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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The weekend effect within and downwind of Sacramento: Part 2. Observational evidence for chemical and dynamical contributions" *by* J. G. Murphy et al.

Anonymous Referee #2

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Overview

This manuscript presents an attempt to derive information about ozone-precursor sensitivity based on ambient measurements, focused mainly on the difference between weekdays and weekends. Many of the results are interesting and original. The use of weekday versus weekend isoprene to infer differences in OH is especially noteworthy. Some of the results are speculative or imprecise, but this reflects the difficult nature of the task. I recommend publication.

The model calculation is weak because it uses an approximate chemical formula rather than a complete calculation. The authors might have done better if they did a straight

0-d calculation of photochemistry, using a standard mechanisms for reactions in the polluted troposphere, rather than their approximation. However, the model calculation adds value to the paper and I recommend publication.

The paper would also be stronger if the authors were to use methods developed elsewhere to interpret their measurements. Previous model calculations have identifed NOx-sensitive and NOx-saturated conditions based on the ratio between VOC reactivity and NOx, and based on correlations between O3 and NOz and between O3 and HNO3. This manuscript and its companion paper describe measurements for all these species. If they used these methods to interpret their measurements, they would find supporting evidence for their conclusions about the NOx-saturated/NOx-sensitive nature of the Sacramento valley.

Detailed comments

1. The text (p. 11985) refers to Ox as having a 4-hour lifetime. I believe this is incorrect if it refers to the lifetime of Ox in the daytime mixed layer with respect to removal (through photochemisry and/or deposition). The lifetime for Ox is usually estimated at 2 days.

It is also not clear where the 4-hour estimate comes from or what it means. Earlier (p.11980-11982) the 4-hour period is introduced as the period of the steepest rise in O3, and as the travel time from Sacramento to the UC-BFRS site. There may be some confusion over terminology.

2. The authors initially use the period between 09:00 and 13:00 to identify trends in Ox that relate to overnight transport and entrainment (represented by Ox at 0900) as opposed to local production (represented by the increase from 0900 to 1300). This is a useful method and yields interesting results in terms of weekday-weekend difference. However, later (p. 11986) it appears that they regard the increase from 0900 to 1300 as a direct measurement of the rate of photochemical production of ozone. I believe this is not correct. The daytime boundary layer increases between 0900 and 1300 by a

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factor of two or more (shown by the large decrease in NOx from 0900 to 1300), and the entrained O3 is usually higher than the 0900 value. The authors apparently recognize that mixing contributes to the rise in O3 (p. 11982, line 5, and p. 11987, line 20), but in the discussion at the bottom of p. 11986, they attempt to match the observed rise in Ox with a model that includes just photochemical production and loss. Please clarify this in the text on p. 11986.

3. The approximate formula for OH and P(O3) is very similar to derivations and equations previously published by Sillman et al., 1990 and 1995 (J. Geophys. Res.), Kleinman, 1997 (Geophys. Res. Lett.) and Tonnesen and Dennis, 2000 (J. Geophys. Res.). These should be cited.

Analysis of p(O3) and OH versus NOx also echoes similar treatments and findings from Liu et al. (1987), Lin et al. (1988), Sillman et al. (1990) and Tonnesen and Dennis(2000), all in J. Geophys. Res.

4. The model calculation (p. 11984-11986) is used to give approximate values for ozone production during the 4-hour transport time from Sacramento to Blodgett, and also for the ozone production rate in Sacramento. These values are then discussed (p. 11986-7) in comparison with the observed rise in ozone from 9am to 1pm at Sacramento and at Blodgett. The overestimate of P(O3) compared to the observed ozone rise is attributed to the impact of deposition and omission of production of PN's.

There are problems with this analysis, as follows:

(i). The observed rise in O3 from 9am to 1pm is influenced by entrainment from aloft (see 2 above), so that the true photochemical PO3 is likely to be smaller than the observed ozone rise. This makes the model result even worse in comparison with the measured change in O3.

(ii) The model NOx distribution assumes that all NOx is emitted in Sacramento (with concentrations based on ambient measurements), and decays exponentially (with no

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additional emissions) as the air mass travels downwind. No allowance is made for decreased NOx due to horizontal dispersion as the plume travels to Blodgett. This is a likely contributor to the overestimate in PO3.

(iii) Measured VOC is not likely to be constant between Sacramento and Blodgett, as assumed. Most VOC is biogenic and has a short lifetime, and the terrain varies widely between Sacramento and Blodgett.

(iv) The rate of NOx removal (0.5 hr-1) is based on the difference between measured NOx at Sacramento and Blodgett, assuming zero emissions downwind of Sacramento. The actual removal rate of NOx could be more rapid if NOx at Blodgett reflects local emissions and/or emissions between Sacramento and Blodgett. This would result in different (lower) NOx along the 4-hour trajectory and different P(O3) in their calculation.

I suggest modifying the treatment on p. 11986-11987 based on these considerations.

More generally, I think that the model lacks credibility if it stood on its own. VOC is represented crudely (as a single 'generic' VOC); there is no link between photochemical production of O3 and removal of NOx; and no evaluation of model results or of the accuracy of numerical approximations.

I think the model is reasonable because its results are consistent with a large body of previous research. The P(O3) vs NOx is comparable with previous studies, including 0-d calculations with more sophisticated photochemistry and 3-d models that are evaluated against measured O3 and NOx reaction products. Previous studies have shown that the impact of VOC can be captured largely by a reactivity-weighted sum (e.g. Kleinman et al., 2005; Chameides et al., 1992).

For this reason, the authors should refer to previous work (see comments 3 and 5) rather than rely on their model for credibility.

5. The measurements shown for VOC and NOx in Sacramento and Blodgett should be compared with the analysis of similar measurements reported by Kleinman et al,

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2005 (J. Geophys. Res.) or with results from Tonnesen and Dennis,2000 (J. Geophys. Res.).

Kleinman et al. (2005) and Tonnesen and Dennis (2000) both calculated instantaneous production of O3 as a function of VOC and NOx. They both found that the crossover between NOx-sensitive and NOx-saturated conditions can be related to ambient NOx and reactivity-weighted VOC. Their calculations are more detailed and extensive than the model used here.

Kleinman et al. (2005) found that NOx-saturated chemistry corresponded to r-VOC/NOx greater than 1 s-1 ppb-1 (where r-VOC is OH-reactivity in s-1, the same units used here). The authors can use Kleinman's results by comparing their measured median r-VOC and NOx at the various sites. These measurements are already shown (Figures 3,4 and 5).

If the authors reported how their median r-VOC and NOx compared with the results from Kleinman et al (2005) it would strengthen their claim for a transition from NOx-saturated to NOx-sensitive conditions between Sacramento and Blodgett.

Ideally, the authors should examine the full range of measured NOx and r-VOC at each of their in comparison with results from Kleinman et al, but this would be a major expansion of the paper. A short analysis based on median measured values could be added easily.

6. The measured of O3, NOz and HNO3 might also be compared with the results of Sillman and He, 2002 (J. Geophys. Res.) to obtain an independent estimate for O3-NOx-VOC sensitivity.

Sillman and He showed values for O3 vs NOz and O3 vs HNO3 that correspond to NOx-sensitive and NOx-saturated conditions in 3-d models, including models for the Sacramento region. As in 5 above, the authors might compare the median values for O3, NOz and HNO3 (already shown in Figures 3, 4, 13 and 14) with the values re-

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ported by Sillman and He for NOx-saturated and NOx-sensitive conditions. This would strengthen their claim for a transition from NOx-saturated to NOx-sensitive conditions between Sacramento and Blodgett.

Again, a complete evaluation would require a display of afternoon O3 vs NOz and O3 vs HNO3 at each site, and would be a major expansion of the paper. A short analysis based on median measured values could be added easily.

Minor comments

p. 11977: “Additionally, in a NOx -limited environment such as is present at the UC-BFRS, the number of O3 molecules produced per NOx emitted is less strongly coupled to the NOx concentration, and P(O3) scales with NOx concentration linearly, reducing the importance of timing.” A reference should be given for this claim.

Table 3: “Change in odd oxygen (dO3)” Probably this should be dOx.

Figure 3 caption should be: (a) NOx and (b) Ox.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11971, 2006.