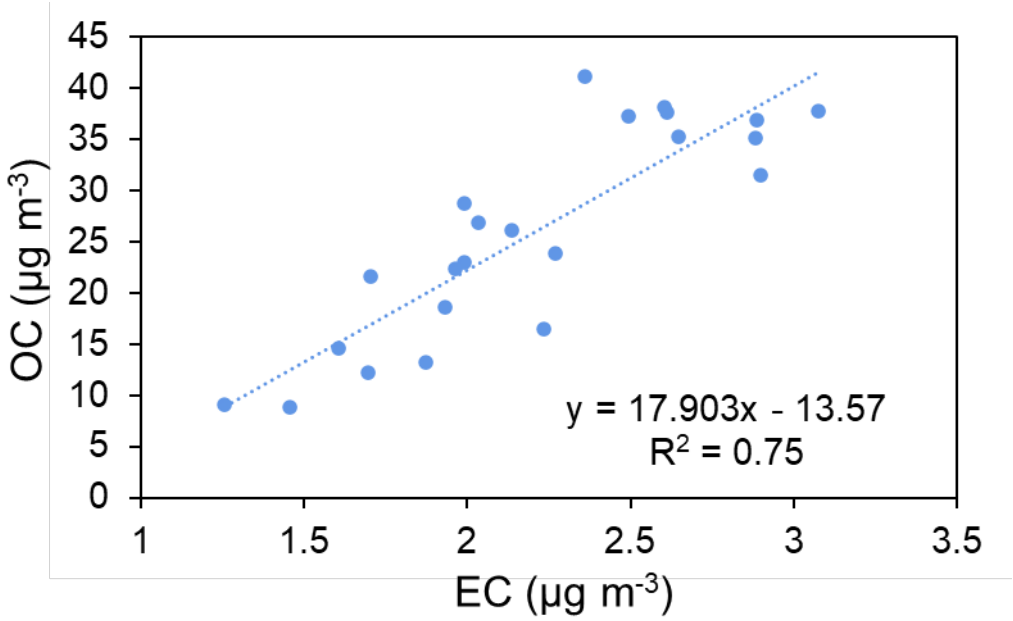

Figure S4. Based on the higher abundances of MSA and diacids in MBA together with nss-$SO4^{2-}$ (0.3 to 10.4 µg m^{-3}), we suggest that these water-soluble organics as well as nss-$SO4^{2-}$ might enhance the hygroscopic growth of the ambient aerosols over the open ocean waters characterized by high biological activity, acting as CCN. GRL High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary OA formation from isoprene

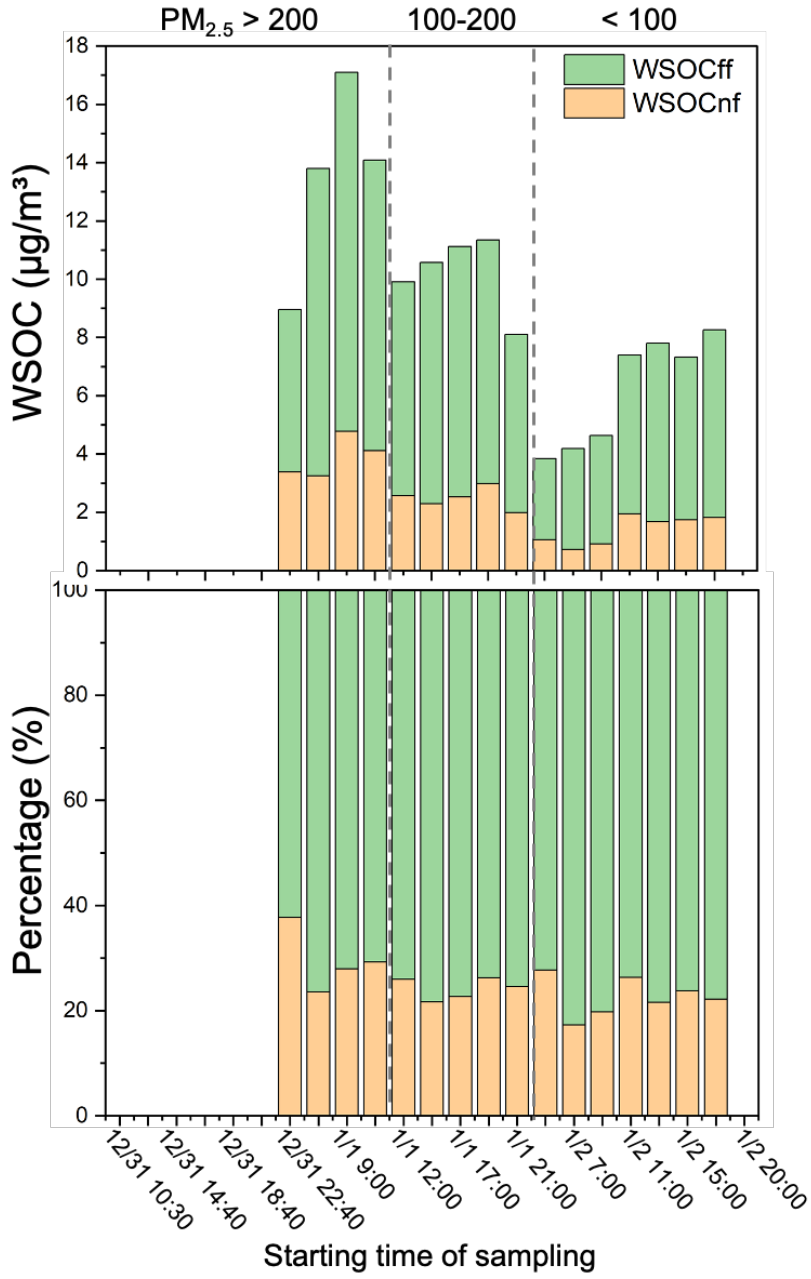

Figure S5. Temporal variations of fossil (ff) and non-fossil (nf) contribution to water-soluble organic carbon (WSOC) in 2-hour $PM_{2.5}$ samples in Nanjing.

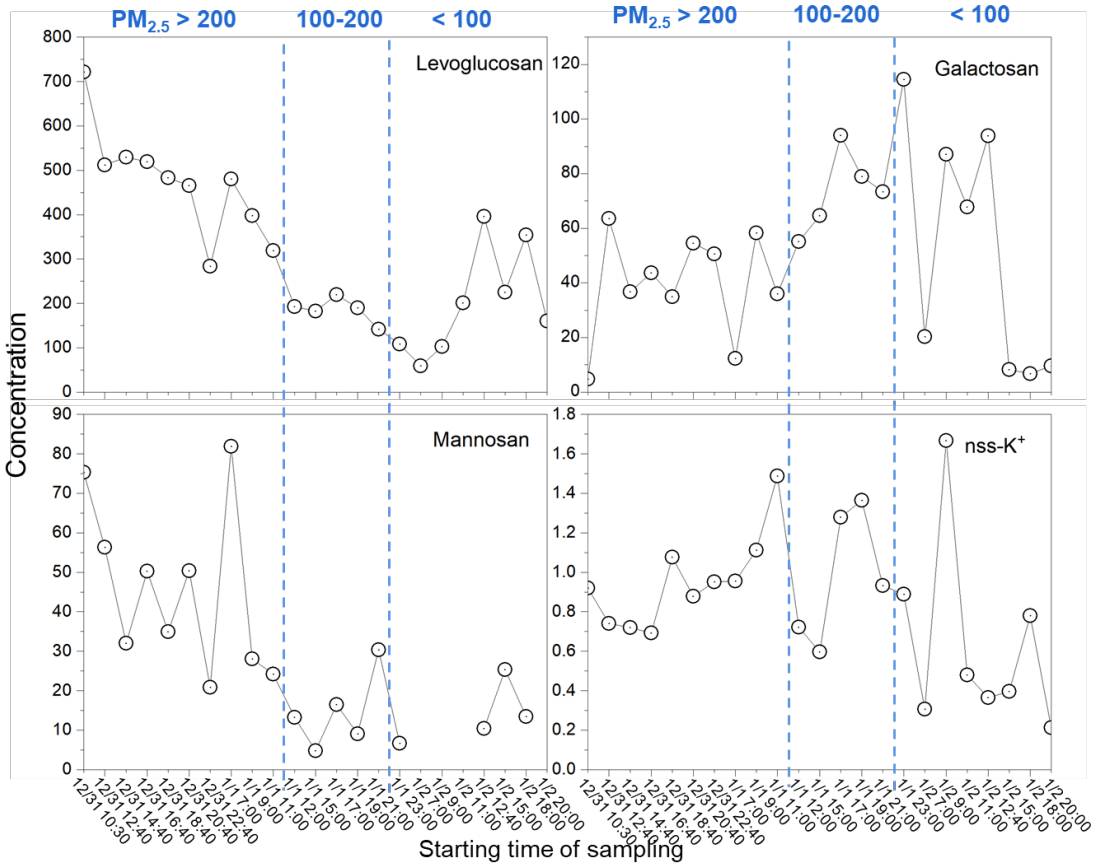

Figure S6. Temporal variations of biomass burning tracers including anhydrosugars (levoglucosan, galactosan, and mannosan, ng m^{-3}) and non-sea-salt K^+ (μg m^{-3}).

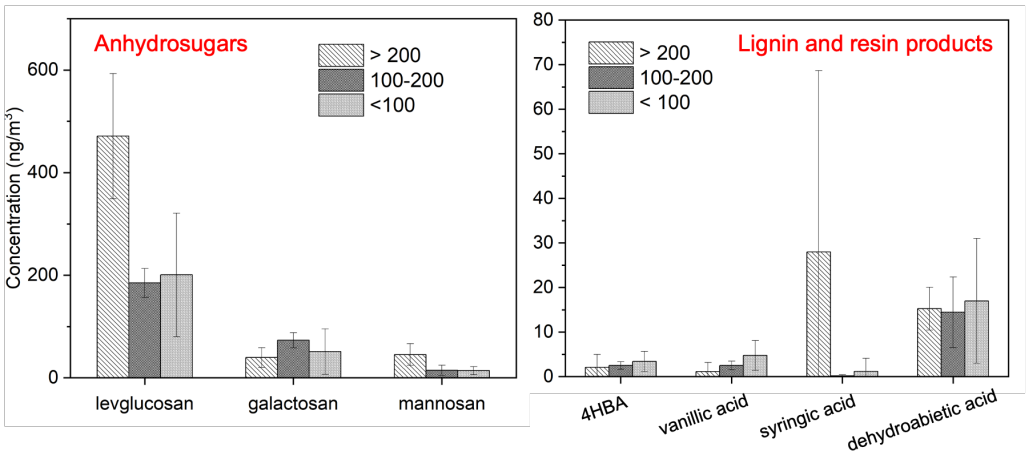

Figure S7. Average concentrations of measured biomass burning tracers during three episodes with $PM_{2.5}$ levels in the ranges of > 200, 100-200, and < 100 μg m^{-3}, respectively.

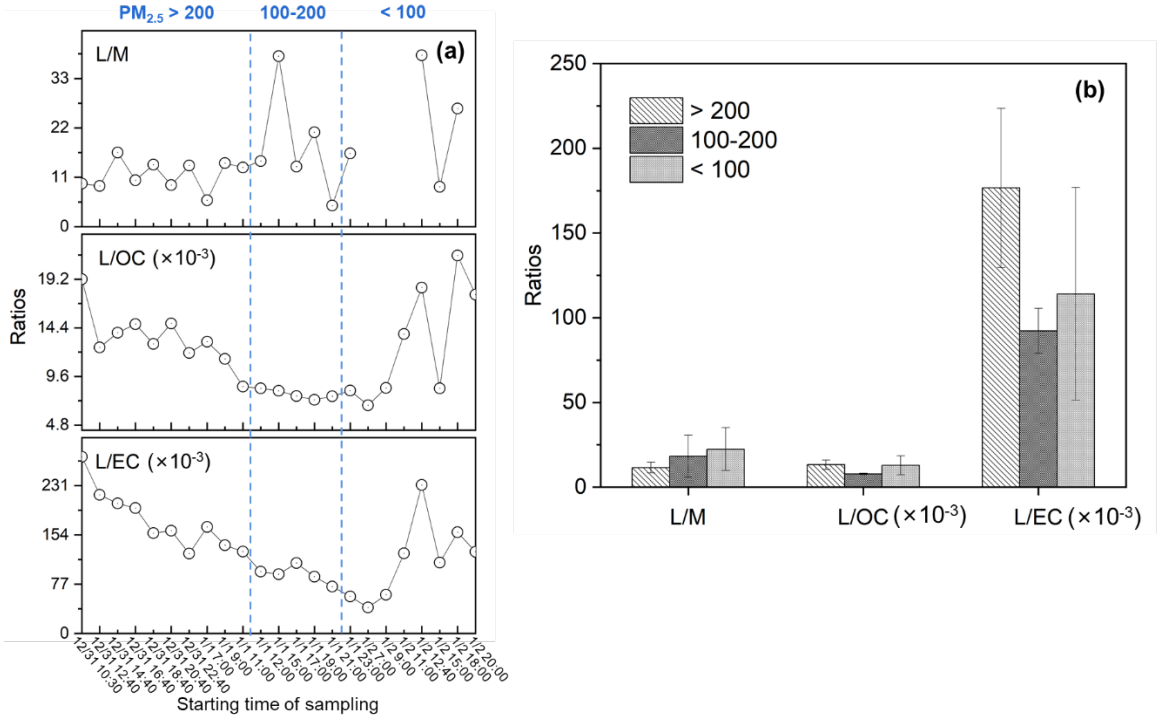

Figure S8. (a) Temporal variations of ratios of L/M, L/OC, and L/EC, and (b) the average ratios during three episodes (> 200, 100-200, and < 100 μg m^{-3}). L refers to levoglucosan, M is mannosan, OC means organic carbon, EC is elemental carbon.

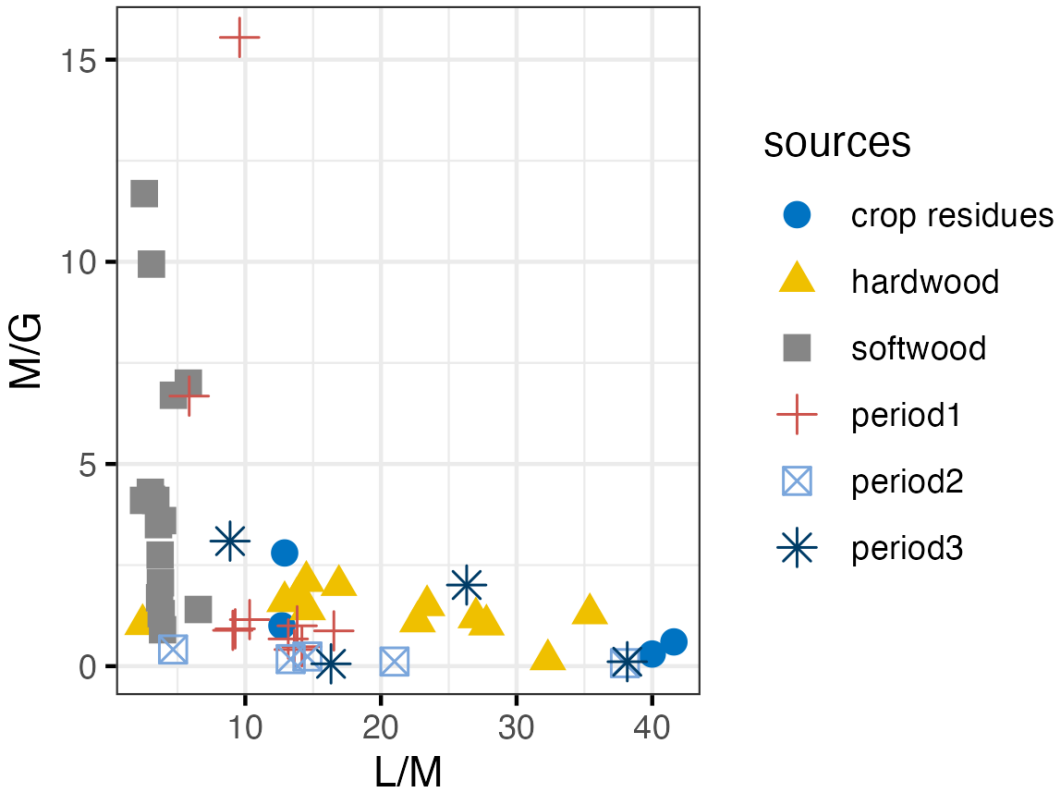

Figure S9. Comparison of L/M and M/G ratios from source emissions (literature values) and ambient aerosols in this study. L/M=levoglucosan to mannosan; M/G=mannosan to galactosan.

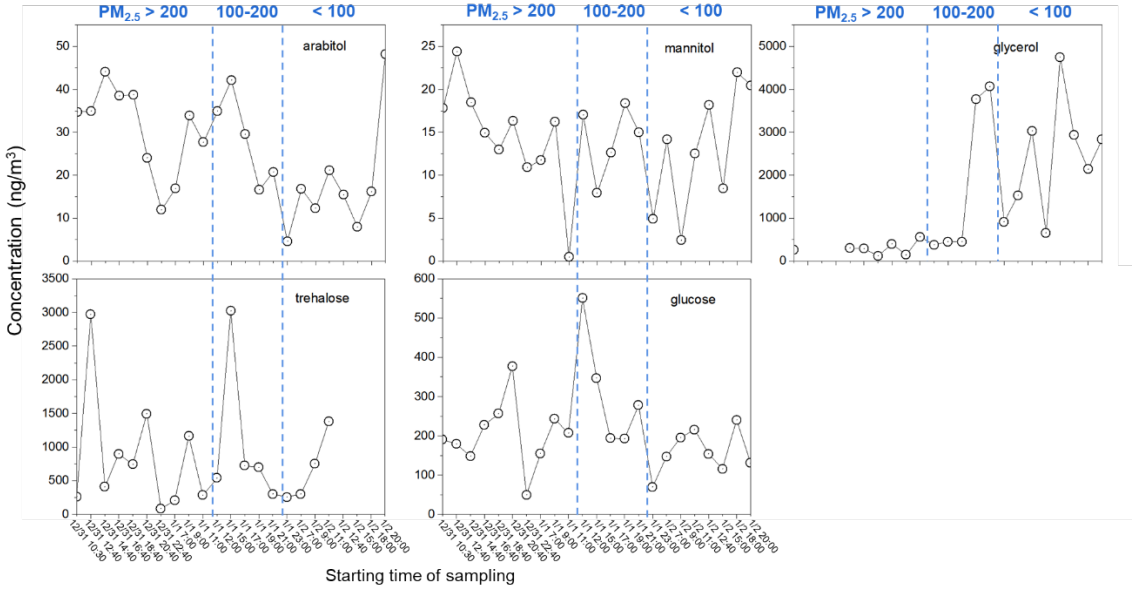

Figure S10. Temporal variations of sugars and sugar alcohols (ng/m^3).

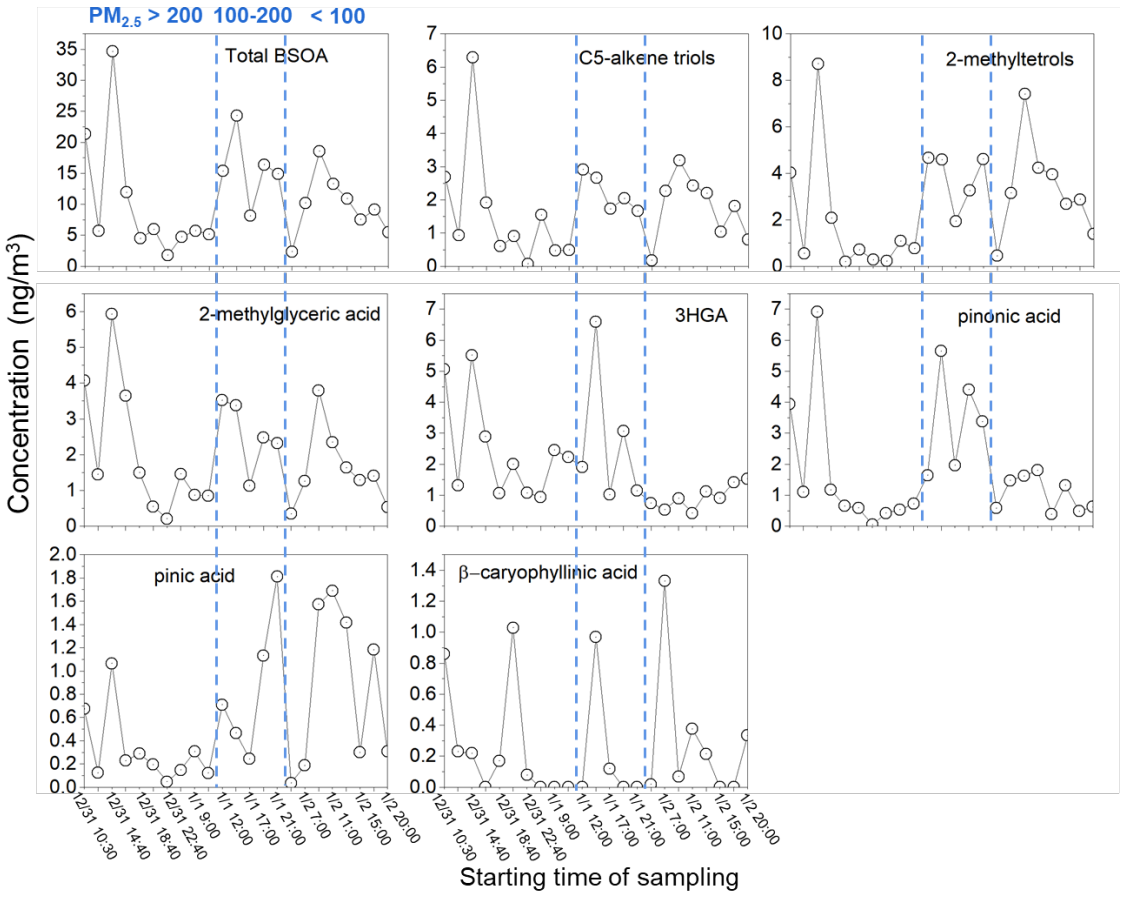

Figure S11. Temporal variations of ratios of biogenic SOA tracers in $PM_{2.5}$.

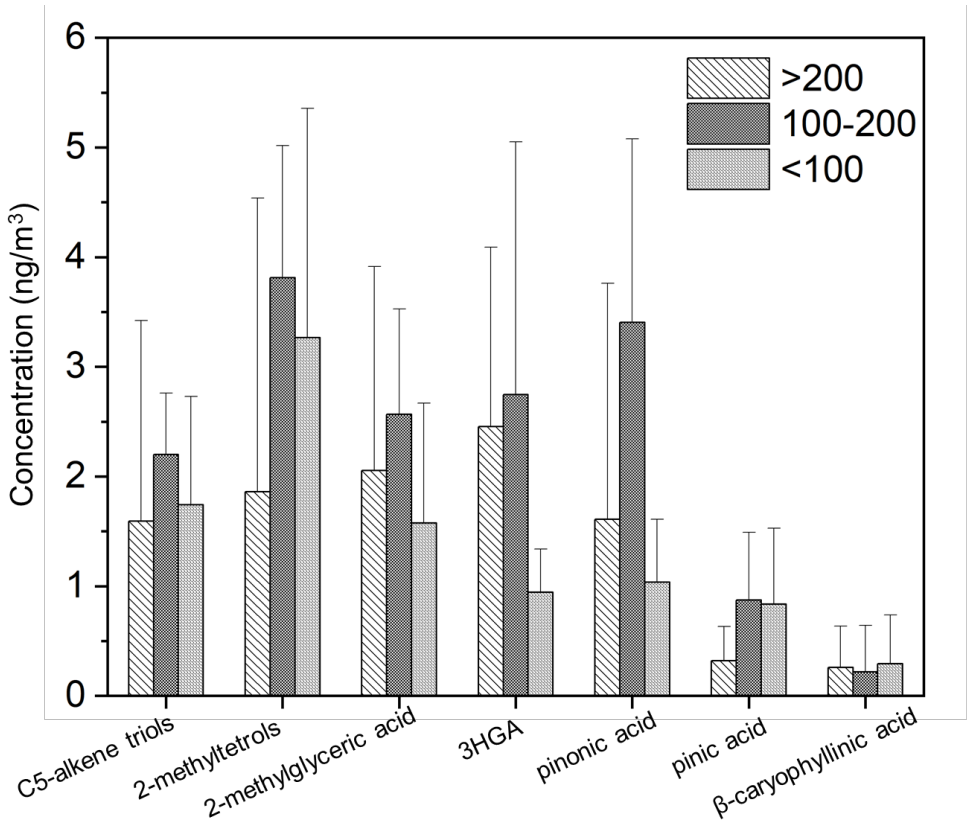

Figure S12. Average concentrations of biogenic SOA tracers detected in three episodes according to $PM_{2.5}$ concentration (i.e., > 200, 100-200, and < 100 μg/m^3).

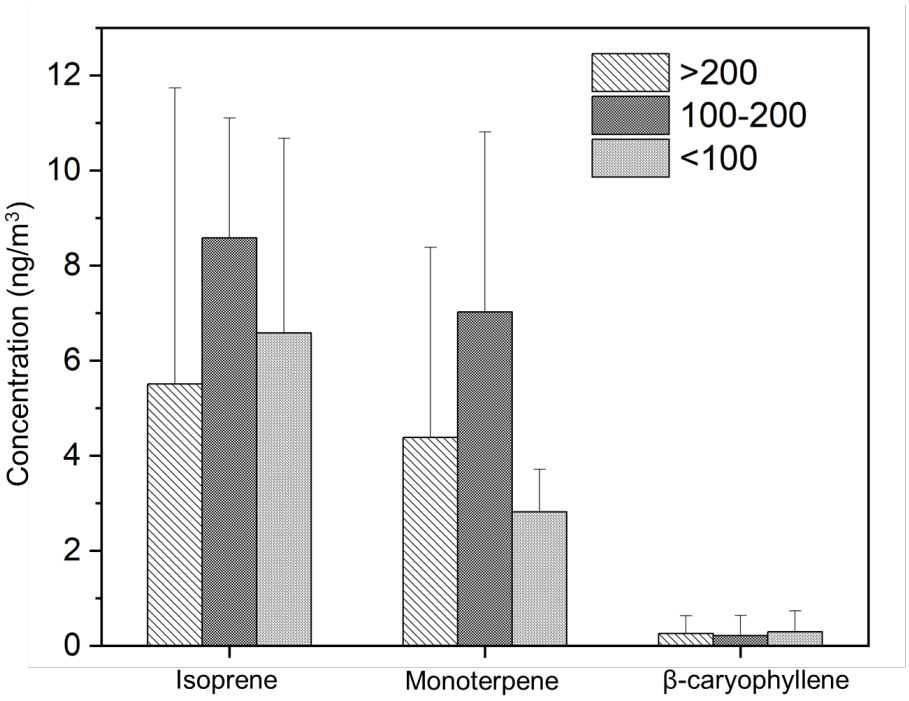

Figure S13. Average concentrations of isoprene, monoterpene, and β-caryophyllene SOA tracers detected in three episodes according to $PM_{2.5}$ concentration (i.e., > 200, 100-200, and < 100 μg/m^3).

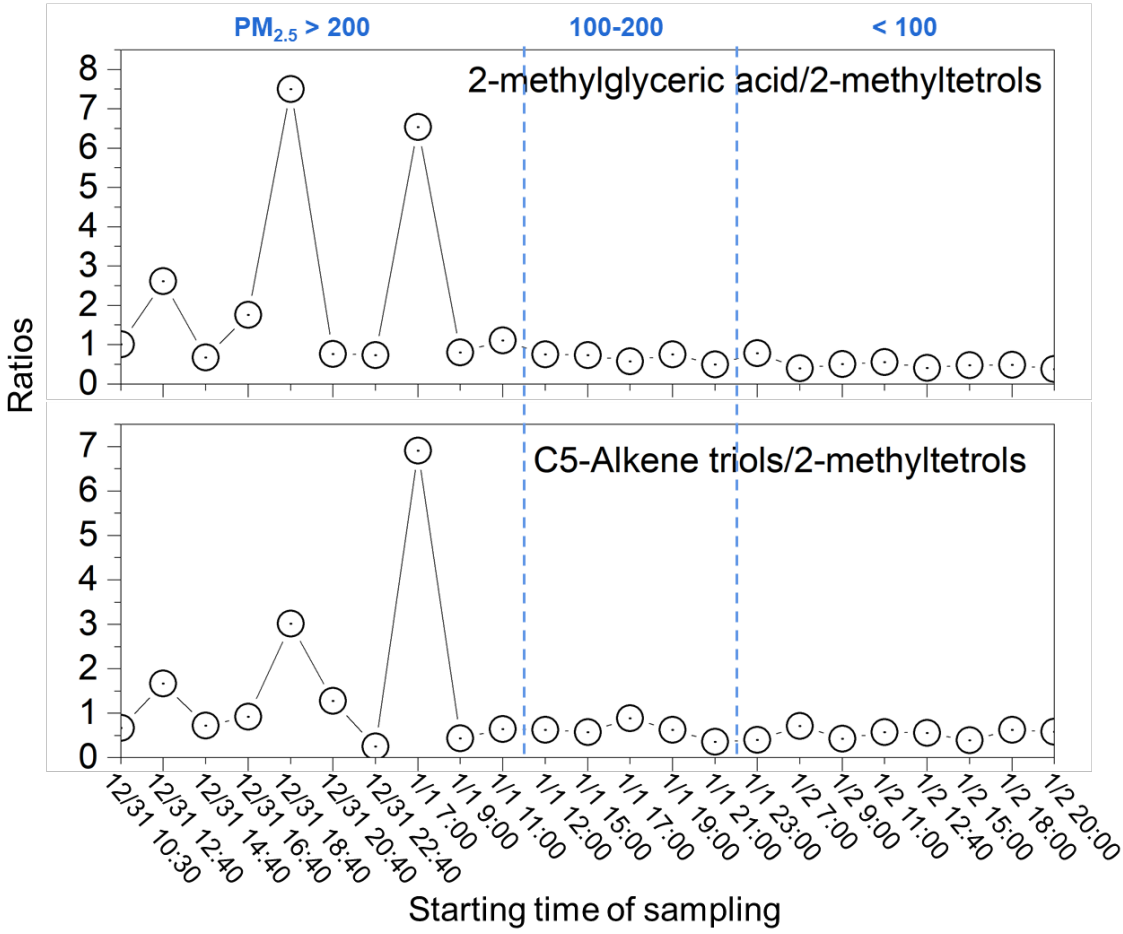

Figure S14. Temporal variations in the concentration ratios of isoprene oxidation products in $PM_{2.5}$.

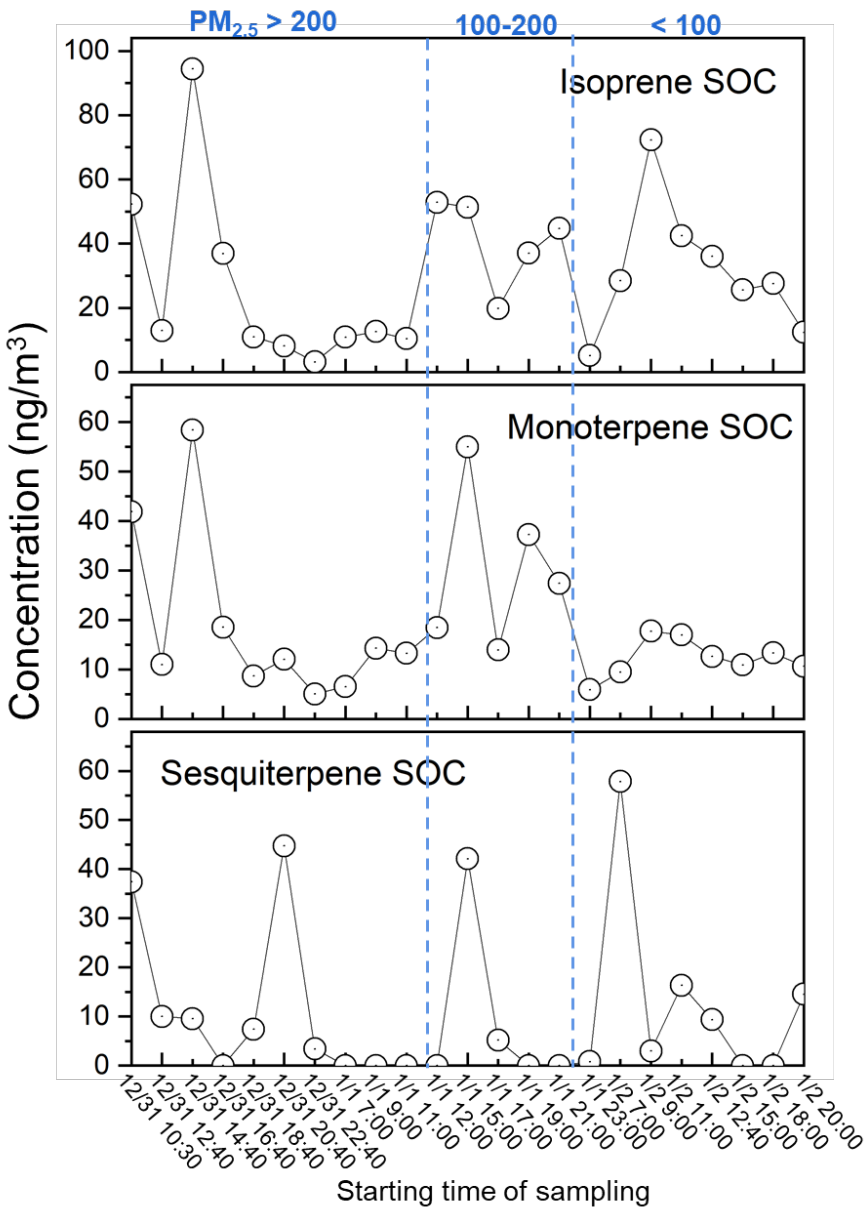

Figure S15. Temporal variations in the biogenic secondary organic carbon (SOC) derived from isoprene, monoterpene, and sesquiterpene in $PM_{2.5}$.

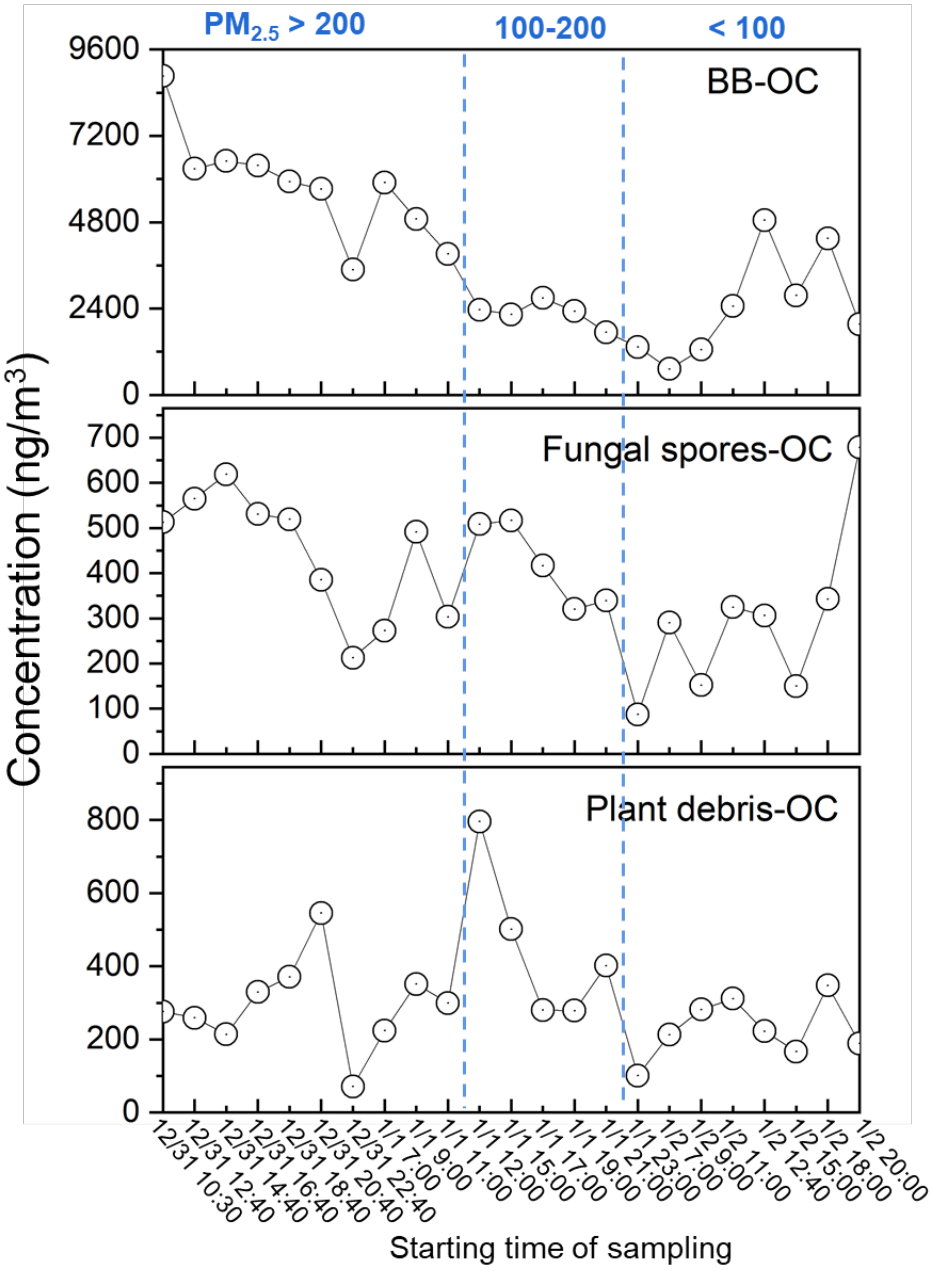

Figure S16. Temporal variations in biomass burning derived OC, fungal spores derived OC, and plant debris derived OC in $PM_{2.5}$.

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