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Comment on acp-2021-1081

Anonymous Referee #2

Referee comment on "Non-reversible aging can increase solar absorption in African biomass burning aerosol plumes of intermediate age" by Amie Dobracki et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1081-RC2>, 2022

Review of Dobracki et al.

The authors present an analysis of aerosol optical properties during a selection of flights from the ORACLES field program that indicate that during aging of biomass burning aerosols the organic aerosol is reduced relative to black carbon which results in a decrease in the single-scattering albedo of the aerosol at a mid-visible wavelength. The authors offer a "parameterization" of this dependency between the optical properties and chemical composition. The authors also find that the organic aerosol has a higher ratio of organic mass to organic carbon than is often considered leading to potential for modelling biases/underestimates. They further argue that it is chemical oxidation that is responsible for the loss of organic aerosol as the plume ages.

In my opinion, the manuscript is unsuitable for publication. The authors make quite forceful interpretations from the data, but the claims are not backed by sufficient evidence and so counter-narratives are easily plausible. The flaws in the analysis are not helped by challenging readability (and some errors). Please consider the points made below as grounds for this assessment.

- The title is misleading. The main finding appears to be that OA is lost with age and SSA is found to decrease. But it is the change of the scattering that is seemingly changing the SSA, not a substantial change to the absorption. Even though the authors find the brown carbon contribution to be small, they do note that it decreases with age. Loss of brown carbon absorption, combined with potential reduction in absorption enhancing effects such as lensing, may instead imply that the absorption is actually decreasing across the ages of the plumes discussed as a result of OA loss – the opposite of claimed in the title.
- The conclusions touch on some climate impacts of the findings (e.g. L476-480) and I had hoped that in “Section 7: Radiative implications and inferences” the authors would have actually provided some analysis of the radiative implications of a reduction of scattering aerosol in an absorbing layer. Instead the authors just reported the optical properties of the aerosol, namely SSA and AAE, in relation to chemical properties. Therefore the climate/radiative implication of the findings is not really part of the study at all. The “parameterization” just seems to be the coefficients of a simple linear regression. It is not clear that the specifics of this relationship (namely the fit coefficients) would hold for any other location/scenario. In general, the discussion around nitrate was quite a large part of the manuscript. I could not understand why the discussion of organic versus inorganic nitrate deserved such a focus given the objectives of the paper. Also, if nitrate (inorganic and organic) was so relevant, why then was it not part of the “parameterization”?
- Thermodynamic partitioning: Section 6 aims to prove that the loss of OA cannot be a consequence of repartitioning of semi-volatiles into the gas phase. The authors use NO₃ to make this case but the thermodynamic arguments are superficial and only related to temperature (or altitude) and humidity but ignore major controlling factors such as the nitric acid vapor pressure or the abundance of other acidic or basic species such as sulfate and ammonium. While it is understood and accepted that the flights may not have the full suite of measurements to support thermodynamic modelling, the authors could have at least offered some discussion and/or calculations to at least constrain their assumptions. The use of NO₃ partitioning to constrain the OA partitioning is further flawed by the fact that OA volatility is variable tending to become lower with age (at least along a functionalization pathway suggested by the VK analysis). Hence the use of the vertical profile of nitrate is not conclusive in anchoring the expected altitude dependence of OA (e.g. all else equal) due to partitioning.
- The argument for chemical oxidation being the driver for OA loss is weak. It appears that it is centered around the fact that for roughly constant BC:CO, an increase in f₄₄ coexists with a decrease in OA:BC somehow implying that increased oxidation causes evaporation. The problem with the reasoning is that if oxidation causes loss of OA, then the signature of oxidation would surely be lost along with the OA. Upon functionalization, a decrease in volatility might be expected (e.g. shift from SV-OOA to LV-OOA with associated increase in f₄₄). Although small carboxylic acids could be volatilized and/or eventually react to CO₂, the authors do not make clear what pathway they are actually describing in relation to further oxidation that leads to OA loss - it is left vague. Also, consider the following: if semi-volatiles – with lower f₄₄ – were liberated from a mixture containing low-volatiles – with higher f₄₄ – as a result of gas vapor pressure dilution, then the f₄₄ of the mixture would go up as the OA went down – i.e. the same as observed, but no chemical mechanism required.
- Transport and meteorology: a brief review of visible satellite imagery on the days of the detailed cases (09/24 and 08/31) and the days prior, suggests that terrestrial convective clouds were exerting an influence on the environment over land in the vicinity of the BBA sources and their near-source transport. The authors do not provide

any context and discussion of the potential for prior processing of BBA by clouds. There are a wide variety of BBA sources active at the time of the case flights spanning a very large geographical extent but little depth of analysis is placed on constraining sources. Significant variability in emissions is known to exist for different fuel types and burn conditions and this could explain the variability in OA even for relatively similar BC:CO. The authors use a forecast product but it is not clear why a forecast product is the correct tool to analyze the meteorology/transport of an event in the past – especially since the purpose of the paper is not to analyze the skill of the forecast. The authors discuss transport age and f_{44} as two methods to describe the age of the BBA and use transport age as a filter for selecting the flights (while also documenting some of the shortfalls/limitations of the age estimate) yet the f_{44} data presented in Fig 6 indicates that all the ORACLES data is bounded by the f_{44} of the six hand-picked cases – therefore if f_{44} is a worthy metric of identifying candidate cases, why then the authors restrict themselves just to the six cases? In the two detailed cases, the vertical structure of the plume is linked to the transport age but the authors do not show what that transport pathway looks like. Given that the vertical structure is important for the mechanistic arguments made by the authors, more evidence is needed supporting how that vertical structure connects back to the described meteorology (e.g. AEJ-S, recirculation, subsidence etc). A reader would benefit from seeing this transport pathway in the form of a trajectory (or some other means), at minimum.

- General structure and readability: Many of the sections describing results of the study contain introductory material. This is particularly notable in the Conclusions section where it becomes challenging to actually summarize/assess the work carried out by this study. Conversely, the last part of the Introduction includes some description of the flights and some preliminary discussion. There are some concepts that are given quite a bit of weight (e.g. recirculation and subsidence of aging plumes) but then discounted elsewhere. Some concepts are only introduced in the Conclusions section (e.g. the “Kalahari heat low” makes an initial appearance with no other description of what this is or why it is relevant). Similar on Fig 7 these elemental ratios are captioned as mass ratios while their magnitude (and convention) would suggest they are molar ratios. Some definitions (e.g. OC, AEJ-S) were not introduced during first instance, also some datasets are not introduced in the dataset section (e.g. temperature, RH and wind data shown in the profiles – were these in situ data during the profile or from another means e.g. dropsondes?). Some of the figures have errors (e.g. Fig. 11 IN:BC is listed in the caption but not in the plots) and readability issue (e.g. Figure 4 has scale bars and axes that overlap and the top-left panel is unreadable). In line references to figures do not match the content of the figure (e.g. L137-138 this is not shown in Fig 5). In Fig 6, what are the pink diamonds clustered near the ORACLES data? Fig 12 is mostly a repeat of Fig 11, just with the temperature recast as potential temperature and the RH as water vapor mixing ratio.
- Other inconsistency: Why does the distribution of BC:CO look so different for 08/31/17 all data (Fig 8d) to the same data broken out by f_{44} shown in Fig 9? Even if only the box containing the vast majority of data is considered (f_{44} : 0.21-0.24) it looks quite different to the distribution of the overall. Based on the argument of using cases with constant BC:CO, from Fig 8 this flight would seem to be a perfect choice.