

Response to reviewers' comments on "Molecular Analysis of Secondary Organic Aerosol and Brown Carbon from the Oxidation of Indole" (egusphere-2023-1804)

The authors kindly thank the reviews for the careful review of the manuscript, and the helpful comments and suggestions, which improve the manuscript a lot. All the comments are addressed below point by point, with our responses in blue, and the corresponding revisions to the manuscript in red. All updates of the original manuscript are marked in the revised version.

Reviewer #1

The manuscript by Jiang et al. investigates the oxidation of indole by selected oxidants (OH radicals and O₃) with/without NO₂. The authors report the chemical composition and optical properties of indole SOA (ind-SOA) under the investigated conditions. In the presence of NO₂, the ind-SOA yields decreased by more than a factor of two, but the mass absorption coefficient at 365 nm of ind-SOA was 5 times higher than that of the SOA form without NO₂. The global emission factors of indole could be around half of the emissions of the most abundant amines, trimethylamine. However, there are only limited studies investigating the formation of SOA and BrC from the oxidation of indole. Overall, this study would be a valuable addition to a better understanding of the ind-SOA formation mechanisms and the influence of NO₂ on the chemical composition and light-absorbing characteristics of ind-SOA. The results may be particularly important for areas with abundant indole emissions, such as large animal husbandries and maize fields. The manuscript is well-presented, and it could be accepted for publication after considering the comments below.

General comments

1. Line 90: To clarify how the OH concentrations were calculated, the authors could consider adding a few sentences explaining the methodology used.

We did not calculate the OH radical concentrations, but Salo et al. (2011) calculated the OH radical concentrations in the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) by using the MCM 3.1 model (Bloss et al., 2005) for similar concentrations of O₃ and TME. We have explained this in the manuscript as follows:

“For comparable levels of ozone and TME in the AIDA chamber, Salo et al. (2011) calculated OH radical levels of $0.2\text{--}1.0\times 10^7$ molecules cm^{-3} employing the Master Chemical Mechanism 3.1 (Bloss et al., 2005).”

2. Lines 95-99 and Figure S2: The O₃ was injected into the chamber at around 600-800 ppb in the REF and seed experiments, while in the Seed-NO₂ experiment, it was initially added at around 100 ppb and then increased to 600-800 ppb after 30 minutes. The authors may want to provide an explanation for this difference.

In REF and seed experiments, the indole was oxidized by OH radical at high concentrations of ozone at around 600-800 ppb. In the seed-NO₂ experiment, NO₂ first reacted with O₃ and led to formation of the NO₃ radicals which reacted with indole. In a second step, the reaction products were oxidized by OH radicals leading to formation of secondary organic aerosol. The difference of the adding O₃ was to test the reaction ratio of indole with O₃ and NO₃ radicals.

“Please note that the difference of adding O₃ in AS-NO₂ experiments, compared with REF and AS experiments, was to investigate the reaction of indole with NO₃ radicals. However, this will not be discussed in this manuscript.”

3. Line 100: It would be helpful if the authors could provide more information about the background samples and whether they would react with the reactants.

Light absorption from Aqualog measurements and chemical compositions from chemical ionization mass spectrometer (CIMS) measurements were corrected by subtracting background filter measurements. Compared to sample filters, the absorption from 240 nm to 800 nm only accounted for 1%. For CIMS measurement, the gas background was relatively low and particle background only contains fluorinated constituents, which don't interfere with sample analysis.

“Compared to sample filters, the absorption of background filters from 240 nm to 800 nm only accounted for 1%. Background measurements for both the gas and particle phase were performed before and after the first addition of indole to identify any contamination inside the chamber. The gas background levels were almost negligible for all experiments. For the measurements by the chemical ionization mass spectrometer, most of the particle background signals were from filter matrix contaminations mainly due to fluorinated constituents. We subtracted the mass spectra of the background filter samples from those of the particle-loaded filter samples for the same experiments. This procedure has been described by Gao et al., (2022).”

4. Line 117: Were the estimated trace gas and particle wall losses corrected?

We estimated the gas and particle wall loss by using model COSIMA. The wall loss of gas and particle mass was lower than 2%. Therefore, we did not correct the gas and particle concentrations.

“Since the wall losses of particles and trace gases were relatively low, we did not correct the gas and particle concentrations”

5. Lines 132 and 152: Why the methanol and acetonitrile were used to extract the filter samples for different analyses? It would be beneficial if the authors could explain their rationale for selecting these solvents and discuss any potential solvent effects.

Compared with the studies of the indole secondary organic aerosol by Montoya-Aguilera et al. (2017), the solution of methanol extraction was used to measure brown carbon aerosol. However, the solution of acetonitrile extraction was used to measure chromophores by using a high-performance liquid chromatography (HPLC) platform coupled to photo diode array (PDA) and high-resolution mass spectrometry (HRMS) detectors. Furthermore, methanol could induce solvent artifacts by reacting with conjugated carbonyl (Bateman et al., 2008; Chen et al. 2022). The acetonitrile, as an inert solvent, is an ideal for proper characterization of BrC chromophores (Chen et al. 2022).

“Please note that we used methanol and also acetonitrile (see next section) to extract the filter samples as to achieve comparability with previous work i.e. by Montoya-Aguilera et al. (2017).”

6. FIGAERO-CIMS part: The manuscript does not mention the mass resolution of the instrument used. Additionally, while the authors assumed a uniform sensitivity for different compounds, it is possible that sensitivities vary by order of magnitude. It would be helpful if

the authors could provide references from the literature supporting their assumption or consider rephrasing statements regarding “XXX% of CIMS detected compounds.” Furthermore, it would be interesting to know if thermal desorption caused any fragmentation of the compounds and if multimodal thermograms were observed.

During the measurement, the mass resolution of FIGAERO-CIMS was relatively stable with about 4000 $m/\Delta m$. The most important issue for a quantitative mass detection efficiency for CIMS is its varying sensitivity for different chemical species. Sensitivity of Iodide-CIMS to individual compounds depends on their polarity and hydrogen bonding capability, and is strongly influenced by molecular geometry and steric factors (Caldwell, et al. 1989). Since it was not possible for us to calibrate the sensitivities of all organic molecules, we assume the same sensitivity of 22 cps/ppt for all compounds (cf. Lopez-Hilfiker et al. 2016). As shown in Figure S2 the major compounds ($C_8H_6O_2N_2$, $C_8H_7O_4N$, $C_8H_7O_3N$, and $C_8H_5O_3N$) detected by FIGAERO-CIMS exhibit only one peak in the thermogram and no substantial indication of fragmentation.

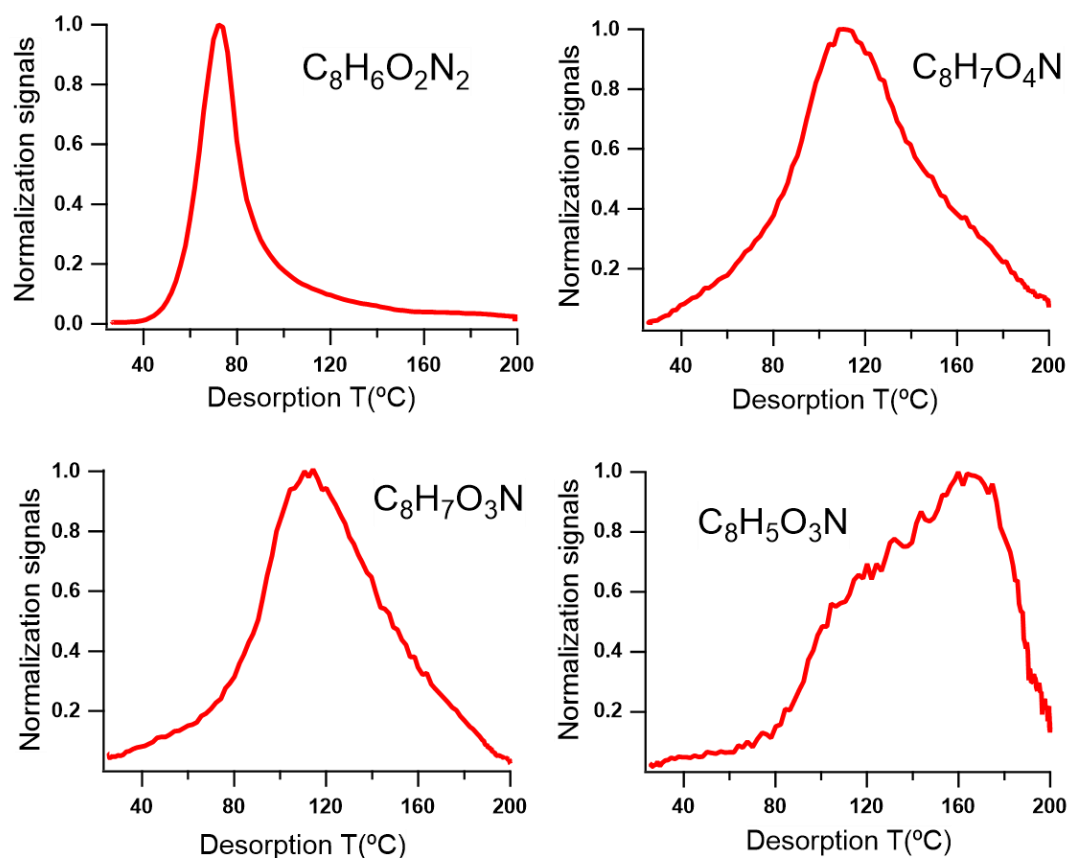


Figure S10. Thermograms of $C_8H_6O_2N_2$, $C_8H_7O_4N$, $C_8H_7O_3N$, and $C_8H_5O_3N$.

“During the measurements, the mass resolution of FIGAERO-CIMS was relatively stable with about 4000 $m/\Delta m$. Since it was not possible for us to calibrate the sensitivities of all organic molecules, we assume the same sensitivity of 22 cps/ppt for all compounds (Lopez-Hilfiker et al. 2016). As shown in Figure S2, the major compounds ($C_8H_6O_2N_2$, $C_8H_7O_4N$, $C_8H_7O_3N$, and $C_8H_5O_3N$) detected by FIGAERO-CIMS exhibit only one peak in the thermogram and no substantial fragmentation.”

7. Line 172: What would be the reasons for the slightly lower SOA yield in the AS seed experiment than that in the REF experiment? Line 183: What is the seed concentration used in Montoya et al.? Would different seed concentrations play a role in the different yields?

The SOA mass was calculated by particle volume and density. Effective densities of indole SOA were derived from comparisons of the aerodynamic size distributions from AMS and the mobility size distributions from SMPS measurements (Saathoff et al. 2009; DeCarlo et al. 2004). The density calculation had relatively high uncertainties. The yield of indole SOA in the AS seed experiment was slightly lower than in the REF experiment but well within the combined uncertainties. Please note, that Montoya-Aguilera et al. (2017) didn't use seed aerosol. Generally, one would expect higher yields for experiments with seed aerosol as it reduces wall losses. However, wall losses were almost negligible in our study. Kamens et al. (2011) showed that experiments with higher initial seed concentrations (and particle phase water) generated more toluene-derived SOA than the lower seed experiments.

8. Figure 1b: When calculating the effective density of indole SOA by comparing the AMS and SMPS data, would the seed density affect the results? Was it excluded?

The density of indole SOA were derived from comparisons of the aerodynamic size distribution from AMS and the mobility size distribution from SMPS measurements. In the AS experiment, the major peaks of the size distributions were from pure indole SOA. Therefore, the seed particles do not affect the indole SOA density determination. However, in the AS-NO₂ experiment, the indole SOA density was calculated by the major peaks of coated particles. Therefore, we used an average particle density including the AS seed and the indole SOA coating. The particle mass concentration was calculated from particle volume and average density. The seed particle mass and volume can be measured by SMPS. We obtained the pure indole SOA mass and volume. Then we calculated the pure indole SOA density.

“The effective density (ρ_{eff}) was derived from the measurement of the vacuum aerodynamic diameter (d_{va}) obtained by AMS and the mobility equivalent diameter (d_m), see figures S11 and S12 (Kostenidou et al., 2007), as shown in the supplemental information (Sect. 3).”

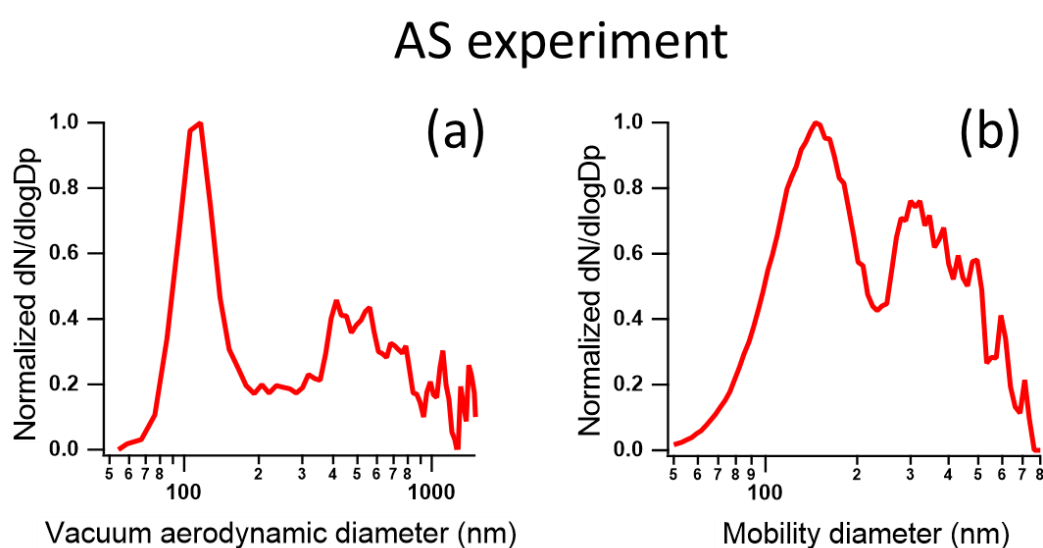


Figure S11. Size distribution of indole SOA at AS experiment.

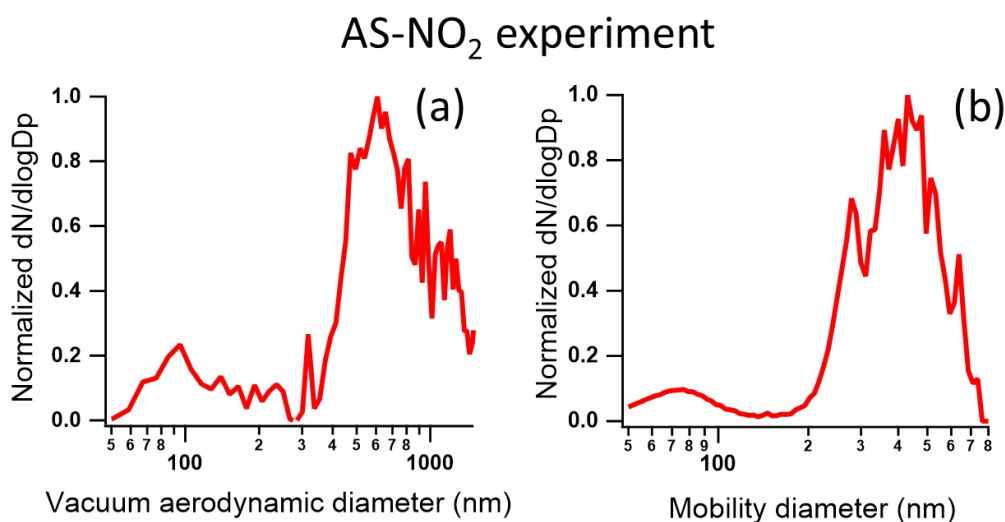


Figure S12. Size distribution of indole SOA at AS-NO₂ experiment.

9. Figure 3: It was mentioned in the figure caption that the Y-axis scale shows the fraction of C_xH_yO_zN₁₋₂ of the total ion intensity, but there are compounds without N atom shown in the Figure.

We agree that and modified the caption of Figure 3.

“The fraction of C_xH_yO_zN₁₋₂ of the total ion intensity is shown on the right.”

10. Line 223: The author attributed the common ions C₆H₄⁺ and C₅H₃⁺ to be fragmented from 3-nitroindole or C₁₆H₁₂O₄N₄ (Figure S8), but these ions were also observed in REF and AS experiments.

We agree it and modified the sentence.

“Consistently, high intensities of large-weight fragment ions such as (C₁₃H₆⁺, C₅H₆NO₃⁺, and C₇H₅⁺, etc.) measured by AMS could be fragments of 3-nitroindole or C₁₆H₁₂O₄N₄ (Fig. S8).”

11. Figure 4: Please check the caption about the description of the color used in the Figure. For example, “The unassigned chromophores (red)”.

We agree and have corrected the caption in the Figure 4.

“...unassigned chromophores (black),...”

12. Line 249: 3-nitroindole contributed 76% of compound signals detected by a CIMS, and ~50% of the BrC absorption. Would this indicate there are compounds with low signal intensities that contribute even more than 3-nitroindole to the BrC absorption?

The mass fraction of 3-nitroindole was measured by a chemical ionization mass spectrometer. As discussed above, the relative abundance determined by this instrument has a substantial uncertainty as we only could assume an average sensitivity. The absorption fraction of 3-nitroindole was measured by HPLC-PDA-MS. The mass fraction values of 3-nitroindole were indeed different from absorption fraction values. This result could be caused by the two

different instruments. CIMS has varying sensitivity for different chemical species. Some chromophores can't be separated by HPLC and directly travel through the column. These could be the reasons why the mass fraction values are different with absorption fractions.

References

- Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, *Atmos. Chem. Phys.*, 5, 641-664, 10.5194/acp-5-641-2005, 2005.
- Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: The Effect of Solvent on the Analysis of Secondary Organic Aerosol Using Electrospray Ionization Mass Spectrometry, *Environ. Sci. Technol.*, 42, 7341-7346, 10.1021/es801226w, 2008.
- Caldwell, G., R. Renneboog, and P. Kebarle. 1989. 'GAS-PHASE ACIDITIES OF ALIPHATIC CARBOXYLIC-ACIDS, BASED ON MEASUREMENTS OF PROTON-TRANSFER EQUILIBRIA', *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, 67: 611-18.
- Chen, Kunpeng, Nilofar Raeofy, Michael Lum, Raphael Mayorga, Megan Woods, Roya Bahreini, Haofei Zhang, and Ying-Hsuan Lin. 2022. 'Solvent effects on chemical composition and optical properties of extracted secondary brown carbon constituents', *Aerosol Science and Technology*, 56: 917-30.
- DeCarlo, P. F., J. G. Slowik, D. R. Worsnop, P. Davidovits, and J. L. Jimenez. 2004. 'Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory', *Aerosol Science and Technology*, 38: 1185-205.
- Gao, L., Song, J., Mohr, C., Huang, W., Vallon, M., Jiang, F., Leisner, T., and Saathoff, H.: Kinetics, SOA yields, and chemical composition of secondary organic aerosol from β -caryophyllene ozonolysis with and without nitrogen oxides between 213 and 313 K, *Atmos. Chem. Phys.*, 22, 6001-6020, 10.5194/acp-22-6001-2022, 2022.
- Lopez-Hilfiker, F. D., S. Iyer, C. Mohr, B. H. Lee, E. L. D'Ambro, T. Kurten, and J. A. Thornton. 2016. 'Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts', *Atmospheric Measurement Techniques*, 9: 1505-12.
- Montoya-Aguilera, J., J. R. Horne, M. L. Hinks, L. T. Fleming, V. Perraud, P. Lin, A. Laskin, J. Laskin, D. Dabdub, and S. A. Nizkorodov. 2017. 'Secondary organic aerosol from atmospheric photooxidation of indole', *Atmospheric Chemistry and Physics*, 17: 11605-21.
- Kamens, R. M., Zhang, H., Chen, E. H., Zhou, Y., Parikh, H. M., Wilson, R. L., Galloway, K. E., and Rosen, E. P.: Secondary organic aerosol formation from toluene in an atmospheric hydrocarbon mixture: Water and particle seed effects, *Atmospheric Environment*, 45, 2324-2334, <https://doi.org/10.1016/j.atmosenv.2010.11.007>, 2011.

Kostenidou, E., Pathak, R. K., and Pandis, S. N.: An Algorithm for the Calculation of Secondary Organic Aerosol Density Combining AMS and SMPS Data, *Aerosol Science and Technology*, 41, 1002-1010, 10.1080/02786820701666270, 2007.

Saathoff, H., K. H. Naumann, O. Mohler, A. M. Jonsson, M. Hallquist, A. Kiendler-Scharr, T. F. Mentel, R. Tillmann, and U. Schurath. 2009. 'Temperature dependence of yields of secondary organic aerosols from the ozonolysis of alpha-pinene and limonene', *Atmospheric Chemistry and Physics*, 9: 1551-77.

Salo, K., M. Hallquist, A. M. Jonsson, H. Saathoff, K. H. Naumann, C. Spindler, R. Tillmann, H. Fuchs, B. Bohn, F. Rubach, T. F. Mentel, L. Muller, M. Reinnig, T. Hoffmann, and N. M. Donahue. 2011. 'Volatility of secondary organic aerosol during OH radical induced ageing', *Atmospheric Chemistry and Physics*, 11: 11055-67.

Reviewer #2

This manuscript by Jiang et al. explores chemical composition, formation mechanisms and optical properties of ind-SOA BrC produced from oxidation of indole in an environmental chamber at atmospherically relevant conditions with/without NO₂. They observed that in the presence of NO₂, the SOA yields decreased by more than a factor of two but the mass absorption coefficient of ind-SOA BrC at 365 nm was 5 times higher as compared to the ind-SOA BrC formed without NO₂. The global emissions of Indole is half of one of the most abundant amines, i.e., trimethylamine. Despite its significant presence in the atmosphere, the chemical composition, formation mechanism, and optical properties of ind-SOA including its BrC remain poorly understood. The study is valuable for atmospheric chemistry and climate modelling community, particularly for areas with high Indole emissions, such as animal husbandry, maize and rice fields and tea manufacturing areas. This manuscript is well written, well-presented, and could be accepted for publication after considering the following comments:

Major issues

1. Line 85-90: How did you make sure that there was no interaction between methanol/indole mixture? How will the volatilization of methanol will affect wall losses? Did you do blanks? Please elaborate.

Sorry, there was a wrong description of the indole injection procedure. We have corrected this description. Actually, no methanol was involved. Instead, synthetic air was flushed through a glass tube coated with indole to inject it into the simulation chamber. The indole coating was generated by evaporating toluene from a solution of indole in toluene in the rotating glass tube. After adding indole into the chamber, we collected filter samples to measure the particle background. In addition, the gas phase background was measured by Iodide-CIMS and Proton Transfer Reaction – Mass Spectrometry (PTR-MS). During the measurement, we did not find any indication of toluene.

“For the REF experiment (Fig. S2a), indole ($\geq 99\%$ purity, Sigma-Aldrich) was dissolved in toluene ($>99.9\%$ p.a. grade, Merk). The solution was used to generate an indole coating on a glass tube of 1.5 m length and 40 mm diameter by evaporating the toluene in the rotating tube. The indole was evaporated into the AIDA chamber with a flow of $0.01 \text{ m}^3 \text{ min}^{-1}$ of synthetic air through the coated tube for 2-3 hours obtaining indole mass concentrations of $90\text{--}150 \mu\text{g m}^{-3}$.”

2. Line 90: Did you use any tracer for OH concentration calculation? If yes, what tracer? Add a brief discussion about OH concentration calculation.

We did not calculate the OH radical concentrations, but Salo et al. (2011) calculated the OH radical concentrations in the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) by using the MCM 3.1 model at comparable concentrations of O₃ and TME. We have explained this in the manuscript as follows:

“For comparable levels of ozone and TME in the AIDA chamber, Salo et al. (2011) calculated OH radical levels of $0.2\text{--}1.0 \times 10^7 \text{ molecules cm}^{-3}$ employing the Master Chemical Mechanism 3.1 (Bloss et al., 2005).”

3. Section 3.2 (Line 195-210): You have used acetonitrile extracted ind-SOA BrC in UPLC-PDA analysis (section 3.3). However, BrC extraction efficiency in methanol and acetonitrile

could be significantly different from each other. Why did you not compare ind-SOA BrC optical properties in methanol and acetonitrile?

We used the methanol extracts to allow direct comparison of our results with the study by Montoya-Aguilera et al. (2017). However, the acetonitrile extraction was used to measure chromophores by using a high-performance liquid chromatography (HPLC) platform coupled to photo diode array (PDA) and high-resolution mass spectrometry (HRMS), for which the filters are commonly extracted by using acetonitrile. We are aware that methanol could induce solvent artifacts by reacting with conjugated carbonyls (Bateman et al., 2008; Chen et al. 2022). In contrast, acetonitrile, as an inert solvent, is ideal for proper characterization of BrC chromophores (Chen et al. 2022). The data for the absorption spectra measured for both extracts are given in Figures 2 & 4.

4. Line 205-210: The MAC values in REF and AS were similar between online-PAS and offline-Aqualog measurements but not for AS-NO₂. Why, elaborate?

In the REF and AS experiment, the major chromophore was C₈H₇O₃N. However, in AS-NO₂ experiment, the major chromophore was C₈H₆O₂N₂ (3-nitroindole). Furthermore, 3-nitroindole becomes the dominant compound, comprising up to 76% of the chemical composition measured by CIMS in the AS-NO₂ experiment. For offline-Aqualog measurement, major absorption was measured from 3-nitroindole molecules dissolved in methanol. However, in the online-PAS measurement, 3-nitroindole was a component of the particle coating, which may cause differences between Aqualog and PAS measurements.

5. Figure 4: How did you calculate the fraction of individual chromophores (known, unassigned, unresolved) to total indi-SOA absorption? Add a brief discussion.

“We added relevant comments on HPLC-PDA data analysis in section 6 of the supplement.”

“Fractions of MAC corresponding to each BrC feature (MAC_{λ_i}) detected in the indole SOA (Figure 4c and f) are calculated using their relative absorptions and MAC_λ as follows (Hettiyadura et al., 2021):

$$MAC_{\lambda} = MAC_{\lambda_i} \left(\frac{I_{\lambda_i} \times \Delta t_i}{I_{\lambda} \times \Delta t} \right)$$

where, I_{λ_i}(μAU) is the averaged absorbance intensity of an individual BrC feature i and Δt_i (min) is its time duration. I_λ (μAU) is the averaged absorbance intensity across Δt = 14 min of LC separation, which excludes the unresolved components eluted at (0 – 1 min). Unassigned fractions correspond to total absorption from 1-15 min, other than C₈H₇O₃N and C₈H₆O₂N₂ chromophores.”

6. Figure 4c: Typo-error "Unassigned"

We have corrected the legend in the Figure 4c.

7. Line 283: "However, in presence of NO₂, a significant shift occurs, and 3-nitroindole becomes the dominant compound, comprising up to 76% of the chemical composition." I think it's 76% of the total CIMS species, not the total composition.

We agree and modify the sentence as follows:

“However, in presence of NO₂, a significant shift occurs, and 3-nitroindole becomes the dominant compound, comprising up to 76% of the chemical composition measured by CIMS.”

Reference

Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, *Atmos. Chem. Phys.*, 5, 641-664, 10.5194/acp-5-641-2005, 2005.

Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: The Effect of Solvent on the Analysis of Secondary Organic Aerosol Using Electrospray Ionization Mass Spectrometry, *Environ. Sci. Technol.*, 42, 7341-7346, 10.1021/es801226w, 2008

Chen, Kunpeng, Nilofar Raeofy, Michael Lum, Raphael Mayorga, Megan Woods, Roya Bahreini, Haofei Zhang, and Ying-Hsuan Lin. 2022. 'Solvent effects on chemical composition and optical properties of extracted secondary brown carbon constituents', *Aerosol Science and Technology*, 56: 917-30.

Hettiyadura, A. P. S., Garcia, V., Li, C., West, C. P., Tomlin, J., He, Q., . . . Laskin, A. (2021). Chemical Composition and Molecular-Specific Optical Properties of Atmospheric Brown Carbon Associated with Biomass Burning. *Environmental Science & Technology*. doi:10.1021/acs.est.0c05883

Montoya-Aguilera, J., J. R. Horne, M. L. Hinks, L. T. Fleming, V. Perraud, P. Lin, A. Laskin, J. Laskin, D. Dabdub, and S. A. Nizkorodov. 2017. 'Secondary organic aerosol from atmospheric photooxidation of indole', *Atmospheric Chemistry and Physics*, 17: 11605-21.

Salo, K., M. Hallquist, A. M. Jonsson, H. Saathoff, K. H. Naumann, C. Spindler, R. Tillmann, H. Fuchs, B. Bohn, F. Rubach, T. F. Mentel, L. Muller, M. Reinnig, T. Hoffmann, and N. M. Donahue. 2011. 'Volatility of secondary organic aerosol during OH radical induced ageing', *Atmospheric Chemistry and Physics*, 11: 11055-67.