Regional Influence of Wildfires on Aerosol Chemistry in the Western US and Insights into Atmospheric Aging of Biomass Burning Organic Aerosol

Shan Zhou1, Sonya Collier1, Daniel A. Jaffe2,3, Nicole L. Briggs2,3,4, Jonathan Hee2,3, Arthur J. Sedlacek III5, Lawrence Kleinman5, Timothy B. Onasch6, Qi Zhang1*

1Department of Environmental Toxicology, University of California, Davis, CA 95616, USA
2School of Science, Technology, Engineering, and Mathematics, University of Washington Bothell, Bothell, WA 98011, USA
3Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, USA
4Gradient, Seattle, WA 98101, USA
5Environmental and Climate Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, USA
6Aerodyne Research Inc., Billerica, MA 01821, USA

*Corresponding Author: Qi Zhang (dkwzhang@ucdavis.edu), (530)752-5779, Department of Environmental Toxicology, University of California, Davis, CA 95616

Abstract. Biomass burning (BB) is one of the most important contributors to atmospheric aerosols on a global scale and wildfires are a large source of emissions that impact regional air quality and global climate. As part of the Biomass Burning Observation Project (BBOP) field campaign in summer 2013, we deployed a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS) coupled with a thermodenuder at the Mt. Bachelor Observatory (MBO, ~2.8 km above sea level) to characterize the impact of wildfire emissions on aerosol loading and properties in the Pacific Northwest region of the United States. MBO represents a remote background site in the western U.S. and it is frequently influenced by transported wildfire plumes during summer. Very clean conditions were observed at this site during periods without BB influence where the 5-min average (± 1σ) concentration of non-refractory submicron aerosols (NR-PM1) was 3.7 ± 4.2 μg m⁻³. Aerosol concentration increased substantially (reaching up to 210 μg m⁻³ of NR-PM1) for periods impacted by transported BB plumes and aerosol composition was overwhelmingly organic. Based on Positive Matrix Factorization (PMF) of the HR-AMS data, three types of BB organic aerosol (BBOA) were identified, including a fresh, semivolatile BBOA-1 (O/C = 0.35; 20% of OA mass) that correlated well with ammonium nitrate, an intermediately oxidized BBOA-2 (O/C = 0.60; 17% of OA mass), and a highly oxidized BBOA-3 (O/C = 1.06; 31% of OA mass) that showed very low volatility with only ~ 40% mass loss at 200°C. The remaining 32% of the organic aerosol (OA) mass was attributed to a boundary layer (BL) OOA (BL-OOA; O/C = 0.69) representing OA influenced by BL dynamics and a low-volatility oxygenated OA (LV-OOA; O/C = 1.09), representing regional free troposphere aerosol. The mass spectrum of BBOA-3 resembled that of LV-OOA and had negligible contributions from the HR-AMS BB tracer ions – C₂H₄O₂⁺ (m/z = 60.021) and C₃H₅O₂⁺ (m/z = 73.029). This finding highlights the possibility that the influence of BB emission could be underestimated in regional air masses where highly oxidized BBOA (e.g. BBOA-3) might be a significant aerosol
component. We also examined OA chemical evolution for persistent BB plume events originating from a single fire source and found that longer solar radiation led to higher mass fraction of the chemically aged BBOA-2 and BBOA-3 and more oxidized aerosol. However, an analysis of the enhancement ratios of OA relative to CO (ΔOA/ΔCO) showed little difference between BB plumes transported primarily at night versus during the day, despite evidence of substantial chemical transformation in OA induced by photo-oxidation. These results indicate negligible net OA production with photo-oxidation for wildfire plumes observed in this study, for which a possible reason is that SOA formation was almost entirely balanced by BBOA volatilization.

1 Introduction

Biomass burning (BB) is estimated to be the largest source of primary carbonaceous aerosols and a major source of reactive trace gases in the Earth’s atmosphere (Bond et al., 2004; Akagi et al., 2011). Emissions from wildfires and other BB sources, such as residential wood combustion and agricultural burning, have been shown to affect the global radiation budget (IPCC, 2013) and degrade air quality in both rural areas and populated locations (e.g. Jaffe et al., 2008; Jaffe and Wigder, 2012). The environmental impacts of BB emissions are strongly correlated with the chemical, optical, and microphysical properties of BB aerosols, which are in turn dependent in a complex manner on fuel type, combustion phase, and atmospheric aging of emitted particles and gas species (e.g., Petters et al., 2009; Liu et al., 2014; Collier et al., 2016).

Organic compounds are a dominant component of BB aerosols (Bond et al., 2004; De Gouw and Jimenez, 2009), but the chemical and physical properties of primary organic aerosol (POA) released directly from burning and secondary organic aerosol (SOA) formed from gaseous precursors emitted by BB are dramatically different. For example, BB POA tends to be semivolatile, smaller in size, and composed of less oxidized compounds, whereas SOA from BB is generally more oxidized, larger in size, and less volatile (Abel et al., 2003; Heringa et al., 2011; May et al., 2013). Furthermore, aerosol composition, optical properties, and hygroscopicity have been found to change substantially in BB plumes undergoing photo-oxidation and cloud processing and the changes are mostly driven by the organic fraction (Abel et al., 2003; de Gouw et al., 2006; Engelhart et al., 2012). Understanding the chemical properties and atmospheric processing of organic aerosols (OA) from BB sources (i.e., BBOA) is thus crucial for improving our ability to quantitatively assess and predict the impacts of BB emissions on climate and air quality. However, the chemical processing of BBOA is highly complex and the net effect of aging on BBOA mass is highly variable. For example, while several laboratory studies reported substantial formation of SOA during chamber aging, others observed a very small increase or even a decrease of BBOA mass (Grieshop et al., 2009; Cubison et al., 2011; Hennigan et al., 2011; Heringa et al., 2011; Ortega et al., 2013). Field studies have also observed enhancement (Yokelson et al., 2009; DeCarlo et al., 2010), depletion (e.g., Akagi et al., 2012; Jolleys et al., 2015), or no change (Brito et al., 2014; May et al., 2015) of dilution-adjusted OA mass in BB plumes after emissions.

In order to decipher which factors affect BBOA evolution and reconcile discrepancies in previous laboratory and atmospheric observational results, the U.S. Department of Energy (DOE) sponsored the Biomass Burning Observation Project (BBOP) campaign, which combined aircraft-based measurements with mountain top observations to characterize the downstream evolution of the chemical, microphysical, and optical properties of
carbonaceous aerosol generated by BB. Wildfires across the western U.S. have been linked to increased PM$_{2.5}$ concentrations at various receptor sites (Jaffe et al., 2008) and high pollution episodes that exceeded the National Ambient Air Quality Standards (Jaffe and Wigder, 2012). Furthermore, due to changes in precipitation, temperature and other meteorological conditions as a result of climate change, wildfire activities in this region have been increasing (Westerling et al., 2006; Dennison et al., 2014) and are predicted to increase summertime OA concentration by 40% from 2000 - 2050 (Spracklen et al., 2009).

A large number of wildfire events originating in the western US were observed during BBOP from the Mount Bachelor Observatory (MBO) – a remote mountain-top site that serves to characterize western U.S. background conditions and is frequently impacted by transported BB plumes during the summer fire season (Wigder et al., 2013). Continuous measurements of BB plumes at MBO allowed for the study of BBOA with different source, age, and formation pathways under realistic atmospheric conditions and can provide rich data for evaluating the impact of BB emissions on regional aerosol chemistry and elucidating their atmospheric aging processes. A number of recent studies conducted at fixed locations in the western U.S. investigated impacts of BB on ozone, gaseous nitrogen species, and organic and elemental carbon (e.g., Wigder et al., 2013; Timonen et al., 2014; Hallar et al., 2015). Yet, only a few ground-based measurements have examined the chemical composition and evolution of BBOA, including a filter-based study of wildfire aerosols in Yosemite National Park (Engling et al., 2006) and a single-particle mass spectrometry study on the mixing state and aging of particles during the 2007 San Diego wildfires (Zauscher et al., 2013).

In this study, we provide an overview of the chemical and physical characteristics of non-refractory submicrometer particles (NR-PM$_{1}$) at MBO and examine the changes in ambient aerosol concentration and composition influenced by BB emissions. The sources of OA are investigated via factor analysis of the HR-AMS data and the aging of BBOA are discussed via combining real-time measurements with trajectory analysis. We also examine the enhancement and chemical transformation of OA in BB plumes transported during day-time and night-time, respectively.

2 Experimental methods

2.1 Sampling site and wildfires in the vicinity

The Mt. Bachelor Observatory (43.981°N 121.691°W, Fig. 1) is situated on the summit of Mt. Bachelor (~ 2.8 km a.s.l.), an isolated volcanic peak in the Deschutes National (coniferous) Forest in central Oregon. The nearest populated areas are Bend (pop. ~80,000), 31 km to the east, and Redmond (pop. ~26,000), 53 km northeast of MBO. Due to its high elevation and distance from local pollution sources, MBO is a remote background site in the western U.S. well positioned for sampling of background free tropospheric air and observation of long-range transport of Asian plumes and North American wildfires (Weiss-Penzias et al., 2006; Wigder et al., 2013; Briggs et al., 2016).

During the sampling period from July 25 to August 25, 2013, various active wildfires in northern California and southeastern and central Oregon were detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (https://firms.modaps.eosdis.nasa.gov) (Fig. 1). Three intense fires, the Salmon River Complex Fire (SRCF),
Whiskey Complex Fire (WCF) and Douglas Complex Fire (DCF), were active for a majority of the time during this study and hence were identified as major fires in the region.

2.2 Real-time measurements at MBO

Continuous observations at MBO included submicron aerosol light scattering (TSI nephelometer; 450, 550, and 700 nm) and absorption (Radiance Research PSAP; 467, 530, and 660 nm), elemental and organic carbon (Sunset Lab), CO and CO₂ (Picarro Cavity Ring-Down Spectroscopy), O₃ (Dasibi), NOₓ (Air Quality Design 2-channel chemiluminescence), peroxyacetyl nitrate (PAN; custom gas chromatograph), and meteorological parameters (e.g., Weiss-Penzias et al., 2006; Briggs et al., 2016). Data reported in this study are 5-min averages. During this study, an HR-AMS (DeCarlo et al., 2006) was deployed downstream of a thermodenuder (TD) to measure the size-resolved composition and volatility of NR-PM₁. These are the first real-time aerosol chemical measurements at MBO. The TD consists of a heated tube followed by a heated adsorption section that uses carbon cloth to prevent recondensation of organic vapors (Fierz et al., 2007). The TD was automated using a custom program to step through 12 different temperatures ranging from 30 to 200°C, at 10 min time intervals. Changes in mass and chemical composition of NR-PM₁ as a result of aerosol evaporation were quantified by the HR-AMS by alternating sampling between the TD and the bypass (BP) ambient sampling mode every 5 min. During BP mode, the temperature in the heated section ramped up to the next setting and reached thermal stability before switching back to TD mode. The switching between sampling modes was triggered by a digital output signal from the HR-AMS which was synchronized to the HR-AMS averaging intervals and was achieved using an actuated 3-way ball valve. Aerosol residence time in the TD was 8.2 s at the experimental flow rate (1.1 L min⁻¹). Particle losses within the TD mode (~ 5%) due to diffusional and thermophoretic forces were quantified based on the behavior of ammonium sulfate.

2.3 HR-AMS data analysis

The HR-AMS was operated in the ion optical “V-mode” with reduced micro-channel plate bandwidth due to signal interference at MBO, and was calibrated following standard protocols described in detail in Collier et al. (2016). Data analyses were performed utilizing AMS analysis toolkit SQUIRREL v1.53 and PIKA v1.12 in Igor Pro 6.34A (Wavemetrics, Inc., Lake Oswego, OR). Default relative ionization efficiency (RIE) values were assumed for organics (1.4), nitrate (1.1), and chloride (1.3), while an RIE value of 5 was determined for ammonium and 1.32 for sulfate following the analysis of pure NH₄NO₃ and (NH₄)₂SO₄, respectively. A time- and composition-dependent collection efficiency (CE) was applied based on the algorithm by Middlebrook et al. (2012), leading to an average (±1σ) CE of 0.56 (±0.12). Time-dependent gas phase CO₂⁻ subtraction was performed to improve the determination of OA, which is critical for low OA concentration periods (Collier and Zhang, 2013). The mass concentrations of ammonium, nitrate, chloride, and sulfate were determined from PIKA analysis of the high-resolution mass spectra (HRMS) whereas organic concentrations came from SQUIRREL analysis of the unit mass resolution (UMR) data. The detection limits of organics, sulfate, nitrate, ammonium, and chloride, defined as 3 times the standard deviations (3σ) of the corresponding signals in particle-free ambient air, were 28.1, 4.5, 2.3, 9.6, and 3.0 ng m⁻³, respectively,
for an averaging time of 5 min. Atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios and the
organic mass-to-carbon (OM/OC) ratio were determined using the Improved-Ambient (IA) method (Canagaratna et
al., 2015). We also reported the ratios determined using the previously published Aiken-Ambient (AA) method
(Aiken et al., 2008) in order to compare with literature results. As shown in Fig. S1 in the Supplement, the O/C, H/C,
and OM/OC values determined from the two methods correlate tightly ($r^2 = 0.99$), and the IA method reports 29%,
5%, and 31%, respectively, higher values compared to the AA method.

Positive Matrix Factorization (PMF) was executed using the PMF2 algorithm (Paatero and Tapper, 1994) in the
PET v2.05 program (Ulbrich et al., 2009). The spectral matrices of organic and inorganic species were combined
(Sun et al., 2012) and the ion signals were expressed in nitrate-equivalent concentrations. Periods with organic
centration below 1.5 µg m$^{-3}$ were excluded from PMF analysis due to low signal-to-noise (S/N) ratios, which
could prevent model convergence. The HRMS of organic ions at $m/z$ 12 – 180 and the UMR signals at $m/z$ 181 –
350 were included. For inorganics, only the major ions for each species were included, i.e., SO$^+$, SO$_2^+$, HSO$_2^+$, SO$_3^+$,
HSO$_3^+$, and H$_2$SO$_4^+$ for sulfate, NO$^+$ and NO$_2^+$ for nitrate, NH$^+$, NH$_2^+$, and NH$_3^+$ for ammonium, and HCl$^+$ for
chloride. Cl$^-$ was not included due to low S/N. Data preparation prior to PMF analysis followed the steps outlined in
the Table 1 of Zhang et al. (2011). After PMF analysis, the mass concentration of each OA factor was derived from
the sum of organic signals in the corresponding mass spectrum after applying proper CE and RIE. The solutions for
3 to 8 factors were explored with varying rotational parameters (-0.5 ≤ FPEAK ≤ 0.5, in increments of 0.1). After a
detailed evaluation of mass spectral profiles, temporal trends, diurnal variations, and correlations with external
tracers, the five-factor solution with FPEAK = 0 was chosen. The diagnostic information for five-factor solution is
shown in Fig. S2. In comparison, the four-factor solution resulted in large residual signals, indicating that an
additional factor was needed to explain the variation in the data, whereas the six-factor solution showed indications
of factor splitting, suggesting that too many factors were introduced (Fig. S3).

The concentrations of OA factors at different TD temperatures were determined via multivariate linear regression
of the HRMS of OA after TD against the HRMS of the 5 OA factors determined from PMF of the ambient OA data
following the procedures given in Zhou et al. (2016). The mass fraction remaining (MFR) of a factor at each TD
temperature was then determined as the slope from orthogonal fit between the time series after TD and the ambient
time series (Fig. S4). Thermograms, which describe the MFR as a function of temperature, have been corrected for
particle losses in the TD mode. Aerosol data reported here have all been converted to concentrations at standard
temperature and pressure (STP, 273 K, 1 atmosphere).

2.4 Back trajectory analysis and calculations of plume transport time and cumulative solar radiation

The HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model backward air mass trajectories
(Draxler, 1998) were initiated from MBO at one-hour intervals throughout the campaign period. Three-day
backward trajectories using the 40 km resolution US Eta Data Assimilation System (EDAS) meteorological data
(http://ready.arl.noaa.gov/HYSPLIT.php) were calculated at a starting height of 1500m above ground level.
Meteorological variables (e.g. solar radiation and relative humidity (RH)) along the trajectories were also output. By
overlapping the back trajectories with MODIS fire hotspots, we estimated the transport times for BB plumes that
unambiguously passed over active fire sources (Collier et al., 2016). In addition, we also estimated the cumulative 
solar radiation exposure and average RH for these plumes during the period between emission at fire source and 
arrival at MBO.

3 Results and discussions

3.1 Observations of wildfire-influenced air masses at MBO

Fig. 2 provides an overview of the meteorological conditions, trace gases mixing ratios, and aerosol 
concentration and composition during the sampling period (July 25 – August 25, 2013). The summit air was cool 
(average temperature of 11.2 ± 4 °C) and dry (average RH of 46 ± 21%), although there were periods (e.g., August 
16 and August 23) when MBO was in low clouds and measured RH reached 98%. Wind was generally strong 
(average = 5.7 ± 3.4 m s⁻¹) with a dominant flow from the west and southwest direction, which provides suitable 
conditions for long-range transport of fire smoke from Northern California and Southwest Oregon. Indeed, the 
bivariate polar plots of total NR-PM₁, submicrometer aerosol light scattering at 550 nm (σ₅₅₀nm), and CO (Fig. 1b, 1d, 
and 1e) calculated using the OpenAir software (Carslaw and Ropkins, 2012) all show the highest values at a wind 
speed of ~ 13 m s⁻¹ from the southwest direction, where the major complex fires were located (Fig. 1a).

The average NR-PM₁ concentration during the entire sampling period was 15.1 µg m⁻³ and 93% was contributed 
by organics (Fig. 1c). However, aerosol concentrations and composition changed dynamically. Clean periods of low 
concentrations of aerosol (NR-PM₁ < 10 µg/m³) and gas-phase pollutants (e.g., CO, NOₓ, and PAN) were observed 
for the first week of sampling (July 25 – 30) and during August 18 – 21 (Fig. 2d – 2f). During these periods, 
ammonium sulfate contributed up to 90% of the NR-PM₁ mass (Fig. 2g) and the OA spectra showed low 
abundances of C₂H₄O₂⁺ (m/z = 60.021) and C₃H₅O₂⁺ (m/z = 73.029), which are ion fragments of anhydrous sugar 
(e.g., levoglucosan) and HR-AMS tracers for BB (Alfarra et al., 2007). The fraction of the signal at m/z = 60 (mostly 
C₂H₄O₂⁺) in OA spectrum (f₆₀) was generally below 0.3% (Fig. 2h), indicating minimal BB influence during “clean” 
periods (Cubison et al., 2011).

In contrast, the other periods were characterized by higher f₆₀ (up to 2%), elevated NR-PM₁ concentration (up to 
~ 210 µg m⁻³), and larger OA fraction (generally > 90% of NR-PM₁; Fig. 2c – 2g). In addition, σ₅₅₀nm (up to ~ 670 
Mm⁻¹), CO (up to ~ 700 ppbv), NOₓ (up to ~ 6.5 ppbv), and PAN (up to ~ 2.2 ppbv) all increased dramatically 
during high f₆₀ periods (Fig. 2d – 2e). In fact, the time series of all these parameters correlate tightly, with Pearson’s 
r² in the range of 0.66 – 0.94 (Fig. S5). These observations highlight the frequent and significant impacts of wildfire 
emissions on air quality and atmospheric chemistry in the Pacific Northwest region. Note that although potassium 
(K) is frequently used as a tracer for BB aerosol, K concentration was very low throughout this study, indicating low 
K contents in wildfire emissions in the western US. Similarly, Maudlin et al. (2015) observed no strong 
enhancement of K in wildfire smokes originated from California and Oregon and concluded that it is not a reliable 
tracer for BB in this region.

3.2 Impacts of wildfires on regional aerosol characteristics
3.2.1. Changes of aerosol concentration and composition due to wildfires

Given that $f_{60}$ is a marker for the influence of BB emissions on OA composition, we divided the entire campaign into three regimes based on the $f_{60}$ value: (1) “No BB” for periods with negligible BB influence and $f_{60} \leq 0.3\%$; (2) “BB Infl” for periods with detectable BB influences and moderately elevated $f_{60}$ values (0.3% - 0.5%); and (3) “BB Plm” for periods with $f_{60} > 0.5\%$, indicating intense and less processed BB events. Note that periods with very low OA concentrations (< 1 µg/m$^3$), e.g., August 18 – 21, were classified as “No BB” regardless of the nominal $f_{60}$ values. The average ($\pm$ 1σ) $f_{60}$ values were 0.18 $\pm$ 0.10%, 0.43 $\pm$ 0.05% and 0.77 $\pm$ 0.29% for “No BB”, “BB Infl”, and “BB Plm” periods, respectively (Fig. 3 and Table S1). Similarly, the average mixing ratios of CO, a gaseous pollutant released from combustion, increased from 87.8 $\pm$ 17.9 ppbv during “No BB” to 121.4 $\pm$ 24.8 ppbv during “BB Infl” and 178.3 $\pm$ 68.8 ppbv during “BB Plm” periods.

Fig. 3 shows the comparisons of gas and particle phase properties among the three regimes to illustrate the strong effects that wildfires have on gases and aerosol composition in the Pacific Northwest region. For example, the average NR-PM$_1$ concentration was only 3.7 ($\pm$ 4.2) µg m$^{-3}$ during “No BB” but increased by ~ 4 and ~ 7 times, respectively, during “BB Infl” (13.4 $\pm$ 7.1 µg m$^{-3}$) and “BB Plm” (25.7 $\pm$ 19.9 µg/m$^3$) periods. Aerosol measured at MBO during “BB Plm” periods was predominantly organic (94.6% of NR-PM$_1$ mass; Fig. S6c). The fraction of OA in BB aerosols may be fuel dependent, for instance, high values have been reported for ponderosa pine smoke emissions (99%) (Lewis et al., 2009) and somewhat lower values have been reported for forest fires in south-western Amazon (93%) (Artaxo et al., 2013) and North America boreal forests (87%) (Kondo et al., 2011), and agricultural fires in west Africa (85%) (Capes et al., 2008). Even lower values were observed in eastern Mediterranean wildfires (51.4%) (Bougiatioti et al., 2014) and Asian fires (60%) (Kondo et al., 2011). Since temperate evergreen vegetation was likely the dominant fuel during this campaign, the high OA/PM$_1$ ratio observed in this study appears consistent with those of ponderosa pine.

In addition to OA, concentrations of nitrate, ammonium, and chloride all showed substantial increases that correlated with wildfire impacts (Fig. 3 and Table S1). Nitrate, in particular, displayed large temporal variations that correlated with wildfire plume influences and its concentration in the “BB Plm” regime was on average ~ 11 times greater than the “No BB” regime. Nitrate appeared to be bulk neutralized based on comparing the total molar equivalent of inorganic anions (i.e., sulfate, nitrate and chloride) to that of ammonium (Zhang et al., 2005) during wildfire-influenced periods (Fig. S7a) and the signal ratios of NO$^+$ to NO$_2^+$ observed in particles during these periods (2.15 $\pm$ 0.006) were very similar to the ratio measured for pure NH$_4$NO$_3$ particles (2.2; Fig. S7b), indicating that nitrate was mostly in the form of NH$_4$NO$_3$. Sulfate, on the other hand, displayed milder temporal variation with poor correlation with BB tracers (Fig. 2d-f), indicating that forest fires in this region are not a significant source of sulfate aerosol. Collier et al. (2016) came to a similar conclusion through examination of aerosol enhancement ratios in transported BB plumes.

Significant enhancements due to wildfires emissions were also observed for PAN and NO$_y$ (Fig. 3). However, the mixing ratios of NO$_x$ (mostly as NO$_2$) were comparable among the three regimes. As a result, the fractional contributions of PAN and particulate nitrate to total NO$_x$ both increased due to wildfire influence (Fig. S8). Considering that MBO was hours downwind of wildfire sources during this study, this observation is consistent with
the findings of Akagi et al. (2012) that NO\textsubscript{x} emitted from BB is rapidly converted to PAN and particulate nitrate during plume transport, which reflects high levels of acetaldehyde in fire plumes (Akagi et al 2011). The influence of wildfire emissions on O\textsubscript{3} at MBO appears to be complex (Fig. 2c). The average O\textsubscript{3} mixing ratio in both “BB Infl” (49.1 ppbv) and “BB Plm” (47.3 ppbv) regimes were higher than during the “No BB” (44.7 ppbv) periods (Fig. 3). Similar observations were made previously, which indicate that O\textsubscript{3} tends to peak downwind of fire sources as a result of the interplay of fire emissions (precursors and reactants) and chemical reactions (Jaffe and Wigder, 2012; Wigder et al., 2013; Briggs et al., 2016).

### 3.2.2. Influence of wildfires on organic aerosol chemical properties

In order to demonstrate the influence of wildfires on bulk OA chemistry at MBO, the average HRMS of OA for each of the three regimes are shown in Fig. S6. OA was generally highly oxidized under all three regimes and the O/C of OA generally decreased as BB influence increased. In addition, ions larger than 100 amu (m/z>100) contributed a larger fraction of the total organic signal during “BB Plm” periods (11%) compared to “No BB” periods (5%), consistent with BBOA containing a larger fraction of high molecular weight compounds (Ge et al., 2012a; Lee et al., 2016). OA in “No BB” air masses had an average O/C of 0.84 (O/C\textsubscript{AA}, i.e., O/C calculated with Aiken-Ambient method, is 0.63) and H/C of 1.48 (H/C\textsubscript{AA} = 1.29), in agreement with previous HR-AMS measurements of free tropospheric OA at mountaintop sites (e.g., Sun et al., 2009; Rinaldi et al., 2015). The average O/C for “BB Infl” and “BB Plm” periods were 0.77 (O/C\textsubscript{AA} = 0.60) and 0.69 (O/C\textsubscript{AA} = 0.53), respectively, substantially higher than previously reported O/C for fresh BB emissions. For example, laboratory experiments reported O/C\textsubscript{AA} in the range of 0.15 – 0.60 for POA from BB, depending on fuel type, burning condition, and burn mass (Heringa et al., 2011; Ortega et al., 2013). The high O/C observed for BB-influenced OA at MBO indicates that they were likely a combination of primary and secondary components with the secondary portion having a substantial contribution to the bulk OA.

### 3.3 Aerosol source apportionment and contributions of primary and secondary BBOA at MBO

In order to gain further insight into the influences of different sources and processes on OA concentration and composition at MBO, we performed PMF analysis on the HRMS of all NR-PM\textsubscript{1} species acquired during this study. PMF is commonly applied to the organic mass spectral matrix to determine distinct OA factors (Zhang et al., 2011 and references therein), but conducting PMF analysis on the combined spectra of organic and inorganic aerosols allows for deriving additional information, e.g., the distributions of inorganic signals among different factors and the nominal acidity of the factors, which benefits the interpretation of the sources, chemical characteristics, and evolution processes of OA (Sun et al., 2012). For this study, a total of five OA factors were identified, including three different BB-related aerosol types, i.e., BBOA-1 (O/C = 0.35), BBOA-2 (O/C = 0.60), and BBOA-3 (O/C = 1.06), and two distinct OOA factors, i.e., a less oxidized OOA associated with boundary layer (BL) dynamics (BL-OOA, O/C = 0.69) and a more oxidized low-volatility OOA representing free-troposphere aerosol (LV-OOA, O/C = 1.09). Unlike the two OOAs, the three distinct BBOA factors all showed high correlations with CO (r\textsuperscript{2} = 0.70 - 0.86; Table S2) and displayed sporadic, high amplitude events with large enhancements in concentrations during wildfire-
influenced periods (Fig. 4a-c). In addition, the polar plots of all the BBOAs showed clear concentration hotspots in the southwest direction at high wind speed (Fig. 5a-c), indicative of their associations with wildfire plumes originating from SW Oregon and NW California (Fig. 1). Nevertheless, the three BBOAs are distinctly different in terms of mass spectral profiles (Fig. 4k-m and Fig. S9), oxidation degrees, and volatility (Fig. 5g), likely due to different extents of aging and/or processing pathways.

Among the three BBOA factors, BBOA-1 had the lowest O/C (0.35) and the highest H/C (1.76) and f60 (2.2%) (Fig. 4k). In addition, the mass spectrum of BBOA-1 showed prominent signals of C2H3+, CHO+, C4H7+, C4H9+, and C6H7+, markers for chemically-reduced aerosols, and a high abundance of ions larger than 100 amu (f m/z>100 = 25%; Fig. 4k and 4k'). The UMR spectrum of BBOA-1 at m/z > 180 exhibited a “picket fence” fragmentation pattern where groups of peaks have 14 amu separation, suggesting the occurrence of molecules with hydrocarbon moieties containing different units of the CH2 group. The time series of BBOA-1 correlated tightly with those of C2H4O2+ and C6H6+ (r2 = 0.94 and 0.95, respectively; Table S2), tracers for primary emissions. Furthermore, BBOA-1 appeared to have a strong point source SW of MBO and peaked in association with high wind speeds suggesting that it could be associated with plumes experiencing shorter transport times relative to plumes from equidistant fire sources (Fig. 5a). Together, these observations suggest that BBOA-1 was primarily associated with fresher and less processed air masses from BB sources. In addition, BBOA-1 was found to be semivolatile (Fig. 5g), which is consistent with previous findings that a majority (50% - 80%) of the POA in BB emissions is semivolatile (May et al., 2013). The semivolatile behavior of BBOA-1 also explains the high degree of correlation between BBOA-1 and nitrate (r2 = 0.60; Fig. 4a and Table S2), a secondary species that is often found to correlate with semivolatile OOA (SV-OOA) (Zhang et al., 2011). However, despite being a secondary component, nitrate displayed tight correlations with primary smoke markers, i.e., C2H4O2+ and C3H5O2+, at MBO (Fig. S10). Therefore, it appears that fast processing near the fire sources led to the rapid conversion of NOx to more oxidized compounds such as PAN and nitrate. Based on these results, we infer that BBOA-1 represents fresher BB emissions and might be a surrogate for primary BB emission sources. On average, BBOA-1 comprised 20% of total OA mass during this study (Fig. 5f), suggesting that fresh BB emissions exerted a significant impact on regional air masses.

The more oxygenated BBOA-2 (O/C = 0.60; H/C = 1.72) accounted for an average 17% of the total OA mass (Fig. 5f). Its mass spectrum displayed characteristics of aged BBOA with lower abundances of C6H4O2+ (f60 = 1.1%), C6H5+ ions (31%), and ions > 100 amu (f m/z>100 = 17%) compared to BBOA-1 (Figs. 4l, 4l' and S9b). BBOA-2 also showed a somewhat less volatile profile compared to BBOA-1, especially at TD temperature < 150°C (Fig. 5g). In addition, the temporal trend of BBOA-2 displayed tight correlations with tracers for carboxylic acids, e.g., CHO2+ and CO2+ (r2 of 0.91 and 0.79, respectively; Fig. 4b and Table S2) but lower correlations with nitrate, C6H4O2+, and C6H6+. These results suggest that BBOA-2 was more chemically processed and likely contained secondary products. Indeed, the polar plot of BBOA-2 (Fig. 5b) displayed a more dispersed pattern of sources compared to BBOA-1 with hotspots located in various directions. Nevertheless, the occurrence of a high concentration band at 5 - 15 m s⁻¹ in the SW direction suggests important BBOA-2 sources from similar distances and locations as BBOA-1. The dispersed source features are further evidence that BBOA-2 is more secondary in nature compared to BBOA-1 and is likely more aged.
BBOA-3 contrasts strongly with BBOA-1 and BBOA-2 in chemical composition. The HRMS of BBOA-3 had a very low $C_2H_4O_2^+$ signal ($f_{60} = 4 \times 10^{-8}$), a relatively high intensity of $CO_2^+$ ($f_{44} = 0.215$) and a high degree of oxidation ($O/C = 1.07$; Fig. 4m), all of which highly resemble those of LV-OOA (Fig. 4o). However, the mass spectra at large $m/z$'s indicated distinct chemical differences between BBOA-3 and LV-OOA (Fig. 4m' and 4o'), as there appeared to be a higher abundance of high molecular weight species in BBOA-3. In addition, the temporal variation patterns of BBOA-3 and LV-OOA were dramatically different ($r^2 = 0.07$) and BBOA-3 closely correlated with CO ($r^2 = 0.86$; Fig. 4c and Table S2) whereas LV-OOA did not ($r^2 = 0.008$). As shown in Fig. 5, the polar plot of BBOA-3 showed a high concentration band from SW at a wind speed of 5 – 15 m s$^{-1}$, which overlaps with the hot spot shown in the BBOA-1 polar plot (Fig. 5a). These results suggest that BBOA-3 was likely formed both through rapid processing near the wildfire source and during transport to MBO.

Another important characteristic of BBOA-3 is that it appeared to be composed of some very low-volatility compounds. As shown in Fig. 5g, ~ 60% of its mass remained in the aerosol phase at a temperature of 200 °C. This observation is consistent with previous studies which have observed the presence of low-volatility and extremely low volatility BBOA materials in aged wildfire plumes (Lee et al., 2016; Paciga et al., 2016) and in SOA produced from major organic gases from BB (e.g., phenols) (Yu et al., 2016). It is important to note that the highly oxidized BBOA-3 on average accounted for 31% of the total OA mass during this study, which implies that a significant fraction of the highly aged BBOA may appear indistinguishable from OOA from other sources due to mass spectral similarities (e.g., low $f_{60}$ and high $f_{44}$) and hence would lead to an underestimation of the influence of BB emissions on a regional scale.

BL-OOA and LV-OOA accounted for the remaining 32% of total OA mass during this study. These two OOAs were not associated with BB, as indicated by low $f_{60}$ (Fig. 4n and 4o) and a lack of correlation with BB tracers (Table S2). BL-OOA was relatively oxidized ($O/C = 0.69$; Fig. 4n) and appeared significantly less volatile than nitrate but more volatile than sulfate (Fig. 5g). BL-OOA showed a distinct diurnal cycle highly resembling that of water vapor (Fig. 5i), which is a tracer for BL upslope flow during the daytime at MBO (Weiss-Penzias et al., 2006). Photochemical production of OA in the early afternoon may also contribute to the daytime increase of BL-OOA. Furthermore, the time series of BL-OOA correlated with $CH_3SO_2^+$ (Fig. 4d and Table S2), a signature ion for methanesulfonic acid (MSA) (Ge et al., 2012b). MSA is typically associated with marine sources but has been found to have terrestrial sources as well (Ge et al., 2012b; Young et al., 2016). All these results suggest the influence of BL dynamics on BL-OOA. In comparison, the LV-OOA was highly oxidized ($O/C = 1.09$) with a pronounced $CO_2^+$ peak in the spectrum (Fig. 4o). In addition, Fig. 5g indicates that LV-OOA shared a similar volatility profile as sulfate, showing no sign of evaporation until the TD temperature reached nearly 130°C, consistent with LV-OOA previously determined in other ambient studies (Huffman et al., 2009; Paciga et al., 2016). The diurnal pattern of LV-OOA appeared to be rather flat (Fig. 4j) and its polar plot had the most dispersed feature among all factors (Fig. 5e). All these observations suggest that this factor is representative of free tropospheric aerosol.

3.4 A case study of the aging of BBOA in wildfire plumes
Based on MODIS fire hotspot information, the Salmon River Complex fire (SRCF) was continuously burning from August 13 to August 17 (Fig. 6a). Three-day HYSPLIT back trajectories suggest that air masses arriving at MBO from August 14 22:00 to August 16 09:00 passed over the SRCF (Fig. 6a), consistent with the observations of persistent SW wind at MBO during this time period (Fig. 6c). MODIS also detected a few hotspots from the Whiskey Complex Fire (~ 43°N, 122.8°W) intermittently on August 15 but the fire was much weaker compared to SRCF as indicated by the lower fire radiative power (FRP, Fig. 6a). We therefore assume that the emissions arriving at MBO during this time period were from a single source and therefore consistent in transport distance and fuel type. Combining MODIS fire hotspots and back-trajectories, we estimated that the transport time of SRCF plumes ranged from 8 to 11 hours before being sampled at MBO.

In order to examine how atmospheric aging affects BBOA chemistry, we calculated cumulative solar radiation ($\Sigma SR$) and average RH over the total transport time (from source to MBO) for each trajectory and plotted them versus air mass arrival time in Fig. 6b. $\Sigma SR$ denotes the total amount of solar radiation that the smoke plumes were exposed to during transport and can be used as an indicator for the extent of photochemical aging assuming the plumes were optically thin. RH in the air mass history was relatively stable, however $\Sigma SR$ clearly varied throughout the measurement period such that some BB plumes experienced more solar radiation than others and some were transported exclusively at night. Furthermore, the burn conditions were modestly constant during this period with an average modified combustion efficiency (MCE) value of 0.88 (± 0.03) for the BB plumes that met the criteria for MCE calculation (Collier et al., 2016). Furthermore, the MCE values showed no differences between nighttime and daytime plumes and didn’t correlate with $\Sigma SR$ (Fig. S11). These conditions, together with the high emissions concentrations for both gas and particle phase components (Fig. 6d-f), provide a near ideal case study where atmospheric aging is likely the largest factor affecting the chemical evolution of BBOA.

During this SRCF case study period, CO, NOy, and PAN mixing ratios observed at MBO exhibited similar trends that varied dynamically and correlated well with the fresh BBOA-1 factor (Fig. 6d - f). In addition, OA was overwhelming dominated by BBOAs, which summed to contribute 80% - 99% of total OA mass (Fig. 6g). The chemical parameters of OA and the fractional contributions of each BBOA factor appear to be related to $\Sigma SR$ (Figs. 6g and 6h). In order to investigate the chemical evolution of BBOA, we reconstructed the time series and the chemistry parameters of total BBOA (= BBOA-1 + BBOA-2 + BBOA-3) from the residual matrix of organic aerosol after subtracting the contributions from BL-OOA and LV-OOA. The carbon oxidation state ($OS_c = 2 \times O/C - H/C$; Kroll et al., 2011) of total BBOA showed a clear increasing trend with respect to $\Sigma SR$, consistent with the trends of O/C and $f_{44}$, while H/C, $f_{60}$, and $f_{m/z>100}$ of total BBOA showed decreasing trends with $\Sigma SR$ (Fig. 7). These results suggest oxidation of anhydrous sugar and other BBOA components due to photochemical aging, consistent with previous observations in the laboratory (Grieshop et al., 2009; Hennigan et al., 2011; Ortega et al., 2013) and field (Cubison et al., 2011; May et al., 2015). In addition, the negative correlation between BBOA-1 and $\Sigma SR$ and the positive correlations of BBOA-2 and BBOA-3 with $\Sigma SR$ (Fig. 7) corroborated our earlier assumption that BBOA-2 and BBOA-3 represented more aged, secondary BBOA whereas BBOA-1 represented primary BBOA.

We classify the plumes according to $\Sigma SR$ and designate those as night-time transported if $\Sigma SR$ was below 500 W m$^{-2}$, and the rest as day-time transported. OA concentration and CO mixing ratio were tightly correlated, with $r^2 =$
0.88 and 0.94 for night- and day-time transported plumes, respectively (Fig. 8a). CO has been commonly used as a stable plume tracer to account for dilution and the slope obtained from orthogonal fitting between OA and CO is defined as the enhancement ratio (i.e., ΔOA/ΔCO). Change of ΔOA/ΔCO during plume transport indicates the influence of factors other than dilution, e.g., SOA formation or OA evaporation. For the SRCF case study, ΔOA/ΔCO was very similar for the day-plumes and the night-plumes: 0.28 ± 0.014 vs. 0.27 ± 0.005 µg m⁻³ ppbv⁻¹ respectively (Fig. 8a), suggesting no net OA mass enhancement due to photochemical aging. This is consistent with the findings of Collier et al. (2016), which compared selected BB events from this dataset measured at MBO to those aboard a research aircraft sampling fresher plume emissions and found very similar OA enhancements between the fresher and more aged emissions. However, compared to daytime-plumes, OA for plumes transported during night time was less oxidized (Fig. 8c and 8d) and was dominated by the fresh BBOA-1 (53%), followed by the most oxidized BBOA-3 (24%), and intermediate oxidized BBOA-2 (15%; Fig. 8b). By contrast, daytime plumes were characterized by a significant decrease in the mass fraction of BBOA-1 (37%) coupled with increases in the BBOA-2 (20%) and BBOA-3 (37%). This is corroborated by the significant differences in chemical composition for the two types of plumes, where the average HRMS (Fig. 8c and 8d) indicated that the BBOA in day-time plumes had a higher degree of oxidation (average O/C = 0.66) compared to the night plumes (O/C = 0.55). These observations together suggest that although net OA production was conserved with higher photochemical aging, BBOA was chemically transformed, likely due to oxidative processing in both gas and particles phases followed by fragmentation and volatilization.

4 Summary and conclusions

We have characterized the chemical composition and properties of aerosols at a high elevation site that was heavily impacted by wildfire smoke plumes in the western US during the BBOP campaign in summer 2013. The sampling site was located on the summit of Mt. Bachelor, an isolated volcanic peak, in central Oregon. It was impacted by regional wildfire emission during a majority of the campaign and saw intense BB plumes with elevated air pollutants (up to 700 ppbv of CO and ~ 210 µg m⁻³ of NR-PM₁). The average (± 1σ) NR-PM₁ mass concentration was 22.4 (± 17.7) µg m⁻³ during fire-impacted periods, mostly due to OA that dominated the NR-PM₁ composition. In contrast, the average NR-PM₁ concentration was only 3.7 µg m⁻³ over periods free of BB influence and the aerosols contained a high mass fraction of ammonium sulfate (up to ~ 90%). In addition to increasing regional aerosol concentrations, wildfires in the Pacific Northwest region also significantly increased the mixing ratios of CO, NOₓ, and PAN, although NOₓ and O₃ displayed more complex behavior.

PMF analysis identified three types of BBOA that together accounted for 68% of the OA mass during this study, in addition to two types of OOA representing regional air conditions. The time series of all BBOA factors displayed dynamic variations that tightly correlated with those of CO and aerosol light scattering. Yet the three BBOAs were significantly different both chemically and physically and appeared to have been subjected to different degrees of atmospheric processing. BBOA-1 appeared to represent fresh wildfire emissions and featured semivolatile behavior, low O/C, a larger fraction of anhydrous sugar (f₆₀ = 2.2%), and a strong association with active wildfire sources. On the other hand, BBOA-2 and BBOA-3 represented more aged BB emissions and showed higher oxidation degree,
lower f_{60}, significantly lower volatilities, and more dispersed source regions. BBOA-3, in particular, had an O/C of 1.06, very low volatility, and almost no contribution from f_{60}, and thus appeared to be chemically similar to highly oxidized SOA observed in the atmosphere. Nevertheless, BBOA-3 is substantially different than the LV-OOA factor identified in this study; in addition to dramatically different temporal variation patterns, BBOA-3 also seemed to be composed of a higher fraction of high molecular weight species as well as compounds of extremely low volatilities.

A case study using consecutive BB plumes transported from the same fire source was performed to examine in detail the environmental factors leading to BBOA evolution. The BB plumes were associated with fires of similar modified combustion efficiencies but were exposed to a wide range of photochemical aging, as indicated by the cumulative solar radiation along the trajectory history from fire source to the sampling site. The results showed that photochemical aging led to more oxidized OA with higher mass fractions of aged BBOA (i.e., BBOA-2 and BBOA-3) and a lower fraction of fresh BBOA-1. Although BBOA in daytime plumes were chemically more processed than nighttime plumes, the enhancement ratios of OA relative to CO were very similar under the night-time and day-time conditions (ΔOA/ΔCO = 0.28 ± 0.014 and 0.27 ± 0.005 μg m⁻³ ppbv⁻¹, respectively). One explanation for this apparent lack of net SOA production in transported BB plumes is that SOA formation in BB emissions was balanced by POA loss, likely due to oxidation followed by fragmentation and volatilization.

Over the entire period of this study, the aged BBOA-2 and BBOA-3, most of which were likely secondary, on average made up ~ 50% of the OA mass observed at MBO. Aged BBOAs were present at significant concentrations even in relatively fresh plumes (~ 6-12 hr of atmospheric aging). These results suggest that BB emissions undergo substantial chemical processing which commences directly after emission and continues during atmospheric transport, forming and transforming aerosols that can significantly influence air quality and atmospheric chemical composition at downwind sites with important implications for health and climate.

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Fig. 1.  a) Map with MBO (black solid triangle) and wildfires detected by MODIS (red open diamonds) in the Northwest Pacific US from July 25 to August 25, 2013. Three fire complexes, Whiskey Complex Fire (WCF), Douglas Complex Fire (DCF), and Salmon River Complex Fire (SRCF) are highlighted with black circles. Bivariate polar plots of (b) NR-PM$_1$ concentrations (in $\mu$g m$^{-3}$), (d) submicrometer aerosol light scattering at 550 nm ($\sigma_{550nm}$ in Mm$^{-1}$) and (e) CO mixing ratio (in ppbv) during the sampling period. c) Average NR-PM$_1$ composition for the sampling period.
Fig. 2. Time series of (a) temperature (T) and relative humidity (RH), (b) wind direction (WD) colored by wind speed (WS), (c) mixing ratios of O₃ and NOₓ, (d) mixing ratios of CO, NOₓ and PAN, (e and f) mass concentrations of NR-PM₁ species and σ₅₅₀nm in STP (T = 273 K, P = 1013.25 hPa), (g) NR-PM₁ composition, and (h) f₆₀ ( = C₂H₄O₂⁺ / OA). The solid and broken lines in (h) indicate f₆₀ = 0.3% and f₆₀ = 0.5%, respectively.
Fig. 3. Box plots that compare f_{60} values, CO mixing ratios, NR-PM1 species concentrations, OA elemental ratios, carbon oxidation states (OSc), σ_{550nm}, and mixing ratios of trace gases among three aerosol regimes (“No BB”, “BB Infl”, and “BB Plm”). The whisks indicate the 90th and 10th percentiles, the upper and lower boundaries indicate the 75th and 25th percentiles, and the lines in the boxes indicate the median values and the markers indicate the mean values.
Fig. 4. (a-e) Time series of OA factors and corresponding tracer compounds. Organic ions are in organic equivalent mass; (f-g) Diurnal variations of OA factors (the whiskers above and below the boxes indicate the 90th and 10th percentiles, the upper and lower boundaries indicate the 75th and 25th percentiles, and the lines in the boxes indicate the median values and the cross symbols indicate the mean values) with the diurnal cycle of mean water vapor in (i); (k-o) HRMS of OA factors colored by eight ion families at m/z < 180 and (k'-o') UMR MS at m/z > 180 for each OA factor. The elemental ratios of each OA factor are shown in the legends of (k-o) with those obtained using the AA method in parenthesis.
Fig. 5. (a-e) Bivariate polar plots that illustrate the variations of the concentrations of each OA factor as a function of wind speed (m s$^{-1}$) and wind direction; (f) Average OA composition during the sampling period; (g) Volatility profiles of OA factors, sulfate, and nitrate.
Fig. 6. (a) Map of the Pacific Northwest with the location of MBO marked by black triangle. Open diamonds represent MODIS satellite fire dots detected during August 13 – 17, 2013, and are sized by fire radiative power (FRP). Twelve-hour HYSPLIT back trajectories of air masses arriving at MBO from August 14 20:00 to August 16 09:00 are colored by time of arrival at MBO. Markers indicate 1-hour interval; (b) Cumulative solar radiation ($\sum$SR) and average RH for each trajectory; (c) Wind direction (WD) colored by wind speed (WS) measured at MBO; Mixing ratios of (d) CO, NOx, (e) nitrate, PAN, and NOy; (f) Five OA factors; (g) OA composition; (h) Average carbon oxidation states and $f_{60}$ of OA during the Salmon River Complex Fire (SRCF) case study period.
Fig. 7. Aerosol chemistry parameters of total BBOA as a function of cumulative solar radiation for the Salmon River Complex Fire case study. The Pearson's correlation coefficients (r) are reported.
Fig. 8. (a) OA vs. CO during August 14 20:00 to August 16 09:00 with night-time transported plumes illustrated as black circles and day-time transported plumes as red crosses. The orthogonal distance regression (ODR) results for the two plume types are shown with the 1-σ uncertainties reported for the fit slopes (s) and intercepts (i); (b) A comparison of the average concentrations of 5 OA factors (stacked) between the night-time and day-time transported plumes. The average mass fractions of the BBOAs to total OA mass in each plume type are reported; (c) Average HRMS of total BBOA for the night-time transported plumes; (d) Average HRMS of total BBOA for the day-time transported plumes and (e) Difference BBOA HRMS between day and night plumes. The elemental ratios of BBOA calculated with the IA method are shown in the legends of (c) and (d) with those obtained using the AA method in parenthesis.