

Response to Anonymous Referee #1

To facilitate review of the referee comments, author responses, and substantial changes to the manuscript, we utilize the following scheme:

Referee comments

Author response

Text additions in block quotes

Text deletions in block quotes

Overview: I find this manuscript to be well written and logically organized. The manuscript describes particle chemical compositional changes measured downwind of two prescribed fire smoke plumes in SE US over 1.5 and 5 hours, respectively. As these measurements are difficult to obtain and there are very few such measurements reported in current literature, this manuscript is both timely and appropriate material for ACP. The manuscript should be published with attention paid to the following minor issues.

We thank the reviewer for these words of support and for the subsequent thoughtful comments, which we have addressed to the best of our ability.

1.) IE's given have units of "ions/molecule".

We thank the reviewer for this note and have added these units to the revised document.

2.) The paragraph about using no gas-phase correction in the AMS data analysis for CO₂ is incorrect and misleading. It needs to be removed or rewritten. The standard AMS analysis directly incorporates a standard CO₂ correction, as it is an important correction, in the fragmentation tables. Please see Allan et al., 2004. It is possible that the intent of the authors was to suggest that differences in gas phase CO₂ concentrations in and out of plume were insignificant, or that the constant pressure inlet reduced gas phase CO₂ concentrations below relevant signal levels, both of which might be true. However, since the authors present total OA, f44, and O:C measurements, all of which can be dramatically impacted by incorrect gas-phase CO₂ corrections, the authors need to clear this issue up.

We thank the reviewer for this comment. The speculation is correct: we did include the standard AMS analysis CO₂ correction but did not explicitly account for the measured CO₂ value. We have re-written this text as the following:

"While we obtained simultaneous measurements of gas-phase CO₂, we ~~have not corrected our data for any potential interference with the signal at m/z 44 (CO₂⁺) in the AMS~~ utilized the standard correction in the fragmentation table from Allan et al. (2004), rather than explicit corrections for CO₂ to account for differences within and without of the plume."

3.) In order to limit the size of this manuscript, Section 2.2.4 should be removed, unless the data in directly used in the manuscript, which I cannot seem to find.

We had originally included this description, since we presented some data in an earlier version of the manuscript derived from the AFTIR that indicated that the plume was photochemically active. We have since removed that figure but retained this text as it described complementary measurements collected during this campaign. Since both reviewers feel that this section is unnecessary, we have deleted the text for Section 2.2.4.

4.) In addition to (3) above, the discussion of Lagrangian or non-Lagrangian could be removed, as again while the data points are duly marked and the description and intent is clear, the differences in L or non-L data points appear to be never discussed or utilized in any way to suggest the differences are important. If the authors' decide to keep this in, then it would be important to at least describe how they differ or why they do not differ.

Our discussion of Lagrangian and non-Lagrangian is a remnant from earlier gas-phase analysis (e.g., Akagi et al., 2013) as this methodology provides some insight to downwind changes due to photochemistry and is not affected by dilution; however, this is complicated for the particle phase since dilution can induce evaporation. Hence, the distinction of data as "Lagrangian" or "non-Lagrangian" no longer has clear or relevant implications. Thus, we have deleted this paragraph and updated the figures accordingly.

5.) One must assume that the significance level assumed in the manuscript for the statistical tests is 0.05. It should be included.

We thank the reviewer for this comment as the assumed significance level is a critical piece of information that we mistakenly excluded from the submitted manuscript. To rectify this, we have added the following text to the second paragraph in the Results and Discussion section, which provides a basic overview of Figures 2-5 (e.g., what boxes and whiskers represent, how error bars were generated):

"To assess whether differences near the source and downwind are statistically significant, we conducted unpaired t-tests. When the corresponding two-tailed p value ≤ 0.05 , we consider the results to be significantly different; conversely, if the p value > 0.05 , we infer that there is no significant difference."

6.) Page 1968 line 22 appears to have the incorrect trend stated, which should read "f60 (Fig. 4c) is significantly lower downwind than at the source: : :"

We thank the reviewer for identifying this error, which has been corrected in the revised draft.

7.) Page 1970 line 10 "decrease" should be "increase".

We thank the reviewer for identifying this error, which has been corrected in the revised draft.

8.) The discussion of O:C and H:C in the same paragraph ends by comparing the trends in changing O:C and H:C downwind with the same trends that were demonstrated for thermal denuded OA. What is left unstated is that these same trends are also true for SOA formation. Can refer to Kroll et al., 2011. Thus, by chemical changes alone, this connection is a bit misleading. It needs to be paired with the decreasing OA loadings to suggest that dilution/evaporation may dominate. Part of the issue here is that the H:C typically goes down with increasing oxidation, as more H's are lost than C's, an explanation that was not included by the authors when attempting to describe why the H:C does not go up with dilution of higher H:C background aerosol.

We thank the reviewer for this comment, as our discussion was perhaps a bit misleading, or at the least, incomplete. We have added text to clarify and have paired this with the observed decrease in OA loading, per the reviewer's suggestion:

“For both fires, the average background H:C ratio was roughly 15% greater than the H:C at the source; downwind H:C values were mostly within the source variability. As the plumes were transported downwind and mixed with background OA, based on measured dilution rates we expected H:C to have increased toward the background values on a 2- to 3-hour timescale if it were a conserved tracer. The lack of a clear decrease increase with time since emission in both experiments suggests either that loss of both H and C occurred in the plume, or increases in C occurred without corresponding addition of H that would maintain the H:C observed at the source. Typically, H:C decreases with increasing oxidation (Heald et al., 2010).

For O:C, about half the downwind values were higher than could be explained by measured variability at the source, and the background OA had O:C within (but at the lower end) of the range at the source. Dilution with background air was thus expected to have had little impact on O:C if O:C were a conserved tracer. Like m/z 44, O:C could have increased with time if photochemical production and condensation of high O:C species or photochemical aging of aerosol had occurred (Kroll et al., 2011).

However, the observed decreases in $NEMR_{OA}$ (whether statistically significant or not) suggests that changes in H:C and O:C may potentially be induced by a solely physical process (i.e., if C were lost from the aerosol phase by preferential evaporation of species that had lower O:C than the average observed at the source). In fact, Huffman et al. (2009b) demonstrated that O:C increased and H:C decreased with increasing evaporation of bulk OA in biomass burning emissions during thermodenuder experiments. Hence, evaporative transformations may be difficult to differentiate from oxidative transformations.”

9.) Given the decrease in measured OA over the short time frames, it is definitely tempting to implicate dilution/evaporation over photochemical oxidation, though photochemical oxidation processes may also reduce the amount of OA in time. However, as the authors’ note, it is not necessarily clear how much of a role photochemical oxidation may have affected the observations. The authors give due time and effort to model the OA measurements as if dilution/evaporation was the only significant process in section 3.2. However, previous work by (some of) these authors reported observations of photochemical activity for these same biomass burning plumes (page 1967 lines 4-6). Why did the authors not try to at least quantify potential photochemical oxidation effects, especially if they might be predicted to be small?

We did, at one point, attempt to quantify these effects via a coupled gas-particle partitioning/ photochemistry box model to predict $NEMR_{OA}$, f_{60} , and f_{44} . Model results suggested that the upper bound prediction of SOA is roughly 30% of total excess OA after 5.5 hours. However, this result may be highly uncertain due to the required assumptions related to SOA precursor concentrations, SOA yields, inferred initial OH concentration, etc. Moreover, when testing this model against different data sets (from other airborne campaigns investigating biomass burning OA), it could not reproduce cases where the downwind $NEMR_{OA}$ increased (DeCarlo et al., 2008; Vakkari et al., 2014; Yokelson et al., 2009), so uncertainties and assumptions with this model appeared to be problematic. Ultimately, we decided to exclude this model and its results from our manuscript. Future work by Matt Alvarado and Chantelle Lonsdale will focus on the modeling of our OA data using the Aerosol Simulation Program (Alvarado and Prinn, 2009).

10.) Page 1972 line 14. “with decreasing plume-integrated COA” should probably read “with decreasing total measured (not background subtracted) COA”.

Per the reviewer’s suggestion, we have modified this text as follows:

“...with decreasing ~~plume-integrated~~ total measured (i.e., not background-corrected) C_{OA} ”

11.) Page 1973 lines 21-24. The authors switch from the discussion of how dilution/evaporation may dominate the biomass burning particle processes during downwind advection and appear to make a more concrete conclusion here and only here in the conclusions, suggesting that not only does the dilution-driven evaporation dominate over photochemical oxidation, but it happens in the first hour, after which the “OA in the plume reaches an equilibrium state with the background in our observations.” It is not clear where this additional information is presented in the results and discussion sections. On page 1967 at the end of section 3.0, the authors note that after 1.5 h from emission, no statistically-significant detectable change was observed in NEMR_OA for either of the two downwind burns. The authors’ should clearly discuss this statement, the associated uncertainties, and the underlying assumptions prior to the conclusions section.

We thank the reviewer for raising this issue since, as written, it lacks the clarification as stated in the comment.

“Our observations and model simulations suggest that dilution-driven evaporation out of the particle phase dominates over condensation of semi-volatile material into the particle phase over roughly the first two ~~one~~ hours of transport during the FJ 9b fire. ~~after which T~~ After this, the OA in the plume reached an apparent ~~equilibrium~~ steady-state with the background in our observations, as there is no net change to NEMR_{OA} (i.e., there is no obvious dilution-driven evaporation or SOA production); thus, OA can be predicted with a simple gas-particle partitioning model. For the Francis Marion fire, ~~due to limited downwind data~~, we cannot draw a similar conclusion ~~from the Francis Marion fire~~ with any certainty due to limited downwind data.”

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