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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley California" *by* S. E. Pusede et al.

Anonymous Referee #1

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Pusede et al. "On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley California"

Recommendation to editor: Minor revision

GENERAL

This paper studied the observed temperature dependence of NOx-VOC-O3 relationship and its implication for the emission regulation. The VOC reactivity (VOCR) with

OH increases significantly as temperature rises. However, NOx reactivity (NOxR) remains invariant with the change of temperature. Such asymmetric responses of VOCR and NOxR to temperature result in different limits on O3 production (PO3) when atmospheric temperature changes: the VOC-limited PO3 at the low and moderate temperatures will become NOx-limited at high temperatures, due to the lower NOxR relative to VOCR at warmer conditions. As a result, the NOx control is efficient to reduce O3 at high temperatures, especially for weekdays with high NOx 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.

SPECIFIC

1. Page 28519, Eq. 1: The equation is essential for your estimate of PO3. Please present the calculation details in appendix for clarification.

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 H2O2 and O3?

3. Page 28521, Line 14: "OH reactivity" is the reactivity with every VOC, NOx, HONO, HNO3, NH3, and SO2? Or the total OH reactivity?

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

5. Page 28523, Paragraph 1, Fig. 1, and Fig. A1: (1) The ΣiVOCRi you estimated includes more than 120 individual VOCs (Table A2) or only the ones you observed directly (Table A1)? (2) Fig. A1 caption shows that some of VOCRi 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.

6. Page 28525, Paragraph 2, and Fig. 2: The authors noted the large difference between ΣiVOCRi 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, NO2, HONO, HNO3, ammonia (NH3), and sulfur dioxide (SO2)". Based on your Table A1, the uncertainties in measurements of HONO, HNO3, NH3, and SO2 may add up to +/- 100%. (2) The VOCR may include other non-VOC sources. (3) VOCRi may enhance when certain VOCs coexist, especially at high temperatures.

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 NOxR 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, HNO3, NH3, and SO2)? Do they affect the VOCR? (2) Lines 2-4: "Equal weekday-to-weekend percent decreases in OH occur alongside decreases in PO3 and an equivalent reduction in the OH-reaction removal rate of organic emissions is implied". Are these changes measured or calculated? (3) VOCR seems only dependent on temperature, and not influenced by NOxR and [OH], how about the impact of changes in VOC emissions?

8. Table 1. This table is very interesting. However, the authors used ΣiVOCRi in their calculation of PO3. Based on Eq. (1)-(6), PO3 is dependent on VOCR, which is very different from ΣiVOCRi. Please clarify.

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

10. One important implication from this study is the climate change penalty. In a warmer future (e.g. increase of 2 °C), VOCR and PO3 are expected to increase. How

much NOx reduction may be required to compensate for such climate change penalty?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 28511, 2013.