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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.

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

I agree that the heterogeneous loss process is one of the likely causes for the HO_x concentrations lower than predicted. However, more information should be provided to convince the readers. For example, averaged vertical profiles of temperature, relative humidity, and aerosol surface density (modeled one) should be presented. Any information about the phase of the particles (liquid or solid), which is critical for the conclusion, should be sought and provided. It is also important to see that the J values are well simulated by the model even when the cloud effect is included.

We now state: “Mean observed temperature and relative humidity (RH) relative to liquid water are 256 K and 73% at 0-3 km, 243 K and 48% at 3-6 km, and 226 K and 48% above 6 km, consistent with the model. Mean observed J (O^1D) and J (NO_2) agree with the model within 25% and 10% respectively. ”

In Section 4, we have added: “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.”

Abstract. As a loss process, HO_2 conversion to HSO_5^- is too much speculative to be mentioned in the Abstract.

We have changed as suggested.

page 6958, line 12. radicals

We have changed as suggested.

By the radical-radical reactions that return water vapor, do the authors mean a single reaction HO_2 + OH reaction? Or any other? In relation, at line 11, which process do the authors indicate by "against conversion to water vapor?"

We now state: “Loss of HO_x eventually takes place by radical-radical reactions. The OH + HO_2 reaction produces water vapor in which case the loss is terminal, but the peroxy + peroxy reactions produce reservoir species such as hydrogen peroxide (H_2O_2) and methyl hydrogen peroxide (CH_3OOH).”

We now state: “The lifetime of HO_y against conversion to water vapor by reaction of OH with HO_2 or peroxides is of the order of a few days . . .”

How do the authors assume the vertical distributions of the total ozone columns?

We now state: “The range of ozone columns during ARCTAS was 380-430 Dobson Units. Fast-JX includes a background climatology of zonal mean profiles of monthly ozone and temperature (Wild et al., 2000).”

Page 6963, from line 23. With respect to wet deposition, was there any significant bias between observed and modeled rainfall distributions/amounts?

We now state: “The same GEOS-Chem simulation is applied in companion papers to interpretation of ARCTAS observations for CO (Fisher et al., 2010a), sulfate (Fisher et al., 2010b), and carbonaceous aerosols (Q. Wang et al., 2010). The latter two studies show that the model reproduces well the observed aerosol concentrations, lending some confidence in the computation of scavenging and heterogeneous uptake.”

Page 6965. What is the expected uncertainty range for HO_2 in the GEOS-Chem model caused by the fact that the J values, H_2O, O_3, and HCHO concentrations were not constrained by the observations? Is the disagreement in the HO_2 concentrations by a factor of 2 under discussion beyond this uncertainty?

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.”

Page 6968. Is there any observational evidence suggesting that the aerosol particles are wet droplets, under the cold temperature conditions? Such as particle shape analysis, humidogram, or H2O signal from the Aerodyne Aerosol Mass Spectrometer?

We could not find any information on aerosol water or phase from the ARCTAS observations. Aerosol water evaporates at the aircraft inlet and does not reach the AMS.

We now state: “This requires that the aerosol be aqueous, which cannot be directly determined from the ARCTAS observations.”

Page 6969, line 6. ranging

We have changed as suggested.

Page 6969, from line 19. Can these successive processes provide a first-order loss for HO_2 where an uptake coefficient can be theoretically defined? Is a reaction step (R7) necessary? Even without (R7), HO_2 can be lost via conversion to SO_5^- (by R6), then to HSO_5^- (oxidation by O_2^- , $HCOO^-$, and HSO_3^- as written in text) and finally to sulfate by R8?

The reaction rate constant for (R6) would need to be quantified to calculate a corresponding reactive uptake coefficient.

We now state: “Jacob (1986) suggested that the subsequent fate of HSO_5^- in acidic solution might follow reactions (R7) or (R8), either of which provides a terminal sink for HO_y by conversion to water. . .”

Page 6972, line 12. Is ozone "production" expected in the arctic troposphere? If not (namely ozone loss regime), it is inappropriate to mention "NO_x-limited production" here.

Even if chemistry provides a net loss there is still gross ozone production. We have added “gross”.

page 6972, lines 25-26. Is the lower troposphere defined with an altitude range 0-2km?

We now state: “the total HO_x sinks balance 50% of the HO_x sources in the lower troposphere (0-3 km) and 70% in upper troposphere (> 6km).”

Figures 5 and 6. Is the radical loss via OH + NMHCs reactions giving organic nitrates negligible?

Yes. We now state: “Formation of organic nitrates is negligible in the HO_x and HO_y budgets, at least in the model, and is not included in Figure 5. ”

page 6974 and Figure 7. Is it better to provide two separate diagrams for lower troposphere and above region, because the importance of the heterogeneous loss is *different?*

Figure 6 already shows the vertical variation of the HO$_y$ budget. For the sake of space we would rather keep a single summary diagram in Figure 7.

When the HO$_2$ loss is governed by the heterogeneous loss of it whose rate is linear with [HO$_2$] (not by the self reaction whose rate is quadratic with [HO$_2$]), HO$_2$ concentration should have more linear dependency against the HO$_x$ production rate. Can the authors show this to test the conclusion?

We now state: "Loss of HO$_2$ by uptake by aerosol has a first-order dependence on HO$_x$ concentration, whereas the gas-phase sinks have a quadratic dependence. However, we find that the total HO$_x$ source P(HO$_x$) computed from Figure 5 is strongly correlated in the upper troposphere with both observed [HO$_2$] (R = 0.87) and [HO$_2$]^2 (R = 0.85), so that it does not test the sink mechanism."

Can the loss of HO$_x$ onto the cloud droplets be also important, in addition to the loss on the aerosol particles?

We now state: "We ignore heterogeneous chemistry of HO$_x$ radicals in clouds because the aircraft sampled almost exclusively in clear sky and the regional effects of clouds on the HO$_x$ budget are limited by the small mass fraction of the atmosphere actually occupied by cloud (Jacob, 2000)."

Can the introduction of the heterogeneous loss process for HO$_2$ into the global chemical transport model damage any past comparisons of the observed/modeled HO$_x$ radicals and thus will we need reanalysis of them? Or is the heterogeneous loss important only in the Arctic troposphere?

We now state: "Uptake of HO$_2$ by aerosol is expected to be particularly efficient as a sink for HO$_x$ in Arctic spring because of the combination of cold temperatures, relatively high aerosol concentrations, and weak UV radiation. On a global scale, however, the OH budget is mainly determined by the tropics and mid-latitudes summer where

aerosol uptake would be less important. We find in our model that the global mean tropospheric OH concentration decreases by 3% when we include uptake of HO$_2$ by aerosols as described here. "

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