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The impact of wildfire smoke on ozone production in an urban area: insights from field observations and photochemical box modeling

Matthew Ninneman[a,*], Daniel A. Jaffe[a]

[a] School of Science, Technology, Engineering and Mathematics, University of Washington Bothell, 18115 Campus Way NE, Bothell, WA, 98011, USA
[*] Corresponding author. *E-mail address:* mn77@uw.edu

Abstract

This study examines the effect of wildfire smoke on ozone (O_3) production at an urban site in Bakersfield, CA. We used data from smoky and non-smoky weekdays in summer 2018. Median surface observations across the smoky and non-smoky weekdays showed that morning and afternoon O_3 concentrations were mainly affected by local photochemistry. Observed daytime median concentrations of O_3, particulate matter with diameters less than 2.5 µm ($PM_{2.5}$), and carbon monoxide (CO) were approximately 8 parts per billion (ppb), 8 micrograms per cubic meter (µg m^{-3}), and 40 ppb higher, respectively, on the smoky weekdays. The observed median sum of the daily-average concentrations of volatile organic compounds (ΣVOCs) was approximately 10 ppb greater on the smoky weekdays. Measured daytime median NO_x levels were almost identical on the smoky and non-smoky weekdays, indicating that the enhancement in NO_x due to smoke was negligible. We used the Framework for 0-D Atmospheric Modeling (F0AM) box model to examine the photochemical processes on the smoky and non-smoky weekdays. The maximum model-predicted instantaneous O_3 production rates (P_{O3}) were about 18 and 9 ppb h^{-1} on the smoky and non-smoky weekdays, respectively. Model sensitivity tests showed that (1) O_3 was sensitive to both NO_x and VOCs on the smoky weekdays, (2) aldehydes significantly affected O_3 formation when wildfire smoke was overhead, and (3) the O_3 production regime on the non-smoky weekdays was likely NO_x-saturated. Our results suggest that a combination of anthropogenic VOC and NO_x reductions will be the most effective strategy for decreasing O_3 on typical non-smoky days. In contrast, due to the high VOC levels in smoke plumes, only reductions in NO_x are expected to have a significant effect on lowering O_3 concentrations on typical smoky days.

Keywords: Wildfires, Smoke, Ozone, Volatile organic compounds, Nitrogen oxides, Box model

1. Introduction

Over the past two decades, the annual area burned in the U.S. by wildland fires has increased dramatically. Data from the National Interagency Fire Center (www.nifc.gov) show that there have been 10 years with more than 3.2 million hectares (ha) burned since 1960, and all have occurred since 2004. The U.S. currently experiences a strong fire season (i.e., more than 3.2 million ha burned) approximately every other year. This increase in wildfire activity is due to climatological factors (e.g., drought, higher summertime temperatures, earlier snowmelt, etc.), forest management, and human ignitions (Aldersley et al., 2011; Balch et al., 2017; Decker et al., 2019; Dennison et al., 2014; Kitzberger et al., 2007; Littell et al., 2009; Miller and Safford, 2012; Westerling et al., 2006). Since wildfires are expected to increase in the future (Moritz et al.,

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2012; Pechony and Shindell, 2010; Spracklen et al., 2009; Val Martin et al., 2015), it is essential to understand how they impact urban air quality and photochemistry.

Wildfires emit large but highly variable amounts of carbon monoxide (CO), particulate matter with diameters less than 2.5 µm ($PM_{2.5}$), volatile organic compounds (VOCs), and oxides of nitrogen (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)); except for $PM_{2.5}$, all are ozone (O_3) precursors (Akagi et al., 2011; Andreae, 2019; Lindaas et al., 2020). Emissions from these fires have had major air quality implications. Laing and Jaffe (2019) show that fires in 2017 and 2018 led to millions of Americans being exposed to some of the highest-ever $PM_{2.5}$ concentrations measured in the U.S. Many sites had daily-average $PM_{2.5}$ concentrations exceeding 500 µg m^{-3}. McClure and Jaffe (2018a) found that smoke from these fires was changing the general long-term downward trend in $PM_{2.5}$ to an upward trend for the policy-relevant 98th percentile days in much of the western U.S. Gong et al. (2017) found that smoke can increase the maximum daily 8-hour average (MDA8) O_3 by up to 40 ppb at some locations, often leading to an exceedance of the O_3 National Ambient Air Quality Standard (NAAQS) of 70 ppb.

Due to large variations in the emissions, plume injection heights, and photochemical processing associated with wildfires, it is challenging to use regional and global air quality models to examine the effect of wildfire smoke on urban O_3 production. Typical Eulerian grid models cannot capture the detailed and rapid photochemical processes that occur in a smoke plume. The most common problem in these applications appears to be significant over-production of O_3 due to rapid plume dilution into a model grid cell or an inadequate chemical mechanism (e.g., Zhang et al., 2014; Baker et al., 2016; Lu et al., 2016). Model underpredictions have also been reported in a few cases (e.g., Singh et al., 2012; Cai et al., 2016). These underpredictions are likely due to modeled meteorology failing to transport smoke to the receptor location and/or inadequate fire emissions.

Due to the difficulty in modeling smoke-produced O_3, several studies have used observational analyses (e.g., Buysse et al., 2019; Dreessen et al., 2016; Lindaas et al., 2017; McClure and Jaffe, 2018b; Rubio et al., 2015) or statistical modeling (Jaffe et al., 2004, 2013; Lu et al., 2016; Gong et al., 2017; McClure and Jaffe, 2018b) to analyze O_3 from fire precursors. Buysse et al. (2019) assessed the impact of wildfire smoke on O_3 in 18 western U.S. cities using surface observations of $PM_{2.5}$, NO_x, and O_3. They also used the NOAA Hazard Mapping System Fire and Smoke Product (HMS FSP) to detect overhead smoke influence. They found that $PM_{2.5}$ and O_3 were usually enhanced on days with smoke, while NO_x did not exhibit a consistent enhancement. However, $PM_{2.5}$ and O_3 on smoke days were nonlinearly related, with O_3 increasing at low to moderate $PM_{2.5}$ concentrations, reaching a maximum when $PM_{2.5}$ concentrations were approximately 30-50 µg m^{-3}, remaining enhanced up to $PM_{2.5}$ concentrations of about 100 µg m^{-3}, and decreasing at higher $PM_{2.5}$ concentrations. The authors also found that the morning rate of O_3 increase (dO_3/dt) was higher and the NO/NO_2 ratios were lower on smoke-influenced days (Buysse et al., 2019). These results suggest that the elevated O_3 on smoke-influenced days in urban areas is likely a result of enhanced in-situ photochemical production, rather than direct transport of O_3 already in the smoke plume.

Statistical modeling identifies the relationship between O_3 and meteorological variables (temperature, winds, humidity, etc.) for non-smoke days (e.g., Camalier et al., 2007) and then uses this relationship to examine observed O_3 on days with and without smoke. This approach has been used in numerous studies to quantify the additional amount of O_3 produced by fire precursors (e.g., Jaffe et al., 2004, 2013; Lu et al., 2016; Gong et al., 2017; McClure and Jaffe,

2018b). This method is also considered acceptable for quantifying smoke impacts on surface O_3 for exceptional event demonstrations (U.S. EPA, 2016). A typical approach uses Generalized Additive Models (GAMs), which are a form of machine learning. Using GAMs, Gong et al. (2017) found that MDA8 O_3 values were on average 3-8 ppb higher on smoke days in eight western U.S. urban areas, with a maximum O_3 enhancement due to wildfire precursors of 40 ppb. The authors also found that 19% of the days with MDA8 O_3 exceeding 75 ppb were influenced by smoke, even though smoke days comprised only a small fraction (4.1%) of all days analyzed (Gong et al., 2017). However, while this approach can provide an estimate of the additional O_3 due to fire emissions, it does not provide much information about the O_3 formation mechanisms or factors controlling O_3 production.

Given the challenge of modeling smoke photochemistry with grid models, several studies have applied 0-D photochemical box models to this problem (Mason et al., 2006; Alvarado et al., 2015; Müller et al., 2016; Coggon et al., 2019; Decker et al., 2019). Although there are differences in the methodologies, each of these studies was reasonably successful at modeling O_3 production in a smoke plume. Key to this success was the ability to link the model to emission data and to use a chemical mechanism that captured the essential chemical features. Despite these successes, to our knowledge, this method has not been applied to smoke in urban areas, where O_3 exceedances have significant regulatory implications.

O_3 production is sensitive to either VOCs, NO_x, or both, and O_3 control strategies have focused on reducing the concentrations of the limiting reagent. Regions with a high VOC/NO_x ratio are in a NO_x-sensitive O_3 production regime, and regions with a low VOC/NO_x ratio are in a NO_x-saturated O_3 production regime (e.g., Sillman, 1999; Farmer et al., 2011; Pusede and Cohen, 2012; Qian et al., 2019). Emissions from wildland fires have relatively high VOC/NO_x ratios (e.g., molar ratios of 25-100; Akagi et al., 2011; Andreae, 2019), so these emissions can be particularly important when mixed into a NO_x-rich urban area. Overall, correctly diagnosing the O_3 production environment during smoke-influenced periods is important when assessing the impact of smoke on O_3 in an urban area. We also note the importance of weekday/weekend differences in NO_x concentrations on O_3 production (Baidar et al., 2015; de Foy et al., 2020).

To address the research gaps highlighted above, we investigated the effect of wildfire smoke on O_3 production at an urban site in Bakersfield, CA. To avoid complications due to weekday/weekend effects, we examine O_3 production on smoky and non-smoky weekdays in summer 2018. The analysis was performed using a combination of surface measurements and a 0-D photochemical box model.

2. Materials and Methods

The Bakersfield Municipal Airport site (BMA; 35.33 °N, 119.00 °W; AQS ID 060292012) is located in the city of Bakersfield, California, and it is operated by the San Joaquin Valley Unified Air Pollution Control District. Some of the measurements made at BMA include O_3, carbon monoxide (CO), oxides of nitrogen (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)), a suite of approximately 50 volatile organic compounds (VOCs), air temperature (T_{air}), barometric pressure (BP), and relative humidity (RH). Since particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) is not measured at BMA, $PM_{2.5}$ data from the California Avenue site (35.36 °N, 119.06 °W; AQS ID 060290014) were used. The California Avenue site is located approximately 6 km to the northwest of BMA, and it is operated by the California Air Resources Board.

Measurements of the above parameters were used to help investigate the impact of wildfire smoke on morning (6:00-11:00 LST) and afternoon (11:00-17:00 LST) O_3 formation at BMA during summer (July-August) 2018. Hour-averaged O_3, CO, NO_x, $PM_{2.5}$, T_{air}, BP, and RH data were obtained from EPA AirNow-Tech (https://www.airnowtech.org/). Daily-averaged speciated VOC data collected by canisters every three hours were retrieved from the EPA Air Data system (https://www.epa.gov/outdoor-air-quality-data). While the VOC data are typical for state monitoring systems, it should be noted that wildfire smoke contains hundreds of VOCs that are not usually measured in this network. Thus, it is likely that VOC concentrations are significantly underestimated for the smoke days.

The effect of wildfire smoke on O_3 production at BMA was assessed using data collected on 13 smoky weekdays and 20 non-smoky weekdays in July and August 2018. The dates of the smoky weekdays were July 6, 24-27, and 30-31 and August 2, 6, 8-10, and 15. The dates of the non-smoky weekdays were July 3-4, 9-10, 12-13, 16, and 18-20 and August 3, 14, 17, 20-21, 23-24, 27, and 29-30. These days were selected for analysis because each had measurements of O_3, CO, VOCs, NO_x, $PM_{2.5}$, T_{air}, BP, and RH. A combination of surface $PM_{2.5}$ measurements, surface CO measurements, and imagery from the NOAA Hazard Mapping System Fire and Smoke Product (HMS FSP; https://www.ospo.noaa.gov) were used to distinguish between the smoky and non-smoky weekdays. We focused on weekdays since numerous studies have reported higher concentrations of O_3 precursors (i.e., VOCs and NO_x) on weekdays than on weekends in southern California (e.g., Blanchard and Tanenbaum, 2003; Fujita et al., 2003). Therefore, weekends were excluded from the analysis so that any differences in O_3 formation chemistry on the smoky versus non-smoky days could be more readily attributed to wildfire smoke. The overhead smoke on the smoky weekdays was likely due in part to the large Ferguson (about 39,000 ha burned), Natchez (about 15,000 ha burned), Carr (about 93,000 ha burned), Mendocino Complex (about 186,000 ha burned), Donnell (about 15,000 ha burned), and/or Hirz (about 19,000 ha burned) fires burning north of BMA. The locations of each of these fires relative to BMA are shown in Fig. 1.

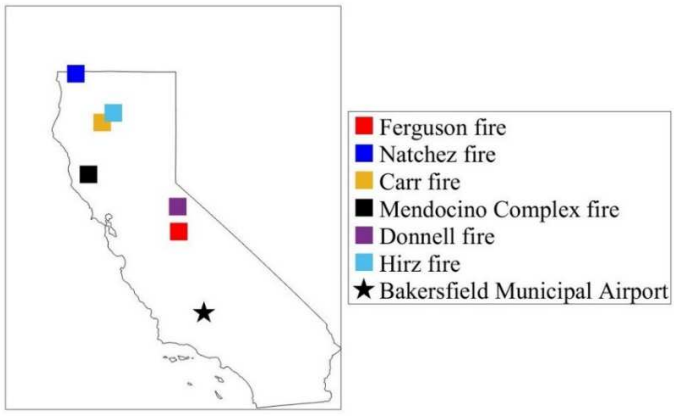

Fig. 1. Site and Wildfire Map Map of California showing the locations of the Bakersfield Municipal Airport (BMA) site and the Ferguson, Natchez, Carr, Mendocino Complex, Donnell, and Hirz fires.

The measurements listed above were used to constrain the Framework for 0-D Atmospheric Modeling photochemical box model (F0AM; Wolfe et al., 2016). Since none of the chemical mechanisms in F0AM include heterogeneous chemistry, $PM_{2.5}$ was not used as a model

constraint. Version 3.3.1 of the Master Chemical Mechanism (MCM v3.3.1, http://mcm.leeds.ac.uk/MCM; Jenkin et al., 1997, 2003, 2015; Bloss et al., 2005; Saunders et al., 2003) was used to drive the model chemistry. One 24-hour simulation was conducted from 0:00-23:00 LST for both the smoky and non-smoky weekdays to investigate the average impact of wildfire smoke on O_3 formation chemistry. Both simulations had a 10-minute integration time for each model time step, and a 2-day model spin-up was performed to ensure that the initial conditions had little to no effect on the modeling. Observed hourly median T_{air}, BP, and RH across the smoky or non-smoky weekdays were used to initialize the meteorology in F0AM for each time step of the simulations. All observed medians of the daily-average VOC concentrations for the smoky weekdays were scaled upward by 30% to account for unmeasured VOCs emitted by wildfires. The individual VOCs used to constrain F0AM for the smoke and non-smoke simulations are shown in Table S1. O_3, CO, VOCs, and methane (CH_4) were initialized at the beginning of the smoke and non-smoke simulations (i.e., 0:00 LST) using (1) the observed median O_3 and CO concentrations at 0:00 LST across the smoky or non-smoky weekdays, (2) the observed medians of the daily-average VOC concentrations, and (3) an assumed CH_4 concentration of 1850 ppb. After O_3, CO, VOCs, and CH_4 were initialized at 0:00 LST for the smoke and non-smoke model runs, their concentrations varied freely for the rest of the 24-hour simulations. Observed hourly median NO_x concentrations across the smoky and non-smoky weekdays were used to initialize F0AM for all hours of the smoke and non-smoke simulations. Specifically, the total NO_x concentrations were set at the beginning of each model time step, while the NO/NO_2 ratio was calculated by the model chemistry.

Fixed background O_3, CO, and VOC concentrations were prescribed for the smoky and non-smoky weekdays. Background O_3 and CO values were specified by determining daily median concentrations on the smoky and non-smoky weekdays. Ultimately, background O_3 and CO concentrations of 45 and 300 ppb, respectively, were prescribed for the smoky weekdays, and background O_3 and CO concentrations of 40 and 240 ppb, respectively, were prescribed for the non-smoky weekdays. Background VOC concentrations for the smoky and non-smoky weekdays were assumed to be equal to the initialized values (Table S1).

Photolysis rates were calculated as a function of solar zenith angle, elevation of BMA (117 m a.s.l.), albedo (0.15), and overhead O_3 column (300 DU) using lookup tables provided in F0AM. The lookup tables are determined using (1) literature-derived cross sections and quantum yields and (2) solar spectra from version 5.2 of the National Center for Atmospheric Research Tropospheric Ultraviolet and Visible (NCAR TUV) radiation model (Wolfe, 2020). We note that the model-calculated photolysis rates were not adjusted for cloud cover or aerosol optical depth (AOD). Sky cover data from Meadows Field Airport (35.43 °N, 119.06 °W; about 12 km north-northwest of BMA) indicate that there was negligible cloud cover on the smoky and non-smoky weekdays (IEM, 2021). In addition, Baylon et al. (2018) reported a minimal impact of AOD on photolysis rates at AOD values up to 0.6, and the daily AODs measured by the Moderate Resolution Imaging Spectroradiometer (MODIS) Aqua satellite on the smoky weekdays in Bakersfield had a median value of approximately 0.4 (data not shown).

Physical processes were accounted for in F0AM by deriving a first-order dilution rate (K_{dil}). K_{dil} was found following an approach adapted from McDuffie et al. (2016) and Ninneman et al. (2020). Namely, different K_{dil} values were tested to determine the best fit of the model-predicted afternoon O_3 concentrations to the observed values. The K_{dil} values that yielded the best fit to the observed afternoon O_3 concentrations for the smoky and non-smoky weekdays were 1×10^{-4} and 3×10^{-5} s^{-1}, respectively. These K_{dil} values also led to reasonable agreement

between modeled and measured NO_x concentrations on the smoky and non-smoky weekdays (Fig. 2 and Table S2). However, we note that the model did not predict the observed decrease in afternoon CO levels, especially on the smoky weekdays. Since CO is highly influenced by transport and emissions, this was likely due in part to the lack of upwind measurements to set the background concentrations of CO and its precursors.

To help assess O_3 production at BMA on the smoky and non-smoky weekdays, model-predicted instantaneous O_3 production rates (P_{O3}) were examined using Eq. (1) (e.g., Thornton et al., 2002):

$$P_{O3}=k_{HO2+NO}\,[HO_2][NO]+\sum_i k_{RiO2+NO}\,[R_iO_2][NO], \quad (1)$$

where k_{HO2+NO} is the rate constant for the reaction of hydroperoxyl radical (HO_2) with NO, and $k_{RiO2+NO}$ is the rate constant for the reaction of speciated organic peroxy radicals (R_iO_2) with NO. P_{O3} differs from the net O_3 production rate in that it does not account for O_3 loss pathways, mainly surface deposition, chemical loss, and advection. Model sensitivity tests were performed to investigate the effect of VOCs and/or NO_x on P_{O3} and O_3 on the smoky and non-smoky weekdays. All VOC sensitivity tests were conducted by varying the initial and background VOC concentrations without changing the other model inputs. All NO_x sensitivity tests were conducted by varying the initialized NO_x concentrations without changing the other model inputs. Initialized NO_x concentrations and initial and background VOC concentrations were the only model inputs that were changed for sensitivity tests examining the impact of both NO_x and VOCs on P_{O3} and O_3. The results of these sensitivity tests will be presented and discussed in the next section.

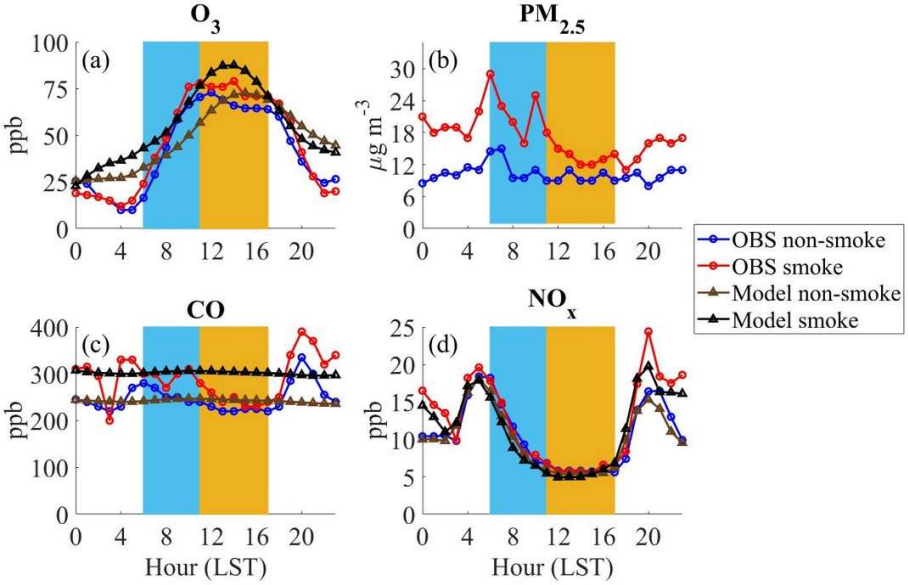

Fig. 2. Model Predictions and Surface Observations Hourly modeled concentrations and/or hourly median observations of (a) O_3 (ppb), (b) $PM_{2.5}$ (μg m^{-3}), (c) CO (ppb), and (d) NO_x (ppb) on the smoky and non-smoky weekdays. O_3, CO, and NO_x were measured at BMA. $PM_{2.5}$ was measured at the California Avenue site, which is approximately 6 km to the northwest of BMA. $PM_{2.5}$ was not modeled, as discussed in section 2. Morning (6:00-11:00 LST) and afternoon (11:00-17:00 LST) hours are denoted by the light blue and gold shading, respectively.

3. Results and Discussion

Observed hourly median and/or hourly modeled O_3, $PM_{2.5}$, CO, and NO_x concentrations for the smoky and non-smoky weekdays are shown in Fig. 2. Measured O_3 concentrations on the smoky and non-smoky weekdays increased rapidly from 24 to 78 ppb and 17 to 71 ppb, respectively, in the morning, reaching a maximum of 79 and 73 ppb, respectively, in the early afternoon. During daytime hours (6:00-17:00 LST), observed O_3 concentrations were approximately 8 ppb greater on smoky weekdays (Table 1). Since there were no corresponding increases in the observed morning $PM_{2.5}$ and CO concentrations, local photochemistry was likely the main factor influencing measured O_3 levels on the smoky and non-smoky weekdays. On the smoky weekdays, observed daytime $PM_{2.5}$ values were about 8 $\mu g\ m^{-3}$ higher, observed daytime CO levels were approximately 40 ppb greater, and the observed median sum of the daily-average concentrations of volatile organic compounds (ΣVOCs) was approximately 10 ppb greater (Table 1). The above differences in the measured concentrations of O_3, $PM_{2.5}$, CO, and ΣVOCs were statistically significant ($p < 0.05$; Table 1). Differences in observed daytime NO_x concentrations on the smoky versus non-smoky weekdays were negligible and statistically insignificant (Fig. 2d and Table 1), suggesting that there is little to no enhancement in NO_x due to smoke.

To ensure that the observed enhancements in O_3, $PM_{2.5}$, CO, and ΣVOCs are consistent with known enhancements due to smoke, we calculated the observed normalized enhancement ratio (NER) of $PM_{2.5}$ relative to CO using Eq. (2):

$$\Delta PM_{2.5}/\Delta CO = (PM_{2.5,S}\text{-}PM_{2.5,NS})/(CO_S\text{-}CO_{NS}), \quad (2)$$

where $PM_{2.5,S}$ and CO_S are the daytime median $PM_{2.5}$ and CO concentrations on the smoky weekdays, and $PM_{2.5,NS}$ and CO_{NS} are the daytime median $PM_{2.5}$ and CO concentrations on the non-smoky weekdays (Table 1). Eq. (2) yielded a $\Delta PM_{2.5}/\Delta CO$ NER of 0.188 $\mu g\ m^{-3}\ ppb^{-1}$, which is within the range of the $\Delta PM_{2.5}/\Delta CO$ NERs of 0.057-0.228 $\mu g\ m^{-3}\ ppb^{-1}$ reported by Laing et al. (2017) for 25 smoke events in eight western U.S. cities. Therefore, the $\Delta PM_{2.5}/\Delta CO$ NER is consistent with other observations of smoke in urban areas.

Type of day or variable	N_{days}	Median O_3 (ppb)	Median $PM_{2.5}$ ($\mu g\ m^{-3}$)[a]	Median NO_x (ppb)	Median CO (ppb)	Median ΣVOCs (ppb)
Smoke	13	69.0	17.5	6.7	280.0	29.4
Non-smoke	20	61.0	10.0	6.3	240.0	19.2
p-value	N/A	< 0.05	< 0.05	0.95	< 0.05	< 0.05

[a] Data taken from California Avenue site, which is approximately 6 km northwest of BMA.

Table 1. Statistics of observations on smoky and non-smoky weekdays Statistical summary of (1) the daytime (6:00-17:00 LST) median hourly observations of O_3, $PM_{2.5}$, NO_x, and CO and (2) the observed median sum of the daily-average concentrations of VOCs (ΣVOCs) at BMA on the smoky and non-smoky weekdays. The ΣVOCs values for the smoky and non-smoky weekdays were calculated by adding the concentrations shown in Table S1. P-values were determined using a 2-tailed t-test. The number of smoky and non-smoky weekdays (N_{days}) are also shown.

Model-predicted morning and afternoon P_{O3} and O_3 at BMA for the smoky and non-smoky weekdays are compared in Fig. 3. Modeled P_{O3} and O_3 were elevated on the smoky

weekdays, the latter being consistent with observations (Fig. 2a). Specifically, maximum P_{O3} on the smoky and non-smoky weekdays were approximately 18 and 9 ppb h^{-1}, respectively, and maximum modeled O_3 levels on the smoky and non-smoky weekdays were about 88 and 73 ppb, respectively.

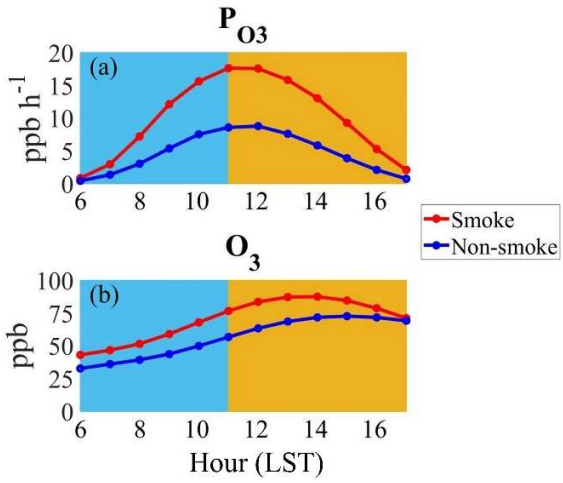

Fig. 3. Modeled O_3 Formation Model-predicted (a) O_3 production rate (P_{O3}; ppb h^{-1}) and (b) O_3 (ppb) at BMA during daytime hours (6:00-17:00 LST) on smoky and non-smoky weekdays. For ease of comparison, the daytime modeled O_3 concentrations shown in Fig. 2a are reshown in (b). The light blue and gold shading have the same meanings as in Fig. 2.

A series of model sensitivity tests were conducted to study the impact of VOCs and NO_x on P_{O3} and O_3 for the smoky and non-smoky weekdays. Initial and background VOC concentrations were reduced by 75% and increased by 100%, and the results of these sensitivity tests are shown in Fig. 4. On smoky weekdays, VOCs significantly impacted P_{O3} and O_3 during morning and afternoon hours. This is because model-predicted P_{O3} increased by up to 12 ppb h^{-1} when VOC concentrations were doubled and decreased by up to 11 ppb h^{-1} when VOC concentrations were reduced by 75%. Meanwhile, modeled hourly O_3 increased by up to 30 ppb when VOC concentrations were doubled and decreased by up to 30 ppb when VOC concentrations were reduced by 75%. Similarly, P_{O3} and O_3 were sensitive to changes in VOC concentrations on the non-smoky weekdays, especially during the afternoon. From 11:00-17:00 LST, increasing VOC values by 100% increased P_{O3} and O_3 by up to 5 ppb h^{-1} and 26 ppb, respectively, and reducing VOC values by 75% decreased P_{O3} and O_3 by up to 4 ppb h^{-1} and 18 ppb, respectively.

Additional model sensitivity tests were performed to determine which VOC class – aldehydes, alkanes, alkenes, and/or aromatics – had the greatest effect on P_{O3} and O_3 on the smoky and non-smoky weekdays (Figs. 5 and 6). We reduced by 75% or increased by 100% the initial and background concentrations of the above VOC classes, while not changing the other model parameters. Figs. 5 and 6 indicate that aldehydes had the greatest influence on P_{O3} and O_3 on the smoky and non-smoky weekdays. The two aldehydes that had the strongest influence on O_3 were acetaldehyde (CH_3CHO) and formaldehyde (HCHO; Table S1). Increasing CH_3CHO and HCHO concentrations by 100% led to P_{O3} and O_3 increasing by up to 8 ppb h^{-1} and 17 ppb, respectively, on the smoky weekdays and 3 ppb h^{-1} and 10 ppb, respectively, on the non-smoky weekdays. In addition, decreasing CH_3CHO and HCHO concentrations by 75% led to reductions

in P_{O3} and O_3 of up to 7 ppb h^{-1} and 15 ppb, respectively, on the smoky weekdays and 2 ppb h^{-1} and 8 ppb, respectively, on the non-smoky weekdays. It is also noteworthy that CH_3CHO and HCHO had a similar impact on P_{O3} and O_3 on the smoky weekdays (Fig. S1), and the same was true for the non-smoky weekdays (Fig. S2). The influence of CH_3CHO and HCHO on P_{O3} and O_3 on the smoky and non-smoky weekdays is consistent with CH_3CHO and HCHO having a high OH reactivity and HCHO providing additional OH and HO_2 upon photolysis (e.g., Luecken et al., 2012, 2018).

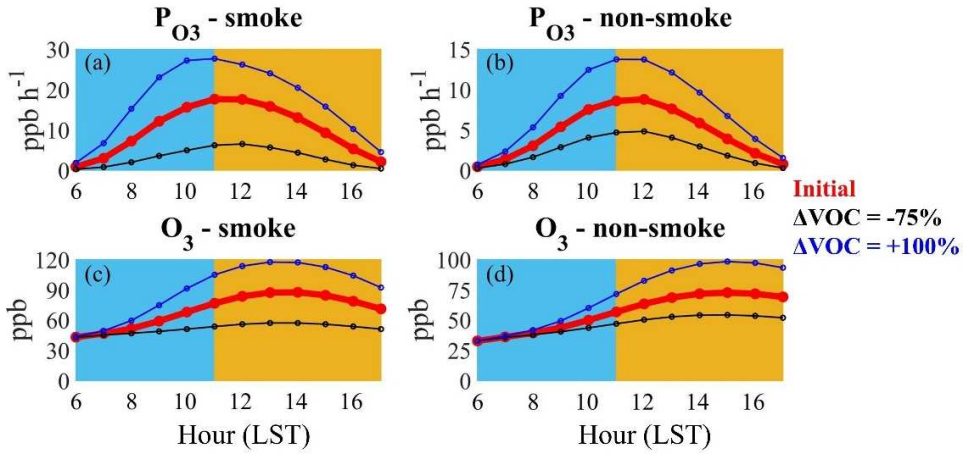

Fig. 4. VOC Sensitivity Tests Model-predicted sensitivity of (a) P_{O3} on smoky weekdays, (b) P_{O3} on non-smoky weekdays, (c) O_3 on smoky weekdays, and (d) O_3 on non-smoky weekdays to changes in VOC concentrations. The results presented by the red and blue lines in Fig. 3 for the smoky and non-smoky weekdays, respectively, are shown in red. For the model sensitivity tests, the initial and background VOC concentrations were the only model inputs that were changed. The light blue and gold shading have the same meanings as in Fig. 2.

Moreover, the lesser effect of alkanes, alkenes, and aromatics on O_3 production (Figs. 5-6) suggests that CH_3CHO and HCHO directly emitted from wildfires and/or anthropogenic activity had the greatest influence on P_{O3} and O_3, rather than the CH_3CHO and HCHO formed via oxidation from other VOC precursors (e.g., ethane, isoprene, benzene, etc.). Still, it must be noted that CH_3CHO and HCHO are short-lived, with lifetimes on the order of a few hours to one day (Jones et al., 2009; Millet et al., 2010). In addition, the large fires burning in California in July-August 2018 were located hundreds of kilometers north of BMA (Fig. 1), implying that much of the smoke affecting the site was well-aged. Therefore, some of the CH_3CHO and HCHO emitted by the fires may have undergone chemical or physical removal prior to the smoke plumes reaching BMA. This suggests that the transport of unmeasured CH_3CHO and HCHO precursors – such as methanol, ethanol, and others – may be influencing the CH_3CHO and HCHO concentrations and impacting O_3 formation on the smoky weekdays. Measurements of these species are needed at urban sites when smoke is present to either support or refute this hypothesis.

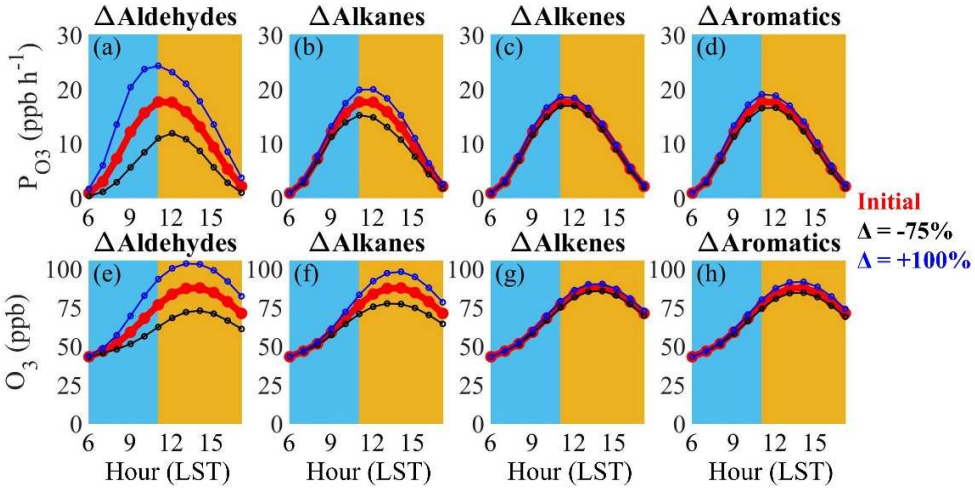

Fig. 5. Sensitivity Tests by VOC Class for Smoky Weekdays Model-predicted sensitivity of P_{O3} (top row; panels (a)-(d)) and O_3 (bottom row; panels (e)-(h)) on smoky weekdays to changes in aldehydes (leftmost column; panels (a) and (e)), alkanes (second column; panels (b) and (f)), alkenes (third column; panels (c) and (g)), and aromatics (rightmost column; panels (d) and (h)). The results presented by the red lines in Fig. 3 for smoky weekdays are shown in red. For the model sensitivity tests, the initial and background concentrations of aldehydes, alkanes, alkenes, or aromatics were the only model inputs that were changed. See Table S1 in the Supporting Information for the VOCs comprising each class. The light blue and gold shading have the same meanings as in Fig. 2.

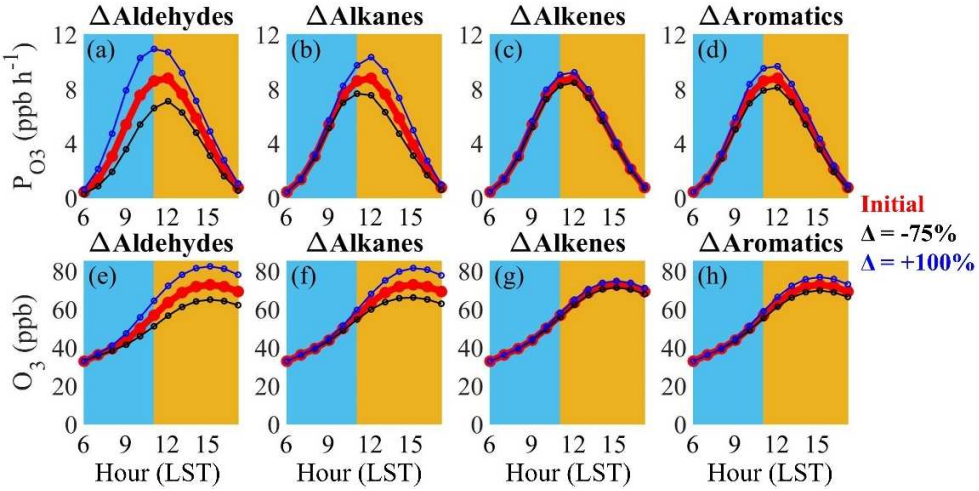

Fig. 6. Sensitivity Tests by VOC Class for Non-smoky Weekdays Model-predicted sensitivity of P_{O3} (top row; panels (a)-(d)) and O_3 (bottom row; panels (e)-(h)) on non-smoky weekdays to changes in aldehydes (leftmost column; panels (a) and (e)), alkanes (second column; panels (b) and (f)), alkenes (third column; panels (c) and (g)), and aromatics (rightmost column; panels (d) and (h)). The results presented by the blue lines in Fig. 3 for non-smoky weekdays are shown in red. For the model sensitivity tests, the initial and background concentrations of aldehydes, alkanes, alkenes, or aromatics were the only model inputs that were changed. See Table S1 in the Supporting Information for the VOCs comprising each class. The light blue and gold shading have the same meanings as in Fig. 2.

The sensitivity of P_{O3} and O_3 to changes in NO_x on the smoky and non-smoky weekdays was examined by reducing and increasing initialized NO_x concentrations by 75% and 100%, respectively, without changing other model inputs (Fig. 7). On the non-smoky weekdays, P_{O3} and O_3 were (1) relatively insensitive to NO_x when NO_x concentrations were reduced by 75% and (2) generally lower when NO_x concentrations were doubled, suggesting that the O_3 production regime at BMA on the non-smoky weekdays was likely NO_x-saturated. In contrast, afternoon P_{O3} and O_3 decreased by up to 8 ppb h^{-1} and 16 ppb, respectively, on the smoky weekdays after NO_x values were lowered by 75%. This result was expected given the higher VOC concentrations on smoky weekdays (Table S1). However, the lower P_{O3} and O_3 on smoky weekdays – particularly during the afternoon hours – after increasing NO_x concentrations by 100% was unexpected. This was because we hypothesized that the O_3 production regime during wildfire smoke events would be NO_x-sensitive due to (1) the abundance of VOCs emitted by wildfires and (2) the lack of an observed enhancement in NO_x concentrations across the smoky weekdays (Fig. 2d). To further investigate this finding, Fig. 8 compares the P_{O3} and O_3 resulting from (1) the initial simulations, (2) doubling VOCs, (3) tripling VOCs, (4) doubling VOCs and NO_x, and (5) tripling VOCs and doubling NO_x. The nearly identical P_{O3} and O_3 after doubling VOCs versus doubling VOCs and NO_x shows that the O_3 production regime during the afternoon remained NO_x-saturated. It was not until VOC concentrations were tripled and NO_x concentrations were doubled that the afternoon P_{O3} and O_3 exhibited behavior characteristic of a NO_x-sensitive O_3 production regime, as indicated by higher P_{O3} and O_3 values. Figs. 7 and 8 suggest that uncertainty in the full range of VOC species is one of the largest uncertainties in our calculations of O_3 production.

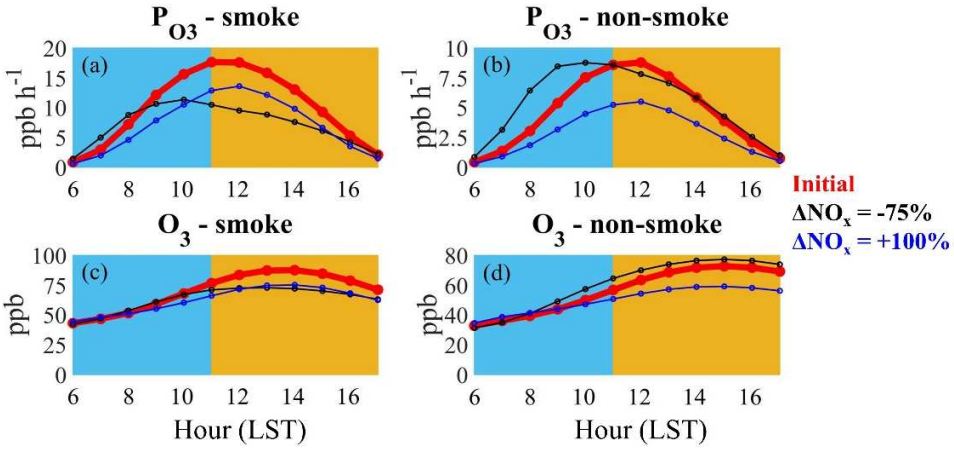

Fig. 7. NO_x Sensitivity Tests Model-predicted sensitivity of (a) P_{O3} on smoky weekdays, (b) P_{O3} on non-smoky weekdays, (c) O_3 on smoky weekdays, and (d) O_3 on non-smoky weekdays to changes in NO_x. The results presented by the red and blue lines in Fig. 3 for the smoky and non-smoky weekdays, respectively, are shown in red. For the model sensitivity tests, the initialized NO_x concentrations were the only model inputs that were changed. The light blue and gold shading have the same meanings as in Fig. 2.

The sensitivity tests described above show that P_{O3} and O_3 are sensitive to the VOC loadings for the higher and lower concentration scenarios. Meanwhile, the response of P_{O3} and O_3 to changes in NO_x varies (Fig. 7). On the non-smoky weekdays, P_{O3} and O_3 are responsive to increasing NO_x concentrations and largely insensitive to decreasing NO_x concentrations. For smoky weekdays, P_{O3} and O_3 are sensitive to lower NO_x concentrations (Fig. 7). In addition, the

black and magenta lines in Fig. 8 demonstrate that afternoon P_{O3} and O_3 are responsive to higher NO_x concentrations in a manner consistent with a NO_x-sensitive O_3 production regime after VOC concentrations were tripled. Thus, we conclude that reductions in both anthropogenic NO_x and VOC concentrations are needed to lower O_3 production at BMA on typical non-smoky days. This conclusion is in line with those made by recent studies conducted in central and southern California (e.g., Nussbaumer and Cohen, 2020). However, due to the high VOC concentrations in smoke plumes, only reductions in NO_x are expected to have a significant impact on lowering O_3 concentrations on typical smoky days.

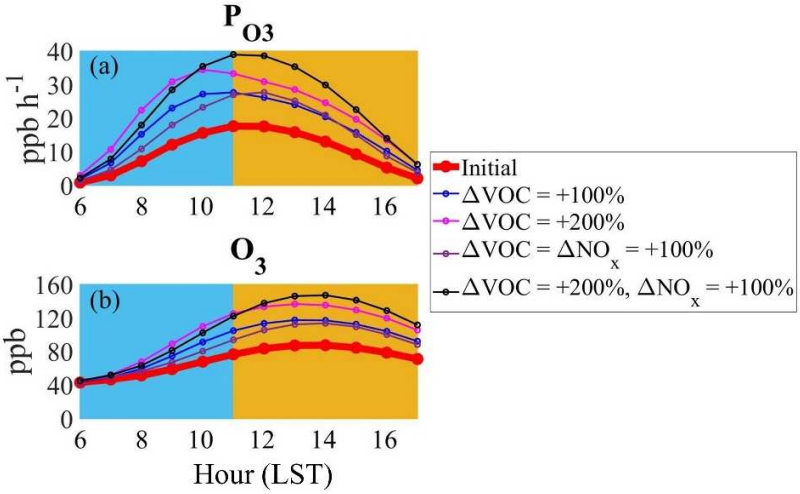

Fig. 8. Additional Sensitivity Tests for Smoky Weekdays Model-predicted sensitivity of (a) P_{O3} and (b) O_3 on smoky weekdays to changes in VOCs or changes in VOCs and NO_x. The results presented by the red and blue lines in Fig. 4 for the smoky weekdays are shown in the same colors. For all model sensitivity tests, the initial and background VOC values or the initial and background VOC and the initialized NO_x values were the only model inputs that were changed. The light blue and gold shading have the same meanings as in Fig. 2.

Two limitations regarding this study need to be discussed. First, the 24-hour time resolution and the comprehensiveness of the VOC data collected at BMA were relatively low (Table S1). Since wildfires emit hundreds of different VOCs of varying OH reactivities (e.g., Hatch et al., 2017; Sekimoto et al., 2018), it is likely that our analysis did not fully account for the temporal variability and number of ambient VOCs at BMA. Therefore, as stated previously, the total VOC concentrations on the smoky weekdays were likely higher than the measurements presented in Table S1 indicate. The lack of a comprehensive suite of hourly measurements of VOCs known to be emitted by fires – such as furfural, methyl furfural, and dimethylfuran (Coggon et al., 2019) – likely led to an underestimate in the total VOCs present. Measurements of more fire-emitted VOCs at a higher time resolution of 1 hour would improve our ability to quantify the impact of wildfire smoke on O_3 chemistry.

Second, there are no formal aerosol parameterizations in F0AM, so the effect of $PM_{2.5}$ on P_{O3} and O_3 could not be investigated. Although previous studies have explored the relationship between $PM_{2.5}$ and O_3 during smoke events (e.g., Baker et al., 2016; Buysse et al., 2019), the influence of interactive aerosol chemistry (i.e., gas-particle reactions, phase partitioning, thermodynamic equilibrium, etc.) on O_3 during urban smoke events has yet to be elucidated. Since aerosols can act as a radical sink (e.g., Emmerson et al., 2007; Stone et al.,

2012) and thus inhibit O_3 formation, investigating the impact of interactive aerosol chemistry on O_3 production during smoke events in urban areas should be a focus of future studies.

4. Conclusions

This study assessed the effect of wildfire smoke on O_3 production at the urban Bakersfield Municipal Airport (BMA) site in California across 13 smoky weekdays and 20 non-smoky weekdays in summer 2018. Median surface observations for the smoky and non-smoky weekdays revealed that afternoon O_3 typically reached values up to 79 and 73 ppb, respectively, and morning and afternoon O_3 were largely influenced by local photochemistry. The observed median concentrations of $PM_{2.5}$, CO, and ΣVOCs were lower on non-smoky weekdays compared to smoky weekdays. Meanwhile, observed daytime median NO_x concentrations were almost identical for the smoky and non-smoky weekdays, indicating that the smoke plumes contained a negligible amount of NO_x. Box model simulations showed that simultaneous reductions in anthropogenic VOCs and NO_x will likely be the best approach for decreasing P_{O3} and O_3 on typical non-smoky days at BMA. For typical smoky days, only anthropogenic NO_x controls are expected to significantly reduce O_3 levels due to the high concentrations of VOCs in smoke plumes.

To further investigate the influence of wildfire smoke on O_3 production at BMA and other urban sites, future work needs to be conducted in the following areas:

1. Make hourly measurements of more fire-emitted VOCs.
2. Assess the impact of interactive aerosol chemistry on O_3 production.
3. Examine individual smoke cases at BMA that are characterized by variable plume age, plume composition, and meteorology (i.e., air mass origin, temperature, etc.).

Addressing the above areas of future research may improve the understanding of urban O_3 production during smoke-influenced periods.

Declaration of interests

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

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