Nitrogen Oxides

- The Berkeley TD-LIF Instrument/Comparisons
- Convection, NO$_2$ peak at 10km, Age of air,
- HO$_x$ chain termination (by NO$_x$) in the continental boundary layer
LIF Detection of NO$_2$

**Multi-pass Cell**

(1 of 2)

To Pump

Nd$^{3+}$:YAG

532 nm

Tunable Dye Laser

585 nm

Sample

Using a supersonic expansion to cool NO$_2$ to about 25K


NO$_2$ Reference Cell Transmission

On-Line

Off-Line

Jet-Cooled

5 Torr

PMT Counts (NO$_2$ Fluorescence)

Etalon Step Number
∑PNs, ∑ANs, & HNO₃ + heat → ROₓ + NO₂

**Thermal Dissociation-LIF**

Oven 2 held at 340 °C

Oven 2 held at 180 °C

Oven 2 held at 40 °C

Temperature of Oven 1 (°C)
Heated inlets

Unheated inlet

Heated inlets

200°C - dissociation of ΣPNs

350°C - dissociation of ΣPNs and ΣANs

580°C - dissociation of ΣPNs, ΣANs and HNO3

to cell 1

to cell 2

to cell 2

to cell 1
DC-8 $\Sigma$PNs PAN Comparison

$\text{NASA PAN} = 0.76 [\Sigma \text{PNs}]_{\text{UCB}} + 54.6 \quad R^2 = 0.64$

1-1 line

NASA PAN = 0.76 [ΣPNs]$_{UCB}$ + 54.6   $R^2 = 0.64$
\[ \text{NO}_{\text{ss}} = \frac{J_{\text{NO}_2} \times [\text{NO}_2]}{k_{\text{HO}_2 + \text{NO}} \times [\text{HO}_2] + k_{\text{O}_3 + \text{NO}} \times [\text{O}_3]} \]
Convection/Age of Air
Fraction of Total Tropospheric Column at LAT = 33.66  LONG = 276.83

Mid-Atlantic continental profile

Assumes tropopause at 10km and BL well mixed and interpolated to the ground
0-D time dependent model: Noon injection, no dilution, 10km
Local Sun Time 11 August 2004

Hours Since Injection

Nitrogen Time
Peroxide Time
Aerosol Time
Lightning hits 10/11 August 2004  2day back trajectory

NLDN Lightning 2 days prior to DC–8 Flight on 11 August 2004

Lightning Hits --> Color-scaled by time prior to DC–8 sampling (hours)
1-min merge data; Model fit to exponential
Isoprene Nitrates
Isoprene Oxidation

$\text{H}_2\text{CO yield is 0.6}$

$\text{O}_3$ yield is $2(1 - \alpha)$ where $
\alpha$ is $k_b/(k_a+k_b)$
Distribution of NO\(_y\)

7/20/2004

*HNO\(_3\) data courtesy of Wennberg et al, CalTech

Observed contributions to RO\(_2\) production

**Pie Chart**

- Isoprene: 66%
- Ethane: 4%
- Propane: 9%
- Butane: 6%
- Pentane: 3%
- Alkenes: 12%
- Alkanes: 31%
- PPNs: 32%
- NO\(_2\): 19%
- HNO\(_3\): 18%

Hydrocarbon data provided by Blake et al, UC Irvine
\[ \Sigma \text{ANs and } O_3 \]

\[
\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{RO}' + \text{O}_2 & \rightarrow \text{R'O} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{RONO}_2 \\
2 \times 97 \text{ O}_3 : 3 \Sigma \text{ANs} \\
65 \text{ O}_3 : \Sigma \text{AN}
\end{align*}
\]
$O_3 = 45 \Sigma ANs + 35,275$

$r^2 = 0.44$

Implied branching ratio = 4.3%
H$_2$CO v. ANs (under 1 km)

\[ \Sigma ANs = 0.067 \text{H}_2\text{CO} - 40.6 \]

\[ r^2 = 0.38 \]

Implied branching ratio = 4.1%
$\text{HO}_x$ Chain Termination
Chain Termination

\[
\begin{align*}
\text{HO}_x - \text{HO}_x & \quad \text{NO}_x - \text{HO}_x \\
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2 + \text{RO}_2 & \rightarrow \text{ROOH} + \text{O}_2 \\
\text{HO}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{NO}_2 + \text{OH} & \xrightarrow{M} \text{HNO}_3 \\
\text{RO}_2 + \text{NO} & \xrightarrow{M} \text{RONO}_2
\end{align*}
\]
$O_3 = 13.7 (HNO_3 + \Sigma ANs) + 32,327$

$R^2 = 0.77$
Plans & Questions

- Describe distribution of age of air between 8 and 12 km. Understand how age affects other photochemical processes. What other short lived species (e.g. H$_2$CO are lofted by convection)? How well can we connect observations of atmospheric composition in the PBL to the observations at 8-12km? Will that provide a way to measure lightning NO$_x$?

- Assess whether data does cleanly constrain isoprene nitrate yield. Characterize $\Sigma$AN/HNO$_3$ roles in HO$_x$ chain termination. Where do the $\Sigma$ANs go?