

## ***Interactive comment on* “Observations of total peroxy nitrates and aldehydes: measurement interpretation and inference of OH radical concentrations” by P. A. Cleary et al.**

**P. A. Cleary et al.**

Received and published: 16 March 2007

Response to referee #1:

We thank the referee for his/her comments. We concur with many of the referee’s general comments, especially on the need for more laboratory studies of the kinetics of production of PNs from the larger aldehydes and additional field studies comparing calculations of OH based on a steady-state analysis of PAN, aldehydes and NO<sub>x</sub> with real-time OH observations. We have addressed the referee’s specific comments (denoted RC) with author comments (denoted AC) below:

Specific Comments

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

RC 1. Page 12936. How are the noontime HO<sub>2</sub>+RO<sub>2</sub> calculated?

AC: Noontime peroxyradicals are calculated using a full photochemical model for the production and loss of RO<sub>2</sub> and HO<sub>2</sub> based on measurements of a suite of 45 VOC at the site. Although the 45 VOC observed are not considered to be a complete representation of the full suite of VOC at the site, they are sufficiently representative of the reactivity at the site, that the calculated RO<sub>2</sub>+HO<sub>2</sub> is not likely to be in error by more than a factor of two (with the true value higher than our calculation). In the original manuscript we chose a high end of the reactivity including estimates for a variety of unmeasured VOC. In the revised manuscript we use only the measured VOC and discuss the sensitivity of our results to the calculated peroxy radical concentrations. The following sentence has been added to Page 12936:

“HO<sub>2</sub>+RO<sub>2</sub> concentrations are estimated to be 0.020 ppb at noon based on a box model calculation of peroxy-radicals generated from the distribution of 45 VOC measured at Granite Bay (the diurnal profile of these compounds was scaled to PAR).”

RC 2. There is likely to be considerable uncertainty in the calculation of [NO]<sub>ss</sub>. Clear skies should mean the value of J(NO<sub>2</sub>) is fairly accurate, although aerosols could scatter radiation. Is the site sufficiently removed from direct emissions for the PSS to be reached? The HO<sub>2</sub>+RO<sub>2</sub> concentration is also needed. Some comment on the uncertainty in [NO]<sub>ss</sub>, and hence the NO/NO<sub>2</sub> used later, would be valuable.

AC: The site is sufficiently removed from sources that steady-state for the NO/NO<sub>2</sub> ratio should be achieved. Peroxy radicals are a minor term in the conversion of NO to NO<sub>2</sub> at this site. A factor of two uncertainty in peroxy radical concentration propagates to a 15% uncertainty in the calculated NO. We conservatively estimate the NO is accurate to 25%. The following text was added:

“The largest uncertainty in the NO<sub>ss</sub> calculation is due to uncertainties in the calculation of peroxy-radicals. Uncertainties of a factor of two in the peroxy radicals propagate to 15% uncertainty in NO<sub>ss</sub>. We conservatively estimate the total uncertainty at 25%”

RC 3. A high noon OH concentration (1.4E7) is used for the calculation of the time dependent PAN - based on some previous results (Dillon). Some further explanation of how this result is obtained, and why this is a reasonable value (lower values are calculated later) is needed.

AC: The text has been modified as follows: "We used as input the median diurnal cycles of the ratio [NO]/[NO<sub>2</sub>], temperature, and an estimate for OH ranging from 1 &#61620;106 to 1.4 &#61620; 107 molecule cm<sup>-3</sup> at noon (the highest value based on the results of Dillon et al. (2002) who fit a Lagrangian model describing mixing and oxidation of a range of VOC measurements to estimate OH)." (page 12941)

RC 4. Using 1E6 appears not to have made a significant difference (line 3 on page 12942) except at certain ratios of NO/NO<sub>2</sub> - was this a surprise? Some further discussion here would be valuable.

AC: We expected the slower production of peroxyacetyl radicals at lower OH to result in more significant breakdown of the steady-state approximation than we observed. However, the calculations did not support this expectation. We have no other results to report at this time but agree with the reviewer's implication that further investigation into the limits of the steady-state expression relating OH, aldehydes and PNs would be useful.

RC 5. In the first section of the analysis Scenarios A, B, C and D are used. Later three models, A, B and C are used. I suggest to avoid confusion that the models are given some other label.

AC: In a revised manuscript, the model calculations will be referred to as M1, M2 and M3.

RC 6. Comparison of the calculated OH with measurements at other sites is given at the end of section 5 on page 12946. Measurements in LA and Munich are cited, but this

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

list of urban measurements is incomplete. For example, there are published measured OH concentrations in Birmingham, UK (mean  $3E6$  molecule  $cm^{-3}$ , Heard, D. et al., GRL, 2004), and also at Writtle (close to London,  $1.2-7.5E6$ , mean  $3E6$ , Emmerson, K. et al, ACPD, 2006). Conditions are likely to vary considerably though (e.g. NO<sub>x</sub>) from one urban area to another.

AC: We have added discussion of these references to the manuscript.

#### Technical Corrections

AC: We have made all of the suggested technical corrections. In order to make Figures 5 and 6 larger, we divided each into two figures.

#### Reference

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A. H. and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, *Journal of Geophysical Research-Atmospheres*, 107, art. no.-4045, 2002.

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 6, 12929, 2006.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)