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On the effect of upwind emission controls on ozone in Sequoia National Park

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Abstract. Sequoia National Park (SNP) experiences the worst ozone (O_3) pollution of any national park in the U.S. SNP is located on the western slope of the Sierra Nevada Mountains, downwind of the San Joaquin Valley (SJV), which is home to numerous cities ranked among the most O_3-polluted in the U.S. Here, we investigate the influence of emission controls in the directly upwind SJV city of Visalia on O_3 concentrations in SNP over a 12-yr time period (2001–2012). We show that export of nitrogen oxides (NO_x) from the SJV plays a larger role in driving high O_3 in SNP than does transport of O_3. As a result, O_3 in SNP has been more responsive to NO_x emission reductions as a function of increasing downwind distance from the SJV. We report O_3 trends by various concentration metrics, but do so separately for when environmental conditions are conducive to plant O_3 uptake and for when high O_3 is most common, which are time periods that occur at different times of day and year. We find that precursor emission controls have been less effective at reducing O_3 concentrations in SNP in springtime, which is when plant O_3 uptake in Sierra Nevada forests has been previously measured to be greatest. We discuss the implications of regulatory focus on high O_3 days in SJV cities on O_3 concentration trends and impacts in SNP.

1 Introduction

Sequoia National Park (SNP) is a unique and treasured ecosystem that is also the most ozone-polluted national park in the U.S. (Meyer and Esperanza, 2016). Ozone (O_3) concentrations in SNP exceeded the current human health-based 8-h O_3 National Ambient Air Quality Standard (NAAQS), defined as 70 ppb, on an average of 119 days per year over the time period 2001–2012. At the same time, there were on average 76 8-h NAAQS exceedances per year in Los Angeles, California, 36 per year in Denver, Colorado, and 55 per year in Phoenix, Arizona, cities which are three of the most O_3-polluted U.S. cities (American Lung Association, 2016).

While O_3 is harmful to humans, it is also damaging to plants and ecosystems (e.g., Reich, 1987), with visible O_3 injury observed in many forests across the U.S. (Costonis, 1970; Pronos and Vogler, 1981; Ashmore, 2005), including in SNP (Peterson et al., 1987; Peterson et al., 1991; Patterson and Rundel, 1995; Grulke et al., 1996; National Park Service, 2013). O_3 exposure also causes a variety of other effects such as decreased plant growth (Wittig et al., 2009), reduced photosynthesis and disrupted carbon assimilation (Wittig et al., 2007; Fares et al., 2013), diminished ecosystem gross and net primary productivity (Ainsworth et al., 2012; Wittig et al., 2009), modified plant resource allocation (Ashmore, 2005), and impaired stomatal response (Paoletti and Grulke, 2010; Hoshika et al., 2014). On multi-decadal timescales, O_3-resistant plants may thrive over O_3-sensitive species, system-level dynamics that would maintain forest productivity and carbon storage, but would induce changes in ecosystem composition (Wang et al., 2016).

SNP is home to more than 1,550 plant taxa with numerous plant species found nowhere else on Earth (Schwartz et al., 2013). One endemic species is the giant sequoia (*Sequoiadendron giganteum*), the largest living tree in the world. Large-tree ecosystems like SNP have been shown to be more sensitive to perturbation (Lutz et al., 2012) because ecological functions are provided primarily by a few large trees, rather than many smaller species. Large-diameter trees disproportionately influence patterns of tree regeneration and forest succession (Keeton and Franklin, 2005), carbon and nutrient storage, forest structure and fuel deposition at death, arboreal wildlife habitats and epiphyte communities (Lutz et al., 2012), and water storage (Sillett and Pelt, 2007), which is of critical importance in drought-prone SNP. While mature sequoias are relatively resistant to O_3, seedlings are sensitive, and high O_3 has been demonstrated to cause both visible injury and altered plant-atmosphere light and gas exchange (Miller et al., 1994). Giant sequoias grow in mixed-conifer groves with companion species ponderosa pine (*Pinus ponderosa*) and Jeffrey pine (*Pinus jeffreyi*). O_3 impacts on these pines have been documented for decades in SNP (Duriscoe, 1987; Pronos and Vogler, 1981) and include early needle loss, reduced growth, decreased photosynthesis, and lowered annual ring width (Peterson et al., 1987; Peterson et al., 1991).

SNP is located in Central California on the western slope of the Sierra Nevada Mountains downwind of the O_3-polluted San Joaquin Valley (SJV) (Figure 1). Previous model estimates suggest at least half of peak daytime O_3 in SNP is produced upwind from anthropogenic precursors (Jacobson, 2001). For the past two decades, regulations have reduced O_3 concentrations in the SJV (Pusede and Cohen, 2012). For example, in Fresno, high O_3 days, defined as days exceeding the 70 ppb 8-h O_3 NAAQS, were 50% less frequent in 2007–2010 than ten years earlier (on high temperature days). At the same time, in Bakersfield, high O_3 days were 15–40% less frequent (on high temperature days). NO_x emission controls contributed to these decreases (Pusede and Cohen, 2012), with summertime (April–October) daytime (10 am–3 pm local time, LT) nitrogen dioxide (NO_2) concentrations falling by 50% from 2001 to 2012, changing linearly by –0.5 ppb yr^{-1} in the SJV city of Visalia. The reductions in precursor emissions that brought about these decreases in high O_3 are likely to have also affected SNP.

The success of O_3 regulatory strategies is generally measured through attainment of human health-based NAAQS rather than ecosystem-impact metrics. While there is a secondary standard requirement aimed at vegetation protection, it has historically been the same as the primary NAAQS (Environmental Protection Agency, 2016). Plants and ecosystems have been shown to be sensitive to lower O_3 concentrations, over longer-term exposures, and at different times of day and year than when

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NAAQS exceedances are frequent (e.g., Kurpius et al., 2002; Panek 2004; Panek and Ustin 2005; Fares et al., 2013). The U.S. Environmental Protection Agency (EPA) has considered redefining the secondary standard to reflect ecological systems, with the W126 metric put forth (Environmental Protection Agency, 2010). W126 is a 12-h daily summation weighted to emphasize higher O_3 concentrations that is used by the U.S. National Park Service. There are a number of other concentration metrics used to quantify ecosystem O_3 impacts. In Europe, the AOT40 index is equal to all daytime (defined as solar radiation ≥50 W m^{-2}) hourly O_3 concentrations greater than 40 ppb. In the U.S., two widely used indices are the SUM0 and SUM06 (Panek et al., 2002), which are the sum of all daytime hourly O_3 mixing ratios greater than or equal to 0 ppb and 60 ppb, respectively.

Even ecosystem-based concentration metrics are proxies of variable quality for O_3 impacts, if O_3 concentrations are not well correlated with plant O_3 uptake (e.g., Emberson et al., 2000; Panek et al., 2002; Panek, 2004; Fares et al., 2010a). This is because of temporal mismatches between when O_3 is high and when plants uptake O_3 from the atmosphere, with differences in high O_3 and efficient O_3 uptake occurring on both diurnal and seasonal timescales. While O_3 impacts are best represented by direct measurements of the O_3 stomatal flux (e.g., Musselman et al., 2006; Fares et al., 2010a; Fares et al., 2010b), exceedances of flux-based standards are difficult to operationalize, as there are few long-term O_3 flux observational records and because reported thresholds, when available, are highly species-specific (Mills et al., 2011).

Under the 1977 Clean Air Act Amendments, selected national parks were designated as Class I Federal areas and, as part of this, the National Park Service began measuring O_3 concentrations in the late 1980s, prioritizing national parks downwind of cities and polluted areas, including SNP (National Park Service, 2015a). Data from these monitors can be used to compute various O_3 concentration metrics; however, direct flux measurements do not exist in SNP, or other national parks, over long enough timescales to assess the effects of multi-year emissions controls. Forest survey data, which assess O_3 impacts by monitoring changes in plants and forests from visible injury records and species population estimates, are limited, as they are labor and time intensive, requiring the evaluation of at least dozens of trees per stand to distinguish moderate levels of injury (Duriscoe et al., 1996). These studies occur at some time interval after exposure, making correlation to specific O_3 concentrations not possible. As a result, there is a need to assess trends using concentration metrics, but to do so with knowledge of when plant O_3 uptake is greatest.

In this paper, we report O_3 trends from 2001 to 2012 in SNP and the upwind SJV city of Visalia to study the effect of SJV emission controls on SNP O_3. We compute trends in human health and ecosystem-based concentration metrics separately when regional environmental conditions favor plant O_3 uptake (springtime) and when high O_3 is most frequent (O_3 season). We describe these O_3 changes in Visalia and SNP as function of distance downwind of Visalia. We demonstrate the importance of transport of urban NO_x from the SJV on O_3 production (PO_3) chemistry in SNP. Finally, we discuss the descriptive power of various O_3 metrics, considering the implications of a regulatory focus on human health-based standards to improve O_3 air pollution and to reduce ecosystem impacts in SNP and polluted downwind ecosystems more broadly.

2 Sequoia National Park (SNP) and the San Joaquin Valley (SJV)

SNP is located in the southern Sierra Nevada Mountains (Figure 1) and is part of the largest continuous wilderness in the contiguous U.S., which includes Kings Canyon NP and Yosemite NP. The SJV extends 250 miles in length and is situated between the Southern Coast Ranges to the west, the Sierra Nevada Mountains to the east, and the Tehachapi Mountains to the south. The southern SJV is the most productive agricultural region in the U.S., an oil and gas development area, and home to the cities of Fresno, Visalia, and Bakersfield. The same climatic conditions that support agriculture in the region, especially the numerous sunny days, are also favorable for PO_3. The high rates of local PO_3 (Pusede and Cohen, 2012; Pusede et al., 2014), diverse local emission sources outside historical regulatory focus, e.g., agricultural and energy development activities (e.g., Gentner et al., 2014a; Gentner et al., 2014b; Pusede and Cohen, 2012; Park et al., 2013), and surrounding mountain ranges that impede air flow out of the valley, have resulted in severe regional O_3 pollution. Four SJV cities rank among the ten most-O_3 polluted cities in the U.S.: Bakersfield (ranked 2), Fresno (3), Visalia (4) and Modesto-Merced (6) (American Lung Association, 2016).

Multiple airflow patterns influence O_3 in SNP and the SJV (Zhong et al., 2004). First, summertime (April–October) afternoon low-level winds in the southern SJV are generally from the west-northwest (represented by Visalia in Figure 2). These winds are strengthened by an extended land-sea breeze, with onshore flow entering central California through the Carquinez Strait near the San Francisco Bay and diverging to the south into the SJV and north to the Sacramento Valley (e.g., Zaremba and Carroll, 1999; Dillon et al., 2002; Beaver and Palazoglu, 2009; Bianco et al., 2011). Second, at night, a recurring local flow pattern in the SJV, known as the Fresno eddy, recirculates air in the southern region of the valley around Bakersfield in the counterclockwise direction back to Fresno and Visalia, further enhancing O_3 pollution and precursors in these cities (e.g., Ewell et al., 1989; Beaver and Palazoglu, 2009). Third, the most populous and O_3 polluted cities in the southern SJV, Fresno, Visalia, and Bakersfield, are located along the eastern valley edge. Here, air movement is also affected by mountain-valley flow (e.g., Lamanna and Goldstein 1999; Zhong et al., 2004; Trousdell et al., 2016). During the day, thermally-driven upslope flow brings air from the valley floor to higher mountain elevations from the west-southwest (Figure 2). In Figure 3, a high elevation SNP site (Moro Rock, 36.5469 N, 118.7656 W, 2050 m ASL) is visibly above the SJV surface layer in the late morning, but within this polluted layer in late afternoon. At night, the direction of flow reverses and air moves downslope from the east-northeast (Figure 2). Due to the prevalence of shallow nighttime surface inversions, evening downslope valley flow at higher elevations may be stored within nocturnal residual layers and entrained into the surface layer the following morning.

3 Results

High O_3 days are most frequent in SNP and the SJV in the summer and early fall (Pusede and Cohen, 2012; Meyer and Esperanza, 2016), as PO_3 chemistry is strongly temperature-dependent (Pusede et al., 2015), particularly in the SJV (Pusede and Cohen, 2012; Pusede et al., 2014). O_3 season is defined here as June–October and 90% of annual 8-h O_3 NAAQS exceedances in SNP occur during O_3 season (2001–2012).

In the Sierra Nevada foothills, high rates of plant O_3 uptake are asynchronous with O_3 season due to the Mediterranean climate (e.g., Kurpius et al., 2002; Kurpius et al., 2003; Panek, 2004). Because plants also capture carbon dioxide required for photosynthesis and transpire through stomata, O_3 uptake is not only a function of the atmospheric O_3 concentration, but also of photosynthetically-active radiation (PAR), the inverse of the atmospheric vapour pressure deficit (VPD) (Kavassalis and Murphy, 2017), and soil moisture (e.g., Reich, 1987; Bauer et al., 2000; Fares et al., 2013). In SNP, PAR is highest in the late spring through early fall and VPD is at a minimum in winter and spring. In the Sierra Nevada Mountains, plant water status (VPD and soil moisture) has been shown to explain up to 80% of day-to-day variability in stomatal conductance, with conductance decreasing with increasing water stress from mid-May to September and remaining low until soils are resaturated by wintertime precipitation. Plant O_3 uptake in Sierra Nevada forests has been reported to be greatest in April–May (Kurpius et al., 2002; Panek, 2004; Panek and Ustin, 2005).

In this context, we separately consider O_3 trends in springtime (April–May), which is when plant O_3 uptake best correlates with variability in atmospheric O_3 concentrations in the region, and during O_3 season (June–October), which is when O_3 concentrations are highest.

3.1 Diurnal O_3 variability

Diurnal O_3 and O_x ($O_x \equiv O_3 + NO_2$) concentrations are shown in Figure 4 in springtime (panel a) and O_3 season (panel b) from 2001–2012. O_3 data in SNP are collected at two monitoring stations, a lower elevation site, SNP-Ash Mountain (36.489 N, 118.829 W), at 515 m above sea level (ASL) and a higher elevation site, SNP-Lower Kaweah (36.566 N, 118.778 W), at 1926 m ASL (Figure 1). We refer to these stations as SEQ1 and SEQ2, respectively. O_3 and NO_2 data are measured in Visalia (36.333 N, 119.291 W), directly upwind of SNP at 102 m ASL. All data are provided by the California Air Resources Board and are available for download at https://www.arb.ca.gov/aqmis2/aqdselect.php. In Figure 4, Visalia data are shown as O_x to account for the portion of O_3 stored as NO_2, which can be substantial in the nearfield of fresh NO_x emissions and at night. NO_2 data are not available in SEQ1 and SEQ2; however, these sites are removed from large NO_x sources (Figure 1) and $O_3 \approx O_x$ is a reasonable approximation.

In Visalia, O_x concentrations increase sharply beginning in early morning (5 am LT) until 2 pm LT, continuing to rise slightly until 4–5 pm LT (Figure 4). This diurnal pattern reflects a combination of local PO_3 (the initial rise) and advection of O_x from the upwind source region (late afternoon maximum). In the morning (8 am LT) 30–40% of O_x is NO_2 and at 12 pm LT ~10% of O_x is NO_2.

Diurnal O_3 variability at SEQ1 and SEQ2 is characterized by two features, an early morning rise (6 am LT) and an increase in the late afternoon (3–4 pm LT). The timing of this morning O_3 increase is consistent with entrainment of O_3 in nocturnal residual layers aloft during morning boundary layer growth. The influence is substantial, as morning O_3 accounts for 50% (springtime and O_3 season) of the daily change in O_3 at SEQ1 and 50% (springtime) and 37% (O_3 season) of the daily

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change in O_3 at SEQ2. The timing of afternoon peak O_3 is consistent with upslope air transport from the SJV (Figures 2). If O_3 attributed to local PO_3 in Visalia is greatest around 2 pm LT, typical of many urban locations, then with mean winds at SEQ1 of 3 m s^{-1} and SEQ2 of 2 m s^{-1}, we expect O_3 to peak in SEQ1 at ~5 pm (45 km downwind of Visalia) and at SEQ2 shortly after (9.6 km downwind of SEQ1), which is generally what we observe. Data in Figure 4 are averaged over 2001–2012 and there has been no change in the hour of peak O_3 at either SNP site from 2001–2012.

3.2 Weekday-weekend O_3 variability

SNP and the SJV are in close geographic proximity but their local PO_3 regimes are different. In 2016, as part of the Korea-U.S. Air Quality (KORUS-AQ) experiment (https://www-air.larc.nasa.gov/missions/korus-aq/index.html) and Student Airborne Research Program (SARP), the NASA DC-8 sampled a low-altitude transect (~130 m above ground level) along the trajectory of SJV mountain-valley outflow. The DC-8 flew at ~10 am LT from Orange Cove, an SJV town 35 km north of Visalia, 24 km up the western slope of the Sierra Nevada Mountains to an elevation of ~1000 m ASL. In Figure 5, the change in NO_x and isoprene along this transect is shown as a function of change in surface elevation. Boundary layer NO_x is observed to decrease with increasing distance downwind of the SJV, while isoprene concentrations increase. Isoprene is a large source of reactivity in the Sierra Nevada foothills (e.g., Beaver et al., 2012) and the combined NO_x and isoprene gradients suggest distinct PO_3 regimes in the SJV and SNP.

If the major source of O_3 in SNP is O_3 produced in the SJV and transported downwind, then the observed NO_x dependence of PO_3 in SNP and the SJV would be the same even if PO_3 regimes in the two locations were different. To test this hypothesis, we consider O_3 in SNP and O_x in the SJV separately on weekdays and weekends. Weekday-weekend NO_x concentration differences are well-documented across the U.S. (e.g., Russell et al., 2012) and California (e.g., Marr and Harley, 2002; Russell et al., 2010), and are caused by reduced weekend heavy-duty diesel truck traffic, where heavy-duty diesel trucks are large sources of NO_x but not O_3 forming organic gases. As a result, NO_x concentrations are typically 30–60% lower on weekends than weekdays and these NO_x changes occur without comparably large decreases in reactive organic compounds (e.g., Pusede et al., 2014). PO_3 is the only term in the O_3 derivative expected to exhibit NO_x dependence.

We focus on the earliest 3-yr time period in our record, 2001–2003, which is when differences in PO_3 chemical sensitivity in the SJV and SNP are expected to be most pronounced (Pusede and Cohen, 2012). We define weekdays as Tuesdays–Fridays and weekends as Sundays to avoid atmospheric memory effects. Statistics were sufficient to minimize any co-occurring variation in meteorology, with no significant weekday-weekend differences observed in daily maximum temperature, wind speed, or wind direction. We focus on afternoon (12–6 pm LT) O_x, when O_3 concentrations in SNP are most influenced by the SJV. We also compare weekday-weekend O_x at high and moderate temperatures, with temperature regimes defined as days above and below the 2001–2012 seasonal mean daily maximum average temperature in Visalia. Temperatures in Visalia are well correlated (R^2 = 0.98) with temperatures in SEQ1 over 2001–2012. During springtime and O_3 season, mean maximum average temperatures in Visalia were 25.1 ± 5.9 and 32.0 ± 5.3 °C (ranges are 1σ variability), respectively.

At high temperatures, weekday-weekend differences in O_x in Visalia and O_3 at SEQ1 and SEQ2 were not statistically distinct in either springtime or during O_3 season. Averaged across sites, percent differences in weekdays and weekends (relative to weekends) were 9.4 ± 5.4% in the springtime and 4.1 ± 2.4% during O_3 season, with greater weekday concentrations implying NO_x-limited chemistry. Errors are the average standard errors of the 3-yr means.

At moderate temperatures, statistically significant weekday-weekend differences were observed. During O_3 season, O_x was 6.3 ± 3.5% higher on weekends than weekdays in Visalia, indicating local PO_3 was NO_x suppressed. At the same time, O_3 was 4.6 ± 3.3% and 4.9 ± 3.9% higher on weekdays than weekends at SEQ1 and SEQ2, respectively, implying PO_3 in SNP was NO_x limited. A similar pattern was observed at moderate temperatures during springtime, as O_x was 7.4 ± 4.6% higher on weekends than weekdays in Visalia and O_3 was 3.5 ± 7.4% and 4.7 ± 5.5% higher on weekdays than weekends in SEQ1 and SEQ2. These weekday-weekend patterns indicate a substantial portion of O_3 in SNP is produced by low-NO_x PO_3 chemistry during air transport from the SJV. At high temperatures, PO_3 during upslope transport is likely occurring, but is not apparent because PO_3 is also NO_x limited in Visalia.

3.3 Interannual O_3 variability

In Table 1, we report 12-yr O_3 trends (2001–2012) in SNP and the SJV in springtime and during O_3 season using four concentration metrics: 8-h O_3 NAAQS; two common vegetative-based indices, SUM0 and W126; and a morning average metric. Trends are represented as the percent change from 2001 through 2012 divided by the fit value in SEQ1 in 2001 (the highest O_3 observed for each metric).

The 8-h O_3 NAAQS is a human health-based metric computed as the maximum unweighted daily 8-h average O_3 mixing ratio. SUM0 is equal to the sum of hourly O_3 concentrations over a 12-h daylight period (8 am–8 pm LT). SUM0 is based on the assumption that the total O_3 dose has a greater impact on plants than shorter duration high O_3 exposures (Kurpius et al., 2002). The summation is unweighted, attributing equal significance to low O_3 concentrations (Musselman et al., 2006). SUM0 averaging is restricted to time periods when stomata are open (daylight), a condition not required for the 8-h O_3 NAAQS. In our SUM0 calculation, we only include days in which there were at least 11 hourly daytime measurements. W126 is a weighted summation (8 am–8 pm LT), assuming higher O_3 is more damaging to plants than lower O_3 levels. W126 weighting is sigmoidal, with hourly O_3 weights equal to $(1 + 4403e^{-126[O3]})^{-1}$ (U.S. Environmental Protection Agency 2015). We have followed the protocol for computing W126, which replaces missing data with the minimum measured concentration in the 8 am–8 pm LT time window. We also compute morning (7 am–12 pm LT) trends (O_x in Visalia and O_3 in SNP), as high O_3 plant uptake rates (morning) and high O_3 concentrations (afternoon) are out of phase within daily timeframes in the Sierra Nevada Mountains. Plant O_3 uptake typically follows a pattern of rapid morning uptake, relatively constant flux through midday, and a decrease in uptake in afternoon as plants close their stomata to prevent water loss in the hot, dry afternoon (Kurpius et al., 2002; Fares et al., 2013). Efficient morning uptake occurs because plants recharge their water supply overnight, which with low morning temperatures and VPD, results in high stomatal conductance (Bauer et al., 2000). Morning uptake in the Sierra Nevada maximizes in springtime around 8 am LT (Kurpius et al., 2002; Panek and Ustin, 2005; Fares et al., 2013).

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Three patterns in interannual O_3 variability in SNP emerge (Table 1): (1) O_3 decreased everywhere over the 12-yr record by all metrics in both seasons; (2) O_3 decreased at a slower rate in the springtime than during O_3 season by all metrics; and (3) O_3 decreased more rapidly in SNP than in Visalia and as a function of downwind distance. Seasonal differences are prominent at each site; for example, O_3 at SEQ1 decreased by 40–60% less in springtime than during O_3 season. Additionally, O_3 decreases were generally greater at SEQ1 than Visalia, and always greater at SEQ2 than SEQ1. Over the 12-yr period, the 8-h O_3 NAAQS declined 63% (springtime) and 46% (O_3 season) more at SEQ1 than Visalia and 77% (springtime) and 63% (O_3 season) more at SEQ2 than Visalia. SUM0 and W126 O_3 decreased 86% and 52% (springtime) and 69% and 43% (O_3 season) more at SEQ1 than Visalia, and 77% and 92% (springtime) and 63% and 78% (O_3 season) more at SEQ2 than Visalia. In the morning, trends at SEQ1 and Visalia were similar in springtime, but O_3 fell by 57% more at SEQ1 than O_x in Visalia during O_3 season. At SEQ2, morning O_3 decreased 38% (springtime) and 65% (O_3 season) more than O_x in Visalia. For each metric, we observe greater interannual variability relative to the net decline in springtime than during O_3 season.

3.4 Past and future exceedances

High O_3 is often defined by exceedances of O_3 thresholds. To better understand the effects of regulatory strategies in SNP, we examine past trends and predict future O_3 levels in the context of protective thresholds. Currently, the human-health based 8-h O_3 NAAQS is 70 ppb and, while there is no standard for SUM0, there are three time-integrated W126 protective thresholds. These are: 5–9 ppm h to protect against visible foliar injury to natural ecosystems, 7–13 ppm h to protect against growth effects to tree seedlings in natural forest stands, and 9–14 ppm h to protect against growth effects to tree seedlings in plantations, with exceedances recorded over a rolling 3-month time window (Heck and Cowling 1997). In Table 2, we show the mean number of 8-h O_3 NAAQS exceedances per year (rounded up) in 2001–2002 and 2011–2012 and the predicted exceedances in 2021–2022 and 2031–2032 in springtime and during O_3 season. We also report the average number of days (rounded up) required to exceed the three W126 protective thresholds (5, 7, and 9 ppm h), summing daily W126 indices starting with the first day of springtime and O_3 season (1 April and 1 June) over the next three months. We only present springtime data, as the W126 metric has been shown to poorly correspond to plant O_3 uptake in late summer in Sierra Nevada forests (Panek et al., 2002; Kurpius et al., 2002; Bauer et al., 2000). Future exceedances are computed assuming individual daily indices continue to decline at the 2001–2012 rate and are projected from 2011–2012 values.

In each case, we find there were fewer exceedances (8-h O_3 NAAQS) or more days until exceedance (W126) in 2011–2012 than at the start of the record, with declines generally linear over the 12-yr period. As with trends in the mean metrics, we observe greater declines at SEQ2 than SEQ1, with 24% (springtime) and 45% (O_3 season) larger reductions in the frequency of NAAQS exceedances at SEQ2 than SEQ1. For comparison, in Visalia there were 15 8-h O_3 NAAQS exceedances in 2001–2002 and 6 in 2011–2012 in springtime and 68 (2001–2002) and 42 (2011–2012) exceedances during O_3 season. Eighteen to 24 more days were required in 2011–2012 than in 2001–2002 for the cumulative daily W126 index to exceed the three protective thresholds at SEQ2 in springtime. Only 3–13 more days were required at SEQ1 and changes at SEQ1 were 20–36% smaller than observed at SEQ2.

If past decreases in O_3 continue over the next two decades, we predict no exceedances of the 8-h O_3 NAAQS at SEQ2 by 2021 in springtime and by 2031 during O_3 season, no exceedance of the 9-ppm h W126 threshold by 2021, and no further exceedances of 5- and 7-ppm h thresholds by 2031. O_3 reductions at past rates are not sizable enough to eliminate future exceedances of either 8-h O_3 NAAQS or W126 thresholds at SEQ1. Models suggest that W126 in the region would be well below these thresholds in the absence of anthropogenic precursor emissions (Lapina et al., 2013), implying further controls would be effective. Because PO_3 in SNP is NO_x limited, future NO_x reductions are expected to have as large an impact on local PO_3 as past reductions. NO_x emissions should continue to decline, as there are significant controls currently in the implementation phase, including more stringent national rules on heavy-duty diesel engines (Environmental Protection Agency, 2000) combined with California Air Resources Board (CARB) diesel engine retrofit-replacement requirements (California Air Resources Board, 2008), and more stringent CARB standards for gasoline-powered vehicles (California Air Resources Board, 2012).

4 Discussion

4.1 O_3 metrics

Long-term measurements of O_3 fluxes rather than O_3 concentrations are required to fully understand the effects of upwind emission controls on O_3 impacts. This is particularly true in Mediterranean ecosystems like SNP and under drought conditions (e.g., Panek et al., 2002), which is where and when plant O_3 uptake and high atmospheric O_3 concentrations may not be correlated. We have based our analysis on results from years of O_3 flux data collected in forests on the eastern slope of the Sierra Nevada Mountains (Bauer et al., 2000; Panek and Goldstein, 2001; Panek et al., 2002; Kurpius et al., 2002; Fares et al., 2010; Fares et al., 2013); however, there are few other O_3 flux datasets that span multiyear timescales and no flux observations in SNP. In California, flux measurements suggest springtime SUM0 trends offer the most insight into trends in O_3 impacts in SNP; that said, we find similar conclusions would be drawn regarding multiyear O_3 variability by assessing trends in SUM0, 8-h O_3 NAAQS, and our morning O_x metric. This can be explained by the upslope-downslope air flow in our study region and is evident in SNP diurnal O_3 patterns (Figure 4), which show considerable O_3 entrained into the boundary layer in the morning. As a result, O_3 concentrations are strongly influenced by afternoon concentrations on the previous day. Comparable trends in morning, afternoon, and daily average O_3 would then arise under conditions of persistence, which are common in Central California, but these results are unlikely to extend to other downwind ecosystems in the absence of an upslope-downslope flow pattern. Dynamically-driven elevated morning O_3 concentrations have important consequences for plants. Vegetation in SNP may be particularly vulnerable because plant O_3 uptake rates are often highest in the morning.

O_3 reductions predicted by W126 are almost twice those of SUM0. We attribute this to the W126 weighting algorithm that makes the metric most sensitive to changes in the highest O_3. A similar result was modeled using GEOS-Chem, which found W126 was more responsive than daily (8 am–7 pm, LT) average O_3 concentrations to decreases in anthropogenic emissions (Lapina et al., 2013). Considering SUM0 has been shown to best correspond to plant O_3 uptake in Sierra Nevada forests (Panek et al., 2002), W126 likely provides an overly optimistic representation of past and future trends in O_3 impacts in SNP.

4.2 Reducing high O_3 in polluted downwind ecosystems

Emission controls have been less effective in SNP when plant O_3 uptake is greatest (springtime), despite comparable NO_x decreases in both seasons. This is in part because regulatory agencies prioritize attainment of the 8-h O_3 NAAQS, with controls developed using models to hindcast past high O_3 episodes and efficacy of NO_x and/or organic emissions reductions tested under conditions typifying O_3 season. In the SJV, high O_3 episodes occur on the hottest days during O_3 season (Pusede and Cohen, 2012; Pusede et al., 2014), leading to policies not optimized to decrease O_3 in cooler springtime conditions.

NO_x decreases have made greater improvements in O_3 with increasing distance downwind of the SJV. This is because the export of NO_x from SJV has a larger impact on SNP O_3 than does transport of O_3 produced in urban SJV. Evidence for this is four-fold. First, O_3 at SEQ1 is greater than O_x in Visalia, at least during O_3 season, suggesting net O_3 formation as air travels from the SJV to SNP. Second, according to observations of O_x (Visalia) and O_3 (SNP) on weekdays versus weekends, PO_3 was simultaneously NO_x suppressed in Visalia and NO_x limited in SNP, with the weekday-weekend dependence of O_3 reflecting the chemical regime in which it is produced. Third, aircraft observations collected in the direction of daytime upslope flow from the SJV to Sierra Nevada foothills reveal substantial decreases in NO_x concentrations relative to isoprene, a key contributor to total organic reactivity (e.g., Beaver et al., 2012). Fourth, O_3 decreases (2001–2012) are observed to be greater in SNP than Visalia, and greater with increasing distance downwind. This implies that PO_3 in Visalia and SNP is differently sensitive to emission controls, with SNP more responsive to NO_x emissions control than Visalia.

An additional challenge to regulators is that high-elevation locations in the Sierra Nevada Mountains are also receptor sites for O_3 and O_3 precursors transported across the Pacific Ocean from east Asia (e.g., Vicars and Sickman, 2001; Heald et al., 2003; Hudman et al., 2004). Northern mid-latitude transport of Asian pollution to the western U.S. is strongest during March–April and weakest in the summertime (e.g., Wild and Akimoto, 2001; Liu et al., 2003; Liu et al., 2005). Hudman et al. (2004) compared surface observations with modeled O_3 enhancements in Asian pollution outflow, finding that, on average, transport events in April–May 2002 led to 8 ± 2 ppb higher 8-h O_3 concentrations at SEQ2. East Asian NO_x emissions have risen over our study window (e.g., Miyazaki et al., 2017), causing an increase in the influence of trans-Pacific transport on O_3 concentrations at SEQ2, and reducing the efficacy of NO_x control in springtime. While we do observe smaller decreases in O_3 in springtime at SEQ2 than during O_3 season, interannual trends have been more downward at SEQ2 than at the lower elevation sites, SEQ1 and Visalia, in both seasons. This suggests that while east-Asian pollution impacts surface O_3 at high-elevations in SNP during individual events, interannual trends in seasonal averages are more influenced by chemistry during upslope outflow from the SJV, and, as such, O_3 can be regulated accordingly.

5 Conclusions

We describe O_3 trends at two locations in SNP and in the upwind SJV city of Visalia. We show that a major portion of the O_3 concentration in SNP is formed during transport from NO_x emitted in the SJV, rather than from O_3 produced in Visalia and subsequently transported downwind. Evidence for this includes greater O_3 at SEQ1 than O_x in Visalia during O_3 season (Figure 4), distinct weekday-weekend O_3 differences in SNP and Visalia, steep gradients in NO_x and isoprene measured in the direction of upslope airflow out of the SJV within the boundary layer (Figure 5), and larger O_3 decreases over 2001–2012 with increasing distance from Visalia (Table 1). NO_x emission controls in Visalia have reduced O_3 in SNP even when PO_3 in Visalia was NO_x-suppressed.

We compute interannual O_3 trends using human health and ecosystem-based concentration metrics in springtime and O_3 season separately, in order to distinguish between O_3 impacts (plant O_3 uptake) and high O_3 concentrations. We find that O_3 has decreased in SNP and Visalia by all metrics in both seasons, but that ongoing NO_x emission controls have been less effective in springtime when uptake is greatest. The metrics, SUM0, 8-h O_3 NAAQS, and morning O_x, indicate comparable reductions in O_3 over 2001–2012, with decreases of ~7% (springtime) and ~13% (O_3 season) at SEQ1 and ~13% (springtime) and ~18% (O_3 season) at SEQ2. We attribute similarity across these three metrics to upslope-downslope airflow at the western edge of the SJV, as morning O_x and SUM0 are strongly affected by high afternoon O_3 concentrations on the previous day due the mixing of O_3-polluted nocturnal residual layers into the surface boundary layer. Past O_3 flux observations in the region indicate the highest plant O_3 uptake in the springtime morning, therefore SNP vegetation experiences greater O_3 exposure than in locations without this memory effect. W126 has predicted O_3 decreases over 2001–2012 that are almost double SUM0. While W126 emphasis of higher O_3 concentrations gives the most optimistic evaluation of the efficacy of past emission controls, our future projections of days required to exceed W126 protective thresholds suggests that much larger decreases in NO_x emissions than took place 2001–2012 are required to eliminate O_3 impacts on vegetation in SNP over the next two decades.

Diurnal and seasonal mismatches between plant O_3 uptake rates and O_3 concentration-based metrics make it challenging to accurately assess vegetative O_3 damage and to quantitatively evaluate the success of regulatory action. Future work would benefit from the development of an environmentally and biologically-relevant metric that captures patterns in plant O_3 uptake over daily and seasonal timescales, especially in Mediterranean ecosystems, where conditions conducive to plant O_3 uptake are asynchronous with conditions that lead to high O_3 concentrations.

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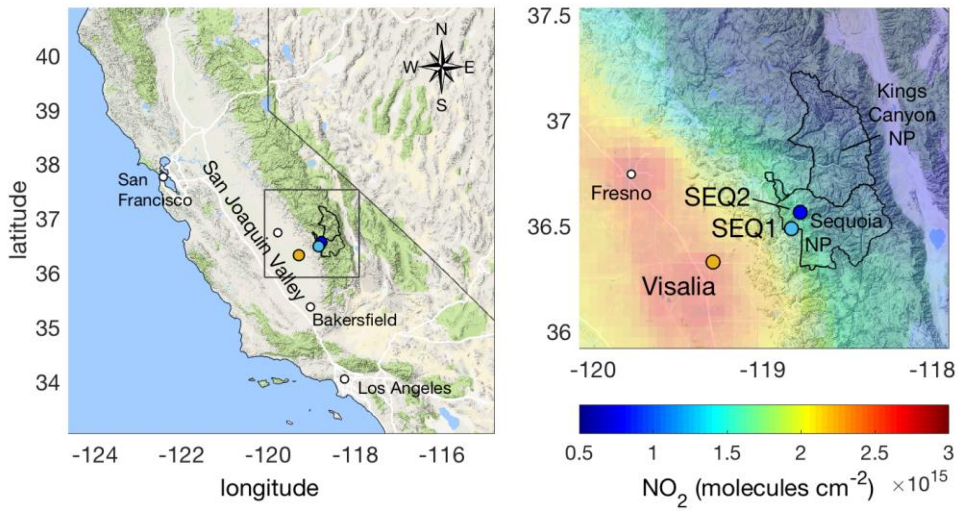

Figure 1. Map of California **(left)** with study region detail **(right)** indicating the locations of the SJV station, Visalia (orange), and two monitoring sites in SNP, SEQ1 (cyan) and SEQ2 (dark blue), with mean April–October, 2010–2012 OMI NO_2 columns using the BEHR (Berkeley High-Resolution) product (Russell et al., 2011).

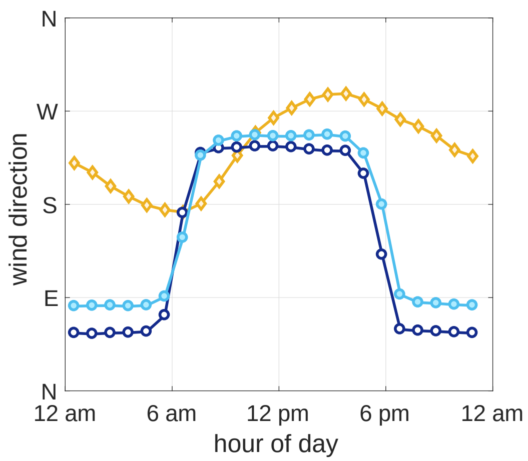

Figure 2. Hourly mean wind directions in Visalia (orange diamonds), SEQ1 (cyan filled circles), and SEQ2 (dark blue open circles) in April–October, 2001–2012.

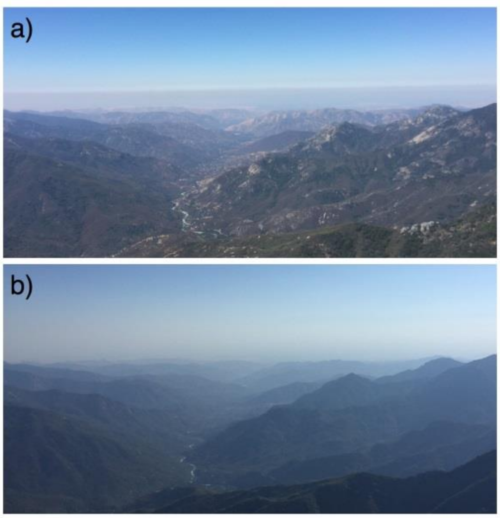

Figure 3. Looking toward the SJV from Moro Rock in SNP (36.5469 N, 118.7656 W; 2050 m ASL) at 11 am LT (panel a) and 5:30 pm LT (panel b). Photographs were taken by the authors on 29 June 2017.

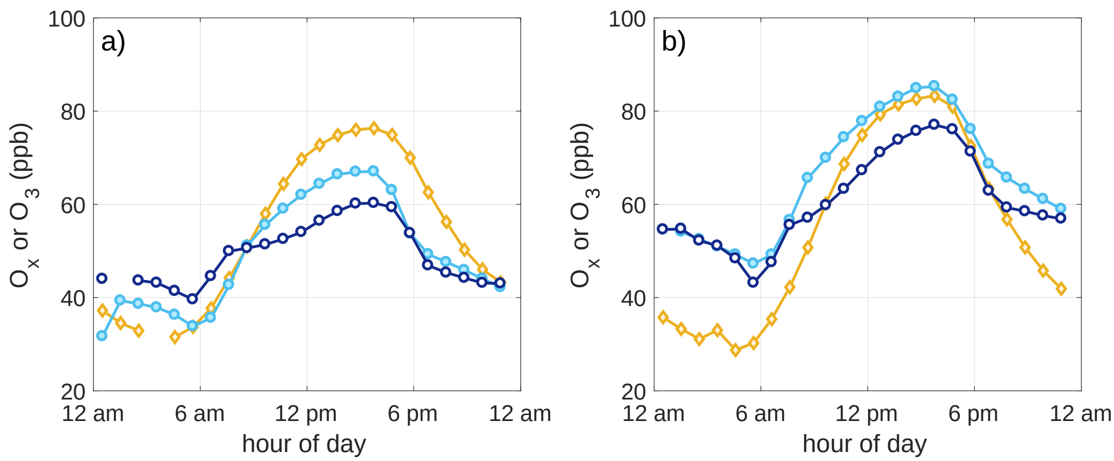

Figure 4. Hourly mean O_x in Visalia (orange diamonds), SEQ1 (cyan filled circles), and SEQ2 (dark blue open circles) in springtime (panel a) and during O_3 season (panel b) 2001–2012. Data gaps are due to routine calibrations.

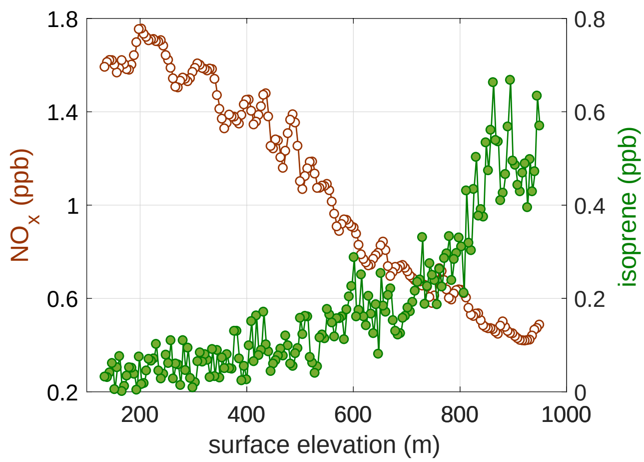

Figure 5. NO_x (brown open circles) and isoprene (green filled circles) measured onboard the NASA DC-8 at ~10 am LT at the Sierra Nevada western slope from a mean altitude of 130 m AGL to 1000 m AGL on 19 June, 2016. The surface elevation is estimated by linearly interpolating across the total elevation change.

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Table 1. Percent change in Visalia, SEQ1, and SEQ2 over 2001–2012 in 8-h O_3 NAAQS, SUM0, W126, and morning O_x metrics based on a linear fit of annual mean data in the springtime and O_3 season with respect to fit value in 2000 at SEQ1 during O_3 season.

O_3 metric	8-h NAAQS	SUM0	W126	Morning O_x
		Springtime (April–May)		
SEQ2	–13	–13	–22	–13
SEQ1	–8	–7	–14	–6
Visalia	–3	–1	–8	–8
		O_3 season (June–October)		
SEQ2	–19	–18	–43	–17
SEQ1	–13	–13	–29	–14
Visalia	–7	–4	–14	–6

Table 2. Mean exceedances per year (rounded up) of the springtime and O_3 season 8-h O_3 NAAQS and days required for an exceedance of the springtime 5-, 7-, and 9-ppm h W126 protective thresholds at SEQ1 and SEQ2. Data are averaged over 2001–2002 and 2011–2012 and projected (*) for years 2021–2022 and 2031–2032 assuming past 12-yr trends continue (from 2011–2012 levels). Italicization indicates no exceedance of the W126 occurred (within 3-months) and *never* indicates the threshold would not be exceeded over the course of the year.

O_3 metric	8-h NAAQS		W126 (springtime)		
	Springtime	O_3 season	5-ppm h	7-ppm h	9-ppm h
SEQ2					
2001–2002	13	103	41	46	49
2011–2012	3	63	59	65	73
2021–2022*	0	4	81	91	*107*
2031–2032*	0	0	*never*	*never*	*never*
SEQ1					
2001–2002	21	121	37	41	45
2011–2012	10	99	40	49	58
2021–2022*	6	67	48	61	68
2031–2032*	2	15	65	75	82