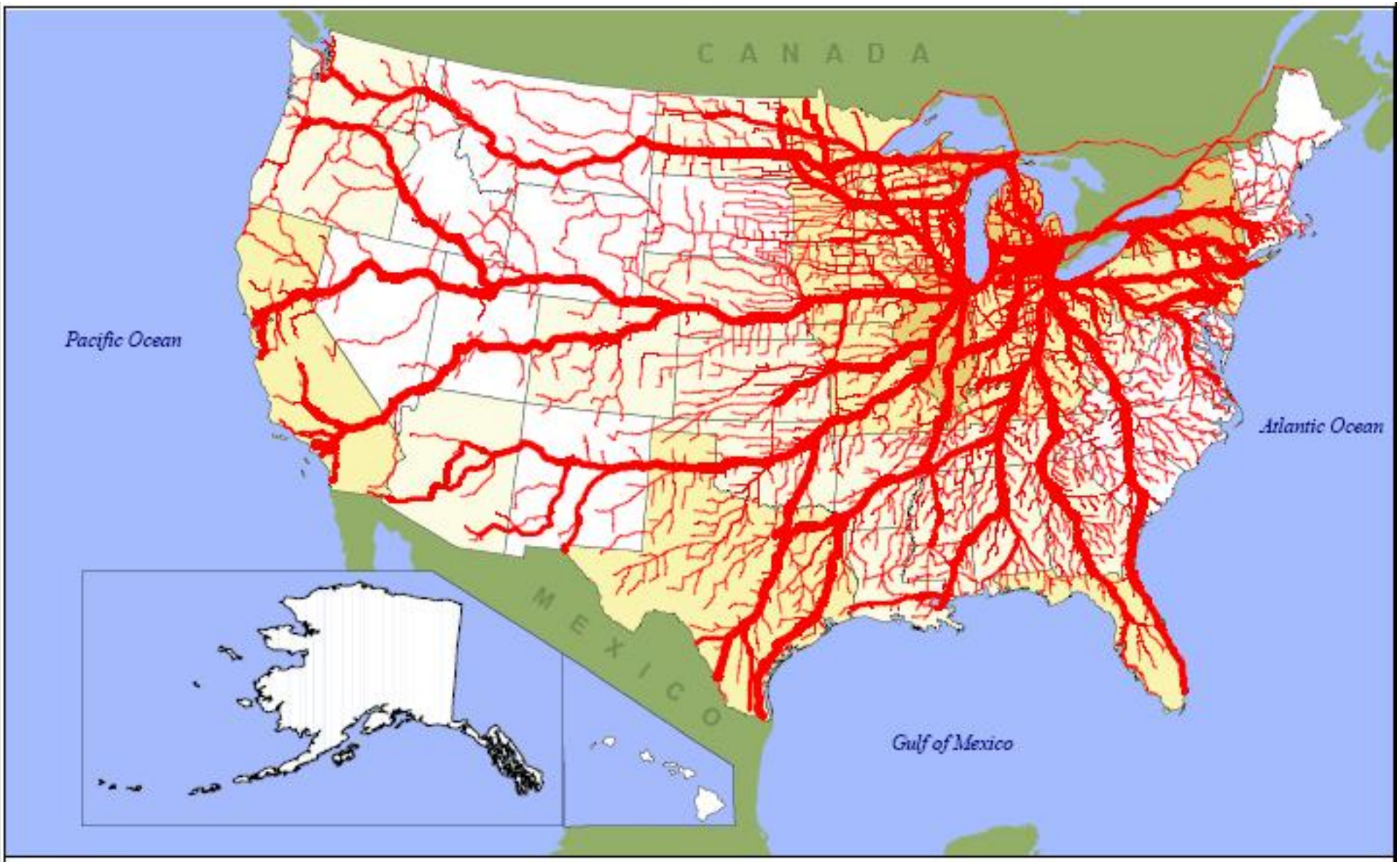
Delray Monitoring Project

Air Toxics Monitoring Conference

October 2 – 4, 2007 Rosemont IL

Mary Ann Heindorf, Amy Robinson, Michigan DEQ
Donna Kenski, LADCO



U.S. Department of Transportation
Federal Highway Administration
Office of Freight Management and Operations
Operations Core Business Unit

MICHIGAN

Total International Truck Flows
(1998)

Network Flows
(Tons)

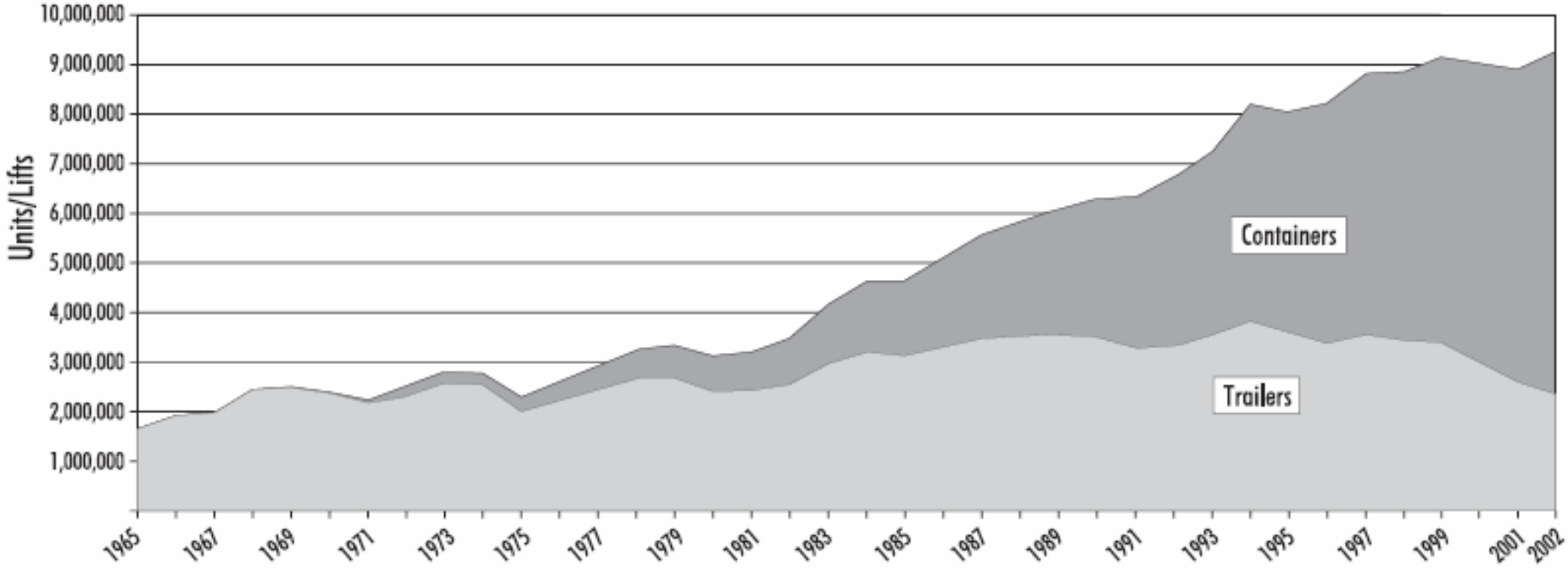
- 0 - 25,000
- 25,001 - 100,000
- 100,001 - 250,000
- 250,001 - 500,000
- More than 500,000

State to State Flows
(Tons)

- 0 to 250,000
- 250,001 to 1,000,000
- 1,000,001 to 5,000,000
- More than 5,000,000

Ambassador Bridge

U.S. Rail Intermodal Traffic

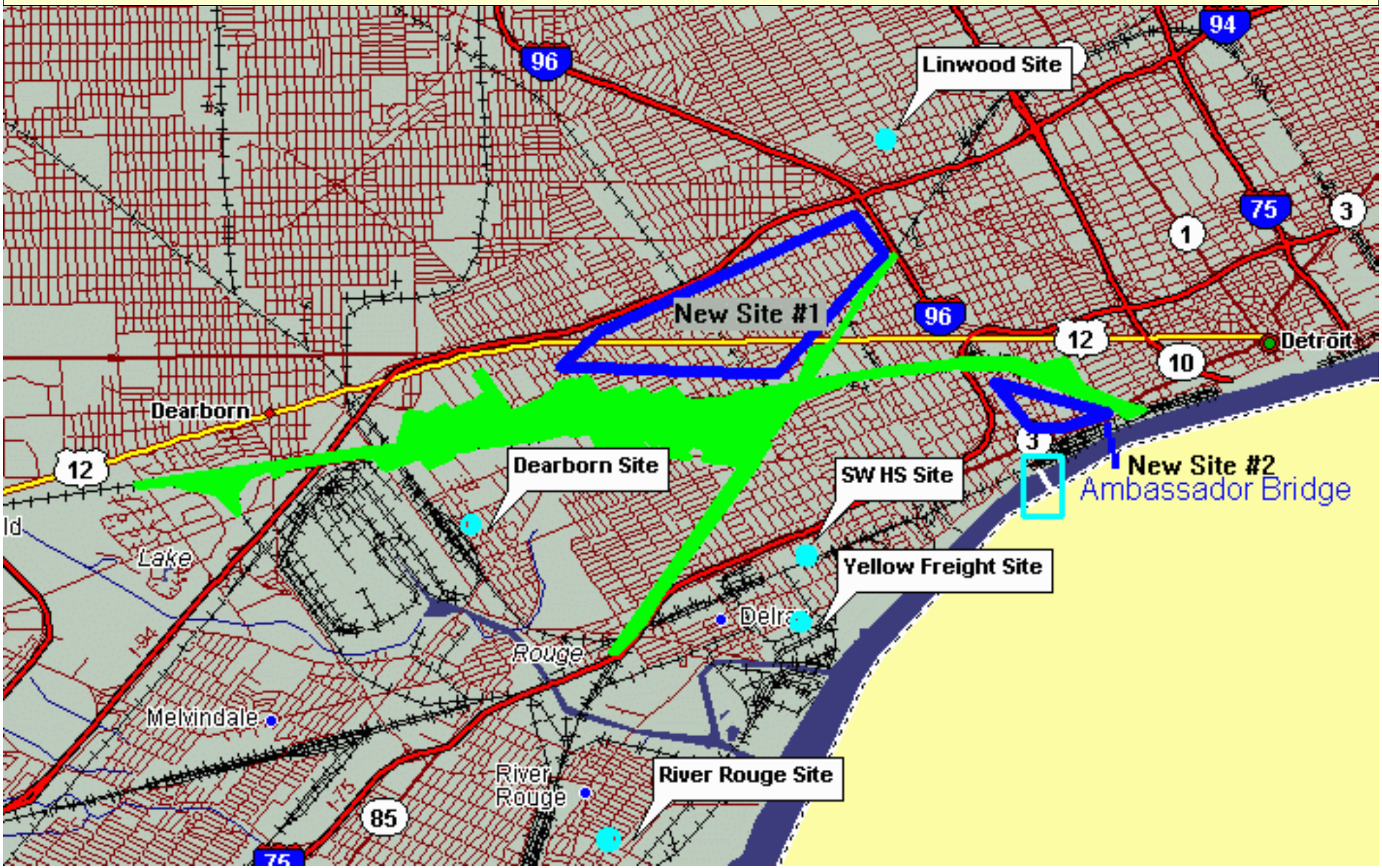


SOURCE: AAR. Container

Projected 2025 Intermodal Demand

	Demand (lifts/year)		Current Capacity (lifts/year)	Deficiency (lifts/year)
	Low	High		
Total	495,000	776,000	345,000	150,000 to 431,000

Proposed Location of Livernois Junction of DIFT



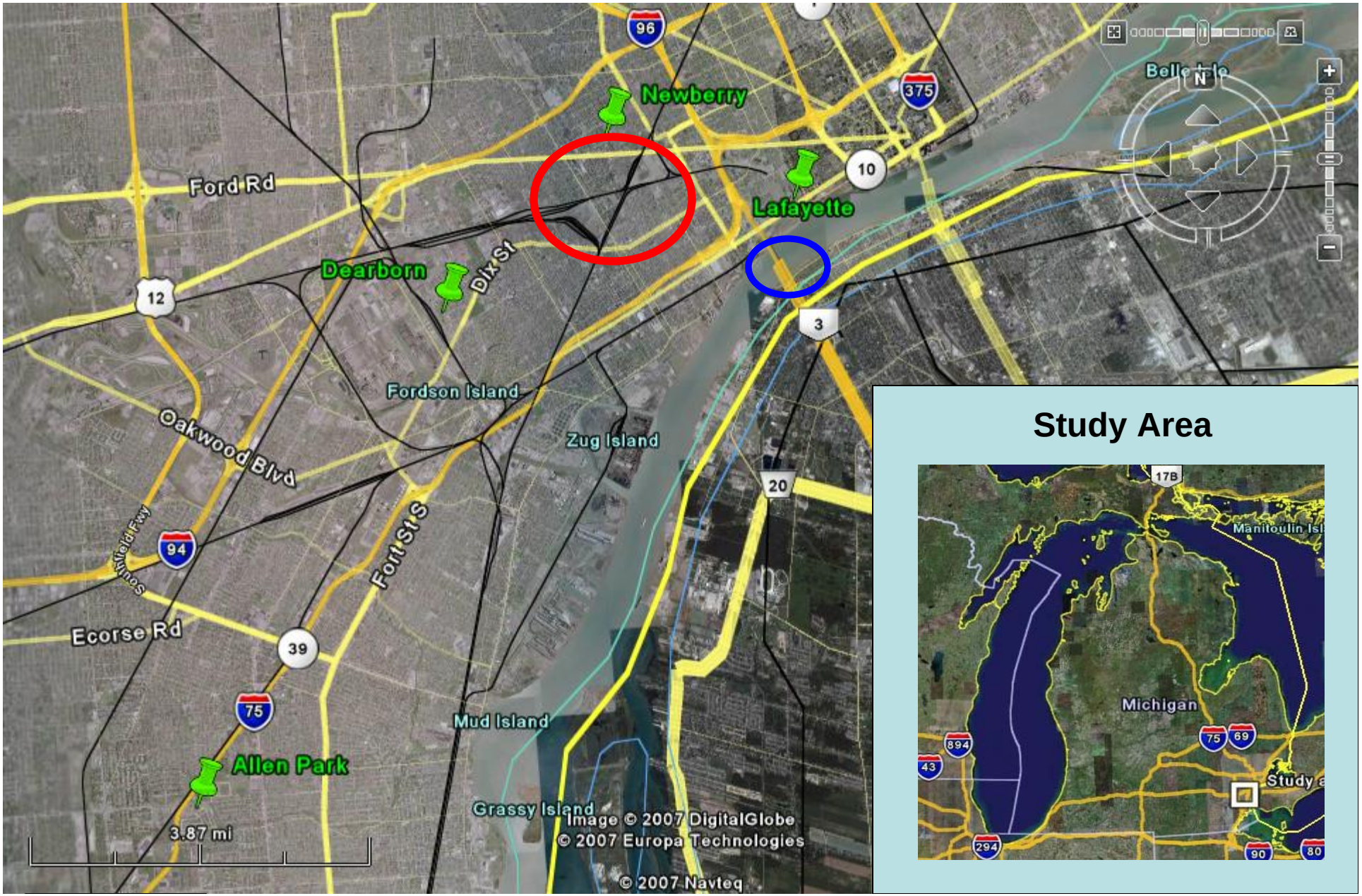
Objectives

- 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

Site	Spec. OC	BC	Trace CO	PM2.5 TEOM	Cont. Form.
Newberry	X	X	X	X	X (Planned)
Lafayette		X	X	X	
Dearborn (NATTS)	X	X		X	X (Planned)
Allen Park (STN)	X	X		X	

Site Locations



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

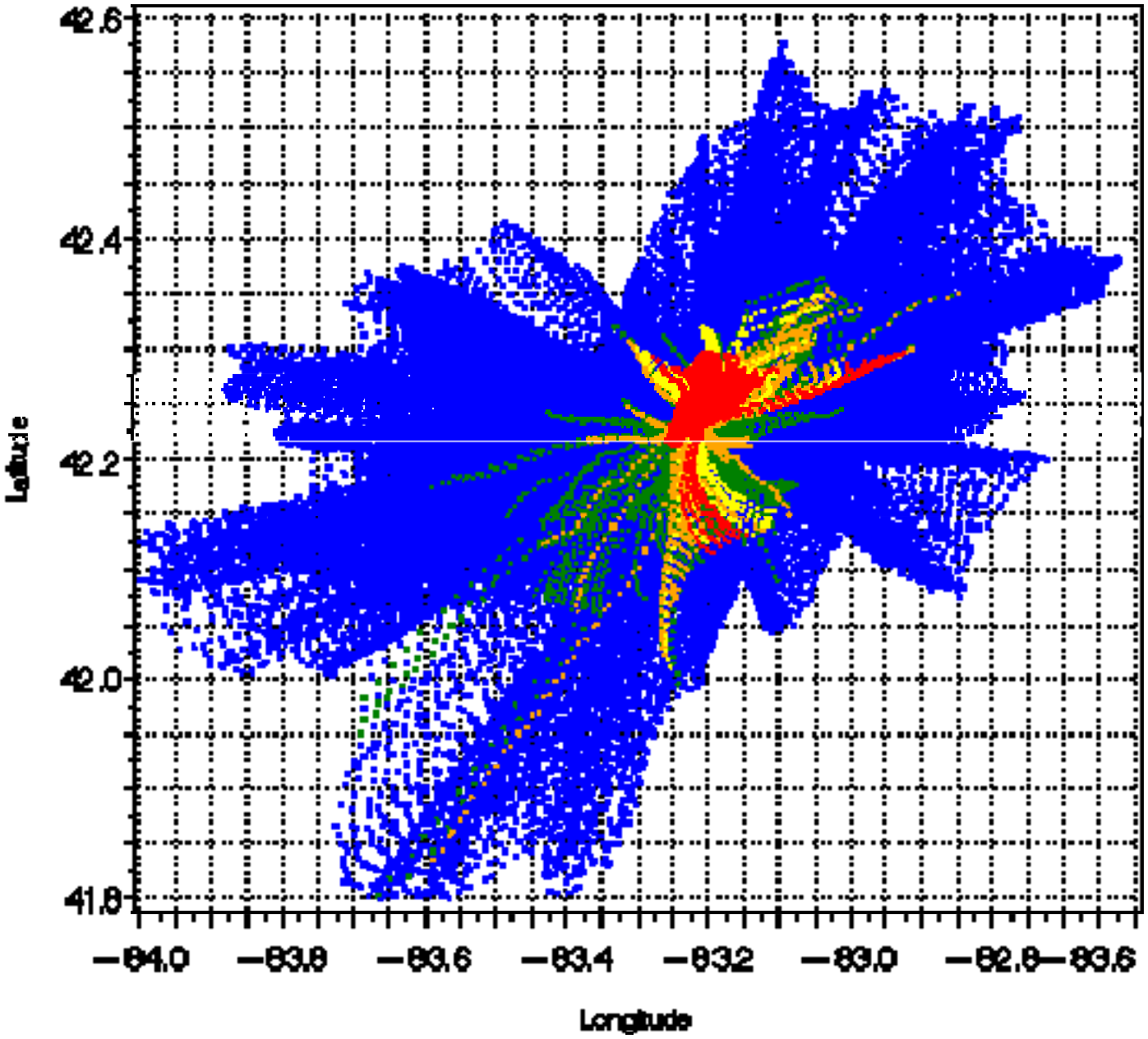
Nonparametric Regression of BC, EC, and OC data at Newberry and Lafayette

- 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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42.4
42.2
42.0
41.8
Latitude
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-83.8
-83.6
-83.4
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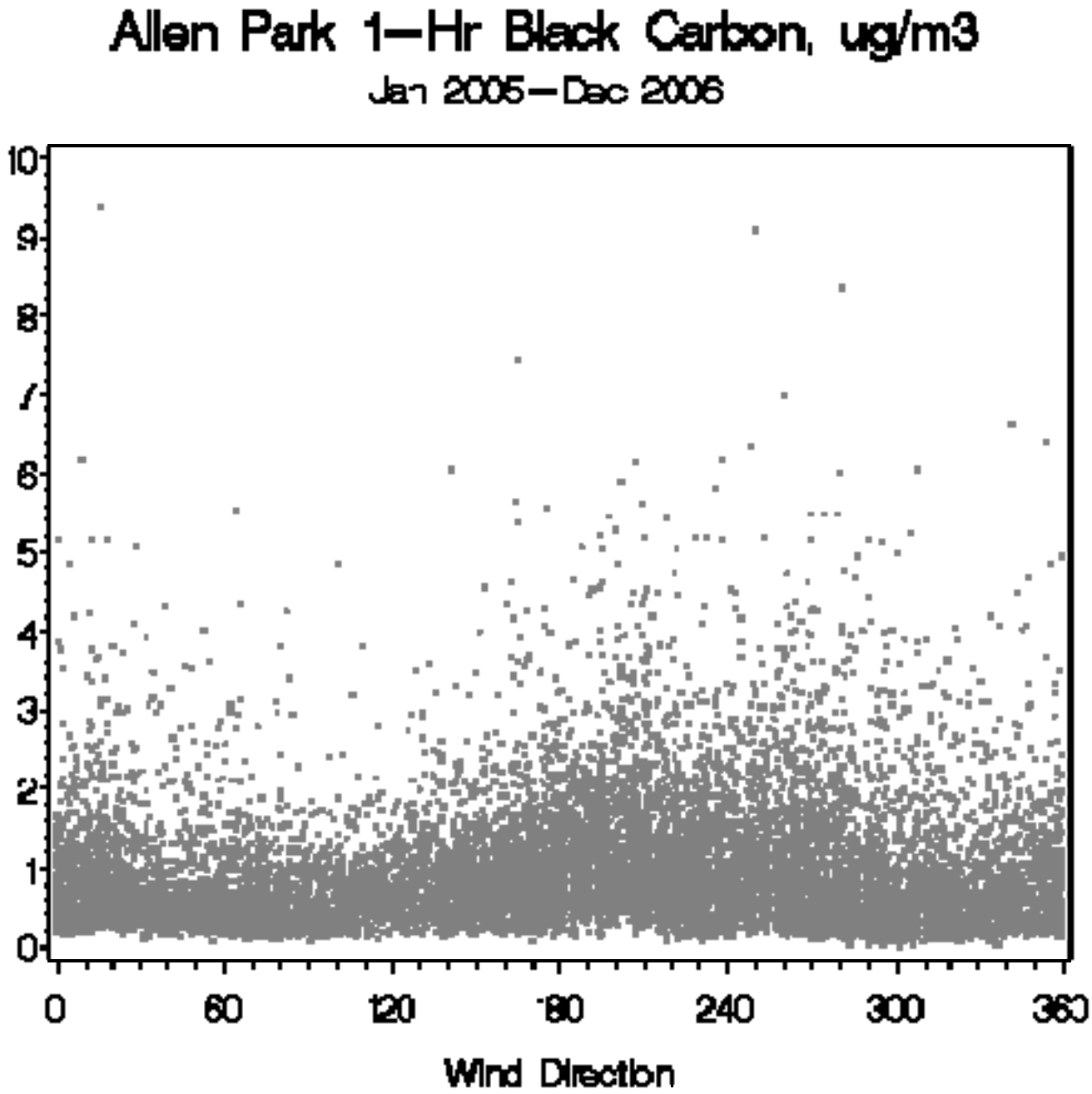
-82.8
-83.6
Longitude


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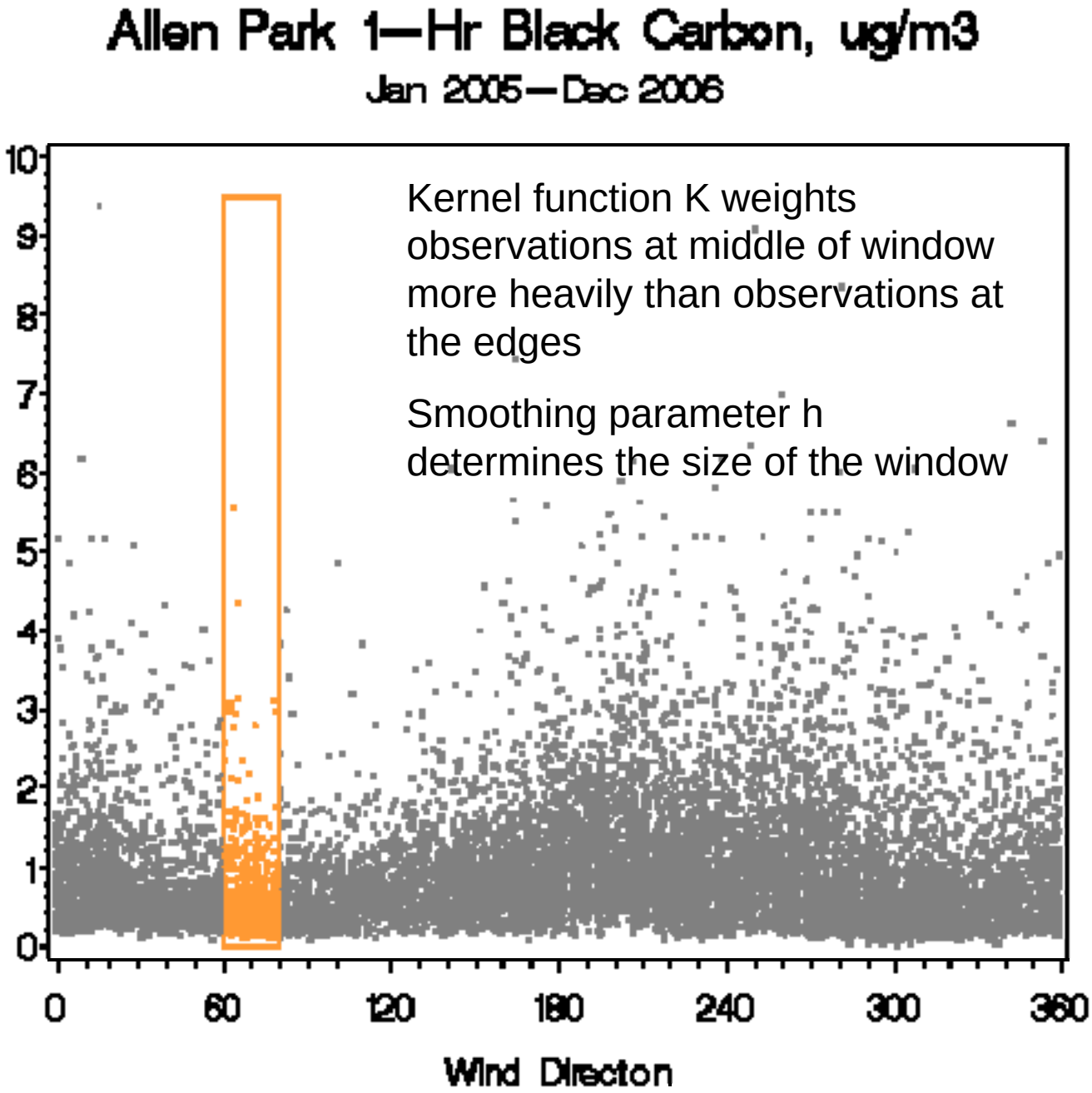
Wind Direction


Allen Park 1—Hr Black Carbon, ug/m3
Jan 2005—Dec 2006
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
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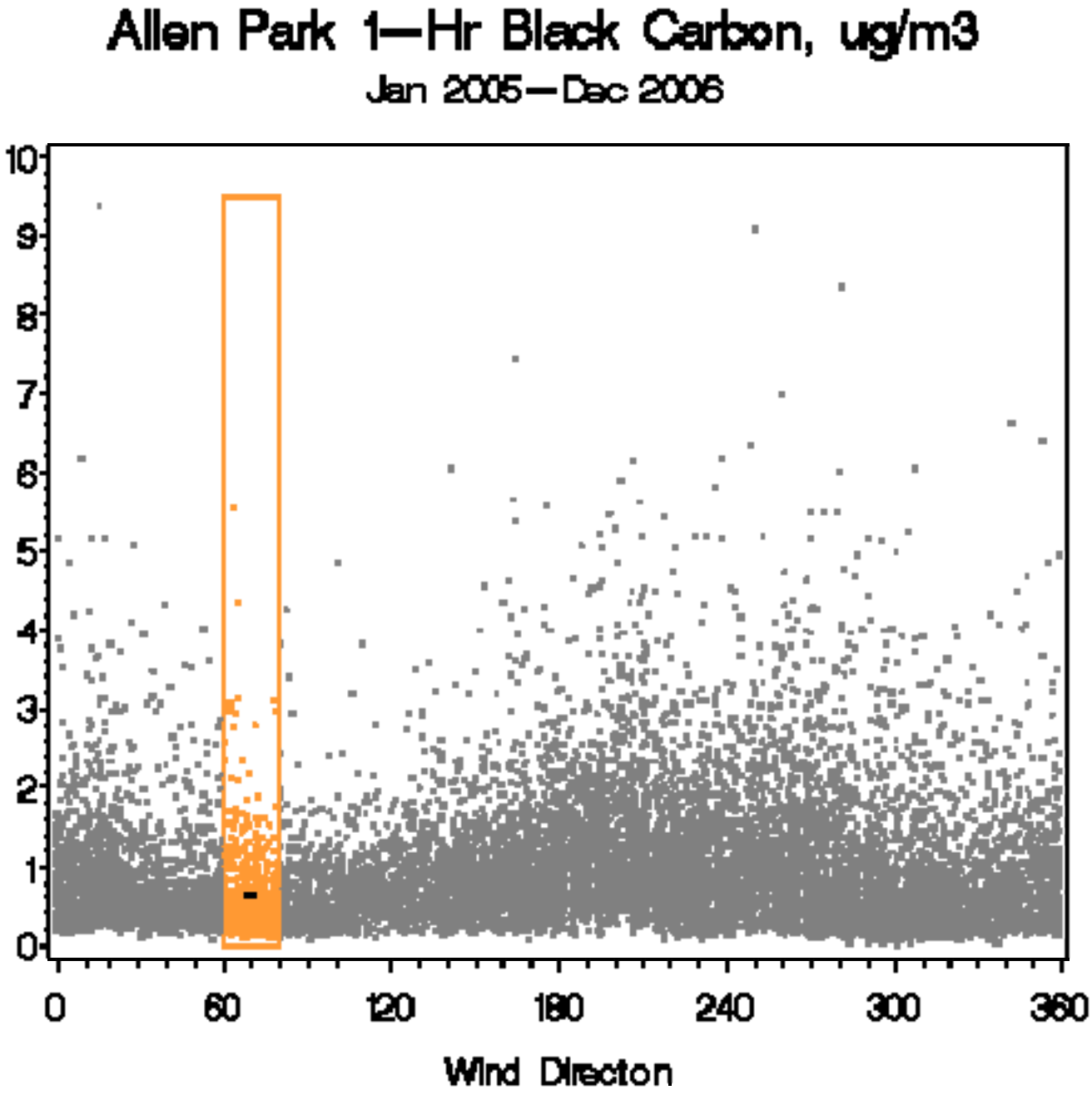
Wind Direction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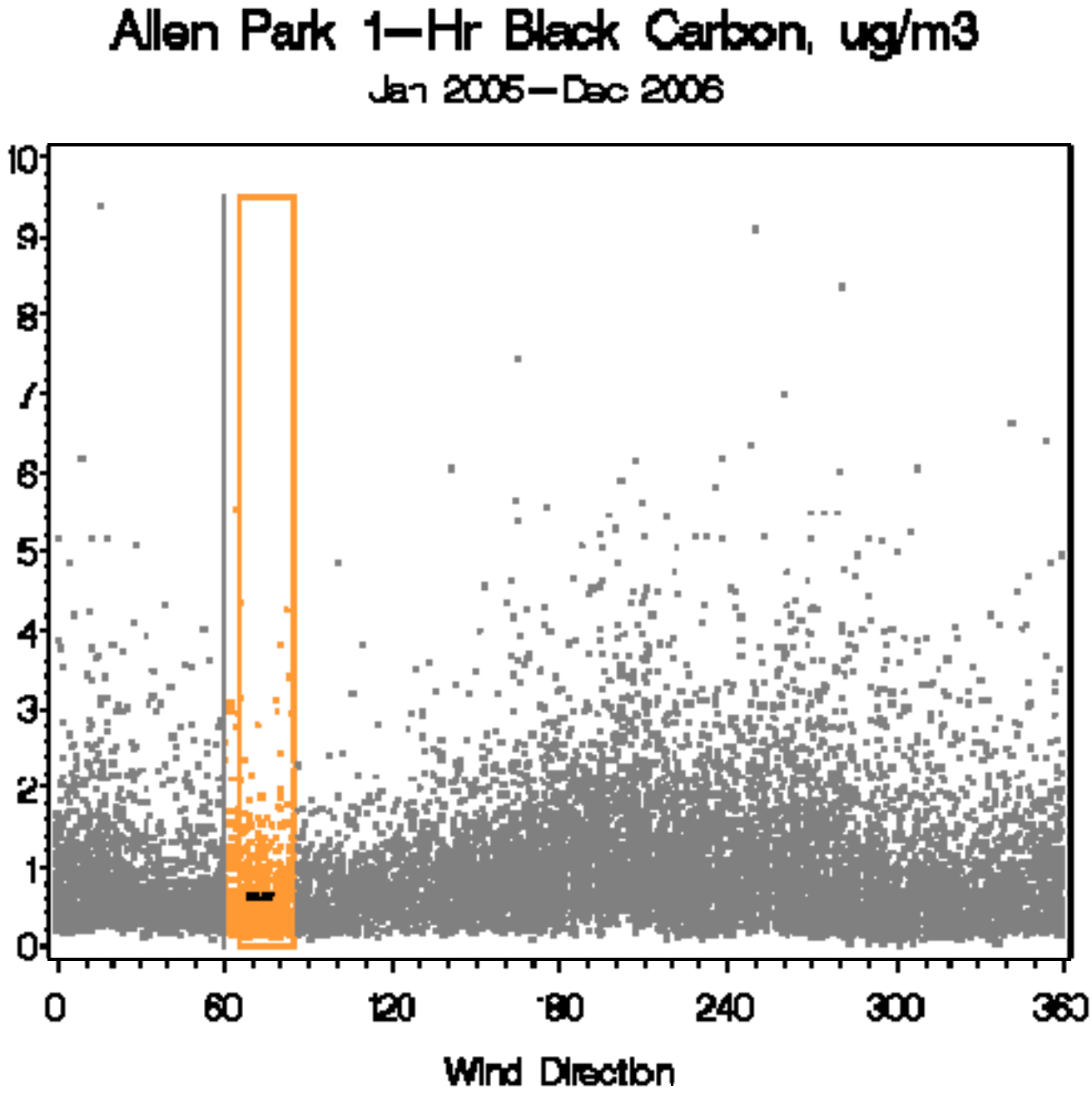
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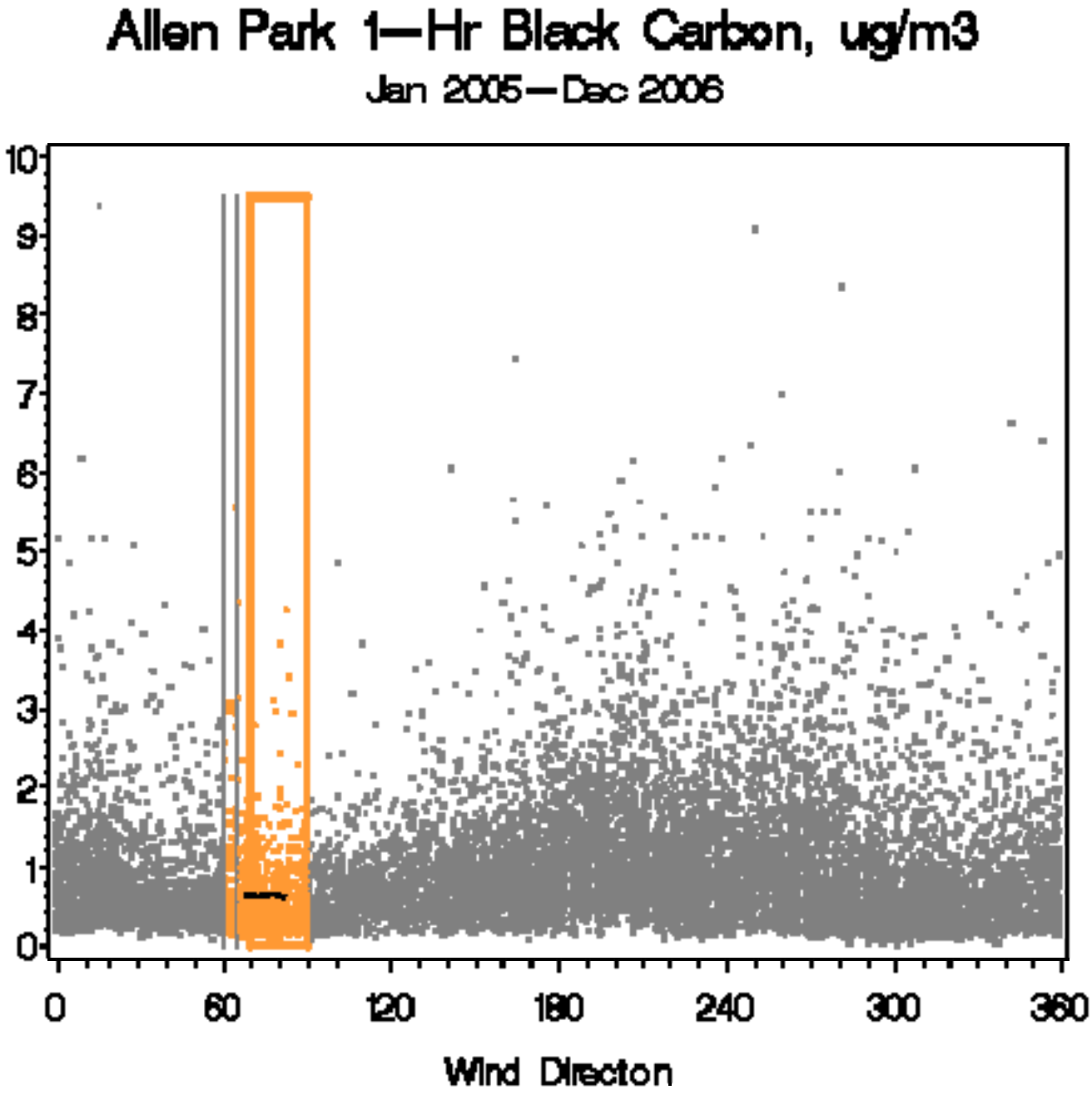
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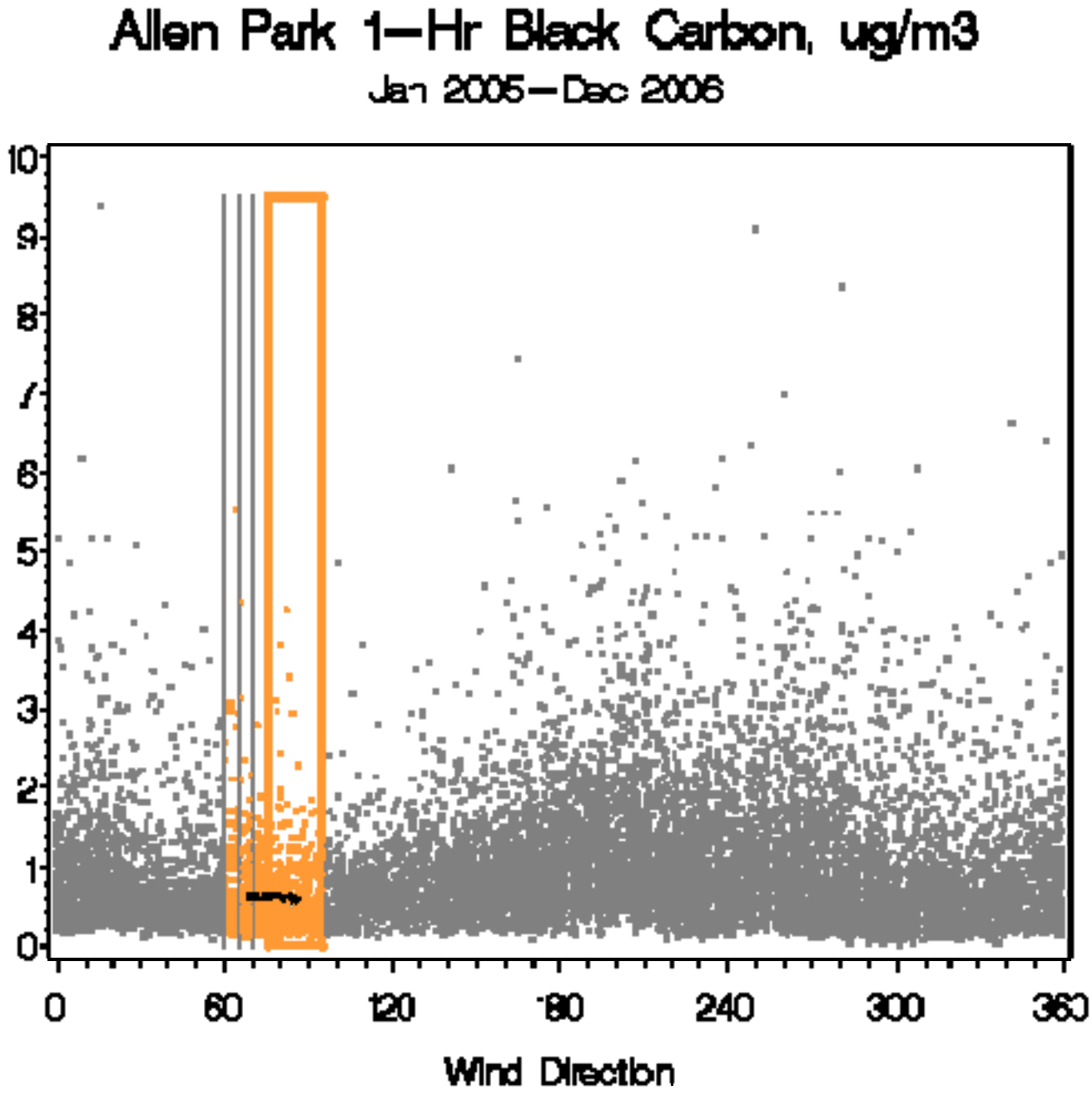
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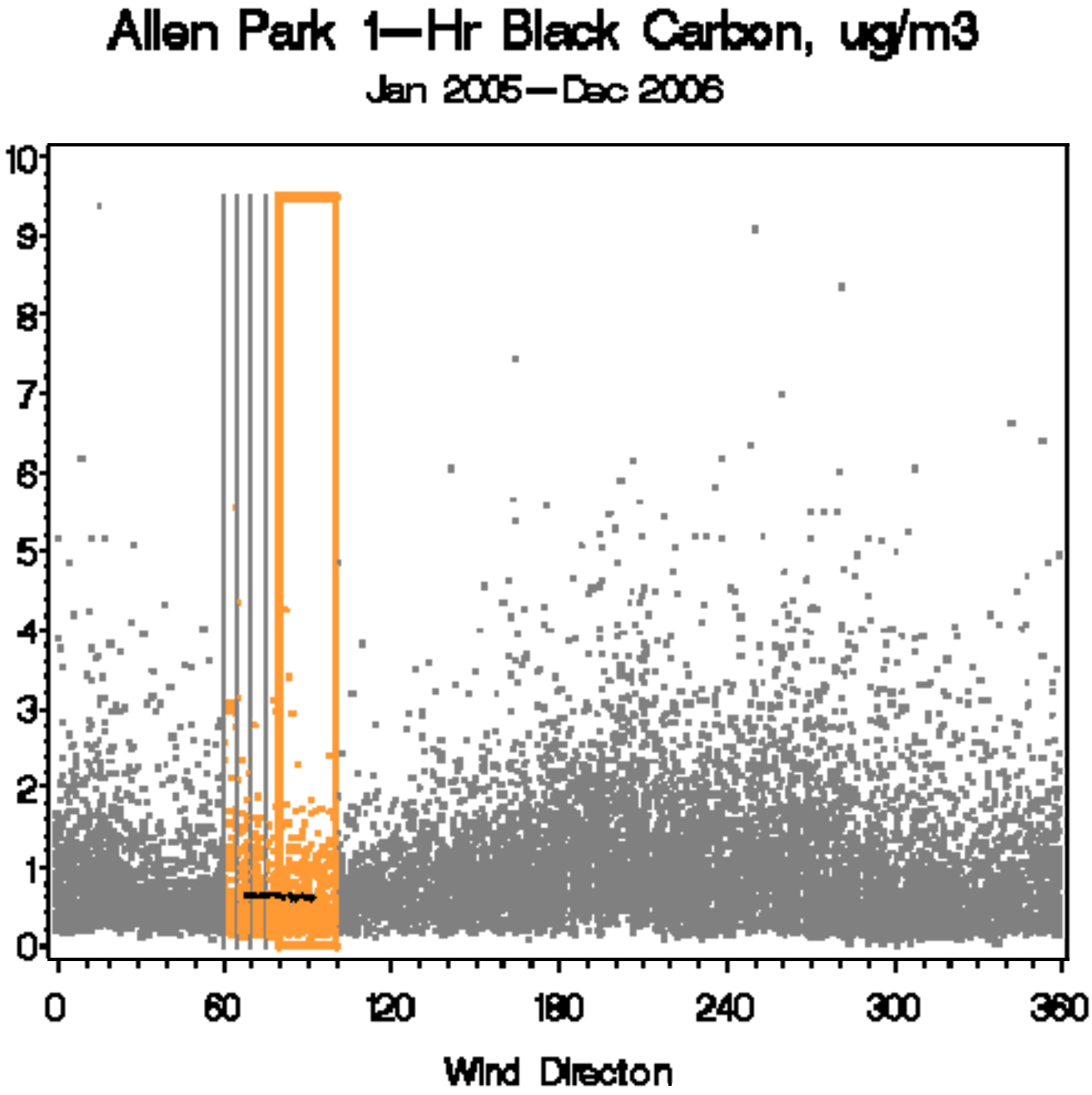
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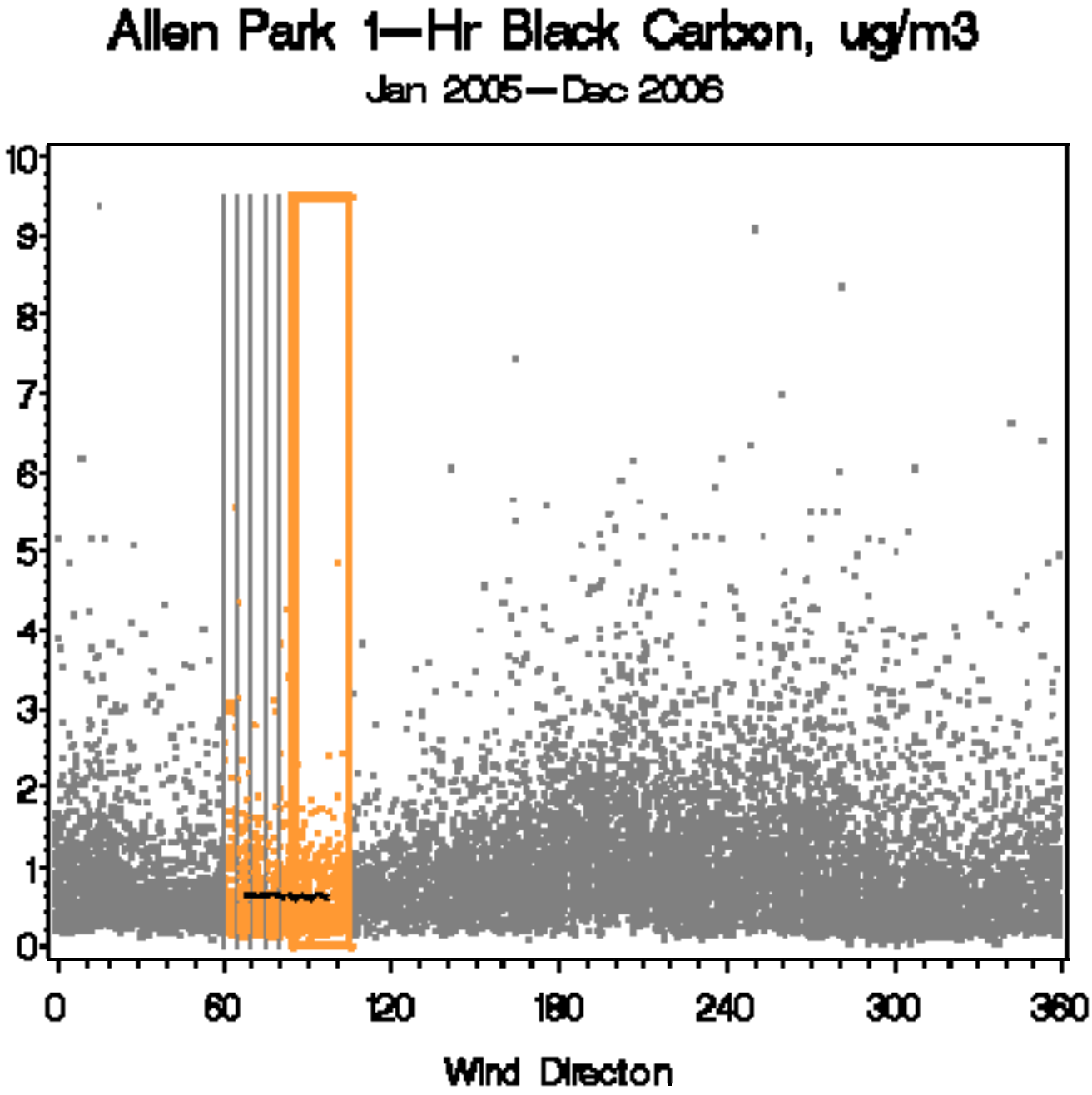
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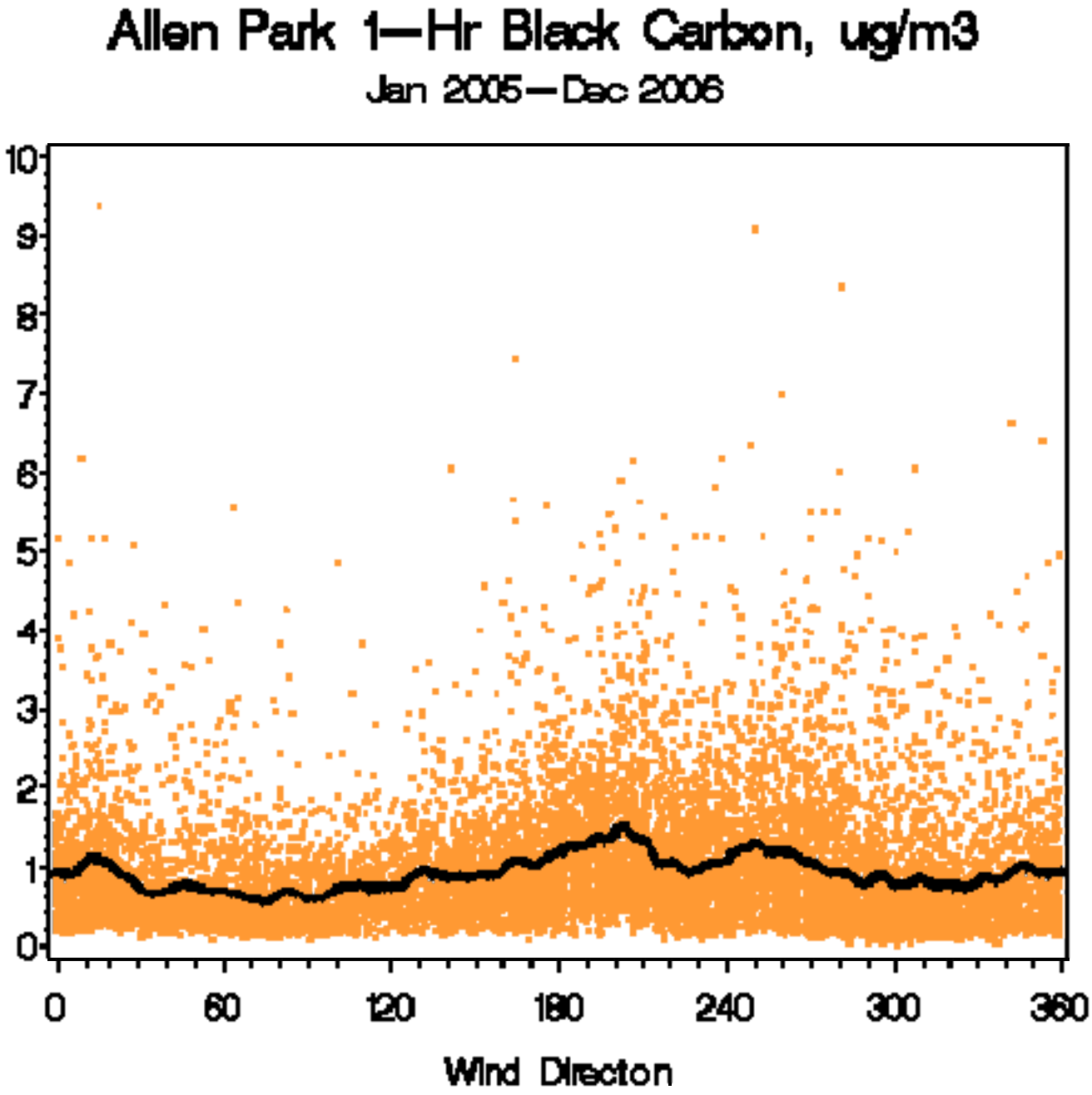
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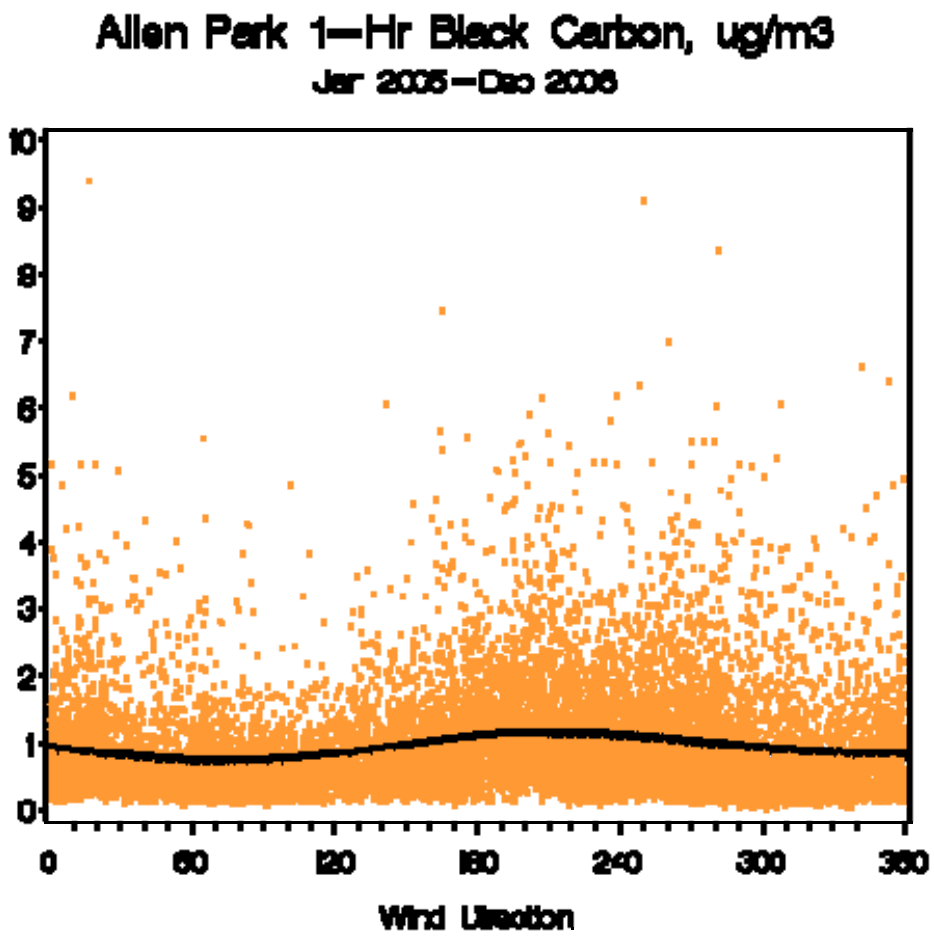
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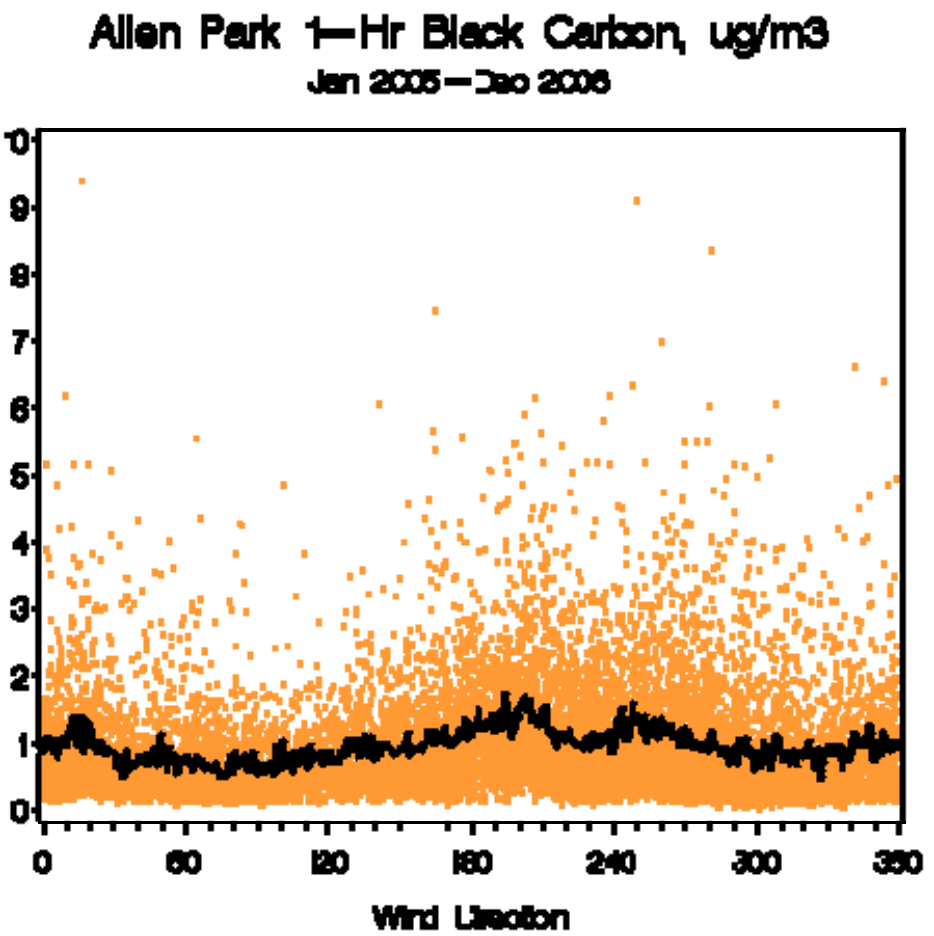
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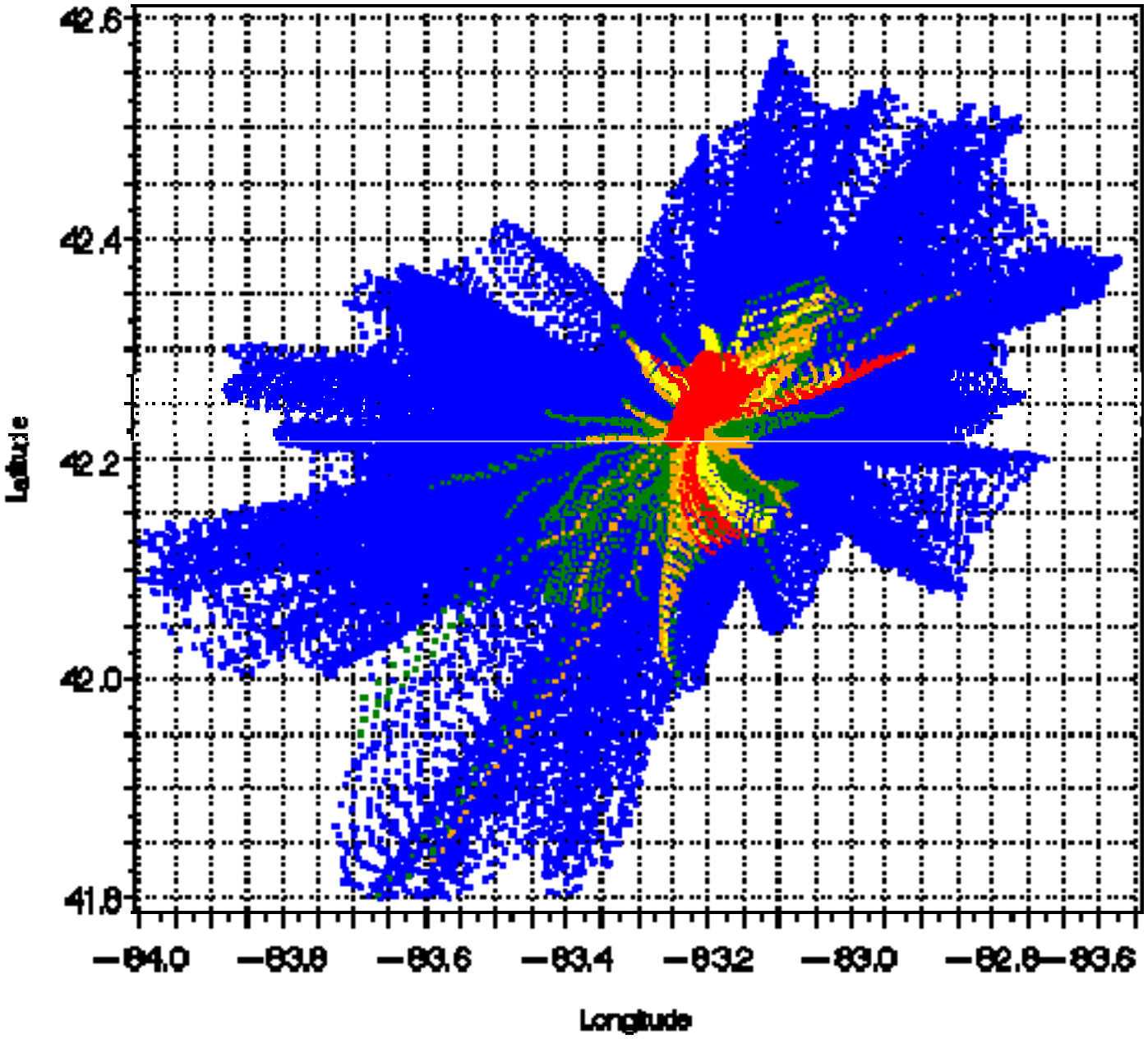
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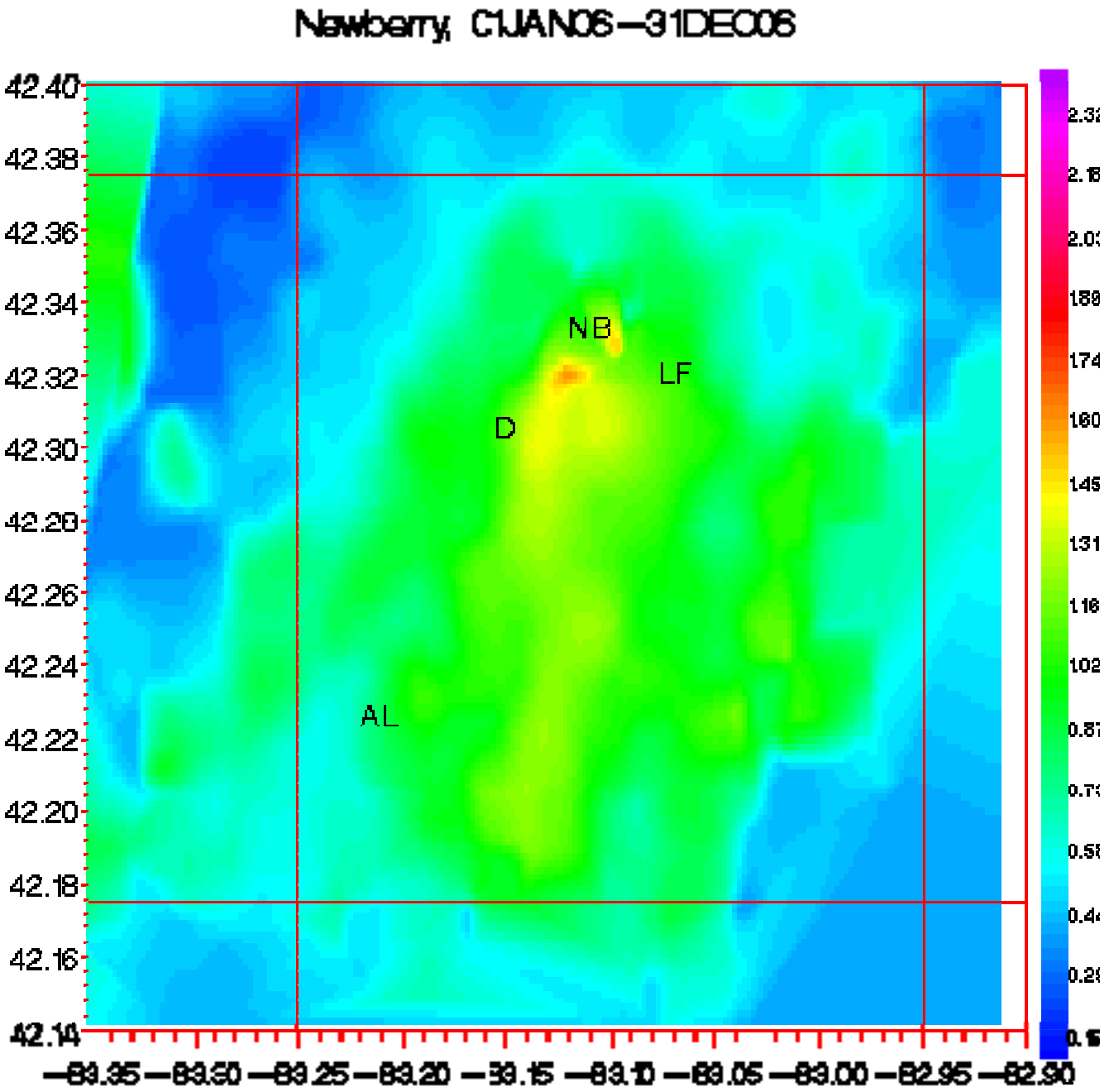
Newberry, C1JAN06–31DEC06
42.40
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42.20
42.18
42.16
42.14
NB
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1.45
1.31
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1.02
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-83.35
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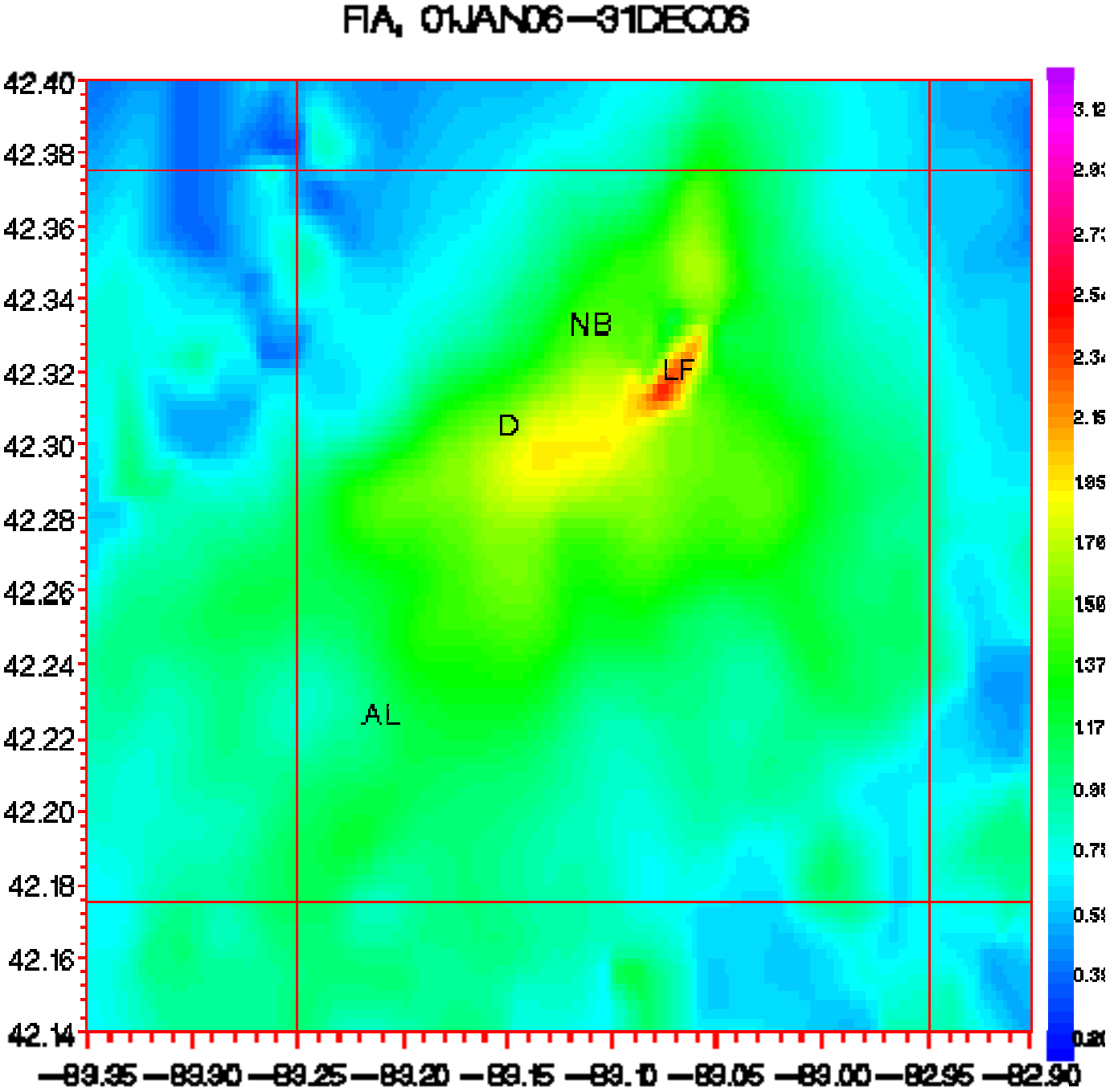
-83.20
-83.15
-83.10
-83.05
-83.00
-82.95
-82.90

Newberry aethalometer data – points very specifically to intermodal freight terminal (1 hr data, 2006)

Newberry
Dix St
Fordson Island


FIA, 01JAN06-31DEC06
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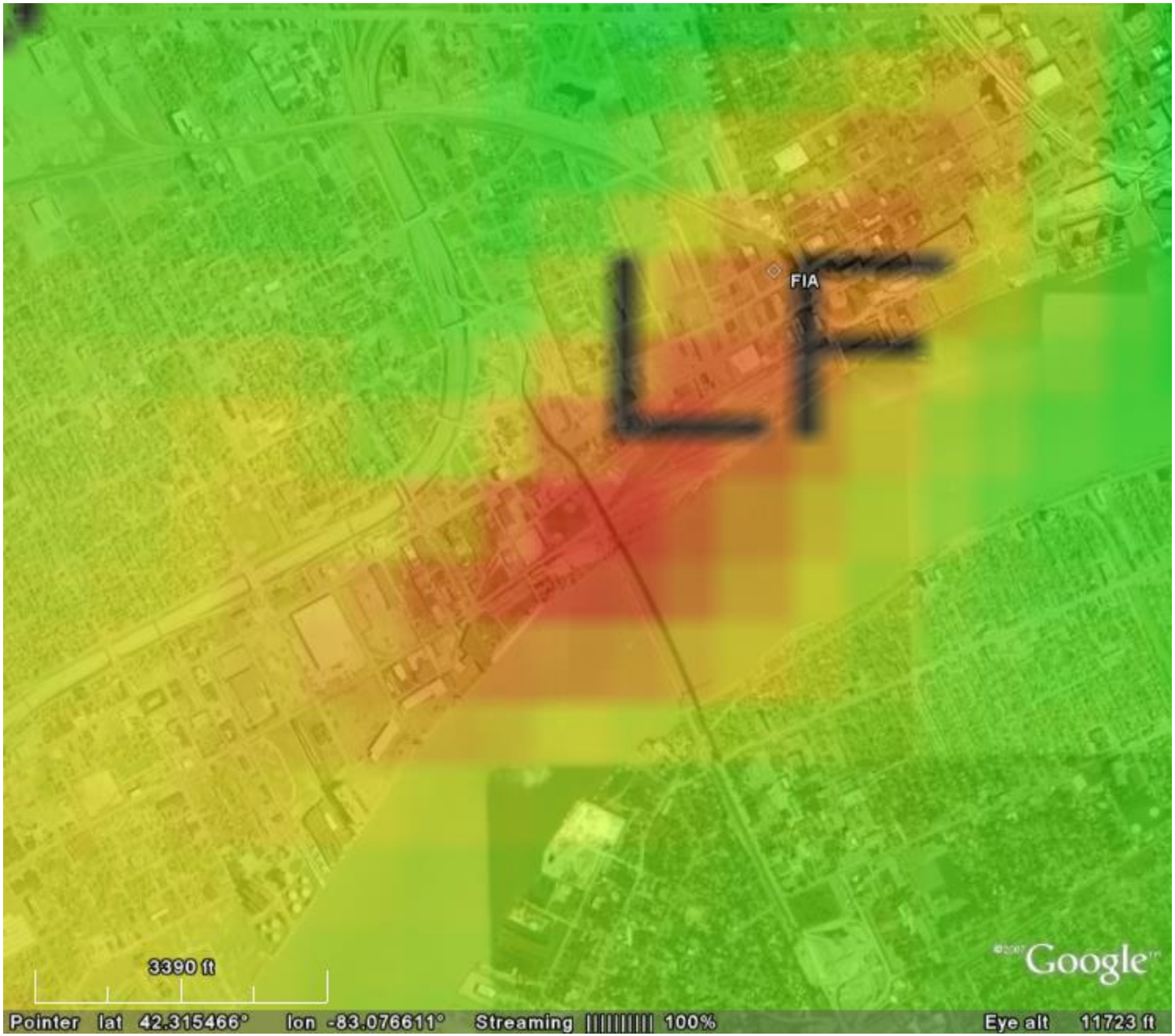


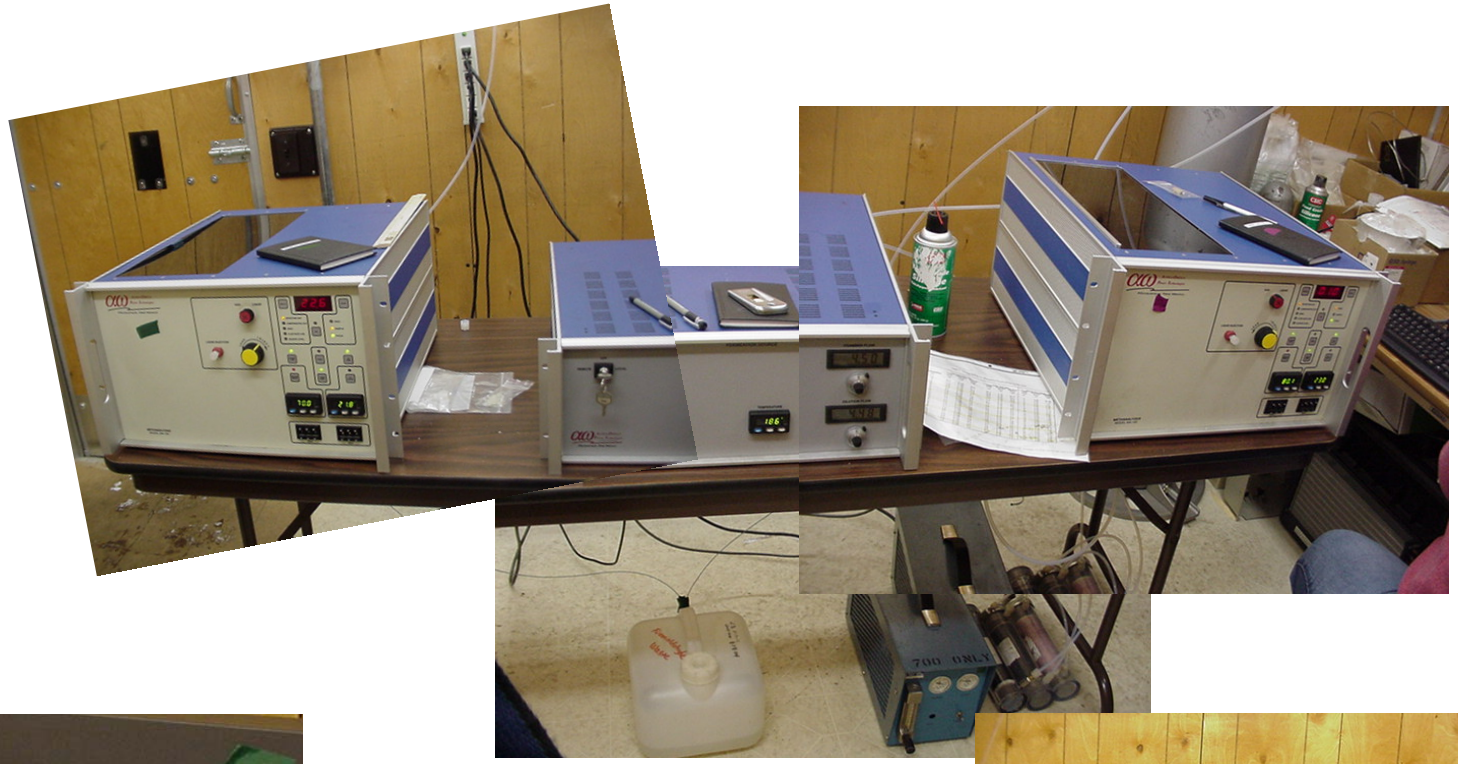
FIA aethalometer data points very specifically to Ambassador Bridge (1-hr data, 2006 annual)

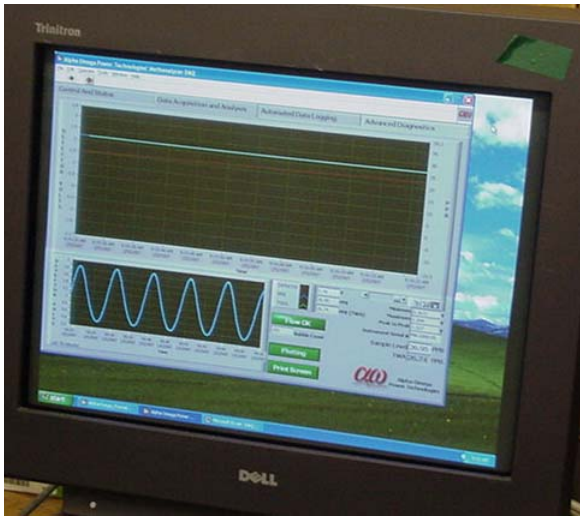
Newberry continuous EC data – identifies same intermodal freight terminal as BC data

Newberry continuous OC data – also identifies freight terminal as source of OC

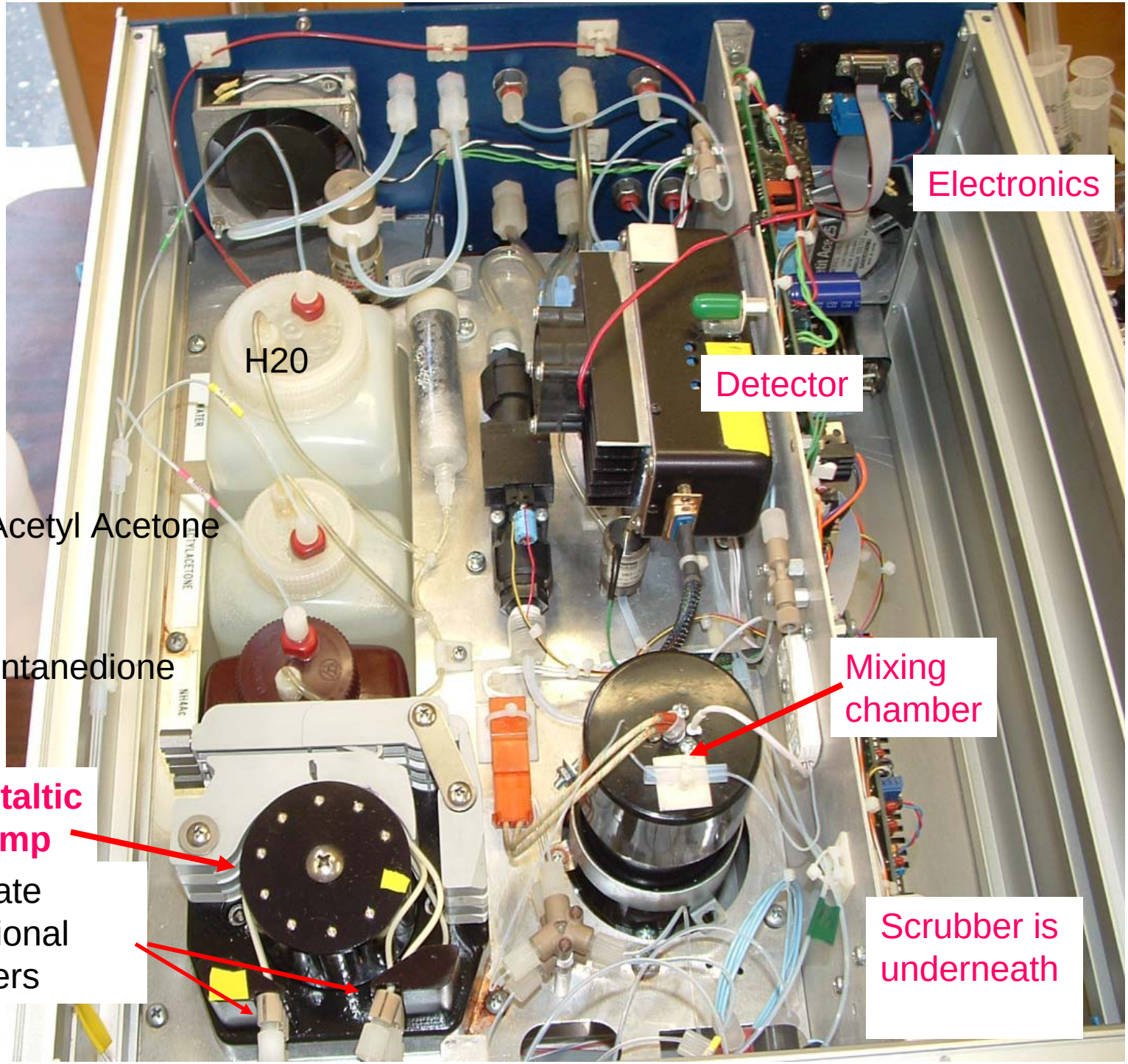
(surprising considering that much OC is secondary and from area sources --point sources not expected to show up)

Continuous Formaldehyde Units





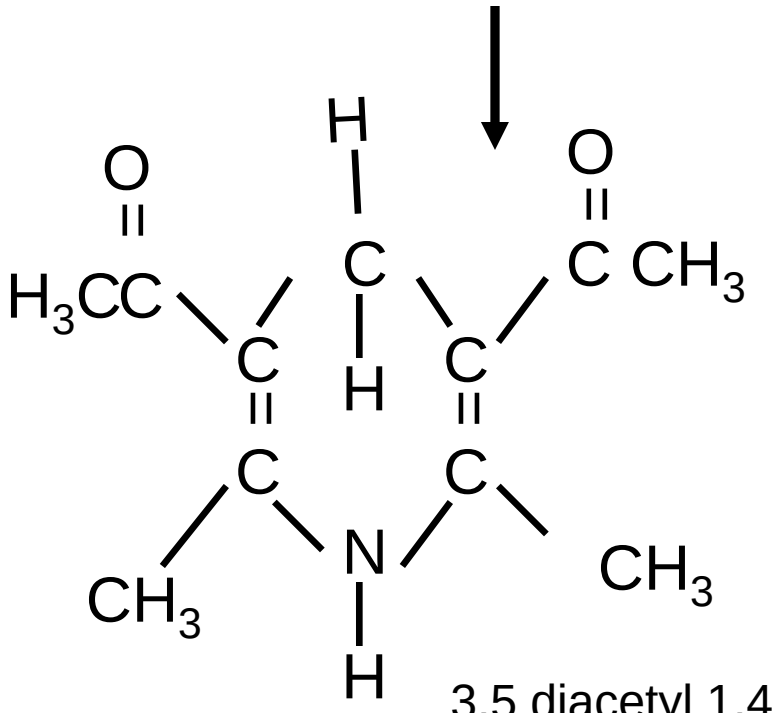
Alpha Omega Power Technologies, Inc Albuquerque New Mexico


Electronics
H20
Detector
Acetyl Acetone
2,4 pentanedione
Mixing chamber
Peristaltic pump
Accurate Directional Markers
Scrubber is underneath

Chemical Reaction

$2\ CH_3COCH_2CO_3 + HCHO + NH_3$

2,4 pentanedione | formaldehyde | ammonia



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

$\lambda_{ex} = 412$ nm

$\lambda_{em} = 410$ nm

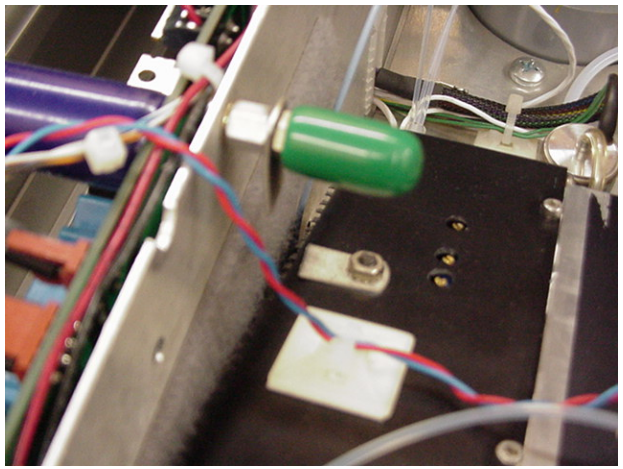
Formaldehyde Units

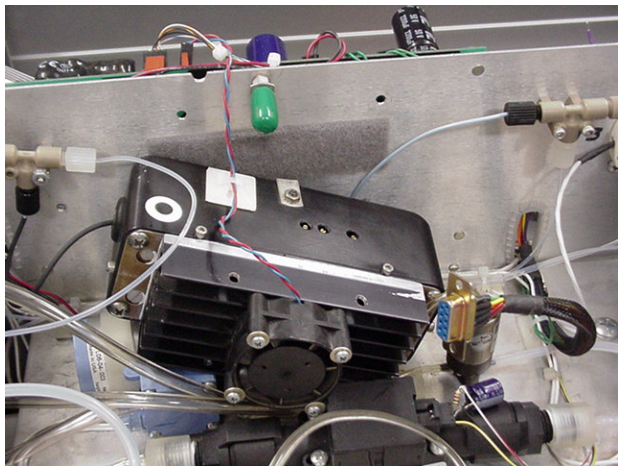
- Goals:
  - Assess inter sampler precision: 6 + weeks
  - Deploy to Newberry & Dearborn NATTS site
    - Spatial variability
    - Diurnal trends
    - Compare w/ other hourly parameters
    - Nonparametric regression
    - Method comparison (24-Hr TO-11a)
    - Short term analysis of risk

Timeline

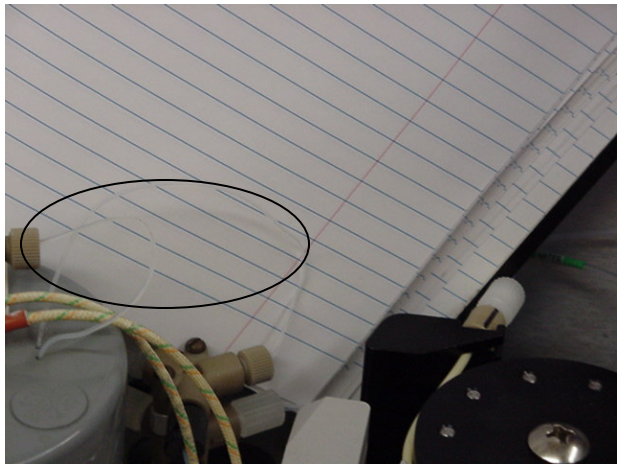
- November 2004 – receive units
- 2005 – ship Permeation source back for repair
- 2005-6 – ship units back for repair – 3x
  - It took 6 mo. for first repair (3/18/05 to 9/20/05)
  - May 2006 Send Amy to NM – training at Alpha Omega's facility
  - More repairs 1/23/06 to 12/21/06 – units received were 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





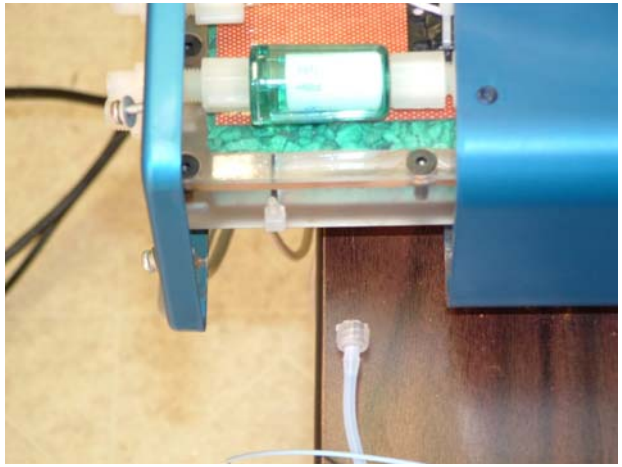
Broken Bracket allowing detector to flop around during shipment



Crimped Line

Permeation source shipping crate

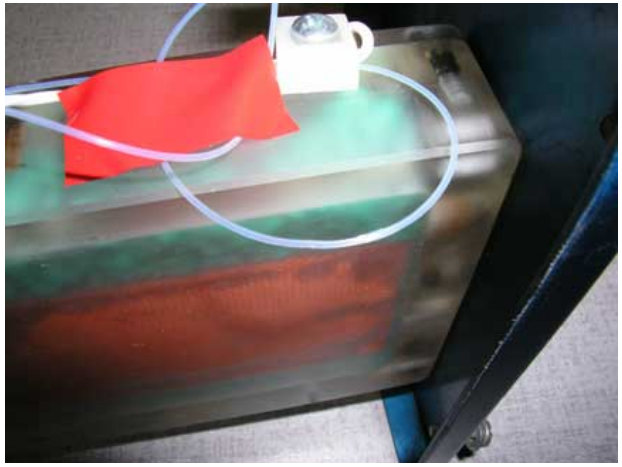
Other issues



Broken Inlet

More Reagent Leaks

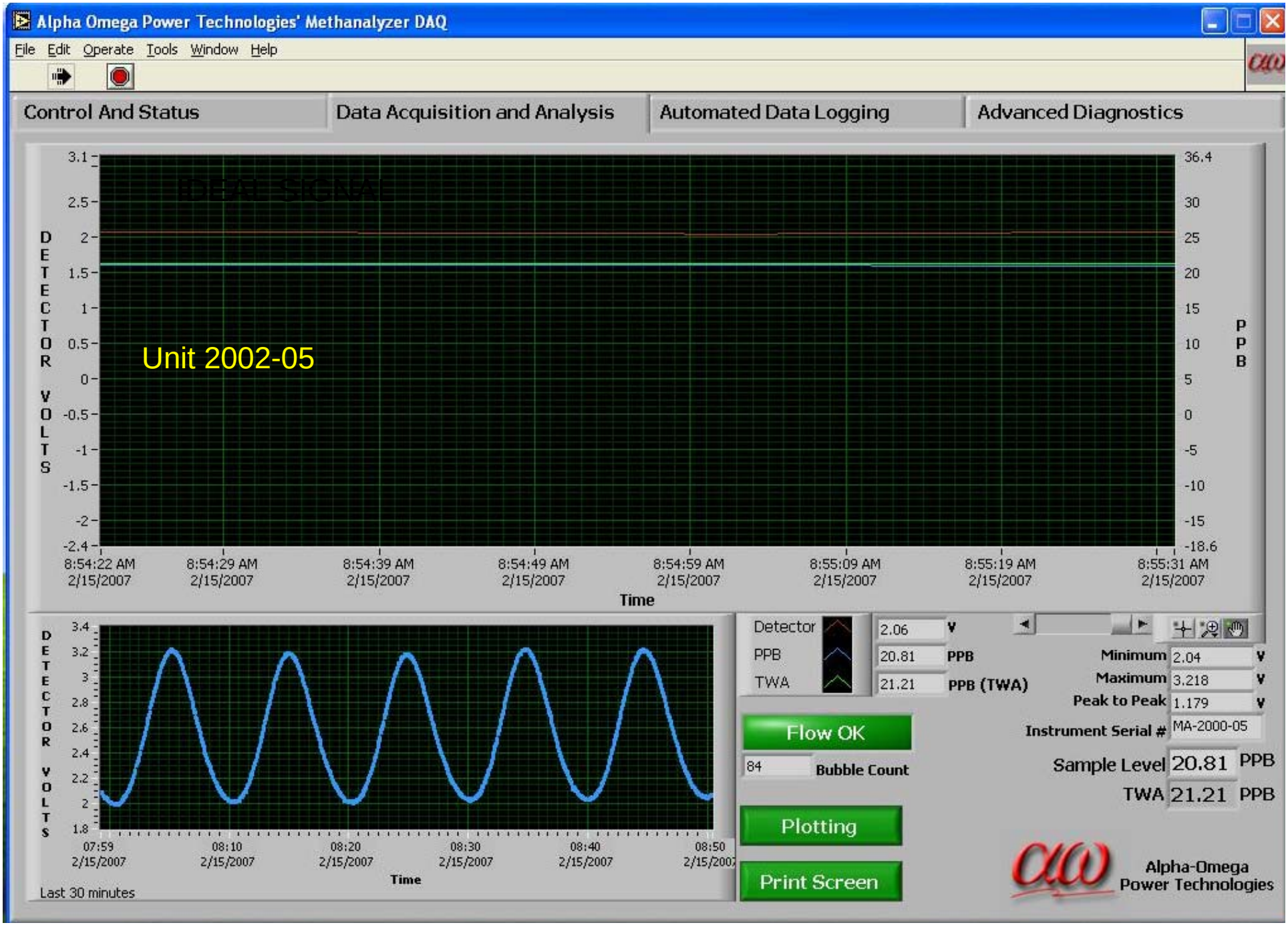
Crushed scrubber tubing



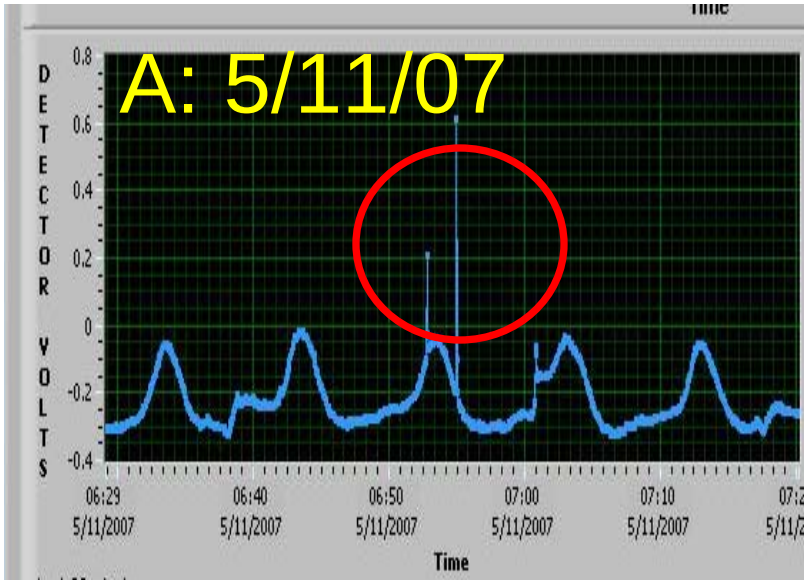
Reagent Leaks

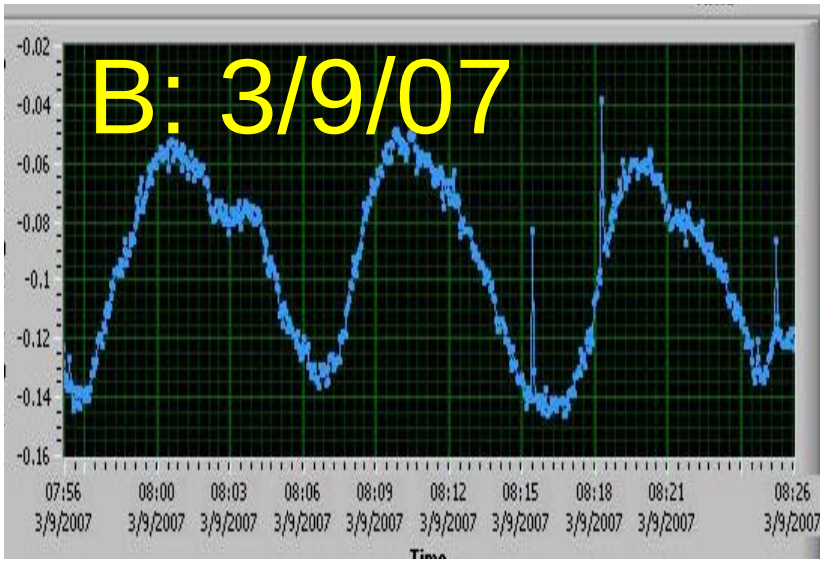
2007 Plan of attack

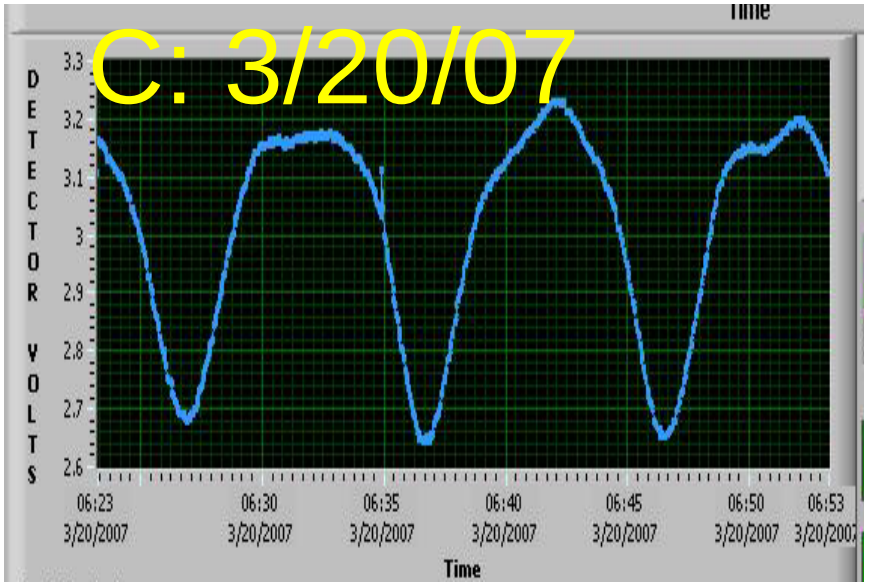
- Learn how to trouble shoot units – use software in diagnosis
- How to quickly change out tubing without line blow outs & floods
- Determine how to minimize bubbles
- Generate stable baselines
- Assess intra and inter sampler precision of liquid system with liquid injections of formaldehyde
- Is the 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

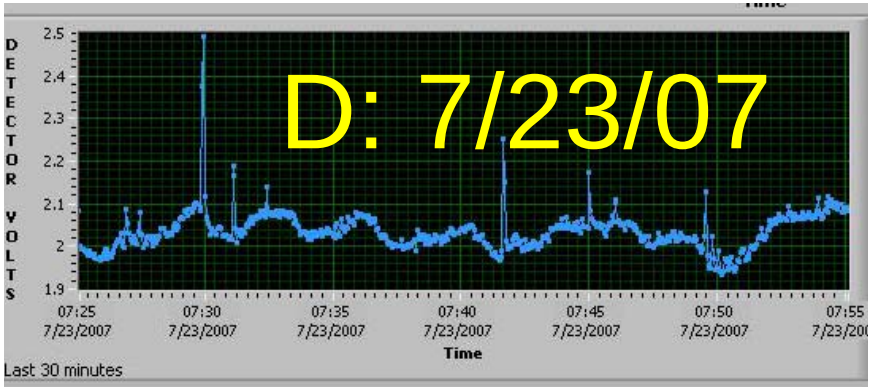

Alpha Omega Power Technologies' Methanalyzer DAQ
File Edit Operate Tools Window Help
Control And Status
Data Acquisition and Analysis
Automated Data Logging
Advanced Diagnostics
DETECTOR VOLTS
PPB
Unit 2002-05
8:54:22 AM 2/15/2007
8:54:29 AM 2/15/2007
8:54:39 AM 2/15/2007
8:54:49 AM 2/15/2007
8:54:59 AM 2/15/2007
8:55:09 AM 2/15/2007
8:55:19 AM 2/15/2007
8:55:31 AM 2/15/2007
Time
07:59 2/15/2007
08:10 2/15/2007
08:20 2/15/2007
08:30 2/15/2007
08:40 2/15/2007
08:50 2/15/2007
Time
Last 30 minutes
Detector
PPB
TWA
2.06 V
20.81 PPB
21.21 PPB (TWA)
Minimum 2.04 V
Maximum 3.218 V
Peak to Peak 1.179 V
Instrument Serial # MA-2000-05
Flow OK
84 Bubble Count
Sample Level 20.81 PPB
TWA 21.21 PPB
Plotting
Print Screen
Alpha-Omega Power Technologies

Utility of Software: Unit 2 Only

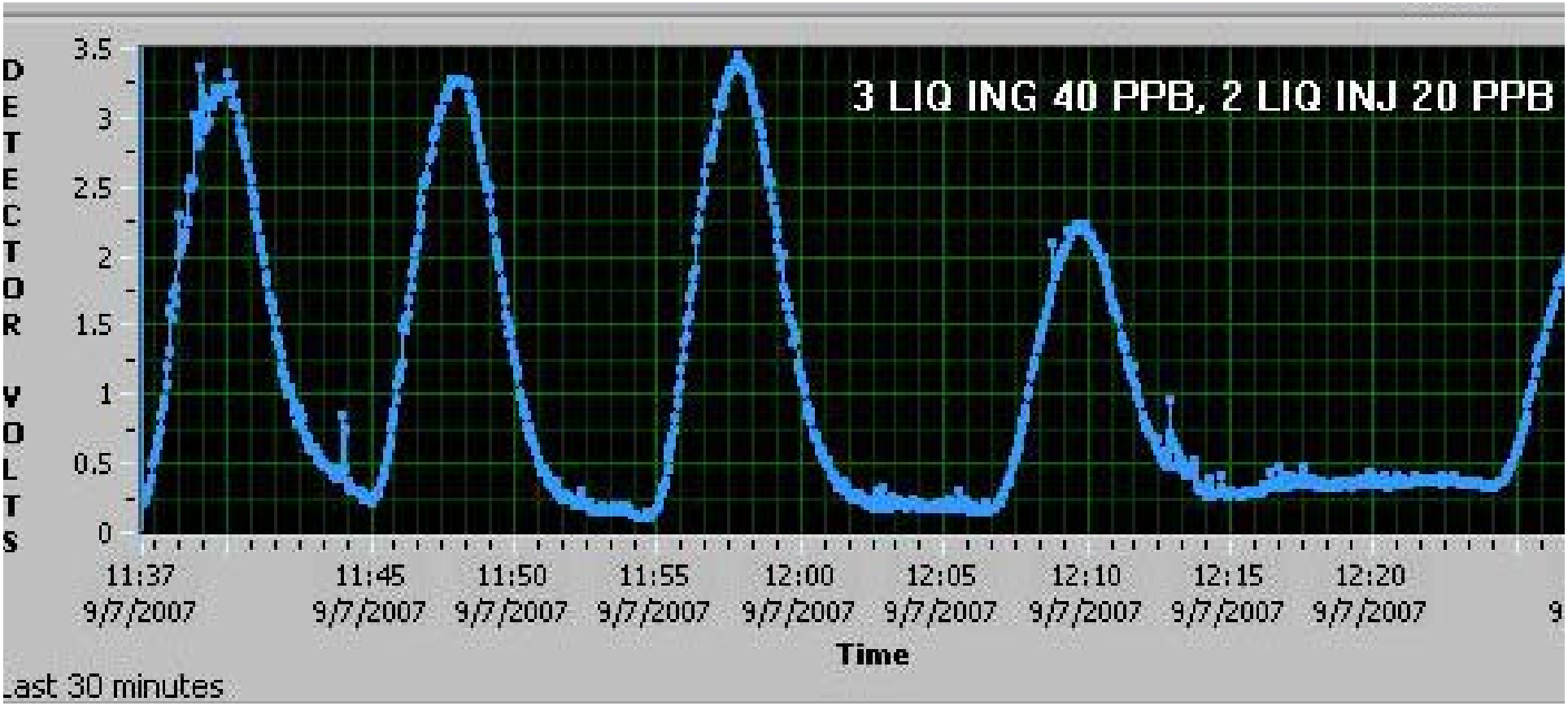






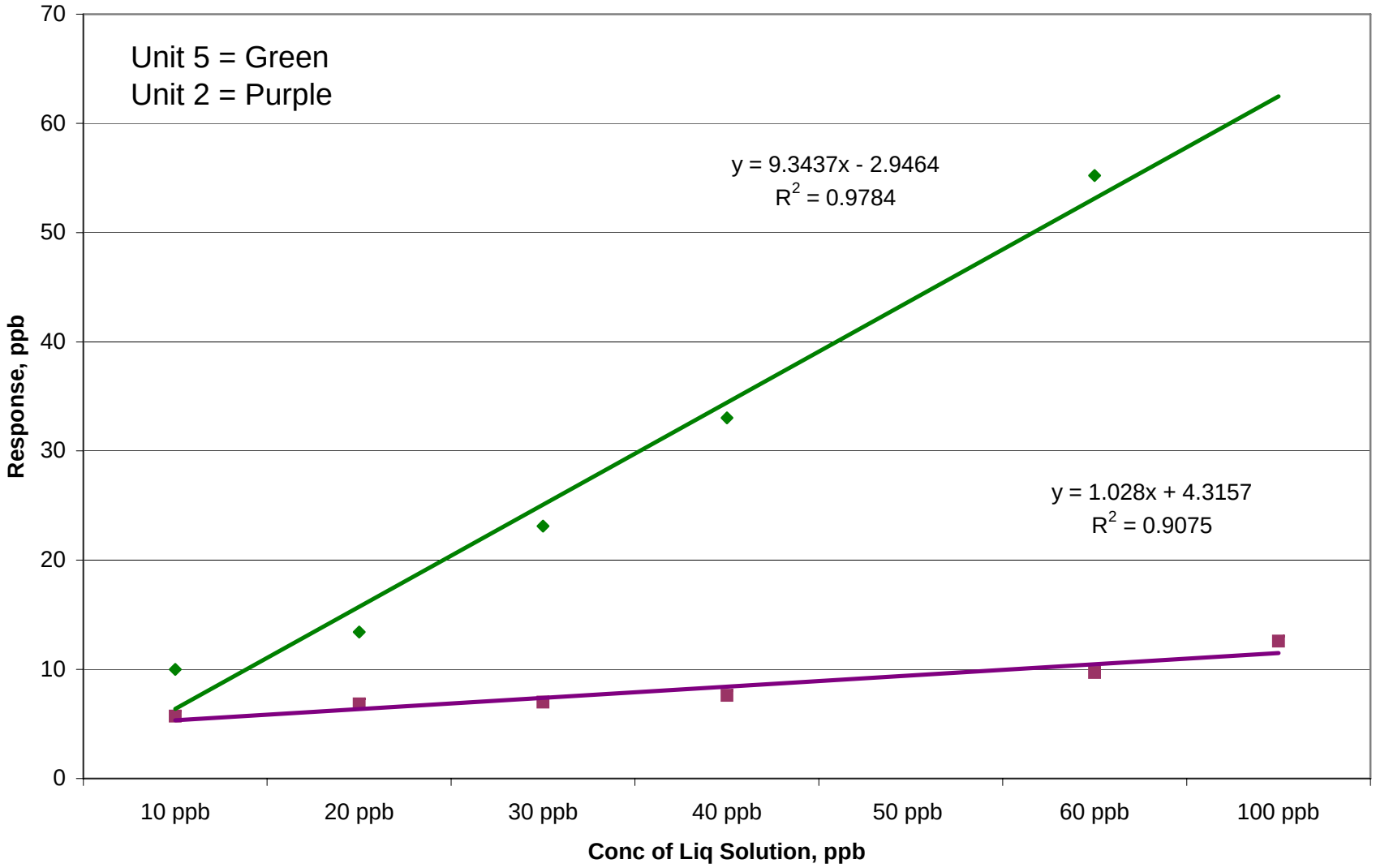


Liquid Mode of Operation: Like a Chromatograph

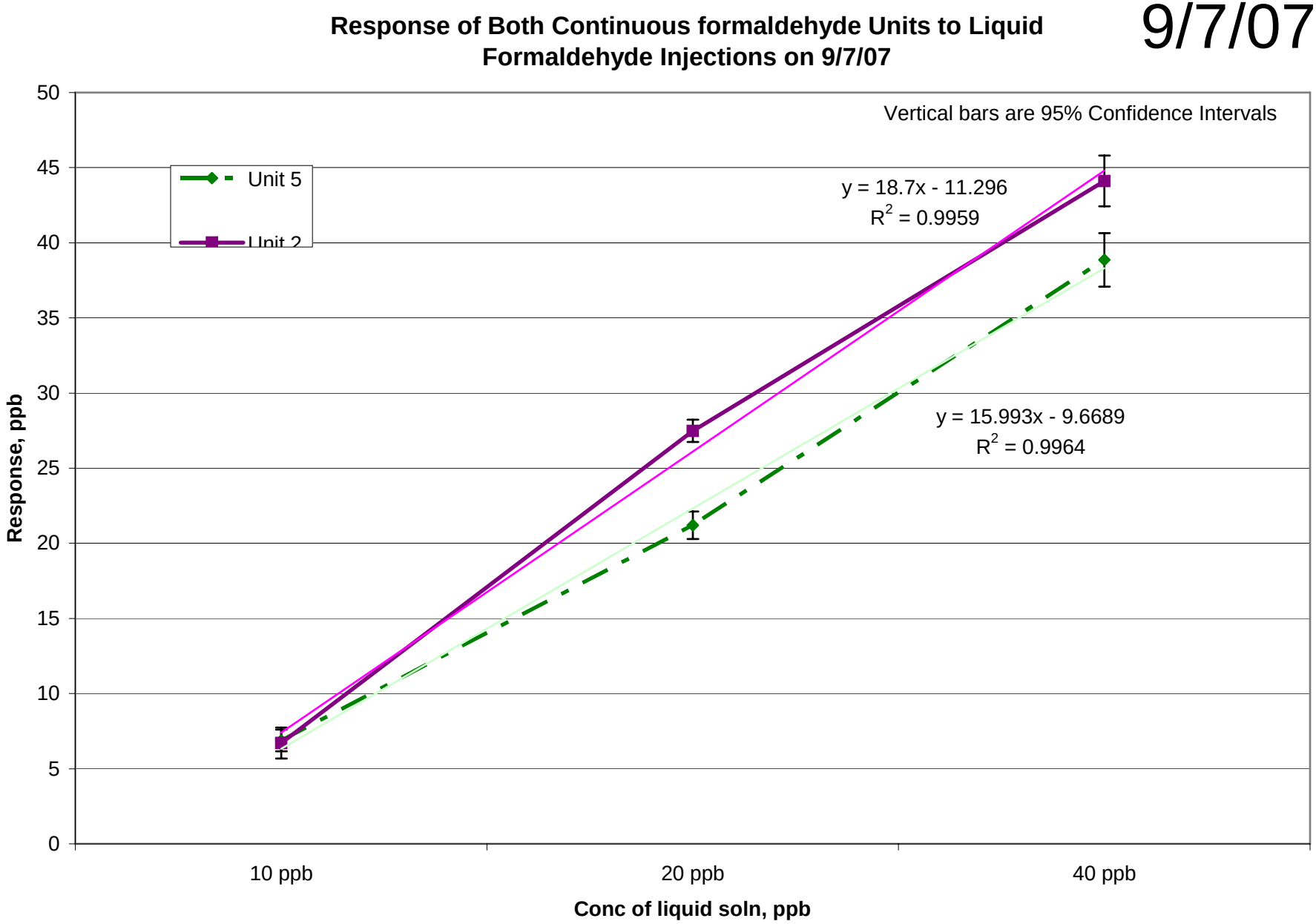


9/4/07

Response of Both Continuous Formaldehyde Units to Liquid Formaldehyde Injections on 9/4/07

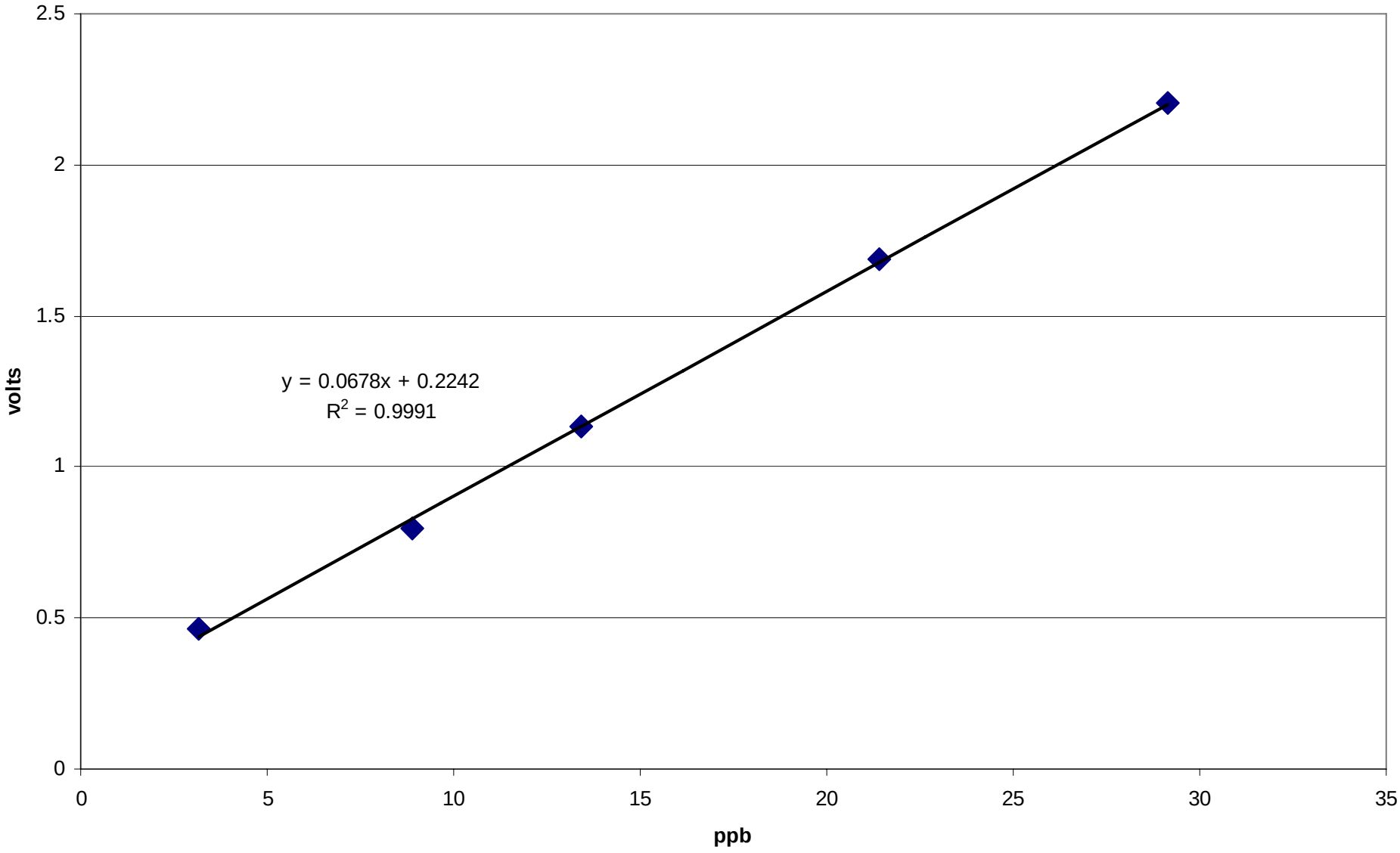


9/7/07


Response of Both Continuous formaldehyde Units to Liquid Formaldehyde Injections on 9/7/07
Vertical bars are 95% Confidence Intervals
Unit 5
Unit 2
y = 18.7x - 11.296
R2 = 0.9959
y = 15.993x - 9.6689
R2 = 0.9964
Response, ppb
0
5
10
15
20
25
30
35
40
45
50
10 ppb
20 ppb
40 ppb
Conc of liquid soln, ppb

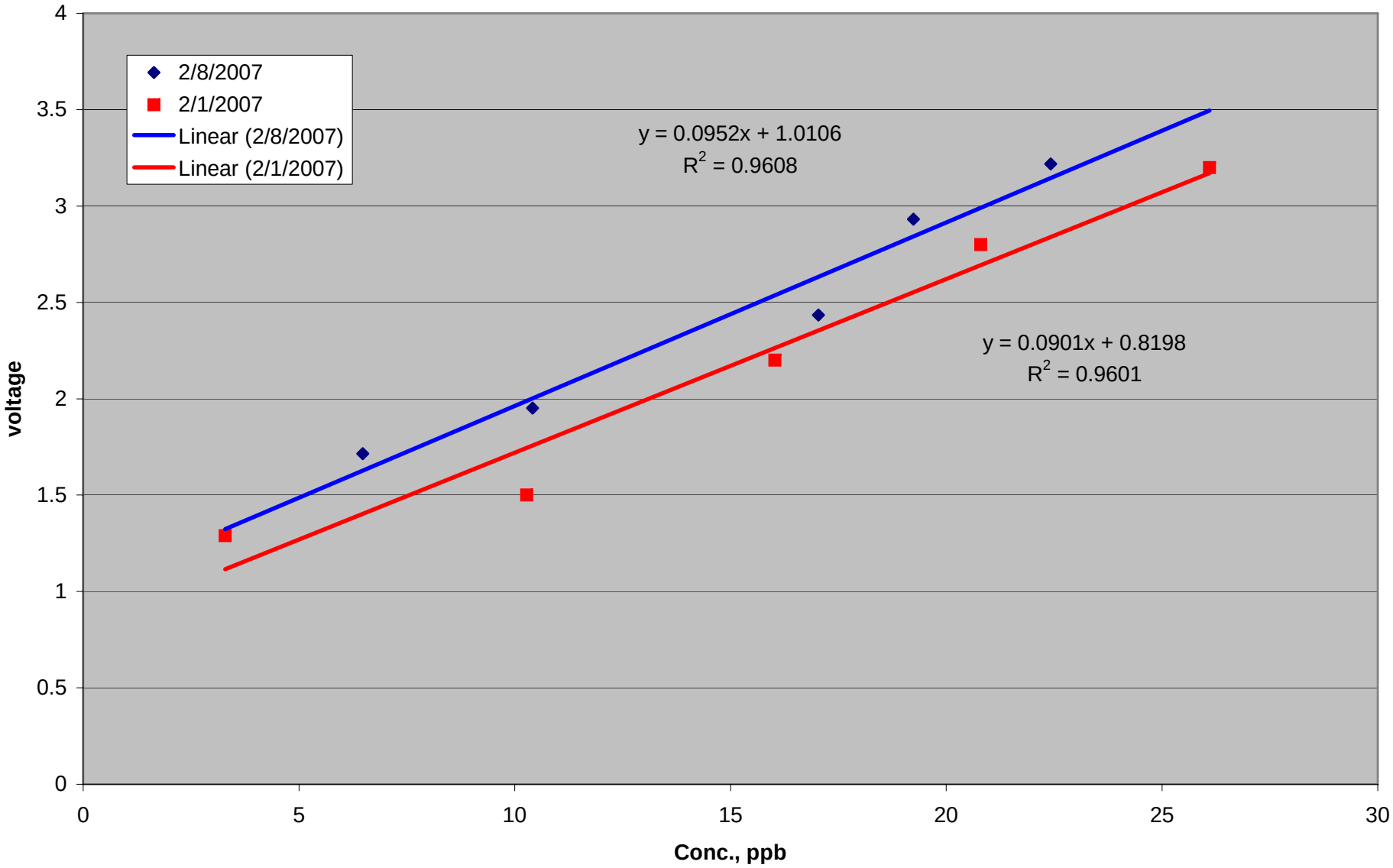
Gaseous Calibration Curve Unit 5

MA-2000-05

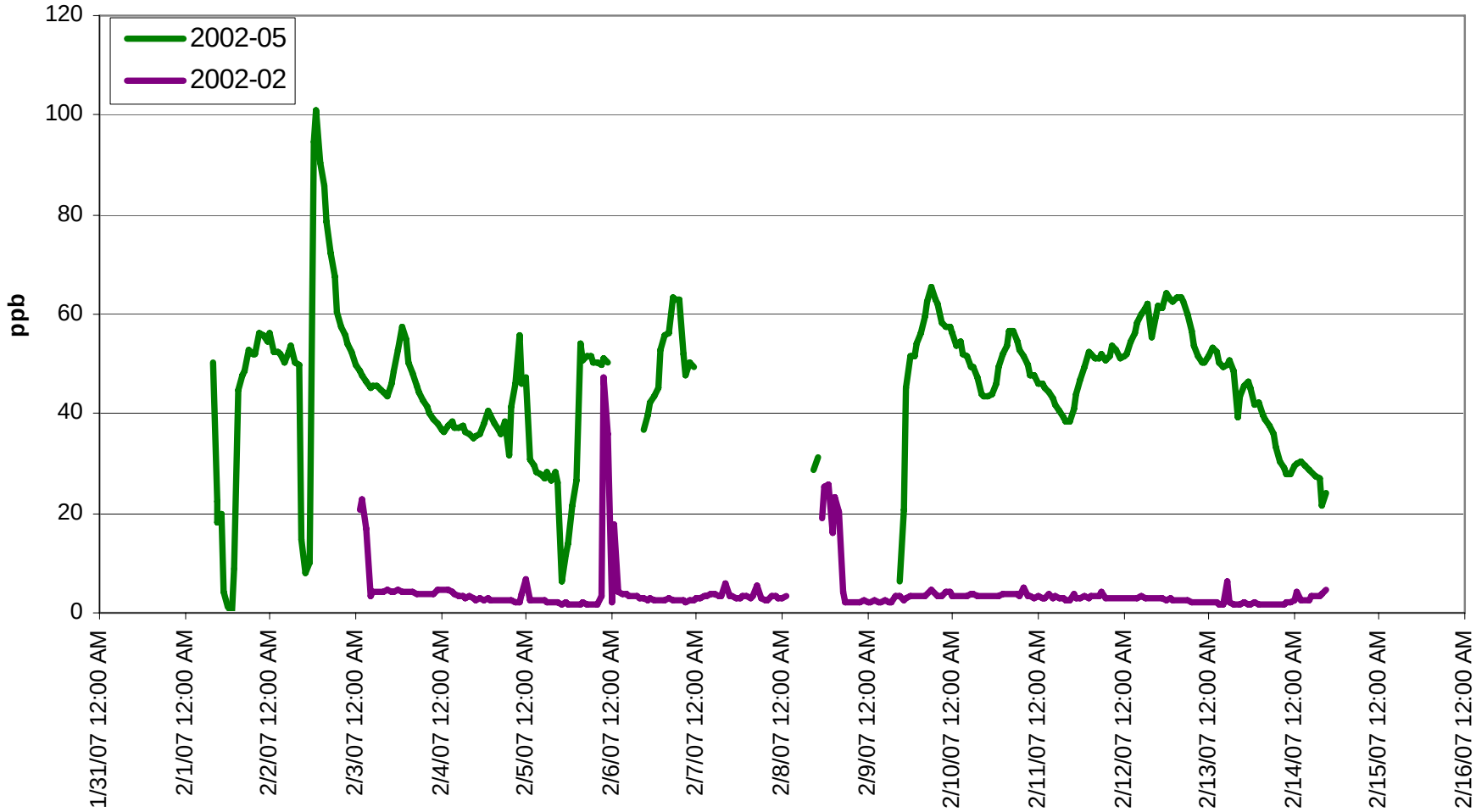


Gaseous Calibration Curves Unit 2

Calibration Curve 2000-02: Pump Tubing Change Out



January 2007



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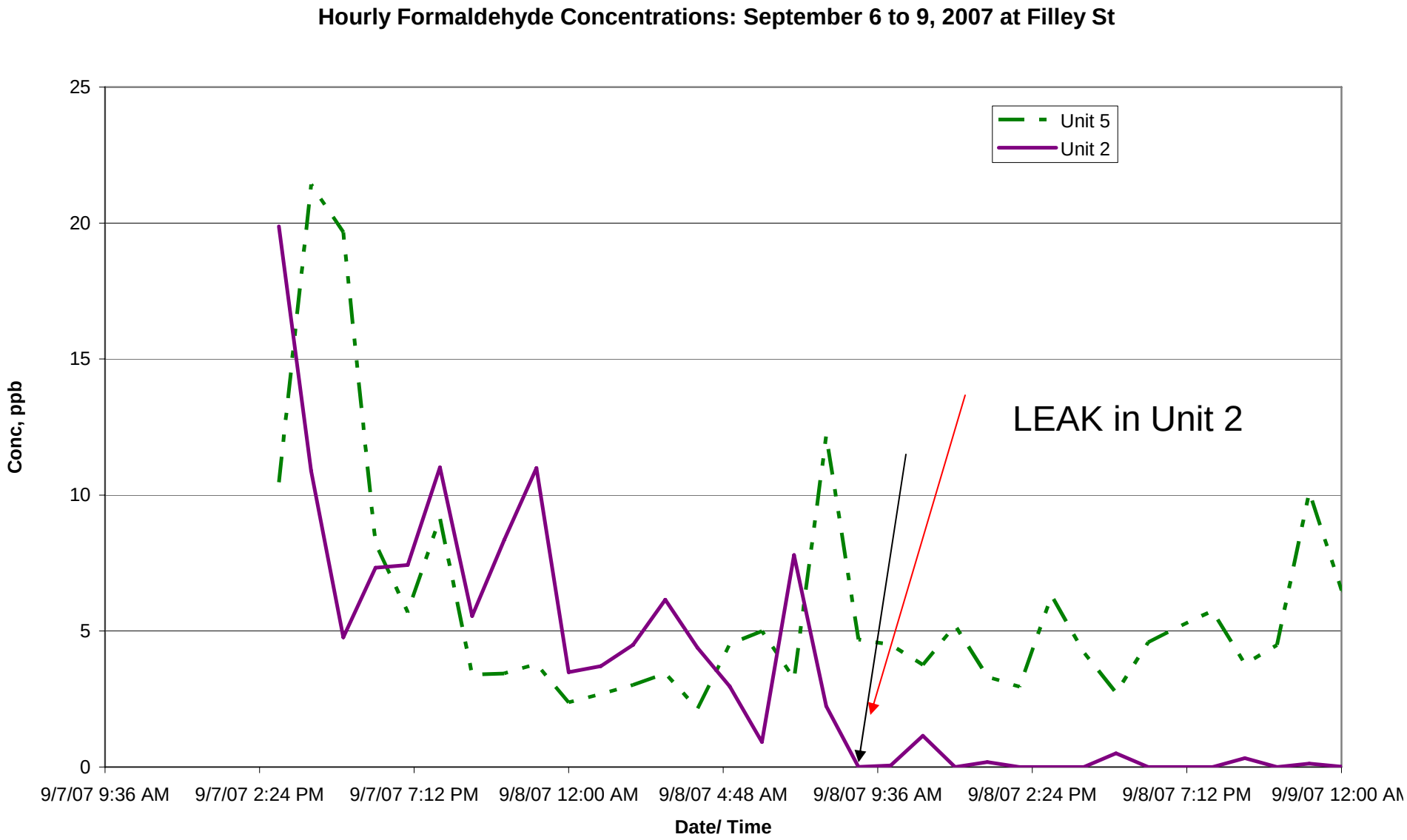
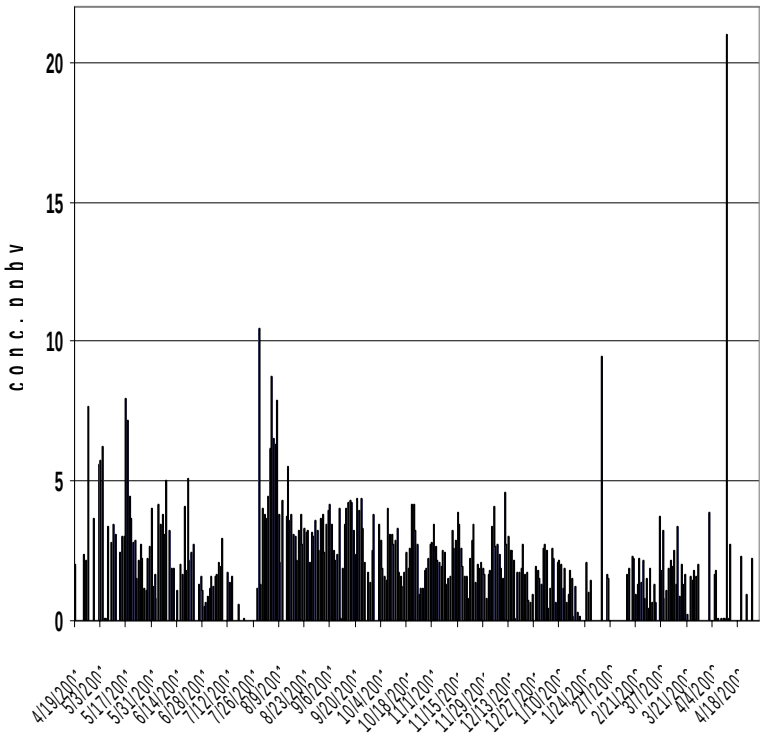
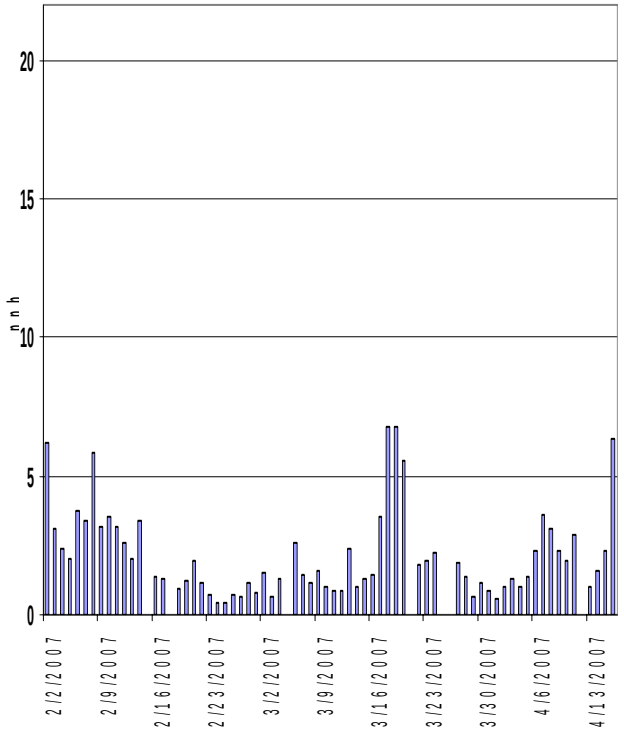


Magnitude of Daily 24-Hr Averages: Encouraging

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 H20 (*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
- Donna Kenski LADCO: consultation & non parametric regression
- Loretta Lehrman, Motria Caudill & Region 5 EPA: funding and support
- EPA OAQPS: funding
- Alpha Omega Power Technologies, Inc Alan Grimmis: patience with us