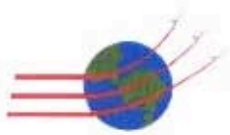


Understanding the Influence of Local and Regional Sources on the Temporal and Spatial Variability of Pollutants in Urban Environments

Joanne H. Shorter, J. Barry McManus, Charles E. Kolb
Aerodyne Research, Inc.

Brian K. Lamb, Susan M. O'Neill, Eugene J. Allwine
Washington State University

Robert W. Talbot, Eric Scheuer
University of New Hampshire

Joseph Ferreira, Jr. and Greg J. McRae
Massachusetts Institute of Technology

Supported by NASA EOS/IDS, Earth Sciences
ARI-VGR-96
August 2000

Issues

- How well do measurements at urban monitoring sites represent actual pollutant levels in the urban area?

  Actual exposure to pollutants?

- Spatial Issue: How well can one monitoring station, or at most just a small number of monitoring sites, in the urban area describe the pollutant levels in the area?

- Temporal Issue: 1 hour averages at monitoring station versus 1 sec data collection rate

Tools and Techniques to Characterize Urban Emissions

- Newly developed high-sensitivity, fast response, mobile instrumentation

  2 channel IR laser spectrometer (TILDAS), ~ 1 ppb in 1 sec.: ARI

- Mobile lab with integrated instrumentation suite: ARI, UNH, WSU

- Mobile measurements for wide area distributions: ARI, UNH, WSU

- Modeling for area flux

  Micro-met urban footprint: WSU

  Transport and chemistry with source modeling: MIT

- Geo-Info Systems for correlation with activity factors: MIT

Measurement Systems

- **Mobile Instrument Suite [ARI Lab]**

Instrument	Measures at 1 sec.
ARI Zeeman-HeNe	CH_4
ARI 2-Channel TDL	2 to 3 of: CO, O_3, N_2O, NO, NO_2, ...
Licor NDIR	CO_2
WSU ECD	SF_6
UNH TSI	Condensation Nuclei
Trimble GPS	Position, Velocity

- **Second Mobile instrument suite [WSU]**

CO, CO_2, NO_x, O_3 at 10 sec.

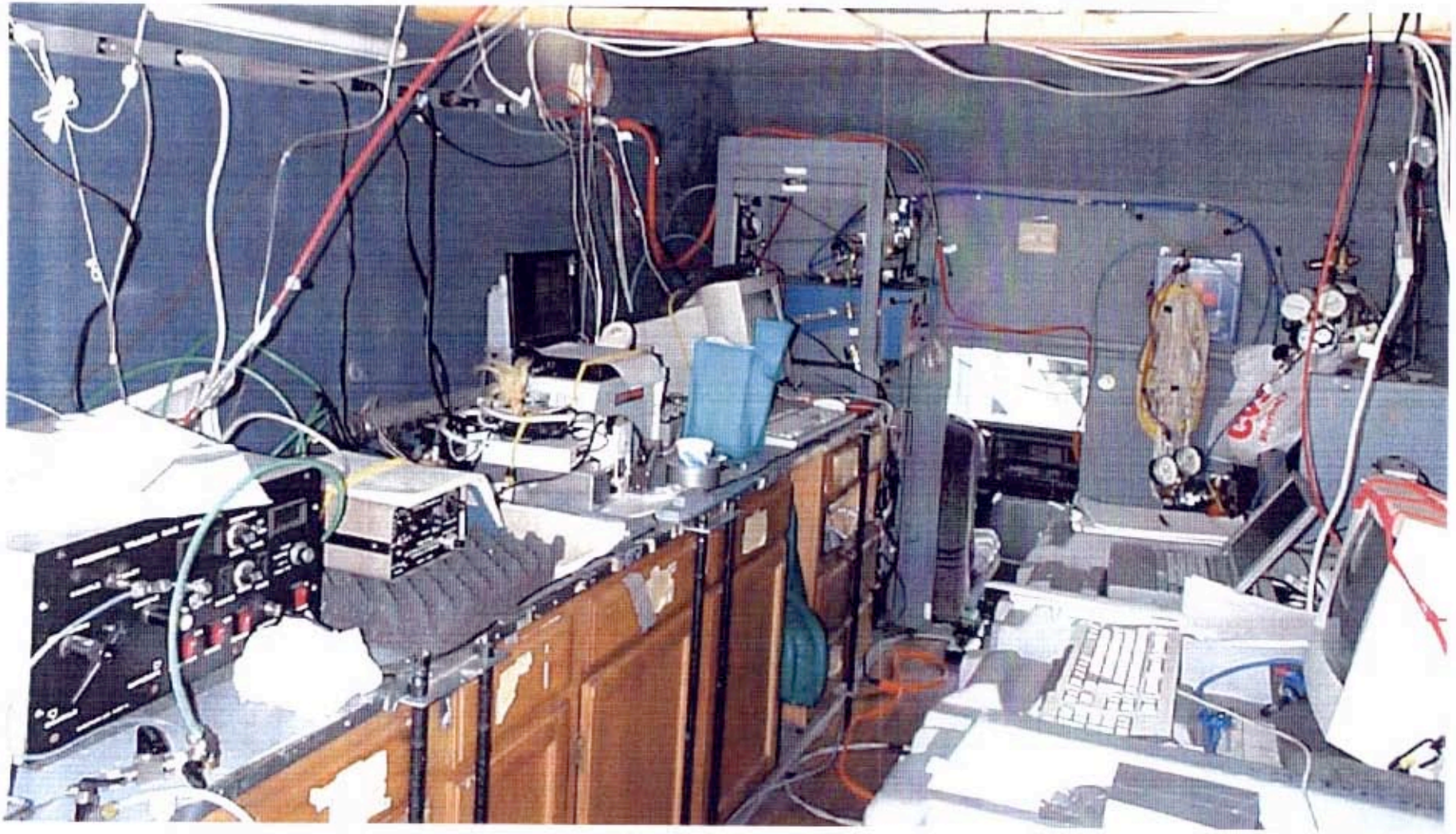
SF_6, Wind (u,v; sonic), GPS at 1 sec.

- **Fixed Site Instruments**

Acoustic Sounder	Boundary Layer Height & Wind Speed to 500 M
Tethered Balloon	Vertical Profiles of Gases
Canister Samplers	Higher Hydrocarbons

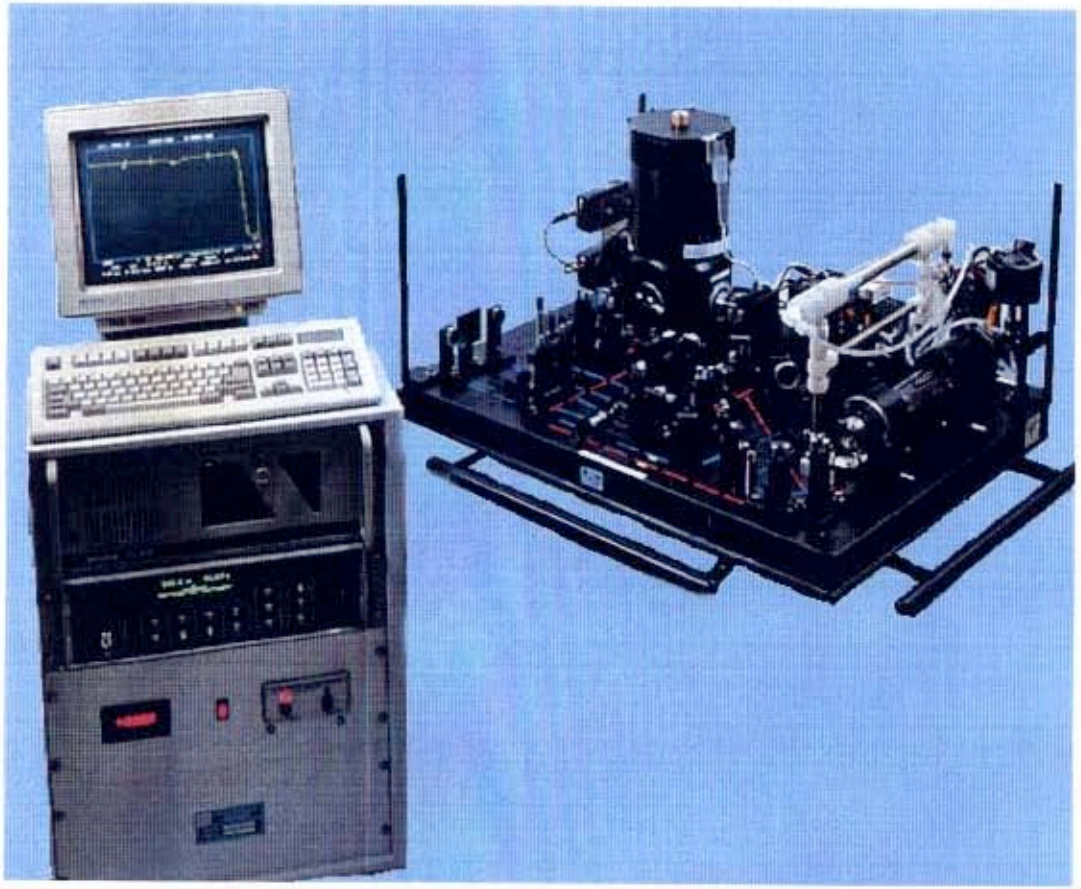
Instrument Vans at Stationary Site
Cambridge, MA May 1999

Instrumented Van for Real-Time Mobile Measurements



Diode Laser Trace Gas Monitor

- **Compact design - All reflective optics**
- **Diode lasers liquid nitrogen cooled**
- **Telescope and/or multipass cell**
- **Data acquisition and analysis software**
- **Applications:**
  - **Automobile emissions**
  - **Greenhouse gas fluxes**
  - **Pollution mapping**
  - **Industrial process monitoring**

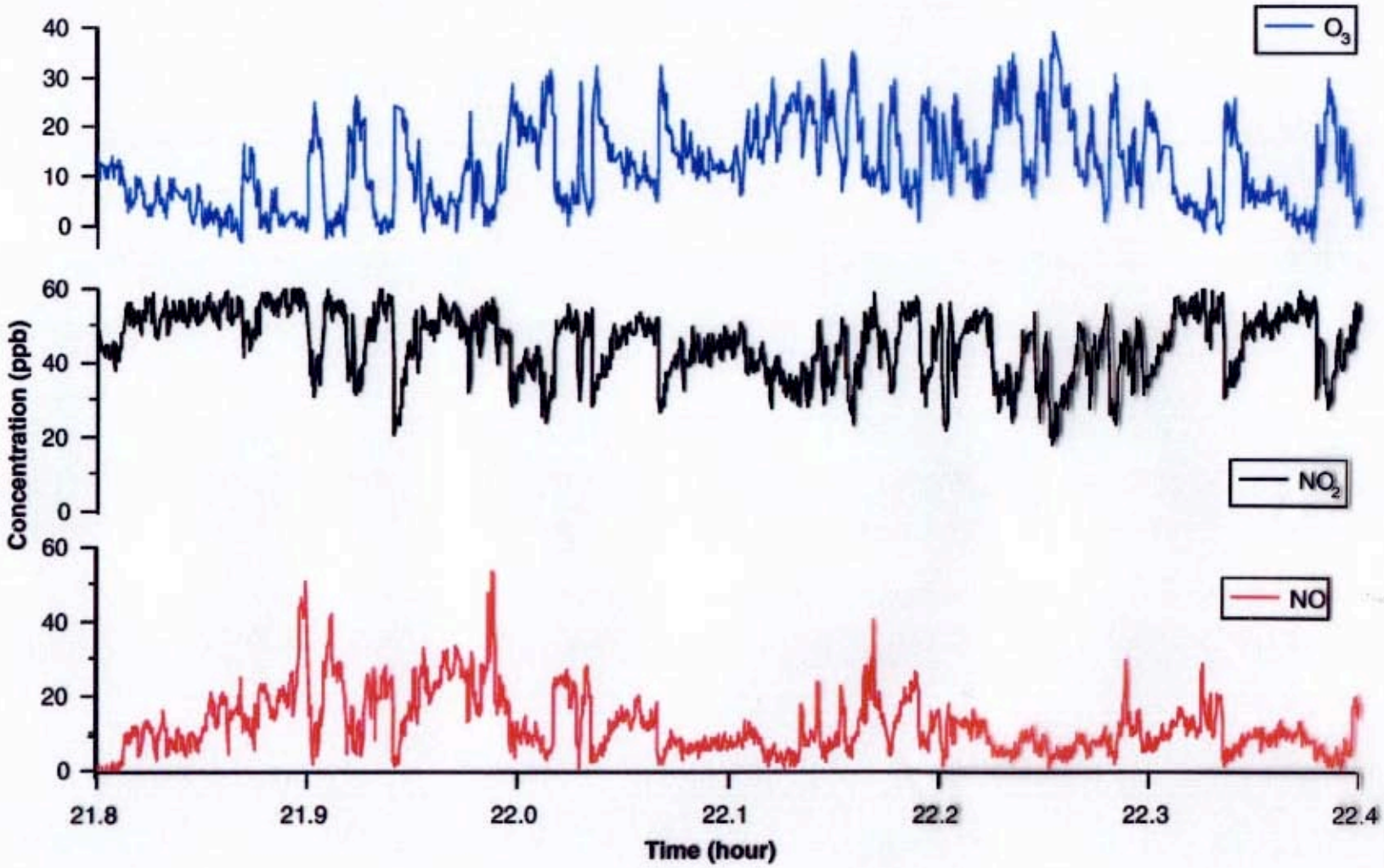


CLOSED-PATH TILDAS DETECTION LIMITS

100 m folded path at 20 Torr

TRACE GAS	SPECTRAL REGION cm^{-1}	DETECTION LIMIT ppbv
CO	2180	0.1
N_2O	2200	0.1
NO	1900	0.5
NO_2	1630	0.3
CH_2O	2803	1.0
SO_2	1370	1.0
O_3	1024	0.5

Simultaneous NO, NO_2 and O_3 Measurements Aug 22, 1996 Evening



Completed Measurement Campaigns

Manchester, NH Compact urban area

1) November 1997: Methods development: CH_4, CO_2

2) June 1998: Greenhouse Gases: N_2O, CH_4, CO_2, + CO, Particulates

3) August 1998: Smog & Smog Precursors:
NO, NO_2, O_3, UV + CO_2, Particulates

Boston, MA

4) May 1999: Smog & Smog Precursors:
NO, NO_2, O_3, UV + CO_2, CO, Particulates

1997-1998 MEASUREMENT CAMPAIGNS

Site: Manchester, NH
Compact industrial city on Merrimack River in southcentral New Hampshire
Population 100,000

November 1997

Greenhouse gas survey

CO_2, CH_4

Mapping
Canister sampling

June 1998

Greenhouse gas study

N_2O, CO, CO_2,CH_4, Particles

Mapping
Canister sampling

Tracer studies

Vertical profiles

August 1998

Pollutants and Precursors

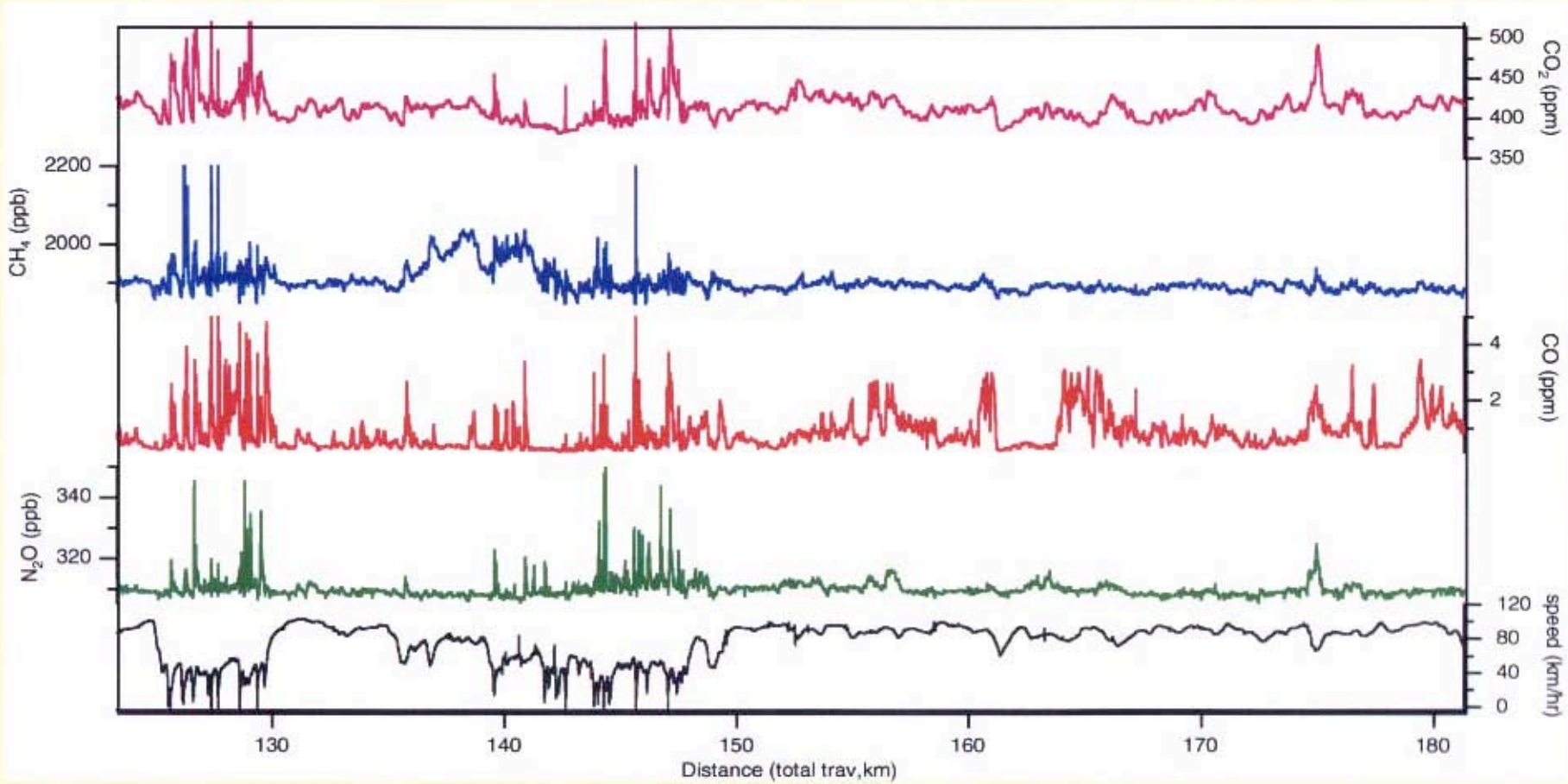
NO, NO_2, O_3, CO_2, UV, Particles

Mapping
Canister sampling

Tracer studies

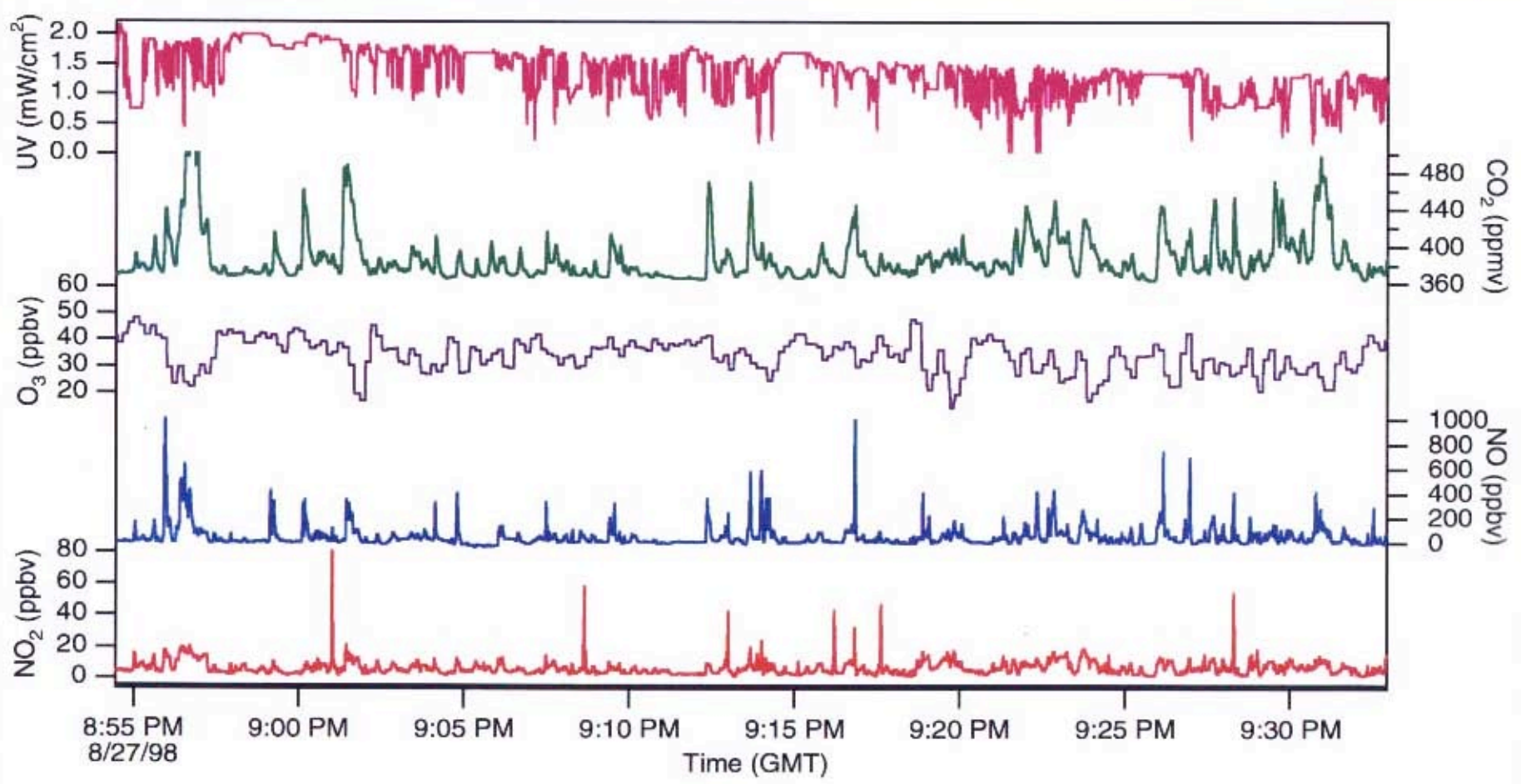
SIMULTANEOUS MEASUREMENT OF TRACE SPECIES

Manchester, NH
June 19, 1998



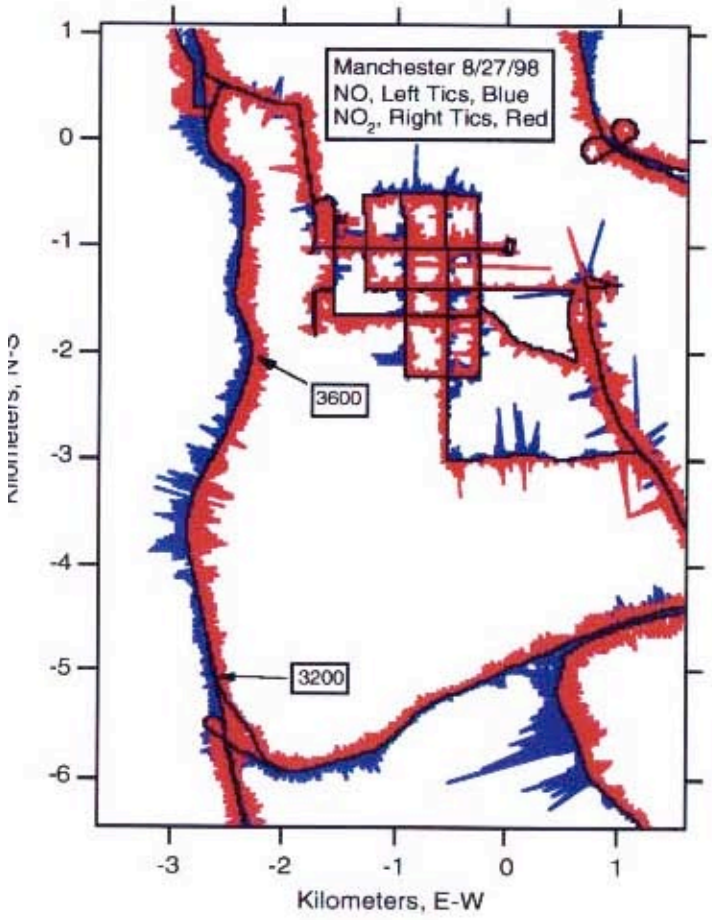
SIMULTANEOUS REAL-TIME MEASUREMENTS OF SMOG PRECURSORS

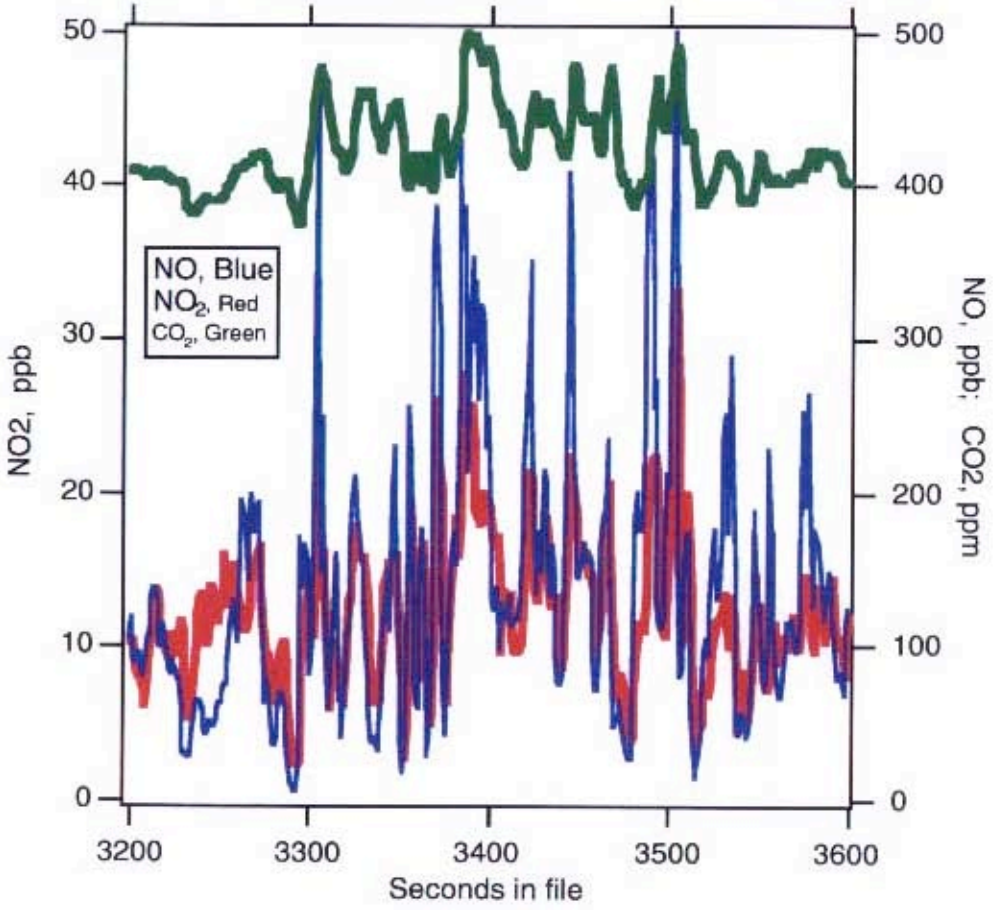
August 27, 1998



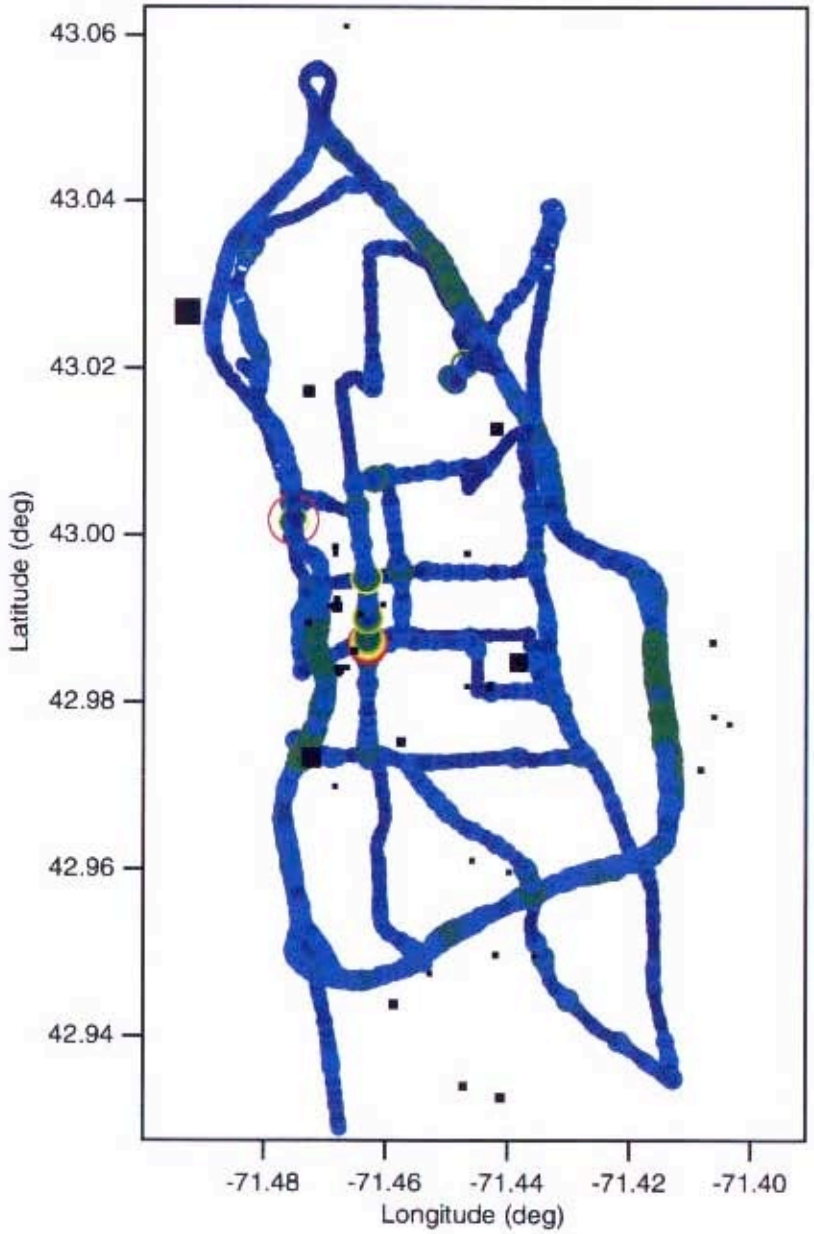
Real-Time Mobile Data Characteristics

Concentration Elevations on a Range of Scales: General elevations, plumes, local sources



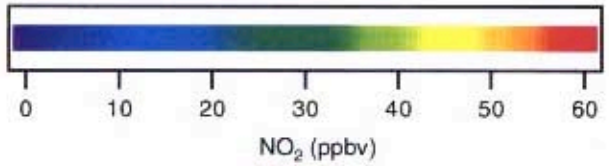


Distribution of NO_2 in an Urban Area
Manchester 8/25/98

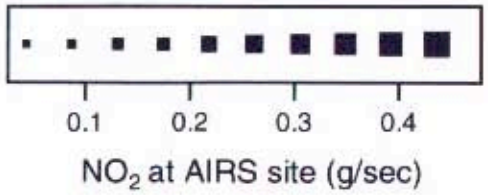


Predominantly South winds

Measured NO_2 mixing ratios are indicated by the size and color of the points on the GPS track.



■ AIRS sites
Symbol size is scaled to NO_2 reported at the site

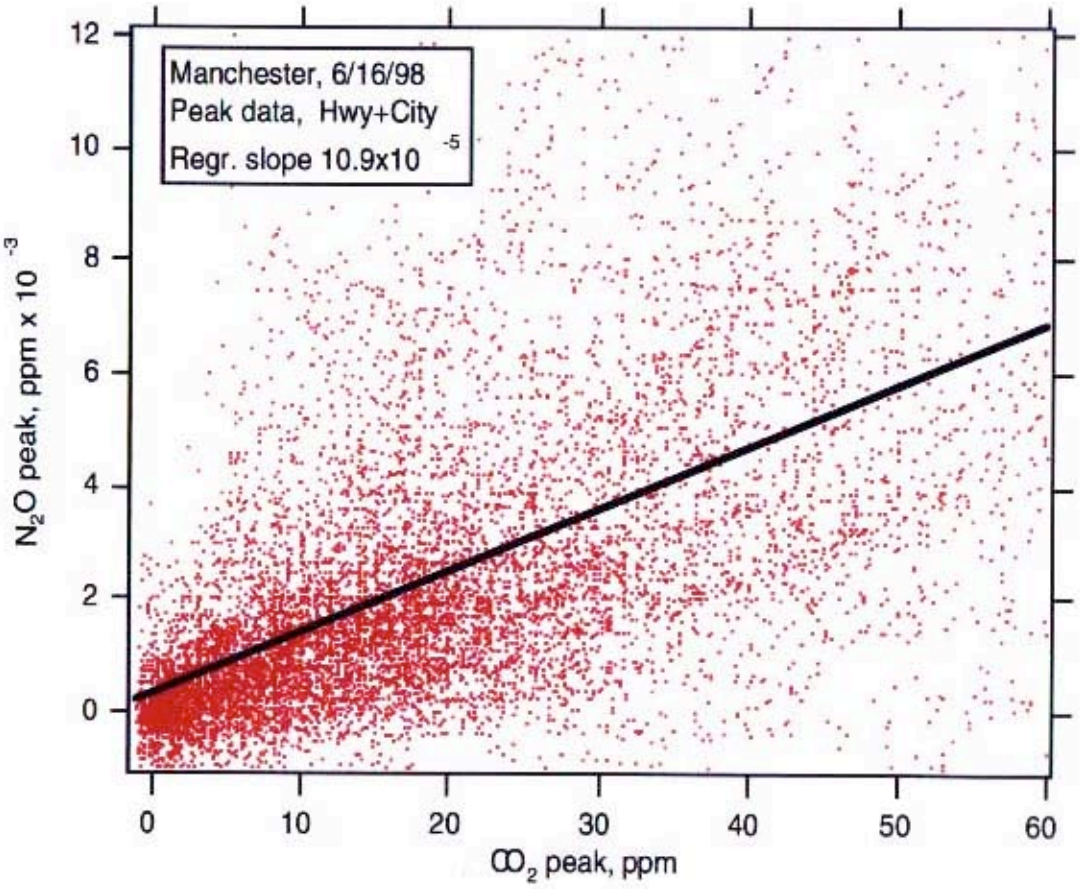


Scatter Plot of N_2O vs CO_2, Manchester, NH, 6/16/98

"Peaks" segment of data
ΔN_2O & ΔCO_2

Highway & City Roads

Regression Slope,
ΔN_2O / ΔCO_2 =(10.9 ±0.1) x10^{-5}

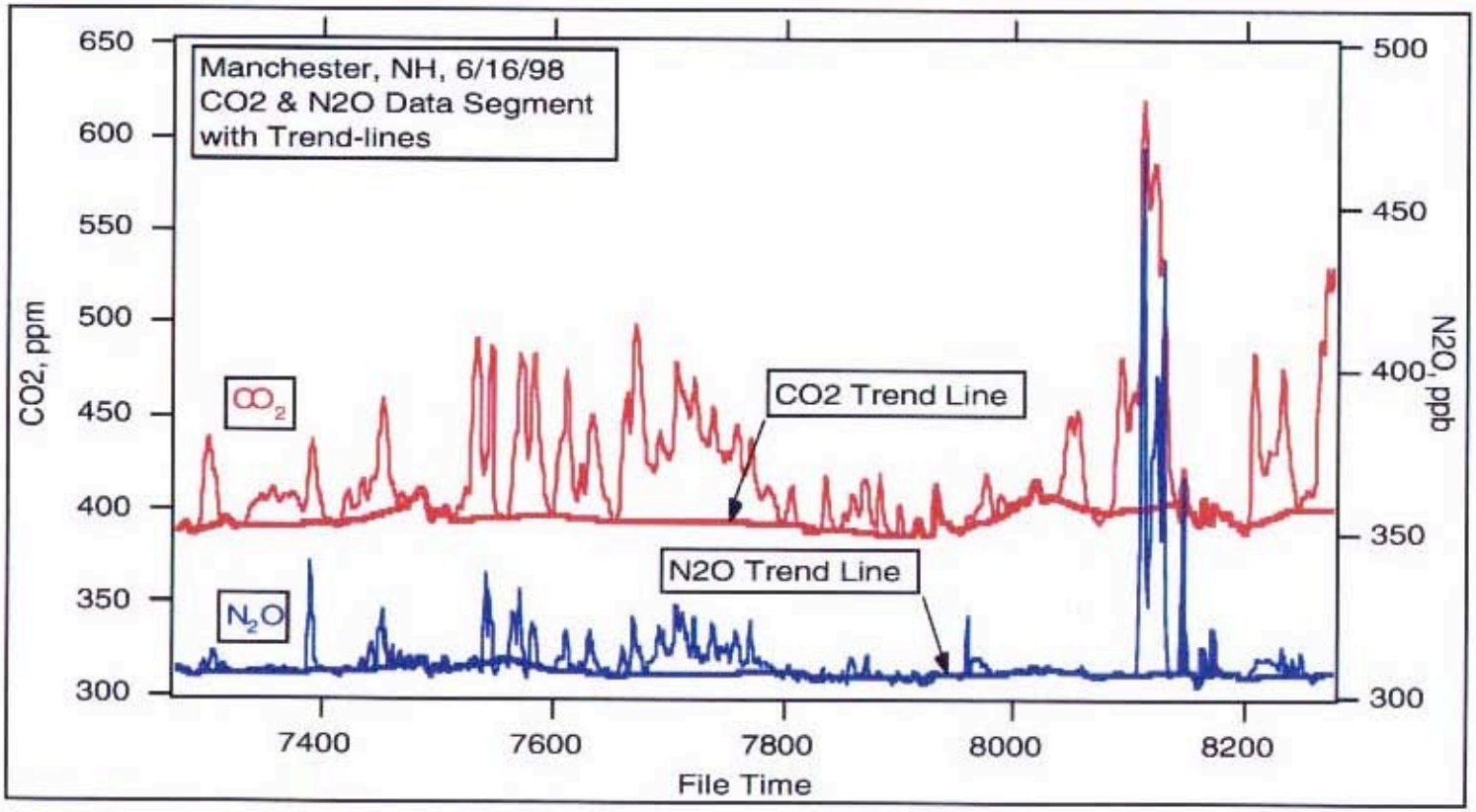


Mobile Measurements: Segmentation of Data

Trend Line and Peaks Above Trend Line

Trend Line: "Local Background"
Slowly Varying
More Mixed

Peaks Above Trend: Local Sources



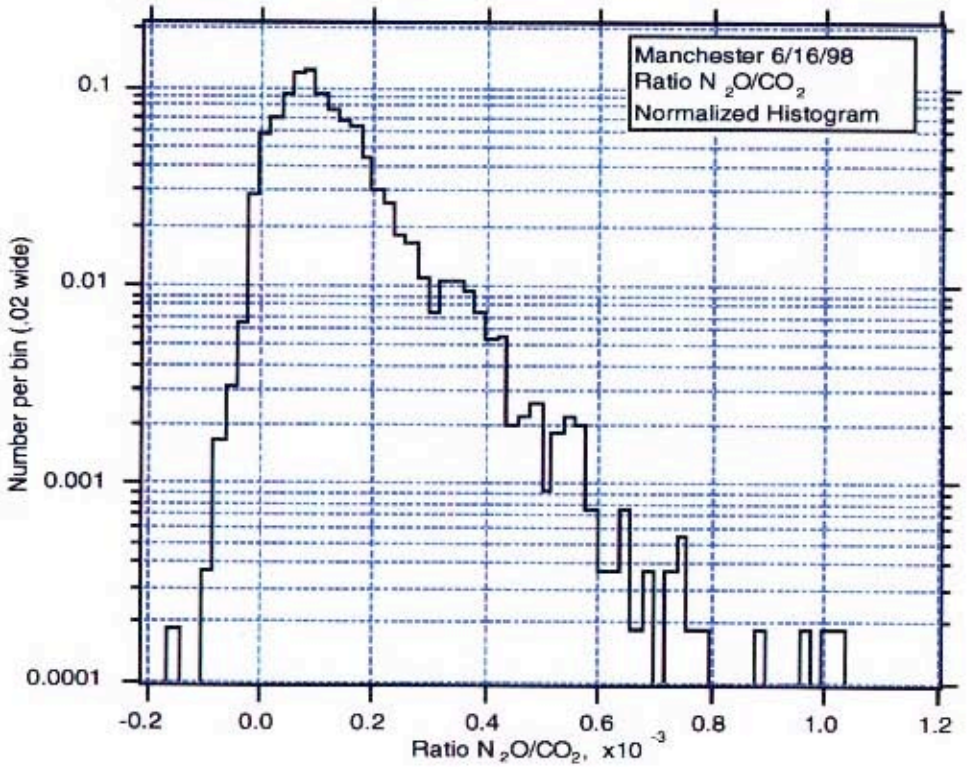
Distribution of N_2O Emission Ratios, Manchester, NH, 6/98

"Peaks" segment of data
ΔN_2O & ΔCO_2

Highway & City Roads

Require ΔCO_2 >15 ppm

For this data cut,
Regression Slope,
ΔN_2O / ΔCO_2 =(12.8 ±0.3) x10^{-5}



Distributions of N_2O Emissions Ratios: Cross-Road & Mobile

Cross-Road Data:
1361 cars in California, 1996

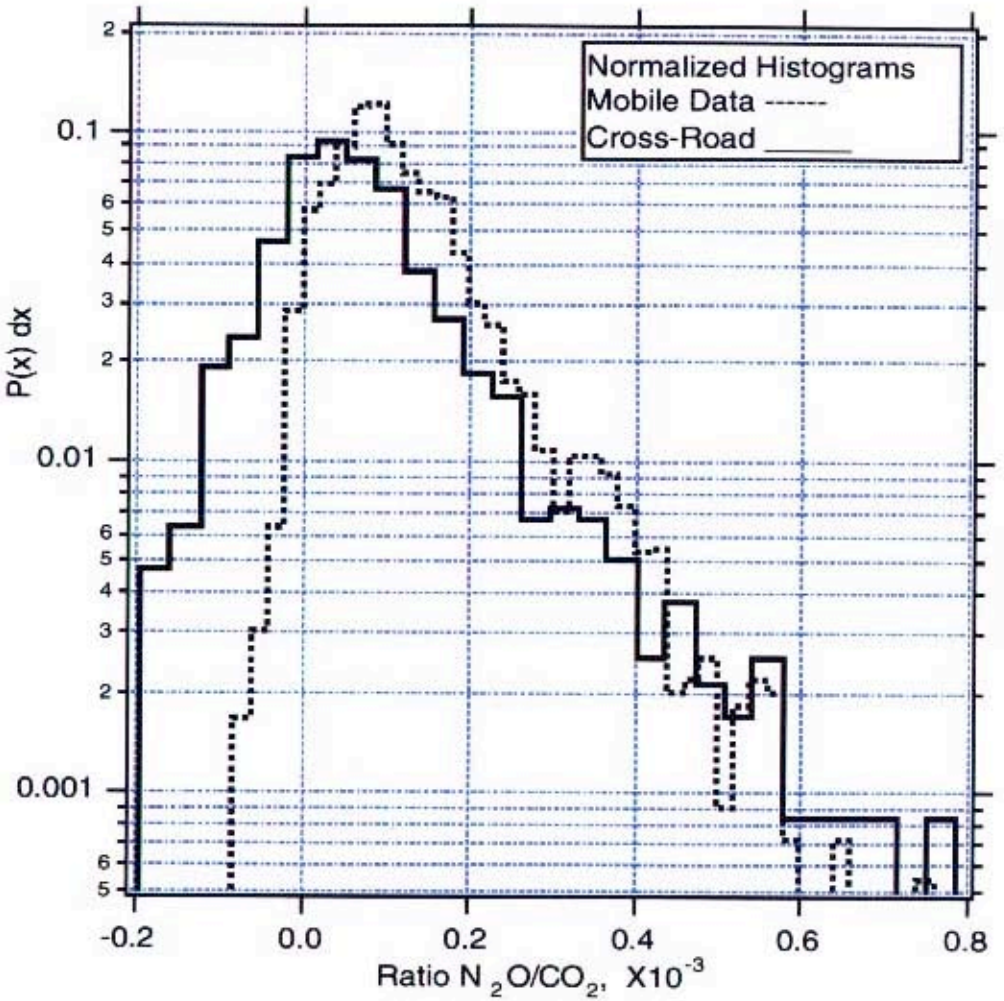
Regression Slope,
ΔN_2O / ΔCO_2 =(8.8 ±2.8) x10^{-5}

Mobile Data: Mixed traffic,
Manchester, NH, 1998

Regression Slope,
ΔN_2O / ΔCO_2 =(12.8 ±0.3) x10^{-5}

For Highway Only,
Regression Slope,
ΔN_2O / ΔCO_2 =(10.9 ±0.3) x10^{-5}

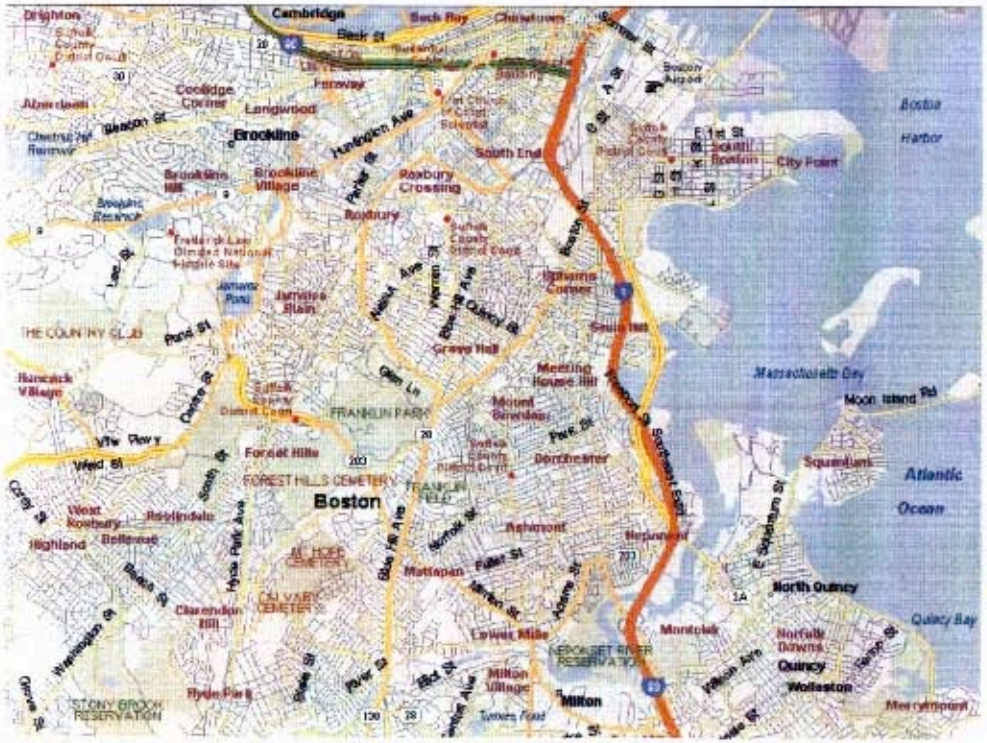
For City Roads Only,
Regression Slope,
ΔN_2O / ΔCO_2 =(15.6 ±0.3) x10^{-5}



Measurement Location

- Boston, MA May 21- 29, 1999

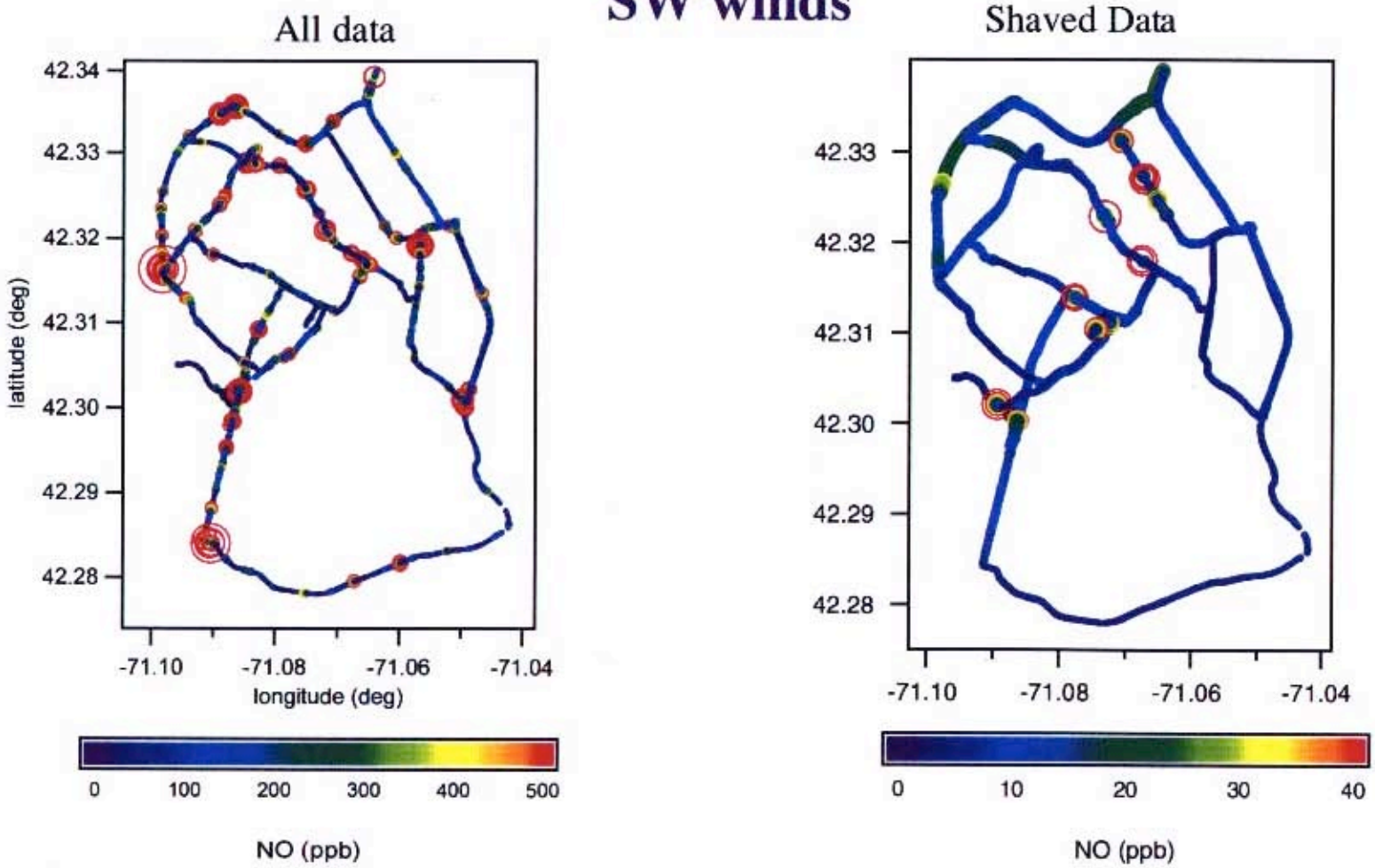
Mobile Measurements in Dorchester/Roxbury



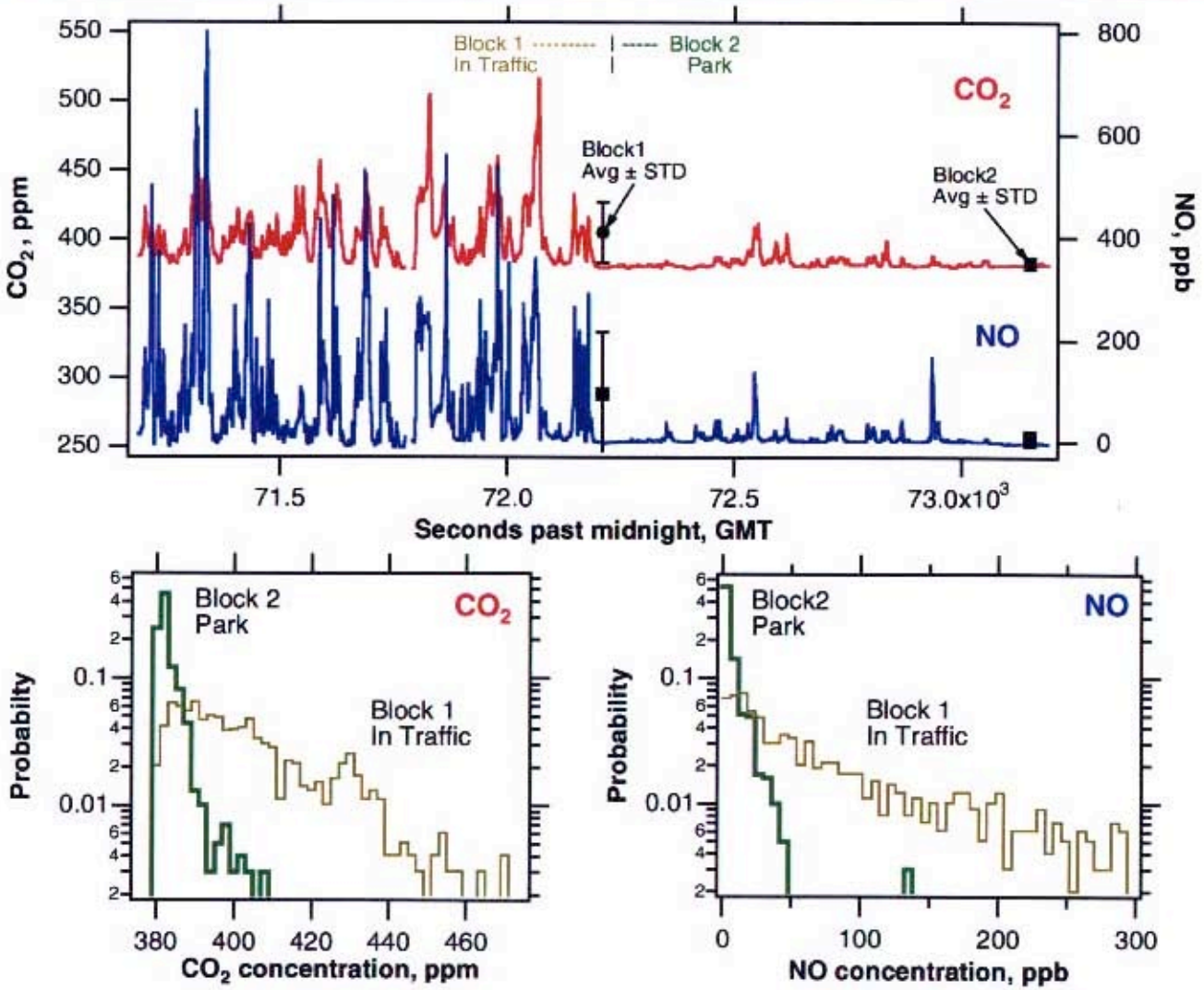
Stationary Measurements at MIT in Cambridge

Spatial Distribution of NO in Dorchester/Roxbury

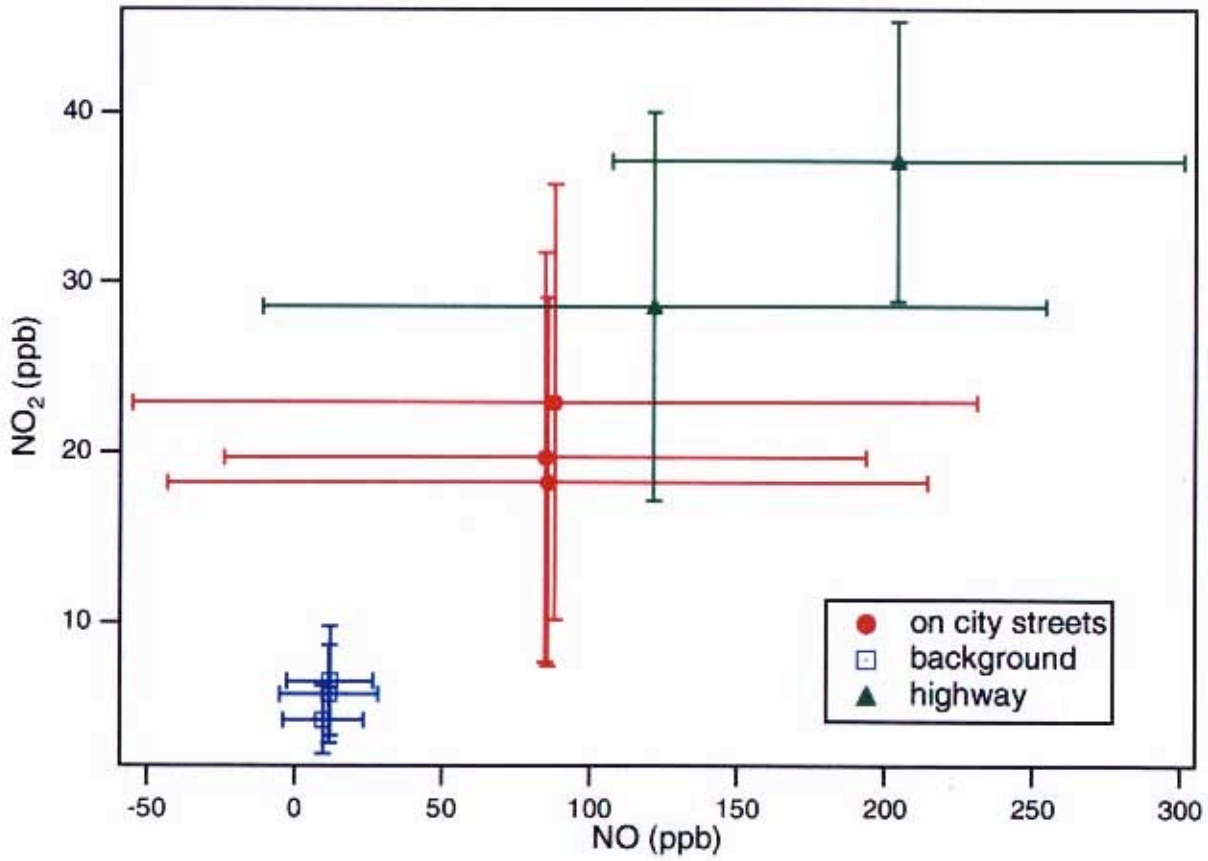
May 25, 1999, afternoon
SW winds



Mobile Data: In-Traffic vs. City Park



Variability of Mobile Data
Effect of Averaging

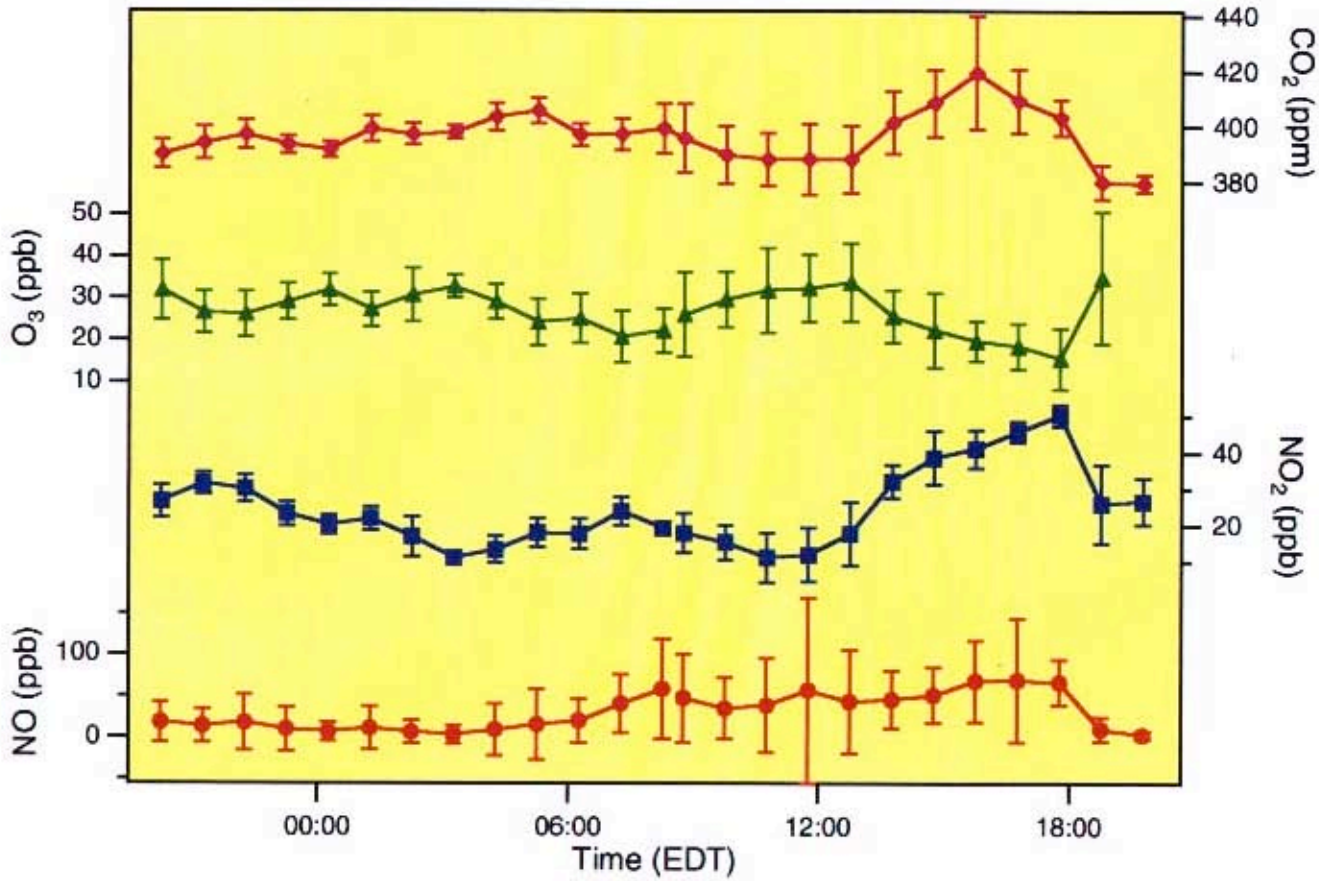


Very large standard deviations in 1 Hour Averages of Mobile Data

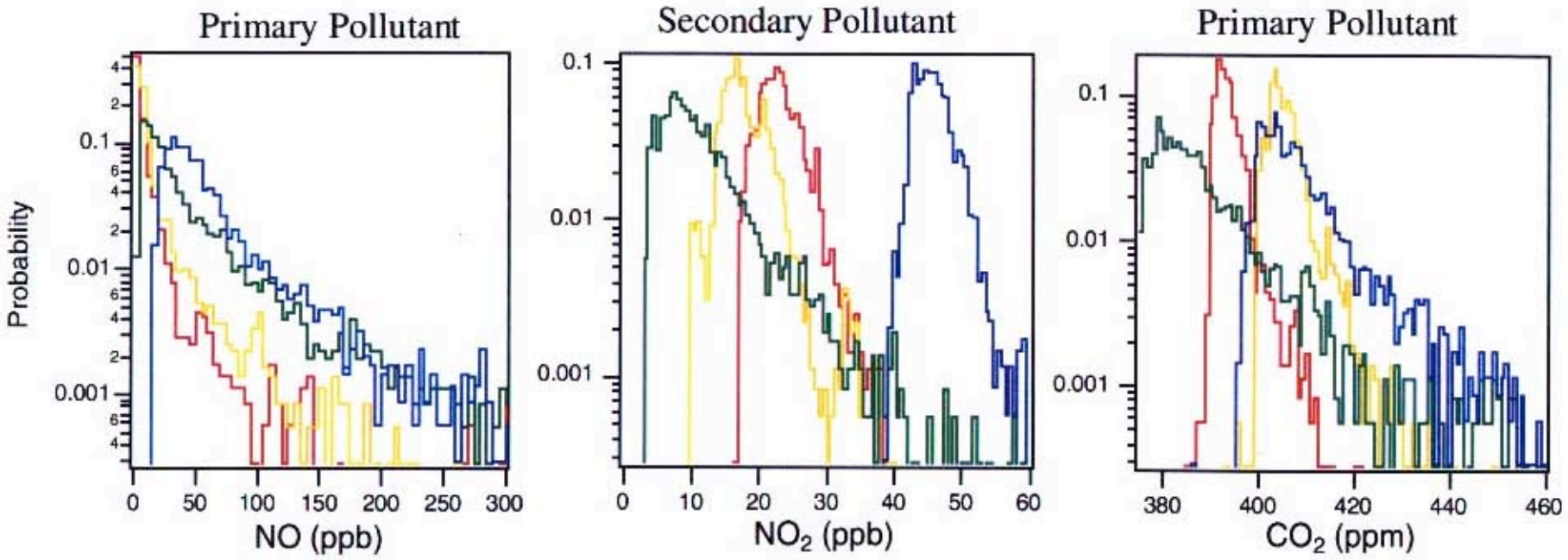
Temporal Variability of Stationary Site Data: Diurnal Data

1 hour averages and stds over 24 hour period

Wind: 0-5 m/s from ~N, shifting to E/SE at ~11 AM



Probability Densities of Pollutants



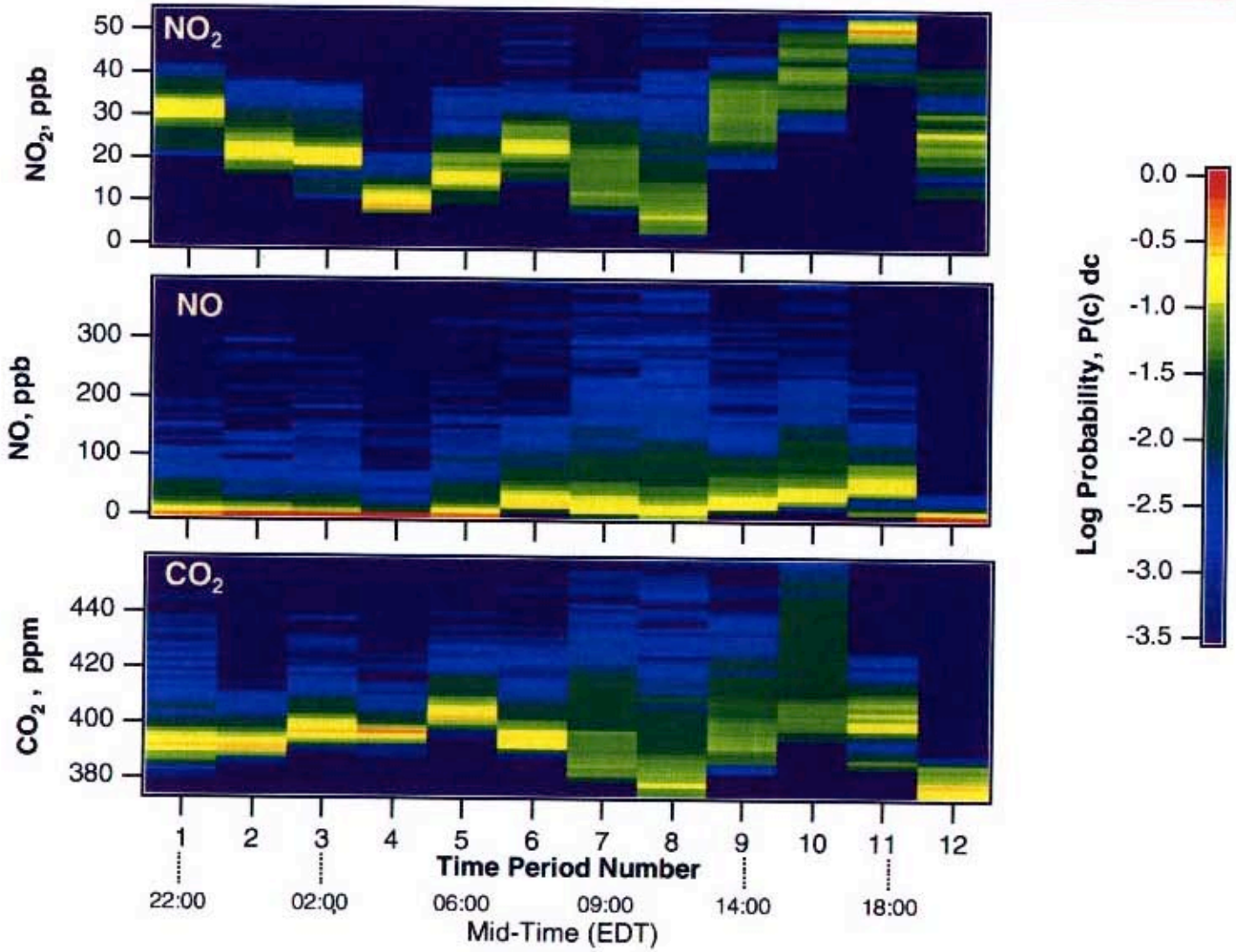
23:15 - 00:15 EDT
5:15 - 6:15
11:45 - 12:45
16:45 - 17:45

General Characteristics of Distributions

Directly Emitted Pollutants: Gaussian-like distribution with exponential tail

Secondary Pollutants: Little or no tail

Normalized Distributions of Pollutants



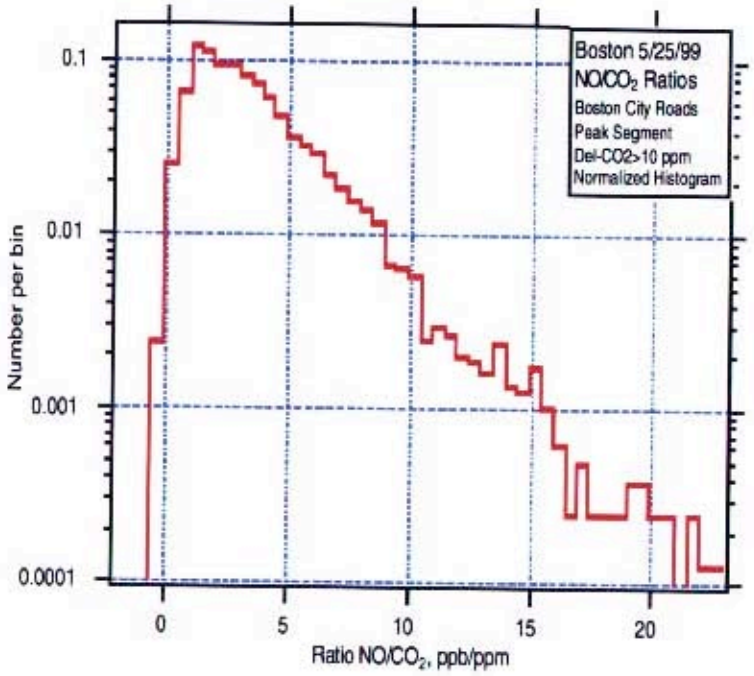
Distributions of NO and NO_2 Emissions Ratios: Boston

Mobile Data, Boston City Roads, May 25, 1999

"Peaks" Data Segment, CO_2 > 10 ppm Above Background

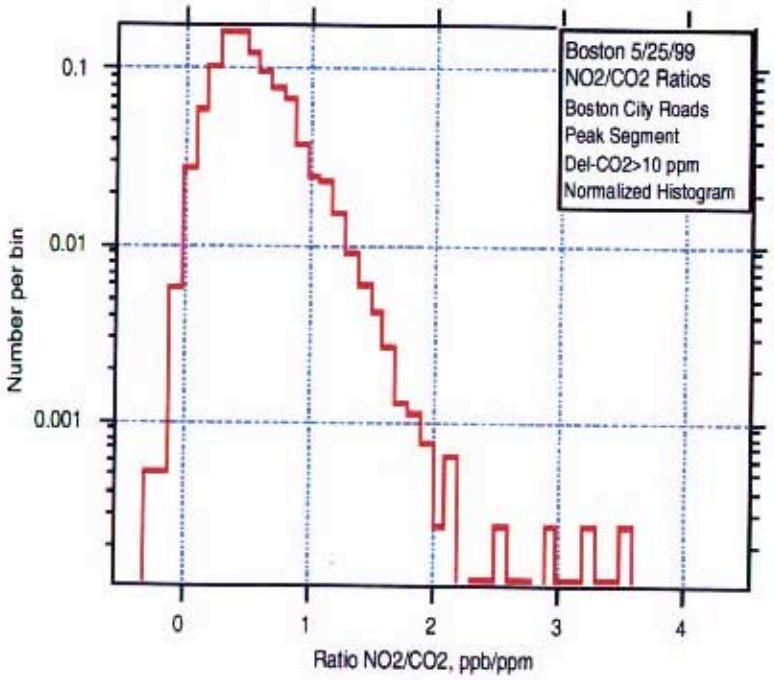
Average NO Emission Ratio

$\Delta NO / \Delta CO_2 = (3.59 \pm 2.77) \times 10^{-3}$



Average NO_2 Emission Ratio

$\Delta NO_2 / \Delta CO_2 = (0.56 \pm 0.33) \times 10^{-3}$



NO and NO_2 Emissions Ratios: Manchester, NH, 8/98

Mobile Data, Highways & Manchester City Roads, August 25 - 28, 1998

23 Data Segments, Highway vs. City
"Peaks" Data, Regression Slopes

Average NO Emission Ratios

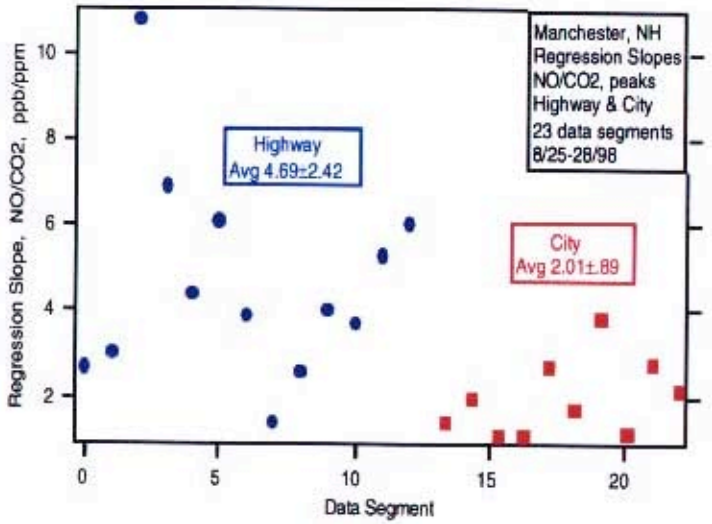
City: $(2.01 \pm 0.89) \times 10^{-3}$

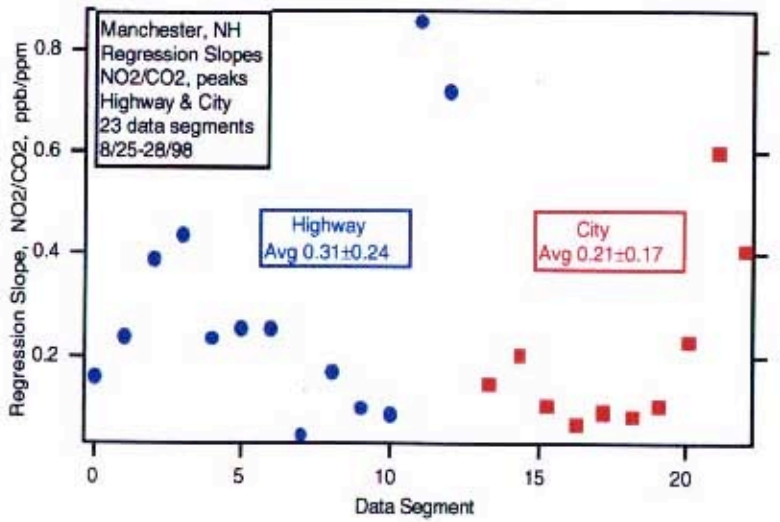
Hwy: $(4.69 \pm 2.42) \times 10^{-3}$

Average NO_2 Emission Ratios

$(0.21 \pm 0.17) \times 10^{-3}$

$(0.31 \pm 0.24) \times 10^{-3}$





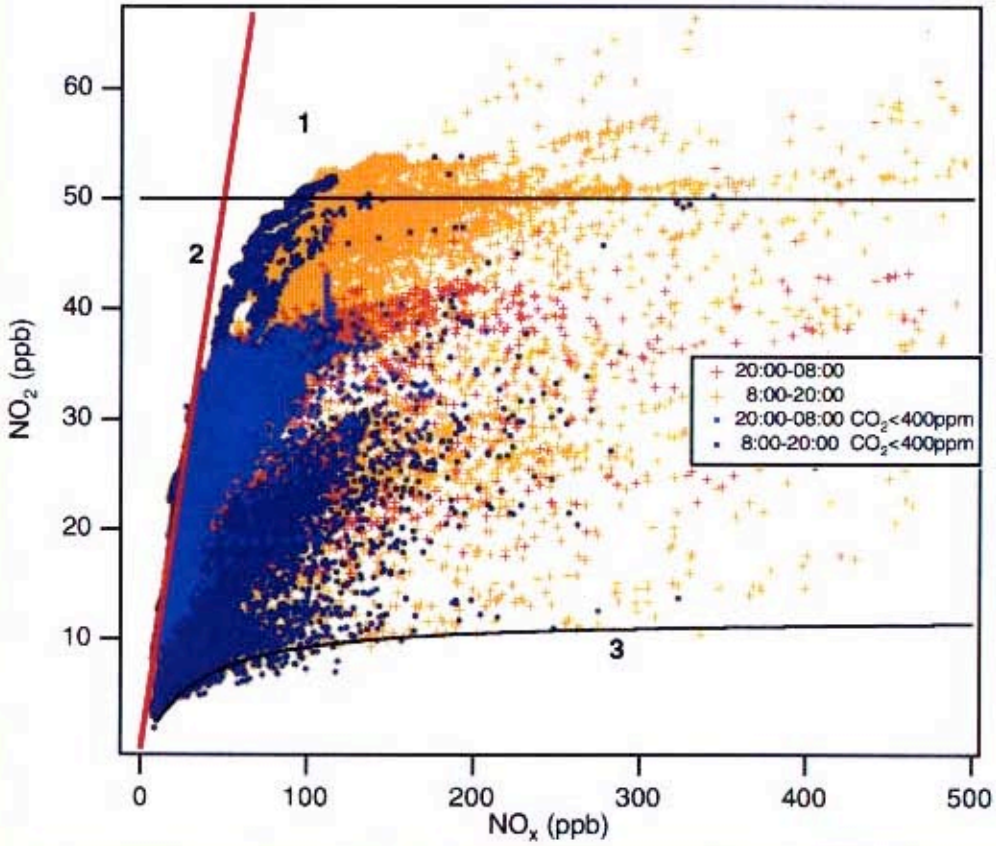
Observed Emission Ratios in Mobile Measurements

Regression slope, [Pollutant gas] / [CO_2]

CH_4	$1 - 2 * 10^{-3}$
CO	$1.5 - 4.5 * 10^{-2}$
N_2O	$5 - 13 * 10^{-5}$
NO	$1 - 10 * 10^{-3}$

Regression Slopes Vary with Location and Roadway Character

Relationship of NO_2 to Total NO_x in Urban Areas



May 27-28, 1999
20:00 - 20:00

Night-time limits:

Line 1. Maximum NO_2 -- All O_3 converted to NO_2

Line 2. All NO_x in form of NO_2

Daytime Limit

Line 3. Photostationary State Limit

$k_1 = 9.7 \times 10^{-3}\ sec^{-1}$

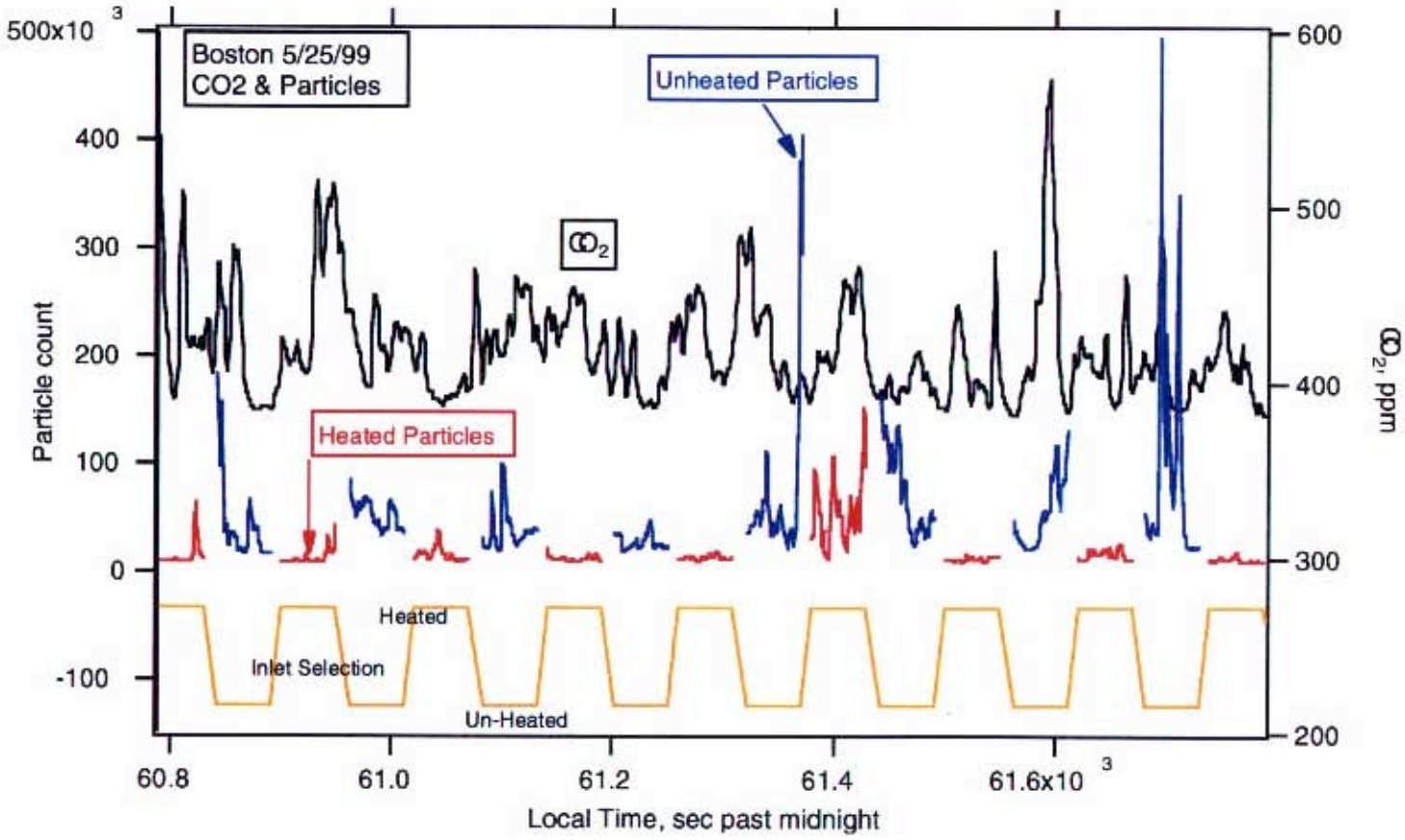
$k_3 = 3.6 \times 10^{-4}\ ppb^{-1}\ sec^{-1}$

Background NO, NO_2 and O_3 :

7, 2.5, and 9.5 ppb, resp.

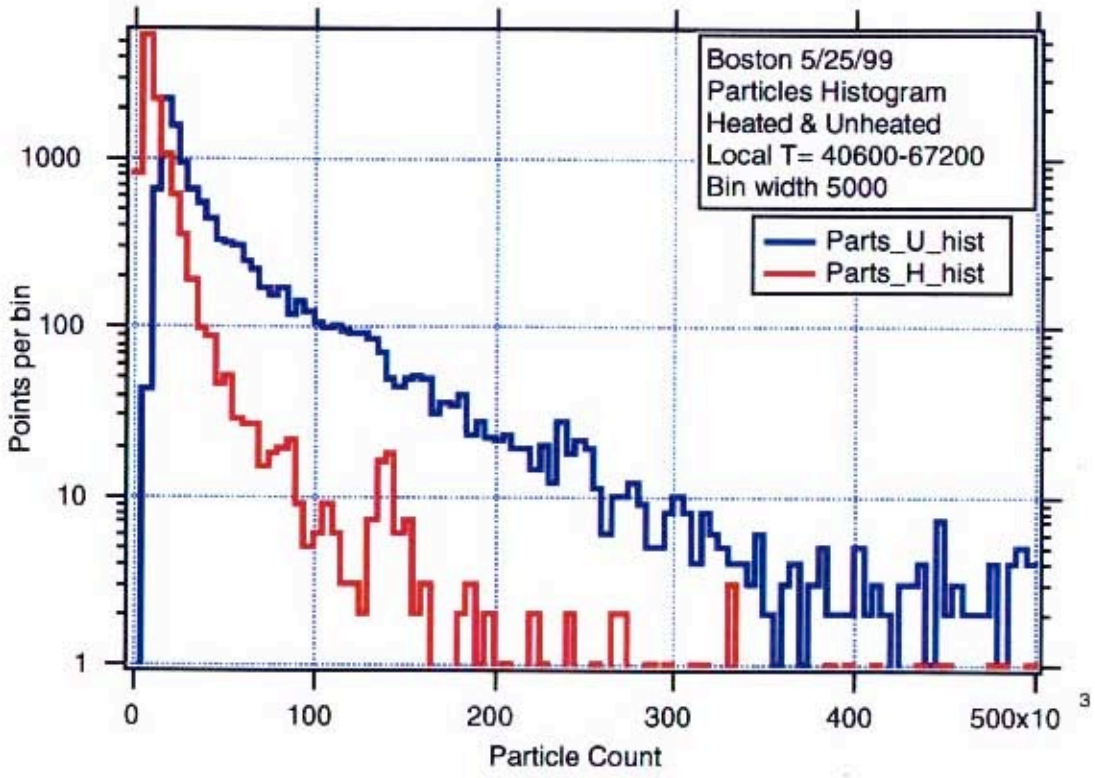
Mobile Particulate Measurements: Boston, May, 1999

Continuous 1 Hz fine aerosol measurements, along with trace gases.
TSI CN counter, 7 - 3000 nm diameter.
Switched Inlets: Unheated and Heated (300 °C) for volatile and non-volatile



Mobile Particulate Measurements: Boston, May, 1999

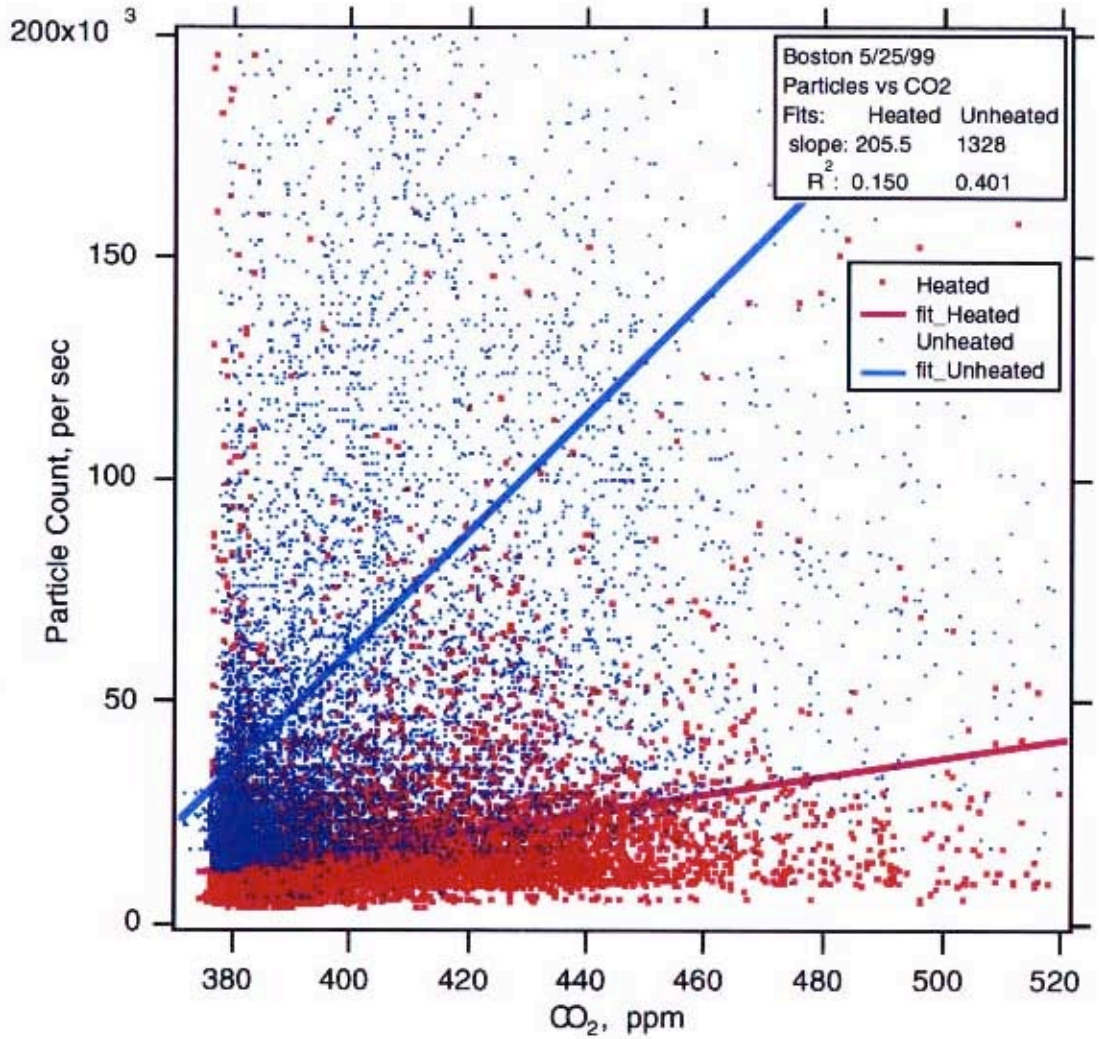
Distribution of Particle Counts



Mobile Particulate Measurements: Boston, May, 1999

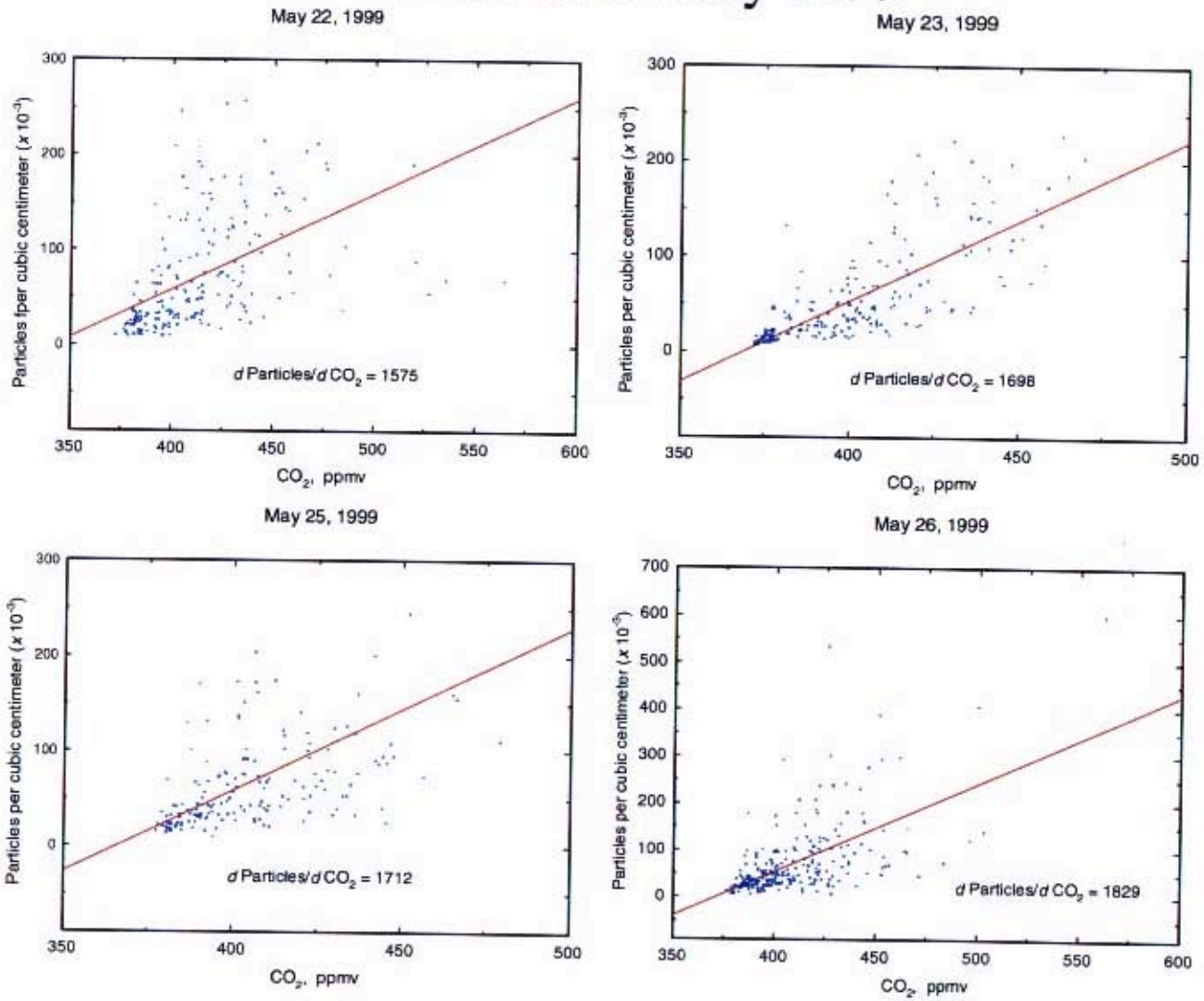
Correlation with CO_2

Correlation generally is weak but real.



Correlation of Total Fine Particle and CO_2

Boston area May 1999



1 HZ data presented as 1 minute averages

Mobile Measurements of Trace Gases: Initial Results

Separation of data into "Peaks" and "Local Background" allows analysis of emissions on different distance scales.

Narrow peaks are generally from local sources, usually motor vehicles.

Analysis of peaks gives vehicle emission ratios, e.g. for N_2O, NO, NO_2, CO.

Emission ratio, (pollutant / CO_2) relates emissions to fuel use, allowing extrapolation of vehicle fleet emissions.

Emissions determinations are available for real-world vehicle mix and driving conditions.

Local background is the local minimum between the peaks, which corresponds to mixed near-surface air, without local sources.

Local background data has been used in studies of wide-area trace gas correlations with land use.

Conclusions

- Spatial and temporal resolution of trace gas distributions in urban areas is critical for understanding
  - pollutant variability
  - human exposure to the pollutants
  - emission sources and strengths
- Observe concentration peaks from local sources + local minimum or background
- Automobiles dominate local sources

Conclusions

- **Distributions of mixing ratios**

  Directly Emitted Pollutants:

  - Gaussian band at low mixing ratios
  - Exponential tail from local sources

  Secondary Pollutants:

  - Narrower distributions
  - Little or no tail