Atmos. Chem. Phys. Discuss., 10, C3921–C3924, 2010
www.atmos-chem-phys-discuss.net/10/C3921/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemistry of hydrogen oxide radicals (HO$_x$) in the Arctic troposphere in spring" *by* J. Mao et al.

J. Mao et al.

mao@fas.harvard.edu

Received and published: 13 June 2010

We thank the reviewer for the helpful comments. Our responses to the comments are provided below, with the reviewer's comments italicized.

Section 3 should be a little more quantitative in describing the differences between the model and the measurements.

For OH, we now state: "The model reproduces the vertical gradient of the observed OH and its concentrations at 1-6 km within 15%, but is too low by 40% in the surface layer (0-1 km) and too high by 40% in upper troposphere (> 6 km). The discrepancy in the surface layer may be due to the effect of halogen chemistry, while the discrepancy in the upper troposphere can be explained by HO$_2$ aerosol uptake as described in section

4. "

For NO$_x$, we now state: "Median observed NO$_x$ concentrations increase from 16 pptv in the boundary layer to 21 pptv in the upper troposphere (>6 km). The model is consistent within the measurement uncertainty (15% ± 10 pptv), increasing from 13 pptv in the boundary layer to 28 pptv in the upper troposphere. "

It is not very clear how the uptake of gases on aerosol is calculated. The authors should be more explicit than simply stating "a general representation for first-order uptake". In addition, how is the aerosol surface area determined? Since they say it was not measured, I assume it was calculated by the model or estimated in some way. Was the measured aerosol composition used to calculate the uptake coefficient, or was an average composition calculated and used? On the same subject, it does not seem that some basic sensitivity study was done. Given the uncertainties in the aerosol characteristics and in the HO$_2$ uptake coefficient itself (and the unknown role of the organics), and the importance of this process for the paper conclusions, it seems important to see how the model would respond to some changes in these parameters.

We have added a description of the aerosol uptake formulation and the model calculation of aerosol surface area in section 2.2.

As pointed out in the text, $\gamma(HO_2)$ > 0.1 is required for aerosol uptake to be important in the HO$_x$ budget. We now restate that in the Implications section. This is somewhat contingent on uncertainty in the aerosol surface area and we now state: "Mean aerosol surface area in the model corrected by hygroscopic growth factors (R. V. Martin et al., 2003) is 26 μm^2 cm^{-3} at 0-3 km, 33 μm^2 cm^{-3} at 3-6 km and 19 μm^2 cm^{-3} above 6 km. The model agrees with the measurements of aerosol surface area aboard the P-3 within a factor of 2."

As the reviewer points out, the largest source of uncertainty lies with the assumed uptake by organic aerosols. These aerosols are mainly from biomass burning, therefore we have conducted a sensitivity simulation with no biomass burning and now report results of that simulation in the Implications section. We now state: “Biomass burning from Siberian wildfires was a major aerosol source to the Arctic in ARCTAS (Warneke et al., 2009), and this aerosol was mainly organic for which we have no information on HO_2 uptake. We find in a sensitivity simulation with no biomass burning that OH and HO_2 concentrations would increase respectively by 10% and 9% in the tropospheric column.”

The model underestimates HCHO and NO in the lower troposphere and overestimates NO in the upper troposphere. NO_2 also seems to be slightly overestimated at higher altitudes. These discrepancies are significant and the authors should at least address them: how would a better agreement between modelled and measured NO_x affect the model results? Better, worse or no improvement, compared to the measurements? What would be the impact on the model results of 2-3 times higher [HCHO] and how would this affect the paper conclusions? Could the HCHO problem be an instrumental/ inlet problem? I think the paper would greatly benefit by a short discussion of these questions.

For NO_x, we now state: “The standard simulation overestimates HO_2 by up to a factor of 2, with the largest discrepancy in the upper troposphere. H_2O_2 is also underestimated. This cannot be explained by model error in the species driving HO_x production, as Olson et al. (2010) find a similar discrepancy for HO_2 in their box model results constrained by ARCTAS observations. They further show that the discrepancy cannot be resolved by adjusting observed concentrations within their measurement uncertainties.”

For HCHO inlet, we now state: “Inlet artifact can be ruled out because zero air was added to the inlet every minute as instrument background signals.”

For the impact from observed HCHO, we now state: “the source of HO_x and HO_y implied by the observed HCHO appears inconsistent with independent calculations of HO_x and HO_y sinks from the ARCTAS observations, leading to an even higher overestimate of HO_2. ”

page 6958, line 12 and elsewhere: "radials" instead of "radicals".

We have changed as suggested.

page 6959, line 5: maybe mention reaction with OH and explain how peroxides are converted to water.

We now state: “Alternatively, they can be converted to water by reacting with OH or deposited resulting in a terminal HO_x sink.”

page 6970, line 21 and elsewhere: don’t use "second simulation" or similar expressions, it is confusing: just say which model is being discussed (e.g.: "model with uptake of HO_2 " or something like that).

We have changed as suggested.

figure 1: adjust the x-axis of CH_3OOH, NO_2 and HNO_4 so that the lines are clearly visible: now they are squeezed together and this might suggest there is a better agreement than there actually is.

We have changed as suggested. The observations of these species are in agreement with the model simulations within their measurement uncertainties and we say so in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6955, 2010.