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Interactive comment on “OH and HO$_2$ chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake” *by* R. Sommariva et al.

Anonymous Referee #2

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General comments. This paper demonstrates that the chemistry of OH and HO2 at Mace Head is highly influenced 1) by the treatment of oxygenates, 2) by the bromine and iodine chemistry, and 3) by the heterogeneous uptake of HO2 on aerosol surfaces by performing many zero-dimensional photochemical box model runs. The model calculations are fully constrained by ancillary observations including aerosol size distributions and, for the first time, by the concentrations of BrO or IO. The model results agreed better with the observed OH and HO2 concentrations when the halogen chemistry and/or the heterogeneous loss of HO2 constrained in such ways are taken into account, suggesting that the processes could be important at coastal sites. The authors

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also specify that the model results are sensitive to the assumed uptake coefficients of HOBr, HOI, and HO2. Generally, the authors provide sound analyses and present their results clearly throughout the manuscript. However, there are still some more points need to be clarified. Especially, there are several cases with Figures 5-7 where the magnitude relation of the HO2 concentrations from several model runs is suspicious. In section 7, the names of the model runs, used for each specific comparison, should be clearly written in text. Overall, the paper fits into the scope of Atmospheric Chemistry and Physics and I recommend publication after minor revision.

Specific comments. 1. Abstract, line 16. The sentence “The best agreement with the measurements was achieved by constraining the model to measured IO and setting gamma(HO2)=1 and gamma(HOI)=0.6.” might give the wrong impression that the model perfectly agreed with the observations by precisely tuning the two gamma parameters. The authors should make it clear that the parameters are selected only from two very different values.

2. page 10951, lines 1-6. The field locations of the past studies of Sommariva et al. (2004), Carslaw et al. (2002), and Kanaya et al. (2001) should be specified.

3. page 10952, lines 15-18 and Figure 1. The authors mention in the caption of Figure 1 that different colors indicate single trajectories calculated by different model runs. What do the authors mean by different model runs?

4. page 10953, lines 2-4. The low [NO]/[NO2] ratio indicates that the measurement is not affected by local NO sources but does not necessarily indicate that the air mass is chemically processed long. The ratio could also be lowered by the reactions of IO and BrO with NO, producing NO2.

5. page 10954, lines 10-11 and Table 2. Although it is indicated in text that the R**2 value for HCHO is lower than 0.9, the values for HCHO in Table 2 are higher than 0.9. Please check this.

6. pages 10953-10954. Although it is mentioned that the photolysis of HOI takes place in the same wavelength to that of NO2 (page 10953, lines 22-23), it is not clearly indicated afterwards that j(HOI) on 15 and 17 August is determined in relation to j(NO2) measured with the filter radiometer.

7. pages 10953-10954. How large is the day-to-day variation of the total column amount of O3? Does it affect the estimation of J values described here?

8. page 10955, lines 4-6. This is just a comment. It is suggested here that short variability due to clouds cannot be taken into account if the calculated j values are used. However, by considering the so-called "cloudiness factor", defined as the ratio of observed j(NO2) to calculated clear-sky j(NO2) for example, j values under the cloudy conditions can be estimated even with the calculated j values.

9. pages 10955 and 10956. In the "clean" and "full" model runs, are the concentrations of oxygenates (aldehydes, carbonyls, and alcohols) and peroxides constrained to zero? Or are they rather calculated simultaneously by considering the degradation chemistry of hydrocarbons and the loss processes of the oxygenates (deposition, photolysis, and reactions with OH)? The deposition velocities of aldehydes and peroxides are figured in page 10956, which might imply that in some model runs the concentrations of these species are rather calculated. If so, are the measured acetaldehyde levels higher than those calculated in the "full" run? This might be important when the impact of acetaldehyde on OH and HO2 is investigated from the difference between the "full" run and the "fulloxy" run.

10. pages 10955 and 10956 and Tables 1 and 3. Table 3 and text in line 18 of page 10955 indicate that the HCHO concentrations are constrained to measured values in all the model runs. Which HCHO measurements are used, UEA or Leeds (Table 1)? How sensitive are the HOx results to the HCHO data set selection?

11. page 10956, lines 22-23. It should be mentioned that heterogeneous uptake was calculated using Eq. (1) "in the four base runs," to distinguish them from the improved

runs described in section 6.

12. page 10960, line 9. The authors wrote that isoprene is a “likely” explanation for the discrepancy between the OH levels from two model runs. However, the processes in the models should be fully analyzable, and thus the authors should avoid the word “likely.”

13. page 10960, lines 17-28. HCHO treatment is not clear. It is implied here that the HCHO concentrations are different in the two model runs “fulloxy” and “clean”, which is inconsistent with the description that HCHO is always constrained at measured levels (From Table 1, it is likely that HCHO measurements are still available on 21 August). It rather seems that the HCHO concentration is calculated for this day. Another inconsistency is present between the sentence in lines 20-21 indicating that k[OH][HCHO] is 1/3 of k’[OH][CO] in the “clean” model run and the sentence in lines 25-26 indicating that k[OH][HCHO] is half of k’[OH][CO] in the same model run.

14. page 10961, lines 11-12 and Figure 4. The NO concentration is figured in ppt in text, while it is in number density in the right axis of Figure 4. The description about the impact of NO pollution on HO2 seems to be repeated here in reference to the earlier paragraph in lines 19-24 of page 10959.

15. page 10962, lines 20-25. It is important to describe the BrO and IO concentration ranges and variations used as input parameters of the model. In this regard, Saiz-Lopez et al. (2004) is a good reference, where the temporal variation of [BrO] on 31 August is described. For [IO] during 15-21 August on the other hand, it would be better to cite Saiz-Lopez et al. (2005b, “Measurements and modelling of I2, IO, OIO, BrO and NO3 ..”) in this special issue of ACP, rather than Saiz-Lopez and Plane (2004).

16. pages 10963 and 10964. What is the size range of the aerosols taken into account? 3 nm to 20 micrometer as described by Coe et al. in this special issue? Instruments used to measure the size distributions of the aerosol number density should be briefly mentioned.

17. page 10964, equation (2). An equal character at the end of the first line should be deleted. An integral is needed immediately after the equal character in the second line.

18. page 10964, lines 14-15. Which values are used for D_g of HO2, HOI, and HOBr?

19. page 10964. Can the authors give the range of the calculated heterogeneous uptake rates of HO2, HOI, and HOBr at least roughly?

20. page 10966, lines 23-25. Figure 5b contains the results from several model runs. It should be mentioned specifically that “fulloxy-io-het_hoi” is the only run using gamma(HOI)=0.06 and its results are compared with the results from the “fulloxy-io-het” run.

21. pages 10966 last line - page10967 line 2. I could not understand the sentence. Which additional effects are expected on OH when NO and NO2 concentrations are higher?

22. page 10967, line 2. Maybe not Fig. 9 but Fig. 5?

23. page 10967, lines 4-7. Maybe not Figure 9 but Fig. 5b? Please specify in text that the results from the “fulloxy-io-het_ho2” and “fulloxy-io-het” runs, with different values of gamma(HO2), are compared here.

24. page 10967, lines 23-25. Please specify which model runs are compared in text. (maybe throughout this section) In this case, the authors should perhaps indicate them by “the uptake coefficient of HOI was decreased from 0.6 in the “fulloxy-io-het” run to 0.06 in the “fulloxy-io-het_hoi” run”...

25. page 10967, line 26-page 10968, line 1. It should be additionally mentioned here that if gamma(HO2)=1.0, the use of the transition regime expression instead of the free-molecular expression could cause a significant difference. This is presented in Figure 5 of Coe et al., in this issue.

26. page 10967, line 26-page 10968, line 1 and Figure 6a. It is strange to me in Figure

6a that HO2[fulloxy-io] is higher than HO2[fullyoxy-io-het]. The use of the transition regime in the “fullyoxy-io-het” run should result in lower heterogeneous uptake rates of HO2 and HOI than those calculated with the free-molecular expression in the “fulloxy-io” run, which should then result in higher HO2 concentrations in the “fullyoxy-io-het” run. I do not understand similarly (1) why HO2[fulloxy] is higher than HO2[fulloxy-het] in Figures 6a and 7b, (2) why OH[fulloxy-io] is higher than OH[fulloxy-io-het] on 16 August in Figure 5a, and (3) why HO2[fulloxy-bro] is higher than HO2[fulloxy-bro-het] in Figure 7b. Please check them.

27. page 10969, lines 17 and 20. Consistency is needed between the factor of 4 (in line 17) and the factor of 3 (in line 20).

28. page 10972, line 13 and Figures 9 &10. It might not be appropriate to refer to the OH + O3 reaction as “oxidation of ozone.” In Figures 9&10, does the series “2OH+O3+H2 -> 2HO2” indicate the sum of the rates of the two reactions of OH + H2 and OH +O3?

29. page 10974, lines 21-22. What do the authors mean by “the lack of the cycling between HOx?”

30. page 10975, line 14. I suppose not only sea-salt particles but also all types of aerosol particles are accounted for in the calculation of the uptake rates.

31. page 10976, line 6. It is suggested here that HOBr is mostly taken up on aerosol, which is not consistent with the sentence in lines 22-23 of page 10973, where it is mentioned that the photolysis of HOBr is still dominant.

32. The authors conclude that the heterogeneous uptake of HO2 on the aerosols could be one of the important processes during daytime. It should be important during nighttime as well, if the aerosol number density and their surface property are not much different from daytime. Does the model reproduce the measured nighttime HO2 levels better with the heterogeneous loss? It should be mentioned at least briefly here even

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though it is described in the author's companion paper.

33. Can the authors make short comments on how the model/measurement comparison in summer 2002 described in this manuscript is compared with the past results at the same site?

34. Table 4. It is written in the caption of Table 4 that H2 on 9 August is estimated at 372 ppb, which is very low. The authors should check this.

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