Evaluation of Wintertime CO and NOx Emissions Inventories from the Treasure Valley PM2.5 Precursor Study

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Treasure Valley PM$_{2.5}$ Precursor Study

- Goal: To characterize atmospheric PM$_{2.5}$, precursor gases, and the relevant meteorology during typical wintertime conditions.
- Two month study in Boise, ID.
- Success!
  - >90% Data completeness for all but two instruments.
  - Sampled a significant wintertime stagnation event.
**Site Overview**

The site is bordered on the south by I-84. Downtown Boise is approximately 7 miles to the east and St. Luke’s Meridian Medical Center is located immediately west of the site.
MACL Instrumentation

**Aerosol**

Particle Size Distribution
- nano SMPS (3-60 nm) (Assembled in house with TSI components)
- long SMPS (40-700nm) (Assembled in house with TSI components)
- APS (0.6-20 um) (TSI)

Bulk Soluble Composition
- Particle-Into-Liquid Sampler – PILS (Brechtel)
- Inorganics (SO$_4^-$, NO$_3^-$, Cl, NH$_4^+$, Na, Mg, ...)
  by Ion Chromatography (Metrohm-Peak)
- Water soluble organic carbon by TOC analysis (Sievers / GE Analytical)

Cloud Condensation Nuclei (DMT)
Aerosol Spatial Variability and Optical Depth (Leosphere Aerosol Lidar)

**Meteorology**

P, T, RH, Wind speed & direction, Precip (Vaisala WXT)
Boundary Layer Height (Leosphere Aerosol Lidar)

**Trace Gases**

Ozone (Dasibi)
Carbon Monoxide (Aerolaser)
NO$_x$ / NO$_y$ (Air Quality Design)
SO$_2$ (Teledyne)
Time Resolved VOCs (PTR-MS, Ionicon)
Speciated VOCs (not deployed in Boise)
  - Varian GC-MS
  - Custom 2-channel VOC preconcentrator
Boise Winds

Wind Rose Plot:

Wind Speed Log Histogram:
Diurnal Average Profile of PBL Height and Aerosol Optical Depth, Dec-Jan
Normalized residence time for Treasure Valley air masses

10 meter height

50 meter height

Graphics courtesy of Ilias Kavouras of The Desert Research Institute and Idaho Department of Environmental Quality.
Use high resolution CO and NOx observations to evaluate emissions

• Parish et al. (2006) compared measured ratios of CO to NOx to emissions inventories.

• Measured CO to NOx ratios are much lower than emissions inventories.

• What is the situation in Boise?
Time series of CO and NOx during January 2009
Diurnal concentrations of automobile exhaust tracers and NO$_x$

![Graph showing diurnal concentrations of various automobile exhaust tracers and NO$_x$.](image)
• CO and NOx levels displayed little wind direction dependence.
• CO/NOx ratios were also not dependent on wind direction
Observed CO vs. NO$_x$ ratio for the entire monitoring period (90s data)

SLOPE $= 4.6 \pm 0.01$

$R^2 = 0.86$
Observed CO vs. NO\textsubscript{x} ratio during morning rush hour (5:00 am to 9:00 am)

SLOPE = 4.0 ± 0.02

R\textsuperscript{2} = 0.88
Diel variation of $\Delta$CO/$\Delta$NOx from Dec 2, 2008 to Jan 31, 2009

Average CO/NOx = 4.6
Standard Deviation = 0.6
max = 5.5; min = 3.4
Emissions generated for AIRPACT-3

- 76% CO emissions mobile
- 57% NOx emissions mobile
Measurement and AIRPACT-3 results for January 2009
AIRPACT-3 Total Emissions

AIRPACT-3 Mobile Emissions

SLOPE = 14.43 ± 0.13
$R^2 = 0.94$

SLOPE = 18.9 ± 0.09
$R^2 = 0.98$
Measured mixing ratios

AIRPACT-3 mixing ratios
Histogram of AIRPACT-3 and measured CO mixing ratios
Histogram of AIRPACT-3 and measured NOx mixing ratios

![Histogram of NOx mixing ratios](image-url)
## Emissions Ratio Summary:

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta$CO/$\Delta$NOx (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measurement</strong></td>
<td></td>
</tr>
<tr>
<td>Entire campaign high res.</td>
<td>4.6</td>
</tr>
<tr>
<td>Rush hour high res.</td>
<td>4.0</td>
</tr>
<tr>
<td>Rush hour median</td>
<td>3.6</td>
</tr>
<tr>
<td>Entire campaign 1hr avg.</td>
<td>4.6</td>
</tr>
<tr>
<td>IDEQ 1 hr</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>Model</strong></td>
<td></td>
</tr>
<tr>
<td>Mixing ratio results</td>
<td>13.8</td>
</tr>
<tr>
<td>Mobile emissions</td>
<td>18.9</td>
</tr>
<tr>
<td>Total Emissions</td>
<td>14.4</td>
</tr>
</tbody>
</table>
VOC Ratios for morning rush hour

Morning Rush Hour Benzene vs. NOx

- Benzene vs. NOx
- fit Benzene vs. NOx
- SLOPE = 0.0054 ± 0.0005
- \( R^2 = 0.77 \)

Morning Rush Hour Toluene vs. NOx

- Rush Hour Toluene vs NOx
- fit Rush Hour Toluene vs NOx
- SLOPE = 0.010 ± 0.001
- \( R^2 = 0.73 \)

Morning Rush Hour Benzene vs. CO

- BENZENE vs. CO
- fit BENZENE vs. CO
- SLOPE = 0.0013 ± 0.00005
- \( R^2 = 0.88 \)

Morning Rush Hour Toluene vs. CO

- Rush Hour Toluene vs CO
- fit Rush Hour Toluene vs CO
- SLOPE = 0.003 ± 0.0005
- \( R^2 = 0.88 \)
Conclusions:

• Model CO/NOx ratios are 3 to 4 times higher than observed.

• Histograms suggest that the emissions inventory captures NOx emissions better than CO emissions.

• How will this change with a new EI and/or with the new MOtor Vehicle Emissions Simulator 2010 (MOVES2010)?

• How do model ratios compare to observations for other species (VOC/NOx)?
Acknowledgements: We would like to thank IDEQ for support, NSF for funding the Mobile Atmospheric Chemistry Lab and NW-AIRQUEST for support of the AIRPACT forecast system.
Instrumentation:

NOx:
• Air Quality Design, Inc. two channel, high sensitivity, chemiluminescent NO detector.
• Molybdenum oxide catalytic converter on channel 1 (NOy).
• Solid state photolytic NO2 converter on channel 2 (NOx).
• Calibration in zero air with 5.03 ppmv ± 1.0% EPA NO standard from Scott Marrin, Inc.
• 90 second average

CO:
• Aero Laser AL5002 Fast CO Monitor.
• Span calibration with 0.250% ± 2% NIST traceable.
• 90 second average