



Air Quality at Devils Postpile National Monument, Sierra Nevada Mountains, California, USA

Joel D. Burley^{1*}, Andrzej Bytnerowicz², Monica Buhler³, Barbara Zielinska⁴, Donald Schweizer⁵, Ricardo Cisneros⁵, Susan Schilling², Jennifer Chapman Varela¹, Mark McDaniel⁴, Michelle Horn⁶, Deanna Dulen³

¹ Department of Chemistry, Saint Mary's College of California, Moraga, CA 94575, USA

² USDA Forest Service, PSW Research Station, Riverside, CA 92507, USA

³ Devils Postpile National Monument, Mammoth Lakes, CA 93546, USA

⁴ Desert Research Institute, Reno, NV 89512, USA

⁵ University of California, Merced, CA 95340, USA

⁶ Technical University of Munich, D-85354 Freising, Germany

ABSTRACT

Ambient concentrations of O₃, PM_{2.5}, NH₃, NO, NO₂, HNO₃, SO₂ and VOCs were measured at Devils Postpile National Monument (DEPO) during the summer seasons of 2013 and 2014. The measurements were impacted by the Aspen and Rim Fires in 2013, and the French and King Fires in 2014. While O₃ concentrations were not discernibly perturbed by the fire events, the 70 ppb threshold (8-hour average) corresponding to both the current California Ambient Air Quality Standard (CAAQS) and the new National Ambient Air Quality Standard (NAAQS) was exceeded on five days during 2013, and on 16 days during 2014. The older NAAQS of 75 ppb (8-hour average) was exceeded once in 2013, and six times in 2014. Exceedances of the CAAQS or NAAQS occurred when background sources of O₃ were augmented by regional-scale transport, at higher altitudes, of polluted air masses that had passed through the San Joaquin Valley before arriving at the DEPO site. The 2013 Aspen Fire elevated PM_{2.5} to a maximum hourly concentration of 214 µg m⁻³ and a maximum 24 h mean of 92.7 µg m⁻³, and resulted in 13 exceedances of the 35 µg m⁻³ (24 h average) NAAQS for PM_{2.5}. The 2013 Rim Fire increased PM_{2.5} to a maximum hourly concentration of 132 µg m⁻³ and a maximum 24 h mean of 69.6 µg m⁻³, and resulted in two exceedances of the 24 h NAAQS. Concentrations of NH₃ increased during all fires, as did those of NO₂ during the Aspen and Rim Fires. Concentrations of benzene increased substantially during the French Fire.

Keywords: Ozone; Passive samplers; PM_{2.5}; VOC; Nitrogen oxides.

INTRODUCTION

Air pollutants that directly impact human health or ecosystem sustainability are regulated in the United States by the Environmental Protection Agency (EPA), which has established National Ambient Air Quality Standards (NAAQS) for ozone, particulate matter, nitrogen dioxide, sulfur dioxide, carbon monoxide, and lead (Environmental Protection Agency, 2016a). The state of California has established similar regulations – the California Ambient Air Quality Standards (CAAQS) – that apply at the state level (California Air Resources Board, 2016a). Compliance with NAAQS and CAAQS regulations is necessary to minimize

threats to human health and detrimental ecological impacts (Vandenberg, 2005; Environmental Protection Agency, 2016b).

While air pollutant concentrations and impacts on human health have been well studied in urban and suburban environments, fewer studies have been conducted in remote mountain locations. Movements of air masses in complex mountain terrain are affected by multiple factors, and consequently the spatial distributions of air pollutants are poorly explained by the available models (Seinfeld and Pandis, 1998; Reff *et al.*, 2007). In addition to improved modeling, more surface-level measurements of pollutant concentrations are needed in remote, high-elevation regions in order to better understand the air quality status of these pollution receptor sites. However, air quality data are typically very limited for high elevation areas, including large sections of the Sierra Nevada Mountains (Bytnerowicz *et al.*, 2000).

Most of the research that has taken place to date in the

* Corresponding author.

E-mail address: jburley@stmarys-ca.edu

Sierra Nevada Mountains has focused on lower elevation sites along the western slope (Bytnerowicz *et al.*, 2003), while considerably less attention has been directed towards more remote locations near the Sierra crest, or towards the eastern slope. In general, these latter regions have been viewed as unpolluted due to their distance from major pollution source areas such as the San Joaquin Valley (SJV) or the San Francisco Bay Area. Air pollution impacts on human health and the biological resources of remote Sierra Nevada sites have therefore been described as low (Cahill *et al.*, 1996). Along these lines, Devils Postpile National Monument (DEPO) – which is located near the Sierra Crest, approximately 85 km east of the SJV – has been perceived as a pristine location with good air quality. This perception has been supported by preliminary passive sampler measurements at locations near DEPO, which showed that 14-day average ozone (O_3) and nitric acid (HNO_3) concentrations were much lower than at other western and central Sierra Nevada locations (Cisneros *et al.*, 2010). However, more recent measurements conducted at the DEPO site with active O_3 monitors in 2007 and 2008 have indicated that the thresholds associated with both the CAAQS (an 8-hour average of 70 ppb) and the NAAQS (formerly an 8-hour average of 75 ppb; now an 8-hour average of 70 ppb) are routinely exceeded during the summer season. These high O_3 episodes have been attributed to regional-scale transport of O_3 from the SJV up the San Joaquin River drainage, with a smaller contribution from local photochemical production (Bytnerowicz *et al.*, 2013).

The general objective of the present study was to follow up on these prior investigations and obtain a more comprehensive understanding of the air quality at DEPO. Specifically, we wanted to measure the spatial variability of surface-level O_3 in the vicinity of the DEPO Visitor Center and assess whether or not local NO_x and VOC emissions from the visitor center bus stop/parking lot were having a discernible influence on the observed O_3 concentrations. We also wanted to investigate the impacts of local topography and dry deposition on the observed O_3 concentrations by operating a second O_3 monitor on top of a nearby granite dome. A third goal was to quantify the concentrations of other pollutants – besides O_3 – present at the DEPO site. To address this latter objective, we therefore measured three additional NAAQS criteria pollutants – fine particulate matter ($PM_{2.5}$), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2) – along with ammonia (NH_3), nitric oxide (NO), HNO_3 , and seventeen C4–C11 volatile organic compounds (VOCs).

The fieldwork for this new study was conducted over two summer seasons (2013, 2014), and utilized multiple sites in the vicinity of the DEPO Visitor Center, as opposed to the single site used in 2007 and 2008. The nearby Aspen and Rim Fires took place during our field measurements in 2013, followed by the French and King Fires in 2014. The occurrence – serendipitous but not unexpected – of these wildland fires during the middle of our fieldwork resulted in the emergence of another objective: to assess how the fires influenced pollutant concentrations at the DEPO receptor site. The issue of fire impacts is very timely because wildfires have become more frequent throughout the Sierra

Nevada Mountains due to the effects of climate change and the ongoing California drought, which started in 2012 (United States Geological Survey, 2016). Information on ambient O_3 and $PM_{2.5}$ is also of high importance to National Park Service administrators who use prescribed fires as a tool for ecosystem management.

METHODOLOGY

DEPO Site, Sampling Locations

DEPO is located approximately 250 km due east of San Jose, and roughly 50 km southeast of Yosemite Valley, just west of the resort town of Mammoth Lakes and the Mammoth Mountain ski area (Fig. 1). It is situated along the middle fork of San Joaquin River, which has its headwaters approximately 15 km to the northwest at Thousand Island Lake, near the Sierra Crest. DEPO is surrounded on all sides by the Inyo National Forest, and the monument boundaries are aligned in a north-south direction, with a rectangular footprint that is 0.8 km wide (west to east) by 4 km tall (north to south). While DEPO is frequently described as an eastern Sierra site – due to the fact that the only vehicular access is from the east, via state highway #203 – the entirety of the monument actually lies along the western slope of the Sierra Nevada Mountains.

Air pollution monitoring was conducted at three different locations within DEPO, all of which were accessed from the Visitor Center near the northern boundary of the monument. The Meadow site (latitude = 37.6293°N; longitude = –119.0848°W; elevation = 2306 masl), utilized in 2013 and 2014, consisted of a lush grassy meadow directly adjacent to the San Joaquin River. The Flagpole site (latitude = 37.6299°N; longitude = –119.0842°W; elevation = 2304 masl), utilized in 2013, was situated on a sand/gravel surface ~100 m north of the Meadow site, directly adjacent to the Visitor Center building and the bus stop/traffic circle. The Granite Dome site (latitude = 37.6253°N; longitude = –119.0896°W; elevation 2493 = masl), utilized in 2014, was located on top of a granite dome near the western boundary of the monument. While the Granite Dome site was only ~625 m southwest of the Meadow site in terms of horizontal travel, it was ~187 m higher in elevation, with different surface cover (granite/gravel vs. lush, ankle-high grass). Readers who wish to view local, higher-resolution images of the sampling sites should access Fig. SI 1(a), a map that shows the locations of the three sampling sites relative to nearby landmarks, and Fig. SI 1(b), an elevated Google Earth view of the local topography.

Sampling Timelines

The active monitors for O_3 and $PM_{2.5}$ were run continuously, with occasional data gaps at the Flagpole site due to loss of AC power. The specific sampling intervals utilized in 2013 were June 4–September 18 (Meadow O_3), June 14–September 21 (Flagpole O_3), and June 9–October 7 (Flagpole $PM_{2.5}$). In 2014 the sampling interval was June 3–October 11 for O_3 and $PM_{2.5}$ at the Meadow site, and June 14–October 11 for O_3 at the Granite Dome site.

The passive samplers collected data as two-week averages

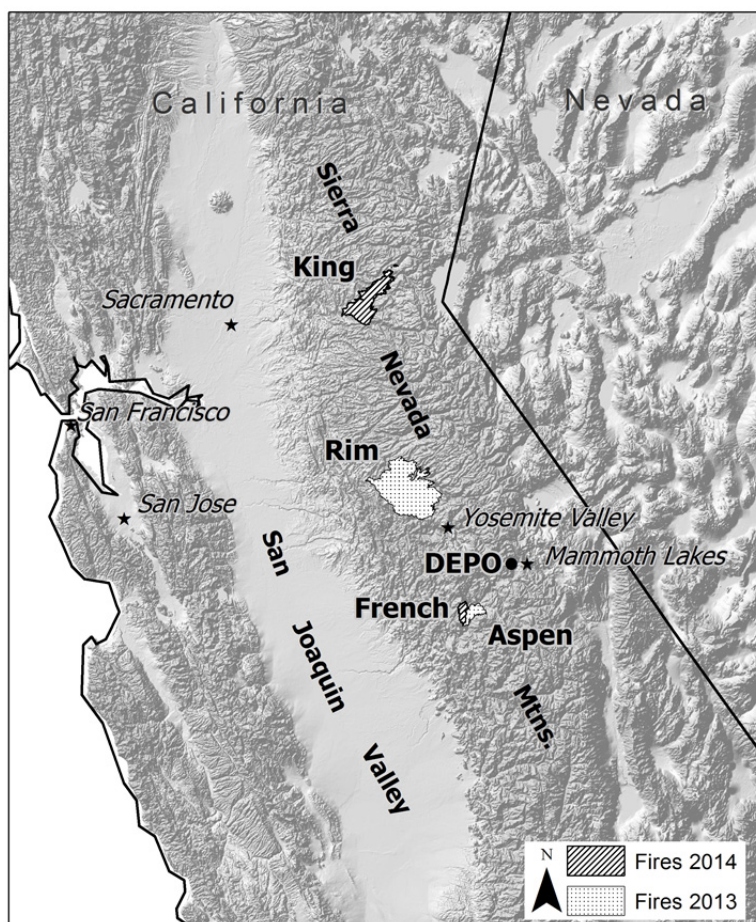


Fig. 1. Location of Devils Postpile National Monument (DEPO) and 2013 and 2014 wildland fires.

such that pollutant concentrations were separated into uniform 14-day sampling intervals. The sampling periods for both 2013 (eight periods, from June 4 through September 25) and 2014 (nine periods from June 3 through October 7) are listed in Table SI 1.

Active Ozone Monitors

Ozone concentrations were measured with 2B Technologies Model 202 UV absorption O_3 monitors, which employ Beer's Law at a wavelength of 254 nm (Bognar and Birks, 1996). Ambient air was sampled approximately 1.75 m above ground level via a 2.5 m length of 6.35 mm o.d. Teflon tubing. The sampling inlet consisted of a downward-facing 47 mm diameter Teflon filter holder equipped with a 1–2 μm Teflon filter membrane, which was shielded from precipitation by a plastic rain shield. Power for the O_3 monitors was provided by either a 12-volt solar power system (Meadow site, Granite Dome site) or by the local AC grid (Flagpole site). To ensure protection from the elements, the O_3 monitors and accompanying electronics were enclosed in weatherproof plastic cases. Ozone concentrations were measured every 10 seconds, and were automatically recorded into internal monitor memory as 5-minute averages. These 5-minute averages were subsequently downloaded from the O_3 monitors and converted into hourly averages. These hourly data were then used to calculate maximum daily 8-

hour averages (MDA8) that could be directly compared to CAAQS and NAAQS thresholds. Multi-point factory calibrations of the O_3 monitors were conducted by 2B Technologies before deployment, and additional calibrations were also carried out after the conclusion of the fieldwork. Based on these multiple comparisons, it is estimated that the hourly data from the O_3 monitors have a precision of ± 5 ppb (worst-case upper limit) and an accuracy of $\pm 5\%$.

$PM_{2.5}$ Measurements

A Met One Instruments Environmental Beta Attenuation Monitor (EBAM) was used to collect hourly $PM_{2.5}$ data. This model of EBAM is designed for temporary field deployment and does not meet the Federal Equivalent Method standard for measuring $PM_{2.5}$. Zero and span tests were conducted before and after deployment to the DEPO site. The zero checks (24-hour averages) yielded a result of $\pm 1 \mu\text{g m}^{-3}$. Audits and calibrations of temperature, barometric pressure, flow rate, and flow integrity (i.e., leak checks) were performed at bi-weekly (or more frequent) intervals. To reduce the sampling errors associated with short-term variability, the hourly data were converted into 24-hour averages. These 24-hour averages were computed when 17 or more hourly values were available during a given calendar day. This method yielded 109 valid days of data in 2013 and 110 valid days of data in 2014, and the daily averages

obtained from this approach were subsequently used to determine the Air Quality Index (AQI) for PM_{2.5}, which is defined as: “good” = 0–12.0 $\mu\text{g m}^{-3}$, “moderate” = 12.1–35.4 $\mu\text{g m}^{-3}$, “unhealthy for sensitive groups” = 35.5–55.4 $\mu\text{g m}^{-3}$, “unhealthy” = 55.5–150.4 $\mu\text{g m}^{-3}$, “very unhealthy” = 150.5–250.4 $\mu\text{g m}^{-3}$, and “hazardous” = 250.5 $\mu\text{g m}^{-3}$ or higher.

Passive Samplers

Ogawa passive samplers were used for determinations of ambient NH₃, NO, and NO₂. Passive NH₃ samplers (Roadman *et al.*, 2003; Ogawa, 2016), contain two replicate filters coated with citric acid. Ammonia reacts with citric acid on the filters producing ammonium citrate. After water extraction, NH₄⁺ concentrations in filter extracts were determined colorimetrically on a TRAACS 2000 Autoanalyzer, and ambient NH₃ concentrations were calculated based on a comparison of passive samplers against co-located annular denuder systems (Koutrakis *et al.*, 1993). Each NO₂ passive sampler contains two filters coated with triethylene amine (TEA) and each NO_x sampler consists of two filters coated with TEA and 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO) as an oxidizer (Ogawa, 2016). Both NO and NO₂ were collected as NO₂[−], which was extracted in water and determined with ion chromatography, and their ambient concentrations were calculated using calibration curves (Alonso *et al.*, 2005). From the difference between NO_x and NO₂ concentrations, NO concentrations were calculated. Passive samplers developed by the US Forest Service were used for HNO₃ and SO₂ determinations. In these samplers ambient air passes through a Teflon membrane and gaseous HNO₃ and SO₂ are absorbed on a Nylasorb nylon filter as NO₃[−] and SO₄^{2−}. Nitrate and SO₄^{2−} concentrations in sample extracts were analyzed by ion chromatography, and concentrations of HNO₃ and SO₂ were calculated using calibration curves (Bytnerowicz *et al.*, 2005). Three replicate

HNO₃ & SO₂ samplers were exposed at each site. The average precision of the NO_x, NO₂, NH₃, HNO₃ and SO₂ passive samplers during the 2013 & 2014 monitoring campaigns, measured as the CV of replicate samples, was 5, 6, 9.5, 14.5 and 10.5%, respectively. The estimated accuracy for these (non-VOC) passive samplers is $\pm 20\%$ (Fujita *et al.*, 2009; Fujita and Campbell, 2010).

To monitor selected VOC species, passive VOC Radiello samplers were used. Radiello diffusive samplers consist of stainless steel mesh cylinders (3 × 8 μm mesh, 4.8 mm diameter × 60 mm length) packed with Carbograph 4 (for all VOC except isoprene and 1,3-butadiene, adsorbing cartridge code R145) and Carbopack X (for isoprene and 1,3-butadiene, R141). The cartridges were deployed in the diffusive sampling bodies according to the manufacturer's instructions (Radiello, 2016). After sample collection, cartridges were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (GC/MS) of individual compounds. The Gerstel Thermal Desorption System (TDS) unit, equipped with a Cooled Injection System (CIS) and a 20-position autosampler, attached to the Varian Saturn 2000 GC/MS, was used for the purpose of sample desorption and cryogenic preconcentration. A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was employed to achieve separation of the target species. For calibration of the GC/MS a set of Radiello passive samplers was prepared by loading the cartridges with known amounts of gaseous calibration standards (purchased from AiR Environmental) containing the most commonly found hydrocarbons. Four different concentrations (plus one blank) were used to construct calibration curves. Table 1 lists the VOC species quantified for this project, along with their method detection limits (MDL) and measurement percent uncertainties at the

Table 1. List of volatile organic compounds measured by passive samplers.

Mnemonic	Compound	MDL (ppbv) ^b	Uncertainty ^b (%) at 2 σ
i_prene	Isoprene ^a	0.040	29.8
a_pine	α -Pinene ^a	0.036	36.7
bud13	1,3-Butadiene	0.077	29.8
n_hex	n-Hexane	0.007	3.6
n_hept	n-Heptane	0.016	5.3
benze	Benzene	0.009	6.4
cyhexa	Cyclohexane	0.007	19.7
tolue	Toluene	0.007	3.2
n_oct	n-Octane	0.021	21.9
n_non	n-Nonane	0.037	28.5
n_dec	n-Decane	0.022	5.7
etbz	Ethylbenzene	0.003	3.4
styr	Styrene	0.007	24.3
mp_xyl	m/p-Xylene	0.006	2.7
o_xyl	o-Xylene	0.002	3.1
bz124m	1,2,4-Trimethylbenzene	0.01	3.5
n_unde	n-Undecane	0.006	14.2

^a biogenic species.

^b MDLs and uncertainties are derived from replicate (n = 7) precision calculations of the lowest calibration level. See text for method description.

2 σ level. MDL's for each compound are based on limits of quantitation (LOQ), which are three times the instrument limit of detection (LOD) for each compound. LOD for each compound are defined as three times the standard deviation of results for each compound in seven analyses of the lowest calibration level. Dividing each compounds' LOQ by the respective sampling rate and 14 day duration gives the MDLs. Measurement percent uncertainty at the 2 σ level is defined as two times the standard deviation of the precision of the seven replicate analyses of lowest calibration level. Precision is the difference between results for each compound in the first replicate and other replicates, relative to their average.

The average ambient concentration of pollutants for 2-week long periods was calculated by dividing the mass of pollutant measured analytically by the product of sampling rate and sampling time:

$$\text{concentration} = \frac{\text{mass of analyte}}{\text{sampling rate} \times \text{sampling time}} \quad (1)$$

The sampling rate for every analyte had to be calculated experimentally since pumps were not used with the passive samplers. (Radiello also supplies these sampling rates for a number of commonly collected compounds.) These sampling rates were validated in chamber experiments for number of VOCs and by comparison with reference methods (Fujita *et al.*, 2009; Mason *et al.*, 2011; Fujita *et al.*, 2013). Masses of analytes were calculated after the average blank result was subtracted from the analytical result. Sampling times were equivalent to the sampler exposure periods and were limited to 14 days due to the limited capacity of the adsorbents.

Since Radiello VOC passive samplers are based on physical adsorption (physisorbents), they have a greater affinity for higher molecular weight compounds. When concentrations of these compounds are high – which can happen during wildfires – over time they tend to replace lower molecular weight compounds. This process is known as back diffusion (Mason *et al.*, 2011), and it is one of the main reasons that exposure times longer than 2 weeks are not recommended (Radiello, 2016). This phenomenon appears to have corrupted the VOC passive sampler data collected during the fourth sampling period of the 2013 season (i.e., during the peak intensity of the Aspen Fire), when near zero values were recorded for all of the measured compounds, such that the sum total of all the measured VOCs (i.e., the total column height in Fig. 7) was less than 0.05 ppb at both the Meadow and the Flagpole sites. The VOC data for this sampling period have therefore been omitted from the analysis.

Wildland Fires

During the study four major wildland fires in the Sierra Nevada Mountains occurred – the Aspen Fire and Rim Fire in 2013, and the French and King Fires in 2014. The locations of these fires are indicated on Fig. 1, and relevant background information about each fire is presented in Table SI 2. The daily growth rate for each fire was computed by calculating

the increase in the reported fire size (in hectares) for each day. Seven-day rolling averages of the daily growth rate were also calculated to reduce the impact of day-to-day errors in the reported fire sizes.

The determination of which passive sampler monitoring periods were affected by fires was achieved by comparing the fire events listed in Table SI 2 with the monitoring periods listed in Table SI 1. Any monitoring period that overlapped with a fire event was treated as a “fire” period, even if only a few days of overlap were present. The only exception to this approach occurred for monitoring period #4 in 2014 (July 15–29), which overlapped by less than one day with the French Fire (July 28–August 17). Because of the extremely small overlap – and after careful consideration of the PM_{2.5} and satellite data – monitoring period #4 was classified as “no-fire.”

Remote Sensing of Wildland Fire Smoke

Satellite images of smoke plumes were obtained from the National Oceanic and Atmospheric Administration (NOAA) Hazard Mapping System (HMS). While originally designed to determine smoke extent, since 2006 HMS data have also included a quantitative estimate of smoke density levels. To prepare these estimates, an analyst uses several hours of visible wavelength animation data from the Geostationary Operational Environmental Satellite (GOES), along with the GOES Aerosol and Smoke Product (GASP). The results are then categorized to three separate levels (low, medium, and heavy) of smoke density (Ruminski *et al.*, 2008; Ruminski, 2013). Although this approach has limitations – particularly when considering low smoke densities – the HMS categories can nonetheless be very useful when assessing the extent (and impacts) of wildland fire smoke, or when attempting to verify ground observations. Readers who are interested in a detailed discussion of how HMS smoke densities can be related to surface level PM_{2.5} should consult Preisler *et al.* (2015).

HYSPLIT Back-Trajectories

Regional-scale transport patterns were investigated by conducting back-trajectory calculations with the online version of the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2016). Calculations were performed using the 40 km EDAS (Eta Data Assimilation System) archived meteorological data, with run times of 72 hours, arrival heights of 100, 500, and 1500 m above ground level, and DEPO arrival times of 17:00 PST.

RESULTS

Ozone

The O₃ results are presented as hourly averages for both 2013 (Fig. 2) and 2014 (Fig. 3), and average diurnal cycles based upon the hourly O₃ data from 2013 and 2014 are shown in Fig. 4, along with the diurnal cycles recorded at the Meadow site in 2007 and 2008 (these latter data have been adapted from Bytnerowicz *et al.* (2013)). In order to facilitate more direct comparisons across multiple years

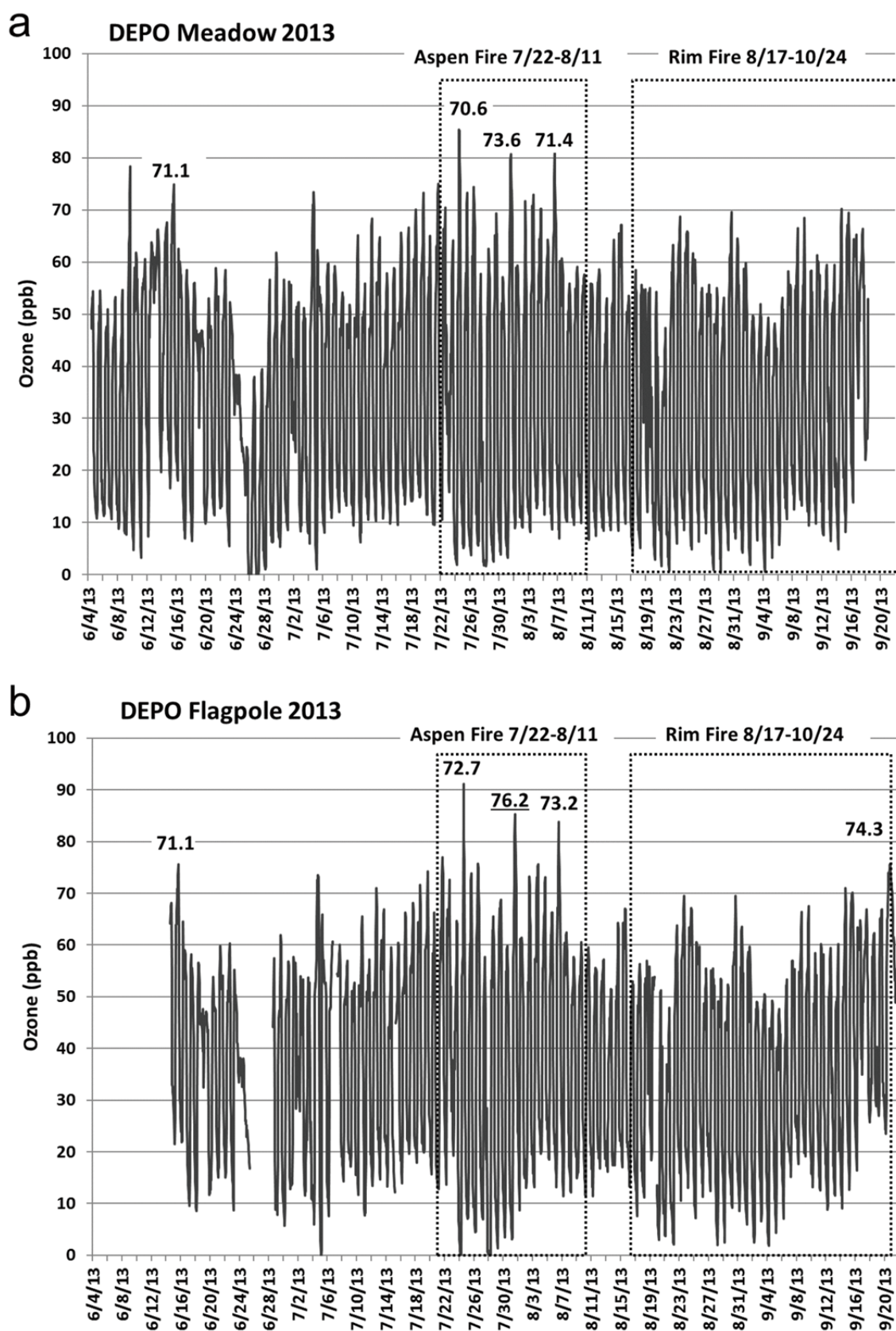


Fig. 2. Hourly O_3 concentrations in 2013. Part a: Meadow site. Part b: Flagpole site. Maximum daily 8-hour averages are noted on the diagram for those days when either the new NAAQS and current CAAQS of 70 ppb (normal typeface) or the old NAAQS of 75 ppb (bold and underlined typeface) was exceeded. The observed exceedances are also summarized in Table SI 3.

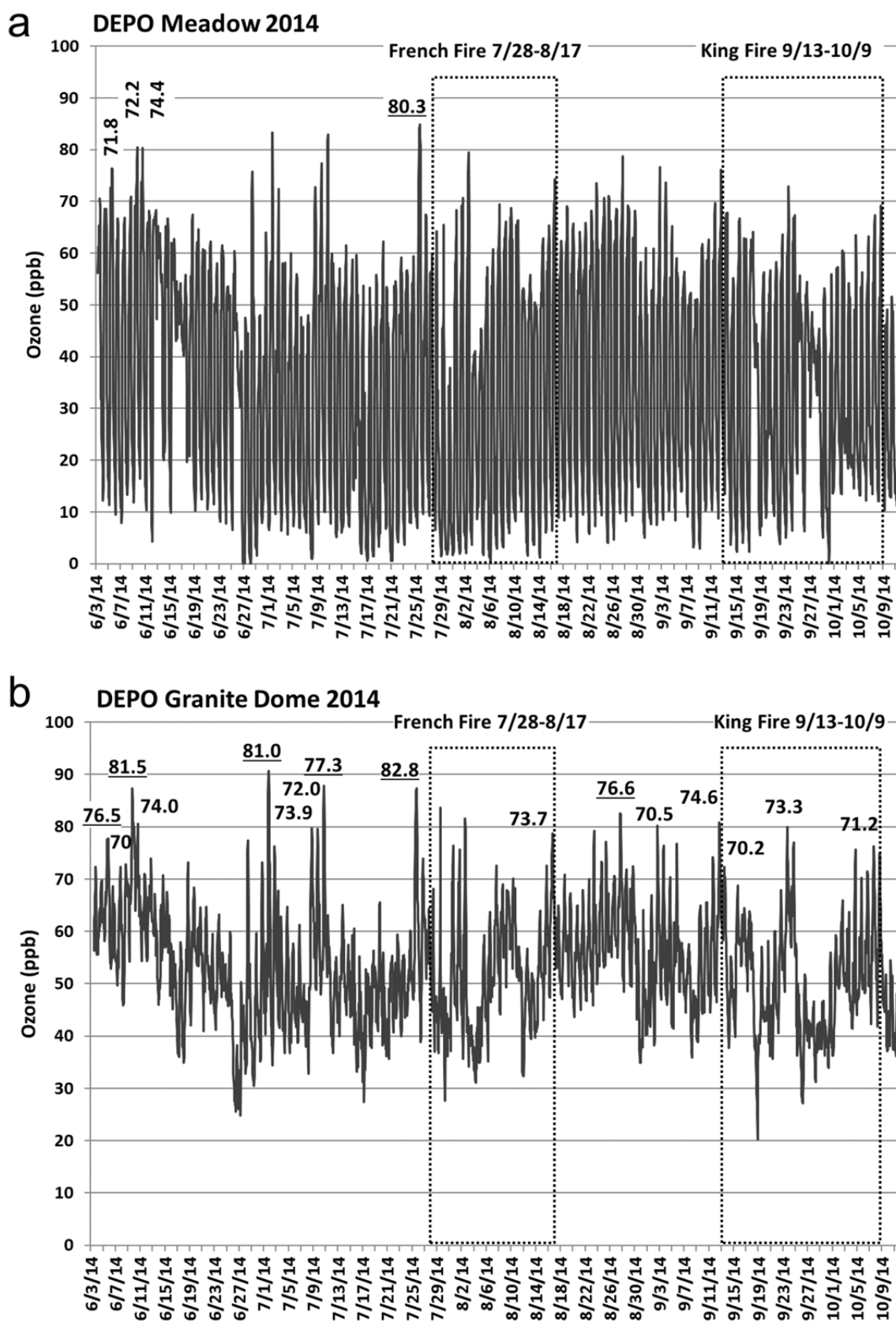


Fig. 3. Hourly O_3 concentrations in 2014. Part a: Meadow site. Part b: Granite Dome site. Maximum daily 8-hour averages are noted on the diagram for those days when either the new NAAQS and current CAAQS of 70 ppb (normal typeface) or the old NAAQS of 75 ppb (bold and underlined typeface) was exceeded. The observed exceedances are also summarized in Table SI 3.

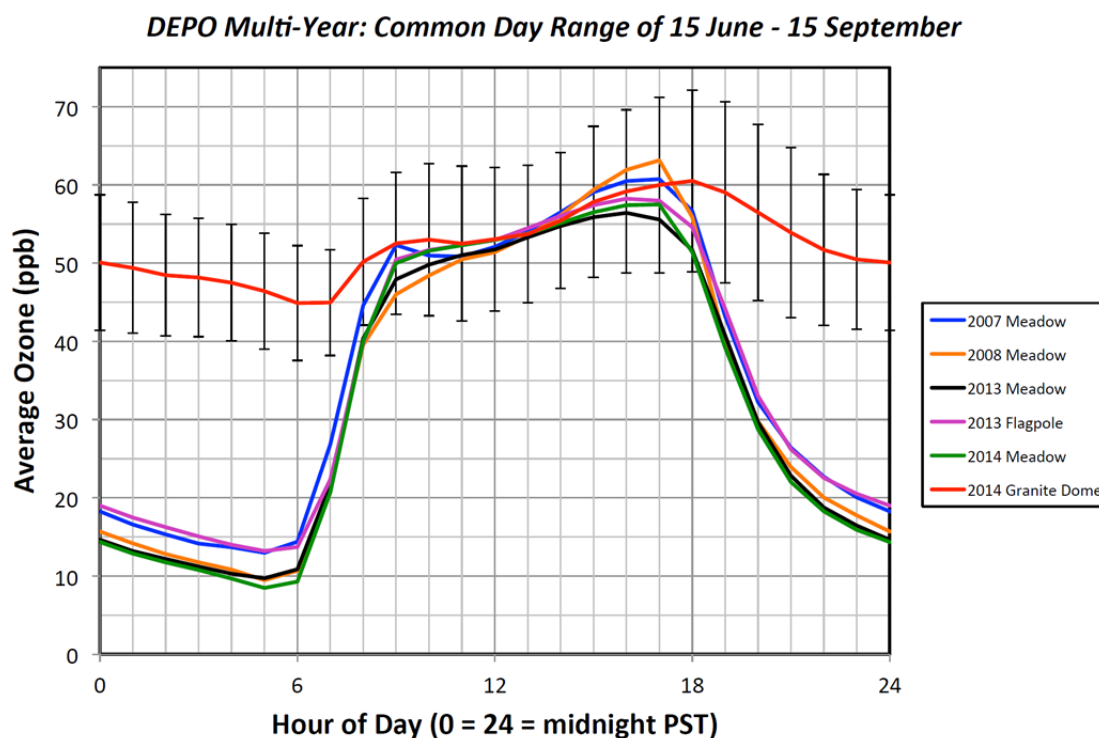


Fig. 4. Average diurnal cycles for DEPO O_3 , observed over a common day range of June 15–September 15, for multiple sites and multiple years. Representative error bars (± 1 standard deviation) have been included for the 2014 Granite Dome results. The 2007 and 2008 data have been adapted from Bytnerowicz *et al.* (2013). A statistical summary of the data used to prepare these diurnal plots is presented in Table 2.

and multiple sites, the data shown in Fig. 4 have been restricted to a common sampling window of 00:00 PST on June 15 through 23:00 PST on September 15. A statistical summary of the multi-site/multi-year comparison shown in Fig. 4 is presented in Table 2.

In 2013, the hourly data from the Meadow (Fig. 2(a)) and Flagpole (Fig. 2(b)) sites – which were separated by only ~100 m – displayed an average difference (Flagpole–Meadow) of 1.9 ppb (based on a comparison of 2230 hourly values), and a scatterplot analysis of Flagpole hourly O_3 (y-axis) vs. Meadow hourly O_3 (x-axis) yielded a linear regression of Flagpole $O_3 = (0.095)(\text{Meadow } O_3) + 3.6$ ppb ($R^2 = 0.980$). These results, along with the average diurnal cycles shown in Fig. 4, indicate an agreement that is within the combined measurement uncertainties for the two sites. During 2013, the new NAAQS and current CAAQS threshold of 70 ppb (8-hour average) was exceeded on four days at the Meadow site and on five days at the Flagpole site (see Fig. 2 annotations and Table SI 3 for details). The old NAAQS threshold of 75 ppb was not exceeded at the Meadow site, but one exceedance was observed at the Flagpole site.

In 2014, the Meadow site yielded hourly O_3 results that were very similar to those observed at the same location in 2013, such that essentially identical results were obtained for both the average diurnal cycles (Fig. 4) and the overall statistical summaries (Table 2). Results from the Granite Dome site, however, were quite different from the Meadow (2013, 2014) or Flagpole (2013) results, and both the average

daily maxima and the average daily minima were higher at the Granite Dome site (Fig. 4). For the daily maxima, the inter-site differences were approximately 0–2 ppb, on average, between the hours of 10:00 and 17:00 PST (Fig. 4) – a difference that is smaller than the combined uncertainties of the measurements. For the daily minima, however, the differences between the two sites were much larger, with average O_3 minima near 45 ppb at the Granite Dome site but under 10 ppb at the Meadow site (Fig. 4). During 2014, the new NAAQS and current CAAQS threshold of 70 ppb was exceeded on four days at the Meadow site and on 16 days at the Granite Dome site. The old NAAQS threshold of 75 ppb was exceeded once at the Meadow site, and six times at the Flagpole site (Table SI 3).

$PM_{2.5}$

The results for $PM_{2.5}$ are presented in Fig. 5 as daily averages (solid black lines). Part a shows the data from 2013, which were impacted by the Aspen and Rim Fires, while part b shows the data from 2014, which were influenced by the French and King Fires. During periods when DEPO was not impacted by wildland fire smoke, the typical maximum 1-hour values were below $62 \mu\text{g m}^{-3}$ and the daily 24-hour average values were below $16 \mu\text{g m}^{-3}$ (Fig. 5, Table SI 4).

Nitrogenous Pollutants and SO_2

Measurements conducted with passive samplers indicated low concentrations of the sampled pollutants (see Table 3

Table 2. Multi-year summary of surface-level O₃ at DEPO (June 15–September 15 data only).

Site	Meadow	Meadow	Meadow	Flagpole	Meadow	Granite Dome
Year	2007	2008	2013	2013	2014	2014
Number of hourly measurements	2232	2200	2231	2131	2232	2232
% data availability	100%	98.6%	~100%	~100%	100%	100%
Mean (ppb)	36.5	34.4	33.4	36.0	33.4	52.5
Median (ppb)	35.6	32.6	32.7	36.1	32.6	52.0
Std. Deviation (ppb)	20.4	21.1	20.5	19.6	21.5	10.3
Maximum (ppb)	86.2	100.0	84.5	91.2	85.0	90.7
Mean MDA8 (ppb)	57.5	57.2	54.9	55.8	56.0	60.2

and Fig. 6 for details). In general, concentrations of all the measured pollutants were similar during the two years of monitoring. The NH₃ concentrations increased slightly during the fire periods in 2013 (averages of 1.9 → 3.2 µg m⁻³) and significantly in 2014 (2.0 → 4.1 µg m⁻³). For NO, the fire periods did not significantly differ from the no-fire periods in either year (3.9 → 3.4 ppb in 2013; 3.4 → 3.6 ppb in 2014). Concentrations of NO₂ increased significantly during the fire periods in 2013 (0.8 → 1.6 ppb), but a slight decrease was seen in 2014 (1.5 → 1.3 ppb). The observed HNO₃ concentrations were not significantly affected by the fires in either year, but a significant decrease in SO₂ concentrations was detected during the 2014 fire periods (0.40 → 0.26 µg m⁻³). Fig. 6 indicates how the observed nitrogenous pollutant concentrations varied as a function of sampling period, and it also specifies the relative contribution of each species to the total budget for reactive nitrogen. The strongest effects on N pollutants were seen during exposure periods No. 4 and 5 (July 17–August 14, 2013; Aspen Fire) and exposure period No. 8 (September 11–25, 2013; Rim Fire). During those periods NH₃ concentrations were elevated, while other pollutants were at levels similar to the no-fire periods.

Volatile Organic Compounds

In general, concentrations of VOCs were quite low, with α -pinene as a dominating species (Fig. 7). During the French Fire at the Meadow site benzene concentrations increased 7- to 14-fold, while at the Granite Dome site 4- to 6-fold increases were seen compared with the no-fire period (Fig. 7(b)). No data are reported for sampling period #4 from 2013 because the VOC results from that period were compromised by back diffusion, as discussed above in the *Methodology* section. The observation that fire-induced enhancements were observed mostly in benzene (and, to a lesser extent, in toluene) is not surprising, as the other VOCs that were measured are not typically produced in woodland fires; they had instead been selected to help assess the effects of local motor vehicle emissions.

Smoke Density

The HMS smoke density data are presented in Fig. 5 as small grayscale squares along the top of the diagram. During the 2013 monitoring campaign, the highest smoke impacts (Fig. 5(a), Table SI 4) were seen during the Aspen Fire (one heavy density and five medium density days) and during the Rim Fire (one heavy density and two medium

density days). One day of medium density was also recorded during the no fire period prior to the Aspen Fire. The HMS-observed smoke was much less pronounced in 2014, when one day of heavy density occurred during the French Fire and one day of medium density occurred during the King Fire (Fig. 5(b), Table SI 4).

DISCUSSION

Ozone

In recent years there have been many observational and attributional investigations of surface-level O₃ in the remote western United States (e.g., Gertler and Bennett, 2015; Lefohn and Cooper, 2015). These investigations indicate that exceedances of the new 70 ppb NAAQS for O₃ are likely to occur more frequently because of increasing background O₃ (Gratz *et al.*, 2014; Fine *et al.*, 2015; Gustin *et al.*, 2015). The importance of elevated background O₃ is especially pronounced during the spring, when both long-range transport (i.e., from outside North America) and stratospheric intrusions exhibit seasonal maxima (Cooper *et al.*, 2011; Lin *et al.*, 2012; Lin *et al.*, 2015).

The O₃ results presented in Figs. 2 through 4 and summarized in Table 2 suggest that DEPO will have difficulty meeting the new NAAQS for O₃, which requires that annual fourth-highest daily maximum 8-hour concentration, averaged over three years, be ≤ 70 ppb. The O₃ concentrations measured at DEPO are generally similar to those obtained at other Sierra Nevada sites such as Yosemite National Park (Burley and Ray, 2007) or Lake Tahoe (Burley *et al.*, 2015), or those from the White Mountains, which are situated approximately 75 km to the east, along the California-Nevada border (Burley and Bytnerowicz, 2011). All of these California-based high elevation locations show average summertime diurnal maxima in the range of approximately 50–60 ppb during daytime hours, with great site-to-site variability at night. The same general trends are also present in the data from the Nevada Rural Ozone Initiative (NVROI), which sampled six different sites at elevations ranging from 1385 to 2082 masl (Fine *et al.*, 2015; Gustin *et al.*, 2015). The observation of a relatively constant/recurring average diurnal maximum across different sites and different years suggests that these rural locations are all influenced primarily by background concentrations of O₃, with smaller contributions (on average) from local photochemical production or regional transport of intact air masses. Under this scenario, solar insolation warms the surface during

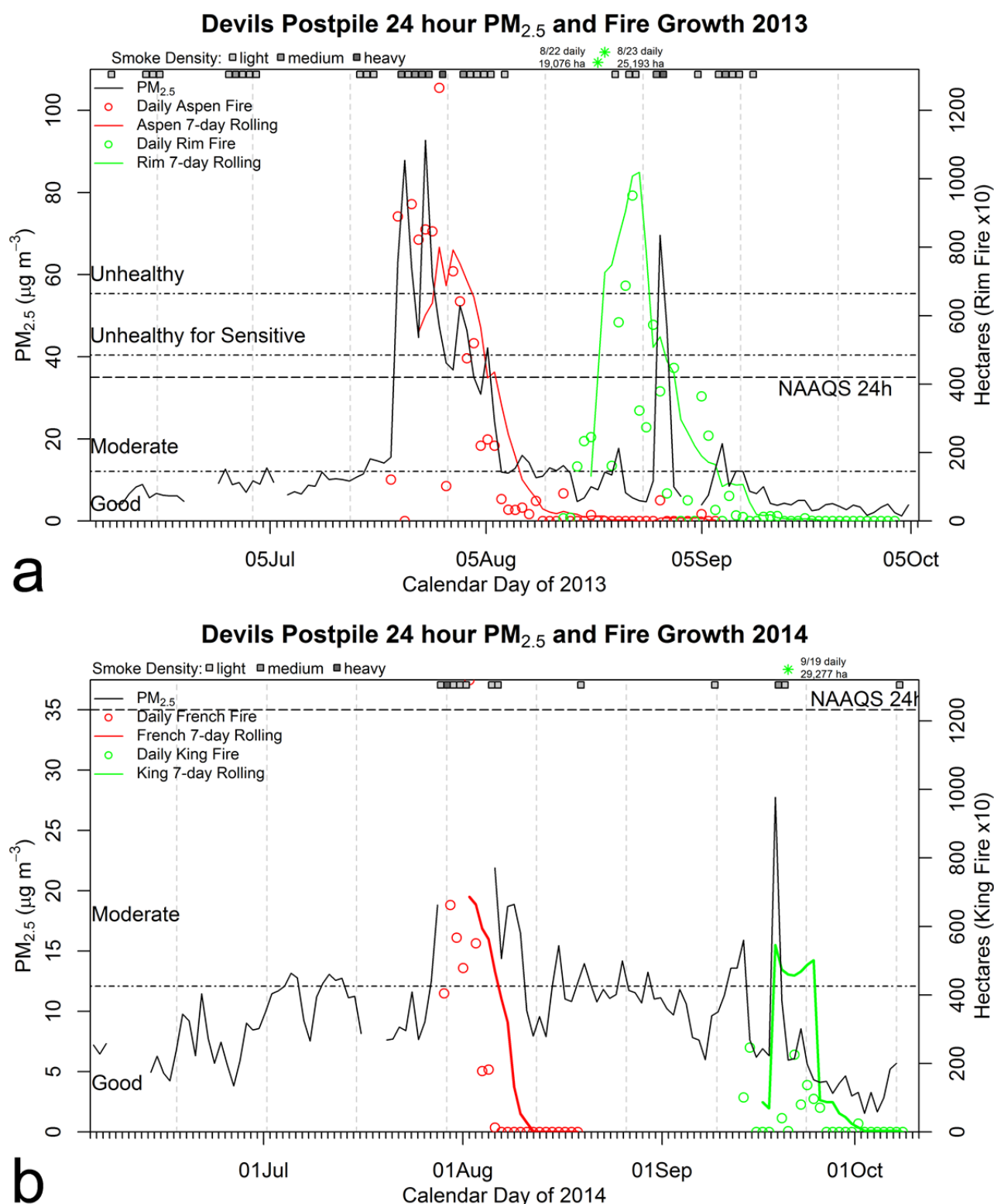


Fig. 5. Daily average PM_{2.5} concentrations at DEPO (black lines) and daily growth rates for fires (colored circles). The colored lines designate 7-day rolling averages for the fire growth rates. The grayscale squares at the top of the panel indicate the HMS smoke density classifications. Dashed horizontal lines indicate the thresholds for the Air Quality Index (AQI) for PM_{2.5}: “good” = 0–12.0 $\mu\text{g m}^{-3}$, “moderate” = 12.1–35.4 $\mu\text{g m}^{-3}$, “unhealthy for sensitive groups” = 35.5–55.4 $\mu\text{g m}^{-3}$, “unhealthy” = 55.5–150.4 $\mu\text{g m}^{-3}$. Part a: 2013 data. Part b: 2014 data. In order to improve clarity and legibility, three off-scale values for the daily growth rates have been omitted: 19,076 ha on 8/22/2013 (Rim Fire, Fig. 5(a)); 25,193 ha on 8/23/2013 (Rim Fire, Fig. 5(a)); and 29,277 ha on 9/19/2014 (King Fire, Fig. 5(b)). These off-scale data have, however, been included in the calculations for the rolling 7-day averages.

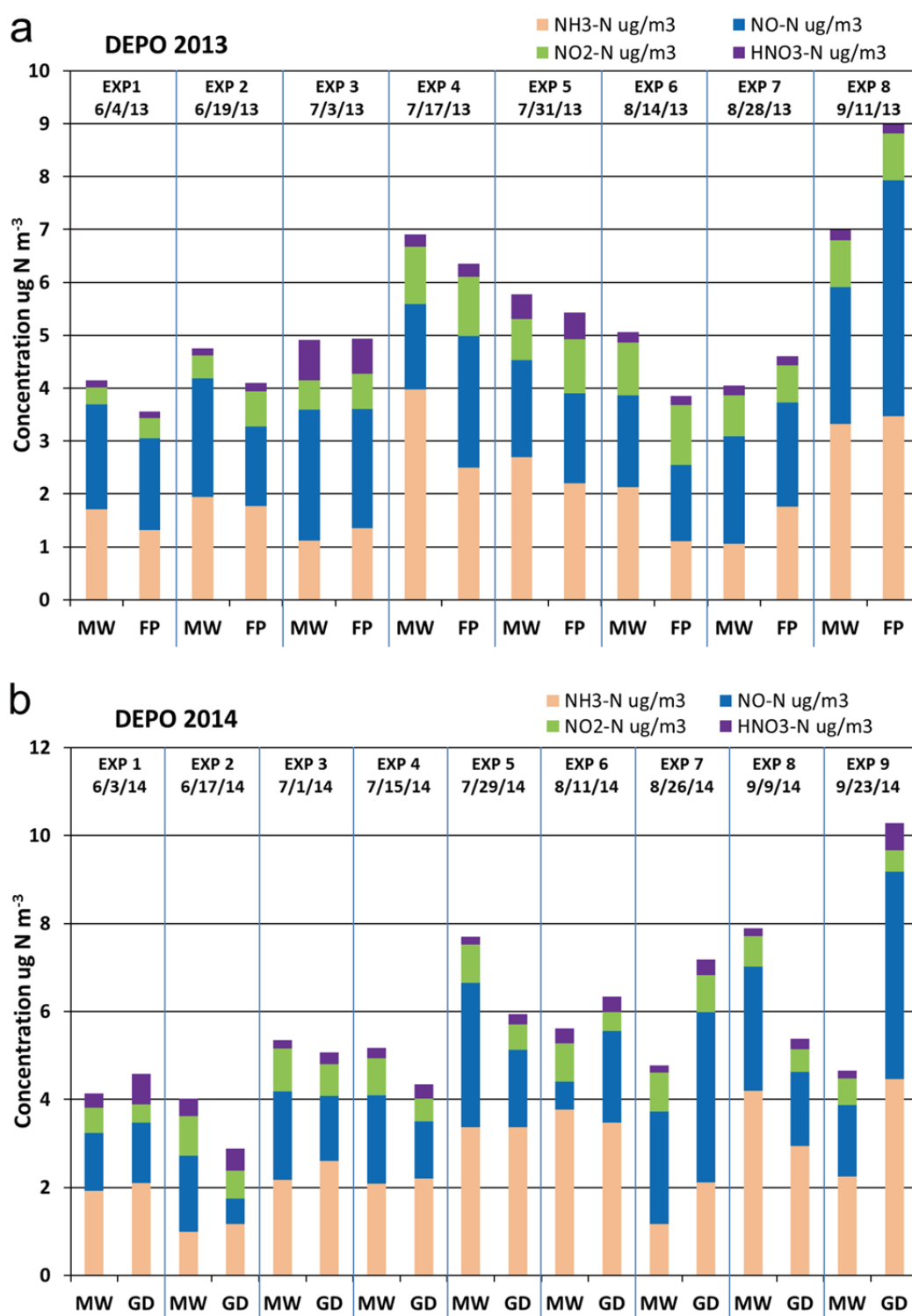


Fig. 6. Concentrations of NH₃, NO, NO₂, and HNO₃ at DEPO, expressed as $\mu\text{g N m}^{-3}$. Part a: 2013 data; MW = Meadow, FP = Flagpole. Part b: 2014 data; MW = Meadow, GD = Granite Dome.

daytime hours, resulting in an increase in the height of the boundary layer and efficient downward mixing of O₃-rich air from aloft. The O₃ measured at the surface therefore increases rapidly after sunrise, and reaches a maximum that reflects the background O₃ that exists in the free troposphere, with local photochemical production of O₃

playing a smaller role. During evening hours, access to the free troposphere may continue unabated for high-elevation sites that have steeply sloped topography, while lower elevation sites with topography that supports the formation of nocturnal temperature inversions will likely experience greatly diminished downward mixing (Burley *et al.*, 2015).

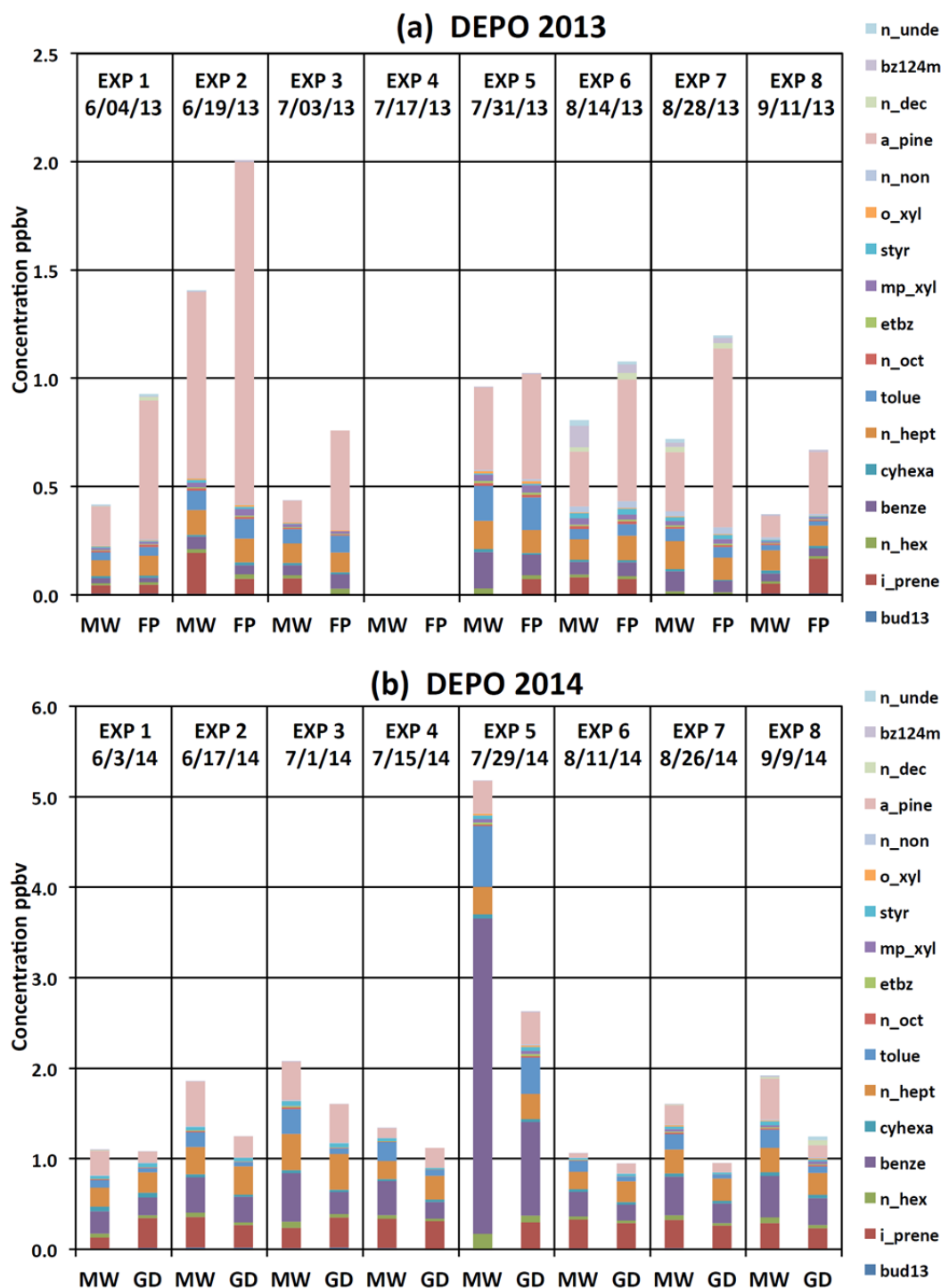


Fig. 7. Concentrations of VOCs at DEPO. Part a: 2013 data; MW = Meadow site, FP = Flagpole site. Part b: 2014 data; MW = Meadow site, GD = Granite Dome site. The data for monitoring period #4 in 2013 have been omitted from Fig. 7(a) because they were compromised by the “back diffusion” sampling problem discussed in the text.

A number of investigations have attempted to quantify the relative contribution of total background O_3 , which they have defined as total modeled O_3 minus anthropogenic O_3 from North America. (Note that the definition of “background” used by these studies differs slightly from the definition used in the preceding paragraph, where the free tropospheric O_3 “background” above DEPO included

anthropogenic contributions from upwind sources.) In some cases these investigations have also quantified transport of anthropogenic O_3 from Asia and stratospheric intrusions. Cooper *et al.* (2011) analyzed six weeks of ozonesonde data (May 10–June 19, 2010) from a network of west coast sites, and concluded that baseline tropospheric ozone coming ashore along the California coast at heights above 2 km

had a major impact on the high elevation terrain of eastern California. Cooper *et al.* (2011) also asserted that, for average daytime conditions, there was no enhancement (i.e., increase due to local photochemical production) of lower tropospheric O₃ in the northern Central Valley, but enhancements of 12–23% in the southern Central Valley. Lin *et al.* (2012) analyzed three months of data (April–June, 2010) from ozonesondes, LIDAR, and surface measurements with the high-resolution GFDL AM3 chemistry-climate model. This analysis, which focused upon 15 high-elevation western U.S. sites, yielded an average (calculated) MDA8 concentration of 61.0 ppb, slightly higher than the observed value of 55.3 ppb. Of the 61.0 ppb produced by the model, 50.0 ppb were attributed to the total background contribution, with the remaining 11.0 ppb attributed to anthropogenic sources over North America. The 50.0 ppb of total background included 4.7 ppb from anthropogenic sources in Asia plus 22.3 ppb from stratospheric intrusions. In a later study, Lin and coworkers (2015) conducted a similar analysis using a March–August timeframe. This latter analysis indicated that total background O₃, O₃ from stratospheric intrusions, and O₃ from anthropogenic sources in Asia decreased by approximately 50%, 67%, and 50%, respectively, when one moved from a timeframe of April–May–June (used in Lin *et al.*, 2012) to a timeframe of July–August (Lin, 2016).

The results from Lin *et al.* (2012, 2015, 2016) suggest that, as the summer measurement period progressed, there was a shift in the relative source contributions for the O₃ observed at DEPO, even though measured O₃ concentrations remained roughly constant. In early June, background O₃ may have contributed ~50 ppb (on average) to the observed MDA8 values, with a much smaller contribution – perhaps ~10 ppb – from anthropogenic sources in California. By late summer (July–August), the contribution from background O₃ had likely decreased to ~25 ppb, with anthropogenic sources in California increasing to ~35 ppb. The hypothesis of an increasing California-based anthropogenic contribution as the summer progressed is consistent with increased

summertime emissions of ozone precursors, warmer temperatures, and increased solar insolation.

The presence of a California-based anthropogenic contribution can also be inferred from the diurnal cycles shown in Fig. 4. Since local photochemical production and regional-scale transport typically occur later in the day compared to the initial break-up of the nocturnal boundary layer, O₃ measurements that are impacted by these latter sources tend to increase throughout the afternoon hours (Seinfeld and Pandis, 1998). The positive slopes of the mid-day diurnal maxima observed at DEPO, which correspond to an increase in the Fig. 4 data from ~50 ppb at 10:00 PST to ~58 ppb at 17:00 PST, suggest that regional and/or local sources of ozone are present. Similar increases in afternoon O₃ have also been observed at other western slope Sierra locations – such as Turtleback Dome in Yosemite National Park (Burley and Ray, 2007) – that have good access to the SJV. Sites that are not significantly impacted (on average), by direct, same-day transport from the SJV – such as White Mountain Summit (Burley and Bytnerowicz, 2011) or high elevation sites at Lake Tahoe (Burley *et al.*, 2015) – instead show diurnal maxima that remain flat during the afternoon hours. In these latter cases, O₃ from California-based anthropogenic sources is still present, but as an addition to the free tropospheric background rather than something that is transported more directly from the SJV.

While the Fig. 4 data indicate the presence of California-based anthropogenic O₃ – specifically from local and/or regional sources – they do not address the relative amounts contributed by (i) local photochemical production at the DEPO site; (ii) surface-level transport of intact, polluted air masses moving up the drainage of the San Joaquin River; or (iii) more diffuse transport of O₃ occurring at higher altitudes in the free troposphere. Given the low values of NO₂ measured by the passive samplers (Table 3) and the near-perfect agreement between the 2013 O₃ data measured at the Meadow and Flagpole sites, it seems unlikely that local sources are contributing more than a few ppb of O₃. If local

Table 3. Concentrations of nitrogenous and sulfurous air pollutants measured with passive samplers.

Pollutant	2013					
	No fires (N = 3)		Fires (N = 5)		All (N = 8)	
	Range	Mean	Range	Mean	Mean	SD
NH ₃ (μg m ⁻³)	1.36–2.37	1.93	1.28–4.83	3.20	2.73	1.25
NO (ppb)	3.46–4.31	3.89	2.82–4.51	3.42	3.59	0.60
NO₂ (ppb)	0.55–0.97	0.76	1.36–1.90	1.58^a	1.27	0.48
HNO ₃ (μg m ⁻³)	0.59–3.46	1.56	0.84–2.08	1.15	1.30	0.99
SO ₂ (μg m ⁻³)	0.22–0.46	0.34	0.18–0.54	0.36	0.35	0.13
Pollutant	2014					
	No fires (N = 5)		Fires (N = 4)		All (N = 9)	
	Range	Mean	Range	Mean	Mean	SD
NH₃ (μg m⁻³)	1.20–2.63	2.02	2.73–5.09	4.12^a	2.96	1.36
NO (ppb)	2.28–4.45	3.35	1.10–5.71	3.64	3.48	1.41
NO ₂ (ppb)	1.00–1.72	1.46	1.07–1.52	1.33	1.40	0.25
HNO ₃ (μg m ⁻³)	0.76–1.85	1.20	0.77–1.54	0.98	1.10	0.41
SO₂ (μg m⁻³)	0.28–0.46	0.40	0.16–0.30	0.26^a	0.34	0.10

^a Bolded data indicate significant differences between the fire and no fire periods ($p < 0.05$).

sources were having a significant impact, then one would expect to see some differences between the O_3 measured at the local traffic hub (Flagpole site) versus the O_3 measured further away from the local traffic (Meadow site). Regional transport of polluted air from the SJV is therefore likely to provide more O_3 than local photochemical production.

In addition to transport phenomena, surface-level O_3 can also be influenced by deposition. For the DEPO site, dry deposition is observed to play an important role at the Meadow site. The very low pre-dawn O_3 concentrations recorded at this location (Figs. 2(a), 3(a), 4) reflect efficient dry deposition to the lush grassy meadow during evening hours, after the establishment of a nocturnal temperature inversion and the cessation of downward mixing of O_3 -rich air from aloft. The Meadow site rests on, and is surrounded on all sides by, lush ankle-high grass, which will act as an efficient O_3 sink due to its high deposition velocity for O_3 (Wesely and Hicks, 2000; Zhang *et al.*, 2003; Meszaros *et al.*, 2009).

At the Granite Dome site, O_3 concentrations remain elevated at night (Figs. 3(b) and 4). This result reflects the higher elevation and steeper topography of the Dome location, which combine to ensure that the Dome site will be less likely to experience nocturnal temperature inversions. During the evening hours, it is therefore more likely to maintain good access to downward mixing of O_3 -rich air from aloft. In addition, the greater distance between the Dome site and the nearby grassy meadow – which acts as an O_3 sink – will also keep O_3 concentrations higher. And the gravel/granite surface of the Granite Dome site will also help to lessen nocturnal loss of O_3 due to reduced dry deposition in the immediate vicinity of the sampling inlet.

Back-Trajectory Calculations

In order to get a better understanding of how regional-scale transport of polluted air masses can influence air quality at DEPO, HYSPLIT back-trajectory calculations were conducted for the 21 high- O_3 days (Table SI 3) when there was an exceedance of the NAAQS or CAAQS threshold for O_3 . In all cases, the trajectories with DEPO arrival heights of 100 or 500 m above ground level “crashed” into the ground prior to arriving at DEPO, rendering the back-trajectory invalid. For the 1500 m arrival height, there were 10 days on which the trajectory “crashed” and 11 days when the trajectory arrived at DEPO without hitting the ground. All 11 of the successful trajectories spent substantial time over the SJV as they made their final approach into DEPO, with six trajectories approaching from the south (see representative example in Fig. SI 2(a)), three moving down the middle of the SJV from the northwest and then turning sharply to the left and ascending the western slope of the Sierra Nevada range (Fig. SI 2(b)), and two approaching from a southwesterly direction (Fig. SI 2(c)).

The HYSPLIT results suggest that exceedances of the NAAQS or CAAQS become more likely when the total background O_3 arriving at DEPO is augmented by regional transport of “dirtier” air parcels that have spent substantial time over the SJV. They also suggest that most of the regional transport that is taking place is occurring at higher

altitudes (as opposed to surface-level transport up the drainage of the San Joaquin River). The observation that transport aloft is more important than transport near the surface is consistent with the previous analyses from Cooper *et al.* (2011), and from VanCuren (2015), who investigated O_3 transport from the Los Angeles and San Joaquin source areas to the Mojave Desert and found that surface-level transport of intact, polluted air masses was not the dominant source of O_3 at rural sites. Instead, he observed that transport at altitudes above approximately 1000 masl played the dominant role. However, it should also be emphasized that the HYSPLIT model is a relatively blunt instrument with limited resolution. It can do a good job of representing regional-scale phenomena, but has insufficient spatial and temporal resolution to accurately model local-scale transport in mountainous terrain. Accurate, high-resolution modeling that includes all of the relevant parameters (topography, surface vegetation, transport, meteorology, emissions, chemistry, etc.) is therefore needed to better address these questions.

PM_{2.5}

Concentrations of PM_{2.5} at DEPO were generally very low during the no-fire periods (Fig. 5, Table SI 4) with means below $13 \mu\text{g m}^{-3}$ and 24 h maximum values below $16 \mu\text{g m}^{-3}$. These results for PM_{2.5} – i.e., summer season highs of ~ 12 to $15 \mu\text{g m}^{-3}$ – are similar to prior results from other Sierra Nevada sites and results from the Owens Valley, which lies just east of the Sierra Nevada range (Cisneros *et al.*, 2014; California Air Resources Board, 2016b; Tribal Environmental Exchange Network, 2016). They are also comparable to the concentrations that have been measured on the western slopes of the Sierra Nevada at elevations above ~ 500 m (Cisneros *et al.*, 2014).

Nitrogenous Compounds, VOCs, and SO₂

Ambient concentrations of NH_3 (~ 2 to $3 \mu\text{g m}^{-3}$), NO (~ 3 to 4 ppb), NO_2 (~ 1 to 2 ppb), HNO_3 ($\sim 1 \mu\text{g m}^{-3}$), and SO_2 ($< 0.4 \mu\text{g m}^{-3}$) were generally low and within ranges typical for remote locations of the Sierra Nevada Mountains (Table 3; Bytnerowicz and Fenn, 1996; Bytnerowicz *et al.*, 2000, 2015). Concentrations of NH_3 , HNO_3 and SO_2 were similar to those determined in 1999 at several remote locations of Sequoia National Park that are not directly affected by emissions from the SJV (Bytnerowicz *et al.*, 2002). Across two summer seasons of monitoring, NH_3 and NO provided the highest contribution of reactive N, while the contributions from NO_2 and HNO_3 were much smaller (Fig. 6).

Concentrations of VOCs were also low during the no-fire periods (Fig. 7), with the biogenic species α -pinene and isoprene being most abundant. While generally similar results were obtained in both 2013 and 2014, the data suggest that DEPO may have been exposed to somewhat “fresher” pollution (i.e., local sources) in 2013, and somewhat “older” pollution (i.e., upwind sources) in 2014. This hypothesis is supported by the VOC data, which indicate lower average concentrations of anthropogenic compounds (i.e., benzene, toluene, n-heptane) in 2013 and higher average concentrations of these compounds in 2014. The toluene/benzene ratios (R),

which provide information regarding the photochemical age of the emissions (de Gouw *et al.*, 2005), were much lower in 2014 ($R < 0.5$) than in 2013 ($2 > R > 0.5$).

Fire Impacts – Ozone

Determining the impacts of wildland fire emissions on downwind concentrations of surface-level O_3 can be very difficult, as fires can both suppress local O_3 (due to increased emissions of NO and decreased solar radiation) and either enhance or decrease downwind O_3 (due to changes in concentrations of NO_x and VOC, which are ozone precursors). Fires can also influence the rates of the photochemical reactions that produce O_3 , and they can affect the meteorological processes that govern the movement of air masses in complex mountain terrain (Seinfeld and Pandis, 1998).

Given that NPS/EPA/CARB managers frequently focus upon surface-level O_3 trends in terms of NAAQS or CAAQS exceedances, one way in which potential fire impacts can be assessed is to compare the number of high O_3 days that exceed either the (old) NAAQS threshold of 75 ppb or the new NAAQS (and current CAAQS) threshold of 70 ppb during fire vs. non-fire periods. While this is admittedly a crude method, it can help to identify any larger-scale trends that may or may not be present.

In 2013, the 70 ppb CAAQS threshold for O_3 was exceeded at DEPO on 5 separate dates (Fig. 2, Table SI 3). The first exceedance occurred on June 15, before the onset of Aspen Fire, and it was therefore unaffected by fire emissions. Three subsequent exceedances (July 24, July 31, and August 6) took place during the Aspen Fire, and were observed at both the Meadow and the Flagpole sites. Careful inspection of the $PM_{2.5}$ data in Fig. 5(a) indicates that all three of these exceedance dates experienced elevated concentrations of $PM_{2.5}$, which is a direct indicator that the DEPO site was impacted by upwind fire emissions on these particular days. Another CAAQS threshold exceedance was observed during the Rim Fire, at the Flagpole site, on September 20. However, the data in Fig. 5(a) indicate that this latter exceedance was probably not impacted by upwind fire emissions, as the $PM_{2.5}$ value remained at the baseline level.

In 2014 CAAQS threshold exceedances were observed on 16 separate dates (Fig. 3, Table SI 3). Four of these exceedances were observed at the Meadow site, but none of them occurred during the French or King Fires. All 16 of these exceedances were observed at the Granite Dome site, with one exceedance taking place during the French Fire (August 16) and 3 exceedances taking place during the King Fire (September 13, September 23, October 7). However, none of these latter four threshold exceedances co-existed with elevated $PM_{2.5}$ (Fig. 5(b)), which indicates that DEPO was not significantly impacted by fire emissions on the dates when the exceedances were observed.

Overall, the emissions from the fires that occurred in 2013 and 2014 appear to have had a small impact on the ambient concentrations of O_3 that were measured at DEPO. While emissions from the Aspen Fire may have contributed to 1–3 exceedances of the CAAQS threshold in 2013, emissions

from the Rim, French, and King Fires do not appear to have influenced any of the CAAQS exceedances that occurred while these three latter fires were underway. Concentrations of O_3 were routinely elevated in the absence of fires (especially at the Granite Dome site in 2014), which suggests that emissions from upwind wildfires did not play a significant role in high- O_3 episodes at DEPO.

Fire Impacts – $PM_{2.5}$

During fire events, DEPO experienced large spikes in $PM_{2.5}$ concentrations due to the sheltered topography of the Meadow site where the EBAM was deployed. At this location, pollutants transported in during well-mixed daylight hours became trapped near the surface at nighttime, when stable temperature inversions occurred. The same meteorological conditions that caused very low O_3 (via enhanced dry deposition to the grassy surface of the meadow) simultaneously contributed to a substantial build-up of $PM_{2.5}$.

The 24-hour daily $PM_{2.5}$ averages ranged from 1.3 to 92.7 $\mu g m^{-3}$ in 2013 and 1.6 to 27.8 $\mu g m^{-3}$ in 2014, with mean concentrations of 14.6 $\mu g m^{-3}$ in 2013 and 9.4 $\mu g m^{-3}$ in 2014. During the 2013 Aspen and Rim Fires the 24 h $PM_{2.5}$ concentrations reached 92.7 and 69.6 $\mu g m^{-3}$, respectively. In 2013, from July 24 through August 4 and again on August 6 (during the Aspen Fire), the daily 24-hour concentrations surpassed the federal NAAQS threshold of 35 $\mu g m^{-3}$. (This threshold is important because the NAAQS for $PM_{2.5}$ specifies that a violation has occurred if the annual 98th percentile of the 24-hour averages, averaged over a three-year period, exceeds 35 $\mu g m^{-3}$. The NAAQS also requires that the annual mean value for $PM_{2.5}$, averaged over three years, be no greater than 12.0 $\mu g m^{-3}$.) For these dates the maximum hourly concentrations for the day ranged from 85 to 214 $\mu g m^{-3}$. During the Rim Fire the 24-hour federal standard threshold was surpassed on August 31 and September 1 with the 24-hour average concentrations reaching 69.6 $\mu g m^{-3}$ and 46.8 $\mu g m^{-3}$, respectively, and 1-hour maxima of 132 $\mu g m^{-3}$ and 115 $\mu g m^{-3}$, respectively. During 2013, the AQI rating for the $PM_{2.5}$ 24-hour average concentration was recorded as “unhealthy” for five days during the Aspen Fire and once during the Rim Fire, while the AQI rating for “unhealthy for sensitive” was observed on five days during the Aspen Fire and once during the Rim Fire (Table SI 4).

In 2014 during the French and King Fires, the 24-hour $PM_{2.5}$ levels were much lower, with maximum 24-hour daily averages of 21.9 and 27.8 $\mu g m^{-3}$, respectively. The largest impacts of smoke on $PM_{2.5}$ were from the French Fire during the period of July 28 through August 9. However, there was a gap in $PM_{2.5}$ data from July 27 to August 5 when the EBAM instrument was malfunctioning (Table SI 4). Smoke was present at the DEPO site from September 9 through September 23, when smoke from the King Fire was widely dispersed throughout California, including the Sierra Nevada Mountains and the Owens Valley.

If one excludes the fire days, the AQI rating for $PM_{2.5}$ at DEPO was usually “good” (76 and 87 days, respectively, during 2013 and 2014) or “moderate” (21 and 23 days).

Emissions from wildland fires, however, drastically changed the ambient PM_{2.5} concentrations at DEPO. The DEPO site received smoke with PM_{2.5} concentrations similar to what can be expected during wildfires of the size and intensity historically seen throughout the Sierra Nevada (Schweizer and Cisneros, 2014). The fires that had the greatest impact on ground level concentrations of PM_{2.5} were not the large, high-intensity Rim and King Fires; prevailing transport patterns and lack of proximity lessened their impacts at DEPO even while these two fires were producing large health impacts at other, more densely populated, locations (Moeltner *et al.*, 2013). The relatively small Aspen Fire instead had the largest impact on PM_{2.5}, highlighting the importance of efficient transport of the emission plume the receptor site. However, even the highly elevated PM_{2.5} levels measured during the Aspen Fire would most likely not cause a violation of the official NAAQS for this pollutant, which – as noted above – is calculated over a three-year window. Our summertime monitoring likely included most of the highest PM_{2.5} concentrations, while the much lower winter concentrations were missed. Therefore, we predict that – even with periodic exposure to wildfires during the summer months – the DEPO site is not likely to violate the three-year NAAQS for PM_{2.5}. This assessment is consistent with what has been observed at other remote Sierra Nevada locations (Cisneros *et al.*, 2014).

Fire Impacts – Nitrogenous Compounds, VOCs, and SO₂

Observed concentrations of NO, HNO₃ and SO₂ remained relatively unchanged during the 2013 and 2014 fire periods. Fire emissions increased levels of ambient NH₃ during both years and those of NO₂ in 2013. These results are consistent with observations made in other areas affected by wildland fires (Goldammer *et al.*, 2009). The observed changes in concentrations of both pollutants could lead to increased N dry deposition, but their impacts at those still low levels would most likely be minimal (Fenn *et al.*, 2010). No direct toxic effects on human or ecosystem health are to be expected from the low N pollutant concentrations reported in Fig. 6 and Table 3 (Bytnerowicz *et al.*, 1998).

VOC concentrations increased significantly during the French Fire in 2014 (Fig. 7), especially concentrations of benzene. Benzene is present in wood smoke in proportionately significant quantities (McDonald *et al.*, 2001). Although benzene is also emitted in automotive exhaust, the benzene enrichment during the French Fire indicates that wood smoke is its main source.

Given the limited accuracy and precision of the passive samplers, and their very coarse temporal resolution (~2 weeks), it should be emphasized that they are not a good method for assessing fire impacts. Our data show some of the changes (increased concentrations of NH₃, NO_x, and benzene) that would be expected with upwind fire activity, but other expected impacts (increased concentrations of NO and HNO₃) are not observed. These inconsistencies in the data likely reflect the experimental limitations of the passive samplers, since there is no reason to expect that the fires included in the present analysis were somehow different or unique compared to the other wildfires that have been

analyzed in previous reports (Goldammer *et al.*, 2009).

CONCLUSIONS

During the summer months, DEPO routinely experiences exceedances of the new NAAQS (and current CAAQS) threshold for O₃ (an 8-hour average of 70 ppb). Exceedances of the old NAAQS threshold (75 ppb) are less frequent. Elevated concentrations of O₃ are observed when total background O₃ is augmented by regional-scale transport, at higher altitudes, of polluted air from the San Joaquin Valley. Local photochemical production is not a significant contributor of O₃, but the observed diurnal patterns are strongly impacted by the topography and ground cover of the sampling site. In the absence of fires, DEPO experiences low concentrations of NH₃, NO, NO₂, HNO₃, SO₂, VOCs and PM_{2.5}. Wildfires do not appear to impact the observed O₃ concentrations, but the Aspen and Rim Fires did cause short-term exceedances of the PM_{2.5} air quality standards. As a result, the Air Quality Index for PM_{2.5} shifted from “good” to “unhealthy” or “unhealthy to sensitive people” while these fires were burning. Concentrations of NH₃ increased during all fires, as did those of NO₂ during the Aspen and Rim Fires. However, those increases are not considered toxic to human health or with any significant ecological consequences. Concentrations of benzene increased substantially during the French Fire.

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SUPPLEMENTARY MATERIAL

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

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