Long-range transported North American wildfire aerosols observed in marine boundary layer of eastern North Atlantic

Guangjie Zheng\textsuperscript{a,b}, Arthur J. Sedlacek\textsuperscript{b}, Allison C. Aiken\textsuperscript{c}, Yan Feng\textsuperscript{d}, Thomas B. Watson\textsuperscript{b}, Shira Raveh-Rubin\textsuperscript{e}, Janek Uin\textsuperscript{b}, Ernie R. Lewis\textsuperscript{b}, Jian Wang\textsuperscript{a,b,\textsuperscript{*}}

\textsuperscript{a} Center for Aerosol Science and Engineering, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, MO, USA
\textsuperscript{b} Environmental and Climate Science Department, Brookhaven National Laboratory, Upton, NY, USA
\textsuperscript{c} Earth System Observations, Los Alamos National Laboratory, Los Alamos, NM, USA
\textsuperscript{d} Environmental Science Division, Argonne National Laboratory, Lemont, IL, USA
\textsuperscript{e} Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel

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\textbf{A B S T R A C T}

Wildfire is a major source of biomass burning aerosols, which greatly impact Earth climate. Tree species in North America (NA) boreal forests can support high-intensity crown fires, resulting in elevated injection height and longer lifetime (on the order of months) of the wildfire aerosols. Given the long lifetime, the properties of aged NA wildfire aerosols are required to understand and quantify their effects on radiation and climate. Here we present comprehensive characterization of climatically relevant properties, including optical properties and cloud condensation nuclei (CCN) activities of aged NA wildfire aerosols, emitted from the record-breaking Canadian wildfires in August 2017. Despite the extreme injection height of ~12 km, some of the wildfire plumes descended into the marine boundary layer in the eastern North Atlantic over a period of ~2 weeks, owing to the dry intrusions behind mid-latitude cyclones. The aged wildfire aerosols have high single scattering albedos at 529 nm ($\omega_{529}$ 0.92–0.95) while low absorption Ångström exponents ($\Lambda_{464}/\Lambda_{648}$ 0.7–0.9). In comparison, $\Lambda_{\text{blue}}$ of fresh/slightly aged ones are typically 1.4–3.5. This low $\Lambda_{\text{blue}}$ indicates a nearly complete loss of brown carbon, likely due to bleaching and/or evaporation, during the long-range transport. The nearly complete loss suggests that on global average, direct radiative forcing of BrC may be minor. Combining Mie calculations and the measured aerosol hygroscopicity, volatility and size distributions, we show that the high $\omega_{529}$ and low $\Lambda_{\text{blue}}$ values are best explained by an external mixture of non-absorbing organic particles and absorbing particles of large BC cores (≥ ~110 nm diameter) with thick non-absorbing coatings. The accelerated descent of the wildfire plume also led to strong increase of CCN concentration at the supersaturation levels representative of marine low clouds. The hygroscopicity parameter, $\kappa_{\text{CCN}}$, of the aged wildfire aerosols varies from 0.2 to 0.4, substantially lower than that of background marine boundary layer aerosols. However, the high fraction of particles with large diameter (i.e., within accumulation size ranges, ~100–250 nm) compensates for the low values of $\kappa$, and as a result, the aged NA wildfire aerosols contribute more efficiently to CCN population. These results provide direct evidence that the long-range transported NA wildfires can strongly influence CCN concentration in remote marine boundary layer, therefore the radiative properties of marine low clouds. Given the expected increases of NA wildfire intensity and frequency and regular occurrence of dry intrusion following mid-latitude cyclones, the influence of NA wildfire aerosols on CCN and clouds in remote marine environment need to be further examined.

1. Introduction

Biomass burning aerosols can greatly impact climate both directly by interacting with solar radiation (Crutzen and Andreae, 1990; Jacobson, 2004; Reid et al., 2005a; Reid et al., 2005b; Bond et al., 2013) and indirectly by modifying the properties of clouds (Johnson et al., 2004; Sakaeda et al., 2011; Wilcox, 2012; Lu et al., 2018). The climatic effects of biomass burning aerosols depend on a number of...
factors, including the injection height (Zhu et al., 2018), dispersion conditions (Adebiyi and Zuidema, 2016; Lievelde et al., 2018), optical properties, and Cloud Condensation Nuclei (CCN) and ice nucleation activity. The optical properties and CCN activities of biomass burning aerosols are strongly influenced by biomass fuel type, fuel load, and combustion conditions (e.g., flaming or smoldering, etc.) (Andreae and Merlet, 2001; Petters et al., 2009a; Bond et al., 2013; Saleh et al., 2014; Liu et al., 2014), and these climate-relevant properties will likely change as the particle size distribution, chemical composition, and mixing state evolve during the transport in the atmosphere (Jacobson, 2001; Janhäll et al., 2010; Levin et al., 2010; Cubison et al., 2011; Ortega et al., 2013; Vakkari et al., 2014; Zhao et al., 2015; Sumlin et al., 2017). Presently, biomass burning aerosols and their evolution remain not well understood and poorly represented in climate models (Stocker, 2001; Janhäll et al., 2010; Levin et al., 2010; Cubison et al., 2011; Ortega et al., 2013; Vakkari et al., 2014; Zhao et al., 2015; Sumlin et al., 2017). Despite the high injection height (up to ~13 km) (Ansmann et al., 2018; Kloss et al., 2019), some of the Canadian wildfire aerosol aloft travelled across the Atlantic ocean and descended into the remote marine boundary layer (MBL) over the eastern North Atlantic (ENA), > 7000 km away from the fires. The well-aged wildfire aerosol dominated the properties of MBL aerosols in ENA from Aug. 24th to 29th, 2017. Here we present comprehensive characterization of climatically relevant properties of the aged wildfire aerosol, including size distribution, chemical composition, optical properties, hygroscopicity, and CCN concentrations. The potential impact of the NA wildfires on the CCN spectrum and therefore cloud properties in remote marine boundary layer is also discussed.

2. Method

This study utilizes comprehensive in-situ measurements conducted at the Atmospheric Radiation Measurement Climate Research Facility ENA site (https://www.arm.gov/capabilities/observatories/ena), which is located on Graciosa Island in the Azores, Portugal (39° 5′ N, 28° 1′ 32″ W, 30.48 m above mean sea level). The site straddles the boundary between the subtopics and mid-latitudes in the eastern North Atlantic, and receives a diverse range of air masses from North America, the Arctic, and northern Europe (Wood et al., 2015; Wang et al., 2016; Zheng et al., 2018). Measurement of the trace gases (e.g., CO and O3), meteorological parameters, and aerosol optical properties are detailed in Zheng et al. (2018). Aerosol size distribution with particle diameter ranging from 0.07 to 1 μm was measured by an Ultra-High Sensitivity Aerosol Spectrometer (UHSAAS, Droplet Measurement Technologies, Boulder, CO, USA). Non-refractory submicron aerosol composition (organics, sulfate, nitrate, ammonium, and chloride) was characterized by an Aerosol Chemical Speciation Monitor (ACSM; Aerodyne Research, Inc., Billerica, MA, USA). Aerosol hygroscopic growth factor at 90% RH was obtained by a Humidified Tandem Differential Mobility Analyzer (HTDMA, Brechtel Manufacturing Inc., CA, USA). These above measurements are part of the routine measurements at the ENA site since October 2013 (Mather and Voyles, 2013). During the Aerosol and Cloud Experiments in Eastern North Atlantic (ACE-ENA) campaign from June 2017 to August 2018, additional measurements were carried out at the ENA site, as detailed below. Only the data collected during the 14-month ACE-ENA campaign are used for further analysis.

2.1. Aerosol size distributions

Aerosol size distribution from 10 to 470 nm was measured by a scanning mobility particle analyzer (SMPS, Model 3938, TSI Incorporated, Shoreview, MN, USA). Concurrently, total aerosol number concentrations (CN) were measured by a standalone condensation particle counter (CPC, Model 3772, TSI Incorporated, Shoreview, MN, USA). The standalone CPC and the SMPS were operated side-by-side, and the measurements alternated every 4 min between ambient samples and samples processed by a custom-made thermal denuder operated at 300 °C. Components that survived the thermal denuder are referred to as non-volatile components hereinafter. Relative humidity of the aerosol sample was reduced to below 25% using a Naftion dryer before being introduced into the system. The flow rates and classifying voltage of the SMPS were calibrated every 3 months and exhibited negligible (< 1%) variation throughout the ACE-ENA campaign.

The measured number size distributions were fitted as a sum of up to three lognormal modes, which were subsequently classified according to the number mode geometric mean diameters (Dnm). For the ambient aerosol size distribution, the modes are classified as: nucleation mode (Dnm < 30 nm), Aitken mode (30 < Dnm < 110 nm) and accumulation mode (Ac, 110 < Dnm < 300 nm). For the non-volatile component, the modes are classified into non-volatile Aitken...
(14 < \(D_{pm}\) < 100 nm) and non-volatile Accumulation (100 < \(D_{pm}\) < 250 nm). For non-volatile aerosol component, the thresholds of mode diameters are generally smaller than those of ambient aerosols, based on the typical non-volatile volume for each mode at ENA. The non-volatile nucleation mode (\(D_{pm}\) < 14 nm) was rarely observed (< 4% annually) and is not considered here. All modes with \(D_{pm}\) above 300 nm for ambient aerosols, or above 250 nm for non-volatile aerosols, are considered as sea spray aerosol modes (Quinn et al., 2017; Zheng et al., 2018).

2.2. Aerosol hygroscopicity from size-resolved CCN activation fraction

The CCN activation spectrum (i.e., activation fraction as a function of super-saturation) of size-selected particles was measured using a Differential Mobility Analyzer (DMA, TSI Inc Model 3081) coupled to a CPC (TSI Inc., Model 3010) and a cloud condensation nuclei counter (CCNC, Droplet Measurement Technologies, Boulder, CO) (Frank et al., 2006; Moore et al., 2010; Petters et al., 2007; Mei et al., 2013b). The operation of the same system is detailed in Thalman et al. (2017), and is only briefly described here. During the ACE-ENA campaign, the DMA stepped through 6 aerosol dry diameters of 40, 50, 75, 100, 125, and 150 nm. At each diameter, the super-saturation level inside the CCNC was changed by changing the flow rates (\(Q_{CCNC}\) ranging from 0.3 to 1 L min \(^{-1}\), temperature gradient (\(\Delta T\), changing among 4, 6.5, and 10 K), or a combination of both. At each super-saturation, sampling time was a minimum of 30 s and until 1500 particles were detected by the CPC, or a maximum of 120 s. A measurement cycle through the 6 particle diameters took between 1 and 2 h. The super-saturation inside the CCNC was calibrated using ammonium sulfate particles following established procedures (e.g., Mei et al., 2013a; Thalman et al., 2017) for each operation condition (\(Q_{CCNC}\) and \(\Delta T\)), and ranged from 0.07% to 1.34% at 298 K. Dependence of super-saturation on the temperature at the top of CCNC column (instrument temperature T1) (Rose et al., 2008; Thalman et al., 2017) was also derived from the calibrations with different T1 values, and applied to retrieve the CCNC super-saturation levels. For the measurements of size-resolved CCN activation spectrum, influence from multiple charged particles is taken into consideration using the same approach described in Thalman et al. (2017). The particle hygroscopicity parameter under supersaturated conditions, \(\kappa\) (Petters and Kreidenweis, 2007), was derived from the activation spectrum at each particle size using approaches detailed in the literature (Lance et al., 2013; Mei et al., 2013a; Thalman et al., 2017).

2.3. Classification of air mass origin

To understand the origin of the air masses arriving at the ENA site, we performed backward trajectory calculations using reanalysis data. Wind data were obtained from the European Centre for Medium-range Weather Forecasts (ECMWF) interim reanalysis (ERA-Interim) (Dee et al., 2011). The 6-hourly ERA-Interim data were interpolated horizontally to 1° by 1° grid, at 60 vertical hybrid levels. The interpolated data were then used in the Lagrangian analysis tool (LAGRANTO) version 2.0 (Sprenger and Wernli, 2015) to calculate 10-day backward air mass trajectories arriving at the ENA site, for the 12 available model levels between the surface and 850-hPa. Calculated every 6 h from 00 UTC 24th August to 00 UTC 29th August 2017, a total of 252 backward trajectories were subsequently classified into 4 origin groups (Fig. S1) with the following criteria. (i) North American origin if a trajectory is found at least once within 120° – 60° W longitude, while at latitude lower than 62° N and at times 96–240 h prior to arrival in the ENA; (ii) Arctic origin if a trajectory is found at least once within 60° – 0° W longitude, while at latitude higher than 62° N and at times 96–240 h prior to arrival in the ENA (and was not recognized as having a North American origin); (iii) Subtropical origin if a trajectory is found at least once at latitude lower than 35° N and at times 6–150 h prior to arrival in the ENA, and is neither recognized as a North American nor Arctic in origin; (iv) Trajectories not meeting any of the above criteria are classified as “others”. This class corresponds to 13% of all trajectories.

3. Strong impact of Canadian wildfire on boundary layer aerosol properties

Abnormally high CO mixing ratio and number concentration of non-volatile accumulation mode aerosol, \(N_{Ac, TD}\) (Fig. 1) were observed at the ENA site from 00 UTC 24th August to 00 UTC 29th August 2017 (referred to as the wildfire episode hereinafter). CO mixing ratio averaged 144 ppb, which is 1.4 times of the average and presenting 99.9th percentile of the measurements during the one-year ACE-ENA campaign. While non-volatile accumulation mode was present nearly all the times during this episode, it was observed for only 12% of the observational time during the ACE-ENA campaign. Average \(N_{Ac, TD}\) during the wildfire episode (227 cm \(^{-3}\)) is 3.3 times higher than the average of those observed outside of the episode. If we consider the concentration of \(N_{Ac, TD}\) as zero in the absence of a non-volatile Ac mode, then the average \(N_{Ac, TD}\) during this episode is 28 times higher than the annual average. Back trajectory analysis (section 2.3) shows that 54% of the air masses arriving at lower troposphere (< 850 hPa) over the ENA site during this episode originated from North America, with the rest from the Arctic (18%), subtropical latitudes (14%) or others (Fig. 1a; Fig. S1). Elevated aerosol number concentration and CO mixing ratio were observed when air masses mostly originated from North America (orange bars in Fig. 1a), while lower values were generally associated with the air masses dominated by those with Arctic origin (blue bars in Fig. 1a). Active Canadian wildfires were observed (Fig. S1) and reported (https://www.bbc.com/news/world-us-canada-41040625) just prior to this episode. The strong impact of the Canadian wildfire on the aerosol in the ENA MBL is further supported by the mixing ratios of trace gases and characteristics of aerosol properties.
(section 3.1), and agreed with the synoptic conditions that facilitated the downward transport of the wildfire plumes into the MBL (section 3.2).

3.1. Trace gas mixing ratios, aerosol number and volume concentrations

During this episode, one prominent feature is the elevated CO mixing ratio, which is especially evident from the correlations with O₃ and water vapor (Fig. 2a, b). Within the ENA MBL, CO usually correlates positively with O₃ while negatively with water vapor (Zheng et al., 2018). During the non-Arctic periods (Fig. 1) of this episode, the CO mixing ratio is much higher than the other periods with similar H₂O or O₃ levels. This is attributed to the higher CO mixing ratio in wildfire plumes than in other types of anthropogenic emissions (Clarke and Kapustin, 2010).

Aerosol properties during non-Arctic periods (Fig. 1) of this episode also exhibit distinct features, including strong linear correlations among the volume concentration of accumulation mode aerosol (Vₐₐc), volume concentration of non-volatile accumulation mode at 300 °C (Vₐₐc, TD), mass concentration of non-refractory organics measured by ACSM, and CO mixing ratios (Fig. 2c-e). Similar linear correlations were also observed in other fresh and slightly aged NA wildfire plumes (Clarke et al., 2004; Petzold et al., 2007). The good correlation between Vₐₐc and CN, and that between Vₐₐc, TD and CN_TD (Fig. 2g, h) suggest relatively uniform spectral shape of size distributions (section 5.1). Both ambient and non-volatile aerosols show higher volume-to-number ratios during the wildfire episode than other periods (Fig. 2g, h), consistent with the larger mode diameter of the accumulation mode aerosols (see section 5.1).

3.2. Vertical transport and dry intrusions

On 12 August 2017, an extremely intense wildfire occurred in western Canadian. The corresponding strong pyrocumulonimbus activity injected aerosols into the upper troposphere and lower stratosphere at ~12 km (Ansmann et al., 2018; Peterson et al., 2018; Khaykin et al., 2018; Kloss et al., 2019). At these high altitudes, it can take over one month for aerosols to descend into the boundary layer (Liang et al., 2009; Bond et al., 2013; Laing et al., 2016). Therefore, one would expect little influence in the boundary layer from this event. However, as shown in section 3.1, the MBL aerosols were strongly influenced by this wildfire after only ~12 days, suggesting an accelerated descent of the plumes.

Fig. 2. Distinct characteristics of trace gases and aerosol properties during the wildfire episode. Orange dots indicate data observed during August 24th to 29th, 2017 when air masses were not from the Arctic, and grey dots indicate data observed at the ENA site during the 14-month ACE-ENA campaign but outside of this wildfire episode. Variables shown include: (i) volume mixing ratios of CO and O₃ in part per billion (ppb), and the water vapor mixing ratios in g kg⁻¹; (ii) the volume concentrations of accumulation mode aerosols under ambient conditions (Ambient Vₐₐc) and those remaining after heated to 300 °C (Vₐₐc, TD); (iii) total number concentrations of ambient aerosols (CN) and those remaining after heated to 300 °C (CN_TD); and (iv) mass concentration of non-refractory organics in sub-micron (diameter < 1 μm) aerosols.
This accelerated descent is attributed to dry intrusions. Dry intrusion (Browning, 1997; Wernli, 1997), also termed as “dry conveyor belt” (Danielsen, 1968), refers to the strong descent of upper-tropospheric dry air in post-cold-front regions, and is often observed over the ENA region (e.g., Naud et al., 2018). Backward trajectories show that the majority of NA air masses arriving at the ENA site indeed descended slantwise from middle-upper troposphere towards the ENA lower troposphere within 10 days prior to reaching the site (Fig. S1).

One example of dry-intrusion air masses is shown in Fig. 3. Fig. 3a shows the 10-day backward trajectory starting from 12:00 UTC, 27 August. This period was characterized by a high CO mixing ratio (> 140 ppb), while all MBL air masses arriving at that time originated from NA (Fig. 1). The backward trajectories suggest that the air masses descended from 500 to 700 hPa to the MBL during 3–4 days as they travelled from Northern Canada to the eastern coast of North America by Aug. 21st (Fig. 3a). At this stage, the air masses were located in the cyclone cold sector, behind the cold front off the east coast. Following this descent, i.e., after Aug. 21st, the air masses were advected at a rather constant altitude towards the ENA site, while turning anti-cyclonically. Similarly, during Aug. 14th – 29th, a series of five extratropical cyclones occurred over eastern North America, each having a cold trailing front with descending air behind it, which later partially reached the ENA site (not shown). During the same time period, cyclones over the North Atlantic governed the descent of Arctic air as well towards ENA. The latter are similar to the cold sector of the cyclone north of ENA in Fig. 3b.

Raveh-Rubin (2017) suggested a Lagrangian descent criterion of 400 hPa descent in 48 h for the identification of dry intrusions. Such a defining criterion resulted in events predominantly in the extended winter season, a third of which indeed occur in association with cold trailing fronts (Catto and Raveh-Rubin, 2019). For the summer case here, however, the descent does not qualify for the criterion in Raveh-Rubin (2017), as air mostly descends < 400 hPa, over a time period longer than 48 h. Yet, the dry northwesterly descending flow is situated between a cyclone-anticyclone dipole, behind a cold front (Fig. 3) as observed in winter dry intrusions (Raveh-Rubin and Catto, 2019), suggesting that the dry intrusions here are qualitatively similar, although shallower and weaker compared to strong winter dry intrusions.

The evidence shown here indicates that dry intrusions are the synoptic-scale pathway that facilitates the relatively fast transport of NA wildfire aerosols into the MBL. The fast transport contrast with the conventional perception of an extended period of time being required for wildfire aerosol aloft to descend into MBL. As dry intrusions frequently occur behind cold fronts in mid-latitudes, (e.g., Naud et al., 2018), we expect substantial impact of NA wildfires on the properties of MBL aerosol and therefore low clouds over the North Atlantic.

4. Optical properties of well-aged wildfire aerosol

The extreme Canadian wildfire and the accelerated descent of the wildfire plume into the ENA boundary layer provided an excellent opportunity to characterize the properties of well-aged wildfire aerosols. As strong pyrocumulonimbus activities were observed on August 12th and 13th (Peterson et al., 2018), we estimate the wildfire aerosols observed from August 24th to 29th had an aging time of around two weeks. Sea spray aerosol can contribute substantially to the aerosol scattering coefficient in the ENA MBL (Zheng et al., 2018) (Fig. 4). As a result, the aerosol scattering coefficient ($B_{sca}$) of the NA wildfire aerosol cannot be measured directly. In this study, the size distribution measured by UHSAS was fitted as sum of lognormal modes, and $B_{sca}$ of the NA wildfire aerosol at 529 nm was calculated from the fitted accumulation mode using Mie theory (see detailed calculations and corrections in SI S1). This approach assumes that the accumulation modes during this episode were dominated by the aged wildfire aerosols, as indicated by the much higher $V_{Ac}$, $V_{Ad}$, $V_T$ and CO than the background values (Fig. 2). Measured aerosol absorption coefficient ($B_{abs}$) is all attributed to the aged wildfire aerosols because the contribution from sea spray aerosols is expected to be negligible.

4.1. Single scattering albedo

During this wildfire episode, measured $B_{abs}$ is linearly correlated with calculated accumulation mode $B_{sca}$ ($r^2 = 0.91$) (Fig. 5a), indicating a relatively constant single scattering albedo at 529 nm ($\omega_{529}$). Here the analysis is focused on the periods with CO > 140 ppb (99% percentile of the 14-month data during the ACE-ENA campaign), when aerosol properties were dominated by wildfire plumes (Figs. 1, 2). During these periods, $B_{sca}$ and $B_{abs}$ were also above 99% percentile of

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**Fig. 3.** Descent of Canadian wildfire air masses by dry intrusions behind a cold front. (a) 10-day backward trajectories of the air masses arriving at the ENA site (red star) at 12:00 UTC, Aug. 27th. The trajectories are colored according to their pressure level (hPa). The blue dots mark the location of the air masses at 00:00 UTC, Aug. 21st, when the front is positioned off the east coast (blue line). (b) Meteorological conditions at 00:00 UTC, Aug. 21st. The 850-hPa equivalent potential temperature $\theta_e$ (in K, shaded), mean sea-level pressure (in hPa, black contours, contours are dashed and unlabeled for 1016 hPa and above) and potential vorticity on 330-K isentropic surface (2-PVU, red contour) are shown. The curved blue line marks the location of the front along the strong $\theta_e$ gradients (verified against NOAA surface analysis, not shown). The schematic orange arrow illustrates the descending airflow at this time behind the upper-tropospheric trough and the cold front.
the 14-month measurements, and were > 22 Mm⁻¹ and 1.6 Mm⁻¹, respectively (Fig. 5, the range of data used in the following calculations indicated by the red dash lines and arrows). Average $\omega_{464}$ of the aged wildfire aerosol is derived as 0.92. This value may represent a lower limit, as the filter-based PSAP can overestimate $B_{sca}$ by up to 70% at high organic loadings (Lack et al., 2008; Cappa et al., 2008). With this taken into consideration, the upper limit of $\omega_{464}$ is estimated as 0.95. The $\omega_{464}$ value of 0.92 – 0.95 is near the upper end of the range reported by previous field studies of NA wildfire aerosols (Table 1). Note that in some studies (e.g., Gyawali et al. (2009), Forrister et al. (2015); Liu et al., (2017); Selimovic et al. (2018)) the $\omega$ were measured at ~400 nm and 870 nm, and exhibit negligible difference at the two wavelengths. Therefore, we expect $\omega_{464}$ to be at same level. While the results listed in Table 1 (including this study) are from different NA wildfires, they suggest a generally increasing $\omega$ with the plume age of the NA wildfire aerosol. Such trend can be explained by the collapse of chain-aggregates and condensation of secondary species (Reid et al., 2005a,b; Ahern et al., 2019), bleaching and/or evaporation of absorbing particles, etc (section 4.2).

4.2. Absorption Ångström exponents

For periods when aerosol was dominated by the aged wildfire particles (i.e., when CO > 140 ppb), values of absorption Ångström exponents ($A_{abs}$) derived from the PSAP measurements at 464 and 648 nm are mostly between 0.6 and 0.8 (Fig. 5c). Early studies show that $A_{abs}$ derived from filter-based PSAP may be underestimated by ~14% when compared to that derived from photoacoustic based measurements (Chow et al., 2009). A 14% increase of the derived $A_{abs}$ leads to a range of 0.7–0.9.

The low $A_{abs}$ observed here indicates negligible contribution of brown carbon (BrC) (Clarke et al., 2007; Shinozuka et al., 2007; Gyawali et al., 2009; Forrister et al., 2015; Laing et al., 2016; Liu et al., 2017; Selimovic et al., 2018; Sedlacek III et al., 2018). In comparison, $A_{abs}$ of fresh wildfire aerosols and those aged for less than a few days typically ranges from ~1.4 to ~3.5 (Table 1), suggesting the presence of substantial BrC upon emission. This apparent reduction of the BrC contribution to absorption is in agreement with Forrister et al. (2015), which examined the BrC concentration and $A_{abs}$ of western U.S. forest fire as a function of aging time up to 50 h. Their result shows that most (~94%) BrC emitted from NA wildfires was lost within a day ($A_{abs}$ reduced from ~3.6 to ~1.4), while the remaining fraction was persistent and not affected by further aging up to 50 h (Forrister et al., 2015). The even lower $A_{abs}$ value observed here essentially suggested a complete loss of BrC following the extended aging time. The reduction of the BrC contribution to absorption could be due to a combination of bleaching (Zhao et al., 2015; Liu et al., 2016a; Sumlin et al., 2017; Schnitzler and Abbatt, 2018) and/or evaporation of volatile BrC (Forrister et al., 2015).

The derived $A_{abs}$ value (i.e., 0.7–0.9) is also near the lower end of the typical range (0.6–1.3) observed for particles consisting of black carbon (BC) without contribution from brown carbon (Bergstrom et al., 2007; Clarke et al., 2007; Gyawali et al., 2009; Bond et al., 2013; Liu et al., 2018). This low $A_{abs}$ value is typically associated with large compact BC particles (diameter > ~110 nm), or large BC core with thick non-absorbing coating (Schnaiter et al., 2005; Gyawali et al., 2009; Lack and Cappa, 2010; Liu et al., 2018; Bergstrom et al., 2007; Li et al., 2016), as also reproduced in our calculations (SI S2). The HTDMA measurement shows that the vast majority of the particles has a hygroscopic growth factor > 1.23 at 80% RH, excluding the possibility of...
Table 1
Summary of optical properties from previous field observations of NA wildfire aerosols.

| Source Region                  | Observation Site                  | Plume type          | Year   | Campaign | Single Scattering Albedo | Absorption Ångström Exponent | Reference                    |
|--------------------------------|-----------------------------------|---------------------|--------|----------|--------------------------|-----------------------------|-------------------------------|
| California Forest fire         | Surface, Reno, NV                 | fresh (several hours) | 2008   | /        | 405 0.88–0.93\(^a\)      | 405/870 1.42–2.07           | Gyawali et al. (2009)          |
| Southwestern U.S. forest (Las Conchas, NM) | Surface, NM                      | fresh               | 2012   | /        | 532 0.90 (0.83–0.95)      | 405/781 2.1 ± 0.5           | Liu et al., (2014)             |
| Northwestern U.S. forest       | Pacific Northwest, Richland, WA   | fresh (< 5h)        | 2013   | BBOP     | 532 ~0.94                 | /                           | Sediacek III et al. (2018)    |
| Southwestern U.S. forest       | Surface, NM                       | slightly aged (~9h) | 2012   | /        | 532 0.91 (0.90–0.93)      | 405/781 3.3 ± 0.4           | Liu et al., (2014)             |
| Northern California            | Mt. Bachelor Observatory, FT in central Oregon, U.S. | slightly aged (10 – 15 h) | 2016   | /        | / 470/660 1.8 or 2.4\(^c\) |                             | Laing et al. (2019)           |
| Western U.S. forest            | western, central, and southeastern regions of continental U.S. | fresh to slightly aged (< 3 days) | 2013   | NASA SEAC4RS | 401 ~0.90\(^b\),\(^d\) | 401/870 ~3.5                  | Forrister et al. (2015); Liu et al., (2017); Selimovic et al. (2018) |
| Western US wildfires           | Mt. Bachelor Observatory, FT in central Oregon, U.S. | fresh to slightly aged (3–5 h) | 2015   | /        | 528 0.978 ± 0.007          | 467/660 3.45 ± 1.04          | Laing et al. (2016)            |
| Canadian Forest fire           | FT of NA east coast               | aged (3–5 days)\(^e\) | 2004   | INTEX / KARRT     | 550 0.96 (0.95–0.97)      | 470/660 2.1 (1–3)           | Clarke et al., (2007)         |
| Canadian Forest fire           | ENA                               | well-aged (> 10 days) | 2017   | ACE-ENA   | 529 0.93–0.96             | 464/648 –0.8                 | This study                    |

\(^a\) Read a ± b as mean ± 1 σ, and read a (c-d) as mean (min - max).
\(^b\) Corresponding single scattering albedo at 529 nm are expected to be in-between that measured at 405 and 870 nm
\(^c\) Depending on the correction method applied.
\(^d\) Estimated through combining the lab studies and field observations of the Rim fires; see Selimovic et al. (2018) for more detail.
\(^e\) Estimated from typical air mass transport time from western to eastern U.S. (Colarco et al., 2004).
a substantial contribution from compact BC particles, which is hydrophobic. Large BC core sizes are consistent with previous observations of NA wildfire plumes, which generally show the geometric mean diameter or BC cores of 120 to 150 nm (Kondo et al., 2011; Taylor et al., 2014; Ditas et al., 2018). The thick coating is supported by earlier studies, which show that the shell-core ratio based on SP2 measurements is 1.3 to 1.6 for fresh NA wildfire plumes (Kondo et al., 2011), and ~2.25 after days of aging (Taylor et al., 2014; Ditas et al., 2018). In addition, BC particles with thick coating also help explain the hygroscopic growth shown by the HTDMA. We note that thickly coated BC particles alone cannot explain the relatively high $\omega_{532}$ (0.92–0.95) (see SI S2). Earlier studies (Lack et al., 2012; Ditas et al., 2018) show that large amounts of particulate organics can be externally mixed with BC-containing particles in biomass burning plumes. The aged wildfire aerosols observed are therefore likely external mixtures of non-absorbing organic particles and thickly coated particles with a large BC core. The averaged shell-core ratio and the number fraction of externally mixed non-absorbing particles are derived from measured optical properties and aerosol size distributions (see SI S2). The results suggest that on average, BC particles have a shell-core ratio above ~2 and non-absorbing particles represent a majority of the aged wildfire aerosols.

4.3. Implications on aerosol direct effects

Given the elevated injection height, wildfire plumes can stay aloft for extended periods of time and spread over large geographic areas, including the tropics (Yu et al., 2019; Khaykin et al., 2018; Kloss et al., 2019). In addition, the radiative forcing efficiency at higher latitudes are much stronger (up to ~10 times) than at the lower altitudes (Zarzycki and Bond, 2016; Samset and Myhre, 2011; Ban-Weiss et al., 2012; Samset et al., 2013). The optical properties presented here help quantify the radiative effects of wildfire aerosols and BrC. When the optical properties of BrC are parameterized using measurements of freshly emitted biomass burning aerosols (Saleh et al., 2014) (i.e., loss of BC is not taken into consideration), simulated global mean direct radiative effects (DRE) of BrC assuming internal mixtures generally ranged from 0.08 to 0.13 W m$^{-2}$ (Saleh et al., 2015; Jo et al., 2016; Brown et al., 2018; Zhang et al., 2019). This is comparable to that of BC. The DRE of BrC decreases by over 50% to ~0.05 W m$^{-2}$ when 25% BrC absorption is assumed to remain following photo-bleaching (Wang et al., 2018; Brown et al., 2018). The DRE further decreases to ~0.013 W m$^{-2}$ if a smaller fraction (i.e., 6%) of primary BrC absorption remains after photo-bleaching (Zhang et al., 2019). Our results here indicate negligible contribution of BrC to absorption in the aged wildfire aerosols. If this finding holds for wildfires in other regions as well, it will suggest that the overall DRE of BrC may be minor on global average.

The optical properties also influence the lifetime and geographic spread of aged wildfire aerosols, which further affect their direct radiative effects. Yu et al (2019) shows that the Canadian wildfire plumes rose from 12 to 23 km within 2 months owing to solar heating of the wildfire aerosols, extending their lifetime and latitudinal spread. In the absence of measurements, model simulations suggest the observed plume rising is best explained by aged wildfire aerosol particles of a coated fractal structure with 2% BC mass and corresponding $\omega_{532}$ of ~0.82, or a coated sphere structure with 3% BC mass and corresponding $\omega_{532}$ of ~0.92. Our measurements of aerosol optical properties, however, are best explained by an external mixture of non-absorbing particles and coated sphere BC particles, which differs from the scenarios above. This provides observational constraints for further evaluations of the transport and direct radiative effects of the wildfire aerosols.

5. Evolutions in CCN concentrations

5.1. Ambient number size distributions

In regional or global models, size distributions of fresh biomass burning aerosols are often assumed to be unimodal, with default number mode diameter ($D_{pn}$) of 80 to 150 nm and mode width ($\sigma_n$) of 1.6 to 2 (Stier et al., 2005; Dentener et al., 2006; Ramnarine et al., 2018). The default mode parameters are based on the observed number size distributions of fresh biomass burning plumes (Janhäll et al., 2010; Levin et al., 2010). These simulation (Sakamoto et al., 2016; Ramnarine et al., 2018) and field observations (Janhäll et al., 2010; Levin et al., 2010) show that the size distribution of biomass burning aerosols remains unimodal, but with increasing $D_{pn}$ (170 ~ 300 nm) and decreasing $\sigma_n$ (1.7 to 1.3) during the aging in the atmosphere. With sufficient time, $\sigma_n$ is expected to converge towards the coagulation limit of ~1.2 (Sakamoto et al., 2016; Ramnarine et al., 2018). To capture the variation trend, some recent models are assuming two size modes for biomass burning aerosols, one fresh mode and one aged mode (Liu et al., 2016b; Rasch et al., 2019). After heating to 300 to 400 °C, most observational studies show an unimodal distribution of biomass burning aerosols (Clarke et al., 2004; Clarke et al., 2007; Rose et al., 2011; Ueda et al., 2016).

Unlike the unimodal size distribution represented in some global models, aerosols observed during this wildfire episode show a bimodal number size distribution (Fig. 6), containing one minor Aitken mode (At: $D_{pn}$ = 88 nm, $\sigma_n$ = 2.11) and a dominant accumulation mode (Ac: $D_{pn}$ = 230 nm, $\sigma_n$ = 1.48). Note that the Aitken mode evident in the number size distribution has a negligible contribution to the volume size distribution (Fig. 4) due to the relatively small particle diameters.

![Fig. 6. Number size distributions observed during the long-range transported Canadian wildfire episode when CO > 140 ppb. The black circles indicate the observed size distribution, based on which the lognormal fittings are conducted to derive modal parameters. For both ambient and non-volatile aerosols, the size distributions are bimodal, including one Aitken (At) mode and one accumulation (Ac) mode.](image-url)
The non-volatile component also exhibited a bimodal number size distribution during this wildfire episode (Fig. 6). The bimodal distributions of non-volatile components are not an artifact due to time-averaging, but was observed continuously during periods when aerosol was dominated by the aged wildfire particles (Fig. 1). While bimodal distribution is rarely observed in fresh or slightly-aged NA wildfire plumes (Kondo et al., 2011; Taylor et al., 2014; Laing et al., 2016), it has been reported for well-aged NA plumes (plumes aged over 6 days) (Fiebig et al., 2003; Petzold et al., 2007) (Table 2).

5.2. Aerosol hygroscopicity and the influencing factors

Aerosol hygroscopicity can be quantified by hygroscopicity parameter, κ (Peters and Kreidenweis, 2007), which ranges from 0 to 1.3 for representative atmospheric aerosol particles. Atmospheric particles consisting mostly of inorganic species typically have higher κ values than those enriched in organic compounds. Particle hygroscopicity parameter κ can be derived under super-saturated conditions from size-resolved CCN activation spectrum (κ_{CCN} section 2.2), or under sub-saturation conditions from particle hygroscopic growth factor (κ_{GF}) measured by HTDMA (section 2). Aerosols observed during the wildfire episode were classified into three groups based on the concurrent measurement of CO mixing ratio: background (CO < 110 ppb), intermediate (110 < CO < 140 ppb), and well-aged wildfire aerosols (CO > 140 ppb). Derived values of κ are shown for each group (Fig. 7).

In background air masses, κ_{CCN} derived at all six diameters (i.e., 40, 50, 75, 100, 125, and 150 nm) were around 0.55. This κ_{CCN} values suggest a mixture dominated by sulfate (including sulphuric acid (κ ~ 0.9), ammonium sulfate (κ ~ 0.6) and ammonium bisulfate (κ ~ 0.7)) and organic compounds (κ generally below 0.4) (Peters and Kreidenweis, 2007; Schmale et al., 2018). This is further supported by the lower κ_{GF} than κ_{CCN} under background conditions, which suggested the presence of organics (see discussions below). Moreover, under the background conditions, while the majority (> 90%) of the 40 and 50 nm particles have κ_{CCN} below 0.6, a substantial fraction (25% to 50%) of particles with diameters of 100, 125, and 150 nm exhibit κ_{CCN} values over 0.6. Such an increase of κ_{CCN} is consistent with condensation of sulfate and in-cloud production of sulfate, which can grow the Aitken mode particles into the accumulation mode size range (Zheng et al., 2018).

As shown in Fig. 7a, both κ_{CCN} and κ_{GF} show strong negative correlation with CO mixing ratio. κ_{CCN} decreased from ~0.55 for background particles to ~0.3 for well-aged wildfire particles. The decrease is especially evident for the accumulation mode (D_p > 75 nm) particles, which is the dominate mode of wildfire aerosols (Fig. 2). The κ_{CCN} value of wildfire aerosols (~0.3) is in good agreement with previous lab studies of aerosols produced using typical biomass fuels consumed in NA wildfires. These studies (Peters et al., 2009a; Engelhart et al., 2012; Lathem et al., 2013) show that, although κ_{CCN} of fresh wildfire aerosols can vary substantially (0.06 to 0.8), the value quickly converges to a range of 0.08 to 0.3 after several hours of aging. The κ_{CCN} value for the wildfire aerosols is also consistent with the range of aged biomass burning aerosols observed in central Amazonia (Thalman et al., 2017; Palm et al., 2018).

The value of κ_{GF} derived from HTDMA measurement shows similar negative correlation with CO, decreasing from ~0.35 under background conditions to ~0.15 for wildfire aerosols. The value of κ_{GF} is consistently lower than that of κ_{CCN} for all three groups. Such difference has been observed in a number of earlier studies (e.g., Wex et al., 2009; Ovdenevaite et al., 2011) when aerosols consist of substantial amounts of organic compounds with higher molecular weights, and was attributed to high non-ideality of compounds in aerosol water under sub-saturated conditions (Peters et al., 2009b), the conversion of hydrogels under sub-saturated conditions into multiple smaller molecules under super-saturated conditions (Ovdenevaite et al., 2011), and/or the difference in solubility and phase states under sub- and super-saturated conditions (Pajunen et al., 2015; Rastak et al., 2017).

The variation in κ can be further explained by the non-volatile volume fractions (κ_{VD}, TD), defined as:

\[ f_{V, TD} = (\text{corresponding } D_p \text{ after heated to } 300 \, ^\circ\text{C} \text{ / selected } D_p \text{ in size-resolved CCN measurements})^3 \]
which can be estimated from the paired size distributions of ambient and thermally denuded aerosols (SI S2; Fig S2). Here we derived $f_{v, TD}$ only during the wildfire-influenced periods (i.e., when CO > 110 ppb). Both $\kappa_{CCN}$ and $\kappa_{GF}$ are negatively correlated with $f_{v, TD}$ (Fig. 8), as non-volatile components are likely water insoluble BC or organics with higher molecular weight, which is shown to result in lower $\kappa$ (Wang et al., 2019). The variations of $\kappa_{CCN}$ and $\kappa_{GF}$ at given $f_{v, TD}$ levels can be caused by differences in the oxygen content of aerosols (e.g., O:C ratio) (Jimenez et al., 2009; Duplissy et al., 2011) or by thermal volatilities (Massoli et al., 2010; Rickards et al., 2013), as well as uncertainties in $f_{v, TD}$ estimations (SI S2).
5.3. Contribution to CCN concentrations and implications on aerosol indirect effects

The shape of number size distribution (section 5.1) and the aerosol hygroscopicity (section 5.2) essentially dictate the fraction of aerosol particles that serve as CCN at given super-saturation level. Compared to background ones (Zheng et al., 2018), the wildfire aerosols show higher number fraction and larger mode diameter in the accumulation mode particles, which compensated the lower κ values, and lead to higher CCN-active fractions (Fig. 9). Under lower super-saturation levels of 0.1% and 0.2% which are representative for marine low clouds (Wood, 2012), average CCN-active fractions are respectively 22% and 36% for background aerosols. In comparison, those during the wildfire-influenced episodes almost doubled (increased to 41% and 62%, respectively). This increase also corresponds to higher absolute CCN concentrations at 0.1% and 0.2% super-saturations during this wildfire episode (302 and 459 cm⁻³, respectively), which are both ~3 times higher than the annual average. The tripled CCN concentrations versus doubled CCN-active fractions are due to the higher CN during wildfire episode.

Given the elevated injection heights, the long-range transported wildfire aerosols are conventionally considered as largely separated from underlying marine low clouds (Painemal et al., 2014; Rajapakse et al., 2017). Therefore, earlier studies of the wildfire aerosol impacts on marine low clouds mainly focused on the cloud adjustment to the warming caused by scattering and absorption of solar radiation by wildfire aerosols above the marine low clouds (Johnson et al., 2004; Wilcox, 2012; Zhang et al., 2016), while the effects on MBL CCN and therefore cloud microphysics have received less attention. Recent satellite and modelling studies suggested contact of biomass burning aerosols with marine cloud decks (Costantino and Bréon, 2010; Costantino and Bréon, 2013; Painemal et al., 2014; Lu et al., 2018). However, direct evidence of such contact is still limited. Our results provide direct evidence that the long-range transported wildfire aerosols can descend into MBL and dominate the CCN population. The elevated CCN concentration due to the influence of wildfire aerosols can result in cooling due to increased albedo (i.e., the Twomey effect) and coverage (cloud lifetime effect) of marine low clouds (Twomey, 1974; Albrecht, 1989; Lu et al., 2018). Given the expected increases of NA wildfire intensity and frequency, the high susceptibility of marine clouds albedo and precipitation to the perturbation of CCN population, wildfire aerosols may have important influences on the climate effects of marine low clouds.

6. Summary

The elevated injection height of North American wildfire plumes leads to extended aerosol lifetimes and geographic spread, therefore enhanced influences on radiation and climate. As the properties of NA wildfire aerosols may evolve substantially during their long transport in the atmosphere, the properties of well-aged wildfire aerosols are needed to quantify their impact on radiation and climate given the long aerosol lifetime. In August 2017, extreme Canadian wildfires injected a large amount of aerosols into the upper troposphere – lower stratosphere (~12 km). Some of the plumes rose from 12 to 23 km in 2 months due to solar heating of absorbing wildfire aerosols (Fig. 10), extending the lifetime (i.e., up to 8 months) and geographic spread (Yu et al., 2019). In contrast, we show some of the wildfire plumes aloft travelled across the Atlantic Ocean and descended into the remote marine boundary layer (MBL) over the eastern North Atlantic (ENA), >7000 km away within about two weeks. These long-range transported wildfire aerosols dominated the properties of MBL aerosol in the ENA from Aug. 24th to 29th, 2017. Our analysis indicates that this accelerated descent is facilitated by dry intrusions associated with mid-latitude cyclones (Fig. 10).

During the episode from Aug 24 to 29, the characteristics of biomass burning plumes are evident from trace gases and aerosol measurements at the ENA site on Graciosa Island, Azores. These characteristics include the extremely high CO mixing ratio and concentration of non-volatile accumulate mode particles, linear correlations among CO, ambient and non-volatile aerosol number and volume concentrations, and the dominance of aerosol composition by organics. As MBL aerosol was dominated by long-ranged transported plume, this provides an excellent opportunity to comprehensively characterize the climate-related properties of well-aged wildfire aerosols. We show that the well-aged wildfire aerosols have high single scattering albedos at 529 nm of...
0.92–0.95, and very low absorption Ångström exponents ($\bar{\Delta}_{\text{abs}}$) at 464 nm / 648 nm of < 1. In contrast, $\bar{\Delta}_{\text{abs}}$ of fresh wildfire aerosols and those aged for less than a few days typically ranges from ~1.4 to ~3.5. The very low $\bar{\Delta}_{\text{abs}}$ value indicates negligible contribution of brown carbon to aerosol absorption, suggesting a nearly complete loss of BrC during the transport of the wildfire aerosols (Fig. 10). This nearly complete loss of BrC suggests that on global average, the direct radiative effect of brown carbon is likely minor (i.e., < 0.05 W m$^{-2}$) (Brown et al., 2018; Wang et al., 2018). Combining the Mie calculations with the measured aerosol hygroscopicity, volatility and size distributions, we show that the high $\omega_{S29}$ and low $\bar{\Delta}_{\text{abs}}$ values are best explained by an external mixture of non-absorbing organic particles and absorbing particles that are large BC cores ($> \sim 110$ nm diameter) and thick non-absorbing coatings.

The accelerated descent of wildfire plumes significantly increased the CCN concentration inside MBL over the Azores (Fig. 10). The number size distribution of the aged wildfire aerosols is dominated by an accumulation mode with mode diameter of 230 nm, much larger than that of typical background marine aerosols ($\sim 157$ nm (Zheng et al., 2018)). Hygroscopicity parameter $\kappa_{\text{CCN}}$ of well-aged wildfire aerosol generally varies between 0.2–0.4, consistent with results from earlier studies and lower than the value of ~0.55 for the background marine aerosols in ENA. Despite the low $\kappa_{\text{CCN}}$ value, aged wildfire aerosols have higher activated fraction at representative super-saturation levels of marine low clouds (0.1%–0.2%) due to the dominance of accumulation mode particles and large mode diameter. Correspondingly, the CCN concentrations at 0.1% and 0.2% super-saturations during the wildfire episode (302 and 459 cm$^{-3}$, respectively) are both ~3 times higher than the annual average. Our results provide direct evidences that the long-range transported wildfire aerosols can descend into MBL and dominate the CCN population. Because the albedo (i.e., reflectivity), drizzle formation, and lifetime of marine low clouds are particularly sensitive to the change in CCN concentration, the higher CCN concentrations are expected to lead to reduced droplet effective radius and drizzle formation, therefore cooling of climate as a result of increased cloud albedo (i.e., the Twomey effect) and increase cloud coverage (cloud lifetime effect) (Twomey, 1974; Albrecht, 1989; Lu et al., 2018). This suggests significant cloud-related climate effects of NA wildfires. The accelerated descent facilitated by dry intrusion is expected to occur regularly following extratropical cyclones (Raveh-Rubin, 2017; Naud et al., 2018). Given the expected increases of NA wildfire intensity and frequency, the effects of NA wildfire on CCN and clouds in remote marine environment therefore need to be further examined.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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