The impact of aged wildfire smoke on atmospheric composition and ozone in the Colorado Front Range in summer 2015

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Abstract. The relative importance of wildfire smoke for air quality over the western U.S. is expected to increase as the climate warms and anthropogenic emissions decline. We report on in situ measurements of ozone (O3), a suite of volatile organic compounds (VOCs), and reactive oxidized nitrogen species collected during summer 2015 at the Boulder Atmospheric Observatory (BAO) in Erie, CO. Aged wildfire smoke impacted BAO during two distinct time periods during summer 2015: 6 – 10 July and 16 – 30 August. The smoke was transported from the Pacific Northwest and Canada across much of the continental U.S. Carbon monoxide and particulate matter increased during the smoke-impacted periods, along with peroxyacyl nitrates and several VOCs that have atmospheric lifetimes longer than the transport timescale of the smoke. During the August smoke-impacted period, nitrogen dioxide was also elevated during the morning and evening compared to the smoke-free periods. There were six days during our study period where the maximum 8-hour average O3 at BAO was greater than 65 ppbv, and two of these days were smoke-impacted. We examined the relationship between O3 and temperature at BAO and found that for a given temperature, O3 mixing ratios were greater (~10 ppbv) during the smoke-impacted periods. Enhancements in O3 during the August smoke-impacted period were also observed at two long-term monitoring sites in Colorado: Rocky Mountain National Park and the Arapahoe National Wildlife Refuge near Walden, CO. Our data provide a new case study of how aged wildfire smoke can influence atmospheric composition at an urban site, and how smoke can contribute to increased O3 abundances across an urban-rural gradient.

Keywords. wildfire smoke, air quality, ozone, in situ observations, biomass burning

1 Introduction

Over the past 30 years, wildfires in the western U.S. have increased in both frequency and intensity, and this trend will likely continue under future climate change (Westerling, 2016). Wildfire smoke can be transported over thousands of kilometers,
and exposure to wildfire smoke has significant impacts on human health (Künzli et al., 2006; Rappold et al., 2011; Elliott et al., 2013). While U.S. emissions of most major air pollutants are declining (Pinder et al., 2008), increasing fire activity suggests that wildfires may have a greater relative impact on U.S. air quality in the future (Val Martin et al., 2015).

Ozone (O$_3$) is formed when hydrocarbons are oxidized in the presence of nitrogen oxides (NO$_x$ = NO + NO$_2$) and sunlight (Sillman, 1999). Wildfires emit many trace gas species that contribute to tropospheric O$_3$ production. Along with carbon monoxide (CO), methane (CH$_4$), and carbon dioxide (CO$_2$), hundreds of different non-methane volatile organic compounds (NMVOCs) with lifetimes ranging from minutes to months (Atkinson and Arey, 2003) are emitted during biomass burning (Akagi et al., 2011; Gilman et al., 2015). Due to relatively large emissions of CO$_2$, CO, CH$_4$ and NO$_x$, the contribution of VOCs to the total emissions from fires on a molar basis is small (<1%). However, VOCs dominate the OH reactivity in smoke plumes (Gilman et al., 2015). Recent observations of the evolution of VOCs within aging smoke plumes indicate that OH can be elevated in young biomass burning plumes (Hobbs et al., 2003; Yokelson et al., 2009; Akagi et al., 2012; Liu et al., 2016) in part due to the photolysis of oxygenated VOCs (Mason et al., 2001), which make a large contribution to the total emitted VOC mass (Stockwell et al., 2015). Elevated OH may reduce the lifetime of emitted VOCs and increase oxidation rates and potential O$_3$ production.

Fires are also a major source of oxidized nitrogen; emissions from biomass and biofuel burning represent approximately 15% of total global NO$_x$ emissions (Jaegle et al., 2005). However, there are major uncertainties in NO$_x$ emission estimates from biomass burning, particularly at a regional scale (Schreier et al., 2015). NO$_x$ emissions depend on the nitrogen content of the fuel (Lacaux et al., 1996; Giordano et al., 2016) as well as the combustion efficiency (Goode et al., 2000; McMeeking et al., 2009; Yokelson et al., 2009). Emitted NO$_x$ is quickly lost in the plume, either by conversion to HNO$_3$ (Mason et al., 2001) or via PAN formation (Alvarado et al., 2010; Yates et al., 2016). HNO$_3$ is not often observed in plumes because it either rapidly forms ammonium nitrate or is efficiently scavenged by other aerosols (Tabazadeh et al., 1998; Trentmann et al., 2005).

There are multiple lines of observational evidence indicating that wildfires in the western U.S. increase the abundance of ground level O$_3$. Background O$_3$ mixing ratios across the western U.S. are positively correlated with wildfire burned area (Jaffe et al., 2008), and daily episodic enhancements in O$_3$ at ground sites can be > 10 ppbv (Lu et al., 2016). There are well-documented case studies of within plume O$_3$ production (Jaffe and Wigder, 2012) and time periods where smoke contributed to exceedances of the U.S. EPA National Ambient Air Quality Standard (NAAQS) for O$_3$ (Morris et al., 2006; Pfister et al., 2008). Brey and Fischer (2016) investigated the impacts of smoke on O$_3$ abundances across the U.S. via an analysis of routine in situ measurements and NOAA satellite products. They found that the presence of smoke is correlated with higher O$_3$ mixing ratios in many areas of the U.S., and that this correlation is not driven by temperature. Regions with the largest
smoke-induced O3 enhancements (e.g. the southeast and Gulf coast) can be located substantially downwind of the wildfires producing the most smoke.

Despite several recent studies showing that smoke contributes to elevated O3, there have been relatively few detailed studies of wildfire smoke mixing with anthropogenic air masses near the surface. Singh et al. (2012) used aircraft measurements from summer 2008 over California to document significant O3 enhancements in nitrogen-rich urban air masses mixed with smoke plumes. Accompanying air quality simulations were not successful in capturing the mechanisms responsible for these enhancements. In general, measurements of O3 precursors are hard to make routinely. Instrumentation and calibration methods tend to be time and labor intensive, and thus unpredictable wildfire smoke plumes and their effects on surface O3 are sparsely sampled.

Here we present a case study of aged wildfire smoke mixed with anthropogenic pollution in the Colorado Front Range and show its impact on atmospheric composition and O3. This region violates the NAAQS for O3, and has been the focus of several recent studies (e.g. McDuffie et al., 2016; Abeleira et al., 2017). First we describe the research location and measurements. Next, we identify the smoke-impacted time periods and show the origin, approximate age, and wide horizontal extent of the smoke plumes. We characterize significant changes in atmospheric composition with respect to the two major classes of O3 precursors, VOCs and oxidized reactive nitrogen (NOx). Finally, we present the impact of smoke on O3 abundances during this period and discuss the underlying causes of this impact.

2 Measurements and Research Site

During summer 2015, we made measurements of a suite of trace gases at the Boulder Atmospheric Observatory (BAO), located north of Denver, CO, in the middle of the rapidly developing northern Colorado Front Range [40.05°N, 105.01°W, 1584m ASL]. BAO has a history of atmospheric trace gas and meteorological measurements stretching back nearly four decades (Kelly et al., 1979; Gilman et al., 2013). Our research campaign from 1 July – 7 September 2015 measured a suite of O3 precursor species as well as several NOx oxidation products and greenhouse gases. The intended goal of the field campaign was to improve our understanding of the complex O3 photochemistry in the Colorado Front Range and the contributions of oil and natural gas activities as well as other anthropogenic emissions to O3 production. All measurements were made by instruments housed in two trailers located at the base of the BAO tower. Here we briefly describe the measurements used in this paper. Data are available at https://esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/.

We measured CO and CH4 at ~3 second time resolution with a commercial cavity ring-down spectrometer (Picarro, model G2401) (Crosson, 2008). The inlet was located 6 m above ground level (a.g.l.), and a 1 µm PTFE filter membrane (Savillex) at the inlet was changed weekly. Laboratory instrument calibrations were performed pre- and post-campaign using three
NOAA standard reference gases (http://www.esrl.noaa.gov/gmd/ccl/refgas.htmls; CA06969, CB10166, and CA08244). Field calibration was performed every 3 hours using high, low and middle reference gas mixtures (Scott Marin Cylinder IDs CB10808, CB10897, CB10881). Mixing ratios were calculated using the WMO-CH4-X2004 and WMO-CO-X2014 scales. The uncertainty associated with the CH4 and CO data is estimated to be 6% and 12% respectively, and it was estimated as the quadrature sum of measurement precision, calibration uncertainty and uncertainty in the water vapor correction.

A custom 4-channel cryogen free gas chromatography (GC) system (Sive et al., 2005) was used to measure selected non-methane hydrocarbons (NMHCs), C1 – C2 halocarbons, alkyl nitrates (ANs), and oxygenated volatile organic compounds (OVOCs) at sub-hourly time resolution. The inlet was located at 6 m a.g.l. with a 1 µm teflon filter. A calibrated whole air mixture was sampled in the field after every ten ambient samples to monitor sensitivity changes and measurement precision. A full description of this instrument is provided in (Abeleira et al., 2017).

Ozone data at BAO for this time period were provided by the NOAA Global Monitoring Division surface ozone network (McClure-Begley et al., 2014; data available at aftp.cmdl.noaa.gov/data/ozwv/SurfaceOzone/BAO/). Ozone was measured via UV-absorption using a commercial analyzer (Thermo-Scientific Inc., model 49), which is calibrated to the NIST standard over the range 0 – 200 ppbv and routinely challenged at the site. The inlet height was 6m a.g.l. on the BAO tower, located about 50 feet from the two trailers, and measurements were reported at a 1 minute averaging interval with an estimated error of 1%.

Nitrogen oxides (NOx=NO+NO2) and total reactive nitrogen (NOy) were measured via NO-O3 chemiluminescence detection (Kley and McFarland, 1980) using a commercial analyzer (Teledyne, model 200EU). Two commercial converters, a 395 nm LED converter (Air Quality Designs, Inc., model BLC) for chemically-selective photolysis of NO2 to NO and a molybdenum in stainless steel converter (Thermo Scientific Inc.) heated to 320 ºC for reduction of NOy to NO, were positioned as close to the inlet tip as possible (<10 cm). A 7 µm stainless steel particulate filter was affixed to the upstream end of the molybdenum converter; otherwise no other filters were used. The analyzer switched between sampling from the LED (NOy) converter and the molybdenum (NOy) converter every 10 seconds, and the LEDs were turned on (to measure NO+NO2) and off (to measure NO only) every minute. NO2 was determined by subtraction of measured NO from measured NO+NO2 divided by the efficiency of the LED converter. All three species are reported on a consistent two-minute average timescale. The detector was calibrated daily by standard addition of a known concentration of NO, NIST-traceable (Scott-Marin Cylinder ID CB098J6), to synthetic ultrapure air. Both converters were calibrated with a known concentration of NO2 generated via gas phase titration of the NO standard. The NO2 channel was further challenged with a known mixing ratio of nitric acid (HNO3) generated using a permeation tube (Kintech, 30.5 ± 0.8 ng/min at 40 ºC), which was used to confirm >90% conversion efficiency of HNO3 by the molybdenum converter. Uncertainties of ±5% for NO, ±7% for NO2, and ±20%
for NO\textsubscript{y} are determined from a quadrature sum of the individual uncertainties associated with the detector, converters, and calibration mixtures; an LOD of 0.4 ppbv for all species is dictated by the specifications of the commercial detector.

Peroxyacyl nitrates (PANs) were measured using the National Center for Atmospheric Research gas chromatograph with an electron capture detector (NCAR GC-ECD) (Flocke et al., 2005). The instrument configuration was the same as was used during the summer 2014 FRAPPE field campaign (Zaragoza, 2016). The NCAR GC-ECD analyzed a sample every five minutes from a 6 m a.g.l. inlet with 1µm teflon filter. A continuous-flow acetone photolysis cell generated a known quantity of PAN used to calibrate the system at 4-hour intervals.

An Aerodyne dual quantum cascade laser spectrometer was used to measure HNO\textsubscript{3} (McManus et al., 2011). The instrument employed a prototype 400 m absorption cell for increased sensitivity during the first month of the campaign, after which it was replaced by a 157 m absorption cell. An active passivation inlet (Roscioli et al., 2016) was used to improve the time response of the measurement to ~0.75 s. This technique utilized a continuous injection of 10-100 ppb of a passivating agent vapor, nonafluorobutane sulfonic acid, into the inlet tip. The inlet tip was made of extruded perfluoroalkoxy Teflon (PFA), followed by a heated, fused silica inertial separator to remove particles larger than 300 nm from the sample stream. The inlet was located 8 m a.g.l. with a 18 m heated sampling line (PFA, 1/2” diameter OD) to the instrument. The system was calibrated every hour by using a permeation tube that was quantified immediately prior to the measurement period.

3 Smoke Events

We observed two distinct smoke-impacted periods at BAO, identified by large enhancements in CO and fine aerosol (PM\textsubscript{2.5}). Figure 1 presents CO observations from BAO and fine particulate matter (PM\textsubscript{2.5}) observations from the Colorado Department of Public Health and Environment (CDPHE) CAMP air quality monitoring site, located in downtown Denver, approximately 35km south of BAO. PM\textsubscript{2.5} was similarly elevated during the smoke-impacted periods at CDPHE monitoring sites across the Colorado Front Range (not shown). For our analysis, we defined a July smoke-impacted period and an August smoke-impacted period. The July smoke-impacted period lasted for 4 days from 00 MDT 6 July 2015 to 00 MDT 10 July 2015. The August smoke-impacted period was significantly longer (~14 days). For the subsequent analysis, we combined three distinct waves of smoke-impact in this 14 day period into one August smoke-impacted period: 00 MDT 16 August 2015 – 18 MDT 21 August 2015, 12 MDT 22 August 2015 – 18 MDT 27 August 2015, and 14 MDT 28 August 2015 – 09 MDT 30 August 2015. We omitted the brief periods between these times from the analysis due to uncertainty on the influence of smoke during them. All other valid measurements were considered part of the smoke-free data.

Figure 2 presents the extent of the presence of smoke in the atmospheric column during representative smoke-impacted days, 7 July and 21 August 2015. The NOAA Hazard Mapping System smoke polygons (grey shading) show that the smoke
...events observed at BAO were large regional events. The HMS smoke product is produced using primarily visible satellite imagery (Rolph et al., 2009). The extent of smoke plumes within the HMS dataset represents a conservative estimate, and no information is provided on the vertical extent or vertical placement of the plumes. The red triangles represent MODIS active fire locations for the previous day (Giglio et al., 2003; Giglio et al., 2006). The thin black lines are NOAA Air Resources Laboratory (ARL) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) 120 hour backward trajectories initialized each hour of the day from BAO at 1000m above ground level (Stein et al., 2015). Trajectories were run using the EDAS (Eta Data Assimilation System) 40 km x 40 km horizontal resolution reanalysis product (Kalnay et al., 1996). Figure 2 shows the smoke that impacted BAO during both periods was transported from large fire complexes in the Pacific Northwest and Canada, with approximate transport timescales on the order of two to three days. Creamean et al. (2016) provide a more detailed description of smoke transport and the sources of the aerosols associated with the August smoke-impacted period.

4 Observed Changes in Ozone and its Precursors

4.1 CO, CH₄, and VOC Abundances

We quantified CO, CH₄, and 40+ VOC species including C₂-C₁₀ non-methane hydrocarbons (NMHCs), C₁-C₂ halocarbons, and several oxygenated species (methyl ethyl ketone, acetone, and acetaldehyde) at BAO. The focus of the BAO field intensive was to study the photochemistry of local emissions from oil and gas development (e.g. Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; Abeleira et al., in review), and we did not quantify species with known large biomass burning emission ratios (e.g. hydrogen cyanide, acetonitrile, most oxygenated organic species). In addition, early campaign issues with the online multichannel gas chromatography system compromised the data for the July smoke period and thus we restrict our comparison of VOCs in smoke-free versus smoke-impacted periods to a comparison between 16 – 30 August, the August smoke-impacted period, and 24 July – 16 August, the smoke-free period. The brief smoke-free times during 16 – 30 August (denoted by white between the red shading in Figure 1) were not included in either period since it is difficult to determine whether they were smoke-impacted. GC measurements were made approximately every 50 minutes and we compared 251 measurements of VOCs during the August smoke-period to 583 measurements during the smoke-free period.

In this section, we describe significant changes in VOC abundances and notable exceptions. The HYSPLIT trajectories (Figure 2) suggest that the age of the smoke impacting the Front Range during the August smoke-period was 2-3 days. We observed enhancements in the abundances of CO, CH₄, and VOCs with lifetimes longer than the transport time of the smoke, with the exception of some alkanes that have a large background concentration in the Front Range due to emissions from oil and gas production. The alkenes we quantified (isoprene, ethene, and propene) were generally near the limit of detection.
during the August smoke-impacted period, although notably cis-2-butene abundances were not changed. Significant differences were not observed in the four oxygenated VOCs quantified between smoke-impacted and smoke-free periods.

Mean CO mixing ratios were significantly enhanced by 86 ppbv, or 65%, during the August smoke-impacted period (Figure 1). This enhancement was present across the diurnal cycle (Figure 3) and a greater range of CO mixing ratios (96 – 402 ppbv versus 70 – 291 ppbv) were measured during the August smoke-impacted period compared to the smoke-free period. Average enhancements of CH₄ were a much smaller percentage of (~3% or 67 ppbv), but comparable in magnitude to, the CO mixing ratio enhancement. Methane has a relatively high background at BAO due to large emissions of CH₄ in nearby Weld County from livestock production and oil and gas development (Pétron et al., 2014; Townsend-Small et al., 2016). Taken together, the larger background of CH₄ and the large local sources of CH₄ in the Front Range served to mute the impact of the August smoke on overall CH₄ abundances. The diurnal cycle of CH₄ did not change during the smoke-impacted period as compared to the smoke-free period and we observed a similar range of mixing ratios (~1,840 – 3,360 ppbv) in the both smoke-free and smoke-impacted periods. We note several large spikes on the order of minutes during the smoke-impacted period, but we do not believe that these are related to the presence of smoke because they were not correlated with similar excursions in CO and PANs, and exhibited strong correlations with propane and other tracers of oil and gas and other anthropogenic activity.

Similar to CO, ethane has an atmospheric lifetime on the order of a month during summertime at mid-latitudes (Rudolph and Ehhalt, 1981) and is emitted by wildfires (Akagi et al., 2011). However, average ethane mixing ratios were not higher during the August smoke-impacted period compared to the smoke-free period. One potential reason for this may be the large local sources of alkanes from oil and natural gas activities within the Denver-Julesberg Basin which contribute to relatively high local mixing ratios of these species (Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; Abeleira et al., 2017). The range of ethane mixing ratios observed at BAO was also not different between smoke-free (0.3 - 337 ppbv) and smoke-impacted periods (1 – 362 ppbv), but the amplitude of the median diurnal cycle was dampened during the August smoke-impacted period (not shown). Median morning ethane mixing ratios were ~10 – 20 ppbv less during smoke-impacted than smoke-free periods, while afternoon and evening median mixing ratios were ~5 – 10 ppbv larger. Most of the C₃ – C₉ alkanes we quantified showed similarly dampened amplitudes in their median smoke-period diurnal cycles. A consistently lower planetary boundary layer (PBL) height during the day and a consistently higher boundary layer at night is one potential explanation for these observations; however an estimate of the PBL height in the grid box surrounding BAO from the North American Regional Reanalysis product (Mesinger et al., 2006) did not show any significant changes in PBL height between the smoke-impacted and smoke-free periods. Likewise estimated PBL heights following methods from Coniglio et al. (2013) and using atmospheric soundings at 0Z and 12Z in Denver (http://mesonet.agron.iastate.edu/archive/raob/) did not show any differences between smoke-impacted and smoke-free periods (Figures S1 and S2). Figure 3 shows there were two exceptions to the general alkane pattern noted above: 2-methylhexane showed a significant decrease in average abundances
(-39 pptv or -45%) and 3-methylhexane showed a significant increase (63 pptv or 75%) during the smoke-impacted period, despite both having similar smoke-free abundances and similar rate constants for reaction with OH radicals (\(\sim 7 \times 10^{12} \text{ cm}^{-3} \text{ molec}^{-1} \text{ s}^{-1}\)).

The atmospheric lifetimes of the four alkenes we quantified (isoprene, propene, ethene, and cis-2-butene) range from tens of minutes to hours. Isoprene, propene, and ethene showed significant decreases in their average abundance: -64% (-143 pptv), -77% (-39 pptv), and -81% (-206 pptv) respectively. The shape of the diurnal cycles did not change (not shown), though propene and ethene were near their respective limits of detection for the majority of each day during the smoke-impacted period. These alkenes were among the most reactive species quantified, and one potential explanation for the reduced abundance of these species during the smoke-impacted period is enhanced oxidation capacity linked to the presence of smoke. However, we do not observe decreased abundances of cis-2-butene, which has a comparable OH-reactivity to propene and lower average abundance. An alternative hypothesis for the reductions in the other three alkene species may be reductions in local biogenic emissions during the smoke-impacted period either due to lower air temperatures or due to a reduction in photosynthetic active radiation (PAR) at the surface during the August smoke-impacted period. Isoprene is emitted by broad leaf vegetation, and emission rates are highly light and temperature sensitive (Guenther et al., 2006). However, while we did observe lower average daytime temperatures at BAO during the August smoke-impacted period compared to the rest of the dataset (-2.3°C), the majority of Front Range emissions of propene and ethene are likely from anthropogenic sources. Thus this hypothesis could possibly help explain reduction in isoprene but not likely explain reductions in ethene and propene. Shifts in local transport could also help explain differences but we did not observe any consistent shifts in wind direction or changes in wind speed that would indicate consistently different local transport during the August smoke-impacted period.

The only alkyne measured was ethyne. Ethyne is emitted by wildfires (Akagi et al., 2011) and has a lifetime of \(~1\) month during summer. We observed a significant increase in the abundance of ethyne during the August smoke-impacted period. These enhancements were small in absolute mixing ratio (0.163 ppbv), but represented a large percentage increase (67%) and were consistently present throughout the day.

It is well known that wildfires produce carcinogenic aromatic hydrocarbons including benzene (Fent et al., 2014). During the smoke-impacted periods, we observed significantly enhanced benzene throughout the day with an average increase of 0.117 ppbv and a percentage increase of 67%. These enhancements followed the pattern of CO and ethyne; there were consistent increases throughout the day and the diurnal cycle retained its shape. Wildfires also produce toluene (Fent et al., 2014); however, it has a substantially shorter lifetime (< 2 days) than benzene (~12 days). Toluene showed no significant changes in its mean mixing ratio, diurnal cycle, or range of values measured at BAO during the smoke-impacted periods. The other aromatic hydrocarbons we quantified (o-xylene and ethyl-benzene) also did not change significantly.
As mentioned in Section 1, oxygenated VOCs are emitted by wildfires and make a large contribution to the total emitted VOC mass in wildfire smoke (Stockwell et al., 2015). Additionally, they are produced as oxidation intermediates (Atkinson and Arey, 2003). Acetaldehyde, acetone, and methyl ethyl ketone (MEK) showed no consistent changes in their abundances, diurnal cycles, or range during the smoke-impacted period compared to the smoke-free period. Small increases in average acetone (~350 pptv) and MEK (~150 pptv) mixing ratios during late afternoon and evening hours were not statistically significant.

Given the diversity of emission sources across the northern Colorado Front Range, previous studies of atmospheric composition at BAO have noted a strong dependence of VOC composition on wind direction (Petron et al., 2012; Gilman et al., 2013). Recent housing development and oil and gas production surrounding the BAO site have made analyses based on wind direction more challenging in recent years (McDuffie et al., 2016). Importantly for our analysis, we found that the statistically significant changes in all species during the smoke-impacted periods occurred across all wind directions. Figure 4 shows this for two example species: benzene and NO₂. We also did not find statistically significant changes in wind direction or wind speed patterns between smoke-free and smoke-impacted periods. Thus we attribute the changes in atmospheric composition during the August smoke-impacted period to the presence of smoke.

### 4.2 Reactive Oxidized Nitrogen (NO₃) Species

Peroxyacetyl nitrates and HNO₃ were successfully measured from 10 July – 7 September and alkyl nitrates were measured from 24 July – 30 August. Thus we report significant changes in these species for the August smoke-impacted period only. We observed significant enhancements in both peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) during the August smoke-impacted period. PAN and PPN abundances were consistently elevated across the day by an average of 183 and 22 pptv respectively, corresponding to a ~100% change for both species. The peak of each diurnal cycle was shifted later in the day by about 3-4 hours for the smoke-impacted period. This cannot be accounted for merely by the shift in the timing of solar noon given that the total decrease in daylight between 10 July and 30 August is ~2 hours. The ratio of PPN to PAN during the August smoke-impacted period exhibited a significant decrease from the smoke-free period ratio (0.14 ± 0.012 versus 0.17 ± 0.006; calculated as the slope of a reduced major axis linear regression on the hourly data from 12PM – 5PM MDT Figure S3). The direction of change in the ratio is consistent with observations of PPN/PAN ratios in Asian urban and aged biomass burning plumes off the coast of California (Roberts et al., 2004). The C₁ – C₂ alkyl nitrates measured at BAO exhibited similar behaviors; methyl nitrates and ethyl nitrates saw average enhancements during the August smoke period of 1.2 and 0.77 pptv, 41% and 31% respectively, though the average mixing ratios of these species are smaller by an order of magnitude compared to other alkyl nitrates quantified. Propyl-, pentyl-, and butyl-nitrate did not display significant changes in their average mixing ratio, though we observed a similar shift in the peak of their diurnal cycles of 2-4 hours. We did not observe significant changes in the abundances of HNO₃. There were no changes to the diurnal cycle or the range of mixing...
ratios observed.

NO and NO\textsubscript{2} measurements were made during the entire campaign, 1 July – 7 September 2015, so both the July and August smoke-impacted periods were analyzed with respect to potential changes in NO\textsubscript{x}. NO was present in the same abundances between the two periods and showed the same diurnal cycle during the August smoke-impacted period as compared to the smoke-free period (Figure 5). During the July smoke-impacted period the morning buildup of NO was slower than the smoke-free period, though the mixing ratios were within the range of smoke-free values and there were fewer days in the July period compared to the August smoke-impacted period.

Figure 5 shows that NO\textsubscript{2} abundances exhibited more significant changes. During the July smoke-impacted period, NO\textsubscript{2} was within the range of smoke-free measurements but the diurnal cycle was shifted later in the day and the average decrease in mixing ratios of NO\textsubscript{2} in the afternoon was not as strong as during the smoke-free periods. In contrast NO\textsubscript{2} during the August smoke-impacted period followed the same diurnal cycle but had pronounced significant increases in average mixing ratios during the morning and evening hours of ~8 ppbv (17%) following sunrise and 3 ppbv (60%) following sunset. These enhanced peak abundances appeared during multiple days during the August smoke-impacted period. We did not find evidence that these enhancements were due to traffic patterns. The concurrently observed PAN abundances can only account for at most 1 ppbv of additional NO\textsubscript{2}, but there could have been significantly higher PAN abundances in the smoke plume prior to reaching BAO and PAN dissociation is one hypothesis for the enhanced abundances. We do not have measurements of other reactive nitrogen species (e.g. HONO, CINO\textsubscript{2}, NO\textsubscript{3}, and \textsubscript{N_2}O\textsubscript{5}) to test potential other hypotheses of a different chemical mechanism to explain the observed NO\textsubscript{2} enhancements.

4.3 Ozone

As discussed in the introduction, wildfire smoke has been found to produce O\textsubscript{3} within plumes and to be correlated with enhanced surface O\textsubscript{3} in areas to which it is advected. The total amount of O\textsubscript{3} at a location is a complex combination of the relative abundances of VOCs and NO\textsubscript{x}, meteorological conditions supporting local O\textsubscript{3} production, and the amount of O\textsubscript{3} present in the air mass before local production. In this section we describe the significant increases in O\textsubscript{3} during both smoke-impacted periods, show that these enhancements were most likely not due to changes in meteorological conditions, and discuss evidence pointing to whether these changes may be due to enhanced local production or transport of O\textsubscript{3} produced within the smoke plume.

Figure 5d shows that there were significant increases in O\textsubscript{3} mixing ratios during nighttime and midday during the August smoke-impacted period compared to the average smoke-free diurnal cycle. The mean O\textsubscript{3} mixing ratio across all hours of the day was 6 ppbv (14%) larger during the August smoke-impacted period than the smoke-free period (Figure 6), significant at
the 99% confidence level based on a two-sample difference of means t-test. There were no significant changes in the average O\textsubscript{3} mixing ratios during the July smoke-impacted period (Figure 5a). The average mixing ratio of O\textsubscript{3} during the July smoke-impacted period was not greater than absolute average during the smoke-free period (Figure 5a). However, as discussed in Section 2, this period in particular was much colder on average than the smoke-free period.

O\textsubscript{3} mixing ratios generally increase with temperature, and this relationship has been attributed to 1) warm and often stagnant anti-cyclonic atmospheric conditions that are conducive to O\textsubscript{3} formation, 2) warmer air temperatures that reduce the lifetime of PAN, releasing NO\textsubscript{2}, and 3) lower relative humidity that reduces the speed of termination reactions to the O\textsubscript{3} production cycle (Jacob et al., 1993; Camalier et al., 2007). Figure 6 presents hourly average O\textsubscript{3} and temperature at BAO and shows a positive relationship between O\textsubscript{3} and temperature for both the smoke-free period in black and August smoke-impacted period in red. The increase in O\textsubscript{3} mixing ratios during the August smoke-impacted period compared to the smoke-free period is present across the entire range of comparable temperatures. Figure S4 shows the same result during the July smoke-period, where for comparable temperatures the July smoke-period has higher O\textsubscript{3} than would be expected from the O\textsubscript{3}-temperature relationship during the smoke-free period. Across both smoke-impacted periods and for a given temperature, the magnitude of the increase in average O\textsubscript{3} was 10 ± 2 ppbv. This was calculated as the mean difference between medians within each temperature bin weighted by the total number of hourly measurements within each bin. The weighted standard deviation was calculated in the same way. The magnitude of this difference is greater than the average difference in means between the smoke-free O\textsubscript{3} mixing ratios and the August smoke-impacted period because there were several periods during the July and August smoke-impacted period where air temperatures were colder (~ 5°C) than most observations during the smoke-free period. Thus the lower O\textsubscript{3} mixing ratios associated with these smoke-impacted periods (e.g. ~ 20 - 40 ppbv) were not included in the weighted difference in medians since there were not commensurate smoke-free O\textsubscript{3} measurements at those same temperatures.

In addition to a positive relationship with surface temperature, elevated O\textsubscript{3} in the western U.S. has also been found to be correlated with 500 hPa geopotential heights, 700 hPa temperatures, and wind speeds (Reddy and Pfister, 2016). We tested the relationship between O\textsubscript{3} and these meteorological variables during our study period using observations from the 0Z and 12Z atmospheric soundings conducted in Denver (http://mesonet.agron.iastate.edu/archive/raob/). We did not find a relationship between O\textsubscript{3} and daily 500 hPa geopotential heights or 700 hPa temperatures, nor were these meteorological variables notably elevated during the August smoke-impacted period (Figures S5, S6, and S7). Additionally we did not find a significant change in wind speed during the August smoke-impacted period. Thus we have no evidence that the enhanced O\textsubscript{3} during the August smoke-impacted period was due to meteorological factors.

To determine if a change in synoptic scale transport in smoke-impacted versus smoke-free periods could have contributed to different abundances, we performed a k-means cluster analysis on 72-hour HYSPLIT back trajectories. The trajectories were
calculated using the methods described above, and initiated each hour at 2000 m a.g.l. from BAO. We chose to initialize the trajectories at 2000 m a.g.l so that fewer trajectories intersect the ground in the Rocky Mountains. Trajectories are unlikely to capture the complex circulations (e.g., potential Denver Cyclones or up/down slope winds) characteristic of summertime in the Front Range, but they should capture synoptic scale air mass motions. The k-means analysis clustered each trajectory into a predetermined number of clusters by minimizing the distance between each trajectory and its nearest neighbor; this technique has been used to classify air mass history in air quality studies (Moody et al., 1998). We found 4 predominate trajectory clusters during our study period: northwesterly flow, westerly flow, southwesterly flow, and local/indeterminate flow (Figure S8). We then compared afternoon (12PM – 5PM MDT) hourly \( \mathrm{O}_3 \) measurements separated by trajectory cluster and binned by temperature between the smoke-free period and the August smoke-impacted period. Most hours during the August smoke-impacted period were associated with northwesterly flow and we found the same enhancement in \( \mathrm{O}_3 \) for a given temperature when comparing smoke-impacted observations to smoke-free observations assigned to this cluster as we found for the complete dataset (Figures S9 and S10). Thus we conclude that potential changes in \( \mathrm{O}_3 \) driven by synoptic scale transport conditions cannot account for the observed \( \mathrm{O}_3 \) enhancements during the August smoke-impacted period at BAO.

We calculated the maximum daily 8 hour average (MDA8) \( \mathrm{O}_3 \) mixing ratios, following methodology from the U.S. EPA, and found that out of 6 high \( \mathrm{O}_3 \) days at BAO (defined as > 65 ppbv MDA8) during our study period, 2 occurred during the August smoke-impacted period (Figure 7). As we stated above, elevated \( \mathrm{O}_3 \) during the smoke period was not a result of abnormal meteorological variables such as higher than normal temperatures, and thus these 2 high \( \mathrm{O}_3 \) days are very likely caused in part due to the presence of wildfire smoke. The lower portion of Figure 7 again shows that maximum daily temperatures during the smoke-impacted periods were the same as or lower than maximum daily temperatures during the smoke-free period.

To assess the spatial extent of the \( \mathrm{O}_3 \) enhancements observed at BAO and to investigate the relative likelihood of \( \mathrm{O}_3 \) enhancements due to transport within the smoke versus greater local production, we analyzed hourly \( \mathrm{O}_3 \) measurements from two nearby National Park Service (NPS) Air Resources Division (http://ard-request.air-resource.com/data.aspx) measurement locations. The Rocky Mountain National Park long-term monitoring site (ROMO; 40.2778’N, 105.5453’W, 2743 meters A.S.L.) is located on the east side of the Continental Divide and co-located with the Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) monitoring sites. Front Range air masses frequently reach this site during summer afternoons (Benedict et al., 2013). The Arapahoe National Wildlife Refuge long-term monitoring site (WALD; 40.8822’N, 106.3061’W, 2417 meters A.S.L.) near Walden, Colorado, is a rural mountain valley site with very little influence from anthropogenic emissions. Figure 8 shows that the August smoke-impacted period produced increases in \( \mathrm{O}_3 \) mixing ratios across all three sites.

When comparing afternoon data for a given temperature, there are enhancements of 10 ± 2 ppbv, 12 ± 3 ppbv, and 4 ± 2 ppbv \( \mathrm{O}_3 \) at BAO, ROMO and WALD respectively. \( \mathrm{O}_3 \) enhancements across all three sites, across an approximate urban to
5 Conclusions

Here we report a time series of detailed gas-phase ground measurements in the northern Colorado Front Range during summer 2015. Clear anomalies in CO and PM$_{2.5}$ showed that aged wildfire smoke was present at ground-level during two distinct periods (6 – 10 July and 16 – 30 August) for a total of nearly three out of the nine weeks sampled. This smoke from wildfires in the Pacific Northwest and Canada impacted a large area across much of the central and western U.S., and was several days old when it was sampled in Colorado. This wildfire smoke mixed with anthropogenic emissions in the Front Range, resulting in significant changes in the abundances of O$_3$ and many of its precursor species. Our measurements are unique because of 1) the length of time we sampled this smoke-impacted anthropogenic air mass, and 2) the detailed composition information that was collected.

During the smoke-impacted periods we observed significantly increased abundances of CO, CH$_4$, and several VOCs with OH oxidation lifetimes longer than the transport time of the smoke. We measured significant decreases in several of the most reactive alkene species, indicating possible enhanced oxidation processes occurring locally. Mixing ratios of peroxyacyl nitrates and some alkyl nitrates were enhanced and peak abundances were delayed by 3-4 hours, but there was no significant change in HNO$_3$ mixing ratios or its diurnal cycle. During the longer August smoke-impacted period we observed significant increases in NO$_2$ mixing ratios just after sunrise and sunset. We did not observe any consistent shifts in wind direction or changes in wind speed that can explain the observed changes in composition, and the changes in abundances that we observed for a given species were generally present across all directions and speeds.

We observed significantly enhanced O$_3$ abundances of about 10 ppbv for any given temperature during both smoke-impacted periods. The enhancements during the August smoke-period led to very high surface O$_3$ levels; out of 6 high O$_3$ days at BAO during our study period, 2 were during the August smoke-period and were impacted by wildfire smoke. These enhancements were not due to higher temperatures, nor anomalous meteorological conditions. We found evidence of O$_3$ produced within the smoke plume during transit, with potentially enhanced local production as well due to enhanced oxidation capacity.
It is important to note that the presence of smoke does not always result in very high O₃ abundances. Many other factors contribute to the overall level of surface O₃, and smoke can also be associated with decreased O₃ at times, such as during the July smoke event described herein. Each smoke event has unique characteristics and thus it is important to study and characterize more events such as these in the future.

Wildfire smoke during these time periods most likely impacted atmospheric composition and photochemistry across much of the mountain west and great plains regions of the U.S. Given the BAO, Rocky Mountain and Walden research locations span an urban-rural gradient as well as a large altitudinal gradient, it is likely that both rural and urban locations impacted by this smoke could have experienced enhanced O₃ levels. Wildfires are increasing in both frequency and intensity throughout the western U.S. due to climate change and thus wildfire smoke events such as this one will likely play an increasingly prevalent role in degrading U.S. air quality.

**Author Contribution:** J. L. compiled and analysed the data, and wrote the manuscript. All authors participated in data collection at BAO and contributed to the writing of or provided comments on the manuscript.

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**References**


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Figure 1. Top panel: Time series of hourly PM\textsubscript{2.5} concentrations for the CDPHE CAMP air quality monitoring site (www.epa.gov/airdata) located in downtown Denver (39.75°, -104.98°). Bottom panel: Time series of hourly CO mixing ratios at the Boulder Atmospheric Observatory (BAO: 40.05°, -105.01°). Red shading denotes periods during which smoke is present at BAO.
Figure 2. Representative days during each smoke period observed at the Boulder Atmospheric Observatory (BAO: blue square). NOAA Hazard Mapping System (http://www.ssd.noaa.gov/PS/FIRE/) smoke polygons are plotted in grey with MODIS fire locations (http://modis-fire.umd.edu/index.php) from the previous day plotted as red triangles. The thin black lines show HYSPLIT back trajectories from the BAO site initiated 1000 m a.g.l. for each hour of the day plotted.
Figure 3. Significant changes (two sided Student’s t-test, 90% confidence interval) in hourly averaged mixing ratios of a subset of species measured at BAO between smoke-free periods and the 16 - 30 August smoke period. Significant increases during smoke-impacted periods compared to smoke-free periods are shown in red, significant decreases are in blue.

<table>
<thead>
<tr>
<th>Species</th>
<th>MDT Hour of Day</th>
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<tbody>
<tr>
<td>Carbon Monoxide (CO)</td>
<td></td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td></td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td></td>
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<tr>
<td>Propane (C₃H₈)</td>
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</tr>
<tr>
<td>2-Methylhexane (C₇H₁₆)</td>
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</tr>
<tr>
<td>3-Methylhexane (C₇H₁₆)</td>
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</tr>
<tr>
<td>Ethene (C₂H₄)</td>
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<tr>
<td>Propene (C₃H₆)</td>
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<tr>
<td>Isoprene (C₅H₁₀)</td>
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<td>Ethyne (C₂H₂)</td>
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<tr>
<td>Benzene (C₆H₆)</td>
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<tr>
<td>Methyl Nitrate (CH₃ONO₂)</td>
<td></td>
</tr>
<tr>
<td>Ethyl Nitrate (C₂H₅NO₃)</td>
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</table>

Figure 4. 95th percentiles of a) benzene and b) NO₂ as a function of wind direction for all data during smoke-free periods (black) and the August smoke period (red).
Figure 5. Average diurnal cycles in MDT of O$_3$ and oxidized reactive nitrogen species at BAO. Panels a), b), and c) compare average diurnal cycles from smoke-free time periods (black) to average diurnal cycles from the July smoke-impacted period (orange). Panels d) – h) show average diurnal cycles during the August smoke-impacted period (red) to the same average diurnal cycles from smoke-free periods (black). PAN and HNO$_3$ measurements were not available during the July smoke-impacted period.
Figure 6. Hourly O₃ data from BAO plotted against hourly temperature data show a positive correlation between temperature and O₃ abundances for both smoke-free time periods in grey and the August smoke-impacted time period in red. Overlaid are boxplots (5th, 25th, 50th, 75th, and 95th percentiles) for each 5 °C bin. On the left normalized histograms of the hourly O₃ data are plotted, with all smoke-free measurements in black, and all hourly measurements made during the August smoke-impacted period in red.
Figure 7. Maximum daily 8-hour average (MDA8) O₃ mixing ratios at BAO plotted in black with maximum daily temperature at BAO in blue. Orange and red boxes denote days that exceed 65 and 70 ppbv respectively.
Figure 8. Hourly O₃ versus temperature for a) BAO, b) the Rocky Mountain National Park long-term monitoring site, and c) the Arapahoe National Wildlife Refuge long-term monitoring site near Walden, CO. Plotted here are hourly afternoon data (12PM – 5PM MDT), with boxplots showing standard percentiles of 5 °C binned O₃ data the same as was shown in Figure 6.