

Review of “Evaluation of simulated photochemical partitioning of oxidized nitrogen in the upper troposphere” by Henderson et al.

This paper presents a stochastic convective modeling approach used in conjunction with both in-situ chemical observations/modeling results and meteorological information in the upper troposphere as a way to compare estimates of air mass photochemical aging. Distributions from a suite of chemical simulations are used to compare various chemical mechanisms. In general, I find this approach very interesting and exciting. As far as I know, this is a new approach for airborne data analysis, and an important addition to the field. I did find several problems/issues within the paper, however, that must be addressed before I can recommend publication.

In the abstract, the authors cite observational based studies that are purported to show that models often over-predict upper tropospheric HO_x, leading to too-fast conversion of NO_x to HNO₃. This claim is incorrect. None of the studies listed show this to be the case, and some, in fact, find the exact opposite (a significant model **under**prediction of upper tropospheric HO_x). Bertram et al. (2007) only use observations of OH and HO₂ in their analysis and make no claims or suppositions about model predictions of HO_x. Ren et al. (2008) looks at INTEX-A data and find a very large model underprediction of HO₂ above 8 km, with a median obs/calc ratio of 2.05 (~3 for the 10-12 km range). OH predictions were within 10% of observations in that same study. Olson et al. (2006) look at the tendency of models to **under**predict HO_x in the upper troposphere with increasing NO_x concentrations and small-scale variability.

Following this, (1. Introduction, top of p. 20128) the following statement is incorrect: “Recent chemistry evaluations suggest that chemical representation could contribute to underpredictions of NO_x via overpredicting HNO₃ formation rates (Olson et al., 2006; Bertram et al., 2007; Ren et al., 2008). These studies do not support this statement.

The authors need to state what value they use for NO. Table 2 does mention that calculated NO is used, rather than observation (and this is a good choice), but this should be brought out in the text as well.

Additionally, Table 2 lists the HNO₃ measurement used as from CIT (similar to NO, I would also suggest this be mentioned in the text).

The measurement of HNO₃ from the UNH instrument is quite different than values from the CIT during INTEX-NA (median ratio between the two for 8-10 km is ~0.68). This would result in NO_x/HNO₃ ratios nearly 50% larger than those derived using CIT-HNO₃. How would these differences impact your calculated mean air parcel lifetimes and conclusions? A discussion of the uncertainty in your results due to the choice of HNO₃ measurement needs to be included.

Figure 5: In calculating the statistical differences for these species, did the authors include instrument uncertainty? For instance, though the statistics identified O₃ from SAPRC99 as statistically distinct from observations for the mid-age and old subsets, I have a hard time believing that such a small difference (few ppb) is significant.

A few minor points:

1. Introduction

Nitric acid is not chemically stable at higher temperatures. Its reactivity is temperature dependent.

2.2 Observations

Line 16 (H₂O < 200 ppb) typo? Should this be ppm?

Whichever the case, this discrimination of stratospheric air confuses me. 200 ppm H₂O is much too high to use to discriminate stratospheric air, but 200 ppb is extraordinarily low (i.e., when I obtain the 10s merged INTEX-A data between 8-10 km, I see no points that have water vapor (from the DLH instrument) less than 18 ppm). On the other hand, I find that 37% have H₂O < 200 ppb, and of those points, 91% have O₃ < 100 ppb (as low as 33 ppb), which is certainly not indicative of stratospheric influence. Why not use a combination of high O₃ and low CO, along with the radioisotope ratios?