

We thank the reviewer for their response in the form of a marked-up pdf manuscript on our third submission. We provide a track changes document and respond here to any specific comments from the review that require a discussion (rather than updating the text). When we refer to line numbers, we will refer to the numbers in the marked-up pdf that the reviewer provided. The line numbers were unfortunately cut off past the one-hundredth place, so for clarity we will refer to page number and the last 2 digits of the line number. We quote reviewer remarks in black text. We will quote original, unaltered text in *pink italics* and new, edited text in red.

The new track-changes manuscript is included at the end of these responses (starting on page 6)

Reviewer response:

"This manuscript provides significant insight into aerosol aging in smoke plumes. However, I suggest revisions because the work needs further data analysis and revision to adequately support their conclusions."

We have enjoyed thinking through and responding to the many scientific issues debated by the anonymous reviewers and editor have brought up over multiple rounds of review. This round of review restates issues that the reviewer had with the previous round of review without building upon or responding to our responses, limiting our ability to further change our analyses.

Page 2 line 55: We do not change our wording (*'Large, thick'* and *'small, thin'*) as we think they are good descriptions of the range of smoke plumes observed.

Page 3, lines 95-96: We agree that some of our initial sentences in the introduction are very similar and have deleted this first sentence to cut down on redundancies.

Page 4, Line 06-07: The reviewer states that they are skeptical of "*The differences in aerosol loading serve as a proxy for differences in initial fire and plume sizes, mass fluxes, and subsequent amount of dilution.*" We hope that the combination of our analyses below and careful language here (that aerosol loading differences serve as a proxy) will bring up similar thoughts and debate within the scientific community. Additionally, we refer to our responses to the reviewer on this topic from earlier rounds of review.

Page 4 line 30: have added temperature

Page 4 line 33: have updated to "Results pertinent to changes in CE due to aging (including physical aging as well as chemical changes including oxidation, coating thickness, and sphericity) in smoke plumes are scarce (see discussion in Kleinman et al., 2020)."

Page 4 line 35: We are using UMR and have added this to the text.

Page 5 line 38: changed

Page 5 line 40: added high-resolution

Page 5 line 58/59: our current text states both the option the reviewer suggested but is also inclusive of e.g. the possibility of downwind sources.

Page 5 line 59: the rest of the paragraph discusses background so we don't think moving this statement will flow well.

Page 5 line 65-66: Original text is "*Mass concentrations of O, H, and C are calculated using the O/C and H/C and OA data from the SP-AMS (assuming all of the OA mass is from O, C, and H)*". The reviewer states that "elemental analysis gives mass concentrations of O, H, C used to calculate O/C, etc". We agree, however the data was provided as O/C and H/C so we had to back-calculate O and C and H. The reviewer also notes that OA mass could have a contribution from N and S, and we now acknowledge this.

Page 6 line 73: The reviewer asks on equation 2 "Why not just use $mz60_{in}$ minus $mz60_{out}$ ".

$$\Delta f = \frac{(f_{in} * OA_{in}) - (f_{out} * OA_{out})}{\Delta OA} \quad \text{Eq. 2}$$

We have access to f and OA , and so found the mass concentrations of the different mz values as the product of $f * OA$.

Page 6 line 76: The reviewer has multiple comments here,

1) Won't "lowest 10%" be more closely related to the amount of time spent in the plume vs out of the smoke plume?

Could you spend <10% our of the smoke plume and therefore your bkgd would be influenced by smoke?

This is true that less than 10% of the time could have been spent out of smoke. Visual inspection of the data collected during the flights (e.g number concentrations Figs S7-S11) indicate that this is almost certainly not the case however. As well, the lowest 10% of CO data fell under the 150 threshold.

2) Check why Figure 2 shows data for DeltaCO 5-15%

Our percentile bins are for Delta(CO) for within the data deemed "in plume" whereas our thresholds are for absolute CO. This is stated in line 74 of page 6, and we include absolute on line 76 to help keep variables straight in the reader's mind.

Page 6 line 96: There was an unnecessary space in the link. Fixed now.

Page 6 line 97: updated

Page 6 line 99-00: Text states *“The FIMS also showed additional smearing in flushing smoky air with cleaner air when exiting the plume with maximum observed flushing timescales around 30 seconds”*

The reviewer wrote

Not sure what “flushing” means? Does this refer to the residence time of air in the FIMS? Do Aerosols have a longer residence time than air?

We have changed to *“The FIMS also showed additional smearing in when transitioning from high concentrations to lower concentrations with maximum observed lags of around 30 seconds behind CO decreases.”*

And

Shouldn't this be the same for high particle concentration air replacing clean air? (referring to “observed flushing timescales around 30 s”)

Yes, we were puzzled by this as well, as the residence time in an instrument should cause the same lag when concentrations are increasing or decreasing. However, this is not what we observed (concentrations rose and peaked in step with CO, but lagged only when concentrations were decreasing) implying some non-linear process in the instrument or tubing.

Page 7 line 18: There was no previous note for BC (it is highlighted on page 5 but not commented on).

Page 7 line 25: The reviewer has highlighted the last portion of *“Note that in Figure 1 (and Figures S14-S18), the points represent the mean values for each transect/percentile and do not include error bars for uncertainty in the mean or measurement uncertainty as characterization of systematic variance (within plume percentiles) with age is beyond the scope of this study.”*

And comments:

without characterization of statistical uncertainty, there is no way of verifying trends in data with physical age or b/w core/intermediat/edge sections of the individual plumes!

We have addressed this concern in detail in our previous responses to reviewer comments. The reviewer has not discussed anything in our response specifically, so we defer to our prior responses.

Page 7 lines 28-30: We think the location of this statement is reasonable given the structure of the paragraph. We have clarified the 4 bins by changing the text to *“edges, intermediate outer and intermediate inner regions, and the core”*

Page 8 line 41: We cannot systematically characterize the variability between the transects, which could yield further insight if we could.

Page 8 lines 57-60: Our text here is

We note that $\Delta OA_{initial}$ does not actually represent the true initial emitted OA from each fire, but instead serves as a proxy for the general fire size, intensity, and emission rate (as larger fires and fires with faster rates of fuel consumption per area will have larger mass fluxes than smaller fires or fires with less fuel consumption per area, all else equal).

The reviewer states

I think this may be a big assumption. Emission factors (e.g. mass_CO/mass_fuel) can vary greatly (Akagi 2011, ACP). (*CO was not a great example)

In our second round of reviews, we discussed emissions factors in great detail, included in R4 and R53. We refer to these detailed responses, but in short, we showed that the variability due to fire size and dilution spans a much larger range than emission factors to the point where emission-factor variability will be in the noise of OA concentration variability due to fuel-burn rates, fire size, and dilution rates. The reviewer has not provided new arguments for us to discuss, and we hope that the community will take up this debate and work to prove or disprove our hypotheses that are supported by this one data set.

Page 9 line 73: The reviewer highlights our first mention of Spearman rank-order correlation tests and states:

This series of analysis does not make any sense to perform when the data are compiled in this way (all single transects together).

It is not expected to show any power and doesn't.

My suggestion is to remove the spearman test. Figure 2 is mildly informative and can stay.

Defn: Spearman Rank-Order Correlation Test.

- 1) convert x/y values to rank_x/rank_y
- 2) pearson's correlation rank_y vs rank_x

We have responded to the reviewer's concerns about the Spearman tests in the 2nd round of reviews, comment R5. The reviewer does not appear to be responding to our prior response but is instead restating their original comments. We understand that the reviewer does not agree with this approach but are unsure what further discussion to present to continue this dialogue.

Page 9 line 91-92: We discussed in round 2 of reviewers why we did the multivariate analysis and why we did not normalize for $\Delta OA_{initial}$, including responses to R5, R4, R52. The reviewer is

not responding to arguments in our prior responses, and is restating their prior comment. We refer to our prior responses.

Page 10 lines 18-21: the heterogeneous chemistry calculation is a quick estimate that is detailed thoroughly in the SI. It is not meant to be a major part of our analysis and we do not think that it needs to be detailed in the methods.

Page 10 line 28: the reviewer doesn't provide a citation(s) for this comment, and we are unsure how to alter the text based on it.

Page 10 lines 34-35: The reviewer highlights *“The relative variability in the OA emission factor is much smaller than the relative variability in $\Delta OA_{initial}$, and other factors contributing to variability in $\Delta OA_{initial}$ will negate an emissions-based covariance between $\Delta OA_{initial}$ with Δf_{60} and Δf_{44} .”*

And comments

Logical flaw:

Variability in $\Delta OA_{initial}$ could be b/c of fuel emission factors and atmospheric processes, e.g. dilution, condensation, evaporation.

If OA fuel emission factors is relatively constant, then the variability in $\Delta OA_{initial}$ (by exclusion) has to do with atm. processes. These processes likely do influence f_{60} and f_{44} , which is stated in Garofalo et al, Lee et al, and in this manuscript.

In R4 of the previous round, we provided 2.5 pages that discussed multiple lines of reasoning as to why emission factors cannot be a significant driver of >2 orders-of-magnitude variability in $\Delta OA_{initial}$. The reviewer is not addressing or acknowledging any of our points/analysis in this response but rather restates their earlier comment. We discuss earlier in the results, “While our observed $\Delta OA_{initial}$ in Figure 2 spans nearly a factor of 100, Andreae (2019) shows that the OA emission factors have a -1σ to $+1\sigma$ range of around a factor 3.” From this work, OA fuel emission factors are relatively constant compared to the variability in $\Delta OA_{initial}$.

Page 13 line 15-16: We note that this statement is for lower normalized number, not total number.

Dilution impacts on smoke aging: Evidence in BBOP data

Anna L. Hodshire¹, Emily Ramnarine¹, Ali Akherati², Matthew L. Alvarado³, Delphine K. Farmer⁴, Shantanu H. Jathar², Sonia M. Kreidenweis¹, Chantelle R. Lonsdale³, Timothy B. Onasch⁵, Stephen R. Springston⁶, Jian Wang^{6,a}, Yang Wang^{7,b}, Lawrence I. Kleinman⁶, Arthur J. Sedlacek III⁶, Jeffrey R. Pierce¹

¹Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, United States

²Department of Mechanical Engineering, Colorado State University, Fort Collins, CO 80523, United States

³Atmospheric and Environmental Research, Inc., Lexington, MA 02421, United States

⁴Department of Chemistry, Colorado State University, Fort Collins, CO 80523, United States

⁵Aerodyne Research Inc., Billerica, MA 01821, United States

⁶Environmental and Climate Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, United States

⁷Center for Aerosol Science and Engineering, Washington University, St. Louis, MO 63130, United States

^aNow at Center for Aerosol Science and Engineering, Washington University, St. Louis, MO 63130, United States

^bNow at Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409, United States

Correspondence to: Anna L. Hodshire (Anna.Hodshire@colostate.edu)

Abstract. Biomass burning emits vapors and aerosols into the atmosphere that can rapidly evolve as smoke plumes travel downwind and dilute, affecting climate- and health-relevant properties of the smoke. To date, theory has been unable to explain observed variability in smoke evolution. Here, we use observational data from the BBOP field campaign and show that initial smoke organic aerosol mass concentrations can help predict changes in smoke aerosol aging markers, number concentration, and number-mean diameter between 40-262 nm. Because initial field measurements of plumes are generally >10 minutes downwind, smaller plumes will have already undergone substantial dilution relative to larger plumes and have lower concentrations of smoke species at these observations closest to the fire. The extent to which dilution has occurred prior to the first observation is not a directly measurable quantity. We show that initial observed plume concentrations can serve as a rough indicator of the extent of dilution prior to the first measurement, which impacts photochemistry, aerosol evaporation, and coagulation. Cores of plumes have higher concentrations than edges. By segregating the observed plumes into cores and edges, we find evidence that particle aging, evaporation, and coagulation occurred before the first measurement. We further find that on the plume edges, the organic aerosol is more oxygenated while a marker for primary

40 biomass burning aerosol emissions has decreased in relative abundance than in the plume cores. Finally, we attempt to
41 decouple the roles of the initial concentrations and physical age since emission by performing multivariate linear regression
42 of various aerosol properties (composition, size) on these two factors.

43 **1 Introduction**

44 Smoke from biomass burning is a major source of atmospheric primary aerosol and vapors (Akagi et al., 2011;
45 Gilman et al., 2015; Hatch et al., 2015, 2017; Jen et al., 2019; Koss et al., 2018; Reid et al., 2005; Yokelson et al., 2009),
46 influencing air quality, local radiation budgets, cloud properties, and climate (Carrico et al., 2008; O'Dell et al., 2019; Petters
47 et al., 2009; Ramnarine et al., 2019; Shrivastava et al., 2017), as well as the health of impacted communities (Ford et al.,
48 2018; Gan et al., 2017; Reid et al., 2016). Dilution of a smoke plume occurs as the plume travels downwind, mixing with
49 regional 'background' air, reducing the concentrations of smoke aerosols and vapors and potentially driving changes in the
50 physical and chemical properties of the emissions (Adachi et al., 2019; Akagi et al., 2012; Bian et al., 2017; Cubison et al.,
51 2011; Hecobian et al., 2011; Hodshire et al., 2019a, 2019b; Jolleys et al., 2012, 2015; Konovalov et al., 2019; May et al.,
52 2015; Noyes et al., 2020; Sakamoto et al., 2015, Palm et al., 2020). Fires span an immense range in size, from small
53 agricultural burns, which may be only a few m² in total area and last a few hours, to massive wildfires, which may burn
54 10,000s of km² over the course of weeks (Andela et al., 2019). This range in size leads to variability in initial plume size and
55 extent of dilution by the time of the first measurement. Plumes can dilute unevenly, with edges of the plume mixing in with
56 surrounding air more rapidly than the core of the plume. Hence overall, these large, thick plumes dilute more slowly than
57 small, thin plumes for similar atmospheric conditions, as the cores of larger plumes are at a greater physical distance to the
58 background air, shielding them from dilution for longer (Akagi et al., 2012; Bian et al., 2017; Cubison et al., 2011; Hecobian
59 et al., 2011; Hodshire et al., 2019a, 2019b; Jolleys et al., 2012, 2015; Konovalov et al., 2019; May et al., 2015; Sakamoto et
60 al., 2015, Lee et al., 2020, Garofalo et al., 2019). Variability in dilution leads to variability in the evolution of smoke
61 emissions as instantaneous plume aerosol concentrations will control shortwave radiative fluxes (and thus photolysis rates
62 and oxidant concentrations), gas-particle partitioning, and particle coagulation rates (Akagi et al., 2012; Bian et al., 2017;
63 Cubison et al., 2011; Hecobian et al., 2011; Hodshire et al., 2019a, 2019b; Jolleys et al., 2012, 2015; Konovalov et al., 2019;
64 May et al., 2015; Sakamoto et al., 2015, Garofalo et al., 2019, Ramnarine et al., 2019; Sakamoto et al., 2016). Thus,
65 capturing variability in plume aerosol concentrations and dilution between fires and within fires can aid in understanding
66 how species change within the first few hours of emission for a range of plume sizes.

67 The evolution of total particulate matter (PM) or organic aerosol (OA) mass from smoke has been the focus of
68 many studies, as PM influences both human health and climate. Secondary organic aerosol (SOA) production occurs through
69 oxidation of gas-phase volatile organic compounds (VOCs) that can form lower-volatility products that partition to the
70 condensed phase (Jimenez et al., 2009; Kroll and Seinfeld, 2008). SOA formation may also arise from heterogeneous and
71 multi-phase reactions in both the organic and aqueous phases (Jimenez et al., 2009; Volkamer et al., 2009). In turn, oxidant

72 concentrations depend on shortwave fluxes (Tang et al., 1998; Tie, 2003; Yang et al., 2009) and the composition of the
73 plume (Yokelson et al. 2009; Akagi et al. 2012; Hobbs et al. 2003; Alvarado et al. 2015). Smoke particles contain
74 semivolatile organic compounds (SVOCs) (Eatough et al., 2003; May et al., 2013), which may evaporate off of particles as
75 the plume becomes more dilute (Huffman et al. 2009; May et al. 2013; Garofalo et al. 2019; Grieshop et al. 2009), leading to
76 losses in total aerosol mass. Field observations of smoke PM and OA mass normalized for dilution (e.g. through a long-lived
77 tracer such as CO) report that for near-field (<24 hours) physical aging, net PM or OA mass can increase (Cachier et al.,
78 1995; Formenti et al., 2003; Liu et al., 2016; Nance et al., 1993; Reid et al., 1998; Vakkari et al., 2014, 2018; Yokelson et al.,
79 2009), decrease (Akagi et al., 2012; Hobbs et al., 2003; Jolleys et al., 2012, 2015; May et al., 2015), or remain nearly
80 constant (Brito et al., 2014; Capes et al., 2008; Collier et al., 2016; Cubison et al., 2011; Forrister et al., 2015; Garofalo et al.,
81 2019; Hecobian et al., 2011; Liu et al., 2016; May et al., 2015; Morgan et al., 2019; Sakamoto et al., 2015; Sedlacek et al.,
82 2018; Zhou et al., 2017). It is theorized that both losses and gains in OA mass are likely happening concurrently in most
83 plumes through condensation and evaporation (May et al. 2015; Hodshire et al. 2019; Hodshire et al. 2019; Bian et al. 2017;
84 Palm et al. 2020), with the balance between the two determining whether net increases or decreases or no change in mass
85 occurs during near-field aging. However, there is currently no reliable predictor of how smoke aerosol mass concentration
86 (normalized for dilution) may change for a given fire.

87 Evolution of total aerosol number, size, and composition is critical for improving quantitative understanding of how
88 biomass burn smoke plumes impact climate. These impacts include smoke aerosols' abilities to both act as cloud
89 condensation nuclei (CCN) and to scatter/absorb solar radiation (Albrecht, 1989; Petters and Kreidenweis, 2007; Seinfeld
90 and Pandis, 2006; Twomey, 1974; Wang et al., 2008). Particles can increase or decrease in size as well as undergo
91 compositional changes through condensation or evaporation of more volatile compounds. In contrast, coagulation always
92 decreases total number concentrations and increases average particle diameter. Plumes with higher aerosol number
93 concentrations will undergo more coagulation than those with lower concentrations (Sakamoto et al., 2016).

94 Fires in the western United States region are predicted to increase in size, intensity, and frequency (Dennison et al.,
95 2014; Ford et al., 2018; Spracklen et al., 2009; Yue et al., 2013). In response, several large field campaigns have taken place
96 in the last 7 years examining wildfires in this region (Kleinman et al., 2020; Garofalo et al. 2019; Palm et al., 2020). Here,
97 we present smoke plume observations from the Biomass Burning Observation Project (BBOP) campaign of aerosol
98 properties from five research flights sampling wildfires downwind in seven pseudo-Lagrangian sets of transects to
99 investigate the evolution of OA mass and oxidation state, aerosol number, and aerosol number mean diameter. A range of
100 initial (at the time of the first plume pass in the aircraft) plume OA mass concentrations were captured within these flights
101 and fast (1 second) measurements of aerosols and key vapors were taken. The time resolution of the data was fast enough to
102 segregate each transect into edge, core, or intermediate regions of the plume and examine aerosol properties within the
103 context of both the location within the plume (edge, core, or intermediate) and the initial OA mass loading of the given
104 location. The differences in aerosol loading serve as a proxy for differences in initial fire and plume sizes, mass fluxes, and
105 subsequent amount of dilution. The extent to which dilution has occurred prior to the first observation is not a measurable

106 quantity, and fire sizes and mass fluxes were not estimated as a part of the BBOP campaign. We create mathematical fits for
107 predicting OA oxidation markers and mean particle diameter given initial plume OA mass concentration and physical age
108 (time) of the smoke. These fits may be used to evaluate other smoke datasets and assist in building parameterizations for
109 regional and global climate models to better-predict smoke aerosol climate and health impacts.

110 **2 Methods**

111 The BBOP field campaign occurred in 2013 and included a deployment of the United States Department of Energy
112 Gulfstream 1 (G-1) research aircraft in the Pacific Northwest region of the United States (Kleinman and Sedlacek, 2016;
113 Sedlacek et al., 2018) from June 15 to September 13. We analyze five cloud-free BBOP research flights that had seven total
114 sets of across-plume transects that followed the smoke plume downwind in a Lagrangian manner (see Figs. S1-S6 for
115 examples; Table S1) from approximately 15 minutes after emission to 2-4 hours downwind (Kleinman and Sedlacek, 2016).
116 The G-1 sampling setup is described in (Kleinman and Sedlacek, 2016; Sedlacek et al., 2018; Kleinman et al., 2020).

117 Number size distributions were obtained with a Fast-integrating Mobility Spectrometer (FIMS), providing particle
118 size distributions nominally from approximately 20-350 nm (Kulkarni and Wang, 2006; Olfert and Wang, 2009); data was
119 available between 20-262 nm for the flights used in this study. A Soot Photometer Aerosol Mass Spectrometer (SP-AMS)
120 provided organic and inorganic (sulfate, chlorine, nitrate, ammonium) aerosol mass concentration of PM1 (sub-micron
121 aerosol) (Canagaratna et al. 2007), select fractional components (the fraction of the AMS OA spectra at a given mass-to-
122 charge ratio) (Onasch et al., 2012), and elemental analysis (O/C and H/C) (Aiken et al., 2008; Canagaratna et al., 2015).
123 Extended details on the SP-AMS are provided in Text S1 in the supplementary information, and a brief overview is given
124 here. The SP-AMS had its highest sensitivity between 70-500 nm, dropping to 50% of peak sensitivity by 1000 nm (Liu et
125 al. 2007). It was characterized to have a collection efficiency of 0.5 when the instrument's laser was off and 0.76 when the
126 instrument's laser was on during the BBOP campaign, and these corrections have been applied to the data. There is evidence
127 from other studies that the CE of the tungsten vaporizer (laser off mode) (Lim et al., 2019) and the laser vaporizer (laser on
128 mode, run nominally at 600° C) (Willis et al., 2014) to change as a function of chemical composition, rBC coating thickness,
129 size, and sphericity in laboratory studies (Middlebrook et al., 2012; Willis et al., 2014; Corbin et al., 2015; Massoli et al.,
130 2015; Collier et al., 2018) and in aircraft observations (Kleinman et al. 2007). Results pertinent to changes in CE due to
131 aging (including physical aging as well as chemical changes including oxidation, coating thickness, and sphericity) in smoke
132 plumes are scarce (see discussion in Kleinman et al., 2020). We assume these CEs for the laser on and off modes are
133 constant in space and time, which is a limitation of this study. We use the calculated f_{60} and f_{44} fractions (the unit mass
134 resolution mass concentration ratios of m/z 60 and 44 normalized by the total OA mass concentration) and O/C and H/C
135 elemental ratios of OA as tracers of smoke and oxidative aging. Elevated f_{60} values are indicative of “levoglucosan-like”
136 species (levoglucosan and other molecules that similarly fragment in the AMS) (Aiken et al., 2009; Cubison et al., 2011; Lee
137 et al., 2010) that are known tracers of smoke primary organic aerosol (POA) (Cubison et al., 2011). f_{44} , the OA fractional

138 component observed by the SP-AMS as the high-resolution ion fragment CO_2^+ as well as some acid groups, is a proxy for
139 SOA arising from oxidative aging (Alfarra et al., 2004; Cappa and Jimenez, 2010; Jimenez et al., 2009; Volkamer et al.,
140 2006). Fractional components f_{60} and f_{44} have been shown to decrease and increase with photochemical aging, respectively,
141 likely due to both evaporation and/or oxidation of semivolatile species that contribute to m/z 60 in the SP-AMS and addition
142 of oxidized species that contribute to m/z 44 in the SP-AMS (Alfarra et al., 2004; Huffman et al., 2009). O/C tends to
143 increase with oxidative aging (Decarlo et al., 2008) whereas H/C ranges from increasing to decreasing with oxidative aging,
144 depending on the types of reactions occurring (Heald et al., 2009). Changes in O/C and H/C (as well as changes in total OA
145 mass, number, f_{44} , and f_{60}) are also influenced by mixing of different air masses and co-oxidation of different VOC
146 precursors (Chen et al. 2015). Tracking H/C with aging may provide clues upon the types of reactions that may be occurring;
147 however, variable oxidation timescales can make inferences of this type difficult (Chen et al. 2015). A Single-Particle Soot
148 Photometer (SP2; Droplet Measurement Technologies) was used to measure refractory black carbon (BC) between 80-500
149 nm (Schwarz et al. 2010) through laser-induced incandescence (Moteki and Kondo, 2010; Schwarz et al., 2006). An Off-
150 Axis Integrated-Cavity Output Spectroscopy instrument (Los Gatos, Model 907) measured CO concentrations. An SPN1
151 radiometer (Badosa et al., 2014; Long et al., 2010) measured total shortwave irradiance. Kleinman et al. (2020) provides
152 extensive details for the BBOP instruments used in this work. The supporting information also includes more details on the
153 instruments used.

154 To determine the contribution to the concentration of species X from smoke emissions (ΔX), the background
155 concentration of X is subtracted off of the measured in-plume species concentrations. To correct for dilution, we normalize
156 ΔX by background-corrected CO (ΔCO), which is inert on timescales of near-field aging (Yokelson et al., 2009). Increases
157 or decreases of $\Delta X/\Delta \text{CO}$ along the Lagrangian flight path indicate whether the total amount of X in the plume has increased
158 or decreased (implying production or removal) since time of emission. The background concentration of X is determined as
159 a regional average of the observed out-of-plume concentrations of X. To avoid using smoke-impacted measurements we
160 apply a threshold of only using measurements of X that occur in regions that correspond to the lowest 10% of CO data. We
161 determine the lowest 10% of CO concentrations for each flight during time periods with a similar altitude, latitude, and
162 longitude as the smoke plume. We perform sensitivity calculations on our assumptions of background regions and discuss
163 them in Section 3.

164 Mass concentrations of O, H, and C are calculated using the O/C and H/C and OA data from the SP-AMS
165 (assuming all of the OA mass is from O, C, and H, and we acknowledge that omitting lower-abundance atoms, such as S and
166 N, contributes to some errors in this assumption), allowing us to calculate the background-corrected OA atomic ratios,
167 $\Delta \text{O}/\Delta \text{C}$, and $\Delta \text{H}/\Delta \text{C}$, following equation 1 (where $X = \text{O}$ or H):

$$168 \frac{\Delta X}{\Delta C} = \frac{(X_{in\ plume} - X_{out\ of\ plume})}{(C_{in\ plume} - C_{out\ of\ plume})} \quad \text{Eq. 1}$$

169 We note that any non-linear changes in chemistry and composition between the plume and background will not perfectly
170 isolate the elemental factors in smoke. We also background-correct fractional f_{60} and f_{44} (using the mass concentrations of

171 m/z 60, m/z 44, and OA inside and outside of the plume), but we do not normalize by CO due to these values already being
172 normalized by OA, following equation 2 (where $f = f_{60}$ or f_{44}):

$$173 \quad \Delta f = \frac{(f_{in} * OA_{in}) - (f_{out} * OA_{out})}{\Delta OA} \quad \text{Eq. 2}$$

174 We only consider data to be in-plume if the absolute CO \geq 150 ppbv. This threshold appears to be capturing clear plume
175 features as seen in the number concentration while excluding background air (Figs. S7-S11). We note that we use different
176 definitions of in-plume and background (i.e. the lowest 10% of absolute CO measurements) in order to provide a buffer
177 between the plume and background to ensure to the best of our abilities that we are capturing non-smoke impacted air for the
178 background and smoke-impacted air for in-plume cases. The regions of the lowest 10% of CO measurements always fall
179 under 150 ppbv (Figs. S7-S11). Similarly, we exclude the lowest 5% of CO data in the in-plume measurements in our
180 analyses to provide a further buffer between smoke-impacted and background air. We perform sensitivity analyses of our
181 results to our assumptions about background and in-plume values in Section 3. Figures S2-S6 indicate the locations of the
182 lowest 10% of CO for each flight.

183 From the FIMS, we examine the background-corrected, normalized number concentrations of particles with
184 mobility diameters between 40-262 nm, $\Delta N / \Delta CO$. This size range allows us to exclude potential influence of fresh
185 nucleation upon the total number concentrations. Occasionally, the background-corrected, normalized number concentration
186 in the FIMS size range between 20-40 nm increases by 1-2 orders of magnitude relative to typical plume conditions,
187 indicating possible nucleation events, primarily at the edges or in between smoke plumes (Figs. S7-S11). Smoke plumes
188 contain particles with diameters larger than 262 nm (Janhäll et al., 2009): thus, we cannot provide total number
189 concentrations, but we can infer how $\Delta N / \Delta CO$ within our observed size range evolves. We also obtain an estimate of how
190 the number mean diameter between 40-262 nm, \overline{D}_p , changes with aging through:

$$192 \quad \overline{D}_p = \frac{\sum N_i * D_{p,i}}{\sum N_i} \quad \text{Eq. 3}$$

193 where N_i and $D_{p,i}$ are the number concentration and geometric mean diameter within each FIMS size bin, respectively.

194 All of the data are provided at 1 Hz and all but the SP-AMS fractional component data are available on the DOE
195 ARM web archive (<https://www.arm.gov/research/campaigns/aaf2013bbop>). As the plane traveled at approximately 100 m s⁻¹
196 on average, the approximate spatial resolution of the data is every 100 m across the plume. The plumes spanned from
197 approximately 5-50 km wide (Figs. S2-6). The instruments used here had a variety of time lags (all <10 seconds) relative to a
198 TSI 3563 nephelometer used as reference. The FIMS also showed additional smearing in flushing smoky air with cleaner air
199 when exiting the plume with maximum observed flushing timescales around 30 seconds, but generally less (Fig. S12). To
200 test if these lags impact our results, we perform an additional analysis where we only consider the first half of each in-plume
201 transect, when concentrations are generally rising with time (Figure S12-S13), and our main conclusions are unaffected. We
202

203 do not test the impacts of other time lags and do not attempt to further correct the data for any time lags. Kleinman et al.
204 (2020) provides further information on instrument time delays during BBOP.

205 We use MODIS Terra and Aqua fire and thermal anomalies detection data to determine fire locations (Giglio et al.,
206 2006, 2008). We estimate the fire center to be the approximate center of all clustered MODIS detection points for a given
207 sampled fire (Figs. S1-S6). The true fire location at the time of sampling is likely different than the MODIS estimates,
208 depending on the speed of the fire front. To estimate the physical age of the plume, we use the estimated fire center as well
209 as the total FIMS number concentration to determine an approximate centerline of the plume as the smoke travels downwind
210 (an example is provided in Fig. S1). The centerline is subjectively chosen to approximately capture the most-concentrated
211 portion of each plume pass (as estimated using total aerosol number concentrations). We use the mean wind speed and this
212 estimated centerline to calculate an estimated physical age for each transect, and this physical age is assumed to be constant
213 across the transect, as plume crossings took between 50-500 seconds; however, transects that were not perfectly tangential to
214 the mean wind would have sampled different plume ages on the opposite sides of the plume. We did not propagate
215 uncertainty in fire location, wind speed, or centerline through to the physical age, which is a limitation of this study.

216 3 Results and discussion

217 As a case example, we examine the aging profiles of smoke from the Colockum fire during the first set of pseudo-
218 Lagrangian transects for flight 730b (Table S1). Figure 1 provides $\Delta OA/\Delta CO$, $\Delta BC/\Delta CO$, Δf_{60} , Δf_{44} , $\Delta H/\Delta C$, $\Delta O/\Delta C$,
219 $\Delta N/\Delta CO$, and $\overline{D_p}$ as a function of the estimated physical age; Figs. S14-S18 provides this information for the other pseudo-
220 Lagrangian transect flight sets studied. (Here, BC represents the refractory BC from the SP2; Sect. 2.) We have divided each
221 transect into four regions: between the 5-15 (edge), 15-50 (intermediate, outer), 50-90 (intermediate, inner), and 90-100
222 (core) percentile of ΔCO within each transect. (As discussed above, we exclude the lowest 5% in order to provide a buffer
223 between the plume edge and background air.) Note that in Figure 1 (and Figures S14-S18), the points represent the mean
224 values for each transect/percentile and do not include error bars for uncertainty in the mean or measurement uncertainty as
225 characterization of systematic variance (within plume percentiles) with age is beyond the scope of this study. Figures S2-S6
226 show the locations of these CO percentile bins for each transect of individual flights. Figure 1 shows the edge and core data,
227 both averaged per transect, and Figs. S14-18 provides all four percentile bins for each flight. These percentile bins correspond
228 with the thinnest (lowest CO mixing ratio) to thickest (highest CO mixing ratio) portions of the plume, respectively. If a fire
229 has uniform emissions ratios across all regions and dilutes evenly downwind, these percentile bins would correspond to the
230 edges, intermediate outer and intermediate inner regions, and the core of the diluting plume. We use this terminology in this
231 study but note that uneven emissions, mixing, and/or dilution lead to the percentile bins not physically corresponding to our
232 defined regions in some cases. We note that some plumes show more than one maxima in CO concentrations within a given
233 plume crossing, which implies that there may be more than one fire or fire front, and that these plumes from separate fires or
234 fronts are not mixing perfectly. Multiple maxima could also imply vertical variations in the location of the core of the

235 plumes that the flights did not capture. As well, in at least one of the fires (in flights ‘730a’ and ‘730b’), the fuels vary
236 between different sides of the fire, as discussed in Kleinman et al., (2020). However, the lowest two ΔCO bins tend towards
237 the physical edges of the plume, and the highest two tend more towards the physical center of the plume (Figs. S2-S6). We
238 do not know where the plane is vertically in the plume, which is a limitation as vertical location will also impact the amount
239 of solar flux able to penetrate through the plume.

240 Figure 1 shows that for this specific plume, $\Delta\text{OA}/\Delta\text{CO}$ and $\Delta\text{BC}/\Delta\text{CO}$ systematically vary little with age for both
241 the 5-15 and 90-100 percentile of ΔCO (p -values >0.5), yet both show non-systematic variability between transects. A true
242 Lagrangian flight with the aircraft sampling the same portion of the plume and no measurement artifacts (e.g. coincidence
243 errors at high concentrations) would have a constant $\Delta\text{BC}/\Delta\text{CO}$ for each transect set. This flight and other flights studied
244 here have variations in $\Delta\text{BC}/\Delta\text{CO}$ (Fig. 1; Figs. S14-S18), which may be indicative of deviations from a Lagrangian flight
245 path with temporal variations in emission and/or measurement uncertainties. The remaining variables plotted also show some
246 noise and few clear trends, but it is apparent that the transect-mean values 5-15 and 90-100 percentiles do show a separation
247 for some of the individual metrics, in particular Δf_{44} and $\Delta\text{O}/\Delta\text{C}$. In order to determine the existence or lack of trends for
248 these metrics, we spend the remainder of this study examining each metric from all of the pseudo-Lagrangian flights
249 together.

250

251 **3.1 Organic aerosol aging: $\Delta\text{OA}/\Delta\text{CO}$, Δf_{60} , Δf_{44} , $\Delta\text{H}/\Delta\text{C}$, and $\Delta\text{O}/\Delta\text{C}$**

252 Figure 2a-e shows available $\Delta\text{OA}/\Delta\text{CO}$, Δf_{60} , Δf_{44} , $\Delta\text{H}/\Delta\text{C}$, and $\Delta\text{O}/\Delta\text{C}$ edge and core data versus physical age for
253 each transect for each flight of this study. We color each line by the mean ΔOA within a ΔCO percentile bin from the
254 transect closest to the fire, $\Delta\text{OA}_{\text{initial}}$, in order to examine whether each variable ($\Delta\text{OA}/\Delta\text{CO}$, Δf_{60} , Δf_{44} , $\Delta\text{H}/\Delta\text{C}$, and $\Delta\text{O}/\Delta\text{C}$)
255 vary with $\Delta\text{OA}_{\text{initial}}$. (Some transects do not have data available for specific instruments.) As with Fig. 1, the points in Fig.
256 2 represent the mean values for each transect and percentile, and we do not include error bars as we do not attempt to
257 characterize systematic variance (within plume percentiles) with age in this study. We note that $\Delta\text{OA}_{\text{initial}}$ does not actually
258 represent the true initial emitted OA from each fire, but instead serves as a proxy for the general fire size, intensity, and
259 emission rate (as larger fires and fires with faster rates of fuel consumption per area will have larger mass fluxes than smaller
260 fires or fires with less fuel consumption per area, all else equal). Thus, $\Delta\text{OA}_{\text{initial}}$ and other “initial” metrics referred to in this
261 study are not to be taken as emission values and direct comparison to studies with direct emissions values is not appropriate,
262 as dilution and chemistry may occur before the initial flight transect, which we discuss further below. We show the 5-15
263 (edge) and 90-100 (core) ΔCO percentile bins in Fig. 2; Fig. S19 shows the same information for all four ΔCO percentiles.
264 We use the simple ‘edge’ and ‘core’ terminology throughout the following discussion but note that the 5-15 and 90-100 ΔCO
265 percentile bins do not necessarily correspond to the physical (spatial) edges and cores of each plume. They instead
266 correspond to the most CO-dense and least CO-dense portions of the plume. We also note that although some of the physical
267 ages appear to start at approximately 0 hours (e.g. over the fire), this is from a limitation of our physical age estimation

268 method (Sect. 2), as no flights captured data before approximately 15 minutes after emission (Kleinman et al., 2016). Flights
269 with two sets of pseudo-Lagrangian transects ('726a' and '730b') have two separate lines in Fig. 2, one for each set. As well,
270 two transects for flight '809a' nearly overlap (Fig. S5), with the transect that is further from the fire occurring first in the
271 flight path, leading to an apparent slight decrease in physical age for the sequential transect (see, e.g., the white dashed line
272 in Fig. 2a).

273 Also included in Fig. 2 are the Spearman rank-order correlation tests (hereafter Spearman tests), which are tests for
274 monotonicity. The Spearman tests show correlation coefficients for each flight set (Table S1) with the initial ΔOA of a flight
275 set ($\Delta\text{OA}_{\text{initial}}$) against $\Delta\text{OA}/\Delta\text{CO}$, Δf_{60} , Δf_{44} , $\Delta\text{H}/\Delta\text{C}$, and $\Delta\text{O}/\Delta\text{C}$ as the smoke aerosol ages downwind. We also include
276 Spearman tests for the calculated physical age of the smoke for each flight set against these same variables. The R values are
277 labeled $R_{\Delta\text{OA},\text{initial}}$ and R_{age} , respectively, in Fig. 2. We calculate these correlation coefficients separately for Figure 2 to
278 determine the strength and direction of association for each variable from $\Delta\text{OA}_{\text{initial}}$ or age alone (and whether the data are
279 correlated vs. anticorrelated with these predictors). To complement these independent correlation coefficients, we also
280 perform multivariate linear regressions (Eqns. 4 and 5 and Figure 3, discussed later) to explicitly decouple the influence of
281 the two predictors. For the correlations with $\Delta\text{OA}_{\text{initial}}$, all transects in a given pseudo-Lagrangian set of transects have the
282 same $\Delta\text{OA}_{\text{initial}}$ value; for flights with two pseudo-Lagrangian sets of transects, each set has its own $\Delta\text{OA}_{\text{initial}}$ value.
283 Correlating to $\Delta\text{OA}_{\text{initial}}$ provides an estimate of how the plume aerosol concentrations at the time of the initial transect
284 impact plume aging (aging both before and after this initial transect). We define the following categories of correlation for
285 the absolute value of R: 0.0-0.19 is 'very weak', 0.2-0.39 is 'weak', 0.4-0.59 is 'moderate', 0.6-0.79 is 'strong', and 0.8-1.0
286 is 'very strong' (Evans 1996).

287 As individual flights show scatter in the metrics of Fig. 2 (Figs. 1, Figs. S14-S18), we also include $R_{\Delta\text{OA},\text{initial}}$ and
288 R_{age} for each metric of Fig. 2 sequentially removing one flight from the statistical analysis. These results are summarized in
289 Table S2. In general, removing single flights does not change our conclusions, particularly when correlations are moderate or
290 stronger. Scatter in $\Delta\text{OA}_{\text{initial}}$ leads to weaker R_{age} values than would be obtained if we normalized changes with aging to the
291 first (normalized) value. However, as plume-density-dependent aging prior to the first transect is one of the potentially
292 interesting findings of this study, we feel that it is important to not normalize our changes further. Figs. S13, S19-S22 show
293 the same details as Fig. 2 but provide sensitivity tests to our methodology. Figure S13 examines potential FIMS
294 measurement artifacts by only using data from the first 50% of each flight leg when particle concentrations are increasing,
295 which lessons response-time-artifacts of the FIMS during transitions from high to low concentration regions. Figure S20
296 tests our assumed in-plume CO threshold value by increasing it from 150 ppbv to 200 ppbv (;Fig. S19). Figure S21 tests
297 ΔCO percentile spacing by changing the bins from 5-15%, 15-50%, 50-90%, and 90-100% to 5-25%, 25-75%, and 75-100%.
298 Figure S22 tests assumed background region by increasing data used from the lowest 10% to the lowest 25% of CO
299 measurements. Although these figures show slight variability, the findings discussed below remain robust, and we constrain
300 the rest of our discussion to the original assumptions made for the FIMS measurements, in-plume CO threshold value, and
301 ΔCO percentiles used in Fig. 2.

302 In general, both the cores and edges do not show any positive or negative trend in $\Delta\text{OA}/\Delta\text{CO}$ with respect to
303 physical aging. The correlation coefficients, $R_{\Delta\text{OA,initial}}$ and R_{age} , show very weak correlations of 0.02 and +0.03 (with
304 $R_{\Delta\text{OA,initial}}$ and R_{age} ranging between -0.25 to +0.17 and 0 to 0.07, respectively, when individual flights are left out
305 sequentially; Table S2). The absolute variability in $\Delta\text{OA}/\Delta\text{CO}$ is dominated by differences between plumes. Many previous
306 field campaigns similarly show little change in $\Delta\text{OA}/\Delta\text{CO}$ with aging (Hodshire et al., 2019a and references therein; Palm et
307 al., 2020). This may be due to a balance between evaporation and condensation over the period of time that the plume is
308 observed (Hodshire et al., 2019a). This hypothesis is supported by the observed Δf_{60} and Δf_{44} : The fractional components
309 Δf_{60} and Δf_{44} show clear signs of changes with aging, consistent with previous studies (Cubison et al. 2011; May et al. 2015;
310 Garofalo et al. 2019; Forrister et al. 2015; Lee et al. 2020). Δf_{60} generally decreases with plume age ($R_{\text{age}} = -0.26$; a weak
311 correlation), consistent with the hypotheses that compounds containing species that can fragment to m/z 60 in the SP-AMS
312 may be evaporating because of dilution, undergoing heterogeneous oxidation to new forms that do not appear at m/z 60,
313 and/or having a decreasing fractional contribution due to condensation of other compounds. In contrast, Δf_{44} generally
314 increases with age ($R_{\text{age}} = +0.5$; a moderate correlation) for all plumes with available data. It appears for the plumes in this
315 study that although there is little change in $\Delta\text{OA}/\Delta\text{CO}$, loss of compounds such as those that contribute to f_{60} fragments (as
316 captured by the SP-AMS) is roughly balanced by condensation of more-oxidized compounds, including those that contain
317 compounds with f_{44} fragments, such as carboxylic acids. This observation also suggests the possibility of heterogeneous or
318 particle-phase oxidation that would alter the balance of Δf_{60} and Δf_{44} . However, estimates of heterogeneous mass losses
319 indicate that after three hours of aging (the range of time the BBOP measurements were taken in) for a range of OH
320 concentrations and reactive uptake coefficients, less than 10% of aerosol mass is lost to heterogeneous reactions (Fig. S23;
321 see SI text S2 for more details on the calculation). These calculations indicate that heterogeneous loss has limited effect on
322 aerosol composition or mass. Hence, the evaporation of compounds that contribute to m/z 60 in the SP-AMS being balanced
323 by gas-phase production of compounds that contribute to m/z 44 in the SP-AMS may be the more likely pathway. When
324 individual flights are left out sequentially, R_{age} ranges from -0.21 to -0.38 and +0.4 to +0.57 for Δf_{60} and Δf_{44} , respectively
325 (Table S2).

326 Two more important features of Δf_{60} and Δf_{44} can be seen within Fig. 2: (1) Δf_{60} and Δf_{44} depend on $\Delta\text{OA}_{\text{initial}}$
327 (moderate correlations of $R_{\Delta\text{OA,initial}} = +0.43$ and -0.55, respectively), with plumes with higher $\Delta\text{OA}_{\text{initial}}$ having
328 consistently higher Δf_{60} and lower Δf_{44} . (2) The differences in Δf_{60} and Δf_{44} are apparent even for the nearest-to-source
329 measurements that are ~15 minutes after the time of emission. Prior studies have shown that f_{60} and f_{44} at the time of
330 emissions correlate with OA emissions factors through variability in burn conditions (Hennigan et al. 2011; Cubison et al.
331 2011; McClure et al. 2020), and this relationship might also contribute to our observed correlation between Δf_{60} and Δf_{44}
332 with $\Delta\text{OA}_{\text{initial}}$. For this emissions relationship to be an important factor, the variability in the OA emission factor needs to be
333 a significant contributor to the variability in $\Delta\text{OA}_{\text{initial}}$. The relative variability in the OA emission factor is much smaller than
334 the relative variability in $\Delta\text{OA}_{\text{initial}}$, and other factors contributing to variability in $\Delta\text{OA}_{\text{initial}}$ will negate an emissions-based
335 covariance between $\Delta\text{OA}_{\text{initial}}$ with Δf_{60} and Δf_{44} . While our observed $\Delta\text{OA}_{\text{initial}}$ in Figure 2 spans nearly a factor of 100,

336 Andreae (2019) shows that the OA emission factors have a -1σ to $+1\sigma$ range of around a factor 3. Hence, variability in fuel
337 consumption rates and dilution prior to the first transect likely dominate the variability in $\Delta\text{OA}_{\text{initial}}$, and the relationships of
338 Δf_{60} and Δf_{44} with $\Delta\text{OA}_{\text{initial}}$ are unlikely to be influenced much by variability in burn conditions. We conclude that
339 evaporation and/or chemistry prior to the first measurement appears to drive the initial relationship between Δf_{60} and Δf_{44}
340 with $\Delta\text{OA}_{\text{initial}}$, consistent with (1) the theoretical work of Hodshire et al. (2019a), (2) an analysis of what chemistry would be
341 missed in laboratory experiments if the initial 10-60 minutes of chemistry was not considered, following field experiments
342 (Hodshire et al., 2019b), and (3) recent field analysis indicating that up to one-third of primary OA from biomass burning
343 evaporates and subsequently reacts to form biomass burning SOA (Palm et al. 2020). We include in the supporting
344 information scatter plots of each parameter of Fig. 1 as a function of $\Delta\text{OA}_{\text{initial}}$ (Fig. S24), and observe no trends other than
345 the cores of the plumes generally having a higher $\Delta\text{OA}_{\text{initial}}$ than the edges of the plumes, as expected. The amount of
346 evaporation and/or chemistry appear to depend on $\Delta\text{OA}_{\text{initial}}$, with higher rates of evaporation and chemistry occurring for
347 lower values of $\Delta\text{OA}_{\text{initial}}$. This result is consistent with the hypothesis that aircraft observations are missing evaporation and
348 chemistry prior to the first aircraft observation (Hodshire et al., 2019b). The differences in $\Delta\text{OA}_{\text{initial}}$ between plumes may be
349 due to different emissions fluxes (e.g., due to different fuels or combustion phases) or plume widths, where larger/thicker
350 plumes dilute more slowly than smaller/thinner plumes. These larger plumes have been predicted to have less evaporation
351 and may undergo relatively less photooxidation (Bian et al., 2017; Hodshire et al., 2019a, 2019b). When individual flights
352 are left out sequentially, $R_{\Delta\text{OA}_{\text{initial}}}$ ranges from +0.3 to +0.58 and -0.42 to -0.63 for Δf_{60} and Δf_{44} , respectively (Table S2).

353 Garofalo et al. (2019) segregated smoke data from the WE-CAN field campaign by distance from the center of a
354 given plume and showed that the edges of one of the fires studied have less fractional f_{60} and more fractional f_{44} (not
355 background-corrected) than the core of the plume. Lee et al. (2020) saw similar patterns in a southwestern United States
356 wildfire. Similarly, we find that the 730b flight shows a very similar pattern in f_{60} and f_{44} (Figs. S25-S26) to that shown in
357 Fig. 6 of Garofalo et al. (2019). The 821b and 809a flights also hint at elevated f_{44} and decreased f_{60} at the edges but the
358 remaining plumes do not show a clear trend from the physical edges to cores in f_{60} and f_{44} . This could be as CO
359 concentrations (and thus presumably other species) do not evenly increase from the edge to the core for many of the plume
360 transects studied (Figs. S2-S6). To more clearly see this, Fig. S27 provides the same style of figure as Figs. S26-S27 for in-
361 plume CO concentrations. Generally CO peaks around the centerline and is highest in the most fresh transect, but shows
362 variability across transects. We do not have UV measurements that allow us to calculate photolysis rates but the in-plume
363 SPN1 shortwave measurements in the visible show a dimming in the fresh cores that has a similar pattern to f_{44} and the
364 inverse of f_{60} (Fig. S28; the rapid oscillations in this figure could be indicative of sporadic cloud cover above the plumes).
365 Lee et al. (2020) similarly saw indications of enhanced photochemical bleaching at the edges of a southwestern United States
366 wildfire when examining aerosol optical properties.

367 We also plot core and edge $\Delta\text{H}/\Delta\text{C}$ and $\Delta\text{O}/\Delta\text{C}$ as a function of physical age (Fig. 2d-e). Similar to Δf_{44} , $\Delta\text{O}/\Delta\text{C}$
368 increases with physical age and is moderately correlated to both physical age and $\Delta\text{OA}_{\text{initial}}$ (moderate correlations of $R_{\text{age}} = +$
369 0.561 and $R_{\Delta\text{OA}_{\text{initial}}} = -0.45$). When individual flights are left out sequentially, R_{age} for $\Delta\text{O}/\Delta\text{C}$ ranges between +0.46 and

370 +0.63 and $R_{\Delta OA, initial}$ ranges between -0.21 and -0.54 (Table S2). Given that Δf_{44} and $\Delta O/\Delta C$ are both metrics for OA aging
371 (Sect. 2), it is unsurprising that we see similar trends between them. Conversely, $\Delta H/\Delta C$ is poorly correlated to physical age
372 and $\Delta OA_{initial}$.

373 Both physical age and $\Delta OA_{initial}$ appear to influence Δf_{60} , Δf_{44} , and $\Delta O/\Delta C$: oxidation reactions and evaporation
374 promoted by dilution occur with aging, and the extent of photochemistry and dilution should depend on plume thickness.
375 Being able to predict biomass burning aerosol aging parameters can provide a framework for interstudy-comparisons and can
376 aid in modeling efforts. We construct mathematical fits for predicting Δf_{60} , Δf_{44} , and $\Delta O/\Delta C$:

$$377 \\ 378 \quad X = a \log_{10}(\Delta OA_{initial}) + b (\text{Physical age}) + c \quad \text{Eq. 4}$$

379 where X is Δf_{60} , Δf_{44} , or $\Delta O/\Delta C$, physical age is in hours, and a , b , and c are fit coefficients. The measured versus fit data are
380 shown in Fig. 3a-c. The values of a , b , and c are provided in Table S3. The Pearson and Spearman coefficients of
381 determination (R_p^2 and R_s^2 , respectively) are also summarized in Fig. 3 and indicate weak-moderate goodness of fits (R_p^2 and
382 R_s^2 of 0.28 and 0.25 for Δf_{60} , R_p^2 and R_s^2 of 0.58 and 0.6 for Δf_{44} , and R_p^2 and R_s^2 of 0.45 and 0.55 for $\Delta O/\Delta C$). We show R^2
383 here to indicate the fraction of variability captured by these fits, whereas calculating R for the trends in Fig. 2 indicate the
384 direction of the correlation. We do not constrain our fits to go through the origin. To provide further metrics of goodness-of-
385 fit, we also include the normalized mean bias (NMB) and normalized mean error (NME) in percent for each metric of Fig. 3.
386 The NMB values are very close to zero (which is anticipated as linear fits seek to minimize the sum of squared residuals).
387 The NME is larger, at 19.8% for Δf_{60} , 14.9% for Δf_{44} , and 10.2% for $\Delta O/\Delta C$. The p-values for each fit are less than 0.01.
388 Although no models that we are aware of currently predict aerosol fractional components (e.g. f_{60} or f_{44}), O/H and H/C are
389 predicted by some models (e.g., Cappa and Wilson (2012) and these fit parameters may assist in modeling of aging biomass
390 burning aerosol. Other functional forms for fits were explored, with the following form showing similar results as Eq. 4:
391

$$392 \\ 393 \quad \ln(\Delta X) = a \ln(\Delta OA_{initial}) + b \ln(\text{Physical age}) + c \quad \text{Eq. 5}$$

394
395 (Fig. S29 and Table S4 for the fit coefficients) and $\Delta N_{initial}$ in the place of $\Delta OA_{initial}$ in Eq. 4 (Fig. S30 and Table S5 for the fit
396 coefficients) providing similar correlation values and NMB and NME values for Δf_{60} , Δf_{44} , and $\Delta O/\Delta C$.

397 The aging values of Δf_{60} , Δf_{44} , and $\Delta O/\Delta C$ show scatter in time (Figs. S14-18), which likely contributes to the
398 limited predictive power of our mathematical fits. The scatter is likely due to variability in emissions due to source fuel or
399 combustion conditions, instrument noise and responses under the large concentration ranges encountered in these smoke
400 plumes, inhomogeneous mixing within the plume, variability in background concentrations not captured by our background
401 correction method, inaccurate characterizations of physical age due to variable wind speed, and/or deviations from a true
402 Lagrangian flight path. Eqs. 4-5 performed the best out of the mathematical fits that we tested. These equations do not have a
403 direct physical interpretation due to their indirect relations to age and initial aerosol mass. But they may be used as a starting

404 point for modeling studies as well as for constructing a more physically based fit. There may be another variable not
405 available to us in the BBOP measurements that can improve these mathematical fits, such as photolysis rates. We do not
406 know whether these fits may well-represent fires in other regions around the world, given variability in fuels and burn
407 conditions. We also do not know how these fits will perform under nighttime conditions, as our fits were made for daytime
408 conditions with different chemistry than would happen at night. We encourage these fits to be tested with further data sets
409 and modeling. These equations are a first step towards parameterizations appropriate for regional and global modeling and
410 need extensive testing to separate influences of oxidation versus dilution-driven evaporation.

411 3.2 Aerosol size distribution properties: $\Delta N/\Delta CO$ and \overline{D}_p

412 The observations of the normalized number concentration between 40-262 nm, $\Delta N/\Delta CO$ (Fig. 2f), show that plume
413 edges and cores generally show decreases in $\Delta N/\Delta CO$ with physical age, with a weak correlation of $R_{\text{age}} = -0.27$ (-0.13 to -
414 0.43 when individual flights are left out, sequentially; Table S2). Although we would anticipate that plume regions with
415 higher initial ΔOA would have lower normalized number concentrations due to coagulation (Sakamoto et al. 2016), a few
416 dense cores have normalized number concentrations comparable or higher than the thinner edges, leading to no correlation
417 with $\Delta OA_{\text{initial}}$. We note that variability in number emissions (e.g., due to burn conditions) adds unexplained variability not
418 captured by the R values.

419 The mean particle size between 40-262 nm, \overline{D}_p (Eq. 3), is shown to statistically increase with aging when
420 considered across the BBOP dataset (Fig. 2g) (a moderate correlation of $R_{\text{age}} = +0.53$, with R_{age} ranging between +0.43 to
421 +0.63 when individual flights are left out sequentially; Table S2). Coagulation and SOA condensation will increase \overline{D}_p . OA
422 evaporation will decrease \overline{D}_p if the particles are in quasi-equilibrium (where evaporation is independent of surface area)
423 (Hodshire et al. 2019b). However, if evaporation is kinetically limited, smaller particles will preferentially evaporate more
424 rapidly than larger particles, which may lead to an increase in \overline{D}_p if the smallest particles evaporate below 40 nm (Hodshire
425 et al. 2019b). The plumes do not show significant changes in $\Delta OA/\Delta CO$ (Fig. 2a), indicating that coagulation is likely
426 responsible for the majority of increases in \overline{D}_p . (We acknowledge that $\Delta OA/\Delta CO$ may be impacted by measurement artifacts
427 as discussed in Sect. 2. For instance, if the collection efficiency of the AMS is actually decreasing with age, then $\Delta OA/\Delta CO$
428 would be increasing and the increases in number mean diameter will be due to SOA condensation as well as coagulation.)
429 We do not have measurements for the volatility of the smoke aerosol, and so cannot refine these conclusions further. We also
430 perform the functional fit analysis following Sect. 3.1 (Eq. 4; where X is \overline{D}_p in this case). The fit can also predict greater than
431 30 percent of the variance in \overline{D}_p (R_p^2 and R_s^2 of 0.37 and 0.33, NME of 5.5%, and p-value less than 0.01; Fig. 3d) but does
432 not predict $\Delta N/\Delta CO$ well (not shown). We show the functional fit for \overline{D}_p for the alternative fit equation (Eq. 5) in Fig. S29
433 and Table S4. We also show the functional fit for \overline{D}_p for Eq. 4 with $\Delta N_{\text{initial}}$ in place of $\Delta OA_{\text{initial}}$ in Fig. 30 and Table S5.
434 Sakamoto et al. (2016) provide fit equations for modeled \overline{D}_p as a function of age, but they include a known initial \overline{D}_p at the
435 time of emission in their parameterization (rather than 15 minutes or greater, as available to us in this study), which is not

436 available here. $\Delta N_{\text{initial}}$ in the place of $\Delta \text{OA}_{\text{initial}}$ in Eq. 4 predicts \overline{D}_p similarly (Fig. S30). As discussed in Section 3.1, scatter
437 in number concentrations limits our prediction skill.

438 Particles appear in the 20-40 nm size range in the FIMS measurements independently of plume OA concentrations
439 (Figs S7-S11), implying that nucleation events may be occurring for some of the transects. Some pseudo-Lagrangian sets of
440 transects also show nucleation-mode particles downwind of fires in between transects (Figs. S7, S8, S9, and S11).
441 Nucleation-mode particles appear to be approximately one order of magnitude less concentrated than the larger particles, and
442 primarily occur in the outer portion of plumes, although one set of transects did show nucleation-mode particles within the
443 core of the plume (Fig. S11). Nucleation at edges could be due to increased photooxidation from higher total irradiance
444 relative to the core (Fig. S26). As well, nucleation is more favorable when the total condensation sink is lower (e.g. reduced
445 particle surface area; Dal Maso et al., 2002), which may occur for outer portions of plumes with little aerosol loading.
446 However, given the relatively small number of data points showing nucleation mode particles and limited photooxidation
447 and gas-phase information, we do not have confidence in the underlying source of the nucleation-mode particles.

448 **4 Summary and outlook**

449 The BBOP field campaign provided high time resolution (1 s) measurements of gas- and particle-phase smoke
450 measurements downwind of western U.S. wildfires along pseudo-Lagrangian transects. These flights have allowed us to
451 examine near-field (<4 hours) aging of smoke particles to provide analyses on how select species vary across a range of initial
452 organic aerosol mass loadings ($\Delta \text{OA}_{\text{initial}}$; a proxy for the relative rates at which the plume is anticipated to dilute as dilution
453 before the first observation is not a measurable quantity). We have also examined how the species studied vary between the
454 edges and cores of each plume. We find that although $\Delta \text{OA}/\Delta \text{CO}$ does not correlate with $\Delta \text{OA}_{\text{initial}}$ or physical age, Δf_{60} (a
455 marker for evaporation) is moderately correlated with $\Delta \text{OA}_{\text{initial}}$ (Spearman rank-order correlation tests correlation coefficient,
456 $R_{\Delta \text{OA}, \text{initial}}$, of +0.43) and weakly correlated with physical age (Spearman rank-order correlation tests correlation coefficient,
457 R_{age} , of -0.26). Δf_{44} and $\Delta \text{O}/\Delta \text{C}$ (markers for photochemical aging) increases with physical aging (moderate correlations of R_{age}
458 of +0.5 and +0.56, respectively) and are inversely related to $\Delta \text{OA}_{\text{initial}}$ (moderate correlations of $R_{\Delta \text{OA}, \text{initial}}$ of -0.55 and -0.45,
459 respectively). $\Delta N/\Delta \text{CO}$ decreases with physical aging, likely through coagulation. Mean aerosol diameter increases with age
460 primarily due to coagulation, as normalized organic aerosol mass does not change significantly, and is moderately correlated
461 with physical age ($R_{\text{age}} = +0.53$). Nucleation is observed within a few of the fires and appears to occur primarily on the edges
462 of the plumes. Differences in initial values of Δf_{60} , Δf_{44} , and $\Delta \text{O}/\Delta \text{C}$ are evidence that evaporation and/or chemistry has
463 occurred before the time of initial measurement and that plumes or plume regions with lower initial aerosol loading can undergo
464 these changes more rapidly than thicker plumes. We have developed fit equations that can weakly to moderately predict Δf_{60}
465, Δf_{44} , $\Delta \text{O}/\Delta \text{C}$, and mean aerosol diameter given a known initial (at the time of first measurement) total organic aerosol mass
466 loading and physical age. We were unable to quantify the impact on potential inter-fire variability in the emission values of
467 the metrics studied here (such as variable emissions of species that can contribute to m/z 60 and m/z 44). We anticipate that

468 being able to capture this additional source of variability may lead to stronger fits and correlation. We encourage future studies
469 to attempt to quantify these chemical and physical changes before the initial measurement using combinations of modeling
470 and laboratory measurements, where sampling is possible at the initial stages of the fire and smoke. We also suggest further
471 refinement of our fit equations, as additional variables (such as photolysis rates) and better quantification of inter-fire
472 variability (such as variable emission rates) are anticipated to improve these fits. We finally urge future near-field (<24 hours)
473 analyses of recent and future biomass burning field campaigns to include differences in initial plume mass concentrations and
474 location within the plume as considerations for understanding chemical and physical processes in plumes.

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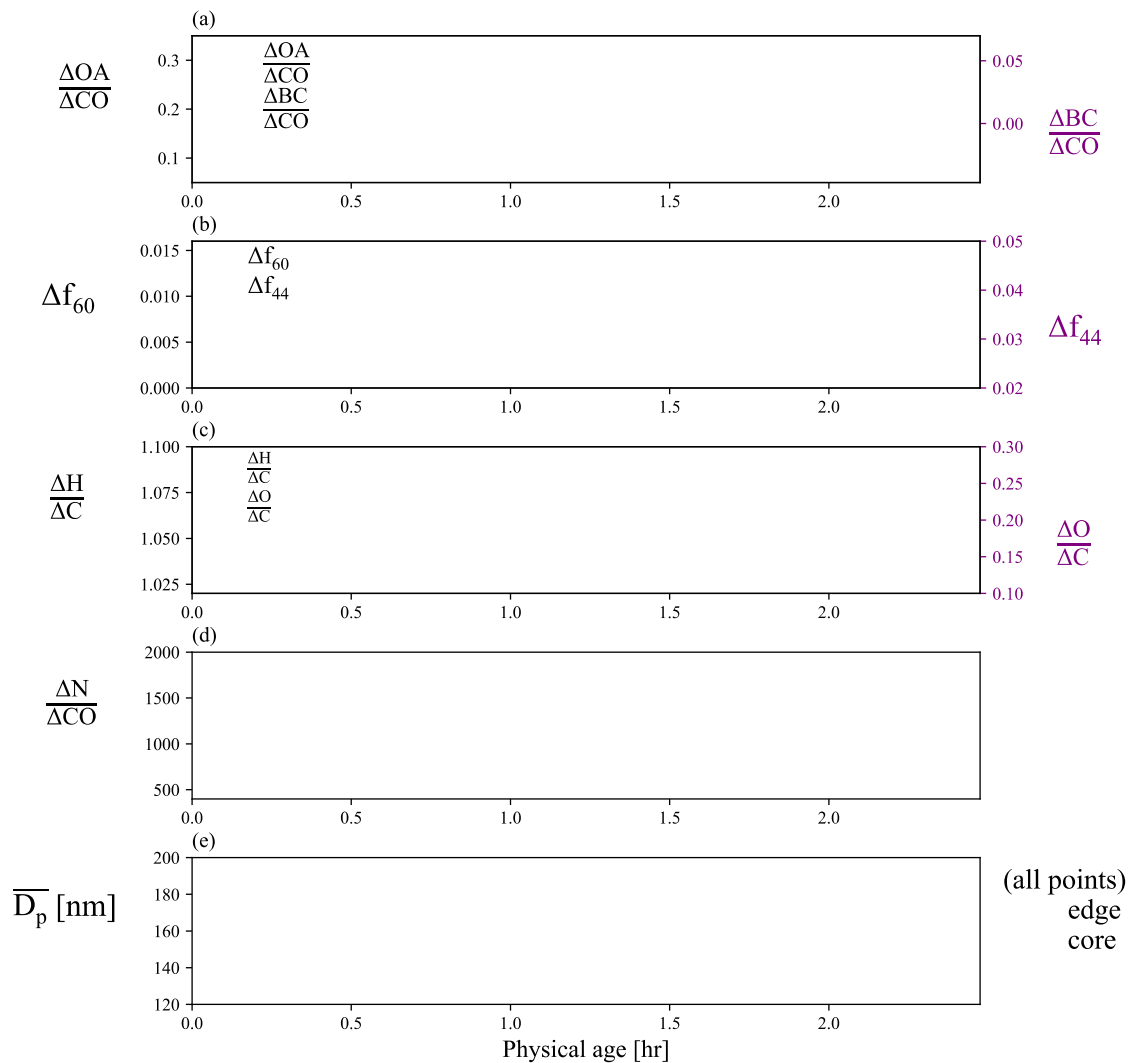
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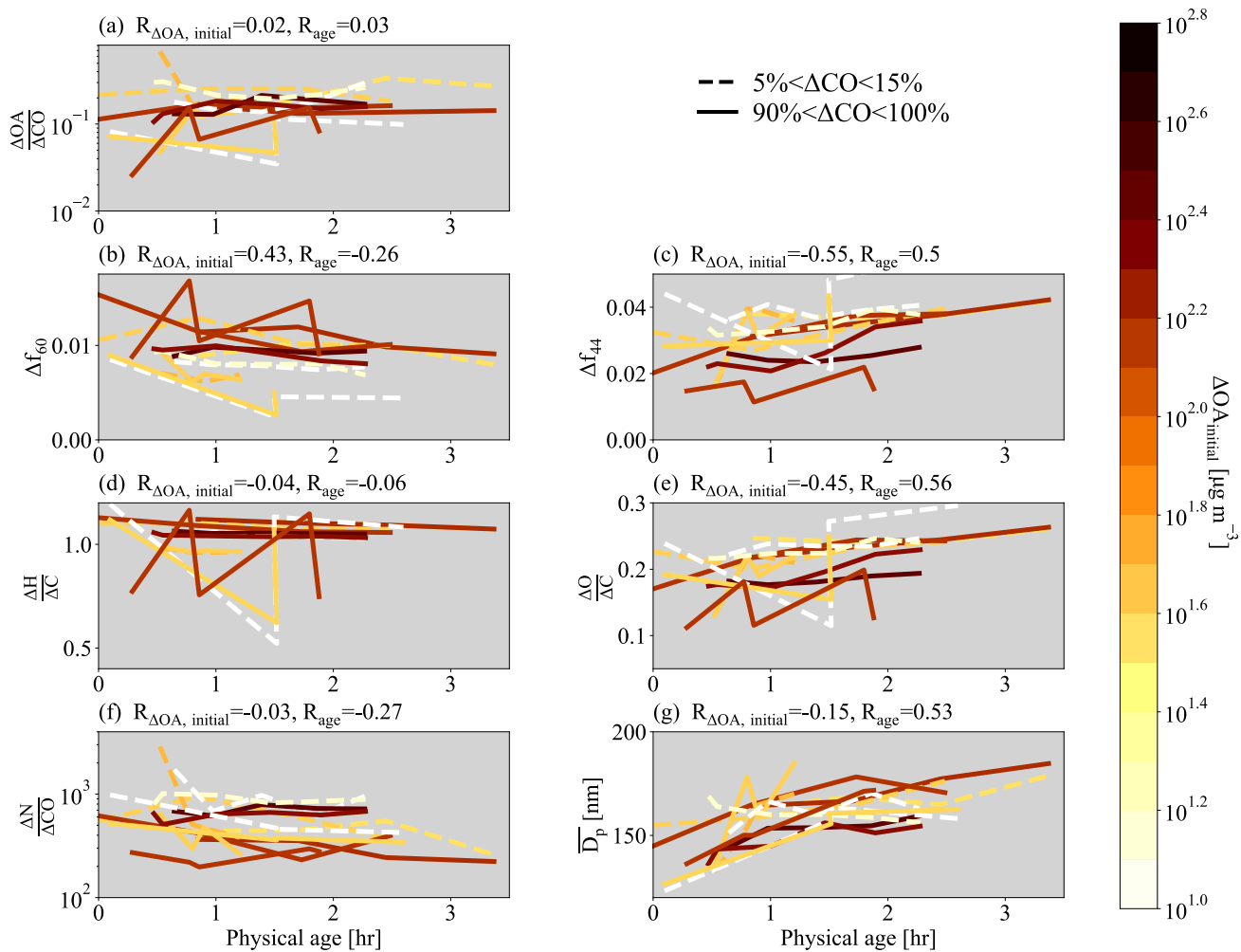
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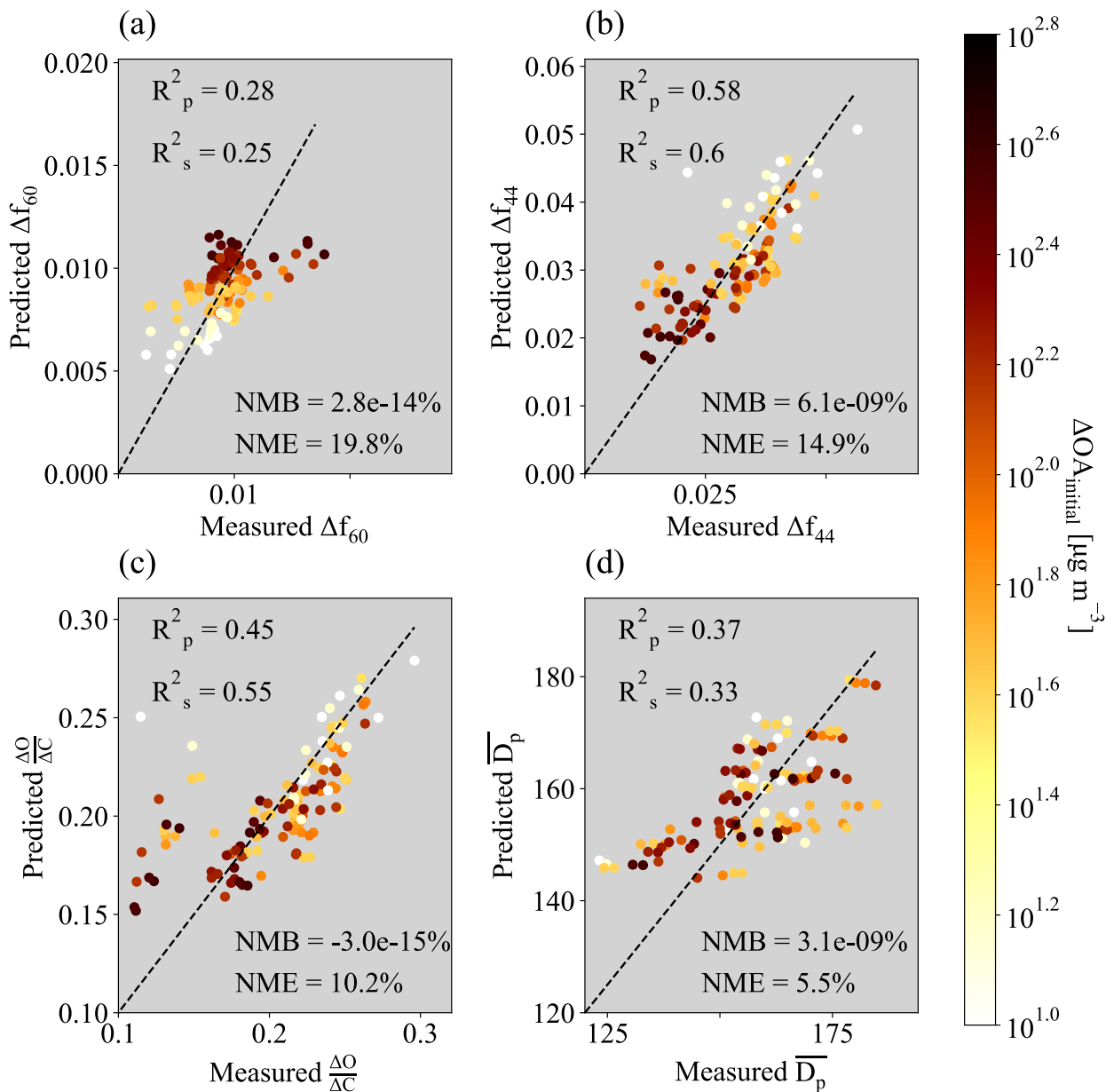
827 **Figure 1: Aerosol properties from the first set of pseudo-Lagrangian transects from the Colockum fire on flight '730b' (a) $\Delta OA/\Delta CO$**
 828 **(right y-axis) and $\Delta BC/\Delta CO$ (left y-axis), (b) Δf_{60} (right y-axis) and Δf_{44} (left y-axis), (c) $\Delta H/\Delta C$ (right y-axis) and $\Delta O/\Delta C$ (left y-**
 829 **axis), (d) $\Delta N/\Delta CO$, and (e) $\overline{D_p}$ against physical age. For each transect, the data is divided into edge (the lowest 5-15% of ΔCO data;**
 830 **red points) and core (90-100% of ΔCO data; blue points).**

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Figure 2. Various normalized parameters as a function of physical age for the 7 sets of pseudo-Lagrangian transects. Separate lines are shown for the edges (lowest 5-15% of ΔCO ; dashed lines) and cores (highest 90-100% of ΔCO ; solid lines). (a) $\Delta OA/\Delta CO$, (b) Δf_{60} , (c) Δf_{44} , (d) $\Delta H/\Delta C$, (e) $\Delta O/\Delta C$, (f) $\Delta N/\Delta CO$, and (g) \overline{D}_p between 40-262 nm against physical age for all flights, colored by $\Delta OA_{initial}$. Some flights have missing data. Also provided is the Spearman correlation coefficient, R , between each variable and $\Delta OA_{initial}$ and physical age for each variable. Note that panels (a) and (f) have a log y-axis.



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Figure 3. Measured versus predicted (a) Δf_{60} , (b) Δf_{44} , (c) $\Delta O/\Delta C$, and (d) \overline{D}_p between 40-262 nm. The predicted values are from the equation $X = a \log_{10}(OA_{initial}) + b (\text{Physical age}) + c$ where $X = \Delta f_{60}$, Δf_{44} , $\Delta O/\Delta C$, or \overline{D}_p . The values of a , b , and c are provided in Table S3. The Pearson and Spearman coefficients of determination (R_p^2 and R_s^2 , respectively) are provided in each panel, along with the normalized mean bias (NMB) and normalized mean error (NME). Note that Fig. 2 provides R values rather than R^2 to provide information upon the trend of the correlation. Included in the fit and figure are points from all four ΔCO regions within the plume (the 5-15%, 15-50%, 50-90%, and 90-100% of ΔCO), all colored by the mean $AOA_{initial}$ of each ΔCO percentile range.