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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Radical chemistry at night: comparisons between observed and modelled HO_x, NO_3 and N_2O_5 during the RONOCO project" *by* D. Stone et al.

Anonymous Referee #2

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General comments

The authors attempt to model interesting aircraft measurements of NO3, N2O5, HO2, and RO2 during the RONOCO campaign using the MCM. The model runs generally struggle to reproduce the measurements (r2 = 0.10 for HO2*, and 0.29 for NO3), in part because the VOC and aerosol data set was quite limited, and because the authors attempted to model the entire data set (which spans several seasons and a wide range of locations) with a single set of parameters. Substantial conclusions or novel insights are not presented, and the manuscript generally is too weak to stand on its own. Because of the extent of the changes that I think would be required to convert this

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manuscript into a publishable form, I need to agree with reviewer #1 and recommend this paper be rejected.

Major comments

-The paper promises "comparisons between observed and modelled HOx, NO3, and N2O5". Unfortunately, neither the observed nor the modelled data are presented in a meaningful way, e.g., by showing figures of time series of the measurements and model results. Instead, only scatter plots (e.g., Figure 2) of modelled vs. observed data for the entire data set are presented, which are neither informative nor useful as there is a lot of scatter, and the slopes were likely affected by relatively few "outlier" points.

- The authors attempted to model all of their data using a single value for gamma(N2O5), which is a highly unrealistic assumption considering the temporal and spatial variability of N2O5 uptake that can occur on ambient aerosol [see, for example, Brown et al., Science 2006, 311, 67-70].

- Most of the campaign took place over the ocean water (Figure 1) at relatively low altitude (the color scale in Figure 1 is clearly mislabeled, and I am guessing below 800 m was the norm) so that it is possible that aircraft entered the marine boundary layer. The oceans are a source of sea salt aerosol and of dimethyl sulphide, which are strong sinks for N2O5 and NO3. Neither chemistry has been considered by the authors.

- Vertical gradients are ignored by the authors, even though Fig 12 of Kennedy et al. suggests an anticorrelation of NO3 and N2O5 chemistry with altitude.

- The authors report having made measurements in July and in January but do not consider seasonal differences in the chemistry, which is unrealistic. In addition, isoprene and terpene emission rates are likely quite different between the summer and winter data set.

- The pie charts (Fig 3-7) are scientifically questionable as they are for campaign aver-

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ages, and the properties plotted are in all likelihood highly variable in time and space (see, for example, Figure 12 in Sommariva et al., 2009). Hence, pie charts of campaign averages are generally are poor choice to present the data. Some of the same info would have been better presented as time series (or maybe as weekly averages plotted against time of day).

- A portion of the paper is spent discussing the model limitations, yet potential measurement errors or biases are by-and-large ignored in the model-measurement comparisons. These could have been substantial, in particular for nocturnal OH and HO2 measurements.

- In their modeling, the authors appear to put infinite trust in most measurements (e.g., NO, NO2, and the VOCs) but zero trust in certain others (NO3, N2O5, HO2, or RO2), because why else would you calculate them. Yet I am sure that Kennedy et al. have a healthy level of trust in their measurements, and that Heard's group feel equally confident about their OH and HO2 measurements. What would have happened if the MCM had been constrained to some of the measured radical species, e.g., NO3, or OH? Does then the model runs agree with the observations? For example, does the MCM reproduce the observed HO2/OH ratio for fixed OH (or HO2)?

- A general limitation of this work is that the list of VOCs used as model input (Table 2) is rather short and lacks entire classes of VOCs (e.g., terpenes, aldehydes). As a result, the MCM (6700 species, 17000 reactions) is underutilized (the authors state $\sim$2000 species, $\sim$8000 reactions are used). I wonder if a data set with such a limited VOC data is a good candidate to attempt a model-measurement comparison from a modeling perspective.

Minor comments

- Table 1 should include the measurements of NO3, N2O5, OH, and HO2 and state detection limits, time resolution, and uncertainties of all of the measurements, not just the auxiliary ones, and give citations to relevant papers.

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It appears that aerosols > 350 nm were not measured. A brief comment on the error this introduces is warranted.

pg 9522, line 15. "Much less emphasis has been placed on the nighttime chemistry" It would be helpful to be more specific here. Nighttime chemistry of what (OH, O(1D), or NO3)?

pg 9523, line 17. "... indicating poor understanding ...." There is also the possibility of measurement errors in the earlier data sets, especially for OH and HO2 at night. These are very challenging measurements to make!

pg 9524, line 23, 25. I believe Sommariva et al., 2009, instead of Sommariva et al., 2006, should be cited here.

pg 9530, line 12. Eq. 1 does not give an expression for the mean molecular speed, and should not be referred to here.

line 18. The parameterization by Evans and Jacob is a questionable choice, as I have yet to see it agree with field observations, and better parameterizations are available in the literature.

pg 9531 line 4. "Species which were not observed are set initially to zero in the model". Please indicate which species and state what magnitude error can be expected.

line 24-26. "potential interferences in HO2 measurements are expected to be small". Please justify this rather important assumption.

pg 9532. lines 1-11 "Model performance" and Figure 2, caption. Please state the numerical values with appropriate numbers of significant digits.

pg 9538, line 25-26. Laboratory and field studies actually span several orders of magnitude of gamma values, so being within range is not particularly difficult.

pg 9541, line 4. Monoterpene emission rates are quite different in summer and winter, which should have been considered here. Further, I would expect monoterpenes to

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be relatively short-lived and therefore to exhibit strong vertical gradients. Are there any vertical trends in the measurement-model comparisons? And what about dimethyl sulphide?

pg 9556. While the BAe146 is surely an impressive aircraft, I doubt that it flew at 6400 km altitude. Not even if Yeager had been at the controls.

pg 9557. Most of the NO3* is likely present as N2O5 in winter, whereas the summertime data likely favors NO3. Thus, a model-measurement comparison of NO3 emphasizes the summer data, whereas one of N2O5 is more sensitive to the winter data. Is that perhaps the reason why the slope in Figure 2c is closer to unity than the data in Figure 2b?

pg 9564, Fig. 8. This figure should have been presented earlier in the manuscript. Further, several reaction pathways, e.g., the transformation of OH to HNO3, or of the Criegee to the HO2 or methylperoxy radical, are missing reactants and hence do not make sense as written.

Fig. 9. The fonts are too small to be readable.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9519, 2013.