Responses to anonymous referee #2

General comment:

While most researchers nowadays focus on light absorption by brown carbon when trying to address the climate effect of aerosols, Shen et al. focused on the overlooked aerosols scattering, which is simplified in a lot of studies, that may induce large uncertainty in radiative forcing estimation. The topic fits well with the scope of ACP. The manuscript is generally well written and adequately organized. I have a few comments before it can be accepted for further consideration.

Response: Thanks for your comments, which really helped improve the manuscript.

Comment: In the abstract and lines 471-474. The authors found an increasing trend of real refractive index with O/C or aging and stated this finding conflicts with most lab results. For example, He et al. (2018) observed a declining trend of real refractive index when OA aged from LO-OOA to MO-OOA for photooxidation of b-pinene and p-xylene. However, He et al (DOI: 10.1021/acs.est.1c07328) and Li et al. (DOI: 10.5194/acp-19-139-2019) also observed increasing refractive index with aging for naphthalene+NOx and biomass burning aerosols. Lab experiments did not conclude on this aspect, as it seems to depend on what kind of aerosol was studied. I would say such of statement exaggerates the significance of the finding in this study.

Response: Thank you for pointing this out. We had not previously noted the findings of these two studies. We agree with the reviewer that the relationship between m_r and O/C can vary depending on aerosol types and oxidation conditions. However, as summarized in Moise et al. (2015), within the O/C range relevant to the LOOA and MOOA identified in our study, most laboratory results show a decreasing trend in m_r with increasing O/C. We have revised the discussion in this section accordingly. This aspect represents only a minor part of our study, and we did not intend to overstate its importance. Our goal is to interpret our results in the context of the broader literature.

"This result suggests that qualitatively, m_r increase with oxidation degree of SOA. Previous laboratory results demonstrate that m_r could increase (Li et al., 2019;He et al., 2022) or decrease (He et al., 2018) with O/C depending on aerosol types, precursors and oxidation conditions. However, as concluded in Moise et al. (2015) , most existing laboratory studies reveal that increase of O/C would decrease m_r, especially at the O/C range of LOOA and MOOA of this study (0.6 to 1.27, and m_r from 1.46 to 1.69). This is likely associated with that MOOA in Guangzhou urban area is mainly formed through multiphase reactions (Zhai et al., 2023) thus has higher m_r as demonstrated by Li et al. (2017) that multiphase reactions enhance m_r. Most laboratory studies on evolution of $m_{r,SOA}$ were conducted in the context of gas-phase reactions."

We also revised the sentence in the abstract as:

"In addition, further analysis reveals m_r of SOA increases substantially with oxidation level which is likely associated with multiphase SOA formation."

Comment: The results obtained from this study are from a single observation site near the emission source. How could the results and conclusions from this unique location be applied to a larger scale or different locations with potentially different emission sources and experiencing different atmospheric processes?

Response: We agree the reviewer that observation at this single observation site might not be applied in regions does not share similar emissions and meteorological conditions with the observation site. The most exciting part of this study for us is the comparisons between scattering refractive index of POA and SOA could be directly revealed, and the resulted have challenged current model settings. We revised the recommendation in the abstract.

"Our analysis recommends m_r values at 525 nm of 1.37 for POA and 1.59 for SOA in urban regions which share similar emissions and meteorological conditions as the observation site."

The following discussions were added in the conclusions

"However, the biggest challenge lies in accurate representations of organic aerosols m_r due to $m_{r,SOA}$ variations, because SOA could be formed through varying pathways (condensational growth or multiphase reactions) of different precursor sources volatile organic compounds (biogenic versus anthropogenic), and existing results already proved that SOA formed from varying precursors and pathways has distinct m_r. Therefore, recommend value of $m_{r,SOA}$ in this study might represent more the m_r of SOA that formed from anthropogenic precursors in urban and humid regions. "

The related sentence in the discussions was modified accordingly

"Based on the above analysis, $m_{r,SOA}$ and $m_{r,POA}$ of 1.37 and 1.59 might be better choice for model settings in regions share similar emissions and meteorological conditions with the observation site. "

Also, we have also revised the title as "Secondary Organic Aerosol Formation Enhances Refractive Index in Humid Southern China Challenging Model Assumptions" to emphasizes both the process, the location, and the implication (model challenge) in a balanced way.

Comment: I am not clear how one could use PMF to do source apportionment for PNSD. The authors also mentioned in their manuscript that LOOA and MOOA are generally not externally mixed and are likely to be prone to internal mixing (lines 463-465). But in the discussion of lines 440-446, the authors stated that POA and SOA tend to be optically independent at the single-particle level. The authors did observe SOA at the observation site. According to our knowledge of new particle formation and condensation growth, SOA and POA would not be completely externally mixed. Condensation of secondary products on existing particles (e.g., POA) would change the size of the particles, but does not change the number. How could PMF deal with this situation?

Response: We agree with the reviewer that SOA and POA are not completely independent. However, their degree of interaction largely depends on the time elapsed since POA emission and the extent to which SOA vapors have condensed onto POA particles. The organic aerosol (OA) observed at a given site typically comprises freshly emitted POA, preexisting SOA transported within the air mass, slightly aged POA (which may sometimes be classified as OOA and thus as SOA), and newly formed, locally produced SOA.

Because our observation site is close to emission sources, a significant fraction of the measured OA signal likely originates from fresh and slightly aged POA. If POA particles differ in size from preexisting aerosols, they can be distinguished using the PMF procedure, as demonstrated by Cai et al. (2020). In our study, PMF analysis revealed that POA exhibited a distinct size distribution from secondary aerosols, with POA mass peaking around 250 nm, whereas the mass of secondary components peaked near 400 nm. A fully internally mixed state would be expected to yield identical mass size distributions for POA and SOA, which is not supported by our observations. Our observations support that POA and SOA reside in distinct size ranges. This indicates that although some internal mixing of POA and SOA may occur, the majority of their mass is likely externally mixed, as they predominantly reside in distinct size modes.

Comment: Figure 1b, for me, it looks like the mr1064,400/mr1064,235 changed suddenly at mr1064,400=1.53. What is the mechanism behind this?

Response: The ratio mr1064,400/mr1064,235 does not exhibit a sudden change at 1.53; instead, it generally increases smoothly with mr1064,400. The number of data points significantly decreases for mr1064,400>1.53, likely because inorganic aerosol components dominate over secondary organic aerosols in most cases, making instances where mr1064,400 exceed 1.53 relatively rare.

Comment: Line 386-387, would the correlation coefficient of R=0.25 and R=-0.24 be significantly different?

Response: Whether this difference is statistically significant depends strongly on the sample size. Given that the sample size exceeds 500 and the trend is clearly visible in Fig. S11, the difference is considered statistically significant.

Comment: The authors used the empirical method proposed by Li et al. (2023). I would say this might not be so relevant for this paper. Li's method was developed based on refractive index data for pure compounds without N element. However, in urban locations, aerosols already have nitrogen-containing species that affect the refractive index of the aerosols. The explanations in lines 474-478 are not well supported, as the aerosols themselves are different. It is not clear how much the formation pathway matters.

Response: We agree with the reviewer that the method proposed by Li et al. does not include nitrogen (N) elements. However, their aim was to develop a scheme for predicting the refractive index of atmospheric aerosols. They evaluated the proposed scheme using laboratory-generated SOA and even included results from field observations. To our knowledge, this is the only available approach that predicts refractive index based on H/C and O/C ratios. Therefore, we believe it is appropriate to include comparisons with their results, as they help illustrate that the parameterization of organic aerosol refractive index remains an open and unresolved issue.

We also agree with the reviewer that it is still unclear how much the formation pathway contributes. However, our previous publication has already demonstrated the prevalence of multiphase SOA formation in the Guangzhou urban area, which likely explains this finding.

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