



Particulate Matter, Ozone, and Nitrogen Species in Aged Wildfire Plumes Observed at the Mount Bachelor Observatory

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ABSTRACT

During the summer of 2012 and 2013, we measured carbon monoxide (CO), carbon dioxide (CO₂), ozone (O₃), nitrogen oxides (NO_x), reactive nitrogen (NO_y), peroxyacetyl nitrate (PAN), aerosol scattering (σ_{sp}) and absorption, elemental and organic carbon (EC and OC), and aerosol chemistry at the Mount Bachelor Observatory (2.8 km above sea level, Oregon, US). Here we analyze 23 of the individual plumes from regional wildfires to better understand production and loss of aerosols and gaseous species. We also developed a new method to calculate enhancement ratios and Modified Combustion Efficiency (MCE), which takes into account possible changes in background concentrations during transport. We compared this new method to existing methods for calculating enhancement ratios. The MCE values ranged from 0.79–0.98, $\Delta O_3/\Delta CO$ ranged from 0.01–0.07 ppbv ppbv⁻¹, $\Delta \sigma_{sp}/\Delta CO$ ranged from 0.23–1.32 Mm⁻¹ (at STP) ppbv⁻¹, $\Delta NO_y/\Delta CO$ ranged from 2.89–12.82 pptv ppbv⁻¹, and $\Delta PAN/\Delta CO$ ranged from 1.46–6.25 pptv ppbv⁻¹. A comparison of three different methods to calculate enhancement ratios (ER) showed that the methods generally resulted in similar $\Delta \sigma_{sp}/\Delta CO$, $\Delta NO_y/\Delta CO$, and $\Delta PAN/\Delta CO$; however, there was a significant bias between the methods when calculating $\Delta O_3/\Delta CO$ due to the small absolute enhancement of O₃ in the plumes. The $\Delta O_3/\Delta CO$ ERs calculated using two common methods were biased low (~20–30%) when compared to the new proposed method. Two pieces of evidence suggest moderate secondary particulate formation in many of the plumes studied: 1) mean observed $\Delta OC/\Delta CO_2$ was 0.028 g particulate-C gC⁻¹ (as CO₂)—27% higher than the midpoint of the biomass burning emission ratio range reported by a recent review—and 2) single scattering albedo (ω) was relatively constant at all MCE values, in contrast with results for fresh plumes. The observed NO_x, PAN, and aerosol nitrate represented 6–48%, 25–57%, and 20–69% of the observed NO_y in the aged plumes, respectively, and other species represented on average 11% of the observed NO_y.

Keywords: Particulate matter; Ozone; NO_y; Enhancement ratio; Modified Combustion Efficiency.

INTRODUCTION

Wildland fires significantly contribute to global air pollution through primary emissions and production of secondary pollutants (Akagi *et al.*, 2011; Urbanski *et al.*, 2011; Jaffe and Wigder, 2012; IPCC, 2013). Many factors impact primary emissions, including fire size, combustion efficiency, and the fuel type (Akagi *et al.*, 2011). The production of secondary pollutants is impacted by these

same factors, as well as influences such as exposure to sunlight during plume transport and mixing of the plume with other pollution sources (e.g., urban emissions) (Akagi *et al.*, 2011; Jaffe and Wigder, 2012). Global inventories indicate that biomass burning emits an average of 49.1 Tg yr⁻¹ of primary organic aerosol (POA) and black carbon (BC), as compared to an average of 15.3 Tg yr⁻¹ of anthropogenic POA and BC (IPCC, 2013). Emissions from wildland fires are also estimated to result in at least 174 Tg yr⁻¹ of net ozone (O₃) production (Jaffe and Wigder, 2012).

In the western United States (US), wildland fires can greatly impact atmospheric pollutant concentrations. On average during 2000–2004, wildland fires contributed 22% of the total carbonaceous aerosol concentrations in the western

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US (Park *et al.*, 2007). Urbanski *et al.* (2011) estimated that during 2003–2008, western US wildland fires contributed 8–39% of the annual PM_{2.5} (particulate matter < 2.5 microns in diameter) emissions and 3–20% of the annual carbon monoxide (CO) emissions. Jaffe *et al.* (2008a, b) showed that wildland fire O₃ and PM_{2.5} enhancements vary from year to year based on the number and size of fires.

Models have been used to understand the air quality impacts of wildland fires in the western US. For example, Strand *et al.* (2012) found that the BlueSky system predicted PM_{2.5} concentrations well for some of the 2007–2008 Californian fires the authors analyzed, but was biased low for others. Herron-Thorpe *et al.* (2014) found that the Air Information Report for Public Access and Community Tracking (AIRPACT) version-3 framework captured the location and transport direction of fire plumes from western US wildfires occurring during 2007–2008, but generally underestimated PM_{2.5} concentrations. Pfister *et al.* (2008) found that the global Model for Ozone and Related Chemical Tracers (MOZART) version-4 accurately identified areas with high O₃ concentrations due to 2007 Californian wildland fires. Jaffe *et al.* (2013) found that a statistical model of O₃ production from 2008 Californian fires showed significant differences in wildland fire O₃ production compared to the Weather and Research Forecasting Model with Chemistry (WRF-Chem).

One factor impacting accurate modeling of wildland fire plumes is uncertainty about aging of particulate and gaseous species within the plumes. In general as fire plumes age, there is a decrease in the concentrations of ammonia (NH₃) and nitrogen oxides (NO_x = NO + NO₂), and an increase in peroxyacetyl nitrate (PAN), nitrate (NO₃⁻), PM_{2.5}, acetic and formic acid, ammonium, sulfate, formaldehyde, acetone, methanol, and usually O₃ (Singh *et al.*, 2000; Hobbs, 2003; Jost *et al.*, 2003; Val Martín *et al.*, 2006; Yokelson *et al.*, 2009; Alvarado *et al.*, 2010; Akagi *et al.*, 2012; Jaffe and Wigder, 2012; Akagi *et al.*, 2013; Wigder *et al.*, 2013). Some studies have observed individual plumes for 45 minutes to 4.5 hours after emission (e.g., Hobbs, 2003; Jost *et al.*, 2003; Yokelson *et al.*, 2009; Akagi *et al.*, 2012, 2013), allowing the authors to quantify changes in species' mixing ratios as a function of time, fuel type, and fire location over these short time periods. Other studies have focused on longer-term production and loss of pollutants in fire plumes by comparing observed concentrations of gases and aerosols in aged fire plumes (i.e., plumes that are hours to weeks downwind of the fire source) with fire emissions. Often, enhancement ratios (ER) of species in wildland fire plumes are calculated and compared with emission factors to understand production and loss of these species in the plumes. However, Yokelson *et al.* (2013a) showed that typical methods for calculating ERs can be inaccurate due to changes in background air masses during plume transport.

Much of the research on aging wildland fire plumes has focused on secondary organic aerosol (SOA) because this topic is poorly understood (Akagi *et al.*, 2011). Yokelson *et al.* (2013b) found that 35–64% of the gas-phase non-methane organic carbon (NMOC) in laboratory and prescribed fire plumes were semivolatile or of intermediate

volatility, suggesting that there is a large quantity of SOA precursors in fire plumes, and Yokelson *et al.* (2009) showed that there can be rapid SOA production in the first few hours of wildland fire plume transport. However, other recent studies have not observed SOA production in wildland fire plumes. May *et al.* (2015) found that evaporation due to dilution can dominate when compared to chemical production of SOA in plumes aged less than five hours, and Jolleys *et al.* (2012) found little SOA production in aged biomass burning plumes. Detailed analyses have been conducted on one prescribed fire, the Williams fire in San Luis Obispo, US. Akagi *et al.* (2012) found that organic aerosol (OA) in that fire plume initially decreased due to evaporation, and eventually increased as condensation began to dominate. Alvarado *et al.* (2015) modeled the Williams fire, and found that inclusion of a parameterization for unknown semi-volatile organic compounds (SVOCs) allowed for more accurate estimation of both OA and O₃ in the plume. This is consistent with other studies that have determined that there are many unknown compounds in wildland fire plumes. For example, Simpson *et al.* (2011) identified 45 previously unknown non-methane volatile organic compounds (VOCs) in boreal fire plumes, Akagi *et al.* (2011) estimated that half of the mass of gas phase NMOC is from unidentified compounds, and Yokelson *et al.* (2013b) measured over 150 unidentified gas species in fire emissions, many of which were likely NMOC. Results from the Fire Lab in Missoula Experiment (FLAME-4) studies have provided further data on the types and quantities of species in fire plumes (e.g., Gilman *et al.*, 2015; Hatch *et al.*, 2015; Stockwell *et al.*, 2015).

Some studies have focused on single scattering albedo (ω), the ratio of aerosol scattering to total extinction (scattering + absorption), to better understand the radiative forcing from fresh and aged PM in wildland fire plumes. In a study of fresh biomass burning emissions, Liu *et al.* (2014) found that there was a strong dependence of aerosol ω on Modified Combustion Efficiency (MCE = $\Delta\text{CO}_2/[\Delta\text{CO} + \Delta\text{CO}_2]$). MCE is an indicator of combustion efficiency, and in wildland fires, MCE generally ranges from 0.80–1.00 (Akagi *et al.*, 2011), with higher MCEs indicating higher proportions of flaming combustion and lower MCEs indicating higher proportions of smoldering combustion. Liu *et al.* (2014) found that MCE explains 60% of the variability in ω , suggesting that MCE could be used to improve parameterization of radiative impacts from fires in models. Vakkari *et al.* (2014) found that ω can increase as wildland fire plumes age, although this increase was more likely to occur in plumes transported during daylight hours. This suggests that the relationship between ω and MCE may not be the same in aged plumes as it is for fresh emissions.

There is also much uncertainty about O₃ production in aging wildland fire plumes. One influence on O₃ production and loss is the amount and proportions of nitrogen species in the plumes. In the immediate vicinity of a wildland fire, O₃ is often titrated due to reaction with nitric oxide (NO). However, the speciation of reactive nitrogen (NO_y) rapidly and continuously changes in fire plumes. For example, Akagi *et al.* (2012) found that NO_x in the Williams fire plume decreased by 76% over four hours due to formation of PAN

and reaction of NO_x with the hydroxyl radical (OH), and Baylon *et al.* (2015) linked O₃ production to the degree of NO_x oxidation in plumes. Some studies have also reported rapid O₃ production in fire plumes (e.g., Hobbs *et al.*, 2003; Jaffe and Wigder, 2012; Baylon *et al.*, 2015). Conversely, rapid conversion of NO_x to PAN can account for a lack of O₃ production in some wildland fire plumes, although eventual decomposition of PAN in warmer temperatures can cause a downwind increase in NO_x leading to O₃ production (Mauzerall *et al.*, 1998; Alvarado *et al.*, 2010; Akagi *et al.*, 2012; Jaffe and Wigder, 2012; Busilacchio *et al.*, 2016).

The Mt. Bachelor Observatory (MBO) is located on a mountain top in central Oregon at 2.76 km above sea level. The observatory has been in operation for the last decade and has been previously used to study long-range transport and wildfire plumes (e.g., Jaffe *et al.*, 2005; Fischer *et al.*, 2011; Wigder *et al.*, 2013; Baylon *et al.*, 2015; McClure *et al.*, 2016). In this study, we analyze wildfire plumes aged 1–2 days that were observed at MBO in 2012 and 2013. We focus on five scientific questions that provide further information on the aging of PM and gaseous species in wildland fire plumes. These questions are:

1. How do different methods for computing ERs in wildland fires compare?
2. What is the variation in observed organic carbon/carbon dioxide ERs ($\Delta\text{OC}/\Delta\text{CO}_2$) in the aged plumes, and how do these ratios compare with wildland fire emission factors?
3. What is the relationship between single scattering albedo and MCE in aged plumes?
4. What do the observed $\Delta\text{OC}/\Delta\text{CO}_2$ and ω suggest about secondary PM production in these aged fire plumes?
5. What is the NO_y speciation in the aged plumes?

METHODS

Data Collected at the Mount Bachelor Observatory

We analyzed data from intensive field campaigns carried out during the summers of 2012 and 2013 at MBO, a mountaintop site located in central Oregon, US (43.98°N, 121.69°W, 2.76 km a.s.l.). Previous studies have shown that MBO regularly observes episodic events, including stratospheric intrusions and long-range transport of Asian pollution in spring, and biomass burning plumes from local and distant fires in spring, summer, and autumn (Jaffe *et al.*, 2005; Weiss-Penzias *et al.*, 2006; Finley *et al.*, 2009; Fischer *et al.*, 2010a, b; Reidmiller *et al.*, 2010; Ambrose *et al.*, 2011; Timonen *et al.*, 2013; Wigder *et al.*, 2013; Baylon *et al.*, 2015).

During July–September 2012, continuous observations at MBO included: aerosol scattering (σ_{sp} ; TSI nephelometer; 450, 550, and 700 nm; 1 μm size cut); aerosol absorption (Radiance Research PSAP; 467, 530, and 660 nm; 1 μm size cut); elemental carbon (EC) and OC (Sunset Lab); CO and CO₂ (Picarro Cavity Ring-Down Spectroscopy G2302); O₃ (Dasibi); NO_x (Air Quality Design 2-channel chemiluminescence); NO_y (custom chemiluminescence); and meteorological parameters. The same instruments were used for a second intensive campaign during June–September

2013, along with continuous observations of PAN (custom gas chromatograph). All of the instruments were regularly calibrated and maintained during the campaigns, as described previously (Weiss-Penzias *et al.*, 2006; Fischer *et al.*, 2010a, b; Ambrose *et al.*, 2011; Baylon *et al.*, 2015). All data were collected as 5-minute averages, and concentrations below the Method Detection Limit (MDL) were set to one-half of the MDL. Multi-point calibrations on the Picarro instrument were performed every eight hours throughout the campaigns. The 1-sigma precision of 5-minute averages was approximately 1.0 ppbv for CO and 0.1 ppmv for CO₂, indicating that even small enhancements of the species could be measured.

NO_x and NO_y were measured as NO using chemiluminescence detectors based on the reaction of NO with O₃. In the NO_x instrument, NO₂ is converted to NO by a Blue Light Converter ($\lambda = 385\text{--}405$ nm) (Baylon *et al.*, 2015). In the NO_y instrument, NO_y species are converted to NO by a molybdenum converter heated to 350°C. The conversion efficiency was evaluated using a nitric acid source, similar to that described by Nunnermacker *et al.* (1989). During the field campaigns, the conversion efficiency was tested onsite every 3–4 weeks and was always >95%.

Studies have shown that the converters used in chemiluminescence NO_y instruments can convert other nitrogen species—such as NH₃—to NO, indicating that these species could be incorrectly included in the total NO_y measurement (e.g., Fahey *et al.*, 1985; Kliner *et al.*, 1997). To evaluate any possible influence from NH₃ on our NO_y measurements, we conducted laboratory tests of the NO_y instrument. These tests showed that the NH₃ conversion efficiency in the molybdenum converter depended on the relative humidity (RH) of the sample, with about 43% conversion in very dry air and less than 1% conversion at 14% RH. The average RH of the fire plumes analyzed in this study was $37 \pm 15\%$. Our laboratory measurement of NH₃ conversion at similar RH (45%) showed that only 0.4% of NH₃ was converted to NO. Given these results, we can assume that NH₃ conversion to NO in the NO_y converter is unimportant at ambient humidity.

Aerosol absorption was measured using a 3 λ Particle Soot Absorption Photometer (PSAP) from Radiance Research. This instrument is filter-based, and the noise increases substantially at filter transmissions below 30% (Snyder and Schauer, 2007). We found that during most of the observed fire events, filter transmission usually went below 30% at some point, due to high concentrations of absorbing aerosols in the plumes.

Because PSAP data were unavailable during most fire periods (due to low filter transmittance or instrument malfunction), we substituted data from the EC analyzer. Snyder and Schauer (2007) performed a comparison of the Sunset Lab organic carbon/elemental carbon (OCEC) and PSAP instruments and found that the correlation between EC and aerosol absorption was good when PSAP transmission was greater than 30% ($R^2 = 0.83$). Using MBO data, we compared the EC and aerosol absorption from summer 2012 and found a strong correlation ($R^2 = 0.94$) when transmission was greater than 30%. Therefore, using the slope of the

Reduced Major Axis (RMA) regression of the Sunset Lab EC and PSAP aerosol absorption observations at 530 nm during non-fire periods, we estimated the aerosol absorption during fire periods. We quantified single scattering albedo (ω) using these estimated absorption data and the aerosol scattering (σ_{sp}) measurements at 550 nm. Note that for this study, the aerosol scattering and absorption observations were first adjusted to 532 nm using a power law relationship and the calculated Angstrom Exponent (Virkkula *et al.*, 2005; Fischer *et al.*, 2010), and then these adjusted observations were used to calculate ω at 532 nm.

Aerosol chemical composition was also measured at MBO for four weeks in 2013 using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) (DeCarlo *et al.*, 2006). The AMS measured size-resolved non-refractory submicron particulate matter (NR-PM₁). Details of design and operation of the AMS instrument are described elsewhere (DeCarlo *et al.*, 2006). In brief, particles are sampled into a high vacuum system ($\sim 10^{-5}$ Pa) through a critical orifice and an aerodynamic lens. The narrow beam of particles is transmitted into the detection chamber, where the non-refractory fraction of the aerosol is flash-vaporized upon impaction on a heated surface (600°C) and ionized by high energy electrons (70 eV). The resulting ions are extracted into the detector region and are analyzed by a time-of-flight mass spectrometer.

During summer 2013, the AMS measured NR-PM₁ with an averaging time of 2.5 minutes. Ambient air was drawn through the inlet where it was treated with a high volume Nafion dryer (PD-200T, Perma Pure LLC) and subsequently sampled by the AMS and a parallel CO₂ gas-phase monitor (Li-COR 840A CO₂/H₂O gas-phase analyzer). Three ammonium nitrate mass calibrations and two particle size calibrations using polystyrene latex spheres were performed onsite according to standard AMS procedures (Jimenez *et al.*, 2003) and various filtered air samples were collected in order to adjust the fragmentation table (Allan *et al.*, 2004). The data were converted to standard temperature and pressure (STP; T = 273 K, P = 1013.25 mb). In this study, we report only limited data from the AMS. More detailed information on the AMS deployment and further data analysis is given in Collier *et al.* (2016) and Zhou *et al.* (in preparation).

Data used in this analysis are permanently archived at the University of Washington's ResearchWorks website (<https://digital.lib.washington.edu/researchworks/>). The data can be easily found by searching the archive using the term "Mt. Bachelor."

Fire Plume Identification

Fire plumes were identified using four criteria: 1) CO and aerosol scattering (σ_{sp}) were elevated above background concentrations, with CO ≥ 150 ppbv and σ_{sp} (at 550 nm) ≥ 20 Mm⁻¹ for at least one hour, 2) CO and σ_{sp} were strongly correlated ($R^2 \geq 0.95$), 3) CO and CO₂ were well correlated ($R^2 \geq 0.85$), and 4) Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) backward trajectories showed transport from a region with active fires. The requirement that CO and CO₂ be well correlated reflects our interest in the calculation of MCE. Notably, McClure

et al. (2016) used MBO data to show that CO and CO₂ are usually well correlated for large plumes and/or plumes transported in the free troposphere, whereas for boundary layer transport, CO₂ uptake often obscures this relationship. The sources of the fire plumes analyzed in this study were confirmed using the HYSPLIT trajectories, Navy Aerosol Analysis and Prediction System model, and Moderate Resolution Imaging Spectroradiometer fire hotspots and imagery (Wigder *et al.*, 2013).

Plume Enhancement ratios, Modified Combustion Efficiency, and Uncertainty

An enhancement ratio (ER) describes the relative enhancement of two species above background concentrations (e.g., $\Delta X/\Delta Y$; Δ is the enhancement over the background concentration), and is typically calculated using either CO or CO₂ in the denominator (Andreae and Merlet, 2001). ERs are often calculated using the absolute enhancement above the local background ($ER = [X_{plume} - X_{bkgnd}]/[Y_{plume} - Y_{bkgnd}]$) or using the slope of the linear correlation of the two species. Throughout this manuscript, we refer to these methods as "Local Background" and "Correlation." Yokelson *et al.* (2013a) argued that ERs calculated using the Local Background and Correlation methods may be inaccurate because changes in the background air mass concentrations can have significant influences on the calculated ERs.

We evaluated the use of the Local Background and Correlation methods and propose a third method, and a technique to evaluate uncertainty in this method's ER, that addresses the concerns raised by Yokelson *et al.* (2013a). The primary issue in calculating ERs is defining the background concentration of each species, since the plume has been transported some distance from the source and may have mixed to some degree with multiple background air masses. This issue is particularly acute when a plume that originated in the boundary layer is observed in the free troposphere (e.g., on a mountaintop or by aircraft). To address this issue, we used three methods to estimate the background concentrations of the species used to calculate the ER. We also quantified the uncertainty in the ER using a statistical analysis based on the uncertainty in the background concentrations. We first developed this method for calculating MCE in fire plumes, and the full set of calculations is described in the Supplement to this manuscript. The background concentrations we used for this method are: 1) the measured concentration of the species immediately before the plume (as is commonly used in the Local Background method), 2) the monthly median concentration of the species at 1600 local solar time (LST) (which is equivalent to 0:00 GMT), and 3) the measured concentration of the species at the 1600 LST that immediately precedes the time that the plume was observed. The third background concentration addresses the fact that fire plumes are sometimes observed during generally smoky periods, which may have relatively high background concentrations of some species. This method uses 1600 LST because this time reflects the boundary conditions at MBO.

We used this method to calculate MCE and all other ERs in this study, and throughout this manuscript we refer to

this method as “Multiple Backgrounds.” The uncertainty calculations used for all text, tables, and figures combine the Multiple Backgrounds method uncertainty (described in the Supplement) and the uncertainty in the measurements (accuracy and precision) using addition in quadrature. For example, the uncertainty in $\Delta X/\Delta Y$ was calculated by adding in quadrature the background uncertainty (calculated using the Multiple Backgrounds method), the uncertainty in the X measurement, and the uncertainty in the Y measurement.

RESULTS

Identified Wildfire Plumes

We identified 23 wildfire plumes observed at MBO in 2012 and 2013 that met the criteria listed in Section 2.2. All of the plumes originated from fires in northern California or southeastern and central Oregon (Fig. 1). Table 1 details the dates and times that the plumes were observed, the source fire locations, the estimated transport time from the source fire locations, the MCE, other ERs ($\Delta\text{PAN}/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$, $\Delta\sigma_{\text{sp}}(\text{at } 550 \text{ nm})/\Delta\text{CO}$, $\Delta\text{O}_3/\Delta\text{CO}$, $\Delta\text{OC}/\Delta\text{CO}_2$), and ω (at 532 nm) of each plume. We estimated transport time using HYSPLIT backward trajectories and HYSPLIT plume dispersion models, and Eta Data Assimilation System (EDAS) 40 km meteorological data. The LANDFIRE vegetation type for all 23 fires shows that the vegetation is dominated by evergreen forests (www.landfire.gov), but there are some regional variations. Collier *et al.* (2016) also analyzes AMS measurements from some of the 2013 plumes. While the reported MCEs of the plumes differ slightly from those reported in this manuscript due to differing calculation methods, all MCEs reported by Collier *et al.* (2016) are within the MCE uncertainty ranges reported here.

Comparison of Plume Enhancement Ratios

The $\Delta\sigma_{\text{sp}}/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$, $\Delta\text{PAN}/\Delta\text{CO}$, and $\Delta\text{O}_3/\Delta\text{CO}$ ERs were calculated using the Local Background, Correlation (Reduced Major Axis [RMA] regressions), and Multiple Backgrounds methods. A comparison of these methods can help identify potential biases between methods and whether the ERs reported in previous studies might be subject to the interferences described by Yokelson *et al.* (2013a).

There was little difference between the $\Delta\sigma_{\text{sp}}/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$, and $\Delta\text{PAN}/\Delta\text{CO}$ ERs calculated using the three methods, reflecting the large enhancement of each of these species in wildfire plumes relative to the background concentration. We plotted the ERs for each pair of methods for each pollutant (σ_{sp} , NO_y , and PAN), and quantified the slope for the RMA regression of the plotted points and the coefficient of determination (R^2) of the data. Fig. 2(a) shows an example of these plots for $\Delta\sigma_{\text{sp}}/\Delta\text{CO}$. When considering these three pollutants, we found that the regression slopes for each pair of methods were close to unity, and the R^2 ranged between 0.92 and 0.99. The degree of correlation for each pair of methods varied by pollutant, and no two methods consistently showed the strongest correlation across all pollutants considered. We conclude that for these 23 fires, all three methods resulted in similar ERs for $\Delta\sigma_{\text{sp}}/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$, and $\Delta\text{PAN}/\Delta\text{CO}$.

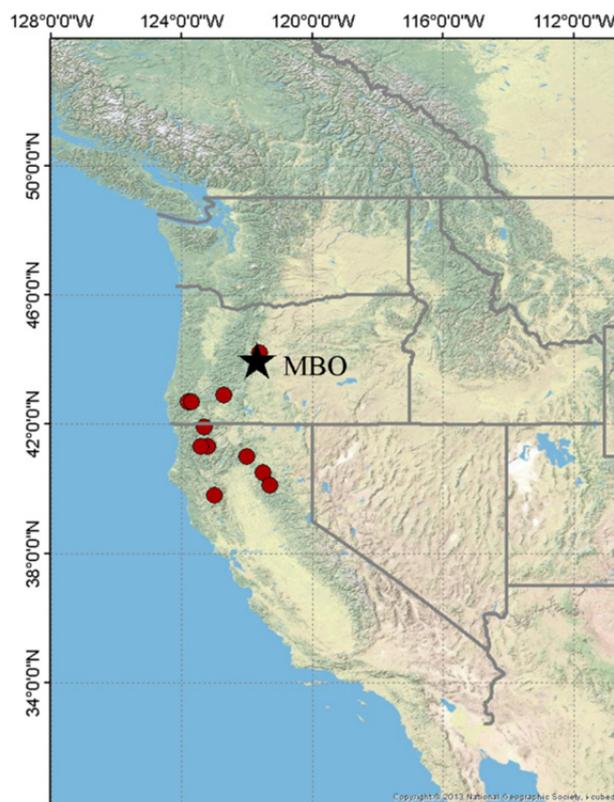


Fig. 1. Locations of the 23 wildfires observed at MBO during summer 2012 and 2013 used in this analysis. Note that some circles represent more than one fire.

However, a similar comparison of $\Delta\text{O}_3/\Delta\text{CO}$ ERs showed that there is not as strong of a correlation between the ERs calculated using the three methods (Fig. 2(b)). There was a strong agreement between the Local Background and Correlation methods ($R^2 = 0.90$), but a weaker relationship between the Multiple Backgrounds method and the other two methods ($R^2 = 0.66$ [with Correlation method] and $R^2 = 0.74$ [with Local Background method]). In addition, the slopes of the regression lines in Fig. 2(b) range between 0.66 and 0.89, indicating that there is a bias in the $\Delta\text{O}_3/\Delta\text{CO}$ calculated using different methods. For the fires included in this analysis, the Multiple Backgrounds method generally resulted in a higher $\Delta\text{O}_3/\Delta\text{CO}$ than the Correlation and Local Background methods, and the Local Background method generally resulted in a slightly higher $\Delta\text{O}_3/\Delta\text{CO}$ than the Correlation method. It is likely that the bias in ER calculation exists because the enhancement of O_3 in wildland fire plumes is generally very small, and therefore the method used for calculating the enhancements and background concentrations has a greater influence on the ER calculation. In summary, considering that wildland fire emissions are often emitted in the boundary layer where background O_3 mixing ratios are generally low, calculating the $\Delta\text{O}_3/\Delta\text{CO}$ ER using the Local Background or Correlation method results in a smaller ER than the Multiple Backgrounds method.

Particulate Matter in Aged Plumes

We measured σ_{sp} continuously during the 2012 and 2013

Table 1. Individual plume data. All ERs calculated using the Multiple Backgrounds method, and uncertainty is calculated by adding the background (equation S3 in the Supplement) and measurement uncertainty in quadrature. Blanks indicate no data.

| Plume number | Date and time (UTC) | Source fire location | Estimated transport time (hours) | MCE | Δ PAN/ Δ CO (pptv ppbv ⁻¹) | Δ NO _y / Δ CO (pptv ppbv ⁻¹) | Δ σ_{sp} (550 nm, at STP) / Δ CO (Mm ⁻¹ ppbv ⁻¹) | Δ O ₃ / Δ CO (ppbv ppbv ⁻¹) | Δ OC/ Δ CO ₂ (mgC gC ⁻¹) | ω (532 nm) |
|--------------|---------------------------------|----------------------|----------------------------------|-------------|--|---|--|--|---|-------------------|
| 1 | 6 Aug. 2012 19:00–22:30 | NW CA | 12–18 | 0.95 ± 0.07 | 6.04 ± 0.31 | 0.97 ± 0.06 | 0.040 ± 0.018 | 15.79 ± 0.49 | 0.95 ± 0.12 | |
| 2 | 7 Aug. 2012 5:15–8:00 | NW CA | 20–36 | 0.96 ± 0.07 | 8.60 ± 0.40 | 0.54 ± 0.05 | 0.051 ± 0.012 | 6.72 ± 0.51 | 0.91 ± 0.12 | |
| 3 | 25 Aug. 2012 14:00–20:20 | NW CA | 12–18 | 0.91 ± 0.08 | 7.46 ± 0.35 | 1.24 ± 0.08 | 0.034 ± 0.011 | 38.36 ± 0.85 | 0.96 ± 0.12 | |
| 4 | 26 Aug. 2012 6:10–11:15 | NW CA | 12–24 | 0.93 ± 0.16 | 10.24 ± 0.73 | 0.94 ± 0.22 | 0.052 ± 0.019 | 22.19 ± 1.48 | 0.96 ± 0.14 | |
| 5 | 27 Aug. 2012 3:30–6:05 | NW CA | 8–18 | 0.79 ± 0.44 | 11.61 ± 0.37 | 0.93 ± 0.08 | 0.060 ± 0.010 | 77.54 ± 2.68 | 0.94 ± 0.12 | |
| 6 | 27 Aug. 2012 6:50–13:20 | NW CA | 8–18 | 0.92 ± 0.08 | 12.82 ± 0.42 | 0.81 ± 0.06 | 0.017 ± 0.020 | 22.31 ± 0.94 | 0.90 ± 0.12 | |
| 7 | 31 Aug. 2012 9:15–12:10 | Northern CA | 12–30 | 0.93 ± 0.18 | 8.85 ± 1.05 | 1.32 ± 0.36 | 0.073 ± 0.038 | 29.01 ± 2.01 | | |
| 8 | 14 Sep. 2012 3:15–4:35 | Central OR | 2–5 | 0.87 ± 0.01 | 4.53 ± 0.14 | 0.63 ± 0.02 | 0.007 ± 0.001 | 30.08 ± 0.74 | | |
| 9 | 14 Sep. 2012 4:35–7:35 | Central OR | 2–5 | 0.90 ± 0.01 | 8.77 ± 0.28 | 0.64 ± 0.03 | 0.013 ± 0.003 | 22.32 ± 0.61 | | |
| 10 | 16 Sep. 2012 16:50–23:00 | Central OR | 2–5 | 0.86 ± 0.04 | 4.05 ± 0.12 | 1.20 ± 0.04 | 0.005 ± 0.001 | 61.58 ± 0.85 | | |
| 11 | 18 Sep. 2012 0:55–5:55 | Central OR | 2–5 | 0.88 ± 0.02 | 5.67 ± 0.15 | | 0.009 ± 0.002 | | 0.92 ± 0.11 | |
| 12 | 18 Sep. 2012 9:50–14:35 | Central OR | 2–5 | 0.90 ± 0.21 | 8.27 ± 0.64 | | 0.019 ± 0.025 | | 0.91 ± 0.12 | |
| 13 | 19 Sep. 2012 1:55–6:35 | Central OR | 2–5 | 0.86 ± 0.01 | 3.61 ± 0.07 | 0.49 ± 0.01 | 0.006 ± 0.0003 | 24.06 ± 0.23 | 0.94 ± 0.11 | |
| 14 | 19 Sep. 2012 23:50–20 Sep. 4:05 | Central OR | 2–5 | 0.85 ± 0.08 | 5.48 ± 0.10 | 0.23 ± 0.02 | 0.006 ± 0.001 | 12.42 ± 0.53 | | |
| 15 | 21 Sep. 2012 0:15–7:25 | Central OR | 2–5 | 0.90 ± 0.03 | 2.89 ± 0.12 | 0.59 ± 0.03 | 0.012 ± 0.003 | 21.69 ± 0.50 | | |
| 16 | 22 Sep. 2012 3:30–9:10 | Central OR | 2–5 | 0.96 ± 0.23 | 7.90 ± 1.91 | 1.12 ± 0.64 | 0.059 ± 0.047 | 15.96 ± 1.89 | | |
| 17 | 3 Oct. 2012 2:30–7:35 | Central OR | 2–5 | 0.87 ± 0.07 | 4.13 ± 0.15 | 0.46 ± 0.05 | 0.022 ± 0.025 | 22.00 ± 2.02 | | |
| 18 | 5 Aug. 2013 16:50–18:10 | SW OR | 14–34 | 0.89 ± 0.25 | 5.64 ± 0.36 | 1.19 ± 0.25 | 0.067 ± 0.027 | 43.02 ± 2.66 | 0.96 ± 0.12 | |
| 19 | 13 Aug. 2013 12:20–16:40 | NW CA | 24–30 | 0.94 ± 0.05 | 8.84 ± 0.31 | 1.29 ± 0.12 | 0.071 ± 0.027 | 24.52 ± 0.65 | 0.97 ± 0.12 | |
| 20 | 13 Aug. 2013 16:40–19:00 | NW CA | 24–30 | 0.87 ± 0.09 | 5.46 ± 0.40 | 1.18 ± 0.09 | 0.046 ± 0.020 | 54.42 ± 1.27 | 0.95 ± 0.12 | |
| 21 | 15 Aug. 2013 7:20–9:35 | NW CA | 10–12 | 0.92 ± 0.11 | 2.00 ± 0.38 | 1.10 ± 0.22 | 0.018 ± 0.004 | 28.16 ± 1.21 | 0.96 ± 0.13 | |
| 22 | 15 Aug. 2013 12:00–14:05 | NW CA | 10–12 | 0.97 ± 0.14 | 2.08 ± 0.79 | 1.03 ± 0.44 | 0.006 ± 0.032 | 11.41 ± 1.41 | 0.94 ± 0.16 | |
| 23 | 22 Aug. 2013 0:30–5:30 | SW OR | 25–45 | 0.98 ± 0.05 | 6.25 ± 0.80 | 1.08 ± 0.28 | 0.056 ± 0.040 | 6.79 ± 0.36 | 0.91 ± 0.14 | |

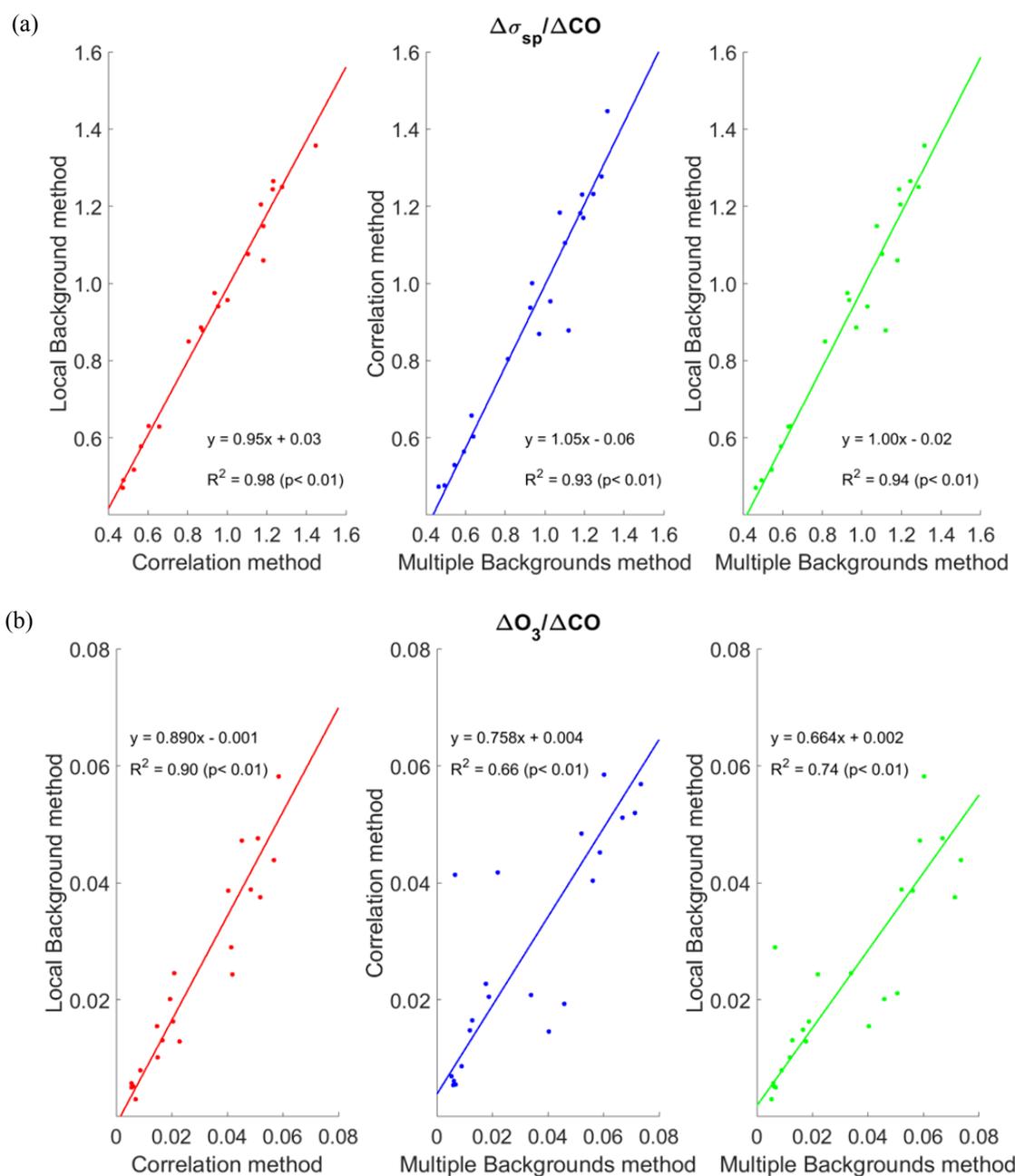


Fig. 2. Comparison of ERs calculated using Correlation (Reduced Major Axis), Local Background, and Multiple Backgrounds methods. Each point represents the ER of one fire plume calculated using two different methods. (a) $\Delta\sigma_{sp}$ (550 nm at STP)/ ΔCO (Mm^{-1} ppbv $^{-1}$) and (b) $\Delta O_3/\Delta CO$ (ppbv ppbv $^{-1}$).

fire seasons, and measured aerosol chemistry with the AMS for four weeks in 2013, including during four of the wildfire plumes analyzed here. Using the simultaneous measurements, we examined the relationship between the AMS organic matter (OM) data and the TSI σ_{sp} data at 550 nm. Fig. 3 shows that there was an excellent correlation between the OM and σ_{sp} data during the fire plumes ($R^2 = 0.98$, $p \leq 0.01$). The AMS data further show that 95% of the non-refractory PM_{10} mass is OM and that the average OM/OC ratio of organic aerosols is 1.7 (Zhou *et al.*, in preparation). The slope of the RMA regression of the σ_{sp} versus OM data is $3.7 \text{ m}^2 \text{ g}^{-1}$ for all data. The slope of RMA regression for σ_{sp}

versus PM_{10} using the AMS data is $3.5 \text{ m}^2 \text{ g}^{-1}$, which is an estimate of the average dry mass scattering efficiency (DMSE) for PM_{10} , given that the nephelometer measures aerosol scattering and the AMS measures non-refractory PM. Individual plumes with AMS and scattering data ($n = 4$) show more variability, with values between 2.8 and $4.8 \text{ m}^2 \text{ g}^{-1}$. These estimated DMSE values are within the range for fine mode mixed composition aerosols ($3.6 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$) (Hand and Malm, 2007).

We used the relationship shown in Fig. 3 to calculate $\Delta OC/\Delta CO_2$ in fire plumes where the AMS data were not available. First, the σ_{sp} (at 550 nm) were converted to STP

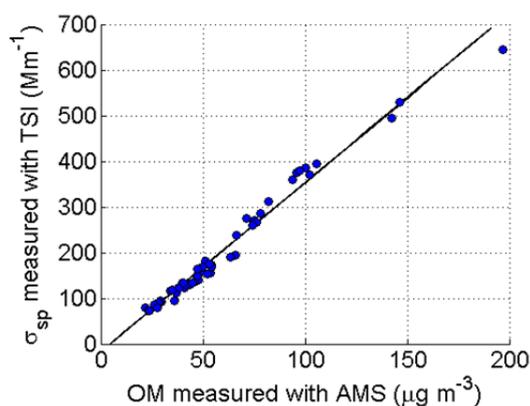


Fig. 3. σ_{sp} (550 nm, STP) versus OM(STP) during wildfire events. 5-minute data points; Reduced Major Axis fit: $y = 3.7x - 18.0$; $R^2 = 0.98$, $p \leq 0.01$.

($T = 273$ K, $P = 1013.25$ mb) to facilitate the comparison with a gas species mixing ratio. Next, we calculated the $\Delta\sigma_{sp}/\Delta\text{CO}_2$ ERs using the Multiple Backgrounds method, and calculated the uncertainty by adding the background and measurement uncertainty in quadrature. We next converted these ERs to grams of particulate carbon per grams of carbon as CO_2 , using the OM/non-refractory PM and OM/OC ratios from our 2013 AMS observations (OM/non-refractory PM = 95%, OM/OC = 1.7), the σ_{sp}/OM ratio of $3.7 \text{ m}^2 \text{ g}^{-1}$, and $T = 273$ K and $P = 1013.25$ mb for the conversion of CO_2 from ppmv to g.

Using this method, we calculated $\Delta\text{OC}/\Delta\text{CO}_2$ for the 21 plumes with available σ_{sp} data, and these ERs ranged from 0.007 – 0.078 gC gC^{-1} (Fig. 4), with a mean of $0.028 \pm 0.018 \text{ (gC gC}^{-1} \text{ as CO}_2, 1 \text{ s.d.)}$. Table 1 presents these ERs in mgC gC^{-1} (rather than as gC gC^{-1}) because the uncertainty in the ERs can be presented in the same format as other uncertainties listed in the table (i.e., using standard notation instead of scientific notation or percents) while still including sufficient significant digits. Fig. 4 also plots a range of

OC/ CO_2 emission ratios for fresh emissions from extratropical forests (in gC gC^{-1} as CO_2), based on CO_2 and OC emission factors and variability (in g kg^{-1}) reported by Akagi *et al.* (2011) in their review of biomass burning emission factors (CO_2 : $1509 \pm 98 \text{ g kg}^{-1}$; OC: 8.6 – 9.7 g kg^{-1}). Our observed ERs have a large degree of variability; however, the mean observed ER (0.028 gC gC^{-1}) is 27% larger than the midpoint of the Akagi *et al.* (2011) emission factor range (0.022 gC gC^{-1}). However, Akagi *et al.* (2011) did not independently calculate an OC emission factor range, and rather reported the range originally reported by Andreae and Merlet (2001) in their review of biomass burning emission factors. The more recent Akagi *et al.* (2012) and Virkkula *et al.* (2014) studies, which reported OC and CO_2 emission factors from biomass burning, are not as broad as the Andreae and Merlet (2001) review, but can be used to further our comparison of $\Delta\text{OC}/\Delta\text{CO}_2$ ERs from aged plumes with OC/ CO_2 emission ratios. Based on the reported emission factors, we calculated that the OC/ CO_2 emission ratio (in gC gC^{-1}) for the temperate fire analyzed by Akagi *et al.* (2012) was 0.008 ± 0.002 , and for the boreal fire analyzed by Virkkula *et al.* (2014) was 0.014 ± 0.023 . Both of these emission ratios are lower than the average observed $\Delta\text{OC}/\Delta\text{CO}_2$ for our fires. Overall, we interpret our $\Delta\text{OC}/\Delta\text{CO}_2$ ERs to suggest moderate production of SOA during transport for some of the plumes we observed. Notably, we do not find a significant relationship between $\Delta\text{OC}/\Delta\text{CO}_2$ ERs in the plumes and the estimated plume transport time.

Fig. 5 shows ω (at 532 nm) versus MCE for the fire plumes observed at MBO. Liu *et al.* (2014) reported that ω drops off sharply at high MCE for fresh fire emissions, based on laboratory burns of various fuels. The authors used their data to develop a parameterization of ω (at 532 nm) as a function of MCE, which is also shown in Fig. 5. All plumes from the present study with MCE uncertainty < 0.1 are plotted, and both the MCE and ω for all plumes were calculated using the Multiple Backgrounds method, and the uncertainty ranges shown include background and measurement uncertainty. For

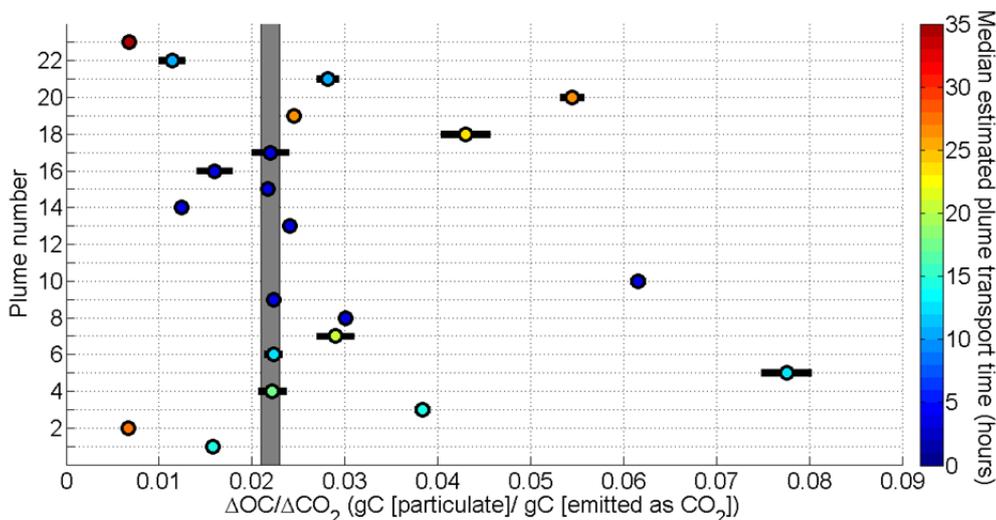


Fig. 4. $\Delta\text{OC}/\Delta\text{CO}_2$ observed in fire plumes at MBO in grams of particulate carbon per grams carbon (as CO_2). Colors represent the median estimated transport time. Grey bar shows the range of emission factors reported by Akagi *et al.* (2011).

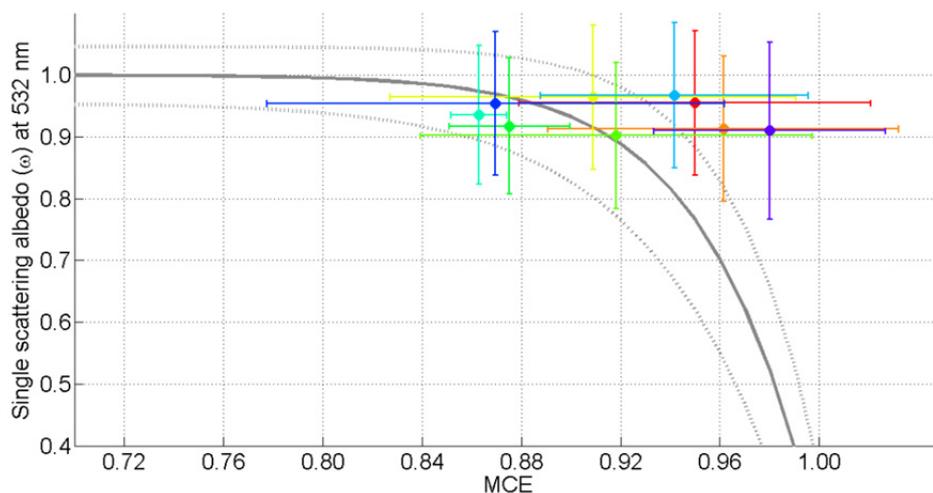


Fig. 5. Single scattering albedo at 532 nm versus MCE (colored points), with the Liu *et al.* (2014) parameterization for fresh emissions (grey lines). Each color represents an individual plume.

the four plumes with MCE > 0.92, the observed ω is 20–74% greater than the parameterization. Due to the large uncertainty in the MCE and ω calculations, the error bars for all of the plumes fall within the uncertainty bounds of the parameterization. However, it is notable that the observed plumes do not follow the pattern of the Liu *et al.* (2014) parameterization, which has an exponential decrease in ω at high MCE. This could be attributed to the aged plumes observed at MBO having a greater OC to total carbon ratio than fresh plumes due to secondary PM production. Another possible explanation is that particle growth (e.g., due to coagulation) led to increasing scattering efficiency of the particles as the particle diameters approached the measurement wavelength (Akagi *et al.*, 2012), and the light scattering was driven by water-soluble inorganic ions. An increase in ω in wildland fire plumes due to aging was also observed by Vakkari *et al.* (2014).

Oxidized Nitrogen Species in Aged Plumes

NO_x , PAN, and aerosol NO_3^- were not continuously measured at MBO. Thus, we have data for these species in only 15, 6, and 4 of the plumes, respectively, and data for all three species in 4 plumes. Fig. 6 shows the median observed NO_x/NO_y , PAN/ NO_y , and p- $\text{NO}_3^-/\text{NO}_y$ in these plumes. In the four plumes where NO_x , PAN, and aerosol NO_3^- were observed, these species represented 77–100% (median: 89%) of the observed NO_y . This indicates that other NO_y species, such as HNO_3 (g), alkyl nitrates, peroxy nitrates other than PAN, and HONO, were on average 11% of the observed NO_y . Other studies have shown relatively small HNO_3 (g) enhancements in aged biomass burning plumes (Yokelson *et al.*, 2009; Alvarado *et al.*, 2010), which can be attributed to low production and/or high conversion of HNO_3 (g) to particulate nitrate. As shown in Fig. 6, the observed NO_x , PAN, and aerosol NO_3^- represented 6–48%, 25–57%, and 20–69% of the observed NO_y in a given plume, respectively. More specifically, the mean and median percent of NO_y that NO_x , PAN, and aerosol NO_3^- represented were as follows: NO_x (mean: 18%; median: 14%), PAN

(mean: 44%; median: 48%), and aerosol NO_3^- (mean: 48%; median: 51%). These average percents exceed 100% because they are based on the differing numbers of plumes in which each species was measured. When considering only the four plumes in which all three species were observed, the mean and median percent of NO_y that NO_x , PAN, and aerosol NO_3^- represented were as follows: NO_x (mean: 11%; median: 10%), PAN (mean: 36%; median: 34%), and aerosol NO_3^- (mean: 51%; median: 53%).

CONCLUSIONS

This study analyzed observations of MCE, ω , and ERs of aerosols and trace gases in 23 western US wildfire plumes aged 1–2 days. Yokelson *et al.* (2013a) showed that the common methods for calculating ERs, the Correlation and Local Background methods, could result in inaccurate ERs due to changes in background air masses. We compared these methods with our newly developed Multiple Backgrounds method, which includes a statistical calculation of uncertainty. There was good agreement between all three methods for $\Delta\sigma_{\text{sp}}/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$, and $\Delta\text{PAN}/\Delta\text{CO}$, indicating that there is little difference between ERs calculated using different methods when the enhancements of the species are large relative to their background concentrations. There was a reasonable agreement between $\Delta\text{O}_3/\Delta\text{CO}$ calculated with the three methods, although there was a bias between methods, which is likely due to the small enhancement of O_3 in the plumes relative to its background mixing ratio. The $\Delta\text{O}_3/\Delta\text{CO}$ ERs calculated in this study are typical of other global calculations of this ER (Jaffe and Wigder, 2012), and therefore we assume that calculations of $\Delta\text{O}_3/\Delta\text{CO}$ ERs for wildland fires in other global regions will show a similar relationship between the methods. Considering that wildland fire emissions are often emitted in the boundary layer where background O_3 mixing ratios are generally low, we believe that the Multiple Backgrounds method is the best approach for calculating $\Delta\text{O}_3/\Delta\text{CO}$, and that ERs calculated using the Local Background or Correlation

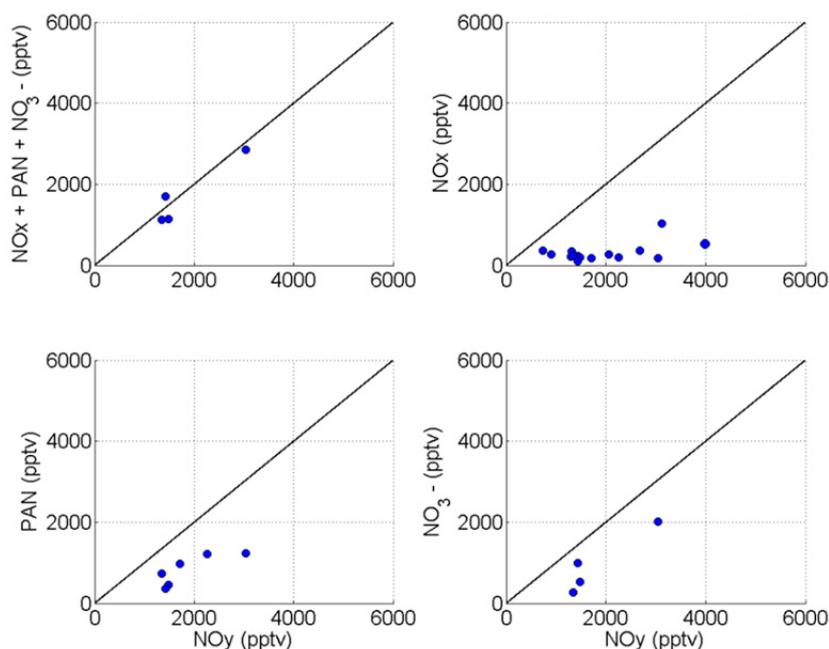


Fig. 6. NO_y species (NO_x , PAN, and aerosol NO_3^-) and their sum versus total observed NO_y for wildfire plumes. Solid lines are 1:1 relationships.

methods are likely biased low by an average of about 20–30%. Overall, our results indicate that caution should be used when comparing wildland fire $\Delta\text{O}_3/\Delta\text{CO}$ when there is only a small difference in magnitude of the ERs compared. We also believe that our new Multiple Backgrounds approach addresses some of the problems with ER calculation raised by Yokelson *et al.* (2013a).

We analyzed the aerosol scattering and absorption measurements in the observed plumes, and found indirect evidence that there was moderate secondary PM production in some plumes. First, a comparison of $\Delta\text{OC}/\Delta\text{CO}_2$ (in gC gC^{-1} [as CO_2]) in the aged plumes showed that the mean observed $\Delta\text{OC}/\Delta\text{CO}_2$ was 27% larger than the midpoint of the Akagi *et al.* (2011) emission ratio range. Second, we found no significant change in ω with MCE in these aged plumes, in contrast to Liu *et al.* (2014), who found that ω decreases exponentially at high MCE for fresh biomass burning emissions. While our data do not include a direct measurement of SOA, we believe that in combination, these two pieces of evidence suggest that there was net secondary PM production in some of the aged wildfire plumes that we observed.

We also analyzed the NO_y speciation in the observed plumes. NO_x , PAN, and aerosol NO_3^- represented 6–48%, 25–57%, and 20–69%, respectively, of the total NO_y in the fire plumes in which each of these species was measured, indicating that other NO_y species represented a relatively small proportion of the reactive nitrogen in these aged plumes. The high proportion of PAN in the observed plumes suggests that there may have been continued O_3 production in the plumes as they were transported further downwind.

Future studies are needed to test the use of the Multiple Backgrounds ER method at other sites, and in particular to compare this method with the Local Background and

Correlation methods for calculating $\Delta\text{O}_3/\Delta\text{CO}$. Further studies are also needed to confirm our finding that ω shows minimal variations with MCE in aged plumes, which we believe is due to secondary PM production within the plumes.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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