Optical and Chemical Analysis of Absorption Enhancement by Mixed Carbonaceous Aerosols in the 2019 Woodbury, AZ, Fire Plume

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Abstract
Wildfires emit mixtures of light-absorbing aerosols (including black and brown carbon, BC and BrC, respectively) and more purely scattering organic aerosol (OA). BC, BrC, and OA interactions are complex and dynamic and evolve with aging in the atmosphere resulting in large uncertainties in their radiative forcing. We report microphysical, optical, and chemical measurements of multiple plumes from the Woodbury Fire (AZ, USA) observed at Los Alamos, NM, after 11–18 hr of atmospheric transit. This includes periods where the plumes exhibited little entrainment as well as periods that had become more dilute after mixing with background aerosol. Aerosol mass absorption cross sections (MAC) were enhanced by a factor of 1.5–2.2 greater than bare BC at 870 nm, suggesting lensing by nonabsorbing coatings following a core-shell morphology. Larger MAC enhancement factors of 1.9–5.1 at 450 nm are greater than core-shell morphology can explain and are attributed to BrC. MAC of OA (MAC_{Org}) at 450 nm was largest in intact portions of the plumes (peak value bounded between 0.6 and 0.9 m^2/g [Org]) and decreased with plume dilution. We report a strong correlation between MAC_{Org}(450 nm) with the f_{C2H4O2} (a tracer for levoglucosan-like species) of coatings and of bulk OA indicating that BrC in the Woodbury Fire was coemitted with levoglucosan, a primary aerosol. f_{C2H4O2} and MAC_{Org}(450 nm) are shown to vary between the edge and the core of plumes, demonstrating enhanced oxidation of OA and BrC bleaching near plume edges. Our process-level finding can inform parameterizations of mixed BC, BrC, and OA properties for wildfire plumes in climate models.

Plain Language Summary
Wildfires generate particles that can cool or warm climate regionally. Organic particles in the atmosphere typically cool climate by redirecting incoming light away from the Earth. Conversely, soot particles absorb light and can cause warming. Additionally, a specific type of organic particle called brown carbon absorbs light at visible and near-ultraviolet wavelengths. Brown carbon’s chemical composition and its ability to absorb light are not well understood, making its climate impacts highly uncertain. We estimate the absorption by aged smoke particles from the Woodbury Fire in Arizona at Los Alamos in New Mexico. Additionally, we propose a chemical tracer to estimate the absorption by brown carbon in wildfire plumes to simulate brown carbon climate impacts in climate models.

1. Introduction
Aerosols contribute significantly to Earth’s radiative budget, masking and/or confounding the greenhouse gas forcing that leads to a warmer and wetter climate (Myhre et al., 2014). By scattering and/or absorbing solar radiation, aerosols reduce surface solar radiation directly as well as indirectly by increasing cloud reflectivity, resulting in net cooling and drying. However, strongly absorbing aerosol such as black carbon (BC) can have a warming effect. Analysis shows that a substantial part of the uncertainty in aerosol climate forcing and sensitivity stems from the large spatiotemporal variations in their light absorption properties and the ways in which composition, mixing, location, and atmospheric conditions impact absorption (Bond et al., 2013; Lesins et al., 2002; Samset et al., 2018).

Wildfires and open biomass burning (BB) account for a significant fraction of global aerosol emissions: approximately 40% of global emissions of aerosol and aerosol precursors by mass and 37% of aerosol BC...
mass (Bond et al., 2004, 2013; Boucher et al., 2013). Absorbing and scattering properties of fire emitted aerosol depend on the fuels and combustion phase and change nonlinearly as the aerosol ages and mixes. Carbonaceous absorbing aerosol (CAA) from BB have a warming effect that is offset by cooling due to scattering, and the sign of the net effect remains uncertain (Myhre et al., 2014; Ramanathan & Carmichael, 2008). These CAAs include predominantly nonabsorbing organic aerosol (OA) and light-absorbing aerosol that include refractory BC (rBC) and a subset of OA that are referred to as brown carbon (BrC). BC and BrC are produced predominantly during flaming combustion (Saleh et al., 2014), while inefficient smoldering combustion primarily generates OAs (Liu et al., 2014).

Light absorption by BC is strong across the solar spectrum and increases at shorter wavelengths as the inverse of wavelength. Laboratory experiments show that OA coatings on BC can enhance its absorptivity through the lensing effect by up to a factor of ~2 (Cross et al., 2010; Schnaiter, 2005), consistent with core-shell Mie theory (Bond et al., 2006; Lack & Cappa, 2010). However, field observations show conflicting results with small enhancements in mixed urban-biogenic regions (Cappa et al., 2012) and aged wildfire plumes (Healy et al., 2015) and moderate enhancements in mixed urban-rural regimes (Liu et al., 2015). The smaller-than-expected absorption enhancement has been attributed to the complex morphology of mixed BC and OA (e.g., partially coated or fractal-like aggregates) (Cappa et al., 2019; China et al., 2013; Girotto et al., 2018; Liu et al., 2015).

Light absorption by BrC is believed to be negligible at red wavelengths but has been found to increase exponentially at shorter wavelengths (Andreae & Gelencsér, 2006; Kirchstetter et al., 2004). Brown carbon's strong wavelength dependence results in a significant contribution by BrC to the wavelength-integrated absorption in wildfire plumes (Lack et al., 2012, 2013) and laboratory biomass burn experiments (Liu et al., 2014; McClure et al., 2020; McMeeking et al., 2014). BrC absorption is also dynamic with both reductions from photo-bleaching (Adler et al., 2011; Forrister et al., 2015; Liu et al., 2016) and increased absorption through atmospheric processing (Fleming et al., 2020) by NOx oxidation (Mohr et al., 2013; Reyes-Villegas et al., 2018) and by cloud processing (Gelencsér et al., 2003) observed.

In laboratory BB experiments, some OA has been shown to absorb in the red with a steep rise in the blue (Chakrabarty et al., 2010; China et al., 2013; Hand et al., 2005; Hoffer et al., 2017; Sedlacek et al., 2018). OA with these characteristics has been hypothesized to be related to “tar balls,” spherical, carbonaceous particles observed by electron microscopy (Chakrabarty et al., 2010; Hand et al., 2005). Recently, tar balls have also been observed in ambient wildfire plumes (Adachi et al., 2019; Girotto et al., 2018). Optical attribution of red absorption to BrC is complicated because its mass is not quantified separately from BC by laser-induced incandescence (Adler et al., 2019; Sedlacek et al., 2018) or by thermal-optical experiments (Adler et al., 2019; Liu et al., 2015). Enhanced absorption treatments of BC and BrC have been included in a few climate models and show that OA significantly affects the aerosol radiative forcing depending on the OA optical properties and composition (Brown et al., 2018; Feng et al., 2013; Jacobson, 2014; Wang et al., 2018).

We investigate the complex dynamic mixing and chemical factors controlling the wavelength-dependent absorption by mixed BC-BrC-OA aerosol with observations of four distinct long-range transported fire plumes from the 2019 Woodbury Fire, AZ, USA. Comprehensive measurements of trace gases (CO, CO2, and CH4), aerosol optical properties at 450 and 870 nm, aerosol size distributions, BC mass and coating thickness, and the chemical composition of OA internally mixed with BC and of the bulk OA are integrated and interpreted. Our analysis quantifies the contributions of coated BC and BrC to the enhanced light absorption. We compare our results with other laboratory and field observations with the goal of simplifying model representations of absorption by aged wildfire aerosol.

2. The Woodbury Fire

From 20–22 June 2019, smoke from the Woodbury Fire was transported to and sampled in real time at Los Alamos National Laboratory (LANL; Los Alamos, NM, USA). The Woodbury Fire was a wildfire located in the Superstition Wilderness near Superior, AZ, USA, about 90 km east of Phoenix, AZ, USA, and 530 km southwest from our location. The fire began on 8 June 2019 and was fully contained by 15 July 2019. It burned approximately 124,000 acres of land, primarily tall grass, brush, and chaparral with stands of pinyon-juniper existing at higher elevations (https://inciweb.nwcg.gov/incident/6382/).
Four distinct plume events were observed over the 3-day period monitored. The first three plumes were observed between 12:00 am and 12:00 pm local time on 21 June 2019 in close proximity to each other and with a background that likely contained residual older smoke in the region. The fourth plume was observed 12 hr later between 12:00 am and 6:00 am on 22 June 2019. Back trajectory analysis using the NOAA HYSPLIT model (Stein et al., 2015) estimates that the plumes were emitted near Superior, AZ, USA, approximately 11–18 hr prior to the time they were observed at LANL (Figure 1). This means that emission of observed aerosol plumes occurred during the day and the sunlight exposure varied between 6.5 and 8.5 hr. Table 1 provides the transport time and sunlight exposure for each plume.

### 3. Instruments and Sampling

A suite of instruments was used to measure the chemical, physical, and optical properties of ambient aerosol and trace gas concentrations (Carrico et al., 2016; Romonosky et al., 2019) in real time. Copper tubing with an outer diameter of 0.5 in. was used as a sampling line attached to the roof of the building at ~10 m height. The inlet was downturned and covered with mesh. A cyclone separator (Model URG-2000-30EHB) was used to remove supermicron particles. A 34 L stainless-steel integration tank was located after the cyclone to split the flow for all instruments. Total flow through the sampling system was approximately 17 standard liters per minute.

Estimates of instrument variability (1-SD), except the soot particle aerosol mass spectrometer (SP-AMS, discussed below), were determined as the mean standard deviation for 30 min periods of measurements of background conditions between 6:30 pm and 10:30 pm, 21 June 2019. This uncertainty is assumed to be independent of systematic instrumental errors related to, for example, calibrations.

### Table 1

| Plume | t_{emission} (local time) | t_{observed} (local time) | A.M. sun (hr:min) | P.M. sun (hr:min) | Dark (hr:min) |
|-------|---------------------------|---------------------------|-------------------|-------------------|--------------|
| A     | 6/20/2019 12:15           | 6/21/2019 0:15            | 8:10              | 3:50              |              |
| B     | 12:40                     | 1:40                      | 7:45              | 5:20              |              |
| C     | 14:10                     | 8:10                      | 6:15              | 9:25              |              |
| D     | 6/21/2019 13:30            | 6/22/2019 0:30            | 6:55              | 4:10              |              |

*Note. Estimated sunlight exposure of each plume.*
Typical atmospheric pressure at Los Alamos, NM, is ~780 mBar. Atmospheric temperature and pressure were measured by several instruments, including the single-particle soot photometer (SP2), cavity attenuated phase shift spectrometer particulate matter single scattering albedo monitor (CAPS-PMssa), and PhotoAcoustic eXtinctiometer (PAX). Measurements have been converted to standard temperature and pressure (STP: 293.15 K and 1013.25 mBar).

Data sets have been smoothed with a LOESS filter (Schlax & Chelton, 1992) with a 30 min smoothing length weighted by measurement uncertainty and were subsampled at 5 min intervals.

3.1. Gas Measurements
Atmospheric mixing ratios of CO, CO₂, CH₄, and H₂O were measured by a G2401 (Picarro, Inc. CA, USA) (Flowers et al., 2012) and NOx mixing ratios by a model 405 NO₂/NOx monitor (2B Technologies, Boulder, CO, USA).

The modified combustion efficiency (MCE) is a parameter describing the fraction of carbon emitted by the fire that is in the form of CO₂ and is defined as

\[ MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \]

High values of MCE imply flaming conditions and efficient conversion of fuel to CO₂ (Liu et al., 2014). Here, MCE was determined by the rate of change of [CO] versus [CO₂] (ΔCO/ΔCO₂) for each individual plume, a strategy used by Collier et al. (2016) and Garofalo et al. (2019), instead of assuming background concentrations (see section S1 in the supporting information for regressions of [CO] and [CO₂]).

3.2. Particle Size Distributions and Number Concentrations
Particle size distribution based on mobility diameter (Dₘ) was measured with a scanning mobility particle spectrometer (SMPS, 3082 Electroclassifier and 3750 Condensation Particle Counter [CPC], TSI, Inc., Shoreview, MN, USA). The SMPS was configured to measure the particle number concentrations from 10.9 to 478.3 nm mobility diameter on a 2 min cycle. Uncertainty in number concentrations, assumed to be independent of instrumental variance, is estimated following the principals of counting statistics and is calculated as

\[ \sigma_{CPC} = \sqrt{\frac{N_{total}}{V_{flow} \times t_{scan}}} \]

Number concentrations were converted to volume-equivalent concentrations assuming spherical particles (DeCarlo et al., 2004). Particle mass concentrations (mₚₚₐₜ) were calculated assuming particle density of 1.4 g/cm³ (Aiken et al., 2010; DeCarlo et al., 2004; Lee et al., 2015, 2016). Particle mass spectra indicate that this size mobility diameter range incorporates the majority of submicron aerosol mass. Total particle number concentration and mass concentration were determined by summing the particle concentrations of the 105 size bins.

3.3. Optical Measurements
Absorption (Bₜₐₜ) and scattering (Bₑₙₑₜ) at 870 nm were measured by PAX (Droplet Measurement Technology, Inc., Longmont, CO, USA) (Flowers et al., 2010). The PAX instrument was calibrated following protocols in Nakayama et al. (2015) and described in Carrico et al. (2016). Single-scatter albedo (SSA) and extinction (Bₑₙₑₜ) at 450 nm were measured with CAPS-PMssa (Aerodyne Research, Inc., Billerica, MA, USA). A Mie model was used to estimate a truncation correction for a particle size distribution typical of the Woodbury plumes. This resulted in a truncation correction of +0.7% applied to the measured SSA (450 nm) values. An additional systematic uncertainty in Bₜₐₜ(870 nm), Bₑₙₑₜ(450 nm), and SSA(450 nm) is assumed to be 1-SD of 10%, 5%, and 1%, respectively (Davies et al., 2018; Massoli et al., 2010; Nakayama et al., 2015; Onasch et al., 2015). Bₜₐₜ(450 nm) is calculated based on this ratio using the following formula:
Both the CAPS and PAX sampled at 1 Hz and automatically perform a zero-calibration using clean filtered air every 5 and 20 min, respectively.

NOx absorbs light at blue wavelengths and therefore can contribute to absorption at 450 nm. Throughout the time period discussed here, the mixing ratio of NOx was stable and thus absorption by NOx is accounted for by the CAPS zero-check.

Aerosol absorption Ångström exponent (AAE) is a measure of the wavelength dependence of absorption and is calculated as

$$\text{AAE}_{450/870} = -\frac{\log(B_{\text{abs}}(450 \text{ nm})/B_{\text{abs}}(870 \text{ nm}))}{\log(450 \text{ nm}/870 \text{ nm})}$$

### 3.4. BC Mass and Coatings

rBC mass concentration was measured using SP2 (Droplet Measurement Technologies, Inc., Longmont, CO, USA) (Schwarz et al., 2006; Slowik et al., 2007). The SP2 directly measures rBC mass using laser-induced incandescence on a particle-by-particle basis. Additionally, the SP2 provides an estimate of particle size based on a scattering signal and positional sensitive channel (split detector). The SP2 was operated at a flow rate of 120 cm$^3$/min.

Aerosolized and mobility-size-selected Aquadag was used to calibrate rBC mass, and polystyrene latex beads (PSLs) of diameters 170 to 350 nm were used to calibrate particle size. Laborde et al. (2012) demonstrated that the SP2 incandescing signal sensitivity (incandescing peak height versus aerosol mass) varies for different rBC types. The SP2 incandescing signal was found to be 20–40% higher for aerosolized Aquadag than for ambient aerosol of the same rBC mass. However, Aquadag was the only surrogate that provided consistent calibration between production batches. We have applied a correction following recommendations by Baumgardner et al. (2012) to account for the lower sensitivity of the SP2 to ambient aerosol. An additional systematic uncertainty of 10% is assumed for this correction.

Aerosol flow to the SP2 was diluted by filtered air, and an empirical dilution factor was applied to the mass concentration (section S2). Briefly, the dilution factor was estimated by a linear orthogonal-distance regression (ODR) (Boggs et al., 1987; Boggs & Rogers, 1990) comparing the SMPS-based number concentration to the SP2-based number concentration for particles between 216 and 478 nm diameter. From this analysis, the dilution factor was estimated to be 48.9 with a 5% uncertainty based on its sensitivity to the selected particle-size window.

rBC coating thickness was determined using a leading-edge fit technique (Gao et al., 2007; Laborde et al., 2012). For this analysis, we assumed a refractive index for coatings (RI = 1.50 + 0i) and for the core (RI = 2.26 + 1.26i) (Laborde et al., 2012; Moteki & Kondo, 2010). Coating mass was estimated assuming spherical core-shell structure of outer diameter determined by the leading-edge of the scattering channel, inner diameter of $D_{\text{core}}$, and assuming a density of organic coatings of $\rho_{\text{org}} = 1.2$ g/cm$^3$ (Arnott et al., 2000; Turpin & Lim, 2001). The coating mass concentration ($m_{\text{coat}}$) was calculated as the mass sum of coatings per STP unit volume of air.

The mass absorption cross section ($\text{MAC}^{\text{SP2}}, \text{m}^2/\text{g} [\text{rBC}]$) was determined from rBC mass concentration ($m_{\text{BC}}$) and the light absorption at the specified wavelength. $\text{MAC}^{\text{SP2}}$ is an empirical estimate of the bulk aerosol mass absorption per unit rBC mass at a given wavelength and is defined as

$$\text{MAC}^{\text{SP2}}(\lambda) = \frac{B_{\text{abs}}(\lambda)}{m_{\text{BC}}}$$

### 3.5. Aerosol Chemical Composition

Aerosol chemical composition was measured with an SP-AMS (Aerodyne Research, Inc., Billerica, MA, USA). The SP-AMS is a high-resolution time-of-flight mass spectrometer (HR-ToF-MS) equipped with a 1,064 nm Nd-YAG laser for vaporization of rBC and associated mass in addition to a thermal vaporizer for detection of nonrefractory (NR) aerosol mass (Canagaratna et al., 2007; Cross et al., 2012; DeCarlo 10.1029/2020JD032399
et al., 2006; Jayne et al., 2000; Onasch et al., 2012). The SP-AMS time-of-flight was operated in the lower mass resolution (V-mode). The SP-AMS sampling was in parallel to the SP2, and aerosol flow to this instrument was diluted by the same factor as the SP2 (see section S2).

During the measurement period, the SP-AMS was operated in one of two vaporization modes: first with the laser vaporizer on and the thermal vaporizer at 100°C and later with the laser on and the thermal vaporizer set to 600°C. With the thermal vaporizer at 100°C, the SP-AMS dominantly measures the composition of rBC-containing aerosol and is referred to as the “rBC mode.” In this setting, the thermal vaporizer is too cool for flash vaporization of OA and NR inorganics (Jayne et al., 2000), but some OA may stick to the vaporizer and evaporate slowly. This mass is subtracted out by analyzing the closed mass spectra (DeCarlo et al., 2006; Drewnick et al., 2005). Increasing the thermal vaporizer to 600°C allows additionally for analysis of externally mixed NR aerosol and is referred to as “rBC + NR” mode.

Vaporization settings were changed between 8:30 am and 9:40 am local time on 21 June 2019. Plumes A, B, and the first part of Plume C were measured while in rBC mode, providing information on rBC-containing aerosol. The later parts of Plumes C and D were measured in rBC + NR mode, which included the externally mixed NR aerosol.

Different vaporization modes can result in different fragmentation patterns, collection, and ionization efficiencies (Canagaratna et al., 2015; Corbin et al., 2014; Lee et al., 2015; Onasch et al., 2012). Vaporization in rBC mode is considered to be “softer” than thermal vaporization at 600°C (Canagaratna, Massoli, et al., 2015; Cross et al., 2012; Onasch et al., 2012), meaning that the thermal vaporizer fragmentation pattern has a higher fraction of low mass ions (m/z < 60) (Canagaratna et al., 2015; Lee et al., 2017). Additionally, a bias has been observed between modes when interpreting the elemental ratios H/C and O/C (Canagaratna, Jimenez, et al., 2015; Lee et al., 2017). A correction of 1.16 and 0.83 has been applied to H/C and O/C elemental ratios, respectively, measured by the laser-only vaporization mode as suggested by Canagaratna, Massoli, et al. (2015) and Lee et al. (2017).

Analysis of SP-AMS mass spectra was performed using the software Squirrel/PIKA (version 1.62D/1.22D) written in IGOR (Wavemetrics, Inc, Lake Oswego, OR, USA). Mass spectra were analyzed with high-resolution peak fitting for ion signals <116 m/z where the majority of the mass was observed in both modes. SP-AMS was calibrated for NR species by atomizing ammonium nitrate in 18.2 MΩ-cm water, drying the aerosol with a diffusion drier, and size-selecting 300 nm mobility diameter particles (Canagaratna et al., 2007; DeCarlo et al., 2006; Jimenez, 2003). The aerosol concentration was varied using a diluter and monitored by a CPC. The measured ion efficiency (IE(NO3)) compares the mass concentration estimate based on the particle size, density, and number concentration to the SP-AMS signal and thus incorporates most losses. For this data, IE(NO3) was determined to be 8.93 × 10^{-8} ions/molecule (NO₃), and we used the relative mass ionization efficiency values from Jimenez (2003) for both vaporization modes as suggested by Healy et al. (2015) and Lee et al. (2016).

Since rBC mass was measured by the SP2, we do not report SP-AMS rBC mass.

Total organic mass concentration (mOrg) is estimated as the product of the SMPS-derived total aerosol volume concentration (Vtotal, section 3.2) multiplied by the average aerosol density and the organic mass fraction (fOrg).

\[
m_{\text{Org}} = V_{\text{total}} \cdot \rho_{\text{aerosol}} \cdot f_{\text{Org}}
\]

\(\rho_{\text{aerosol}}\) is assumed to be 1.2 g/cm³ (Aiken et al., 2010; DeCarlo et al., 2004; Lee et al., 2015, 2016). For the Woodbury plume events, fOrg is estimated to be 0.873 ± 0.015 (95% confidence interval, section S3) based on measurements made with the SP-AMS. mOrg is compared to the mass concentration of rBC (section 3.4) to describe the externally mixed mass ratio (referred to as Org/rBC) and to the coating mass concentration (section 3.4) (referred to as Coating/Org).

4. Characterization of Woodbury Plumes: Optical, Physical, and Chemical Properties

A time series of measurements for the Woodbury plume events is shown in Figure 2. We resolved four major plume events labeled “A” to “D” (boxes in Figure 2). Plume events were identified by synchronous increases
in CO, particle mass concentration, $B_{\text{abs}}(450 \text{ nm})$, and $B_{\text{abs}}(450 \text{ nm})$, and respective peak enhancement factors were 14, 54, 70, and 350 above background for Plume B and 3, 10, 10, and 50 during the other plumes (Figures 2a–2c). The duration of each plume sampling ranged from 1.5 to 5.5 hr. At the onset of each plume event, we observed a step change in the mode mobility diameter particle size from $D_m < 60 \text{ nm}$, representative of background periods, to $D_m > 100 \text{ nm}$ throughout the duration of the plumes (Figure 2c). Additionally, OA, rBC, and nitrate mass concentrations all peaked during each plume (Figure 2e). As noted earlier, all the smoke plumes were emitted during the day and were sampled 11–18 hr after emission with solar exposure varying between ~6.5 and 8.5 hr (Table 1).

### 4.1. Plume B: Core of the Intact Wildfire Aerosol Plume

The largest values of CO, particle mass concentration, and $B_{\text{abs}}(450 \text{ nm})$, and $B_{\text{abs}}(450 \text{ nm})$, were observed during Plume B. Plume B exhibited high mean MCE (0.90) indicative of a mix of smoldering and flaming fire conditions (Collier et al., 2016; Liu et al., 2014) and was the lowest value observed for all the plumes (Figure 2a). The emission ratio of $\Delta rBC/\Delta CO$ is a conservative tracer of smoke in the plume as it mixes with ambient air. Lower values of $\Delta rBC/\Delta CO$ during Plume B ($2.6 \mu g \cdot m^{-3} \cdot ppm^{-1}$, Figure 2d) than the other plumes are consistent with mixed smoldering-flaming conditions indicated by its lowest mean MCE value (Figure 2a).
Furthermore, Plume B exhibited the highest values of $\text{AAE}_{450/870}$ (2.4, Figure 2c) among all plumes, indicating that it contained the most BrC (Chylek et al., 2019; Kirchstetter et al., 2004). Plume B also had a higher fraction of OA internally mixed with rBC particles ($m_{\text{coat}}/m_{\text{Org}} = 0.05$, Figure 2b). Plume B was likely the core of the intact transported plume to our site and experienced the least aging and dilution by entrainment with background air.

### 4.2. Plumes A and C: Aerosol in Periphery to the Core of the Plume

Several intensive properties of Plumes A and C, such as MCE (0.95) and $\text{AAE}_{450/870}$ (2.0), were similar to Plume B. These plumes occurred immediately before and after Plume B. All three plumes were emitted during the same daytime period and sampled within a 12 hr timespan. Background conditions were not observed between Plumes A and C. Lower peak values of $B_{\text{abs}}$ (450 nm) and $m_{\text{part}}$ and the short time period between plumes indicate that Plumes A and C likely represent similar primary emissions as Plume B but had experienced greater mixing with background air and a higher degree of atmospheric processing. Plume A exhibited similar $m_{\text{coat}}/m_{\text{Org}}$ (0.05) as Plume B while Plume C exhibited a significantly lower fraction (0.03). Lower $\Delta \text{rBC}/\Delta \text{CO}$ during Plume C (2.8 $\mu g \cdot m^{-3} \cdot ppm^{-1}$) in comparison to Plume A (3.1 $\mu g \cdot m^{-3} \cdot ppm^{-1}$), potentially indicating mixing with residual smoke from Plume B.

### 4.3. Plume D: A Different Primary Emission Mixed With Background Aerosol

Plume D was observed after a 12 hr period of background conditions. We hypothesize that the lower peak values of $B_{\text{abs}}$ and particle mass concentration indicate that Plume D experienced more aging and mixed with cleaner ambient air than Plumes B and C. $[\text{CO}]$ and $[\text{CO}_2]$ over this period did not covary likely due to mixing and resulted in MCE values (1.01) statistically the same as complete combustion (see section S1). Characteristics of this plume were distinct from the others despite similar (11 hr) transport and sampling times. Plume D exhibited noticeably higher MCE, lower $m_{\text{coat}}/m_{\text{Org}}$ (0.03), and lower $\text{AAE}_{450/870}$ values (1.3–1.9) than others. The different characteristics of Plume D and its separation in time from the other plumes likely result from a change in primary emissions and a larger contribution from mixing with background air along the trajectory of the less intact plume.

### 5. Enhanced Absorption by Internal Mixing With rBC and Brown Carbon

#### 5.1. MAC Dependence on Mixing State and Composition

The observed MAC$^{\text{SP2}}$ for the aged Woodbury smoke ranged from 6.6–9.7 $m^2/g$ (rBC) at 870 nm and 16.7–43.7 $m^2/g$ (rBC) at 450 nm that is much larger than the respective ~4 and ~9 $m^2/g$ (rBC) values reported for pure BC (Bond & Bergstrom, 2006; Cross et al., 2010; Zanatta et al., 2016). To understand the mechanisms causing the MAC$^{\text{SP2}}$ enhancements, we related it to the independent measurements of the internally mixed and externally mixed OA/rBC composition in Figure 3. First, the coating mass determined by the SP2 and compared to rBC mass (Coating/rBC, section 3.4) ranges from 2.6 to 6.2 (Figures 3a and 3c). Second, the total submicron mass concentration that was determined from the measured size distributions (section 3.2) and divided by the SP2 measured rBC mass concentration (Org/rBC, section 3.5) ranges from 28 to 45 (Figures 3b and 3d). The top panels (Figures 3a and 3b) plot the observed MAC$^{\text{SP2}}$ values at 870 nm against the Coating/rBC and Org/rBC, and the bottom panels plot the observed MAC$^{\text{SP2}}$ values at 450 nm.

While there was significant variability among the plumes, a correlation between MAC$^{\text{SP2}}$ and both the Coating/rBC and total OA/rBC compositions is clear. The correlation is present in all plumes and most evident in Plume B, which had the largest signal and underwent the least mixing with ambient background air. The other plumes exhibited a higher degree of mixing with background, which is apparent in Figure 3 as deviations from the trend line—particularly for Plume D (blue symbols). We also compared averaged MAC$^{\text{SP2}}$ values and mixing states at the peak of each plume in Figure 3 (represented by diamond symbols), which show consistent trends across the four observed Woodbury plumes, with Plume D a slight outlier due to reasons discussed earlier.

The fit of the observed MAC$^{\text{SP2}}$ values in comparison to Coating/rBC at 870 nm was determined using an ODR technique (Boggs et al., 1987; Boggs & Rogers, 1990). This resulted in a maximum likelihood intercept of $4.4 \pm 0.9 \text{m}^2/\text{g}$ (rBC) (Figure 3a), which corresponds to a MAC value of uncoated rBC (MAC$_{\text{rBC}}$) and agrees well with previously published values (Bond & Bergstrom, 2006; Cross et al., 2010). Org/rBC at
870 nm spanned a smaller range than Coating/rBC, and, despite this, fitting the observed MACSP2 to Org/rBC yielded an intercept of 3.1 ± 1.3 m²/g (rBC) (Figure 3b) also consistent within uncertainties of MACrBC. We used the former value (4.4) to derive absorption enhancements as this value was based on the larger range of Coating/rBC. Uncertainty in MACrBC is propagated through the following calculations.

We estimate the absorption enhancements from the derived MACrBC value as follows:

$$E_{\text{abs}}(\lambda) = \frac{\text{MAC}_{\text{SP2}}(\lambda)}{\text{MAC}_{\text{rBC}}(\lambda)} = \frac{\text{MAC}_{\text{SP2}}(\lambda)}{4.4 \cdot \frac{1}{\text{AAE}_{\text{rBC}}}}$$

Here we assumed an AAE for pure rBC of 1 (Bond & Bergstrom, 2006). The expected MACrBC(450 nm) was then assumed to be 8.6 ± 1.9 m²/g (rBC). This was useful to interpret the relationships in Figure 3. In addition, the enhanced absorptions relative to pure rBC observed in the Woodbury plumes ranged from 1.5 – 2.2 at 870 nm and 1.9 – 5.1 at 450 nm (Figure 4a).

A factor of ~2 enhancement can be explained by core shell Mie theory via transparent coatings alone (Ahern et al., 2016; Bond et al., 2006; Schnaiter, 2005). This mechanism could account for most of the observed enhancement at 870 nm. In contrast, we observed much larger absorption enhancements of 1.9 – 5.1 at 450 nm that cannot be explained by core shell alone and signifying the presence of light-absorbing BrC. The trend of MACrBC(450 nm) with Org/rBC is captured by a linear fit that is forced with an intercept of 8.4 m²/g (rBC).

Our results are consistent with past studies that show small enhancements at red and green wavelengths and larger enhancements in the blue. Liu et al. (2015) observed some enhancements at 781 nm (factor of 1.4) in ambient aerosol of mixed sources from residential heating, traffic, and long-range transport and attributed them to coatings. They also report larger enhancements at 405 nm (factor of 2) that they attribute to BrC that have been characterized as nitrogen-containing organic compounds (Mohr et al., 2013). Lack et al. (2012)
found similar results for wildfire smoke measured in the near-field, with an enhancement factor of 1.4 for 532 nm and 2 for 404 nm. Other ambient fire studies have reported no enhancement at green or red wavelengths (Healy et al., 2015; Lack et al., 2012).

### 5.2. Absorption Enhancement Attribution and MACs of BrC

The large absorption enhancements at the blue wavelength could result from the lensing effect and by the absorption by BrC present in OA. To separate the two effects, we quantitatively bounded the bulk absorption efficiency of OA (MAC\(_{\text{Org}}\)) using an optical closure calculation. In this estimate, we assumed that OA internally mixed with rBC had the same absorption efficiency as the bulk OA. The following equation expresses absorption at wavelength \(\lambda\) by the different components in terms of their MAC values and their mass quantity with the absorption by rBC enhanced by a lensing effect (\(K_{\text{lens}}\)):

\[
B_{\text{abs,Obs}}(\lambda) = MAC_{\text{Org}}(\lambda) \times m_{\text{Org}} + K_{\text{lens}} \times MAC_{\text{BC}}(\lambda) \times m_{\text{BC}}
\]

We use the term “MAC\(_{\text{Org}}\)” instead of “MAC\(_{\text{BrC}}\)” as we did not identify the specific organic compounds which contributed to absorption. MAC\(_{\text{Org}}\) is therefore the effective absorption efficiency of OA, which includes BrC and nonabsorbing OA. MAC\(_{\text{Org}}\) likely varied between different wildfires and within a smoke plume as the composition and properties of OA changed.

Here we bound MAC\(_{\text{Org}}\) for the Woodbury plumes with three estimates that assumed distinct contributions to absorption and lensing enhancements in the red as follows:

**Minimum estimate of MAC\(_{\text{Org}}\):**

\[
MAC_{\text{Org}}(870 \text{ nm}) = \frac{B_{\text{abs}}(870 \text{ nm}) - K_{\text{lens}} \times MAC_{\text{BC}}(870 \text{ nm}) \times m_{\text{BC}}}{m_{\text{Org}}}
\]

**Maximum estimate of MAC\(_{\text{Org}}\):**

\[
MAC_{\text{Org}}(870 \text{ nm}) = \frac{B_{\text{abs}}(870 \text{ nm}) - MAC_{\text{BC}}(870 \text{ nm}) \times m_{\text{BC}}}{m_{\text{Org}}}
\]

\[K_{\text{lens}} = 1\]

MAC\(_{\text{Org}}\) estimated for each wavelength following Mie approximations by Bond et al. (2006) which were used to estimate MAC\(_{\text{Org}}\)(870 nm) and MAC\(_{\text{Org}}\)(450 nm).

Our minimum and maximum estimate represent the lower and upper bounds of MAC\(_{\text{Org}}\) based on physical constraints. Mie approximations were made with the assumptions of transparent OA coatings on an rBC
particle in a core-shell structure (Bond et al., 2006). Dcore is based on mrBC measurements and assuming an rBC density of 1.8 g/cm³. These assumptions provided a theoretical maximum estimate of the lensing, and therefore a minimum estimate of MACOrg, but with significant uncertainty. The three estimates of MACOrg are shown in Figures 4b and 4c.

During the peak of Plume B, we observed high values of MACOrg(450 nm) (Figure 4b) between 0.61 ± 0.24 m²/g (Org) (lower bound ±1-SD) and 0.86 ± 0.22 m²/g (Org) (upper bound ±1-SD). At the beginning of Plumes A and D, presumed to be the peripheries of the plumes with the largest degree of mixing, MACorg(450 nm) was estimated to be between 0.15 ± 0.25 m²/g (Org) (lower bound ±1-SD) and 0.45 ± 0.22 m²/g (Org) (upper bound ±1-SD). Upper bounds of MACOrg(870 nm) ranged between 0.07 ± 0.01 m²/g (Org) (1-SD) during Plume C and 0.15 ± 0.16 m²/g (Org) (1-SD) during Plume A. Estimates of MACOrg(870 nm) were not significantly different than 0 m²/g (Org), and we could not exclude large values of kOrg (blue lines, Figure 4c).

Our estimates of MACOrg(450 nm) for the Woodbury plumes are in broad agreement with previous reported values of MACOrg for blue wavelengths for ambient wildfire aerosol (0.5–1.5 m²/g [Org]) (Lack et al., 2012, 2013) and from laboratory biomass burns (0.2–1.3 m²/g [Org]) (Chakrabarty et al., 2016; McClure et al., 2020). In the Woodbury plumes, MACOrg(450 nm) covaried with Babs(450 nm) and particle mass concentration implying variations in BrC fraction of OA, where less diluted/aged aerosol corresponded with a larger BrC fraction of OA.

At 870 nm, we saw independent evidence of significant enhancements due to lensing on rBC (Figures 3c and 3d). In this analysis, MACOrg(870 nm) could not be distinguished from 0 with high confidence. Modeled values (Model iii, medium case) ranged from 0.03 ± .06 to 0.08 ± .07 m²/g (Org) (1-SD) in the red. Our fire plume data are therefore consistent with most prior observations that show either no absorption by OA in the field at green and red wavelengths (Cappa et al., 2012; Healy et al., 2015; Kirchstetter et al., 2004; Lack et al., 2012) or very weak enhancements (Chakrabarty et al., 2016; McClure et al., 2020; Yang et al., 2009). In addition, our MAC (870 nm) in the fire plume was more than an order of magnitude lower than the MACOrg(661 nm) of 0.9–2.0 m²/g observed by Adler et al. (2019) for laboratory burns. This underscores the need for more field observations to quantify absorption efficiency of OA at red wavelengths to resolve the issue raised by Adler et al. (2019).

5.3. Mie Inversions of Refractive Index

Climate models often use prognostic treatments of aerosol where optical properties are calculated using refractive indices and Mie theory (Feng et al., 2013; Jacobson, 2014; Saleh et al., 2015). Typically, the refractive index of aerosol is calculated from the pure components using volume mixing rules (Lesins et al., 2002). Although the spherical, internally mixed Mie scattering model may be an oversimplification, it has been found to be a reasonable approximation for thickly coated and aged aerosol (Lesins et al., 2002; Romonosky et al., 2019; Washenfelder et al., 2015). This model does tend to overestimate absorption enhancement when compared to the core-shell model using the same value of kOrg (Bond et al., 2006; Jacobson, 2000) and would therefore represent a lower limit for the imaginary part of the refractive index of OA (kOrg).

Figure S5 shows the Mie scattering model results of the refractive indices of BrC with real part of 1.46 (Chylek et al., 2019; Schmid et al., 2009). Model results indicate kOrg at 870 nm is a maximum of 0.010i ± 0.005i for all plumes assuming the upper bound scenario and 0.050i ± 0.005i for Model iii. Values of kOrg at 450 nm (0.010i to 0.020i based on Model iii) compare reasonably well to previous estimates of kOrg for blue wavelengths (Chylek et al., 2019; Romonosky et al., 2019; Washenfelder et al., 2015).

5.4. Chemical Markers for Wildfire-OA Associated With rBC and Bulk OA

During the four Woodbury wildfire plumes, we measured chemical composition with the SP-AMS in rBC and rBC + NR modes (section 3.5). Here, we present a novel comparison of the rBC-associated OA with the more historically well characterized bulk NR OA as it is relevant to light-absorbing properties (Lack et al., 2012, 2013).

In Figure 5a, we present the first high-resolution version of the BB OA aging plot (Cubison et al., 2011; Ortega et al., 2013) sampled with the SP-AMS from an ambient wildfire. Building upon the unit mass resolution OA fractions at m/z 44 (f44) and m/z 60 (f60) that are ratios of the signal at that nominal mass to total OA...
signal, we present the dominant exact ion species at each nominal mass: CO$_2^+$ (m/z = 43.990) at m/z 44 and C$_2$H$_4$O$_2^+$ (m/z = 60.021) at m/z 60. f$_{CO2}$ is the fraction of CO$_2^+$ signal attributable to OA to the total submicron OA measured by the SP-AMS. This fraction is the high-resolution version of $f_{44}$ which can include other fragment ions, such as C$_2$H$_4$O$^+$ and C$_2$H$_6$N$^+$ (Aiken et al., 2010; Canagaratna, Jimenez, et al., 2015). For the Woodbury data, CO$_2^+$ was 99% (± 3%) and C$_2$H$_4$O$_2^+$ was 89% (± 1%) of the total ion signal at each nominal m/z (see section S5). In this way, we use the exact ion tracers for oxygen content within $f_{44}$ that have been used to study photochemical processes via changing oxidation of OA (Alfarra et al., 2004; Canagaratna et al., 2007; Zhang et al., 2005) and for primary BB OA within $f_{60}$ using the main levoglucosan fragment ion (Alfarra et al., 2007; Simoneit et al., 1999).

A negative relationship was observed between f$_{C2H4O2}$ when plotted against f$_{CO2}$ that is interpreted as aging of the primary BB OA and/or dilution via mixing with more oxidized and cleaner background air masses (Cubison et al., 2011; Garofalo et al., 2019; Jolleys et al., 2015). Plumes A and B had the highest f$_{C2H4O2}$ and lowest f$_{CO2}$, typical for near-source wildfire NR submicron OA that have been aged less than a day in the atmosphere (Lack et al., 2013; Sedlacek et al., 2018; Zhou et al., 2017). The plume average data in the rBC mode (Plumes A, B, and C diamonds) fell within the range that has been previously reported for bulk wildfire NR OA (Cubison et al., 2011; Jolleys et al., 2015). Plumes C and D had lower total mass concentrations as well as lower f$_{C2H4O2}$ and higher f$_{CO2}$ as have been observed in more aged BB plumes in the field and laboratory (Ortega et al., 2013; Zhou et al., 2017). When the SP-AMS was switched to rBC + NR mode during Plume C, both factors decreased (f$_{CO2}$ decreased from 0.14 to 0.11 and f$_{C2H4O2}$ from 0.015 to 0.014), which could be due to changes in the plume chemical composition, fragmentation patterns, and/or OA detection efficiencies. Enhanced f$_{CO2}$ has been previously reported for the SP-AMS in rBC-mode (Canagaratna, Massoli, et al., 2015; Corbin et al., 2014; Onasch et al., 2015). Potential explanations include the presence of refractory OA species bound to the rBC in addition to differences in the fragmentation pattern of OA in comparison to rBC + NR mode. For these reasons, we did not pursue comparison of the ratio of f$_{CO2}$ to f$_{C2H4O2}$ across different vaporization modes in the SP-AMS.

In the Woodbury plumes, a positive trend was observed for the primary wildfire OA fraction (f$_{C2H4O2}$) with the ratio of coating thickness to rBC (Coating/rBC) for the rBC-containing particles as measured by the SP2. This relationship can be seen in Figure 5b and was preserved across the different vaporization modes and plumes. For all four plumes, thicker coatings and higher primary BB OA fractions were observed during peak signals, when plumes were the most intact and exhibited the highest mass concentrations. The consistent correlation within measurement uncertainties across the different vaporization modes suggests that the bulk NR-OA that dominated in total mass had similar f$_{C2H4O2}$ to OA that was internally mixed with rBC. Further study is required since primary BB OA is known to have higher volatility than other OA factors (Huffman et al., 2009) and as such may have partially vaporized from the non-rBC-containing particles during peaks of the plumes or fragmented less. In the future, operating colocated instruments, one operating in rBC mode and one with standard 600°C thermal vaporization (bulk NR OA), could be used to resolve this
further (e.g., Lee et al., 2017). A positive trend was also observed for the relationship between the bulk OA to rBC mass ratio (Org/rBC) for Plumes A–C, but Plume D represented an outlier with high Org/rBC and low \( f_{C_2H_4O_2} \) values (Figure S8a), likely due to mixing with background OA from different sources and possibly confounded by the different sampling modes.

Using the high-resolution data, we determined the elemental ratios of the rBC-associated OA and NR OA (Aiken et al., 2007, 2008; Canagaratna, Jimenez, et al., 2015). In Figure 5c, we plot the hydrogen-to-carbon ratio (H/C) versus the oxygen-to-carbon ratio (O/C) in a van Krevelen diagram for all four plumes. The four plumes did not span across a large range in values (H/C from 1.27–1.41 and O/C from 0.68–0.80 for plume peak averages), which was consistent with sampling intact plumes with similar aging times on top of a relatively clean background aerosol. The H/C versus O/C of the plumes fell between the 1:1 and 0.5:1 space of the diagram consistent with reported aged fire aerosol field and laboratory observations (Cubison et al., 2011; Ortega et al., 2013). The observed slopes were also consistent with the addition of both acid and alcohol functional groups with no fragmentation to form a hydroxycarbonyl or carboxylic acid during oxidation (Heald et al., 2010; Kroll et al., 2011).

5.5. Associations of Brown Carbon With Chemical Proxies

Here we relate our derived MAC_{Org} to the observed chemical markers in the Woodbury plumes. Since BrC mass and composition evolve, it is important to identify a proxy to trace BrC emissions and its atmospheric processing (Flowers et al., 2010; Forristeer et al., 2015; Lack et al., 2013; Mohr et al., 2013; Washenfelder et al., 2015). \( f_{60} \) is an established and widely used tracer for fresh BB emissions. We found a strong correlation between MAC_{Org}(450 nm) and \( f_{60} \) and the high-resolution analog \( f_{C_2H_4O_2} \) (Figure 6a). \( f_{C_2H_4O_2} \) is related to the relative abundance of levoglucosan in OA, but levoglucosan does not absorb radiation at the wavelengths measured here and is not BrC. The correlation was consistent across all plumes with varying Org/rBC mass ratios despite varying relationships of MAC_{Org}(450 nm) with Org/rBC between plumes (Figure 6b). The strong correlation provided evidence that BrC in the Woodbury Fire was most likely coproduced with levoglucosan as a primary OA formed during flaming conditions.

Lack et al. (2013), Washenfelder et al. (2015), and Forristeer et al. (2015) have also noted a relationship between levoglucosan and BrC absorption at 404, 365, and 360 nm, respectively. While we also observed some correlation of \( f_{60}/f_{44} \) with MAC_{Org}(450 nm) for the Woodbury Fire plumes, we found the relationship to be weaker than it was for \( f_{C_2H_4O_2} \) (Figure 6c). The positive trend
was not surprising given the positive relationship of BrC with levoglucosan, but the slope of the regression was much lower than that estimated by Lack et al. (2013). This is possibly due to Lack et al. (2013) having measured the bulk NR-OA composition close to the fires in comparison to our measurements that sampled OA internally mixed with rBC from more aged plumes. It has previously been observed that different plumes follow distinct evolutions of $f_{45}$ in comparison to $f_{44}$ (Garofalo et al., 2019; Jolleys et al., 2015), implying the relationship of BrC with $f_{45}/f_{44}$ is specific to the plume being measured. Regardless, we found $f_{C2H4O2}$ to be a better indicator of BrC in the Woodbury Fire plumes and was shown to be a viable predictor of BrC for other wildfire plumes including those discussed in Lack et al. (2013), Washenfelder et al. (2015), and Forrister et al. (2015).

5.6. Cross-Plume Variability of BrC MAC$_{Org}(450 \text{ nm})$ and Oxidation State

We expect our observations of BrC absorption in the Woodbury plumes, which have undergone 11–18 hr of atmospheric transport, about half of it during daytime (Table 1), to include some effects from photochemical bleaching that can occur on similar time scales (Fleming et al., 2020; Forrister et al., 2015; Wong et al., 2019). In this case, the shortwave absorption enhancements from BrC at the time the plumes were observed at LANL should have been reduced relative to the fresh emissions. While we were unable to quantify the potential bleaching during transport, we did analyze the variation in MAC$_{Org}(450 \text{ nm})$ (inferred from Model iii) compared to [CO] across the plumes as shown in Figure S9a. CO has a relatively long lifetime compared to our plume transit times (Zheng et al., 2019), and we used [CO] as a proxy for plume dilution, with higher CO concentrations indicating closer proximity to the core of the plume. For the most prominent and intact Plume B and Plume A, the MAC$_{Org}(450 \text{ nm})$ decreased linearly with [CO] from the core of the plumes to their edges. For Plume B, MAC$_{Org}(450 \text{ nm})$ increased when the plume was first observed, peaking at 0.66 m$^2$/g (Org). Following the peak, MAC$_{Org}(450 \text{ nm})$ decreased and plateaued at 0.44 m$^2$/g (Org) for [CO] concentrations below 300 ppb. For Plume A, MAC$_{Org}(450 \text{ nm})$ varied more strongly with [CO] than Plume B with MAC$_{Org}(450 \text{ nm})$ at the beginning edge of the plume at 45% of the peak value. We note that Plumes A and B are asymmetric as Plume A started with clean background conditions but did not return to background conditions prior to the beginning of when we observed Plume B. Plume B followed the opposite trend, mixed with Plume A in the beginning and achieved near background conditions following its peak. For Plume D, which was more mixed and had a broader peak in [CO] and B$_{abs}(450)$, we also observed a steady decrease in MAC$_{Org}(450 \text{ nm})$ with [CO] with values of MAC$_{Org}(450 \text{ nm})$ at the beginning edge of the plume about 28% of the peak value. The background values for all these plumes were different possibly because the background air was mixed with earlier smoke or reflecting the dynamic processes of bleaching of volatile BrC species and production of less volatile BrC species in ambient plumes (Fleming et al., 2020). Finally, since the background between Plumes A and C was likely mixed with previous smoke, we were unable to resolve the edge effects for Plume C.

In addition to lower values of MAC$_{Org}(450 \text{ nm})$ at plume edges, we also observed enhanced chemical oxidation of the aerosol (including internally and externally mixed with rBC) with our SP-AMS using $f_{45}/f_{44}$ (Figures S9b and S9c). This enhanced oxidation has recently been reported in other BB plumes (Garofalo et al., 2019). However, this study did not include analysis of optical properties. Our inferred values MAC$_{Org}(450 \text{ nm})$ increased with $f_{C2H4O2}$ and $f_{45}/f_{44}$ (less oxidation) as shown in Figure 6. While our observations indicate enhanced photochemical bleaching is likely to have occurred at plume edges, we stress that BrC photochemistry is complex, has been found to depend on the fuel burned and the burn conditions, and maybe better described as an evolution involving aerosol bleaching, recalcitrant BrC, and BrC production instead of simply BrC degradation (Dasari et al., 2019; Fleming et al., 2020; Wong et al., 2019).

6. Conclusions

We report comprehensive optical, microphysical, and chemical observations of multiple Woodbury Fire smoke aerosol plumes measured in real time at LANL (Los Alamos, NM), approximately 11–18 hr after emissions in Arizona. We sampled the core of the plumes as well as the peripheries that exhibited a higher degree of photochemical processing (aging) and mixing with more aged background air. Our analysis showed that BC (rBC) was coated with OA and that absorption enhancements at 870 and 450 nm correlated with coating thickness. Most of the inferred $B_{abs}(870 \text{ nm})$ values of 1.5–2.2 can be accounted for by core-shell enhancements, and the fit MAC$^{\text{SPC}}(870 \text{ nm})$ value representing uncoated rBC supports this mechanism. We also
reported $E_{\text{abs}}(450 \text{ nm})$ values of 1.9–5.1 that were much larger than core-shell models can explain and require absorption by BrC. We constrained the MAC$_{\text{Org}}$ values at 450 nm and found that it peaked at the core of the plume with peak values bounded between 0.6 ± 0.2 and 0.9 ± 0.2 m$^2$/g (Org) and decreased with mixing and aging observed on the peripheries.

We report a strong correlation between MAC$_{\text{Org}}(450 \text{ nm})$ and our multimode SP-AMS $f_{\text{C}_2\text{H}_4\text{O}_2}$ (a tracer of the primary OA species levoglucosan) measurements for rBC-associated OA and bulk OA, which indicates that BrC was most likely coemitted at the source as primary OA. Additionally, we observed a decrease in MAC$_{\text{Org}}(450 \text{ nm})$ and primary BB OA (e.g., $f_{\text{C}_2\text{H}_4\text{O}_2}$) and an increase in oxidized internally mixed rBC organics (e.g., $f_{\text{CO}_2}$) at plume edges that are consistent with enhanced photochemical bleaching. Our peak MAC$_{\text{Org}}$ (450 nm) values are in the range used in global model sensitivity studies that show BrC top-of-atmosphere radiative forcing to be 10–25% of BC (Brown et al., 2018; Feng et al., 2013). However, our reported peak MAC$_{\text{Org}}(450 \text{ nm})$ likely represents an upper limit since we show that the MAC$_{\text{Org}}(450 \text{ nm})$ decreased when the plume mixed with background ambient air. Furthermore, the effects of BrC bleaching (Forrister et al., 2015; Liu et al., 2014) significantly reduce the global BrC forcing in models (Brown et al., 2018; Wang et al., 2018). However, we stress that the processes controlling MAC$_{\text{Org}}(450 \text{ nm})$ are complex, involving mixing, bleaching, recalcitrant BrC, and BrC production (Dasari et al., 2019; Fleming et al., 2020; Wong et al., 2019) and that we do not fully resolve their effects here. Our study develops an observational framework to better represent the treatments of BrC properties and the effects of mixing-state and dynamical changes related to aging and mixing in climate models.

Data Availability Statement

Data used in this research are available at: https://doi.org/10.17632/j6c6trjvf3.4.

References

Adachi, K., Sedlacek, A. J., Kleinman, L., Springfield, S. R., Wang, J., Chand, D., et al. (2019). Spherical tarball particles form through rapid chemical and physical changes of organic matter in biomass-burning smoke. *Proceedings of the National Academy of Sciences*, 116(39), 19336–19341. https://doi.org/10.1073/pnas.1900129116

Adler, G., Flores, J. M., Abo Riziq, A., Burmann, S., & Rudich, Y. (2011). Chemical, physical, and optical evolution of biomass burning aerosols: A case study. *Atmospheric Chemistry and Physics*, 11(4), 1491–1503. https://doi.org/10.5194/acp-11-1491-2011

Adler, G., Wagner, N. L., Lamb, K. D., Manfred, K. M., Schwarz, J. P., Franchin, A., et al. (2019). Evidence in biomass burning smoke for a climate impact of enhanced photochemical bleaching. *Atmospheric Chemistry and Physics*, 19(11), 6117–6137. https://doi.org/10.5194/acp-19-6117-2019

Ahern, A. T., Subramanian, R., Salisbury, G., Lipsky, E. M., Donahue, N. M., & Sullivan, R. C. (2016). Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass-burning soot by two particle mass spectrometers. *Atmospheric Measurement Techniques*, 9(12), 6117–6137. https://doi.org/10.5194/amt-9-6117-2016

Aiken, A. C., de Foy, B., Wiedinmyer, C., DeCarlo, P. F., Ulbrich, I. M., Wehrl, M. N., et al. (2010). Mexico city aerosol analysis during the Visiting Faculty Program (VFP) and the New Mexico Consortium is gratefully supported by LANL’s Laboratory Directed Research and Development (LDRD) Program (20200035DR) (J. E. L., M. K. D., and A. C. A.). The New Mexico Consortium is grateful for financial support in this research. NMT students Jamie Karacoglou and Sabina Gulick are acknowledged for their contributions. We thank Ethan Emerson for providing IGOR scripts to analyze rBC coating thickness and Andrew Freedman for guidance on the CAPS-PM$_{\text{Ana}}$ uncertainties.

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Liu, J., Lin, P., Laskin, A., Laskin, J., Kauthmann, S. M., Wise, M., et al. (2016). Optical properties and aging of light-absorbing secondary organic aerosol. *Atmospheric Chemistry and Physics, 16*(18), 12,815–12,827. https://doi.org/10.5194/acp-16-12815-2016

Liu, S., Aiken, A. C., Gorkowski, K., Dubey, M. K., Cappa, C. D., Williams, I. R., et al. (2015). Enhanced light absorption by mixed source black and brown carbon particles in UK winter. *Nature Communications, 6*(1), 8435. https://doi.org/10.1038/ncomms9435

Liu, S., Aiken, A. C., Arata, C., Dubey, M. K., Stossel, C. E., Yokelson, R. J., et al. (2014). Aerosol single scattering albedo dependence on biomass combustion efficiency: Laboratory and field studies. *Geophysical Research Letters, 41*, 742–748. https://doi.org/10.1002/2013GL058392

Massoli, P., Kehabian, P. L., Onasch, T. B., Hills, F. R., & Freedman, A. (2010). Aerosol light extinction measurements by cavity attenuated phase shift (CAPS) spectroscopy: Laboratory validation and field deployment of a compact aerosol particle extinction monitor. *Aerosol Science and Technology, 44*(6), 428–435. https://doi.org/10.1080/02786821003716599

McClure, C. D., Lim, C. Y., Hagan, D. H., Kroll, J. H., & Cappa, C. D. (2020). Biomass-burning derived particles from a wide variety of fuels — Part 1: Properties of primary particles. *Atmospheric Chemistry and Physics, 20*(3), 1531–1547. https://doi.org/10.5194/acp-20-1531-2020

McMeeking, G. R., Fortner, E., Onasch, T. B., Taylor, J. W., Flynn, M., Coe, H., & Kreidenweis, S. M. (2014). Impacts of nonrefractory material on light absorption by aerosols emitted from biomass burning. *Journal of Geophysical Research: Atmospheres, 119*, 12,272–12,286. https://doi.org/10.1002/2014JD021750

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prevot, A. S., Xu, L., Ng, N. L., et al. (2013). Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time. *Environmental Science & Technology, 47*(12), 6316–6324. https://doi.org/10.1021/es400683v

Moteki, N., & Kondo, Y. (2010). Dependence of laser-induced incandescence on physical properties of black carbon aerosols: Measurements and theoretical interpretation. *Aerosol Science and Technology, 44*(8), 663–675. https://doi.org/10.1080/0278682100376450

Myhre, G., Shindell, D., Bréon, F.-M., Collins, W., Fuglestvedt, J., Huang, J., et al. (2013). Anthropogenic and natural radiative forcing. In *Intergovernmental Panel on Climate Change, Climate Change 2013—The Physical Science Basis: Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Chap. 8). Cambridge: Cambridge University Press.

Nakayama, T., Suzuki, H., Kagamitani, S., Ikeda, Y.,UCHIYAMA, A., & Matsumi, Y. (2015). Characterization of a three wavelength photoacoustic spectrometer (PASS-3) and a photoacoustic extinction monitor (PAX). *Journal of the Meteorological Society of Japan. Ser. II*, 93(8), 285–308. https://doi.org/10.2151/jmsj.2015-016

Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., et al. (2012). Soot particle aerosol mass spectrometer: Development, validation, and initial application. *Aerosol Science and Technology, 46*(7), 804–817. https://doi.org/10.1080/02786826.2012.663948

Onasch, T. B., Trimborn, A. C., Lambe, A. T., Tiwari, A. J., Marr, L. C., et al. (2015). Investigations of SP-AMS carbon ion distributions as a function of refractory black carbon particle type. *Aerosol Science and Technology, 49*(6), 409–422. https://doi.org/10.1080/02786826.2015.1039995

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., De Gouw, J. A., & Jimenez, J. L. (2013). Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME 3. *Atmospheric Chemistry and Physics, 13*(8), 11,551–11,571. https://doi.org/10.5194/acp-13-11551-2013

Ramanathan, V., & Carmichael, G. (2008). Global and regional climate changes due to black carbon. *Nature Geoscience, 1*(4), 223–227. https://doi.org/10.1038/ngeo156

Reyes-Villegas, E., Priestley, M., Ting, Y.-C., Haslett, S., Bannan, T., Le Breton, M., et al. (2018). Simultaneous aerosol mass spectrometry and chemical ionisation mass spectrometry measurements during a biomass burning event in the UK: Insights into nitrate chemistry. *Atmospheric Chemistry and Physics, 18*(6), 4093–4111. https://doi.org/10.5194/acp-18-4093-2018

Romzynsky, D. E., Gomez, S. L., Lam, J., Carrico, C. M., Aiken, A. C., Chylik, P., & Dubey, M. K. (2019). Optical properties of laboratory and ambient biomass burning aerosols: Elucidating black, brown, and organic carbon components and mixing regimes. *Journal of Geophysical Research: Atmospheres, 124*, 5088–5105. https://doi.org/10.1029/2018JD029892

Saleh, R., Marks, M., Heo, J., Adams, P. J., Donahue, N. M., & Robinson, A. L. (2015). Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions. *Journal of Geophysical Research: Atmospheres, 120*, 10,285–10,296. https://doi.org/10.1002/2015JD023697

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., et al. (2014). Brownness of organics in aerosols from biomass burning linked to their black carbon content. *Nature Geoscience, 7*(9), 647–650. https://doi.org/10.1038/ngeo2220

Samet, B. H., Stjern, C. W., Andrews, E., Kuhn, R. A., Myhre, G., Schulz, M., & Schuster, G. L. (2018). Aerosol absorption: Progress towards global and regional constraints. *Current climate change reports, 4*(2), 65–83. https://doi.org/10.1007/s40641-018-0091-4

Schlax, M. G., & Chelton, D. B. (1992). Frequency domain diagnostics for linear smoothers. *Journal of the American Statistical Association, 87*(420), 1070–1081. https://doi.org/10.1080/01621459.1992.10476262

Schmid, O., Chand, D., Karg, E., Guyon, P., Frank, G. P., Swietlicki, E., & Andreae, M. O. (2009). Derivation of the density and refractive index of organic matter and elemental carbon from observation between physical and chemical aerosol properties. *Environmental Science & Technology, 43*(4), 1166–1172. https://doi.org/10.1021/es803570p

Schmaitner, M. (2005). Absorption amplification of black carbon internally mixed with secondary organic aerosol. *Journal of Geophysical Research, 110*, D19204. https://doi.org/10.1029/2005JD006046

Schoeberl, W., Oliva, P., Giglio, L., & Ciurapi, I. A. (2014). The new VIIRS 375m active fire detection data product: Algorithm description and initial assessment. *Remote Sensing of Environment, 143*, 85–96. https://doi.org/10.1016/j.rse.2013.12.008

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., et al. (2006). Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere. *Journal of Geophysical Research, 111*, D16207. https://doi.org/10.1029/2006JD007076

Sedlacek, A. J., Onasch, T. B., Nickman, L., Lewis, E. R., Davidovits, P., Freedman, A., & Williams, L. (2018). Formation of refractory black carbon by SP2-induced charring of organic aerosol. *Aerosol Science and Technology, 52*(12), 1345–1350. https://doi.org/10.1080/02786826.2018.1531107

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., et al. (1999). Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Aerosol Environment, 33*(2), 173–182. https://doi.org/10.1016/S1352-2310(98)00145-9
