Importance of nighttime processing of emissions in the marine boundary layer

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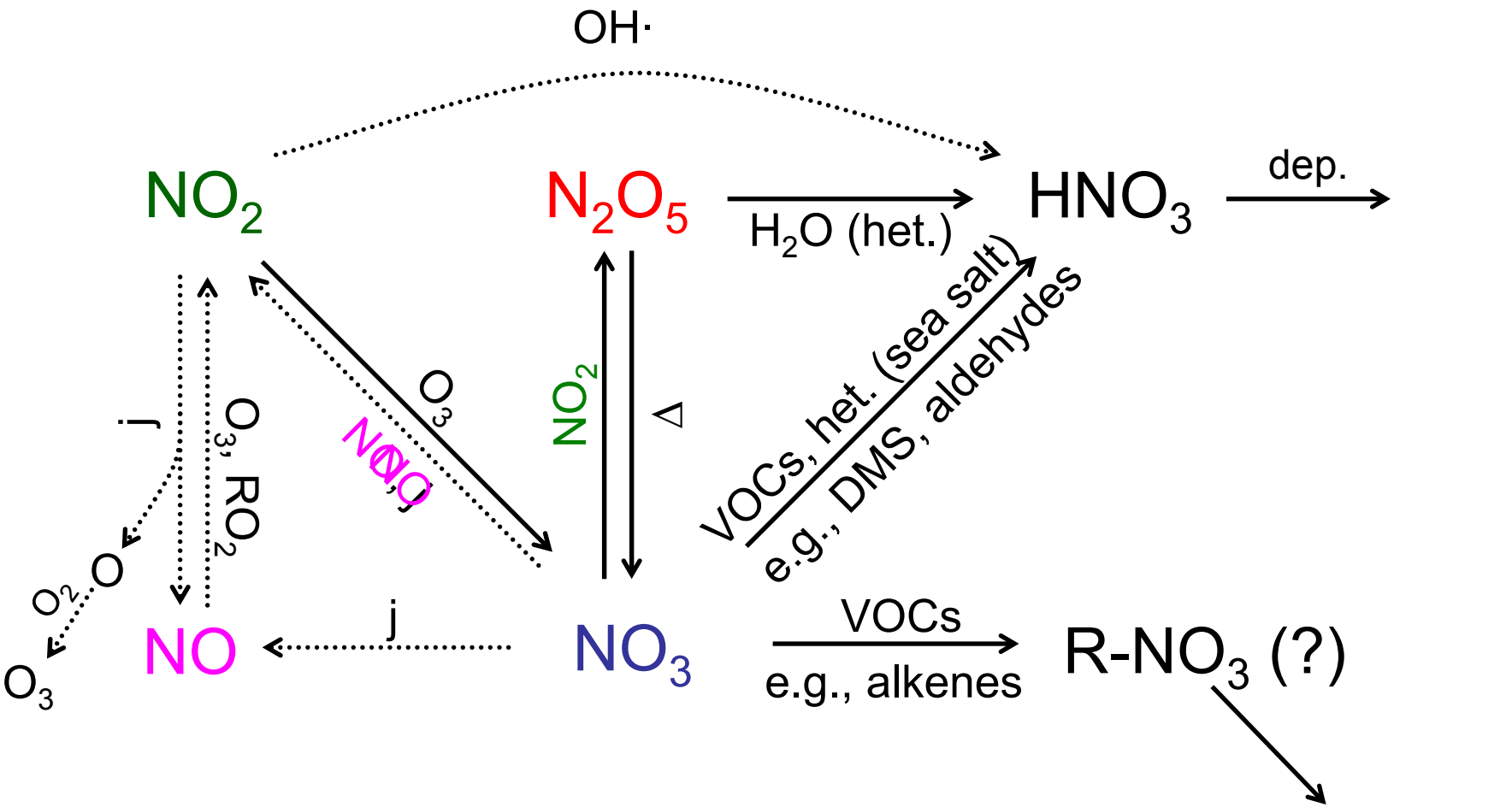
Austin, TX, Oct 12th, 2006

- NO_x loss via NO_3 and N_2O_5
- O_3 loss via NO_3 and N_2O_5
- VOC oxidation by NO_3

Examples:

- Houston ship channel (Aug 11)
- Barbour's cut (Sept 8)
- Plumes in Gulf of Texas (Aug 23)

Nitrogen oxide processing

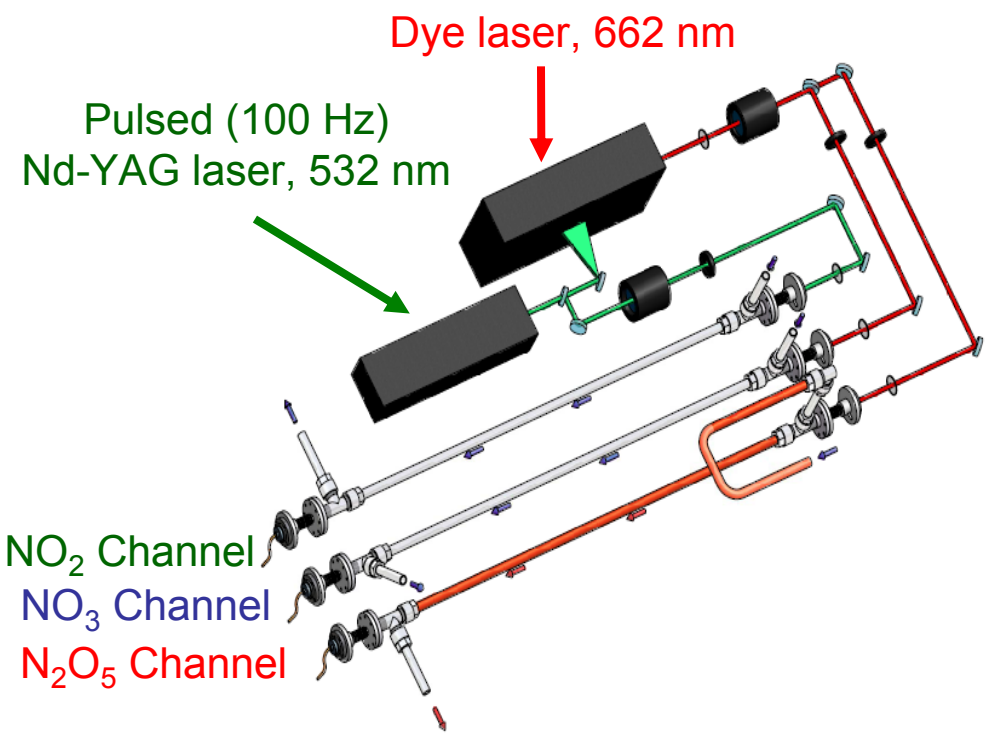


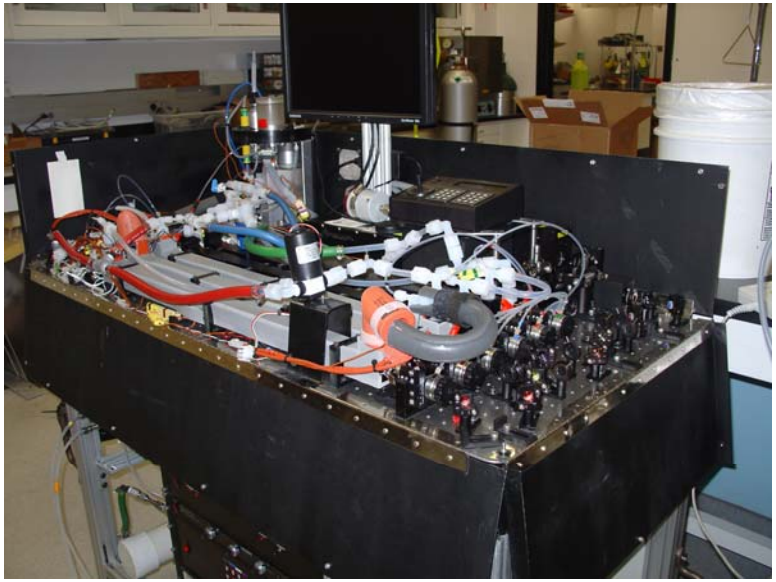
Goal:

- qu… NO_x, O_3 and VOC removal from troposphere

daytime

Measurements of NO_3, N_2O_5, and NO_2 by cavity ring-down spectroscopy on RHB





Some concepts and tools...

$NO_x = NO + NO_2 + NO_3 + 2\ N_2O_5$

Odd oxygen ≡ O_x "O_3 equivalent"

$O_x = O_3 + NO_2 + 2\ NO_3 + 3\ N_2O_5$

Brown, et al., GRL **33**, L08801 (2006).

Assume: NO_3 and N_2O_5 are not conserved; absence of NO

k_x = NO_3 loss rate coefficient; k_y = N_2O_5 loss rate coefficient

NO_x loss

$$dNO_x/dt = \underbrace{-k[NO_2][O_3]}_{\substack{NO_3 \text{ production term} \\ k=3\times10^{-17}\ cm^3\ molec^{-1}}} \times \underbrace{\left(\frac{1*k_x[NO_3]+2*k_y[N_2O_5]}{k_x[NO_3]+k_y[N_2O_5]}\right)}_{1 < S_{NOx} < 2}$$

O_x loss

$$dO_x/dt = \overbrace{-k[NO_2][O_3]} \times \underbrace{\left(\frac{2*k_x[NO_3]+3*k_y[N_2O_5]}{k_x[NO_3]+k_y[N_2O_5]}\right)}_{2 < S_{Ox} < 3}$$

additional losses: deposition, O_3 + VOC...

Texas:

- relatively warm
  - ⇒ short thermal lifetime of N_2O_5
  - ⇒ N_2O_5 likely not a reservoir species
  - ⇒ NO_3 reactions more important (except for very high [NO_2])

- lots of anthropogenic VOCs
  - ⇒ NO_3 gas phase reactions likely dominant
  - ⇒ NO_3 as initiator of secondary, radical chemistry
  - ⇒ anthropogenic emissions "overwhelm" NO_3 and deplete NO_x

Case I: Close to big sources, [NO]>[O_3]

O_3 O_3 slow

slow → NO_2

NO shuts down nighttime chemistry!

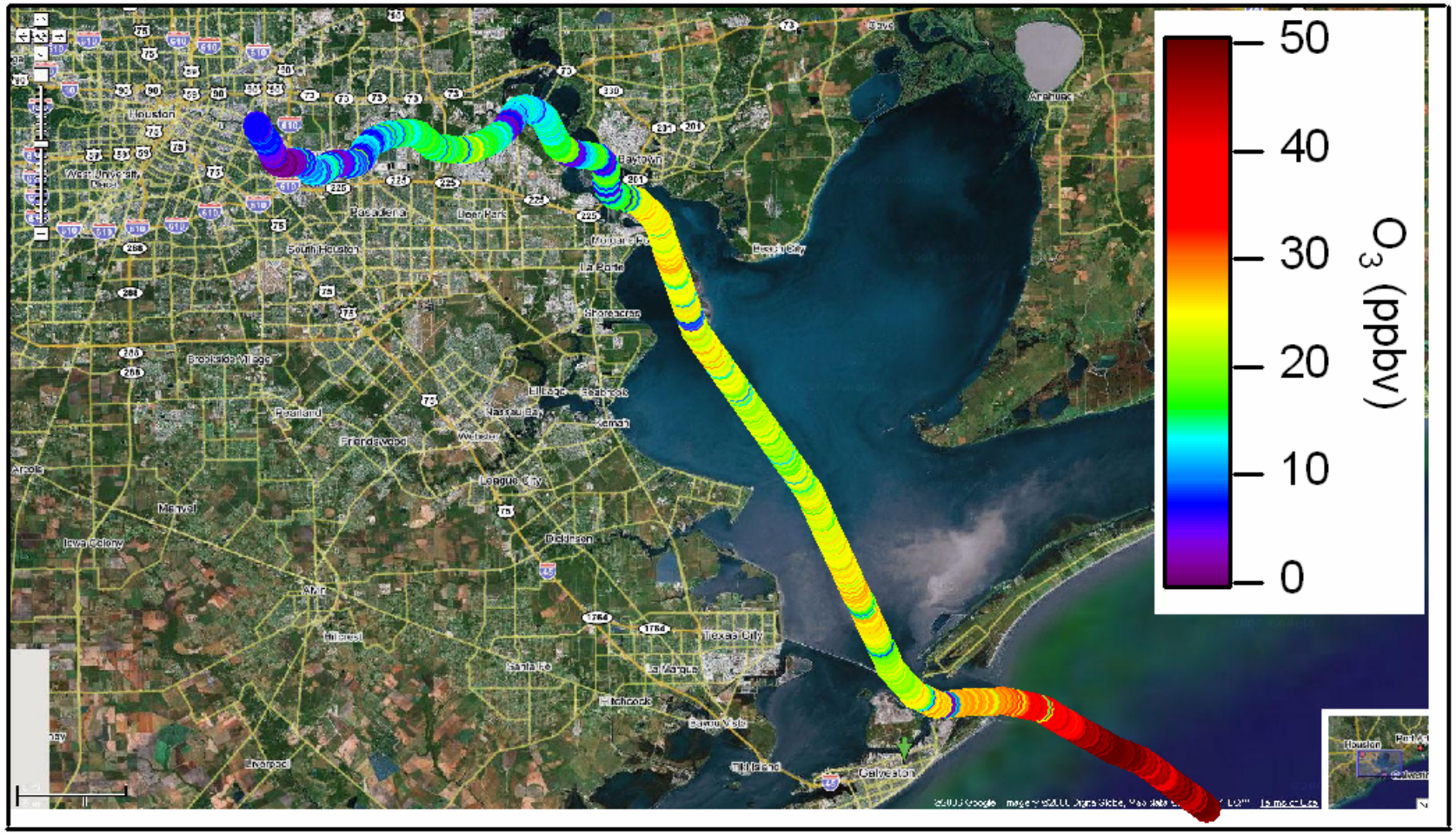
$$NO_3 + NO \rightarrow 2\ NO_2$$

e.g., 100 pptv NO: $\tau(NO_3)$ = 27 s

Production of NO_3 is slow (O_3 limited)

$$O_3 + NO_2 \rightarrow NO_3$$

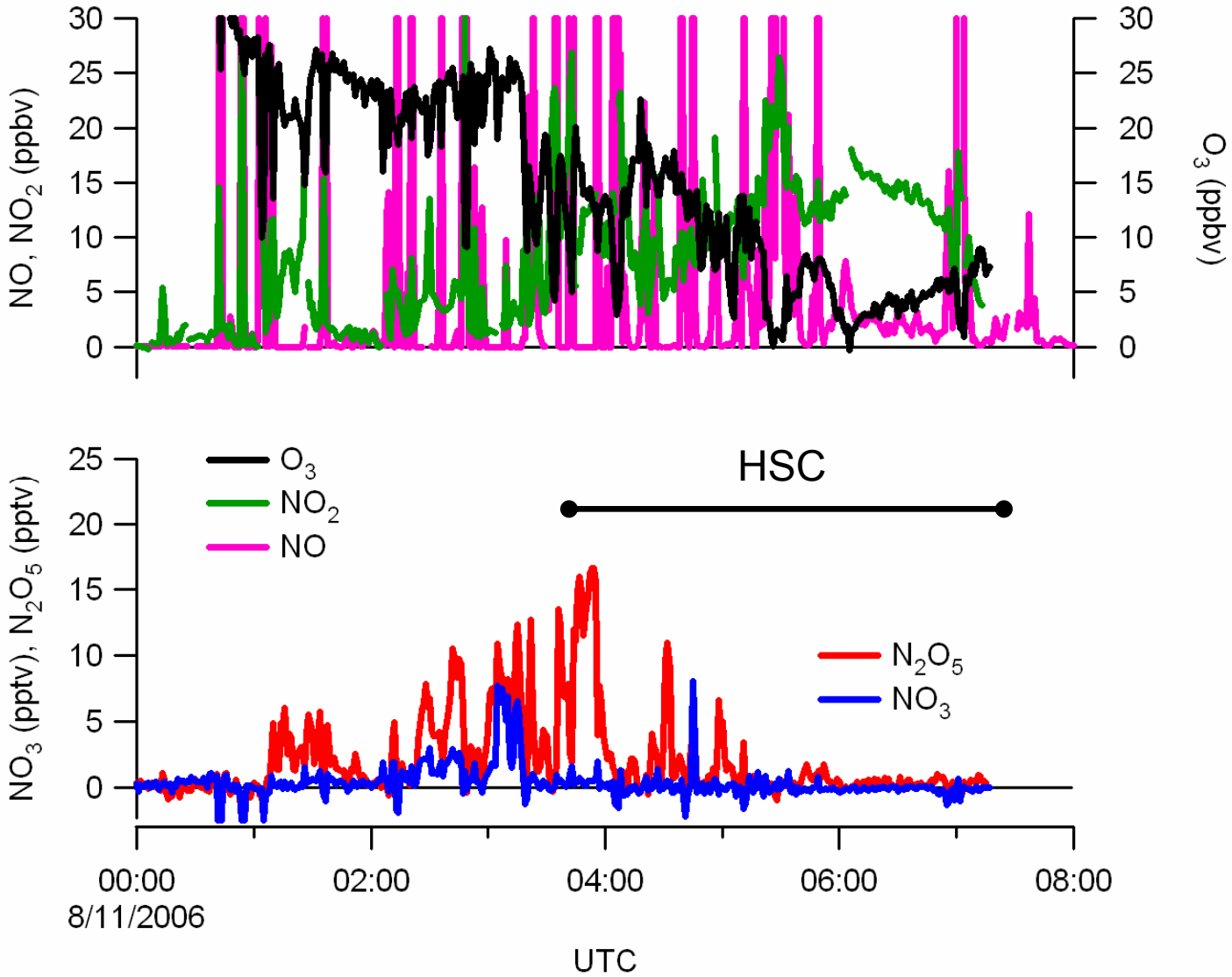
Case I: Close to sources, [NO]>[O_3]



Aug 11, 2006: Nighttime transit of Houston ship channel (HSC)

picture courtesy of Dan Welsh-Bon

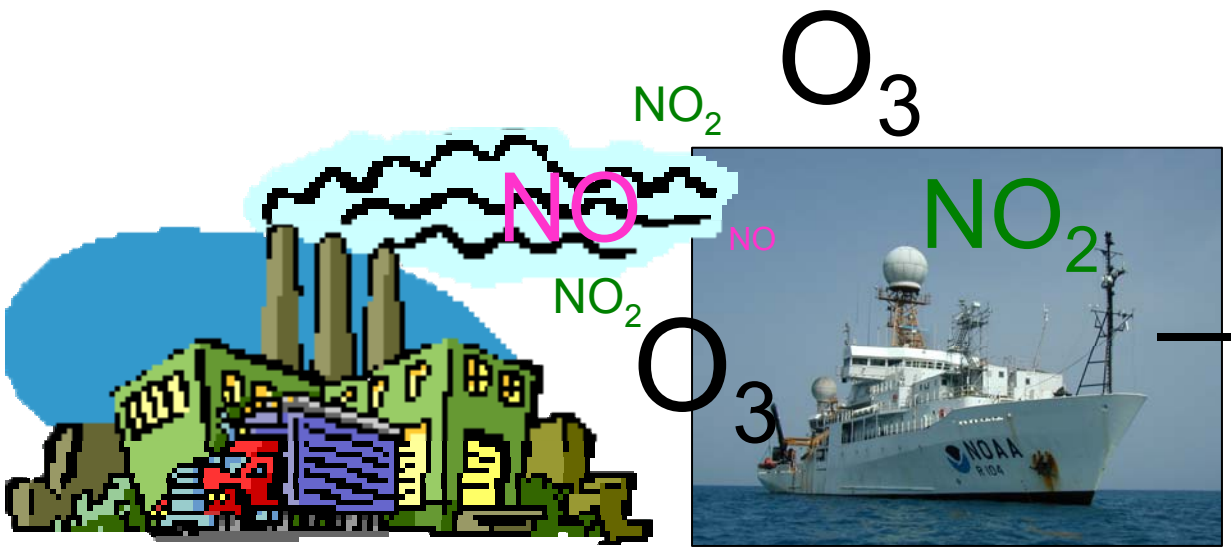
Case I: Close to sources, [NO]>[O_3]



small NO_3/N_2O_5 signals; fast sinks (mainly NO_3+NO); slow production of NO_3;

slow processing of NO_x and O_x

Case II: Intermediate distance, $[O_3]>[NO]$



$\longrightarrow$ NO_3, N_2O_5

Rapid conversion of NO to NO_2

$$O_3 + NO \rightarrow NO_2$$

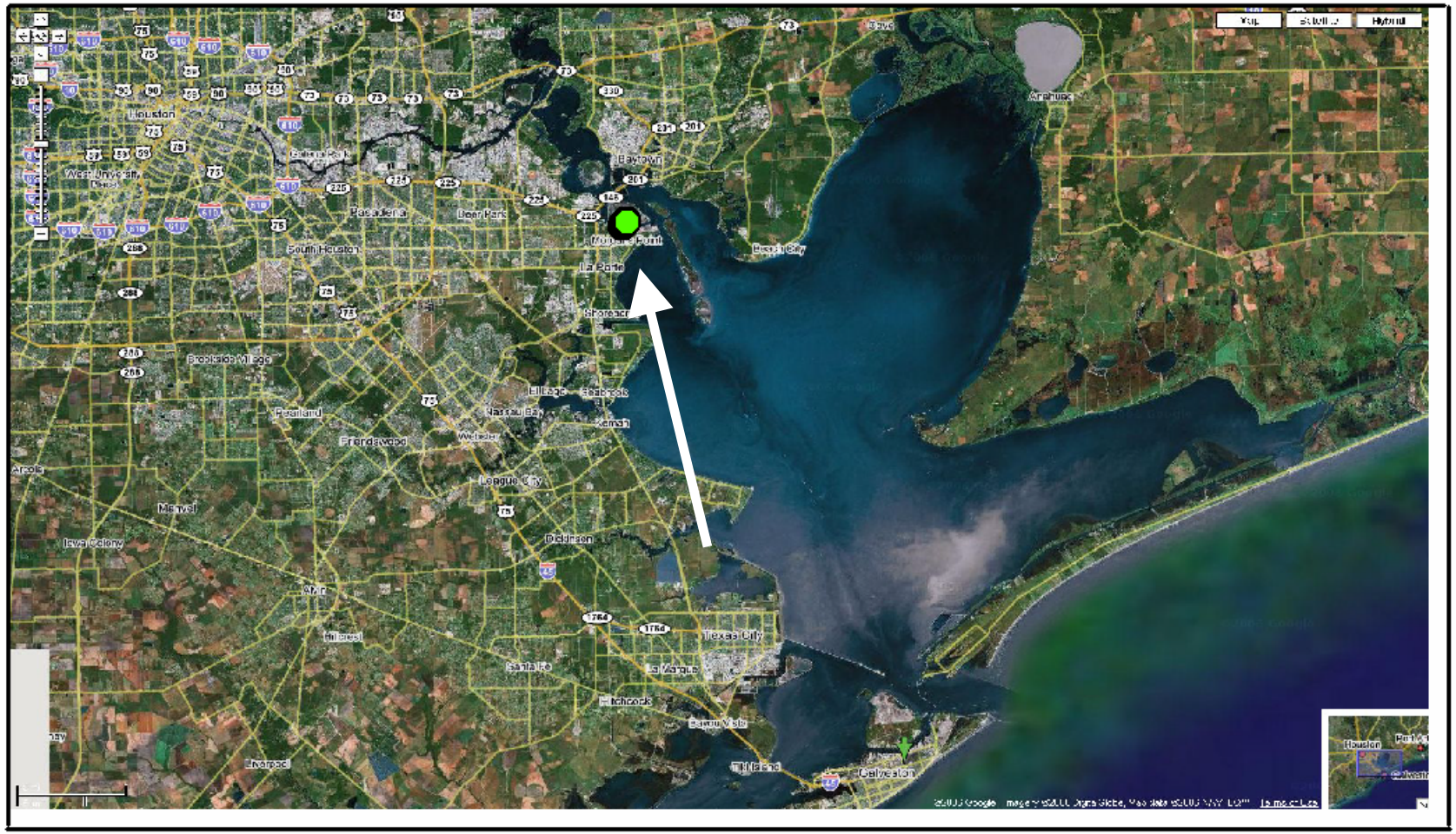
e.g., 50 ppbv O_3: $\tau(NO) = 42$ s

Production of NO_3:

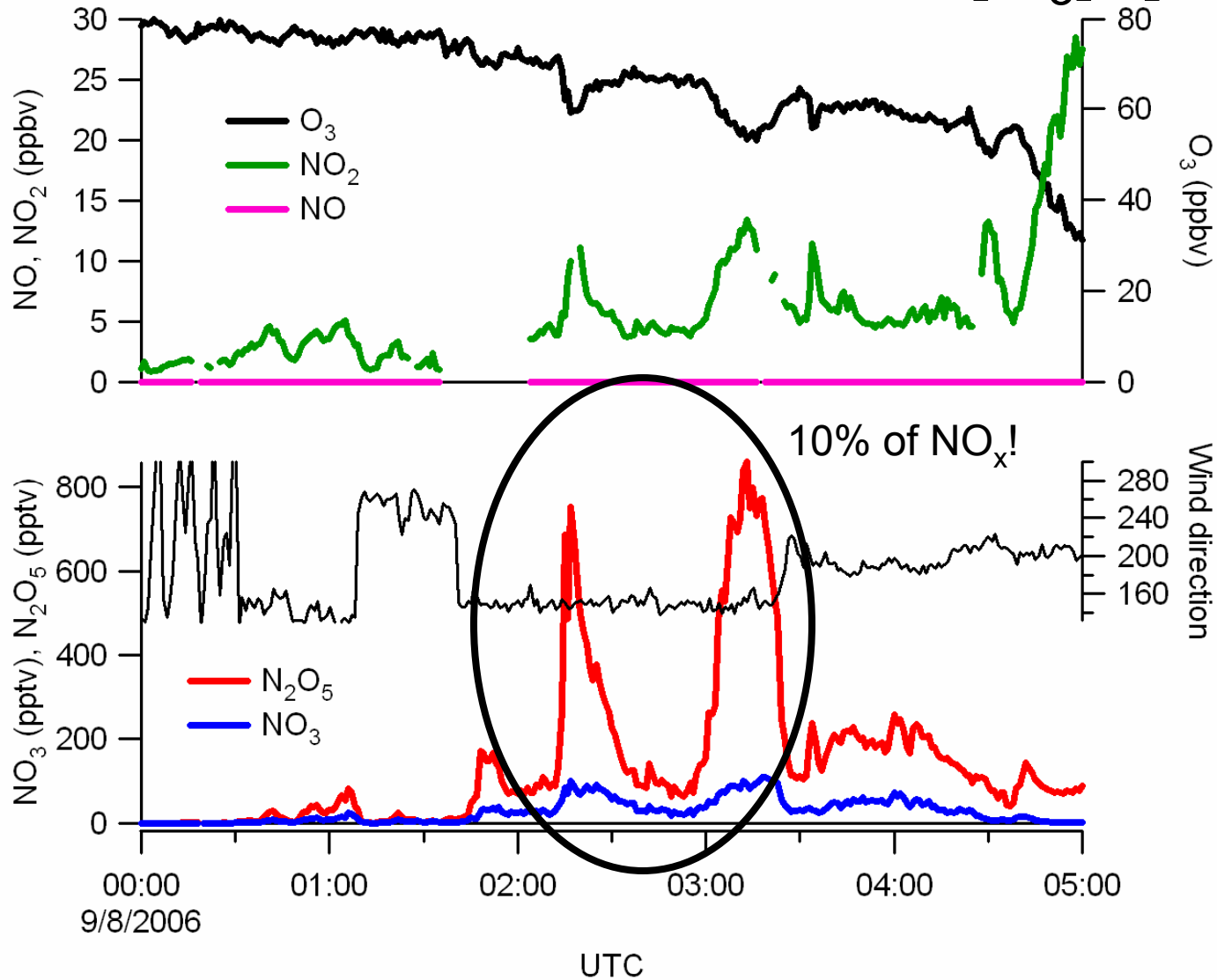
$$O_3 + NO_2 \rightarrow NO_3$$

e.g., 10 ppbv NO_2, 50 ppbv O_3:
1.4 ppbv hr^{-1}

Case II: Intermediate distance, $[O_3]>[NO]$


Map
Satellite
Hybrid
Houston
Baytown
Pasadena
Deer Park
South Houston
La Porte
Bacliff
Clear Lake Shores
Kemah
Nassau Bay
Friendswood
Webster
Alvin
Dickinson
Texas City
La Marque
Santa Fe
Hitchcock
Galveston
Bolivar Peninsula
Arcadia
Manvel
Iowa Colony
Hillcrest
Alvin
Angleton
Freeport
Surfside Beach
Jones Creek
Brookside Village
Pearland
Lake Jackson
Clute
Sargent
Matagorda
Palacios
Port Lavaca
Port Aransas
Aransas Pass
Rockport
Fulton
Bayside
Tivoli
Port O'Connor
Seadrift
Port Alto
Point Comfort
Indianola
Magnolia Beach
Cox Point
Lake Ivanhoe
Lake Jackson
Lake Bryan
Lake Bryan
Lake Bryan

Case II: Intermediate distance, $[O_3]>[NO]$

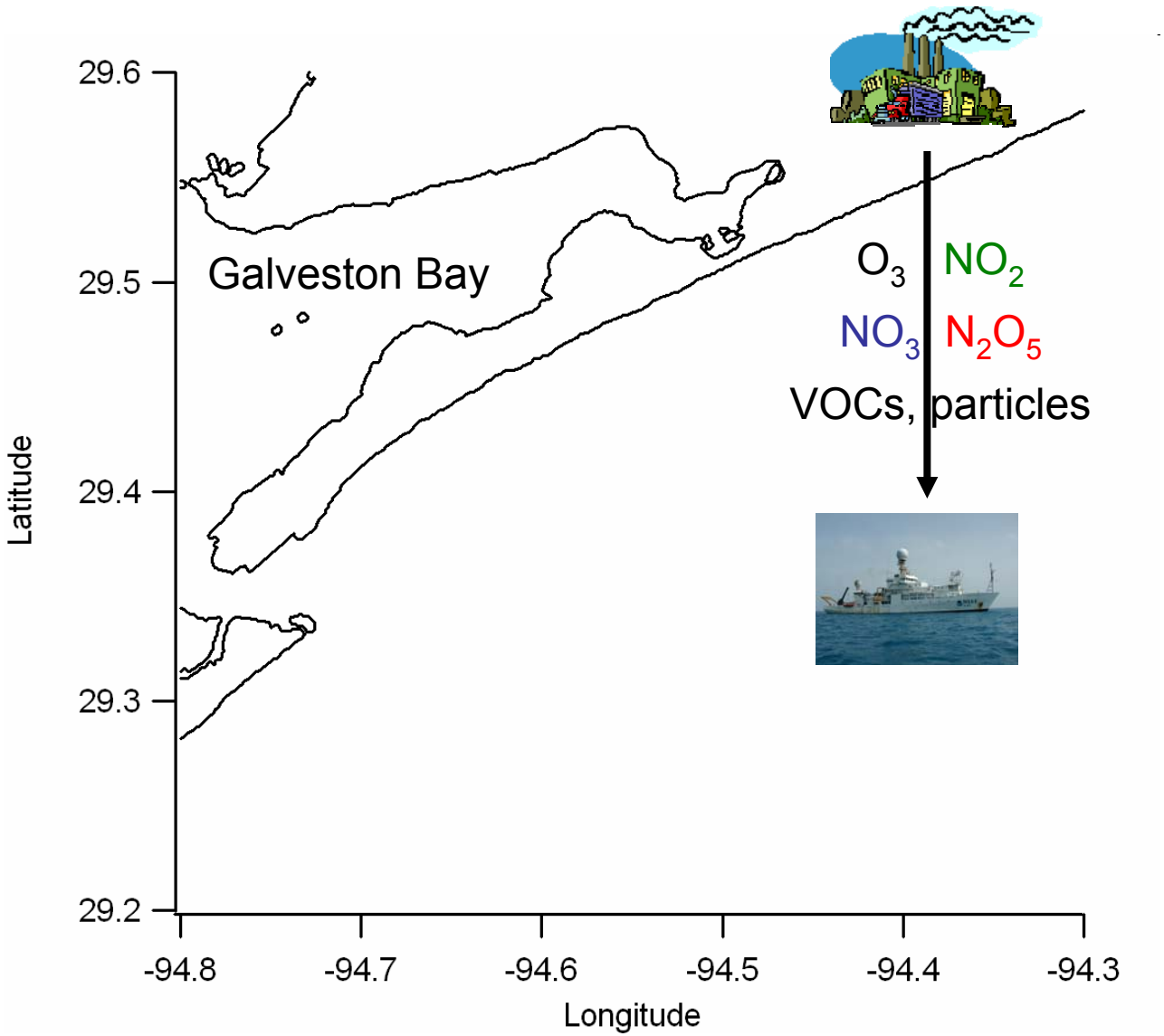


higher concentrations (i.e. lower loss rate coefficient (τ_{N2O5} up to 20 min))

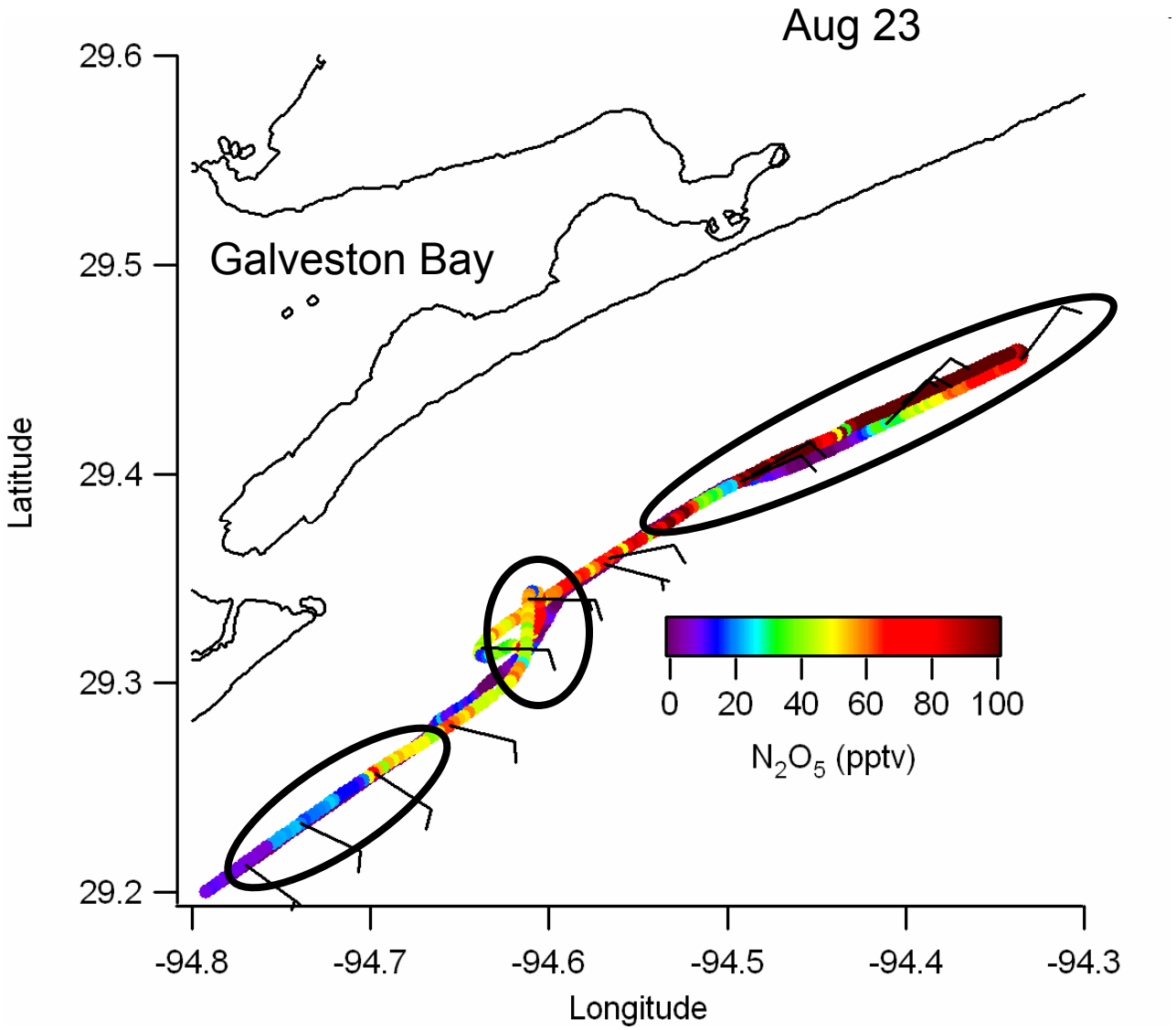
N_2O_5 becomes temporary NO_x reservoir; heterogeneous losses important

processing: 1.8×(-2.4 ppbv, or 15% hr^{-1}) NO_x; 2.8×(-2.4 ppbv hr^{-1}) O_x

Case III: Downwind from sources



Case III: Downwind from sources

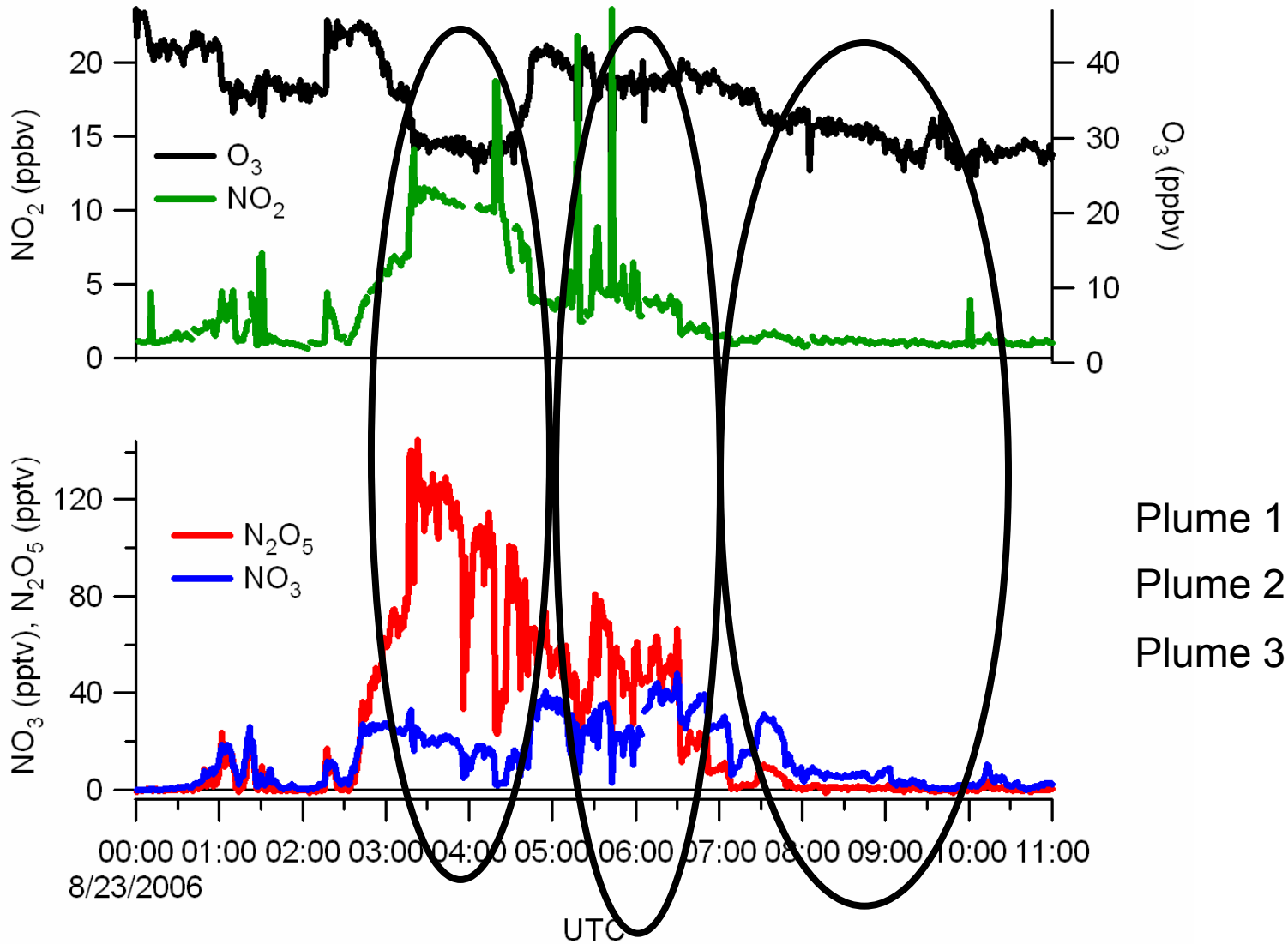


Plume 1:
RHB traveled within anthropogenic plume to the SW; winds NE

Plume 2:
RHB crossed a second anthropogenic plume, likely of different origin winds E
Plume was older, i.e. more processed

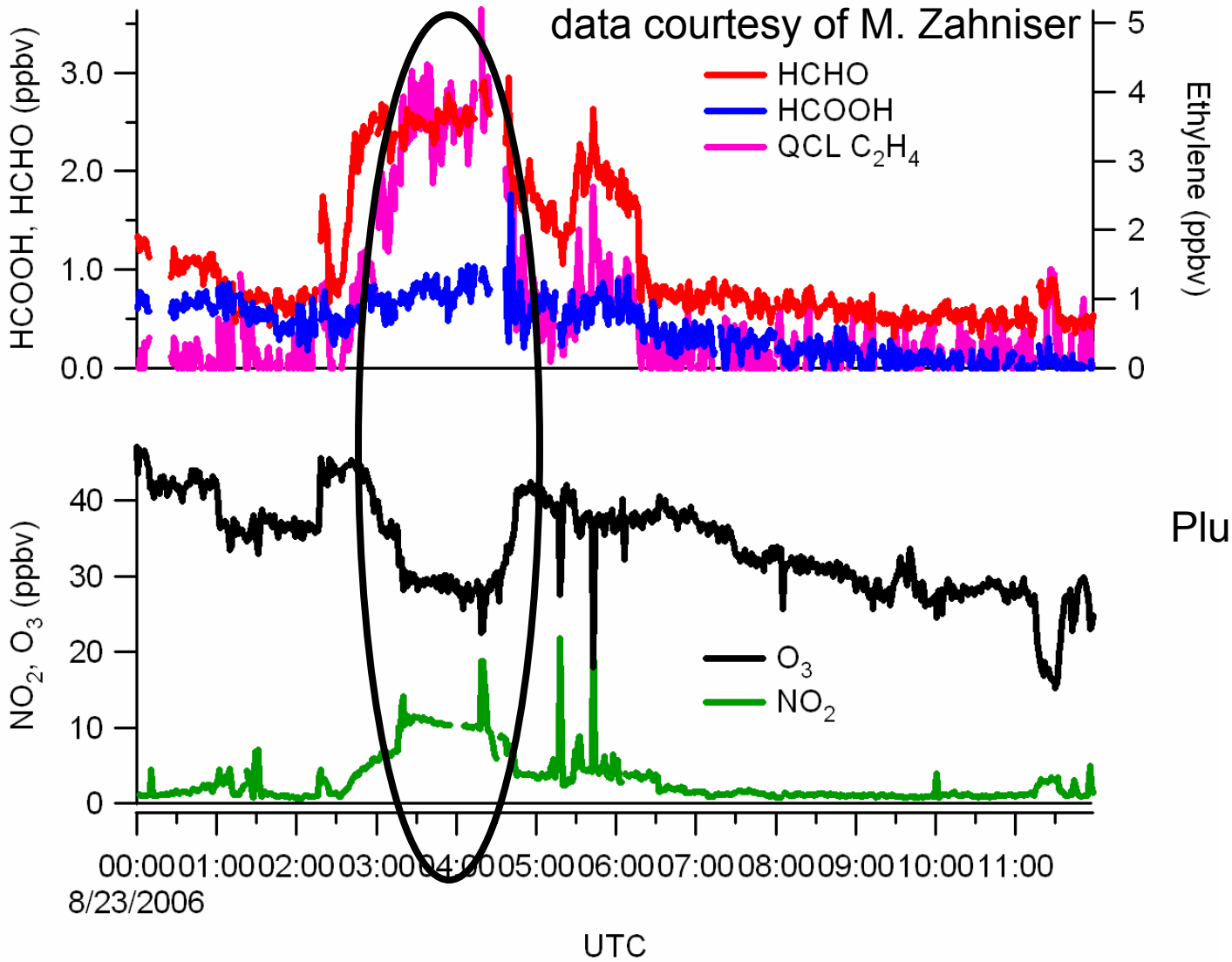
Plume 3:
Old, NO_x-depleted air mass

Case III: Downwind from sources



Notice that ratios of N_2O_5:NO_3 are different

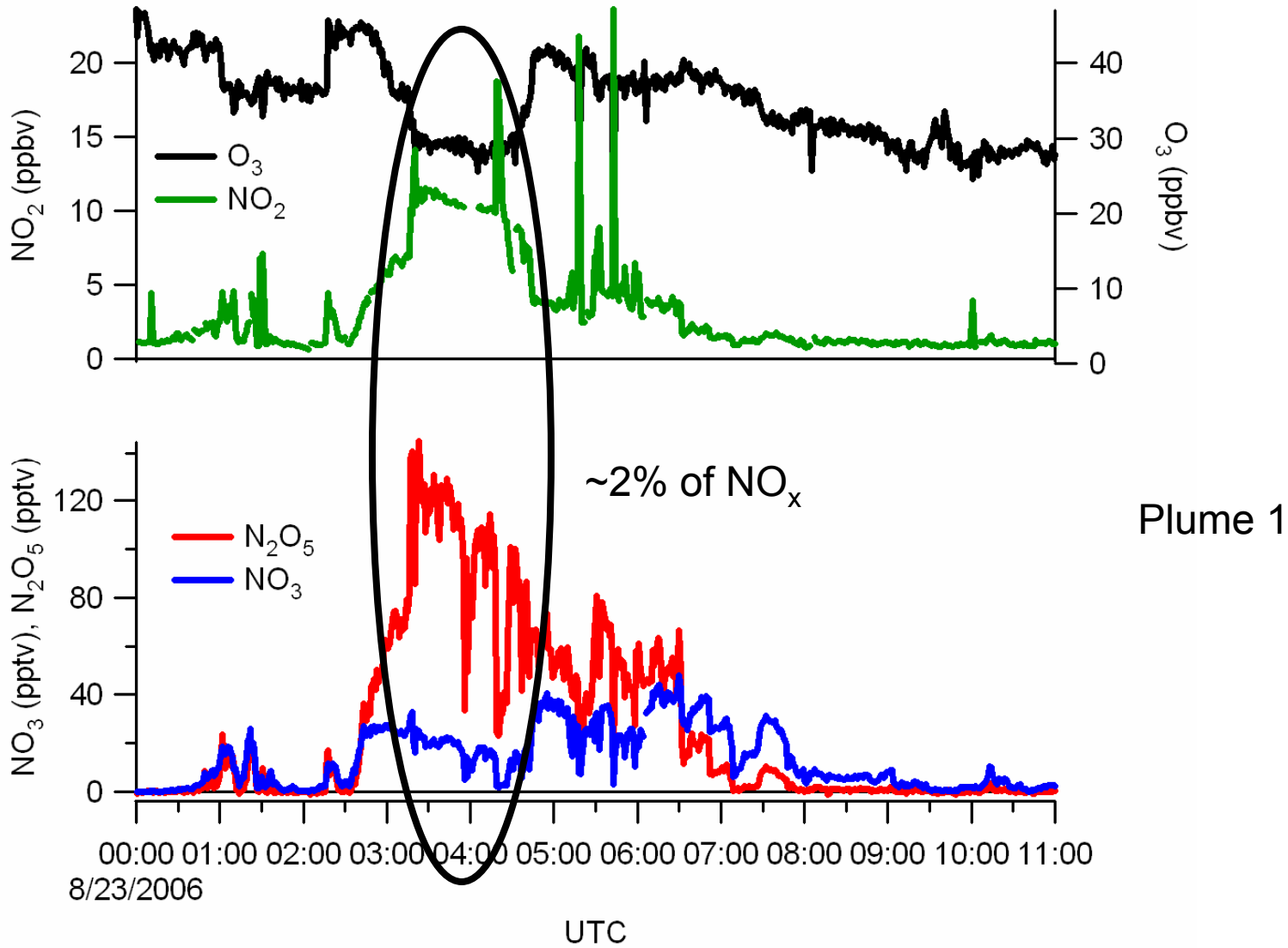
Case IIIa: Downwind from sources



Plume 1

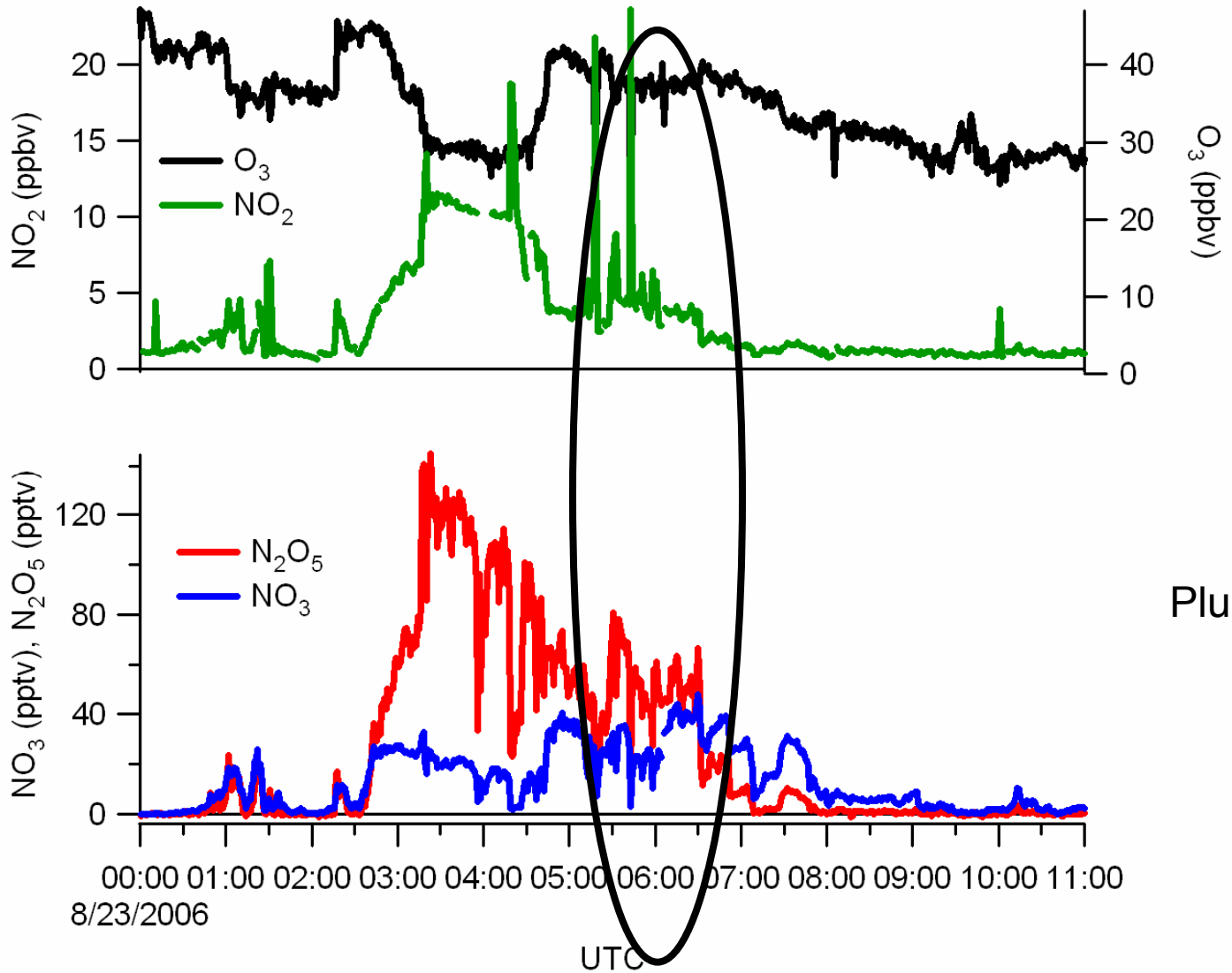
[O_3], [NO_2] decrease ↓
HCHO, HCOOH, C_2H_4 (used as tracers) →

Case IIIa: Downwind from sources



- NO_3 reacting with VOCs
- evidence for heterogeneous uptake of N_2O_5 processing: 1.6×(-0.9 ppbv, or 10% hr^{-1}) NO_x; 2.6×(-0.9 ppbv hr^{-1}) O_x

Case IIIb: Downwind from sources

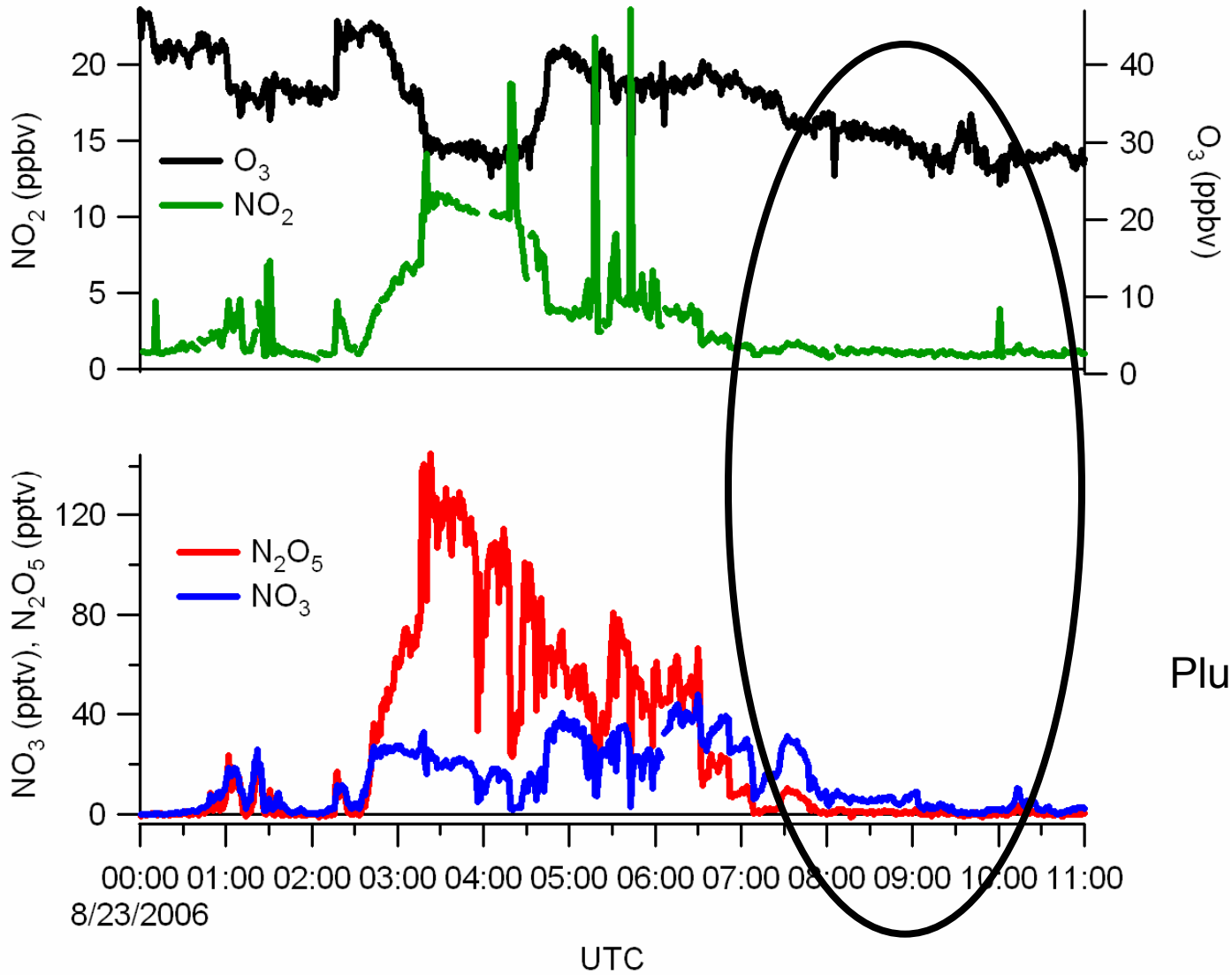


Plume 2

Older, more processed plume

1.3×(-0.4 ppbv, or 10% hr^{-1}) NO_x; 2.3×(-0.4 ppbv hr^{-1}) O_x

Case IIIc: Downwind from sources



Plume 3

- highly processed air mass
- mostly NO_3 reactions due to low [NO_2]

losses NO_x limited; long NO_3 lifetimes (~ ½ hour)

$1\times(-0.1\ \text{ppbv hr}^{-1})\ NO_x$; $2\times(-0.1\ \text{ppbv hr}^{-1})\ O_x$

Summary/Conclusions

NO_3 and N_2O_5:

- remove NO_x and O_3 at night
  - slowly near sources
    - O_3 – limited, e.g., Houston ship channel
  - rapidly in intermediate distance plumes
    - heterogeneous uptake of N_2O_5
    - NO_3 + VOCs (especially biogenics, e.g., isoprene)
  - slowly in distant plumes
    - NO_2 (or O_3) limited production of NO_3
    - low [NO_2], high temperatures → processing through NO_3
- Oxidation of VOCs by NO_3:
  - little impact on anthropogenic VOCs
  - interesting secondary chemistry (e.g., oxidation products, SOA)

Nighttime chemistry is working for you while you sleep!