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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Lagrangian analysis of low level anthropogenic plume processing across the North Atlantic" *by* E. Real et al.

E. Real et al.

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First of all I would like to thank the 2 referees for their useful remarks that have helped to increase the quality of our paper.

One of the main criticisms made by both referees concerned the lack of heterogeneous reactions on aerosols in the model runs. Both referees suggested that it would have been interesting to estimate the impact of heterogeneous reaction of N2O5 on simulated concentrations of HNO3 and O3 . Therefore, in the new version of the paper we have carried out a sensitivity test where we included N2O5 hydrolysis (section 4.2.3): 8220;In the runs discussed in the previous sections, heterogeneous loss of trace species on aerosols was not taken into account in the model. This can be important for N_2O_5 which can be converted to HNO_3 through heterogeneous reactions. At night the conversion of NO_x into N_2O_5 becomes the major NO_x sink and if no hydrolysis

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occurs N_2O_5 decomposes back into NO_x the following day. However, heterogeneous reaction may be difficult to simulate as there are still some uncertainties on the reaction probability value and its dependence on water vapour and temperature. Here, the sensitivity of results to heterogeneous loss of N_2O_5 has been examined using a parametrisation from **?**. Loss rates were calculated based on recommended temperature and relative humidity dependent uptake coefficient and measurement derived surface aerosol densities using observations made in the plume on 20 July. Since wet deposition and dilution may decrease aerosol density, an exponential decrease was applied with a half life time of 2 days in order to mimic the decrease in aerosol number between 20 and 21 July. Results of these simulations with and without deposition are represented in Figure 8. When no wet or dry deposition is included, the impact of N_2O_5 hydrolysis on NO_x and O_3 concentrations is important (see Figure 8a). O_3 concentrations decrease by about 5-6 ppbv over 6 days and NO_x are lower by almost 50In runs including wet deposition (see Figure 8b) the impact of including or not including N_2O_5 hydrolysis on O_3, NO and NO_2 levels is less important even if NO_x are significantly reduced with hydrolysis (by about 20

In the following we answer each of the referees remarks:

REFEREE 2

Major issues:

1)N2O5 hydrolysis : see previous comment and text

2)HNO3 and OX : The impact of HNO3 on O3 levels is discussed in the text (sections 4.1.3). In the chemistry only simulations the main impact is through HNO3 photolysis which maintains NOx levels in the plume. Wet deposition reduces HNO3 and therefore NOx levels and net O3 production. We do not consider that HNO3 is part of the Ox budget for this purpose.

3)The use of NO/CO correlation : we agree that NO is fast reacting and thus, the

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NO/CO analysis performed as part of the correlation study is not appropriate. As suggested by the referee we have removed this part from the correlation discussion.

4)Wet deposition of soluble species: as suggested by the referee, we performed a sensitivity test where only HNO3 was removed by wet deposition. Results show very small changes (< 2

Minor issues:

Page 7528: The text has been changed to be clearer - see section 4.3.1

Page 7529: The mixing rates estimated by Arnold et al. for the entire campaign (10 days) were used to prescribe the mixing rates used in our study. Arnold et al. involved a detailed analysis of VOC changes in the Lagrangian cases reported by Methven et al.

Page 7530: The discussion on measured VOCs has been reinforced in the new version (see section 4.3.2).

It is true that sometimes the text was confusing regarding the direct/indirect effect of wet deposition on O3 8211; the text has been clarified. (see in particular end of section 4.2.2 : 8220;8220;The impact of wet deposition is not only important for HNO_3 but also for species that are not soluble but dependant on HNO_3 concentrations. Modelled NO_x is now almost equal to zero after 6 days (much less HNO_3 photolysis) leading to a reduction in O_3 production rates which decrease by 60 % due to this wet deposition indirect effect.8221;8221; Also conclusions is clearer.

Conclusions: We think that the discussion about Lagrangian matches on 22 and 26 July is covered several times in the text and our results provide some confidence in our conclusion that these 2 samplings were not truly Lagrangian. On 26 July, the large increase in NOy and NO clearly shows that there was an important influence of mixing with air masses containing more recent emissions and therefore the word Lagrangian match is not appropriate any more. On 22 July there may still be some doubts but the

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increase in VOC concentrations, the decrease in O3 concentrations (which is not reproduced by the model), the strong decrease in correlations and the differences between the trajectories used in our study and the Lagrangian balloons all suggest a problem with the 22 July Lagrangian match. However the sentence 8220;the analyse shows that some of the links identified as Lagrangian are not truly Lagrangian8221; has been replaced by 8220;the analyse suggests that some of the links identified as Lagrangian are not truly Lagrangian8221;

Figure and tables: changed has been added for caption of table2 and 4.

REFEREE 1

Specific comments:

Page 7515-line25-26: At this part of the text, the statements 8220;Therefore it appears that the Lagrangian match on 22 July is less good8221; does not come from any other study but is based on comparison between the location of the Lagrangian balloon (Riddle et al., 2006) and the position of the Lagrangian match. It is also based on the fact that VOC concentrations in the match increase compared to the previous 2 days which suggests a mismatch or strong mixing and in both cases?? the Lagrangian match is 8220;less good8221; than the matches between the 20 and 21 July. Moreover, John Methven (a co-author on our paper), who has established the Lagrangian matches, confirmed that this match was 8220;less good8221; compared to the others. In the new paper version, the text has been slightly changed to make this point clearer

Page 7519, line 11: more detail about the chemical scheme has been added and additional references added.

Page 7521, line 5 to 13: a simulation with N2O5 hydrolysis has been conducted (see beginning of this reply).

Page 7525, section 4.2.2 : done

Page 7527, lines 15 to 20: all along the new version of the paper, 8220;slightly8221;

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has been or removed or accompanied by more quantitative information.

Page 7528, lines 25 to 30: The sentences on mixing have been slightly re-written to try to make it clearer. The mixing rate of 10 days was chosen according to results of Arnold et al., 2007 that analysed mixing rates based on hydrocarbons measurements made during the ICARTT campaign during the Lagrangian matches. We agree that the change to a mixing rate of 2 days is somewhat arbitrary but appears necessary in order to obtain better agreement with the measured mean values of NOy and NO during the 26 July match.

Page 7541: All measured hydrocarbons that were simulated by the model are shown in Table 1 noting that fewer measurements were taken on the Falcon compared to the P3. Hydrocarbons can indeed be useful to estimate mixing and OH levels in the plume. It was shown (section 4.3.2) that with the simulated OH concentrations and the choice of mixing rates, the modelled evolution of C2H2, C2H6 and C4H10 (relatively long-lived VOCs) agreed reasonably well with the data. This was not the case for shorter lived VOCs due to the possible local influence of mixing with biogenic or oceanic emissions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7509, 2008.