

Author response

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

Referee Comments (bold)

5 *Author Response (italics)*

Author Changes to Manuscript (standard)

We thank the reviewer for their feedback, which has improved the quality of the manuscript. We address each point below.

Anonymous Referee #3

10 **Buysee et al provide an analysis of ozone data and trends in Sequoia National Park and in the upwind source area of the San Joaquin Valley represented by a site in Visalia, CA. They focus their analysis on the relationship between these two areas and on a comparison of metrics typically used for human health assessments versus metrics relevant to vegetation effects. This is a useful exploration of ozone in an area where**
15 **ozone is expected to have substantial impacts on vegetation and ecosystem health especially since relatively few ambient ozone analyses in the literature focus on ecosystem impacts. The paper is generally well written and the data analysis is sound. There are some improvements that could be made in terms of background information and references. In addition, there are some places where minor clarifications/updates to**
20 **the analysis and presentation of the results would be beneficial. I recommend the paper be published after the following comments are addressed.**

Introduction:

1) Lines 28-30: I think this comparison is misleading for a few reasons. First, as the
25 authors clearly understand, ozone is not highest near emissions sources but rather downwind within a metro area. While the number of days above 70 ppb in LA proper may be 76, the number of days above 70 in the LA metro area (defined as the Los Angeles Nonattainment area which includes portions of Riverside and San Bernardino) is actually in the range of 150-175. I think that is a more appropriate comparison,
30 otherwise the authors give the false impression that SNP experiences more days above 70 ppb than the LA metro area. In addition, while determinations of the three most ozone polluted cities in the US by the ALA is likely based on the US standard of the 4th highest MD8A value, the number of days above a threshold has a lot to do with regional climate. Therefore, it would be more appropriate to compare SNP to other local urban
35 areas (such as those listed on line 14 of page 4) than to Denver and Phoenix. Also note

that the number of days above 70 ppb in Phoenix has decreased dramatically over the time-period evaluated (more than 100 days in 2001).

Deleted.

2) The recent Tropospheric Ozone Assessment Report (TOAR) presented analysis that is relevant to the work described here. There are two articles of particular significance: Lefohn et al (2018) describe the relationship between various ozone health and vegetation metrics and show how trends in different metrics compare across the US, EU and Asia. Mills et al (2018) specifically focus on characterizing ozone levels and trends for metrics most important to vegetation health. These articles should be discussed in the introduction. In addition, it would be worthwhile to put your results in context of those other recent findings both within California and globally.

We thank the reviewer for the references, which were published after our initial submission in October 2017. We have added a discussion of findings from TOAR as follows:

Page 2, Lines 32–34: “While trends toward median O₃ levels observed at a large number of U.S. sites (Lefohn et al., 2017) may have decreased the number of NAAQS exceedances, benefits to plants and ecosystems may be limited (Lefohn et al., 2018).”

Page 3, Lines 9–11: “For a global assessment of O₃ distribution and trends using a variety of ecosystem concentration metrics see Mills et al. (2018), which is part of the Total Ozone Assessment Report (TOAR).”

Page 10, Lines 31–32; Page 11, Lines 1–2: “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 O₃ uptake and high atmospheric O₃ concentrations may be uncorrelated. This may also be true in European Mediterranean climate regions, where high concentrations of ecosystem-based O₃ metrics have also been observed (Mills et al., 2018).”

Page 11, Lines 20–22: “In the TOAR global analysis, Mills et al. (2018) found April–September W126 downward trends over 1995–2014 in California of between 1–2 ppm h yr⁻¹ to be among the most rapid W126 declines in the world.”

Page 9, Lines 5–8: “Table 2 coloration indicates trend significance computed using the Mann-Kendall non-parametric test following the categorization developed by TOAR authors (Chang et al., 2017; Mills et al., 2018; Lefohn et al., 2018), with p-values categorized as statistically significant (0–0.05), indicative of a trend (0.05–0.10), a weak indication of change (0.10–0.34), and weak or no change (0.34–1).”

3) EPA, 2015 would be a more appropriate reference for statements at the top of page 3 than EPA, 2016 and EPA, 2010. Also, EPA, 2010 is not listed in the references section.

5 *We thank the reviewer for catching this error. We have added the EPA, 2010 reference to the references section. We have also adjusted the first EPA reference to cite EPA, 2015. We retain the subsequent EPA, 2010 reference, which includes the proposal of the weighted W126 metric as the secondary O₃ standard, as well as the EPA, 2016 reference, which provides specific detail on the W126 metric.*

10 Page 2, Lines 28–34; Page 3, Lines 1–3: “While there is a secondary NAAQS requirement aimed at vegetation protection, this has historically been the same metric (based on the MD8A O₃) at the same threshold as the primary NAAQS (Environmental Protection Agency, 2015b). Plants and ecosystems have been shown to be sensitive to lower O₃ concentrations, over longer-term exposures, and at different times of day and year than when NAAQS exceedances are frequent (e.g., Kurpius et al., 2002; Panek 2004; Panek and Ustin, 2005; Fares et al., 2013). While trends toward median O₃ levels observed at a large number of U.S. sites (Lefohn et al., 15 2017) may have decreased the number of NAAQS exceedances, benefits to plants and ecosystems may be limited (Lefohn et al., 2018). 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 3-month summation weighted to emphasize higher O₃ concentrations (Environmental Protection Agency, 2006; Environmental Protection Agency, 2016) that is 20 used by the U.S. National Park Service.”

4) Line 9, Page 3: Is SUM0 the same as the M12 metric from the TOAR analysis?

25 *The M12 metric is an average exposure metric, while SUM0 is a cumulative exposure metric. Since both are over the same time window (8 am–8 pm LT), they represent the same concentrations when computed over a 3-month period. In this work, we retain the cumulative exposure framework that aligns with SUM06 and W126 metrics, which have been explicitly compared to O₃ eddy-covariance flux measurements in Sierra Nevada forests.*

30 Page 3, Lines 7–9: “Similarly, the M12 metric is an average exposure metric computed over the same daily time window (8 am–8 pm LT) and representing the same hourly O₃ concentrations when computed over a 3-month period as SUM0 (e.g., Tingey et al., 1991; Lefohn and Foley, 1993).”

Methods:

1) **Much of the methods description appears to be in the results section with bits included in the introduction. I think the article would be clearer if the methods were broken out into a separate section. The methods section could include: description of monitoring sites (currently lines 23-29 on page 5), description of where data were retrieved from, gap filling methodology (currently lines 10-14 on page 8), calculation of metrics (currently mentioned in various places in the introduction and results section), and description of trends calculation methodology (not currently included in the text at all).**

10 *We have opted for the referee's second suggestion and moved the measurement description to the general results section (section 3). We have added a description of the trend and significance calculation methodology, referencing the TOAR reports.*

15 Page 5, Lines 24–29: “Hourly O₃ data have been routinely collected in SNP 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. O₃ and NO₂ data are measured in Visalia (36.333 N, 119.291 W), which is in the upwind direction of SNP at 102 m ASL (Figure 2). The data are collected by various agencies, including the National Park Service, and are hosted by the California Air Resources Board and available for download at <https://www.arb.ca.gov/aqmis2/aqdselect.php>.”

20 Page 9, Lines 1–2: “In Figure 6, mean seasonal daily MD8A and morning metrics and cumulative SUM0 and W126 metrics are shown for Visalia, SEQ1, and SEQ2 with their fit derived using an ordinary least squares linear regression.”

25 **2) Why did analysis only use data through 2012? Certified ozone data is available through 2017. I suggest that the authors extend their analysis to include more recent data.**

California has recently experienced the worst drought in recorded history. Because this manuscript focuses on the effects of upwind emission controls on O₃, we stopped the analysis before this severe drought period. We have added text to this point.

30 Page 3, Lines 29–33: “In this paper, we report O₃ trends from 2001 to 2012 in SNP and the upwind SJV city of Visalia to study the effects of SJV emission controls on SNP O₃. We do not extend the analyses beyond 2012 as, beginning in late 2012, California experienced the worst drought in recorded history (Griffin and

Anchukaitis, 2014; Diffenbaugh et al., 2015). Because O₃ concentrations are influenced by drought conditions (e.g., Jacob and Winner, 2009; Huang et al., 2016), we focus on the 2001 to 2012 time period.”

3) What methods did the authors use to calculate trends? There are many different linear regression and other methods that could be used to determine trend magnitudes and significance. For instance, other trends analysis have used ordinary least squares regressions, Thiel-Sen regressions, Spearman rank order regression etc. Some regression methods also account for temporal variability on different time scales (inter-annual variability versus seasonal variability etc). Please specify the method used here. Also, please add p-values to the trends magnitudes reported in Table 1 and include some description of which trends were statistically significant in the results section.

We have stated our regression methodology and indicated which trends were statistically significantly different than the null hypothesis (i.e. no trend).

Page 9, Lines 1–2: “In Figure 6, mean seasonal daily MD8A and morning metrics and cumulative SUM0 and W126 metrics are shown for Visalia, SEQ1, and SEQ2 with their fit derived using an ordinary least squares linear regression.”

Page 9, Lines 5–8: “Table 2 coloration indicates trend significance computed using the Mann-Kendall non-parametric test following the categorization developed by TOAR authors (Chang et al., 2017; Mills et al., 2018; Lefohn et al., 2018), with p-values categorized as statistically significant (0–0.05), indicative of a trend (0.05–0.10), a weak indication of change (0.10–0.34), and weak or no change (0.34–1).”

Page 9, Lines 30–34: “This site-dependence is reflected in the O₃ trend p-values (Table 2), where at SEQ2, slopes are either statistically significant at the 0.05 level or indicative of a trend (0.05–0.10) for each metric in both seasons. At SEQ1, slopes are statistically significant during O₃ season, but only indicative (W126), weakly indicative (MD8A), or suggestive of weak to no change (SUM0 and Morning O_x) in springtime. Trends in Visalia are the least robust, with p-values typically only weakly indicative or suggestive of minor to no change in both springtime and O₃ season.”

Table 2. O₃ changes in Visalia, SEQ1, and SEQ2 over 2001–2012 according to MD8A, SUM0, W126, and morning O_x metrics based on a linear fit of annual mean data (shown in Figure 6) in the springtime and O₃ season. Each left column is the percent change with respect to fit value in 2001 at SEQ1 during O₃ season for comparison, which is the highest O₃ observed for each metric. Each right column is the fit slope with slope errors in O₃ abundance units per year. Coloration is based on the TOAR categorization for trend significance (Lefohn et al., 2018), with p-values calculated using the Mann-Kendall non-parametric test: yellow, 0–0.05, statistically significant trend; green, 0.05–0.10, indicative of a trend; violet, 0.10–0.034, weak indication of change; and pink, 0.34–1, weak or no change.

O ₃ metric	MD8A		SUM0		W126		Morning O _x	
O ₃ season (June–October)								
	%	ppb yr ⁻¹	%	ppm h yr ⁻¹	%	ppm h yr ⁻¹	%	ppb yr ⁻¹
SEQ2	-19	-1.4 ± 0.41	-15	-1.2 ± 0.46	-37	-2.2 ± 0.72	-17	-1.0 ± 0.32
SEQ1	-13	-1.0 ± 0.27	-12	-0.96 ± 0.21	-28	-1.7 ± 0.36	-14	-0.83 ± 0.21
Visalia	-7	-0.54 ± 0.30	-3	-0.20 ± 0.28	-11	-0.69 ± 0.41	-6	-0.50 ± 0.30
Springtime (April–May)								
	%	ppb yr ⁻¹	%	ppm h yr ⁻¹	%	ppm h yr ⁻¹	%	ppb yr ⁻¹
SEQ2	-13	-1.0 ± 0.38	-16	-1.2 ± 0.47	-30	-1.8 ± 0.62	-13	-0.78 ± 0.34
SEQ1	-8	-0.59 ± 0.42	-6	-0.50 ± 0.53	-24	-1.5 ± 0.62	-6	-0.35 ± 0.32
Visalia	-3	-0.23 ± 0.39	-4	-0.31 ± 0.38	-11	-0.69 ± 0.49	-8	-0.39 ± 0.35

4) Metrics: I suggest that the authors also include an analysis of the AOT40 metric which is commonly used in Europe and is mentioned in the introduction.

5 *We have opted to use SUM0 because it has been shown to best correlate with springtime stomatal O₃ uptake in a Sierra Nevada forest according to O₃ eddy-covariance flux measurements (Panek et al., 2002; Fares et al., 2010). We used W126 because it is a standard metric of the U.S. National Park Service. Past O₃ eddy-covariance observations indicate poor correlation between AOT40 and O₃ uptake in both the springtime and*
10 *summer at a Sierra Nevada forest measurement site (Fares et al., 2010). For this reason, we decided to exclude trends in the AOT40 metric. We have added text to this clarify our decision.*

Page 8, Lines 1–4: “In Figure 6 and Table 2, we report 12-yr O₃ trends (2001–2012) in SNP and the SJV in springtime and during O₃ season using four concentration metrics: MD8A; two common vegetative-based indices, SUM0 and W126; and a morning average metric. We do not report trends in SUM06 or AOT40
15 vegetative indices, as they have been shown to poorly correlate with O₃ uptake at a Sierra Nevada forest site even in springtime (Panek et al., 2002; Fares et al., 2010b).”

5) The authors have some limited analysis of number of days above 70 ppb (lines 20-25 on page 9) but they should also calculate trends in this metric similar to the other metrics. These trends for # of days > 70 could be included in both Table 1 and Figure 6.

20 *It is our aim discuss trends in the metrics that have been shown to be best correlated to past O₃ flux measurements in the region, not to provide a comprehensive survey of trends*

in all metrics. The TOAR reports have now done this in a more spatially comprehensive fashion. To keep the manuscript focused, we do not add a new figure, but do add the trend and significant information to the text.

5 Page 10, Lines 7–10: “Patterns in high MD8A O₃ days follow trends in other metrics, with the largest rates of change occurring during O₃ season in SEQ2 (–4.7 days yr^{–1}, $p = 0.02$), then SEQ1 (–2.8 days yr^{–1}, $p = 0.05$) and Visalia (–2.5 days yr^{–1}, $p = 0.05$). In springtime, smaller decreases are observed with similar spatial patterns, SEQ2 (–1.0 days yr^{–1}, $p = 0.02$), SEQ1 (–1.0 days yr^{–1}, $p = 0.15$) and Visalia (–0.5 days yr^{–1}, $p = 0.37$).”

10 **6) The authors use a cutoff of 70.4 ppb for the US ozone standard, but the US EPA actually truncates rather than rounds fractional ppb values when calculating days above the standard. So, the correct threshold should actually be 70.9 ppb. See description in 40 CFR Appendix U to Part 50 from October 2015 (https://www.law.cornell.edu/cfr/text/40/appendix-U_to_part_50)**

We have adjusted our threshold calculation, corresponding text, and numerical results.

15 Page 1, Lines 27–29: “Ozone (O₃) concentrations in SNP exceeded the current U.S. human health-based O₃ National Ambient Air Quality Standard (NAAQS), defined as maximum daily 8-h average (MD8A) O₃ greater than 70 ppb, on an average of 117 days per year over the time period 2001–2012.”

Page 8, Lines 7–8: “In this work, we utilize the seasonal mean MD8A and discuss O₃ exceedances as individual days in which MD8A O₃ > 70.9 ppb, the current 8-h NAAQS (CFR 40, 2015).”

20 Page 10, Lines 1–6: “High O₃, as defined by exceedances of protective thresholds, also became less frequent over the 12-yr record. The number of days in which MD8A O₃ was greater than 70.9 ppb in 2001–2002 (averages are rounded up) was 66 yr^{–1} (O₃ season) and 14 yr^{–1} (springtime) in Visalia. In 2011–2012, the number of exceedances fell to 39 yr^{–1} (O₃ season) and 6 yr^{–1} (springtime). At SEQ1 in 2001–2002, there were 119 exceedance days yr^{–1} (O₃ season) and 20 yr^{–1} (springtime), declining in 2011–2012 to 97 yr^{–1} (O₃ season) and 10 yr^{–1} (springtime). At SEQ2 in 2001–2002, there were 103 exceedance days yr^{–1} (O₃ season) and 13 yr^{–1} (springtime). In 2011–2012, this decreased to 62 exceedance days yr^{–1} (O₃ season) and 3 yr^{–1} in 2011–2012 (springtime).”

25 Page 13, Line 8: “Even in SEQ1 and SEQ2, days with MD8A > 70.9 ppb are far more common in the summer.”

30

Results:

1) If the authors decide not to include a separate methods section, then I suggest the authors at least move the general description of monitoring sites (lines 23-28 on page 5) up to the general results section (section 3) instead of having it buried in section 3.1.

5 *We have moved this description to section 3 as recommended.*

Page 5, Lines 24–29: “Hourly O₃ data have been routinely collected in SNP 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. O₃ and NO₂ data are measured in Visalia (36.333 N, 119.291 W),
10 which is in the upwind direction of SNP at 102 m ASL (Figure 2). The data are collected by various agencies, including the National Park Service, and are hosted by the California Air Resources Board and available for download at <https://www.arb.ca.gov/aqmis2/aqdselect.php>.”

2) Line 2, page 6: Additionally, rush-hour NO_x emissions are likely to impact the diurnal pattern of O_x described here for Visalia.

15 *We have added text to this point.*

Page 6, Lines 3–7: “In Visalia, O_x concentrations increase sharply beginning in early morning (7 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 PO₃ (the initial rise) and advection of O_x from the upwind source region (late afternoon maximum). In the morning, enhanced rush-hour NO_x emissions overlap in time with the initial increase in O_x with 30–
20 40% of O_x as NO₂ at 7–8 am LT. In the afternoon, from 12–4 pm LT ~10–15% of O_x is NO₂. At 5 pm, NO₂ concentrations increase with evening rush hour with 30–40% of O_x as NO₂ at 5–6 pm LT.”

3) Section 3.2: If this analysis is important enough to warrant its own section, then the authors should include a Table or Figure displaying the results described in lines 16-27 of page 7, so that readers will easily be able to see a summary of these results.

25 *We have added a table of these results and modified the discussion to reference this table.*

Page 7, Lines 20–31: “At moderate temperatures, statistically significant weekday-weekend differences were observed (Table 1). During O₃ season, O_x was $6.3 \pm 3.5\%$ higher on weekends than weekdays in Visalia, indicating local PO₃ was NO_x suppressed. At the same time, O₃ was $4.6 \pm 3.3\%$ and $4.9 \pm 3.9\%$ higher on weekdays than weekends at SEQ1 and SEQ2, respectively, implying PO₃ in SNP was NO_x limited. A similar
30 pattern was observed during springtime, as O_x was $7.4 \pm 4.6\%$ higher on weekends than weekdays in Visalia

and O₃ was 3.5 ± 7.4% and 4.7 ± 5.5% higher on weekdays than weekends in SEQ1 and SEQ2. These weekday-weekend patterns imply that a substantial portion of O₃ in SNP is produced by low-NO_x PO₃ chemistry during air transport from the SJV. At high temperatures, greater weekday concentrations in O_x in Visalia and O₃ at SEQ1 and SEQ2 imply NO_x-limited chemistry in all three locations (Table 1). Averaged across sites, percent differences in weekdays and weekends (relative to weekdays) were 8.7 ± 4.8% in the springtime and 4.3 ± 2.3% during O₃ season. PO₃ during upslope transport is not apparent by this method because PO₃ was also NO_x limited in Visalia, indicating a portion of O₃-forming organic reactivity in Visalia was temperature dependent, consistent with past analyses in other SJV cities (Steiner et al., 2006; Pusede and Cohen, 2012; Pusede et al., 2014; Rasmussen et al., 2014).”

Table 1. Percent difference in afternoon (12–6 pm LT) O_x or O₃ on weekdays and weekends calculated as: $(O_{x, \text{weekday}} - O_{x, \text{weekend}}) / O_{x, \text{weekday}}$ in Visalia, SEQ1, and SEQ2 in 2001–2003 on moderate and high temperature days. Errors are reported as standard errors of the mean.

Temperature	Moderate	High
O₃ season (June–October) 2001–2003		
	%	%
SEQ2	4.9 ± 3.9	3.5 ± 2.4
SEQ1	4.6 ± 3.3	4.2 ± 1.9
Visalia	–6.3 ± 3.5	5.3 ± 2.6
Springtime (April–May) 2001–2003		
	%	%
SEQ2	4.7 ± 5.5	5.2 ± 4.6
SEQ1	3.5 ± 7.4	8.6 ± 4.9
Visalia	–7.4 ± 4.6	12.2 ± 4.8

4) Lines 16-20 on page 7: Is it also possible that SNP becomes VOC limited on hot days? Maybe due to changes in biogenic VOC emissions?

In locations with substantial biogenic emissions like SNP, increases in temperature drive chemistry to be more NO_x-limited. We have stated this more explicitly.

Page 7, Lines 26–31: “At high temperatures, greater weekday concentrations in O_x in Visalia and O₃ at SEQ1 and SEQ2 imply NO_x-limited chemistry in all three locations (Table 1). Averaged across sites, percent

differences in weekdays and weekends (relative to weekdays) were $8.7 \pm 4.8\%$ in the springtime and $4.3 \pm 2.3\%$ during O₃ season. PO₃ during upslope transport is not apparent by this method because PO₃ was also NO_x limited in Visalia, indicating a portion of O₃-forming organic reactivity in Visalia was temperature dependent, consistent with past analyses in other SJV cities (Steiner et al., 2006; Pusede and Cohen, 2012; Pusede et al., 2014; Rasmussen et al., 2014).”

5) Lines 7-8, page 8: It might be useful to note in the description of W126 that the sigmoidal weighting function has an inflection point at around 60 ppb, so days below 60 ppb receive little weighting while days above 60 ppb are weighted heavily.

We have added text to this point.

10 Page 8, Lines 14–15: “W126 weighting is sigmoidal, with hourly O₃ weights equal to $(1 + 4403e^{-126[O_3]})^{-1}$, such that hourly mixing ratios below (above) 60 ppb receive less (more) weight (Environmental Protection Agency, 2016).”

6) Lines 10-11, page 8: How many months had less than 75% complete data at these three sites?

15 *We have added text to this point.*

Page 8, Lines 19–20: “From 2001–2012, 0, 8, and 3 months were initially less than 75% complete in Visalia, SEQ1, and SEQ2, respectively.”

7) Lines 26-29, page 9: The authors may also wish to note that in EPA’s 2015 review of the ozone standard, they considered potential secondary W126 ozone standard levels between 7 and 17 ppm-hrs and the Clean Air Science Advisory Committee recommended a W126 standard level between 7 and 15 ppm-hrs (See EPA, 2015). These levels are consistent with the levels discussed here from other literature sources.

We have added text to this point.

20 Page 10, Lines 14–16: “The EPA has considered a potential secondary W126 ozone standard between 7 and 17 ppm h (Environmental Protection Agency, 2015a); likewise, the Clean Air Science Advisory Committee recommended a W126 standard level between 7 and 15 ppm h (Environmental Protection Agency, 2015a).”

8) Lines 24-25, page 11: There are more recent EPA regulations on heavy-duty onroad and nonroad emissions that could be cited here. See: <https://www.epa.gov/emission-standards-reference-guide/epa-emission-standards-regulations>

30 *We have updated references at both the federal and state levels.*

Page 12, Lines 15–19: “Local NO_x emissions should continue to decline into the future, as there are significant controls currently ongoing or in the implementation phase, including more stringent national rules on heavy-duty diesel engines (Environmental Protection Agency, 2000; 2010), combined with California Air Resources Board (CARB) diesel engine retrofit-replacement requirements (California Air Resources Board, 2008; 5 2014), and more stringent CARB standards for gasoline-powered vehicles (California Air Resources Board, 2012).”

9) Lines 3-23, page 12: Authors may want to note that less substantial trends in the spring may also be due to a larger fraction of ozone coming from background ozone sources in the spring than in the summer. The authors discuss background ozone in the 10 next paragraph but never explicitly state this.

We have stated this more explicitly.

Page 13, Lines 13–15: “Deeper cuts in emissions appear to be required in the springtime in SNP, as decreases in anthropogenic emissions have a smaller effect, both relatively and in the absolute, on the total O₃ abundance than during O₃ season, in part because background O₃ makes the greatest contribution to daily O₃ in the 15 springtime SNP (Figure 4).”

10) Line 5, page 13: Also note, that satellite observations as well as Chinese emissions estimates indicate that Chinese NO_x emissions have been decreasing since 2011 so the influence from Asia may have become less important since 2011.

We have included this information.

20 Page 13, Lines 29–33: “East Asian NO_x emissions have risen over our study window (e.g., Miyazaki et al., 2017), potentially causing an increase in the influence of trans-Pacific transport on O₃ concentrations at SEQ2 and reducing the efficacy of local NO_x control in springtime. However, NO_x emission and concentration declines have been observed over China since 2011 (Liu et al., 2016), potentially diminishing the influence of Asian transport events in SNP.”

25 11) Figure 6: in caption or figure headings clarify that MD8A is the seasonal average.

We have clarified this.

Page 27, Lines 7–10: “**Figure 6.** O₃ trends in Visalia (orange diamonds), SEQ1 (cyan filled circles), and SEQ2 (dark blue open circles) computed using MD8A (a–b), SUM0 (c–d), W126 (e–f), and morning O_x (g–h) metrics during O₃ season (top row) and springtime (bottom row). Both MD8A and morning O_x are

computed as seasonal averages. Error bars in panels a–b and g–h are standard errors of the mean. Error bars in panels c and e are standard errors of the mean of the three O₃ season 3-month summations.”

References:

- 5 **Policy Assessment for the Review of the Ozone National Ambient Air Quality Standards, Final Report, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-452/R-14-006, August 2014, available at: <https://www.epa.gov/naaqs/ozone-o3-standards-policy-assessments-review-completed-2015>**
- 10 **Lefohn AS, Malley CS, Smith L, Wells B, Hazucha M, Simon H, et al.. Tropospheric ozone assessment report: Global ozone metrics for climate change, human health, and crop/ecosystem research. Elem Sci Anth. 2018;6(1):28. DOI: <http://doi.org/10.1525/elementa.279>**
- 15 **Mills G, Pleijel H, Malley CS, Sinha B, Cooper OR, Schultz MG, et al.. Tropospheric Ozone Assessment Report: Present-day tropospheric ozone distribution and trends relevant to vegetation. Elem Sci Anth. 2018;6(1):47. DOI: <http://doi.org/10.1525/elementa.302>**

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

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Abstract. Ozone (O₃) air pollution in Sequoia National Park (SNP) is among the worst 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 in the top ten most O₃-polluted in the U.S. Here, we investigate the influence of emission controls in the upwind-SJV city of Visalia on O₃ concentrations in SNP over a 12-yr time period (2001–2012). We show that the export of nitrogen oxides (NO_x) from the SJV has played a larger role in driving high O₃ in SNP than transport of O₃. As a result, O₃ in SNP has been more responsive to NO_x emission reductions than in the upwind SJV city of Visalia, and, in SNP, O₃ concentrations have declined faster at a higher elevation monitoring station than at a low elevation site nearer to the SJV. We report O₃ trends by various concentration metrics but do so separately for when environmental conditions are conducive to plant O₃ uptake and for when high O₃ 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 O₃ concentrations in SNP in springtime, which is when plant O₃ uptake in Sierra Nevada forests has been previously measured to be greatest. We discuss the implications of regulatory focus on high O₃ days in SJV cities on O₃ concentration trends and ecosystem impacts in SNP.

25 1 Introduction

Sequoia National Park (SNP) is a unique and treasured ecosystem that is also one of the most ozone-polluted national parks in the U.S. (National Park Service, 2015a). Ozone (O₃) concentrations in SNP exceeded the current U.S. human health-based O₃ National Ambient Air Quality Standard (NAAQS), defined as 8-h maximum daily 8-h average (MD8A) O₃ greater than 70 ppb, on an average of 449117 days per year over the time period 2001–2012. At the same time, there were an average of 76 days per year with MD8A O₃ greater than 70 ppb in Los Angeles, California, 36 per year in Denver, Colorado, and 55 per year in Phoenix, Arizona, cities which are three of the most O₃-polluted in the U.S. (American Lung Association, 2016).

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While O₃ is harmful to humans, it is also damaging to plants and ecosystems (e.g., Reich, 1987), with visible O₃ 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). O₃ exposure ~~also causes~~ affects ecosystems in a variety of ~~other effects such as decreased ways, potentially decreasing~~ plant growth (Wittig et al., 2009), ~~reduced~~ reducing photosynthesis and ~~disrupted~~ disrupting carbon assimilation (Wittig et al., 2007; Fares et al., 2013), ~~diminished~~ diminishing ecosystem gross and net primary productivity (Ainsworth et al., 2012; Wittig et al., 2009), ~~modified~~ modifying plant resource allocation (Ashmore, 2005), and ~~impaired~~ impairing stomatal response (Paoletti and Grulke, 2010; Hoshika et al., 2014). ~~On multi-decadal timescales, O₃-resistant plants may thrive over O₃-sensitive species, and these system-level dynamics 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 O₃, seedlings are sensitive, ~~and with~~ high O₃ ~~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*). O₃ 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 O₃-polluted San Joaquin Valley (SJV) (Figure 1). Previous model estimates of a pollution episode in August 1990 suggest at least half of peak daytime O₃ in SNP is produced upwind from anthropogenic precursors (Jacobson, 2001). For the past two decades, regulations have reduced O₃ concentrations in the SJV (Pusede and Cohen, 2012). For example, in Fresno, high O₃ days, defined as days when the MD8A exceeded 70 ppb, were 50% less frequent in 2007–2010 than ten years earlier (on high temperature days). At the same time, in Bakersfield, high O₃ 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 (NO₂) concentrations falling by 50% from 2001 to 2012, changing linearly by –0.5 ppb yr⁻¹ in the SJV city of Visalia. The precursor reductions that brought about these decreases in high O₃ are likely to have also affected O₃ in SNP.

The success of O₃ regulatory strategies can be measured through attainment of human health-based NAAQS and ecosystem-impact metrics. ~~However, while~~ While there is a secondary NAAQS requirement aimed at vegetation protection,

~~it~~has historically ~~used been~~ the same metric ([based on the MD8A O₃](#)) ~~and been set~~ at the same threshold as the primary NAAQS (Environmental Protection Agency, [20162015b](#)). Plants and ecosystems have been shown to be sensitive to lower O₃ concentrations, over longer-term exposures, and at different times of day and year than when NAAQS exceedances are frequent (e.g., Kurpius et al., 2002; Panek 2004; Panek and Ustin, 2005; Fares et al., 2013). [While trends toward median O₃ levels observed at a large number of U.S. sites \(Lefohn et al., 2017\) may have decreased the number of NAAQS exceedances, benefits to plants and ecosystems may be limited \(Lefohn et al., 2018\)](#). 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 3-month summation weighted to emphasize higher O₃ concentrations (Environmental Protection Agency, 2006; Environmental Protection Agency, 2016) that is used by the U.S. National Park Service. There are a number of other concentration metrics used to quantify ecosystem O₃ impacts. In Europe, the AOT40 index is common, and is equal to all daytime (defined as solar radiation $\geq 50 \text{ W m}^{-2}$) hourly O₃ concentrations greater than 40 ppb. In the U.S., two widely used indices are the SUM0 and SUM06 (e.g., Panek et al., 2002), which are the sum of all daytime hourly O₃ mixing ratios greater than or equal to 0 ppb and 60 ppb, respectively. [Similarly, the M12 metric is an average exposure metric computed over the same daily time window \(8 am–8 pm LT\) and representing the same hourly O₃ concentrations when computed over a 3-month period as SUM0 \(e.g., Tingey et al., 1991; Lefohn and Foley, 1993\). For a global assessment of O₃ distribution and trends using a variety of ecosystem concentration metrics see Mills et al. \(2018\), which is part of the Total Ozone Assessment Report \(TOAR\).](#)

Even ecosystem-based concentration metrics are proxies of variable quality for O₃ impacts, if O₃ concentrations are not well-correlated with plant O₃ 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 O₃ is high and when plants uptake O₃ from the atmosphere, with differences in high O₃ and efficient O₃ uptake occurring on both diurnal and seasonal timescales. While ecosystem O₃ impacts are best represented by direct measurements of the O₃ 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 O₃ 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 O₃ concentrations in the 1980s, prioritizing national parks downwind of cities and polluted areas, including SNP (National Park Service, 2015b). Data from these monitors can be used to compute various O₃ 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 O₃ 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 O₃ 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 O₃ uptake is greatest.

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In this paper, we report O₃ trends from 2001 to 2012 in SNP and the upwind SJV city of Visalia to study the effects of SJV emission controls on SNP O₃. [We do not extend the analyses beyond 2012 as, beginning in late 2012, California experienced the worst drought in recorded history \(Griffin and Anchukaitis, 2014; Diffenbaugh et al., 2015\). Because O₃ concentrations are influenced by drought conditions \(e.g., Jacob and Winner, 2009; Huang et al., 2016\), we focus on the 2001 to 2012 time period.](#) We compute trends in human health- and ecosystem-based concentration metrics separately when regional environmental conditions favor plant O₃ uptake (springtime) and when high O₃ is most frequent (O₃ season). We describe these O₃ changes in Visalia and SNP as function of distance downwind of Visalia by way of data collected at two monitoring stations located on the western slope of the Sierra Nevada Mountains. We demonstrate the importance of transport of urban NO_x from the SJV on trends in O₃ production (*PO*₃) chemistry in SNP. Finally, we discuss the descriptive power of various O₃ metrics and consider implications of a regulatory focus on human health-based standards to reduce ecosystem O₃ impacts in SNP.

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 O₃ pollution. Four SJV cities rank among the ten most O₃-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 O₃ in SNP and the SJV (see Zhong et al. (2004) for a diagram). First, summertime (April–October) afternoon low-level winds in the southern SJV are generally from the west-northwest (represented by Visalia in Figure 2a). 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 O₃ pollution and precursors in these cities (e.g., Ewell et al., 1989; Beaver and Palazoglu, 2009). Third, the most populous and O₃-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). The prevalence of shallow nighttime surface inversions in the SJV means that 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 O₃ days are most frequent in SNP and the SJV in the summer through early fall (Pusede and Cohen, 2012; Meyer and Esperanza, 2016), as PO₃ chemistry is often temperature-dependent (reviewed in Pusede et al., 2015) and this effect is particularly strong in the SJV (Pusede and Cohen, 2012; Pusede et al., 2014). The O₃ season is defined here as June–October and with ~90% of annual O₃ 8-h NAAQS exceedances in SNP occur during O₃ season (2001–2012).

In the Sierra Nevada foothills, high rates of plant O₃ uptake are asynchronous with O₃ season because of the Mediterranean climate (e.g., Kurpius et al., 2002; Kurpius et al., 2003; Panek, 2004). Plants also capture carbon dioxide required for photosynthesis and transpire through stomata; therefore, O₃ uptake is not only a function of the atmospheric O₃ 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 O₃ 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 O₃ trends in springtime (April–May), which is when plant O₃ uptake best correlates with variability in atmospheric O₃ concentrations in the region, and during O₃ season (June–October), which is when O₃ concentrations are highest. In this manuscript, for clarity we generally use the term *impacts* when discussing ecosystem metrics and *concentrations* when talking about human health metrics; O₃ ecosystem and human health effects are of course both O₃ impacts.

Hourly O₃ data have been routinely collected in SNP

3.1 Diurnal O₃ variability

Diurnal O₂ and O₃ (O₃ = O₂ + NO₂) concentrations are shown in Figure 4 in springtime (panel a) and O₃ season (panel b) over the 2001–2012 time period. Hourly O₃ 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. O₃ and NO₂ data are measured in Visalia (36.333 N, 119.291 W), which is in the upwind direction of SNP at 102 m ASL (Figure 2). The data are collected by various agencies, including the National Park Service, and are hosted by the California Air Resources Board and available for download at <https://www.arb.ca.gov/aqmis2/aqdselect.php>.

5 **3.1 Diurnal O₃ variability**

Diurnal O₃ and O_x (O₃ ≡ O₃ + NO₂) concentrations are shown in Figure 4 in springtime (panel a) and O₃ season (panel b) over the 2001–2012 time period. ~~In Figure 4,~~ Visalia data are shown as O_x to account for the portion of O₃ stored as NO₂, which can be substantial in the nearfield of fresh NO_x emissions and at night. NO₂ data are not available in SEQ1 and SEQ2; however, these sites are removed from large NO_x sources (Figure 1) and O₃ ≈ O_x is a reasonable approximation.

10 In Visalia, O_x concentrations increase sharply beginning in early morning (57 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 PO₃ (the initial rise) and advection of O_x from the upwind source region (late afternoon maximum). In the morning ~~(8 am LT), enhanced rush-hour NO_x emissions overlap in time with the initial increase in O_x with~~ 30–40% of O_x is as NO₂ ~~and~~ at 7–8 am LT. In the afternoon, from 12–4 pm LT ~10% of O_x is NO₂ ~15% of O_x is NO₂. At 5 pm, NO₂ concentrations increase with evening rush hour with 30–40% of O_x as NO₂ at 5–6 pm LT.

15 Diurnal O₃ 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 O₃ increase is consistent with entrainment of O₃ in nocturnal residual layers aloft during morning boundary layer growth. The influence is substantial, as morning O₃ accounts for 50% (springtime and O₃ season) of the daily change in O₃ at SEQ1 and 50% (springtime) and 37% (O₃ season) of the daily change in O₃ at SEQ2. The timing of afternoon peak O₃ is consistent with upslope air transport from the SJV (Figure 2). If O₃ attributed to local PO₃ in Visalia is greatest around 2 pm LT, typical of many urban locations, with mean winds at SEQ1 of 3 m s⁻¹ and SEQ2 of 2 m s⁻¹, we expect O₃ to peak in SEQ1 at ~5 pm (45 km downwind of Visalia) and at SEQ2 shortly after (9.7 km downwind of SEQ1, which includes the change in elevation using the Pythagorean theorem). This is broadly what we observe. While the actual distance of airflow is dictated by the mountain terrain and a parcel of air will travel a distance longer than the straight-line path on a smooth surface, the timing of the O₃ diurnal patterns is consistent with airflow travel time roughly equal to that determined by the horizontal distance and mean wind speed. There has been no change in the hour of peak O₃ mixing ratio at either SEQ1 or SEQ2 over the 2001 to 2012 period.

3.2 Weekday-weekend O₃ variability

30 SNP and the SJV are in close geographic proximity but their local PO₃ 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; Dreyfus et al., 2002) and the combined NO_x and isoprene gradients suggest potentially distinct PO₃ regimes in the SJV and SNP. While these data were collected on one day in a different year from our study, the relative pattern of NO_x to organic compound emissions is likely representative, as there have been no substantial changes in the locations of urban NO_x and biogenic organic emitters. This NO_x to organic compound gradient is consistent with observations over longer sampling periods downwind of the Central California city of Sacramento, where the NO_x-enriched Sacramento urban plume is transported up the western slope of the vegetated Sierra Nevada Mountains (e.g., Beaver et al., 2012; Dillion et al., 2002; Murphy et al., 2006).

If the major source of O₃ in SNP is O₃ produced in the SJV and transported downwind, then the observed NO_x dependence of PO₃ in SNP and the SJV would be the same even if PO₃ regimes in the two locations were different. To test this hypothesis, we consider O₃ 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 O₃-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). PO₃ is the only term in the O₃ 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 PO₃ 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 O₃ concentrations in SNP are most influenced by the SJV (from Figure 4). 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 (R² = 0.98) with temperatures in SEQ1 over 2001–2012. During springtime and O₃ 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 O₃ at SEQ1 and SEQ2 were not statistically distinct in either springtime or during O₃ 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 O₃ 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 (Table 1). During O₃ season, O_x was 6.3 ± 3.5% higher on weekends than weekdays (relative to weekdays) in Visalia, indicating local PO₃ was NO_x suppressed. At the same time, O₃ 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 during springtime, as O_x was $7.4 \pm 4.6\%$ higher on weekends than weekdays in Visalia and O_3 was $3.5 \pm 7.4\%$ and $4.7 \pm 5.5\%$ higher on weekdays than weekends in SEQ1 and SEQ2. These weekday-weekend patterns indicate that 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, greater weekday concentrations in O_x in Visalia and O_3 at SEQ1 and SEQ2 imply NO_x -limited chemistry in all three locations (Table 1). Averaged across sites, percent differences in weekdays and weekends were $8.7 \pm 4.8\%$ in the springtime and $4.3 \pm 2.3\%$ during O_3 season. PO_3 during upslope transport is not apparent by this method because O_3 -season PO_3 is also NO_x limited in Visalia, indicating a portion of O_3 -forming organic reactivity in Visalia was temperature dependent, consistent with past analyses in other SJV cities (Steiner et al., 2006; Pusede and Cohen, 2012; Pusede et al., 2014; Rasmussen et al., 2014).

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3.3 O_3 trends over time

In Figure 6 and Table 4, 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: MD8A; two common vegetative-based indices, SUM0 and W126; and a morning average metric. We do not report trends in SUM06 or AOT40 vegetative indices, as they have been shown to poorly correlate with O_3 uptake at a Sierra Nevada forest site even in springtime (PANEK et al., 2002; Fares et al., 2010b). MD8A O_3 is a human health-based metric computed as the maximum unweighted daily 8-h average O_3 mixing ratio. A region is classified as in nonattainment of the NAAQS when the fourth-highest MD8A O_3 over a 3-yr period, known as the design value, exceeds a given standard. In this work, we utilize the seasonal mean MD8A and discuss O_3 exceedances as individual days in which MD8A $O_3 > 70.49$ ppb, the current 8-h NAAQS (CFR 40, 2015). SUM0 is equal to the sum of hourly O_3 concentrations over a 12-h daylight period (8 am–8 pm LT), as opposed to SUM06, which is limited to hourly O_3 mixing ratios greater than 60 ppb. 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 high and 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 MD8A. 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 $(1 + 4403e^{-126(O_3)})^{-1}$ (U.S. Environmental Protection Agency, 2015). W126 weighting is sigmoidal, with hourly O_3 weights equal to $(1 + 4403e^{-126(O_3)})^{-1}$, such that hourly mixing ratios below (above) 60 ppb receive less (more) weight (Environmental Protection Agency, 2016). Here, SUM0 and W126 summations are computed following the W126 protocol (Environmental Protection Agency, 2016), affording straightforward comparisons between the metrics. First, in months with less than 75% of hourly data coverage in the 8 am–8 pm LT window, missing values are replaced with the lowest observed hourly measurement over the study period (April–October) only until the dataset is 75% complete. From 2001–2012, 0, 8, and 3 months were initially less than 75% complete in Visalia, SEQ1, and SEQ2, respectively. Second, monthly summations of daily indices, comprised of hourly data (8 am–7 pm), are computed; when data are missing, the summation is divided by the data completeness fraction. Consecutive 3-month metrics are computed by adding monthly indices. In practice, SUM0 and W126 are computed as 3-yr averages of the

highest 3-month summation; however, we define springtime SUM0 and W126 as the 3-month summation over April–June and O₃ season SUM0 and W126 as the mean of the 3-month summations over June–August, July–September, and August–October (not the highest of the three 3-month sums). Because less than 15% of data were available for August 2008 at SEQ1, O₃ season SUM0 and W126 were computed as the mean of 3-month summations over June, July, and September, and July, September, and October only for this site and year. We compute morning (7 am–12 pm LT) trends (O_x in Visalia and O₃ in SNP), as high O₃ plant uptake rates (in the morning) and high O₃ concentrations (in the afternoon) are out of phase within daily timeframes in the Sierra Nevada Mountains. Plant O₃ 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).

In Figure 6, mean seasonal daily MD8A and morning metrics and cumulative SUM0 and W126 metrics are shown for Visalia, SEQ1, and SEQ2 with their fit derived using a [simple linear regression](#). Table 42 reports both the regression slope value (right columns) and the change in O₃ relative to the O₃ season fit value in SEQ1 in 2001 reported as a percent (left columns). SEQ1 experiences the highest O₃ observed for each metric and using a standard denominator facilitates comparison between monitoring sites and between seasons. [Table 2 coloration indicates trend significance computed using the Mann-Kendall non-parametric test following the categorization developed by TOAR authors \(Chang et al., 2017; Mills et al., 2018; Lefohn et al., 2018\), with p-values deemed statistically significant \(0–0.05\), indicative of a trend \(0.05–0.10\), weakly indicative of change \(0.10–0.34\), and indicative of weak or no change \(0.34–1\).](#)

Three patterns emerge in SNP O₃ trends over time: (1) O₃ decreased everywhere over the 12-yr record by all metrics in both seasons; (2) O₃ decreased at a slower rate in the springtime than during O₃ season by most metrics; and (3) O₃ decreased more rapidly in SNP versus Visalia and at SEQ2 versus SEQ1.

Seasonal differences in O₃ trends are prominent at each site. For example, O₃ at SEQ1 generally decreased less in springtime than during O₃ season (Table 42). For context in SEQ1, during O₃ season the mean MD8A declined from 82.3 ppb (2001–2002) to 73.8 ppb (2011–2012), but in the springtime the MD8A fell from 61.7 ppb (2001–2002) to 55.6 ppb (2011–2012). SUM0 O₃ fell from 87.0 ppm h (2001–2002) to 79.0 ppm h (2011–2012) during O₃ season and from 69.9 ppm h (2001–2002) to 61.8 ppm h (2011–2012) in the springtime. W126 O₃ decreased from 67.8 ppm h (2001–2002) to 53.7 ppm h (2011–2012) during O₃ season and from 39.8 ppm h (2001–2002) to 25.4 ppm h (2011–2012) in springtime. Morning O₃ fell from 67.1 ppb (2001–2002) to 59.6 ppb (2011–2012) during O₃ season and from 49.0 ppb (2001–2002) to 45.1 ppb (2011–2012). This pattern was not observed in one instance: SUM0 in SEQ2. Here, seasonal differences were comparable; however, mean daily indices were observed to differ, where SUM0 O₃ decreased from 0.914 ppm h (2001–2002) to 0.816 ppm h (2011–2011) during O₃ season, and, in the springtime, fell from 0.673 ppm h (2001–2002) to 0.616 ppm h (2011–2012), which amount to a change of –11% during O₃ season [and](#) –8% in the springtime.

Additionally, greater O₃ decreases were observed at SEQ1 than Visalia and at SEQ2 compared to SEQ1. Over the 12-yr⁴ period, MD8A O₃ declined at a rate of ~~5046~~ (O₃ season) and 61% (springtime) faster at SEQ1 than in Visalia, and 29% (O₃ season) and 41% (springtime) faster at SEQ2 than SEQ1 (based on the slopes reported in Table 42). SUM0 and W126 O₃ decreased 79% and 59% (O₃ season) and 38% and 54% (springtime) faster at SEQ1 than in Visalia and 20% and 23% (O₃ season) and 58% and 17% (springtime) faster at SEQ2 than SEQ1. Morning O_x trends at SEQ1 and Visalia were similar in springtime, but O_x decreased 40% more rapidly at SEQ1 during O₃ season and faster at SEQ2 than SEQ1 by 17% (O₃ season) and 55% (springtime). For each metric, we observe greater interannual variability relative to the net decline in springtime than during O₃ season. This site-dependence is reflected in the O₃ trend p-values (Table 2), where at SEQ2, slopes are either statistically significant at the 0.05 level or indicative of a trend (0.05–0.10) for each metric in both seasons. At SEQ1, slopes are statistically significant during O₃ season, but only indicative (W126), weakly indicative (MD8A), or suggestive of weak to no change (SUM0 and Morning O_x) in springtime. Trends in Visalia are the least robust, with p-values typically only weakly indicative or suggestive of minor to no change in both springtime and O₃ season.

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High O₃, as defined by exceedances of protective thresholds, also became less frequent over the 12-yr record. The number of days in which MD8A O₃ was greater than 70.49 ppb in 2001–2002 (averages are rounded up) was ~~6866~~ yr⁻¹ (O₃ season) and ~~4514~~ yr⁻¹ (springtime) in Visalia. In 2011–2012, the number of exceedances fell to ~~4239~~ yr⁻¹ (O₃ season) and 6 yr⁻¹ (springtime). At SEQ1 in 2001–2002, there were ~~424119~~ exceedance days yr⁻¹ (O₃ season) and ~~2420~~ yr⁻¹ (springtime), declining in 2011–2012 to ~~9997~~ yr⁻¹ (O₃ season) and 10 yr⁻¹ (springtime). At SEQ2 in 2001–2002, there were 103 exceedance days yr⁻¹ (O₃ season) and 13 yr⁻¹ (springtime). In 2011–2012, this decreased to ~~63~~ ~~exceedance days yr⁻¹ (O₃ season) and 3 yr⁻¹ in 2011–2012 (springtime).~~ 62 exceedance days yr⁻¹ (O₃ season) and 3 yr⁻¹ in 2011–2012 (springtime). Patterns in high MD8A O₃ days follow trends in other metrics, with the largest rates of change occurring during O₃ season in SEQ2 (–4.7 days yr⁻¹, $p = 0.02$), then SEQ1 (–2.8 days yr⁻¹, $p = 0.05$) and Visalia (–2.5 days yr⁻¹, $p = 0.05$). In springtime, smaller decreases are observed with similar spatial patterns, SEQ2 (–1.0 days yr⁻¹, $p = 0.02$), SEQ1 (–1.0 days yr⁻¹, $p = 0.15$) and Visalia (–0.5 days yr⁻¹, $p = 0.37$).

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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, known as the 5, 7, and 9 ppm h standards (Heck and Cowling 1997). RatherThe EPA has considered a potential secondary W126 ozone standard between 7 and 17 ppm h (Environmental Protection Agency, 2015a); likewise, the Clean Air Science Advisory Committee recommended a W126 standard level between 7 and 15 ppm h (Environmental Protection Agency, 2015a). In this work, rather than calculate W126 exceedances using a 3-month summation of monthly indices, we instead count the number of days required for an exceedance to occur, summing daily W126 indices from the first day of the springtime (1 April). A larger number of days indicates improved air quality. We do this to generate information in addition to exceedance frequency, as W126 O₃ at SEQ1 and SEQ2 is greater than all three standards in all years in both seasons. We only consider springtime, as this is when W126 is reported to better correlate with plant O₃ uptake (Panek et al., 2002; Kurpius et al., 2002; Bauer et al.,

2000). At SEQ1 from 1 April in 2001–2002, 37, 41, and 45 days of O₃ accumulation reached exceedances of the 5, 7, and 9 ppm h thresholds, respectively (averages are rounded up). In 2011–2012, 3 to 13 more days were needed at SEQ1, as 40, 49, and 58 days of O₃ accumulation were required to exceed the 5, 7, and 9 ppm h thresholds. At SEQ2 from 1 April in 2001–2002, 41, 46, and 49 days of accumulation led to exceedance of the 5, 7, and 9 ppm h thresholds, respectively. In 2011–2012, 59, 65, and 73 days were required at SEQ2, or 18–24 more days.

4 Discussion

4.1 O₃ metrics

10 Long-term measurements of O₃ fluxes rather than O₃ concentrations are required to fully understand the effects of upwind emission controls on ecosystem O₃ 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 O₃ uptake and high atmospheric O₃ concentrations may be uncorrelated (e.g., Panek et al., 2002). This may also be true in European Mediterranean climate regions, where high concentrations of ecosystem-based O₃ metrics have also been observed (Mills et al., 2018). We have based our analysis on results from years of O₃ flux data collected in forests on the western 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 O₃ 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 ecosystem O₃ impacts in SNP; that said, we find similar conclusions would be drawn regarding multiyear O₃ variability by location by assessing trends in SUM0, MD8A O₃, and the morning O_x metric. This can be explained by the upslope-downslope air flow in our study region and is evident in SNP diurnal O₃ patterns (Figure 4), which show considerable O₃ entrained into the boundary layer in the morning. O₃ concentrations are strongly influenced by afternoon concentrations on the previous day. Comparable trends in morning, afternoon, and daily average O₃ would then arise under conditions of persistence, which are common in Central California, but these results may not extend to other downwind ecosystems in the absence of an upslope-downslope flow pattern. The dynamically-driven elevated morning O₃ concentrations have important consequences for plants, as vegetation in SNP may be particularly vulnerable because plant O₃ uptake rates are often highest in the morning.

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30 Reductions in ecosystem O₃ impacts as represented by declines in W126 are greater than those of SUM0. We attribute this difference to the W126 weighting algorithm that makes the metric most sensitive to changes in the highest O₃. Using the GEOS-Chem model with a focus on national parks, Lapina et al. (2014) also found W126 was more responsive to decreases in anthropogenic emissions than daily (8 am–7 pm, LT) average O₃ concentrations. With the Community Earth System Model, Val Martin et al. (2015) modeled air quality in national parks under two Representative Concentration Pathway (RCP) scenarios, computing substantially larger decreases over a 50-yr period in W126 O₃ compared to the MD8A. In the TOAR global analysis, Mills et al. (2018) found April–September W126 downward trends over 1995–2014 in California of between

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[1–2 ppm h yr⁻¹ to be among the most rapid W126 declines in the world.](#) Considering that the SUM0 metric has been shown to best correspond to plant O₃ uptake in Sierra Nevada forests using O₃ flux observations (Panek et al., 2002) and that we observe W126 O₃ has declined at approximately twice the rate of SUM0 over 2001–2012, W126 trends may provide an overly optimistic representation of past declines in ecosystem O₃ impacts in SNP.

5 4.2 Reducing high O₃ in SNP and polluted downwind ecosystems

NO_x decreases have generally made greater improvements in O₃ in SEQ1 than Visalia and in SEQ2 than SEQ1, a trend that corresponds to increasing distance downwind of the SJV. We attribute this to the importance of export of NO_x from the SJV on O₃ in SNP, combined with distinct PO₃ chemical regimes in SNP versus Visalia. Evidence for this is four-fold. First, O₃ at SEQ1 is greater than O_x in Visalia, at least during O₃ season, suggesting net O₃ formation as air travels from the SJV to SNP.

10 Second, according to observations of O_x (Visalia) and O₃ (SNP) on weekdays versus weekends, PO₃ was simultaneously NO_x-suppressed in Visalia and NO_x-limited in SNP, with the weekday-weekend dependence of O₃ 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, O₃ decreases (2001–2012) are observed to be greater in SNP than Visalia, and
15 greater with increasing distance downwind. Distinct local PO₃ regimes lead to PO₃ chemistry in Visalia and SNP that is differently sensitive to emission controls, with NO_x-limited SNP historically more responsive to NO_x emission control than Visalia. SNP NO_x-limitation is enhanced by NO_x dilution during transport, which further decreases NO_x relative to the abundance of local organic compounds. Downwind sites usually experience PO₃ chemistry that is more NO_x-limited than in the often NO_x-suppressed (or at least more NO_x-suppressed) urban core. As a result, we expect similar location-specific O₃
20 trends in other ecosystems and national parks downwind of major NO_x sources like cities. However, while the extent of observed O₃ improvements in SNP follows the pattern of increasing distance downwind of Visalia with sustained NO_x emission control in the SJV (Russell et al., 2010; Pusede and Cohen, 2012), PO₃ chemistry is non-linear and the direction of location-specific trends may vary. That said, at some distance downwind this conclusion breaks down, as areas become less and less influenced by the upwind source.

25 Because PO₃ in SNP is NO_x-limited, future NO_x reductions are expected to have at least as large an impact on local PO₃ as past reductions. Seasonal mean NO₂ concentrations have decreased by 58% and 53% in Visalia in springtime and O₃ season [over our study window](#), respectively. Local NO_x emissions should continue to decline into the future, as there are significant controls currently ongoing or in the implementation phase, including more stringent national rules on heavy-duty diesel engines (Environmental Protection Agency, 2000; 2010), combined with California Air Resources Board (CARB) diesel engine retrofit-replacement requirements (California Air Resources Board, 2008; 2014), and more stringent CARB standards for
30 gasoline-powered vehicles (California Air Resources Board, 2012). While O₃ declines near or greater than those that occurred from 2001 to 2012 are required to eliminate exceedances in SNP, modeling analysis by Lapina et al. (2014) suggests that W126 in the region would be well below these thresholds in the absence of anthropogenic precursor emissions, implying further

emissions controls would be effective. Under the stringent precursor controls of RCP4.5, Val Martin et al. (2015) projected decreases of 11% and 67% for the MD8A and W126 in 2050, respectively, from the base year of 2000, with mean O₃ decreasing from 58.9 ppb (MD8A) and 45.5 ppm h (W126) in 2000 to 52.7 ppb (MD8A) and 15.1 ppm h (W126). Under the RCP8.5, smaller O₃ declines were predicted, with MD8A unchanged and W126 falling by 38% to 28.3 ppm h. Given that these scenarios represent a reasonable spread of possible future climatic conditions, Val Martin et al. (2015) suggest at least W126 will remain well above protective thresholds in 2050.

Over 2001–2012, O₃ declines have mostly been smaller in SNP when plant O₃ uptake is greatest (springtime), despite comparable NO_x decreases in both seasons. This may be in part because regulatory strategies prioritize attainment of the O₃ NAAQS in polluted urban areas like the SJV basin, where air parcels influenced by the results of these controls are then transported downwind to locations with different PO₃ chemistry. In the development of regulatory plans, agencies use models to hindcast past O₃ episodes, facilitating testing of the efficacy of specific NO_x and/or organic emissions reductions over that episode to meet the 8-h O₃ NAAQS or progress goals (Environmental Protection Agency, 2007; Environmental Protection Agency, 2014). In nonattainment areas, U.S. EPA guidance recommends modeling past time periods that meet a number of specific criteria, such as typifying the meteorological conditions that correspond to high O₃ days as defined by the MD8A greater than the NAAQS value and focusing on the ten highest modeled O₃ days (Environmental Protection Agency, 2007; Environmental Protection Agency, 2014). Regulatory modeling in the SJV (Visalia, SEQ1, and SEQ2 are included in this attainment demonstration) is more comprehensive, as it was recently updated to span the full O₃ season (defined as May–September); still potential reductions (known as relative reduction factors, RRFs) are based on the MD8A and restricted to high O₃ days (San Joaquin Valley Air Pollution Control District, 2007; San Joaquin Valley Air Pollution Control District, 2014). In the SJV, high O₃ days are most frequent in the late summer (O₃ season) and on the hottest days of the year (Pusede and Cohen, 2012). Even in SEQ1 and SEQ2, days with MD8A > 70.49 ppb are far more common in the summer. Because of chemical and meteorological differences between seasons, this may lead to policies not optimized to decrease O₃ in cooler springtime conditions, which in the SJV are more NO_x-suppressed and therefore more sensitive to controls on reactive organic compounds (Pusede et al., 2014). In addition, we observe greater year-to-year O₃ variability in the springtime than during O₃ season (Figure 6), suggestive of a larger relative role of interannual meteorological variability controlling O₃ concentrations. Deeper cuts in emissions would appear to be required in the springtime in SNP, as decreases in anthropogenic emissions have a proportionally smaller effect, both relatively and in the absolute, on the total O₃ abundance than during O₃ season, in part because background O₃ makes the greatest contribution to daily O₃ in the springtime SNP (Figure 4).

An additional challenge to regulators is the contribution of background O₃ concentrations to O₃ levels and non-local sources challenges regulators (Cooper et al., 2015), as natural sources produce O₃ even in the absence of anthropogenic precursor emissions, O₃ can be transported over significant distances, and O₃ concentrations are influenced by large-scale meteorological and climatic events. Multiple studies have identified an increasing trend in O₃ at rural sites (often used as a proxy for background O₃) in the western U.S., particularly in the springtime (e.g., Cooper et al., 2012, Lin et al., 2017). Parrish et al. (2017) presented observational evidence of a slowdown and reversal of this trend on the California west coast since 2000,

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though the reversal was stronger in the summer than springtime. Using observations and the GFDL-AM3 model, Lin et al. (2017) computed that Asian anthropogenic emissions accounted for 50% of simulated springtime O₃ increases at western U.S. rural sites, followed by rising global methane (13%) and variability in biomass burning (6%). 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), with high-elevation locations in the Sierra Nevada Mountains being more vulnerable to reception of Asian O₃ and O₃ precursors (e.g., Vicars and Sickman, 2001; Heald et al., 2003; Hudman et al., 2004). Hudman et al. (2004) compared surface observations with GEOS-Chem-modeled O₃ enhancements in Asian pollution outflow, finding that, on average, transport events in April–May 2002 led to 8 ± 2 ppb higher MD8A O₃ concentrations at SEQ2. East Asian NO_x emissions have risen over our study window (e.g., Miyazaki et al., 2017), potentially causing an increase in the influence of trans-Pacific transport on O₃ concentrations at SEQ2 and reducing the efficacy of local NO_x control in springtime. [However, NO_x emission and concentration declines have been observed over China since 2011 \(Liu et al., 2016\), diminishing possible influence of Asian transport events in SNP.](#) Background O₃ concentrations are also responsive to large-scale climatic events, and elevated springtime O₃ at rural sites in the western U.S. has been linked to strong La Niña winters (Lin et al., 2015; Xu et al., 2017), which are associated with an increased frequency of deep tropopause folds that entrain O₃-rich stratospheric air into the troposphere (Lin et al., 2015). Over our study period, strong La Niña events occurred during the winter of 2007–2008 and 2010–2011. In general, transport of Asian pollution and tropopause folds are expected to have a greater impact in the springtime and at the higher-elevation SEQ2. While we do observe smaller decreases in O₃ in springtime at SEQ2 than during O₃ season, interannual trends have been more downward at SEQ2 than at the lower elevation sites, SEQ1 and Visalia, in both seasons. This suggests that these factors may impact surface O₃ at high-elevations in SNP during individual events (e.g., Hudman et al., 2004) but that interannual trends in seasonal averages are more influenced by chemistry during upslope outflow from the SJV.

5 Conclusions

We describe O₃ trends at two monitoring stations in SNP and in the SJV city of Visalia, which is located in the upwind direction from SNP. We show that a major portion of the O₃ concentration in SNP is formed during transport from NO_x emitted in the SJV, rather than from O₃ produced in Visalia and subsequently transported downwind. This has contributed to reductions in O₃ in SNP over the 12-yr period of 2001–2012, even while PO₃ in Visalia was NO_x suppressed. Evidence for this includes greater O₃ at SEQ1 than O_x in Visalia during O₃ season (Figure 4), distinct weekday-weekend O₃ differences in SNP and Visalia, [\(Table 1\)](#), 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 O₃ decreases over 2001–2012 at SEQ1 versus Visalia and at SEQ2 versus SEQ1 [\(Figure 6, Table 42\)](#).

We compute interannual O₃ trends using human health- and ecosystem-based concentration metrics in springtime and O₃ season separately in order to distinguish between ecosystem O₃ impacts (plant O₃ uptake) and high O₃ concentrations. We find

that O₃ has decreased in SNP and Visalia by all metrics in both seasons consistent with ongoing NO_x emission controls but observe smaller O₃ declines in springtime when plant uptake is greatest. The three metrics, MD8A, SUM0, and morning O_x, all indicate comparable reductions in O₃ over 2001–2012, with decreases of ~7% (springtime) and ~13% (O₃ season) at SEQ1 and 13–16% (springtime) and 15–19% (O₃ season) at SEQ2. We attribute similarity across these three metrics to upslope-downslope airflow at the eastern edge of the SJV, as morning O_x and SUM0 are strongly affected by high afternoon O₃ concentrations on the previous day which results from the mixing of O₃-polluted nocturnal residual layers into the surface boundary layer. Past O₃ flux measurements in the region indicate the highest plant O₃ uptake in the springtime morning, therefore SNP vegetation experiences greater O₃ exposure than in locations without this memory effect. O₃ decreases over 2001–2012 computed with W126 are almost double those for SUM0, with the W126 emphasis of higher O₃ concentrations giving the most optimistic evaluation of the efficacy of past emission controls.

Diurnal and seasonal mismatches between plant O₃ uptake rates and O₃ concentration-based metrics make it challenging to accurately assess vegetative O₃ damage and to quantitatively evaluate the success of regulatory action on ecosystems. Future work would benefit from the development of an environmentally- and biologically-relevant metric that captures patterns in plant O₃ uptake over daily and seasonal timescales, especially in Mediterranean ecosystems, where conditions conducive to plant O₃ uptake are asynchronous with conditions that lead to high O₃ concentrations.

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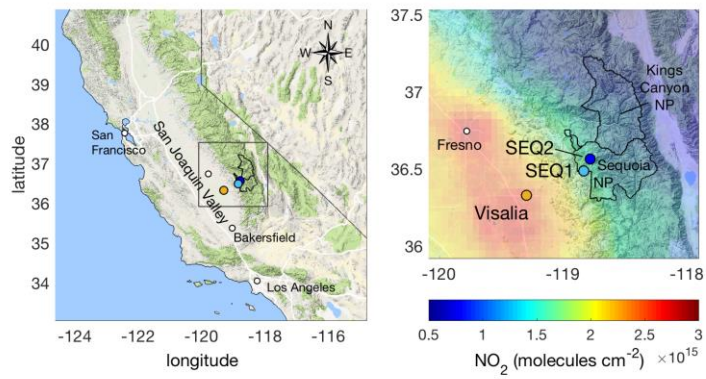


Figure 1. Map of California (**left**) with study region detail (**right**) indicating the locations of the SJV station, Visalia (orange), and two monitoring sites in SNP, SEQ1 (cyan) and SEQ2 (dark blue), with mean April–October, 2010–2012 OMI NO₂ columns using the BEHR (Berkeley High-Resolution) product ([Russell et al., 2014](#)), ([Russell et al., 2011](#)).

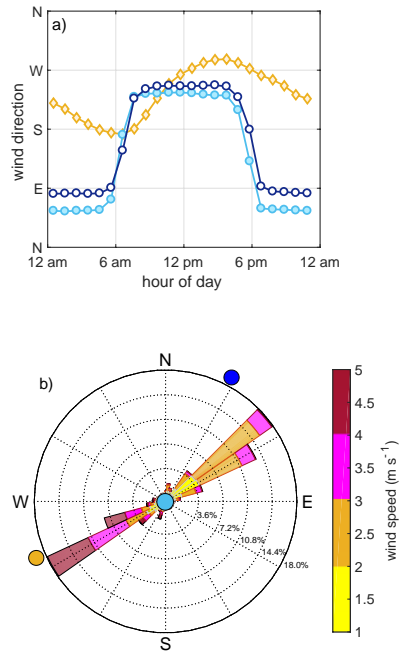


Figure 2. Hourly mean wind directions in Visalia (orange diamonds), SEQ1 (cyan filled circles), and SEQ2 (dark blue open circles) in April–October, 2001–2012 (panel a). Wind rose for SEQ1 (panel b) with the direction of the neighboring sites of Visalia (orange), SEQ1 (cyan), and SEQ2 (dark blue) indicated.

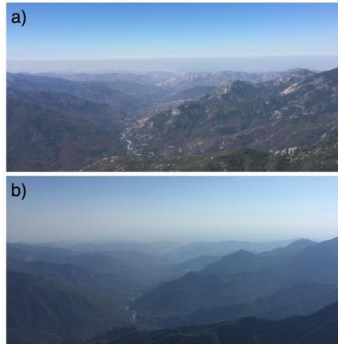
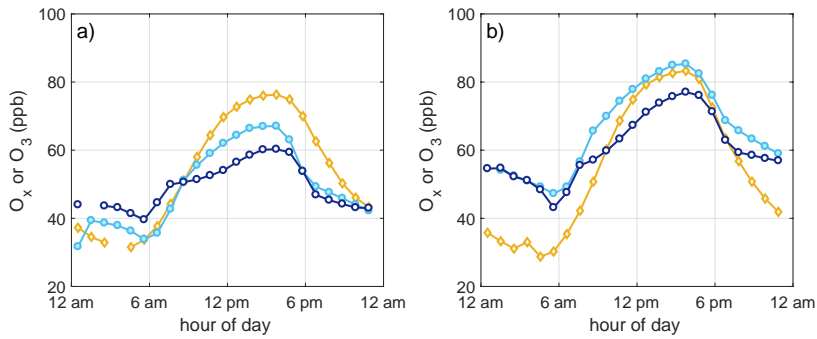


Figure 3. Looking toward the SJV from Moro Rock in SNP (36.5469 N, 118.7656 W; 2050 m ASL) at 11 am LT (panel a) and 5:30 pm LT (panel b). Photographs were taken by the authors on 29 June 2017.



5

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.

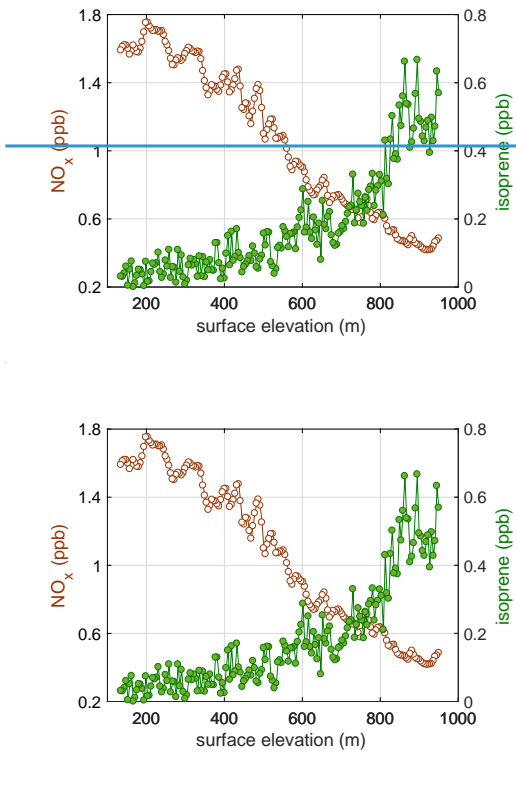


Figure 5. NO_x (brown open circles) and isoprene (green filled circles) measured onboard the NASA DC-8 at ~10 am LT at the Sierra Nevada western slope from a mean altitude of 130 m AGL to 1000 m AGL on 19 June, 2016. The surface elevation is estimated by linearly interpolating across the total elevation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

Table 1. Percent difference in afternoon (12–6 pm LT) O_x or O₃ on weekdays and weekends calculated as: $(O_{x,weekday} - O_{x,weekend}) / O_{x,weekday}$ in Visalia, SEQ1, and SEQ2 in 2001–2003 on moderate and high temperature days. Errors are reported as standard errors of the mean.

Temperature	Moderate	High
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O ₃ season (June–October) 2001–2003		
-	%	%
SEQ2	4.9 ± 3.9	3.5 ± 2.4
SEQ1	4.6 ± 3.3	4.2 ± 1.9
Visalia	-6.3 ± 3.5	5.3 ± 2.6
Springtime (April–May) 2001–2003		
-	%	%
SEQ2	4.7 ± 5.5	5.2 ± 4.6
SEQ1	3.5 ± 7.4	8.6 ± 4.9
Visalia	-7.4 ± 4.6	12.2 ± 4.8

Table 2. O₃ changes in Visalia, SEQ1, and SEQ2 over 2001–2012 according to MD8A, SUM0, W126, and morning O_x metrics based on a linear fit of annual mean data (shown in Figure 6) in the springtime and O₃ season. Each left column is the percent change with respect to fit value in 2001 at SEQ1 during O₃ season for comparison, which is the highest O₃ observed for each metric. Each right column is the fit slope with slope errors in O₃ abundance units per year. [Coloration is based on the TOAR categorization for trend significance \(Lefohn et al., 2018\), with p-values calculated using the Mann-Kendell non-parametric test: yellow, 0–0.05, statistically significant trend; green, 0.05–0.10, indicative of a trend; violet, 0.10–0.034, weak indication of change; and pink, 0.34–1, weak or no change.](#)

O ₃ metric	MD8A		SUM0		W126		Morning O _x	
	%	ppb $\frac{\text{yr}^{-1}}$	%	ppm h $\frac{\text{yr}^{-1}}$	%	ppm h $\frac{\text{yr}^{-1}}$	%	ppb $\frac{\text{yr}^{-1}}$
O₃ season (June–October)								
SEQ2	-19	-1.4 ± 0.41	-15	-1.2 ± 0.46	-37	-2.2 ± 0.72	-17	-1.0 ± 0.32
SEQ1	-13	-1.0 ± 0.27	-12	-0.96 ± 0.21	-28	-1.7 ± 0.36	-14	-0.83 ± 0.21
Visalia	-7	-0.54 ± 0.30	-3	-0.20 ± 0.28	-11	-0.69 ± 0.41	-6	-0.50 ± 0.30
Springtime (April–May)								
SEQ2	-13	-1.0 ± 0.38	-16	-1.2 ± 0.47	-30	-1.8 ± 0.62	-13	-0.78 ± 0.34
SEQ1	-8	-0.59 ± 0.42	-6	-0.50 ± 0.53	-24	-1.5 ± 0.62	-6	-0.35 ± 0.32
Visalia	-3	-0.23 ± 0.39	-4	-0.31 ± 0.38	-11	-0.69 ± 0.49	-8	-0.39 ± 0.35

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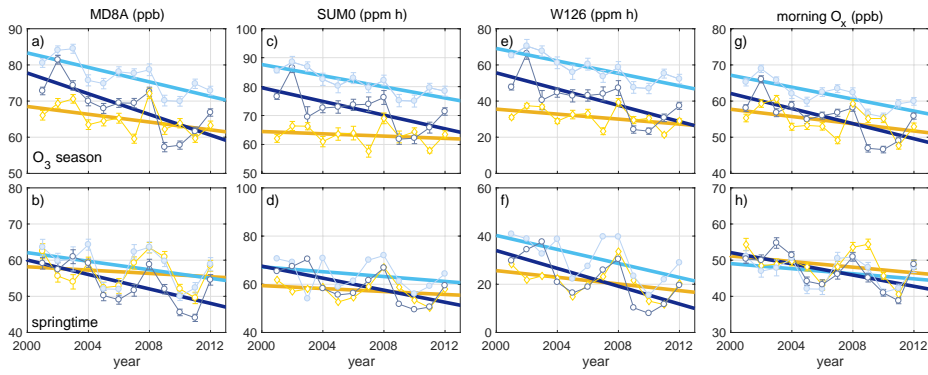


Figure 6. O₃ trends in Visalia (orange diamonds), SEQ1 (cyan filled circles), and SEQ2 (dark blue open circles) computed using MD8A (a–b), SUM0 (c–d), W126 (e–f), and morning O_x (g–h) metrics during O₃ season (top row) and springtime (bottom row). [Both MD8A and morning O_x are computed as seasonal averages.](#) Error bars in panels a–b and g–h are standard errors of the mean. Error bars in panels c and e are standard errors of the mean of the three O₃ season 3-month summations.

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