The paper provides a comprehensive analysis of SOA formation and aging processes in the PRD region, using advanced measurements from a FIGAERO-CIMS coupled with PMF analysis. The study identifies and characterizes different SOA factors based on their volatility and formation pathways. The results highlight the significant role of gas-particle partitioning and photochemical aging in SOA formation, with variations driven by environmental factors such as NOx levels. The authors also compare these findings with data from AMS and discuss the limitations of FIGAERO-CIMS in detecting certain OA components. This manuscript is suitable for publication in ACP and I recommend it for publication after the following comments have been addressed.

1. The author mentioned that six daytime FIGAERO factors were positively correlated with LOOA in AMS OA. I wonder whether the relationship between FIGAERO factors and LOOA varies across different periods.

   Reply: We appreciate the reviewer for this valuable suggestion. We examined the relationship between FIGAERO factors and LOOA during urban both air massed and long-range transport period. The sum of six daytime FIGAERO factors showed a positive relationship (R=0.80 and 0.76, respectively) with LOOA during both periods. However, the slope (0.81) of the linear regression during the urban air masses period was higher than that (0.58) during the long-range transport period, indicating that a higher fraction of LOOA could be detected by the FIGAERO-CIMS during urban air masses period. This difference could be related to the difference in OA volatility. According to Cai et al. (2024), the volatility of OA was higher during the urban air masses period.

   We added some discussion in line 415-421,

   "**Note that the sum of six daytime FIGAERO factors showed a positive relationship (R=0.80 and 0.76, respectively) with LOOA during both periods (Fig. S20). However, the slope (0.81) of the linear regression during the urban air masses period was higher than that (0.58) during the long-range transport period, indicating that a higher fraction of LOOA could be detected by the FIGAERO-CIMS during urban air masses period. This difference could be related to the discrepancy in OA volatility. According to Cai et al. (2024), the volatility of OA was higher during the urban air masses period.**"

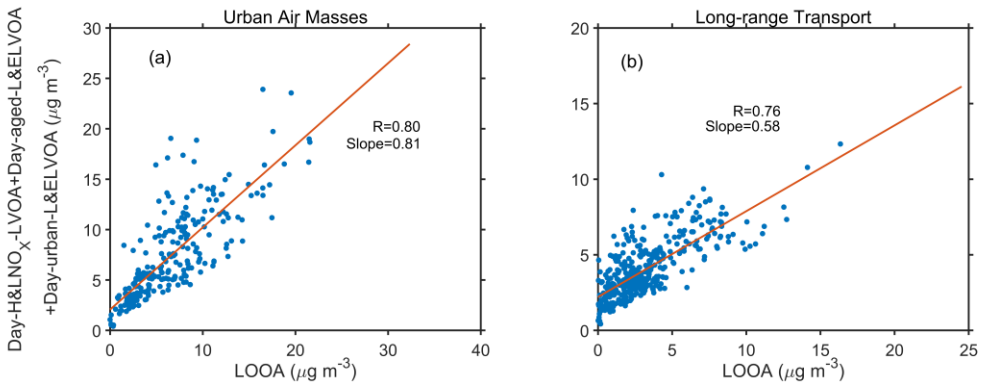

Figure S20. Correlation between the sum of six daytime FIGAERO-OA factors and LOOA during different periods.

2. The calibration experiment regarding the relationship between Tmax and saturation vapor concentration is important. Could the authors provide more details about this calibration experiment in the main text? Specifically, why were the fitting parameters chosen?

   Reply: We appreciate the reviewer for this valuable suggestion. We have added some introduction about the calibration experiment and the selection of fitting parameters in line 221-232:

   "The fitting parameters of a and b were calibrated by a series of polyethylene glycol (PEG 5-8) compounds before the campaign. PEG standards (dissolved in acetonitrile) were atomized using a homemade atomizer, and the resulting particles were size-classified by a differential mobility analyzer (DMA; model 3081L, TSI Inc.) to target diameters of 100 and 200 nm. The size-selected particles were then split into two flows: one directed go to a CPC (3775, TSI) for the measurements of number concentration, and the other to the FIGAERO-CIMS particle inlet. The collected mass by CIMS was calculated based on the particle diameter, number concentration, FIGAERO-CIMS inlet flow rate, and collection time. The details of the calibration experiments and selection of fitting coefficients (a and b) can be found in table S1 and Cai et al. (2024). In this study, the fitting parameters (a=-0.206 and b=3.732) were chosen, as the mass loading (407 ng) and diameter (200 nm) are closest to the ambient samples, since the collected mass loading centered at about 620 ng and the particle volume size distribution (PVSD) centered at about 400 nm (Cai et al., 2024)."

3. The study finds discrepancies between nighttime SOA measured by AMS and that characterized by FIGAERO-CIMS, suggesting that the nighttime processes may not be fully captured by the FIGAERO-CIMS thermogram data. Is there any evidence about the low volatility of nighttime

OA?

Reply: We appreciated the reviewer for this valuable suggestion. It is indeed challenging for FIGAERO-CIMS to fully capture the relatively low volatile fraction of OA, owing to the "relatively low heating temperature (~175℃)". During the same campaign, a thermodenuder (TD) coupled with an AMS was also deployed to characterize OA volatility. The TD operated at temperatures up to ~270 °C, enabling the detection of substantially lower-volatility OA. We are currently preparing our next manuscript focusing the volatility of nighttime OA and a comparison between the FIGAERO-CIMS and TD-AMS approaches. As the TD-AMS dataset is still under analysis, we are unable to include those results in the present manuscript.

Previous studies also support the likelihood of lower nighttime OA volatility. For example, Xu et al. (2019) found that volatility of MO-OOA was lower at nighttime than daytime, likely due to differences in precursor emissions, formation pathways, and meteorological conditions. In addition, organic nitrates have lower volatility than hydroxylated products with the same carbon number(Donahue et al., 2011; Ren et al., 2022). Taken together, these findings suggest that nighttime chemistry, which produces a higher fraction of organic nitrates, may generate OA with substantially lower volatility. (Kiendler-Scharr et al., 2016)"

We added some discussion to the revised manuscript in line 591-595,

"**Xu et al. (2019) found that nighttime MO-OOA exhibited lower volatility compared with daytime MO-OOA, likely due to differences in precursors, formation mechanisms, and meteorological conditions. Moreover, organic nitrates generally have lower volatility than hydroxylated species with the same carbon number (Donahue et al., 2011; Ren et al., 2022). It suggested that a higher fraction of nighttime organic nitrates could lead to lower OA volatility (Kiendler-Scharr et al., 2016).**"

4. The authors suggest that an increase in NOx levels could enhance the volatility of SOA. I recommend that the authors compare this finding with other studies on the impact of NOx on OA volatility.

Reply: We appreciate the reviewer for this valuable suggestion. To our current knowledge, most studies investigating the influence of NO_x on the volatility of OA have been conducted under controlled laboratory conditions, while field-based evidence remains limited. D'ambro et al. (2017) investigate the molecular composition and volatility of isoprene derived SOA under high and low NO_x condition in an environmental simulation chamber. Their results showed that SOA exhibited lower volatility under high-NO_x conditions, corresponding to a greater contribution of organic nitrates. However, the experimental conditions were restricted to two scenarios: high NO_x and low NO_x. Furthermore, in the high-NO_x experiments, the NO input

was 20 ppb, without accounting for the nonlinear dependence of SOA formation pathways on NO_x concentrations (Pye et al., 2019).

Xu et al. (2014) further investigated the variation of SOA volatility over a wide range of NO_x levels (<1 ppb to 738.1 ppb) in a series of chamber experiments. They found that both SOA volatility and oxidation state exhibited a nonlinear response to NO_x. SOA volatility decreases with increasing NO_x level when the ratio of initial NO to isoprene was lower than 3. At higher NO_x level, higher volatile SOA was produced, probably owing to the more competitive RO_2+NO pathway. This study highlights the important nonlinear impacts of NO_x concentrations on SOA formation and volatility. More field measurements were needed to investigate these effects in the ambient environment.

We added some discussion to the revised manuscript in line 482-486,

"**Xu et al. (2014) found that both SOA volatility and oxidation state exhibited a nonlinear response to NO_x in a series of chamber environment. SOA volatility decreases with increasing NO_x level when the ratio of initial NO to isoprene was lower than 3. At higher NO_x level, higher volatile SOA was produced, probably owing to the more competitive RO_2+NO pathway**."

5. The paper finds that FIGAERO-OA cannot explain MO-OOA and HOA in AMS, but it does not further analyze the reasons. For MO-OOA, it is unclear whether it is a "very low-volatility species not desorbed by heating". For HOA, the undetection may be due to the low response efficiency of the ionization method (I^- reagent) in FIGAERO-CIMS, which weakens the discussion on the data complementarity of the two instruments.

Reply: We would like to thank the reviewer for this valuable suggestion. We acknowledge that capturing the full spectrum of OA using FIGAERO-CIMS remains challenging. One limitation arises from the relatively low maximum heating temperature (~175 °C), which prevents full desorption of low-volatility OA. Xu et al. (2019) investigate the volatility of different OA factors using the TD+AMS method and found that MO-OOA evaporated ~52% at T=175°C. Another TD+AMS field study in the North China Plain suggested that the volatility of MO-OOA varied with RH levels(Xu et al., 2021), more MO-OOA evaporate at higher RH levels (RH>70%). During this campaign, the RH varied from 25% to 92% which likely caused variability in MO-OOA volatility and thus in the fraction desorbed at 175 °C. This variability might explain the low correlation between MO-OOA in AMS and all FIGAERO-OA factors.

In addition, the iodide source of the FIGAREO-CIMS is selective towards multi-functional organic compounds(Lee et al., 2014), making it less sensitive to detection hydrocarbon-like species. Ye et al. (2023) preformed factorization analysis of data obtained from the FIGAERO-

CIMS and AMS and suggested that FIGAERO-derived OA factors could not account for all primary OA components resolved by AMS, including COA, NOA, and HOA. These findings highlight the need for further investigations into the chemical characteristics of primary OA to better understand their emission signatures and atmospheric evolution.

We added some discussion to the revised manuscript in line 545-552,

"**Xu et al. (2019) investigate the volatility of different OA factors using the TD+AMS method and found that MO-OOA evaporated ~52% at T=175°C. Another TD+AMS field study in the North China Plain suggested that the volatility of MO-OOA varied with RH levels, more MO-OOA evaporate at higher RH levels (RH>70, Xu et al., 2021), suggesting that MO-OOA compounds formed at high RH condition could be higher volatile. During this campaign, the RH varied from 25% to 92% which likely caused variability in MO-OOA volatility and thus in the fraction desorbed at 175 °C. This variability might explain the low correlation between MO-OOA in AMS and all FIGAERO-OA factors.**"

and in line 553-560,

"**The iodide source of the FIGAREO-CIMS is selective towards multi-functional organic compounds(Lee et al., 2014), making it less sensitive to detection hydrocarbon-like species. Ye et al. (2023) preformed factorization analysis of data obtained from the FIGAERO-CIMS and AMS and suggested that FIGAERO-derived OA factors could not account for all primary OA components resolved by AMS, including COA, NOA, and HOA. These findings highlight the need for further investigations into the chemical characteristics of primary OA to better understand their emission signatures and atmospheric evolution.**"

6. Figure 2 a: please add "" to the x-axis label.

   Reply: The character in the "" is missing. We thought it could be "$\overline{OS_c}$" and revised figure 2 a.

7. Table 1: It should be "average elemental composition" in the heading.

   Reply: It has been revised.

8. Eq (5) and (6) are missing in the main text. This is presumably a typesetting omission.

   Reply: It has been revised.

Reference:

Cai, M., Ye, C., Yuan, B., Huang, S., Zheng, E., Yang, S., Wang, Z., Lin, Y., Li, T., Hu, W., Chen, W., Song, Q., Li, W., Peng, Y., Liang, B., Sun, Q., Zhao, J., Chen, D., Sun, J., Yang, Z., and Shao, M.: Enhanced daytime secondary aerosol formation driven by gas–particle partitioning in downwind urban plumes, Atmos. Chem. Phys., 24, 13065-13079, 10.5194/acp-24-13065-2024, 2024.

D'Ambro, E. L., Lee, B. H., Liu, J., Shilling, J. E., Gaston, C. J., Lopez-Hilfiker, F. D., Schobesberger, S., Zaveri, R. A., Mohr, C., Lutz, A., Zhang, Z., Gold, A., Surratt, J. D., Rivera-Rios, J. C., Keutsch, F. N., and Thornton, J. A.: Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low- and high-NOx conditions, Atmos. Chem. Phys., 17, 159-174, 10.5194/acp-17-159-2017, 2017.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303-3318, 10.5194/acp-11-3303-2011, 2011.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophysical Research Letters, 43, 7735-7744, https://doi.org/10.1002/2016GL069239, 2016.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, Environmental Science & Technology, 48, 6309-6317, 10.1021/es500362a, 2014.

Pye, H. O. T., D'Ambro, E. L., Lee, B. H., Schobesberger, S., Takeuchi, M., Zhao, Y., Lopez-Hilfiker, F., Liu, J., Shilling, J. E., Xing, J., Mathur, R., Middlebrook, A. M., Liao, J., Welti, A., Graus, M., Warneke, C., de Gouw, J. A., Holloway, J. S., Ryerson, T. B., Pollack, I. B., and Thornton, J. A.: Anthropogenic enhancements to production of highly oxygenated molecules from autoxidation, Proceedings of the National Academy of Sciences, 116, 6641-6646, 10.1073/pnas.1810774116, 2019.

Ren, S., Yao, L., Wang, Y., Yang, G., Liu, Y., Li, Y., Lu, Y., Wang, L., and Wang, L.: Volatility parameterization of ambient organic aerosols at a rural site of the North China Plain, Atmos. Chem. Phys., 22, 9283-9297, 10.5194/acp-22-9283-2022, 2022.

Xu, L., Kollman, M. S., Song, C., Shilling, J. E., and Ng, N. L.: Effects of NOx on the Volatility of Secondary Organic Aerosol from Isoprene Photooxidation, Environmental Science & Technology, 48, 2253-2262, 10.1021/es404842g, 2014.

Xu, W., Chen, C., Qiu, Y., Li, Y., Zhang, Z., Karnezi, E., Pandis, S. N., Xie, C., Li, Z., Sun, J., Ma, N., Xu, W., Fu, P., Wang, Z., Zhu, J., Worsnop, D. R., Ng, N. L., and Sun, Y.: Organic aerosol volatility and viscosity in the North China Plain: contrast between summer and winter, Atmos. Chem. Phys., 21, 5463-5476, 10.5194/acp-21-5463-2021, 2021.

Xu, W., Xie, C., Karnezi, E., Zhang, Q., Wang, J., Pandis, S. N., Ge, X., Zhang, J., An, J., Wang, Q., Zhao, J., Du, W., Qiu, Y., Zhou, W., He, Y., Li, Y., Li, J., Fu, P., Wang, Z., Worsnop, D. R.,

and Sun, Y.: Summertime aerosol volatility measurements in Beijing, China, Atmos. Chem. Phys., 19, 10205-10216, 10.5194/acp-19-10205-2019, 2019.
Ye, C., Liu, Y., Yuan, B., Wang, Z., Lin, Y., Hu, W., Chen, W., Li, T., Song, W., Wang, X., Lv, D., Gu, D., and Shao, M.: Low-NO-like Oxidation Pathway Makes a Significant Contribution to Secondary Organic Aerosol in Polluted Urban Air, Environmental Science & Technology, 10.1021/acs.est.3c01055, 2023.