We thank the referees for their constructive and helpful comments.

Referee 1

This paper studied the observed temperature dependence of NO_x-VOC-O_3 relationship and its implication for the emission regulation. The VOC reactivity (VOCR) with OH increases significantly as temperature rises. However, NO_x reactivity (NO_xR) remains invariant with the change of temperature. Such asymmetric responses of VOCR and NO_xR to temperature result in different limits on O_3 production (PO_3) when atmospheric temperature changes: the VOC-limited PO_3 at the low and moderate temperatures will become NO_x-limited at high temperatures, due to the lower NO_xR relative to VOCR at warmer conditions. As a result, the NO_x control is efficient to reduce O_3 at high temperatures, especially for weekdays with high NO_x emissions. On the other hand, VOC control will be useful for days with low and moderate temperatures.

The subject is interesting and appropriate for ACP. The results are also very useful for policy makers to determine strategies of emission regulation. The logical structure and language of the paper are excellent. Some minor revisions are required for clarifications.

1. Page 28519, Eq. 1: The equation is essential for your estimate of PO_3. Please present the calculation details in appendix for clarification.

There are errors in equations 1 and 5 in the ACPD version incurred during typesetting that we did not notice when we approved the proofs. We have corrected these errors and we have added a new Appendix A that gives the complete set of equations (page 26).

2. Page 28520, Lines 8-10: "Noontime HONO concentrations during CalNex-SJV were between 30–250 ppt ... making HONO an important radical source throughout the day." Could you estimate the fraction of OH from HONO, like the values for H_2O_2 and O_3?

We have changed the text as follows:

"PHO_x is the summed HO_x production rates of O_3, H_2CO, HONO, and H_2O_2 photolysis and O_3 reactions with alkenes. The contributions of O_3 and H_2CO were 34% and 26%, respectively. Noontime HONO concentrations during CalNex-SJV were between 30–250 ppt (Ren et al., 2011; VandenBoer et al., 2013) making HONO an important daytime radical source (32%). H_2O_2 photolysis (1%) and O_3 + alkene reactions (7%) are less important to the daytime total."

3. Page 28521, Line 14: "OH reactivity" is the reactivity with every VOC, NO_x, HONO, HNO_3, NH_3, and SO_2? Or the total OH reactivity?

We have added the word "total" before "OH reactivity" in this sentence.

4. Page 28522, Lines 20-28: Why do you use two different temperatures? Please clarify how you use them separately in the analysis.

We have added this sentence (page 14 line 6):

"We use the average temperatures to streamline the discussion of our results."

5. Page 28523, Paragraph 1, Fig. 1, and Fig. A1: (1) The $\Sigma_i VOCR_i$ you estimated includes more than 120 individual VOCs (Table A2) or only the ones you observed directly (Table A1)?

We have changed the text to improve the clarity. The first paragraph of this section (pages 14–15 lines 16–5) now reads:

"We examine observed daytime (10 am–2 pm LT) relationships between reactivity and temperature of more than 120 individual organic compounds and find that reactivities can be broadly categorized as either temperature independent or temperature dependent. We emphasize the observed temperature dependence is driven primarily by temperature's effect on VOC concentrations (presumably emissions) rather than by acceleration of the OH reaction rates. In Fig. 1 we show the empirically determined fits of all observed organic molecules (10 a.m.–2 p.m. LT) as a function of the daily maximum temperature. The $\Sigma_i VOCR_i$ are grouped by chemical functionality when possible and we prioritize simplicity (the fewest number of groupings) over groupings by source category. Fig. 1 also includes reactivity contributions from four unmeasured species using computed concentrations; each VOC included in Fig. 1 is listed in Table B2 (see Appendix B for details). The data points summarized in Fig. 1 are shown in Fig. B1."

(2) Fig. A1 caption shows that some of $VOCR_i$ are calculated using measured concentrations. Please explain how to do such calculation. (3) Please explain what's the meaning of each point in every panel. I guess that some of them are from measurements, while others are estimated based on Table A2.

We present a detailed discussion of this in Appendix B (formerly Appendix A). The calculated species are marked with a star in Table B2 (formerly Table A2), as noted in the caption. For MVK, benzene, and ethane the contributions are very small and have no impact on our conclusion that there is a missing temperature-dependent source of organic reactivity. In the case of acetaldehyde we discuss the impact of the uncertainty associated with our calculation by presenting the calculation two ways.

6. Page 28525, Paragraph 2, and Fig. 2: The authors noted the large difference between $\Sigma_i VOCR_i$ and VOCR. They tried to explore the possible causes. Please also discuss the following possible uncertainties in your estimate: (1) uncertainties in estimate of VOCR. "Total VOCR is equal to the measured OH reactivity minus the OH reactivities of NO, NO_2, HONO, HNO_3, ammonia (NH_3), and sulfur dioxide (SO_2)". Based on your Table A1, the uncertainties in measurements of HONO, HNO_3, NH_3, and SO_2 may add up to +/- 100%.

The reactivity contributions of HONO, HNO_3, NH_3, and SO_2 are far too to small to affect our conclusion that there are unidentified molecules contributing to the VOCR at high temperatures. We have added this sentence (page 16 line 15–18):

"Measurement uncertainties in HONO, HNO_3, NH_3, and SO_2 cannot fill the observed gap in reactivity at high temperatures. The total mean high-temperature reactivity of these species is $0.15 \text{ s}^{-1} \pm 21\%$, or at most 0.18 s^{-1}, as $> 85\%$ of this reactivity is from NH_3 (Table B1)."

(2) The VOCR may include other non-VOC sources.

We have included all the inorganic species that were measured and now include mention of O_3 loss in Appendix A. The mean O_3 reactivity with OH at high temperatures is $0.13\ \text{s}^{-1}$ and we have added this fact to Appendix A (page 27 lines 15–16). Does the Referee have another inorganic source in mind?

(3) $VOCR_i$ may enhance when certain VOCs coexist, especially at high temperatures.

We list organic oxidation products as reactivity sources that are likely temperature dependent (page 17 lines 2–3).

7. Page 28528, Paragraph 1, and Fig. 5a: The authors noted that VOCR shows no day of-week variations but failed to explain it. (1) The NO_xR shows a significant difference between weekdays and weekends (Fig. 4a). How about the weekly variations of the reactivity for other non-VOC species (such as $HONO$, HNO_3, NH_3, and SO_2)? Do they affect the VOCR?

OH rate constants for $HONO$, HNO_3, NH_3, and SO_2 are too slow for day-of-week variability in the concentrations of these species to affect the total VOCR. We have added this sentence (page 16 line 15–18):

"Measurement uncertainties in $HONO$, HNO_3, NH_3, and SO_2 cannot fill the observed gap in reactivity at high temperatures. The total mean high-temperature reactivity of these species is $0.15\ \text{s}^{-1}\ \pm21\%$, or at most $0.18\ \text{s}^{-1}$, as $> 85\%$ of this reactivity is from NH_3 (Table B1)."

(2) Lines 2-4: "Equal weekday-to-weekend percent decreases in OH occur alongside decreases in PO_3 and an equivalent reduction in the OH-reaction removal rate of organic emissions is implied". Are these changes measured or calculated?

We mean that the NO_x dependence of PO_3 follows from that of OH. We have divided this sentence into two to separate the ideas to make our point more clear.

(3) VOCR seems only dependent on temperature, and not influenced by NO_xR and [OH], how about the impact of changes in VOC emissions?

Concerning emissions, we have this text (page 20 lines 4–8):

"A compensating increase in organic emissions on weekends is unlikely, as high-temperature reactivity is dominated by molecules with emissions rates controlled by temperature and not by human activity (Sect. 4.1). Temperature-independent $\Sigma_i VOCR_i$ is also invariant with day of week (not shown)."

Ultimately the statistics are limited, both due to the short time frame of the experiment (6 weeks) and the sharp temperature dependence of VOCR. We present independent evidence in the subsequent section that supports our assessment of the high-temperature OH and PO_3 being NO_x limited. This evidence is the observed day-of-week pattern in the 2010 exceedance frequency.

8. Table 1. This table is very interesting. However, the authors used $\Sigma_i VOCR_i$ in their calculation of PO_3. Based on Eq. (1)-(6), PO_3 is dependent on VOCR, which is very different from $\Sigma_i VOCR_i$. Please clarify.

We use VOCR in our calculation of PO_3 not $\Sigma_i VOCR_i$. We have changed the first sentence in the table caption to read:

"PO_3 (ppb h^{-1}) computed with an analytical model parameterized with CalNex-SJV observations (the organic reactivity is equal to VOCR, not $\Sigma_i VOCR_i$)."

9. Fig. 2 and Fig. 5a. The VOCR in these two figures are slightly different. Please clarify.

We have changed our description of Fig. 5 panel a to clarify this. It now reads:

"Total VOCR (s^{-1}) (measured OH reactivity minus the OH reactivity contributions of NO_2, NO, HONO, HNO_3, NH_3, and SO_2; this is equivalent to the sum of the green and blue data in Fig. 2)."

10. One important implication from this study is the climate change penalty. In a warmer future (e.g. increase of 2°C), VOCR and PO_3 are expected to increase. How much NO_x reduction may be required to compensate for such climate change penalty?

A discussion of how the frequency of exceedances in the SJV will change in a warmer climate is beyond the scope of this work and our expertise. Among other potential changes, we do not know how the distribution of temperatures will shift or how meteorology in Valley is expected to respond. We have created a picture of chemical ozone production as a function of temperature that we expect to be useful to researchers studying the frequency of high O_3 in a warmer climate.

We have however somewhat expanded the last paragraph of the discussion (page 24 lines 7–13) to show that our Fig. 7 offers insight into how to anticipate how PO_3 versus temperature will change in the future if NO_x emission controls occur. The text now reads:

"One consequence of the local photochemistry moving to a NO_x-limited regime is that in the future the temperature dependence of PO_3 will diminish; at low enough NO_x levels PO_3 will be temperature independent, as temperature-driven increases in VOCR will not increase PO_3. This is visualized in in Fig. 7 in the comparison of the black solid (higher NO_x emissions) and brown dashed line (lower NO_x emissions). In the future, we therefore expect less variability in PO_3 and, by extension, less variability in the frequency of O_3 exceedances with temperature."

This manuscript contains an excellent treatment of the relative importance of nitrogen oxides and VOCs to ozone production in the southern San Joaquin Valley of California, an area with a long history of exceedances of the US National Ambient Air Quality Standard for ozone. The authors used in this analysis a very substantial air chemistry dataset from a ground site downwind of the city of Bakersfield, CA that was collected during the CalNex campaign of May - June 2010, along with observations from the routine air monitoring sites in this region. They performed detailed calculations of HO_x and O_3 production rates from the available data, and then made perturbations to the emissions of NO_x and VOCs to simulate possible future controls. The results of these calculations show that there are two distinct sets of VOCs present, those with temperature-dependent OH reactivity and those that are temperature independent. The latter have been reduced substantially over the last couple of decades, but the results of this analysis show that further such reductions will do little to further reduce exceedances of the ozone standard. Instead, NO_x emission reductions will be much more beneficial.

The authors have produced a very well written paper, and it should send a strong message to air regulators concerning the types of future emission controls would have the most benefit in terms of reducing ozone mixing ratios in this region. I suggest that the manuscript be accepted with minor revisions as I have outlined below.

p. 28513, line 11: Should mention possible sources of these VOCs with temperature dependent reactivity here in the abstract.

Our focus is on describing observed relationships between VOC reactivities and temperature. We do not attempt an analysis to assign sources to these reactivities and so would rather keep the abstract as is.

p. 28519: Here the authors detail their calculation scheme for PO_3. The observed O_3 mixing ratios are a function of both PO_3 and LO_3 (ie: both production and loss). Shouldn't the NET PO_3 be used here, considering both production and loss (probably most important would be O_3 + OH and O_3 photolysis, which could be calculated quite easily). I would think at least a sample calculation of the net production should be included. Perhaps that would be highly correlated with the PO_3 during the 10 AM to 2 PM period that is considered. If so, that should be demonstrated.

We have added this information to our new model appendix (Appendix A). The exact text reads (page 27 lines 9–16):

"Throughout this analysis we consider instantaneous PO_3 rather than net PO_3 (production minus O_3 chemical loss). Pathways of O_3 loss are O_3 photolysis to yield two OH (R13–R14) and reactions between O_3 and OH, HO_2, and alkenes. Using observations of each species we find the total mean O_3 loss rate to be 0.7, 1.1, and 1.4 ppb h^{-1} at low, moderate, and high temperatures, respectively. The largest contributor to O_3 loss is O_3 photolysis (66%). Losses due to reactions with OH, HO_2, and alkenes are approximately equal in importance. Ozone's mean reactivity with OH is 0.08 s^{-1} at low, 0.1 s^{-1} at moderate, and 0.13 s^{-1} at high temperatures and is not included."

p. 28520, lines 20-21: I know you need HO$_x$ to be in steady state over 10 AM - 2 PM for your calculations. But, having to adjust the photolysis rates by 10% means that HO$_x$ was not really in steady state. Can you discuss why this might have been the case?

We think the steady-state assumption is correct. We attribute the adjustment in photolysis rates to the lack of measured photolysis rates during the experiment. We have added this comment to the text (page 11 lines 12–14):

"We attribute the adjustment in photolysis frequencies to error associated with selection of TUV model input parameters."

p. 28522, lines 3-6: I don't understand why you don't use the average temperature over the same interval as the chemistry measurements (10 AM to 2 PM). What is the correlation between daily max T and the average over 10 AM - 2 PM?

We chose to use the daily maximum, as this was the temperature used in manuscript Pusede and Cohen (2012), to which we frequently compare our work. We reported the correlation between the daily average (10 am–2 pm LT) and daily maximum (page 13 lines 5–7). The sentence reads:

"The daily maximum is well-correlated to with the daily average: slope = 0.91(±0.03), y-intercept = 4.72(±0.70)$^{\circ}$C, and R^2=0.99)."

We use temperatures over the same time interval as the chemistry measurements when we compute the $\Sigma_i VOCR_i$. This is stated in Appendix B (formerly Appendix A) (page 28 lines 18–20).

"If a temperature dependent OH rate expression is available we use the time varying temperature over the same time interval, not the daily maximum temperature."

p. 28527, line 8: not on weekdays. It looks to be < 10 on weekdays from the figure.

We have changed this to read:

"On weekdays and weekends the observed VOCR/NO$_x$R increases across the temperature range of 15–40°C by a factor of 5 and 10, respectively."

p. 28530, line 22: Should this be 20 -27 deg., rather than 2 - 20?

Yes, this has been corrected.

Figure 6 caption: Please further clarify the meaning of the wind direction arrow on the right side of the figure. I think it is referring to the fact that the wind is blowing from a high NO$_x$ region to a low NO$_x$ region, but it took me a while to figure that out.

We have modified the last sentence of the Fig. 6 caption to read:

"The arrow along the right-hand side represents the prevailing daytime (10 am–2 pm LT) wind direction with respect to NO$_x$ to the CalNex-SJV site, i.e. the wind travels from the higher NO$_x$ Bakersfield city center to the lower NO$_x$ measurement site."