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# ***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**

Received and published: 25 December 2013

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 NO<sub>x</sub>-VOC-O<sub>3</sub> relationship and its implication for the emission regulation. The VOC reactivity (VOCR) with

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OH increases significantly as temperature rises. However, NO<sub>x</sub> reactivity (NO<sub>x</sub>R) remains invariant with the change of temperature. Such asymmetric responses of VOCR and NO<sub>x</sub>R to temperature result in different limits on O<sub>3</sub> production (PO<sub>3</sub>) when atmospheric temperature changes: the VOC-limited PO<sub>3</sub> at the low and moderate temperatures will become NO<sub>x</sub>-limited at high temperatures, due to the lower NO<sub>x</sub>R relative to VOCR at warmer conditions. As a result, the NO<sub>x</sub> control is efficient to reduce O<sub>3</sub> at high temperatures, especially for weekdays with high NO<sub>x</sub> 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 PO<sub>3</sub>. 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 H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>?
3. Page 28521, Line 14: "OH reactivity" is the reactivity with every VOC, NO<sub>x</sub>, HONO, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>? 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  $\sum \text{VOCR}_i$  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 VOCR<sub>i</sub> are calculated

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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  $\Sigma i\text{VOCR}_i$  and  $\text{VOCR}$ . They tried to explore the possible causes. Please also discuss the following possible uncertainties in your estimate: (1) uncertainties in estimate of  $\text{VOCR}$ . "Total  $\text{VOCR}$  is equal to the measured OH reactivity minus the OH reactivities of NO, NO<sub>2</sub>, HONO, HNO<sub>3</sub>, ammonia (NH<sub>3</sub>), and sulfur dioxide (SO<sub>2</sub>)". Based on your Table A1, the uncertainties in measurements of HONO, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub> may add up to +/- 100%. (2) The  $\text{VOCR}$  may include other non-VOC sources. (3)  $\text{VOCR}_i$  may enhance when certain VOCs coexist, especially at high temperatures.

7. Page 28528, Paragraph 1, and Fig. 5a: The authors noted that  $\text{VOCR}$  shows no day-of-week variations but failed to explain it. (1) The  $\text{NO}_x\text{R}$  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<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>)? Do they affect the  $\text{VOCR}$ ? (2) Lines 2-4: "Equal weekday-to-weekend percent decreases in OH occur alongside decreases in PO<sub>3</sub> and an equivalent reduction in the OH-reaction removal rate of organic emissions is implied". Are these changes measured or calculated? (3)  $\text{VOCR}$  seems only dependent on temperature, and not influenced by  $\text{NO}_x\text{R}$  and [OH], how about the impact of changes in VOC emissions?

8. Table 1. This table is very interesting. However, the authors used  $\Sigma i\text{VOCR}_i$  in their calculation of PO<sub>3</sub>. Based on Eq. (1)-(6), PO<sub>3</sub> is dependent on  $\text{VOCR}$ , which is very different from  $\Sigma i\text{VOCR}_i$ . Please clarify.

9. Fig. 2 and Fig. 5a. The  $\text{VOCR}$  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),  $\text{VOCR}$  and PO<sub>3</sub> are expected to increase. How

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much NO<sub>x</sub> reduction may be required to compensate for such climate change penalty?

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

**ACPD**

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