Nighttime Tropospheric Chemistry

Nocturnal Reactions of NO_x, O_3, VOC and Aerosol

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Atmospheric Chemistry Review

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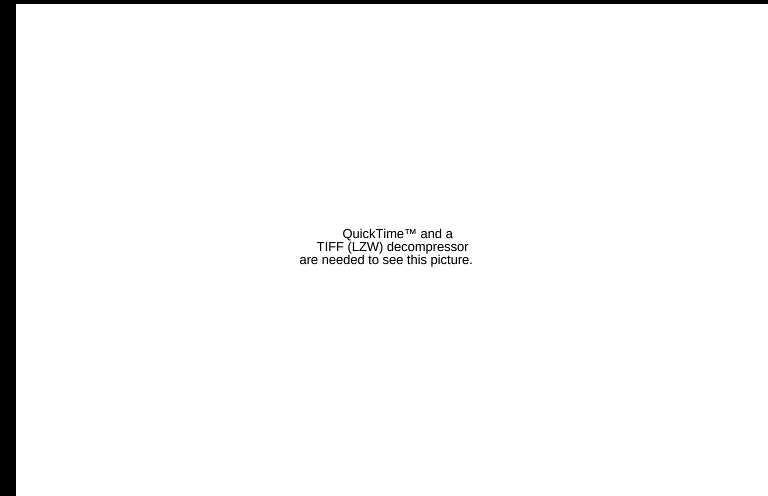
Ozone (O_3) and Air Quality

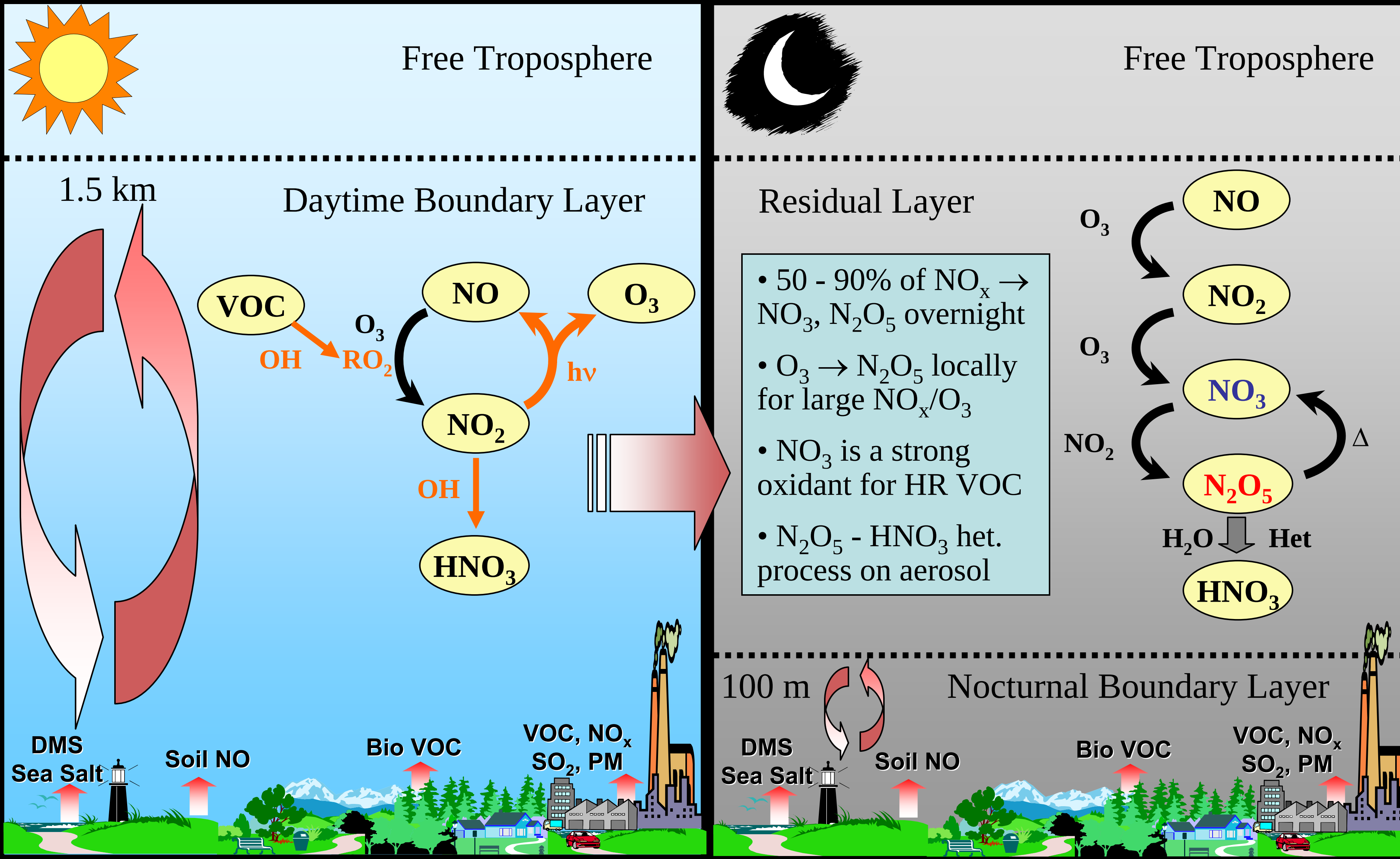


Relevance
- Health Impacts
- Greenhouse gas

Ingredients
- Nitrogen Oxides ($NO_x = NO + NO_2$)
  - Produced mainly from fossil fuel combustion
- VOC (Volatile Organic Compounds)
  - Both anthropogenic and natural sources
- Sunlight !
  - Key steps = radical formation, NO_2 photolysis

Scientific Requirements
- Emissions
- Process Chemistry
- Meteorology & Transport

Diurnal Nitrogen Oxide Cycles



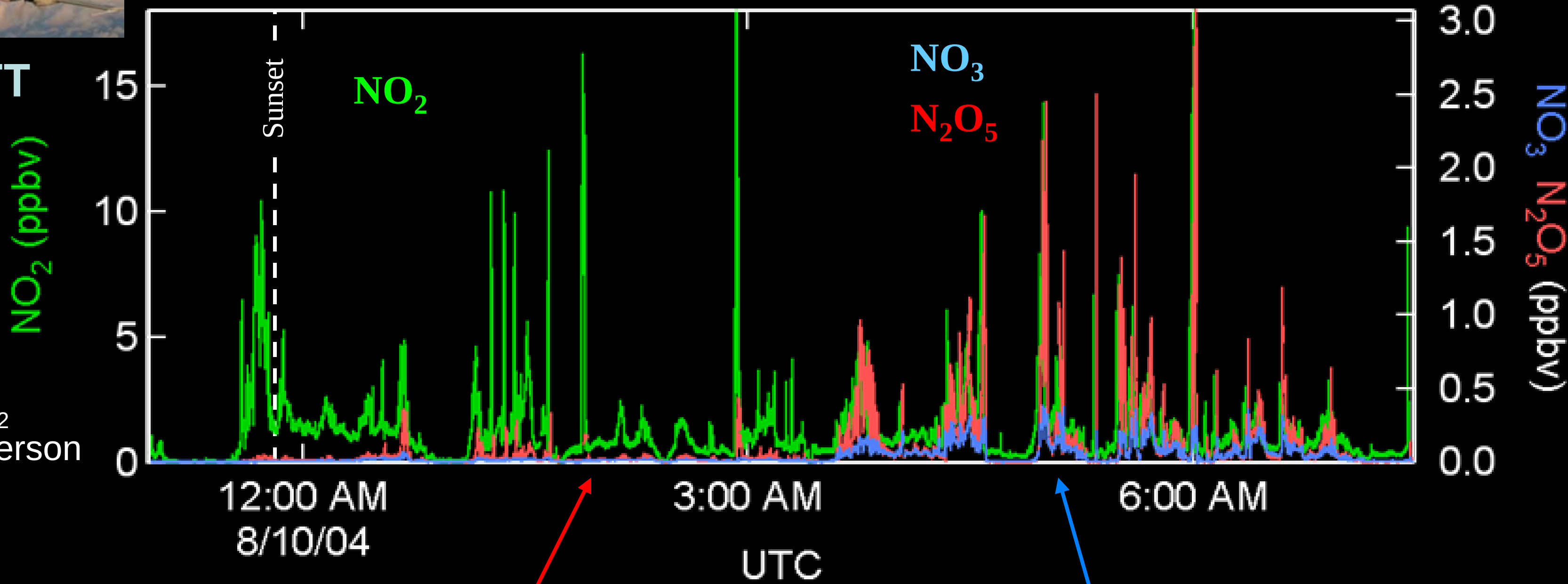
NO_x, VOC ,O_3 transformed at night

Nighttime Chemistry - Topics

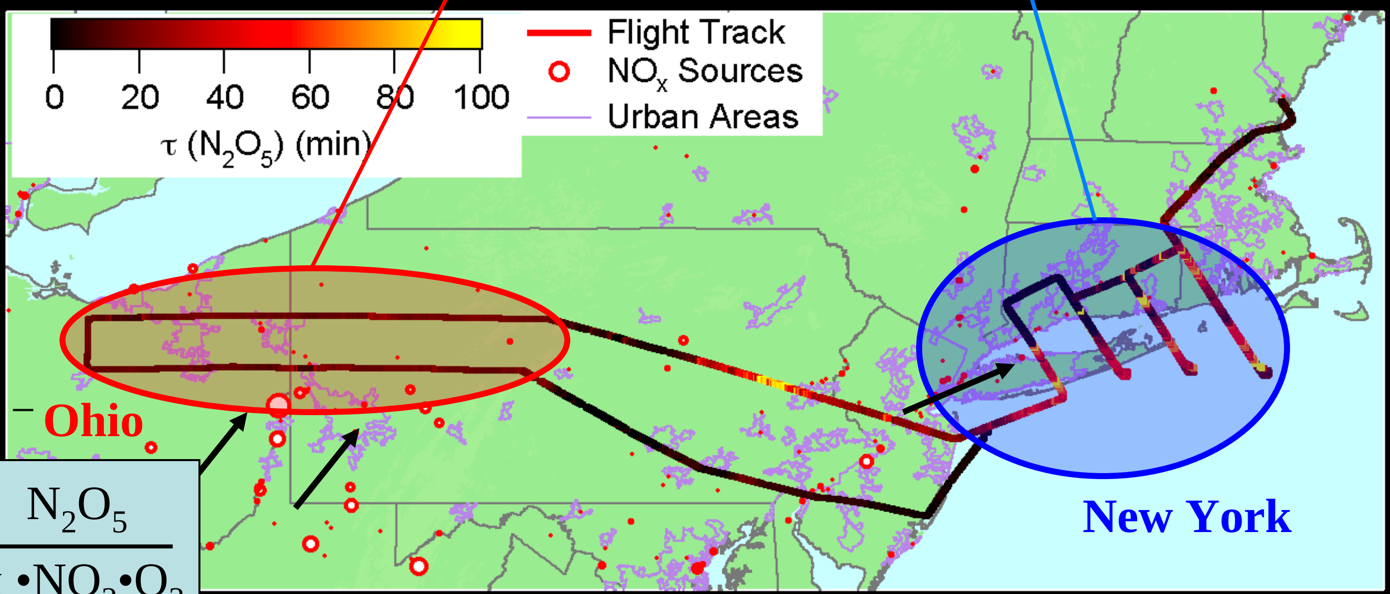
- Variability in the heterogeneous hydrolysis of N_2O_5
- Halogen activation in polluted coastal or marine environments
- Oxidation of marine sulfur emissions in continental outflow
- Daytime vs. nighttime NO_x loss in the marine boundary layer
- Laboratory studies of key kinetic parameters
- NO_x- driven oxidation of biogenic VOC and HR VOC
- Vertical stratification and nighttime chemical transformation
- Seasonal and regional variation of NO_x impacts - ozone vs. PM

Regional Variability in N_2O_5 Lifetimes

ICARTT 2004



NO_2
Tom Ryerson



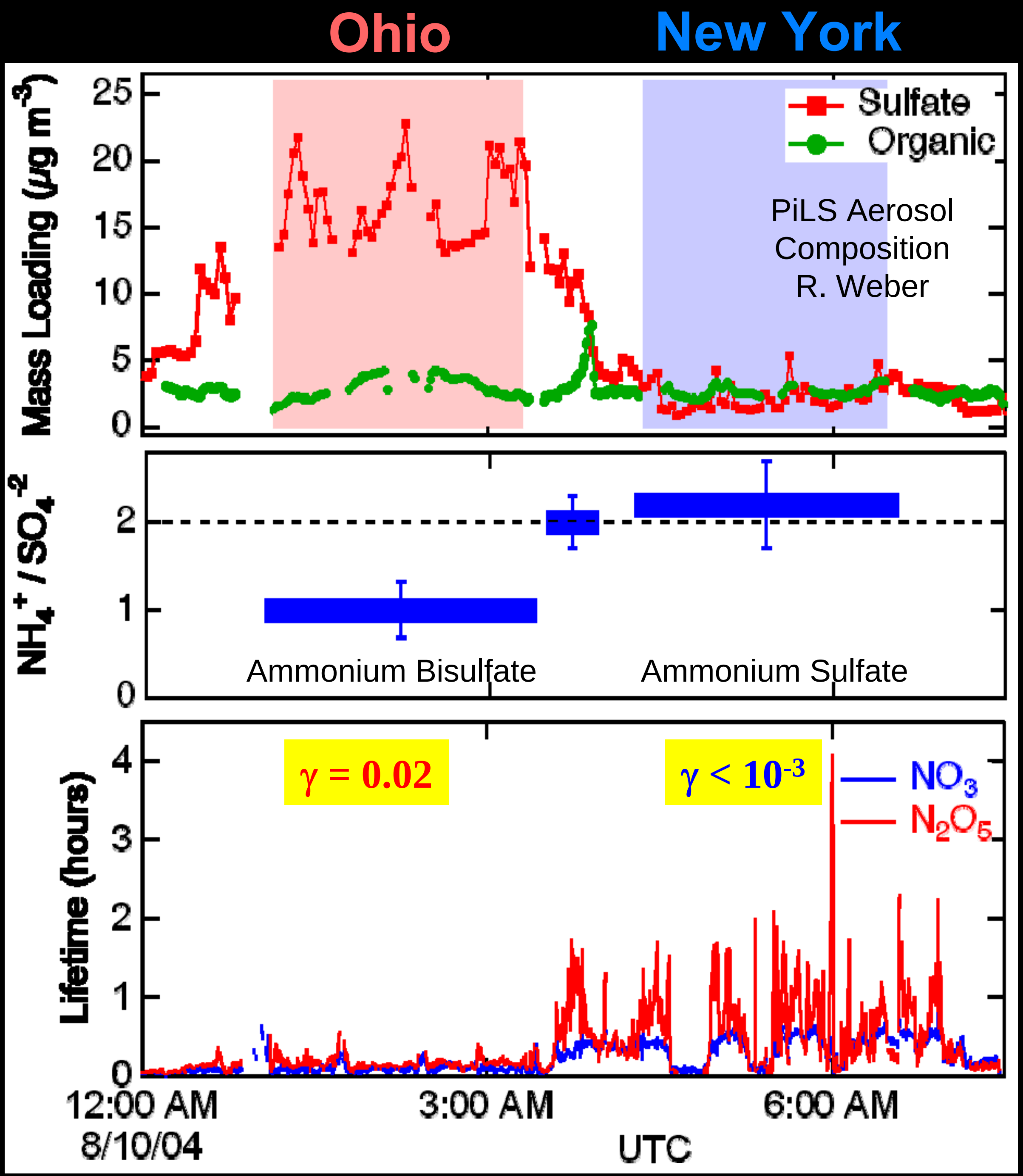
$$\tau(N_2O_5) = \frac{N_2O_5}{k_s \cdot NO_2 \cdot O_3}$$

S. S. Brown, *et al.*, Science, 311, 67-70, 2006

N_2O_5 Uptake & Aerosol Composition

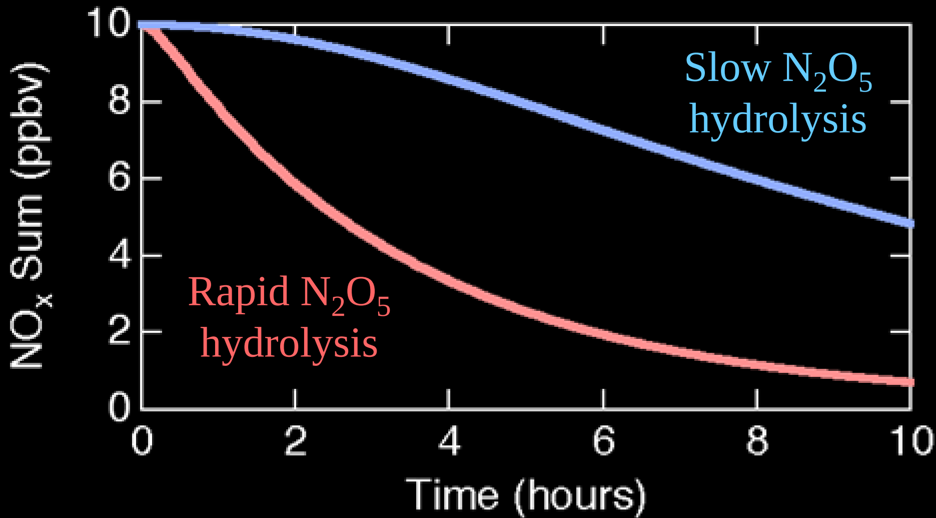
Ohio → New York Changes:

- **Sulfate Loading**
- **Aerosol Organic Fraction**
- **Aerosol Acidity**
- **Relative Humidity**



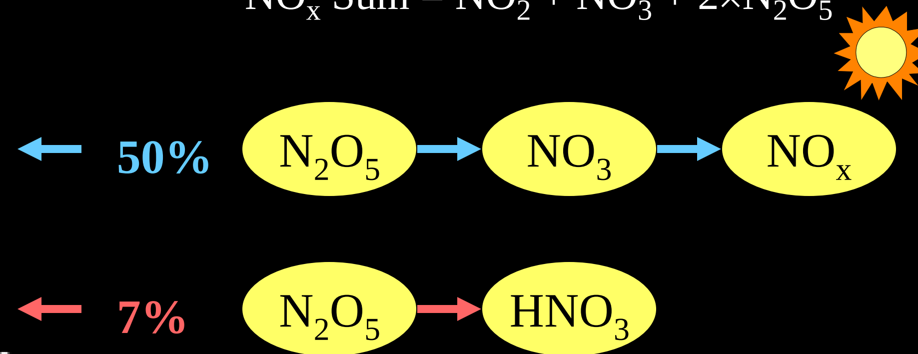
Nocturnal NO_x lifetime strongly correlated to the aerosol loading, particularly sulfate

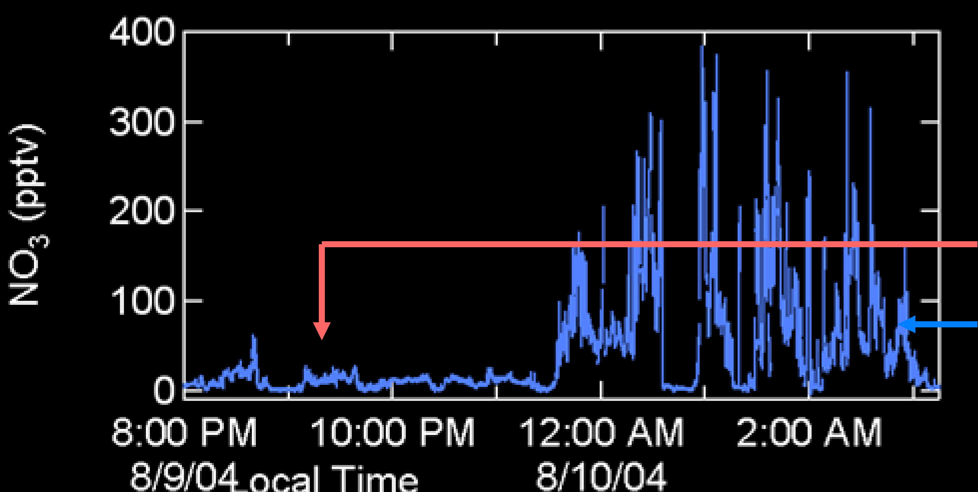
N_2O_5 Lifetimes and O_3 precursors



NO_x processing overnight

NO_x Sum = $NO_2 + NO_3 + 2 \times N_2O_5$





Nocturnal Oxidative Capacity

Reactive VOC (e.g. alkenes, aldehydes)

$\gamma = 0.02$ τ(VOC) ~ 60 hours 15% loss

$\gamma < 0.001$ τ(VOC) ~ 6 hours 82% loss

Variability in $\tau(N_2O_5)$ affects the 2 components of photochemical ozone

Payoffs - Variability in N_2O_5 hydrolysis

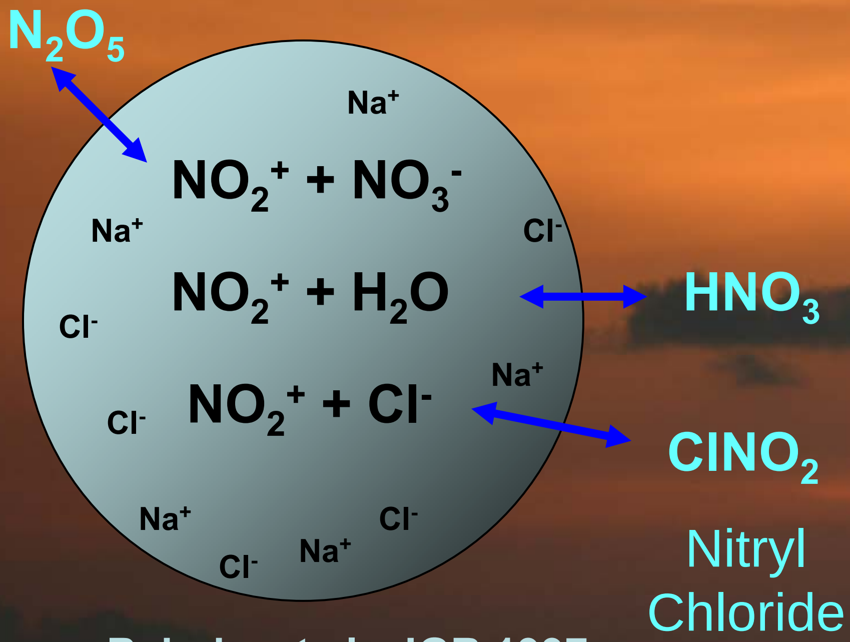
• Actual reactivity of N_2O_5 on real atmospheric aerosol much different than suggested by laboratory studies on proxy substrates (e.g., inorganic salts)

• Uptake of N_2O_5 to aerosol a key input to regional air quality models for both ozone (summer) and particulate matter (winter)

Future

• Expand field database, develop parameterization of N_2O_5 uptake from field measurements, compare to laboratory studies and implement in models

Halogen Activation in Polluted Marine Environments



Behnke et al., JGR 1997
$\Phi(ClNO_2) \approx 1$, $[Cl^-] \geq 1$ M

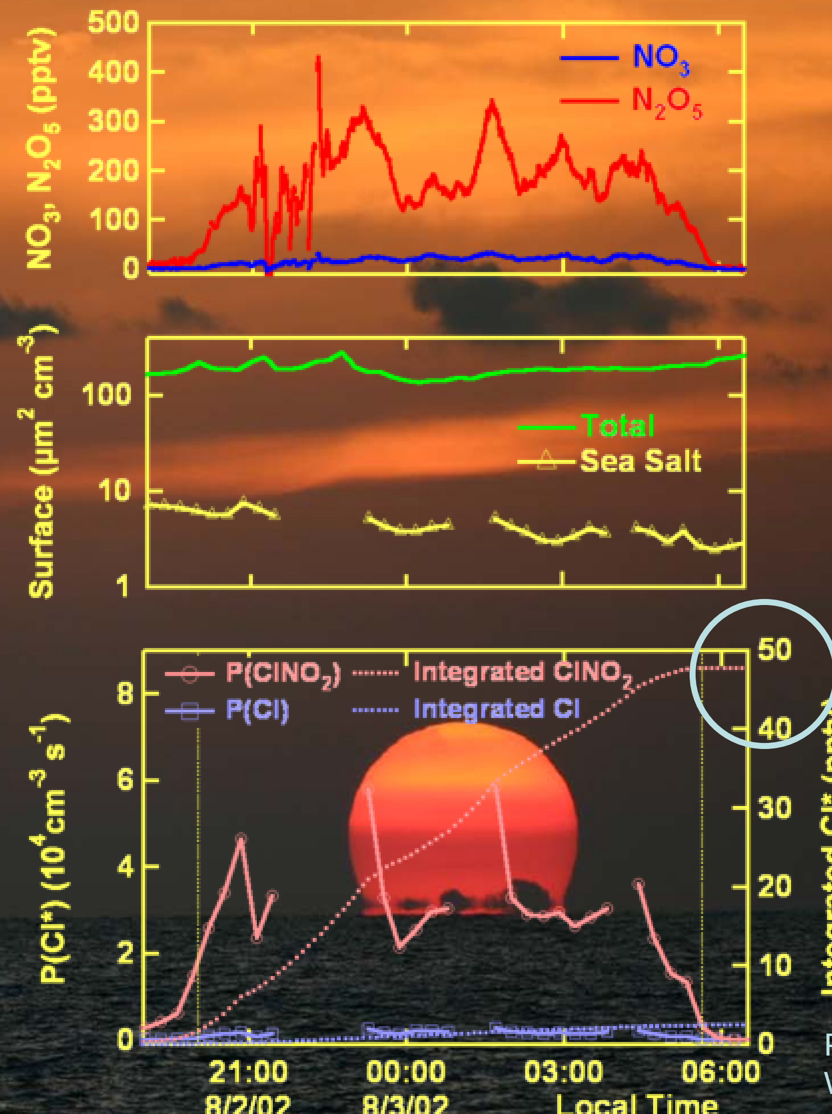
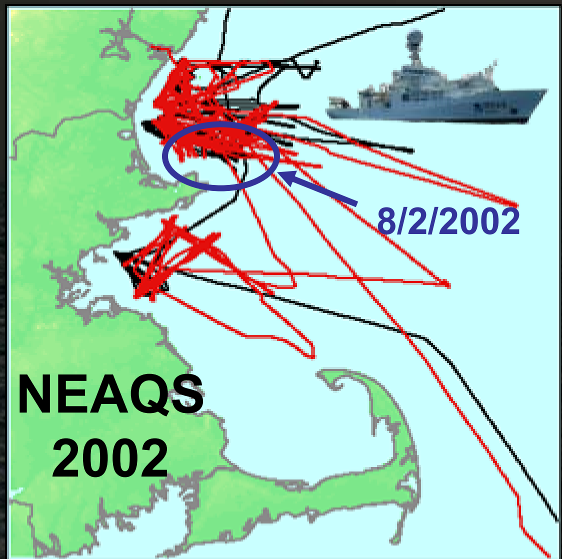


Photo: Dan Welsh-Bon



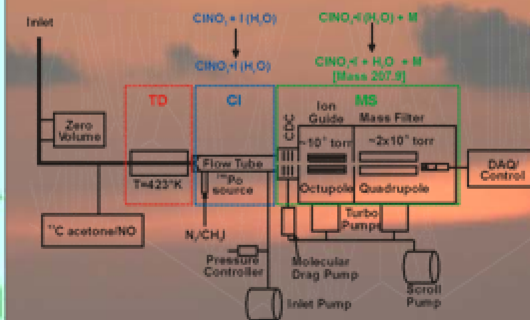
Simple calculation: Modest (50 pptv integrated) halogen activation even for strong N_2O_5 production

TexAQS / GoMACCS 2006: N_2O_5 & $ClNO_2$

July 26 - September 15, 2006

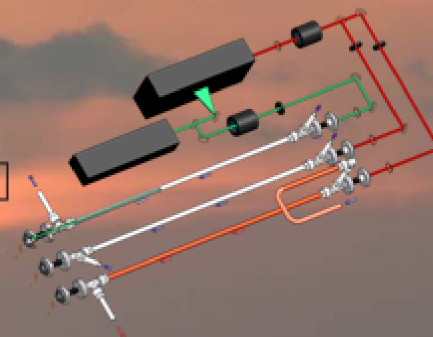
$ClNO_2$: CIMS

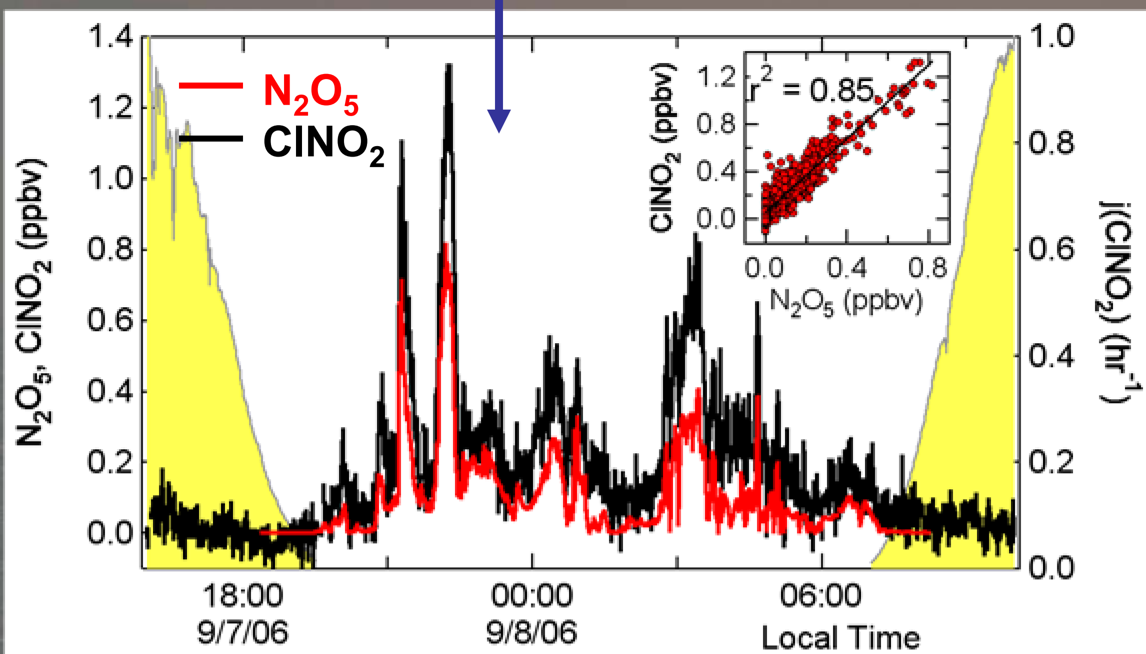
Jim Roberts



N_2O_5: CRDS

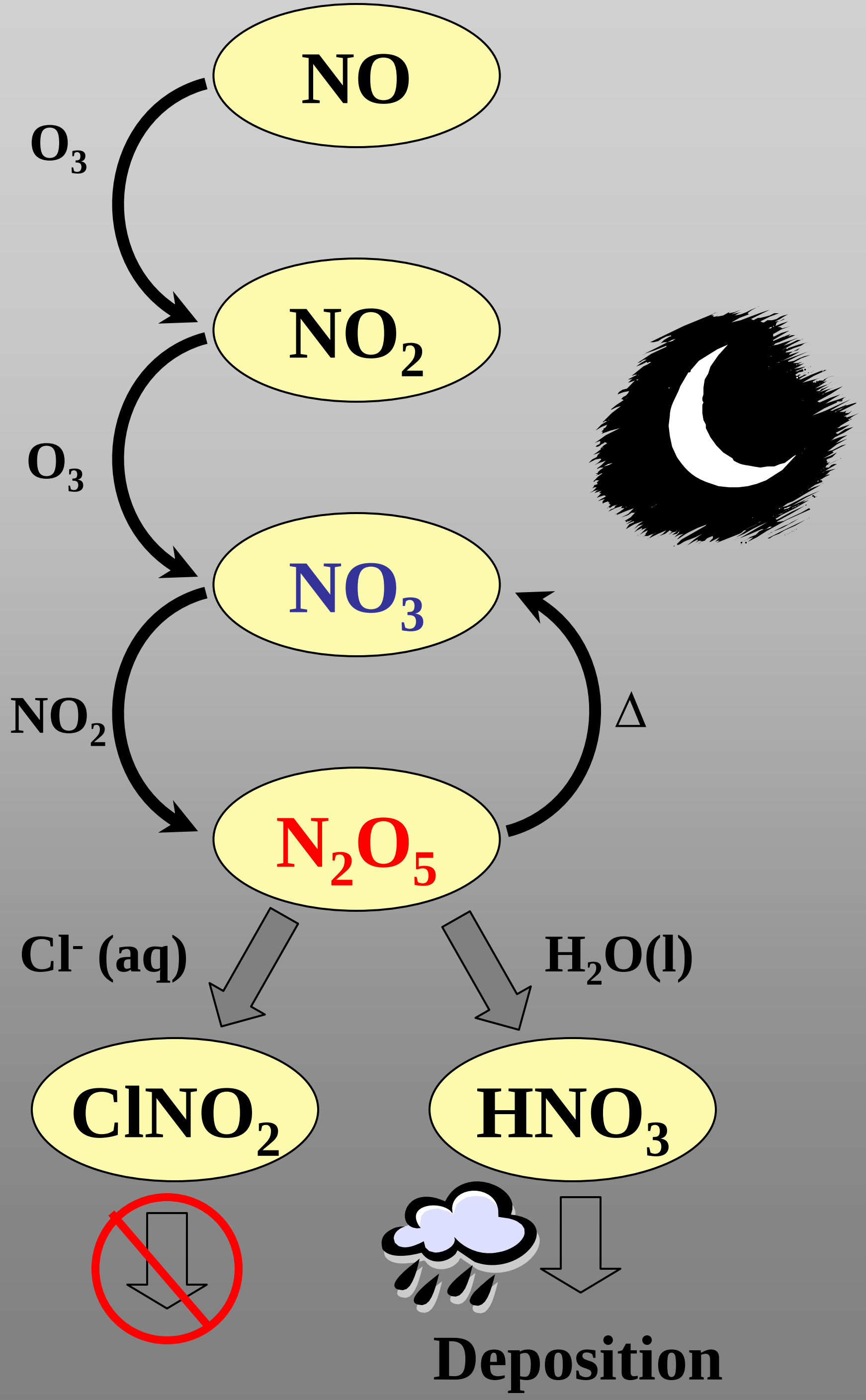
Hans Osthoff



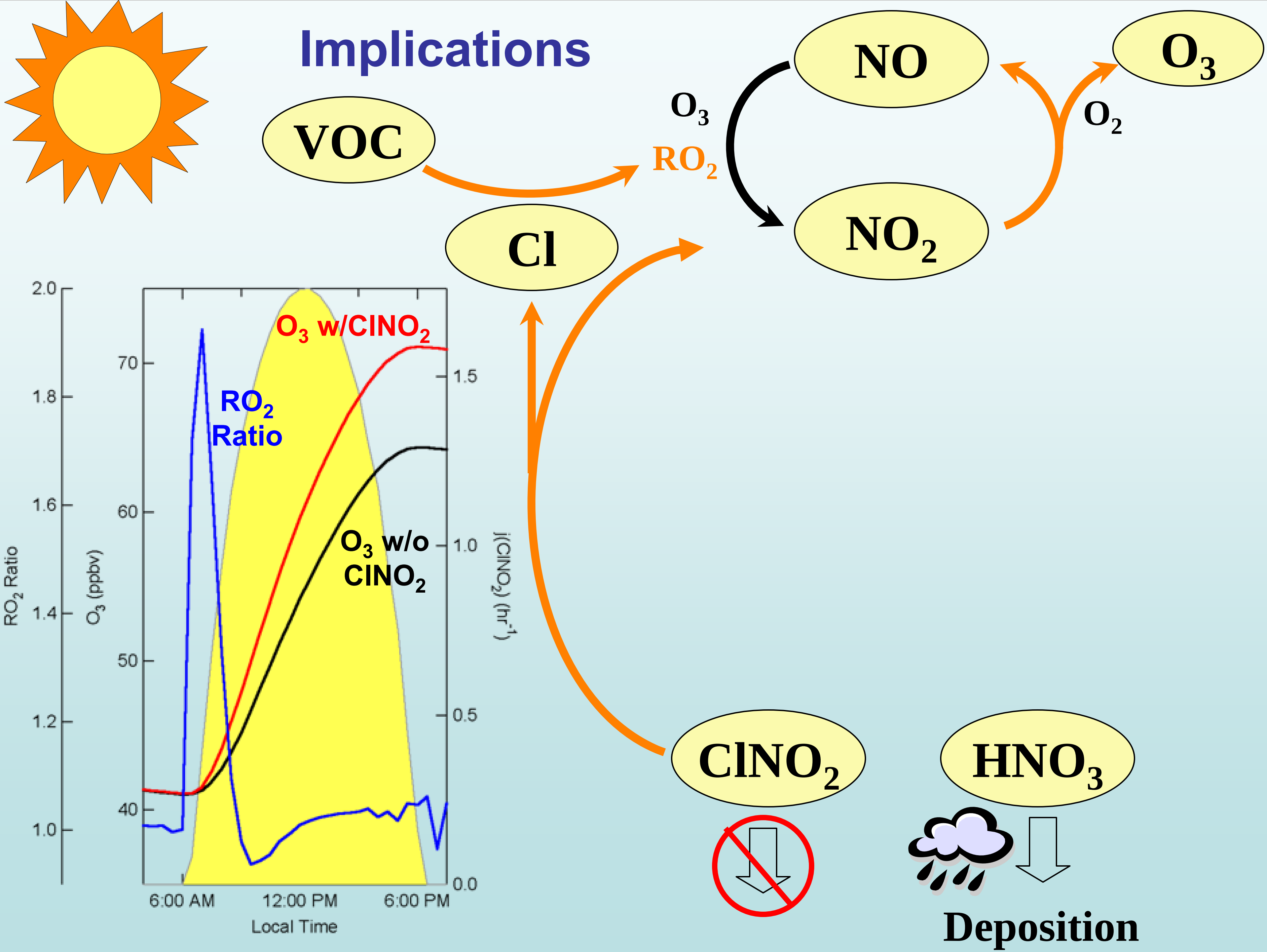


- Observed $ClNO_2$ levels inconsistent with N_2O_5 uptake on sea salt alone !
- Implies role for submicron aerosol
- High efficiency for $ClNO_2$ production: up to ~ 50% yield per NO_x oxidized

Implications



Implications



Payoffs - Halogen Activation

• Efficiency of nocturnal halogen activation from N_2O_5 much greater than previously recognized

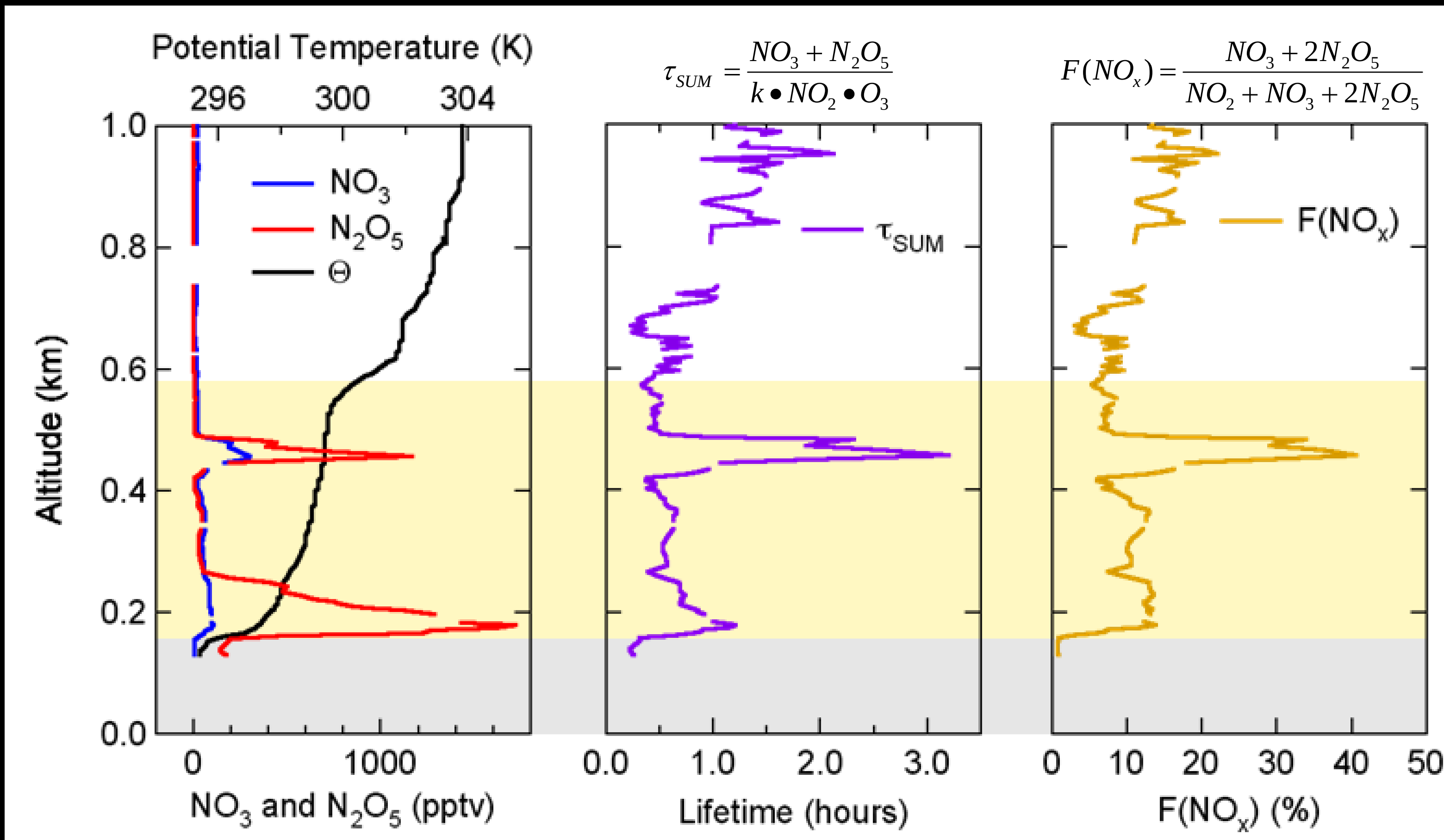
• May have regional effects on oxidant chemistry and ozone formation relevant for air quality modeling in coastal areas

Future

• Impact in winter coastal New England, the Arctic (2008) and California (2010)

Vertical Stratification & Nighttime Chemistry

TexAQS 2006

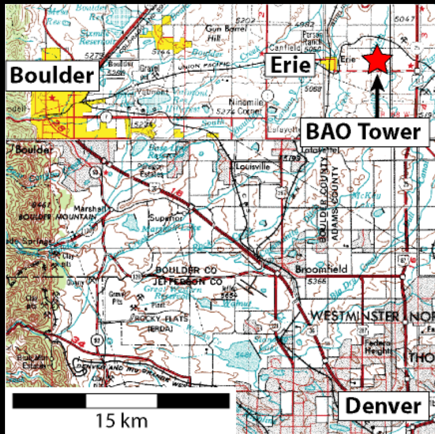


Residual Daytime Boundary Layer

Intermediate Layer

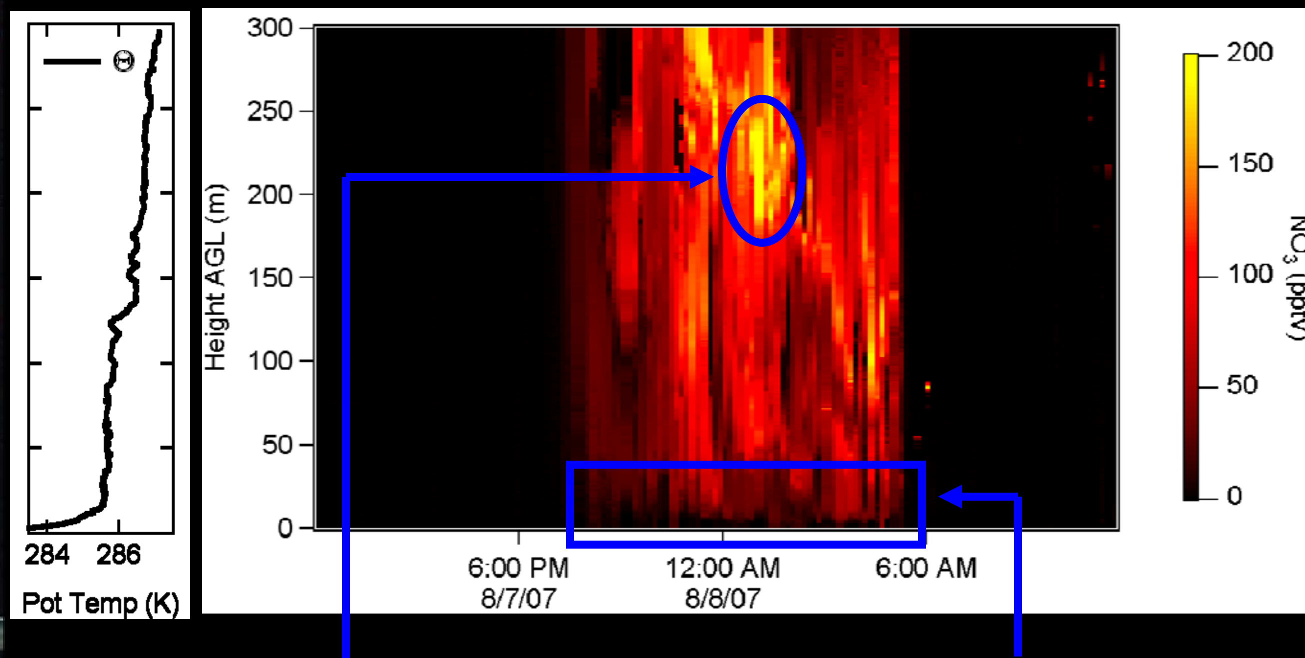
Nocturnal Boundary Layer (NBL)

- NO_x & VOC plumes occur in discrete layers at night
- Chemical transformation within different layers differs markedly



Boundary Layer Vertical Profiles Erie (BAO) Tower

- 300 m w/ vertical resolution ~ 0.5 m
- Movable carriage on *outside* with > 1 ton payload
- Studies in 2004 (fall) and 2007 (summer)



- Large [NO_3] routinely observed aloft
- Often associated with complex layering

Surface layer commonly observed

Payoffs - Vertical Profiles

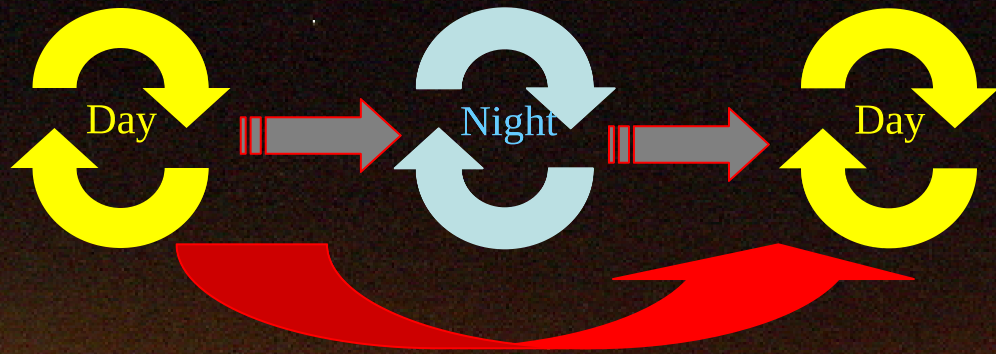
• Large differences observed between measurements at surface level and aloft - aircraft, tower measurements change view of nighttime chemistry

• High resolution vertical data shed light on interaction between emissions, vertical stratification and chemistry

Future

• Future: Incorporation of micrometeorology and modeling to data analysis; winter measurements

Conclusions
The Dark Side of Atmospheric Chemistry



“Photochemical” O_3 & PM production depends on more than just ***photo***-chemistry

Nocturnal reactions transform the mixture of NO_x, VOC, radicals, O_3 and aerosol

Nighttime chemistry, transport and mixing are complex, interrelated problems