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Interactive comment on "Secondary Organic Aerosol from Atmospheric Photooxidation of Indole" *by* Julia Montoya et al.

Anonymous Referee #3

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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. 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. 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. 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. 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

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Discussion paper

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.

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 12: the losses should be seen in the PTR-MS Page 8, line 29: spectrometer "of" Page 10, line 31: should be Figure 7 Figure 7: did the authors check the retention time with authentic standards? This would strongly support their assignment Figure 8: replace ingigo by indigo Figure S2.1: Why does indole still decrease after lights off? 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?

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