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Atmospheric
Chemistry
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Discussions

Interactive comment on "Measurements of the sum of HO_2NO_2 and $CH_3O_2NO_2$ in the remote troposphere" *by* J. G. Murphy et al.

J. G. Murphy et al.

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We thank the reviewers for their suggestions and have revised the manuscript to try to clarify the issues raised. We first address concerns raised by both reviewers and then deal with the rest separately.

The referees call for further discussion of systematic differences in the calibration of the instruments used in this analysis (comments 2,3 from Referee 1 and comments 4,5 from Referee 2). Neither technique is known to have a humidity-dependent bias or interference of the magnitude observed. We examined a wide range of variables and considered many possible sources of instrument error in the effort to understand the calibration difference between the instruments. Humidity provided the clearest correction. A more detailed discussion of the humidity correction will be included in the revised text. Because the abundance of ΔPNs has no humidity dependence, this correction does not introduce a bias to our inferred observations. Data where $\Delta\text{PNs}<10$

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% of PAN was selected for Figure 1 to compare the relative calibrations for conditions where ΣPNs $\sim$(PAN+PPN), however the correction was applied to the full dataset. The application of the correction does not affect the conclusions of this paper. The absolute magnitude of the $\Sigma NO_yi/NO_y$ ratio depends on the correction and would change by about 10% if the correction were applied to only the TD-LIF data or only the GC-ECD data.

If the modelled ΔPNs are added to the PAN and PPN measurements, the average $\Sigma NO_yi/NO_y$ ratio over the whole campaign is 1.2. If the humidity correction is not applied to the data, the $\Sigma NO_yi/NO_y$ ratio using the ΣPN measurements is a constant 1.1, and the ratio using PAN + PPN varies from above 1.2 where ΔPNs are insignificant to 0.8 where ΔPNs are calculated to be 45% of NO_y. The systematic difference between ΣNO_yi and NO_y is within the combined measurement uncertainties of the techniques used. The exact magnitude of the bias depends on the whether the humidity correction is applied and to which instruments.

Reviewer 1

Comment 1 - More details have been added regarding the TD-LIF instrument design used during the campaign. Briefly, TD-LIF relies on a heated inlet (50 ms residence time at 180 ° C) to dissociate RO_2NO_2 to yield NO_2 and RO_2. The resultant NO_2 is quantified along with ambient NO_2 using laser-induced fluorescence (LIF). By operating the heated inlet in parallel with an inlet maintained at ambient temperature, ΣPN mixing ratios can be derived from the difference between the NO_2 signals of the two channels. In addition to acyl and non-acyl peroxynitrates, N_2O_5 will also dissociate in the heated inlet, though we expect it was removed through contact with the walls prior to the heated portion of the inlet, and made a negligible contribution to NO_y in the low NO_x conditions sampled during TOPSE. NO_y species such as alkyl nitrates and nitric acid have significantly higher O-NO_2 bond energies than peroxynitrates and would not have dissociated under the inlet conditions used.

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Comment 4 - The reviewer encouraged discussion of the possible importance of IR photodissociation of $CH_3O_2NO_2$. In this molecule, the mechanism would require an overtone of the CH stretch which is sufficiently energetic to overcome the O-NO_2 bond energy and with a large enough absorption cross section to substantially change the lifetime of the molecule. Because the thermal decomposition of the molecule is so fast, even down to 220 K, it is unlikely that the IR photodissociation mechanism would alter the abundance of this compound.

Reviewer 2

Comment 1 - A more qualititative description of ΔPN and ΣPN abundances has been added to the paper. During the spring high latitude conditions sampled during the TOPSE experiment, the model predictions of the contribution of (HO_2NO_2 + $CH_3O_2NO_2$) to NO_y are highly temperature dependent: on average 30 % of NO_y at 230 K, 15 % of NOy at 240 K, and < 5 % of NOy above 250 K. The temperature dependence of the inferred concentrations corroborates the contribution of overtone photolysis to the photochemistry of peroxynitric acid. A model that includes IR photolysis (J=1x10$^-5$ s$^-1$) agreed with observed sum of HO_2NO_2 + $CH_3O_2NO_2$ to better than 35 % below 240 K where the concentration of these species is largest.

Comment 2 - A table has been added to the paper which lists the contribution of each NO_yi species to the overall reactive nitrogen budget above and below 240 K. The observations show ΔPNs contributing 17% to NO_y below 240 K. A model with IR photolysis for HO_2NO_2 predicts a contribution of 22% while a model with the IR term predicts 34%.

Comment 3 - Information about the geographical extent of the TOPSE campaign and the conditions encountered have been added to the introduction. TOPSE flights focused on tropospheric sampling over mid- to high-latitude continental North America during the winter and spring of 2000. Data used in this paper are limited to latitudes north of 50 ° N and altitudes above 500 m to avoid the effects of recent surface emis-

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sions or losses. The data were collected during the daytime at temperatures between 220 and 290 K.

Comment 6 - We would agree that part of the scatter in the observations of ΔPNs displayed in the lower panel of Figure 3 results from measurement precision. However, the overlaid averages sorted by NO_2 concentration demonstrate that the abundance of radicals (NO_2, HO_2, and CH_3O_2) also contributes to the spread in the ΔPNs observed at any particular temperature.

Comment 7 - As discussed in the text describing Figure 6, the observed and modelled ΔPNs agree to within twice the standard deviation of the mean for each concentration bin, though the consistently low bias in the observations compared to the model at high concentrations is suggestive of a discrepancy that exists under conditions where the model predicts high ΔPNs. The width of the bins was determined by the number of data points existing in the concentration range, and thus they are further apart for the less frequently encountered high concentrations of ΔPNs. The mean and standard deviation bars represent the span of the dataset, and the figure is too cluttered to interpret usefully with the individual points plotted. The figure includes the full dataset used in the analysis and the text will be revised to note that.

Tech Comment 1 - TD-LIF measurements were, on average, 20 ppt higher than chemiluminescence measurements of NO_2, but the ΣPN measurements are the difference between two channels, and observations with the inlet heater turned off confirm that both channels measure the same amount of NO_2. Therefore we do not expect this offset to affect for ΣPN measurements

Tech Comment 2 - All the data were merged to a 1 minute time base. The 1433 measurements occur during the last nineteen flights of TOPSE and exclude data acquired below 500 m or south of 50 ° N.

Tech Comment 3 - Total NO_y and NO_y are the same thing, the Figure 2 caption has been fixed.

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Tech Comment 4 - The legend for Figure 3 has been corrected to show squares for $NO_2 > 11$ ppt and circles for $NO_2 < 11$ ppt.

Tech Comment 5 - Figure 6 uses all data for the measurement/model comparison, not just May 22.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 5689, 2003.

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