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

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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]**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measures at 1 sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARI Zeeman-HeNe</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>ARI 2-Channel TDL</td>
<td>2 to 3 of: CO, O$_3$, N$_2$O, NO, NO$_2$, ...</td>
</tr>
<tr>
<td>Licor NDIR</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>WSU ECD</td>
<td>SF$_6$</td>
</tr>
<tr>
<td>UNH TSI</td>
<td>Condensation Nuclei</td>
</tr>
<tr>
<td>Trimble GPS</td>
<td>Position, Velocity</td>
</tr>
</tbody>
</table>

- **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**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic Sounder</td>
<td>Boundary Layer Height &amp; Wind Speed to 500 M</td>
</tr>
<tr>
<td>Tethered Balloon</td>
<td>Vertical Profiles of Gases</td>
</tr>
<tr>
<td>Canister Samplers</td>
<td>Higher Hydrocarbons</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>TRACE GAS</th>
<th>SPECTRAL REGION cm(^{-1})</th>
<th>DETECTION LIMIT ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2180</td>
<td>0.1</td>
</tr>
<tr>
<td>(\text{N}_2\text{O})</td>
<td>2200</td>
<td>0.1</td>
</tr>
<tr>
<td>NO</td>
<td>1900</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{NO}_2)</td>
<td>1630</td>
<td>0.3</td>
</tr>
<tr>
<td>(\text{CH}_2\text{O})</td>
<td>2803</td>
<td>1.0</td>
</tr>
<tr>
<td>(\text{SO}_2)</td>
<td>1370</td>
<td>1.0</td>
</tr>
<tr>
<td>(\text{O}_3)</td>
<td>1024</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Simultaneous NO, NO₂ and O₃ Measurements
Aug 22, 1996 Evening

![Graph showing concentrations of NO, NO₂, and O₃ over time.](image)
Completed Measurement Campaigns

Manchester, NH  Compact urban area

1) November 1997: Methods development: CH₄, CO₂


3) August 1998: Smog & Smog Precursors:
   NO, NO₂, O₃, UV + CO₂, Particulates

Boston, MA

4) May 1999: Smog & Smog Precursors:
   NO, NO₂, O₃, UV + CO₂, 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

NO$_2$ at AIRS site (g/sec)
Scatter Plot of $\text{N}_2\text{O}$ vs $\text{CO}_2$, Manchester, NH, 6/16/98

"Peaks" segment of data
$\Delta \text{N}_2\text{O}$ & $\Delta \text{CO}_2$

Highway & City Roads

Regression Slope,
$\Delta \text{N}_2\text{O} / \Delta \text{CO}_2 = (10.9 \pm 0.1) \times 10^{-5}$
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

- Manchester, NH, 6/16/98
- CO2 & N2O Data Segment
- with Trend-lines

- CO2 Trend Line
- N2O Trend Line
"Peaks" segment of data
ΔN₂O & ΔCO₂

Highway & City Roads

Require ΔCO₂ >15 ppm

For this data cut,
Regression Slope,
ΔN₂O / ΔCO₂ = (12.8 ± 0.3) x10⁻⁵
Distributions of $\text{N}_2\text{O}$ Emissions Ratios: Cross-Road & Mobile

Cross-Road Data:
1361 cars in California, 1996

Regression Slope,
$\Delta \text{N}_2\text{O} / \Delta \text{CO}_2 = (8.8 \pm 2.8) \times 10^{-5}$

Mobile Data: Mixed traffic,
Manchester, NH, 1998

Regression Slope,
$\Delta \text{N}_2\text{O} / \Delta \text{CO}_2 = (12.8 \pm 0.3) \times 10^{-5}$

For Highway Only,
Regression Slope,
$\Delta \text{N}_2\text{O} / \Delta \text{CO}_2 = (10.9 \pm 0.3) \times 10^{-5}$

For City Roads Only,
Regression Slope,
$\Delta \text{N}_2\text{O} / \Delta \text{CO}_2 = (15.6 \pm 0.3) \times 10^{-5}$
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

All data

Shaved Data

NO (ppb)
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

General Characteristics of Distributions

Directly Emitted Pollutants: Gaussian-like distribution with exponential tail
Secondary Pollutants: Little or no tail
Normalized Distributions of Pollutants

NO₂, ppb

NO, ppb

CO₂, ppm

Log Probability, P(x|dc)

Time Period Number

Mid-Time (EDT)

22:00 02:00 06:00 09:00 14:00 18:00
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**
\[
\Delta \text{NO} / \Delta \text{CO}_2 = (3.59 \pm 2.77) \times 10^{-3}
\]

**Average NO$_2$ Emission Ratio**
\[
\Delta \text{NO}_2 / \Delta \text{CO}_2 = (0.56 \pm 0.33) \times 10^{-3}
\]
NO and NO\textsubscript{2} Emissions Ratios: Manchester, NH, 8/98


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\textsubscript{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, \([\text{Pollutant gas}] / [\text{CO}_2]\)

- \(\text{CH}_4\) \(1 - 2 \times 10^{-3}\)
- \(\text{CO}\) \(1.5 - 4.5 \times 10^{-2}\)
- \(\text{N}_2\text{O}\) \(5 - 13 \times 10^{-5}\)
- \(\text{NO}\) \(1 - 10 \times 10^{-3}\)

Regression Slopes Vary with Location and Roadway Character
Relationship of NO$_2$ to Total NO$_x$ in Urban Areas

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
Distribution of Particle Counts

Boston 5/25/99
Particles Histogram
Heated & Unheated
Local T = 40600-67200
Bin width 5000
Mobile Particulate Measurements: Boston, May, 1999

Correlation with CO$_2$

Correlation generally is weak but real.
Correlation of Total Fine Particle and CO₂

Boston area May 1999

May 22, 1999

May 23, 1999

May 25, 1999

May 26, 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, $\left( \text{pollutant} / \text{CO}_2 \right)$ 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