

## Response to Anonymous Referee #1

This manuscript describes a laboratory study on the photo-oxidation of indole under low-NO<sub>x</sub> conditions. Secondary organic aerosols (SOA) were chemically characterized to determine the importance of indole chemistry in the formation of brown carbon (BrC) constituents. State of art analytical techniques (high-resolution mass spectrometers) used in this study, provide novel and important insights into the understanding of the formation of BrC in the atmosphere. In addition, the authors have evaluated the importance of their findings using a regional model and have highlighted that oxidation of indole could have an important role in SOA formation as well as BrC compounds. Since these results help to provide accurate atmospheric chemistry models for the oxidation of BVOC, they are an important contribution to the literature. While the results are interesting and are appropriate for Atmospheric Chemistry and Physics, few clarifications (c.f. comments below) should be provided and would benefit from clarifying revisions.

- 1.1** Page 2. Lines 7-15: The authors should consider adding some information on the emissions of indole in the atmosphere and compare them with the emissions of other BVOCs. In addition, what is the contribution of the human activities (e.g. agriculture, pharmaceutical application) in the global emission of indole?

The literature review on the emission sources of indole that was included in the introduction section manuscript was fairly comprehensive. However, we have added additional references dealing with emissions of indole from animal husbandry (see response 4.1 to reviewer #4).

- 1.2** Page 4. Line 5: Could the authors provide more information on the settings of the PTR as well as the time and mass resolutions?

We added information on the PTR-ToF-MS settings to the first paragraph in section 2.

- 1.3** Line 7. The authors mentioned Page 7, line 7 that “The particles had a geometric mean diameter of approximately 0.3  $\mu\text{m}$ ”. What was the mean diameter of the seed aerosol?

No seeds were used in this experiment because the seed material would interfere with HRMS analysis. A clarification has been added to the beginning of section 2.

- 1.4** Line 9. Hallquist et al. is not an appropriate reference. It is a review and they have not determined any aerosol density. Please provide a better reference(s). The authors decided to use a density of 1.2 g cm<sup>-3</sup>, could they explain why? Previous studies have reported a density of ~1.4 g cm<sup>-3</sup> for SOA generated from the oxidation of mono- and polyaromatic compounds, such as naphthalene (Ng et al., 2007; Chan et al., 2009; Chen et al., 2016). It is worth noting that such compounds could form oligomers as proposed in the manuscript (Healy et al., 2012). Could the authors further support their choice and discuss the potential impact of using a density of 1.4 g cm<sup>-3</sup> in their model?

This is an excellent point. We wish we had tools for measuring aerosol particle density at our disposal. The assumed SOA density was changed from 1.2 to 1.4 g cm<sup>-3</sup> based on the reported values for naphthalene SOA in Chan et al., 2009 and Chen et al., 2016, and based on densities of known indole oxidation products. This increased the reported aerosol yield by ~15% and decreased the reported MAC by ~15%.

- 1.5** The authors haven't discussed the potential wall losses of organic vapors. Have they considered them in the determination of the SOA yields? If not, by looking at the decay of the main products they should be

able to provide an estimation.

We suspect that the wall loss effects are minimal because of the fast aerosol formation and high apparent yield. We added the following statement regarding the possible effect of the wall loss of oxidation products on the yield, "Indole oxidation products could be lost to the walls reducing the apparent yield and contributing to its scatter. However, this effect is probably minor given that the apparent yield is quite high." in section 4.1, paragraph 2.

**1.6** Lines 14-16: The authors mentioned page 4 lines 2-3: "In some experiments, mixing was not complete by the time the lamps were turned on as evidenced by the measured indole concentrations continuing to increase". How did they determine the SOA yields in such experiments?

In all yield calculations, we relied on the actual amount of injected indole so we do not view incomplete mixing at the state of the reaction as a huge problem. As long as mixing timescale is shorter than the oxidation timescale (which is the case) the yield calculation should work reasonably well. We added the following statement, "Although mixing was not fast, it was faster than the time scale of the reaction, so it should not have affected the SOA mass yield calculations." to the first paragraph in section 2.

**1.7** Page 7. Lines 27-28: The time series of the species presented in Figure S2.5 is not clear. The products are continuously produced over the course of the experiments (c.f. formic acid) disregarding the presence of OH radicals (i.e. lights On or Off). The authors should further discuss the time evolution of the identified products. In addition, the authors proposed that the oxidation of indole form 3-oxyindole. But according to Figure S2.4, this product is an impurity from the indole and it is not formed during the oxidation process (no increase after the lamps were turned on). The decay of 3-oxyindole is much slower than the decay of indole. Therefore, if the 3-oxyindole was really formed from the oxidation of indole it should have shown up, such as 2-formylformanilide. Please clarify.

We found the time dependence of some of the observed ion abundances puzzling. After some more experiments with PTR-ToF-MS we suspect that some of the behavior results from slow-adsorption-desorption kinetics on the sampling lines. The PTR-ToF-MS flexible heated inlet is not long enough to reach into the chamber, and we have to sample through segments of unheated Teflon tubing. Stickier compounds take longer to pass through the tubing to the PTR-ToF-MS instrument, and also compete with other compounds for surface sites. This complicates the interpretation. In response to this comment, as well as related comments from other reviewers we did the following changes:

- better explained the limitations of PTR-ToF-MS measurements in the supporting information section
- removed a statement that the time dependence of isatin implied a complex mechanism of its production
- removed Figure S2.5

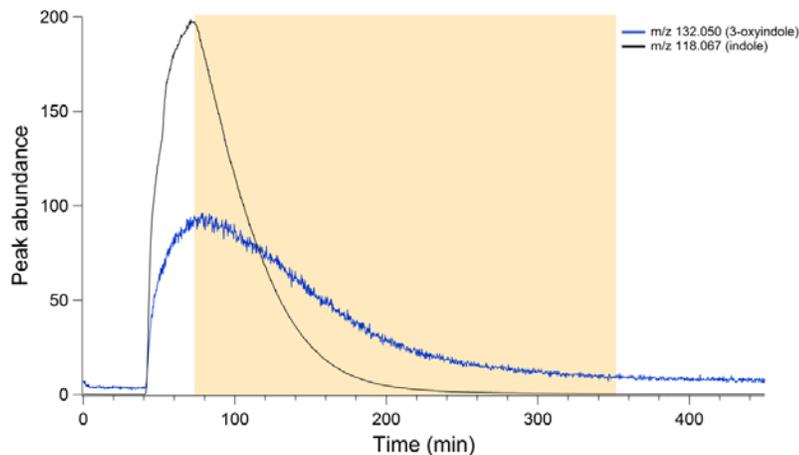
**1.8** Page 10. Lines 19-22: It is not clear if the authors claim that the formation of the oligomers (BrC compounds) occur in the gas phase. The authors used a reference that described similar oxidation process occurring in the liquid phase. If the authors expect that the formation of oligomers happened in the gas phase, they need suspect this reaction to occur in the particle phase rather than in the gas phase. Have the authors performed any experiments at different RH and/or without seed aerosols? Further experiments are needed if they want to conclude that.

We have added a new paragraph at the end of section 4.1 to address this point. The added discussion emphasizes the tentative nature of the proposed mechanism.

We agree that multiple further experiments are needed to clarify the mechanism and establish where and how different processes take place. Our focus was not a complete analysis of the mechanism – this would take a prohibitively long time, well beyond a lifetime of a typical graduate student. We hope this publication inspires additional work on this interesting SOA system.

**1.9** Lines 23-24: With the data presented in Figures S2 it seems difficult to propose that 3-oxyindole is directly formed from the oxidation of indole (c.f. previous comments).

We agree that the fact that 3-oxyindole is present as an impurity complicates the interpretation. However, it appears to be also a product of indole photooxidation. To make it easier to see we replotted the figure on a linear scale in this response. The “bulge” observed at ~130 minutes would not be there if 3-oxyindole was only being removed.



\*In the graph above, the indole peak abundance was scaled to 1/50 of its actual peak abundance.

**1.10** Moreover, the authors should consider the mechanism proposed by Healy et al. 2012. In this previous study, they have reported the formation of dimers and oligomers from the photolysis of nitro-naphthalene through gas-phase processes. Could such chemical pathways contribute to the formation of some compounds identified in this manuscript?

Thank you for this suggestion. We have added the following to the discussion of the mechanism in section 4.1, paragraph 11: “For example, Healy et al. (2012) observed efficient dimerization of naphthoxy radicals in the gas phase leading to rapid formation of SOA following photolysis of 1-nitronaphthalene. The dimerization of oxindole to dihydro indigo dye, as well as other oligomerization processes in indole SOA, could follow a mechanism similar to the one described by Healy et al. (2012).”