Convection Signatures and the Age of Air in the Upper Troposphere

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1. Motivation

Observations of Nitrogen Dioxide (NO_2) over the continental United States reveal strong signatures of convective pumping of both boundary layer and lighting NO_x to the Upper Troposphere (UT) (8-12.5km) during the summer (INTEX-NA July-August 2004). This influence may require adjustments to *a priori* assumptions about NO_2 profiles used in OMI or SCIAMACHY NO_2 retrievals. As expected, similar profiles during the winter (PAVE January 2005) show no signs of enhanced NO_x in the UT. Quantifying the role of convection and lightning is a long standing challenge for tropospheric chemistry. Another challenge has been to provide a clock indicating the time that air has spent in the free troposphere since convection. Following on the suggestion of Jaegle et al. [1998] that convective injection of boundary layer NO_x is responsible for holding the observed NO_x/NO_y ratio above steady state during the summer months and that this ratio provides timing information we use the ratio of NO_2/HNO_3; the number of condensation nuclei and the ratio CH_3OOH/H_2O_2 as indicators of convective influence and a measure of the timing of that influence.

In the following analysis we use the results of a 0-D chemical box model to assign time-stamps to air masses sampled from the DC-8 during the INTEX-NA campaign. This analysis will allow us to address the following questions:

1. Under what conditions do time indicators derived from NO_x/HNO_3, CH_3OOH/H_2O_2 and UCN agree?

2. Using these time indicators how accurately can we estimate the export efficiency of various BL species in convective events?

3. To what extent does chemical processing vs. entrainment dictate the fate of these convective injections?

Additionally, we discuss the implications of recent NO_2 profiles on the retrieval of tropospheric NO_2 columns from space-based instruments.

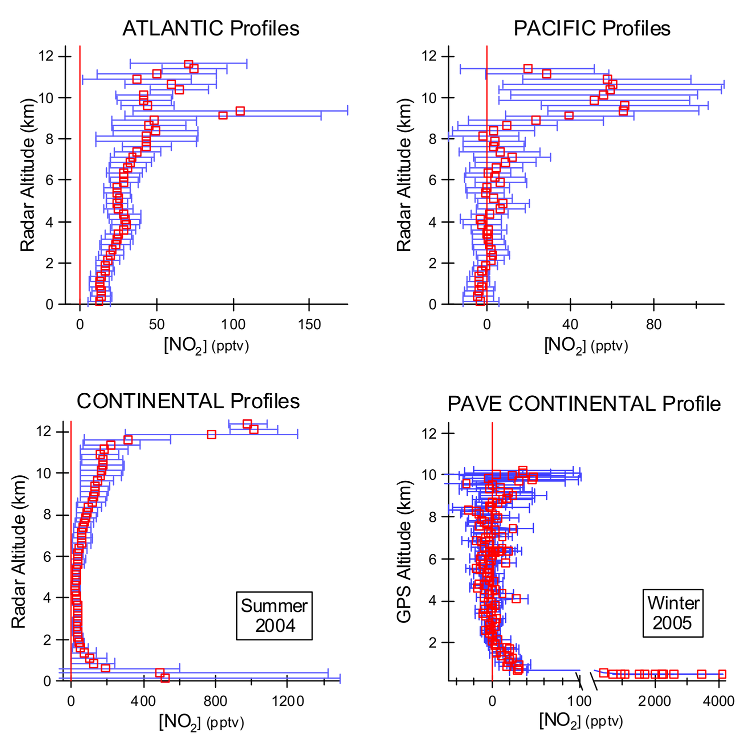

Figure 1: *Upper Panel* Mean NO_2 mixing ratios during profiles over the Atlantic (left) and Pacific (right) averaged in 250m bins. *Lower Panel* Mean NO_2 mixing ratios during continental profiles in the summer (INTEX) (left) and winter (PAVE) (right) separated into 250m bins.

2. Methods

A simple time-dependent 0-D box model, was constructed to assign time-stamps to measured ratios of NO_x/HNO_3 and CH_3OOH/H_2O_2 and UCN (3-7nm). The model was initialized with t=0 defined as the point of injection. The initial conditions correspond to observations made at 10km during July at 40 N.

Nitrogen Module – Reactive nitrogen in the injection is considered to be comprised of NO_x and PAN, assuming all other NO_y species are scrubbed completely. Photolysis rates are varied with SZA and NO_y is comprised of NO_2, NO, PAN, HNO_3, PNA and N_2O_5.

Peroxide Module – The initial peroxide ratio was taken as the maximum value observed during INTEX (representing a lower bound).

Aerosol Module – Aerosol Coagulation rates were based on coagulation constants (K) derived from Brownian diffusivities (Stokes-Einstein Expression), assuming D_{p1}=5nm with a background aerosol population of D_{p2}=100nm and taking N_0=max(UCN-coldCN)$_{INTEX}$.

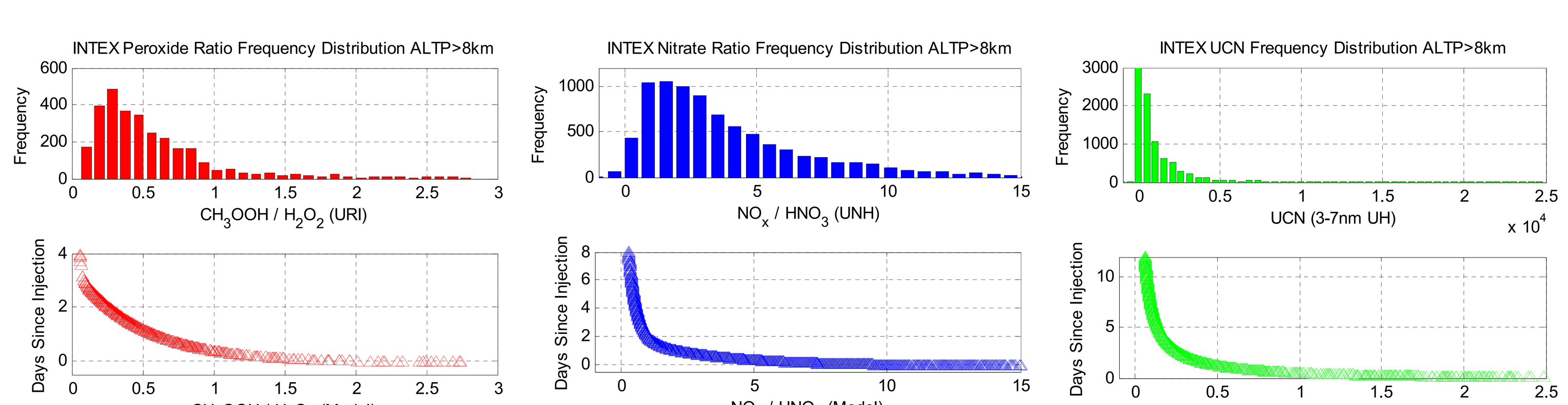

Figure 2 *Upper Panels* Measured frequency distributions of species used in 0-D time-dependent model (ALT>8km). *Bottom Panels* Calculated time since convection as determined from 0-D model for each of the three time indicators (Model results were fitted to a double exponential to calculate time from the observed ratios)

3. Preliminary Analysis

Case Study: 11 August 2004

As indicated in Figure 2, the DC-8 routinely sampled air in the UT that had recently been influenced by convection. Figure 3 shows a two day back-trajectory from the DC-8 sampling location over Northern Maine the morning of August 11th. Using lightning as a proxy for convective activity, it is clear that the air sampled during this leg had been influenced by convection during the past 24 hours.

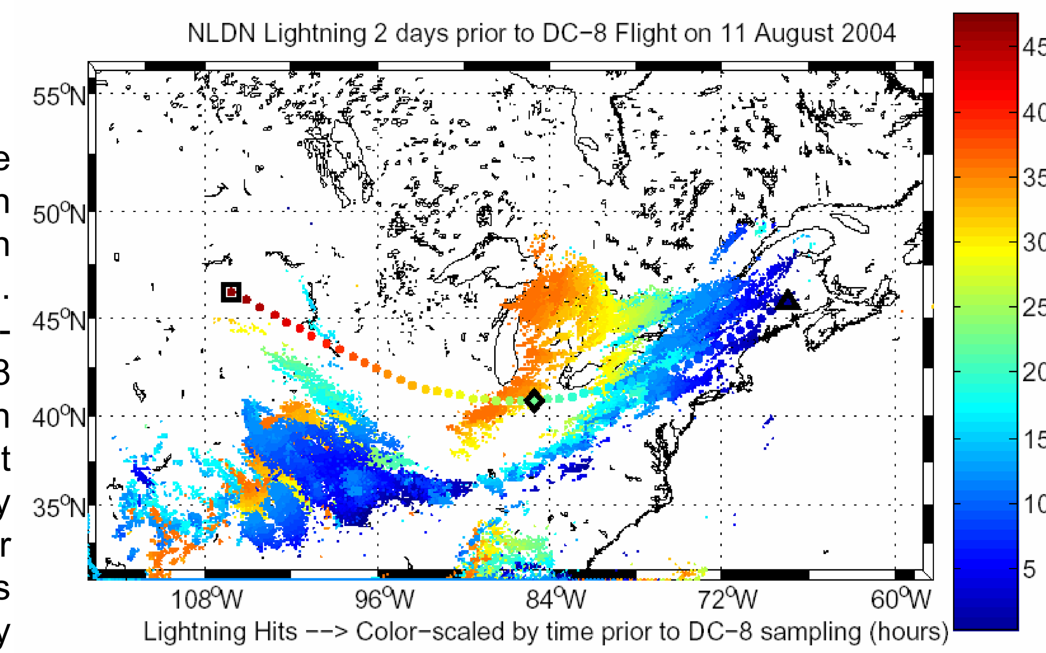

Figure 3 NLDN Lightning Hits on the 10th and 11th of August color-coded by time (hours) prior to DC-8 Sampling Time. The DC-8 sampling location (Δ) and 1-day (◊) and 2-day (□) back-trajectory points have been included in addition to the two day flight level back trajectory (Fuelberg *et al.*).

• Figure 4 (*left*) shows the agreement of the convection time indicators calculated from measured ratios of CH_3OOH / H_2O_2 (URI), NO_x / HNO_3 (PS,UCB and UNH) and UCN (UH) during the same 30min sampling leg described in Figure 3. The consistency between the chemical signatures of convection and the NLDN data implies that the sampled air mass had been influenced by varying degrees of convective activity during the past 24 hours.

• The observed structure in formaldehyde (Figure 4 *right*, H_2CO Fried *et al.*) further supports the conclusion of recent convective influence. This structure could either be attributed to entrainment of background UT air depleted in H_2CO with respect to the injection, photolysis of H_2CO following convection or a combination of the two factors. Regardless, characterizing air masses in this manner will prove useful for generating export efficiencies of various BL species to the UT. (e.g. Alkyl Nitrates (ΣANs) among others)

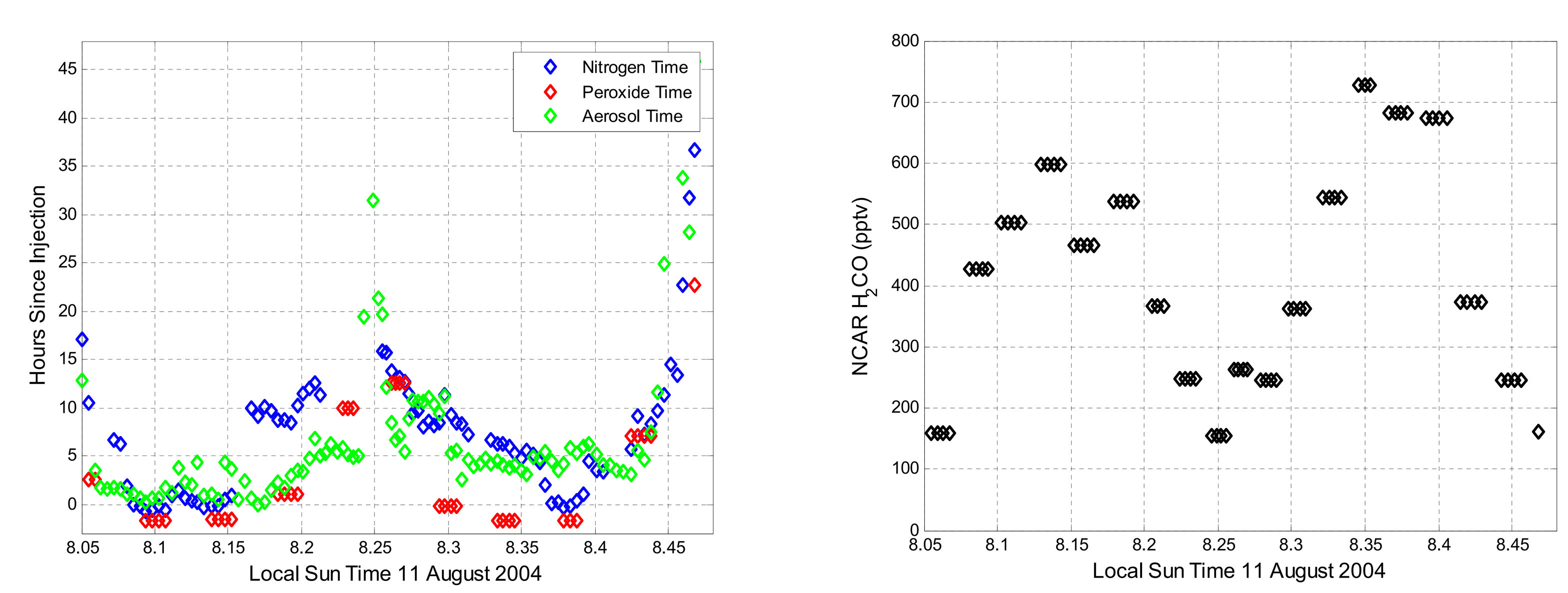

Figure 4 *Left* Calculated time indicators using measured ratios of NO_x/HNO_3, CH_3OOH/H_2O_2 and UCN for a 30min sampling leg at 9km on 11 August 2004. *Right* Observed H_2CO (NCAR) during the same time window.

4. Future Directions

In order to calculate accurate export efficiencies for BL species we will first need to investigate the dependence of our approach on the following:

1. Time of day of the convection

2. Entrainment rate of background air

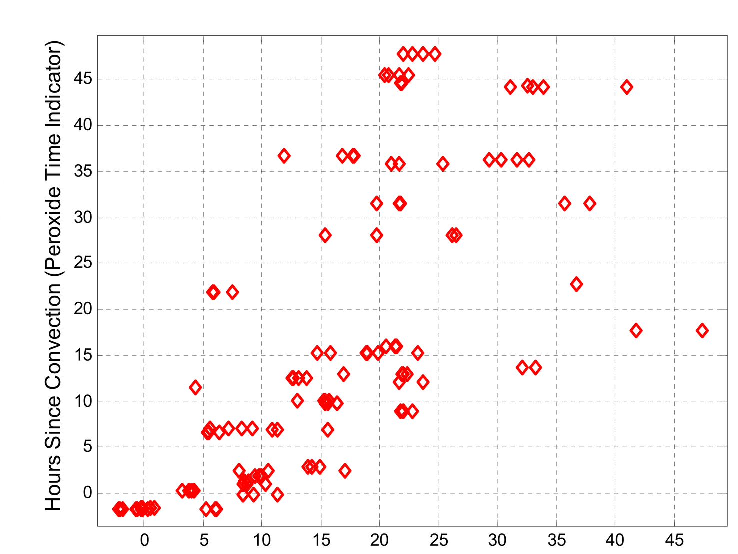

Figure 5 Correlation of convection time indicators in the upper troposphere (ALTP>8km) on 11 August 2004.

5. Implications for Remote Sensing Instruments

• Convective pumping of BL air to the free troposphere coupled with long NO_x lifetimes at high altitude (τ_{NOx} > 6 days at 10km) can result in significant fractions of the total tropospheric NO_2 column at altitudes greater than 5km during the summer over the continent.

• Current NO_2 satellite retrieval algorithms use an *a priori* assumption that the tropospheric column is confined to the BL.

• Analysis of continental NO_2 profiles from INTEX (Figure 1) suggests that during the summer NO_2 at altitudes greater than 5 km represents more than half of the total column NO_2 on 24 of 52 profiles.

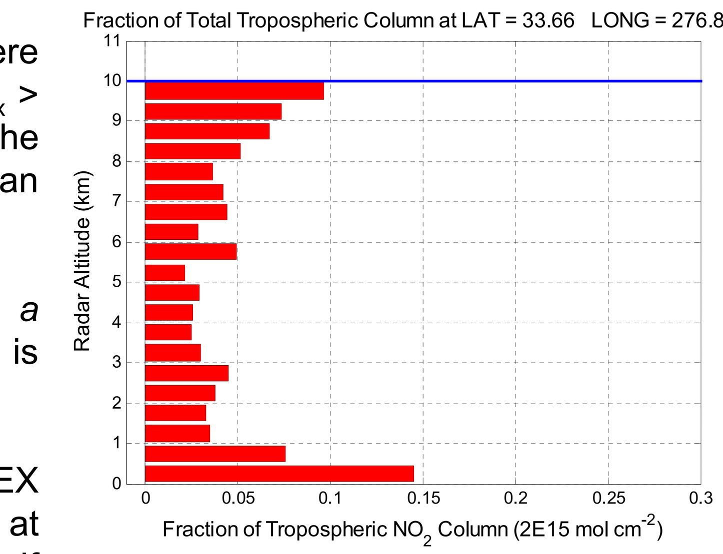

Figure 6 Fraction of Total Column NO_2 in 500m bins from 0-10km.

6. SCIAMACHY and AURA Validation and Future Directions

• We have begun an extensive comparison of BL NO_2 mixing ratios derived from SCIAMACHY column measurements with NO_2 measured by the California Air Resource Board (CARB) network of ground stations (Figure 7).

• Preliminary results show a systematic bias of elevated NO_2 measured by CARB as a result of heterogeneity of NO_2 in the SCIA pixel with respect to the CARB station it is compared with. This is because the ground stations are located near sources and not a representative sampling of the region.

• Our future work will focus on using weekday/weekend NO_2 ratios from CARB, SCIA, AURA and our own network of sampling stations to constrain the California NO_x emissions inventory (Figure 8).

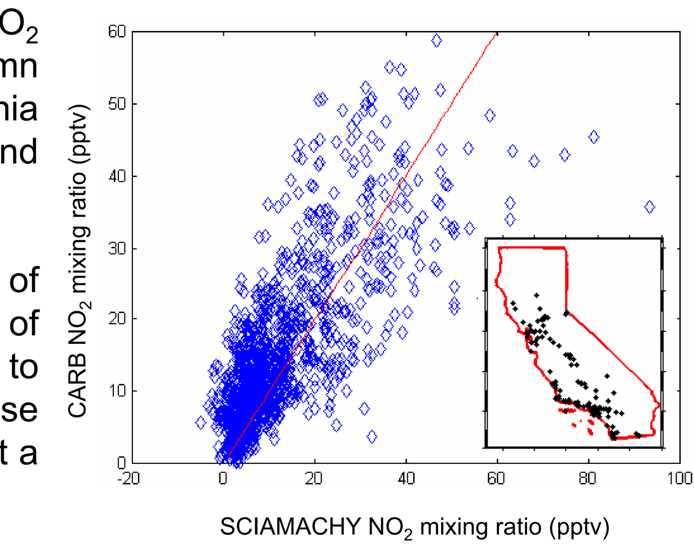

Figure 7 Boundary layer NO_2 comparison between SCIAMACHY and CARB (10AM) Summer 2003.

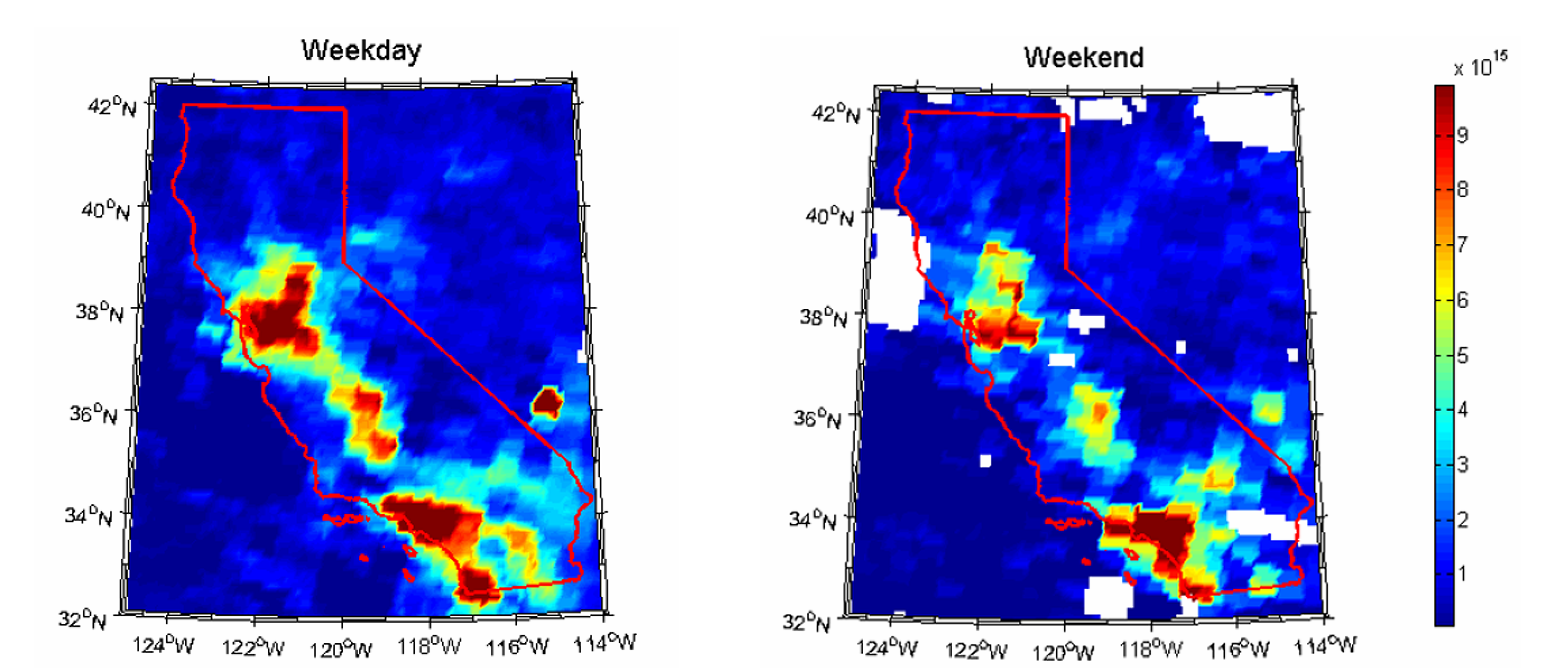

Figure 8 Monthly averaged SCIAMACHY NO_2 column densities for October 2004 weekday (left) and weekend (right) 10AM overpass time.

7. References

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8. Acknowledgements

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INTEX-NA Science Team

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