

Response to William Morgan

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

Reviewer comments

Author response

Text additions in block quotes

Text deletions in block quotes

The manuscript is well written and adds to the relatively scarce number of observations of fresh smoke plumes and their subsequent evolution. This is a timely and helpful addition to the literature, given the somewhat conflicting nature of previous observations. The manuscript adds insights into the potential drivers of the transformation of organic aerosol in the initial stages of smoke plume evolution, which is appropriate for ACP. The manuscript is suitable for publication once some issues with the data analysis have been cleared up and some minor issues have been addressed.

We thank the reviewer for his praise of our manuscript and thoughtful comments, which we have addressed individually below.

P1955, L19-20: The authors suggest that ‘increases in f44 are typically interpreted as indicating chemical production of SOA’ – I would say that typically, increases in f44 are thought to ‘typically’ indicate aging of SOA, rather than formation. It can be indicative of formation. I would suggest clarifying the text here.

Per the reviewer’s suggestion, we have replaced “production” with “aging”.

P1957, L21-26: Is it really necessary to say that this is the first study to use that combination of instruments, especially when most of them have little or no use in this manuscript? If it is necessary, a sentence to illustrate why would be useful. At the moment it just seems like unnecessary boasting.

We have modified the text to read “The SCREAM campaign combined simultaneous aircraft...”

Section 2.1: It would be useful to include the typical altitudes for the sampling e.g. at what altitude was the close-to-source sampling conducted and what altitude was the downwind sampling conducted? Approximately how old was the initial smoke that was sampled close-to-source? This is useful context for both this manuscript and future studies that will likely cite this work.

The reviewer raises two valid points in this comment, both of which we have addressed in the text. To respond to the first point, we moved from Section 2.3 to Section 2.1 with text related to smoke age added for clarification, while the response to the latter point is a combination of text moved from Section 2.3 and additional text added for clarification.

On smoke age we added:

“For consistency with May et al. (2014), we defined “near-source” samples as those collected within 5 km of the fire (always less than 30 minutes of aging, but most of the smoke had an age < 10 minutes based on average ambient wind speed), while downwind samples were those collected at distances greater than 5 km.”

On sampling altitude we clarify:

“The first 1-2 hours of flight time was typically spent sampling near the source at ~100-600 m altitude. Following this characterization period, it was possible to sample smoke downwind with 1-2 hours of atmospheric aging, so we then alternated downwind cross-plume samples with occasional additional source sampling. A challenge was that emissions were rapidly diluted and mixed within the boundary layer (within roughly 30 min downwind), and the plumes did not penetrate into the free troposphere, so visual tracking of the plumes was difficult. In fact, the flight path was guided via consultation with real-time instrument output, which enabled the identification of plume center and extent as well as the marking of way points. Furthermore, the plume from the FJ 22b fire entered restricted air space near Columbia, SC, so it was only possible to follow this plume for a short distance from the point of emission.

Downwind, the Twin Otter typically flew at altitudes between 500 m and 1500 m, but not with sufficient detail to develop vertical profiles. All data, regardless of sampling altitude (or latitude/longitude), are categorized as “within the plume” or “outside of the plume” along with the additional distinction of “estimated time since emission” (please refer to Section 2.3.1).”

P1960, L6: What does ‘adjusted’ mean in this context? Was the data simply averaged to the AMS time base or were the time series shifted to account for differences in inlet and/or instrument lag times? If so, how was this done?

In our analysis, we adjusted times via the latter approach suggested by the reviewer and subsequently integrated the peaks; we did not average any data to the AMS time base. We have noted this change in the text:

“For consistency, all data were adjusted to the same timestamp via alignment of peaks (thus accounting for differences in both instrument clocks and instrument response times), which we defined from HR-ToF-AMS.”

Section 2.2.1: The uncertainties relating to the AMS collection efficiency (CE) should be expanded on here and a discussion of how they may affect the latter analysis should be included.

It is not clear how appropriate the Middlebrook et al. CE calculator is for aerosol that is dominated by organic material (such as biomass burning). As the authors are aware, there is a large range of AMS CE values (approx. 0.5 to 1.0) reported in the literature for biomass burning aerosol, which can introduce an additional uncertainty of a factor of two. Was an external measurement available during SCREAM that could be used to validate the AMS CE calculation? Furthermore, do the authors have any insights from their prior biomass burning datasets that may help to validate the use of this procedure?

As the reviewer states, there is a large range of AMS CE reported for biomass burning aerosol. Unfortunately, there was no external measurement available that might validate our AMS CE calculation as the only instruments deployed on the aircraft were an AMS, an SP2, an AFTIR, and a fraction collector for water-soluble compounds.

Rather than assume a value based on literature, we elected to utilize the empirical calculator. Furthermore, in these samples, we are dealing with both in-plume and out-of-plume aerosol. While the CE for biomass burning emissions (as derived from laboratory data) may vary from 0.5 to 1.0 based on the literature (Hennigan et al., 2011; Heringa et al., 2011; Weimer et al., 2008), the general consensus for ambient aerosol is a CE = 0.5. Since the smoke plumes are mixing with ambient air, it is likely that the

CE will evolve over time due to the mixing of smoke aerosol with regional background aerosol. Hence, we feel that calculating CE is more appropriate than applying different CE to in-plume and out-of-plume data.

To address the potential uncertainty of an “unvalidated” CE based on the Middlebrook et al. (2012) calculator, we have added a similar line of text to that in the May et al. (2014) paper which focused solely on primary emissions from this aircraft campaign (as well as another aircraft campaign and a laboratory campaign):

“As stated in May et al. (2014), our results are potentially biased by up to a factor of two due to the inherent uncertainty in our estimation of CE.”

The authors refer to May et al. (2014) for further details regarding the AMS data quality assurance for the inorganic species and I see that they have made fairly typical adjustments to the fragmentation table for nitrate and sulphate ions. Given that the Middlebrook et al. CE calculator evaluates the CE depending on the contribution of the inorganic species, I wonder how much impact any composition changes in the plumes downwind will impact on the CE? Does nitrate form in the plumes downwind and does this impact the CE? Does the acidity of the aerosol evolve downwind (this requires careful and uncertain analysis of the ammonium contribution also, which is challenging for biomass burning aerosol with the AMS)? Discussion of these issues is required and how the uncertainty in the CE may impact the reported significance of the observed trends downwind should be included in the revised manuscript.

While the reviewer raises very good points in this comment, we cannot fully respond to these points in the revised manuscript. We have made no attempts to quantify the evolution of aerosol acidity. At one point, we did attempt to investigate nitrate aerosol formation downwind for comparison with AMS data as part of a modeling study focused on gas-phase chemistry, but this never progressed beyond preliminary efforts. Ultimately, we chose to focus solely on OA for this work.

However, as the reviewer notes, changes in composition downwind may impact the CE, which further supports our choice of using the composition-dependent CE calculator, as this likely provides a more robust estimate than the arbitrary assumption that $CE = 0.5$ or $CE = 1$, based on prior work.

P1961, L1: Clarify that with no particle time-of-flight data being collected, no size resolved information is available from the AMS.

We have added this clarification per the reviewer’s suggestion as follows:

“During operation, data were exclusively collected using the “V-mode” of the ion time-of-flight within the mass spectrometer; since no particle time-of-flight data were collected, no size-resolved information is available.”

P1961, L3-L11: As noted by Referee #1, this is misleading regarding the CO₂ correction for the AMS.

As described in the response to Referee #1, we have modified this text as follows:

“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.”

Section 2.2.4: As noted by Referee #1, is this section necessary?

As noted in the response to Referee #1, we have removed this text.

P1966, L15: Is it appropriate to call these ‘Lagrangian’? This assumes that the fire characteristics and emissions are fixed over the time span between sampling the initial smoke and its subsequent evolution downwind. Do the measurements support this (the manuscript suggests not on P1966, L25)? Just flying along the plume does not guarantee this given that the speed of the aircraft and the speed by which the smoke is transported is not synchronised. I would suggest changing the terminology here or better defending this classification.

The discussion of Lagrangian versus non-Lagrangian originally followed the discussion of the gas-phase data presented in Akagi et al. (2013). However, based on the reviewer comments and discussion among co-authors, we no longer feel that this distinction is appropriate. We have deleted the paragraph in question and have updated figures accordingly.

P1967, L25-28: This framework was also demonstrated in a partner paper to the Ng et al. (2010) paper in Morgan et al. (2010), which should be referenced here. The reference is included below.

Morgan, W. T., Allan, J. D., Bower, K. N., Highwood, E. J., Liu, D., McMeeking, G. R., : : : Coe, H. (2010). Airborne measurements of the spatial distribution of aerosol chemical composition across Europe and evolution of the organic fraction. *Atmospheric Chemistry and Physics*, 10(8), 4065–4083. <http://doi.org/10.5194/acp-10-4065-2010>.

We have added the reviewer’s reference.

P1968, L2: This is a somewhat confusing definition of f₄₄ for those unfamiliar with the AMS, as it suggests that C₄₄ is the mass concentration of particulate CO₂⁺. While this is correct as far as the AMS fragmentation pattern is concerned, the CO₂⁺ particulate signal is thought to arise due to decarboxylation on the vaporiser surface, rather than carbon dioxide being present in the actual aerosol sample. This should be clarified in the revised manuscript.

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

“C₄₄ is the mass concentration of particulate CO₂⁺, which is likely due to decarboxylation on the vaporizer surface rather than CO₂ molecules being present in the aerosol sample”

Figure 1: I suggest using a more colour-blind friendly scale on these flight tracks. Panel a) is particularly difficult to judge the differences. Color Brewer (<http://colorbrewer2.org/>) is a very useful resource for colour-blind friendly scales.

We have modified the color scale in this figure to a “yellow-hot” scheme rather than “rainbow” that appears to be color-blind friendly. If our new scheme is still problematic, we encourage the reviewer to follow up with us regarding this.

Figure 2: There is a seemingly large variation in the emission factors for CO and CO₂ in these figures. What do the authors attribute this to and how does it affect the interpretation of the results?

The total variation in EF_{CO_2} is only about 5%, but the total variation in EF_{CO} is closer to 50%. Since the EF_{CO} values should ideally be conserved with aging, the variation in EF_{CO} likely arises from three sources: a) lower S:N in the excess CO measurement by CRDS for CO than for CO₂, b) imperfect mixing of the source smoke so that even pseudo-Lagrangian (retaining this argument here since it is applicable to gas-phase data) samples can be impacted to some extent by spatial variability in smoke composition near the source, or c) excess CO₂ values (10s of ppmv) that are small compared to the background (~400 ppmv). Since OA and CO emissions are both from smoldering and should be somewhat correlated, the lack of correlation between the NEMR for OA/CO and EF_{CO} suggests the variation is mainly the higher noise in the CO measurement. The average downwind value is not significantly different from the source average so no bias is indicated. It is possible that source variability is larger than indicated by the box-whisper plot, but those measurements were made at higher concentrations with more S:N than downwind so we have retained the estimate of source variability based on source samples in our analysis. However, given that only the reported EF have substantial noise (e.g., Figure 2c-d, Figure 3c-d, Figure 6), we speculate that argument c) may be the primary driver of this variability. Ultimately, we do not feel that these variations affect our interpretation of results.

Figure 6: There appears to be significant overlap between the near-source and downwind data for FJ 9b and Francis Marion fires. What do the authors attribute this to? As noted previously, it would be useful to include more details regarding the near-source samples.

The overlap to which the reviewer has referred is also apparent in Figures 2 and 3. Based on these figures, it is likely that the largest factor contributing to this is source variability. For example, the interquartile range for the FJ 9b fire is roughly $10 \mu\text{g m}^{-3} \text{ppmv-CO}^{-1}$ while it is roughly $15 \mu\text{g m}^{-3} \text{ppmv-CO}^{-1}$ for the Francis Marion fire. Furthermore, our statistical test suggests that there is no significant difference between the near-source and downwind NEMR_{OA} data for the Francis Marion fire, so it is not surprising that when converted to OA concentration, these data overlap.

The sampling details do contribute to this figure showing OA loading and the corresponding emission factor. The main point of this figure is that on average, a laboratory-derived parameterization of the impact of dilution on the gas-particle partitioning can reproduce the EF_{OA} observed for real-world (prescribed) fires, within measurement/model uncertainty, for both near-source and downwind data at different loadings. Variability in near-source data arises due to proximity to the source and to the center of the plume as well as the smoke production rate.

References:

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