Proposed Analysis of Results from the 2005 SETTS and 2006 Houston Triangle Field Studies

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TOPICS - Overview

- **Texas 2006 AQS – The Houston Triangle**

1. Emission inventory
2. Source Identification/Trajectory Paths
3. Particulate and Heterogeneous Chemistry/Inter-annual Variability

- **Texas 2005: Southeast Texas Transport Study**

4. Particulate and Heterogeneous Chemistry

The Houston Triangle

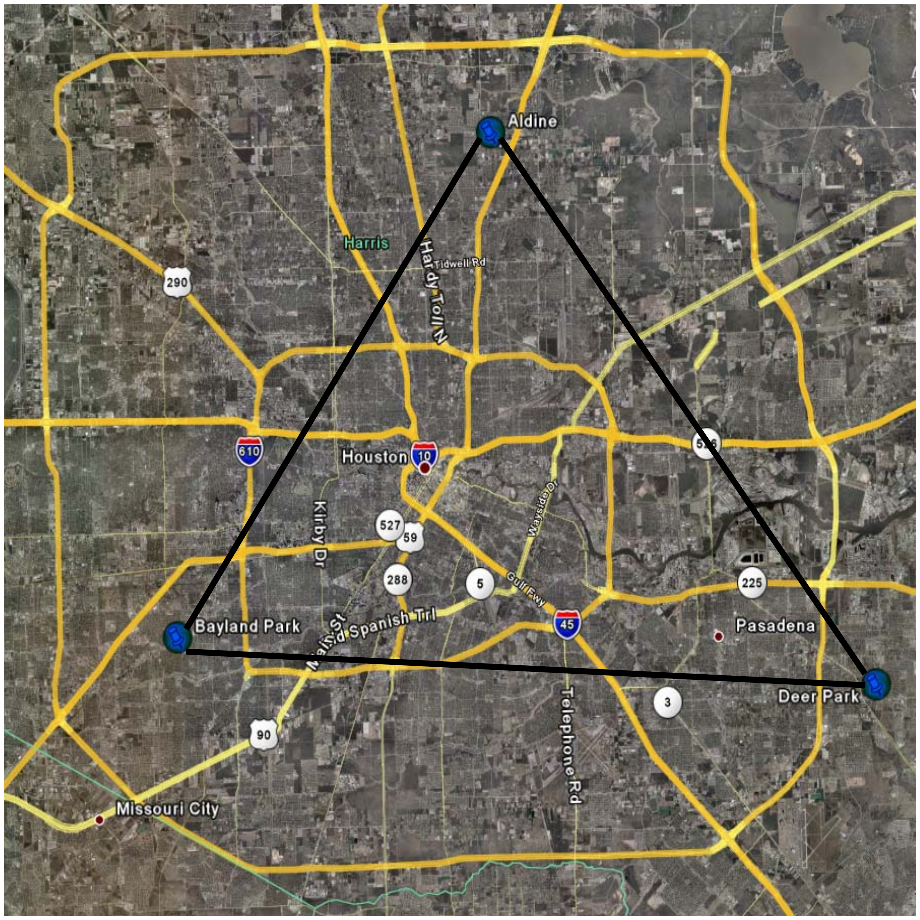
Three PTR-MS and three Aerodyne Aerosol Mass Spectrometers (AMS) units deployed between September 5-27th, 2005

•The PTR-MS measured 22 NMHC.

•The AMS measured aerosol composition and size (~40nm - ~800nm)

Resulted in an almost continuous set of co-located VOC/aerosol observations at three TCEQ air monitoring stations

- **Aldine: urban emission sources and transported emissions from Ship Channel**
- **Deer Park: upwind of Houston Ship Channel under S. flow**
- **Bayland Park: west side of city**



1. Use of PTR-MS Observations to Evaluate Emission Inventory

- **Are TCEQ emissions inventories consistent with concentrations measured by the PTR-MS and canisters during the Triangle Campaign?**

  - **Ambient ratio analysis**
    - **e.g., (ambient CO/ambient NMHC)/(emission CO/emission NMHC)**
    - **CO: ppm, NMHC: ppm-carbon**

  - **Strengths:**
    - **Ratios are less influenced by day to day variations in insolation, transport, etc.**
    - **Don’t need absolute concentrations: relatively robust technique**

  - **Weaknesses:**
    - **Little information on actual magnitude of emissions**
    - **Not so good for photochemically active pollutants**
    - **Difficult to asses if discrepancy associated with numerator or denominator**

  - **Modeling analysis (small cluster of column models for short-term simulations**

1. Use of PTR-MS Observations to Evaluate Emission Inventory

- **Continuous Speciated NMHC data from PTR-MS**
  - **Different NMHC associated with different source categories (area-wide, mobile, stationary, etc.)**

- **TCEQ CO and NO_X data and auto-GC observations**
  - **From Deer Park, Aldine and Bayland Park**

- **Propose to break assessment into**
  - **Nighttime & daytime, sunrise & sunset, weekday & weekend**
  - **Use 'local' emissions vs. entire inventory.**
    - **'zone of influence' concept**
  - **Fresh emissions vs. 'aged' emissions: canisters at Bayland Park**
    - **suggested by Dr. Eric Fujita's study of California emissions**
    - **Fresh emissions: alkenes/alkanes is 'big'**
    - **Aged emissions: alkenes/alkanes is 'small'**

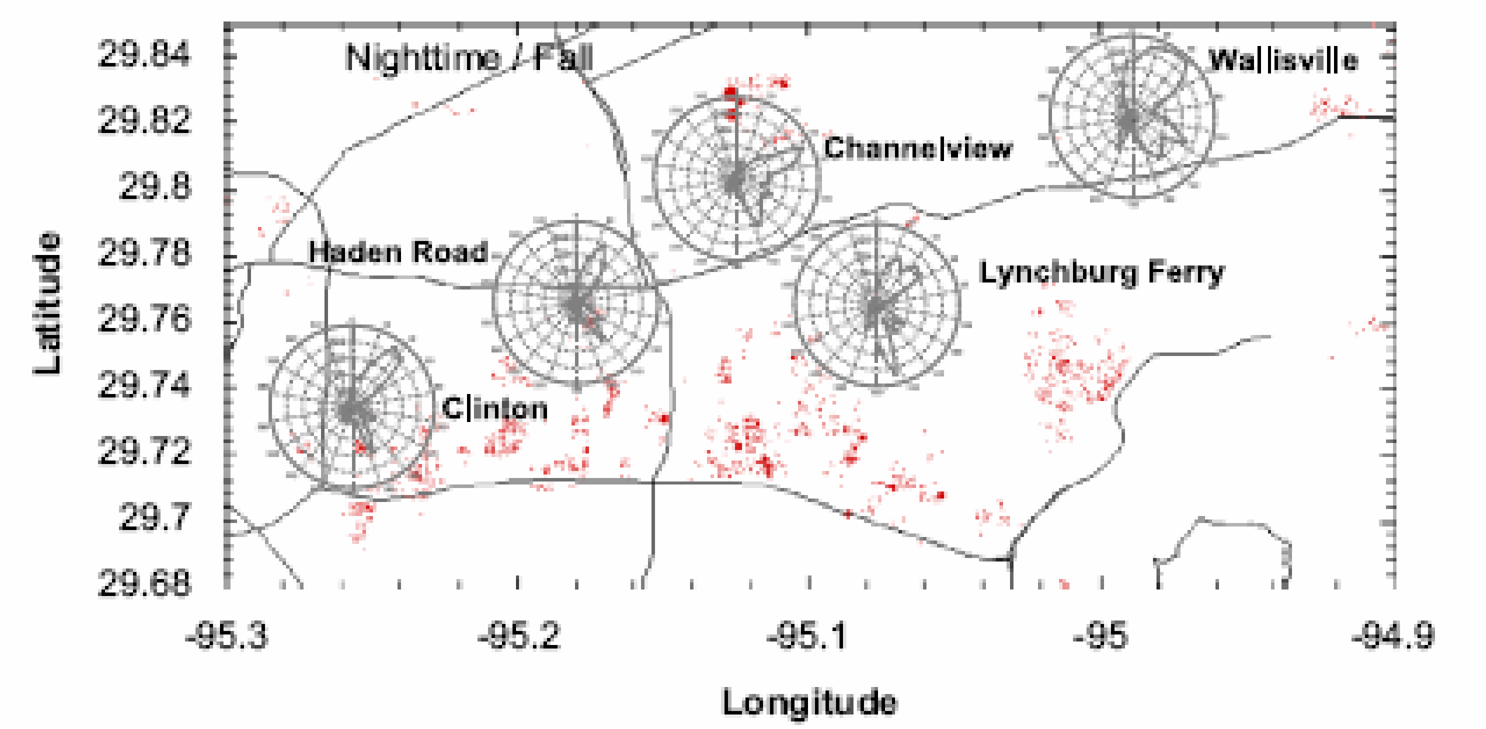
The 23 masses that were monitored by PTR-MS and their nominal identification:

Mass	Compound	Formula
M33	methanol	CH_3OH
M35	hydrogen sulfide	H_2S
M42	acetonitrile	C_2H_3N
M43	propene	C_3H_6
M45	acetaldehyde	C_2H_4O
M47	ethanol	C_2H_6O
M57	butenes	C_3H_6O
M59	acetone	C_3H_6O
M61	acetic acid	$C_2H_4O_2$
M63	dimethyl sulfide	C_2H_6S
M69	isoprene	C_5H_8

Mass	Compound	Formula
M71	MVK+MACR+ pentenes	C_4H_6O, C_5H_{10}
M73	MEK	C_4H_8O
M79	benzene	C_6H_6
M93	toluene	C_7H_8
M95	phenol	C_6H_6O
M105	styrene	C_8H_8
M106	isopropyl nitrate	$C_3H_7NO_3$
M107	xylenes	C_8H_{10}
M109	cresols	C_7H_8O
M121	C3-benzenes	C_9H_{11}
M135	C4 benzenes	$C_{10}H_{14}$
M137	monoterpenes	$C_{10}H_{16}$

2. Identify Source Regions and Advection Pathways of Hydrocarbon Emissions

- Conditional Probability Functions combine directional information with high concentrations of VOCs.
  - defined as ratio of the number of samples in the wind sector y with mixing ratios greater than some ''high'' concentration, to the total number of samples in the same wind sector

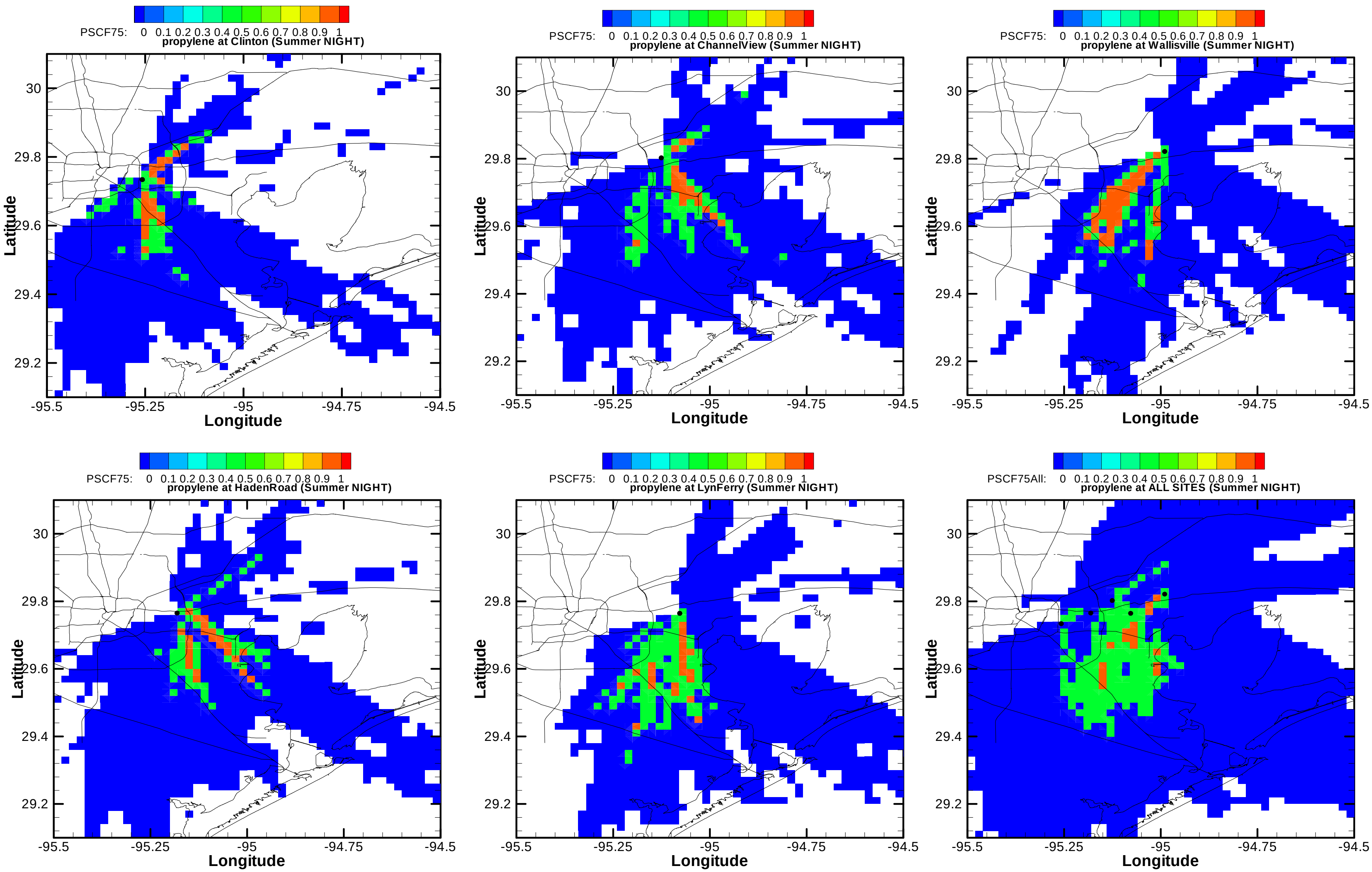


2. Identify Source Regions and Advection Pathways of Hydrocarbon Emissions

- Potential Source Contribution Function analysis: based on time series of the location of simulated air parcels released from each of the Triangle sites.

- Associates each back trajectory with an observation at a given receptor site and evaluates the time of the arriving parcel at points along its back trajectory.

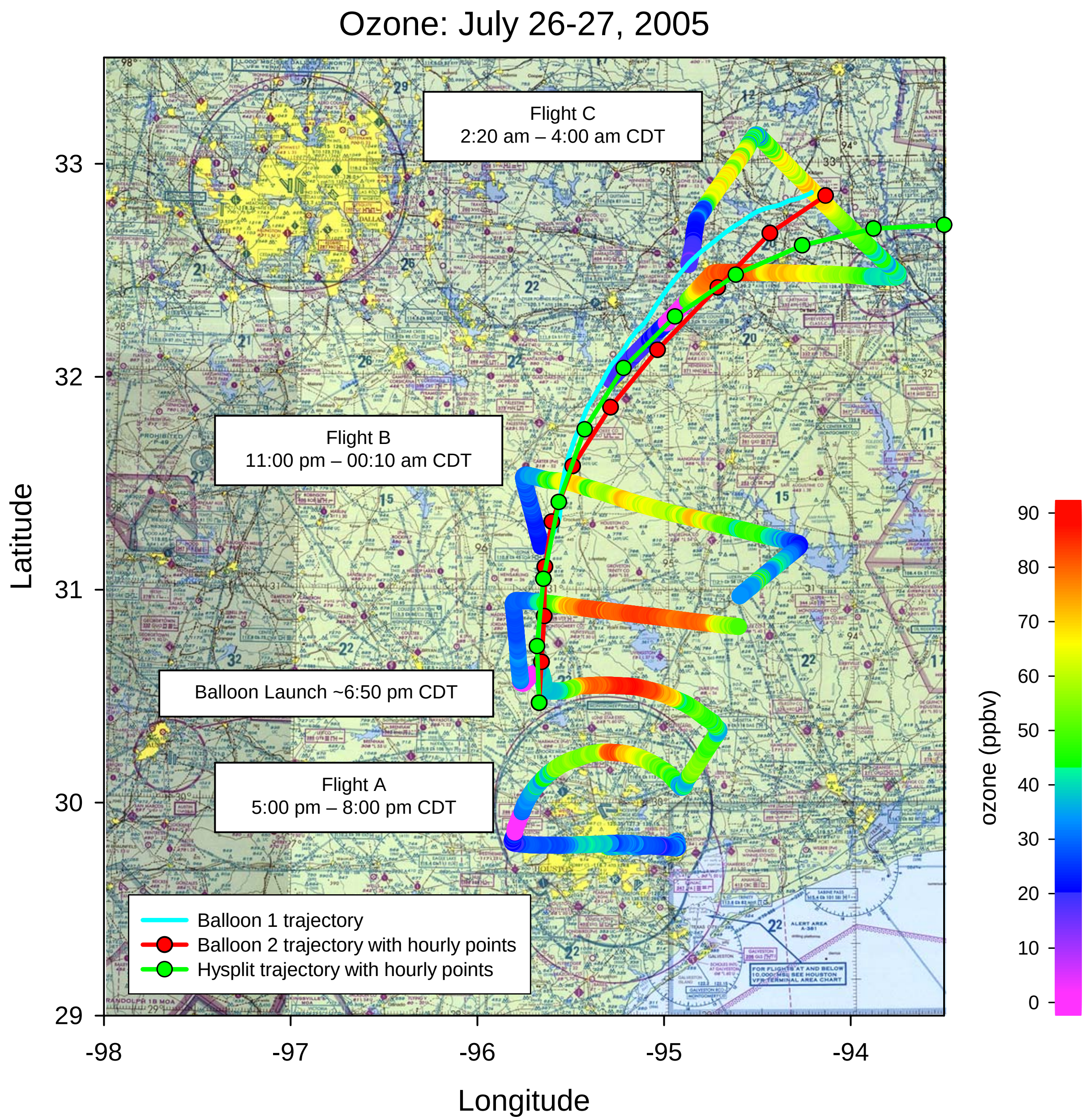
- Results in a map showing the probability of a given cell being associated with an elevated measurement at the receptor site of interest.


PSCF75: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at Clinton (Summer NIGHT)
PSCF75: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at ChannelView (Summer NIGHT)
PSCF75: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at Wallisville (Summer NIGHT)
PSCF75: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at HadenRoad (Summer NIGHT)
PSCF75: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at LynFerry (Summer NIGHT)
PSCF75All: 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
propylene at ALL SITES (Summer NIGHT)
Latitude
30
29.8
29.6
29.4
29.2
Longitude
-95.5
-95.25
-95
-94.75
-94.5

3. Particulate and Heterogeneous Chemistry/Inter-annual Variability

- Comparison of Houston Triangle Results with September 2000 observations from the Gulf Coast Aerosol Research and Characterization Study (Allen and Fraser, 2006):
- Triangle Study: continuous aerosol size and composition.
  - Size resolved composition data at Deer Park, Bayland Park
- A partial list of features to be examined in Triangle data:
  - Homogeneity of aerosol concentrations
  - Lack of homogeneity in particle size distributions (can we use size distribution to evaluate new particle formation vs. coagulation?)
  - Diurnal patterns (primary AM peak, weaker PM peak)?
  - Major components (sulfate, ammonium, organics…) of aerosols.
  - Dominant source of acidity as function of size? Sulfate?
  - Source characterization/chemical signatures to identify primary mobile sources, geological sources, cooking, etc.
  - Relation of primary SO2 to total sulfate aerosol mass at each site

4. Particulates and Heterogeneous Chemistry 2005 Southeast Texas Transport Study (SETTS)



Background & Motivation

Nighttime Chemical Processing of NO_x

Gas-phase Reactions

$$O_3 + NO \rightarrow NO_2$$

$$O_3 + NO_2 \rightarrow NO_3$$

$$NO_3 + NO_2 \;\square\; N_2O_5$$

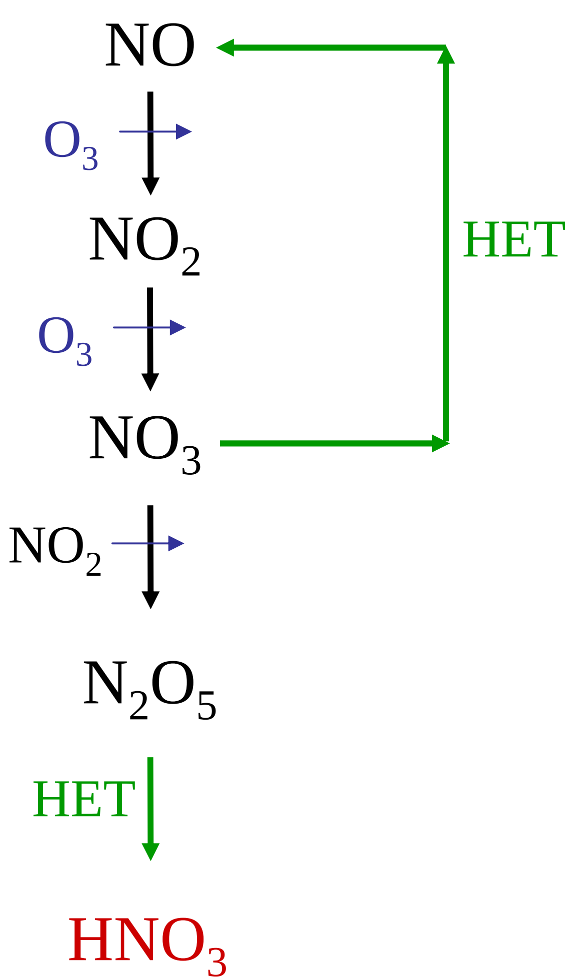
Heterogeneous Reactions

$$N_2O_5 + H_2O \xrightarrow{\text{HET.}} 2HNO_3 \quad (\gamma_{N_2O_5})$$

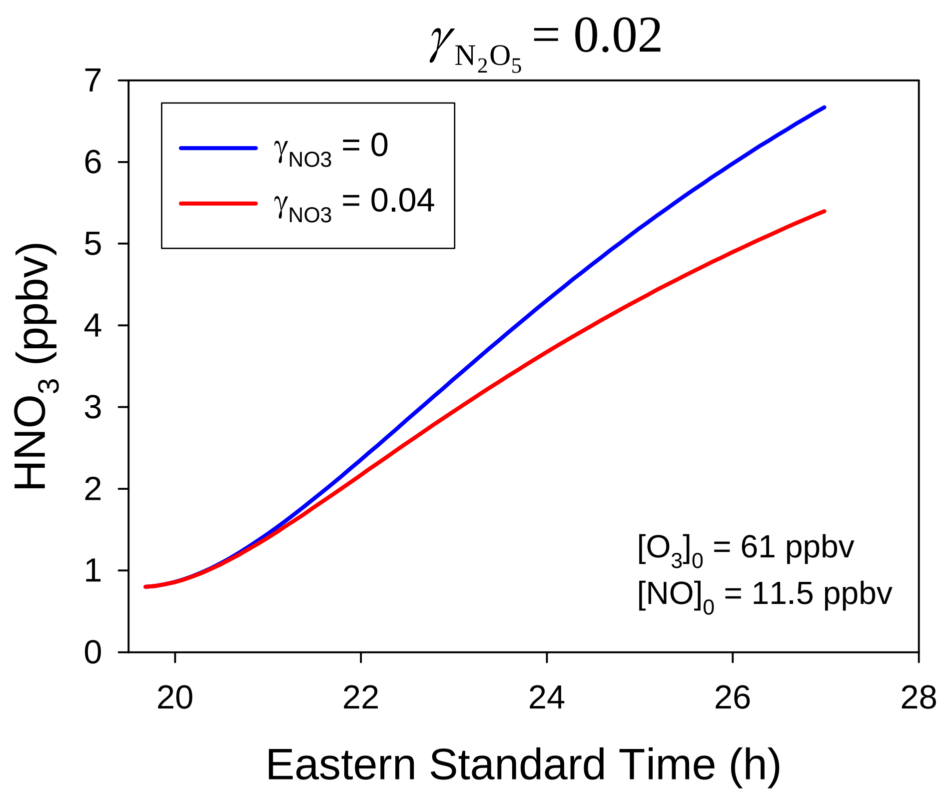
$$NO_3 \xrightarrow{\text{HET.}} NO \text{ or } NO_2 \quad (\gamma_{NO_3})$$

- **Reactions of N_2O_5 and NO_3 are important at night**
- **Laboratory and field studies show large variability of N_2O_5 uptake**
- **Reactive uptake of NO_3 on aerosols still rather poorly understood**

Role of NO_3 Heterogeneous Reaction



Slows down conversion of NO_x to HNO_3



HNO_3 production decreased by 20% over a period of 8 hours

Data Analysis and Paper Ideas for SETTS 2005

- Nighttime Gas-phase and Heterogeneous Chemistry
  - Role of nighttime radical and VOC (alkene) chemistry on the loss of O_3 and NO_x during overnight transport of Houston plume
  - Oxidation of NO_x to HNO_3 via hydrolysis of N_2O_5 and the potential role of NO_3 radical heterogeneous chemistry

- Evidence of overnight transport of concentrated Houston urban and ship channel emissions.
  - Precise quasi-Lagrangian measurements during SETTS are the first to show that the Houston plume remained nearly intact as it was advected nearly 300 km over 10 hours (July 26, 2005 episode).

- Effect of Houston emissions on downwind photochemical O_3 production the next day.
  - Modeling study constrained by observations made during the SETTS campaign

Thank you!