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Interactive comment on "Concentrations of OH and HO$_2$ radicals during NAMBLEX: measurements and steady state analysis" *by* S. C. Smith et al.

S. C. Smith et al.

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The authors would like to thank both anonymous referees and Professor Thornton for their comments, all of which have been taken into account in the revised manuscript. The discussion below contains our response to the more general comments from the referees and Professor Thornton, and also our point-by-point response to the specific comments from the two anonymous referees.

1. Response to general comments

The four case study days were selected to be representative of the different conditions encountered during the NAMBLEX campaign, allowing a detailed description of the response of OH and HO_2 radicals to their controlling variables. The days selected as case studies are also used throughout sections 5.2 and 5.3 for the steady state analysis of the OH and HO_2 measurements. However, we would also like to keep the paper as concise as possible in order to focus on the main scientific results and have therefore removed the section on case study days from the revised manuscript, as suggested by the referees. This shortens the paper by eight pages.

In response to the comments of both Professor Thornton and Referee One, the authors would like to clarify that this paper along with that by Sommariva et al. (2005a) (also part of the NAMBLEX special issue) are being used to investigate potential HO_2 sinks which may account for model over-predictions of HO_2. Both papers use a reaction probability, γ_{HO_2}, of (up to) 1.0 to investigate the maximum possible impact of heterogeneous chemistry upon HO_2 concentrations (as a direct sink of HO_2). We are not suggesting that a value of 1.0 is correct or appropriate for uptake on sea salt aerosol in the MBL, and have made comments to this effect in the revised manuscript, including a reference to the recent HO_2 uptake work by Thornton and Abbatt (Thornton and Abbatt, 2005). Calculations of HO_2 concentrations using the cubic equation (5) and several adaptations of it, as displayed in Figs. 8 and 9, and also those from MCM modelling shown in Fig. 6 of Sommariva et al. (2005a), clearly illustrate that even using the maximum possible theoretical value for γ_{HO_2} of 1.0, uptake of HO_2 onto aerosols cannot fully account for the discrepancy between calculated and measured HO_2 concentrations. It is only upon inclusion of the reaction of HO_2 with ($[IO]_{meas} \times 10$) that the calculated / measured HO_2 ratio is found to be significantly closer to unity. Further to this, Sommariva et al. (2005a) find that if the hypothesis that IO concentrations at the

HO_2 measurement site are a factor of 10 greater than those measured as the average across the DOAS light-path (Saiz-Lopez et al., 2005b), then γ_{HO_2} is likely to be significantly smaller than 1, as otherwise HO_2 would be significantly underestimated by the model (see Sommariva et al. (2005a) Figs. 6 and 8). So it would appear that the influence of halogen species is more important than heterogeneous loss for perturbing the model-measurement HO_2 bias under the conditions at Mace Head, consistent with the comment of Professor Thornton that γ_{HO_2} is likely to be < 0.1. We plotted the calculated / measured HO_2 ratio versus aerosol surface area as suggested by Professor Thornton, but there is not sufficient dynamic range to draw any definitive conclusions. We also plotted the calculated / measured HO_2 ratio versus aerosol composition (concentrations of nitrate, sulphate, organics and ammonium in the aerosol particles (Coe et al., 2005)), and again found no correlation.

2. Point-by-point response to specific comments

2.1. Referee One

p12412 line 23/24. The laser to nozzle distance in the OH cell is 90 mm (see p12412 line 21). The laser to nozzle distance in the HO_2 cell is 400 mm because of the presence of both the NO injection ring and a spacer which increases the distance below the nozzle at which NO is injected improving the HO_2 to OH conversion efficiency.

p12415 line 20. Calculations of the effect of H_2O collisional quenching on the OH ($A^2\Sigma^+$) fluorescence quantum yield have been carried out using rate constants from Bailey et al. (1997 and 1999). These calculations show that over the range of ambient water vapour mixing ratios ($0.5 - 2.0\%$) experienced during the NAMBLEX campaign there should be an 18% decrease in the OH fluorescence quantum yield and hence the instrument sensitivity for a cell pressure of 1 Torr. However, several experiments carried out on the instrument both in the NAMBLEX configuration (nozzle sizes, pressures, laser to nozzle distances etc) and other configurations show that the sensitivity is independent of water vapour in the mixing ratio range $0.5 - 2.0\%$. Clearly there are other controlling factors involving water vapour which balance the expected quenching decrease.

p 12416 line 24. This is a typographical error and should say that solar background, S_{sb}, is zero during the night. This has been corrected in the revised manuscript.

All figures. The font is larger for all axes annotations in the revised manuscript.

p12419 line 7. The case study section has been removed from the paper as suggested.

Fig. 6 The measurements are plotted as blue diamonds in the revised figure.

p12430 line 1. The total OH reactivity was not measured during NAMBLEX, as the Leeds instrument was still at the building stage at this time. The instrument's first deployment was in 2003 as part of the Tropospheric Organic CHemistry experiment (TORCH 2003) (Ingham et al., in preparation).

p12430 line14. Steady state concentrations of HO_2 have been calculated both with and without the term for HO_2 production from the reaction of H_2 with OH. These calculations illustrated that the HO_2 concentrations were on average 4.2% lower for steady state calculations which omitted HO_2 production from H_2. A comment on this calculation has been included in the revised manuscript. Rate of production analyses carried out using the Master Chemical Mechanism by Sommariva et al. (2005a) found that the OH + H_2 reaction contributed on average 6% to HO_2 production.

p 12435 line 7. Dealt with already in the response to the general comments.

p 12438. The modelled to measured OH ratio shows no dependence on measured NO. However, it must be noted that the majority of the data points (855 out 968) lie in the NO range between $0-50$ pptv, and over half (584 out of 968) are in the range $0-20$ pptv. Hence it would be difficult to carry out any NO_x dependence analyses on the NAMBLEX HO_x data set due to this very limited dynamic range.

2.2. Referee Two

The following deals with replies to specific comments from Referee Two (as four separate points) that have not been dealt with in the general reply above:

1) The eight days used for the OH steady state analyses were 10 and $15-21$ August. The six days used for the HO_2 steady state analysis were 13, $15-16$ and $18-20$ August. These dates are already stated several times in the main text (for example, p. 12426 line 11 and p.12431 line 7) as well as in the figure and table captions related to the calculations (Fig. 7 - 9, Tables 3 and 4) and hence the authors do not feel that any revisions to the manuscript are necessary for this comment.

2) We believe that using a simple approach to simulate / interpret the measured data is likely to give a clear scientific understanding. The OH data are amenable to a steady

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state treatment and so the greater complexity of numerical integration, i.e. a box model, is not necessary in this paper. For HO_2, an approximate analytical treatment can be developed, as described in the paper, and used for comparison with measured values to obtain an insight into the gross importance of reactions with halogen oxide species and aerosol loss as HO_2 sinks. The non-linear dependence upon $[HO_2]$ introduced by the HO_2 and RO_2 self- and cross-reactions necessitates a fuller model approach for exact simulation, as presented in the accompanying paper by Sommariva et al. (2005a).

By carrying out steady state analyses on the NAMBLEX OH and HO_2 data we have also emphasised the caution with which comparisons between OH and HO_2 measurements and model calculations should be interpreted. The steady state analyses reported in this paper, which clearly omit many of the less crucial OH and HO_2 sources and sinks, nevertheless reproduce the measured OH and HO_2 concentrations with a similar level of accuracy as obtained when using a full chemical mechanism based on the MCM (discussed in Sommariva et al. (2005a)). Whilst recent improvements in chemical mechanisms for predicting OH and HO_2 have led to better agreement with measurements, good agreement can also be obtained via the balancing out of missing sources and sinks, a point that ought not to be forgotten when interpreting model / measured ratios.

One of the underpinning results from the steady state analysis of the NAMBLEX OH data was the very clear diurnal pattern in the calculated / measured OH ratio (Fig. 7). This finding provides further evidence to support the importance of non-primary OH production through photolysis of precursors at longer wavelengths than those required for O_2 photolysis, which are of particular importance in the early morning and evening, and not included in the steady-state analysis.

3) The rate constant used in the steady state analyses in this paper was the new value, $k_{O(^1D)+N_2} = 2.1 \times 10^{-11} exp^{(115/T)}$ cm^3 $molecule^{-1}$ s^{-1}, as reported in Ravishankara

et al. (2002). This value is the average of recent measurements from three separate universities, including our own, and is an 18% increase (at room temperature) on the previous recommended value (Atkinson et al., 2001). The effect of using this new rate constant compared to that reported in the earlier evaluation (Atkinson et al., 2001) has been investigated using the NAMBLEX data, and it was found that the new rate constant decreased the calculated OH concentration by an average of 10.9%.

4) The source of the free-radicals observed at night-time is NO_3 chemistry augmented by a small contribution from the ozonolysis of alkenes. The night-time radical data are the subject of a forthcoming paper to be submitted to this NAMBLEX special issue (Sommariva et al., 2005b), in which the night-time free-radical chemistry during NAMBLEX is investigated using a number of observationally constrained zero-dimensional box models, based on the MCM.

We wish to thank Dr. Roberto Sommariva for discussions concerning the comments regarding uptake of HO_2 onto aerosols.

References

[Atkinson, R. (2001)] Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson Jr, R. F., Kerr, J. A., Rossi, M. J., and Troe, J.: Summary of evaluated kinetic and photochemical data for atmospheric chemistry, 2001.

[Bailey(1997)] Bailey, A. E., Heard, D. E., Paul, P. H., and Pilling, M. J.: Collisional quenching of OH ($A^2\Sigma^+$, $\nu' = 0$) by N_2, O_2 and CO_2 between 204 and 294 K. Implications for atmospheric measurements of OH by laser-induced fluorescence, J. Chem. Soc. Far. Trans., 93 (16), 2915-2920, 1997.

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[Bailey(1999)] Bailey, A. E., Heard, D. E., Henderson, D. A., and Paul, P. H.: Collisional quenching of OH ($A^2\Sigma^+$, $\nu' = 0$) by H_2O between 211 and 294 K and the development of a unified model for quenching, Chemical Physics Letters, 302 (1-2), 132-138, 1999.

[Coe(2005)] Coe, H., Allan, J. D., Alfarra, M. R., Bower, K. N., Flynn, M. J., McFiggans, G. B., Topping, D. O., Williams, P. I., O'Dowd, C. D., Dall'Osto, M., Beddows, D. C. S., and Harrison, R. M.: Chemical and Physical Characteristics of Aerosol Particles at a remote Coastal location, Mace Head, Ireland, during NAMBLEX, Atmos. Chem. Phys. Discuss., accepted, 2005.

[Ingham(2006)] Ingham, T., Self, D. E., Read, K. R., Johnson, G. P., and Heard, D. E.: An instrument for the measurement of ambient OH reactivity using low-pressure laser induced fluorescence., in preparation.

[Saiz-Lopez(2005)] Saiz-Lopez, A., Shillito, J. A., Coe, H., and Plane, J. M. C.: Measurements and modelling of I_2, IO, OIO, BrO and NO_3 in the mid-latitude marine boundary layer, Atmos. Chem. Phys. Discuss., 5, 9731-9767, 2005b, SRef-ID 1680-7375/acpd/2005-5-9731.

[Sommariva(2005b)] Sommariva, R., Ball, S. M., Bitter, M., Bloss, W. J., Brough, N., Fleming, Z. L., Heard, D. E., Jones, R. L., Lee, J. D., Monks, P. S., Penkett, S. A., Pilling, M. J., Plane, J. M. C., and Saiz-Lopez, A.: Night-time radical chemistry during the NAMBLEX campaign, Atmos. Chem. Phys. Discuss., to be submitted, 2005b.

[Sommariva(2005a)] Sommariva, R., Bloss, W. J., Brough, N., Carslaw, N., Flynn, M., Haggerstone, A. L., Heard, D. E., Hopkins, J. R., Lee, J. D., Lewis, A. C., McFiggans, G., Monks, P. S., Penkett, S. A., Pilling, M. J., Plane, J. M. C., Read, K. A., Saiz-Lopez, A., Rickard, A. R., and Williams, P. I.: OH and HO_2 chemistry during the NAMBLEX: Roles of oxygenates, halogen oxides and heterogeneous uptake, Atmos.

Chem. Phys. Discuss., 5, 10947-10996, 2005a, SRef-ID: 1683-7375/acpd/2005-5-5405.

[Sommariva(2004)] Sommariva, R., Haggerstone, A. L., Carpenter, L. J., Creasey, D. J., Carslaw, N., Heard, D. E., Lee, J. D., Lewis, A. C., Pilling, M. J., and Zador, J.: OH and HO_2 chemistry in clean marine air during SOAPEX-2, Atmos. Chem. Phys., 4, 839-856, 2004, SRef-ID: 1680-7324/acp/2004-4-839.

[Thornton(2005)] Thornton, J., and Abbatt, J. P. D.: Measurements of HO_2 uptake to aqueous aerosol; Mass accommodation coefficients and net reactive loss, J. of Geophys. Res.-Atmos., 110 (D8), doi:10.1029/2004JD005402, 2005.

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