

## Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Page and line numbers in the responses correspond to those in the ACPD paper.

### Review #1

**The authors report measurements of real and imaginary refractive indices for secondary organic matter derived from photooxidation of toluene and m-xylene with different levels of NO<sub>x</sub>. They find that the SOMs are somewhat absorbing even with zero NO<sub>x</sub>, but that the extent of absorption increases with NO<sub>x</sub>. Overall, the paper is well presented and straight-forward. I can recommend publication, once the authors address the comments below.**

We thank the reviewer for the careful reading of the manuscript and the associated questions and feedback that were provided. The revised manuscript takes into account these aspects. Detailed responses to each question are given below.

**1. My primary concern is that it is a bit difficult to tell when the derived refractive indices (in particular, the imaginary components) come from the ellipsometry measurements or the methanol extracts. This needs to be clarified. I am not certain that the methanol extracts are used at all.**

In the revised manuscript, there are new clarifications in several places. Please refer the responses for comments #4, #5, and #9 for details. In short, however, the imaginary refractive indices  $k$  were retrieved from UV-visible spectroscopy, and the real parts  $n$  were retrieved from spectroscopic ellipsometry.

**2. Also, it should be noted more clearly that these measurements were made for SOM produced at very high mass loadings. There is some evidence in the literature that the refractive indices of SOM depend on mass loading (Kim et al., 2012; Kim and Paulson, 2013).**

The reviewer brings up an important point. We agree that high mass concentrations may influence the chemical composition of SOM and consequently affect the refractive indices. This point is discussed in section 3.1 in the revised manuscript, as follows:

*As a caveat, the SOMs of this study were produced at mass concentrations much higher than typical atmospheric concentrations. Both elemental composition and refractive index can depend on mass concentration (Shilling et al., 2009; Kim et al., 2012; Kim and Paulson, 2013), and further investigations are needed to quantify this possible effect.*

**Additional comments follow below.**

**3. P20588/L18: I suggest also including the VOC/NO<sub>x</sub> ratio (ppbC/ppbNO<sub>x</sub>) for reference when discussion “high” NO<sub>x</sub> conditions. The “high” vs. “low” paradigm is really related to the fate of peroxy radicals: do they react with NO or with something else? This depends not on the absolute NO<sub>x</sub>, but more-so on the VOC/NO<sub>x</sub> ratio.**

We agree with the reviewer on this point. A column of hydrocarbon:NO<sub>x</sub> ratios is included in Table 1. In the main text, the description reads as follows:

Page 20588 Line 18:

*The SOMs were produced from the photooxidation of toluene and m-xylene in an oxidation flow reactor, both in the absence of NO<sub>x</sub> (hereafter "low NO<sub>x</sub>"; < 70 ppt) and in the presence of NO<sub>x</sub> at different levels (hereafter "high NO<sub>x</sub>"). For the high-NO<sub>x</sub> experiments, the initial NO<sub>x</sub> concentration varied from 2.5 to 10 ppm, corresponding to initial hydrocarbon:NO<sub>x</sub> ratios of 3.5 to 16 ppbC ppbN<sup>-1</sup>.*

**4. P20590: It is not clear if the uncertainty in  $k$  reported as 15% applies just to that derived from the UV-Vis spectroscopy of the extracts, or the ellipsometry measurements as well. If it does not apply to the ellipsometry, what is the uncertainty for that method?**

The uncertainty of 15% applies to the  $k$  values derived from UV-Vis spectroscopy. This point is clarified in the revised manuscript, as follows:

Page 20590 Line 20:

*For the  $k$  values derived from UV-Visible spectroscopy, propagation of uncertainties in  $\rho$ ,  $c$ , and  $A(\lambda)$  leads to an overall uncertainty of  $\pm 15\%$  (10 and 90% confidence interval) for  $\lambda < 420$  nm.*

A comparison of  $k$  values derived from ellipsometry and UV-visible spectroscopy is added in the revised manuscript (cf. section 2.3 and Fig. S1). The uncertainty of ellipsometry-derived  $k$ , although not used in the main analysis, is discussed.

Section 2.3:

*For the smallest  $k$  values ( $< 0.005$ ), the ellipsometry retrievals have uncertainties approaching  $> 50\%$ . The uncertainties for UV-visible spectroscopy are considerably smaller ( $< 15\%$ ).*

**5. P20591/Fig. 2: It is unclear if these  $k$  values are from ellipsometry or from UV-Vis of extracts.**

This information is added in the figure caption. In the revised manuscript, the caption of Fig. 2 reads as:

Figure 2, caption:

*Absorptive component  $k$  of the refractive indices of (column 1) toluene-derived SOMs and (column 2) m-xylene-derived SOMs for several different initial NO concentrations. Row 1 shows the  $k$  values, and row 2 shows  $\Delta k$  values (i.e.,  $\Delta k = k - k_{NO_0=0}$ ). The  $k$  values are derived from UV-visible measurements (see main text). The shaded regions show confidence intervals of 10% to 90%, as calculated by propagation of individual uncertainties for the parameters of Eq. 1.*

**6. P20594/L4: Should state “The FT-IR spectra...” not just “The spectra...”**

The correction is made.

**7. P20594/L5: I suggest the sentence starting “This similarity...” be changed to “This similarity suggests that the oxygen-containing functional groups, excluding nitrogen containing groups, are not substantially different between SOM produced at the different NO<sub>x</sub> concentrations.”**

This sentence is revised as suggested.

**8. Section 3.4: I find the figure associated with this section (Fig. 8) to be a bit confusing. The authors are assessing the optical effects of brown carbon from anthropogenic sources, but these need to be better understood in the context of the BC contributions. By plotting the SSA values separately for brown and black carbon (+ sulfate) it is difficult to really understand the importance of the brown carbon absorption. Just as the authors specify different BC/Sulfate ratios, I think that this might be better if the authors also specify different BC/OA mass ratios (or BC/BrC ratios) and plot the resulting overall SSA for the combined system. There will be some point where the BC/OA ratio is sufficiently large that the contributions of BrC start to become noticeable/important. The authors should be able to bound this based on their low vs. high NO<sub>x</sub> characterization. Put another way, if BC/BrC = 1, then BrC probably doesn't much matter. But if BC/BrC = 0.1, then BrC will alter the SSA. This is what doesn't quite come through in the current presentation. However, they might also want to consider that OA from urban sources does not only come from aromatics, but also from alkanes. Alkanes are likely to form SOA that is comparably much less absorbing.**

We agree with the reviewer that the importance of brown carbon absorption depends on the BrC/BC mass ratio. In the revised manuscript, a new figure panel is added (Fig. 8b). The contribution of BrC absorption is plotted as a function of the ratio of the mass concentration of organic matter to that of black carbon for three different wavelengths. Discussion about the new panel is added in the main text, as follows.

Section 3.4, first paragraph:

*The relative contribution of BrC absorption to total light absorption (i.e.,  $\text{BrC}/(\text{BrC} + \text{BC})$ ) is calculated as a function of the mass ratio of organic matter to black carbon. The calculated results for  $\lambda = 320, 405, \text{ and } 550 \text{ nm}$  are plotted in Fig. 8b. These three wavelengths are selected because solar radiation in these bands respectively regulates  $\text{O}_3$  photolysis,  $\text{NO}_2$  photolysis, and energy balance (cf. Fig. 8a).*

Section 3.4, second paragraph:

*When externally mixed with BC, the studied BrC has a negligible contribution to light absorption at 550 nm (Fig. 8b). These results indicate that these BrC populations have a net cooling effect.*

*The case study suggests that BrC populations can have a substantial contribution for light absorption in this band (Fig. 8b). For a mass ratio of organic matter to BC in a range of 2 to 20, which is typical for urban atmosphere (Turpin et al., 1991), BrC accounts for 15-80% of the UV absorption at 320 nm.*

## **Review #2**

**This paper reported the real and imaginary parts of refractive index (RI) in the UV and visible region for two types of secondary organic materials (SOMs) generated in the photooxidation of toluene and m-xylene. The initial  $\text{NO}_x$  concentration dependence of these RI values was discussed based on the chemical properties of the SOMs measured using infrared spectroscopy. Their results are interesting and should provide useful information to improve our understanding of the SOMs on the radiation balance and photochemical reactions including the production of OH and  $\text{O}_3$ . Manuscript is logically written and the topics are relevant to this journal. I therefore recommend publication once the comments and questions below are addressed.**

We acknowledge the reviewer for the valuable questions and comments that were provided. These aspects are considered in the revision. Detailed replies to each question are given below.

### **Major Comments:**

**9. In this study, the authors determined  $n$  value using the spectroscopic ellipsometry and  $k$  values by measuring the UV-vis spectrum of the SOMs extracted by methanol after filter sampling. In their previous study (Liu et al. 2013), they determined both  $n$  and  $k$  values using the spectroscopic ellipsometry. Some explanation on the reasons that the author did not used the spectroscopic ellipsometry to determine  $k$  value should be added. In the analysis of the spectroscopic ellipsometry data, how do you treat the  $k$  values in this study? (Did you adopt the  $k$  values determined by the UV-vis spectroscopy in the analysis of the spectroscopic ellipsometry?)**

We agree with the reviewer that some explanations are needed to justify why we use UV-visible spectroscopy instead of ellipsometry to determine  $k$ , which is different from our previous publication (Liu et al., 2013). The  $k$  values derived from spectroscopic ellipsometry have a larger relative error than that derived from UV-visible spectroscopy, especially when the  $k$  values are small. This problem is also common for other optical techniques that simultaneously retrieve  $n$  and  $k$ , such as the cavity ring-down spectrometry (e.g., Nakayama et al., 2010). UV-visible spectroscopy provides additional information about absorption, thus improving the estimate of  $k$ . In the revised manuscript, a comparison of  $k$  values derived from UV-visible spectroscopy and spectroscopic ellipsometry is added (cf. section 2.3 and Fig. S1 in the revised manuscript). The ellipsometry measurement was independent to UV-visible spectroscopy, i.e.,  $k$  values retrieved from UV-vis were not used in ellipsometry.

Section 2.3:

*In an alternative to the UV-visible spectroscopy, the  $k$  values are also retrieved by ellipsometry (Liu et al., 2013). A comparison of  $k$  values derived from UV-visible spectroscopy and to those from ellipsometry is provided in the supporting information (cf. Fig. S1). Overall agreement is good. For the smallest  $k$  values ( $<0.005$ ), the ellipsometry retrievals have uncertainties approaching  $>50\%$ . The uncertainties for UV-visible spectroscopy are considerably smaller ( $<15\%$ ). Even so, this method requires sample extraction, and artifacts associated with extraction efficiency, material density, and solvent effect can be introduced. All factors considered, the  $k$  values derived from UV-visible spectroscopy were adopted in this study for further analysis.*

**10. The author suggested that “An absence of systematic error in retrieved refractive indices, as related to film thickness, was confirmed previously (Liu et al., 2013).” However, the systematic errors in retrieved RI possibly depend on physical and chemical properties of the particles to form film. Especially, the viscosity of the SOMs should depend on their precursors, degree of oxidation, relative humidity, and so on. It will be nice if the authors will add some comments on this issue.**

We agree with the reviewer that the systematic errors in retrieved refractive indices possibly depend on physical and chemical properties, e.g., viscosity. In this study, however, we do not have sufficient information to comment on this issue.

**11. The author used equation (1) to determine  $k$  values. Do you have any information that the obtained  $k$  values can represent the  $k$  values for aerosol particles suspended in air?**

Yes. The imaginary refractive index  $k$  is an intrinsic physical property of a material, meaning that it does not depend on the form of the material. In our previous

publication (Liu et al., 2013), we compared the  $k$  values of nigrosin dye (a light-absorbing standard) retrieved from (1) ellipsometry for thin film form, (2) UV-visible spectroscopy using Eq. 1 for bulk solution form, and (3) cavity ring-down spectroscopy for aerosol particles (Dinar et al., 2008; Lack et al., 2006). The results agreed well.

#### **Minor Comments:**

##### **12. Page 20591, line 25**

**“from 0.0018 to 0.0150” should be “from 0.0017-0.0153” ? (from Table 1).**

This correction is made.

##### **13. Figure 6**

**“Spectra are normalized to the peak height at  $1100\text{ cm}^{-1}$ , corresponding to a C–O stretch, to compensate for different masses on the filter samples.”**

**It seems to be better to show the spectra normalized to the peak area of C-H, because the C-H was used as reference in the discussions in this study.**

Here we used the peak height of C–O stretch to normalize the IR spectra because the C–O group is the largest peak in the IR spectra and comprises a major mass fraction. We do not think that the method of normalization is important in the analysis because the spectra shown in Fig. 6 are in arbitrary units.

##### **14. Figure 7**

**“See Sect. S1 ...” should be “See Sect. S2 ...”**

This correction is made.

#### **Review #3**

**In this paper Liu et al study the optical properties of anthropogenic SOA based on collection of the aerosols on a filter and deriving the optical constants using ellipsometry and UV-VIS spectrometry over a broad wavelength range. The study claims that anthropogenic precursors can lead to brown carbon formation at different NO<sub>x</sub> levels by forming nitrogen-containing species. As such this is an interesting and timely paper that sets a new paradigm regarding brown carbon formation, which has not been so far substantiated for biogenic or anthropogenic precursors. However, the method for deriving the optical constants used in this study is new and has not been well established. In addition, it follows a previous study by the same group in which the used solely ellipsometry. The question then arises why the difference between the two studies and if there are inherent issues with the experimental methods (i.e.; can ellipsometry alone be used for derivation of the refractive indices for films of collected aerosols of unknown thickness and density?). These issues, together with others, are mentioned below:**

We thank the reviewer for careful reading of the manuscript and for acknowledging the worth of the present manuscript. The questions and comments are taken into account in the revised manuscript. Detailed replies are below.

**15. Page 20589 line 5: specify how was the gas phase precursor concentration was determined.**

This information is added into the revised manuscript.

Page 20589 line 5:

*The injected precursor concentration was  $5.0 \pm 0.5$  ppm, which was calculated from the injection rate of the liquid into the flow rate of the reactor.*

**16. Line 12--15: The experimental analysis assumes complete removal of O<sub>3</sub> from the reactor and conversion to OH, so that the only oxidant is hydroxyl radicals. Was this assumption validated? What is this assumption based on? Please include O<sub>3</sub> concentration measurement or theoretical rate constants calculation?**

We do not assume complete removal of O<sub>3</sub>. The presence of O<sub>3</sub>, however, plays a minor role for producing particles. This point is discussed in the revised manuscript.

Section 2.1, third paragraph:

*In a control experiment to assess the possible importance of ozonolysis, in the dark the produced particle mass concentration was 0.1% of that obtained when the ultraviolet lamps were illuminated, indicating that photooxidation was the major pathway of SOM production.*

**17. Line 24--30: Explain the method. Explain how the aerosols films were deposited, how they were characterized. How was the film thickness determined? how homogenous it is? How reproducible is the film and how many repetitions were made for each determination. What are the errors associated with this method. What validations were made to ensure that the method produces physically sound values?**

Spectroscopic ellipsometry, as a method for measuring refractive indices of SOM, was introduced in our previous publication (Liu et al., 2013). The questions raised by the reviewer were largely discussed in that first paper. The thickness and homogeneity of the SOM thin films were retrieved from ellipsometry data fitting and subsequently validated by optical and atomic force microscopic techniques. Validation experiments of refractive indices from ellipsometry were made for both non-absorbing (squalane) and light-absorbing (nigrosin dye) standards, and the values agreed well with literature (cf. supporting information in Liu et al., 2013).

In the revised manuscript, we add some more discussion to further explain the method, especially as related to the reviewer's questions. The updated paragraph reads as follows.

Section 2.2:

*From the data sets, film thickness, film non-uniformity, and wavelength-dependent real refractive indices  $n$  were retrieved using the WVASE32 software package (J.A. Woollam VASE). Individual film thickness ranged from 100 to 350 nm. The non-uniformity in film thickness was 5 to 10% over the ellipsometric sampling spot. An absence of systematic error in retrieved refractive indices, as related to film thickness or film non-uniformity, was confirmed previously (Liu et al., 2013).*

*For each thin film sample, duplicate measurements were conducted at two or more different spots. The retrieved  $n$  values agreed with each other within an absolute difference of 0.015. An overall uncertainty of  $n$ , taking both the reproducibility and the fitting error into account, was within  $\pm 0.015$  (10 and 90% confidence interval) across the studied wavelength range from 280 to 1200 nm. As a confirmation of the overall approach, the  $n$  values retrieved for squalane, a non-absorbing standard, and nigrosin dye, a light-absorbing standard, were consistent with literature values (cf. supporting information in Liu et al., 2013).*

**18. Page 20590 line 1-4: in this study only the real part of the complex RI was retrieved using ellipsometry. In previous publication by the same group (also referenced in this work, Liu et al., 2013) the authors used ellipsometry to retrieve both the real and imaginary parts of the complex RI. Why this method was not used this time? Is there a problem determining the imaginary part with this method? If yes, please discuss the problem. Why did you need to derive the imaginary part in a separate experiment using UV-VIS spectrometry of extracts? What are the possible artifacts using the UV-VIS methods? What is the absorption by the water soluble component of the SOA and by the organic soluble component? How was this new approach verified? Did you measure standard materials to verify the validity of the method? What are the associated errors?**

We agree with the reviewer that some explanations are needed to justify the use of UV-visible spectroscopy for  $k$ . In the revised manuscript, a comparison of  $k$  values for toluene-derived SOM retrieved from both ellipsometry and UV-visible spectroscopy is provided (cf. section 2.3 and Fig. S1). Merits, drawbacks, and associated errors for both techniques are discussed in the revised main text, as follows:

Section 2.3:

*In an alternative to the UV-visible spectroscopy, the  $k$  values are also retrieved by ellipsometry (Liu et al., 2013). A comparison of  $k$  values derived from UV-visible*

*spectroscopy and to those from ellipsometry is provided in the supporting information (cf. Fig. S1). Overall agreement is good. For the smallest  $k$  values ( $<0.005$ ), the ellipsometry retrievals have uncertainties approaching  $>50\%$ . The uncertainties for UV-visible spectroscopy are considerably smaller ( $< 15\%$ ). Even so, this method requires sample extraction, and artifacts associated with extraction efficiency, material density, and solvent effect can be introduced. All factors considered, the  $k$  values derived from UV-visible spectroscopy were adopted in this study for further analysis.*

The absorption by water-soluble component of SOM is not discussed because the scope of the present study mainly focuses on the absorption of total SOM.

The  $k$  values retrieved from both ellipsometry and UV-visible spectroscopy were validated by comparing retrieved values of a light-absorbing standard (nigrosin dye) against literature values (cf. supporting information in Liu et al., 2013). Please refer the response to comment #11 by reviewer #2.

**19. In the previous publication (Liu et al., 2013) the authors indicated that the film thickness measured by the ellipsometer should not vary by more than 10% and that the surface roughness should be less than 10% of the light wavelength. In both papers the film thickness is reported to be up to hundreds of nm and the wavelength range starts at about 300nm up to microns. This suggests that in order to satisfy the thickness uniformity and surface roughness, collected particles should be in the size range of less than 100nm. Unless there is evidence that particles become flat by impaction on the surface, this is probably not the case. Please explain how this was done, how it was verified, how film uniformity was assured and how the roughness was measured. What were implications of the film roughness on the associated errors?**

The reviewer brings up an important question. We did find that SOM particles coagulate and form a flat bulk film on the surface of silicon substrate. Surface roughness of such a SOM film was typically below 1 nm, which was characterized by an atomic force microscope (AFM) in our previous study (Liu et al., 2013). Film uniformity can be obtained from the inversion of ellipsometry data. In the revised manuscript, discussions about the film uniformity are included.

Section 2.2:

*From the data sets, film thickness, film non-uniformity, and wavelength-dependent real refractive indices  $n$  were retrieved using the WVASE32 software package (J.A. Woollam VASE). Individual film thickness ranged from 100 to 350 nm. The non-uniformity in film thickness was 5 to 10% over the ellipsometric sampling spot. An absence of systematic error in retrieved refractive indices, as related to film thickness or film non-uniformity, was confirmed previously (Liu et al., 2013).*

**20. Page 20590 section 2.3: The authors used an equation taken from sun et al., 2007. In that publication, the equation should be**

$$k = \frac{\ln(10)}{4\pi} \frac{\rho\lambda}{cL} A(\lambda)\xi(n,k)$$

**And not as presented in the manuscript, Equation 1.**

**In Sun et al 2007,  $\xi$  is a weak function of BOTH  $n$  and  $k$  with a values that ranges between 0.7 and 0.8. This factor can introduce an error (0.25-0.45% over estimation) and should not be neglected in the analysis as was done in this study.**

**Equation (1) in the current manuscript should not be equal to  $k$  but to  $k/\xi(n,k)$ . Using  $n$  from the ellipsometry measurements, if justified, one can then calculate  $k$ .**

Regarding the use of the equation from Sun et al., 2007, there seems to be a point of confusion. To be clear, the equation in Sun et al (2007) is written as follows, corresponding to Eq. 1 in the original paper:

$$\frac{\alpha(\lambda)}{\rho} = 1000\ln(10) \frac{\varepsilon(\lambda)}{M_w} = 1000\ln(10) \frac{A(\lambda)}{cL}$$

The absorption coefficient of bulk organic liquid,  $\alpha(\lambda)$  ( $\text{cm}^{-1}$ ), can be determined from spectroscopic data for the dissolved compounds, using the absorbance  $A$ , the optical path length  $L$  (cm), and the concentration  $c$  (g/L). The imaginary part  $k$  is related to the absorption coefficient by the equation:  $\alpha = 4\pi k / \lambda$ .

The Eq. 1 in the manuscript was derived by plugging the expression  $\alpha = 4\pi k / \lambda$  into the Eq. 1 in Sun et al. (2007), followed by unit conversions. The method used in our manuscript to retrieve  $k$  from absorbance  $A(\lambda)$  is exactly the same as what was suggested by Sun et al. (2007).

The correction factor  $\xi$  was called “particulate effect” by Sun et al. (2007). It appears in the conversion from bulk absorption coefficient  $\alpha$  to particulate mass-normalized absorption cross section  $MAC$  ( $\text{m}^2/\text{g}$ ), as follows (Sun et al., 2007, Eq. 3):

$$MAC = \frac{\alpha}{\rho} \xi$$

In our manuscript, Eq. 1 was used to calculate the imaginary part  $k$  from the absorbance  $A$  measured for bulk solution (not in particulate form). The parameter  $\xi$  representing the particulate effect does not appear in this calculation. In this study, when the optical properties for particulate form are calculated, as for the single-scattering albedo of particle populations in section 3.4, the particulate effect is a natural result of using a Mie-theory-based optical model. This approach is more

accurate than using the weak form function, which relies on the assumption of small-particle limit.

Another piece of evidence is that the  $k$  values calculated from Eq. 1 are not systemically higher than those derived from ellipsometry, as shown in Fig. S1, indicating that Eq. 1 does not overestimate  $k$ .

**21. According to Chen and Bond 2010, the error introduced by selection of a density value, as was done here (1.4) is nulled out only when calculating the particulate absorption per mass using the same density. Because in this work the authors calculate the imaginary part, the uncertainty in the density should not be ignored.**

We agree with the reviewer that the uncertainty in the material density should not be ignored for calculating the imaginary part  $k$ . The uncertainty in the material density is actually considered in the analysis of the overall uncertainty for  $k$ . The sentence was misleading and is deleted in the revised manuscript.

Page 20590 Line 18:

~~*Although the use of a literature value for material density introduces uncertainty for  $k$ , this uncertainty nulls out in the calculation of the mass absorption coefficient in a Mie-based optical model (Chen and Bond, 2010).*~~

**22. In addition, the authors do not specify how the value of  $c$  (concentration) was obtained. Were the filters weighted and a 100% extraction efficiency was assumed? If not, what was assumed and how the error was calculated? This should be discussed.**

This information is added in the revised manuscript.

Page 20590 Line 18:

*Particles were collected onto Teflon filters (Millipore FGLP, 0.2  $\mu\text{m}$  pore size). The collected SOM mass was determined by weighing the filter before and after sample collection using an analytical balance (Sartorius, LA120S; 2.0 to 10.0 mg, with an uncertainty of 0.1 mg). The filters were extracted in methanol (40.0 to 100.0 mL) while ultrasonating (Branson 2510; 20 min). The concentration  $c$  was calculated from the measured SOM mass and the volume of solvent. An extraction efficiency of 100% was assumed (Updyke et al., 2012).*

**23. Page 20594 line 4: “the spectra in the...” the IR spectra?**

The change is made.

**24. Page 20596 line 24-28: Do particle phase reactions depend on humidity? Does water play a role in these reactions? The experiment in this work started at 13% RH and water molecules were converted to hydroxyl radicals. These experiments should be conducted at several relative humidities to determine what is the potential role of water in the products formation.**

We agree with the reviewer that water can potentially play a role in the particle phase reactions. The scope of the present study, however, mainly focuses on the influence of NO<sub>x</sub> on optical properties. We do not have sufficient data to discuss the effect of water on particle-phase reactions because the relative humidity was not changed during our experiments. This leaves an interesting topic for future studies.

**25. Page 20598 line 1: sentence not clear, please rephrase.**

This sentence is rewritten in the revised manuscript, as follows.

*The implication is that, as an effective UV absorber, BrC influences the production of O<sub>3</sub> and OH by reducing UV irradiance and consequently affects the oxidation capacity of the regional atmosphere.*

**26. Table 1. Please provide some information regarding the choice of the size distribution in table 2.**

Information about the choice of the size distribution is added in the main text of revised manuscript.

Section 3.4:

*The number-diameter distributions of the BrC and sulfate particle populations are representative of polluted urban regions (Wu et al., 2008). The BC particle population having a relatively smaller mode diameter is typical for fresh soot particles emitted from motor vehicles (Kleeman et al., 2000).*

**27. Table 2. Provide reference for the complex RI values of black carbon and sulfate?**

The references are provided in the revised manuscript.

Table 2:

<sup>d</sup>*Value recommended by Bond and Bergstrom, 2006.*

<sup>e</sup>*Value taken from Toon et al., 1976.*

**28. Figure 3. Add error bars to figures 3c and 3d like you have done in figures 3a and 3b.**

In the revised manuscript, the error bars are added to Fig. 3c and Fig. 3d.

**29. Figure 4. How were the  $k$  values for Suwannee river fulvic acid derived? With equation 1? If yes, what density was assumed? Please justify**

Yes. The  $k$  values for Suwannee river fulvic acid were also derived with Eq 1. Information about material density is added in the revised manuscript.

Page 20590 Line 17

*A material density of  $(1.4 \pm 0.1) \times 10^3 \text{ kg m}^{-3}$  was used in the analysis for toluene- and m-xylene-derived SOMs (Ng et al., 2007). For Suwannee river fulvic acid, a material density of  $(1.47 \pm 0.02) \times 10^3 \text{ kg m}^{-3}$  was used (Dinar et al., 2006).*

**30. Figure 6. The upper information segment is shifted relative to the figure.**

This is corrected in the revised manuscript.

**31. Figure 8. Blue lines are missing in the legend.**

This figure legend is updated, as follows.

Figure 8, legend:

*Calculated single-scattering albedo of light absorbing particles for a scenario of an urban plume. Cumulative distributions for solar irradiance (orange) and photolysis rate coefficients (light blue) are also shown.*

**32. Concluding remarks: the authors emphasize the decrease in UV power available for photochemistry as a result of light absorption in the atmosphere. It would be interesting to discuss also implications to the direct or semi -direct radiative effect. If this is the case, a quantitative estimation of the decrease (even only for a case study) and a qualitative estimation of its significance are needed.**

The implications for direct radiative effect were briefly discussed in the original manuscript (page 20597 line 17-19). The main point was that the studied brown carbon populations have single-scattering albedo values close to unity in the visible range, thus having a net cooling effect when they are externally mixed with black carbon. In the revised manuscript, this point is further explained, as follows.

Page 20597 Line 17:

*Results of the case study have several implications for climate and atmospheric chemistry modeling. The  $\omega$  values of the BrC particle populations are close to unity for  $\lambda > 500 \text{ nm}$  (Fig. 8a). When externally mixed with black carbon, the studied BrC has a negligible contribution to light absorption at 550 nm (Fig. 8b). These results*

*indicate that these BrC populations have a net cooling effect.*

Spectroscopic data of complex refractive indices for studied brown carbon are tabulated in the supporting information (cf. Table S1). Readers interested in the quantitative estimate of radiative forcing of brown carbon can calculate this value using the provided data.

## References

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- Chen, Y., and Bond, T. C.: Light absorption by organic carbon from wood combustion, *Atmos. Chem. Phys.*, 10, 1773-1787, 10.5194/acp-10-1773-2010, 2010.
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