

Interactive comment on “Hohenpeissenberg Photochemical Experiment (HOPE 2000): Measurements and photostationary state calculations of OH and peroxy radicals” by G. M. Handisides et al.

G. M. Handisides et al.

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The authors wish to thank reviewer #1 for his/her comments. We will respond to each of the points in detail below.

1. We will follow the suggestion, and the conclusion has been changed to reflect this recommendation.
2. There are only a limited number of studies which have been carried out in similar conditions to those experienced during HOPE. A further problem is that most published RO_x measurements were made using the chemical amplifier and were published before the discovery of the water effect. As a result, almost all of the previously pub-

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lished results using a chemical amplifier do not take the water effect into account and consequently the RO_x mixing ratios need to be adjusted upwards. Nevertheless, the published results do indicate the range to be expected for RO_x mixing ratios. Mixing ratios as high as 300 pptv were measured by [Cantrell et al.(1993)] during ROSE, under conditions of high biogenic emissions.

The RO_x measurements made during BERLIOZ did include an adjustment for water vapour [Platt et al.(2002)]. Typical daily maximum RO_x mixing ratios were 15-30 pptv, with mixing ratios of 40-50 pptv being observed on three days. Daily maximum HO_2 mixing ratios of 10-20 pptv (over 30 pptv on one day) were also observed. The daily maximum OH concentration ranged from $5-8 \times 10^6 \text{ cm}^{-3}$. The presence of high NO_x levels depressed the HO_2 and RO_2^* mixing ratios greatly, and the OH concentration by a factor of 2.

During PROPHET, [Tan et al.(2001)] measured HO_2 using LIF and used these results to model RO_2 . The daily median of the HO_2 mixing ratio was around 10 pptv, with a daily maximum of 20 pptv. Nighttime levels were around 2-3 pptv. The modelled RO_2 mixing ratio was 30-50 pptv, resulting in total maximum RO_2^* levels in the range of 50-70 pptv. The OH concentration was around $2-3 \times 10^6 \text{ cm}^{-3}$ (median), a daily maximum of about $7 \times 10^6 \text{ cm}^{-3}$, and a nighttime concentration of $0-4 \times 10^6 \text{ cm}^{-3}$. However, the conditions during PROPHET appear to have been quite different to those experienced during HOPE 2000, with the PROPHET chemistry being dominated by isoprene. Monoterpenes seem to have played a much lesser role during PROPHET. Thus, it is difficult to make a simple comparison.

These measurements indicate that the current RO_x measurements, while higher than some recent studies, are still within the expected range. Further measurements are required. A short statement has been added to the text to reflect this.

3. [Salisbury et al.(2001)] reported higher nighttime RO_x production rates due to alkene-ozone reactions than due to alkene- NO_3 reactions in the oceanic environ-

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ment. However, NO_2 mixing ratios were substantially lower than those observed during HOPE, e.g. by factors of 2-10. Consequently, the role played by NO_3 chemistry in the marine boundary layer investigated by [Salisbury et al.(2001)] is expected to have been much smaller than its role in the mid-continental rural environment investigated in the present study. In Scenario V, we estimated that the effect of ozonolysis of alkenes on the RO_x level at night was smaller than that of NO_3 by a factor of 8 on average. If we include the production rate of OH from ozone-alkene reactions in this estimate, the ratio would be 3.5. However, since these considerations are based on an estimate of the upper limit for RO_2 production from NO_3 -alkene reactions, the reference to the role of NO_3 chemistry at night has been reworded in Section 4.4. NO levels of 6 pptv do not present a major sink for NO_3 .

4. The potential role of oxidation products of biogenic hydrocarbons was considered by assuming that oxygenated hydrocarbons made a contribution equal to the measured hydrocarbons. This led to an overprediction of RO_x and an underprediction of OH during most of the measurement period. As the presence of oxygenated hydrocarbons is already taken into account by assuming the presence of 3 ppbv HCHO, doubling the effect of the NMHCs is probably an extreme assumption. This is discussed in the text in Section 4.4.

5. Heterogeneous loss of HO_2 was not considered. However, we have added a comment to this point in section 4. Sampling of scrubbed gases appears to be highly unlikely. A remark has been added. We checked the possibility of uptake of OH on surfaces and commented on this in the revised manuscript. The ratio between measured/modelled data did not show any correlation with the local wind speed.

6. The text is correct (1.6 m). The reaction time in the tube is 0.66 s.

7. Please refer to the response to Point 9 of Reviewer #2 in the accompanying authors' response.

8. The NO mixing ratio has been included in two panels with different scales in Figure

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2. In the lower panel the scale is extended to allow the general level of NO to be determined. As a consequence the spikes are cut off in the lower panel. The NO concentration has been retained in the upper panel to allow a direct comparison with NO₂.

9. We have added detailed information to the end of Section 2 concerning this point.

10. We have added a sentence towards the end of Section 2 concerning peak separation. The problem of the potential presence of organic compounds which were not included in the measurements is now addressed more thoroughly in section 4.4.

11. The role of NO has been checked, and proved to be of minor importance at night as the NO mixing ratio was below 6 pptv at night. A corresponding sentence has been included in the revised manuscript.

12. Photolysis frequencies for clear sky conditions obtained using the STAR model (j_{NO_2} and $j_{\text{O}_1\text{D}}$) were compared to measurements by filter radiometer for a 4-year period at Hohenpeissenberg. Great care was taken concerning calibration of the filter radiometers and current recommendations for quantum yield and cross sections have been used. Excellent agreement was found within the range of the stated uncertainties. Thus, the STAR model is expected to provide realistic photolysis frequencies for daytime clear sky conditions, such as those which prevailed during HOPE 2000 (C. Plass-Dülmer, H. Berresheim, J. Reuder, and E. Tensing, unpublished results).

13. We agree, although a more complex model such as MCM does not necessarily render better agreement with "reality" for any given conditions, for one reason because it is likewise limited by the measured parameters. In the conclusions we express our intentions to pursue a broader based measurement and model study in the future.

14. In Section 4.1, the OH lifetime is stated as being ≤ 0.5 sec. Most of the time it was much smaller, and only approached 0.5 sec at night. However, we wanted to give an upper limit in order to justify the steady state assumption made.

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15. Not necessarily, it could also be due to modelling problems! However, in this case the reviewer is quite right and we have removed this sentence.
16. We agree. The variability of the HO₂/RO₂ ratio was commented on in Section 4.4. As pointed out in the conclusion, this ratio definitely needs to be considered in future studies.
17. We indeed hope that more measurements will be carried out!
18. Thank you!

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