Direct Measurements of the Convective Recycling of the Upper Troposphere

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We present a statistical representation of the aggregate effects of deep convection on the chemistry and dynamics of the Upper Troposphere (UT) based on direct aircraft observations of the chemical composition of the UT over the Eastern United States and Canada during summer. These measurements provide new and unique observational constraints on the chemistry occurring downwind of convection and the rate at which air in the UT is recycled, previously only the province of model analyses. These results provide quantitative measures that can be used to evaluate global climate and chemistry models.
Deep convection is a highly efficient mechanism for the vertical transport of air from
near the Earth’s surface (0-2 km) to the Upper Troposphere (UT) (6-12 km) (1-5).
Typical convective storms have spatial scales of tens of kilometers and vertical velocities
as large as 15 m sec\(^{-1}\) (6), making their local influence in the UT extremely strong. The
rapid upward flow is balanced by much slower descending flow that occurs over a larger
spatial scale (7). Convection is also associated with lightning a significant source of NO\(_x\)
(NO\(_x\) ≡ NO + NO\(_2\)) in the UT (8, 9). The source strength and spatial distribution of
lightning NO\(_x\) emissions are not well known, with estimates ranging from 2-20 Tg(N) yr\(^{-1}\)
for the global average (10), compared to 25 Tg(N) yr\(^{-1}\) from fossil fuel combustion (11).
Although there have been a number of case studies of the chemical effects of individual
storms (12), studies of the aggregate effects of convection on the chemical composition
and radiative forcing of the UT have been largely the province of modeling and theory
(13, 14). Here we describe measurements that provide a direct link between an
observable property and the ensemble of convective events.

The chemical and radiative consequences of convection and lightning are known to be
large (2, 3, 15). Upper tropospheric O\(_3\), either transported directly from the boundary
layer via convection or formed in situ following detrainment of convectively lofted O\(_3\)
precursors (NO\(_x\), odd hydrogen radicals (HO\(_x\)) and hydrocarbons) in the outflow region,
directly impacts climate through a positive radiative forcing (15). Additionally, deep
convection accounts for a significant fraction of the net flux of moisture from near the
Earth’s surface to the UT (16). Thus, the rate at which the UT is turned over by
convection has important implications on the hydrological cycle and the magnitude of the
water vapor feedback on global temperature (17).

In this study we describe a method for calculating the time air spends in the upper
troposphere following convection from in situ measurements of the chemical composition
of the UT and discuss the chemistry occurring in the outflow region as a function of time
since convection. We use measurements of NO$_2$ (18, 19) (NO$_x$ is calculated from NO$_2$,
O$_3$, HO$_2$ and photolysis rates), HNO$_3$ (20, 21), OH and HO$_2$ (22), O$_3$ (23), aerosol number
density (24), actinic flux (25), CO (26) and CO$_2$ (27) obtained during the Intercontinental
Chemical Transport Experiment – North America (INTEX-NA) aboard the NASA DC-8
(28). Measurements were made at altitudes between the surface and 12.5 km, over a wide
area of the US and Canada, west of 40º W and between 30 and 50º N. There were a large
number of vertical profiles allowing a reasonably unbiased statistical sampling of air over
this region during July and August of 2004.

We use the deviation of the observed NO$_x$ to HNO$_3$ ratio from steady-state as an indicator
of convective influence. The NO$_x$ to HNO$_3$ ratio is reset to near infinity in moist
convection as a result of preferential wet scavenging of HNO$_3$ relative to NO$_x$ (i.e., the
Henry’s Law Constant for HNO$_3$ is $\sim 10^8$ times larger than for NO$_x$) (29). Further,
lightning initiated NO$_x$ production, often coincident with convection, dramatically
enhances NO$_x$ in the outflow region. The coupling of these processes makes the NO$_x$ to
HNO$_3$ ratio in the UT an effective indicator of convective influence, where NO$_x$/HNO$_3$
$>> 1$ is indicative of recent cloud outflow (30, 31). In the days following convection, the
ratio decays toward steady-state providing a chemical clock that marks the time an air-

mass has spent in the UT following convection (32). A number of previous studies have

used species which have no upper tropospheric source (e.g. CH$_3$I) (33), or alternative

chemical ratios to provide estimates of age of air in the UT (34, 35). Our study is unique

because of the availability of high time resolution NO$_2$, OH and HNO$_3$ measurements that

allow us to build a much more extensive data set than previous studies. After the initial

turbulent mixing in the near field of the convection, mixing is slow, thus the time

evolution of NO$_x$/HNO$_3$ following convection depends largely on the partitioning of NO$_x$

(between NO and NO$_2$), the concentration of OH and the actinic flux.

11 Reactive Nitrogen Partitioning in the UT

The only significant chemical sinks of UT NO$_x$ are reaction with OH to produce HNO$_3$

(Equation 1) and nighttime loss through NO$_3$ (Equation 2a-b) followed by hydrolysis of

N$_2$O$_5$ to produce HNO$_3$ (36). NO$_x$ is regenerated by nitric acid photolysis (and

subsequent NO$_3$ photolysis to NO$_2$) and reaction of OH with HNO$_3$ (Equations 3 and 4).

\[
NO_2 + OH \rightarrow HNO_3 \tag{1}
\]

\[
NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2a}
\]

\[
NO_3 + NO_2 \rightarrow N_2O_5 \tag{2b}
\]

\[
HNO_3 \xrightleftharpoons[^h\nu]{} OH + NO_2 \tag{3}
\]

\[
HNO_3 + OH \rightarrow NO_3 + H_2O \tag{4}
\]

Including the altitude dependent rain-out rate for HNO$_3$ (k$_{\text{rain-out}}$) as derived by Giorgi and

Chameides (37), the expected steady-state NO$_x$/HNO$_3$ is:
\[
\left( \frac{[NO_x]}{[HNO_3]} \right)_{\text{Steady-State}} = \frac{J_{HNO_3} + k_{HNO_3+OH}[OH] + k_{HNO_3\text{rainout}}}{k_{NO_x+OH}[OH] + 2k_{N_2O_5+H_2O} \frac{[N_2O_5]}{[NO_2]} x \left( \frac{[NO_2]}{[NO_x]} \right)}
\]

Our observations show the NO\textsubscript{x} to HNO\textsubscript{3} ratio to be much higher than the ratio described by equation 3 at altitudes greater than 6 km (c.f. Fig. 2). The difference between the observed ratio and that predicted by equation 3 grows with altitude, reaching a maximum at 10 km. Previous observations of NO\textsubscript{x} and HNO\textsubscript{3} (either measured directly or calculated from observations of NO\textsubscript{x}, PAN and NO\textsubscript{y}) have shown the NO\textsubscript{x}/HNO\textsubscript{3} ratio to be significantly larger than the steady-state prediction in the UT (30, 31, 38-42). This has been shown to be primarily a result of convection and lightning reinitializing the system before steady-state is achieved (30, 31). Although a series of other hypotheses have been put forth (40-42), we (like Jaegle et al.) find no evidence for a mechanism other than convection responsible for holding NO\textsubscript{x}/HNO\textsubscript{3} out of steady-state in the UT.

### Chemical Signatures of Convection

Fig. 3 depicts one of many convectively influenced air-masses sampled in the UT during INTEX-NA. Three distinct convective events (40–80 km wide) are identified by enhancements in NO\textsubscript{x}/HNO\textsubscript{3} in Fig. 3a. Coincident enhancements are present in SO\textsubscript{2}, an indicator of a recent boundary layer source for this air, and Ultra-fine Cloud Condensation Nuclei (UCN) \((3 \leq D_p \leq 10 \text{ nm})\), an indicator of cloud detrainment (Fig. 3b) (43, 44). Sharp decreases in CO\textsubscript{2} also indicate the convective lofting of boundary layer air depleted in CO\textsubscript{2}, a result of photosynthetic activity (Fig. 3c) (44). Enhancements in CO, CH\textsubscript{2}O and various hydrocarbons, relative to the surrounding UT
air, were also observed in these plumes, further indicating that these parcels originate from the Planetary Boundary Layer (PBL). Backward air trajectories, initialized along the flight track, coupled to the spatial and temporal distribution of cloud-to-ground lightning strikes, indicate that the sampled air-mass was recently influenced by lightning approximately one day prior to DC-8 sampling (c.f. Fig. 3 bottom panel) (45). Such features with high NOx/HNO3 were observed throughout the UT during INTEX-NA.

To assess the extent to which the UT over the Eastern U.S. and Canada during the summer of 2004 was influenced by convection and describe the chemical evolution of convective outflow, we use a constrained time-dependent photo-chemical box model to map the observed NOx/HNO3 to the time since the ratio was last reinitialized. The model is described in the supplemental information included with this article. It is initialized with observations at 1km vertical intervals from 6 to 12 km. The derived timing indicator for the convectively influenced air sampled on 11 August 2006 is shown in Fig. 3d. The properties of the ensemble of our measurements are shown in Figs. 4-6.

The aerosol size distribution provides an independent indicator of air recently detrained from clouds. Cloud-processed air is depleted of aerosol surface area permitting new particle formation in the outflow region (43, 44). Fig. 4a depicts the fraction of condensation nuclei found in the 3-10 nm bin as a function of time since convective influence. The fraction of particles in this ultra-fine mode is largest during the first few days confirming that the NOx to HNO3 ratio, and the timing indicator derived from it, is reinitialized in the UT by cloud processing. Strong enhancements in CH3OOH/H2O2 (not
shown), also an indicator of recent cloud processing (33, 46), were observed during the first two days after cloud processing.

As expected, both elevated NO\textsubscript{x} and suppressed HNO\textsubscript{3} are observed at short times (c.f. Figs. 4b-c). Enhancements in NO\textsubscript{x} during the first few days is indicative of convection of boundary layer and/or lightning NO\textsubscript{x} (47, 48). The suppression of HNO\textsubscript{3} at short times is clear indication of HNO\textsubscript{3} scavenging during convection. Fig. 4d confirms that reactive nitrogen (NO\textsubscript{y} \equiv NO_{x} + total peroxy nitrates + HNO\textsubscript{3}) is conserved during the chemical processing following convection, a fact which provides further support for the use of NO\textsubscript{x}/HNO\textsubscript{3} as a marker representing time since convection.

**Chemical Processing in Convective Outflow**

Mapping the ensemble of observations made throughout the UT onto the coordinate of time since convection allows us to assess the chemical and dynamical processes occurring following convection, without attempting a Lagrangian convection study. In this analysis we concentrate on the time evolution of CO and O\textsubscript{3}.

The time evolution of CO, following detrainment into the UT, is set by the abundance of OH and the rate at which the convective plume entrains air from the background UT (c.f. Fig. 5a). Due to the direct dependence of the chemical clock on HO\textsubscript{x}, we constrained both OH and HO\textsubscript{2} to the observations as a function of NO\textsubscript{x} and pressure in the time-dependent model used to generate time. As a result, we can iterate the model to determine the proper mixing rate of the convective plume by matching the modeled and
observed time evolution of CO following convection. Using this approach for a series of
long lived species (e.g. CO, CH$_4$, CH$_3$OH and others), we calculate an average mixing
rate of 0.05 ± 0.02 day$^{-1}$ following detrainment into the UT. This is in good agreement
with the upper limit of 0.06 - 0.1 day$^{-1}$ determined by Ray et al. from observations of
convective plumes observed in the stratosphere during the CRYSTAL-FACE mission
(49), however it is slower than the 2 day dilution time-scale determined by Wang et al.
from observations during the SONEX Experiment (32). Since the DC-8 did not routinely
sample in the turbulent environment directly surrounding convective outflow, this mixing
rate likely reflects diffusive and shear induced mixing subsequent to the initial turbulent
mixing occurring during detrainment from the convective system. Entrainment of UT air
either during convective lofting or cloud detrainment is discussed in the next section.

The O$_3$ mixing ratio as a function of time since convection is shown in Fig. 5b. We find
that on average, convectively lofted air-masses contain less O$_3$ than the background UT.
This result is consistent with the observed vertical gradient in O$_3$ observed over the
continental US during INTEX-NA, with lower O$_3$ in the PBL than above (50). Rapid
changes in the O$_3$ mixing ratio are observed during the first two days following
detrainment, with the observed O$_3$ 15 nmol mol$^{-1}$ above the initial value by the end of day
two. The observed rate of increase slows exponentially with an asymptote at long time
approaching zero and the O$_3$ mixing ratio approaching a constant value of 85 nmol mol$^{-1}$.
This is a surprising result, as our model of the O$_3$ rate of change never approaches zero,
but continues to predict a net increase of 3 nmol mol$^{-1}$ O$_3$ day$^{-1}$ at the end of day five
(51).
Constraints on the Convective Turnover Rate of the UT

The convective turnover rate of the upper troposphere is critical for accurately describing NOx, HOx and O3 chemistry in the UT (52). However, at present there is a paucity of observation based constraints available (either meteorological or chemical) to test the aggregate effects of convection in the current generation of global chemistry and climate models. To determine the convective turnover rate of the UT from the observations presented here, both the extent to which the UT is influenced by convection and the fraction of PBL air in the convectively influenced air-masses must be known with high confidence.

To determine the fraction of PBL air contained in fresh convective outflow, we use observations of insoluble long-lived species made throughout the INTEX-NA campaign over the continent. Assuming that we conducted a statistically unbiased sampling of both the boundary layer and free troposphere during INTEX-NA, we can calculate the fraction of PBL air present in fresh convection (f) through the following equation:

\[
[X]_{UT(\tau=0)} = f [X]_{surface} + (1 - f) [X]_{UT}
\]

where \([X]_{UT (\tau=0)}\) is the mean mixing ratio of species X in fresh convective outflow (as identified using our timing indicator), \([X]_{UT}\) is the mean mixing ratio of species X in the UT (7.5-11.5 km) and \([X]_{surface}\) is the mean mixing ratio of species X between 0-1.5 km. Using observations of CO, CO2, CH3OH, CH4 and C2H6 we calculate the fraction of PBL
air in fresh convection to be $0.19 \pm 0.05, 0.11 \pm 0.03, 0.26 \pm 0.05, 0.15 \pm 0.05, \text{ and } 0.34 \pm 0.09$, respectively. We calculate a weighted average for the fraction of PBL air in convective outflow of $0.17 \pm 0.02$ by weighting each value by the inverse square of its uncertainty. This implies that convectively lofted PBL air rapidly entrains the surrounding air either during ascent or in the turbulent environment of the detraining flow. These results are consistent with: i.) the observations of Ray et al., who determined the fraction of tropospheric air in convective plumes sampled in the stratosphere to be between 0.1 and 0.4 (49), ii.) the observations of Cohan et al., who calculate the fraction of BL air in fresh convection outflow to be between 0.32 and 0.64 from observations of CHBr$_3$, CH$_3$OOH and CH$_3$I in fresh convection (33) and iii.) the modeling studies of Mullendore et al., who calculate the fraction of PBL air present in the convective outflow region of a supercell storm to be 0.26, 10 hours after storm initialization (53).

Fig. 6a shows the normalized frequency distribution of the observed time since convection based on the ratio of NO$_x$ to HNO$_3$. We find that 54% of the air sampled between 7.5 and 11.5 km had been influenced by convection during the past two days. The convective outflow was strongest between 9.5 and 10.5 km, where the fraction of sampled air that is less than two days old exceeds 69%. The vertical distribution presented here is consistent with previous observations and model analyses of convective outflow to the UT from individual storms (4, 54) and the vertical distribution of convectively influenced laminae observed in O$_3$ sonde data from the summer of 2004 over the northeastern U.S. (55). The shift toward longer times between 10.5 and 11.5 km suggests that either convective cloud tops on average do not extend higher than 10.5 km
over the mid-latitude during the summer (56) or that transport of stratospheric air, rich in HNO₃, contributes to keeping the NOₓ to HNO₃ ratio low at altitudes greater than 10.5 km (57).

To constrain the turnover rate of the UT from the ensemble statistics generated from our calculated time since convective influence (Fig. 6a), we constructed a two dimensional model of the UT. We assume that it takes 4 days for any individual box to pass through the sampling region and that each box has not been influenced by convection upon entering the sampling window. Every six hours we: i.) represent convection by randomly reinitializing the age of x% of the boxes in the sampling domain to 0 (the value of x is determined by the turnover rate (varied between 0.05 and 0.2 day⁻¹) and the fraction of PBL air contained in fresh convection (assumed to be a constant at 0.17)) and ii.) dilute each box with the mean value of the adjacent 8 boxes at the rate of 0.05 day⁻¹.

Fig. 6b depicts the observed and three calculated normalized frequency distribution of time since convective influence between 7.5 and 11.5 km. The shape of the distribution suggests that UT air sampled during INTEX-NA was largely influenced by convection, and that convectively lofted plumes did not have sufficient time to either mix or age prior to sampling by the DC-8, but instead were transported to the East out of the domain. Frequency distributions of time since convection, using three different convective turnover rates, in the Eastern half of the 2-D UT model analysis (where we sampled most frequently) are also shown in Fig. 6b. Assuming the DC-8 made a statistically unbiased sampling of the continental UT during summer, the best match between the model and
observations would imply a convective turnover rate between 0.1 - 0.2 day$^{-1}$. However, if we assume the DC-8 had a positive bias toward sampling fresh convection in accordance with Fuelberg et al., our observed frequency distributions are consistent with a convective turnover rate closer to 0.1 day$^{-1}$ (45, 58).

For comparison, the model detrainment cloud mass flux between 400 and 200 hPa (approximately 7.2 - 11.8 km based on standard atmosphere) for the INTEX-NA sampling domain (80° - 100°W for 30° - 35°N and 70° - 100° W for 35° - 50° N) between July 1st and August 15th 2004 was 0.0085 kg m$^{-2}$ sec$^{-1}$. This corresponds to a turnover rate of 0.37 day$^{-1}$ (using a column mass of 1.9x10$^3$ kg m$^{-2}$ between 7.2 - 11.8 km). As expected, the observed and modeled detrainment rates for the extratropics are slower than in the tropics. For example, Folkins and Martin determine a maximum convective detrainment rate of 0.4 day$^{-1}$ at 12.5 km from calculation of the clear-sky radiative and precipitation induced evaporative cooling rates using a one-dimensional model constrained by observations of temperature and water vapor (59).

**Conclusions**

We present a statistical representation of the aggregate effects of convection on the chemistry and dynamics of the upper troposphere using in situ measurements taken aboard the NASA DC-8 during the summer of 2004 over the Eastern U.S. and Canada. These observations provide a new and unique constraint on: i.) the extent to which convection perturbs the continental UT during summer, ii.) the fraction of boundary layer air present in convective outflow, and iii.) the convective overturn rate of the upper
troposphere. In addition, the chemical clock described here defines a coordinate that can
be used to assess the chemistry occurring down-wind of convective injection. These
direct measures of atmospheric rates present a new opportunity for quantitative tests of
model representations of processes governing UT ozone, convection, lightning and their
impact on climate.
Figure 1: In moist convection, air from near the Earth’s Surface is rapidly transported upwards and detrained into the Upper Troposphere. In this process, Nitric Acid (highly soluble) is efficiently scavenged, while NO\textsubscript{x} (insoluble) remains. NO\textsubscript{x} is dramatically elevated by concurrent lightning NO production, resulting in high NO\textsubscript{x} to HNO\textsubscript{3} ratios in the convective outflow region. Following detrainment into the UT, NO\textsubscript{x} is converted to HNO\textsubscript{3} by OH during the day and via NO\textsubscript{3}/N\textsubscript{2}O\textsubscript{5} at night. The chemical evolution of the NO\textsubscript{x}/HNO\textsubscript{3} ratio provides a unique indicator of the time a sampled air-mass has been in the UT following convection.
Figure 2: The observed deviation of the NO$_x$ to HNO$_3$ ratio from steady-state as a function of altitude in the UT. The mean values within 500 m vertical bins are shown with circles ($\circ$). The steady-state NO$_x$ to HNO$_3$ ratio was calculated from measured NO$_x$, OH and $J_{\text{HNO}_3}$ and includes the rain out parameterization of Giorgi and Chameides (1985).
Figure 3: *top panel* Time series of measurements taken in the vicinity of recent convective activity on 11 August 2004 between 5 and 9 km. Panel A suggests the sampling of a series of fresh convective plumes, indicated by a sharp increase in the NOx/HNO3 ratio. Panels B & C depict coincident enhancements in SO2 and UCN (3nm > Dp > 10nm) and coincident sharp drops in CO2, indicative of the convective lofting of boundary layer air depleted in CO2. The derived time since the sampled air-mass had been influenced by convection is shown in Panel D. *bottom panel* NLDN lightning hits (small dots) on the 10th and 11th of August. The color-code represents the time of the hit (hours) prior to aircraft sampling. The DC-8 sampling location corresponding to measurements shown in Figure 1 is located on the Maine – New Brunswick border [46ºN 67ºW]. The two day back trajectory [●] (initialized at the point of the second convective plume shown in Panel A) is also color-coded by time prior to DC-8 sampling (dots with black edges).
Figure 4: Observations of the fraction of ultra-fine condensation nuclei [number density of aerosol (3-10 nm) / total aerosol number density] (Panel A), NO\(_x\) (Panel B), HNO\(_3\) (Panel C) and NO\(_y\) (Panel D) as a function of modeled time since convective influence. The mean (-○-) and median (-□-) of the observations, within 8 hour bins, is shown along with interquartile range (shaded region). Results from the time-dependent box model, initialized at 10 km and 12PM, are shown with dashed lines for the gas phase species (B-D).
Figure 5: Observations of CO (Panel A) and Ozone (Panel B) as a function of modeled time since cloud processing in the UT. The mean (-□-) and median (-○-) of the observations, within 8 hour bins, is shown along with the interquartile range (shaded region). Results from the time-dependent box model, initialized at 10 km and 12PM, are shown with dashed lines.
Figure 6: **left panel** Normalized frequency distribution in the time since convective influence, as calculated from observations of the NO$_x$ to HNO$_3$ ratio made during the summer of 2004. Calculations are separated into 1 km altitude bins (ranging from 7.5-11.5 km). The fraction of air that had been influenced by convection within the past two days ($f < 2$ days) is included in the figure legend. **right panel** Comparison of observed frequency distribution (7.5-11.5 km) with various modeled representations of the convective turnover rate.
References and Notes:

47. R. C. Hudman et al., Accepted J. Geophys. Res. (2006).
51. Net ∆Ozone of 0 nmol mol⁻¹ day⁻¹ could be achieved if the air parcel: i.) subsided to where H₂O abundances are large enough to provide a sink of O₃ through O¹D that balanced production from NO+HO₂ (~6 km), ii.) entrained air containing lower O₃ mixing ratios or iii.) contained additional O₃ loss terms beyond NOₓ, HOₓ, H₂O (via O¹D removal). To match the deviation between the model and measurement, we would require an additional 2-3 nmol mol⁻¹ day⁻¹ of chemical ozone loss. In order for mixing to explain the deviation, air of lower O₃ would need to be mixed into the air parcel. As shown in Fig. 5b, the only air in the UT containing significantly less O₃ is that pumped directly from the PBL. While mixing fresh and aged outflow could help to explain the discrepancy in O₃, it is inconsistent with the observed decay in CO at long time (2-5 days).
58. Fuelberg et al. use 10-day back trajectories to National Weather Service Global Forecast System (GFS) derived convection and National Lightning Detection Network (NLDN) measured lightning strikes to assess the fraction of time that the DC-8 sampled either convection or lightning influenced air. Using the GFS statistics, Fuelberg et al. calculate that 63% of the sampled air on INTEX-NA had encountered convection and ~57% had been influenced by lightning during the
past 2 days. In Fuelberg et al., the authors determine that when considering the entire INTEX-NA sampling domain (both in space and time), convection was present in 12.5% of the grid points. This is substantially smaller than the percent of observations within 6 hours of convection (21.4%), suggesting that the DC-8 had a positive bias toward sampling fresh convection. This bias is reflected in the sharp drop in population between day 1 and 2 as shown in Fig. 6a. Correcting for this bias has little effect on our assessment of the fraction of air less than 2 days old, lowering our results from 0.43, 0.56, 0.69, and 0.43 to 0.38, 0.50, 0.62, and 0.39 at 8, 9, 10, and 11 km respectively.

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Supplemental Online Information

1. INTEX-NA Experiment Description and Instrument Descriptions

The Intercontinental Chemical Transport Experiment – North America (INTEX-NA) took place between 1 July and 14 August 2004. Research flights were conducted out of Dryden Flight Research Center (Edwards AFB, CA), Mid-America Airfield (Mascoutah, IL); and PEASE International Trade-Port (Portsmouth, NH). Figure S1 depicts the vertical and horizontal extent of research flights conducted aboard the NASA DC-8 during INTEX-NA. DC-8 flight tracks are shown in the left panel of Figure 1 and the number of samples (10 second averaging time) in 1km vertical bins are shown in the right panel. In situ observations relevant to this study include; NO$_2$, HNO$_3$, OH, O$_3$, CO, CO$_2$, SO$_2$ and Ultra-fine Condensation Nuclei (UCN). Table S1 describes the detection threshold, uncertainty and time response for each measurement used in this analysis.

NO$_2$ LIF Instrument The NO$_2$ instrument flown aboard the DC-8 was described in detail by Thornton et al. (2), with specifics of the jet-expansion described by Cleary et al. (3). Briefly, NO$_2$ fluorescence is detected at 1Hz following excitation of a specific jet-cooled rovibronic transition in NO$_2$ at 585 nm. Red-shifted fluorescence is imaged at 90º onto an air cooled photomultiplier tube that is both optically and temporally filtered to remove laser scatter. NO$_2$ mixing ratios are calculated directly from fluorescence counts following calibration to NO$_2$ gas standards and measurements of the instrument zero from compressed air mixtures containing zero NO$_2$. Selectivity to NO$_2$ is demonstrated by tuning on and off of a specific NO$_2$ resonance, where the difference in observed fluorescence at the two different frequencies is attributed solely to NO$_2$. We calculate a
2. 0-D Time Dependent Model

The chemical evolution of convective outflow was modeled using a 0-D time dependent model. The model was initialized with chemical conditions, altitudes and detrainment times consistent with observations of fresh convection made during INTEX-NA. As time propagates in the model, we calculate the production and loss of O₃, CO, NO, NO₂, NO₃, N₂O₅, PAN, HO₂NO₂, HNO₃, OH, HO₂, RO₂, H₂O₂, CH₃OOH, H₂CO and C₁-C₆ Hydrocarbons for 20 days following cloud detrainment. The conversion of NOₓ to HNO₃ in the outflow region is used as an indicator of time since convection. Figure S2 depicts the results of a single run initialized at 10km with a noon detrainment time. Initial conditions correspond to [NOₓ]₀ = 800 pptv, [O₃]₀ = 65 ppbv and [CO]₀ = 105 ppbv. Rapid conversion of NOₓ to HNO₃ is observed during the first few days as the system approaches steady-state. In this analysis we assume: i.) HNO₃ is scavenged with unit efficiency in deep convection, ii.) γ_{N₂O₅} = 0.01 and iii.) HNO₃ is not scavenged by aerosols (or rain) following injection into the UT. All kinetic rates used in this analysis were taken from the NASA JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14 (4).

2.1 Treatment of OH and HO₂

The calculated time since convective detrainment is directly coupled to the HOₓ budget through the daytime NOₓ sink to HNO₃ via reaction with OH. As in other model
descriptions of the UT during INTEX-NA (5, 6), our unconstrained model over-estimates OH by nearly a factor of two in the UT and under-estimates HO_2 by a similar amount.

Due to the direct dependence of our timing indicator on HO_x, we constrain the mixing ratios of OH and HO_2 to the observed values as a function of NO_x and altitude. Figure S3 depicts the modeled mixing ratios of OH and HO_2 (lines), constrained to the observations (dots), as a function of NO_x and SZA at 10km. The observed OH is a strong function of NO_x, while observations of HO_2 remain insensitive to NO_x. Constraints for OH and HO_2 were derived independently for each 1km altitude bin. Constraining OH and HO_2 to the observations increases the time required for the NO_x-HNO_3 system to reach steady-state (by slowing the rate of OH + NO_2) and enhances the modeled O_3 production in the outflow region (by speeding up the rate of HO_2+NO).

2.2 Calculation of Time since Convection

The time since a sampled air-mass had been cloud processed is calculated by applying the mapping of time to NO_x/ HNO_3 derived in the box model to the observed NO_x to HNO_3 ratio. Figure S4 depicts the best-fit relation between the modeled NO_x to HNO_3 ratio and time since cloud processing at 10km. This function is calculated at 1km increments from 6-12km and applied to the measured NO_x to HNO_3 ratio.

2.3 Model Assumptions and Uncertainty

In order to access the uncertainty in the calculated time, we ran the time-dependent model under various different conditions encountered during INTEX-NA (e.g. \([\text{NO}_x]_i\) (0.2-3.0 ppbv), \([\text{O}_3]_i\) (40-100 ppbv), \([\text{CO}]_i\) (80-150 ppbv), detrainment time (noon, 4PM,
midnight), altitude (6-12km) and time of year (June-September). As illustrated in figure S4, the NO\textsubscript{x} to HNO\textsubscript{3} ratio has good resolution (i.e. large rate of change per unit time) during the first five days following convection. Beyond five days small changes in NO\textsubscript{x}/HNO\textsubscript{3} correspond to larger changes in the derived time. From the variance in the calculated time of individual model runs, we estimate the uncertainty in our modeled time to be ±6 hours at 1 day, ±12 hours at 2 days and ±1 day at 4 days. In addition, the INTEX-NA sampling domain did not permit frequent measurement of aged convection (>5 days). For these reasons we limit our analysis to the first five days following convection.

2.4 Treatment of Mixing

The mixing rate was determined by iterating the model until we had closure between the observed and modeled time evolution of a suite of long-lived species (e.g. CO, CH\textsubscript{4}, CH\textsubscript{3}OH and others). The modeled time rate of change of species X is determined as:

$$\frac{d[X]}{dt} = P(X) - L(X) - k_{\text{dilution}} ([X] - [X]_{\text{background}})$$

where P(X) represents the chemical production of species X, L(X) represents the chemical loss of species X and $k_{\text{dilution}}$ is the mixing rate of the convective plume with background UT. We find this mixing term to be on average 0.05 ± 0.02 day\textsuperscript{-1}. That is, after 5 days, the plume still has 75% of its original contents. While individual convective plumes may mix faster (or slower) that this, the aggregate mixing rate of all the sampled plumes can be described by this rate. This rate supports the conclusion that over the course of 5 days, the convective plume remains relatively isolated from the background.
Background mixing ratios used in the dilution calculation were taken as the mean observed UT mixing ratios outside of fresh convective plumes.

Due to subsidence of convectively lofted air parcels following injection, our calculated time represents a lower bound for age as the chemical clock speeds up (due to NO\textsubscript{x} repartitioning) as the parcel descends in altitude. However, this is a relatively small effect as calculated subsidence rates are approximately 35 hPa day\textsuperscript{-1} (7).

### 3.0 Comparison of Chemical and Meteorological Convective Influence Calculations

The results presented here provide a chemical constraint on the rate at which the UT over the continental US is influenced by convection during summer. In addition to the meteorological analysis of Fuelberg et al., presented in this manuscript, Thompson et al. assessed the effects of convection on the O\textsubscript{3} budget in the UT, over eastern North America, during the summer of 2004. Using results from the INTEX Ozone Sonde Network Study (IONS), the authors conclude that 10-15% (lower-limit) of the below tropopause O\textsubscript{3} can be attributed to the interaction of regional pollution with convection and lightning (8).

The INTEX-NA sampling period (June-August) and region (Eastern North America) is characterized by intense lightning activity. Cooper et al. calculated that 13% of the global annual lightning NO\textsubscript{x} emissions occurred between 108° W – 18 ° E and 18 ° -72° N the between June 21 and August 15, 2004 (9). In terms of lightning flash counts, Hudman et al., conclude that 2004 was typical (within 20% of the mean) of the past 5
years (6). Persistent frontal passages prevented the formation of stagnant high pressure systems, typically observed during the summer over the northeastern United States (10). These frequent passages led to both record low temperatures and number of O₃ exceedances in the northeast (11). In contrast UT/LS O₃, as observed from the IONS network, was comparable to the climatology (11).

4.0 Measurement Uncertainties

In this analysis we calculate NOₓ from observations of NO₂, O₃, HO₂ and photolysis rates measured directly on the DC-8. NO was measured directly on the DC-8 via a commercial grade chemiluminescence detector. The sensitivity of the chemiluminescence instrument (detection threshold > 50 pptv) and long integration time (1 minute) prohibited its use in these calculations. NO was calculated from steady-state using the following equation:

\[
\left[ NO \right]_{\text{Steady-State}} = \frac{J_{NO_2} \left[ NO_2 \right]}{k_{NO+O_3} \left[ O_3 \right] + k_{NO+HO_2} \left[ HO_2 \right]}
\]

We calculate the accuracy of the derived NO to be better than ± 30% based on the propagation of the individual errors used on the calculation. Observations of Nitrogen Dioxide, Ozone and JNO₂ made during the INTEX-NA campaign were compared directly with measurements made aboard the NOAA WP-3D during a series of in-flight comparisons. During these experiments the principal individual components (NO₂, O₃ and JNO₂) showed agreement to within their stated instrumental uncertainty.
In Figure S6 we compare the measured NO$_x$ (using the chemiluminescence and the Laser Induced Fluorescence measurements) and NO$_x$ calculated from steady-state for the entire INTEX-NA campaign. The steady-state NO$_x$ agrees with the measured NO$_x$ to within the calculated uncertainty when averaged to 1-minute and divided into 1km vertical bins. The observed upper tropospheric NO$_x$ concentrations during INTEX-NA are on average much higher than previous reported on intensive aircraft field campaigns over North America. During the SUCCESS campaign, Jaegle et al. report mean NO concentrations of 0.030 ± 0.022 ppbv and 0.061 ± 0.045 ppbv, for the altitude ranges of 8-10 km and 10-12 km, respectively (12). However, it must be noted that the scientific objective of SUCCESS was the sampling of aircraft exhaust and contrails, thus the values reported in Jaegle et al., were filtered to exclude fresh aircraft exhaust (CO$_2$ > 368 ppmv and NO > 300 pptv). Crawford et al., report mean NO concentrations of 0.1 ppbv for observations made between 6-12 km during the SONEX campaign during the fall of 1997 over the North Eastern United States and the North Atlantic (13). Neither of these studies provides a direct comparison to the INTEX-NA data-set as SUCCESS was conducted in the spring and SONEX in the fall, while peak lightning and convection occurs over the continental North America during summer. The best comparison comes from NO$_x$ measured aboard a commercial passenger aircraft during the NOXAR program between 1995 and 1997. Brunner et al. report a mean UT NO$_x$ concentration of 0.4 ppbv during June, July and August over North America (14). As seen in Figure S6, our observations during the summer of 2004 are consistent with this.
We use the Caltech CIMS HNO$_3$ due to its fast time response (5 seconds as compared to 105 seconds for the UNH Mist Chamber Technique) and the UNH MC results when the fast HNO$_3$ was unavailable. To account for the systematic bias between the two observations in the UT ($[\text{HNO}_3]_{\text{UNH}} = 0.6 \times [\text{HNO}_3]_{\text{Caltech}}$), we scale both the CIMS and MC observations to split the difference between the two measurements (i.e. we increase $[\text{HNO}_3]_{\text{UNH}}$ by 20% and decrease $[\text{HNO}_3]_{\text{CIM}}$ by 20%).

Due to the observed systematic bias, the choice of which HNO$_3$ measurement to use in the analysis has the potential to complicate our conclusions. To address these effects we have conducted the analysis using Nitric Acid as measured from: i.) the Mist Chamber – Ion Chromatography Instrument, ii.) the Chemical Ionization Mass Spectrometer and iii.) the scaled difference between the two techniques. The results are compared in Figures S7 and S8. Figure S7 shows the normalized frequency distribution in the time since convective influence, as calculated from observations of the NO$_x$ to HNO$_3$ ratio made during the summer of 2004. Figure S8 depicts the fraction of air that had been influenced by convection within the past two days ($f < 2\ \text{days}$) as a function of altitude. Calculations derived from the Mist Chamber – Ion Chromatography Instrument result in a higher fraction of convectively influenced air when compared with calculations made using measurements from the CIMS instrument. When compared with the results shown in Figure 6B of the manuscript, on which our conclusions regarding the convective overturn rate are drawn from, calculations using either the CIMS, MC-IC or the scaled difference result in a convective overturn rate between 0.1 and 0.2 day$^{-1}$. 
2. Supplemental Figures

**Figure S1:** left panel INTEX-NA flight tracks made between 1 July 2004 and 14 August 2004 aboard the NASA DC-8. right panel Number of samples (using 10-sec averaged data) within 1km altitude bins between 0-12 km during the entire campaign.
Figure S2: Time-dependent model illustrating the conversion of NO\textsubscript{x} to Nitric Acid in the days subsequent to a cloud processing event occurring at 10km. The above model was initialized at 12PM local time at 30ºN in August using [NO\textsubscript{x}]\textsubscript{i} = 800 pptv, [CO]\textsubscript{i} = 105 ppbv at [O\textsubscript{3}]\textsubscript{i} = 65 ppbv.
Figure S3: Model representation of OH (left panel) and HO$_2$ (right panel) as a function of SZA and [NO$_x$]. Model results (solid lines) are shown on top of the *in situ* observations (dots). The model was initialized at noon at 10km with [NO$_x$]$_i$ = 800 pptv, [CO]$_i$ = 105 ppbv at [O$_3$]$_i$ = 65 ppbv. Observations shown were taken aboard the DC-8 between 9 and 11 km.
Figure S4: Observed NO\textsubscript{x} to HNO\textsubscript{3} ratios are converted to a time since last convective influence using the best fit equation relating the NO\textsubscript{x}/HNO\textsubscript{3} ratio to time as calculated using the time-dependent model in 1km altitude bins from 7.5-11.5 km. The above equation is valid for pressure altitudes between 9.5 and 10.5 km.
Figure S5: Comparison of chemical (grey bars) and meteorological constraints (-○-, -□-) on convective influence during INTEX-NA. Convective influence on air sampled by the DC-8 is shown with blue circles (-○-), while convective influence on the entire INTEX-NA domain is shown with red squares (-□-).
Figure S6: Comparison of observed (grey lines) and steady-state (black lines) NO_{x} for the entire INTEX-NA field campaign. The shaded region represents the interquartile range of the calculated NO_{x}.
Figure S7: Normalized frequency distribution in the time since convective influence, as calculated from observations of the NOx to HNO3 ratio made during the summer of 2004. Calculations were conducted using Nitric Acid as measured from: i.) the Mist Chamber – Ion Chromatography Instrument (-□-), the Chemical Ionization Mass Spectrometer (-○-) and the scaled difference (-■-).
Figure S8: Fraction of air that had been influenced by convection within the past two days ($f_{<2 \text{ days}}$) as a function of altitude. Calculations were conducted using Nitric Acid as measured from: i.) the Mist Chamber – Ion Chromatography Instrument (---), the Chemical Ionization Mass Spectrometer (---), and the scaled difference (■—■).
<table>
<thead>
<tr>
<th>Species</th>
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<th>Detection Threshold</th>
<th>Accuracy</th>
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<td>NO₂</td>
<td>LIF¹</td>
<td>8 pptv / 10 sec</td>
<td>±10% 1σ</td>
<td>1 Hz</td>
<td>(2, 3)</td>
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<td>HNO₃</td>
<td>CIMS³</td>
<td>10 pptv / 0.5s</td>
<td>±30%</td>
<td>0.5s sample every 5s</td>
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<td>Mist Chamber – IC⁴</td>
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<td>105 sec</td>
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<td>OH</td>
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<td>20 sec</td>
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<td>O₃</td>
<td>Chemiluminescence</td>
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<td>Precision = ±1ppbv, ±1.5% of reading</td>
<td>±1.4 ppbv, ±2.6% 2σ</td>
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<tr>
<td>JNO₂</td>
<td>Actinic Flux Spectroradiometer</td>
<td>4.1 x 10⁻⁷ Precision = ±4.5%</td>
<td>±8%</td>
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<td>(22)</td>
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</table>

¹LIF – Laser Induced Fluorescence
²NO₂ detection threshold is 8 pptv / 10 sec at 760 Torr (ground) and 20 pptv / 10 sec at 200 Torr (10 km)
³CIMS – Chemical Ionization Mass Spectrometry
⁴IC – Ion Chromatography
⁵UCN (Ultra-fine Condensation Nuclei) was obtained by the difference of the UCN (Dₚ>3nm, TSI 3025) and CN (Dₚ>10nm, TSI 3010) Condensation Nuclei (CN) instruments.

**Table S1:** Detection thresholds, measurement uncertainty and time response of the *in situ* measurements used in this study. (Note: ppmv = µmol mol⁻¹, ppbv = nmol mol⁻¹ and pptv = pmol mol⁻¹)
References and Notes:

4. S. P. Sander *et al.*, “Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14” (National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 2003).