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# **RESEARCH ARTICLE**

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#### **Key Points:**

- Anthropogenic VOC precursors dominate APN production when ozone is most elevated in the Colorado Front Range in summer 2015
- Propane and n-pentane, primarily from oil and natural gas emissions, drive elevated PPN/PAN ratios during high-ozone events
- Emissions from the oil and natural gas sector contribute to O<sub>3</sub> production on high O<sub>3</sub> days

#### **Supporting Information:**

• Supporting Information S1

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# Acyl Peroxy Nitrates Link Oil and Natural Gas Emissions to High Ozone Abundances in the Colorado Front Range During Summer 2015

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**Abstract** We present measurements of ozone (O<sub>3</sub>), acyl peroxy nitrates (APNs), and a suite of O<sub>3</sub> precursors made at the Boulder Atmospheric Observatory in Erie, Colorado, during summer 2015. We employ an empirical analysis of the APNs and a previously described positive matrix factorization of the volatile organic compounds (VOCs) to investigate the contribution of different VOC sources to high O<sub>3</sub> abundances at Boulder Atmospheric Observatory. Based on the ratio of peroxypropionyl nitrate (PPN) to peroxyacetyl nitrate (PAN), we find that anthropogenic VOC precursors dominate APN production when O<sub>3</sub> is most elevated. Propane and larger alkanes, primarily from oil and natural gas emissions in the Colorado Front Range, drive these elevated PPN to PAN ratios during high O<sub>3</sub> events. The percentage of OH reactivity associated with oil and gas emissions is also positively correlated with O<sub>3</sub> and PPN/PAN. Idealized box model simulations are used to probe the chemical mechanisms potentially responsible for these observations. We find that observed abundances of long-lived oil and natural gas-related VOCs are likely high enough such that the oxidation of these VOCs in a single photochemical day produces sufficient peroxy radicals to contribute to O<sub>3</sub> formation in the northern Colorado Front Range. Based on our empirical observations and box model simulations, we conclude that oil and natural gas emissions contribute to O<sub>3</sub> production on high O<sub>3</sub> days in this region during summer 2015.

#### 1. Introduction

Formed by the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides ( $NO_x$ ) and sunlight (Haagen-Smit & Fox, 1956; Sillman, 1999), tropospheric ozone ( $O_3$ ) negatively affects human health (e.g., Bates, 2005; Ito et al., 2005; Young et al., 1964), especially in sensitive populations such as children and the elderly, and has adverse effects on vegetation (Fowler, 1992). As such, ground-level  $O_3$  is regulated by the U.S. Environmental Protection Agency (EPA) as one of six key criteria pollutants, with the National Ambient Air Quality Standard recently revised to a 70 ppbv maximum 8-hr average (EPA, 2015).

The northern Colorado Front Range metropolitan area (NFRMA) has been in violation of the EPA National Ambient Air Quality Standard for O<sub>3</sub> since 2008 (CDPHE, 2009). Rapid population growth and increasing oil and natural gas development since the early 2000s have changed the quantity and distribution of emissions of many important O<sub>3</sub> precursors (e.g., Evans & Helmig, 2017; McDuffie et al., 2016). However, these emission sources are heterogeneously distributed across the NFRMA (Pfister, Reddy, et al., 2017). NO<sub>x</sub> (=NO + NO<sub>2</sub>) is emitted predominately from traffic and power generation, and in the NFRMA NO<sub>x</sub> is most abundant near major roadways and population centers (Wild et al., 2017; yellow lines and gray areas in Figure 1). These urban areas are also sources of aromatic hydrocarbons, hydrocarbons associated with traffic (e.g., ethyne), and industrial solvents, among other compounds (Swarthout et al., 2013). Oil and natural gas extraction operations in the Denver-Julesberg Basin are clustered in Weld Country around Greeley, Colorado, and extend into areas to the south and west that abut the northern Denver metropolitan area (blue dots in Figure 1). Oil and natural gas activities emit a range of alkanes and aromatic hydrocarbons (Gilman et al., 2013; Halliday et al., 2016; Pétron et al., 2012; Pétron et al., 2014; Thompson et al., 2014). Biogenic emissions from dispersed broadleaf trees throughout urban neighborhoods in the NFRMA contribute small amounts of isoprene, and needle-leaf forests in the Rocky Mountain foothills along the western edge of the NFRMA have been shown to emit small amounts of several alkene species (Rhew et al., 2017).

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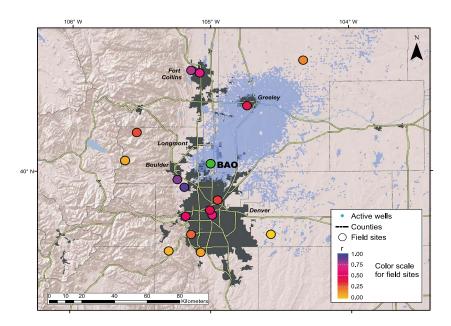


Figure 1. Positive correlations of maximum daily  $O_3$  at Boulder Atmospheric Observatory (BAO) with air quality monitoring sites in the Northern Colorado Front Range for the study period 11 July to 15 August 2015. Dark gray regions are urban areas, with yellow lines representing major roads and dotted lines delineating county boundaries. Small blue dots are the locations of active oil and natural gas wells. Large points are 14 CDPHE air quality monitoring sites, as well as the CASTNET Rocky Mountain National Park site and the NOAA Niwot Ridge location. These are sites that measure  $O_3$  and are colored by the correlation coefficient between daily maximum hour-averaged  $O_3$  mixing ratios the measured that location and BAO. For sites that routinely exceed the National Ambient Air Quality Standard (https://www.colorado.gov/airquality/html\_resources/ozone\_summary\_table.pdf; Rocky Flats N, NREL, Fort Collins West, Welch, Chatfield State Park, and Greeley Weld Tower), correlation coefficients with BAO are r = 0.77, 0.67, 0.76, 0.76, 0.76, 0.47, and 0.57, respectively.

Photolysis of  $NO_2$  is the only known mechanism for chemically producing  $O_3$  in the troposphere (Monks et al., 2015). Net  $O_3$  production occurs when NO is recycled back to  $NO_2$  without the subsequent destruction of  $O_3$ . Oxidation of VOCs offers a way to convert NO to  $NO_2$  while cycling  $HO_x$ , thereby propagating or catalyzing the formation of  $O_3$ . This formation of  $O_3$  is initiated by the reaction of OH with a VOC, which begins a process whereby  $NO_x$  is interconverted as the VOC oxidation products are further oxidized.

The hydroxyl radical (OH) is the primary daytime oxidant for most VOC species. The VOC OH reactivity (OHR) is then defined as the product of the rate constant associated with the reaction of a species with OH ( $k_{OH, VOC}$ ) and the concentration of that species. OHR provides information on which species are likely to initiate the catalytic  $O_3$  production cycle. OHR does not, however, give insight into how oxidation products of that VOC may propagate or terminate the  $NO_x$  and  $HO_x$  catalytic cycles.

The oxidation pathways of most VOCs are complex, and the fate of oxidation products (such as RO and RO $_2$  radicals) plays a large role in the extent to which the reactions supporting catalytic O $_3$  production continue or whether these cycles terminate. This leads to complex and nonlinear chemistry that is impacted by the relative abundances of NO $_x$  and VOCs. Reactions that terminate the cycling of NO $_x$  and HO $_x$  can be temporary or permanent sinks for these radical families and include the production of nitric acid, hydrogen peroxide, organic nitrates, and acyl peroxy nitrates (APNs; e.g., Farmer et al., 2011; Sillman et al., 1995; Thornton et al., 2002).

Acyl peroxy nitrates are secondary species that are formed concurrently with  $O_3$  from specific VOC precursors. Therefore, the relative abundances of different APN species offer important evidence for the extent to which their respective parent VOCs impacted the photochemistry of a given air mass. The most common APN, peroxyacetyl nitrate (PAN), also has the widest variety of VOC precursors (Fischer et al., 2014). Comparatively, two other commonly measured APNs, peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN), have more limited VOC precursors. PPN is formed from oxidation products of primarily anthropogenic VOCs (Roberts et al., 2001), and the main precursor of MPAN is isoprene, a primarily

biogenic species (Williams et al., 1997). APNs are only a temporary sink for  $NO_x$ , due to thermal dissociation. The effective thermal lifetime depends on the ratio of  $NO_2$  to NO in a given environment. APNs are also lost via dry deposition, photolysis, and reaction with OH; the rate constants for the reaction with OH differ substantially for individual APNs. Deposition in the nighttime boundary layer likely contributes to the low observed APN abundances overnight at Boulder Atmospheric Observatory (BAO). Thus, most of the variability in day-to-day daytime measured APN mixing ratios in the Front Range is due to local photochemical production or to the movement of different Front Range air masses toward BAO. One notable exception is the presence of wildfire smoke, which can contain substantial amounts of PAN (e.g., Lindaas et al., 2017).

In this study we explore the contribution of different VOC precursors to high  $O_3$  events at the BAO in summer 2015. We build upon previous measurements made at BAO during summer 2014 and report similar patterns in the relationships between measured APN species and  $O_3$ . We pair this analysis with a concurrently measured data set of 40+ VOCs (Abeleira et al., 2017) and examine the empirical relationships between different VOC sources,  $O_3$ , and APNs. Next, we present several idealized box model simulations to probe the underlying mechanisms for the empirical relationships we observe. Lastly, we use the box model to investigate the primary precursors of PPN and provide support for the hypothesis presented in Zaragoza et al. (2017) that alkane precursors dominate the production of APNs in the NFRMA.

# 2. Data and Methods

#### 2.1. Research Location and Data

During summer 2015 (1 July to 7 September 2015), a suite of trace gasses were measured at the BAO, located north of Denver, Colorado, in the middle of the northern Colorado Front Range (40.05°N, 105.01°W, 1584 m above sea level). Decommissioned in 2016, BAO had a long history of atmospheric trace gas and meteorological measurements (Gilman et al., 2013; Kelly et al., 1979). The suite of O<sub>3</sub> precursor species and photochemical products measured in summer 2015 included nitrogen oxides (NO and NO<sub>2</sub>), total reactive nitrogen (NO<sub>v</sub>), a set of 45 organic compounds (including selected alkanes, alkenes, C -C<sub>2</sub> halocarbons, alkyl nitrates, and several oxygenated VOCs), three APN species (PAN, PPN, and MPAN), CO, and CH4. These measurements were made by instruments housed in two trailers located at the base of the BAO tower with inlet heights of 6 m above ground level [agl]; all data are available at the National Oceanic and Atmospheric Administration (NOAA) website (https://esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/). Full details of the measurement techniques and instrument descriptions have been previously published in Abeleira et al. (2017) and Lindaas et al. (2017). O<sub>3</sub> data used in this analysis were collected by the NOAA Global Monitoring Division surface ozone network (data available at aftp.cmdl.noaa.gov/data/ ozwy/SurfaceOzone/BAO/). The inlet location was about 50 feet from the two trailers at 6 m agl on the BAO tower. A full description of the measurement technique used in the collection of these data is presented in McClure-Begley et al. (2014).

This analysis uses measurements from the period 11 July to 15 August 15. The days within the campaign study period but before and after 11 July to 15 August have been determined to be impacted by aged wildfire smoke (Lindaas et al., 2017). Data used in this analysis are further restricted in two ways. Analysis using the APN measurements is restricted to 18 July to 15 August because prior to this date the MPAN peak was compromised. Valid VOC measurements for this analysis were likewise restricted to 24 July to 14 August due to water issues in the gas chromatograph system (Abeleira et al., 2017).

#### 2.2. PMF Factors

Abeleira et al. (2017) characterized the VOC measurements made at BAO during summer 2015. They used positive matrix factorization (PMF) to differentiate multiple source classifications and to partition the species measured among these factors. For summer 2015 they identified six source factors: short-lived oil and gas, long-lived oil and gas, traffic, secondary, biogenic, and background.

Here we use the reconstructed time series of the summed OH reactivity (OHR) for these factors to investigate the empirical connections between these source classifications and our secondary species of interest,  $O_3$ , and the APNs. The reconstructed OHR time series was created by calculating the OHR of each species, using the time series of the reconstructed mixing ratios for that species, the temperature-dependent  $k_{\rm OH,\ VOC}$ , and the



ambient 10-m air temperature time series, and then aggregating the reconstructed OHR time series across all species in a given factor. For simplicity, we group the short- and long-lived oil and gas factors into one oil and gas factor and note that the biogenic factor solely consists of isoprene.

# 2.3. Box Model Setup

We use BOXMOX (Knote et al., 2015; https://boxmodeling.meteo.physik.uni-muenchen.de/online tools/ boxmox.html), an online extension to the Kinetic PreProcessor (Sandu et al., 2003), to investigate mechanisms that may be responsible for our empirical observations. We use the full set of equations from the Master Chemical Mechanism (MCM) version 3.3 (Emmerson & Evans, 2009; Jenkin et al., 2015) with fixed environmental parameters in a zero-dimensional framework to simulate idealized photochemistry in the Front Range, summarized in Table 1. The MCM explicitly simulates thousands of reactions and has been extensively used in past studies of urban photochemistry (e.g., Sommariva et al., 2011). For all simulations, we held the mixing height constant at 1 km and the ambient temperature at 300 K. The mixing height value is only used to guide the calculation of the immediate even mixing of chemical emissions. In this way the mixing ratio achieved by addition of emissions can be changed by either adjusting the emissions or the mixing height. Here we keep mixing height constant and adjust emissions to change abundances of relevant species, fully described below. No deposition, turbulent mixing, or entrainment/dilution parameters are included. The simulations are run for 8 hr at a 10-min time step. While we are not attempting to recreate specific high-O<sub>3</sub> events, 8 hr is roughly the length of the photochemically active part of 1 day, and it is long enough for us to test and compare mechanisms behind 1 day of photochemical O<sub>3</sub> production under different mixtures of O<sub>3</sub> precursors. We did test the sensitivity of our inferences to the length of time we ran the model for. The conclusions we draw from our 8-hr simulations are not changed when the model is run for 24 hr. Photolysis rates were calculated from the National Center for Atmospheric Research Tropospheric Ultraviolet and Visible (TUV; Madronich, 1992) radiation model for 40°N and 105°W, 1,700 m agl. The full set of TUV parameters are listed in Table S1 in the supporting information. The photolysis rates were held constant for the duration of each simulation.

Additionally, NO and  $NO_2$  emissions are added at each time step such that  $NO_x$  mixing ratios stay approximately constant throughout each simulation. The goal of this setting is to allow VOC oxidation to proceed under an approximately consistent  $VOC/NO_x$  regime in each simulation.

BOXMOX simulations are initialized with four different VOC mixtures. The four mixtures include a baseline mixture ("baseline"), a high oil and natural gas influenced mixture ("high ONG"), a high traffic influenced mixture ("high traffic"), and a high biogenic mixture wherein a small quantity of isoprene (3  $\times$  10<sup>11</sup> molec·cm<sup>-2</sup>·s<sup>-1</sup>) was emitted into the box at every time step to keep isoprene approximately constant throughout the simulation ("isoprene addition"). Initial mixing ratios in the "baseline" are initialized with the median value of every measured VOC for the measurement period between daytime hours of 10 a.m. to 6 p.m. MDT, while the three other mixtures are created by adding the mixing ratio equivalent of  $0.5 \, \mathrm{s}^{-1}$ of OH reactivity, distributed among respective sets of species, to the baseline initial conditions. Thus, the high ONG mixture has an additional 0.5 s<sup>-1</sup> of OHR, achieved by proportionately increasing the initial mixing ratios of species that were unambiguously factored into the combined oil and gas PMF factor in Abeleira et al. (2017). Accordingly, species that are predominately associated with the traffic PMF factor are proportionately increased by  $0.5 \, \mathrm{s}^{-1}$  OHR mixing ratio equivalent to create the high-traffic mixture. VOCs that were not measured at our research location were initialized in all simulations to 0 ppbv. We recognize that this decision means we are missing potentially important sources of OHR. However, we measured many of the most abundant VOCs (Abeleira et al., 2017), and a full representation of all possible species is not needed for our primary goal: to investigate chemical mechanisms that may underpin our empirical observations. APNs and alkyl nitrates were also not given initial concentrations, meaning the presence of these species in the output of the simulations is solely due to secondary production.

Values for all initial mixing ratios of species present in each mixture are summarized in Table 1. Species that were not unambiguously factored into a single PMF factor are initialized at constant mixing ratios across the simulations. These species are listed at the bottom of Table 1 (mixed source species). This is a limitation to our approach, because we expect there to be influences from certain sectors on their abundances. For example, of the VOCs measured in summer 2015, acetaldehyde is the largest contributor to OHR (17%). Several of



Table 1 Initial Conditions for All BOXMOX Simulations

	Baseline	High ONG	Isoprene addition	High traffic
Temperature		300		
Mixing Height		1000		
Deposition	NA			
Turbulent Mixing	NA			
Entrainment	NA _			
Photolysis Rațes	constant, from TUY <sup>a</sup>			
NO emissions <sup>b</sup> NO <sub>2</sub> emissions <sup>b</sup>	$3 \times 10^{11}$ molec·cm <sup>-2</sup> ·s <sup>-1</sup>			
NO <sub>2</sub> emissions <sup>b</sup>	$3 \times 10^{11} \text{ molec} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ $3 \times 10^{10} \text{ molec} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$			
Isoprene emissions	0	0	0	
•	Ü	Ç	$3 \times 10^{11} \text{ molec·cm}^{-2} \cdot \text{s}^{-1}$	v
NO <sup>b</sup> .		0.5 p	nhv	
NO <sub>2</sub> <sup>b</sup>	1 ppbv			
$O_3$		50 ppbv 1%		
$H_20$		1,900 ppbv		
CH <sub>4</sub>				
CO	110.9 ppbv			
M	1e9 ppbv			
$N_2$	78.084%			
$O_2$	20.946%			
ОН	0 ppbv			
Initial $\Sigma$ OHR <sub>voc</sub> (s <sup>-1</sup> )	1.58	2.08	2.08	2.08
Oil and natural gas species (ppbv)				
	Baseline	High ONG	Isoprene addition	High traffic
Ethane	5.4	12.5	5.4	5.4
Propane	2.39	5.5	2.39	2.39
i-butane	0.41	0.96	0.41	0.41
n-butane	1.0	2.32	1.0	1.0
i-pentane	0.9	2.08	0.9	0.9
-	0.71		0.71	0.71
n-pentane		1.64		
n-hexane	0.1	0.23	0.1	0.1
Cyclohexane	0.053	0.12	0.053	0.053
2-methylhexane	0.024	0.056	0.024	0.024
n-heptane	0.042	0.097	0.042	0.042
n-octane	0.021	0.049	0.021	0.021
cis-2-butene	0.016	0.037	0.016	0.016
Benzene	0.091	0.211	0.091	0.091
Traffic species (ppbv)				
Traine species (ppov)	Baseline	High ONG	Isoprene addition	High traffic
Toluene	0.111	0.111	0.111	2.07
Ethylbenzene	0.012	0.012	0.012	0.22
Ortho-xylene	0.015	0.015	0.015	0.28
Ethyne	0.14	0.14	0.14	2.61
3-methylhexane	0.02	0.02	0.02	0.372
Š				
Biogenic species (ppbv)	Baseline	High ONG	Isoprene addition	High traffic
Isoprene	0.167	0.167	0.167	0.167
•				
Mixed source species (ppbv)	Baseline	High ONG	Isopropa addition	High troffic
		riigii ONG	Isoprene addition	High traffic
Ethene	0.123	0.123	0.123	0.123
Propene	0.035	0.035	0.035	0.035
Acetaldehyde	1.915	1.915	1.915	1.915
Acetone	3.16	3.16	3.16	3.16
MEK	0.344	0.344	0.344	0.344
CH <sub>2</sub> Cl <sub>2</sub>	0.021	0.021	0.021	0.021
CHCl <sub>3</sub>	0.021	0.021	0.007	0.021

Note. All environmental parameters and  $NO_x$  emissions were held constant throughout the simulations, which were run for 8 hr at 10-min time steps. Initial conditions for the simulations are given for a  $NO_x$  scaling factor of 1.  $^aTUV$  input parameters given in Table S1.  $^bMultiply$  by the  $NO_x$  scaling factor if needed.



the alkanes are precursors for acetaldehyde (Millet et al., 2010), but the background and secondary factors in Abeleira et al. (2017) accounted for the majority of this species.

We compared the NO<sub>2</sub>/NO ratio in our simulations to that observed at BAO. For all of our simulations, the initial NO2/NO ratio was ~2, but the NO2/NO ratio adjusts within 2-3 time steps (10 min each) to a level consistent with the average ratio of the BAO field measurements (~5). OH concentrations in all simulations were also similar to those measured in the NFRMA during the Front Range Air Pollution and Photochemistry Experiment aircraft campaign in summer 2014 (Ebben et al., 2017). Additionally, we tested the sensitivity of each simulation to NO<sub>x</sub> by running each VOC mixture with a series of five NO<sub>x</sub> scaling factors: 0.25, 0.5, 1, 2, and 3. With all other initial conditions held constant, both the NO and NO2 initial conditions and NO and NO<sub>2</sub> emissions at each time step are multiplied by the given NO<sub>x</sub> scaling factor (i.e., a simulation run with a NO<sub>x</sub> scaling factor of 2 contains twice as much NO<sub>x</sub> as a simulation run with a scaling factor of 1). At the original level of NO<sub>x</sub> (NO<sub>x</sub> scaling factor of 1), we find that our simulations are close to peak O<sub>3</sub> production efficiency. For NO<sub>x</sub> scaling factors of 0.5 and 2, O<sub>3</sub> production does not change significantly, but for a factor of 3 increase or decrease in NO<sub>x</sub> (scaling factors of 3 and 0.25), we find much less efficient O<sub>3</sub> production in all simulations. Abeleira and Farmer (2017) used an empirical analysis to find that O<sub>3</sub> production in the northern Colorado Front Range is likely near peak O<sub>3</sub> production efficiency. Though their analysis was specific to the Denver metro area and spatial heterogeneity likely exists in the O<sub>3</sub> production efficiency across the northern Colorado Front Range, our conclusions are not affected by changing the  $NO_x$  scaling factor by a factor of 2. Thus, we use a  $NO_x$  scaling factor of 1 in all simulations discussed in this paper.

# 3. Empirical Results

#### 3.1. Spatial Variability in NRFMA O<sub>3</sub> and Its Precursors

Strong spatial gradients in emissions and meteorology in the NFRMA make this region particularly heterogeneous (Pfister, Reddy, et al., 2017). The sources of  $O_3$  precursors differentially impact ground-level  $O_3$  across the Front Range. Denver and surrounding suburban and industrial areas (large gray area in Figure 1) are characterized by large  $NO_x$  emissions and certain VOC emissions. Outside of Denver and its suburbs there are also several more disperse population centers (e.g., the cities of Boulder, Longmont, Fort Collins, and Greeley), and oil and natural gas production closely border, if not overlap these population centers (small blue dots in Figure 1). Though likely less relevant for  $O_3$  production, agricultural activities are also a major source of atmospheric compounds in the Front Range (Eilerman et al., 2016; Tevlin et al., 2017; Townsend-Small et al., 2016). Recirculation and upslope-downslope regimes mix these sources of emissions throughout the NFRMA (Pfister, Reddy, et al., 2017; Sullivan et al., 2016; Vu et al., 2016).

The BAO was located north of the Denver urban area and at the southeast corner of the region with the most dense oil and gas development. This site has hosted a variety of recent field experiments focused on atmospheric chemistry and air quality. For example, in situ observations from this location have been used to investigate specific aspects of nighttime chemistry (Brown et al., 2013), the relative importance of different sources on VOC abundances in the Colorado Front Range (e.g., Abeleira et al., 2017; Gilman et al., 2013; Pétron et al., 2014; Swarthout et al., 2013), and the impact of oil and gas emissions on summertime O<sub>3</sub> chemistry in this region (McDuffie et al., 2016). Recent measurements near BAO in Erie, Colorado, indicate that atmospheric composition near BAO is similar to other sites throughout the northern Colorado Front Range in the types of species present and their relative abundances (Thompson et al., 2014). Analogously, we find that O<sub>3</sub> measurements at BAO are positively correlated with O<sub>3</sub> measurements across the Front Range. Figure 1 shows the correlation coefficient (r) of the relationship between daily maximum hour-averaged O<sub>3</sub> mixing ratios at BAO and daily maximum 1-hr averaged O<sub>3</sub> mixing ratios at 14 CDPHE air quality monitoring sites as well as the CASTNET Rocky Mountain National Park site and the NOAA Niwot Ridge location. Correlation coefficients >0.6 exist for most sites along the Denver to Fort Collins corridor, with lower correlations between BAO and further afield sites such as rural Weld County and east Aurora. Variability of O<sub>3</sub> abundances is also similar at BAO as compared to other sites. Specifically, the standard deviation in maximum hourly O<sub>3</sub> mixing ratios at BAO (10.5 ppbv) is comparable to the median standard deviation (9.9 ppbv) of all locations, and it is also within the range of standard deviations (5.5-12.2 ppbv) at other Front Range locations.

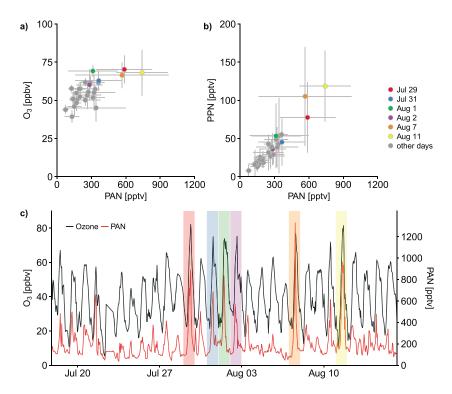


Figure 2. Relationship between (a)  $O_3$  and peroxyacetyl nitrate (PAN) and (b) peroxypropionyl nitrate and PAN. Points represent afternoon (12 p.m. to 6 p.m. MDT) average mixing ratios for each day during the study period. Error bars indicate +/-1 standard deviation. (c) Time series of  $O_3$  in black and PAN in red. The colors of the rectangular shading denote the corresponding days in panels (a) and (b).

# 3.2. Ozone and APNs

APNs are considered to be excellent tracers of photochemical activity because they are not directly emitted (Fischer et al., 2014). Prior work based on observations from summer 2014 showed that APN species at BAO are good tracers of local photochemistry (Zaragoza et al., 2017). Conversely, periods of elevated  $O_3$  driven by long-range transport or a large contribution of  $O_3$  from the upper troposphere in 2014 were not found to be associated with elevated APNs (Zaragoza et al., 2017). During summer 2015, we do not find any days in our study period that display evidence of long-range transport or stratospheric intrusion. Significant periods during our measurement campaign were influenced by wildfire smoke (Lindaas et al., 2017), including several days with high  $O_3$ , but these periods are not included in this analysis.

Similar to prior measurements at BAO and other locations, Figure 2a shows a positive relationship  $(R^2=0.51)$  between afternoon average (12 p.m. to 6 p.m. MDT)  $O_3$  and PAN mixing ratios over the study period. Zaragoza et al. (2017) also found a strong relationship between PPN and PAN, and Figure 2b indicates a similar strong relationship during summer 2015 ( $R^2=0.93$ ). The ratio of PPN to PAN can tell us about the precursors that dominated the secondary production preceding a given measurement (Roberts et al., 1998). Zaragoza et al. (2017) hypothesized that PPN/PAN ratios >0.15 were indicative of alkane-dominated photochemistry in the Front Range, and we discuss this further in later sections. Figure 2c presents the time series of hourly average  $O_3$  and PAN mixing ratios for summer 2015. The shaded colors designate 6 days with the highest maximum hourly average  $O_3$  abundances. These same colors are used to denote the corresponding points in panels (2a) and (2b). These 6 days are not only among the days with the highest daily average  $O_3$  but are also associated with hourly PAN mixing ratios >500 pptv. Similar to the observations from summer 2014 (Zaragoza et al., 2017), we again find that MPAN is closely correlated with PAN ( $R^2=0.69$ ) and PPN ( $R^2=0.72$ ) as well, but the absolute mixing ratios we observe (afternoon mean = 8.3 pptv) are low compared to other regions, such as the southeastern or northeastern United States, which have larger isoprene emissions (e.g., Roberts et al., 1998, 2003, 2007).

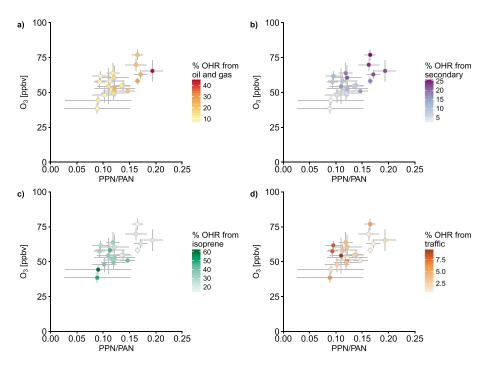


Figure 3. Afternoon (12 p.m. to 6 p.m. MDT) average  $O_3$  mixing ratios versus the ratio of peroxypropionyl nitrate (PPN) to peroxyacetyl nitrate (PAN) at Boulder Atmospheric Observatory for each day during the study period. Error bars indicate +/-1 standard deviation. Points are colored by (a) the percentage of total calculated hydroxyl radical reactivity (OHR) from the oil and natural gas positive matrix factorization (PMF) factor; (b) the percentage of total calculated OHR from the secondary PMF factor; (c) the percentage of total calculated OHR from the biogenic PMF factor, which consists exclusively of isoprene; and (d) the percentage of total calculated OHR from the traffic PMF factor.

#### 3.3. Ozone, PPN/PAN, and VOCs

We observe a positive relationship between afternoon average (12 p.m. to 6 p.m. MDT)  $O_3$  mixing ratios and the ratio of PPN/PAN ( $R^2 = 0.41$ ; Figure 3), suggesting that there is increasing influence from PPN precursors when  $O_3$  abundances are higher in the Front Range. The colors in Figure 3 designate the percentage of total calculated VOC OH reactivity (OHR) from various PMF VOC factors identified by Abeleira et al. (2017); see section 2.3. This percentage is calculated as the sum of OHR for individual species in the factor divided by the summed OHR across all species in all factors. Figure 3a shows that when the PPN/PAN ratio is high, the percentage contribution of oil and gas OHR to total OHR is also high. Conversely, Figure 3c shows that when PPN/PAN is low, the percentage contribution of biogenic species (largely isoprene) to OHR is high. The ratio of MPAN/PAN is also anticorrelated with  $O_3$ , following the same pattern as the percentage of biogenic OHR. Other measured secondary species such as alkyl nitrates that are included in the secondary factor are positively correlated with PPN/PAN (Figure 3b). This is to be expected, given this group of secondary species predominately have alkane precursors. Lastly, the percentage of OHR attributed to traffic shows no relationship with PPN/PAN and is consistently below 10% of the total estimated OHR (Figure 3d).

While these observations support the conclusion that oil and natural gas emissions make an important contribution to high  $O_3$  abundances at BAO, it is clear that the variability in PPN/PAN and OHR from the oil and gas factor do not explain all of the variability in  $O_3$  mixing ratios. Meteorological factors such as temperature, relative humidity, and stagnation events have been shown to drive variability on multiple time scales in the NFRMA (Reddy & Pfister, 2016) and other regions (e.g., Camalier et al., 2007; Jacob et al., 1993; Sillman & Samson, 1995). We do not find a relationship between mean afternoon air temperatures or mean afternoon relative humidity measured at BAO and mean afternoon  $O_3$  abundances during our time period. We do, however, find a negative relationship between mean afternoon wind speed and mean afternoon  $O_3$  ( $R^2 = 0.52$ ), such that lower wind speeds are linked to high  $O_3$  and vice versa. These low wind speed days likely exhibit lower ventilation or stagnation. This relationship is strong enough to explain some of the

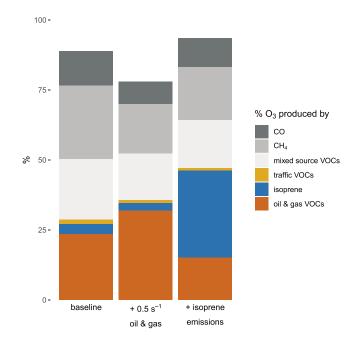


variability unexplained by PPN/PAN. This is not necessarily inconsistent with our inferences based on atmospheric composition made above; under more calm conditions emissions would have time to build up and react, increasing the potential for oil and gas emissions to contribute to O<sub>3</sub> production. Lower wind speeds are typical of mountain-valley circulation patterns, which often drive local circulation during summer high-pressure events in the NFRMA (Vu et al., 2016).

Another factor that may contribute to variability in measured surface mean afternoon O<sub>3</sub> is the residual O<sub>3</sub> from the previous day. O<sub>3</sub> produced during the previous day persists in the residual layer and can be entrained into the planetary boundary layer the next day as it develops. This residual O<sub>3</sub> will then influence the "starting" mixing ratio as O<sub>3</sub> production begins. There can be considerable variability in this residual O<sub>3</sub> (McDuffie et al., 2016), but without coincident O<sub>3</sub> LIDAR measurements at BAO such as those during summer 2014 (Wang et al., 2017), it is difficult to estimate. We also expect that PAN and PPN will remain aloft in the residual layer and that they are likely also entrained into the planetary boundary layer during the next day. Thus, we acknowledge this as a source of variability, but we lack the tools to effectively separate out the O<sub>3</sub> or PAN production from the current day from the residual O<sub>3</sub> or PAN component. There are other sources that would contribute to variability in either the PAN or O<sub>3</sub> mixing ratios observed at BAO. APN species and O<sub>3</sub> are produced concurrently in the air mass as it is transported to BAO and reflect the chemistry influenced by the same mixtures. However, it is possible that the air masses reaching BAO started with low NO<sub>x</sub> abundances and high VOC mixing ratios. This would be likely for air masses that originated in Weld County, outside of the city of Greeley. En route to BAO, there are multiple opportunities for fresh NO<sub>x</sub> emission to be injected into traveling air masses. The changing ratios of NO/NO<sub>2</sub> will affect the thermal lifetime of APNs, as discussed in section 1. In short, there is ample heterogeneity in O<sub>3</sub> and APN precursors to contribute to scatter in the APN-O<sub>3</sub> relationship that is observed at BAO.

It is also worth noting several possible complications to using the mean afternoon estimated PMF factor percentage contributions to total OHR (i.e., VOC measurements made at the same time as O<sub>3</sub> and APNs) as the basis for supporting the conclusions reached by the APN and O<sub>3</sub> relationship analysis. While the VOCs measured in the afternoon may represent different mixtures from those that influenced earlier photochemistry. A possible method for addressing this potential issue could be to use VOC measurements from earlier in the day. However, in that case one must assume that the earlier measurements represent the same air mass and the same emission sources as the air mass measured in the afternoon. We know that there is considerable recirculation in the NFRMA and that complex circulation patterns are common (Sullivan et al., 2016; Vu et al., 2016). Thus, this assumption may not be valid. A more conservative assumption is that the coincident afternoon VOC mixture reflects the same mixture that produced O<sub>3</sub> and APNs, though short-lived species may no longer be present. Very short lived VOCs may contribute to the photochemistry of the air masses en route to BAO, but these VOCs may not have been quantified at BAO because they were also consumed en route. For example, isoprene has a lifetime on the order of an hour (for [OH] = 10<sup>6</sup> molec/cm<sup>3</sup>) and a light and temperature dependent emission rate (Guenther et al., 2006). Isoprene could have been emitted into an air mass en route to BAO but may have been oxidized before the air mass reaches BAO. However, this oxidization of isoprene would likely produce MPAN, and the very low MPAN abundances observed at BAO do not support the hypothesis that isoprene abundances are large in the region.

Our inference that oil and gas emissions significantly influence high  $O_3$  mixing ratios at BAO is consistent with other recent research. McDuffie et al. (2016) combined observations from two summers (2012 and 2014) at BAO and employed the MCM box model to estimate the average contribution of oil and gas emissions to  $O_3$  production in summer 2014. They found that oil and gas emissions are responsible for about 17% of average local  $O_3$  production at BAO. It is important to note that this was an estimate of the average contribution, as McDuffie et al. (2016) did not have temporally collocated measurements available to make specific estimates during high  $O_3$  days in 2014. Evans and Helmig (2017) partitioned  $O_3$  measurements made over 4 years (2009–2012) at two Front Range locations by wind direction and observed that a majority of elevated  $O_3$  measurements were characterized by transport from areas with large oil and gas emissions. Cheadle et al. (2017) used measurements from three individual days in Greeley as case studies to show that a larger abundance of oil- and gas-related species is correlated with higher  $O_3$  mixing ratios. And lastly, regional chemical transport modeling conducted by NCAR as a follow up to the Front Range Air Pollution and Photochemistry Experiment indicates that oil and gas and traffic emissions generally make



**Figure 4.** Cumulative percentage contribution to  $O_3$  production by hydrocarbon group for the baseline, high ONG, and isoprene addition simulations, estimated via a local first-order sensitivity analysis over an 8-hr period. VOC = volatile organic compound.

the largest contributions to local O<sub>3</sub> production during summer 2014 in the NFRMA (Pfister, Flocke, et al., 2017).

# 4. Insights From Idealized Modeling

In this section, we turn to our set of idealized box model simulations to identify possible mechanisms responsible for our empirical results using an explicit chemical framework. For a simulation to be more useful for identifying possible relevant chemical mechanisms than the baseline simulation, it should meet two simple analogy criteria. (1) The initial conditions must be within the measurement ranges for all species, and (2) patterns in the simulated O<sub>3</sub> and APNs must be consistent with the empirical observations. In the empirical analysis outlined in sections 3.2 and 3.3, O<sub>3</sub> and the PPN/PAN ratio are positively related (Figure 3). Of our simulations, only the high ONG simulation meets both of these requirements. After adding  $0.5 \text{ s}^{-1}$  of OHR equivalent mixing ratios to the ONG species, their total initial mixing ratios still fell within the range of measured abundances. Compared to the baseline simulation, a larger ONG OHR in the high ONG simulation led to increased O3 production as well as an increase in the PPN/PAN ratio. These outcomes are consistent with the patterns observed in the measurements. Conversely, both the high traffic simulation and the isoprene addition simulation failed at least one of our analogy criteria. With 0.5 s<sup>-1</sup> of added traffic VOC OHR, the initial mixing ratios of traffic VOCs in the high traffic simulation were nearly an order of magnitude higher than the maximum abundances measured. And though

 $O_3$  production was higher than baseline, ratios of PPN/PAN did not increase. Thus, the high traffic simulation is less useful in interpreting the empirical results. As for the isoprene addition simulation, the initial conditions do fall within the bounds of the measurements. However, this simulation produces a lower PPN/PAN ratio compared to the baseline, and a much higher MPAN/PAN ratio. This pattern is inconsistent with the observations, which show that the MPAN/PAN ratio and the amount of isoprene observed at BAO are lower during high  $O_3$  events in summer 2015 compared to low- $O_3$  periods. This simulation may also be less useful for another reason. Isoprene mixing ratios in the boundary layer are unlikely to be well mixed because it has a shorter chemical lifetime than the likely mixing time for the boundary layer. Initial isoprene abundances and isoprene emissions best reflect surface observations, which are unlikely to represent a boundary layer mean. Thus, based on the application of our two criteria, the high ONG influenced mixture appears to be the most analogous to the observations during high- $O_3$  events at BAO in summer 2015.

To confirm that the increased  $O_3$  production in the high ONG simulation is driven by the increased abundances of ONG species, we employ a local first-order sensitivity test similar to that performed by Jin et al. (2008) in their investigation of a local high- $O_3$  episode in the Central Valley of California. In this sensitivity analysis the initial mixing ratios of each group of VOCs as well as CO and  $CH_4$  are perturbed by -10% in separate additional simulations. The difference in the final  $O_3$  abundances between the end of each sensitivity simulation and the original simulation is calculated and multiplied by 10 to approximate the total percentage contribution of that group of VOCs (or CO or  $CH_4$ ) to the overall  $O_3$  production in the original simulation. This estimate of the total contribution implicitly assumes the impact of each perturbation is linear, and in theory the sum of all percentage contributions will be 1. In practice, given the nonlinearity of  $O_3$  chemistry and the potential for interactions between species, this linearization of the effect is subject to small errors. However, we achieve greater than 80% closure of the overall  $O_3$  production for every simulation. Thus, this local first-order sensitivity analysis is a reasonable approximation of the contribution of each VOC factor to  $O_3$  production in each simulation.

Figure 4 presents the results of this sensitivity analysis for three mixtures: the baseline, the high oil and gas influenced mixture, and the isoprene addition simulation. As expected, the high ONG simulation displays a larger percentage contribution to  $O_3$  production from ONG species (~31% compared to ~23%), and the contribution from isoprene is highest in the isoprene addition simulation. For the reasons outlined above, the

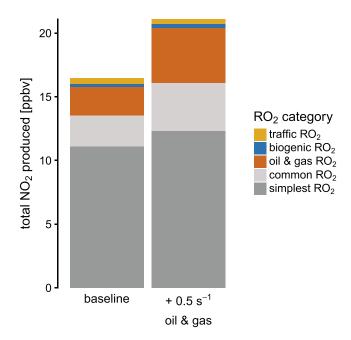


isoprene addition simulation is less representative of the observations and likely contains higher mixing ratios than would exist throughout the full boundary layer. Thus, the contribution from isoprene to O<sub>3</sub> production in the isoprene addition simulation is likely an upper bound, well in excess of the true contribution on high O<sub>3</sub> days. On the other hand, it is possible that the ONG species contribution estimate in the high ONG simulation could actually be a lower bound, given that full closure of O<sub>3</sub> production was not fully achieved by this sensitivity analysis and that the "mixed source VOCs" category includes secondary species such as acetaldehyde and methyl ethyl ketone (MEK) (see Table 1), which have oil- and natural gas-related precursors. For instance, the largest precursor of MEK in the Front Range is likely n-butane, which is largely emitted from oil and natural gas activities. Given that these secondary VOCs have other sources as well, they were not lumped with the group of VOCs we used to represent VOCs largely from oil and gas operations in the region. Traffic VOCs make only a small contribution to O<sub>3</sub> production (< 2%) in all simulations, which is consistent with the empirical observation of low overall percentage contributions of traffic VOCs to measured VOC OHR. CO and  $CH_4$  make significant contributions to O<sub>3</sub> production (8-12% and 17-26%, respectively) in each simulation, which reflects the combination of contributions from background abundances and their local sources in the NFRMA. A large fraction of the locally emitted CH<sub>4</sub> is likely from oil and gas sources, around 75% according to Pétron et al. (2014), but the high hemispheric background of CH<sub>4</sub> means that CH<sub>4</sub> from oil and gas sources contributes a relatively small fraction of the total O<sub>3</sub> production. In our simulations the contribution of the regional oil and gas emissions of CH<sub>4</sub> to total O<sub>3</sub> production is 2%. Overall, the local first-order sensitivity analysis confirms that ONG VOCs are responsible for the increased production of O<sub>3</sub> in the high ONG simulation, which is the most useful simulation for interpreting the observations.

To gain insight into the mechanism behind the increased contribution of ONG VOCs to  $O_3$  production, we tracked the production of peroxy radicals ( $RO_2$ ) by our different VOC factors.  $RO_2$  species have different parent VOCs, meaning that the relative abundance of certain  $RO_2$  species can offer insight into which parent VOCs are contributing the most to the rate-limiting step in  $O_3$  production. To investigate this, we calculate the relative contribution of different reaction pathways to the formation of  $NO_2$  (and thereby  $O_3$ ) by tagging  $RO_2$  species according to their precursors and then aggregating the rate at which they produce  $NO_2$  by PMF factor. In this way, we can use  $RO_2$  radicals as a lens into the contribution of different VOCs to  $O_3$  production in our simulations in addition to the first-order sensitivity analysis.

For each VOC associated with a given factor (oil and gas, traffic, or biogenic) we identify every RO<sub>2</sub> produced during the oxidation of that group of VOCs. RO2 radicals that react with NO to produce NO2 were then combined into one of five categories: (1) RO2 radicals that are formed solely from the precursors largely associated with oil and gas activities; (2) RO<sub>2</sub> radicals that are only produced from isoprene oxidation; (3) RO<sub>2</sub> radicals that are only produced from the oxidation of traffic-related precursors; (4) RO<sub>2</sub> radicals with VOC precursors in multiple factors (i.e., they are common products to species in different precursor classes); and (5) the three simplest RO<sub>2</sub> radicals (methyl peroxy, acetyl peroxy, and ethyl peroxy radicals), which are a subset of the common category of RO2 radicals but were not included in the common category, and often the most abundant RO<sub>2</sub> radicals. We separated out the simplest RO<sub>2</sub> to demonstrate that a large proportion of the RO<sub>2</sub> in all simulations exist as one of these simple  $C_1$ – $C_2$  alkyl peroxy radicals. Thus, we have classified all the RO2 in the simulations into five categories named "oil and gas RO2," "biogenic RO2," "traffic RO2," "common RO2," and "simplest RO2." As an example of a species in the common RO2 group, both propane and propene are potential precursors for HYPROPO2 (C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>) in the MCM, which is a propanol peroxy radical. Since propane is in the oil and gas factor and propene is not assigned to a specific factor, HYPROPO2 is classified as a common RO2. A total of 768 out of 1,130 peroxy radicals in the MCM have common precursors among the factors. To calculate the total production of NO2 via RO2 radical reaction with NO, and therefore gross O<sub>3</sub> production, we multiply the individual concentration of each RO<sub>2</sub> species in a given group by the concentration of NO and the rate constant for each time step. Lastly, we aggregate the results across all RO2 species in the group and across all time steps in the simulation. The final product is the integrated contribution of a given set of representative VOCs to the total gross production of NO2, and by extension O<sub>3</sub>, for a given simulation.

Figure 5 displays the results of this RO<sub>2</sub> categorization and calculation of total NO<sub>2</sub> production for the baseline and high ONG simulations. The high oil and gas mixture produces more RO<sub>2</sub> radicals specific to oil and



**Figure 5.** The sum of the  $RO_2$  reactions that generate  $NO_2$  for the baseline and high ONG 8-hr BOXMOX simulations, broken down by the precursor category of the  $RO_2$  radical. Traffic, biogenic, and oil and gas  $RO_2$  categories include  $RO_2$  radicals that are solely products of parent species within each representative group of volatile organic compounds (VOCs). Common  $RO_2$  radicals include those with precursors from multiple groups of precursor VOCs, and the simplest  $RO_2$  radicals consist of the methyl-, ethyl-, and acetyl- peroxy radicals, which are common products of all the VOCs.

gas as compared to the baseline simulation. The high oil and gas mixture also produces more NO<sub>2</sub> in general than the baseline, and proportionately more simple and common RO2 as well. Even though most of the individual trace gasses associated with the oil and gas activities (i.e., alkanes) have relatively low initial OHR, the abundances of these VOCs in the high ONG simulation are sufficient to create appreciable amounts of RO<sub>2</sub> radicals in a short period of time, in this case one photochemical day in the explicit MCM chemical framework. In this way, VOCs associated with the oil and gas activities appear to provide abundant opportunities to recycle NO<sub>x</sub> through RO<sub>2</sub> production at multiple stages of oxidation, thus enhancing O<sub>3</sub> production. One possible pathway for this could be through the thermal decomposition of alkoxy radicals (RO) into an aldehyde and alkyl radical, which readily participate in further oxidation. For small (≤3 carbon) RO, decomposition reactions are likely too slow as compared to reaction with O2 to be relevant. For larger RO, however, thermal decomposition may be an important reaction pathway (Calvert et al., 2008; Orlando et al., 2003), especially on warmer days given the temperature dependence. Thermal decomposition of RO is included in the MCM, but the relative rates of these reactions are difficult to extract and examine. We considered trying to track RO radicals in the BOXMOX simulations similar to how we tracked RO<sub>2</sub>. Naming conventions in the MCM make this difficult to do comprehensively as we have done for RO2 species. Further research into the relative importance of this oxidation pathway in mixtures with high alkane abundances would be useful.

Lastly, we can use the BOXMOX simulations to investigate which measured VOCs are the most dominant PPN precursors. As discussed above, nearly any VOC can serve as a precursor to PAN, though the yields vary

widely (Fischer et al., 2014; Roberts, 2008). In contrast, propanal is the main oxidation intermediate for PPN (Roberts et al., 2001, 2007). We test the sensitivity of PPN and PAN formation to a series of perturbations in individual precursors using the baseline simulation with a  $NO_x$  scaling factor of 1. We tested the sensitivity of PPN and PAN production to the full set of possible PPN precursors that were measured during the summer 2015 field campaign at BAO using a final set of simulations where the initial mixing ratio for each species was individually increased by 10% (Figures S1 and S2). All other precursors were set to the median mixing ratio observed during the campaign (the same as the baseline simulation). We find that propane and n-pentane are the dominant precursors for PPN in our simulations. Given that alkanes are attributed primarily to oil and gas activities in the NFRMA, these sensitivity results support the hypothesis that alkane emissions from oil and gas activities dominate the production of PPN and PAN in the NFRMA and are responsible for periods with high (>0.15) PPN/PAN ratios reported here and in Zaragoza et al. (2017).

# 5. Summary

Empirical observations and idealized box model simulations support the hypothesis that emissions from oil and gas extraction activities in the northern Colorado Front Range contribute to  $O_3$  photochemical production in the region. We have four main conclusions.

- 1. The highest mixing ratios of PAN occur on the same days with the highest abundance of  $O_3$ , and these periods of elevated secondary species are consistently associated with ratios of PPN/PAN > 0.15. Additionally, when  $O_3$  and the PPN/PAN ratio are most elevated, a large (25–45%) percent of the concurrently estimated VOC OHR is attributed to VOCs from oil and natural gas development. While a large percentage of VOC OHR from the oil and natural gas sector does not translate directly to  $O_3$  production, the colocation of high PPN/PAN ratios suggest that emissions of VOCs from oil and natural gas production contribute to high  $O_3$  days at BAO in summer 2015.
- 2. A larger percentage (30–60%) of the measured VOC OHR is attributed to isoprene when O<sub>3</sub> and PPN/PAN ratios are lower (<6 ppbv and <0.13). MPAN mixing ratios are also low, and MPAN/PAN



- ratios are anticorrelated with  $O_3$  abundance. This suggests that biogenic VOCs do not drive high  $O_3$  events at BAO in summer 2015.
- 3. Based on the observations, the high ONG BOXMOX simulation is the most similar of our simulations to photochemistry on high O<sub>3</sub> days during our study period because (A) the abundances of VOCs used to initialize that simulation are within the bounds of what we observed on high O<sub>3</sub> days and (B) the PPN/PAN ratio increased from the baseline simulation to this high ONG simulation consistent with observations of higher PPN/PAN ratios on days with high O<sub>3</sub>. It is clear in this simulation that even over a short period of time (i.e., one photochemical day) the oxidation of long-lived ONG VOCs with high abundances can still produce an appreciable amount of peroxy radicals. Thus, the idealized BOXMOX simulations support our empirical conclusion that VOCs from oil and natural gas activities contribute to O<sub>3</sub> production on high O<sub>3</sub> days. This is consistent with the findings from several other recent studies on O<sub>3</sub> in the northern Colorado Front Range using a variety of different methods (e.g., Cheadle et al., 2017; Evans & Helmig, 2017; McDuffie et al., 2016; Pfister, Flocke, et al., 2017).
- 4. Out of the VOC species that were measured, propane and several larger alkanes such as n-pentane are the dominant contributors to PPN production in the BOXMOX simulations. In the northern Colorado Front Range, these species predominately come from oil and natural gas sources (e.g., Abeleira et al., 2017; Gilman et al., 2013) and thus indicate that high ratios of PPN/PAN observed in the northern Colorado Front Range are driven by the oxidation of emissions from oil and natural gas production.

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