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On the observed response of ozone to NO_x and VOC reactivity reductions in San Joaquin Valley California 1995–present

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Abstract

We present a statistical approach to describe the effects of nitrogen oxide (NO_x) and organic reactivity reductions on the frequency of high ozone days. We use sixteen years of observations of ozone, nitrogen oxides, and temperature at sites upwind, within, and downwind of three cities in California's San Joaquin Valley to assess the probability of exceeding of the California 8-h average ozone standard of 70.4 ppb at each location. We demonstrate that the comprehensive data records in the region and the steep decreases in emissions over the last decade are sufficient to constrain the relative import of NO_x and organic reactivity reductions on the frequency of violations. We show that high ozone has a large component that is due to local production, as the probability of exceeding the state standard is lowest for each city at the upwind site, increases across the city center, is highest at downwind locations, and then decreases at the receptor city to the south. We see that reductions in organic reactivity have been very effective in the central and northern regions of the San Joaquin but not in the southern portion of the Valley. We find evidence for two distinct categories of reactivity sources: one source that has decreased and dominates at moderate temperatures, and a second source that dominates at high temperatures in the southern San Joaquin, which has not changed over the last twelve years. We show that NO_x reductions are already effective or are poised to become so in the southern and central Valley, where violations are most frequent, as conditions in these regions have or are transitioning to NO_x-limited chemistry when temperatures are hottest and high ozone most probable.

1 Introduction

Ozone formation is a nonlinear function of nitrogen oxides (NO_x) and the reactivity of gas phase organic molecules and consequently, reductions in the emissions of these precursors can decrease, increase, or leave unchanged the rate of ozone production. Emissions control policies aimed at improving ozone (O_3) air quality therefore require

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sufficient information on how the chemical system at a given location will respond to reductions in precursor concentrations. Over the last decade there have been dramatic reductions in NO_x concentrations across North America and Europe (e.g. Richter et al., 2005; Kim et al., 2006, 2009; Stavrakou et al., 2008; van der A et al., 2008; Konovalov et al., 2010; Russell et al., 2010, 2012). At many locations there are reports of decreases in organic emissions (e.g. Environmental Protection Agency, 2003; Parrish, 2006; Bishop and Stedman, 2008; Monks et al., 2009; Wilson et al., 2012) but changes to the total organic reactivity are not well documented. These precursor changes are predicted to have substantially affected the photochemical ozone production rate and thus the probability of exceeding health-based standards. Reports of improved air quality are mixed and there has been little success in attributing quantitative measures of changes in ozone concentrations to the reductions of specific emissions.

A variety of observational and modeling approaches have been used to evaluate ozone's sensitivity to NO_x and organic reactivity. These include analyses of ratios of peroxides to nitric acid (e.g. Sillman et al., 1995, 1997), relationships between measured nitrogen oxides and organic molecules (e.g. Kleinman et al., 2000, 2005; Trainer et al., 2000; Martin et al., 2004; Stephens et al., 2008; Pollack et al., 2012), rates of ozone production derived from observed reactant concentrations (e.g. Thornton et al., 2002; Martinez et al., 2003; Ren et al., 2003), and, very recently, the direct measurement of the instantaneous ozone formation rate (Cazorla and Brune, 2010; Cazorla et al., 2012). These methods each work to constrain the chemistry of ozone production at the specific local NO_x and organic reactivity. Predictions of the effects of emissions reductions are usually based on models that hindcast a small subset of historical high ozone episodes. These studies typically implement a given percentage reduction in NO_x and/or organic emissions and calculate whether O_3 would have indeed been reduced during that episode. However, the short-time and/or limited-spatial scales of these measurement and modeling analyses make it difficult to assess the accuracy of the predictions. For example, we know of no case where a quantitative prediction of the

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reduction in the number of annual violations of a health-based standard was made in advance of a policy and then explicitly verified with observations after the fact.

Growth in the observational database and the increase in computational power have made it possible to think about ozone statistics over wide regions of space and over long periods of time instead of focusing on individual episodes. Here we take a statistical approach describing changes in the frequency of high ozone days and showing that existing routine observations of ozone, nitrogen oxides, and temperature can provide direct insight into the probabilistic response of ozone to emission reductions. We develop our methodology using the example of California's San Joaquin Valley (SJV), a region competing with the Los Angeles basin for the most frequent number of high ozone days in the US (American Lung Association, 2011), where ambient O_3 concentrations persistently violate health-based air quality standards (Cox et al., 2009) despite sustained scientific attention (Venkatram et al., 1994; Andreani-Aksoyoglu et al., 2001; Marr et al., 2002a, b; Steiner et al., 2006, 2008; Lin et al., 2008; Howard et al., 2008, 2010a, b; Hu et al., 2012) and regulatory efforts at both the local (e.g. San Joaquin Valley Air Pollution Control District, 2007) and state level (California Air Resources Board, 2011). We use the results from our statistical approach to make policy-relevant conclusions about how the frequency of high O_3 in the SJV will respond to NO_x and organic reactivity emissions reductions. We note that the data to support this type of analysis are available at many locations in North America and Europe.

2 Conceptual framework

2.1 Ozone production

Photochemical ozone production results from a pair of catalytic cycles initiated by creation of odd-hydrogen (OH or HO_2) or organic peroxy radicals (RO_2), collectively referred to as HO_x ($HO_x \equiv OH + HO_2 + RO_2$). Entering the HO_x cycle, a generic organic molecule is oxidized by OH, forming RO_2, then HO_2, and subsequently regenerating

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OH (Fig. 1a). This cycle drives the oxidation of NO to NO_2 twice (Fig. 1b). The photolysis of NO_2 is rapid and the product oxygen atom combines with O_2 to yield O_3. During the daytime reactions propagating the HO_x cycle are much more important than those that are chain terminating and the ratio of HO_2 to RO_2 is near one.

Figure 2 shows the nonlinear dependence of the instantaneous rate of O_3 production (PO_3) on NO_x ($NO_2 + NO$) and the organic reactivity (VOCR). Moving left to right, i.e. from a scenario of remote continental to urban photochemistry, PO_3 grows steeply with increasing NO_x abundance, reaches a peak, and then decreases with continued NO_x increases. This initial rise results from NO_x's role as modulator of the ($HO_2 + RO_2$) to OH ratio. At low NO_x, adding NO enhances OH via reactions between NO and HO_2 or RO_2, and thereby the oxidation rate of organic molecules (NO_x-limited chemistry). Because OH is typically 100 times less abundant than HO_2 or RO_2, this has little effect on the comparatively large $HO_2 + RO_2$ reservoir. At high NO_x, OH reacts with NO_2 to form nitric acid reducing the HO_x radical pool (NO_x-suppressed chemistry). In the intermediate regime, reactions forming alkyl and peroxy nitrates are important to the absolute rate but do not strongly affect the shape of the curves (Farmer et al., 2011).

Participating organic molecules are commonly referred to as volatile organic compounds (VOCs), distinguishing them from low vapor pressure species that are instead more likely to condense onto aerosol surfaces. The impact of any individual VOC to ozone production depends primarily on its reaction rate with OH; rapidly reacting molecules such as alkenes and aldehydes are disproportionally important compared to less reactive alkanes, acids, and ketones. The rate at which the sum of all VOCs reacts with OH is defined as the VOC reactivity (VOCR). This is a condensed parameter summarizing the integrated effects of the local VOC mixture. In Fig. 2, we show PO_3 calculated with three different VOCRs: a base case, twice the base VOCR, and three times the base VOCR. Note that at the left of Fig. 2 (low NO_x), VOCR has no effect on the rate of O_3 production, while at the right, PO_3 increases with VOCR almost linearly (VOC-limited chemistry).

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Just as decreases in VOCR decrease PO_3, so will reductions in the rate of HO_x production (PHO_x), as a shrinking HO_x pool will slow VOC oxidation rates (not shown). PO_3 scales nearly linearly with PHO_x, its response to increasing PHO_x smaller at low than high NO_x. The photolysis of O_3 is typically the single largest HO_x source and so lower O_3 concentrations impact PHO_x in a positive feedback that results in further decreased ozone production rates. In the SJV, the average Valley-wide summertime (June–August) 8-h O_3 has varied by less than 16 ppb in the last twelve years (it was 70.2 ppb in 1999 and 66.4 ppb in 2010). The second largest source of PHO_x is often the photolysis of formaldehyde. Formaldehyde is both a primary anthropogenic emission and is an oxidation product of virtually every gas phase organic molecule. Formaldehyde is reactive with OH as well and, after oxidation, enters the HO_x cycle at HO_2 formation directly. VOC emissions reductions targeting formaldehyde and/or any of its precursors will have the combined effect of simultaneously reducing VOCR and radical production.

The atmospheric O_3 concentration is a function of the time-integrated effects of PO_3, chemical and depositional O_3 loss, and mixing. Of these, PO_3 dominates the variability, as day-to-day variations in the other terms are much smaller. Consequently, the curves representing PO_3 in Fig. 2 also describe the statistics of ozone variability and the number of high ozone days as a function of VOCR and NO_x.

We illustrate the change in frequency of high ozone days in response to three scenarios of NO_x and/or VOCR reductions with dashed lines in Fig. 2:

- Scenario A decreases NO_x at constant VOCR. This scenario is shown as the transition between points (1) → (2) → (3). NO_x reductions initially increase PO_3 at high NO_x (1 → 2) followed by a decrease in PO_3 at low NO_x (2 → 3). This scenario occurs on weekends in locations where dramatic reductions in diesel truck traffic result in lower NO_x emissions alongside small changes in VOCR.

- Scenario B decreases VOCR at constant NO_x (2 → 4) and has the effect of proportionally reducing PO_3 at high NO_x and of negligibly changing PO_3 at low NO_x.

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This scenario occurs in regions where NO_x emissions are constant and VOC emissions are exponential with temperature. One such example is in forested regions downwind of cities, where VOCR is largely biogenic and higher at hotter temperatures (e.g. LaFranchi et al., 2011).

– Scenario C reduces NO_x and VOCR simultaneously (2 → 5) and is typical of what has occurred over the last decade in cities where vehicular emissions dominate both NO_x and VOCR.

We use this conceptual framework to interpret the observed changes in the probability of high ozone days defined as the fraction of days exceeding the 8-h O_3 California Ambient Air Quality Standard (CAAQS) of 70 ppb (>70.4 ppb).

2.2 NO_x

NO_x abundances across California have fallen at near constant rates over the last decade; this is according to emissions inventories (Cox et al., 2009; Millstein and Harley, 2010), surface measurements (Ban-Weiss et al., 2008; Lafranchi et al., 2011; Parrish et al., 2011), and space-based observations (Kim et al., 2009; Russell et al., 2010). These NO_x decreases have had led to striking improvements in ozone air quality in the Sacramento Valley (Lafranchi et al., 2011) but less so in the Los Angeles basin, where chemistry remains NO_x-suppressed and the dramatic improvements of the 1980's and 1990's have slowed (e.g. Pollack et al., 2012). In the SJV, both satellite NO_2 and the ground-based nitrogen oxide data records indicate steady decreases of approximately 5 % per year Valley-wide (Russell et al., 2010).

In addition to long-term reductions, NO_x concentrations have a well known day-of-week dependence. In the SJV, NO_x is typically 30–50 % lower on weekends than weekdays, a phenomenon largely due to reduced weekend heavy-duty diesel truck traffic (e.g. Marr et al., 2002b; Millstein and Harley, 2010). Meteorological and chemical conditions, such as VOCR, are far less day-of-week dependent than are changes in NO_x and, as a result, comparison of weekdays to weekends is an effective and widely used

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tool to study the NO_x dependence of O_3 formation (e.g. Murphy et al., 2006, 2007; Stephens et al., 2009; LaFranchi et al., 2011; Pollack et al., 2012).

In this work, we consider both annual and day-of-week NO_x trends comparing curves describing weekday and weekend O_3 CAAQS exceedance probabilities over the past sixteen years. We note that the NO_2 data presented here are obtained by chemiluminescence coupled with a heated molybdenum catalyst, a technique with a known positive interference from the higher oxides of nitrogen (alkyl and peroxy nitrates and nitric acid). We refer to measured "NO_2" as NO_2* hereafter (more detailed description of all measurements is found in the Appendix). To a reasonable approximation NO_2 is a constant fraction of NO_2* at a given location at a given time of day (Dunlea et al., 2007).

2.3 VOCR and temperature

Tailpipe emissions from vehicles are only weakly temperature dependent, for example due to the increase in fuel consumption for air conditioning on hot days (Rubin et al., 2006). By contrast, biogenic VOCs from forests (e.g. Guenther et al., 1993; Schade and Goldstein, 2001) and agriculture (e.g. Ormeño et al., 2010) are emitted as an exponential function of temperature until, for certain species, inhibited by extreme heat. Vapor pressures rise exponentially with temperature and so evaporative emissions, such as from fuels and farm residues, are also strongly temperature dependent. There is evidence for decreases in both the concentrations (Harley et al., 2006) and emissions (Cox et al., 2009) of some VOCs in the SJV over the last twenty years. However, how or if these reductions have broadly translated to decreases to total VOCR is not known. Observations of VOCR are not generally available, as techniques for direct measurement have only recently been developed (Kovacs et al., 2001; Sadanaga et al., 2004a; Sinha et al., 2008; Ingham et al., 2009). The use of these techniques is still limited to large-scale field experiments and at most sites observations of individual VOCs do not add up to the total VOCR measured (e.g. Kovacs et al., 2003; Di Carlo et al., 2004; Sinha et al., 2008, 2010; Ingham et al., 2009; Lou et al., 2010). In the SJV,

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we show temperature is a useful surrogate for VOCR insofar as we recreate distinct curves analogous to Fig. 2 by organizing observations by temperature (see below for details).

Meteorological conditions conducive to high ozone, including stagnation events and clear skies, correlate with increasing temperature. As such, in this analysis, grouping data at a common temperature decouples the effects of chemistry from those of meteorology. We note however that in the SJV, we do not expect meteorological factors that are particularly different to vary with temperature during ozone season.

3 Probability of high ozone

The SJV is characterized by regular airflow through the Valley from north to south during ozone season (~May–October) with background O_3 well mixed Valley-wide (Zhong et al., 2004). Here we divide the SJV (Fig. 3a) into three distinct urban photochemical plumes each captured by California Air Resources Board's (CARB) monitoring stations and refer to these three regions as *Southern SJV* (Fig. 3b), *Central SJV* (Fig. 3c), and *Northern SJV* (Fig. 3d). Within each plume, we identify an upwind, city center, and downwind location, each along the axis of air movement (nine locations total). We see the lowest exceedance probabilities at upwind sites (Figs. 4–10, panels a), increased probabilities across the city center (Figs. 4–10, panels b), and the highest probabilities at locations downwind (Figs. 4–10, panels c). At the upwind site of adjacent study regions to the south, the likelihood of a violation is again at a minimum – evidencing the production of ozone within each transect (details in Sect. 4.4).

The bottom panels in Fig. 3 show observations of NO_2 from the Ozone Monitoring Instrument (OMI) averaged for weekdays in June–August in 2007–2010 using the Berkeley High-Resolution (BEHR) product (Russell et al., 2011). The OMI images highlight three separate NO_2 plumes in our three study areas and show the local nature of NO_x emissions in the SJV. In what follows, we discuss each region in turn, starting in the south and moving north.

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4 Results

4.1 Southern San Joaquin Valley

In Fig. 4 we show the Southern SJV 8-h O_3 CAAQS exceedance probability vs. NO_2* and in Fig. 5 we show the trend in this probability vs. year (year increases right to left analogous to NO_2* concentration). The red symbols are statistics for high temperatures (34–45 °C) and the blue for moderate temperatures (28–33 °C). Solid symbols are weekdays (Tuesday–Friday) and open diamonds are weekends (Saturday–Sunday). Mondays and Saturdays are considered transition days as they are influenced by carryover from the previous day. We omit Mondays for this reason but retain Saturdays to improve the statistics for weekends. Uncertainties in exceedance probabilities are treated as counting errors and computed as $0.5(N)^{1/2}/N$, where N is the total number of days in that bin. Uncertainties are typically less than ±0.09 (1 σ) for weekdays and ±0.12 (1 σ) for weekends. Uncertainties in the four-year median probabilities are less than ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends.

At high temperatures, the probability of an ozone violation at the upwind site, Shafter, decreased from 80 % on weekdays when NO_2* was 9.8 ppb in 1996 to 30 % on weekends in 2010 when NO_2* was 4.6 ppb (Fig. 4a). In Bakersfield, the exceedance probability fell from greater than 90 % on weekdays at 10.7 ppb NO_2* to 75 % on weekdays at 5.7 ppb NO_2* and 50 % on weekends at 4.0 ppb NO_2* in 2010 (Fig. 4b). Downwind in Arvin, the probability held constant and near unity on weekdays despite an NO_2* decrease from 9.2 to 4.4 ppb over the window of the measurements; in the last two years it fell to 60–70 % on weekends at ~3.7 ppb NO_2* (Fig. 4c)[1].

A key observation from Fig. 4b and c is that the probability of an exceedance on weekends, when NO_x is 30–50 % lower within a given year, is essentially identical to

[1]Titration of O_3 by NO can affect the frequency of violations even when the odd oxygen, O_x ($O_x = O_3 + NO_2$), is constant. We checked our results using O_x instead of O_3 and found no significant differences.

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the weekday probability years later when the same NO_x decrease is achieved. This can only occur if VOCR remained constant over that same interval (Scenario A). From the shape of the curves in Fig. 4a, we infer that PO_3 in Shafter is presently NO_x-limited (to the left of peak production). In Bakersfield, the exceedance probability is NO_x-limited on weekends and appears to have recently transitioned to NO_x-limited chemistry on weekdays at NO_2* less than ~9 ppb. In Arvin, while the weekday probability of exceeding the state ozone standard has been at or near unity for the last sixteen years, we do observe a small decrease in the probability of high ozone on weekends at NO_2* less than ~4 ppb. We interpret the shape of these curves to indicate that we are at or near the peak of ozone production as a function of NO_x in Bakersfield and Arvin. Consequently, reductions in the frequency of ozone exceedances have been slow to accrue despite a more than two-fold decrease in NO_2*.

We estimate the effects of future NO_x reductions from weekend observations (Fig. 5). Regionally, over the past four years, exceedances are less likely on weekends than weekdays at high temperatures (20 % in Shafter, 25 % in Bakersfield, and 20 % in Arvin), indicating that at each point along the Southern SJV transect at these temperatures the frequency of exceedances has indeed crossed the peak in probability and is now in a regime of NO_x-limited chemistry on weekends. Although NO_x decreases substantially larger than those occurring on weekends are required to eliminate violations, those reductions that do occur will be immediately effective on weekdays and even more so on weekends.

At moderate temperatures, although NO_2* is unchanged, the observed exceedance probabilities are lower than at high temperatures. This is evidence that temperature is a proxy for VOCR (Figs. 4 and 5). A second piece of evidence is that the weekday and weekend curves vs. NO_2* do not overlap in this temperature regime (Fig. 4). Rather, we see a different functional dependence in the probability of violations by day of week. When weekday NO_2* matches the weekend value of several years earlier the probability of violations is noticeably lower. This implies that annual NO_x reductions are attended by year-to-year changes in VOCR (Scenario C) at moderate temperatures.

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As shown in Fig. 5, exceedances were much more frequent on weekends than weekdays for 1996–2005, placing regional ozone chemistry to the right of peak PO_3 (NO_x-suppressed). At all three locations in the last four years, the probability of a high ozone day is identical on weekdays and weekends indicating that at moderate temperatures Southern SJV ozone chemistry is near the peak, where the derivative with respect to NO_x at the current VOCR is small.

Another perspective on the impact of NO_x and VOCR reductions is shown in Fig. 6. Here, four-year median exceedance probabilities are shown as a function of NO_2* with lines tethering weekday (solid circles) and weekend (open diamonds) conjugates. For each measurement point shown, because day-of-week variability in VOCR and meteorology is small, the weekday-weekend pair describes the NO_x dependence along a single PO_3 curve. For visual aid, we have included a set of dashed lines as a qualitative description of the PO_3 curves corresponding to the data, which were created with the same equations (with tuned parameters) used to draw the curves in Fig. 2. If interannual decreases in NO_x have occurred without simultaneous changes in VOCR, as in Scenario A, consecutive yearly weekday-weekend pairs would trace a single curve. This is what we observe at high temperatures. If VOCR changes occurred in concert with NO_x reductions, as in Scenario C, the weekday-weekend pairs will each lie on separate curves. This is what we observe at moderate temperatures. We also see in Fig. 6 that the relationship between high- and moderate-temperature curves is consistent with overall lower VOCR at moderate-temperatures. We observe a shift of peak ozone production to lower rates and that the peak occurs at lower NO_x concentrations.

When temperatures are highest, Fig. 6 reinforces the conclusions drawn from Fig. 4 that VOCR in Bakersfield and Arvin has been almost constant over the last twelve years, as subsequent weekday-weekend pairs each trace the same curve. Decreases in the frequency of violations are recent and appear to be solely a result of sustained NO_x reductions. In contrast in Shafter, VOCR reductions also appear to have influenced the trends over time. At high temperatures, throughout the metropolitan region spanned by these three sites, conditions have transitioned to NO_x-limited chemistry

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on weekends as depicted by the steep positive slopes of the most recent conjugates (green).

In contrast, at moderate temperatures the exceedance probability has been largely NO_x-suppressed over the past twelve years. In Shafter and Bakersfield, ozone production has remained NO_x-suppressed since 1999 (negative slopes) with PO_3 nearing the peak (small slopes) in the last eight years as shown in Fig. 6a and b. In Arvin, early in the data record the sign of the slope fluctuated at constant NO_x; if the NO_x level corresponds to peak ozone production then the slope is more sensitive to changes in VOCR. In 2007–2010, the slope is near zero and ozone chemistry close to peak production. Although it appears from Fig. 4 that at moderate temperatures the percentage of violations has fallen because of decreasing NO_2*, Fig. 6 shows that VOCR reductions are the primary cause of the smaller observed exceedance probabilities at moderate temperatures. This situation is best described by Scenario C, where VOCR reductions decrease the frequency of violations and also shift peak PO_3 to lower NO_x.

Taken together, distinct behavior in the two temperature regimes provides evidence for two classes of VOCR sources in the Southern SJV. One class has decreased over the last twelve years and is a large VOCR source at moderate temperatures. Another class that dominates at high temperatures, has not decreased, and at high temperatures far exceeds the moderate-range source.

4.2 Central San Joaquin Valley

The past decade has seen the 8-h O_3 CAAQS exceedance probability in the Central SJV fall by almost 50 % both on weekdays and weekends when temperatures are highest (Fig. 7, note that year increases right to left in analogy to NO_2* concentration). In the last four years, at high temperatures, exceedances became slightly less likely on weekends at all locations in the Central SJV suggesting O_3 conditions are transitioning to NO_x-limited chemistry. Unlike in the Southern SJV, in the Central SJV there is evidence for a significant role played by VOCR reductions in decreasing the number of violations at high temperatures (Fig. 8). In Fresno, we infer VOCR decreases from

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1999–2002 to 2003–2006 have amounted to 20 % fewer O_3 violations at the same NO_2* (Fig. 8b, top panel). From 2003–2006 to 2007–2010, VOCR changes contributed a 20 % decrease in O_3 exceedances. Similar trends are seen upwind in Madera and downwind in Parlier.

At moderate temperatures, the frequency of violations has decreased dramatically. In 2007–2010, the probability was less than 25 % at all three locations, with the largest changes in Parlier, where violations occurred at a frequency of more than 75 % on weekends a decade ago. We show this decrease in the exceedance probability is due to VOCR decreases, as exceedances are more likely on weekends (Fig. 7, bottom panel) and as probabilities consistently exhibit negative day-of-week slopes vs. NO_2* (Fig. 8, bottom panel). Figure 8 suggests that the magnitude of the decrease in the likelihood of violations from 1999–2002 to 2003–2006 is approximately twice that at high temperatures. This is similar to the results for the Southern SJV (Fig. 6) and it again indicates the presence of two distinct classes of VOCR emission, where at moderate temperatures, the controlled class is a larger fraction. These changes are explained if we assume that at high temperatures VOCR is a mixture of a controlled class and an uncontrolled class with both terms being important.

4.3 Northern San Joaquin Valley

From 2007–2010 at Stockton, the upwind location of the Northern SJV region, there is a less than 10 % probability that ozone concentrations will exceed the 8-h CAAQS at high temperatures on either weekdays or weekends (Fig. 9a). Downwind, probabilities are higher. At all three sites, there have been steep weekday decreases in the last sixteen years: in Stockton from 20 % to 5 %, in Turlock from 75 % to 35 %, and in Merced from 95 % to 55 % (Fig. 9b and c). In Stockton and Turlock, more frequent weekend exceedances (Fig. 9a and b) and negative day-of-week slopes vs. NO_2* (Fig. 10a and b) show these locations are in a NO_x-suppressed chemical regime. In contrast, in Merced at high temperatures, chemistry became NO_x-limited in the last four years. Overall, in the Northern SJV, the observed decreases in the frequency of high O_3 apparently are

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due to VOCR reductions. However, Fig. 10c (top panel) indicates that the frequency of high O_3 in Merced will fall with continued NO_x reductions and Fig. 10b (top panel) shows that Turlock is near the threshold where NO_x reductions become effective.

At moderate temperatures, exceedances from 2007–2010 were highly unlikely, occurring on fewer than 10 % of days at any of the three locations in the Northern SJV (Figs. 9 and 10). Violations were more frequent earlier in the record (e.g. Fig. 10c, bottom panel) and we infer the observed decreases are due to reductions in VOCR.

4.4 Evidence for local ozone production

There are two pieces of evidence that support local ozone production to be a large contributor to the frequency of high ozone days in the SJV. First, the observed exceedance probability is lowest for each of the upwind sites, Shafter (Southern SJV), Madera (Central SJV), and Stockton (Northern SJV), increases along the plume transect (at Bakersfield, Fresno, and Turlock), and is highest at the corresponding downwind locations, Arvin, Parlier, and Merced, respectively. In the Southern SJV in 2007–2010 at high temperatures, we see an increase in the probability of a violation by 45 % on weekdays and by 40 % on weekends between Shafter and Arvin. In the Central SJV, over the same time period and in the same temperature regime, the percentage of violations is shown to increase by 20 % on weekends and 35 % on weekdays from Madera to downwind Parlier. In the Northern SJV in 2007–2010 at high temperatures, the probability increases by 35 % on weekdays and 45 % on weekends between Stockton and downwind Merced. The second piece of evidence is that there is a ∼10 % drop in the exceedance percentage between Parlier (downwind Central) and Shafter (upwind Southern) and a ∼20–35 % decrease between Merced (downwind Northern) and Madera (upwind Central). If local production were not important, we would expect to observe a single Valley-wide ozone plume and, therefore, to see the exceedance probability to smoothly rise (or fall) the length of the SJV. This is not the case however. Rather, the exceedance probably increases across each sub-region but then decreases again at the next site to the south (at the upwind sites Shafter and Madera). Exceedances

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are presently unlikely at moderate temperatures in the Central and Northern SJV but a comparison of past four-year median exceedance probabilities also illustrates this same effect.

5 Discussion

From 1995–2010, reductions in NO_x emissions in California have been mostly due to more stringent standards on stationary sources and light-duty vehicles. In contrast, emissions from heavy-duty diesel engines, the largest source of NO_x emissions in the SJV, have increased over the past fifteen years (Cox et al., 2009). Nationally, new rules require heavy-duty diesel engines to meet more stringent NO_x emissions standards (Environmental Protection Agency, 2000); however, these engines have long service lifetimes and slow fleet turnover rates. In California, in an effort to expedite benefits from new diesel engine regulations, the California Air Resources Board (CARB) is requiring all vehicle owners to retrofit or replace older diesel engines by 2023 and half of the in-use heavy duty-engines in large fleets must meet new NO_x standards by 2014 (California Air Resources Board, 2007). Millstein and Harley (2010) show that in Los Angeles, as a result of this accelerated engine retrofit/replacement program, reductions in summertime diesel NO_x emissions could be greater than 50 % over the next five years (2010–2015), with slower reductions (−20 % in tons day^{-1}) predicted in the following ten years 2015–2025. Additionally, the SJV Air Pollution Control District is also partnering with the Environmental Protection Agency (EPA) under the National Clean Diesel Campaign to replace diesel locomotives and diesel engines on agricultural equipment (Environmental Protection Agency, 2012a).

NO_x emissions reductions can still be expected from cars and light-duty trucks in the next twenty-five years. In 2012, CARB announced the Advanced Clean Cars Program, which aims to further reduce these NO_x emissions by 75 % from 2014 levels through new emissions standards (in the 2015 model year) and by requiring one in

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seven news cars sold in California be zero-emission or plug-in hybrid vehicles by 2025 (Environmental Protection Agency, 2012b).

In summary, policymakers at the local (San Joaquin Valley Unified Air Pollution Control District), state (CARB), and federal level (EPA Region 9) have expressed a commitment to reducing NO_x emissions in the SJV and we therefore expect NO_x concentrations to continue to decrease Valley-wide.

The outlook for VOCR in the SJV is less clear. We show that at moderate temperatures, VOCR throughout the SJV has decreased over the last twelve years and that these decreases have resulted in fewer high O_3 days. This implies that the dominant sources of organic reactivity in this temperature regime are currently being controlled. VOC emissions from mobile sources have been thought to be largest source of O_3 forming organic precursors in the Valley (Hu et al., 2012). Regulatory efforts during our study window have focused on VOC emissions from light-duty vehicles and reduced these emissions through a combination of stricter standards and gasoline reformulation (Kirchstetter et al., 1999; Harley et al., 2006). At high temperatures in the Central and Northern SJV, we also show that reductions in VOCR have significantly decreased the frequency of violations. However, in the Central SJV, these decreases in VOCR are smaller than those observed at moderate temperatures. This same temperature dependence is seen to a more dramatic extent in the Southern SJV, where over the last twelve years at high temperatures the VOCR in Bakersfield and Arvin has not changed. Therefore in this temperature regime, we infer the existence of a VOCR source that both overwhelms the moderate-temperature source and that has gone unregulated over the last twelve years.

Recent model calculations have indicated non-mobile VOCR sources are important to PO_3 in the SJV but to our knowledge this manuscript provides the first direct observational evidence. For example, Steiner et al. (2009) computed the total reactivity in the SJV, finding that the biogenic VOC emissions important in most other locations, such as isoprene and monterpenes (α-pinene), were only a small fraction of the total VOCR in this region. The authors suggested that the regional reactivity was dominated

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by oxygenates, although they noted that the sources of these species were very poorly quantified.

VOC emissions from animal feeds have been proposed to be a large component of SJV VOCR (Alanis et al., 2008; Howard et al., 2010a, b; Malkina et al., 2011). This source is not currently included in official inventories. In a first step toward understanding their impacts, inclusion of animal feed emissions in a regional air quality model (focusing on a single O_3 episode 24 July–2 August 2000) found that they were less important than mobile source VOC emissions to PO_3 (Hu et al., 2012), that PO_3 was still under-predicted SJV, and that there is still likely missing VOCR. Clearly, more research is needed to identify the source(s) of VOCR in the SJV, but whatever the non-mobile source, our analysis suggests it has been unchanged over the last decade.

With this background on the expected changes in San Joaquin emissions, we present policy-relevant conclusions for the Southern, Central, and Northern SJV below, addressing the impacts of additional NO_x and VOCR reductions on the frequencies of future CAAQS 8-h O_3 exceedances in the region.

5.1 Southern San Joaquin Valley

When temperatures are hottest, ozone production in Bakersfield and Arvin has been at peak for much of the last sixteen years and at constant VOCR. This explains why, despite a decade of NO_x emission reductions, violations remain highly probable. At both sites ozone production has recently transitioned to NO_x-limited chemistry and, as a result, continued NO_x controls are poised to improve O_3 air quality. Sizable NO_x reductions are required before gains are seen in Arvin, as the exceedance probability at this site is still at peak on weekdays and very near unity. Current decreases in the high-temperature exceedance percentage in Arvin from 90 % on weekdays to 70 % on weekends suggest there will be 20 % fewer weekday violations in response to the next 50 % NO_x reduction. Fifty percent NO_x reductions will reduce the frequency of high ozone on weekdays in Bakersfield to 50 % and in Shafter to 30 %. At all three locations at moderate temperatures, ozone production is still at peak PO_3 or slightly

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NO_x-suppressed (with a small slope) and so NO_x reductions in this temperature regime will not immediately improve local O_3 air quality but will also not exacerbate it.

At the highest temperatures, observations suggest VOCR has not appreciably changed in the past decade. New strategies are therefore needed both to identify what organic molecules drive VOCR at the hottest temperatures and to reduce these precursor species. That said, because Southern SJV ozone production has transitioned to NO_x-limited chemistry at high temperatures, additional VOCR reductions will provide diminished returns. At moderate temperatures, there is still the potential for VOCR reductions to decrease the frequency of violations.

5.2 Central San Joaquin Valley

At high temperatures, the exceedance probability has in the last four years transitioned to NO_x-limited chemistry. It is difficult to be quantitative, but a comparison of the steepness of the 2007–2010 high-temperature slopes in Figs. 8 and 6 shows ozone chemistry in this region nearer to peak production than in the Southern SJV. As such, NO_x controls will improve O_3 air quality but gains will lag those anticipated in the south. At moderate temperatures, NO_x reductions will be slow to decrease the frequency of exceedances because chemistry is still NO_x-suppressed.

VOCR reductions have been a powerful force in decreasing the exceedance probability under both high- and moderate-temperature conditions. Continued controls on mobile source emissions will further reduce the frequency of violations in both regimes but the impact of further controls is checked by the onset of NO_x-limited ozone chemistry and by the fraction of VOCR that is due to uncontrolled sources. This fraction is important at high temperatures.

5.3 Northern San Joaquin Valley

In Stockton, NO_2* abundances are high, the frequency of violations is NO_x-suppressed, and high O_3 days are uncommon. As a result, NO_x controls will not improve local O_3

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air quality in this location. In Turlock under both high- and moderate-temperature conditions, the exceedance probability remains NO_x-suppressed. The payoff from continued NO_x reductions will be delayed until a transition to NO_x-limited chemistry takes place. The difference in the percentage of violations on weekdays and weekends is small and so chemistry is proximate to peak PO_3. This gives confidence that NO_x controls will not degrade Turlock O_3 air quality. In Merced, at high and moderate temperatures, PO_3 is NO_x-limited as of 2007–2010. We anticipate continued NO_x reductions will decrease the exceedance probability at this location and note that NO_x reductions upwind in Stockton and Turlock are important to decreasing NO_x abundances in Merced.

At high temperatures, continued reduction of VOC emissions is expected to decrease the frequency of high ozone days in Turlock. We predict that the impact of VOC emission reductions will be smaller than previously seen, as the decrease in O_3 exceedance probability in the last four years was only half that seen earlier in the decade. In Merced, in both temperature regimes, VOCR reductions have made profound improvements to O_3 air quality. At moderate temperatures, exceedances are below 15 %. At the high temperatures, VOCR reductions have resulted in exceedances being 50 % less probable than a decade ago. Now that ozone production is NO_x-limited, further VOCR reductions will be unable to drive substantial decreases in the number of violations.

6 Conclusions

We present a statistical approach to describe ozone's dependence on NO_x and organic reactivity (VOCR) in San Joaquin Valley California using sixteen years of routine measurements of O_3, NO_2*, and temperature.

We show that local ozone production plays a large role in the frequency of high ozone days, as the exceedance probability is seen to increase from upwind to downwind within each of our study regions and because the probability of a violation between regions is, in each case, higher at the downwind site to the north than at the receptor

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city to the south. This underscores the importance of controlling precursor emissions from local sources in the SJV.

We give location-specific policy-relevant conclusions for the Southern SJV, Central SJV, and Northern SJV in Sects. 5.1, 5.2, and 5.3, respectively. Broadly speaking, we show that in the Central and Northern SJV, decreases in VOCR have dramatically reduced the frequency of violations. We report a temperature dependence in the effects of VOCR reductions in the Central SJV, finding they are larger at moderate-range temperatures than at high. This is likewise true in the Southern SJV, where reductions in the VOCR have decreased the frequency of violations at moderate temperatures but have made no impact when temperatures are hottest. That the VOCR has remained unchanged over the past twelve years at high temperatures reveals a need for finer spatial resolution accounting in VOC emissions inventories. Secondly, this observation evidences two distinct types of VOCR sources and frames an outstanding question for future research. *What organic molecules drive the observed temperature dependence of VOCR Valley-wide?*

Finally, we find that NO_x reductions are poised to improve ozone air quality where violations are most frequent – the Southern and Central SJV. We see that these regions have or soon will transition to NO_x-limited conditions when temperatures are highest, which is when the likelihood of high ozone is greatest. We show that exceedances in the Southern SJV have remained highly probable despite NO_x emissions control efforts because the ozone chemistry in Bakersfield and Arvin has been near peak PO_3 and at constant VOCR for more than a decade.

The data described here have been collected across North America and around the world for over a decade. We expect that our statistical approach should be applicable to other locations and we look forward to analyses providing perspective on the effectiveness of NO_x and VOCR controls in other places.

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Appendix A

Measurements

CARB maintains an extensive network of ground-based monitors statewide. In this paper we use the 8-h maximum O_3 and hourly NO_2 data from thirteen CARB sites in the San Joaquin Valley Air Basin. These sites are Arvin, Arvin-Bear Mountain Blvd (35.209, −118.779) (this site closed in November 2010); California Avenue, Bakersfield-5558 California Avenue (35.357, −119.063); Clovis, Clovis-N Villa Avenue (36.819, −119.716); Edison, Edison (35.346, −118.852); Drummond, Fresno-Drummond Street (36.705, −119.741); First Street, Fresno-1st Street (36.782, −119.773); Madera, Madera-Pump Yard (36.867, −120.010); Merced, Merced-S Coffee Avenue (37.282, −120.434); Parlier, Parlier (36.597, −119.504); Shafter, Shafter-Walker Street (35.503, −119.273); Skypark, Fresno-Sierra Skypark #2 (36.842, −119.883); Stockton, Stockton-Hazelton Street (37.952, −121.269); and Turlock, Turlock-S Minaret Street (37.488, −120.836). "Bakersfield" is the median of the California Avenue and Edison stations and "Fresno" is the median of the Skypark, First Street, Drummond, and Clovis stations. Data at Madera-Pump Yard are available starting in 1998 and data from Clovis in 2008 were not reported. Data at Merced-S Coffee Avenue are not available in 2000 (NO_2*) and 2006 (O_3). All data and detailed information about the location of each monitor are available for download on the CARB website: http://www.arb.ca.gov/adam/index.html.

We removed any concentration data exactly equal to 0.000 ppm believing this to be a physically unreasonable daytime concentration for either the 8-h maximum O_3 or the hourly NO_2*. The daytime NO_2* concentration is the daily mean value between 10:00 a.m. and 02:00 p.m. local time. For Fresno and Bakersfield we use medians of the individual sites and in the absence of data at a single site for a given day that day is omitted. Yearly NO_2* data are averaged for weekdays (Tuesdays–Fridays) and weekends (Saturdays–Sundays).

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CARB NO_2* is measured by chemiluminescence coupled with a heated molybdenum catalyst. NO_2 measurements with this technique are attended by a known positive interference from higher oxides of nitrogen, for example organic nitrates and nitric acid, which also thermally decompose (Williams et al., 1998; Dunlea et al., 2007). Ammonia (NH_3) has also been seen to positively interfere (0–10 %) with NO_2 chemiluminescence (Williams et al., 1998; Dunlea et al., 2007). NH_3 concentrations in the SJV are high (Clarisse et al., 2010) but we take confidence in the usefulness of the CARB NO_2* data, as the NO_2* abundances are decreasing across the Valley at rates similar to those observed from space by OMI (Russell et al., 2010). NO_2* data are reported by CARB to be accurate to at least 15 %.

Temperature data are the 1-h maximum daily temperatures and data are used from three sites, Merced-S Coffee Avenue (37.282, −120.434), Fresno Air Terminal (36.776, −119.718), and Bakersfield Airport (35.325, −118.998); one site in each of our three study areas. The average maximum temperature is not statistically different from 1995 to 2010. We do not separate NO_2* by temperature finding no significant temperature dependence in its concentration by day of week.

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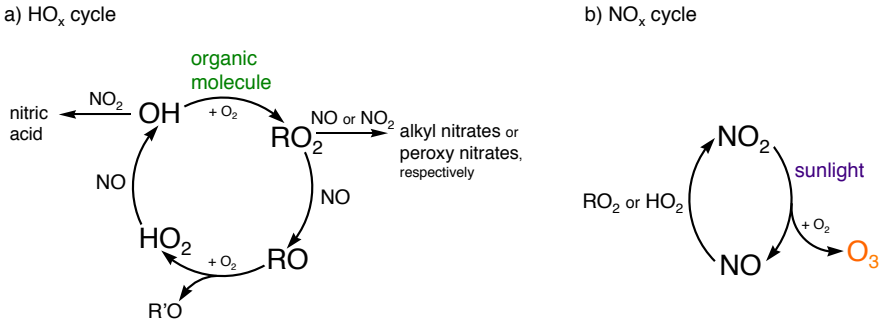

Fig. 1. Schematic of photochemical production of two new O_3 molecules from the oxidation of one generic organic molecule at the overlap of the HO_x **(a)** and NO_x **(b)** catalytic cycles. Only the NO_x termination channels are shown. HO_x chain terminations are reactions among peroxy radicals and OH.

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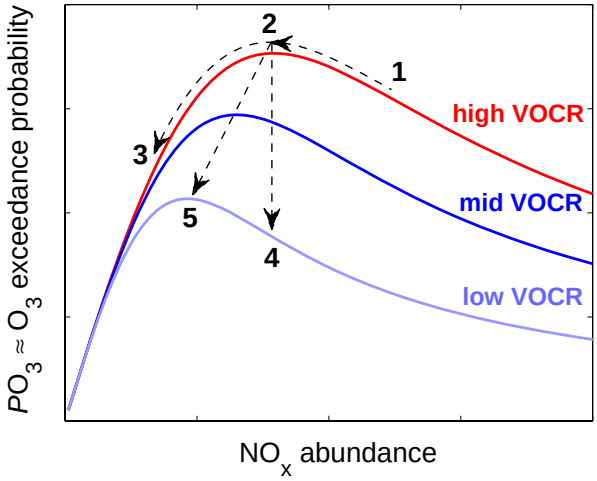

Fig. 2. The instantaneous ozone production rate (PO_3) and, by analogy, the ozone exceedance probability as a function of NO_x is shown for three categories of organic reactivity (VOCR): high (red), mid (blue), and low (violet). The mid- and high-VOCR curves correspond to scaling the base VOCR by 2 and 3, respectively. If temperature serves as an adequate proxy for VOCR then the three curves will also describe high- (red), moderate- (blue), and low- (violet) temperature regimes.

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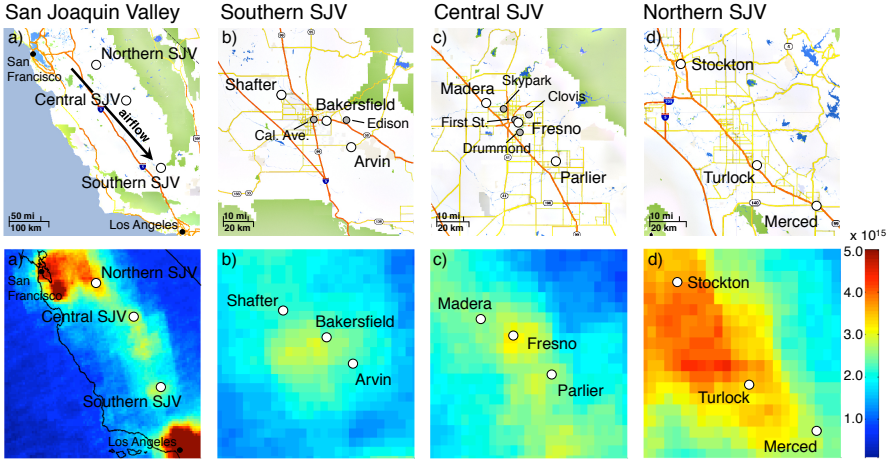

Fig. 3. Map of the California San Joaquin Valley (SJV) (**a**, top) and details of each region for this study: Southern SJV (**b**, top), Central SJV (**c**, top), and Northern SJV (**d**, top). CARB 8-h maximum average O_3 and NO_2* data are used from thirteen CARB sites: Shafter (upwind), Bakersfield, and Arvin (downwind), where Bakersfield is the median of the California Avenue and Edison stations; Madera (upwind), Fresno, and Parlier (downwind), where Fresno is the median of the Skypark, First Street, Drummond, and Clovis stations; Stockton (upwind), Turlock, and Merced (downwind). OMI NO_2 columns (molecules cm^{-2}) are shown over the same regions. These images are June–August weekday averages from 2007–2010 for the California San Joaquin Valley (**a**, bottom), Southern SJV (**b**, bottom), Central SJV (**c**, bottom), and Northern SJV (**d**, bottom).

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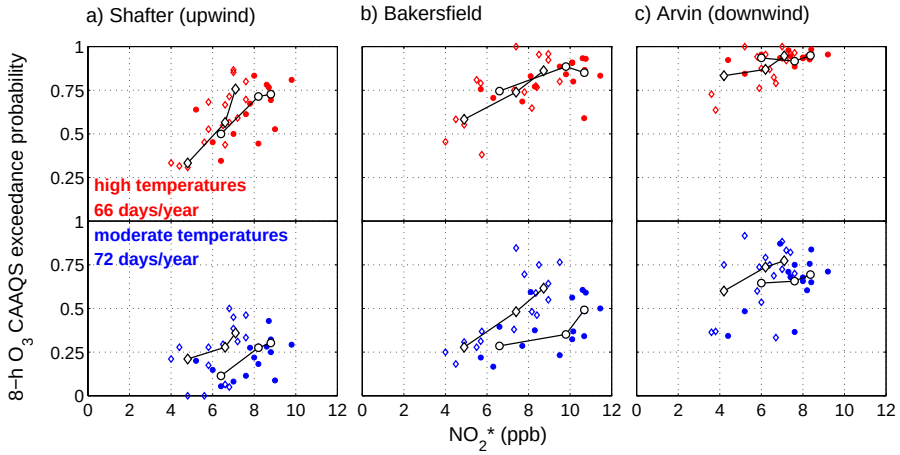

Fig. 4. Southern SJV, Shafter **(a)**, Bakersfield **(b)**, and Arvin **(c)**, exceedance probabilities vs. NO_2* at high (34–45 °C) and moderate (28–33 °C) temperatures in red and blue respectively. Data from weekdays (closed circles) and weekends (open diamonds) are shown as separate symbols. NO_2* are averages (10:00 a.m.–02:00 p.m. local time) of hourly data at each site. Uncertainties are typically less than ±0.09 (1 σ) for weekdays and less than ±0.12 (1 σ) for weekends. NO_2* data are reported by CARB to be accurate to at least 15 %. Black lines connect the median percentage of violations at every 5th NO_2* data point. Over the past sixteen years, the average annual number of days per year (rounded up) in the Southern SJV with a maximum temperature in the high-temperature range is 66 and the average number in the moderate-temperature range is 72.

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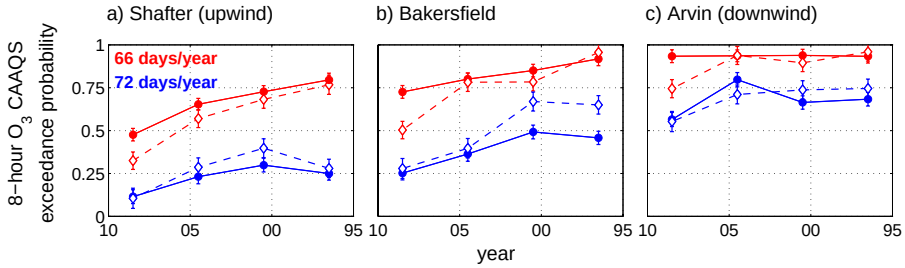

Fig. 5. Four-year median exceedance probabilities of the 8-h O_3 CAAQS vs. year (increasing right to left) in the Southern SJV: Shafter **(a)**, Bakersfield **(b)**, and Arvin **(c)**. Data are shown separated into the temperature regimes: high (34–45 ˚C) and moderate (28–33 ˚C) in red and blue, respectively and divided into weekdays (closed circles) and weekends (open diamonds). Error bars are uncertainties in the four-year median exceedance probabilities, are calculated as counting errors, and are typically less than ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends. The average annual number of days per year (rounded up) over the past sixteen years for both temperature regimes is given.

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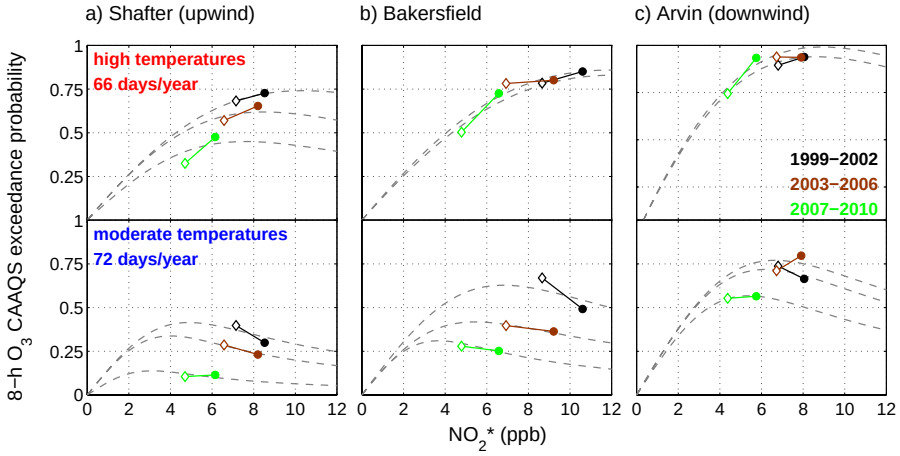

Fig. 6. Southern SJV four-year median 8-h O_3 CAAQS exceedance probabilities vs. NO_2* tethering weekday (circles) and weekend (diamonds) conjugates for 1999–2002 (black), 2003–2006 (brown), and 2007–2010 (green). Data are shown separated by high- (top) and moderate-temperature (bottom) regimes for Shafter **(a)**, Bakersfield **(b)**, and Arvin **(c)**. Uncertainties in the probability of violations (by counting statistics) are typically less than ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends and are much smaller than the observed year-to-year variability. Curves (dashed grey lines) are included for visual aid and are not meant to be quantitative; the lines were generated with an analytical model where only VOCR was tuned and PO_3 scaled arbitrarily to fit.

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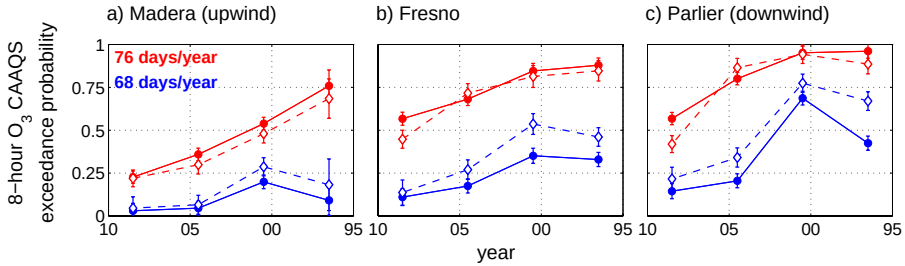

Fig. 7. Central SJV four-year median exceedance probabilities of the 8-h O_3 CAAQS vs. year (increasing right to left) are shown separated into high- (34–45 °C) and moderate- (28–33 °C) temperature regimes in red and blue, respectively, where on average over the past sixteen years there were 76 high-temperature days and 68 moderate-temperature days (the number of days is rounded up), and into weekdays (circles) and weekends (diamonds) for Madera **(a)**, Fresno **(b)**, and Parlier **(c)**.

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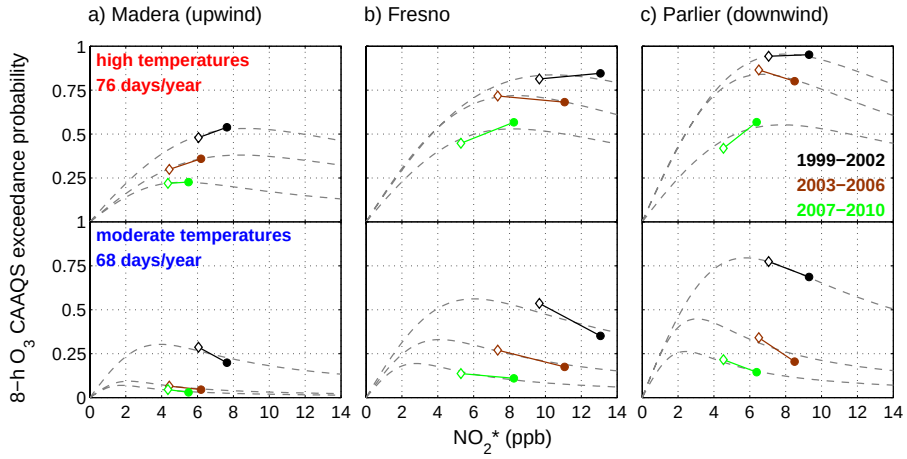

Fig. 8. Tethered four-year median weekday (closed circles) and weekend (open diamonds) 8-h O_3 CAAQS exceedance probabilities vs. NO_2* in the Central SJV for 1999–2002 (black), 2003–2006 (brown), and 2007–2010 (green). Data are separated into high- (top) and moderate-temperature (bottom) regimes for Madera **(a)**, Fresno **(b)**, and Parlier **(c)**. Uncertainties in the probability of violations are computed with counting statistics, are typically less than ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends, and are much smaller than the observed year-to-year variability. Curves (dashed grey lines) are included for visual aid and are not meant to be quantitative. These curves were produced with an analytical model where only VOCR was tuned and PO_3 scaled arbitrarily to fit.

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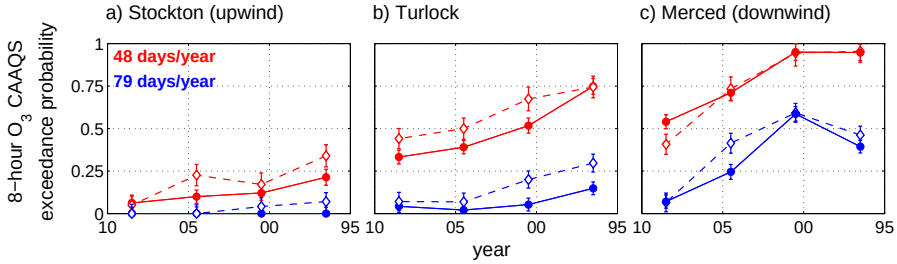

Fig. 9. Northern SJV four-year median 8-h O_3 CAAQS exceedance probabilities vs. year (increasing right to left) are plotted separated into high- (34–45˚C) and moderate- (28–33˚C) temperature regimes in red and blue respectively and into weekdays (circles) and weekends (diamonds) for Stockton **(a)**, Turlock **(b)**, and Merced **(c)**. The average number of days (rounded up) with a maximum temperature in each temperature range over the past sixteen years is given. Error bars are the uncertainties calculated as counting errors and are typically ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends for four-year averages.

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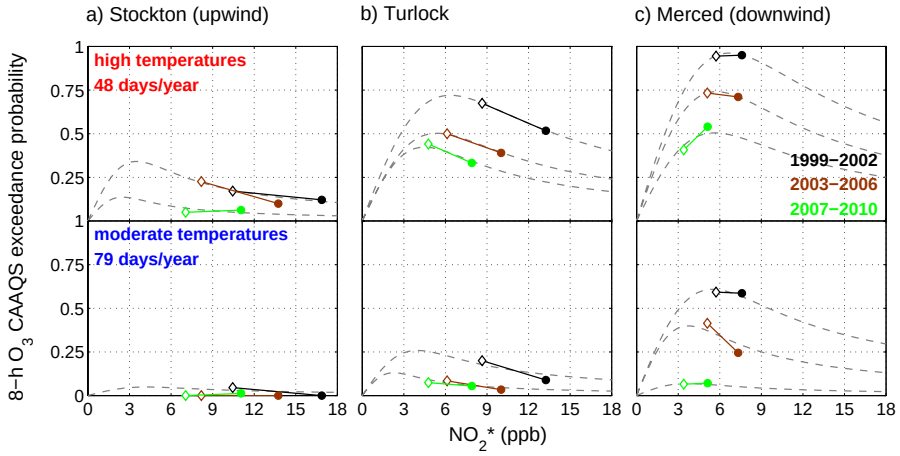

Fig. 10. Northern SJV four-year medians of 8-h O_3 exceedance probabilities vs. NO_2* tethering weekdays (circles) and weekends (diamonds) for 1999–2002 (black), 2003–2006 (brown), and 2007–2010 (green). Data are separated into high- (top) and moderate-temperature (bottom) regimes for Stockton **(a)**, Turlock **(b)**, and Merced **(c)**. Uncertainties in the probability of violations are smaller than the observed year-to-year variability at ±0.04 (1 σ) for weekdays and ±0.06 (1 σ) for weekends. Curves (dashed grey lines) are for visual aid only and were produced with an analytical model where only VOCR was tuned and PO_3 scaled arbitrarily to fit.

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Ozone, NO_x, and VOC reactivity in the San Joaquin Valley

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