Ambient Measurements to Support Coal Combustion Emission Research

International Workshop on Mercury Control from Coal Combustion

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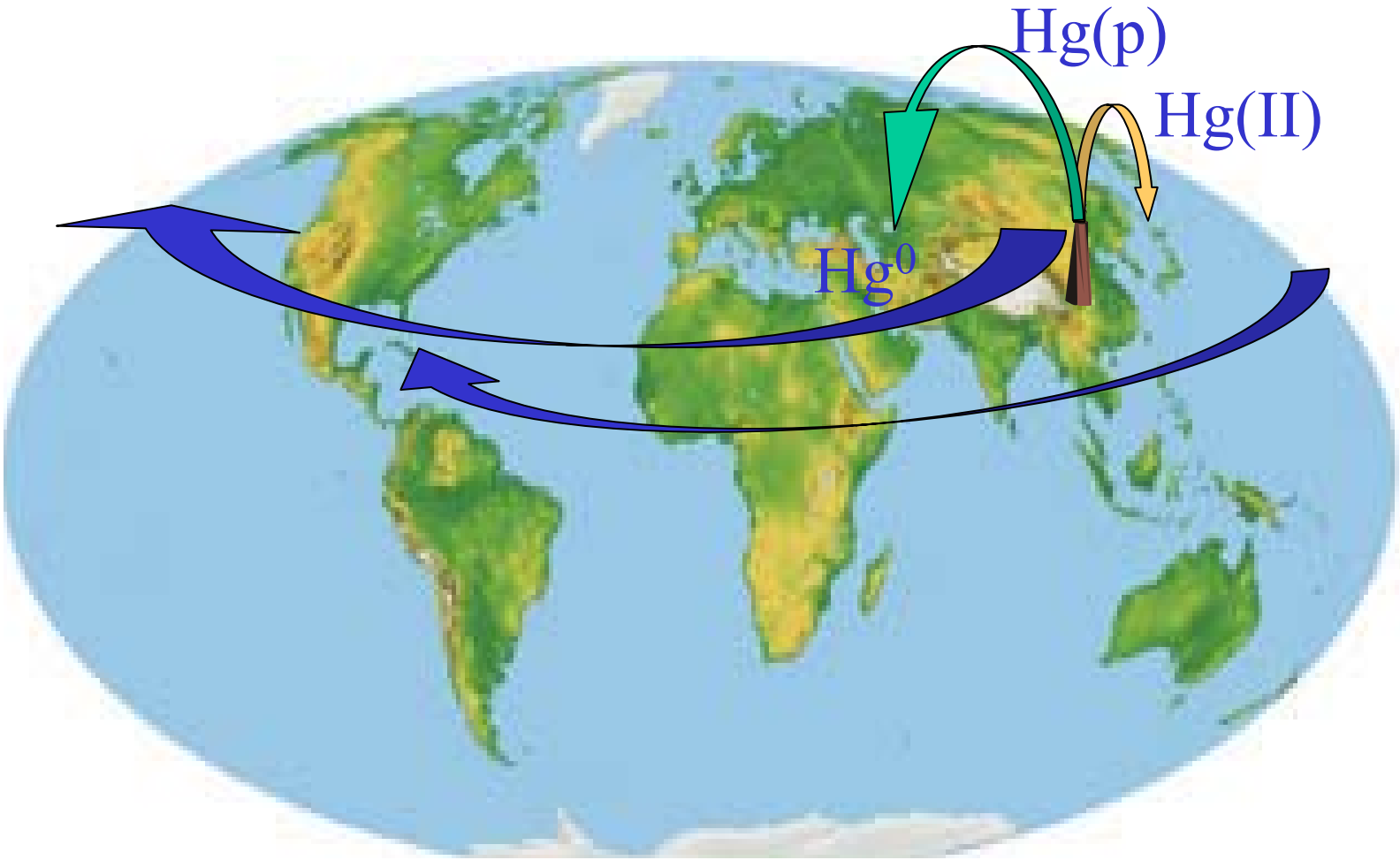
Ambient Measurements to Support Coal Combustion Emission Research

- **Atmospheric Mercury Model Validation**
- **Quantify Deposition Impacts from Specific Sources**
- **Emission Reduction Accountability**

Overview of Source Apportionment

- Source apportionment relates sources and environmental concentrations
- Approaches to source apportionment
  - Deterministic modeling (e.g., CMAQ)
    - Requires emission inventory, chemistry, and meteorology
    - Models emission source impacts on predicted concentrations
  - Receptor modeling
    - Requires comprehensive environmental measurements
    - Statistically identifies sources impacting measured concentrations
- Approaches are independent and complementary

Contemporary Atmospheric Mercury Conceptual Model



Global - Regional - Local

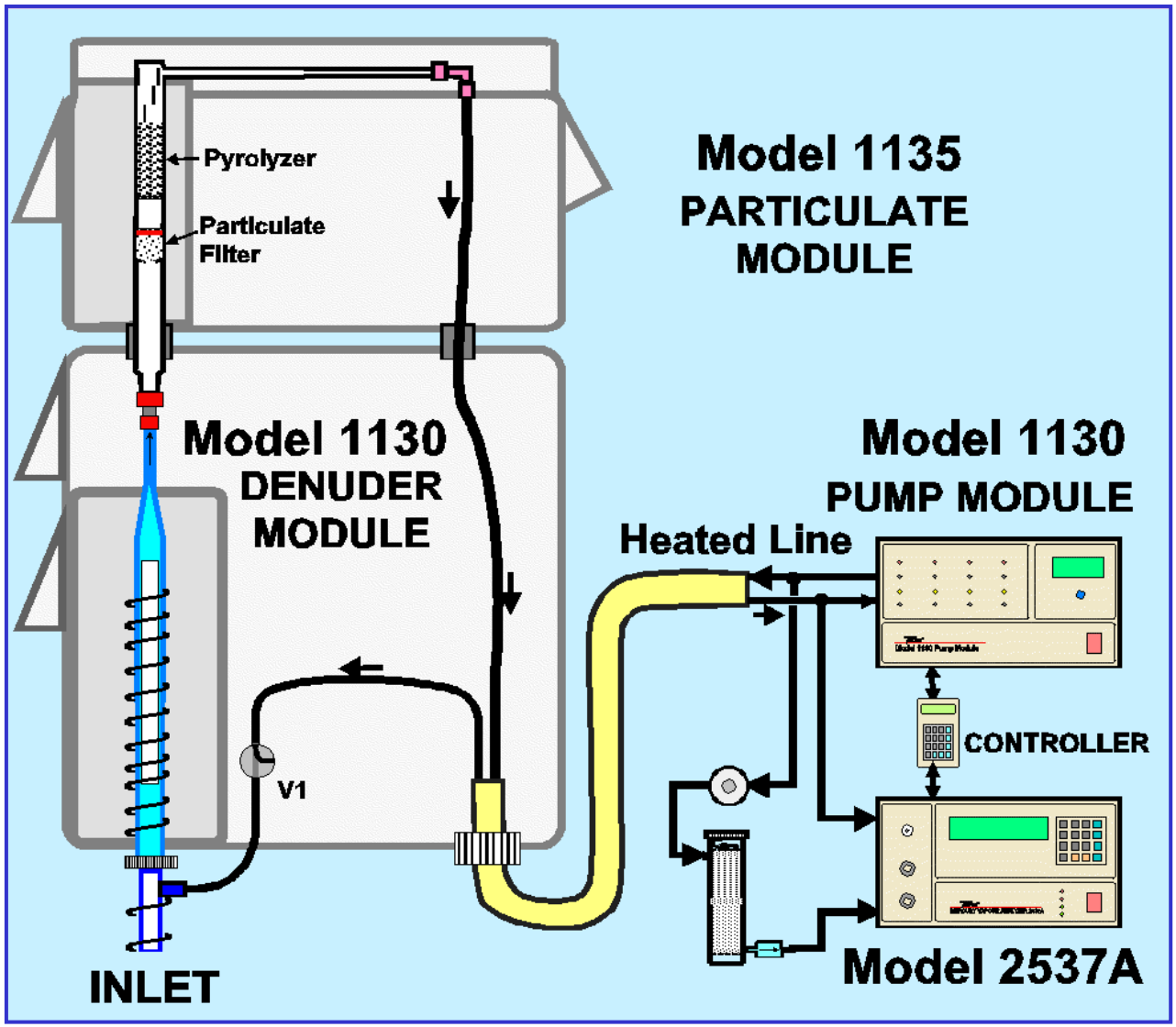
Mercury Modeling Limitations

- Current Deterministic Models
  - Need Comprehensive Global Emission Inventories
  - Need Improved Understanding of Hg Kinetics
  - Need Improved Dry Deposition Parameterizations
- Source Apportionment Modeling Requires Comprehensive Monitoring
  - Need Automated Ambient Speciation Measurements
  - Need Event Precipitation
  - Need Comprehensive Tracer Species
  - Need Coordinated Monitoring Strategy

Multivariate Receptor Modeling

- Identify major “factors” by statistical analysis of an element measurement matrix
- Relate “factors” to source type using tracer compounds
- Example tracer compounds
  - Coal Combustion – S, Se
  - Oil Combustion – Ni, V
- Requires many samples (150 or more)
- Ohio River Valley Study
  - Applied both positive matrix factorization (PMF) and UNMIX models
  - Estimated source contributors to measured wet Hg deposition

Automated Speciation Instrumentation



* Landis et al. *Environ. Sci. Technol.*, **2002**, 36, 3000-3009

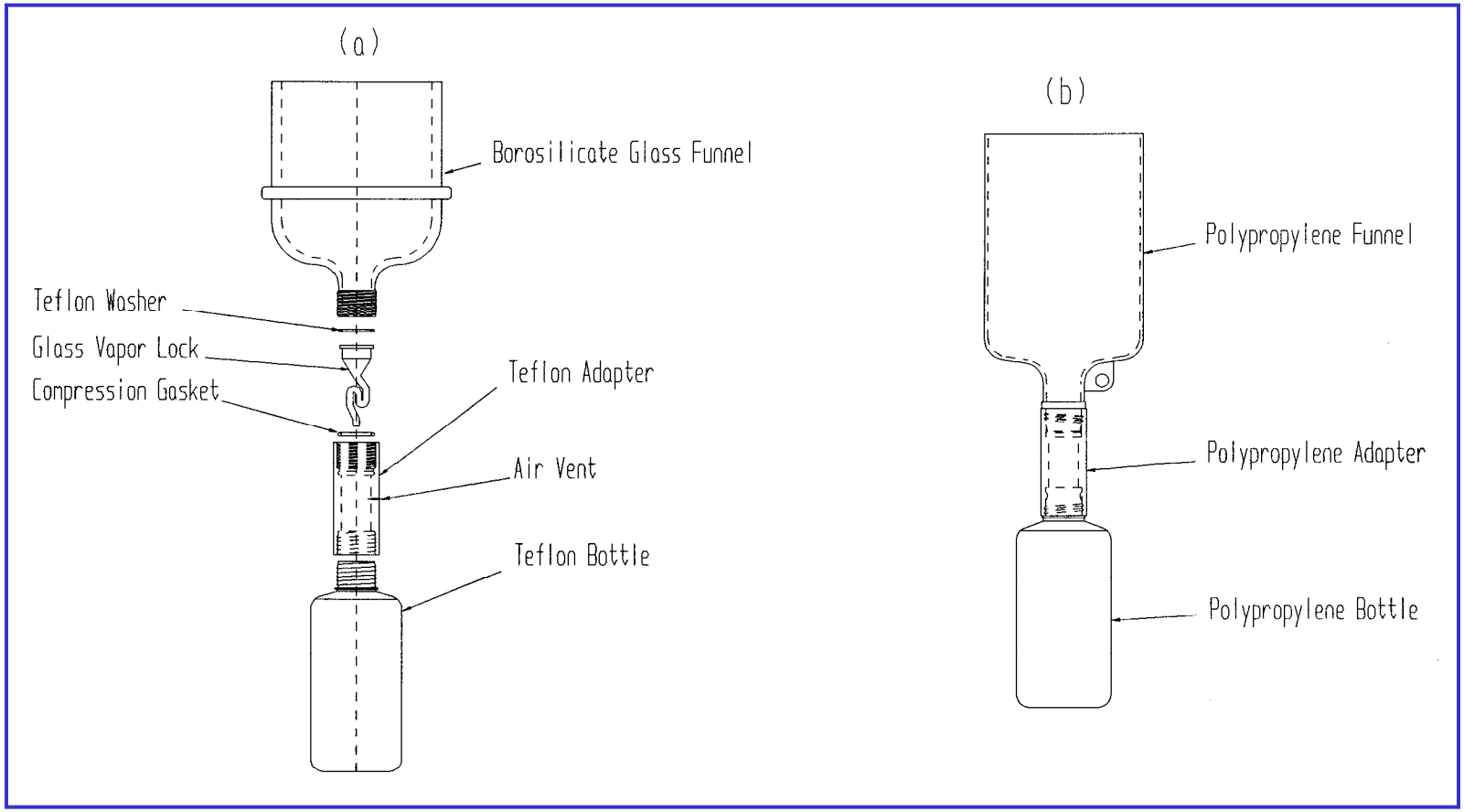
Speciation Methods Summary

- KCl-Coated Quartz Annular Denuders Quantitatively Collect RGM Without Known Interconversion or Interference Problems.
- RGM is Thermally (~500°C) Converted to Hg^0
- Hg(p) is Thermally (~800°C) Converted to Hg^0
- Low Denuder MDL's Allow High Resolution Sampling
- Manual Sampling is Inexpensive, Simple, and Mobile
- Automated Sampling Provides High Resolution Hg Speciation

Wet-Only Precipitation Collection

* Landis and Keeler
Environ. Sci. Technol.,
1997, 31, 2610-2615

Analyte Specific Sampling Trains



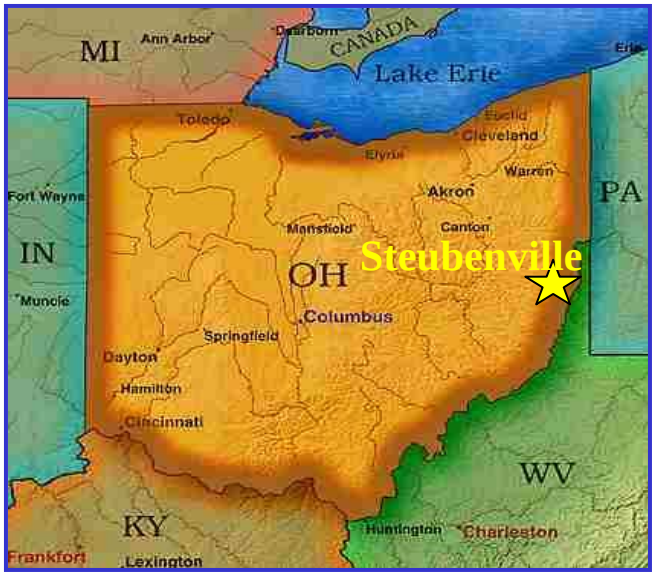
Temperature Controlled Storage Module

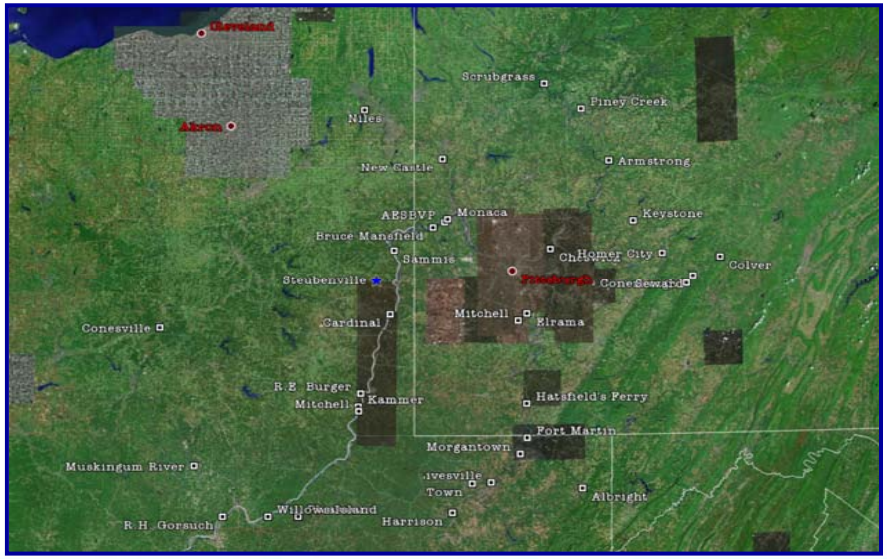
Pinch Valves

1 L sample bottles

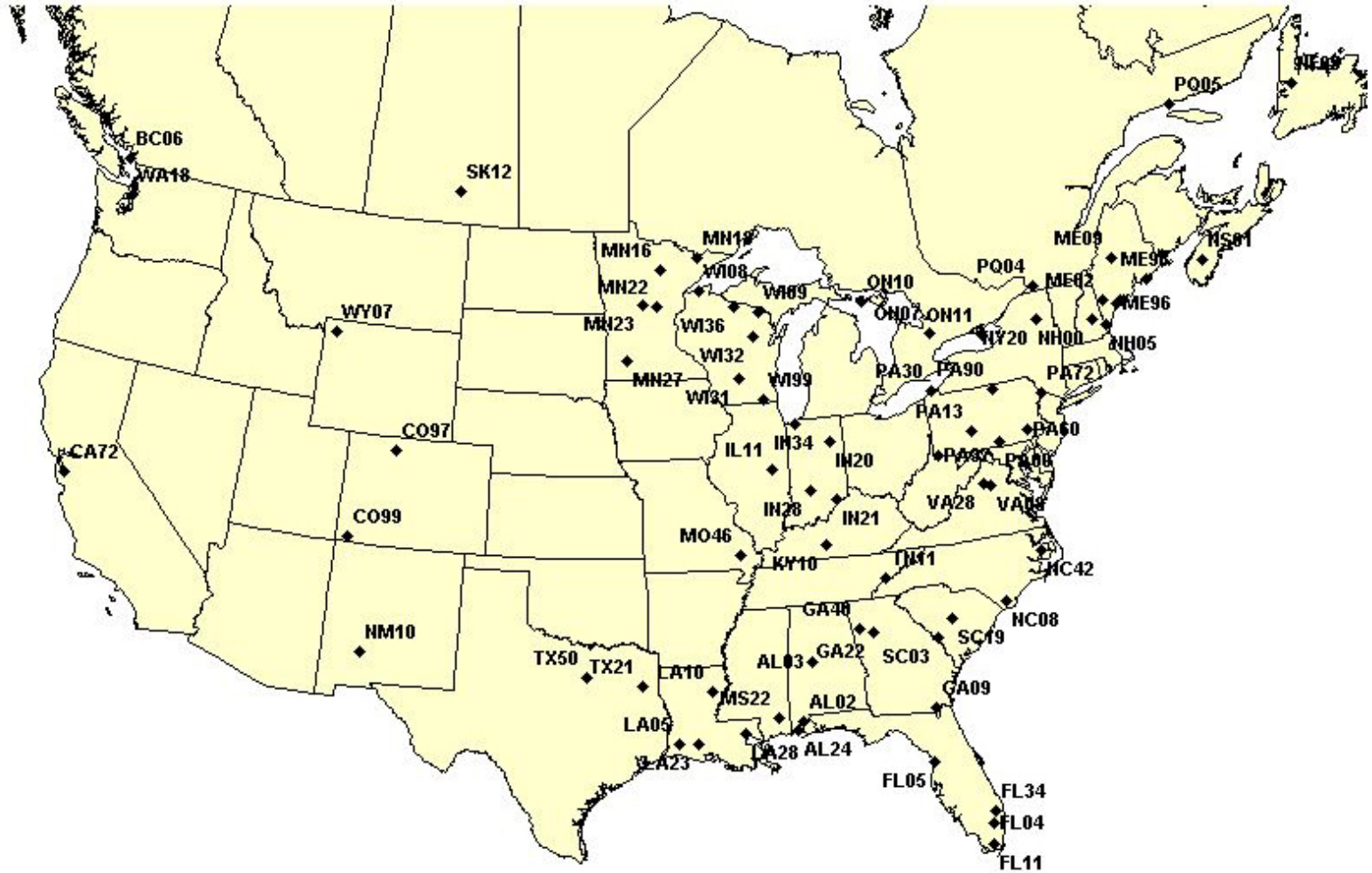
Ohio Mercury Source Apportionment Study

- Objective
  - Determine the impact of local/regional coal combustion sources on Hg deposition in the Ohio River Valley
- Time Line
  - Study designed in 1999
  - Study began January 2002
  - Study will run to end of 2006





NADP Mercury Deposition Network Site Map



Ohio Study Overview

- Comprehensive state-of-the-art measurement & analyses
  - Aerosols - Integrated and Continuous
  - Wet Deposition - Daily Event
  - Criteria Gases - Continuous
  - Meteorology - Continuous
- Receptor Modeling
  - UNMIX, and PMF
  - Hybrid Modeling (Regional Transport)

Steubenville EPA PMF v1.1 Apportionment Results 2003 & 2004

Analyte	Factor 1 (Iron/Steel)	Factor 2 (P Source)	Factor 3 (Coal)	Factor 4 (Crustal)	Factor 5 (Metals)	Factor 6 (Oil/Incineration)
Mg	187.14	95.11	*	**539.31**	29.58	*
Al	49.19	*	75.71	**346.68**	34.67	52.20
P	*	**64.36**	*	*	*	*
S	*	172.33	**11187.00**	363.19	*	*
Cl	257.26	*	602.59	186.41	647.79	**1745.00**
V	**2.82**	*	*	*	*	**1.26**
Cr	**2.40**	*	*	*	*	0.62
Mn	**53.93**	14.02	*	33.01	*	*
Fe	**337.11**	15.32	22.52	12.40	*	136.26
Ni	*	0.53	*	*	*	**3.93**
Cu	*	2.29	19.90	*	8.23	14.38
Zn	3.31	4.20	*	*	13.78	**44.79**
As	*	0.04	0.70	0.09	0.27	0.60
Se	*	*	**2.39**	*	1.25	0.26
Rb	*	0.26	0.23	0.14	0.08	0.20
Sr	0.51	1.53	1.77	**5.54**	*	2.19
Mo	*	*	*	*	**3.60**	*
Cd	0.09	*	0.33	*	0.25	0.25
La	*	*	*	**0.61**	0.01	0.07
Ce	0.02	*	*	**1.19**	*	*
Hg	0.011	0.003	0.136	*	*	*
Pb	0.91	*	3.83	*	*	6.26
NO_3	*	216.00	**5993.80**	1325.70	*	5296.70
% Hg	4 ± 3	2 ± 1	67 ± 14	*	*	*

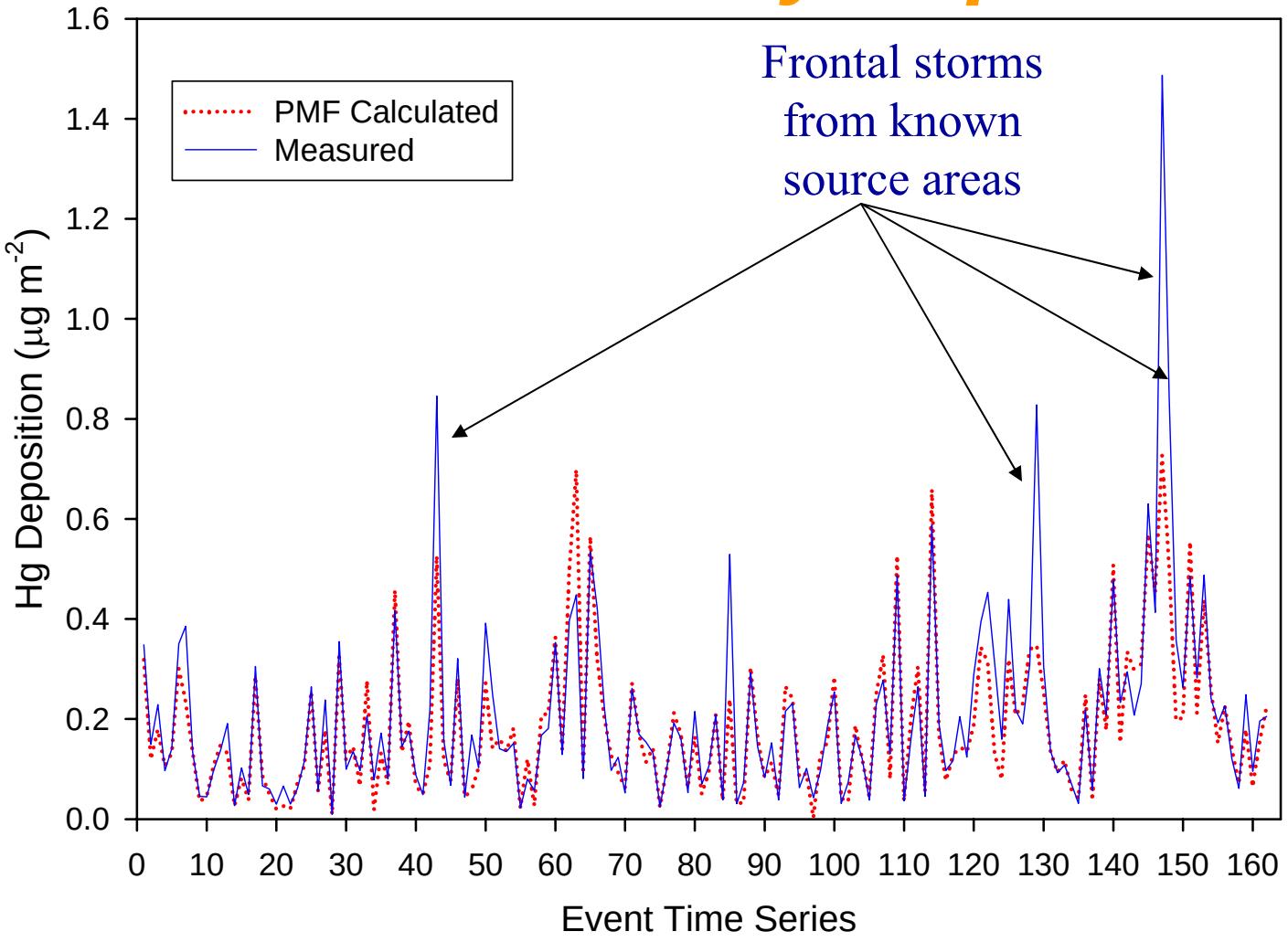
* = Not Significant at 95% confidence interval

Preliminary Steubenville Source Apportionment Results

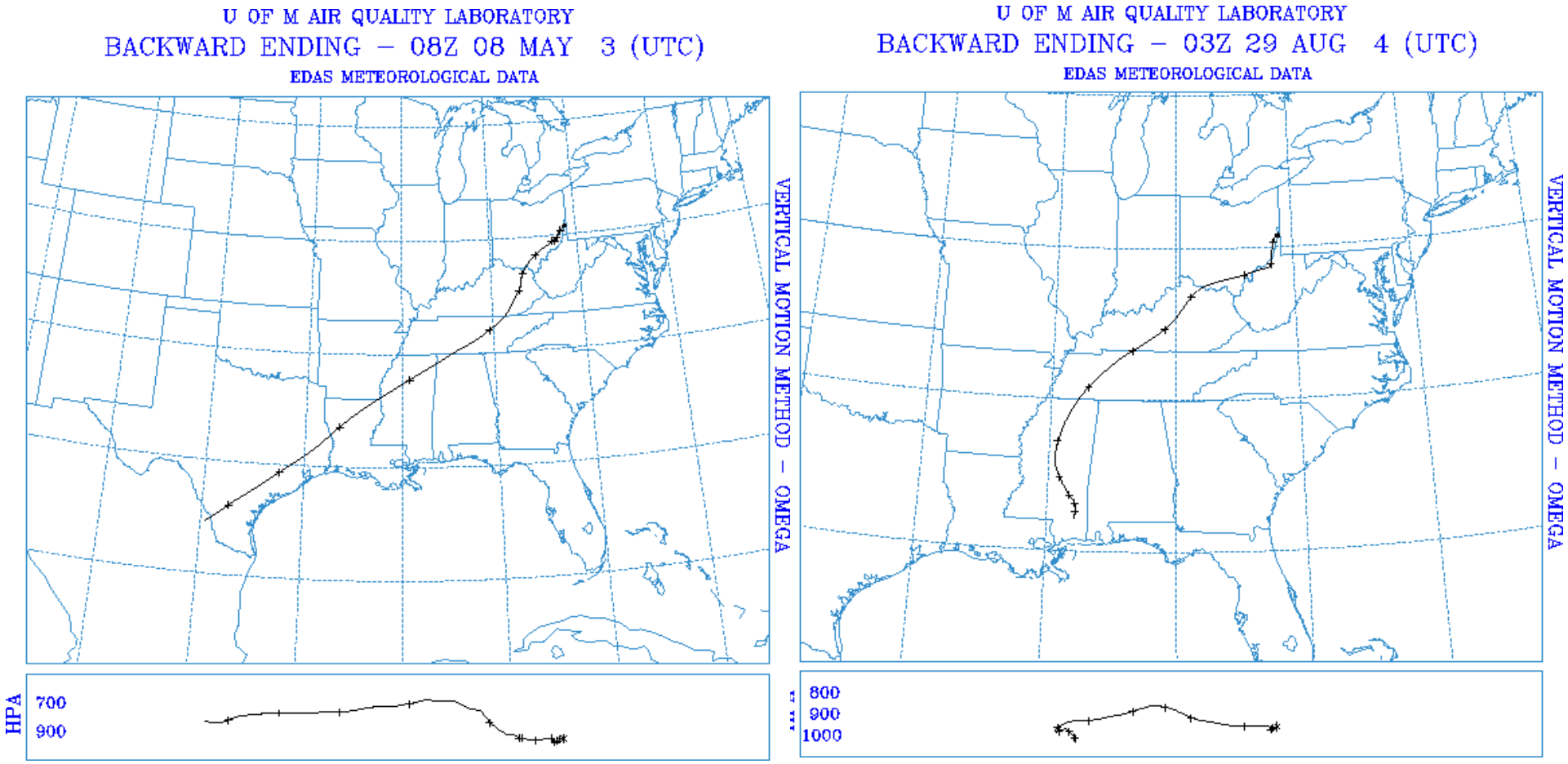
	Measured Hg Wet Deposition ($\mu g\ m^{-2}$)	PMF Estimated CFUB* Contribution ($\mu g\ m^{-2}$)	Unmix Estimated CFUB* Contribution ($\mu g\ m^{-2}$)
2003	13.1	9.3 (73%)	7.9 (60%)
2004	18.0	11.2 (62%)	10.5 (59%)

***Coal-fired Utility Boiler**

EPA PMF Estimated versus Measured Mercury Deposition



HY-SPLIT Back Trajectories

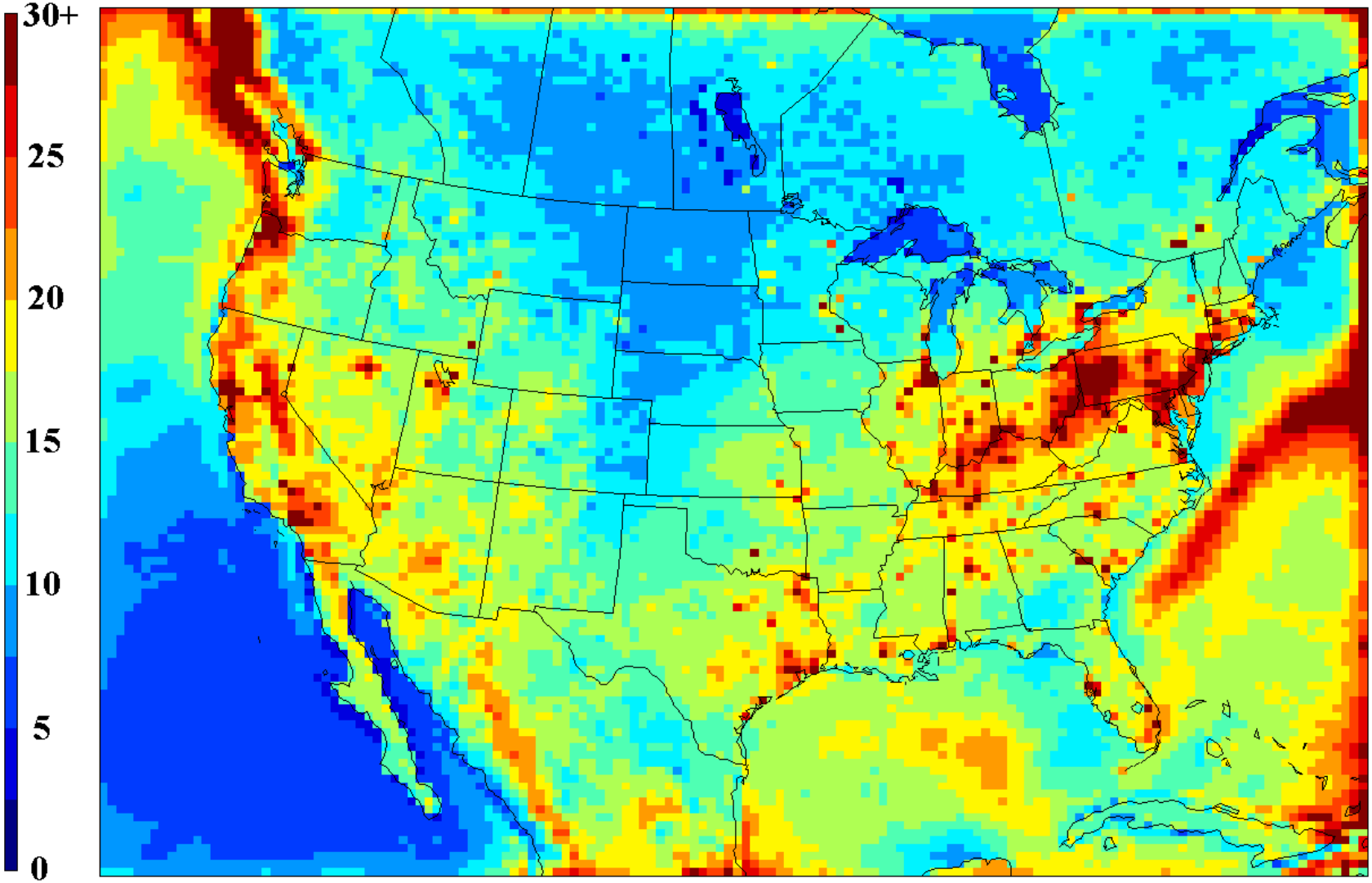


Summary of Steubenville Receptor Modeling

- Hg wet deposition at Steubenville
  - ~ 75% is attributable to local/regional anthropogenic sources
  - ~ 65% is attributable to coal combustion
  - ~ 25% from reemission/global background
- A significant portion of total Hg wet deposition is driven by a few local coal combustion dominated precipitation events
  - In 2004, >8% of total wet Hg deposition occurred during one event
  - S/Se ratio may be useful to evaluate relative importance of regional CFUBs not equipped with FGD

CMAQ-simulated total mercury deposition for 2001

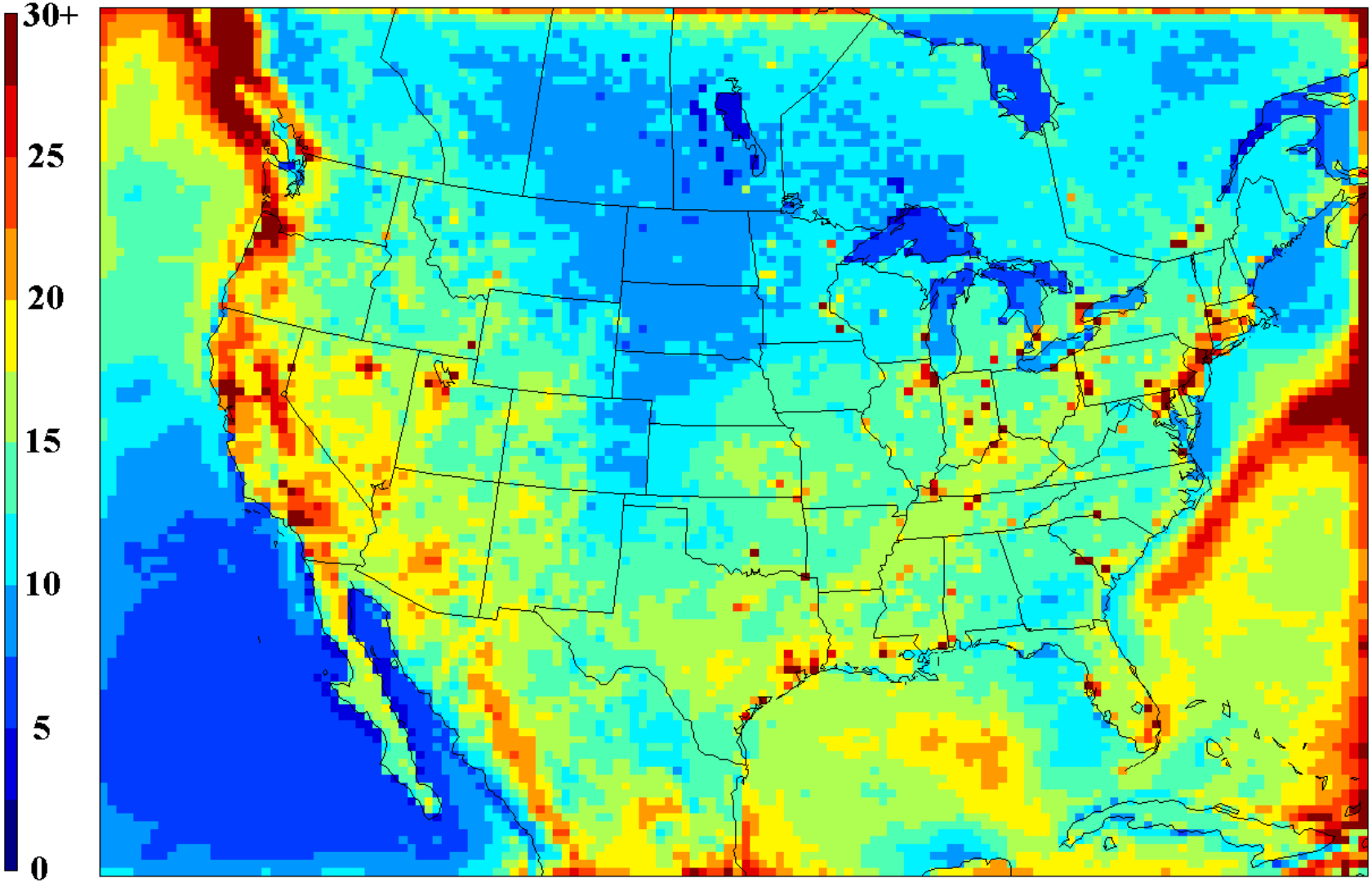
(micrograms per square meter)



Base case

CMAQ-simulated total mercury deposition for 2001

(micrograms per square meter)



Utility Zero Out

Comparison of CMAQ Model Results to Measured Mercury Wet Deposition at Steubenville

CMAQ Simulations performed by CSC for EPA (6FEB04)

	Hg Deposition ($\mu g\ m^{-2}$)	CFUB Contribution (%)
CMAQ 2001	13.6	43
PMF & UNMIX 2003 & 2004	15.6	65

Comparison of CMAQ Modeled versus UMAQL Measured Hg Wet Deposition 2001

Site	CMAQ Wet Deposition ($\mu g\ m^{-2}$)	Measured ($\mu g\ m^{-2}$)
Dexter, MI	8.3	12.5
Pellston, MI	4.6	10.5
Eagle Harbor, MI	4.7	7.7
Underhill, VT	4.4	8.6

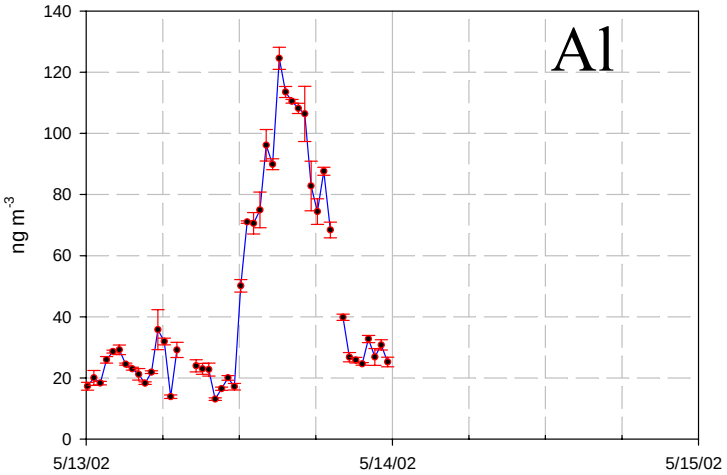
High Volume Slurry Sampler

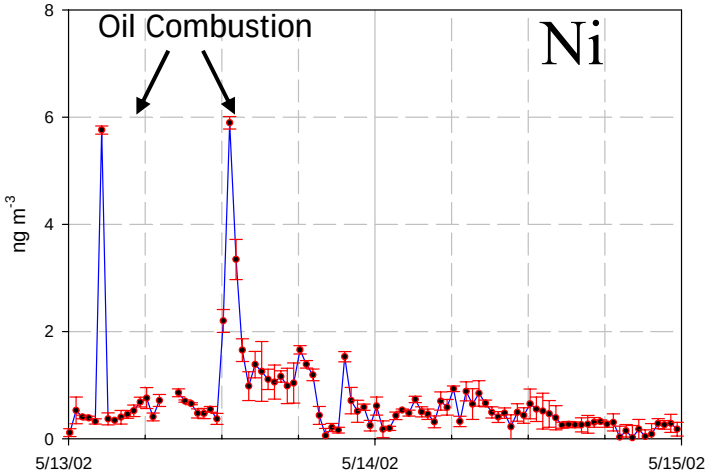
* 30 minute $PM_{2.5}$ samples

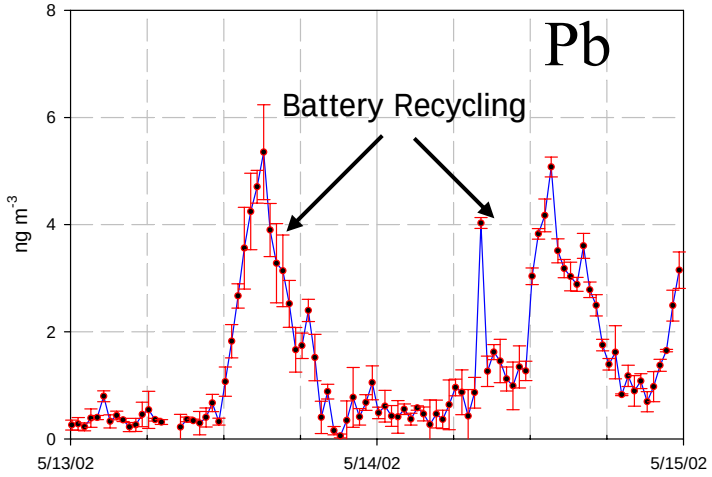
High Resolution ICP-MS Capability
(Slurry Sample Aerosol Samples)

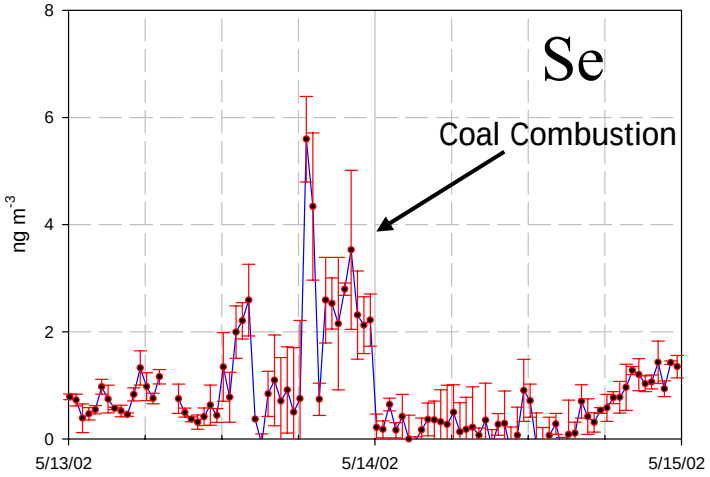
- Low Resolution
  - Li, Be, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb
    Cs, Ba, La, Ce, Nd, Sm, W, Tl, Pb, U
- Medium Resolution
  - Na, Mg, Al, P, S, Ca, Sc, Ti, V, Cr
    Mn, Fe, Co, Ni, Cu, Zn
- High Resolution
  - K, As, Se
- Stable Isotope Ratios
  - Pb

Example Slurry Sampler Data

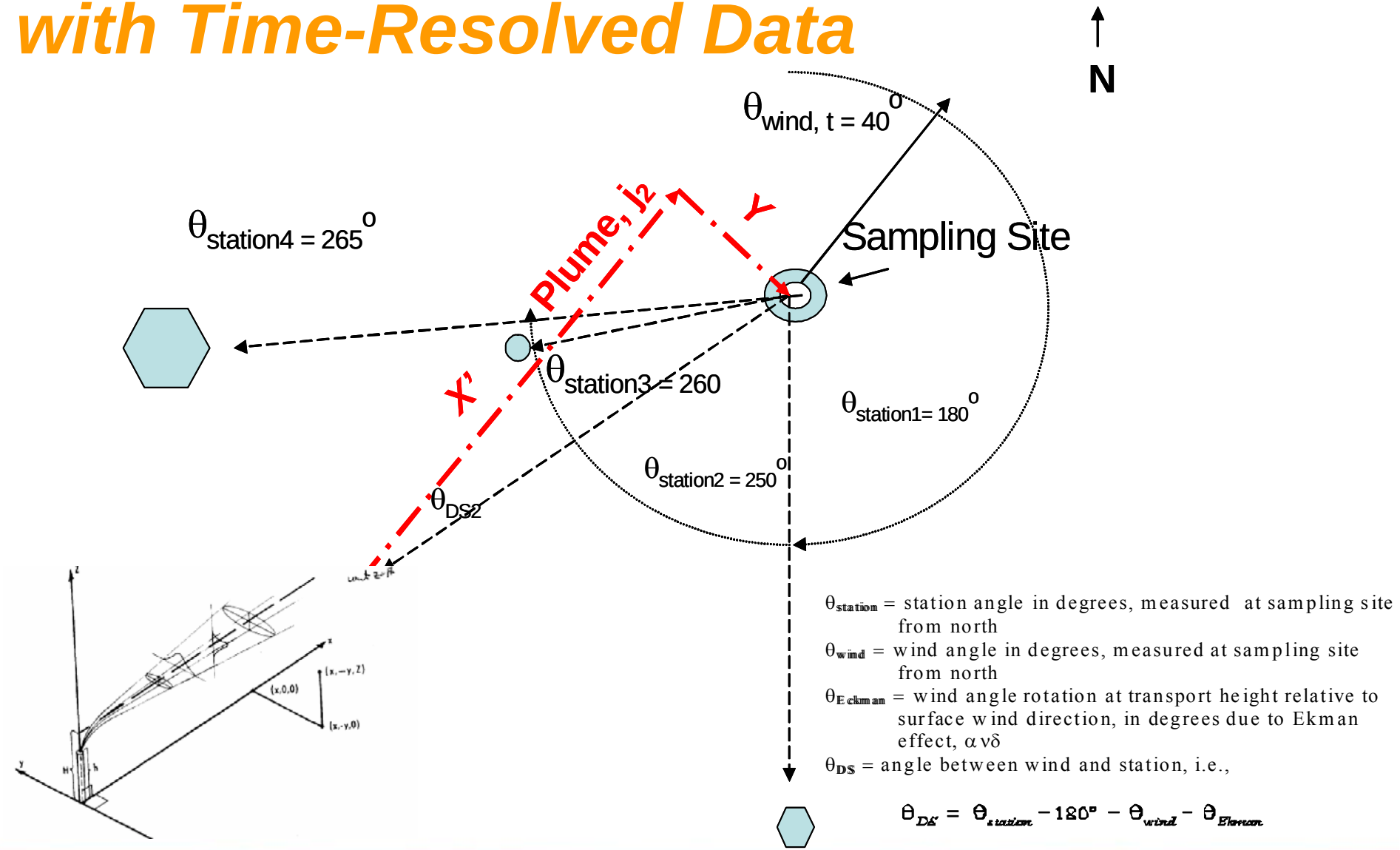








Directionality: A Powerful Constraint with Time-Resolved Data



Sources Near the Sydney Site

Model Description

- **Basic Mass Balance with Meteorological Dispersion**
- **Our goal is to determine the emission rates of species, i, which are of interest from power plant plumes, from j sources, using highly time-resolved concentration measurements from SEAS and SO_2 monitors, as the products of emission rates and P/Q, meteorological dispersion factor for each source. This is given by the following equation:**

$$[E_i]_t = \sum_{j=1}^{n} ER_{i,j} \cdot \chi/Q_{j,t} + [E_{bkgnd_i}]_t \qquad (1)$$

$[E_i]_t$ = Ambient conc. species i at time (sample) t, $\mu g\ m^{-3}$
(SO_2, Se, As, Ni, Pb, Zn, Cd, Cu, Cr, Al, Fe, Mn)

$ER_{i,t,j}$ = Emission Rate of species i at time, t, from source j, $\mu g\ s^{-1}$

$X/Q_{j,t}$ = Dispersion Factor for each source j at time t, $s\ m^{-3}$

$$\chi/Q = \frac{1}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\frac{y^2}{\sigma_y^2}\right] \cdot \exp\left[-\frac{1}{2}\frac{H^2}{\sigma_z^2}\right] \qquad (2)$$

Volumetric dilution rate

directionality

Vertical dispersion

Predicted Emission Rates of SO_2 and Metal Species

Species	Unit	Gannon	Big Bend	Bartow	Manatee
SO_2 observed	g/s	2,600	311	1140	1280
SO_2 predicted	g/s	2,700	430	1200	1135
Al	g/s	2.059	1.743	0.262	11.084
As	g/s	0.019	0.016	0.021	0.017
Cr	g/s	0.029	0.031	0.023	0.178
Cu	g/s	0.033	0.044	0.025	0.160
Fe	g/s	1.496	1.359	0.749	6.514
Mn	g/s	0.024	0.031	0.020	0.254
Ni	g/s	0.022	0.074	0.021	0.635
Pb	g/s	0.055	0.069	0.043	0.188
Se	g/s	0.035	0.019	0.030	0.050
Zn	g/s	0.099	0.142	0.085	1.045