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Measurements of the sum of HO₂NO₂ and CH₃O₂NO₂ in the remote troposphere

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Abstract

The chemistry of peroxyxynitric acid (HO_2NO_2) and methyl peroxyxynitrate ($\text{CH}_3\text{O}_2\text{NO}_2$) is predicted to be particularly important in the upper troposphere where temperatures are frequently low enough that these compounds do not rapidly decompose. At temperatures below 240 K, we calculate that about 20% of NO_y in the mid and polar latitude upper troposphere is HO_2NO_2 . Under these conditions, the reaction of OH with HO_2NO_2 is estimated to account for as much as one third of the permanent loss of hydrogen radicals. During the Tropospheric Ozone Production about the Spring Equinox (TOPSE) campaign, we used thermal dissociation laser-induced fluorescence (TD-LIF) to measure the sum of peroxyxynitrates ($\Sigma\text{PNs} \equiv \text{HO}_2\text{NO}_2 + \text{CH}_3\text{O}_2\text{NO}_2 + \text{PAN} + \text{PPN} + \dots$), aboard the NCAR C-130 research aircraft. We infer the sum of HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$ as the difference between ΣPN measurements and gas chromatographic measurements of the two major peroxy acyl nitrates, peroxy acetyl nitrate (PAN) and peroxy propionyl nitrate (PPN). Comparison with NO_y and other nitrogen oxide measurements confirms the importance of HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$ to the reactive nitrogen budget and shows that current thinking about the chemistry of these species is approximately correct. The temperature dependence of the inferred concentrations corroborates the contribution of overtone photolysis to the photochemistry of peroxyxynitric acid.

1. Introduction

Reactions of hydrogen radicals ($\text{HO}_x \equiv \text{OH} + \text{HO}_2$, and RO_2) and nitrogen radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) affect atmospheric composition and climate by regulating global tropospheric ozone and the Earth's oxidative capacity. Peroxyxynitrates (RO_2NO_2) link these chemical families, thereby influencing tropospheric ozone production and the abundance of OH in both the troposphere and stratosphere. Non-acyl peroxyxynitrates such as HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$ are increasingly important at temperatures below

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240 K, because the molecules are very weakly bound (~ 95 kJ/mol) and rapidly dissociate at higher temperature. Consequently these molecules are most important in the stratosphere and upper troposphere.

Knowledge of the chemistry of alkyl RO_2NO_2 species is limited because they are difficult to isolate in the laboratory or to observe directly in the atmosphere. Remote sensing measurements of peroxyacetic acid concentrations in the stratosphere show that HO_2NO_2 mixing ratios peak at approximately 200 ppt near 27 km altitude (Rinsland et al., 1996; Rinsland et al., 1986; Sen et al., 1998). The only other measurements are from the Antarctic surface where Slusher et al. (2001) used chemical ionization mass spectrometry to observe HO_2NO_2 mixing ratios on the order of 20 ppt, showing they were nearly equal to nitric acid mixing ratios. Recent OH and HO_2 measurements made in the lower stratosphere at high solar zenith angles (SZA) indicate that there is a source of HO_x that dissociates following absorption of low energy photons (Salawitch et al., 1994; Wennberg et al., 1999). Overtone photodissociation of HO_2NO_2 , as suggested by Donaldson et al. (1997), can explain these observations and some of the temporal variability seen in remote sensing of HO_2NO_2 (Salawitch et al., 2002). These observations and calculations of HO_2NO_2 abundances and their effect on stratospheric HOx have been the impetus for revisiting the long-wavelength photolysis and kinetics of peroxy nitrates in the laboratory (Knight et al., 2002; Roehl et al., 2002; Zhang et al., 2000).

Here we describe the first in situ measurements of these peroxy nitrates in the free troposphere. The measurements were made during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment (Atlas et al., 2003). Analysis along chemical coordinates (Cohen et al., 2000), in this case temperature and NO_2 , and consideration of the NO_y budget are used to evaluate current understanding of photolytic and thermal decomposition rates of HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$.

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2. Instrumentation

NO_y and its components were measured from the NCAR C-130 aircraft during the TOPSE experiment. Ridley et al. measured NO, NO₂ and NO_y by conversion to NO followed by O₃ + NO chemiluminescence (Ridley et al., 2000). The NO₂ measurements were precise to ±4 ppt and accurate to 5%. C1–C4 alkyl nitrates were quantified by GC analysis of whole air samples (Blake et al., 2003). In our analysis, the sum of C1–C4 alkyl nitrate observations was linearly interpolated to a 1 min time base. Nitric acid was measured using a mist chamber followed by ion chromatography (Talbot et al., 1990). PAN and PPN were measured in situ by the NCAR Gas Chromatography with Electron Capture Detection (GC-ECD) instrument (The behavior of PANs and the balance of NO_y during TOPSE, Flocke et al., in prep). The PAN and PPN measurements represent 1–3 s samples with a precision of ±5 ppt at 20 ppt, ±3 ppt at 100 ppt, ±5–7 ppt at 500 ppt. The accuracy of the PAN and PPN measurements is 10%. Because they were made with the same instrument, we assume their uncertainties are correlated, that is, if necessary, both could be brought to the “true” value by multiplying by a single constant. During a 5 min interval, two PAN measurements and one PPN are obtained.

A two-channel thermal dissociation laser-induced fluorescence (TD-LIF) instrument was used for observations of total peroxy nitrates (Σ PNs \equiv PAN + PPN + HO₂NO₂ + CH₃O₂NO₂ + ...) and of NO₂. TD-LIF is described in detail in Day et al. (2002). The specific instrument configuration used during TOPSE is presented by Thornton (2002). Briefly, TD-LIF relies on a heated inlet to dissociate RO₂NO₂ to yield NO₂ and RO₂. The resultant NO₂ is quantified along with ambient NO₂ using laser-induced fluorescence (LIF). By operating the heated inlet in parallel with an inlet maintained at ambient temperature, Σ PN mixing ratios can be derived from the difference between the NO₂ signals of the two channels. The first third of the campaign was used to test and improve some aspects of instrument performance. High time resolution measurements of NO₂ and Σ PNs were obtained simultaneously and continuously during the final nineteen flights of the TOPSE experiment. The

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precision of the measurements for a 1 min average in each channel under optimal conditions was ± 20 ppt which is dominated by uncertainty in the instrument zero. Under some conditions, usually after steep altitude changes, the apparent precision is ± 50 ppt. The accuracy of channel 1 is estimated to be 10% and the accuracy of channel 2 to be 15%. The precision of Σ PNs is given by:

$$\sigma(\Sigma\text{PNs}) = [(\sigma_{\text{channel 1}})^2 + (\sigma_{\text{channel 2}})^2]^{1/2} \quad (1)$$

and for a typical scenario $\sigma(\Sigma\text{PNs})$ is ± 28 ppt for 1 min averaging. The accuracy is estimated to be 15% since the accuracy of the two channels is largely correlated and most of the signal is in channel 2. While TD-LIF NO₂ measurements were used for calculating Σ PN, in the model calculations below we use the NCAR photolysis-chemiluminescence measurements of NO₂ because of their superior precision in the low concentration ranges encountered during TOPSE.

Measurements suggest that PAN is the dominant contribution to Σ PNs and that PPN is the only other major acyl peroxyxynitrate in the air sampled during TOPSE. In order to infer abundances of non-acyl peroxyxynitrates (hereafter referred to as Σ PNs) we subtract speciated measurements of PAN and PPN obtained by the NCAR GC-ECD instrument from the TD-LIF measurements of Σ PNs.

$$\Delta\text{PNs} = \Sigma\text{PNs} - \text{PAN} - \text{PPN}. \quad (2)$$

We averaged 1 min of TD-LIF data about each PAN measurement and interpolated PPN to generate a dataset of all species coincident in time.

The uncertainty in Δ PNs has components associated with both the precision and accuracy of the TD-LIF and GC measurements. In what follows, we do not draw any conclusions based on individual measurements, rather our conclusions are based on averages over a large enough sample that uncertainty in mean quantities is entirely a function of the instruments' accuracies. The techniques are thought to be accurate to 10% (GC) and 15% (LIF) and for both techniques one single multiplicative correction (if it could be known) would bring the observed values to the "true" values (to within

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the precision uncertainty). The accuracy of these instruments depends on a chain of calibration that connects to NIST traceable reference standards of NO or NO₂, on the accuracy of flow controllers used to dilute these standards and on titration reactions. None of these factors depend on environmental parameters. Thus the associated accuracy in the average value of a combined quantity like ΔPNs adds in quadrature, since the accuracy of the GC and LIF measurements are assumed to be uncorrelated, resulting in a combined accuracy of 18%. The random error associated with an individual ΔPNs measurement is obtained by standard propagation of error based on Eq. (2);

$$\sigma(\Delta\text{PNs}) = [(\sigma_{\Sigma\text{PNs}})^2 + (\sigma_{\text{PAN}})^2 + (\sigma_{\text{PPN}})^2]^{1/2}, \quad (3)$$

which results in an uncertainty of ±29 ppt.

Figure 1a shows the ratio of ΣPNs/(PAN+PPN) versus humidity for data that calculations suggest have negligible amounts of ΔPNs (ΔPNs less than 10% of PAN). In contrast to the expectations outlined above, Fig. 1 shows that the two techniques differ by 35% at high relative humidity and agree at low humidity. The absolute difference is larger than expected and the accuracy is not observed to be independent of environmental parameters. One or both instruments are not accurate to within the 10 or 15% quoted.

Neither technique is known to have a humidity-dependent bias or interference of this magnitude. Applying a constraint that

$$\Delta\text{PNs} \geq 0 \quad (4)$$

permits the derivation of a constant that implicitly couples the calibration constants for the two instruments and corrects for this difference as a function of humidity. A correction factor, $C = (1 + 0.0025 * \% \text{ RH})$, was generated that brings the average (PAN + PPN)/ΣPNs near one when ΔPNs are insignificant. Since we have no reason to apply the correction to one or the other instrument, the TD-LIF data was multiplied by the correction factor C, and the GC data was divided by this factor. This removed the humidity bias (Fig. 1b). Throughout the remainder of this paper we use these adjusted

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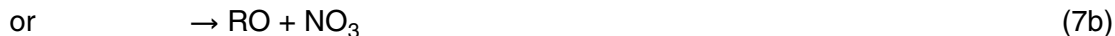
datasets. Applying the factor C to the two data sets alters them by 12% on average (+12% ΣPNs and −12% PAN and PPN). Using Eq. (2) with the corrected datasets provides 1433 measurements of ΔPNs, which calculations suggest are predominantly HO₂NO₂ and CH₃O₂NO₂. We estimate the uncertainty in ΔPNs is 25%.

Measurements of NO_y and comparison to the sum of individual NO_y compounds (ΣNO_y) provide another means to evaluate the relative calibration of the GC-ECD, TD-LIF and NO_y techniques, as well as our ability to infer ΔPNs from the adjusted difference of the two sets of measurements. Figure 2 demonstrates the importance of HO₂NO₂ in the reactive nitrogen budget and the ability of TD-LIF ΔPN measurements to account for this compound. The ratio ΣNO_{yi}/total NO_y, with the above correction applied to each peroxyxynitrate dataset, is plotted against fraction of NO_y that is predicted by a model to be HO₂NO₂. The ratio where ΣNO_{yi} = NO_x + HNO₃ + ΣANs + PAN + PPN (gray circle) decreases from a value of 1.2 where ΔPNs are insignificant to close to 0.8 where HO₂NO₂ contributes nearly half of total NO_y. Conversely, the NO_y budget using TD-LIF measurements ΣNO_{yi} = NO_x + HNO₃ + ΣANs + ΔPN (black square) suggests that our measurements account for the predicted contribution of HO₂NO₂ to the reactive nitrogen budget. If the modelled ΔPNs are added to the PAN and PPN measurements, the average ΣNO_{yi}/total NO_y ratio over the whole campaign is 1.2.

3. Model description and comparison to observations

Peroxyxynitrates are formed when an RO₂ radical (where R = H, alkyl, or acyl group) reacts with NO₂ (R5). In the remote atmosphere, HO₂ and CH₃O₂ make up a large fraction of RO₂. Sinks of HO₂NO₂ and CH₃O₂NO₂ include thermal decomposition (R6), photolysis (R7), and for HO₂NO₂, reaction with OH (R8). Note that the products given for (R8) have not been measured. Models all assume that water is a product of (R8) and consequently that (R8) is a sink for HO_x radicals.





5 Uncertainties associated with this chemistry are large. For example, for the thermal decomposition of HO₂NO₂ the JPL panel recommends an uncertainty factor of 5 at 298 K and of 13 at 230 K (Sander et al., 2003). Recent laboratory measurements of the UV (Knight et al., 2002) and IR (Roehl et al., 2002) cross sections of peroxyacetic acid greatly improve our understanding of its photolysis rate, (J≡R7), although the temperature and pressure dependencies of the quantum yield require further investigation. We know little about the photolysis of CH₃O₂NO₂.

We use an instantaneous steady state model representing (R5)–(R8) to predict the abundances of HO₂NO₂ and CH₃O₂NO₂.

$$[\text{HO}_2\text{NO}_2]_{\text{SS}} = \frac{k_5[\text{HO}_2][\text{NO}_2][\text{M}]}{k_6[\text{M}] + J + k_8[\text{OH}]} \quad (9)$$

$$[\text{CH}_3\text{O}_2\text{NO}_2]_{\text{SS}} = \frac{k_{5'}[\text{CH}_3\text{O}_2][\text{NO}_2][\text{M}]}{k_{6'}[\text{M}] + J'}. \quad (10)$$

Measurements of NO₂, the spectrally resolved actinic flux, temperature, and pressure are used in the calculations. As a result of the low mixing ratios of NO₂ (50% of the observations have NO₂ below 11 ppt) the precision of the model calculations are roughly proportional to the precision of the NO₂ measurements, for example ±40% at 10 ppt NO₂. Although OH and HO₂ were measured during the TOPSE campaign, the observations were too infrequent to use in the model. Steady state concentrations of OH, HO₂, and CH₃O₂ were calculated using the photochemical model described by Cantrell et al. (2003), which included the steady state equations for HO₂NO₂ and

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CH₃O₂NO₂. Four individual calculations in which radicals and reservoirs were solved self-consistently were used to investigate the main sources of uncertainty in the kinetics of HO₂NO₂. Rate constants used in the model are from the JPL-2000 recommendations except for the self-reaction of HO₂ (Christensen et al., 2002) and for the reaction HO₂ + O₃ and OH + O₃ for which we use JPL-97 recommendations (see Lanzendorf et al., 2001). Photolysis rates were determined using measured actinic flux and made use of the recent molecular data for H₂CO (Smith et al., 2002) and HO₂NO₂ (Knight et al., 2002; Roehl et al., 2002). The UV cross section of CH₃O₂NO₂ is assumed to be equal to that of HO₂NO₂, and we assume it has no infrared component because it lacks the OH group required for significant IR overtone photodissociation. In the first calculation (Model A), the IR photolysis rate of HO₂NO₂ is set at $1 \times 10^{-5} \text{ s}^{-1}$, slightly higher than the recommendation of $8.3 \times 10^{-6} \text{ s}^{-1}$ from Roehl et al., which was given for a system with no albedo. In a second calculation (Model B), the IR photolysis rate for HO₂NO₂ was set to zero. In two separate calculations, the rate of thermal decomposition of HO₂NO₂ was varied to the maximum (Model C) and minimum (Model D) limits given in JPL-2003. Model A, with standard thermal decomposition and IR photolysis, calculates peak HO₂NO₂ and CH₃O₂NO₂ mixing ratios during the last 19 flights of the TOPSE experiment that range as high as 300 ppt and 100 ppt respectively. It predicts HO₂NO₂ reaching as much as 50% of measured NO_y and CH₃O₂NO₂ as much as 15% of measured NO_y.

Figure 3 depicts the temperature dependence of the thermal and photochemical sinks of these two peroxy nitrates. The photochemical sinks (R7 and R8) are nearly independent of temperature. HO₂NO₂ has a slower thermal decomposition rate and a faster photochemical loss than CH₃O₂NO₂ because of its large infrared photodissociation cross section and because its reaction with OH also contributes to photochemical loss. For HO₂NO₂, thermal decomposition becomes faster than the photochemical sinks above 240 K, while the crossing point for CH₃O₂NO₂ is near 220 K. One consequence of this is that the lifetime of HO₂NO₂ (~12 h in sunlit conditions) is independent of temperature for the colder conditions sampled during TOPSE.

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The instantaneous steady state model is valid only when the lifetime of the HO₂NO₂ or CH₃O₂NO₂ is short compared to the rate of change of its sources and sinks. This is not always true for these peroxy nitrates under the coldest conditions sampled during TOPSE. However, many of the data points were collected at high latitudes during the late spring, where the photochemistry has a fairly shallow diurnal profile, making the model steady state predictions reasonable estimates. To help avoid any bias due to being strongly out of steady state, model results in which the lifetime of either compound exceeded 12 h were discarded, unless there were more than 20 h of sunlight per day at that location.

In the lower panel of Fig. 3, the ΔPN concentrations inferred from our observations are displayed versus temperature. The mixing ratios below approximately 250 K are larger than at warmer temperatures. The wide range of concentrations at each temperature derives partly from variation in the abundance of HO₂, CH₃O₂ and NO₂ radicals in the airmass. As an example, the large symbols are the mean ΔPNs within a 5 K bin for NO₂ mixing ratios above (black squares) and below (open circles) 11 ppt, which was the median NO₂ during the last 19 flights of TOPSE. On average, higher values of ΔPNs were observed when NO₂ mixing ratios were higher than average and vice versa. In addition to being proportional to NO₂, below 250 K ΔPNs are calculated to depend strongly on the IR photolysis of HO₂NO₂, which has only recently been recognized as large enough to affect its atmospheric mixing ratio. Our data provides direct observational evidence for this term. In the upper panel of Fig. 4 we show the difference between the ΔPN observations and model B (no IR photolysis) and in the lower panel we show the difference between ΔPNs and model A. The relative significance of IR photolysis increases strongly as a function of decreasing temperature and dominates over thermal decomposition as a sink of HO₂NO₂ below 235 K. At 230 K, the model without IR photolysis has, on average, 200 ppt more HO₂NO₂ than the observed ΔPNs. There are specific events where modeled ΔPNs exceed the measurements by 400 ppt without the infrared sink of HO₂NO₂.

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The model A peroxyxynitrate (HO₂NO₂ + CH₃O₂NO₂) predictions are compared to ΔPN measurements in a time series during a TOPSE flight on 22 May (Fig. 5 upper panel). This flight between Thule and Winnipeg sampled a wide range of tropospheric conditions and encountered air of mixed stratospheric-tropospheric character (O₃ > 100 ppb) near the end of the flight. HNO₃ and NO_x make significant contributions to NO_y in this particular airmass, which nonetheless has quite high PAN mixing ratios. The ΔPN measurements are generally scattered around the model predictions and tend to be highest under the coldest conditions as expected based on the chemistry described above. During this flight, NO_x and ΔPNs are nearly equal.

The figures above show that ΔPNs vary as expected in response to two of the individual terms in the steady-state equations (J and NO₂) and vary along a flight track as the steady state calculation suggests they should. Figure 6 shows a direct comparison of calculations of ΔPNs and the observations. Within the statistical variance, the observations and model agree. However model predictions exceed the observations at higher mixing ratios and the fact that nearly all calculated concentrations above 150 ppt are higher than observations suggests the effect is statistically reliable. If the steady state approximation is correct, then this could indicate an error in the photochemistry of HO₂NO₂ or the thermal decomposition of CH₃O₂NO₂. We investigated the factor of 5–15 uncertainty in the HO₂NO₂ thermal decomposition rate at temperatures in the 220–298 K range. Model calculations (C, D) that incorporated the most extreme values for rates of thermal decomposition predicted ΔPN concentrations that differed at most by 100 ppt, with the greatest effect occurring between 235 and 250 K. Both models were less consistent with the observations than Model A, but because HO₂NO₂ is largest where thermal decomposition is slow compared to photolysis we are unable to define substantially more precise limits on the rate of thermal decomposition than recommended by the JPL panel. We examined other possible effects but found no single explanation that would bring the model-measurement comparison into agreement.

4. Discussion

In the upper troposphere, several studies (Folkins et al., 1997; Jaegle et al., 2000; Jaegle et al., 2001) have described calculations indicating that reaction of OH with HO₂NO₂ is a dominant sink for HO_x. Analysis of HO_x observations by Faloona et al. (2000) suggest that a model in which the HO₂NO₂ equilibrium constant is reduced by a factor of five, or with HO₂NO₂ formation suppressed entirely, provides a more accurate representation of upper tropospheric HO_x observations than the standard model. We estimate that inclusion of the IR photolysis of HO₂NO₂ should have nearly the same effect on HO₂NO₂ concentrations at the altitudes where most of the observations described by Faloona et al. were collected. The main consequence is a decrease in the modelled abundance of HO₂NO₂. However, the IR photolysis will have a distinctly different temperature dependence than the suggested change to the equilibrium constant. For the coldest conditions sampled during TOPSE, between 220 K and 240 K, Model A, which includes IR photolysis, predicts ~10% more HO_x than Model B, and also results in slightly different HO_x partitioning.

Another interesting aspect of HO₂NO₂ and CH₃O₂NO₂ chemistry is their behavior as a short-term reservoir for HO_x and NO_x radicals. Under sunlit conditions, the radicals and alkyl peroxy nitrates should reach steady state, yet once the sun sets, formation diminishes and the only remaining sink is thermal decomposition. During 12 h of darkness in the upper troposphere at 240 K, all the CH₃O₂NO₂ and over half of the HO₂NO₂ will have thermally dissociated, releasing on the order of tens to hundreds ppt of CH₃O₂ and HO₂. The fate of these radicals during the night will depend strongly on the abundance of NO_x and O₃. This fact underscores the importance of making measurements at night to challenge our understanding of radical sources and sinks.

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5. Conclusions

We describe observations of Δ PNs and demonstrate that they are HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$. The observations show that during the spring high latitude conditions sampled during the TOPSE experiment, the contribution of Δ PNs to NO_y is highly temperature dependent, with Δ PNs on average 30% of NO_y at 230 K and 7% of NO_y at 250 K. The magnitude and observed temperature dependence of the mixing ratios is consistent with recent laboratory evidence that the J value for HO_2NO_2 has a large IR component. Prior analyses of the NO_y budget in the upper troposphere that did not take into account HO_2NO_2 or the new J value should be revisited.

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References

- Atlas, E. L., Ridley, B. A., and Cantrell, C. A.: The Tropospheric Ozone Production about the Spring Equinox (TOPSE) Experiment: Introduction, *J. Geophys. Res.-Atmos.*, 108, 8353, doi:8310.1029/2002JD003172, 2003.
- Blake, N. J., Blake, D. R., Sive, B. C., Katzenstein, A. S., Meinardi, S., Wingenter, O. W., Atlas, E. L., Flocke, F., Ridley, B. A., and Rowland, F. S.: The seasonal evolution of NMHCs and light alkyl nitrates at middle to high northern latitudes during TOPSE, *J. Geophys. Res.-Atmos.*, 108, 8359, doi:8310.1029/2001JD001467, 2003.
- Cantrell, C. A., Mauldin, L., Zondlo, M., Eisele, F., Kosciuch, E., Shetter, R., Lefer, B., Hall, S., Campos, T., Ridley, B., Walega, J., Fried, A., Wert, B., Flocke, F., Weinheimer, A., Hannigan, J., Coffey, M., Atlas, E., Stephens, S., Heikes, B., Snow, J., Blake, D., Blake, N., Katzenstein, A., Lopez, J., et al.: Steady state free radical budgets and ozone photochemistry during TOPSE, *J. Geophys. Res.-Atmos.*, 108, 8361, doi:8310.1029/2002JD002198, 2003.

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Christensen, L. E., Okumura, M., Sander, S. P., Salawitch, R. J., Toon, G. C., Sen, B., Blavier, J.-F., and Jucks, K. W.: Kinetics of HO₂ + HO₂ to H₂O₂ + O₂: Implications for Stratospheric H₂O₂, *Geophys. Res. Lett.*, 29, 1299, doi:10.1029/2001GL014525, 2002.

5 Cohen, R. C., Perkins, K. K., Koch, L. C., Stimpfle, R. M., Wennberg, P. O., Hanisco, T. F., Lanzendorf, E. J., Bonne, G. P., Voss, P. B., Salawitch, R. J., Del Negro, L. A., Wilson, J. C., McElroy, C. T., and Bui, T. P.: Quantitative constraints on the atmospheric chemistry of nitrogen oxides: An analysis along chemical coordinates, *J. Geophys. Res.-Atmos.*, 105, 24 283–24 304, 2000.

10 Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO₂, peroxy nitrates, alkyl nitrates, and HNO₃, *J. Geophys. Res.-Atmos.*, 107, 4046, doi:10.1029/2001JD000779, 2002.

Donaldson, D. J., Frost, G. J., Rosenlof, K. H., Tuck, A. F., and Vaida, V.: Atmospheric radical production by excitation of vibrational overtones via absorption of visible light, *Geophys. Res. Lett.*, 24, 2651–2654, 1997.

15 Faloon, I., Tan, D., Brune, W. H., Jaegle, L., Jacob, D. J., Kondo, Y., Koike, M., Chatfield, R., Pueschel, R., Ferry, G., Sachse, G., Vay, S., Anderson, B., Hannon, J., and Fuelberg, H.: Observations of HO_x and its relationship with NO_x in the upper troposphere during SONEX, *J. Geophys. Res.-Atmos.*, 105, 3771–3783, 2000.

20 Folkins, I., Wennberg, P. O., Hanisco, T. F., Anderson, J. G., and Salawitch, R. J.: OH, HO₂, and NO in two biomass burning plumes: Sources of HO_x and implications for ozone production, *Geophys. Res. Lett.*, 24, 3185–3188, 1997.

Jaegle, L., Jacob, D. J., Brune, W. H., Faloon, I., Tan, D., Heikes, B. G., Kondo, Y., Sachse, G. W., Anderson, B., Gregory, G. L., Singh, H. B., Pueschel, R., Ferry, G., Blake, D. R., and Shetter, R. E.: Photochemistry of HO_x in the upper troposphere at northern midlatitudes, *J. Geophys. Res.-Atmos.*, 105, 3877–3892, 2000.

Jaegle, L., Jacob, D. J., Brune, W. H., and Wennberg, P. O.: Chemistry of HO_x radicals in the upper troposphere, *Atmos Environ*, 35, 469–489, 2001.

30 Knight, G., Ravishankara, A. R., and Burkholder, J. B.: UV absorption cross sections of HO₂NO₂ between 343 and 273 K, *Phys Chem Chem Phys*, 4, 1432–1437, 2002.

Lanzendorf, E. J., Hanisco, T. F., Wennberg, P. O., Cohen, R. C., Stimpfle, R. M., and Anderson, J. G.: Comparing atmospheric [HO₂]/[OH] to modeled [HO₂]/[OH]: Identifying discrepancies with reaction rates, *Geophys. Res. Lett.*, 28, 967–970, 2001.

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Ridley, B., Walega, J., Montzka, D., Grahek, F., Atlas, E., Flocke, F., Stroud, V., Deary, J., Gallant, A., Boudries, H., Bottenheim, J., Anlauf, K., Worthy, D., Sumner, A. L., Splawn, B., and Shepson, P.: Is the Arctic surface layer a source and sink of NO_x in winter/spring?, *J Atmos Chem*, 36, 1–22, 2000.

5 Rinsland, C. P., Gunson, M. R., Salawitch, R. J., Michelsen, H. A., Zander, R., Newchurch, M. J., Abbas, M. M., Abrams, M. C., Manney, G. L., Chang, A. Y., Irion, F. W., Goldman, A., and Mahieu, E.: Atmos/Atlas-3 Measurements of Stratospheric Chlorine and Reactive Nitrogen Partitioning Inside and Outside the November 1994 Antarctic Vortex, *Geophys. Res. Lett.*, 23, 2365–2368, 1996.

10 Rinsland, C. P., R., Z., C.B., F., R.H., N., L.R., B., J.M., R., and J.H., P.: Evidence for the presence of 802.7 cm⁻¹ band Q branch of HO₂NO₂ in high-resolution solar absorption-spectra of the stratosphere, *Geophys. Res. Lett.*, 13, 761–764, 1986.

Roehl, C. M., Nizkorodov, S. A., Zhang, H., Blake, G. A., and Wennberg, P. O.: Photodissociation of peroxyntiric acid in the near-IR, *J. Phys. Chem. A*, 106, 3766–3772, 2002.

15 Salawitch, R. J., Wennberg, P. O., Toon, G. C., Sen, B., and Blavier, J. F.: Near IR photolysis of HO₂NO₂: Implications for HO_x, *Geophys. Res. Lett.*, 29, 1762, 1710.1029/2002GL015006, 2002.

Salawitch, R. J., Wofsy, S. C., Wennberg, P. O., Cohen, R. C., Anderson, J. G., Fahey, D. W., Gao, R. S., Keim, E. R., Woodbridge, E. L., Stimpfle, R. M., Koplów, J. P., Kohn, D. W., Webster, C. R., May, R. D., Pfister, L., Gottlieb, E. W., Michelsen, H. A., Yue, G. K., Prather, M. J., Wilson, J. C., Brock, C. A., Jonsson, H. H., Dye, J. E., Baumgardner, D., Proffitt, M. H., Loewenstein, M., Podolske, J. R., Elkins, J. W., Dutton, G. S., Hintsä, E. J., Dessler, A. E., Weinstock, E. M., Kelly, K. K., Boering, K. A., Daube, B. C., Chan, K. R., and Bowen, S. W.: The Diurnal Variation of Hydrogen, Nitrogen, and Chlorine Radicals - Implications For the Heterogeneous Production of HNO₂, *Geophys. Res. Lett.*, 21, 2551–2554, 1994.

25 Sander, S. P., Kurylo, J. M., Orkin, V. L., Golden, D. M., Huie, R. E., Finlayson-Pitts, B. J., Kolb, C. E., Molina, M. J., Friedl, R. R., Ravishankara, A. R., and Moortgat, G. K.: Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, evaluation number 14, NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 2003.

30 Sen, B., Toon, G. C., Osterman, G. B., Blavier, J. F., Margitan, J. J., Salawitch, R. J., and Yue, G. K.: Measurements of reactive nitrogen in the stratosphere, *J. Geophys. Res.-Atmos.*, 103, 3571–3585, 1998.

Slusher, D. L., Pittner, S. J., Haman, B. J., Tanner, D. J., and Huey, L. G.: A chemical ionization

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technique for measurement of pernitric acid in the upper troposphere and the polar boundary layer, *Geophys. Res. Lett.*, 28, 3875–3878, 2001.

Smith, G. D., Molina, L. T., and Molina, M. J.: Measurement of radical quantum yields from formaldehyde photolysis between 269 and 339 nm, *J. Phys. Chem. A*, 106, 1233–1240, 2002.

Talbot, R. W., Vijgen, A. S., and Harriss, R. C.: Measuring Tropospheric HNO₃ – Problems and Prospects For Nylon Filter and Mist Chamber Techniques, *J. Geophys. Res.-Atmos.*, 95, 7553–7561, 1990.

Thornton, J. A.: Nitrogen Dioxide, Peroxynitrates, and the Chemistry of Tropospheric O₃ Production: New Insights from In Situ Measurements, Doctoral thesis, University of California, Berkeley, 2002.

Wennberg, P. O., Salawitch, R. J., Donaldson, D. J., Hanisco, T. F., Lanzendorf, E. J., Perkins, K. K., Lloyd, S. A., Vaida, V., Gao, R. S., Hints, E. J., Cohen, R. C., Swartz, W. H., Kusterer, T. L., and Anderson, D. E.: Twilight observations suggest unknown sources of HOx, *Geophys. Res. Lett.*, 26, 1373–1376, 1999.

Zhang, H., Roehl, C. M., Sander, S. P., and Wennberg, P. O.: Intensity of the second and third OH overtones of H₂O₂, HNO₃, and HO₂NO₂, *J. Geophys. Res.-Atmos.*, 105, 14 593–14 598, 2000.

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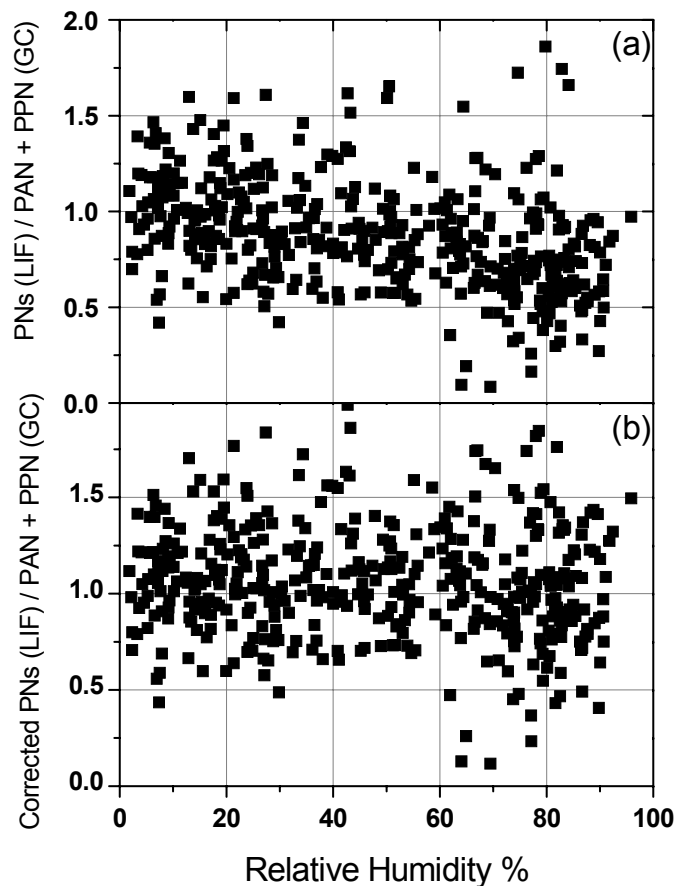


Fig. 1. (a) Humidity trend in ratio of LIF to GC measurements where HO_2NO_2 is predicted be less than 10% of PAN (b) Ratio after the humidity-dependent correction has been applied.

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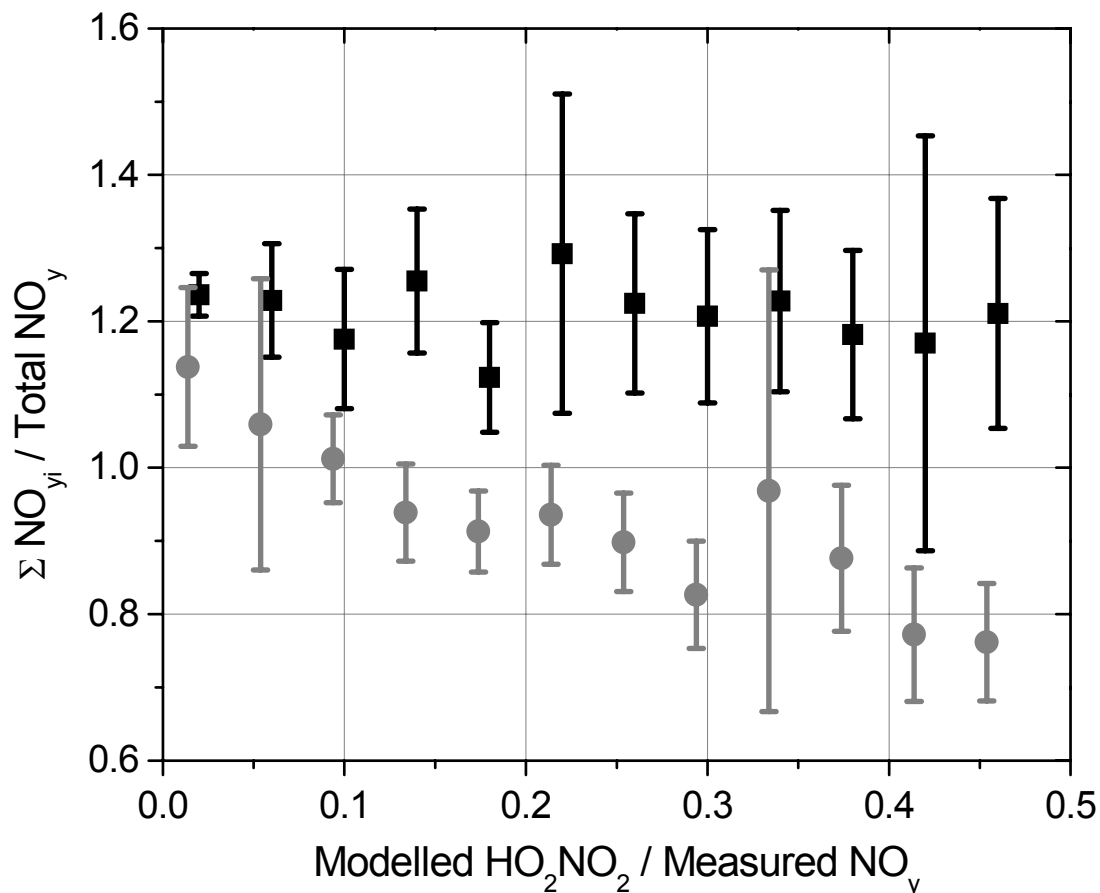


Fig. 2. $\Sigma\text{NO}_{y_i}/\text{NO}_y$ vs calculated $\text{HO}_2\text{NO}_2/\text{NO}_y$, using $\Sigma\text{NO}_{y_i} = \text{NO}_x + \text{HNO}_3 + \Sigma\text{ANs} + \text{PAN} + \text{PPN}$ (grey) and $\Sigma\text{NO}_{y_i} = \text{NO}_x + \text{HNO}_3 + \Sigma\text{ANs} + \Sigma\text{PNs}$ (black). The data were averaged within ± 0.04 of $\text{HO}_2\text{NO}_2/\text{NO}_y$ and the error bars represent twice the standard deviation of the mean.

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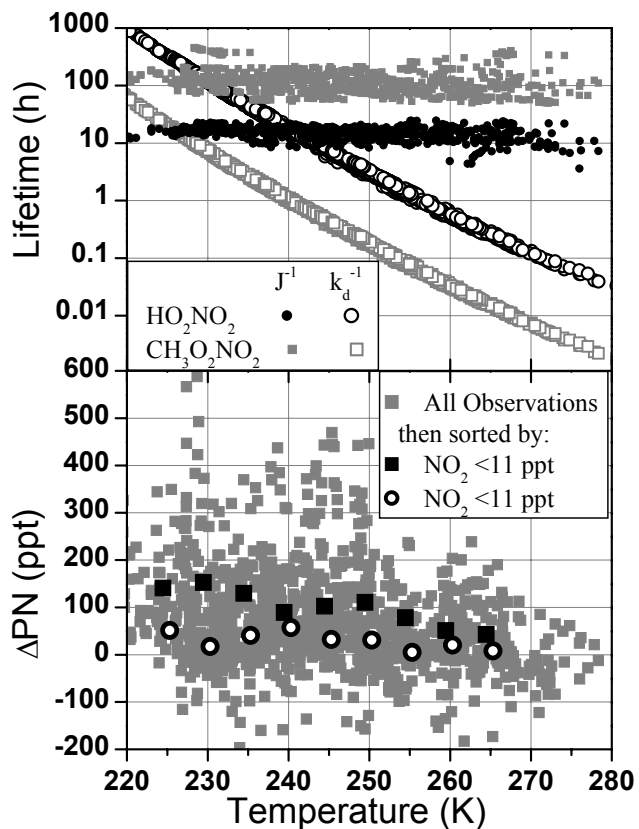


Fig. 3. (Upper panel) lifetime of HO_2NO_2 with respect to thermal decomposition (large black circle) and the sum of photolysis and reaction with OH (large black dot) and of $\text{CH}_3\text{O}_2\text{NO}_2$ with respect to thermal decomposition (large grey square) and photolysis (small grey square). **(Lower panel)** ΔPN measurements (small grey square) as a function of temperature, averaged into separate temperature bins for $\text{NO}_2 < 11$ ppt (big black circle) and for $\text{NO}_2 > 11$ ppt (large black square).

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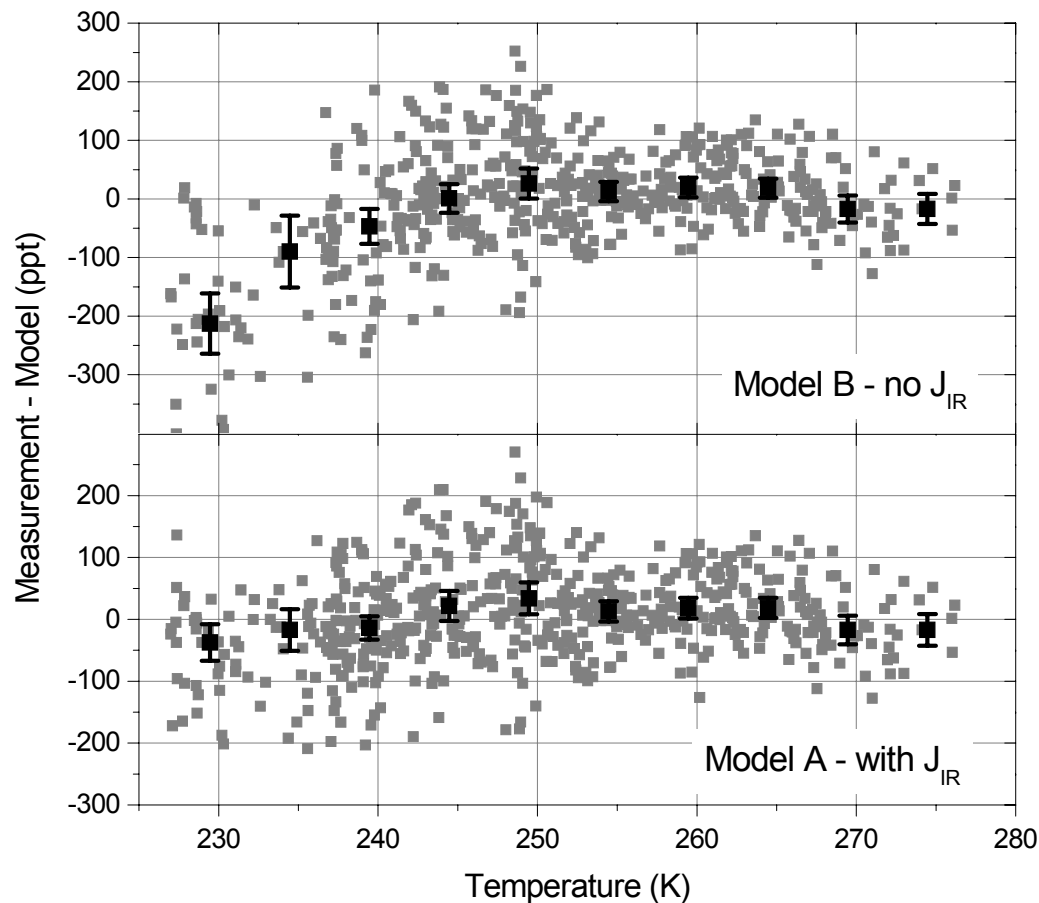


Fig. 4. Difference between measured and modelled ΔPNs for a model without IR photolysis (**upper panel**) and a model including IR photolysis for HO_2NO_2 (**lower panel**). The black squares represent the median of each 5 K bin and the error bars are twice the standard deviation of the mean.

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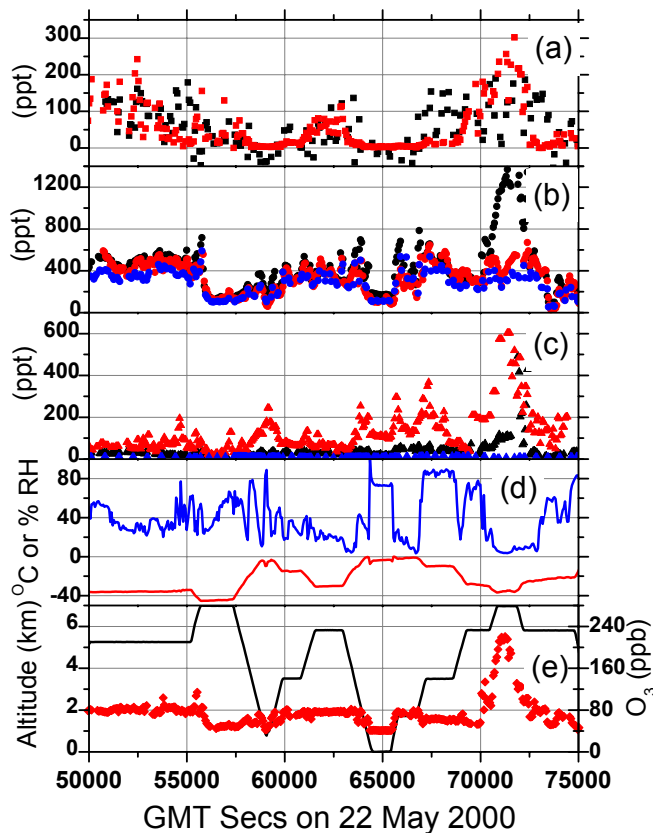


Fig. 5. Observations during a flight between Thule and Winnipeg on 22 May 2000, **(a)** ΔPN measurements (small black square) and predictions from Model A (small red square), **(b)** NO_y (black dot), PAN + PPN (blue dot), ΣPN (red dot), **(c)** HNO_3 (red triangle), NO_x (black triangle), ΣAlkyls (blue triangle), **(d)** temperature (red line), % relative humidity (blue line), **(e)** altitude (black line), O_3 (red diamond).

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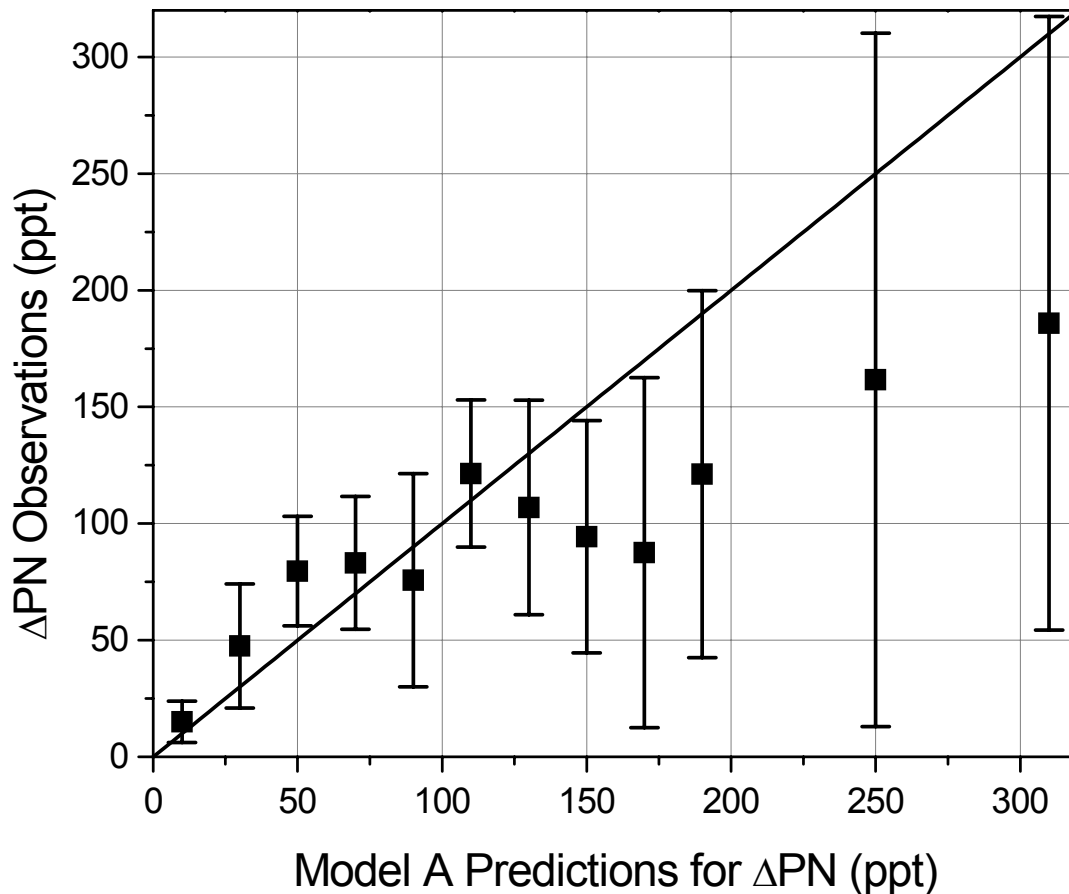


Fig. 6. Comparison of average Δ PN observations and Model A predictions with the error bars representing twice the standard deviation on the mean and a 1:1 line shown.

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