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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the observed response of ozone to NO_X and VOC reactivity reductions in San Joaquin Valley California 1995–present" *by* S. E. Pusede and R. C. Cohen

Anonymous Referee #2

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On the observed response of ozone to NOx 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 NOx 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 NOx 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 dependant. The different curves illustrated in Fig 2 could be generated by increasing any one of the three parameters represented by VOCR. Additional text should be added to emphasize these points.

3. Fig 2 should be modified to show units for NO2*, PO3, and VOCR (corresponding to each curve). Recommend creating a figure that corresponds as closely as possible to actual conditions in the SJV.

4. The authors assume a linear relationship between ozone production rate (PO3) 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 PO3 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 PO3 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 PO3 and the probability of

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exceeding the ozone standard.

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. NO2* and VOCR. If the authors can show a proportional relationship between PO3 and the probability of exceeding the standard, then all is well. If not, then some additional thought needs to be given to the dependant variable used in Figs 4, 6, 8, and 10.

6. Page 9775 statement starting on line 2 “During the day. . .” is not universally true. In regimes with excess NOx 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.

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.

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

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

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

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PO3 may be the dominant effect.

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.

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?

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?

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9771, 2012.