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Interactive comment on "Dilution impacts on smoke aging: Evidence in BBOP data" *by* Anna L. Hodshire et al.

Anonymous Referee #1

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Overall, I find this an interesting paper that addresses an important topic and builds nicely on previous work by the authors. However, I have a number of concerns regarding the inherent assumptions made or implied throughout and how thoroughly they are justified, and regarding the consistency of the interpretations provided. I find there are also a number of areas where more detail is required. I think that this work might be publishable after substantial revision. My specific comments and questions follow below.

L54: It is not clear to me how plume thickness controls gas-particle partitioning or particle coagulation rates. Both depend on concentrations, not thickness. I suggest the authors clarify whether they really mean "thickness" here and on L58.

L65: Do oxidant concentrations not also depend on the composition of the plume?

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Discussion paper

L67: The authors cite Formenti et al. (2003) as support of dilution occurring. However, they might note that the particular conclusion in Formenti et al. (2003) really derives from the observation of a single, high concentration point for the “fresh” samples that controls the linear regression. If that point is excluded, the slopes of the fresh and aged EC vs. OC curves are nearly identical.

L79: Much of this paragraph seems redundant with material already presented. I suggest it be streamlined. The only new information is the slightly greater information regarding coagulation.

L94: I suggest that the authors here define what they mean by “initial.” This is a critical feature of this study. Only later is it clear that "initial" means "the closest we got to the fire for a given flight."

L112: The authors should note the size range of the SP-AMS measurements, and the size range of the SP2 measurements (L126).

L125: The authors might also note that the atomic ratios are strongly affected by mixing of different air masses and the co-oxidation of different VOC precursors, which start at different points on a van Krevelen diagram. Different VOCs in the plumes will age on a variety of timescales, giving rise to an evolving O:C and H:C regardless of “aging” of the sort implied here. Mixing and co-oxidation affect the H:C, especially, making inferences of the “types of reactions occurring” challenging. This is discussed in (Chen et al., 2015). See later comment on the same subject.

L130: The authors note that the supporting info provides “more details on the instruments used.” I find this misleading. The information provided in the SI is extremely limited, hardly greater than that provided in this paragraph. I suggest the authors provide in the SI some discussion at least of instrumental uncertainties.

L138: I suggest it be clarified how f60 and f44 are background corrected. Presumably this is not a straight difference, as the denominators ([OA]) differ. Is it, for example

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f60_corrected = (f60_plume*[OA]_plume – f60_bgd*[OA]_bgd)/[OA]_plume? If the authors used a straight difference, this must be justified as it does not seem appropriate to me. Similarly, more details on how the other intensive properties (O:C, H:C) are corrected are needed.

L140: It would be helpful if in Figs. S2-S6 and S7-S11 the authors would number each plume so that the two can be related to each other. It would also help if the time-series were shown as an additional panel with the spatial plots, again so comparisons can be made. I think this is important because the authors discuss "plumes" here, but they do not discuss how it is, for example, that in a given transect there can be multiple maxima in CO. Does this imply there are two plumes? Or is this the same plume? What drives this behavior, and what might it indicate about the evolution of the plumes? What does it mean to define a "centerline" of the plume if there are clearly two distinct maxima on either side (see Fig. S3, for example).

From Figs. S7-S11, it appears that the background [CO] varies from flight-to-flight. For example, in Fig. S7 the background is clearly lower than the 150 ppb threshold the authors have used, but in Fig. S9 it is barely sufficient. Why not define a flight-specific background [CO] based on the observations?

L156: The authors note that the instruments had various time lags, but it is not clear whether they were all adjusted to account for these varying time lags. This should be clarified. Also, it would be helpful if the authors clarified whether they really mean a "lag" but with a fast response time (i.e., two instruments both show sharp changes but are offset) or whether they are referring to some amount of smearing in which previous measurements affect the current measurement. From the FIMS discussion, it sounds as if they are actually talking about smearing (related to instrument response time) and not a lag.

L165: Further details regarding how the FIMS data were used to establish the centerline are needed. How were the number distributions used specifically? How were these

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determined for different transects to give a single straight line? Also, is wind speed as measured by the aircraft?

Fig. 1: The figure lacks error bars. Given the analysis, it would seem that precision-based propagated uncertainties would be appropriate, as the authors seem interested more in characterizing changes than they are absolute values. I suggest appropriate error bars are added.

L182: While it seems that the 5-15 percentile values are primarily found at the physical edges of the plumes shown in the supplemental, as often as not the 90-100 percentile values exhibit bimodal behavior across a transect, often occurring relatively close to the physical edge. From what is shown, I do not believe it is justified to say that the 90-100 percentile "core" corresponds to the physical "core" of the plume as observed. I strongly suggest the authors to define a quantitative metric to relate the percentiles to the spatial distribution. Perhaps a normalized distance from the centerline.

L191: I suggest the authors be more precise in their claims. The normalized number concentration in the "core" does not change with age, and at the edge the entirety of the change is observed from the first transect to the second. And there is perhaps an increase in diameter from the first transect to the next, but the diameter is constant (within variability) for all transects further downwind. Also, the deltaO/C does not increase with aging. The authors indicate that the delta_f44 changes with age, but it is not clear how this was determined. Was some sort of linear fit done? Is this just the difference between the first point and the last? Visually, the points look scattered about a flat line. Overall, for this discussion I think that the authors need to be more specific and precise and quantitative. As currently written, it is not always clear how the authors came to the conclusions that they did.

L203: I find it exceptionally difficult to understand exactly what the authors have done with the Spearman rank-order correlation tests. The authors need to be much more specific. The authors have one value for (e.g.,) initial plume OA mass but then have

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multiple values for the deltaOA/deltaCO for each transect of a given plume. Then there are multiple plumes. How are the data merged to allow comparison across all plumes? Physical age makes more sense, as (for example) deltaOA/deltaCO can be regressed versus physical age for each plume. But, to me, how the other parameters are used (OA initial and deltaOAinitial) is unclear. Are all the initial OA values repeated for a given flight? Are the authors using only the initial values for the other parameters to compare with initial OA?

L213: What does it mean for something to "evaporate off through heterogeneous aging?" Things can evaporate, or they can be heterogeneously oxidized. These are distinct processes.

L210: The authors note that the changes in deltaOA/deltaCO with aging are small. A recent review by the authors (Hodshire et al., 2019) indicates a variety of reasons for such behavior. Another recent paper (Lim et al., 2019) introduces another potential reason for this behavior, specifically potential biases in the measurement of OA as the particle composition evolves. Have the authors considered this?

With reporting the Spearman's correlation coefficient I suggest the authors use consistent language that links to typical interpretation of the level of significance (that a relationship is monotonic). For example, a value of -0.25 (as determined for f60) might be considered "weak" while a value of 0.54 (for f44) is "moderate." Also, the authors might note when introducing the Spearman's test that it is a test for monotonicity.

There appears to be a good deal of flight-to-flight variability in behavior, from Fig. 2. This raises a question of how much of the inferred behavior (from the Spearman's test) derives from fairly strong changes in one flight. The authors might consider testing the sensitivity to their analysis by determining Spearman's coefficients when systematically leaving out individual flights or transects one at a time. This would give a broader sense of the robustness of the results, given the notable scatter.

L217: Nitpicky, but compounds do not "contain f44." Certain compounds fragment in

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such a way that they show up at m/z 44 in the AMS. But overall this sentence is a run on with a second half that does not logically follow from the first. The sentence starts by talking about a balance between condensation and evaporation but shifts abruptly to note something about heterogeneous oxidation or particle-phase reactions. I suggest the authors clarify the point they are aiming to make here.

L219: The authors note that deltaOA/deltaCO does not change much. This would be consistent with the little mass loss that the authors note from heterogeneous oxidation here, correct? Are the authors aiming to make a point more specifically about the efficiency with which heterogeneous oxidation might degrade the f60 signal and not about mass loss? I find it unclear.

Laboratory observations (Cubison et al., 2011;Hennigan et al., 2011;Hodshire et al., 2019;McClure et al., 2020) have demonstrated that the f60 and f44 of freshly emitted particles vary over large ranges dependent on the fuel type and specific burn condition. Is it not possible that the differences in deltaf60 and deltaf44 between flights result from intrinsic differences in the emitted particle properties? The authors seem to discount this without explicit justification when they state that their interpretation assumes that "emitted deltaf60 and deltaf44 do not correlate with deltaOAinitial." Might there not be an initial correlation, as this might indicate some difference in the burn conditions or the particular fuel mix? I can certainly believe that "evaporation and/or chemistry likely occurred before the time of" the first measurements, however it is not clear to me that the observations as presented here demonstrate this conclusively. Also, given that different sources produce particles that have different initial f60 and f44, would they be expected to exhibit the same deltaf60 and deltaf44 even if initial OA and dilution were identical? Is there evidence that this is expected?

L243: I disagree with the authors interpretation of the van Krevelen diagram here. The authors interpret this in a process based way related to chemistry. However, this does not account for the fact that this is, likely, ultimately a mixing experiment wherein primary OA is being increasingly mixed with secondary OA. This cannot be interpreted in

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terms of functional group addition. Additionally, it is not clear that a plot of deltaO/deltaC vs deltaH/deltaC should behave in the same way as a plot of O/C vs H/C. The authors must demonstrate the equivalency of these.

deltaO/deltaC ratios: I am somewhat surprised that these values are positive. O:C ratios of fresh biomass burning tend to be around 0.3-0.4 whereas O:C of background OA are typically large. (The same is true for f44.) The authors should comment on the very fact that their deltaO/deltaC values are positive.

Eqn. 2: First, what is the justification for this functional form? Is there some other form that would better explain the data? Second, in terms of utility, is it really most useful to predict the delta values, as these will depend explicitly on the background, which may vary between locations? Do the authors expect these relationships will prove robust and applicable to other regions? Would these be appropriate at night as well as during the day? The authors have not been able to distinguish between dilution-driven changes and oxidation-driven changes, so there may be distinct day/night differences? When would they expect them applicable? How could these parameters assist specifically in biomass burning models? Presumably such models would aim to be processed based, differentiating between oxidation and dilution.

When the authors report the Pearson's coefficients, are these constrained to go through the origin? The authors show only the 1-1 lines, but visually it seems that any linear fit to the calculated vs. observed relationship will have a non-zero intercept unless constrained. In this context, having a good r^2 value is simply an indication of a linear relationship but it is not an indication of the goodness of the calculated vs. observed. Instead, the authors would need to provide some metric such as normalized mean bias. As presented, I am not convinced that the r^2 values are particularly meaningful.

L263: It is not clear to me what the authors are getting at when they state that aged deltaf60 and deltaf44 show scatter, limiting the predictive skill of measurements available from BBOP. They had just discussed how there are "moderate goodness of fits." It

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seems now that they are contradicting themselves. Or perhaps they are just providing more context for what “moderate” means.

L273: While the authors state here that highest initial deltaOA generally has the lowest normalized number concentrations, this seems to contradict their near zero Spearman’s coefficient reported in Fig. 2. In fact, the authors state this two lines later. This needs to be revised. Either there is a correlation or there is not.

L276: Is variability in number emissions really “noise?” It seems like an inherent feature.

L278: Does the particle size really increase for “all” plumes, or does it statistically increase when considered across all plumes? There seem to be some lines in the graph that are basically flat when considered individually; thus, I am not certain that the “all” applies.

L280: As mentioned above, have the authors considered other potential artifacts in their deltaOA/deltaCO that might lead to this parameter remaining flat while the apparent particle size increases? I suggest this be discussed in the context of the authors’ conclusion that coagulation drives the size change.

L283: The authors have been assuming that it is acceptable to use as an “initial” OA and particle concentration the value measured in the closest transect for each flight. Given this assumption, it is unclear why the authors now indicate it is essentially inappropriate to estimate an initial particle diameter from the closest transect to use for comparison with the model of Sakamoto et al. (2016). If the assumption is poor for one variable how is it justified that it is okay for two other variables?

Equation 2: What units must the time have?

L290: Nucleation is generally more favorable when existing particle surface area is smaller, as the condensation sink is reduced. Might this also be an explanation for the greater incidence of nucleation near plume edges?

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L294: The authors note that the nucleation mode “appears to be coagulating or evaporating away as the plumes travel downwind.” It would be useful if they show this explicitly in some way. Which figures should the reader look at specifically and which intersects? I find this overall too vague and suggest that it needs to be made more explicit.

L303: Again, does “thicker” here mean “more concentrated”? Thickness, which I would interpret to mean some spatial thickness, is not discussed in this paper as best I can tell. Regardless, the authors cannot conclude that deltaN/deltaCO is lower for “thicker” plumes since their Spearman’s coefficient is essentially zero.

L308: Again, how can the authors rule out differences in the initial conditions that are independent of physical or chemical aging? This seems to be an underlying assumption throughout this entire study, but I do not find that the authors have really justified this assumption. Given how central it is to everything, I strongly suggest that an explicit discussion must be included wherein the authors review the evidence for and against their assumption.

Minor:

L47: It might be more accurate to say that the smoke plumes dilute through entrainment of background air rather than that they dilute and entrain background air.

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