

Response to Anonymous Referee #3

Indole is emitted from the biosphere by plants under stressed conditions. The SOA yield of Indole was measured in a smog chamber. The particles were collected and the mass absorption coefficient determined at various wavelengths. With nanospray desorption electrospray high resolution mass spectrometry and DART-MS the molecular formula of a series of species in the aerosol phase was identified and attributed to possible compounds. Some of these were confirmed by their UV spectra with HPLC-PDA-HRMS. Since many of the products determined absorb in the UV, the authors hypothesize, that indole SOA may considerably contribute to brown carbon. They investigate this with the help of an airshed model, which they updated with some new indole oxidation reactions. They conclude that indole SOA can considerably contribute to decreased visibility and poor air quality in rural and agricultural areas. The paper is well presented. The experimental work is well done and adds new information to a potentially important, but largely unexplored field of biogenic emissions. However, the interpretation or speculation of chemical mechanisms on product formation and the potential impact on brown carbon are in my view not very solid.

- 3.1** The authors propose that the dimer dihydro indigo dye is formed by recombination of two alkyl radicals. At ambient concentrations of indole oxygen would add on much faster than such a recombination of alkyl radicals. The authors may estimate if this mechanism is at all possible at the high concentrations of the experiments. In case of dihydro indoxyl red formation the authors suggest a reaction of the 3-oxindole alkyl radical with indole. As indole is present at really high concentrations this might be an option. However, in both cases such reactions might only be possible in their smog chamber due to the high concentrations. They are most probably not relevant at all for the ambient atmosphere.

This is an excellent point. We have revised Figure 9 to eliminate reactions that would require recombination of two carbon-centered radicals. We have also added a reference to Healy et al. (2012) that discussed a related mechanism of oligomerization in naphthalene oxidation, which was interpreted by efficient reaction of two resonance-stabilized free radicals. Finally, we added a paragraph to the end of section 4.1 intended to emphasize the tentative nature of the outlined mechanism.

- 3.2** In Figure 9b, do the authors believe that anthranilic acid and isatin react in the gas phase to tryptanthrin? Such complex non-radical reactions are very slow.

Indeed, the reaction would be very slow in the gas phase. We therefore suspect it should occur in the particle-phase. We have added a statement in the paper suggesting that some of the products may result from particle-phase chemistry (even though we cannot directly prove it with our data). The new text appears in the last paragraph of section 4.1.

- 3.3** Similarly, the oxidation of isatin is formally the addition of two OH radicals or H₂O₂. Mechanistically, it is quite difficult to imagine this happening in the gas phase. Novotna did the experiments in dichloromethane solution, a fairly different chemical environment. Both of these proposed mechanisms are very speculative and would need further support by literature data or experiments. As already mentioned many products might only have been formed due to the high concentrations used in these experiments. This makes it difficult to extrapolate the results to the real atmosphere.

Indeed, the processes in the Novotna et al. experiments in dichloromethane took longer time compared to the timescale of chamber reaction in aerosol, and it is not obvious whether they would occur any faster under chamber conditions. We therefore view the proposed explanation for the formation of this particular chromophore as tentative, and acknowledge this in the revised version.

3.4 Furthermore, the airshed model includes a reaction of indole to indigo dye, which then partitions into the aerosol. As far as I understand all reacted indole ends up in indigo dye and contributes to SOA. This is a large overestimation. Indigo dye, which is still very reactive, does also not further react. This is unrealistic and all this leads to a large overestimation of the brown carbon effect. It is not very likely that the SOA from indole has finally such a low degree of oxidation at the modelled aerosol concentrations. The reaction time or OH exposure in these experiments was rather low, only 2-3 hours of ambient background OH exposure. Further oxidation reactions would break the chromophore at some point and decrease the brown carbon effect. The paper does not convincingly demonstrate that the species measured and included in the model are relevant for the ambient. Thus, the paper should include also measurements at lower concentrations and higher OH exposure to demonstrate their relevance.

We have added a statement in the paper that we hope better explains that the choice of the surrogate oxidation product is not too important for this system because most of the products have fairly low volatility. Any of the choices of the surrogate product would suffer from the same issue the reviewer is referring to – many of them can be expected to react further via various aging mechanisms. The indole SOA will indeed continue to age, likely in a very interesting way. We have not explored OH-driven aging or photolysis-driven aging of indole SOA in this study but we fully intend to do so in a follow up work. At present time it is hard for us to estimate the effect of the increased OH exposure but we are getting an oxidation flow reactor soon that will make such experiments possible.

We also agree that experiments at lower concentrations would be more environmentally relevant. The choice of concentration for this initial study was high because we were concerned about getting sufficient signal-to-noise ratio in mass spectrometry and UV/Vis measurements. Now that we know what to expect we can move to better designed experiments at lower concentrations.

Minor comments:

Page 6, line 17: delete “to the”

Page 7, line 32: Figure S2.3 instead of S2.2

Page 8, line 4: suggesting that. . . (delete “the”)

Page 8, line 29: spectrometer “of”

Page 10, line 31: should be Figure 7

All of these corrections have been made.

Page 8, line 12: the losses should be seen in the PTR-MS

We have reworded the SOA yield discussion to avoid ambiguities

Figure 7: did the authors check the retention time with authentic standards? This would strongly support their assignment

We were not able to get authentic standards in time for this experimental campaign. Fortunately, the optical absorption spectra are sufficiently complex and coincidence in peaks in the absorption spectra with the corresponding peaks of the reported standards is in our opinion quite convincing.

Figure 8: replace ingigo by indigo

Corrected

Figure S2.1: Why does indole still decrease after lights off?

When we collect the sample we allow make up air to enter the chamber and dilute its content. The indole

would not decrease if we were not collecting. We added a note to the caption of Figure S2.1.

Figure S2.5: m/z 98 and 99 do already continuously increase before light on? Is there really additional formation when light is turned on?

We have elected to remove Figure S2.5 from the SI section and focus on larger PTR-ToF-MS signals, which have less ambiguous interpretation.