

## Response to Anonymous Referee #1

*The manuscript by Nakayama et al. investigates the optical properties, specifically the complex refractive index, of the SOA formed by the photooxidation of toluene under different (high) levels of NO<sub>x</sub> and the SOA formed by the photooxidation of 1,3,5-trimethylbenzene in the presence of NO<sub>x</sub> using a photoacoustic spectrometer at 405, 532, and 781 nm and a cavity ring-down spectroscopy at 532 nm. The study shows there's only slight absorption at 405 nm for the Toluene-SOA and no absorption in any wavelength for the 1,3,5-TMB-SOA. The study also shows that absorption increases with higher NO<sub>x</sub> concentrations. They explain their results by the increase in the nitrate to organics ratio in a H-ToF-AMS and correlate this to the hypotheses that nitrated aromatic compounds in the particle phase are likely to be the major contributors to the absorption in the UV. The study shows the influence anthropogenic emissions can have on SOA and how nitro-aromatic compounds affect both the real and imaginary components of the complex refractive index.*

*I would like to mention it is a shame the authors did not use (or show) their 355 nm CRD in this study. I believe the study is relevant and an important contribution to the gap of knowledge concerning optical properties of SOA; however, I have some concerns which should be address before I recommend the manuscript for publication.*

(reply)

We appreciate the valuable comments from the reviewer. We have considered the comments carefully and revised our manuscript.

- 1) *The authors mention on page 14560 and in the conclusions that “The imaginary part of the RI value (k) for the toluene-SOAs was found to increase steeply to shorter wavelengths at 405 nm, while the real part of the RI (n) gradually increases to shorter wavelengths”, I disagree with this conclusion. On Fig. 5 the authors show the result from their previous publication (open circles) to justify this; however, the error bars on the k value are large and the result from Zhong and Jang (2011) does not show a “steep” jump in the absorption. Moreover, the real part may also show a “steep” jump, as two of the three values retrieved jump from values around n = 1.45 to n > 1.6. This change in n is quite large and not a gradual step. The author should explain these changes in the components of the RI.*

(reply)

We agree with the suggestions. We have removed the words “steep” and “gradually” in the revised manuscript. The increase in the k values at shorter wavelength suggests the existence of a resonance wavelength at shorter wavelength. For a light absorbing material, the n value principally has a normal dispersion (i.e., n decreases with increasing wavelength) for wavelengths well above the resonance wavelength. As shown in Fig.6, the n values depend on [NO<sub>x</sub>]<sub>ini</sub>. If we compare the n value (n = 1.632) at 355 nm determined under the high [NO<sub>x</sub>]<sub>ini</sub> condition (= 540 ppbv), with that (n = 1.567) at 405 nm determined under high [NO<sub>x</sub>]<sub>ini</sub> condition (= 571 ppbv), the wavelength dependence does not show the steep jump.

- 2) *In page 14569 the authors mention that “The bulk absorption per soluble carbon*

*can be compared with the particulate absorption coefficients using the following relationship, assuming that the particles are small relative to the wavelength" and use the relationship to calculate the mass absorption cross section; however, the size of the particles is in the same range as the wavelength (one of the reasons the authors used Mie theory to calculate the RI). How can the authors justified using this relationship? The authors need to give a stronger justification for the whole analysis presented in the "Atmospheric implications" section.*

(reply)

Thank you for the important comments. Because we are considering the weak light absorbing particles in this study, the relationship can be used, even when the particle size is comparable with the wavelength, as described below.

The MAC values for the particles are defined by Bohren and Hoffmann (1983):

$$\text{MAC} = \frac{6\pi}{\rho\lambda} \text{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \left[ 1 - \frac{4\pi D_p^3}{3\lambda^3} \text{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\}^2 \right].$$

For the particles with  $D_p < 600$  nm and  $k < 0.01$  at  $\lambda = 405$  nm, the term  $(4\pi D_p^3/3)\text{Im}\{(m^2-1)/(m^2+2)\}^2$  is less than 0.001. Therefore, the MAC is approximately,

$$\text{MAC} = \frac{6\pi}{\rho\lambda} \text{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\}.$$

As shown by Sun et al. (2007), by expanding the term in brackets and substituting for  $\alpha$ , the MAC can be related to the bulk absorption:

$$\text{MAC} = \xi \times \alpha/\rho.$$

These points have been added in the revised manuscript.

3) *The error analysis in the text is not clear and should be expanded. The authors mention in page 14556 that there is at least a 6% error associated with the calibration, since they use a TSI SMPS there is a 10% error in the concentration count, there is a further error in the mean diameter, but the error bars in Fig. 3 – specially for 532 and 781 nm – do not seem to reflect the cumulative error in the measurements. Moreover, the authors do not seem to incorporate the errors investigated by Miles et al. 2010 for CRDS refractive index retrievals. It is also not clear to me how the error in the RI retrieved for 781nm can be smaller than for 532 and 405 nm; specially, because the  $Q_{ext}$  values are quite small.*

(reply)

The errors in the retrieved RI values have been recalculated in the revised manuscript by reevaluating the uncertainties in the optical properties and size distribution measurements. The uncertainties in the size distribution measurements were estimated to be <8% based on the calibration data provided by the manufacturer and the uncertainties in the diameters of the PSL particles used for the calibration of the SMPS. Miles et al. (2010) reported that uncertainties in the particle size and RI of PSL particles, which were used for the calibration of the instrument, contributed to systematic errors in the retrieved RI of other aerosols. The uncertainties in the particle diameters of the PSL particles used for the calibration of the CRDS and PASS-3 were

also taken into account in the estimation of the uncertainties for these instruments. Because the uncertainties in the RI of the PSL particles was not taken into account in the estimation of the uncertainties of the  $b_{\text{ext}}$  and  $b_{\text{sca}}$  measurements in the original manuscript, these uncertainties have been corrected in the revised manuscript. As suggested by the referee, the error bars in Figs.3 and 4 were incorrect. These error bars have also been corrected in the revised manuscript.

*4) Equation 2 on page 14559.  $f(D_p)$  – the normalized surface area weighted size distribution function – does this refer to the measured size distribution from the SMPS normalized to the total area? Weighted to what? It should be made clear on the text from where you get this size distribution as it is crucial to your retrieval algorithm.*

(reply)

Yes,  $f(D_p)$  represents the surface area weighted size distribution function normalized to the total surface area, and was obtained from the SMPS data. An explanation of  $f(D_p)$  has been added in the revised manuscript.

*Technical corrections:*

*In Table 2 and throughout the text write out the  $k$  values. For example, it is clearer to have  $k=0.0018$  than  $k = 1.8$  and in an above parenthesis (  $\times 1000$  ) – which should actually be (  $\div 1000$  ) – and it will also clarify to how many significant figures the  $k$  values can be retrieved.*

(reply)

We have revised the descriptions of the  $k$  values in Table 2, Figs. 5, 6, and 8, and in the text.

*p 14553, 21: change “was” to “were”*

*p 14554, 4: add “,” after closing parenthesis*

*p 14554, 22: change “and” to “in the”*

*p 14555, 5: change “and” to “in the”*

*p 14556, 7: delete “a” between “adding” and “purified”*

*P 14559, 2 and 7: delete “the” before “Mie theory”*

*p 14568, 9: change “Fig. 8” to “Fig. 9”*

*p 14568, 17: delete “the” before “Mexico” and change “city” to “City”*

*p 14568, 18: delete “the” after “reported”*

(reply)

We have corrected these words in the revised manuscript. We appreciate the careful reading.

*p 14570, 6-7: Rephrase: “In addition, the MAC values for combustion-OA may several times larger than those for the toluene-SOAs as discussed above” As it is written in is not clear what you mean.*

(reply)

We have removed the sentence in the revised manuscript.

## Response to Anonymous Referee #2

*Nakayama et al. investigate the optical properties of toluene SOA formed in the presence of high levels of NOx using photoacoustic spectrometry and cavity ring-down spectroscopy at 405, 532, and 781 nm. In particular, the authors retrieve the complex refractive index at these wavelengths and are therefore able to study the wavelength dependence of the real and imaginary components of this property. The study contributes to understanding a finding from field observations in urban areas, namely that there is a marked increase in particle absorption at short wavelengths. The resulting attenuation of near-ultraviolet light by particles can significantly alter the local and regional radiative balance and photochemistry, e.g., through lower photolysis rates of O3 and NOx. As Jacobsen (1999) has pointed out, nitrated aromatic compounds in the particle phase are likely to be major contributors to this absorption. Consistent with this hypothesis, Nakayama et al. find that the absorption of toluene SOA becomes appreciable at 405 nm, and increasingly so with higher NOx concentrations. The NOx dependence is rationalised on basis of the concentration of nitro-cresols, which are known products of OH oxidation chemistry. In contrast, absorption at longer wavelengths is small or negligible and particles are almost purely scattering (SSA  $\sim 1$ ). Nakayama et al. also studied the optical properties of 1,3, 5-trimethylbenzene, whose photooxidation and SOA does not produce nitroaromatic compounds to any significant extent. In this case, no absorption was observed even in under high NOx conditions. These observations are evidence in support of the particular importance of nitroaromatic compounds in affecting the optical properties of anthropogenically-influenced SOA.*

*I have no major criticisms of the work, and the experimental results in the paper appear robust and with low enough uncertainty for the subsequent level of analysis. In this regard, it should be noted that measuring the particle absorption with sufficient accuracy remains an experimental challenge. Nevertheless, it is regrettable that the paper does not explore the near-UV optical properties directly. Although previous work (including that by the authors) has shown that toluene SOA absorption is much larger at 355 nm, measurements at even shorter wavelengths (e.g., below 330 nm) are desirable to evaluate the influence of particle absorption on O3 photolysis rates. Nakayama et al. estimate the mass absorption cross-sections (MAC) at shorter wavelengths based on angstrom exponents from field work. Although commonly done, it is not clear that this approach is sound for these particles: the extrapolation starts from 405 nm (which is in the tail-end of the absorption) and estimates an extinction near the maximum of the strong absorption band of the nitro-cresols. The authors should provide a stronger justification for this approach in the text, particularly with reference to the absorption spectra of these nitro-cresols. The findings of this paper therefore highlight the need for further measurements in the near-UV, and for new experimental systems or methods to study the optical properties of particles in this region. Doing so will contribute to a deeper understanding of particles on the influence on local photochemistry and radiative balance.*

(reply)

We appreciate the valuable comments from the reviewer. We agree with the comments

on the importance of further measurement of light absorption properties at shorter wavelengths (e.g., below 330 nm) in order to evaluate the influence of particle absorption on O<sub>3</sub> photolysis rates. We have added sentences about the importance of further research at shorter wavelengths in the revised manuscript.

We estimated the MAC values at 405 nm for the particles observed in LA by Zhang et al. (2012) from the  $\alpha(365 \text{ nm})/\rho$  value, using their reported absorption Ångström exponent ( $3.2 \pm 1.2$ ), because the linear relationship between  $\log(b_{\text{abs}})$  and  $\log(\lambda)$  between 365 and 405 nm was shown in Fig. 2 of Zhang et al. (2012). However, we agree with the comment that it is important to note that there is possibly a difference in the wavelength dependence of the light absorption between the toluene-SOAs and the particles observed in LA. These points have been added in the revised manuscript.

*Technical corrections:*

*p.14552,3: “light absorbing”*

*p.14552, 16: “high-resolution”*

*p.14554, 1: “gas phase”*

*p.14557,26: should this be “V-mode”?*

*“phenoxy-type” on p.14565 lines 18,20, p.14566, 4, p.14571, 5*

*p.14570, 3: Define “AAE”*

*p. 14570, 6: “. . . combustion-OA may be several times. . .”*

*p.14571, 5: “2,4,6-trimethylphenol”*

(reply)

We have corrected these words in the revised manuscript. We appreciate the careful reading.

### Response to Anonymous Referee #3

*This study investigates the dependence of the complex reflective index at 405nm, 532nm, and 781nm of SOA formed from toluene and 1,3,5-trimethylbenzene as a function of NOx. It is found that the k values for toluene SOA increase to shorter wavelengths at <405nm, and the k value at 405nm increases with NOx concentration. The authors note that the light absorption for 1,3,5-trimethylbenzene SOA is negligible at all wavelengths. It is hypothesized that nitro-aromatic compounds such as nitro cresols are the major contributors to light absorption of toluene SOA. While this work can provide further information for understanding the optical properties of aerosols, in many places the discussions are inadequate and/or not clear (see specific comments below). The authors need to address these issues before the manuscript can be recommended for publication.*

(reply)

We appreciate the valuable comments from the reviewer. We have considered the comments carefully and revised our manuscript.

*Specific comments:*

*1. Page 14556, experiment section. The initial hydrocarbon concentration used is about 4ppm for toluene experiments and 2 ppm for 1,3,5-TMB experiments, which leads to the formation of > 100 ug/m<sup>3</sup> SOA in some experiments. With such a high SOA loading, more semi-volatile species would partition into the particle phase and result in an SOA composition that is very different from experiments performed at more atmospherically relevant loadings. How would this potentially affect their measurements and conclusions? The authors need to comment on the atmospheric relevance of their experiments. (with the exception of some very polluted places, typical ambient aerosol loading is much lower than 100 ug/m<sup>3</sup>).*

(reply)

We agree with the suggestion regarding the possible contribution of the difference in the partitioning of semi-volatile organic compounds between the gas phase and the aerosol phase. Unfortunately, however, these initial concentrations were used due to the instrumental limitations. We have added the following sentences in the revised manuscript.

“In addition, the initial concentrations of the VOCs may also contribute to the optical properties of the SOAs, because the partitioning of semi-volatile species between gas and particle phases may be changed. Therefore, further studies on the contribution of other possible factors, such as the presence of seed particles, the initial VOC concentrations, and the generation of SOAs from other anthropogenic VOCs, to the RI values of the SOAs are needed.”

*2. Page 14556, lines 26-29. The authors noted that the bscs (532nm) was not used in this study as a strong particle size dependence of the calibration factors was found. The authors need to include more details and discussions regarding this. Why is such size dependence calibration only found in the 532nm case? What sizes of PSL particles are used? Further, how are the uncertainties noted in line 29 calculated?*

(reply)

The information on the calibration of the PASS-3 is provided in the supplemental material and will be submitted as a separate paper (Nakayama et al., manuscript in preparation). In our calibration experiments for the scattering measurements, PSL particles with diameters of 203, 299, and 400 nm were used. The calibration factors for  $b_{\text{sca}}(\lambda)$  were estimated by comparing the  $b_{\text{sca}}(\lambda)$  data obtained using the PASS-3 with those calculated based on Mie theory and applying the particle diameter, particle number density, and literature refractive index. As a result, a strong particle size dependence of the calibration factors for  $b_{\text{sca}}(532 \text{ nm})$  were found, while no significant size dependence was observed for  $b_{\text{sca}}(405 \text{ nm})$  and  $b_{\text{sca}}(781 \text{ nm})$ . The results may be explained by the difference in the truncation errors, because the polarization plane of the 532 nm laser beam is perpendicular to the view plane, while those of the 405 and 781 nm laser beams are parallel. The uncertainties for the PASS-3 were estimated from a combination of the statistical and estimated systematic uncertainties (including the uncertainties in the particle size and refractive index of the PSL particles) in the determination of the calibration factors. Descriptions of the estimations of the uncertainties associated with the calibration have been added to the supplemental material in the revised manuscript.

*3. Page 14557, line 15. I would imagine with all absorption and scattering coefficient measurements at 405nm, 532nm, and 781nm, the authors would also measure the extinction coefficients at these 3 wavelengths. Is there a reason why only the extinction coefficient at 532nm is measured?*

(reply)

Due to the instrumental limitations, extinction coefficients were measured only at 532 nm using a home-made CRDS instrument. The extinction measurements at 532 nm were required to determine the RI values at 532 nm, because the scattering measurements using the PASS-3 at 532 nm potentially had large uncertainties due to the truncation errors as described above.

*4. Page 14558. The authors wrote “significant light absorption was found at 405 and 532nm in run A4”. However, it is difficult to tell how “significant” the light absorption is at 532nm from Figure 3b (it looks like the values are around zero from the scale in Figure 3b).*

(reply)

We agree with the comments. The scale for  $Q_{\text{abs}}$  at 532 and 781 nm in Fig. 3b has been changed in the revised manuscript. As shown in revised Fig. 3b,  $Q_{\text{abs}}$  at 532 nm have non-negligible values. The sentence was revised as follows: “Significant light absorption at 405 nm and non-negligible light absorption at 532 nm were found for “run A4” (Fig. 3b)”.

*5. Page 14560, lines 11-22. The authors noted that at 532nm, a non-negligible  $k$  value (1e-3) is obtained under high NOx conditions. Later, the authors wrote that the typical uncertainty in  $k$  value determined by PASS-3 is \_ 1e-3. Therefore, it would seem like the measured  $k$  value is just in the uncertainties? If so, I do not think the author can read too*

*much into the value. The authors also need to be more explicit as how they calculate the uncertainties.*

(reply)

The uncertainties in the determination of the RI values were estimated from the  $2\sigma$  for the differences between the  $Q^*(\bar{D}_s, \lambda)$  values obtained using eqs. (1) and (2) and the uncertainties in the measurements of the optical properties and size distributions of the SOAs. The uncertainties in the size distribution measurements were estimated to be  $<8\%$  based on the calibration data provided by the manufacturer and the uncertainties in the diameters of the PSL particles used for the calibration of the SMPS. Milles et al. (2010) reported that uncertainties in the particle size and RI of PSL particles, which were used for the calibration of a CRDS instrument, contributed to the uncertainties in the retrieved RI of other aerosols. In the present study, the uncertainties in the particle diameters of the PSL particles used for the calibration of the CRDS and PASS-3 were taken into account in the estimation of the uncertainties for these instruments. The uncertainties in the determination of the  $k$  values actually varied, partly due to differences in the abundance of the SOAs, and partly due to the drift in the absorption and scattering signals for each experimental run. Because the larger abundance of SOAs during “run A4” led to smaller uncertainties, the  $k$  value at 532 nm for run A4 was slightly larger than the estimated uncertainties for this run. This explanation has been added in the revised manuscript.

*6. Page 14560, last paragraph. The authors wrote “the light absorption of toluene SOA steeply increases to short wavelengths at  $<405\text{nm}$ ”. This work does not have any measurements at  $<405\text{nm}$ , and it seems to me that this statement is made by including the data from Nakayama et al and Zhong and Jang. However, the error bar in the  $k$  value in the earlier Nakayama work is very large. I do not think that the authors can conclude from Figure 5 that there is a steep increase at  $<405\text{nm}$ . Further, while the experimental conditions in the earlier Nakayama work are probably similar to the current work, it is not clear if this is the same case for the work by Zhong and Jang. The authors need to comment on this.*

(reply)

We agree with the comments. We have removed the word “steep” in the revised manuscript. The initial  $\text{NO}_x$  concentrations used by Zhong and Jang (2011) were 62 and 70 ppbv. The following sentence has been added in the revised manuscript. “The difference in the  $k$  values at  $\sim 350$  nm reported by Nakayama et al. (2010a) and Zhong and Jang (2011) may be explained by the difference in the  $[\text{NO}_x]_{\text{ini}}$  conditions: 540 ppbv (Nakayama et al. 2010a) and 62-70 ppbv (Zhong and Jang 2011).”

*7. Page 14561, lines 9-11. The authors wrote”. I do not understand this. The  $n$  value at 405nm increases from 1.45 to 1.57, the  $n$  value of at 532 nm increases from 1.43 to 1.50. From these results it seems like there is a larger increase in  $n$  value at shorter wavelength?*

(reply)

As suggested by the referee, there is a larger increase in the  $n$  value at shorter

wavelength. The “long-wavelength side” in the original manuscript meant the “the long-wavelength side from the resonance wavelength”. To avoid the confusing expression, the sentence has been revised as follows:

“...because the stronger light absorption under high  $[NO_x]_{ini}$  conditions would cause a larger increase in the  $n$  values at 405 nm than at 532 nm. ”.

8. *Page 14561, lines 15-24. Again, from the uncertainties, I do not agree with the authors that the  $k$  value at 532nm is also increasing. Further, why does the  $k$  value show a clear increase with  $NO_x$  at 405nm, but no so much at 532nm? The authors need to discuss this.*

(reply)

As suggested by the referee, it is difficult to discuss the  $NO_x$  dependence of the  $k$  values at 532 nm based on these results. Therefore, the following comments have been added in the revised manuscript:

“At 532 nm, the  $k$  value was slightly larger than the uncertainties under the high  $[NO_x]_{ini}$  condition (571 ppbv); however, it is difficult to discuss the  $[NO_x]_{ini}$  dependence of the  $k$  value based on these results.”

In addition, the discussion on the MAC value at 532 nm has also been removed from the “Atmospheric implication” section in the revised manuscript.

9. *Page 14564, lines 18-19. Given that most of toluene is still no reacted at the end of the experiment (Figure 2) and that the reaction time is not too long (~4 hours), it is surprising that the O/C of toluene SOA is as high as 0.73. What is the [OH] in the chamber? The authors need to comment on how these O/C values compared to those in literature.*

(reply)

The  $[OH]$  concentrations are estimated to be  $\sim 10^6$ . The O/C ratios observed in the present study (0.64-0.73) are consistent with those reported in recent papers (e.g., Sato et al. 2012 (Fig. 1) and Chhabra et al. 2011 (Fig. 9B)). Their results indicate that the O/C ratios for the toluene-SOAs are not particularly high among the SOAs generated from aromatic hydrocarbons.

10. *Page 14580. Table 1. The results show that more SOA is formed in experiments with a higher  $NO_x$  concentration. Is this a result of the enhanced radical reaction with  $NO_2$  (owing to the high  $NO_2$  in the chamber)?*

(reply)

Under our experimental conditions ( $[HC]_{ini} > [NO_x]_{ini}$ ), the reaction cycles should slow down after the  $NO_x$  is consumed. In this case, a larger portion of the HCs is used for the reaction cycles leading to greater SOA formation under higher  $[NO_x]_{ini}$  conditions.

*Technical comments:*

1. *Page 14553, line 16. Missing comma before “corn”.*
2. *Page 14553, line 17. Missing comma before “coal”.*
3. *Page 14554, line 4. Missing comma before “the”.*

(reply)

We have corrected these words in the revised manuscript. We appreciate the careful reading.

*4. The authors should box all the figure legends to avoid confusion of the legend with the actual data points. (Especially Figures 5 and 6).*

(reply)

We have boxed all of the figure legends in the revised manuscript.

## References

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