Delray Monitoring Project

Air Toxics Monitoring Conference
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Mary Ann Heindorf, Amy Robinson, Michigan DEQ
Donna Kenski, LADCO
Ambassador Bridge
U.S. Rail Intermodal Traffic

Projected 2025 Intermodal Demand

<table>
<thead>
<tr>
<th></th>
<th>Demand (lifts/year)</th>
<th>Current Capacity (lifts/year)</th>
<th>Deficiency (lifts/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>495,000</td>
<td>776,000</td>
<td>150,000 to 431,000</td>
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Objectives

• Establish 2 new sites down wind of proposed DIFT and Ambassador Bridge areas
• Collect baseline data before and after DIFT is built
• Collect Speciated Organic Carbon at Newberry (downwind of DIFT) w/ eventual source apportionment objective (SA not included in this grant)
• Collect hourly measurements to ground truth SA results: BC, EC/OC, PM2.5 TEOM
• Continuous formaldehyde (precision, diurnal profiles, spatial variability)
## Leverage of Infrastructure to Assess Spatial Variability

<table>
<thead>
<tr>
<th>Site</th>
<th>Spec. OC</th>
<th>BC</th>
<th>Trace CO</th>
<th>PM2.5 TEOM</th>
<th>Cont. Form.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newberry</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Lafayette</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X (Planned)</td>
</tr>
<tr>
<td>Dearborn (NATTS)</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X (Planned)</td>
</tr>
<tr>
<td>Allen Park (STN)</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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</table>
Site Locations

Study Area
Newberry School (261630038)

- Speciated OC includes EC/OC ions & metals (J. Shauer)
- Hrly EC/OC (Sunset)
- BC (small spot)
- Trace CO
- PM2.5 TEOM (no FDMS)
- Met
- PM2.5 FRM
- Cont. Formaldehyde (planned, not yet deployed. When deployed 24-hr carbonyls via TO-11A will be added)
Lafayette St (261630039)

- PM2.5 TEOM (FDMS)
- PM2.5 TEOM
- BC
- Trace CO
- PM2.5 FRM
- Met
Breaks in at Newberry: September 2005

• Incomplete year speciated OC
• Missing months never to be regained
• Monitoring in 2006- Newberry
  – Temporal variability in speciated OC
  – June, July & August 2005 & 2006 Newberry
• Allen Park & Dearborn
  – Use archived STN to determine speciated OC
  – Mo Composites June, July, Aug 2005 & 2006
Newberry Source Apportionment

• Will be performed in 2008 as part of a community monitoring grant investigating the impact of temporal and spatial variability on source apportionment results

• Allen Park, Dearborn & Newberry data used
Nonparametric Regression of BC, EC, and OC data at Newberry and Lafayette

- Black carbon/elemental carbon surrogate measures for diesel
- Nonparametric regression uses high-time-resolution data to identify areas associated with high concentrations.
- Only ambient data used – no emissions information
- Model regresses concentration on wind direction and speed (as x,y vectors) to locate areas associated with peak concentrations (i.e., source locations)
- Kernel density estimate, weighted by no. of observations
- Like a moving average, but with a smoothing parameter

\[
\overline{C}(X_i, Y_j) = \frac{\sum_k K\left(\frac{X_j - x_k}{h}\right) K\left(\frac{Y_j - y_k}{h}\right) c_k}{\sum_k K\left(\frac{X_j - x_k}{h}\right) K\left(\frac{Y_j - y_k}{h}\right)}
\]

Where K is the Epanechnikov kernel (or Gaussian) and h is the smoothing parameter.
Allen Park 1-Hr Black Carbon, ug/m³

Jan 2005 – Dec 2006

Wind Direction
Kernel function $K$ weights observations at middle of window more heavily than observations at the edges.

Smoothing parameter $h$ determines the size of the window.
Allen Park 1-Hr Black Carbon, ug/m³
Jan 2005–Dec 2006
Allen Park 1-Hr Black Carbon, ug/m³

Jan 2005–Dec 2006

Wind Direction
Allen Park 1-Hr Black Carbon, ug/m³

Jan 2005–Dec 2006
Allen Park 1-Hr Black Carbon, ug/m³

Jan 2005 – Dec 2006

Wind Direction
Allen Park 1-Hr Black Carbon, ug/m³

Jan 2005–Dec 2006
Newberry aethalometer data – points very specifically to intermodal freight terminal (1 hr data, 2006)
FIA aethalometer data points very specifically to Ambassador Bridge (1-hr data, 2006 annual)
Newberry continuous EC data – identifies same intermodal freight terminal as BC data
Newberry continuous OC data – also identifies freight terminal as source of OC
(surprising considering that much OC is secondary and from area sources --point sources not expected to show up)
Continuous Formaldehyde Units

Alpha Omega Power Technologies, Inc
Albuquerque New Mexico
Peristaltic pump

H2O

Mixing chamber

Accurate Directional Markers

Acetyl Acetone

2,4 pentanedione

Detector

Electronics

Scrubber is underneath
Chemical Reaction

$2 \text{CH}_3\text{COCH}_2\text{CO}_3 + \text{HCHO} + \text{NH}_3$

2,4 pentanedione  formaldehyde  ammonia

3,5 diacetyl 1,4 dihydrolutidine  
(yellow chromophore)

$\lambda_{ex} = 412 \text{ nm}$

$\lambda_{em} = 410 \text{ nm}$
Formaldehyde Units

• Goals:
  – Assess inter sampler precision: 6 + weeks
  – Deploy to Newberry & Dearborn NATTS site
    • Spatial variability
    • Diurnal trends
    • Compare w/ other hourly parameters
    • Nonparametric regression
    • Method comparison (24-Hr TO-11a)
    • Short term analysis of risk
Timeline

• November 2004 – receive units
• 2005 – ship Permeation source back for repair
• 2005-6 – ship units back for repair – 3x
  – It took 6 mo. for first repair (3/18/05 to 9/20/05)
  – May 2006 Send Amy to NM – training at Alpha Omega’s facility
  – More repairs 1/23/06 to 12/21/06 – units received were broken & returned immediately
  – December 2006 – units are driven to Michigan from New Mexico!

• 2007 – Team approach to operation
  – June 2007 – scrubber sent back for repair
  – Unit operational 7/26/07
Shipping - Related Issues

Broken Bracket allowing detector to flop around during shipment

Crimped Line

Permeation source shipping crate
Other issues

- Broken Inlet
- Crushed scrubber tubing
- More Reagent Leaks
- Reagent Leaks
2007 Plan of attack

- Learn how to troubleshoot units – use software in diagnosis
- How to quickly change out tubing without line blowouts & floods
- Determine how to minimize bubbles
- Generate stable baselines
- Assess intra and inter sampler precision of liquid system with liquid injections of formaldehyde
- Is the precision reproducible from day to day?
  - Challenge with gas phase formaldehyde
  - Determine accuracy
  - Adjust set points for calibration curves
  - Collect co-located data
  - Deploy to two sites in the field
Unit 2002-05
Utility of Software: Unit 2 Only

A: 5/11/07
B: 3/9/07
C: 3/20/07
D: 7/23/07
Liquid Mode of Operation: Like a Chromatograph
Response of Both Continuous Formaldehyde Units to Liquid Formaldehyde Injections on 9/4/07

Unit 5 = Green
Unit 2 = Purple

y = 9.3437x - 2.9464
R² = 0.9784

y = 1.028x + 4.3157
R² = 0.9075
Response of Both Continuous formaldehyde Units to Liquid Formaldehyde Injections on 9/7/07

Vertical bars are 95% Confidence Intervals

y = 18.7x - 11.296
R² = 0.9959

y = 15.993x - 9.6689
R² = 0.9964

Conc of liquid soln, ppb

Response, ppb
Gaseous Calibration Curve Unit 5

y = 0.0678x + 0.2242
R^2 = 0.9991
Gaseous Calibration Curves Unit 2

Calibration Curve 2000-02: Pump Tubing Change Out

y = 0.0952x + 1.0106
R² = 0.9608

y = 0.0901x + 0.8198
R² = 0.9601

2/8/2007
2/1/2007
Linear (2/8/2007)
Linear (2/1/2007)
Hourly Formaldehyde Concentrations: September 6 to 9, 2007 at Filley St

LEAK in Unit 2
Magnitude of Daily 24-Hr Averages: Encouraging

TO-11A Dearborn: 2001

Continuous Unit: Filly St: 2007
Factors Contributing to Sensitivity

• Bubbles impacted by fittings/ leaks
• Flow Rates impacted by peristaltic pump tubing age
• Freshness of DI H2O *(and storage location – not in trailer!)*
• Zero/ baseline settings – impacted by solutions
• Filters – impact flow rates
• Integrity of tubing/ plumbing system/ back pressure
General Lessons Learned

• Team work essential – site location, access negotiation, POWER INSTALLATION, site set up
• Communication + data sharing – ie non parametric regression
• Partnerships – Region 5 EPA
• Control scope of grant – split large projects
Lessons Learned - Formaldehyde

• Team approach to complex instrumentation
• **Patience and time spent with the units is invaluable**
• Don’t believe what the manual says
• Software is a valuable tool in diagnosing problems
• Need to create our own manual that links software displays with performance
• Will likely need to rebuild units w/ syringe pumps
Suggested Modifications to Formaldehyde Units

• Replace peristaltic pumps with syringe pumps eliminating the need for tubing change outs
• Electronic controls of flow rates?
• Configure flush ports to front of unit so 1 user can flush and see detector output
• Larger fluid reservoirs housed AWAY from electronics, chilled if necessary
• Relocate scrubber ABOVE & AWAY from solvents
• Software should allow users more control over screen formatting
Will the Work Continue?

Assuming adequate funding & FTE’s etc:

- If/when DIFT is built, it will be important to assess the environmental impact
- The Newberry and FIA sites have been rated by DEQ mgmt as some of the most critical locations in the network, valuable data
- Progress is continuing with the formaldehyde monitors
Acknowledgements

• Matt Landis ORD: Loan of BC & TEOM
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