

Responses to Referee #2:

We thank the reviewer for thoughtful and constructive suggestions that help us improve our manuscript. According to the comments, we have added the related statements in the Results and Discussion section. In the following, please find our responses to the comments one by one and the corresponding revisions made to the manuscript (highlighted in yellow color). The original comments are shown in italics, and our point-by-point responses are listed below. We believe that the current form of the manuscript is much improved, and we hope the new version is now suitable for publication in ACP.

General comments:

In this article the authors investigated the effects of SO₂ and RH on the optical properties of secondary organic aerosol (SOA) produced by toluene photooxidation using smog chamber experiments. Photooxidation of toluene was performed in a 5 m³ dualreactor smog chamber under the condition of dry (D), dry with SO₂ (DS), wet (W), or wet with SO₂ (WS). Optical properties of SOA were measured by a photoacoustic extinctionsmeter (PAX) and a cavity ring-down spectrometer (CRDS) at the wavelength of 375 nm as well as 532 nm. Particle composition was measured by an electrospray ionization time-of-flight mass spectrometry. The authors found that RH enhanced light absorption and scattering of SOA and indicated that it was due to the formation of highly conjugated oligomers formed through multiphase reactions. They also found that adding SO₂ slightly lowered the real part of complex refractive index (n) but increased the imaginary part (k) for dry condition and explained by the partitioning of low oxidation state products and the formation of charge transfer complexes with SO₂ appeared. The authors concluded that their results have significant implication for evaluating the impacts of SOA on the regional haze, global radiative balance, and climate change. Overall, the topic is suitable for the readership of Atmos. Chem. Phys. I recommend publication of this work, provided that the following issues have been adequately addressed.

Response: We thank the reviewer for these positive and constructive comments.

The authors explained the differences in the optical properties with adding SO₂ by larger amounts of new particles formation and higher particle surface concentrations. Since particle concentration and size distribution were measured in the experiments, direct evidence of NPF needed to be provided to support this argument. Also, an increase of particle surface concentration increases the rate of uptake but could not help to stabilize the volatile compounds in the particle phase. There needs some discussion on the chemical mechanism leading to their measured optical properties of secondary organic aerosol. For example, it has been recently proposed that the toluene oxidation proceeds dominantly via the cresol pathway (Ji et al., Reassessing the atmospheric oxidation mechanism of toluene, Proc. Natl. Acad. Sci. USA 114, 8169–8174, 2017). How do the different mechanisms of toluene oxidation impact their optical measurements and conclusions. Also, toluene oxidation is known as a major source for small alpha-dicarbonyls (glyoxal and methylglyoxal), which can be a source for brown carbon (Marrero-Ortiz et al., Formation and Optical Properties of Brown Carbon from Small - Dicarbonyls and Amines, Environ. Sci. Technol. 53(1), 117-126, 2019). Such an aspect needs to be addressed in this paper.

Response: Thanks for the suggestions. As the previous studies reported, the addition of SO₂ would cause large amounts of new particle formation. We observed the same phenomenon and added a comparison diagram about the maximum of total number concentration of SOA (Figure S1). In the discussion part, we added “As shown in Figure S1, the maximum of total number concentrations of toluene SOA was almost doubled under conditions with SO₂, which implied that the addition of SO₂ could promote new particle formation.” (Line 10-13, page 6).

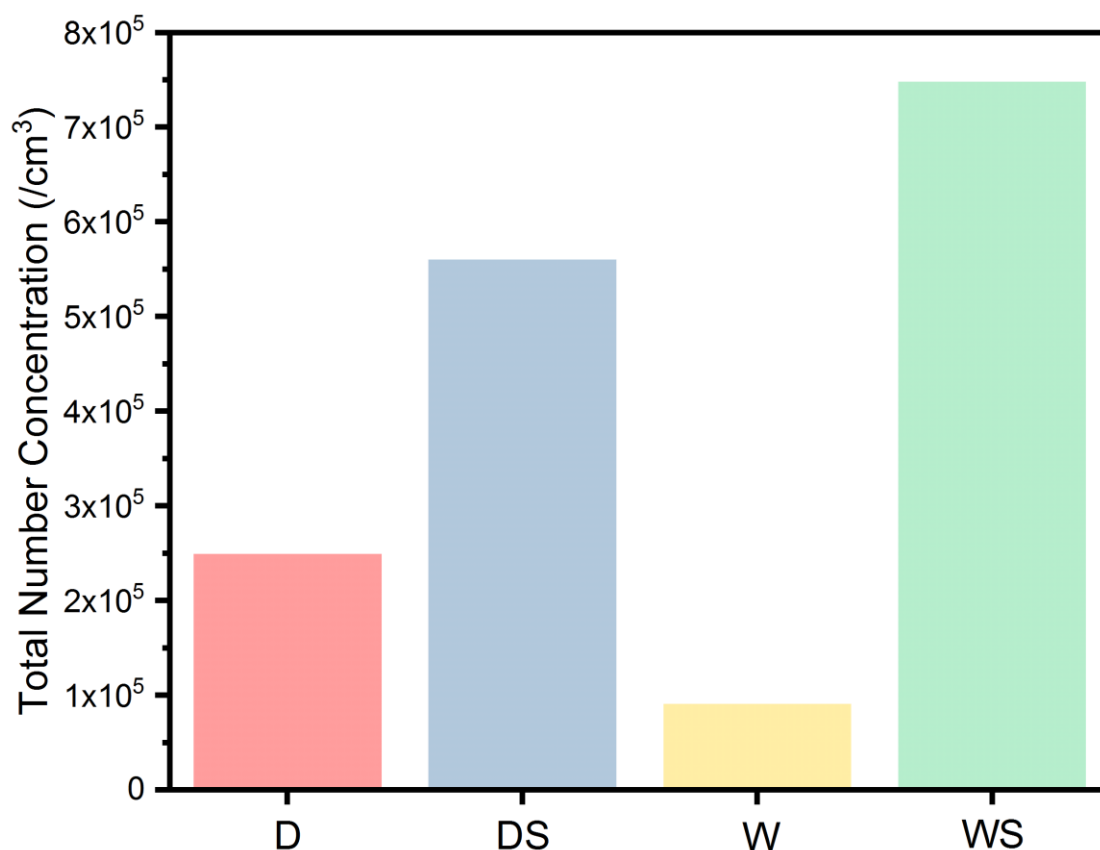


Figure S1. The maximum of total number concentrations of SOA derived from toluene under the D, DS, W and WS conditions.

As for the mechanism, we have changed Paragraph 3 in Section 3.3 to “Light absorption properties of SOA are related to its composition, the contribution of each product to light absorption and so on (Laskin et al., 2015; Moise et al., 2015). Small α -dicarbonyls compounds such as glyoxal and methylglyoxal are important intermediate products of toluene that undergo polymerization to produce low-volatility oligomers (Ji et al., 2017; Fu et al., 2009; Fu et al., 2008). These products might undergo particle phase reactions, e.g., acid-catalysed aldol condensation reactions under SO₂ conditions, plausibly contributing to the observed light absorption. Nakayama et al. (2018) reported the same phenomenon on isoprene SOA (Nakayama et al., 2018; Nakayama et al., 2015), while Marrero-Ortiz et al. (2019) found BrC particles were formed from small α -dicarbonyls and amines (Marrero-Ortiz et al., 2019). Formation of charge transfer (CT) complexes might be another reason for light absorption enhancement, which could lead to optical transitions through a transfer of charge from a donor group, such as hydroxyls, to an acceptor group, such as a ketone or aldehyde (Phillips and Smith, 2014). For

organosulfate, another kind of BrC, we did not detect them under the DS condition, which is in accordance with previous studies (Staudt et al., 2014).” (Line 11-24, paragraph 3 in Section 3.3, page 9). And we have revised the abstract part to “.....The imaginary part of the complex refractive index, $RI(k)$, is enhanced under dry condition with SO_2 compared to that of only dry condition, which might be due to acid-catalysed aldol condensation reactions.....” (Line 11-14, page 1) In conclusion part, we have rewritten to “.....The increase in $RI(k)$ is probably related to acid-catalysed reactions on acidic particles.....” (Line 23-24, page 11).

Under different conditions, the peak of the absorption spectrum can shift due to the different functionalities, which could also be a reason for different optical properties at certain wavelength. Since the PAX and CRDS only measure the optical properties at 375 nm and 532 nm, it would help if the full spectrum is provided.

Response: The full UV-Vis absorption spectrum of toluene under four conditions has been conducted and provided in Figure S3. As shown in the figure, the absorption of toluene SOA decreased with increasing wavelength (in the range of 300–600 nm, typical range of sunlight).

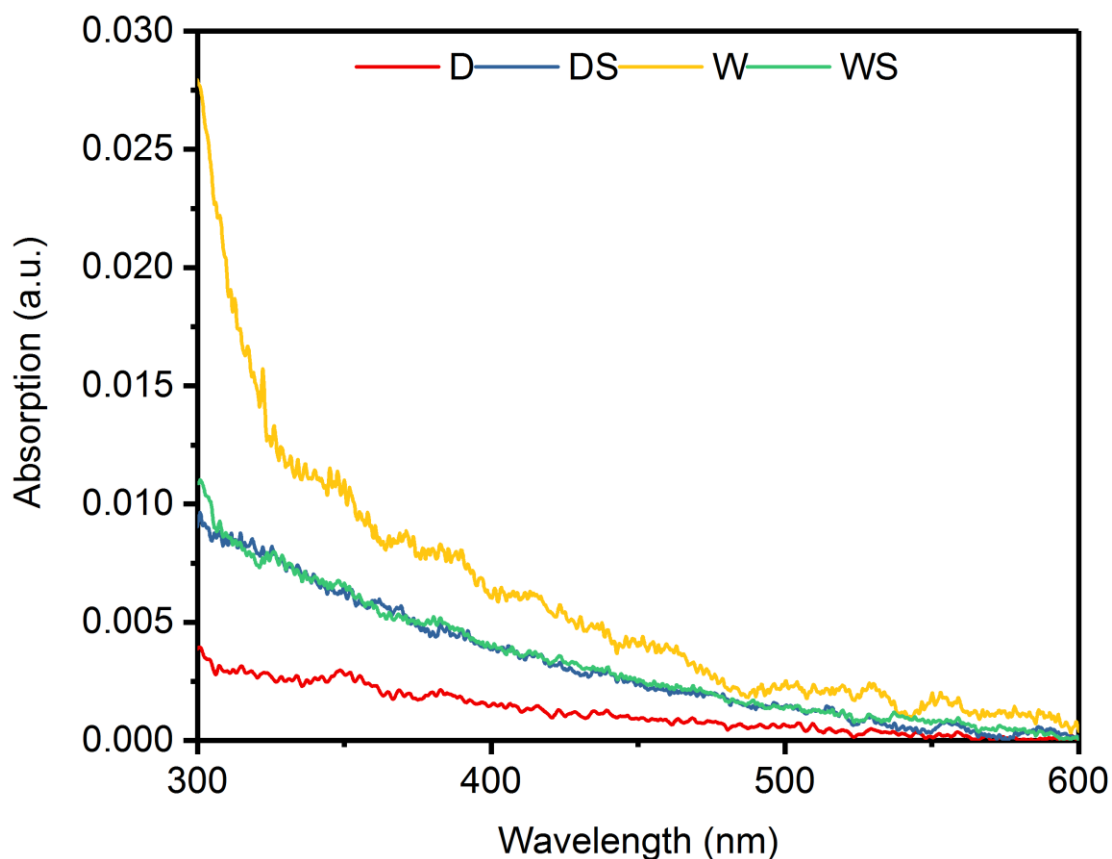


Figure S3. UV-Vis absorption spectrum of toluene SOA under four different conditions.

In the introduction, the role of light-absorption aerosols on radiative forcing and pollution development needs to be discussed. In particular, several key references are missing here (An et al., Severe haze in Northern China: A synergy of anthropogenic emissions and atmospheric processes, Proc. Natl. Acad. Sci. USA 116, 8657–8666, 2019; Peng et al., Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proc. Natl. Acad. Sci. USA 113, 4266–4271, 2016; Wang et al., Light absorbing aerosols and their atmospheric impacts, Atmos. Environ. 81, 713-715, 2013). Those studies have discussed the atmospheric impacts of light-absorbing. It would also be necessary that discussions are provided to compare the results from this work to those of literature.

Response: Thanks for the suggestions. We have added “Light-absorbing aerosols (including black carbon (BC), mineral dust, and brown carbon (BrC)) are recognized as playing important roles in climate radiative forcing because of the strong dependence

of their optical properties on the aerosol composition, the complexity of their production and the poor constraints on their contribution to radiative forcing (Peng et al., 2016; Wang et al., 2013).” (Line 8-12, page 2). We also added “According to An’s study, the concentrations of NO₂ and nitrate were also quite high in China, especially in the North China Plain (NCP) (An et al., 2019).” (Line 30-33, page 2).

Minor points

The font size of chemical formulas in Fig. 4 is too small to be read clearly.

Response: Thanks for the suggestions. The sizes of chemical formulae have been enlarged from 12 to 16 in Figures 4, S4 and S6.

P7 Line 32, “that” is repeated.

Response: The mistake has been corrected.