

We thank the referees for their constructive and helpful comments. We believe changes made in response have strengthened this manuscript.

Referee 1

This paper describes a unique statistical approach that appears to provide explanations for ozone sensitivity to NO_x and VOC precursors. Aside from some minor clarifications I have only two major comments.

The authors make definitive statements on the causes for the responses in ozone probability responses to NO_x and VOCs. Given the non-linearity of the chemistry and the many coupled processes in the atmosphere could there be another unknown and permissible explanation that could also explain the model results? It is unclear as written whether the authors considered or pursued other permissible explanations and had data that excluded these thus leading to the conclusion presented in the manuscript.

We have not thought of any other explanations that simultaneously explain all of the observations. If the reviewer has something specific in mind that we should have mentioned we would be interested to consider it.

The authors state that they would like to see this approach applied to other locations. Are the unique conditions found in the SJV making this approach possible? In other location must there be the sustained one way valley flow that sets up the highly statistical likelihood of having an upwind and downwind region? This possible limitation is not discussed in the manuscript.

We think the only condition required is an isolated plume. We added text explicitly stating this opinion in the Conclusions. We suggest that analyses along the lines of this manuscript in city centers alone would likely be interesting making consistent winds less necessary. We also added text suggesting that one could define upwind/downwind based on the observed winds in locations where the winds are not as persistently from the same direction as they are in the SJV.

“Finally, O₃, NO₂*, and temperature measurements have been collected across North America and around the world for more than a decade. We expect that the statistical approach described herein should be applicable to other isolated urban plumes. Even if wind directions are not as persistent as in the SJV, we imagine an analysis at the city center alone or one sorted by wind direction in addition to temperature will be interesting. We look forward to such analyses providing broader observational perspective on the effectiveness of NO_x and VOCR controls in other locations.”

Minor Comments

Page 9774 line 1: The authors note that “For example, we know of no case where a quantitative prediction of the 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.” The authors may want to consider the following citation. A.B. Gilliland et al. “Dynamic evaluation of regional air quality models: Assessing changes in O₃ stemming from changes in emissions and meteorology” *Atmospheric Environment* 42 (2008) 5110– 5123.

We thank the referee for pointing out this reference. It does pursue a large-scale statistical approach to interpreting the response of ozone to NO_x decreases and we now mention it in the Introduction.

“For example, Gilliland et al. (2008) examined models and observations before and after implementation of controls on the electric generating utilities in the eastern U.S. and used the ensemble to suggest that air quality models underestimated the benefits of the NO_x reductions.”

Page 9775 line 15: Missing the Farmer et al 2011 from reference list.

We have added the reference.

Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., Vargas, O., and Cohen, R. C.: Impact of organic nitrates on urban ozone production, *Atmos. Chem. Phys.*, 11, 4085–4094, doi:10.5194/acp-11-4085-2011, 2011.

Page 9776 line 23: It would help the reader to have a condensed version of these bullets as a table with a column that includes the paths linked with Figure 2.

We have changed the starting sentence of each bullet point so that for each there is a title and numbered scenario. We hope this is satisfactory; we would like to avoid adding a table.

- *Scenario A decreases NO_x at constant VOCR (1 → 2 → 3).* NO_x reductions initially increase PO₃ at high NO_x (1 → 2) followed by a decrease in PO₃ 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).* VOC reductions have the effect of proportionally reducing PO₃ at high NO_x and of negligibly changing PO₃ at low NO_x. 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)*. This transition is typical of what has occurred over the last decade in cities where vehicular emissions dominate both NO_x and VOCR.

Page 9777 line 8: Could the author provide more text making it clearer the relationship between probability and ozone production $P(O_3)$ and why its treated as equivalent such as in Figure 6.

We have added a new section describing our thinking on this point:

2.2 Ozone production, O_3 concentration, and the frequency of high O_3 days

The atmospheric O_3 concentration is a function of the time-integrated effects of PO_3 , chemical and depositional loss, and mixing. All of these terms vary and often co-vary. Over the time interval of our study, we expect no significant variability in the chemical or depositional loss terms or in the frequency of stagnation in the SJV. Trends in the mean, median, and width of the distribution of ozone concentrations—observed to be Gaussian in our dataset—are thus dominated by the statistics of changes in PO_3 . Moreover, O_3 exceedances varying in the nonlinear manner shown in Fig. 2, as we will show they do, bolster the notion that production is the principal term changing over time. To make the association between the O_3 concentration and the frequency of high ozone days, we take advantage of the statistical properties of normal distributions. Specifically that the cumulative probability of the portion of a normal distribution above a particular threshold varies linearly with shifts in the mean (assuming the width is constant) so long as the threshold is within one standard deviation of the mean, or between approximately 15% and 85%. On this basis, we hypothesize that the curves representing PO_3 in Fig. 2 also describe the statistics of high ozone days and use this conceptual framework, which in our analysis we support empirically, to interpret observed changes in the probability of high ozone defined as the fraction of days exceeding the 8-hour O_3 California Ambient Air Quality Standard (CAAQS) of 70 ppb (>70.4 ppb).

Page 9780 line 6: What determined these ranges is it based on any meteorological record?

We have added this text in response:

“...We group data into two temperature regimes, high (34–45°C) and moderate (28–33°C); we find these ranges are sufficiently distinct to identify differences in production of ozone (see below) while still maintaining sufficient statistics to characterize the ensemble of ozone at each site. We note that in the SJV, boundary layer dynamics are strongly influenced by mountain valley flow and as a result we do not expect meteorological factors (e.g. wind speeds) that are particularly different between high and moderate temperatures.”

Page 9781 line 3: Was there any additional analysis (i.e. Sillman Ratio) done by authors that can help confirm the inferences made here concerning the NO_x sensitivity.

Data do not exist in the SJV (or at any location) with which to analyze decadal and regional trends in the H₂O₂/HNO₃ ratio. To our understanding, the various other indicator ratios—for example O₃/HNO₃, O₃/NO_z, O₃/NO_y, and O₃/PAN—are less consistent predictors (Sillman and West, 2009). If approximations were made, perhaps NO+NO₂*~NO_y, the O₃/NO_y ratio could be investigated with the routine monitoring data on inter-annual timescales and regional spatial scales. That said indicator ratios are only a proxies for the local NO_x-VOCR sensitivity. In contrast, weekend/weekday analysis is a direct test of the local chemical conditions. With weekend/weekday analysis there is no need to interpret the meaning of an indicator ratio and the NO_x dependence can be tested without a surrogate metric.

Sillman, S. and West, J. J.: Reactive nitrogen in Mexico City and its relation to ozone-precursor sensitivity: results from photochemical models, *Atmos. Chem. Phys.*, 9, 3477–3489, 2009.

Page 9782 line 1: Text refers to P(O₃) but figure shows exceedance probability.

We have clarified the relationship between the exceedance probability and PO₃ and we think page 9782 line 1 is correct as is. See our response to the comment regarding page 9777 line 8.

Figure 1 Difference between gray and white circles?

We have added a description of the difference between the white and grey circles in the Fig. 3 caption.

Figure 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-hour maximum average O₃ and NO₂* data are used from thirteen CARB sites: Shafter (upwind), Bakersfield, and Arvin (downwind) (**white circles**), where Bakersfield is the median of the California Avenue and Edison stations (**grey circles**); Madera (upwind), Fresno, and Parlier (downwind) (**white circles**), where Fresno is the median of the Skypark, First Street,

Drummond, and Clovis stations (**grey circles**); Stockton (upwind), Turlock, and Merced (downwind) (**white circles**). OMI NO₂ 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**).

Figure 5: It is difficult to discern what four-year window each dot represents.

We now state the time windows explicitly in the caption.

“...The exceedance probabilities are shown for 1995–1998, 1999–2002, 2003–2006, and 2007–2010.”

Figure 6 P(O₃) in caption but exceedance probability shown on graph.

In Fig. 6, we write that we plot the “Southern SJV four-year median 8-hour O₃ CAAQS exceedance probabilities vs. NO₂*” and that the dashed grey curves are PO₃ generated from an analytical model.

Appendix A: Rationale for 10am – 2pm averaging time for NO₂?

We want to represent the average daytime NO₂* concentration and found the average value to be similar regardless of the exact time window selected, i.e. versus 9am–2pm or 11am–3pm. We now say this in the Appendix (text below). Our work is especially insensitive to this distinction as we are concerned with the relative NO₂* concentration rather than the absolute concentration. This is emphasized by our naming the NO₂ data “NO₂*”, as the chemiluminescence technique is known to have significant positive interferences from HNO₃ and organic nitrates. We believe the NO₂* dataset is useful in describing trends/changes in NO₂ but is a largely an uncalibrated metric for the NO₂ concentration.

“The daytime NO₂* concentration is the daily mean value between 10 am and 2 pm local time. The average NO₂* is not very sensitive to a change in this window and our work uses relative rather than absolute NO₂* concentration. 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 NO₂* data are averaged for weekdays (Tuesdays–Fridays) and weekends (Saturdays–Sundays).”

Referee 2

On the observed response of ozone to NO_x and VOC reactivity reductions in San Joaquin Valley California 1995-present. Pusede and Cohen Summary: This paper uses measured concentrations of NO₂ and ozone over a +15 year period to infer the NO_x vs. VOC sensitivity for ozone formation in the San Joaquin Valley. The variation of NO₂ and ozone on weekdays vs. weekends and the variation of NO₂ and ozone over the multiyear time period are both used to infer sensitivity relationships. The difference in ozone concentrations upwind, within, and downwind of urban locations is used to infer the importance of local production. The major conclusions of this paper are that (1) a large fraction of the ozone production is caused by local emissions, (2) changes in VOC reactivity have influenced ozone formation in the northern and central portions of the San Joaquin Valley but not in the southern SJV, (3) there is an unknown source of VOC reactivity in the southern San Joaquin Valley that is dominant at higher temperatures and that has not decreased over the 16 year study period, (4) the atmosphere in the northern and central San Joaquin Valley is entering a regime where NO_x reductions decrease ozone concentrations.

Comments

1. The paper addresses an important question using a novel approach to analyze routine monitoring data. The results have important policy implications. The paper should be published after attention to the remaining comments.

2. Page 9775 line 23: VOC reactivity is a complex parameter that is influenced by the VOC concentration, the mixture of detailed compounds that contribute to overall VOC concentrations, and the reaction rates of those compounds with oxidants. This final parameter is extremely temperature dependent. The different curves illustrated in Fig 2 could be generated by increasing any one of the three parameters represented by VO_{CR}. Additional text should be added to emphasize these points.

We feel that we have adequately discussed temperature's impact on the VOC abundance (Sect. 2.4) and on how changing the temperature will change the composition of the VOC mix. We use this second point to infer that VOC reactivity in the Southern SJV is dominated by an uncontrolled and strongly temperature dependent VOC source when temperatures are hottest compared to when temperatures are moderate and controlled VOCs are more important. We agree with the reviewer that we had not addressed the impact of temperature on reaction rates and we have added the following text:

“Temperature also influences the rates of reaction of organic molecules with OH and of radical cycling, but this effect is much smaller than that due to the increase in VOC abundance (Steiner et al., 2006).”

Steiner, A. L., Cohen, R. C., Harley, R. A., Tonse, S., Millet, D. B., Schade, G. W., and Goldstein, A. H.: VOC reactivity in central California: comparing an air quality model to

ground-based measurements, Atmos. Chem. Phys., 8, 351–368, doi:10.5194/acp-8-351-2008, 2008.

3. Fig 2 should be modified to show units for NO_2^* , PO_3 , and VOCR (corresponding to each curve). Recommend creating a figure that corresponds as closely as possible to actual conditions in the SJV.

We strongly prefer not to put units on the figures as we believe the numbers would distract from the more important point that the relative shapes of the curves are teaching us how the system is responding to changes in NO_x and VOCR.

The data do not exist in the SJV (or at any location) on inter-annual timescales and regional special scales to do this from a measurement-based perspective. While we believe the shapes of the curves and the relative positions are reliable, these relative shapes could be reproduced with more than one choice of PHO_x , VOCR, and the relationship between NO_2^* and true NO_2 .

4. The authors assume a linear relationship between ozone production rate (PO_3) and probability of exceeding the ozone standard in Fig 2 with little proof. This linear relationship doesn't seem to make sense. Consider a case where ozone concentrations are below the standard. A 10% increase in PO_3 may well lead to an increase in the probability of exceeding the standard. Consider a second case where ozone concentrations are already above the standard. A 10% increase in PO_3 has no effect on the probability of exceeding the standard (which is already 1). This "saturation" effect seems almost certain to produce a non-linear relationship between PO_3 and the probability of exceeding the ozone standard.

The reviewer makes good points. We added a section to the revised manuscript explaining our thinking on this set of issues and discussing why a linear relationship does make sense for this dataset.

2.2 Ozone production, O_3 concentration, and the frequency of high O_3 days

The atmospheric O_3 concentration is a function of the time-integrated effects of PO_3 , chemical and depositional loss, and mixing. All of these terms vary and often co-vary. Over the time interval of our study, we expect no significant variability in the chemical or depositional loss terms or in the frequency of stagnation in the SJV. Trends in the mean, median, and width of the distribution of ozone concentrations—observed to be Gaussian in our dataset—are thus dominated by the statistics of changes in PO_3 . Moreover, O_3 exceedances varying in the nonlinear manner shown in Fig. 2, as we will show they do, bolster the notion that production is the principal term changing over time. To make the association between the O_3 concentration and the frequency of high ozone days, we take advantage of the statistical properties of normal distributions. Specifically that the cumulative probability of the portion of a normal distribution

above a particular threshold varies linearly with shifts in the mean (assuming the width is constant) so long as the threshold is within one standard deviation of the mean, or between approximately 15% and 85%. On this basis, we hypothesize that the curves representing PO_3 in Fig. 2 also describe the statistics of high ozone days and use this conceptual framework, which in our analysis we support empirically, to interpret observed changes in the probability of high ozone defined as the fraction of days exceeding the 8-hour O_3 California Ambient Air Quality Standard (CAAQS) of 70 ppb (>70.4 ppb).

We also check that the reviewer's hypothetical example is not realized for this particular dataset. We included a description of this in the new text.

“With the near unity exceedance probabilities observed in Arvin, it is possible that the O_3 concentration did actually decrease but that the normal distribution did not shift sufficiently to move any of the population below the threshold of 70.4 ppb. If this is the case, then the VOCR may have also decreased. To check our conclusion in the Southern SJV, we use exceedance thresholds of 80.4 and 90.4 ppb, where the probability of exceeding these higher standards is low enough (with maximum values of 83% and 63%, respectively) that we expect a linear response in violations to changes in PO_3 . In Shafter, we find no difference in the slopes of the NO_2^* and VOCR relationships depicted in Fig. 6 for either the 80.4 or 90.4 ppb standard. In Bakersfield, the shape of the curves for the 90.4 ppb standard is the same as for the 70.4 ppb; however, we find some evidence for VOCR decreases using the 80.4 ppb standard. We attribute this behavior to Bakersfield's transitional location within the plume between upwind Shafter and downwind Arvin. In Arvin (perhaps most importantly) the slopes of the three weekend-weekday conjugates and the chemical conditions they describe are unchanged; using either the 80.4 or 90.4 ppb standard we find no evidence for VOCR reductions.”

5. Closely related to comment 4, the authors need to provide additional justification for the assumed relationship between the probability of exceeding the ozone standard vs. NO_2^* and VOCR. If the authors can show a proportional relationship between PO_3 and the probability of exceeding the standard, then all is well. If not, then some additional thought needs to be given to the dependent variable used in Figs 4, 6, 8, and 10.

Please see comment 4.

6. Page 9775 statement starting on line 2 “During the day. . .” is not universally true. In regimes with excess NO_x that quench radical chemistry, the termination reactions are more important than the radical propagation reactions. This has commonly been the case in large urban locations throughout California in past decades.

We revised the text to be clear about our meaning.

“During the daytime, HO_x chain lengths are long enough that the ratio of HO_2 to RO_2 is near one.”

7. Page 9775 line 19 statement starting with “The impact of any individual VOC to ozone production depends primarily on its reaction rate with OH. . .” is not universally true. Radical chemistry from several important VOCs can be initiated through photolysis as the authors later point out page 9776 line 9.

We have changed the text as follows:

“The impact of any individual VOC to ozone production depends mainly on its reaction rate with OH (except for a small subset of VOCs that are photolabile); rapidly reacting molecules such as alkenes and aldehydes are disproportionately important compared to less reactive alkanes, acids, and ketones.”

8. Page 9776 first three sentences are convoluted. The HO_x pool is a direct product of VOCR, and it seems confusing to discuss reductions in HO_x as a cause rather than a symptom of reductions in VOCR. The exogenous variables that control VOCR (and the HO_x pool as a consequence) are listed in comment 2.

We have revised our text to clarify our meaning. In general, we understand urban HO_x sources to be dominated by $O^1D + H_2O$ and HONO photolysis with a smaller but still significant contribution from formaldehyde photolysis. The latter is dependent on VOC as we have mentioned in several places in the text.

9. Page 9776 reference to formaldehyde as the second largest source of PHO_x in the San Joaquin Valley needs a reference and brief discussion. What measurement technique was employed to reach this conclusion, and under what conditions?

We were only speculating about O_3 and formaldehyde as they have been seen to be important HO_x sources in other locations. We do not have the measurements or references to support this claim for the SJV as a result we removed this text and rewrote the paragraph. Our new text also addresses the concerns in comment 8.

“...Net sources of HO_x include the photolysis of O_3 , formaldehyde and other aldehydes, nitrous acid, and nitril chloride, reactions between O_3 and alkenes, and organic radical reactions that

amplify rather than merely propagate OH and HO₂. PHO_x and VOCR are linked. For example, formaldehyde is both a primary anthropogenic emission and is an oxidation product of virtually every gas phase organic molecule. Formaldehyde is also reactive with OH and, after oxidation, enters the HO_x cycle at HO₂ formation directly. Emissions reductions targeting formaldehyde and/or any of its precursors will have the combined effect of simultaneously reducing PHO_x and VOCR. In addition, VOC emission controls that improve O₃ air quality will also decrease PHO_x. The photolysis of O₃ is the single largest HO_x source in many locations and lower O₃ concentrations impact PHO_x in a positive feedback resulting in further decreased ozone production rates. That said, in the SJV the average Valley-wide summertime (June–August) 8-hour O₃ 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). In the analysis that follows, we make no attempt to tease apart the effects of PHO_x from those of VOCR, as data do not exist with which to do this; we acknowledge that our “VOCR” likely includes a component due to changes in HO_x sources.”

10. Page 9776 line 16 statement “Of these, PO₃ dominates the variability, as day-to-day variability in other terms is much smaller. . .” is not correct. Variability in wind speed and mixing depth have a dominant effect on ozone concentrations in the San Joaquin Valley on a daily basis. There are no ozone episodes unless conditions are stagnant. Averaged over 16 years of data, the meteorology is relatively constant, and changes to PO₃ may be the dominant effect.

We have modified the text:

“The atmospheric O₃ concentration is a function of the time-integrated effects of PO₃, chemical and depositional loss, and mixing. All of these terms vary and often co-vary. Over the time interval of our study, we expect no significant variability in the chemical or depositional loss terms or in the frequency of stagnation in the SJV. Trends in the mean, median, and width of the distribution of ozone concentrations—observed to be Gaussian in our dataset—are thus dominated by the statistics of changes in PO₃. Moreover, O₃ exceedances varying in the nonlinear manner shown in Fig. 2, as we will show they do, bolster the notion that production is the principal term changing over time.”

11. Page 9779 statement starting on line 5 “As such, in this analysis, grouping data at a common temperature decouples the effects of chemistry from those of meteorology” does not describe the analysis performed. Only two temperature groups are selected, with significant

temperature range within each group. It still seems likely that the effects of temperature, stagnation, and photolysis rates are convoluted with the effects of VOC emissions rates

We modified the text as follows:

“Meteorological conditions conducive to high ozone, including stagnation events and clear skies, correlate with increasing temperature. We group data into two temperature regimes, high (34–45°C) and moderate (28–33°C); we find these ranges are sufficiently distinct to identify differences in production of ozone (see below) while still maintaining sufficient statistics to characterize the ensemble of ozone at each site. We note that in the SJV, boundary layer dynamics are strongly influenced by mountain valley flow and as a result we do not expect meteorological factors (e.g. wind speeds) that are particularly different between high and moderate temperatures.”

12. Page 9779 statement starting on line 7 “We note however that in the SJV, we do not expect meteorological factors that are particularly different to vary with temperature during ozone season.” What does this mean?

We have changed the text in response. Also, see comment 11.

“We note that in the SJV, boundary layer dynamics are strongly influenced by mountain valley flow and as a result we do not expect meteorological factors (e.g. wind speeds) that are particularly different between high and moderate temperatures.”

13. The VOCR values used to generate the smooth curves in Figs 6, 8, and 10 should be listed. Are these values realistic given measured / expected VOCR?

As with reviewer’s comment 2, we prefer not to insert numerical values. We believe strongly in the relationships implied by these curves and not in the specific numbers we used to generate them. We hope our manuscript inspires research using 3-D CTMs and other approaches to directly calculating O₃ to study this location and time period and to provide specific numbers for comparison.

14. Fig 4 uses open and closed symbols that are hard to distinguish. Consider using larger symbols or otherwise modify to make more readable.

We made the symbols larger to make figure more readable.