Review of "Dilution impacts on smoke aging: Evidence in BBOP data"

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Anonymous Reviewer

Summary:

This manuscript uses airborne data of wildfire smoke plumes, measured as pseudo-lagrangian transects of the plumes during the 2013 BBOP field campaign. Physical ages of the plumes ranged from approximately 15 minutes to 2-4 hours.

The authors analyze the oxidation state (through f44, f60, O/C, and H/C) as well as mean particle diameter and the OA/CO emission ratio of aerosol in terms of physical plume age and the aerosol's proximity to the plume core. They demonstrate enhanced chemical aging/oxidation at the edges of plumes that they argue is related to enhanced photolysis in more dilute BBOA-containing air.

Only a couple studies have discussed the effects of chemical aging in terms of plume thickness and edge-to-core position. This is a very informative and fascinating approach and is a great use of archived data BBOP data to build upon previous modeling research. The paper is well cited and the figures are generally aesthetically pleasing. Please don't be dismayed by the criticism to follow as I tend to focus on the things that need to be fixed. There are a lot of good observations and analysis in this paper which I don't, but maybe should, highlight.

I believe that many of the conclusions are likely true, however the way the data was analyzed does not always support this and I have made quite a few comments regarding this. In my opinion, a focus should be made on comparisons within transect sets regarding how things evolve with physical age and generalizations of plume cores vs plume edges instead of on bulk regressions (Spearman's correlations) which are not particularly convincing (either low R-values or R-values reflective of outlier data). Additionally, there seems to be a lot of contradicting statements made in interpreting the results. This is potentially a very good and interesting paper relevant to the subject areas of ACP and eventually should be published, but obviously will require significant edits.

General Comments:

1) Figures are aesthetically pleasing but could use some minor changes.
2) Format of citations need to be fixed.
3) There are a lot of typos and issues with word choice which will need to be fixed before final publication.
4) I am curious, how wide were the plumes and how long did it take to fly through them? It seems like you explored whether instrument lags affected your results, but during a

transect did the physical age of the leading the plume edge vary significantly from the edge when you left the plume?

5) I think you can better clarify how you estimate physical age. In the supplementary files, the "core" trajectory is a straight line, presumably because you use a single wind speed and direction, but the core of the transect frequently does not lie on that line. Could this be improved with Hysplit/WRF models? Would that help the core of the transect fall along the dashed line?
6) Data are broken down into physical age and further into fringe-vs-core (such as shown in Figure 1). These data-points represent a range of data subsample in time and space and therefore should include error bars representing the variance in data represented by each data point as well as the measurement uncertainty.
7) Δf60 and Δf44 are known to vary in primary emissions, even in laboratory experiments where nascent soot can be analyzed (i.e. not after 10+ minutes of aging). However, a key assumption in many of the conclusions seems to be that all primary BBOA has the same initial Δf60 and Δf44. This is a problem when the authors try to support their conclusions.
8) The use of Spearman's rank-correlation is fine as you may not expect linearly increasing/decreasing values with physical (or even chemical) age. But it needs to be clearly stated that this is a test of monotonically increasing/decreasing values, which does not give the same predictive interpretations as a Pearson's correlation.

   Interpretation of Spearman's correlation coefficients and the strength of these coefficients, in many cases, do not support the interpretations presented in this work. Part of this is because the authors chose to combine all data from all flights together for the regressions. This means that data representing older physical age of a plume with high initial concentrations is mixed together with data representing young physical age but low concentrations. The result is that there is not a strong relationship between these parameters (e.g. $\Delta N/\Delta CO$) and physical age (or $\Delta OA_{initial}$). If these transects were normalized in some other way, maybe these statements may be more supportive of the conclusions.

9) The supplementary text provides very little additional information. There seems to be some confusion regarding methodology which could be explained in more detail here. I would suggest a cartoon of a flight path showing how you chose your background for a transect.
10) Were all supplementary sections/figures referenced in the text? I lost count.

Specific Comments:

L30: Be more specific about what you mean by "smoke concentrations… aging markers, number, diameter."

L34-35: You state that it is not quantifiable how diluted a plume is when first measured; does this contradict the next statement that (hence) the initially measured (number?) concentration is a proxy for dilution?

L37: Do you mean “increases in oxidative tracers” or that the oxidation-state of OA at the edges was higher?

L44-47: “...rapidly evolve as smoke travels downwind, diluting and entraining background air.” I think you mean that dilution and entrainment can rapidly cause aerosol & vapor evolution, but that is not how it reads.

L49: I think you mean “dilution at time of measurement”.

L54: Does this refer to radiative fluxes?

L 55-57: Please fix the brackets around citations.

L93: Should read “aging and oxidation of OA mass and aerosol number concentration and mean diameter.”

L112: 20-262 nm size range is not ideal, but I guess it is what you have.

L134-135: Also background correct m/z=44 and m/z=60?

L 136: Conceptually, where does the lowest 10% of CO occur? Just outside of the plume as the plane circles back through? Is the background fairly constant for a flight leg? Do you adjust background each time the plane turns around and goes back to transect the plume again?

L137: Is elemental O, H, and C calculated from O/C, H/C & OA or is H/C and O/C calculated from the elemental O, H, C concentrations? Aiken et al (2007) estimate it in the later (Eqn 1).

L 139: Typo (“…, we but do not…”)

L164-165: Sentence grammar

L165-167: Why use the FIMS # distribution to determine plume center? Why not [CO], [mrBC], total number concentration, etc? In the supplemental figures, it says the center-flow is determined by number concentration (not distribution).

L170: Fix heading

L189: Measurement uncertainty should be plotted in Figures (sum of variance in data represented by each data point + uncertainty in each instrumental recording)

L189-190: Changes in f60 and f44 should be provided as fractional (as displayed on axis of Figure 1, etc). Relative changes (%) are confusing.

L192: Replace “number concentration” with either “normalized number concentration” or “$\Delta N_{40\text{-}262\ nm}/\Delta CO$”.

L192: I only see a decrease in $\Delta N_{40\text{-}262\ nm}/\Delta CO$ between ~0.6 and 1.0 hours physical age. Saying that it decreases with age implies a consistent trend. For Dp, this trend is hard to tell if it is statistically significant.

L197: What do you mean by “available …”?

L197-199: Really long sentence. I have had to read it 6-7 times to parse out what is shown.

L200-201: Physical age is the distance between the transect-center to the fire-center divided by the average windspeed? So does 0 physical age imply infinite or 0 windspeed?

L203: The “…correlation coefficients (R) with initial plume OA mass,…” is not shown. Do you mean to say that this is represented by $\Delta OA_{initial}$?

L202-204: Is the Spearman coefficient for concatenation of all data points from all transects? If so, I am not sure it would make sense to do this way. Spearman’s test tests for monotonically increasing/decreasing values. Given that each transect set starts at a different initial value you wouldn’t expect the grouped transect sets to display a strong R-value. If you want to use Spearman’s test in this way, for R_{age} you could normalize each normalized value to the initial normalized value to get a % change and plot that in Figure 2 and relevant supplementary figures.

L206: Spell out “Figs.” And lower case.

L207-208: Type in list “…FIMS measurements AND BACKGROUND and ΔCO percentile spacings…”

L209: Previous line said you would only discuss FIMS, background and ΔCO.

L209-210: $R_{\Delta OA,initial}$ just says 0 in figure.

L209-210: This figure shows orders of magnitude changes in $\Delta OA/\Delta CO$ with age. I think you mean there is not a clear positive or negative trend (as stated in the first clause of the next sentence), not that there is no change.

L212: Here and elsewhwere, spell out “vs.” Check grammar.

L213: For positive R values, consider putting a “+” sign in front of the value.

L214-218: Consider breaking this into multiple, shorter sentences. Check for redundancy with L212-214, i.e. a negative R value means there is a decreasing trend.

L214-218: Is it only evaporation or condensation (phase changes) happening or does O attack volatile and semivolatile species (levoglucosan) changing its molecular composition to more oxidized/refractory species without a phase change?

L218-220: If you didn't expect a change in normalized-OA anyway based on your model, why do you suggest a balance between evaporation particle mass loss and condensation mass gain?

L221: Those are not very strong R values to base your interpretations on, but I wouldn't expect them to be for the reasons discussed above. This statement is not particularly true for f60.

L224: But you just said that Δf60 and Δf44 correlate with $\Delta OA_{initial}$. Differences in your initial Δf60 or Δf44 don't necessary need a mechanistic explanation. We see variance these parameters in fresh emission in laboratory experiments and would expect to also see variance in primary emissions of wildfires. This is not good support for your next conclusion (that aircraft observations are missing evaporation and/or condensation).

L227: Is this logic circular? That differences in $\Delta OA_{initial}$ is due to different emission fluxes?

L228: should not be a comma after the bracket.

L231 & 234: Reference format needs to be changed.

L234: Grammar. Reference to figure in Garofalo should be something like "(Fig. 6 in Garofalo et al, 2019)"

L235-236: Isn't that why you normalize?

L237-239: You imply that patterns of f60 and f44 compared to shortwave irradiance is related by photolysis rates. I don't necessarily agree with this interpretation. If the plume is thicker it means that a higher fraction of aerosol mass is from the fire and because fire-emitted aerosol has higher f60 and lower f44 than background a simple mechanism of mixing explains your observations.

L242-243: $\Delta O/\Delta C$ and f44 are both proxies for OOA and would be expected to have the same trends. $\Delta H/\Delta C$ and f60, while not conceptually the same, both reflect primary BBOA and would also be expected to show the same trends It is a little redundant to analyze both sets.

L242-243: See issues raised earlier regarding interpreting Spearman's test results for these data sets.

L249-264: You should provide explanation for why you used these equations to try and fit f44 and f60. Is there a conceptual justification for them? Do they have meaning outside of a mathematical fit?

L263-268: What do you mean by “Aged Δf60 and Δf44”? Does “limiting the predictive skill” mean that your fits are not particularly informative?

L264-265: typos/grammar

L271-272: The decrease in normalized number concentration with physical age mostly appears to be caused by 2-3 outlier measurements (the initial points for leg 730b edge, the initial value of another edge, and the tailing value of leg 726a 1). This does not seem like a statistically robust claim and I think the R value verifies it. Lines 275-277 seem to agree with my assessment.

L273-274: “generally have lower normalized … by the time of the first measurement”. This implies that there was a measurement made before the first measurement. Please explain.

L273-274: “plume edges and cores with the highest ΔOA generally have lower normalized number concentrations…” This is not true based on figure 2f. The two lowest $\Delta OA_{initial}$ values (white dashed lines) have two of the highest $\Delta N/\Delta CO$ values.

L279: Evaporation (mass loss/time) is, partially, a function of available surface area. Since small particles have a higher surface area-to-volume, it is plausible that evaporation will decrease the number of small particles more than large particles and therefore increase the mean particle size. You state this possibility of preferential loss of small particles on lines 293-295.

L282-283: should be R_P^2 instead of $R^2_{P.}$

L282-283: you were previously using R and not R^2 (L272, Fig 2, etc). In my opinion, this is fine and depends on how you use them, but I have been reviewed differently. Did you intend to calculate R and R2? Please check to make sure that you they are used and calculated correctly. I only state this because there are a number of typos in the manuscript and want to make sure that this is not one.

L287: Do you mean “legs” instead of “days”?

L294: Replace “~” with “approximately”

L301-302: As mentioned above, I do not agree that the data supports the statement regarding correlation. I think there is a lot of good analysis in this paper and I don’t think you need to make this statement.

L302-304: I also do not agree that the data supports the statement regarding $\Delta N/\Delta CO$.

L304: You don't need to keep specifying that diameter size range of 40-262.

L306-308: I don't like saying this, I don't agree that your data support this statement. The only way that differences in $\Delta f44_{initial}$, $\Delta f60_{initial}$ and $\Delta O/C_{initial}$ support this statement is if all primary OA from all wildfires have the same value which has been shown to not be true.

Figure 1: Change "BC" to "rBC" in the legend and axis. Also in Figures S14-S18

Figure 1: Change $\Delta N/\Delta CO$ to $\Delta N_{40\text{-}262\ nm}/\Delta CO$ to be consistent with text.

Figure 2: Caption should be "function of physical age"

Figure 2: This figure is pretty confusing. If I look at Figure S2, I see that for leg 726a there were 2 sets of transects with each comprising of 4 transects. So, theoretically, the same air mass was sampled 4 times corresponding to 4 different physical ages. So a line in figure 2 contains ~4 data points which correspond with either the edge or core of a transect in the transect set? Am I reading this correct?

How does the white dashed line in 2a go backwards in physical age?

Figure 2: Change to $R_{\Delta OA,initial}$ instead of double subscript to be consistent with that used in text.

Figure S1: I don't see a black star or dashed line.

Figure S1: Leg number not indicated. ("The numbers are the leg number")

Figure S1: I would suggest that you use a different symbol and symbol color for the MODIS thermal anomalies so that it contrasts with the color code of the # concentration.

Figure S1: Please change the colorcode to a color-blind friendly one.

Figure S5: Is the black star the fire center for 8/9/2013 or 8/8/2013? The caption does not say what symbol is used for 8/8/2013, only that "The black star indicates the approximate center of the fire…"

Figure S24-S25: The y-axis scale changes between graphs, with a wide range for data that do not look like they have much variation (leg 730a) and a smaller range for others (730b). Is this why there is not consistent patterns in 730a and 730b?

Figure S26: is shortwave irradiance a measure of photo-chemical rate, the amount of scattering/absorbing aerosol above you, or a combination of both?

Figure S27: Please complete the drawing of the Van Krevelen diagram with the 1:1, 2:1, and 0.5:1 lines.