Nocturnal Processing of NO_x, O_3 and VOC aloft over Houston

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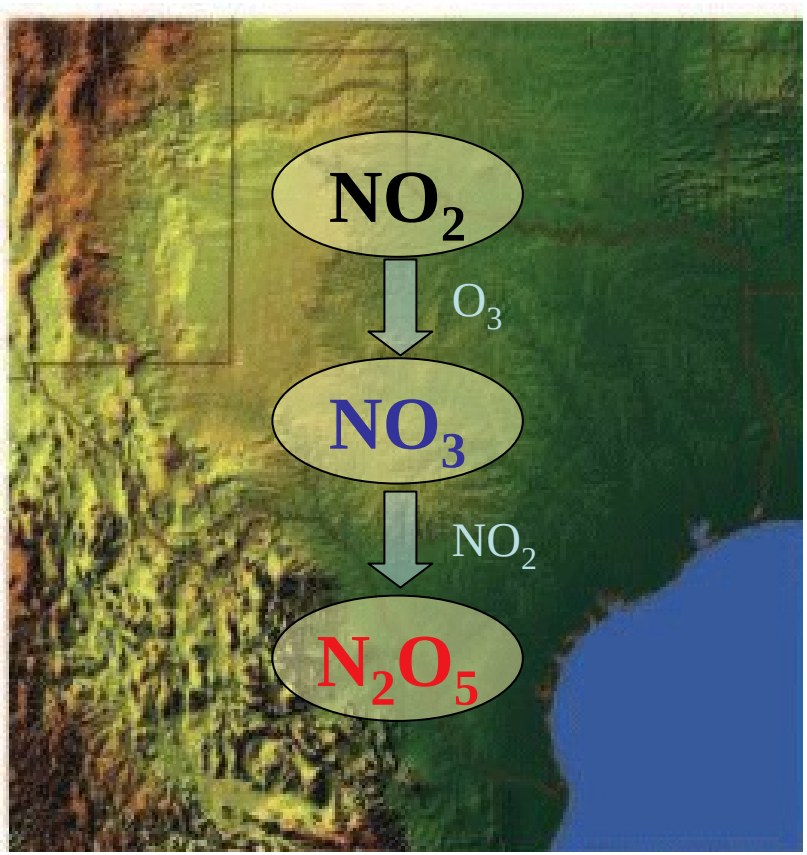
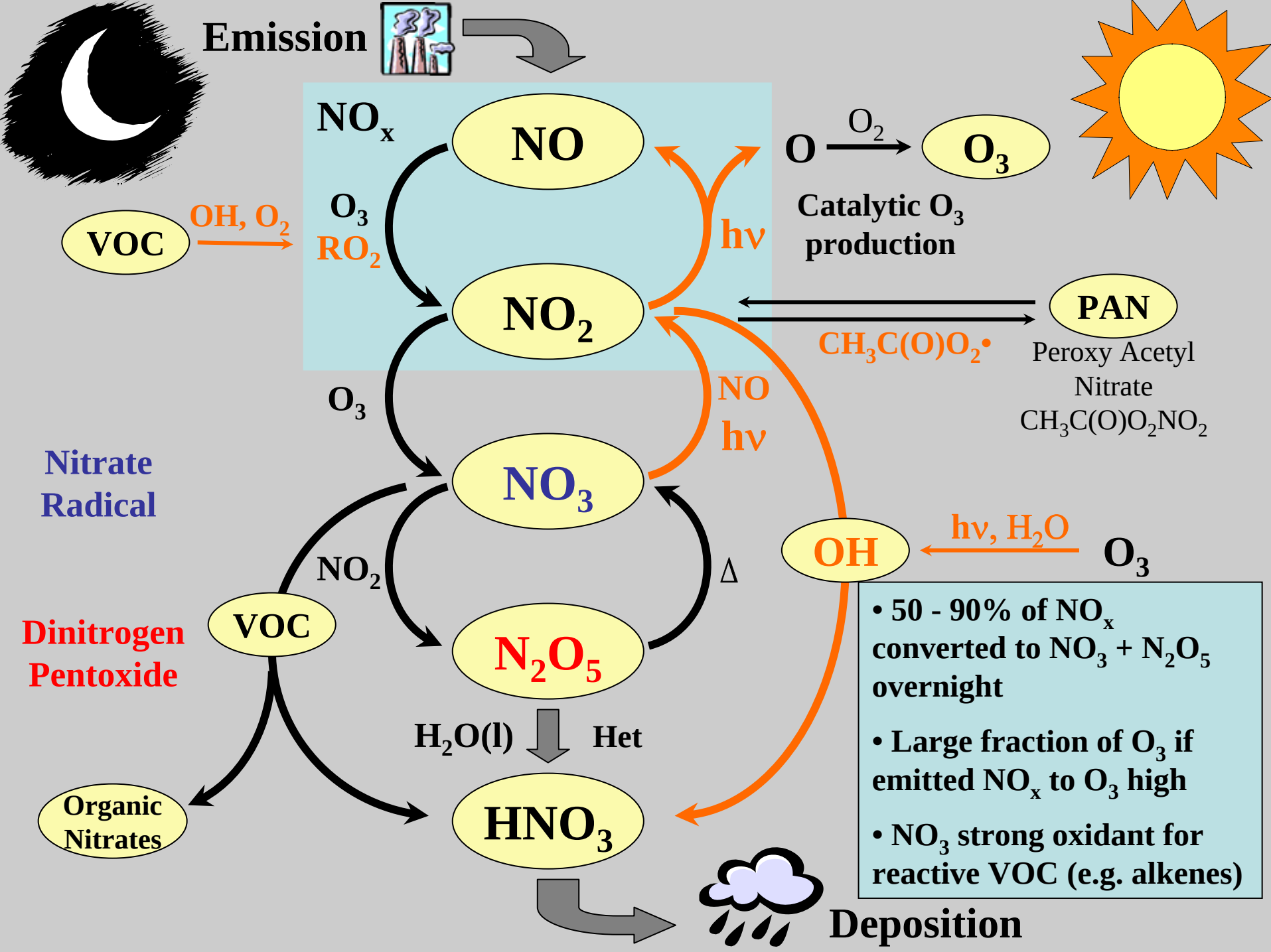
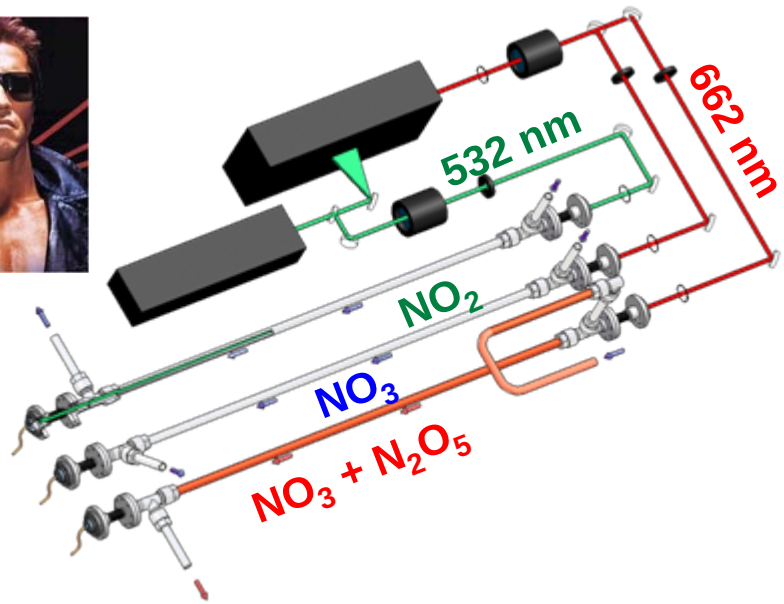
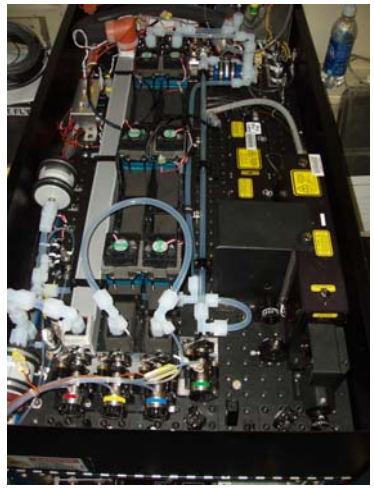



Emission
NO_x
NO
NO_2
O_3
RO_2
VOC
OH, O_2
hν
O
O_2
O_3
Catalytic O_3 production
PAN
$CH_3C(O)O_2$•
Peroxy Acetyl Nitrate
$CH_3C(O)O_2NO_2$
O_3
NO
hν
Nitrate Radical
NO_3
NO_2
Δ
OH
hν, H_2O
O_3
Dinitrogen Pentoxide
VOC
N_2O_5
$H_2O(l)$
Het
Organic Nitrates
HNO_3
Deposition
• 50 - 90% of NO_x converted to NO_3 + N_2O_5 overnight
• Large fraction of O_3 if emitted NO_x to O_3 high
• NO_3 strong oxidant for reactive VOC (e.g. alkenes)

NO_3 and N_2O_5 Instrument

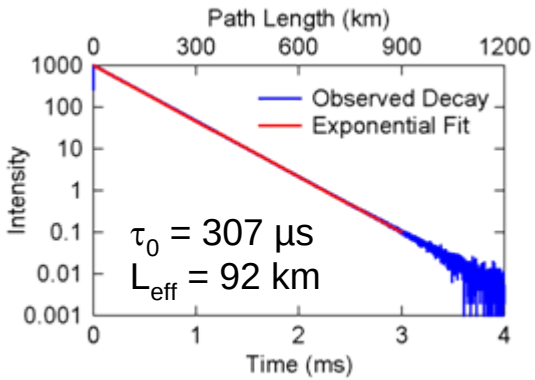
"ARNOLD" = Airborne Ringdown Nitrogen Oxide Laser Detector





Bill Dubé

Pulsed Cavity Ring-down Spectroscopy



Measure first-order decay rate coefficient of light intensity from an optical cavity

NO_2: 532-nm optical extinction
L.O.D. = 0.1 ppbv @ 1 Hz
Accuracy = 5%

NO_3: 662 nm optical extinction
L.O.D = 0.2 - 2 pptv @ 1 Hz
Accuracy = 20%

N_2O_5: Thermal conversion + 662 nm optical extinction
L.O.D. = 0.5 - 2 pptv @ 1 Hz
Accuracy = 20%

Outline

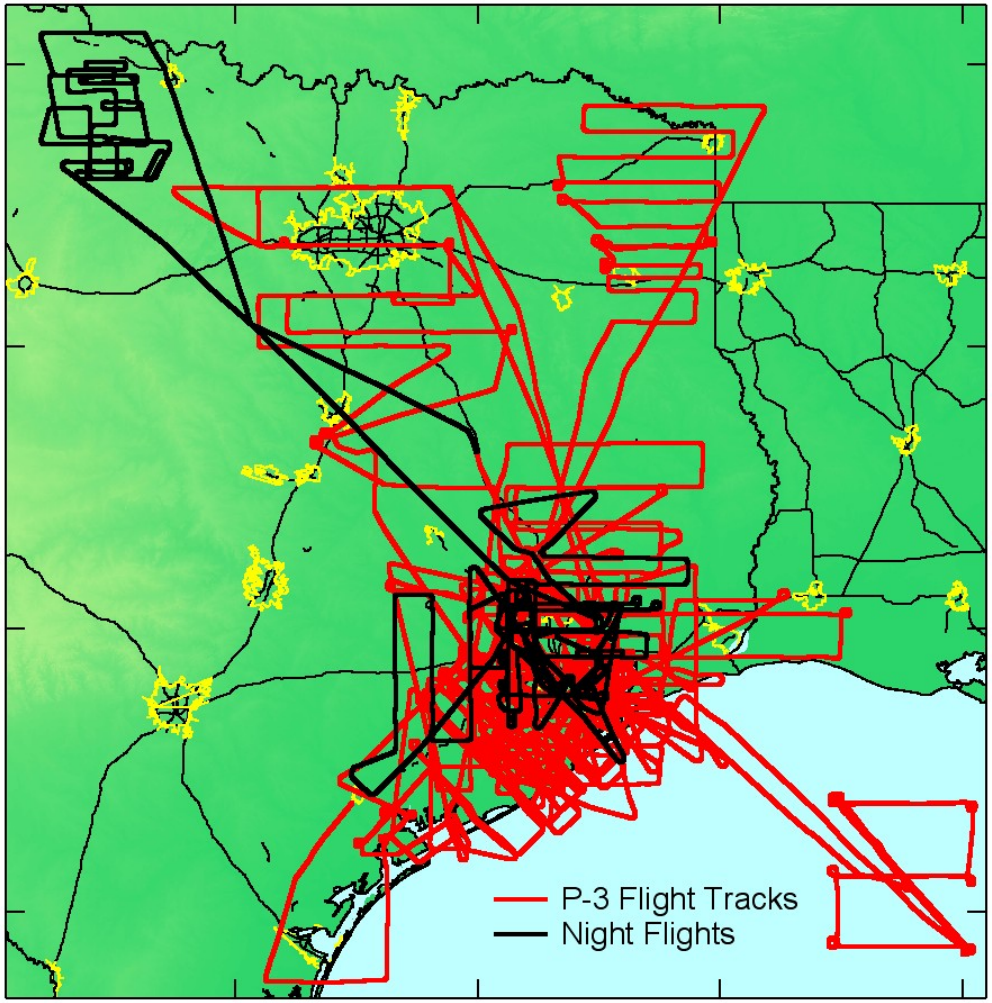
1. Nocturnal NO_x Loss vs. Transport
   Key = Stability / Reactivity of N_2O_5

2. O_3 Loss and transport
   Key = Nocturnal Odd Oxygen (O_x)

3. Nocturnal VOC Oxidation
   Key = Availability of NO_3 & Highly Reactive VOC

4. Vertical Stratification
   Difference between surface and aloft

Night Flights during TexAQS 2006



September 29

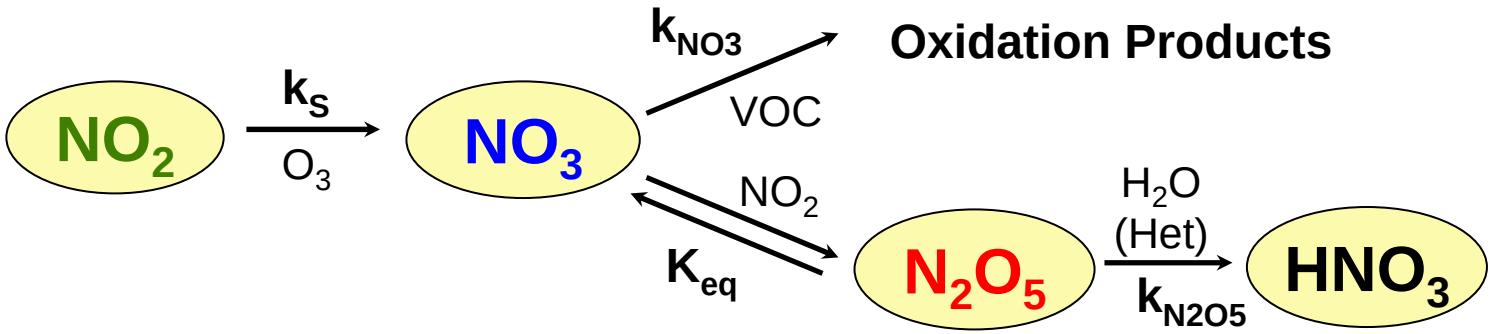
October 8

October 10

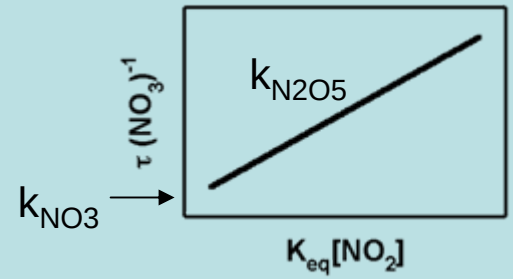
October 12

- Limited set of nighttime data
- Draw the most general conclusions possible

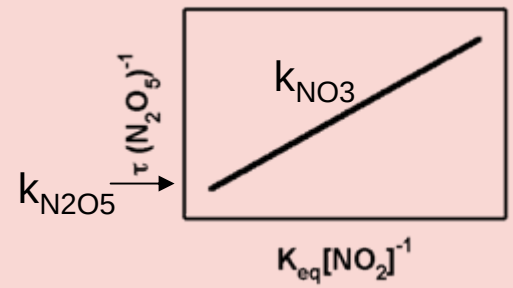
Data Analysis I - Steady State Lifetimes



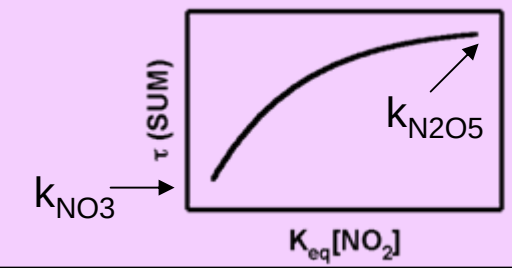
$$\tau(NO_3) \equiv \frac{[NO_3]}{k_S[NO_2][O_3]} \qquad \tau(NO_3)^{-1} \approx k_{NO_3} + k_{N_2O_5}K_{eq}[NO_2]$$



$$\tau(N_2O_5) \equiv \frac{[N_2O_5]}{k_S[NO_2][O_3]} \qquad \tau(N_2O_5)^{-1} \approx k_{N_2O_5} + \frac{k_{NO_3}}{K_{eq}[NO_2]}$$

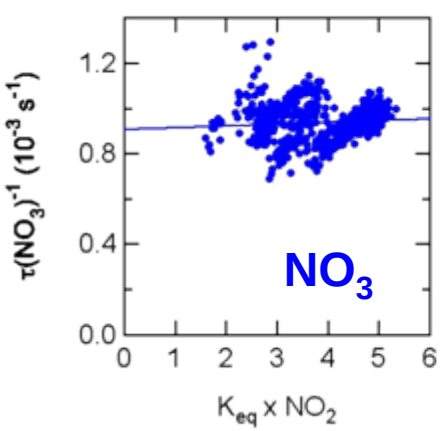


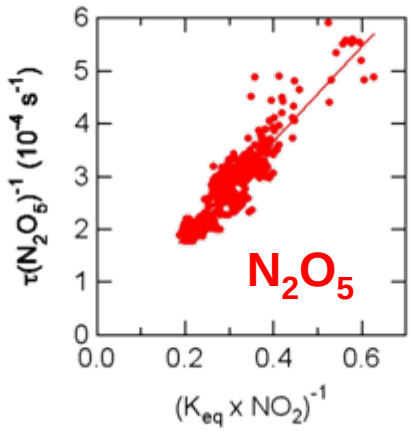
$$\tau(SUM) \equiv \frac{[NO_3]+[N_2O_5]}{k_S[NO_2][O_3]} \qquad \tau(SUM) \approx \frac{1+K_{eq}[NO_2]}{k_{NO_3} + k_{N_2O_5}K_{eq}[NO_2]}$$

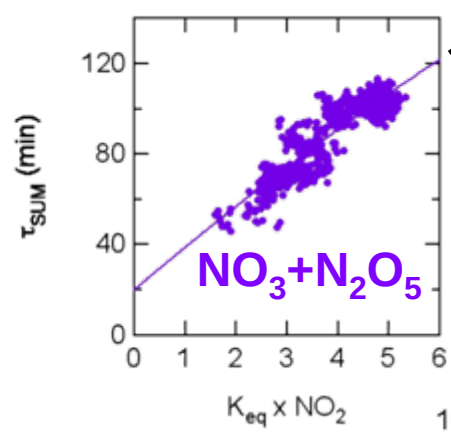


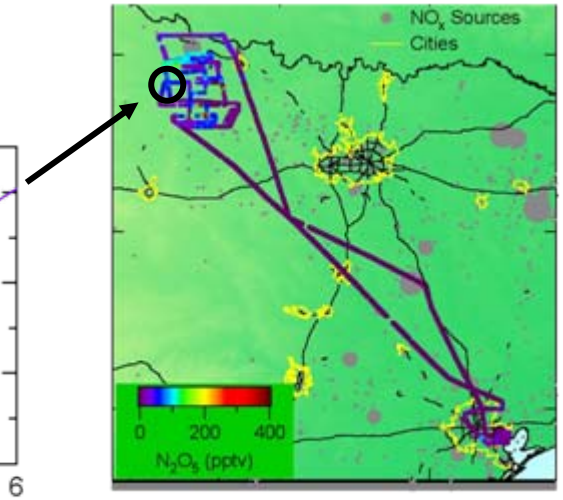
Caveats: • System must reach steady state • No covariance between k_{NO3}, k_{N2O5} & NO_2

Example 1: North Texas



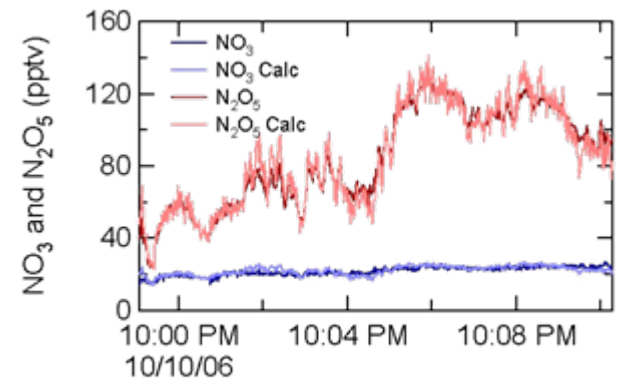






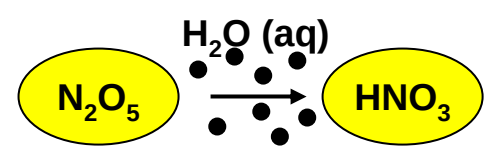
k_{NO3}^{-1} = 19 ± 1 min

k_{N2O5}^{-1} > 10 hours



N_2O_5 Hydrolysis *very slow*

$$k_{N_2O_5} \approx \frac{1}{4} \times \bar{c} \times \gamma(N_2O_5) \times S_{Aerosol} \qquad \gamma < 10^{-3}$$



Aerosol:

- Neutral $(NH_4)_2SO_4$ aerosol
  NH_4^+/SO_4^{2-} > 2
- Measurable aerosol NO_3^-
- Large Organic / Sulfate Ratio

- $\gamma(N_2O_5)$ similar to that seen on this aerosol type in previous campaigns (e.g. New England)

Data Analysis II - Nocturnal Odd Oxygen (O_x)

Daytime: $O_x \equiv O_3 + NO_2$

$NO + O_3 \rightarrow NO_2 + O_2$ $\quad$ $NO_2 = 1\ O_x$

Nighttime: $O_x \equiv O_3 + NO_2 + 2NO_3 + 3N_2O_5$

$NO + O_3 \rightarrow NO_2 + O_2$ $\quad$ $NO_2 = 1\ O_x$

$NO_2 + O_3 \rightarrow NO_3 + O_2$ $\quad$ $NO_3 = 2\ O_x$

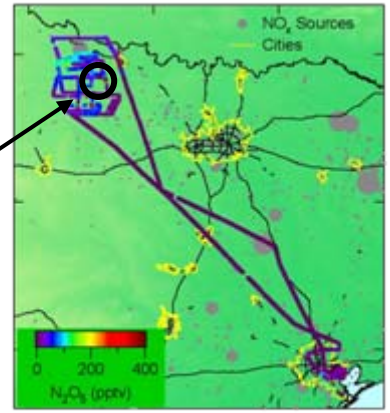
$NO_3 + NO_2 \rightarrow N_2O_5$ $\quad$ $N_2O_5 = 3\ O_x$

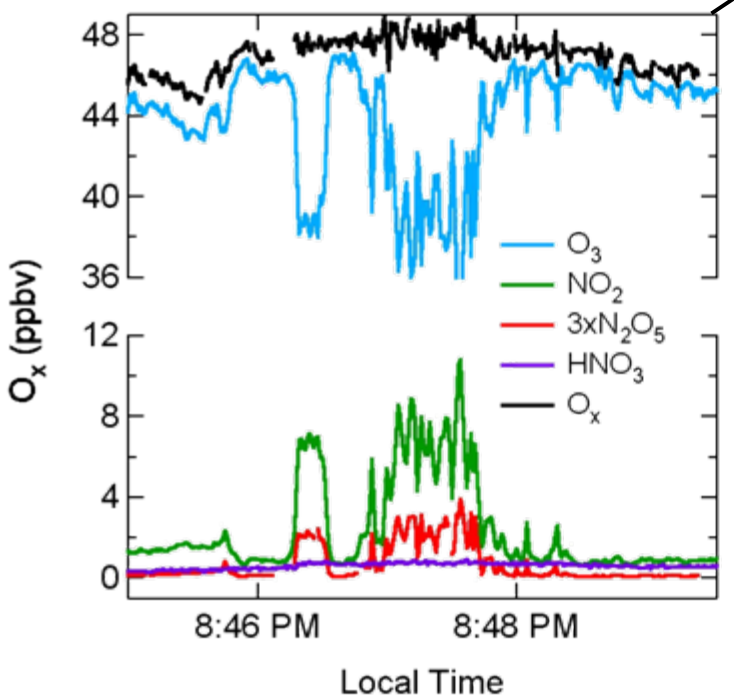
Nocturnal Losses for O_x

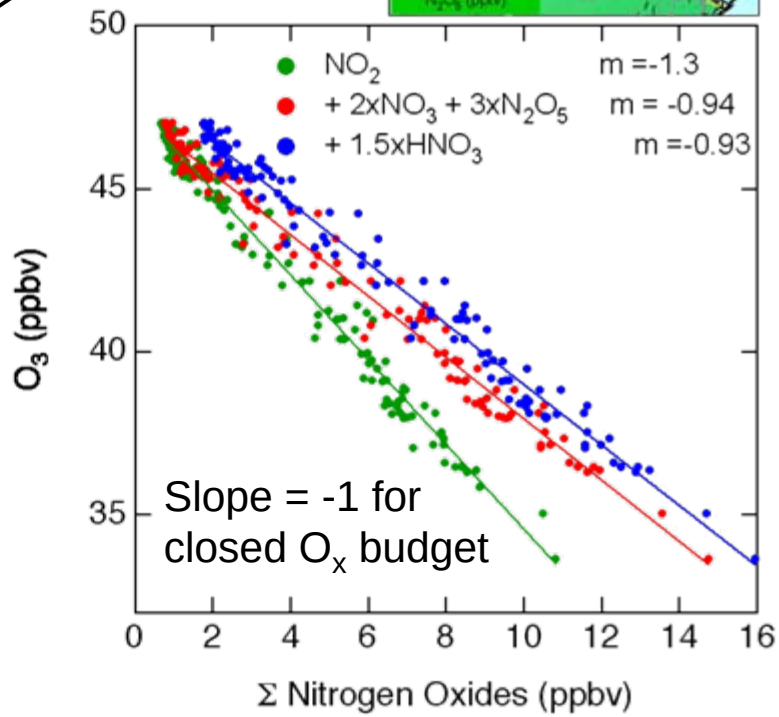
$N_2O_5 + H_2O \rightarrow 2HNO_3$ $\quad$ HNO_3 = loss of 1.5 O_x

NO_3 + VOC reactions $\quad$ Variable, loss of 1-2 O_x

O_x Budget - Oklaunion Power Plant Plume (North Texas)

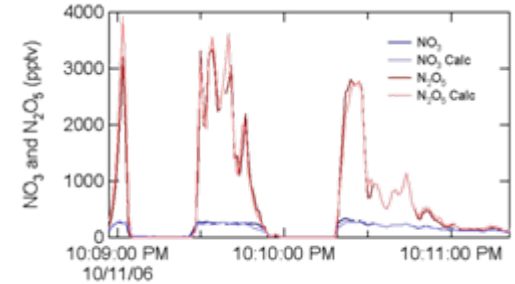




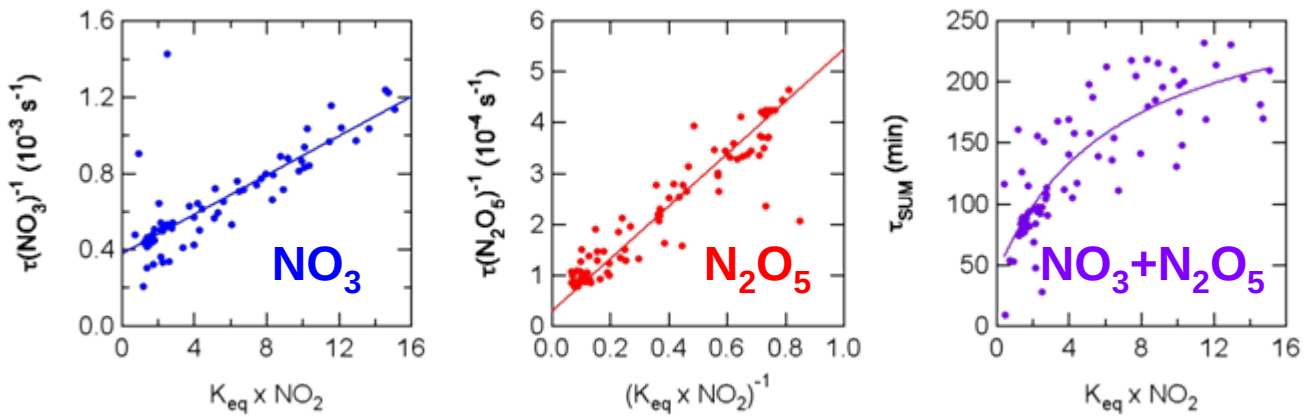


- NO_3 and N_2O_5 account for most of lost O_x in plumes
- Little to no enhancement of HNO_3
- Corroborates lifetime analysis - *slow* N_2O_5 hydrolysis

Example 2: Parish Power Plant Intercept - October 12



Steady State Analysis

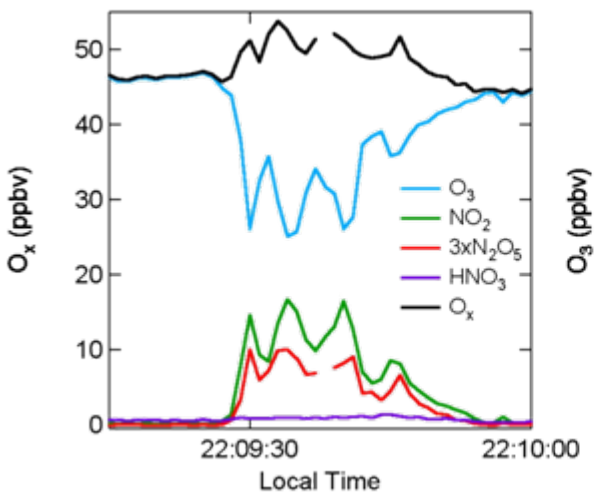


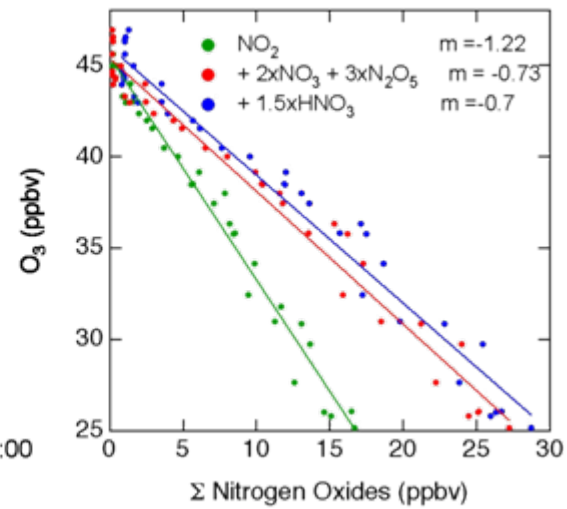
k_{NO3}^{-1} > 40 ± 1 min

k_{N2O5}^{-1} > 6 hours

N_2O_5 hydrolysis *slow*
$\gamma < 5x10^{-3}$

Odd-Oxygen Analysis

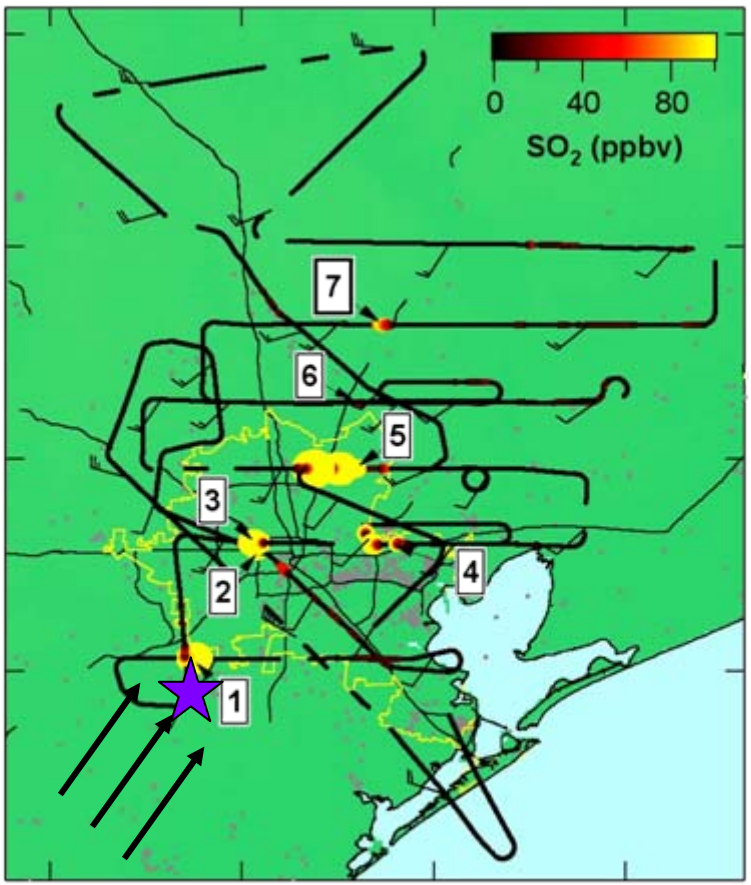


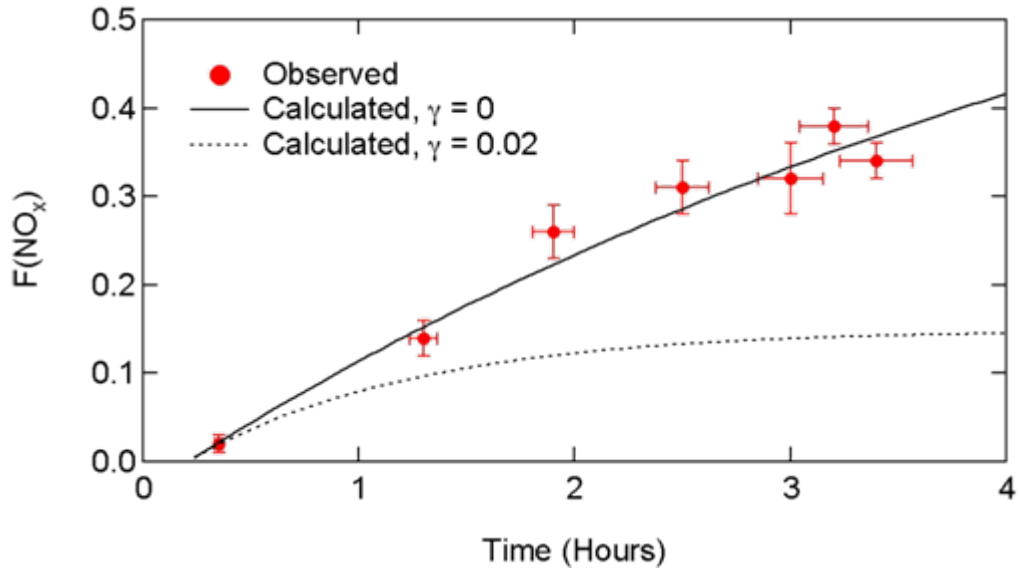


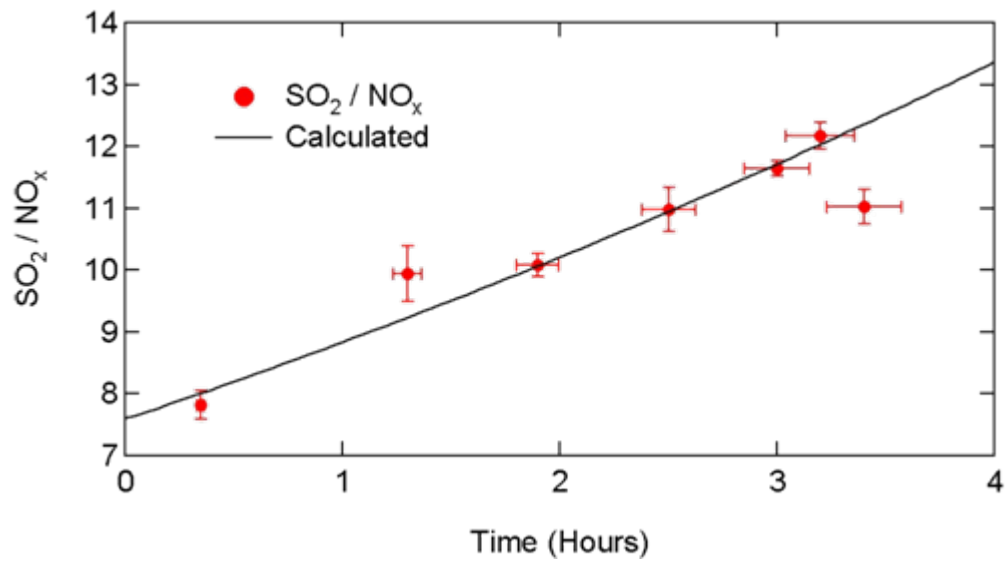
- NO_3 and N_2O_5 (more than) account for lost O_x
- Little to no enhancement in HNO_3
- Transport of NO_x and O_x

NO_x Transport - Parish Plume

$$F(NO_x) = \frac{NO_3 + 2N_2O_5}{NO_2 + NO_3 + 2N_2O_5}$$



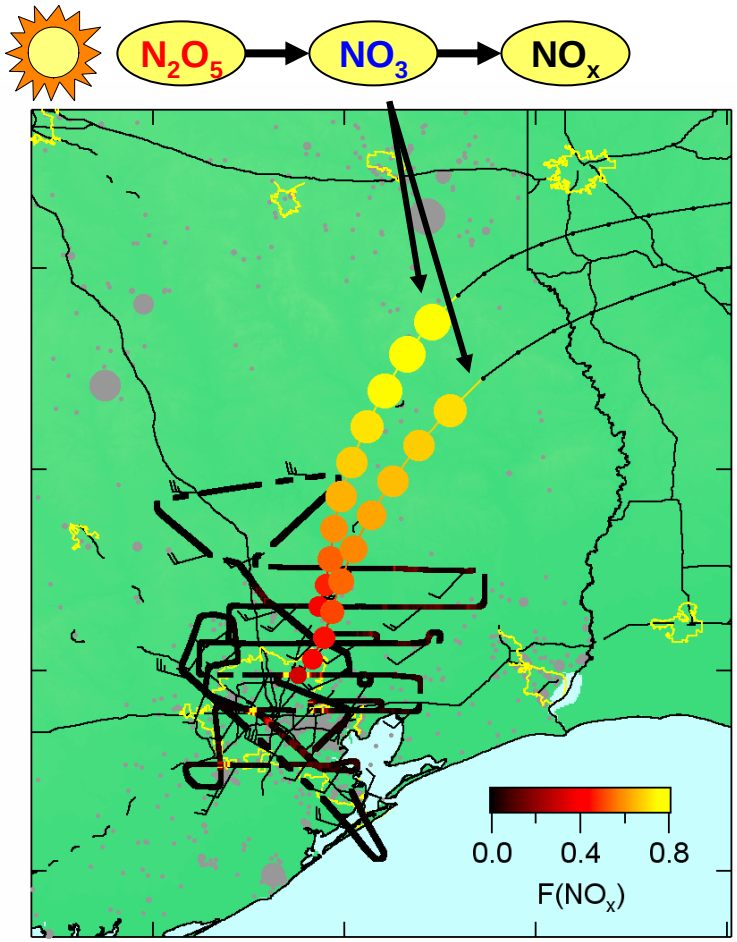




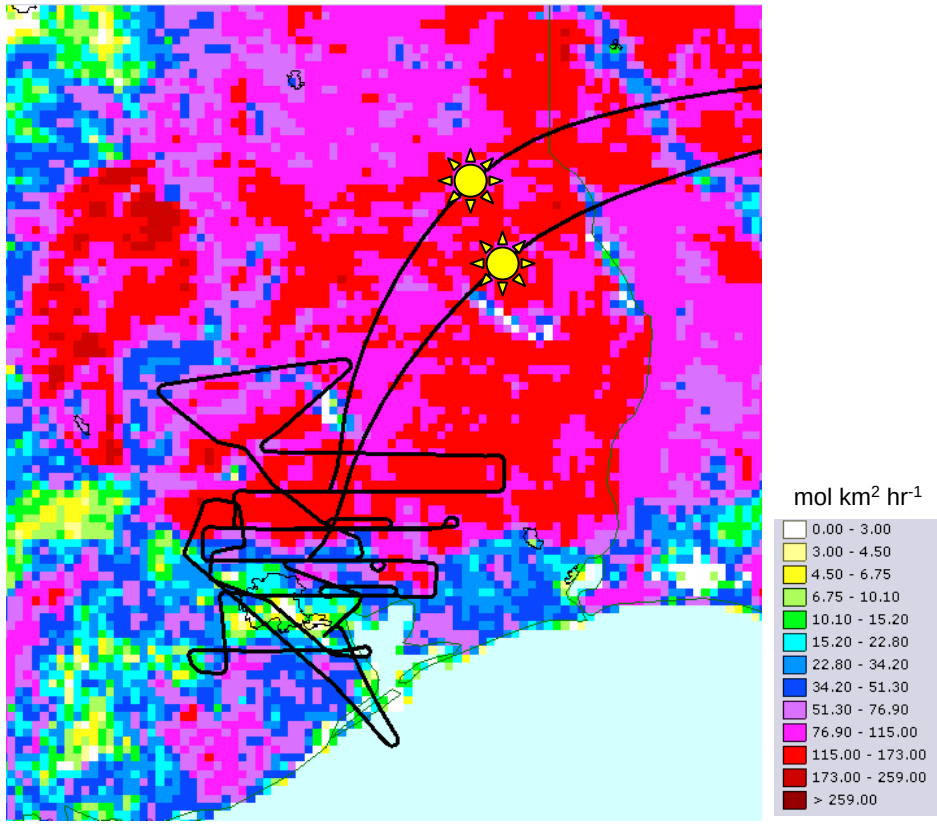
NO_x conserved within this plume

note: Low VOC case

Where Does It Go ?



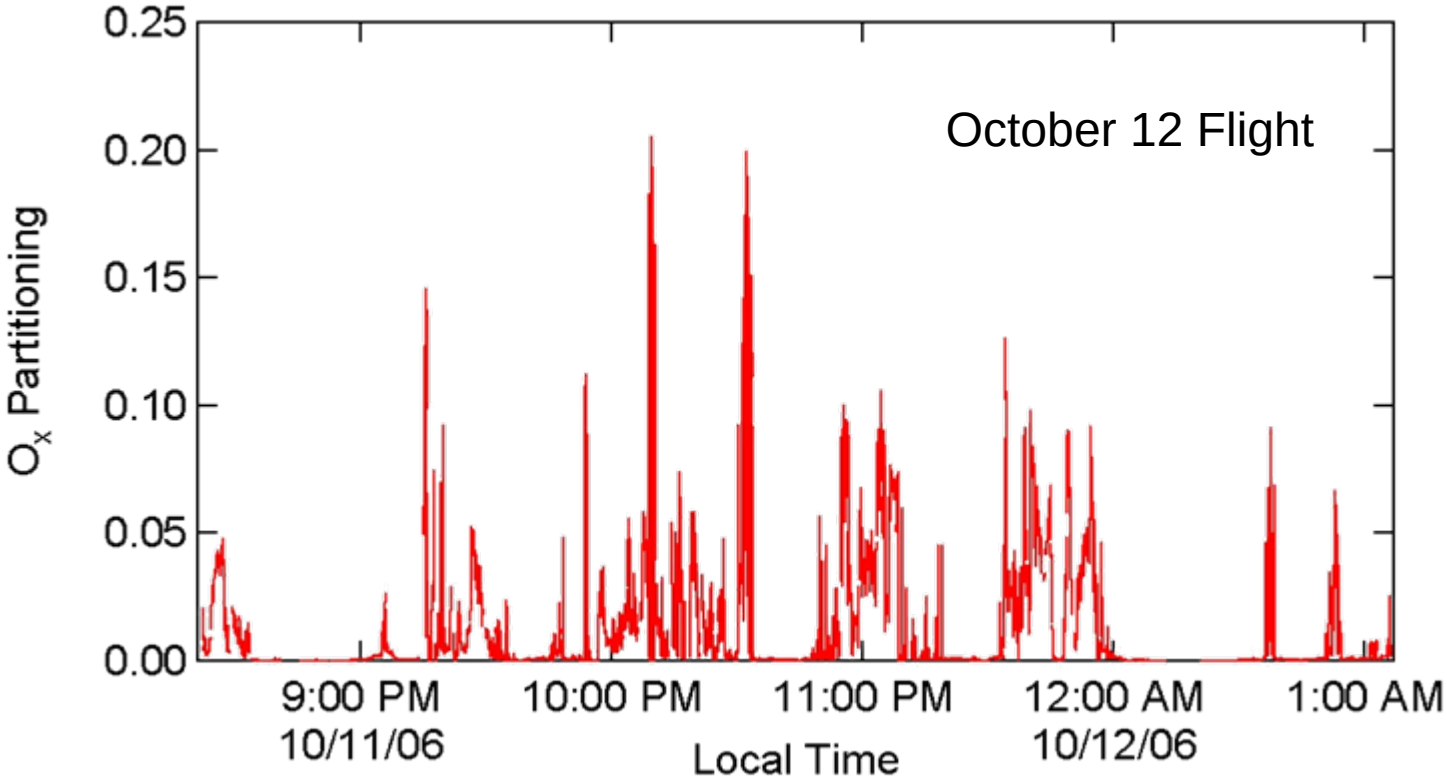
Isoprene Emission Map



- Overnight transport to region with higher biogenic emissions
- O_3 formation potential in rural regions, well removed from urban sources

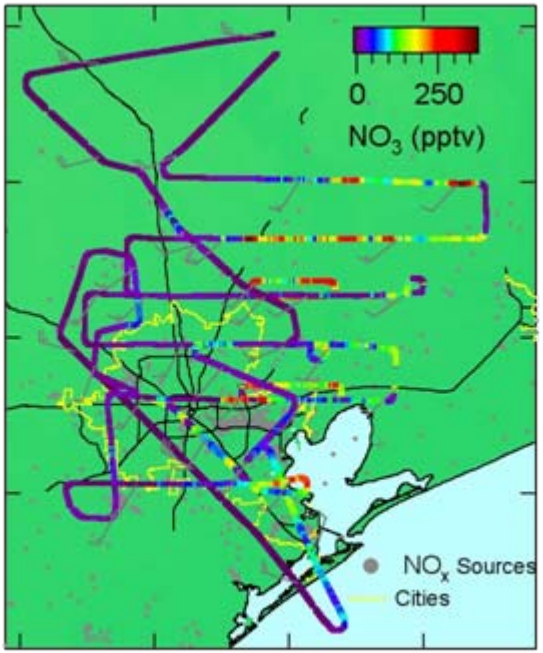
Nocturnal O_x Partitioning

$$F(O_x) = \frac{2NO_3 + 3N_2O_5}{O_3 + NO_2 + 2NO_3 + 3N_2O_5}$$



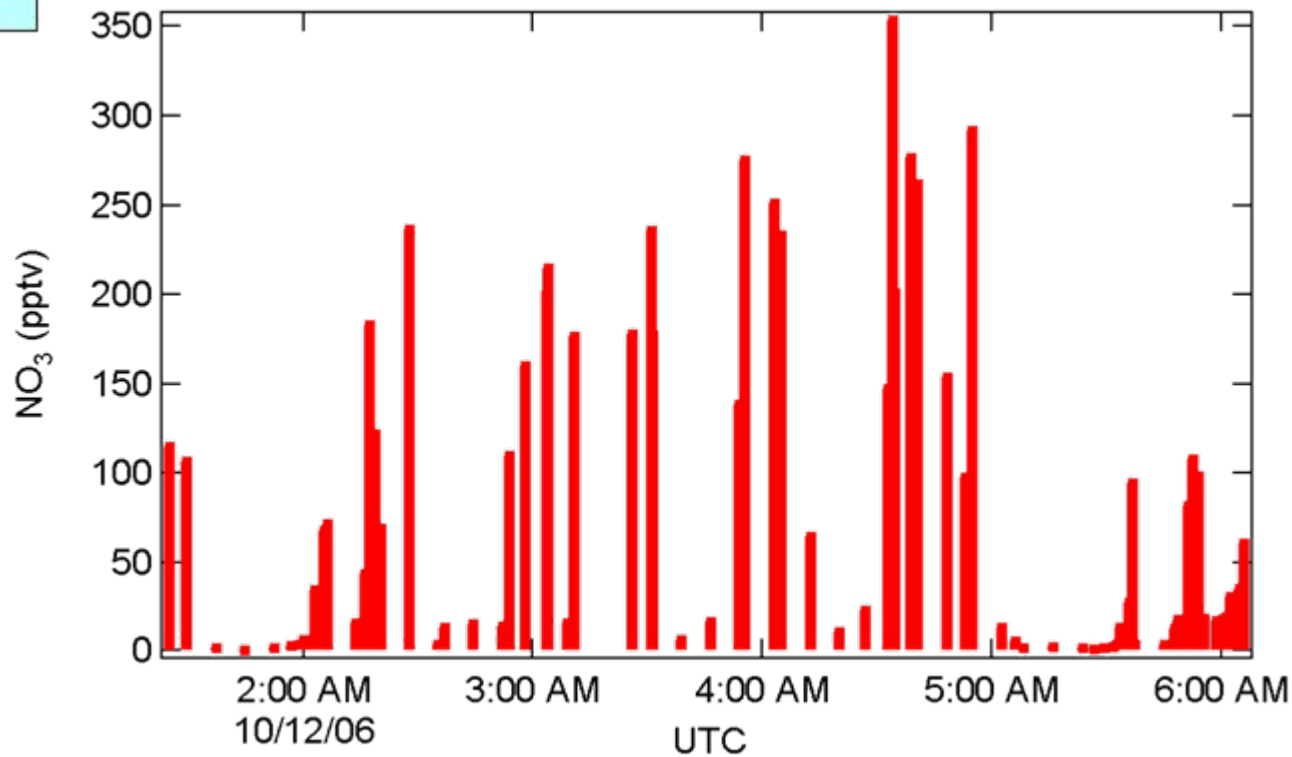
- $F(O_x)$ depends on ratio of emitted NO_x to O_3 and the stability of N_2O_5
- 5 - 20% (2 - 11 ppbv) O_x stored as N_2O_5 within plumes October 12

Nocturnal VOC Oxidation



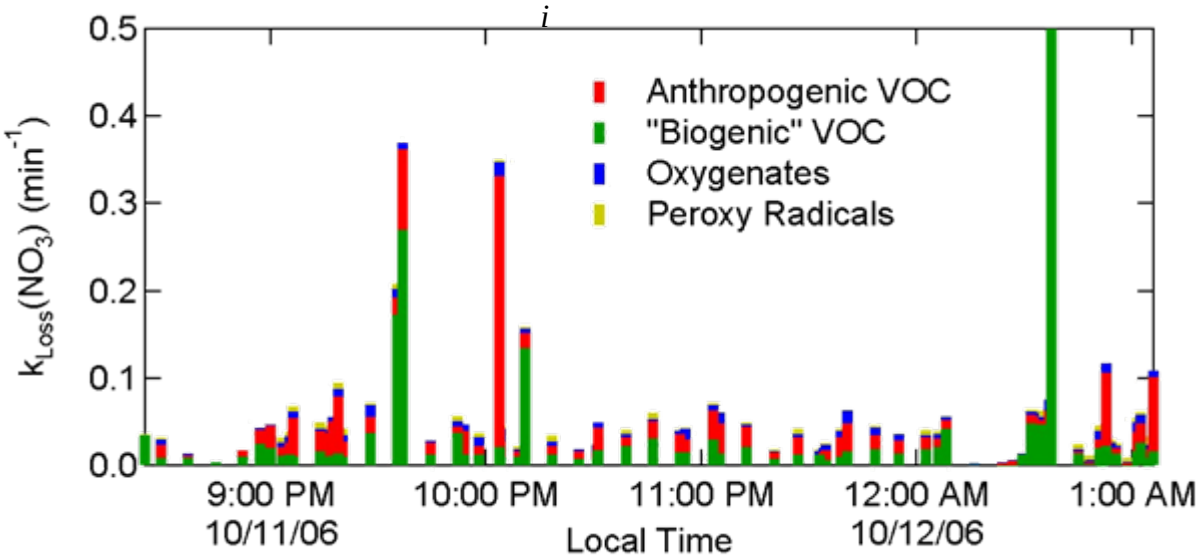
- Stability of N_2O_5 regulates availability of NO_3
- NO_3 on October 12 reached 350 pptv
- Potentially *very* strong oxidant - depends on VOC mixture
  - Alkenes (but ethylene very slow)
  - Aldehydes (but formaldehyde very slow)
  - Some aromatics

NO_3 averaged to whole air sampler (WAS) time base for October 12 flight

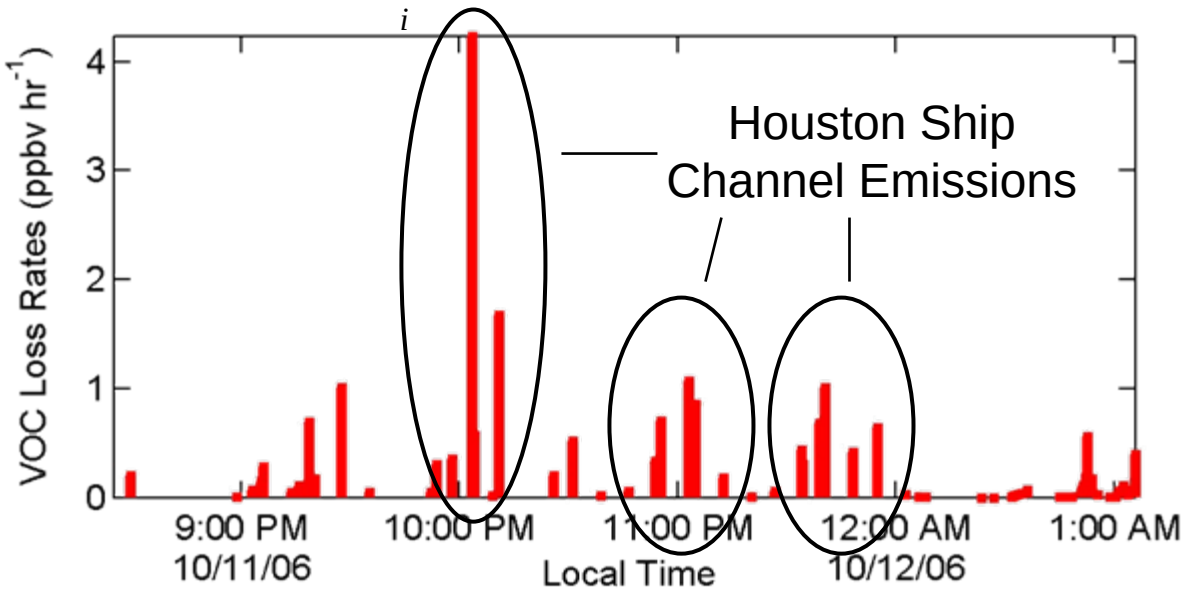


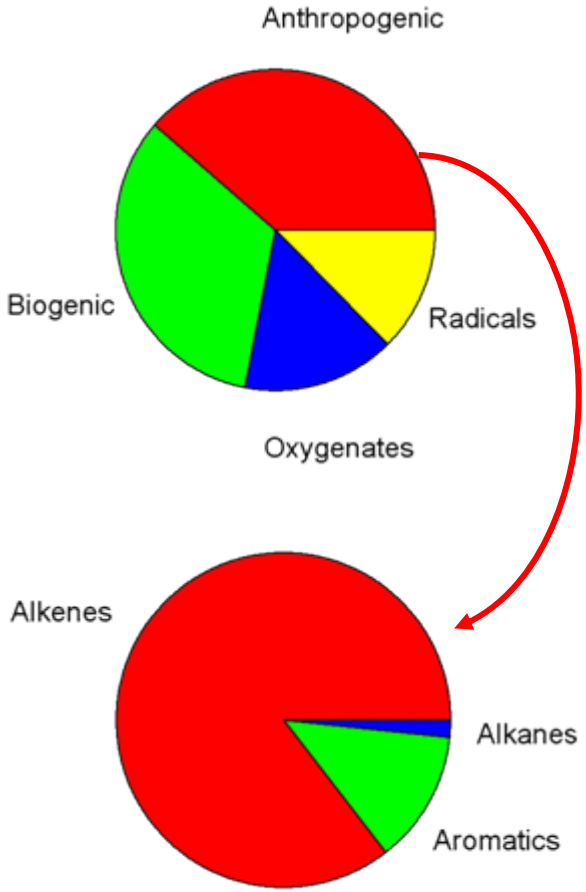
NO_3 - VOC Loss Rates & Sink Partitioning

$$k_{Loss}(NO_3) = \sum_i k(NO_3 + VOC_i) \times [VOC]_i$$



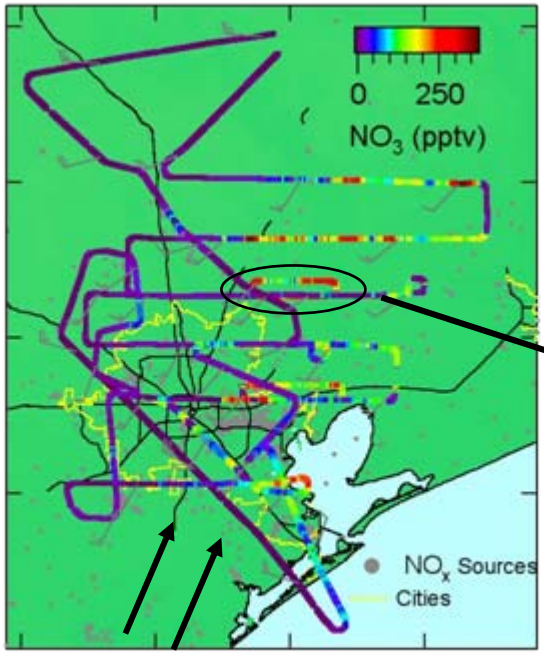
$$R_{VOC} = \sum_i k(NO_3 + VOC_i) \times [NO_3] \times VOC_i$$



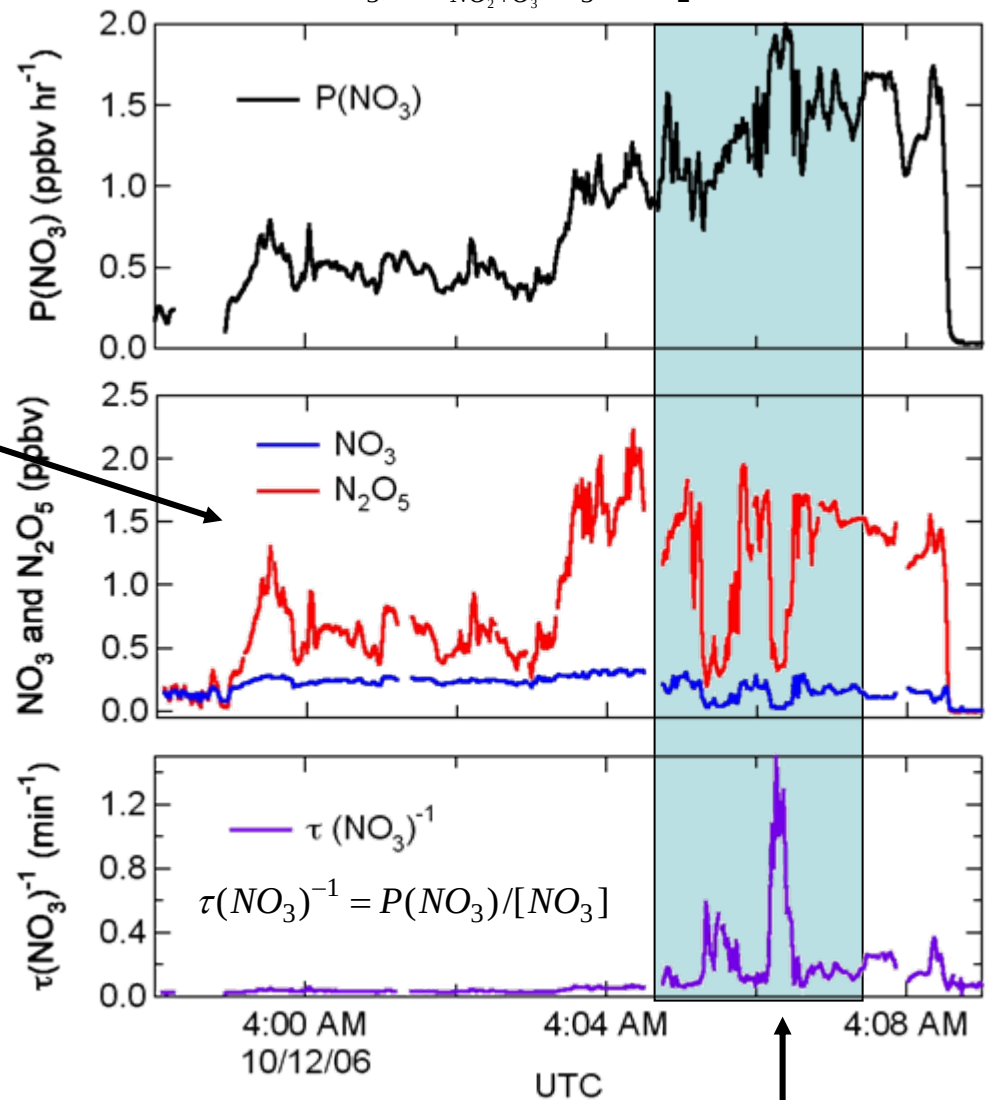


VOC Loss Rates of 0.5 - 4 ppbv hr^{-1} within plumes emitted from industrial sources

Evidence for oxidation of highly reactive VOC

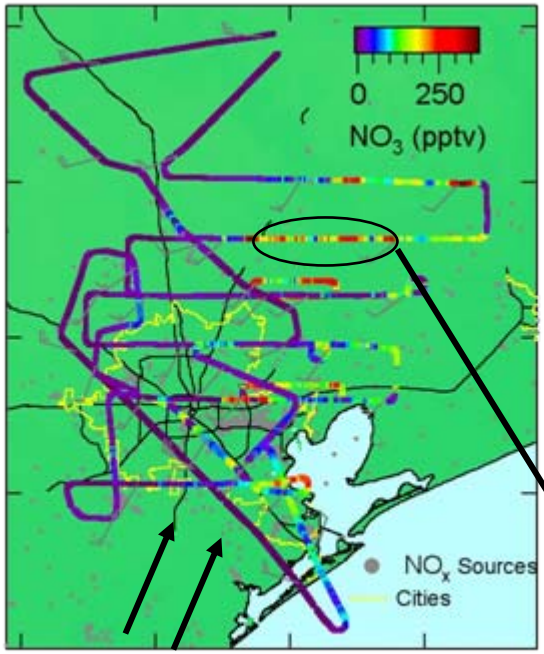


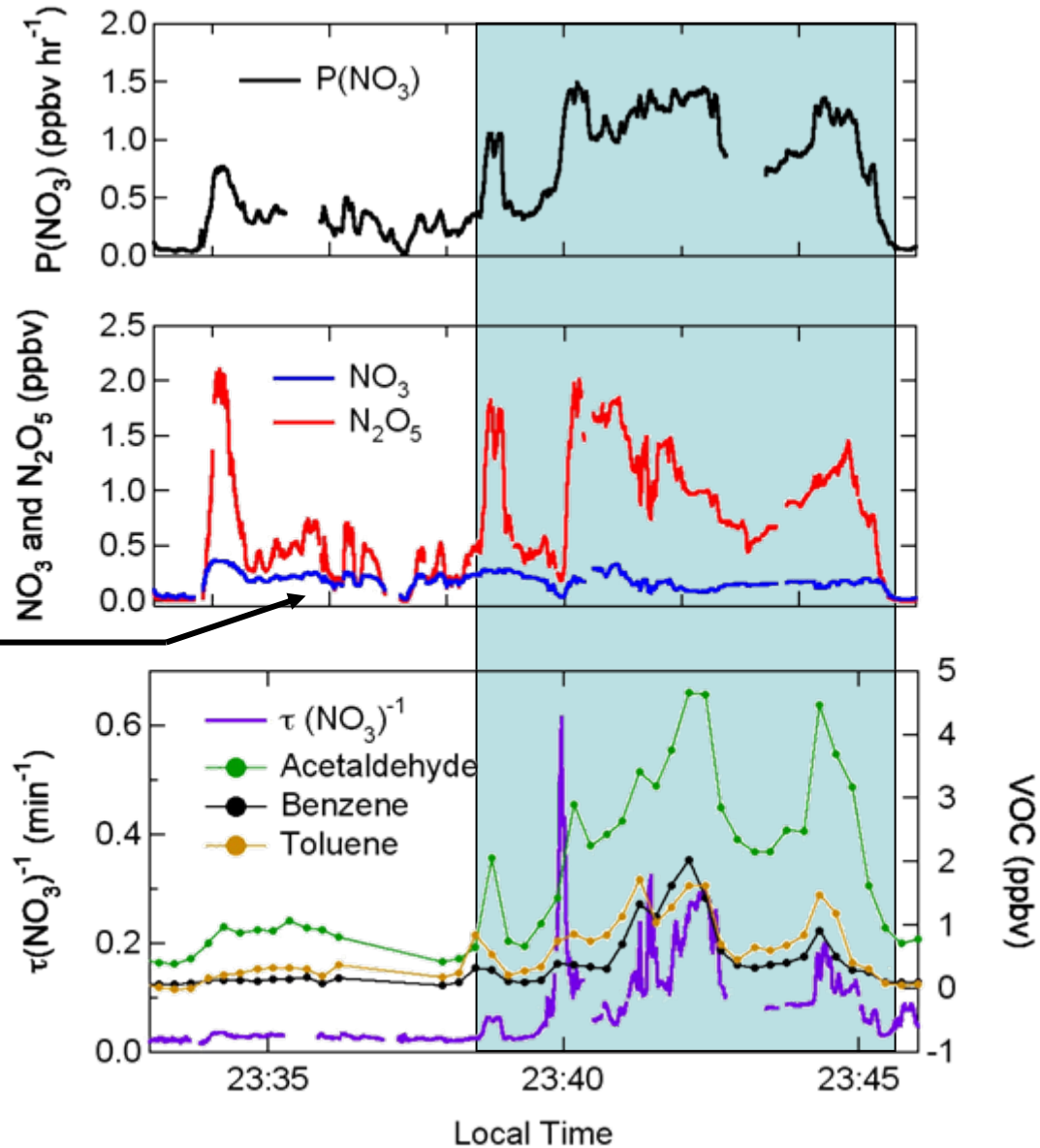
$$P(NO_3) = k_{NO_2+O_3}[O_3][NO_2]$$



Emission of very highly reactive VOC ?
(e.g., butadienes, styrene, phenols)

Oxidation of highly reactive VOC - Second Chance



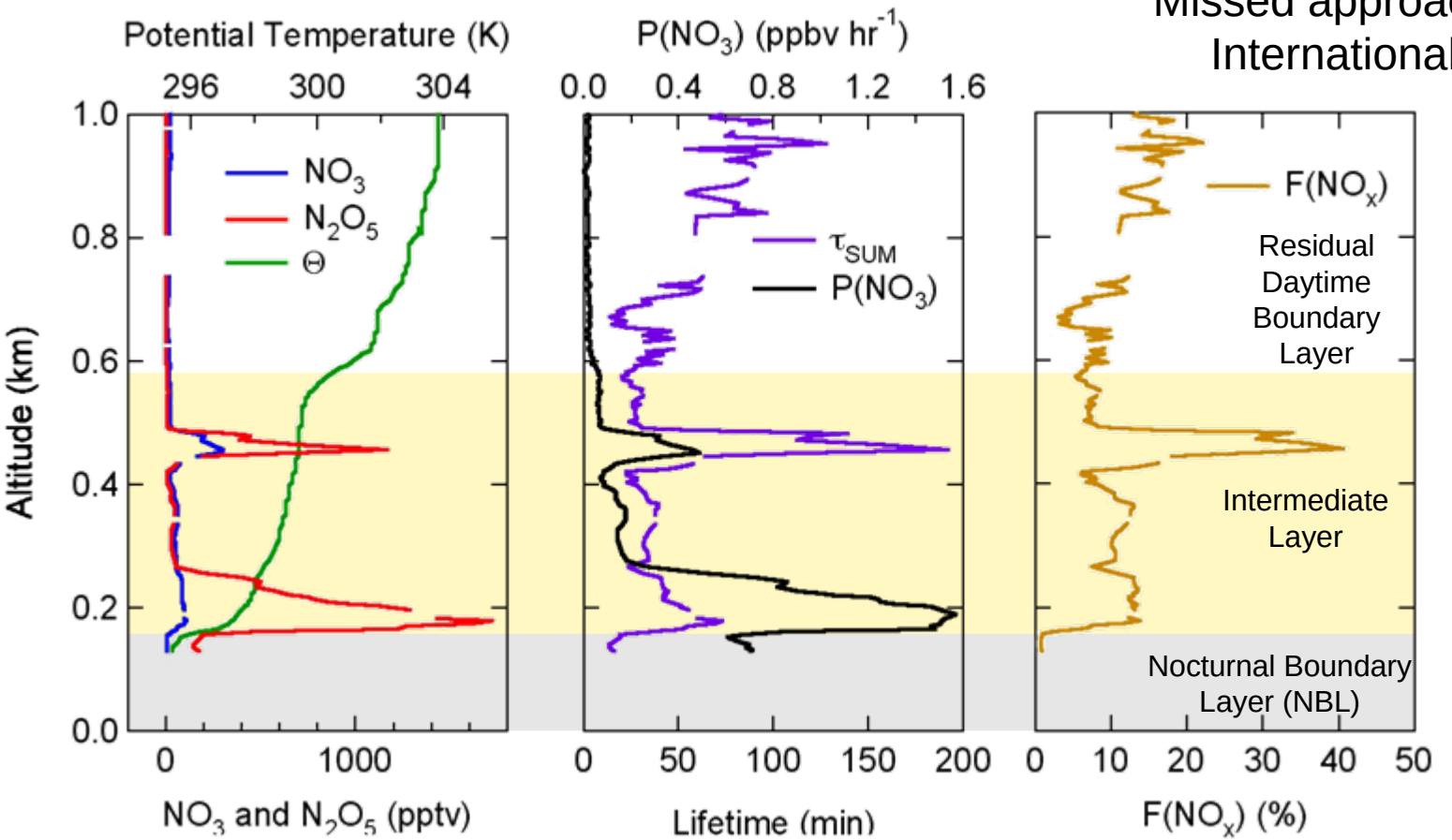


- Measured VOC *not* responsible for increase in NO_3 loss rate

- *But* likely correlated with emission of more reactive VOC

Vertical Stratification of Nighttime Chemistry

Missed approach to Bush International Airport



- NO_x & VOC plumes occur in discrete layers at night
- Can be more concentrated, and difficult to find !
- Chemistry in Nocturnal Boundary Layer differs significantly
  (see Hans Osthoff, Roberto Sommariva Posters for details)

Conclusions

- N_2O_5 hydrolysis *generally* inefficient during TexAQS
  - Consistency between lifetime and O_x analysis
  - Aerosol = Neutral $(NH_4)_2SO_4$ + Organics

- Overnight transport of NO_x and O_x in the form of N_2O_5
  - Most obvious in power plant plumes (low VOC)

- NO_3 available as an oxidant in industrial emissions
  - VOC loss rates 0.5 - 4 ppbv hr^{-1} in ship channel plumes
  - Evidence for oxidation of extremely reactive VOC

- Vertical Stratification
  - Shallow, concentrated NO_x plumes
  - Large difference between surface and aloft
    - P-3 vs. Ron Brown