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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxy radical chemistry and the control of ozone photochemistry at Mace Head, Ireland during the summer of 2002" *by* Z. L. Fleming et al.

Anonymous Referee #2

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General comments:

This paper describes peroxy radical (HO2 + RO2) measurements during the NAMBLEX campaign at Mace Head, Ireland, during summer 2002. The data are analysed with respect to their major dependencies (photolysis frequencies, NOx, VOC) based on a discussion of (mean) diurnal cycles and correlation analyses. The same approach was used to discuss the net ozone production which was deduced from the peroxy radical measurements. While most of the presented analyses are based on observations a small part of the paper deals with peroxy radical model calculations. At this point my

feeling is that the paper looses some of its strength since the model approach as well as the results are presented in such a brief manner only that I found it quite difficult to follow the discussion concerning differences between observations and model results. In my opinion modelling of the peroxy radical measurements is important and therefore deserves and needs more space than the 'bits and pieces' in the present manuscript. However, as the paper is already quite long, the authors may consider to publish these results in an accompanying publication. Overall writing of the paper is clear and it is well within the scope of ACP so that I recommend publication after some revision.

Specific comments:

p12316, line above R10: OH oxidation of ...

p12316, line 22: omit 'that'

p12320, line 10: ... for any given ...

p12321, line 5: omit dot after b)

p12321, line 10: I guess the model was also constrained to NO, NO2, O3?

p12321, line 18: I suggest to rename the section 3.1 to 'Meteorological conditions and chemical climatology', drop the present title of section 3.2 and continue with 'Peroxy radical levels and diurnal cycles' as section 3.2

p12323, line 10: Generally, the average day-time ...

p12324, line 17-21: How was the slope of the regression line determined? What weighting of data was used in the fit? The usual least-squares linear regression approach is only valid if the precision of the x-axis data is much higher than the precision of the y-axis data which certainly is not the case for the present data set. For data sets with errors in both coordinates the 'fitexy' routine can be used instead (W. H. Press and S. A. Teukolsky and W. T. Vetterling and B. P. Flannery, 1992, Numerical Recipes in FORTRAN, 2nd Ed., Cambridge University Press, New York).

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p12324, line 22: Correlations of j(O1D), ...

p12324, line 25: I suggest to provide some information about the (average) concentrations of these compounds on the two days either in the figure or in the text.

p12325, 2nd paragraph: Here the authors discuss the influence of different photolytic sources on the production of peroxy radicals on two particular days. In order to provide some more quantitative information I think it would be helpful to show a time-series plot of the photolysis rates (J*[conc]) of the different molecules considered.

p12325, 4th paragraph: Please provide correlation coefficients as a quantitative measure of the 'goodness' of the correlations.

p12326: I would omit R13 since your discussion is on the radical channel only.

p12326, R15: Write HCO instead of CHO

p12326, R16: HCHO + 2O2 + hv

p12326, line 5-6: In the list of days I miss the 21st of August

p12326, last paragraph: Why is there no increase in HO2 from HCHO photolysis?

p12327, line 3: I can not deduce these NOx levels from Fig. 2

p12327, 2nd paragraph: Some of the sentences got mixed up

p12327, 2nd paragraph: I can see prominent NOx spikes on 8 August but not on 16 August.

p12327, 3rd paragraph: Fig. 8 needs some more technical explanation (in the text) on how the authors arrived at the data set shown in this plot (and others to follow later). What NOx bin width was used? What is plotted - the average (or median?) peroxy radical concentration in each NOx bin against the centre of the NOx bin? I am missing error bars in Fig. 8a. You could omit the blue trace which is not discussed in the text. Why does the red trace in Fig. 8b look so different from the red trace in Fig. 8a? Both

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are daylight peroxy radical concentrations plotted against NOx?

p12328, 2nd paragraph: Rather than showing all the different VOC's on a relative scale in Fig. 8b I would suggest to show the corresponding OH reactivities (limited to those which substantially contribute to the total reactivity) on an absolute scale since this is the quantity of interest in this context.

p12330, 1st paragraph: Fig. 9a shows that the observed HO2/(HO2+RO2) ratio varies considerably on 16. August. However, I can not deduce from this figure that this is the case for the modelled ratio as well. Fig. 9a does not show data for 21 August (which are referred to in the text).

p12330, 2nd paragraph: From the logical point of view the last sentence in this paragraph (RO2 reacts rapidly ...) seems to be meant as an explanation why the HO2/(HO2+RO2) ratio drops at high NOx. But in my understanding the last sentence proposes just the opposite (increasing ratio with increasing NOx)?

p12330, line 22: '... via Reaction (16) and (17) ...' should be '... via Reaction (17) and (18) ...'

p12331, Eq. 1: Since the quantity 0(CO + HCHO) is a dimensionless fraction the OH concentration (on the right hand side of this equation) must not show up. Further below the authors discuss possible reasons why this ratio does not match the observations. They argue that photolysis of HCHO is an additional important source of HO2 which is not taken into account by this fraction. So, why not include the HCHO photolysis rate (radical channel) into the equation?

p12332, Fig. 10: This figure shows peroxy radical and ozone data plotted against the HCHO/CO ratio. The authors have added a third-order polynomial but do not discuss the purpose of that in the text. I suggest not to include to polynomial in the figure.

p12333, section 3.6: I am missing a figure showing a 'typical' night-time series of HO2+RO2 measurements together with NO3 data.

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p12333, line 17: Increasing night-time HO2+RO2 with increasing NOx can be seen for 8. August (Fig. 7c) not for 16. August.

p12333, line 19-22: For the analysis of the dependency of HO2+RO2 on NO3 the authors discuss the dependency on NOx shown in Fig. 8a. Wouldn't it be a better approach to look at the dependence (HO2+RO2) vs. NO2*O3, the latter being the production term of NO3?

p12335, 1st paragraph: Additional reference for RO2-NO3 measurements and their interpretation: Geyer et al., Nighttime formation of peroxy and hydroxyl radicals during the BERLIOZ campaign: observations and modeling studies, JGR, 108 (2003)

p12336, line 16-19: Sign and magnitude of the net ozone production very much depend on the wind sector considered. I therefore suggest to replace the mean N(O3) diurnal cycle averaging over all wind sectors in Fig. 14 by two graphs for the clean and the polluted wind sector regimes.

p12337, line 17-18: Are the dlnP(O3)/dln(NO) values of the different campaigns in Table 6 statistically different?

p12337, line 19-21: The authors state that, not unexpected, the loss rate of ozone does not depend on NO. While this is true for most of the campaigns listed in Table 6 it's the NAMBLEX campaign which makes an exception with a surprisingly large value of dlnL(O3)/dln(NO). The authors should comment on that.

p12349, Table 1: I am missing an entry for O3.

p12350, Table 2: Why is N(O3) listed in Table 2 but not in tables 1 or 3?.

p12353, table caption: The table lists only the mean but not the min and max values of N(O3).

p12359, Fig. 5: I suggest to show NO instead of NOx in the diurnal cycles since the concentration of NO rather than NOx determines the HO2 and RO2 levels. I further

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suggest to omit the regression lines in the plots of the third raw in Fig. 5 since they are not discussed in the text. Furthermore, for the 23. August a linear regression is completely meaningless.

p12367, Fig. 13: Please comment on the low loss rates of ozone on 17. and 18. August. According to Fig. 2 photolysis frequencies where quite within the range of the other days.

Technical notes on Figures:

In general the layout of the graphics needs to be improved. Many of the figures are hard to read since they contain too much information or are too small and/or are not well reproduced neither in the online nor in the printed version of the manuscript.

In general:

- Quite often the axes titles run into the axes labels.

- I recommend not to put additional axes inside of a plot since this leads to very obscure figures.

- The same is true if x-axis labels are inside rather then below the plot.

- On most of the axes titles the parameter name is separated from the unit using a '/'. On some axes titles the separator is missing.

- Some figure captions refer to panels (a), (b), ... which are not denoted as such.

- Some figures show up in a 'box style' manner (box around the plot area) while others do not. This is the case even for different panels in the same figure. I suggest to put a box around every plot.

In detail:

Fig. 1: (a) The pie chart doesn't really help. The fraction of each wind sector can easily be judged from the bar plot. If the authors wish to provide more quantitative information

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in the plot I suggest to put the fractional numbers below the wind sector labels. (b) The 3 trajectory plots are too small, enlargement of the figures doesn't help due to their very limited resolution. The contour lines are hard to see.

Fig. 2: The axis label reads 'NO' while legend and figure caption show 'NOx'.

Fig. 3: Choose the same order of axes in figs. 2 and 3. Choose the same width, time scale and time axis labels for all three panels of fig. 3. Figure caption: '... diurnal cycles for all campaign data and W and NE air-mass sector data subsets.'

Fig. 5: The trajectory as well as the correlation plots are much too small. In the latter I can't read axes titles or legends. There seem to be no marks along the trajectories to indicate the position of the air mass on the different days. Does the photolysis frequency 'j(HCHO)' refer to the radical channel only?

Fig. 6: Figure caption: '... diurnal cycles ...', omit 'h-1'. Does the photolysis rate 'j(HCHO)x[HCHO]' refer to the radical channel only?

Fig. 7: The order of the plots is different from what is listed in the figure caption. Either use an increasing or decreasing date to order the plots. Mixing the chronology generates confusion. The plots should be correctly aligned to have the same time-of-day mark on every vertical line.

Fig. 8: These figures are too small and very hard if not impossible to read. Choose the same unit for NOx in all 6 panels.

Fig. 9: The correlation plot shows data from 21. Aug. which are not part of the time series plot (wrong date in figure caption).

Fig. 10: What is the data basis? A mean diurnal cycles? Meaning of the error bars is missing.

Fig. 12: (a) Misleading numbers on y axis scale. (b) Difference in colour hard to tell on printout.

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Fig. 13: I suggest to expand the time scale so that some more details can be seen.

Fig. 14, 15: Shouldn't the ozone loss show up with a negative sign in the plots?

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12313, 2005.