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 CO_2 correction but did not explicitly account for the measured CO_2 value. We have re-written this text as the following:

"While we obtained simultaneous measurements of gas-phase CO_2, we ~~have not corrected our data for any potential interference with the signal at m/z 44 (CO_2^+) in the AMS~~ utilized the standard correction in the fragmentation table from Allan et al. (2004), rather than explicit corrections for CO_2 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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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 CO_2, we ~~have not corrected our data for any potential interference with the signal at m/z 44 (CO_2^+) in the AMS~~ utilized the standard correction in

the fragmentation table from Allan et al. (2004), rather than explicit corrections for CO_2 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:

"C_{44} is the mass concentration of particulate CO_2^+, which is likely due to decarboxylation on the vaporizer surface rather than CO_2 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_{CO2} 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 CO_2, 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 CO_2 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 $\mu g\ m^{-3}$ ppmv-CO^{-1} while it is roughly 15 $\mu g\ m^{-3}$ 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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Observations and Analysis of Organic Aerosol Evolution in Some Prescribed Fire Smoke Plumes

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Abstract

Open biomass burning is a significant source of primary air pollutants such as particulate matter (PM) and non-methane organic gases (NMOG). However, the physical and chemical atmospheric processing of these emissions during transport is poorly understood. Atmospheric transformations of biomass burning emissions have been investigated in environmental chambers, but there have been limited opportunities to investigate these transformations in the atmosphere. In this study, we deployed a suite of real-time instrumentation on a Twin Otter aircraft to sample smoke from prescribed fires in South Carolina, conducting measurements at both the source and downwind to characterize smoke evolution with atmospheric aging. Organic aerosol (OA) within the smoke plumes was quantified using an Aerosol Mass Spectrometer (AMS), along with refractory black carbon (rBC) using a Single Particle Soot Photometer and carbon monoxide (CO) and carbon dioxide (CO_2) using a Cavity Ring-Down Spectrometer. During the two fires for which we were able to obtain aerosol aging data, normalized excess mixing ratios and "export factors" of conserved species (rBC, CO, CO_2) ~~were unchanged~~suggested that changes in emissions at the source did not account for most of the differences observed in samples ~~with~~of increasing ~~sample~~ age. Investigation of AMS mass fragments indicated that the in-plume fractional contribution ($f_{m/z}$) to OA of the primary fragment (m/z 60) decreased downwind, while the fractional contribution of the secondary fragment (m/z 44) increased. Increases in f_{44} are typically interpreted as indicating chemical ~~production~~ aging of ~~secondary~~ OA ~~(SOA)~~. Likewise, we observed an increase in the O:C elemental ratio downwind, which is usually associated with aerosol aging. However, the rapid mixing of these plumes into the background air suggests that these chemical transformations may be attributable to the different volatilities of the compounds that fragment to these m/z in the AMS. The gas-particle

partitioning behavior of the bulk OA observed during the study was consistent with the predictions from a parameterization developed for open biomass burning emissions in the laboratory. Furthermore, we observed no statistically-significant increase in total organic mass with atmospheric transport. Hence, our results suggest that dilution-driven evaporation likely dominated over chemical production of SOA within our smoke plumes, likely due to the fast dilution and limited aging times (< ~5 hr) that we could sample.

1. Introduction

Open biomass burning is estimated to be the largest contributor on a global scale to atmospheric fine carbonaceous particulate matter (PM) (Bond et al., 2013) and the second largest contributor to atmospheric non-methane organic gases (NMOG) (Akagi et al., 2011). Substantial research has been focused on characterizing gas- and particle-phase primary emissions from biomass burning and the development of emission inventories (Akagi et al., 2011; Burling et al., 2010, 2011; Christian et al., 2003; Hosseini et al., 2013; May et al., 2014; McMeeking et al., 2009; Reid et al., 2005; Urbanski, 2013; Urbanski et al., 2011; Watson et al., 2011; van der Werf et al., 2010; Wiedinmyer et al., 2006, 2011; Yokelson et al., 2013a). These emissions are ultimately integrated into chemical transport models used to predict regional air quality and global climate impacts.

Organic aerosol (OA) species represent the major component by mass in the submicron carbonaceous PM emitted from fires (May et al., 2014; McMeeking et al., 2009; Reid et al., 2005). In general, the physical and chemical evolution of biomass-burning-derived OA in the atmosphere after emission is poorly understood, in part ~~since~~ because OA is a "metastable intermediate" (Donahue et al., 2013). Since OA consists of thousands of species with a spectrum of temperature-dependent saturation vapor pressures, the portion of OA that is observable as PM

varies with dilution and with atmospheric temperature. Further, many of the species comprising OA have been shown to undergo oxidation reactions, forming secondary products with their own range of volatilities. In field studies, OA in biomass burning plumes has been observed to be enhanced, be depleted, or remain constant with time after emission (Akagi et al., 2012; Capes et al., 2008; Cubison et al., 2011; DeCarlo et al., 2008; Jolleys et al., 2012; Vakkari et al., 2014; Yokelson et al., 2009), but due to the complexities described above, attribution of these transformations to specific physical and chemical processes is difficult (Heilman et al., 2014).

Laboratory studies have been conducted to attempt to separate these processes for biomass-burning-derived OA. As part of the third Fire Lab at Missoula Experiment (FLAME-III), May et al. (2013) derived a volatility distribution and related thermodynamic parameters representative of the primary emissions from all of the biomass fuels studied. In that same study, Hennigan et al. (2011) and Ortega et al. (2013) investigated chemical transformations of the emissions using an environmental chamber and a potential aerosol mass chamber, respectively. Results from both chambers demonstrated that the OA mass can be enhanced, depleted, or remain roughly constant with oxidation, similar to field measurements, yet the OA always became apparently more oxidized with photochemical aging, as interpreted from the organic mass fragments measured via online aerosol mass spectrometry.

In this work, we report and interpret observations from the South Carolina fiRe Emissions And Measurements (SCREAM) campaign conducted in October-November 2011 (Akagi et al., 2013, 2014; May et al., 2014; Sullivan et al., 2014). The objectives of SCREAM were to: (1) simulate moderately intense wildfires by conducting prescribed burns at sites with high fuel loadings, ~~to~~ (2) characterize the emissions and develop estimates of emission factors and emission ratios from both ground- and aircraft-based sampling, and (3) ~~to~~ sample plumes

downwind as they evolved during atmospheric transport. We also sampled fires of opportunity during the study. The SCREAM campaign ~~was the first study, to our knowledge, to include~~combined simultaneous aircraft-based online measurements of refractory black carbon (rBC), time-resolved non-refractory sub-micron PM measurements (including OA), and time-resolved water-soluble organic carbon (WSOC) and levoglucosan (LEV) measurements~~;~~, in addition to a suite of gas-phase compounds. Companion papers have reported airborne trace gas emissions (Akagi et al., 2013), ground-based trace gas emissions (Akagi et al., 2014), airborne WSOC and smoke marker emissions (Sullivan et al., 2014), and airborne primary PM emissions (May et al., 2014). This paper focuses on airborne observations of the OA mass concentrations and composition near the source and transformations to OA mass concentration and composition during the first hours of atmospheric transport.

2. Methods

Emissions from five of the seven fires sampled during SCREAM are discussed in this paper. Details including fuel type, area burned, meteorology and stand history were provided by Akagi et al. (2013) and are summarized briefly here. Two of the burns were conducted on the Fort Jackson (FJ) Army Base (located northeast of Columbia, SC) in Blocks 9b (FJ 9b; 34º0'15" N, 80º52'37" W; 1 November 2011) and 22b (FJ 22b; 34º5'4" N, 80º52'16" W; 2 November 2011). These burns occurred in older stands that had not been treated for a number of years, and were intended to simulate wildfires. Fuel inventories indicated that the vegetation comprised primarily of mature longleaf pine (*Pinus palustris*) and loblolly pine (*Pinus taeda*) with some contributions of turkey oak (*Quercus laevis Walter*) and farkleberry (*Vaccinium arboretum Marsh.*). Complementary ground-based measurements of emissions from the FJ burns were reported by

Akagi et al. (2014). The three other sampled fires were designated Georgetown (33°12'9" N, 79°24'6" W; 7 November 2011), Francis Marion (33°12'55" N, 79°28'34" W; 8 November 2011), and Bamberg (33°14'5" N, 80°56'41" W; 10 November 2011), based on the location in SC where the fire occurred. Georgetown and Francis Marion were located in coastal SC, likely burning coastal grasses and longleaf pine understory, respectively, based on in-flight observations. The Bamberg fire, located roughly 80 km due south of the Fort Jackson site in inland SC, was likely comprised of multiple fuel types, including longleaf/loblolly pine understory as well as marsh grasses, based on smoke marker ratio measurements reported in Sullivan et al. (2014).

2.1. Sample Collection

Smoke plumes during SCREAM were sampled via airborne measurements onboard a United States Forest Service DHC-6 Twin Otter aircraft. Sampling strategies and flight tracks are described in prior literature from the SCREAM study (Akagi et al., 2013; May et al., 2014; Sullivan et al., 2014). Fires were initiated in mid-morning, and the aircraft initially sampled the emissions near the source. Following the source characterization period, the downwind plume was sampled to investigate the effect of chemical and physical aging during atmospheric transport. 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 of < 10 minutes based on average ambient wind speed), while downwind samples were those collected at distances greater than 5 km. During flights, there were also periods of out-of-plume background sampling to establish time-dependent background concentrations of the species that were quantified in the plume.

The flight path for the FJ 9b burn is provided in Figure 1 as one example. Figure 1a provides total (i.e., not background-corrected) OA mass concentration (C_{OA}), which was

typically between 3-7 μg m^{-3} (average = 4.6 μg m^{-3}) outside of the plume throughout the sampling domain, with the exception of ~~a band of data collected to the southwest of the fire source~~higher concentrations ~~that is~~ attributable to the smoke plume. Correcting the data for the background OA results in Figure 1b; here, the plume transport is more distinct.

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 ~~E~~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 challenging. 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.

~~During flights~~Downwind, the Twin Otter typically flew at altitudes between 500 m and 1500 m, but not with sufficient detail to ~~. However, as with flight pathes, sampling elevation was not systematic in nature, and we have made no attempt 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).

2.2. Instrumentation

The instrumentation installed on the Twin Otter used to characterize emissions included a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne

Research, Inc.), a Single Particle Soot Photometer (SP2; Droplet Measurement Technologies, Inc.), a Cavity Ring-Down Spectrometer (CRDS; Picarro G2401; Picarro, Inc.), an airborne Fourier-transform infrared spectrometer (AFTIR), a Particle-into-Liquid Sampler/Total Organic Carbon and fraction collector system (Sullivan et al., 2014) and an Aircraft Integrated Meteorological Measuring System (AIMMS-20) probe (Aventech Research, Inc.). The AIMMS-20 provided meteorological data such as three-dimensional wind vectors, three-dimensional position of the aircraft (i.e., latitude, longitude, and altitude), ambient temperature, and ambient relative humidity. All sampling was conducted from a low turbulence inlet (Wilson et al., 2004) followed by a non-rotating Micro Orifice Uniform Deposit Impactor (MOUDI; Marple et al., 1991). The MOUDI was operated such that it served as a PM_1 ~~impactor~~ selecter (i.e., having 50% particle transmission efficiency for particulate matter of 1 μm aerodynamic diameter with a sharpness of 1.08 – particles less than roughly 900 nm will be transmitted with 100% efficiency). ~~For consistency, a~~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~~referenced to the HR-ToF-AMS.

2.2.1. Aerosol Mass Spectrometer

The HR-ToF-AMS (hereafter AMS) characterizes non-refractory sub-micron aerosol by focusing sampled particles through an aerodynamic lens, collecting particles on a thermal vaporizer, ionizing the vaporized particles via electron impaction, and detecting ions (m/z) in the high-resolution time-of-flight mass spectrometer (DeCarlo et al., 2006). Using the ToF-AMS data analysis toolkit SQUIRREL/PIKA (Sueper et al., 2013), aerosol mass concentrations can be reconstructed from the m/z signal; for this study, we fit HR peaks for $m/z \leq 200$. These concentrations are dependent on instrument parameters (e.g., ionization efficiency and vaporizer collection efficiency). Ionization efficiency calibrations were performed with 350 nm ammonium

nitrate particles throughout the campaign, with values ranging from 1.83×10^{-7} to 2.91×10^{-7} ions molecule^{-1}. Composition-dependent collection efficiencies were calculated following the algorithm of Middlebrook et al. (2012), which is now built into the SQUIRREL software, for each AMS sample and ranged from roughly 0.5-0.9, with a campaign-average value of 0.53. We report AMS-derived emissions data of nitrate, sulfate, ammonium, and chloride elsewhere (May et al., 2014). 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 AMS was mounted into National Center for Atmospheric Research GV-type aircraft racks with a pressure-controlled inlet to reduce fluctuations of the pressure within the aerodynamic lens (Bahreini et al., 2008). 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. AMS data were typically collected with a time resolution of 6 seconds (corresponding to a distance of roughly 250-300 m).

While we obtained simultaneous measurements of gas-phase CO_2, we ~~have not corrected our data for any potential interference with the signal at *m*/*z* 44 (CO_2^+) in the AMS.~~utilized the standard correction in the fragmentation table from Allan et al. (2004), rather than explicit corrections for CO_2 to account for differences within and without ~~of~~ the plume. The AMS samples particles roughly 10^7 times more efficiently than the gas-phase. We estimate that on average, our plume OA concentrations are positively biased by 0.0044 ± 0.0019% (both near the source and downwind), our background OA concentrations are positively biased by 0.025 ± 0.021%, and our *m*/*z* 44 measurements are positively biased by 0.20 ± 0.11%, all based on

co-located gas-phase CO_2 measurements. Consequently, we deemed this correction unnecessary as this interference represents < 0.5% of our reported values.

2.2.2. Single Particle Soot Photometer

The SP2 provides operationally-defined rBC mass concentrations via laser-induced incandescence (Stephens et al., 2003; Schwarz et al., 2006). Absorbing material present in particles is heated to its vaporization temperature and emits radiation, which is measured by optical detectors. This approach removes uncertainties due to interferences of artifacts that have been observed during filter-based approaches (Kirchstetter et al., 2004) and excludes the influence of "brown" carbon that can bias optical absorption methods (Andreae and Gelencsér, 2006; Lack et al., 2012), although it has been shown the method responds to some metals. Signal is related to rBC mass via calibration procedures; during SCREAM, calibrations were performed using fullerene soot. Generally, rBC mass concentrations were recorded every 6 seconds, similar to the AMS. Additional details related to the SP2 operation during this campaign can be found in May et al. (2014).

2.2.3. Cavity Ring-Down Spectrometer

A Picarro G2401 provided ~~1~~ 0.5 Hz measurements of CO_2, CO, CH_4, and H_2O, which are the major gas-phase emissions from combustion sources. The CRDS was calibrated in-flight using mixed standards of CO_2/CO/CH_4 and procedures similar to those described by Urbanski (2013). These data were applied to calculate emission ratios and emission factors of particle-phase species, as described below.

~~### 2.2.4. Airborne Fourier-Transform Infrared Spectrometer~~

~~The AFTIR data used and obtained during this study are described in detail by Akagi et al. (2013). "Grab samples" were collected in background air and as the Twin Otter traversed the smoke plume; these samples were held for 2-3 minutes of signal-averaging in order to improve~~

~~sensitivity. Compound mixing ratios were quantified via a non-linear least-squares method for the majority of the identifiable trace gases (Burling et al., 2011; Yokelson et al., 2007); however, nitrogen monoxide (NO) and nitrogen dioxide (NO_2) were quantified by integration of selected peaks in the spectra. These AFTIR data provide complementary results describing gas-phase chemistry that assist the interpretation of particle-phase measurements.~~

2.3. Data Processing

2.3.1 Plume Identification and Age

~~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 challenging. 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.~~ As discussed previously, visual plume identification was challenging. Positive downwind plume intercepts were confirmed through simultaneous spikes in measured values of OA, BC, and CO. These confirmed intercepts were corroborated by simultaneous increases in smoke markers (Sullivan et al., 2014) and trace gases (Akagi et al., 2013). Intercept-averaged concentrations for each transect were derived by integrating the excess area (above background) under the data time series curves and dividing by the elapsed time in the window of integration.

Sample ages (times since emission) were estimated using the distance from the source and mean wind speed. Distance from the source was computed using the haversine formula and the spatial coordinates measured by the AIMMS-20. Mean wind speed was also measured using the AIMMS-20. Akagi et al. (2013) estimated that this approach has an uncertainty of roughly 30%, largely due to uncertainties in the wind speed data. Due to the ~~nature of the flight path~~plume tracking challenges, plume intercepts were rarely ~~occurred~~ perfectly perpendicular to

the plume~~; in fact, they~~ and were often diagonal transects. Thus, a given sample can be associated with a range of estimated ages. In subsequent figures, we plot the average age of a plume intercept along with error bars representing the range of ages; in these figures, we do not include the estimated uncertainty of 30% on this range.

~~This~~ Based on the time since emission ~~calculation~~ we can identify ~~provides a pseudo-Lagrangian estimate of plume~~ samples that were emitted during the time period that we were ~~sampling at the source and thus we have higher confidence in the initial value for theseage, and hence, a downwind samples~~ and they can be termed pseudo-Lagrangian. ~~can be related to emissions measured directly at the source at the appropriate earlier time. Therefore, some of the data we present in figures are labeled "Lagrangian" when we had corresponding source measurements, whereas for others (labeled "non-Lagrangian") we can estimate time since emission based on distance from the source and ambient wind speed but do not have a corresponding source samples. For consistency with May et al. (2014), we defined "near-source" samples as those collected within 5 km of the fire, while downwind samples were those collected at distances greater than 5 km.~~

In-plume data from all research flights were corrected for local background concentrations via integration under the curves in data time series between out-of-plume measurements. The resulting species concentrations are "excess" concentrations and denoted by the delta symbol, i.e., ΔX is the excess concentration of species X. We show background values of some parameters in some of the following figures; these background concentrations represent the median background concentration for the duration of the given flight. Sample background-corrected data are provided in Figure 1.

2.3.2. Excess Emission Ratios and Emission Factors

Normalized excess mixing ratios (NEMR) are often used to account for transient fire behavior and the dilution and mixing of plumes with background air during transport (e.g., Hobbs et al., 2003) and are defined as:

$$NEMR_X = \frac{\Delta X}{\Delta CO} \qquad (1)$$

where ΔX is the excess concentration of species X, and ΔCO is the background-corrected value of CO. Since both numerator and denominator are excess quantities, uncertainties in their values increase as the plume dilutes and in-plume concentrations approach the background concentrations. Here, we report ~~instantaneous~~ plume-integrated $NEMR_X$ for each plume interception, so our values ~~will~~ differ from the "fire-integrated" values (based on consideration of all the plume intercepts) reported in May et al. (May et al., 2014). $NEMR_X$ are reported here in units of μg m^{-3} ppmv-CO^{-1}; this value can be converted to g g-CO^{-1} by multiplying by a factor of 8.7 x 10^{-4} ppmv-CO (μg-CO m^{-3})$^{-1}$. Strictly speaking, $NEMR_X$ is a misnomer for aerosol mass concentrations, but we utilize this terminology for consistency with the vast body of prior literature.

Time series of instantaneous $NEMR_X$ provide information on transient smoke behavior (Jolleys et al., 2014). By associating instantaneous $NEMR_X$ with time since emission, physicochemical transformations can be investigated, since $NEMR_X$ accounts for dilution and thus should be constant with time in the absence of sources or sinks of the species X or changes in the initial emissions. The net formation of secondary organic aerosol (SOA) in smoke plumes can be inferred from an increase in $NEMR_{OA}$ with distance downwind (Yokelson et al., 2009). On the other hand, since OA emitted from biomass burning sources is semi-volatile, net

evaporation of particle-phase mass as dilution proceeds would appear as a decrease in $NEMR_{OA}$ (Akagi et al., 2012).

Emission factors (EF) are widely used descriptors of fire emissions (Ward and Radke, 1993; Andreae and Merlet, 2001). Their calculation relates the mass of X emitted (M_X) to the mass of dry fuel consumed (M_{fuel}). In cases where the mass of fuel consumed is unknown, a carbon mass balance approach can be applied, which relates the change in the concentration of X relative to the background (ΔX; μg m^{-3}) to the excess carbon concentrations (i.e., background-corrected concentrations that have been converted to mg-C m^{-3}) of CO_2, CO, total organic gases (TOG = CH_4 + NMOG), and carbonaceous PM (PM_C):

$$EF_X = \frac{M_X}{M_{fuel}} = \frac{\Delta X}{\Delta CO_2 + \Delta CO + \Delta TOG + \Delta PM_c} f_C \qquad (2)$$

In Equation 2, the term f_C is a conversion factor representing fuel carbon content. Since we lack detailed fuel information, we assume that f_C = 0.50, roughly the average fuel carbon content of southeastern (SE) US coastal plain biomass fuels reported in laboratory studies (Burling et al., 2010; May et al., 2014; McMeeking et al., 2009)[.; we also lack an estimate of]Since [Δ]TOG [in the emissions. Furthermore,]and $\Delta PM_C << (\Delta CO_2 + \Delta CO$[).), Hence,]for convenience we approximate EF_X neglecting both ΔTOG and ΔPM_C, which [may]result[s] in an over-estimate in EF_X of [~]3-[45]% (Yokelson et al., 2013b). Like $NEMR_X$, EF_x are based on excess concentrations and account for dilution, but if an "emission factor" is computed with downwind data, the value obtained reflects [changes in the initial emission factor plus the effect of]any sources or sinks of the originally-emitted species X. Hereafter, we will refer to downwind "emission factors" as "export factors", also denoted as EF_X and calculated from Equation 2; the main distinction is that an export factor describes X downwind from the source, and thus[, except for pseudo-Lagrangian samples] may be

subject to both changes in the emissions as the fire burns and atmospheric transformations. We report EF_X as g or mg kg-dry-fuel^{-1}.

3. Results and Discussion

During the study, only two fires provided adequate downwind aerosol data allowing us to investigate in-plume aerosol physicochemical transformations: the FJ 9b fire and the Francis Marion fire. As mentioned earlier, the plume from the FJ 22b fire entered restricted airspace and could not be pursued. Further, the Georgetown fire was a small fire whose plume rapidly mixed with the background, so downwind ΔOA was small and uncertain; the Bamberg samples represented two distinct fuel types as shown elsewhere (May et al., 2014; Sullivan et al., 2014), making it difficult to distinguish transformations during transport from differences in the sources.

In Figure 2, we present composition data versus estimated time since emission ~~of~~ for the NEMR or EF ~~of~~ for four major components present in the biomass burning smoke sampled for the FJ 9b fire: OA ($NEMR_{OA}$; Figure 2a), rBC ($NEMR_{rBC}$; Figure 2b), CO (EF_{CO}; Figure 2c), and CO_2 (EF_{CO2}; Figure 2d). Data near the source are presented as box-and-whisker plots (25^{th}-75^{th} and 10^{th}-90^{th} percentiles); these data were collected ~~over~~ during roughly 2.5 hours of ~~real-time,~~sampling during which the modified combustion efficiency (MCE) (Ward and Radke, 1993) varied between 0.900 and 0.930, which explains some of the variability in the data. Data up to five hours downwind were obtained and are shown as closed symbols for Lagrangian points, or open symbols for non-Lagrangian data. For downwind samples, vertical errors bars represent estimated measurement uncertainties while horizontal error bars represent the range of estimated plume ages for non-perpendicular plume transects; horizontal error bars do not account for the estimated 30% measurement uncertainty in wind speed. 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.

We expect rBC, CO, and CO_2 to be conserved with transport since they are stable in the atmosphere on the timescales considered here. Indeed, unpaired *t*-tests for the data shown in Figures 2b-d indicate that there was no significant difference ~~between~~ in the average value of these species at the source and downwind (two-tailed *p* values > 0.13). Differences in mean downwind EFs are attributable to measurement uncertainties, including identification of the plume edges, and variability in the combustion ~~phase~~ at the source. ~~Based on the~~Fitting an exponential decay with distance from the source of absolute mixing ratios of CO and CO_2, we infer an average mixing rate (the inverse of the dilution timescale, or the time to decay by 1/e) of 1.6 hr^{-1} during the FJ 9b experiment.

Since OA is reactive and semi-volatile, it is perhaps not surprising that the downwind $NEMR_{OA}$ over 2-5 hr of atmospheric aging is significantly lower than the $NEMR_{OA}$ at the source (Figure 2a; two-tailed *p* value = 0.015), suggesting a net loss of emitted OA via evaporation and/or reaction. As demonstrated by Akagi et al. (2013), the smoke plume was photochemically active, as evident through enhancements of ozone and formaldehyde relative to the source.

Figure 3 is identical to Figure 2 but represents the Francis Marion burn, the only other case with downwind aerosol measurements adequate to assess aging ~~downwind aerosol measurements~~ (here, up to 1.5 hr after emission) ~~and no other known biomass burning emission sources~~. Akagi et al. (2013) inferred photochemical processing was occurring in the Francis Marion plume, based on observed downwind enhancements of ozone and formaldehyde relative to the source. However, unlike the FJ 9b fire, none of the computed downwind NEMR and EF

shown in Fig. 3 were significantly different from the source (all two-tailed p values > 0.32). The background OA concentrations, which we assume contribute to gas-particle partitioning of emitted OA by providing additional absorptive material, were roughly 50% greater during the Francis Marion fire compared to the FJ 9b fire; furthermore, the ~~dilution~~ mixing rate was 20% slower for the Francis Marion plume (1.3 hr^{-1}), and the plume aging was observed over a much shorter time period. These factors would slow the evaporation of emitted OA, and limit the time over which chemical transformations could occur and be observed. Indeed, over the first 1.5 hr after emission, the data for FJ 9b shown in Figure 2 also indicated no statistically-significant ~~detectable~~ change in $NEMR_{OA}$.

3.1. Chemical Transformations of Organic Aerosol

In this section, we investigate chemical transformations of the organic aerosol, fragment evolution (Figure 4), and elemental ratio analyses (Figure 5) ~~utilize~~ using two approaches to ~~investigate chemical transformations of the organic aerosol~~ for ~~the two cases~~both fires with adequate downwind data~~:~~, the FJ 9b and Francis Marion burns~~: fragment evolution (Figure 4) and elemental ratio analyses (Figure 5)~~. Both Ng et al. (2010) and Morgan et al. (2010) demonstrated that "fresh" OA in ambient samples can be distinguished by organic fragment signatures in the mass spectra (e.g., $C_3H_7^+$ at m/z 43), while "aged" OA is more highly oxidized and can be distinguished by a strong contribution of CO_2^+ (m/z 44). The fractional contributions of each of these fragments to the total OA concentration (e.g., f_{44} = C_{44}/C_{OA}, where C_{44} is the mass concentration of particulate CO_2^+, which is likely due to decarboxylation on the vaporizer surface rather than CO_2 molecules being present in the aerosol sample) change with atmospheric aging: f_{43} is expected to decrease and f_{44} to increase.

However, neither Ng et al. (2010) nor Morgan et al. (2010) directly considered the influence of biomass burning. Cubison et al. (2011) and Ortega et al. (2013) thus modified the approach and compared f_{60} and f_{44} to infer photochemical aging of BBOA. Levoglucosan and other anhydrosugars ~~that~~ are ~~combustion~~ pyrolysis products of cellulose, and thus are used as molecular markers for biomass burning emissions (Simoneit et al., 1999; Sullivan et al., 2008); these compounds~~,~~ contribute ~~an be identified~~ to~~in~~ AMS spectra at m/z 60 ($C_2H_4O_2^+$) (Alfarra et al., 2007; Lee et al., 2010). May et al. (2012) and references therein demonstrated that levoglucosan is semi-volatile at ambient conditions~~; hence,~~ and thus m/z 60 ~~is expected to~~could decrease due to evaporation~~e~~ during dilution, if this finding is extrapolated to all ~~anhydrosugars in general~~contributing species. Furthermore, Hennigan et al. (2010) demonstrated that levoglucosan is reactive and chemically decays similar to the hydrocarbon-like (m/z 43) fragments. Thus, f_{60} may change due to both dilution-driven evaporation and photo-oxidation processes.~~Cubison et al. (2011) and Ortega et al. (2013) thus modified the Ng et al. (2010) approach and , compareding f_{60} and f_{44} to infer photochemical aging of BBOA.~~

In Figure 4, we present excess f_{60} (Δf_{60}) and excess f_{44} (Δf_{44}) for the FJ 9b and Francis Marion fires. These excess fragment fractional contributions were computed from background-corrected m/z 60 or m/z 44 mass concentrations by dividing that excess concentration by ΔOA. Thus, as the plume dilutes and becomes less distinguishable from the background, Δf_{60} and Δf_{44} should remain constant if neither preferentially evaporates, reacts, or accumulates within the plume. For the FJ 9b fire, the source-downwind differences for both Δf_{60} (Figure 4a) and Δf_{44} (Figure 4b) are statistically significant (two-tailed p value < 0.0001). For the Francis Marion fire, Δf_{60} (Figure 4c) is significantly lower ~~at the source than~~ downwind than at the source (two-tailed p value < 0.0001), while Δf_{44} (Figure 4d) is significantly higher downwind than at the source

(two-tailed p value = 0.029). The result for Δf_{60} is consistent with Figure 2a; that is, the decrease in Δf_{60} downwind during the FJ 9b fire reflects the decrease in $NEMR_{OA}$. An observed decrease in Δf_{60} with no decrease in OA concentration during the Francis Marion fire may be related to chemical reactions of compounds that fragment to m/z 60 or to differences in the volatility of these compounds compared to the bulk OA. The mechanistic driver of all transformations will be explored below.

The increase in Δf_{44} with plume age for both fires indicates a compositional change toward increasing mass fractional contributions from molecules that fragment to CO_2^+. If only dilution (and hence, evaporation) was occurring in the plumes as they moved downwind, Δf_{44} should be conserved, provided its parent's volatility is similar to that of the bulk of the emitted OA. The observed increase in CO_2^+ in these photochemically-active environments may indicate that production of SOA occurred within the plumes, although there were no statistically-significant increases in the measured downwind $NEMR_{OA}$, as also found in some previous field studies (e.g., Capes et al., 2008; Cubison et al., 2011). On the other hand, this increase could also indicate that the species fragmenting to m/z 44 are relatively less volatile than the bulk OA that evaporates during transport and dilution.

There is experimental evidence investigating chemically-resolved volatility that is consistent with the evaporation of bulk OA resulting in a relative increase in m/z 44 and a relative decrease in m/z 60. Huffman et al. (2009a) demonstrated for ambient samples in two different megacities that, at a given temperature in a thermodenuder, m/z 60 evaporated to a greater extent than the bulk OA, while m/z 44 evaporated to a lesser extent than the bulk OA. While heating OA is technically not the same as diluting OA, the response of OA to increased temperature is analogous to the response of OA to increased dilution. Furthermore, Collier and

Zhang (2013) demonstrated that f_{44} increased with decreasing C_{OA} for vehicle test data in the absence of chemistry and hypothesized that this observation was attributable to preferential evaporation of less-oxidized OA species. Thus, the observed changes during SCREAM in Δf_{44} and Δf_{60} may be due, at least in part, to physical changes occurring as some of the emitted OA is volatilized upon dilution with ambient air.

Another framework for tracking the chemical evolution of OA was suggested by Heald et al. (2010), who proposed the use of elemental ratios (hydrogen to carbon, H:C, and oxygen to carbon, O:C) to describe photochemical aging of OA. Similar to the fragment evolution, with increasing OH exposure, H:C is expected to decrease (e.g., due to hydrogen abstraction reactions) and O:C is expected to increase (e.g., due to oxygen addition to alkyl radicals). In Figure 5 we present the evolution of the elemental ratio of H:C and O:C during atmospheric transport of the biomass burning plumes from both fires; values of the ratios for the average background, out-of-plume ratio for each fire are shown as dotted lines. We assume uncertainties of 31% of O:C and 10% for H:C, based on Aiken et al. (2008).

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.

3.2. Physical Transformations of Organic Aerosol

A net loss of OA due solely to dilution-driven evaporation may thus be consistent with the observations in Figures 2-5. However, we note that we cannot definitively state that no aerosol chemistry has occurred within the plumes as they age. In the following, we assume a priori knowledge that dilution-driven evaporation dominates over chemical processing and explore if the volatility distribution derived by May et al. (2013) for laboratory biomass burning POA can reproduce our airborne observations. If it can, no oxidative chemistry is required to

explain the data, although it is possible that some occurs.~~apply results obtained in prior lab studies of biomass burning emissions to simulate plume evolution to test this assumption.~~

Simulations representing the process of dilution alone are presented in Figure 6, which shows EF_{OA} data (representing the emission factors near the source and export factors downwind) as a function of the total mass concentration of observed organic aerosol (i.e., not background corrected), C_{OA}, for six flights. Model curves were calculated using the following equation (Donahue et al., 2006; Robinson et al., 2010):

$$EF_{OA} = EF_{tot} \sum_i f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (3)$$

where *i* represents arbitrarily-chosen surrogate compounds defined by their saturation concentration (C_i*; related to saturation vapor pressure through the ideal gas law), and f_i is the mass fraction of each species *i* relative to the total emitted organics. The set of f_i and C_i* is referred to as a volatility distribution. Here, we utilize the volatility distribution for emissions from open biomass burning that was proposed by May et al. (2013), which is comprised of surrogate compounds representing seven logarithmically-spaced C_i* bins. C_{OA} represents the total OA concentration (emissions + background).

EF_{tot} is the emission factor of total organics (gas + particle phase) that are constrained by the volatility distribution (here, all material between $C_i^* = 3\text{x}10^{-3}$ μg m^{-3} and $3\text{x}10^{4}$ μg m^{-3}, so this is not equivalent to NMOG), and hence, contribute to gas-particle partitioning; EF_{tot} is likely dominated by biomass-burning-derived organics but may include background semi-volatile organic material that can partition into the particle phase due to the presence of the biomass burning smoke. Values of EF_{tot} were inferred using Equation 3 with measured C_{OA}, calculated EF_{OA} (from Equation 2), and the volatility distribution from May et al. (2013) as inputs for each plume intercept. In Figure 6, the lines represent predictions based on the average EF_{tot} inferred

for each fire, while the shaded areas represent ± one standard deviation in EF_{tot}. Values of EF_{tot} ranged from roughly 2 g kg-fuel^{-1} (Bamberg B) to 12 g kg-fuel^{-1} (FJ 22b); both the FJ 9b and Francis Marion fires had inferred EF_{tot} of roughly 6 g kg-fuel^{-1}. Equation 3 implies that EF_{OA} (regardless of whether this represents an emission factor or export factor) decreases with increasing dilution, due to the physical repartitioning of semi-volatile species.

There are some key assumptions to our use of Equation 3. We assume that the gas-particle partitioning of the OA can be described using a parameterization derived for laboratory fires, even though the OA in our samples has originated from prescribed fires in the field and may be enhanced by background semi-volatile organics. We are also assuming that EF_{tot} is constant in time for a given prescribed fire (i.e., it does not vary due to source variability, mixing with background air, or atmospheric chemistry). Finally, we are inherently assuming that the plume temperature is constant at 298 K, so dilution is the only process affecting gas-particle partitioning. While these assumptions are not strictly true, they should not affect our conclusions significantly on average.

Figures 6a and 6b provide EF_{OA} calculated near the source and downwind for the FJ 9b and Francis Marion fires, respectively. Near-source data from the FJ 22b and Georgetown fires are presented in Figure 6c, and from the Bamberg fires in Figure 6d. Generally, the near-source data for all fires follow the expected trend, exhibiting a decrease in EF_{OA} with decreasing ~~plume-integrated~~ total measured (i.e., not background-corrected) C_{OA}, as would be expected for a semi-volatile tracer with the characteristics summarized by May et al. (2013); 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. ~~-~~ Downwind data (only available for Figures 6a and 6b) also generally follow the trend predicted by Equation 3; indeed, downwind OA concentrations appear to be

lower than predicted, suggesting evaporation of emitted OA dominates over production and condensation of SOA if occurring. Performing a t-test on the inferred EF_{tot} for both the FJ 9b and Francis Marion fires indicates that the differences between near-source and downwind values are not statistically significant (p-value > 0.1), suggesting no observable SOA production from oxidation reactions (e.g., excess OA has reached equilibrium).

We also note that the predictions in Figure 6 are based on a composite volatility distribution that best represented biomass fuels investigated in the laboratory during the FLAME-III study, which has been extrapolated to the field in this study. Also, fire behavior was variable during the several hours over which data were collected, as evident in the MCE variability (Akagi et al., 2013); the emissions of organics has been demonstrated to vary with MCE (May et al., 2014; McMeeking et al., 2009). All data are represented using a single set of model inputs, which does not account for this variability with MCE. While other factors likely play a role, these two are likely to be the most important. Regardless, the differences in OA observed at the source and downwind for these plumes can be explained by a simple model of gas-particle partitioning.

4. Conclusions

In this work, we present field observations of the physicochemical evolution of the organic aerosol present in biomass burning plumes from two prescribed fires in South Carolina. Downwind observations of rBC to CO ratios and emission factors of CO, and CO_2 are not statistically different on average from those at the source. The downwind ratio of OA to CO was significantly lower than at the source ~~during~~ for the fire that we were able to follow downwind for up to five hours of atmospheric aging. ~~, but this~~The downwind OA to CO ratio was not

significantly different downwind for the other fire, which may be related to the much shorter observable atmospheric aging time (~2 hr).

We observed significant differences in downwind ratios of AMS mass fragments thought to be indicative of fresh biomass burning emissions (*m*/*z* 60, which decreased) and more oxidized OA species (*m*/*z* 44, which increased), consistent with prior reported laboratory photo-oxidation experiments. While the observed increases in Δf_{44} (and the O:C ratio) imply the possibility of SOA production within the plume, these observed changes are also consistent with differences in the volatilities of the species fragmenting to *m*/*z* 60 and *m*/*z* 44 relative to the bulk OA, resulting in differences in evaporation as the plume dilutes into background air.

Our observations and model simulations suggest that dilution-driven evaporation out of the particle phase dominateds over condensation of semi-volatile material into the particle phase over roughly the first two hours of transport during the FJ 9b fire. ~~,~~ ~~after which t~~After this, t~~T~~he 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 transformation 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 ~~for the Francis Marion fire~~ with any certainty. The~~is finding~~ decrease in $NEMR_{OA}$ for the FJ 9b fire is consistent with results from previous literature (Akagi et al., 2012; Jolleys et al., 2012, 2015); however, other studies report increases in OA with increasing plume age (DeCarlo et al., 2008; Vakkari et al., 2014; Yokelson et al., 2009). The exact cause of this variability in observations is unclear. These remaining unexplained differences among different field studies highlight the need for additional research on atmospheric physicochemical transformations of biomass burning plumes.

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Figures

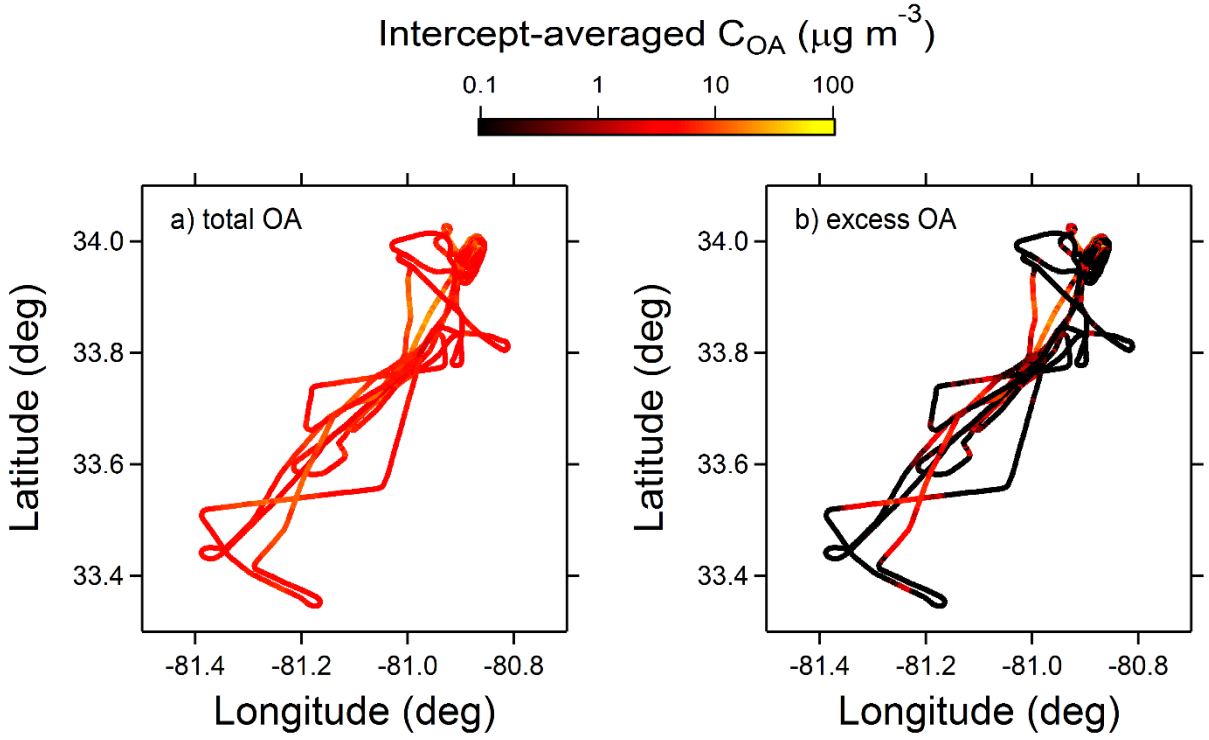


Figure 1.

Flight tracks colored by **a)** total OA concentration and **b)** excess OA concentration. Due to the log-scaling of intercept-averaged concentrations, the minimum value in panel b) is set to 0.1 μg m^{-3}. Removing the background OA elucidates distinct plume transport to the southwest.

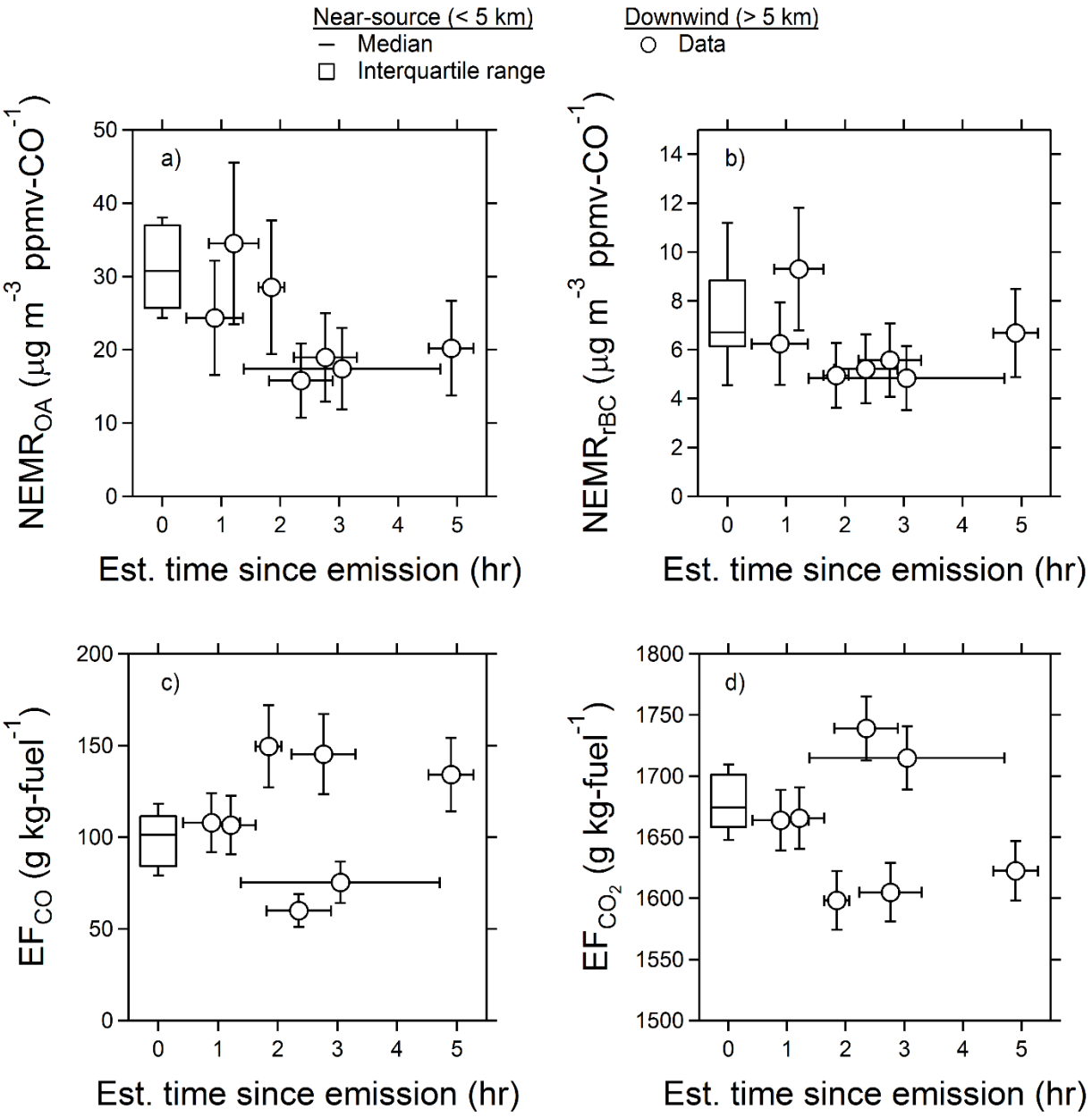
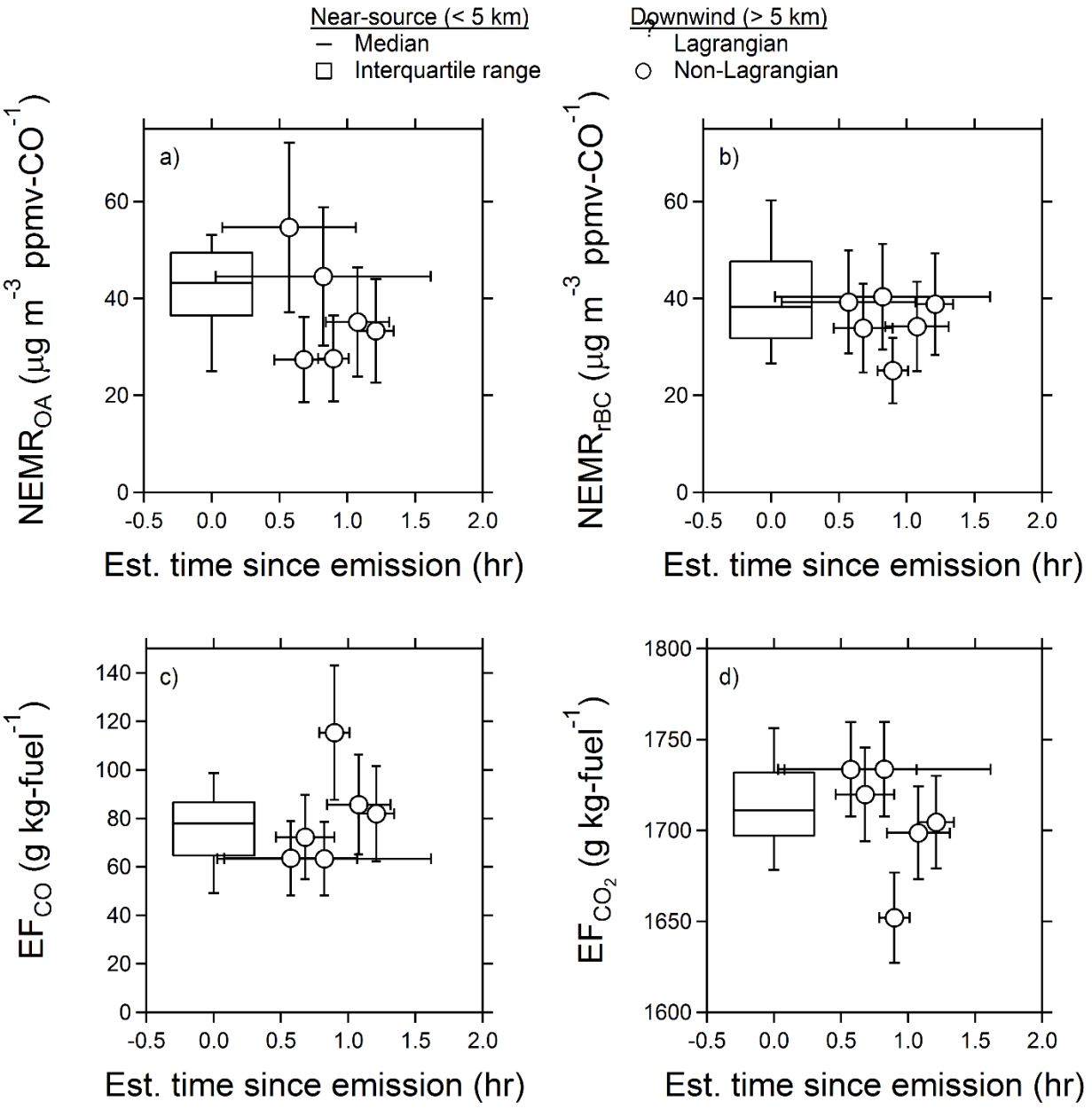


Figure 2.

Near-source and downwind data collected during the FJ 9b prescribed fire. **a)** the ratio of excess OA to CO; **b)** the ratio of excess rBC to CO; **c)** emission/export factor for CO; and **d)** emission/export factor of CO_2. Near-source data are represented by box-and-whisker plots (boxes: 25th and 75th percentiles; whiskers: 10th and 90th percentiles; horizontal lines: median) while downwind data are represented by markers (closed markers: Lagrangian data; open markers: non-Lagrangian data). Error bars associated with the markers indicate range of estimated time since emission (x-direction) and measurement uncertainty (y-direction). Error bars in x direction do not account for estimated 30% accuracy of windspeed.



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868 Figure 3.

869 As in Figure 2, but for the Francis Marion prescribed fire.

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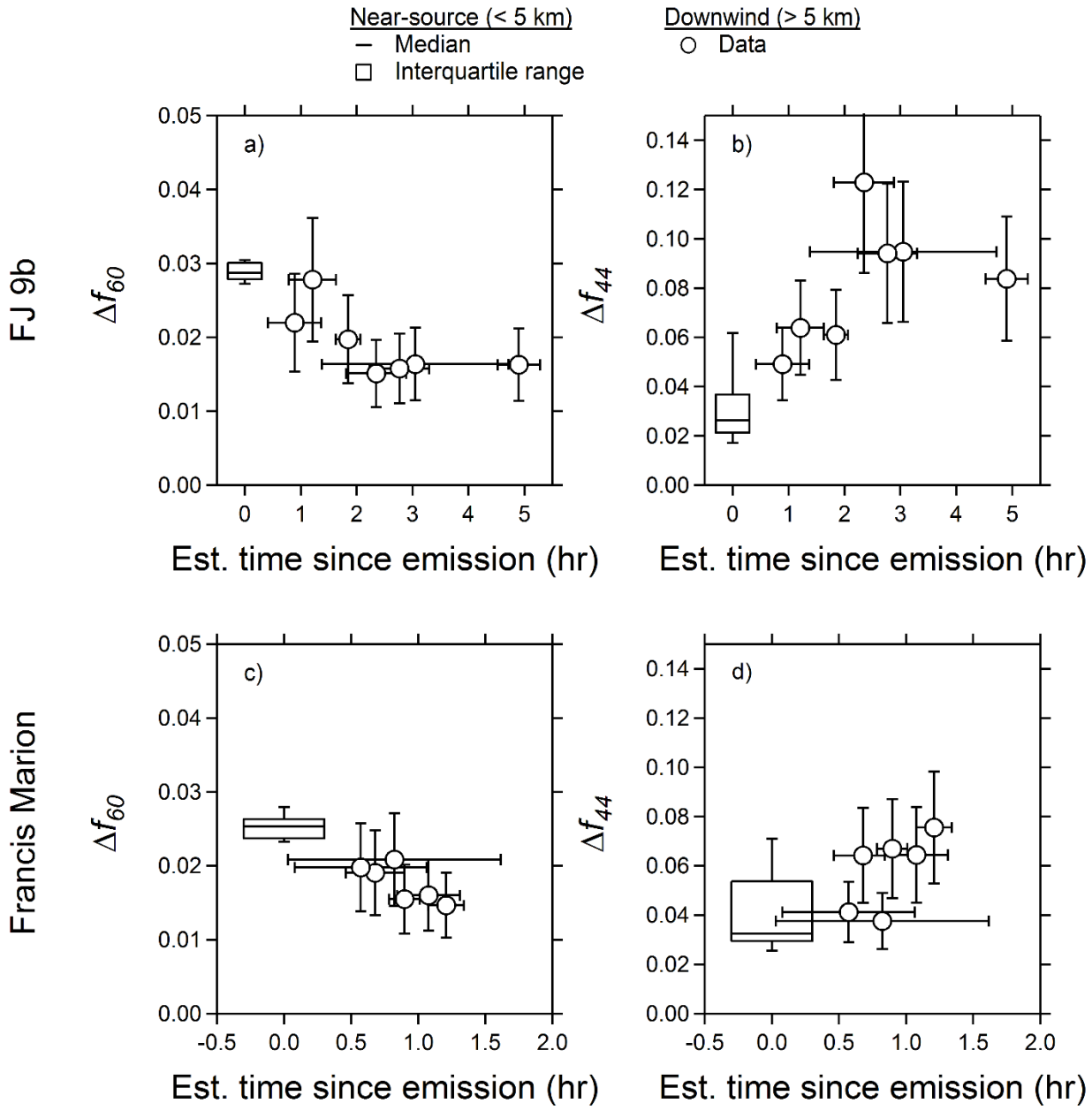

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872 Figure 4.

873 Evolution of background-corrected AMS mass fractions. **a)** Δf_{60} for the FJ 9b fire; **b)** Δf_{44} for the
874 FJ 9b fire; **c)** Δf_{60} for the Francis Marion fire; **d)** Δf_{44} for the Francis Marion fire. In all panels,
875 there is a statistically-significant difference between data collected near the source and
876 downwind. Box-and-whisker plots and markers are identical to those in Figures 2 and 3.
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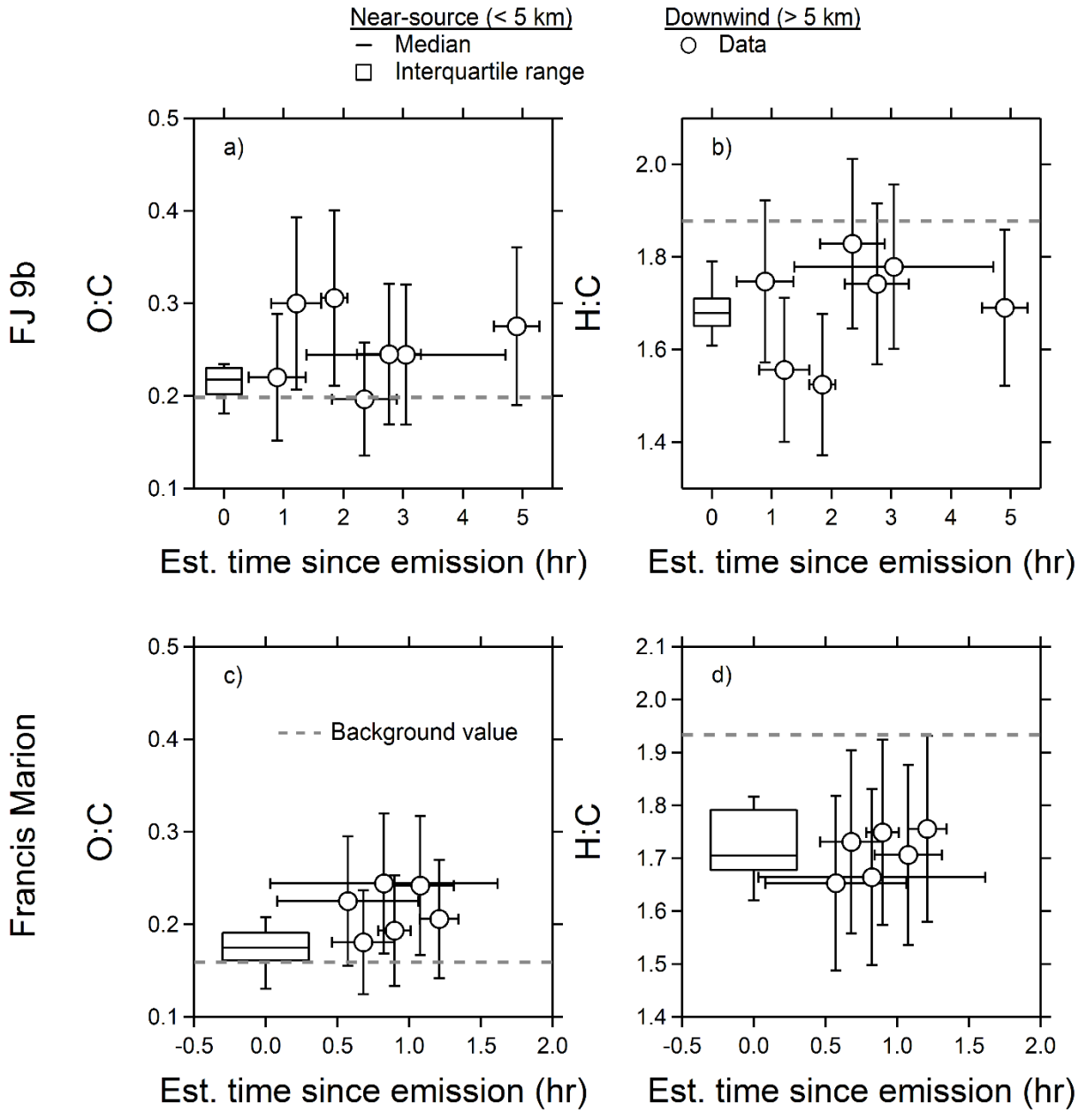

Figure 5.

Evolution of elemental ratios derived from AMS data. **a)** O:C for the FJ 9b fire; **b)** H:C for the FJ 9b fire; **c)** O:C for the Francis Marion fire; **d)** H:C for the Francis Marion fire. For both fires, changes in O:C with increasing estimated time since emission are statistically significant. Dashed line is the value of the parameter in the background measurements outside of plume penetrations. Box-and-whisker plots and markers are identical to those in Figures 2 and 3.

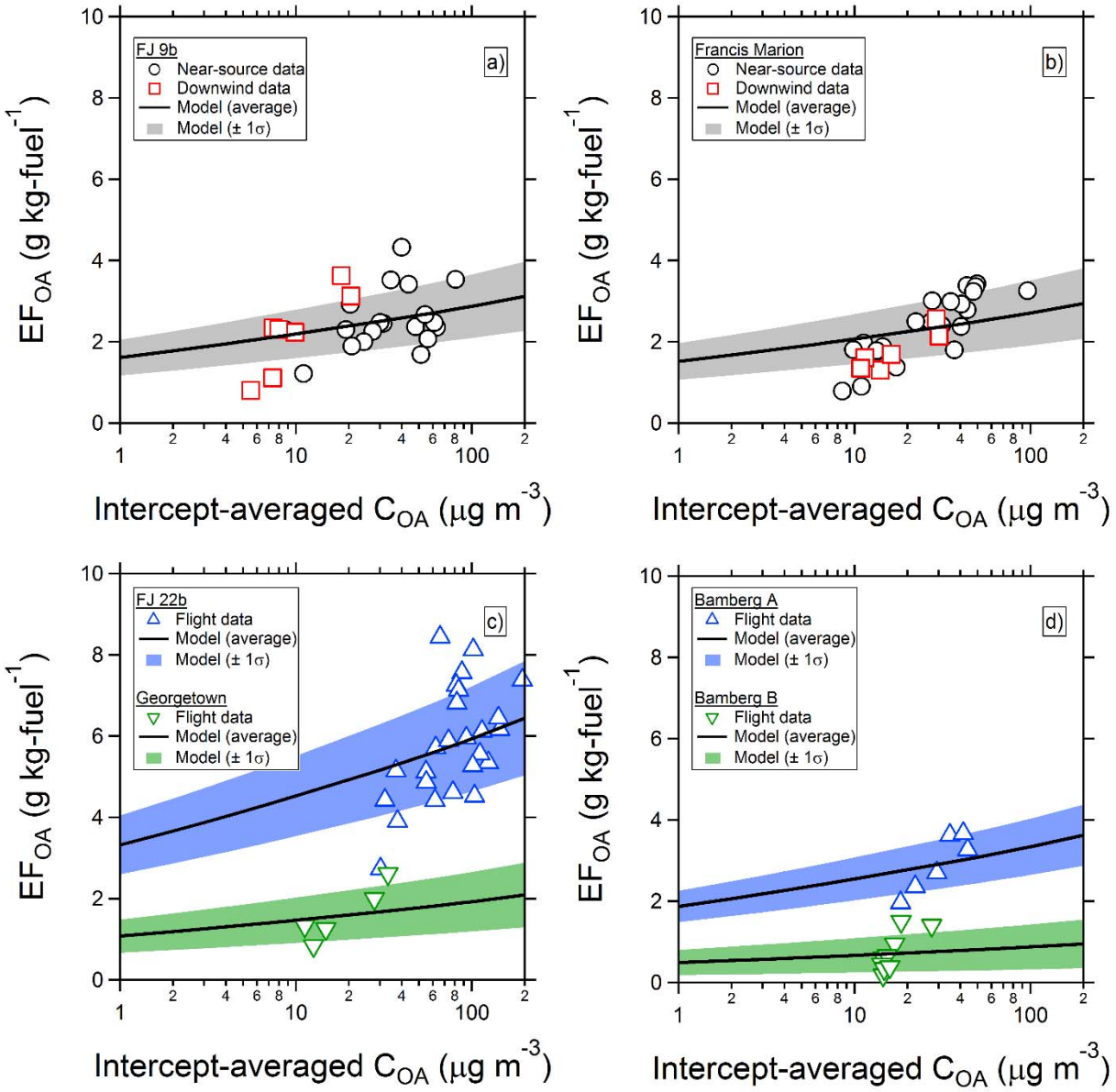

Figure 6.

Changes in the emission factor of excess OA due to gas-particle partitioning as a function of total observed OA. **a)** near-source (circles) and downwind (squares) data for the FJ 9b fire; **b)** near-source (circles) and downwind (squares) data for the Francis Marion fire; **c)** near-source data for the FJ 22b (upward-facing triangles) and Georgetown (downward-facing triangles) fires; and **d)** near-source data for the two fires attributed to the Bamberg site ("A": upward-facing triangles; "B": downward-facing triangles). Curves represent predictions using the laboratory parameterization from May et al. (2013).