Atmos. Chem. Phys. Discuss., 5, S5248–S5258, 2005
www.atmos-chem-phys.org/acpd/5/S5248/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on “OH and HO_2 chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake” *by* R. Sommariva et al.

R. Sommariva et al.

Received and published: 26 January 2006

We would like to thank both referees for their useful comments.

—– REPLY TO COMMENTS BY REFEREE #2 —–

We agree with most of the comments of Referee #2 and we will modify the manuscript accordingly. We would like to reply to some specific comments here:

COMMENT:
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

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

model runs?
REPLY:
The back trajectories are calculated using the same ECMWF analyses and differ because they are released from different points. The seven trajectories in each plot arrive in a cluster around a point above Mace Head. There is one in the centre (53.32 N, 9.9 W, 900 hPa) and the others are displaced by ± 0.25 deg latitude, ± 0.40 deg longitude and ± 50 hPa. Please refer to Methven et al., JGR, 2001 and the NAMBLEX overview paper (Heard et al., this issue) for more details on the trajectories.

COMMENT:
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.
REPLY:
We agree with this comment and this paragraph will be rewritten using a different chemical tracer (such as toluene/benzene ratio) to indicate the photochemical age of the air masses.

COMMENT:
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.
REPLY:
This sentence will be rephrased as: "The correlation was usually very good with R$^2 \geq 0.9$ for all species. The data for HCHO showed a larger scatter than for the other compounds. While HCHO photolyzes..."

COMMENT:
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.
REPLY:
It was necessary to estimate j(HOI) for a few hours in the period 15-20 August. The correlation will be added to the table and j(HOI) will be mentioned in the text were appropriate. It was not necessary to use correlations for j(HOBr) so the reference to j(HOBr) will be removed from the text.

COMMENT:
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?
REPLY:
The variation of the total ozone column is implicit in the measurements of the j values (also see Monks et al., 2004).

COMMENT:
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.
REPLY:
This is correct. The thing you have to be careful about is that using j(NO2) to scale all j values is that clouds affect all spectral regions identically. This issue was dealt with in Monks et al., 2004, which showed that you have to be careful about this assumption especially with j(O1D).

COMMENT:
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.
REPLY:
In the "clean" and "full" models, the concentrations of the oxygenates and peroxides are calculated by the models from the degradation of their precursors and their loss processes. Note that when the model was not constrained to oxygenates and hydroperoxides concentrations, these species were calculated as intermediates, but the concentrations obtained were, for most species and especially those with longer lifetimes more than an order of magnitude less than the measured concentrations, because of the importance of transport. This sentence will be added to the text.

COMMENT:
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?
REPLY:
The UEA measurements of HCHO were used in the model, because the UEA instrument was located closer to the radical measurements location than the Leeds instrument. Using the Leeds dataset had a negligible influence on the calculated [OH], but could increase calculated [HO2] by up to 15%. For a complete discussion of the differences between the two datasets see Still et al. in this issue.

COMMENT:
13. page 10960, lines 17-28. HCHO treatment is not clear. It is implied here that the

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

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.
REPLY:
HCHO measurements on 21 August were available only for a few hours and therefore the models were not constrained to HCHO on this day. The values shown in Table 1 refer only to the few available data. The inconsistency in the figures of the fluxes is a typo and will be corrected.

COMMENT:
21. pages 10966 last line - page 10967 line 2. I could not understand the sentence. Which additional effects are expected on OH when NO and NO2 concentrations are higher?
REPLY:
This sentence is not very clear and will be rephrased as following: "... upon the particles. Uptake of HONO can increase the effectiveness of reaction with NO as an OH sink. Normally, under daylight conditions HONO photolyzes to regenerate OH, but uptake could reduce [HONO] and hence the rate of regeneration. Under the conditions considered, however, [NO] was too small to make this an important reaction. The main impact on OH is likely to be through HO2 uptake on aerosol, reducing the rate of OH production through HO2+NO."

COMMENT:
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 "fulloxyio" 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.
REPLY:
The use of transition regime expression should indeed result in higher [HO2]. However in the models ‘fulloxy-het’, ‘fulloxy-io-het’ and ‘fulloxy-bro-het’ the use of the transition regime espression was not the only improvement. A higher uptake coefficient was also used for HCHO resulting in faster removal of HCHO and, hence, lower [HO2]. Since the decrease in HO2 concentration is only a few percent between 15 and 21 August and less than 10% on 31 August we concluded that, as is stated in the paper, "the use of the transition regime expression instead of the free-molecular expression to describe the heterogeneous uptake did not cause a significant change in the concentration of HO2, due to the low value of the uptake coefficient". A sentence clarifying this will be added to the text.

COMMENT:
29. page 10974, lines 21-22. What do the authors mean by "the lack of the cycling between HOx?"
REPLY:
The simple model used by Bloss et al. (2005) calculates the impact of IO on HO2 destruction and on OH formation. However it does not include the HO2 → OH reactions, so it does not consider the effect of IO on HO2 formation via OH.

COMMENT:
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.
REPLY:

In the calculation of the uptake rates it was assumed that all particles were sea-salt particles. While this a simplification, we think that for our purpose and in the conditions of the modelled days (i.e. mostly unpolluted conditions) it is a reasonably safe assumption. See also Coe et al., this issue.

COMMENT:
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 though it is described in the author's companion paper.
REPLY:
The choice of the treatment to describe heterogeneous uptake (free-molecular vs. transition regime expressions) has the same impact during the day and during the night. However, since the agreement between the model and the measurements is better during the night than during the day an increase in γ_{HO2} in the model results in a worse agreements with the measurements. The discussion of the night-time chemistry will be in the companion paper (Sommariva et al., to be submitted), but we will mention it here.

COMMENT:
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.
REPLY:
This is an error and will be corrected (H2 = 512 ppb).

—– REPLY TO COMMENTS BY REFEREE #1 —–

COMMENT:
Page 10953, line 2: I have my doubts that the NO/NO2 ratio is a good indicator for

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

long chemical processing time, in particular if halogens are present. I am sure there are better indicators to make a statement on chemical processing time. If not, please explain why the NO/NO2 ratio is advantageous.
REPLY:
We agree with this comment and this paragraph will be rewritten using a different chemical tracer (such as toluene/benzene ratio) to indicate the photochemical age of the air masses.

COMMENT:
Page 10955, line 18: How reasonable is it to constrain a model with NO and NO2 values, while leaving out chemistry such as the various IO reactions that can change the NO/NO2 ratio? Omitting the influence of IO, which is present at high enough concentrations to impact the NO/NO2 ratio considerably, could lead to erroneous OH and HO2 levels. Please comment on this question in the manuscript.
REPLY:
NO and NO2 were measured during the campaign. Therefore, constraining the models to the measured concentrations of NO and NO2 implicitly include in the models the influence of IO on NOx.

COMMENT:
Page 10954, line 19: It would be helpful to give the accuracy of the photolysis estimates for those days without spectral radiometer data. The statement, that the agreement between measured and estimated photolysis rates was better than 50
REPLY:
The following sentence will be added to the text: "The difference between the measured and estimated photolysis rates is in most cases less than 30% and occasionally within 50%. This is comparable to the instrumental uncertainties, so we think these estimates are reasonably safe to use in the model."

COMMENT:
Page 10956, top Table 1: Please specify which of the HCHO data listed in Table 1 sets

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

have been used to constrain the model. Why was one chosen over the other?
REPLY:
The UEA measurements of HCHO were used in the model, because the UEA instrument was located closer to the radical measurements location than the Leeds instrument. Using the Leeds dataset had a negligible influence on the calculated [OH], but could increase calculated [HO2] by up to 15%. For a complete discussion of the differences between the two datasets see Still et al. in this issue.

COMMENT:
Page 10957, line 17: Please specify the accuracy (including the uncertainty of the calibration) of the OH and HO2 measurement. Citing standard deviations gives the impression of a statistical error, which is not the case for the influence of calibration uncertainties on the field observations. In the text, please use statements such as "agreement within the error of the measurements". For example, statements such as that on page 10958 that the agreement was better than 10
REPLY:
A complete discussion of the accuracy and the uncertainties of the OH and HO2 measurements is best given in the paper dealing with the measurements. Please see Smith et al. in this issue. The expression "within the combined uncertainties of the measurements and the likely uncertainties of the model" will be used throughout the text.

COMMENT:
Page 10957, line 15: I would like to applaud the authors for giving a "model uncertainty". However, I do not believe that this uncertainty was actually used in the manuscript. At least in the figures, the model data does not have uncertainties. The authors may consider the bold step of putting error bars on model results.
REPLY:
The uncertainty cited in the paper is not the real model uncertainty (and this is why it was not put in the figures), but an estimated uncertainty calculated using a simpler version of the model, which is similar to the "clean" model used in this work. Please see

Sommariva et al., ACP, 2004 for more details on this and the problems associated to the estimate of the uncertainty in a "full" model. The following sentence will be added to the text: "the model uncertainty is likely to be larger for the more complex models, but the uncertainty in the model input parameters is not sufficiently well defined to warrant a full uncertainty analysis."

COMMENT:
Page 10981, line 21: One expects the concentration of halogen oxides to be lower at higher NOx. The omission of XO in the model would therefore have a smaller influence at higher NOx.
REPLY:
Since both NOx and XO are constraints of the model this effect is implicitly taken into account.

COMMENT:
Page 10970: It is becoming increasingly clear that IO is indeed spatially unevenly distributed, as discussed at the beginning of this page. Therefore, the question arises whether using the DOAS IO measurements is the correct approach to constrain the model. One could argue that the DOAS measurements are only a lower limit for the IO concentrations, and that the impact of IO is larger than described in most of the manuscript, or that the averaged DOAS values are not necessarily representative for the local observations at the Mace Head observatory. It appears that for days such as 18 August the agreement between measurements and model with 50ppt of IO is quite good. It would improve the manuscript if this point would be discussed in more detail.
REPLY:
We agree on this point. In fact, Saiz-Lopez et al. in this issue have shown that IO was likely to be concentrated near the coast at Mace Head. However, during the campaign IO was measured only by DOAS. Therefore, the model was constrained only to the available measurements and only an attempt to estimate the impact of higher [IO] was made. Given the absence of reliable information on the distribution of IO, however, we

feel that the conservative, lower concentration values are the ones that must be used, with a more limited analysis at higher [IO], as has been done in the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10947, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper