Using DC3 Observations to Assess Chemistry Occurring in the Upper Troposphere after Convection

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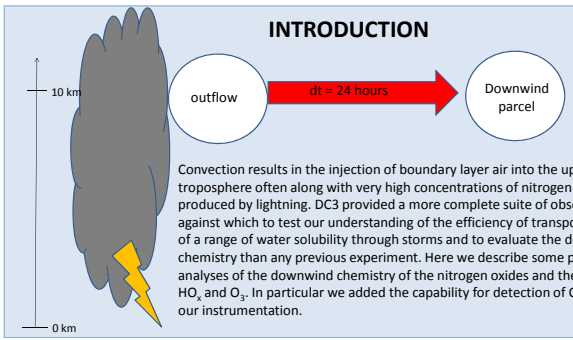
INTRODUCTION



Convection results in the injection of boundary layer air into the upper troposphere often along with very high concentrations of nitrogen oxides produced by lightning. DC3 provided a more complete suite of observations against which to test our understanding of the efficiency of transport of chemicals of a range of water solubility through storms and to evaluate the downwind chemistry than any previous experiment. Here we describe some preliminary analyses of the downwind chemistry of the nitrogen oxides and their coupling to HO_x and O_3. In particular we added the capability for detection of $CH_3O_2NO_2$ to our instrumentation.

OBSERVATIONS AND INSTRUMENTATION

Observations of NO_2, MPN, ΣPNs, and ΣANs were made using Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) (Thornton et al, 2000; Day et al., 2002). Briefly, NO_2 is detected via excitation of an individual rovibronic feature in the NO2 spectrum at 585 nm; then, the resulting fluorescence is collected by a PMT orthogonal to the laser axis. The instrument is calibrated with a 4.67(±0.26) ppm NO_2 standard (Praxair). $CH_3O_2NO_2$, total peroxynitrates (ΣPNs= PAN+PPN+$CH_3O_2NO_2$+HNO_4+N_2O_5+…), and total alkyl and multifunctional alkyl nitrates (ΣANs) are observed by coupling thermal dissociation with NO_2 detection (Day et al., 2002). Ambient air is heated to 60°C for $CH_3O_2NO_2$ detection, 200°C for ΣPNs, and 400°C for ΣANs. The individual quantities are determined by subtraction (e.g., total PNs are defined as the difference between the 200°C channel and the unheated NO_2 channel after correcting for a modest interference of $CH_3O_2NO_2$ in the NO_2 channel. The $CH_3O_2NO_2$ channel was a new feature to this instrument, added for DC-3 based on the results of Browne et al (2011) who showed that $CH_3O_2NO_2$ is abundant in the upper troposphere where temperatures are below 240K. $CH_3O_2NO_2$ rapidly dissociates at room temperature (τ = 980 ms at 25°C) making it essential to either correct NO_2 measurements for its presence or to interpret "NO_2" measurements as the sum of NO_2 and $CH_3O_2NO_2$ if the residence time within the airplane prior to detection is long compared to this lifetime. The residence time prior to detection in our NO_2 channel was reduced to 500 ms for DC-3. We use the 60°C measurements to infer an interference in that channel that was a maximum of 10% of the NO_2.

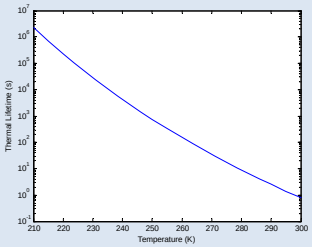


Figure 1. The thermal lifetime of $CH_3O_2NO_2$ versus temperature. In areas of the outflow (T < 240 K), $CH_3O_2NO_2$ has lifetimes greater than 1 hour, but at temperatures characteristic of the interior of the aircraft airplane, the lifetime is approximately 1 second.

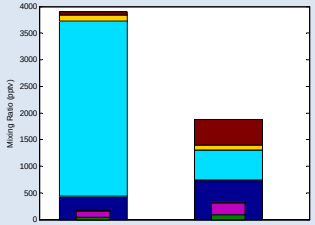


Figure 2. The average NO_y concentrations for 05/29 (left) and 05/30 (right). ΣPNs (dark blue) and the ΣPN components $CH_3O_2NO_2$ (green) and PAN (purple) were measured. The balance of the ΣPNs are most likely HO_2NO_2. NO_x is light blue, sum of ANs is yellow, and HNO_3 is brown. As expected, HNO_3 and ΣPNs both become much larger fractions of NO_y downwind of convection.

MODEL

A box model with dilution is used to simulate the first ~48 hours of chemistry. Chemistry in the model is taken from the Master Chemical Mechanism, version 3.2 with rate constants updated to JPL Publication 10-6, IUPAC, and Henderson et al., 2012. For N_2O_5 uptake onto aerosol, the parameterization from Bertram and Thornton, 2011 was used. The model is initialized with the mean values measured on the DC8 in the outflow of the storm during 05/29; background values are also set to the mean of air sampled by the DC8 with CH_4 values below 1840 ppbv.

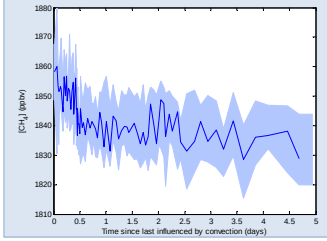


Figure 3. The box model includes dilution of the air parcel into background air. Compounds with long chemical lifetimes (e.g., CH_4) have been used before to determine the rate of dilution into background air (Bertram et al., 2007). Shown to the right are all CH_4 measurements made above 8 km during the DC3 campaign against the determined age of air parcel (see Figures 4 and 5 for more information). It is shown that the first 12 hours has a rate of dilution of ~ 2 day^{-1}; then, the rate of dilution decreases to ~ 0.2 day^{-1} The latter rate of dilution is a factor of 2 higher than what Bertram et al., 2007 measured during INTEX-NA. This is consistent with other typically used long-lived tracers for dilution (e.g., CO, CH_3OH).

INITIAL RESULTS

Frequency of Time Since Air was Influenced by Convection

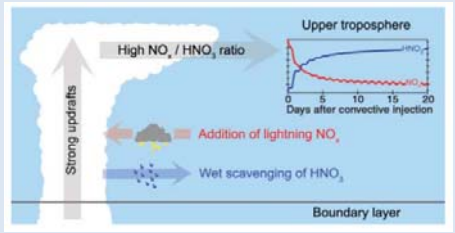


Figure 4. As described in Bertram et al. 2007, high NO_x:HNO_3 ratios in the outflow of convection result from scavenging of HNO_3 in cloud droplets that fall to lower altitudes. Even in the absence of lightning injection of NO_x high ratios are expected due to HNO_3 removal. The return of the ratio of NO_x/HNO_3 to its background value serves as a clock with a well-defined zero of time at the convective outflow. In the simplest conceptual model, NO_x decays due to reaction with OH and HNO_3 is produced such that the sum of the two is conserved—and the sum only decreases due to dilution. In more full detail, other weakly bound oxides of nitrogen (PAN, HO_2NO_2, $CH_3O_2NO_2$) are important. Figure 5 (left) shows the mapping between time and NO_x/HNO_3 has high resolution for about two days with the high dilution rate inferred in this analysis. After that memory is lost as dilution makes the air indistinguishable form the background.

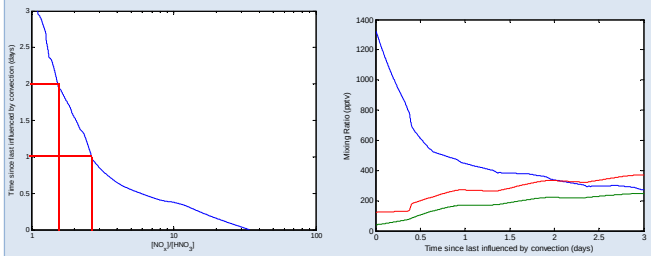


Figure 5. Left figure is shows $[NO_x]/[HNO_3]$ for 3 days. Red lines show what he approximate $[NO_x]/[HNO_3]$ would be for 1 and 2 days after convection (~3 and 1.5, respectively). These are similar ratios found in Bertram et al., 2007. On the right, NO_x (blue), HNO_3 (green) and PAN (red) vs. time since convection.

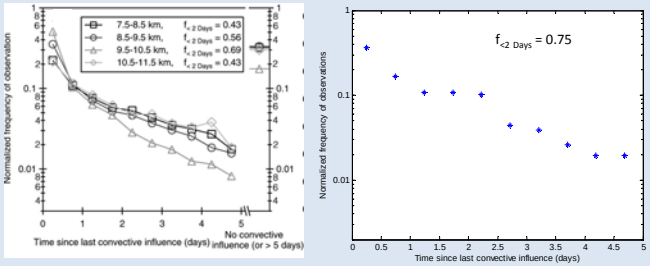


Figure 6. (Left) Normalized frequency of observations of time since convective influence at four altitudes as observed during INTEX-NA (Bertram et al., 2007). That experiment sampled relatively randomly compared to DC-3 and found that about 50% of the air over the Eastern US at altitudes above 7.5 km was influenced by convection within the last two days. (Right) Same for DC-3 for all measurements from the DC-8 above 8 km. The distributions are quite similar. The frequency of measurement for air parcels less than .5 days and less than 2 days are highlighted in the figure.

Evolution of NO_y Downwind from Convection

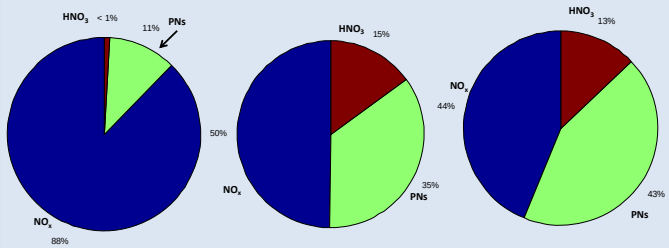


Figure 7. Observed partitioning of NOy at the convective outflow (left) and calculated partitioning 1 day later (center). The parcel is initially over 90% NO_x. The change in partitioning with substantial increases in total peroxynitrates (PAN + PPN + HNO_4 + $CH_3O_2NO_2$ + N_2O_5) results both from chemical production of HNO_3 and the various peroxynitrates, but also from mixing of background air. Based on observations of air that was the most aged in the campaign, we set the background NO_y partitioning as shown in the right panel. In the model, the peroxynitrates in this background are allowed to equilibrate to the local temperature if it is warm enough to result in net formation or dissociation of $CH_3O_2NO_2$ or HNO_4.

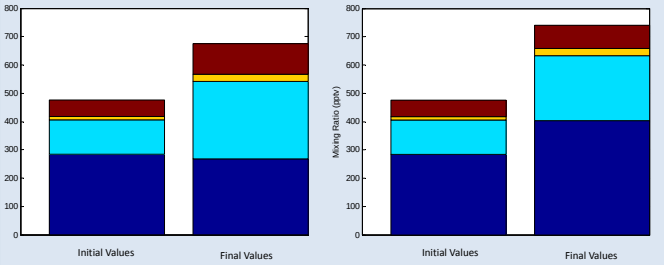


Figure 8. Comparison of modeled (left) and measured (right) HNO_4, determined from subtraction of (PAN + $CH_3O_2NO_2$ + PPN) from ΣPNs, (dark blue), PAN (light blue), PPN (yellow) and $CH_3O_2NO_2$(brown). The left bar corresponds to the mean values measured on the DC8 on 05/29 in the outflow, and the final values corresponds to the average values measured by the DC8 on 05/30 and the end on a 1 day model run. During the one day run, the model shows a -5% decrease in HNO_4, and a 124%, 107%, and 89% increase in PAN, PPN, and $CH_3O_2NO_2$. The average increase in the observations is 43%, 88%, 89%, and 43%. The much smaller increases in the observations suggest there is room to improve the kinetics in the model using these data as constraints.

REFERENCES

Bertram, T.H., et al. *Science*, 315, 816-820, 2007.
Bertram, T. H. and Thornton, J. A. *Atmos. Chem. Phys.*, 9, 8351-8363, 2009.
Bloss et al. *Atmos. Chem. Phys.*, 5, 641, 2005.
Browne et al. *Atmos. Chem. Phys.*, 11, 4209-4219, 2011.
Day D. A., et al., *J. Geophys. Res.*, 107, D6, 2002.
Henderson, B. H., et al. *Atmos. Chem. Phys.*, 11, 275-291, 2011.
Henderson, B. H., et al. *Atmos. Chem. Phys.*, 12, 653-667, 2012.
Jenkin et al.. *Atmos. Envrion.*, 31, 81, 1997.
Jenkin et al. *Atmos. Chem. Phys.*, 3, 181, 2003.
Sander, S. P., et al. "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," 2011.
Saunders et al. *Atmos. Chem. Phys.*, 3, 161, 2003.
Thornton J. A. et al., *Anal. Chem.*, 72, 526-539, 2000.

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