This study conducted by Cai et al. demonstrates the significant role of volatile organic compounds (VOCs) from urban plumes in the formation of daytime secondary organic aerosols (SOA) in suburban areas by gas-particle partition through observation using a time-of-flight chemical ionization mass spectrometer coupled with a Filter Inlet for Gases and Aerosol (FIGAERO-CIMS) and other instruments at a suburban site. This manuscript is well-written and fits well to the scope of ACP. I recommend it for publication after the following comments have been addressed.

Major Comments:

1. It is noted that this manuscript utilizes Positive Matrix Factorization (PMF) to distinguish different types of organic compounds. It is necessary to supplement the PMF spectra and diagnosed plot in the supporting information.

Reply: We appreciate the reviewer for this valuable suggestion. A comment from reviewer 3 states that the lower O:C and higher H:C of aBBOA factor is contrary to what it is expected for aging. Our results indicate that this factor was likely formed through oxidation of biomass burning precursors rather the aging process of BBOA. In order to avoid any confusion, we renamed this factor as biomass burning SOA (BBSOA). We added some discussion in section 2.2.2 by providing detailed description of the PMF analysis and PMF spectra in the supporting information.

"The PM_1 chemical composition was measured by a soot particle aerosol mass spectrometer (SP-AMS, Aerodyne Research, Inc., USA). The details of the operation and data analysis can be found in Kuang et al. (2021). Source apportionment was performed for organic aerosols in the bulk PM_1 using positive matrix factorization (PMF). The organic aerosol could be divided into six components, including two primary OA factors and four secondary OA factors. The mass spectral profiles of six OA factors are shown in Figure S3. The timeseries and diurnal variation of these factors are presented in Figure S4.

The primary OA factors include hydrocarbon-like OA (HOA), mainly contributed by traffic and cooking emissions and biomass burning OA (BBOA) originating from biomass burning combustion. The HOA was identified by hydrocarbon ions $C_xH_y^+$. Owing to the prominent hydrocarbon ions and low O:C value (0.10), HOA could be attributed to primary emission from cooking and traffic. The BBOA was recognized by the markers $C_2H_4O_2^+$ (m/z 60.022, 0.5%) and $C_3H_5O_2^+$ (m/z 73.029, 0.4%), which are considered tracers for biomass burning OA (Ng et al., 2011).

The SOA factors include biomass burning SOA (BBSOA) likely formed from oxidation of biomass burning emission, less oxygenated OA (LOOA) provided by strong daytime photochemical formation, more oxygenated OA (MOOA) related to regional transport, and nighttime-formed OA (Night-OA) contributed by secondary formation during nighttime. The BBSOA was likely formed through oxidation of biomass burning precursors, which was supported by the evening peak at about 19:00 LT (Fig. S4). BBSOA showed a similar variation trend with $C_6H_2NO_4^+$, which might be contributed by oxidation of gaseous precursors from biomass burning emissions (Wang et al., 2019; Bertrand et al., 2018). The significant afternoon peak of LOOA indicates its formation through photochemical reactions, which would be detailly discussed in section 3.1. The negligible diurnal

variation and the highest O:C value (1.0) of MOOA suggested that it could be aged OA resulting from long-range transport. Night-OA was formed through NO_3 nighttime chemistry, supported by a pronounced evening elevation and positive correlation with nitrate (R=0.67).The detailed determination of PMF factors has been found in Kuang et al. (2021) and Luo et al. (2022).
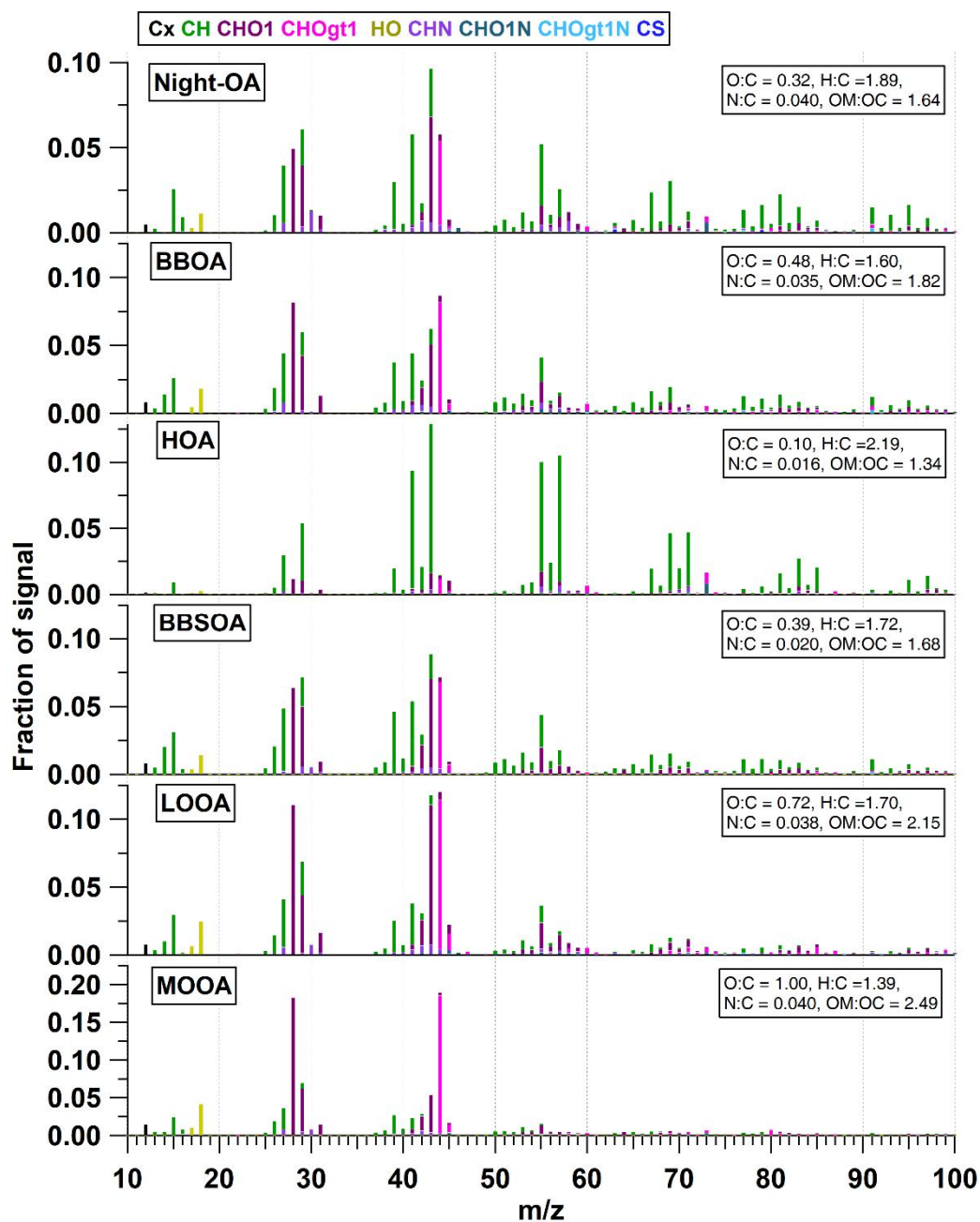

Figure S3. Mass spectral profile of six OA factors. The colors represent different family groups.
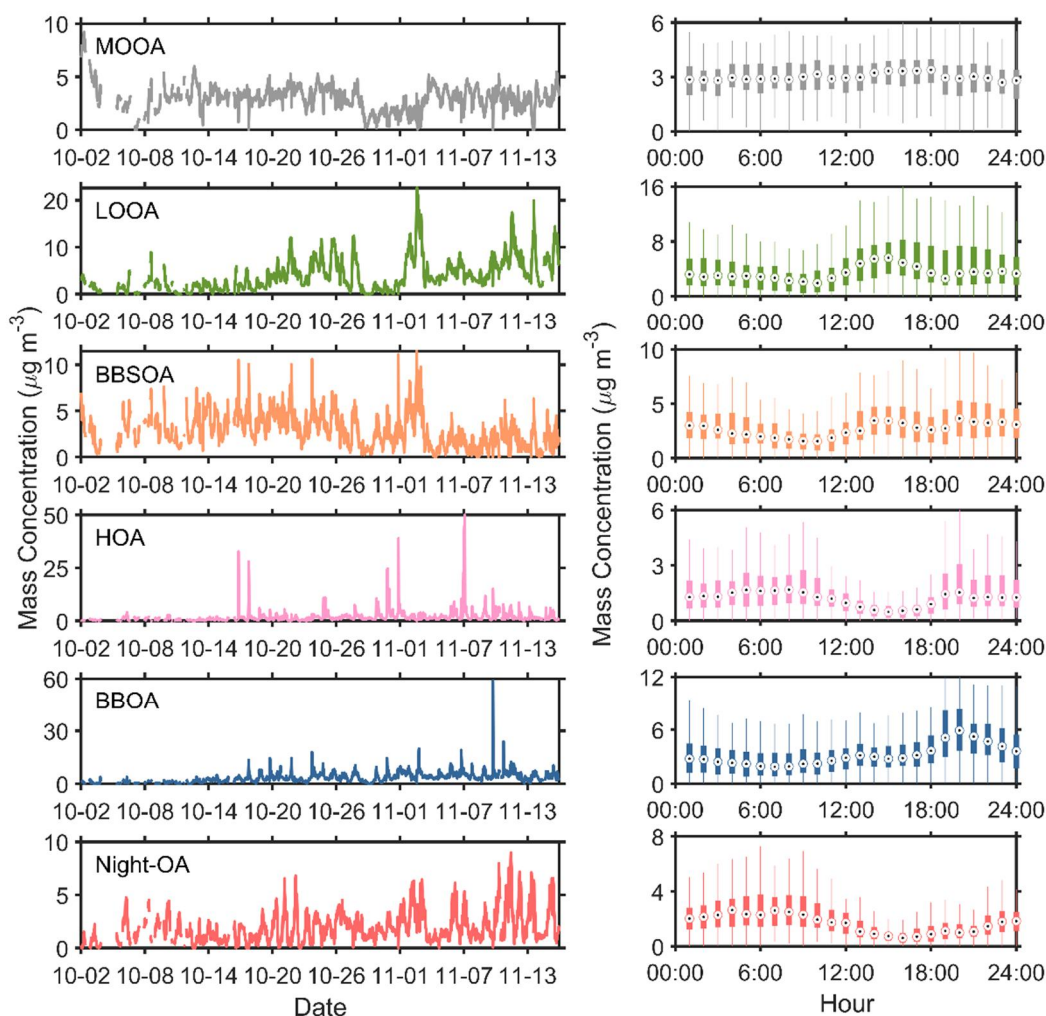
2. Figure 6 illustrates the difference in carbon oxidation state () between different periods. However, the description of Figure 6 in the text is insufficient. The authors should provide further explanation on Figure 6, detailing the observed differences in organic aerosol states in different carbon numbers during various periods.

Reply: We appreciate the reviewer for this suggestion. We have added some discussion in Line 433-436:

"This trend was more significant for carbon number between 2 and 5, indicating a higher concentration of small molecules with low $\overline{OS_C}$ during urban air masses period. The $\overline{OS_C}$ of major C_5 compounds was about -1.33, which was mainly contributed by $C_5H_8NOI^-$, highlighting the role of NO_x chemistry."

3. Figure 7 present the different production of OH and RO_2 in different VOC and NO_X Adding the boundary of VOCs and NOx limited region could help reader better understanding the change of production of OH and RO_2 in different periods.

Reply: We appreciate the reviewer for this suggestion. We have modified figure 7 (now figure 9) by adding the boundary of VOCs and NO_x control regime.
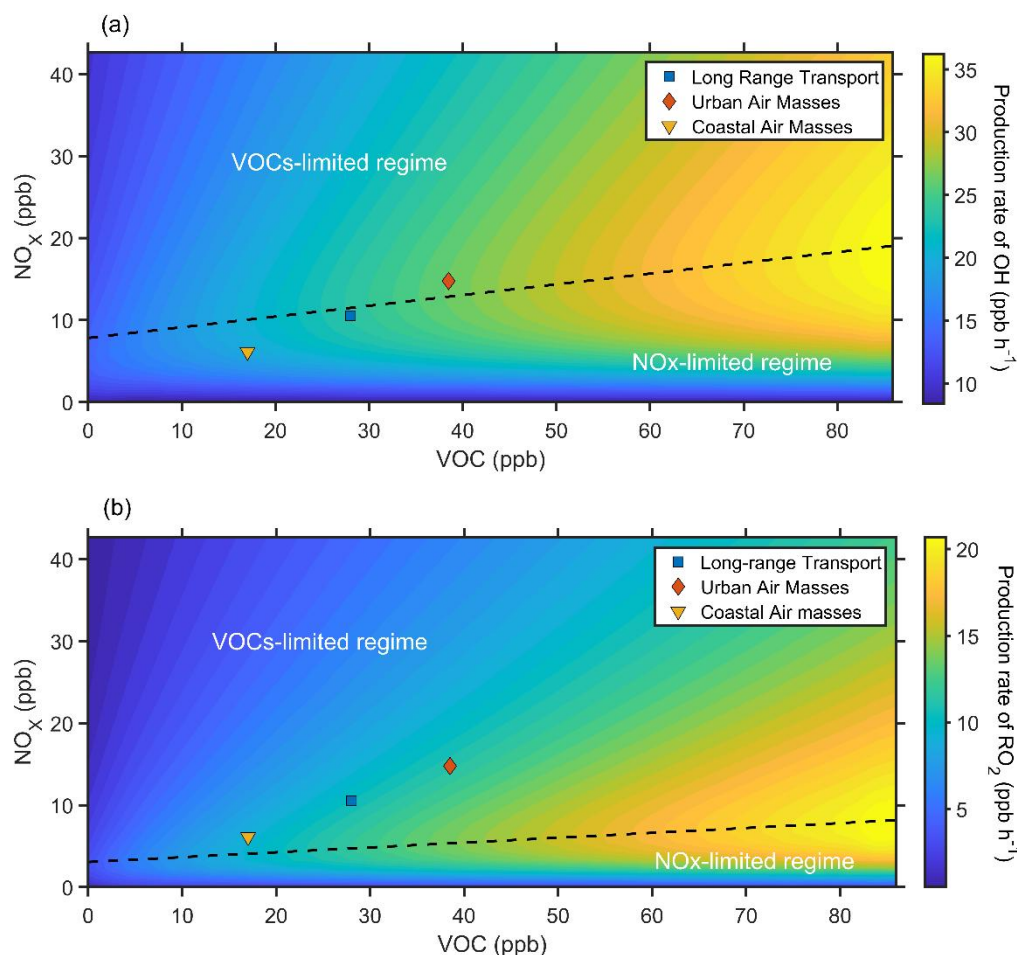

Figure 9. The simulated production rate of OH(a) and RO_2(b) with NOx and VOCs concentration predicted by an observation-constrained box model under campaign average condition. Blue square, red diamond, and yellow triangle represent the average conditions during long-range transport, urban air masses, and coastal air masses period, respectively.

4. Line 243: The author mentions that the correlation between LOOA concentration and particle surface area suggests a relationship between gas-particle partitioning and LOOA formation. However, particle mass concentration is also positively correlated with the particle surface area. The authors should provide more evidence about the contribution of gas-particle partitioning on LOOA formation.

Reply: We thank the reviewer for this suggestion. We agree that particle mass concentration is positively correlated with the particle surface area. The positive relationship between the LOOA and particle surface area might not be strong evidence of the contribution of gas-particle partitioning. We further analysis the relationship between organic vapors and six OA factors. It was shown that

the LOOA was highly correlated with organic vapors (R=0.84), while we did not observe such high correlation for other OA factors. These results suggest that the formation of LOOA could be contributed by gas-particle partitioning. We have modified the corresponding sentences in Line 292-296:

"LOOA showed a noticeable increase corresponding to the particle surface area (Fig. S8), while we did not observe such correlation for other SOA factors (MOOA and BBSOA). Furthermore, LOOA exhibited a stronger positive correlation with organic vapors measured by the FIGAERO-CIMS compared to other OA factors (Fig. S9). These results suggested that the daytime formation of LOOA was attributed to gas-particle partitioning."

5. Line 367: In urban plumes, the production rate of OH increases with the increase of NOx and VOC, transitioning to the VOC-limited regime. Why is it stated that NOx suppressed the production rate of OH at this period?

Reply: We are grateful to the reviewer for this valuable suggestion. Compared with the period influenced by coastal air masses, the P(OH) in urban plumes was elevated owing to the increase of VOCs and NO_x. However, the sensitivity regime of P(OH) shifted towards being VOCs-limited during the urban air masses period. It suggests that the P(OH) might be suppressed with further increases in NO_x. To avoid any confusion, this sentence (Line 456-458) has been revised to:

"Interestingly, the sensitivity regime of P(OH) changed to the VOCs-limited during the urban air masses period, suggesting that the production of OH would be suppressed with continued increases in NO_x."

Specific comments:
1. Line 259: It should be "long-range transport".
   Reply: It has been revised.
2. Figure S8: please provide R value.
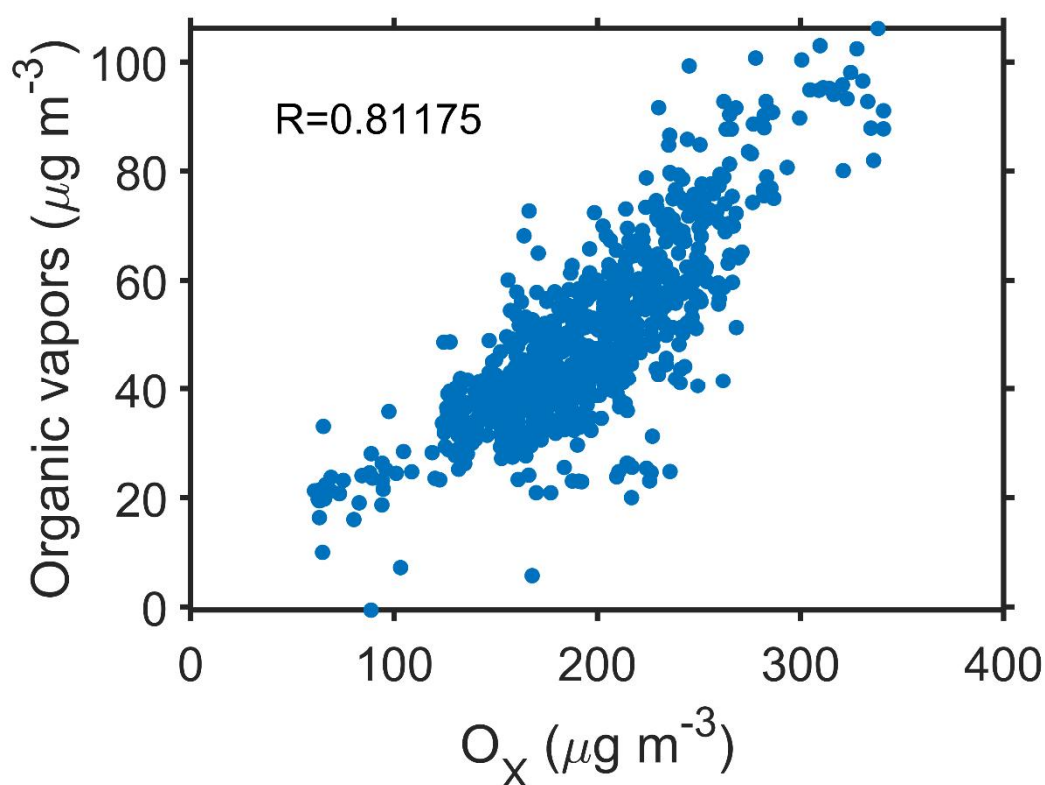   Reply: The R value has been added.

Figure S10. Relationship between odd-oxygen (O_X, $O_X=O_3+NO_2$) and the concentration of organic vapors measured by the FIGAERO-CIMS in the afternoon (10:00-16:00 LT).

3. Line 389: It should be "dramatic".
Reply: It has been revised.

Reference

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