

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

Anonymous Referee #1

Received and published: 3 January 2007

General Comments

In this paper measurements are described of peroxy nitrates (PN) (sum of), NO₂, O₃ and aldehydes at an Urban site in Sacramento during summer 2001. Assuming formation of the precursor peroxy acetyl (PA) radicals only from reaction of OH with a single aldehyde (no photolysis considered at all), and loss via reaction with NO only, and propagation through PN (with reversible thermal decomposition back to PA), a simple steady state [PN] is calculated. Using PAN as an example, comparison is made with a time-dependent model using various assumptions for the diurnal variation of the concentration of acetaldehyde- considered the only source of PAN. Starting concentrations

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

of PAN and acetaldehyde at sunrise are based on measurements. There is reasonable agreement between the two calculated [PAN] for all of the scenarios, the scenario that fits best depends upon the day chosen - showing that the steady-state model for PAN is reasonable. However, the fraction of total PN due to PAN is too low based on measurements of PAN and other PN elsewhere, suggesting there is another source of PAN in addition to OH+acetaldehyde. Photolysis of methylglyoxal or OH+methylglyoxal are suggested possibilities - although other additional PAN sources are needed too. Making assumptions about the fraction of PN that is PAN and MPAN, the steady-state concentrations of individual larger PN species are calculated assuming steady state from measured aldehydes and the total measured PN, but PN molecules never measured before are calculated to be present in significant concentration. The results suggest that the steady-state model is a poor one for the higher PN. Finally, the total measured PN and the measured aldehydes are used to calculate [OH], assuming that the only sink for the aldehydes is reaction with OH to form PA and then PN. Sensible OH concentrations are calculated, but the assumptions used in its calculation are severe, and really the values are only an indication that the whole approach is generally valid.

The measurement of total PN and HNO₃ in real time using thermal dissociation (with detection of NO₂ produced, NO₂ is also measured at low temperature) at different temperatures is unique to this group, and provides abundant data. When combined with the aldehyde measurements one can begin to examine the speciation of PN in some detail by use of the simple model described here, which is novel. Although there are many assumptions (e.g. one aldehyde gives one PA and hence PN) much has been learnt about these photochemical processes and the budget of PAN throughout a day - and the assumptions can be tested - e.g. the results would appear to indicate that there is another source of PAN other than OH+acetaldehyde. The results also indicate that PN and NO_x are interconverted quite quickly, and so downwind of the NO_x source at high temperature the decomposition of PN provides a constant source of NO_x, and so NO_x should really be replaced by NO_x+PN as the latter is continually releasing NO_x.

The OH calculations obtained from the analysis, as the authors point out, should be viewed with caution, due the unknowns in the model (e.g. what the sources of the individual PA species are), but show sensible values, over a 2 month period. A future field experiment comparing OH calculated from the total PN and aldehyde measurements with actual measured OH concentrations, would be very valuable, as it would provide a* validation of the approach used. For example, including photolysis of methylglyoxal and its reaction with OH as sources of PA (to make more PAN), rather than just increasing the amount of acetaldehyde, changes the calculated OH significantly (a factor of 2 in the analysis presented) and field measurements of OH would enable bounds to be put on the possible additional sources of PAN.

Specific Comments

1. Page 12936. How are the noontime HO₂+RO₂ calculated?
2. There is likely to be considerable uncertainty in the calculation of [NO]_{ss}. Clear skies should mean the value of J(NO₂) is fairly accurate, although aerosols could scatter radiation. Is the site sufficiently removed from direct emissions for the PSS to be reached? The HO₂+RO₂ concentration is also needed. Some comment on the uncertainty in [NO]_{ss}, and hence the NO/NO₂ used later, would be valuable.
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.
4. Using 1E6 appears not to have made a significant difference (line 3 on page 12942) except at certain ratios of NO/NO₂ - was this a surprise? Some further discussion here would be valuable.
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

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

some other label.

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 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_x) from one urban area to another.

D. E. Heard, N. Carslaw, L. J. Carpenter, D. J. Creasey, J. R. Hopkins, A. C. Lewis, M. J. Pilling, P. W. Seakins, "High levels of the hydroxyl radical in the winter urban atmosphere", Geophys. Res. Lett., 31, L18112, 10.1029/2004GL020544 (2004).

Emmerson, K. M. , Carslaw, N., Carslaw, D. C., Lee, J. D., McFiggans, G., Bloss, W. J., Gravestock, T., Heard, D. E., Hopkins, J., Ingham, T., Pilling, M. J., Smith, S. C., Jacob, M. J. and Monks, P. S., "Free radical modelling studies during the UK TORCH Campaign in summer 2003", Atmospheric Chemistry and Physics Discussions, Vol. 6, pp 10523-10565 (2006).

Technical corrections

1. Page 12930. Line 9, "of are be .." needs to be sorted out.
2. Page 12933. Line 8. Should there be a latitude here as N not E?
3. Page 12937. Line 20. 08:00 pm, should be 8:00 pm.
4. Several places: concentration units are molecule cm^{-3} and not molecules cm^{-3} . e.g. page 12939, line 23.
5. Line 21, page 12940, to be absolutely clear, put () around $2/3$.
6. Figure 6c. For scenario D, there is nothing before noon? 12941, line 28 during the scenario D discussion "PAN in the morning \ddot{E} " but the plot does not show the morning.

7. Page 12945, line 27 - “midday peaks” is confusing here, as it occurs after solar noon. Probably “peaks” is better. Line 28, concentration units again.
8. Line 28, 12945, Fig 4b
9. Page 12946, line 26, 27, units of concentration
10. Page 12946, line 21, the symbol is a diamond not a square
11. Page 12947, line 15, unit of concentration
12. Table 1. Footnote d. Add “see section 5 of text” after “estimated” so the reader knows where to go to see how the propanal is estimated.
13. Table 2. Footnote a, the Troe formula, there are two instances of “F” without the subscript c.
14. Table 3. title line 2, units of concentration
15. Table 4. Suggest changing models A, B, C to something else to avoid confusion with the earlier scenarios. Also, footnote a, “data are ..”. Footnote d, space after Orlando
16. Figure 4, spelling of September
17. Figure 5, concentration units on figure. I found it hard to distinguish the different lines on this figure - partly due to the small size of the figure. It might be better on screen, but not good on a hard copy. Also, the acetaldehyde concentration is given in molecule cm^{-3} , whereas the measured concentrations in Fig 4(a) are in ppb so hard to compare values. Keep the same?
18. Figure 6. Needs to be bigger, struggled to distinguish the various lines. For (c), scenario D, there does not appear to be a line before noon? The caption needs sorting out, there is only (a) and (b) given, despite there being 3 panels (a), (b) and (c). There is a bit missing. Plot (a) is mislabelled as scenario D. Plot (b) in caption should be plot

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

(c) and there is no plot (b) in the caption.

19. Fig 7, units of concentration. They are black diamonds and not squares?

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

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper