

## ***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.***

**Z. L. Fleming et al.**

Received and published: 3 March 2006

The authors are grateful to the referee for his/her insightful comments on the paper.

The referee suggests an expanded modelling section or another paper dealing with the model/measurement comparison. The NAMBLEX radical model results are dealt with at length by Sommariva et al. (ACP(D), 2006) in two papers looking at daytime and night-time radical chemistry. The results in the Fleming paper deal with the specific peroxy radical model/measurement and it is not thought necessary to duplicate information in the other papers.

We have dealt with all the typographic errors in the paper, in accordance with the ref-

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

eree's suggestions. The comments in relation to scientific points are dealt with below.

The referee is correct in respect of the requirement for a bivariate linear regression for the data in Figure 4. Unfortunately, this software was not available. In order to test the need for a FITEXY type analysis, a number of statistical indicators were run. A bivariate correlation analysis, suggests the Pearson correlation (significant at the 0.01 level) was 0.838 for  $x_1$  vs  $x_2$  and v.v. When this is compared to the normal regression analysis the derived value of  $r^2$  was identical the standard error was different. This suggests in this case the assumption of a normal linear regression model does not make a large difference.

The average concentrations have been added to Figure legend 5, as suggested. The data in the lower panels of Figure 5, illustrate the very point the referee raises with respect to the quantification of  $j.[X]$ , in that for HCHO the data is shown, this as the text points out is the major contributor.

The correlation coefficients have been added to Figure 6 to illustrate the arguments on pg 12325 paragraph 4.

With respect to reaction (13), it is felt better to leave both channels in for completeness. We feel it is misleading to only display one channel.

It is not clear why the  $\text{HO}_2$  measurements do not respond in the same way to cloud modulation. The phenomenon bears more research.

With respect to the  $\text{NO}_x$  spikes, inspection of Figure 7 clearly shows the spikes on the 16th August. Both the 8<sup>th</sup> and 16<sup>th</sup> experienced high  $\text{NO}_x$  levels, the 8<sup>th</sup>, in the form of a few hours of high  $\text{NO}_x$  in the morning, that suppressed the radicals throughout the day, but as the  $\text{NO}_x$  died down towards the afternoon, the radicals formed in the late afternoon, leading to a shifted diurnal, with the highest concentrations around 17-18.00. On the 16th August there was a sudden  $\text{NO}_x$  spike, lasting about an hour or so around midday, when the radicals would have been highest, this meant that the ap-

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

parent/observed diurnal cycle was shifted towards the late afternoon, as the reduction in NO<sub>x</sub> after the spike lead to a sudden high radical production in the afternoon which persisted until after 18.00.

In general, the binning used for data (including that displayed in Figure 8) was using equal log normal (NO) bin widths. This follows the method used for example in the Berlioz experiments (Holland *et al.*, 2003). A sentence has been added to the text to explain this. The mean peroxy radical concentration for that bin is then plotted against the mean NO. The figure legend clearly states the data-subsetting (daytime) used for the averaging process.

For Figure 8b, as the referee suggested the OH reactivity has been moved onto an absolute scale, giving clearer results.

The data for Figure 9 has been replotted to make it clearer in respect of the variation of the modelled HO<sub>2</sub>/HO<sub>2</sub>+RO<sub>2</sub> and the measured data. The agreement is best on the 16<sup>th</sup> August. Further, the data series has been extended to the 21<sup>st</sup> August.

The referee is correct with respect to the contradiction in the text at high NO<sub>x</sub> in the original text on pg 12330. The repartitioning of OH to HO<sub>2</sub> by NO will be dominant, it is the relative rate of RO<sub>2</sub>+NO *vs.* HO<sub>2</sub>+NO, that must control the HO<sub>2</sub>/HO<sub>2</sub>+RO<sub>2</sub> ratio.

With respect to equation (1), the referee is correct that this is a dimensionless fraction. The analysis centred around equation (1) was to investigate OH reactivity hence the preclusion of  $j(\text{HCHO})$  chemistry.

The night of 28th/29th of August has been added to Figure 11 to show a typical night.

For the night of the August 16th (Figure 7b), there is a clear increase in NO<sub>3</sub> with NO<sub>x</sub> not present on the 8th, this has been added to the text.

The referee is correct the dependency with NO<sub>2</sub>+O<sub>3</sub> (O<sub>x</sub>) would be more appropriate for the night time chemistry. Figure 8a was constructed to provide a common chemical co-ordinate for comparison.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

As suggested by the referee, Figure 14 has been changed to two panels containing the average diurnal cycles in N/L/P(O<sub>3</sub>) under clean and polluted (as defined in the figure legend) conditions.

For the data in Table 6, values for the  $1\sigma$  standard deviation have been added to give the reader a feel for the statistical significance. The original NAMBLEX value of  $d\ln L(\text{O}_3)/d(\text{NO})$  in Table 6 was erroneous, the real value being 0.32, in line with the other semi-polluted values.

N(O<sub>3</sub>) is listed only in Table 2, as it is a daylight average quantity. If listed in Table 1 it would have to be a 24 hour average and in Table 3 it would be equal to zero (i.e. night).

The apparent low ozone loss rates observed were an artefact of some error in the ozone measurements, with ozone apparently dropping from ca. 30 ppbv to 2 ppbv on these dates. These data have been excluded from the analysis.

In line with the referee's comments, the figures have been extensively revised. The general style points have been carried out as far as possible.

In reference to specific comments raised in relation to individual figures.

Figure 1 - Pie chart and trajectory panels removed.

Figure 5 - The figure has been substantially revised in line with the referee's comments. Values for the correlation coefficients have been added to the text.

Figure 14, 15 - It is our preference not to plot  $L(\text{O}_3)$  with a negative sign, as this allows direct comparison of the magnitude of P L (O<sub>3</sub>).

---

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

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)