

# Direct Measurement of Mercury Reactions in Power Plant Plumes

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EPRI

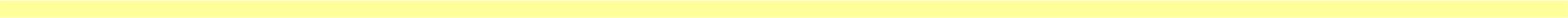
*DOE NETL Mercury Control Technology  
R&D Program Review Meeting*

*Pittsburgh, PA*

*August 12-13, 2003*

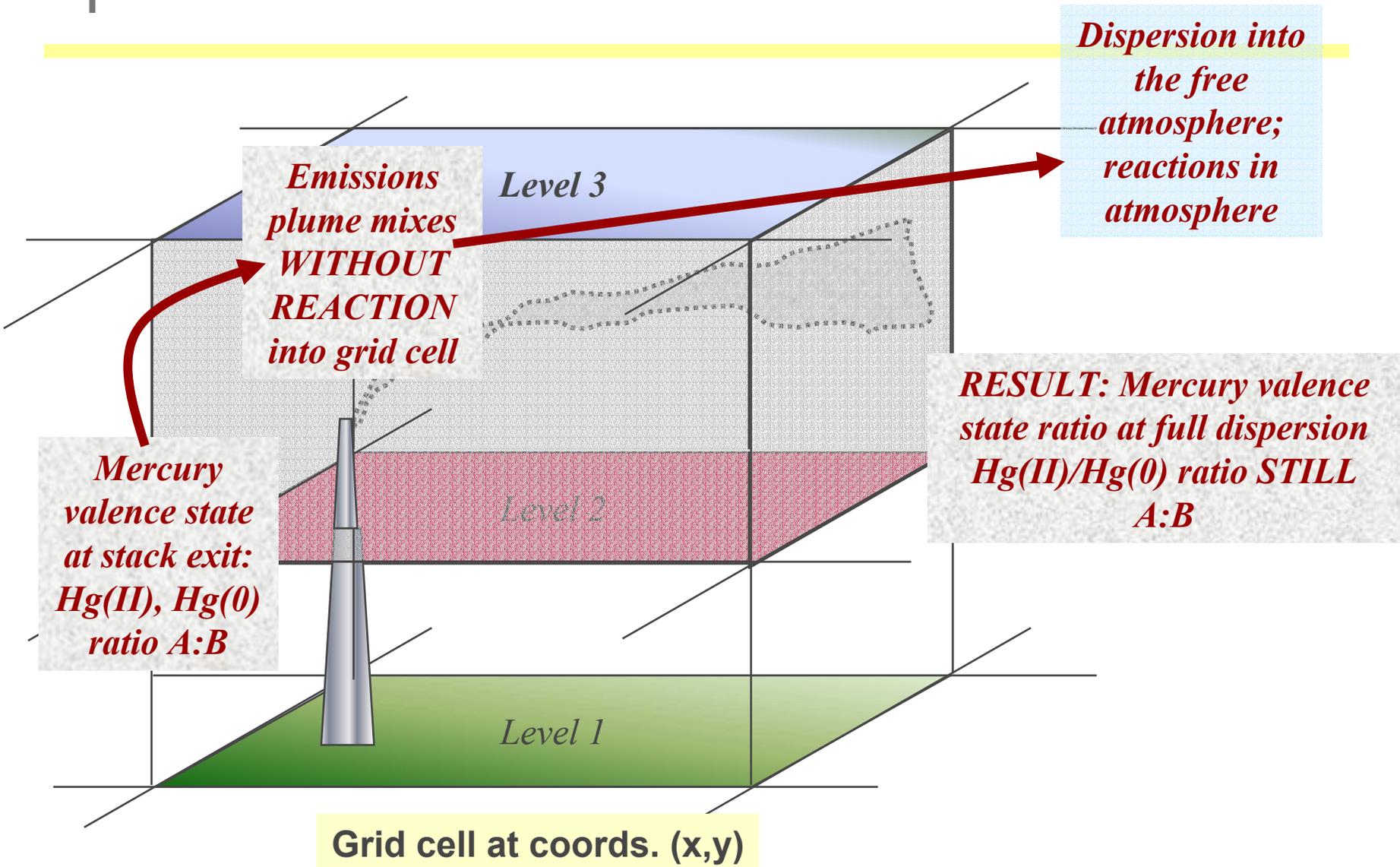
# Power plant plumes may promote rapid mercury chemistry

- ***Ionic*** mercury (6 orders of magnitude more water soluble, easily washed out of plume) → rapidly reduced to ...
- ***Elemental*** mercury (much less soluble in precipitation, likely to go into regional, global background) in power plant plumes.

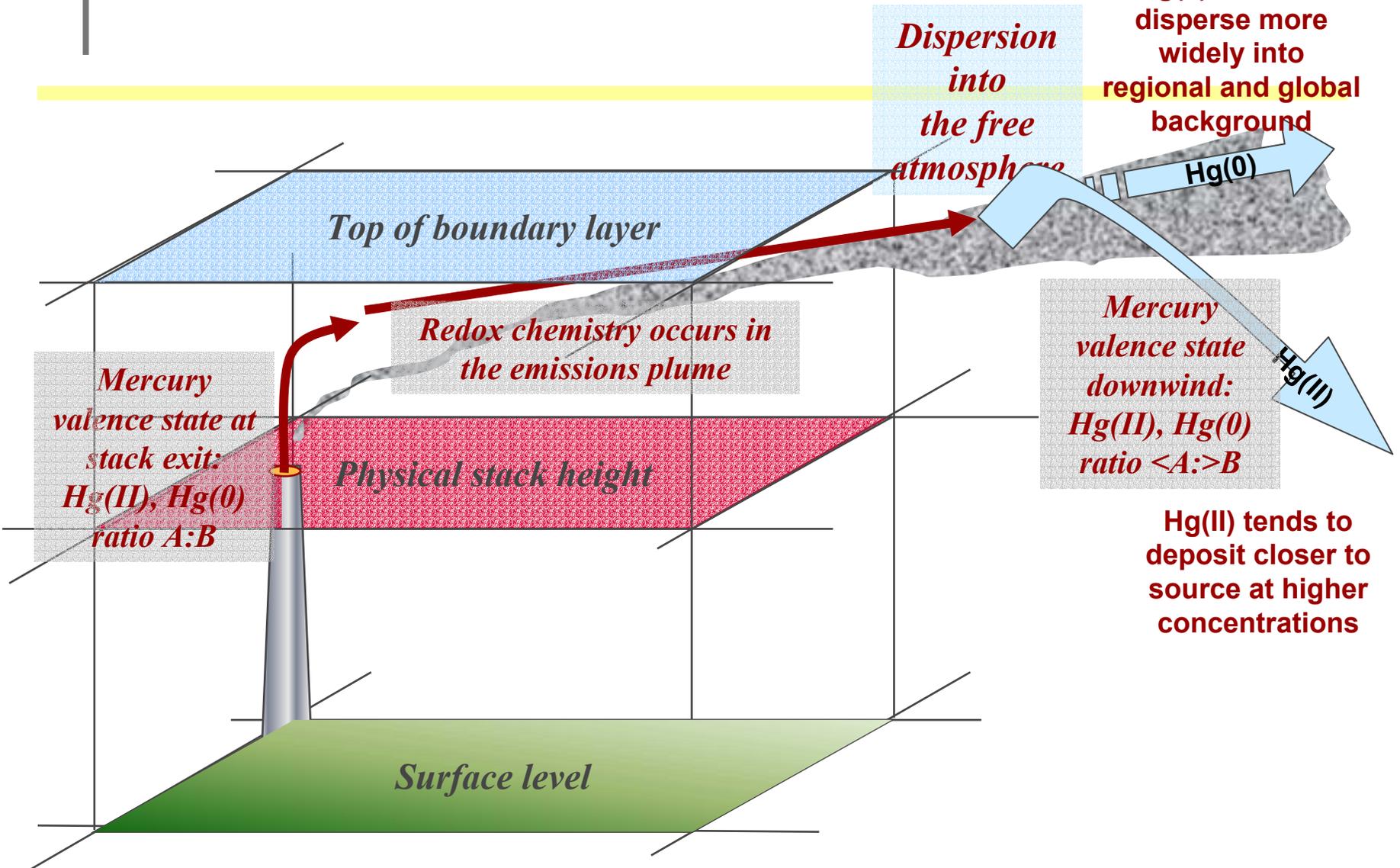


# **CURRENT MODELING OF MERCURY IN PLUMES**

# Plume behavior in model atmosphere



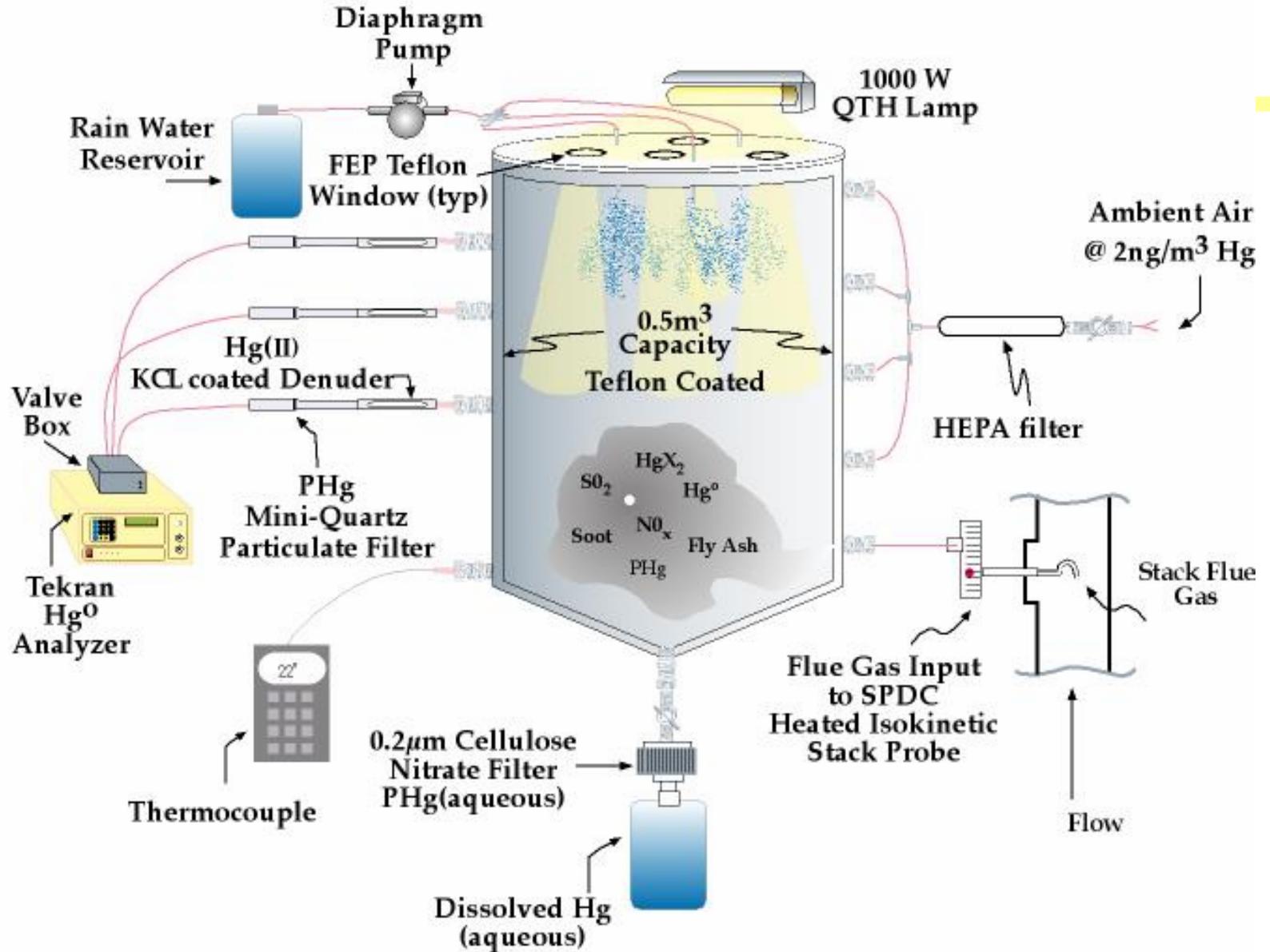
# Plume behavior in “real” atmosphere





# – PLUME DILUTION SIMULATIONS

# Static Plume Dilution Chamber (SPDC) Schematic

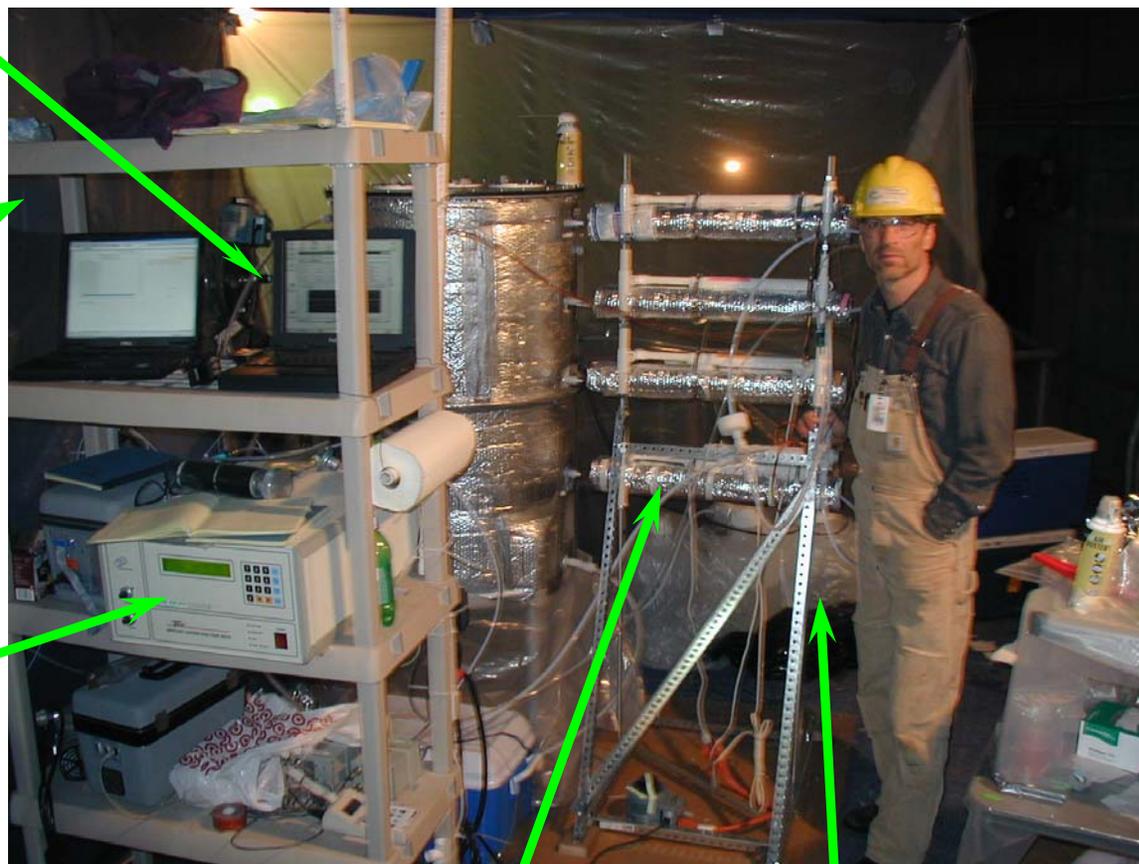


# SPDC at Plant Bowen

Duct to SPDC Interface

Flue gas Duct

Tekran  
Real-Time  
Hg(0)



SPDC Speciation  
Denuder/Filter System

Rainwater  
Wash System

# Some SPDC Study Locations

- October 2002 at Plant Bowen, EPRI (Levin), Southern Company, (Jansen), in collaboration with TVA (Valente) and EERC (Laudal and Schulz)
- March 2000 @ EERC UARG-EPRI (Michaud and Levin), CATM-EERC (Laudal), EPA-ORD (Kilgroe) and FGS (Prestbo)
- May 1997 @ Dickerson and Mont. Co. Waste Inc. Maryland DNR-PPRP (Sherwell) and ERM (J. Ross)
- February 1995 @ WEPCO-PIPP Wisconsin DNR (Knauer) and EPA GLNPO(A. Bandemeier)

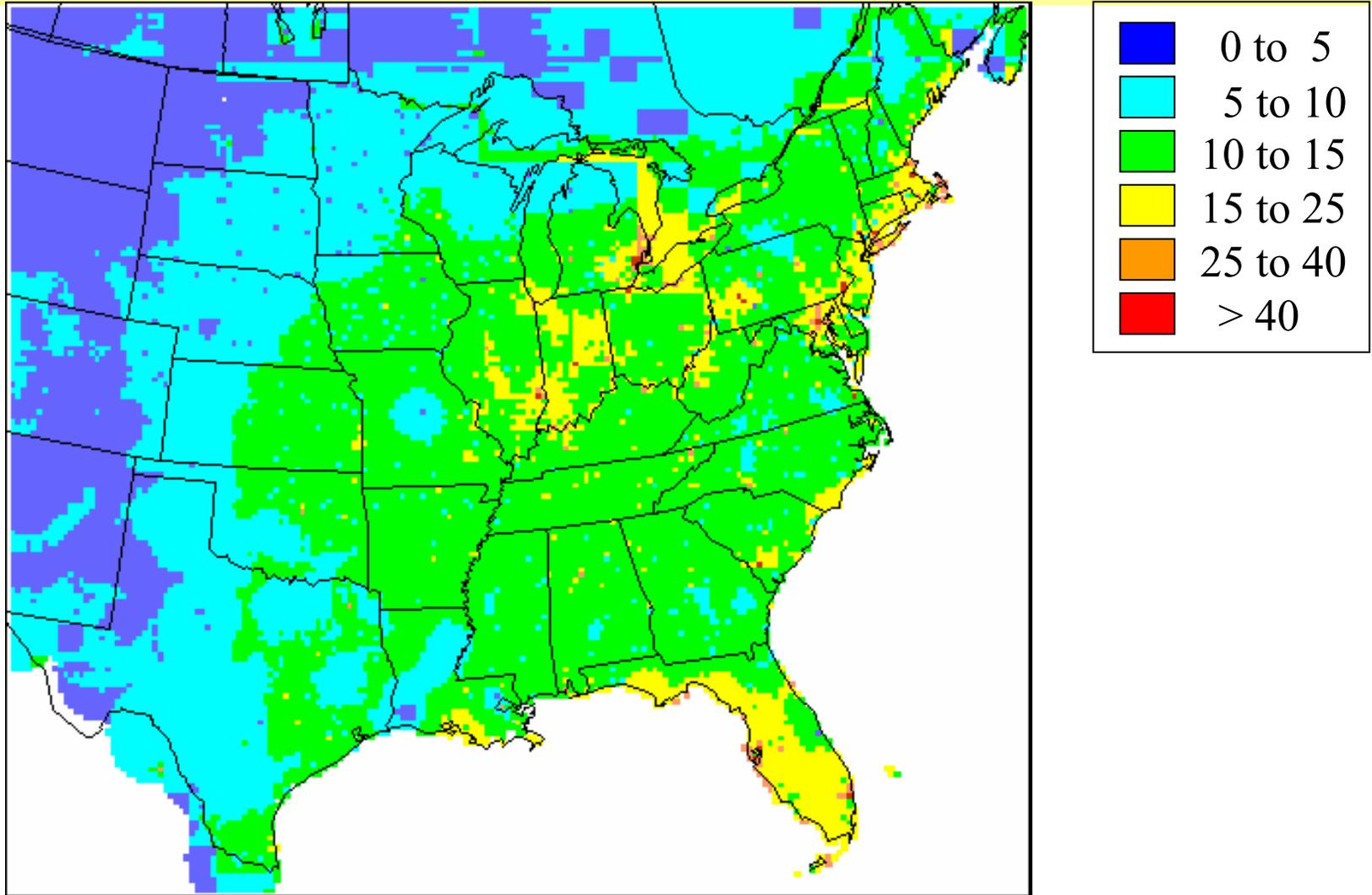
# SPDC EERC Pilot Plant Study Conclusions: Hg(II) → Hg(0) in Plume

- Hg(0)/Hg<sub>TOT</sub> at end > ratio injected into the SPDC – Hg(II)→Hg(0)?
- Conversion is fast (<5 minutes), significant
- Greater conversion of Hg(II) to Hg(0) for SPDC “daytime” runs.
- Conversion of Hg(II) to Hg(0): typically x1.5-3, largest (x6) when O<sub>3</sub> added at 200 ppb.
- No SPDC runs showed significant amounts of gaseous Hg(II) adsorbing to the particulate phase

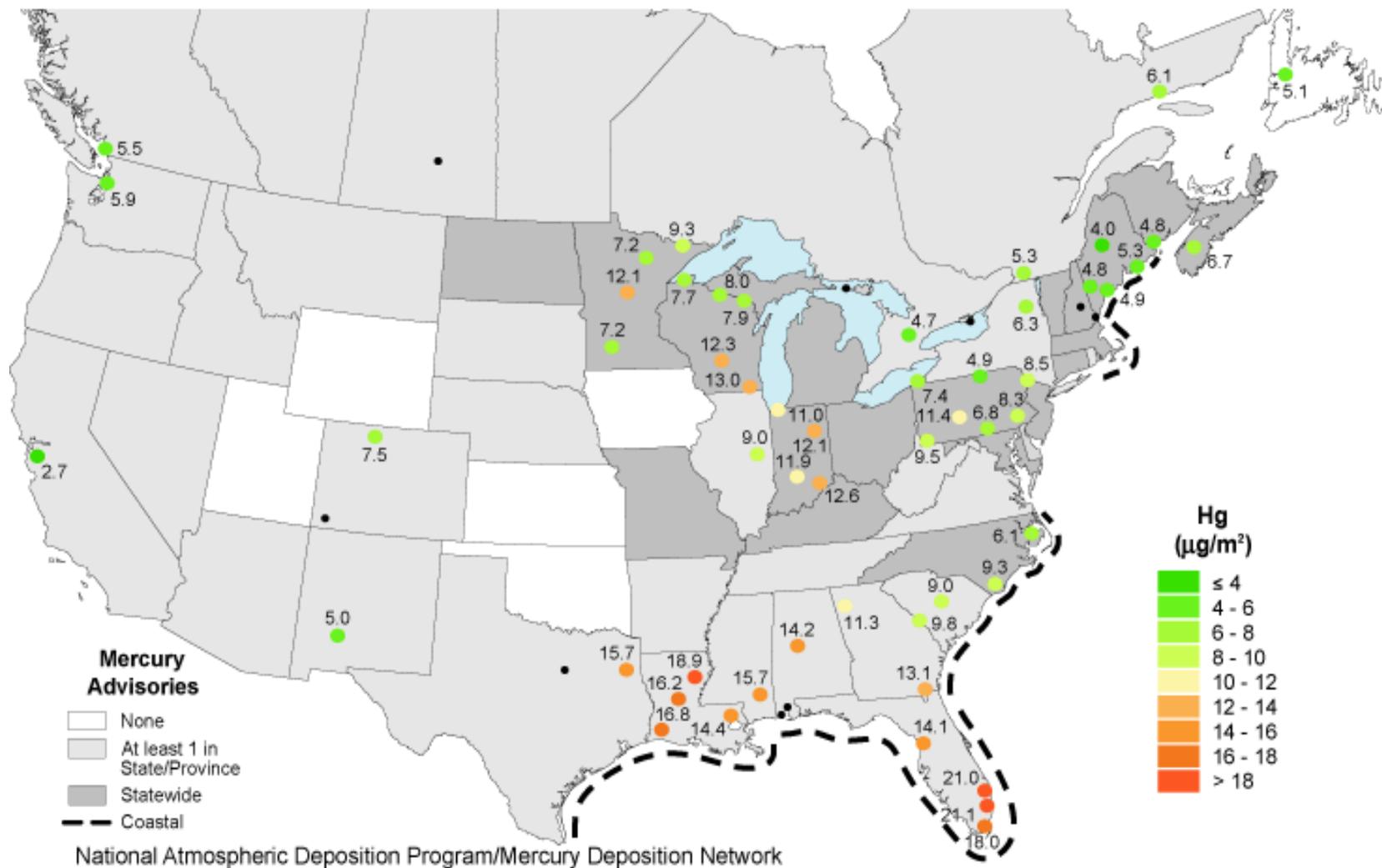
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**– REGIONAL MODEL  
SIMULATIONS vs.  
OBSERVATIONAL DATA**

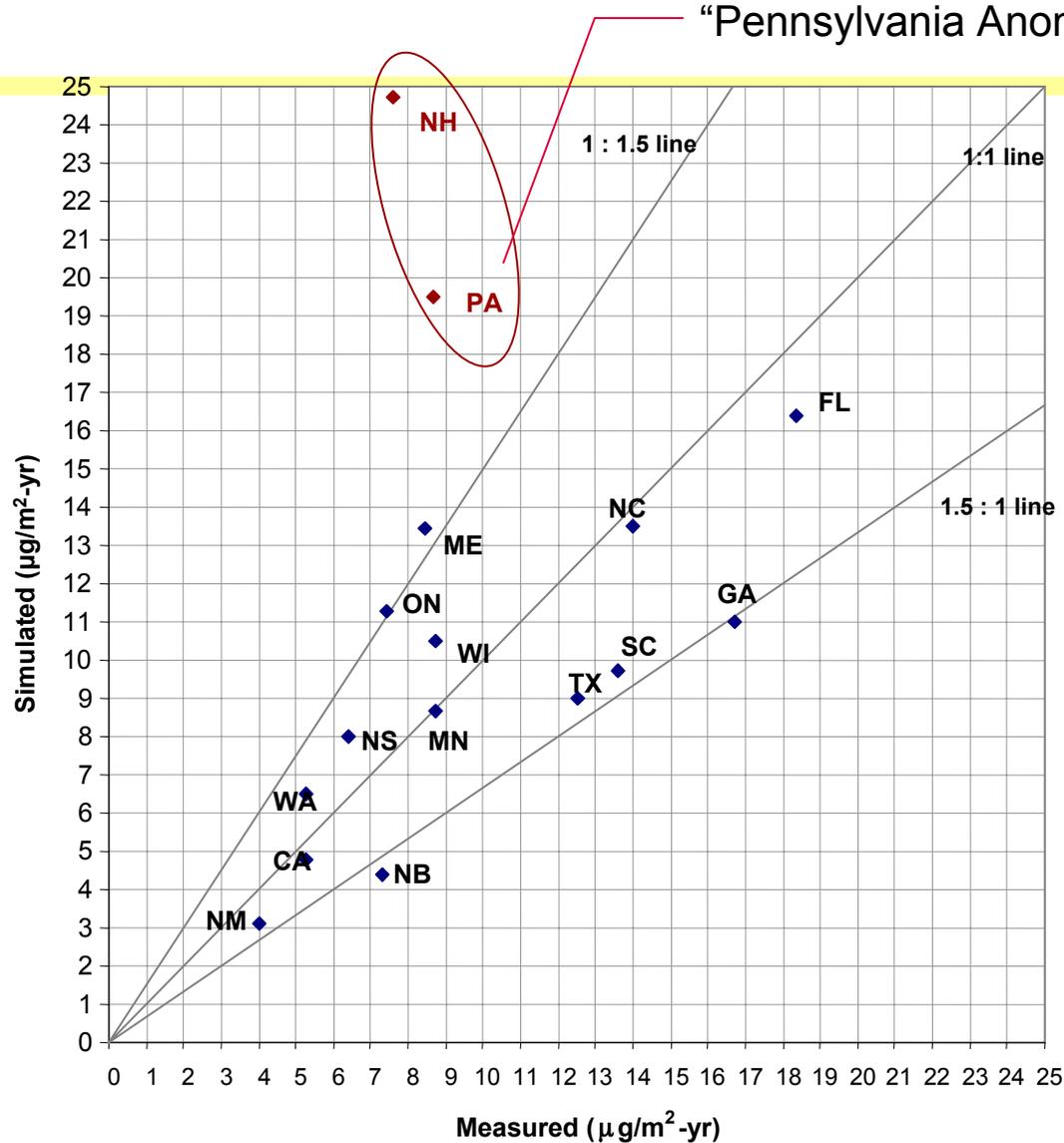
# Annual wet deposition flux of total Hg ( $\mu\text{g}/\text{m}^2\text{-y}$ ) (EPRI TEAM Regional Model, 20-km resolution)



# Observed Mercury Wet Deposition ( $\mu\text{g}/\text{m}^2\text{-y}$ ), Mercury Deposition Network, 2001



# EPRI TEAM Model Prediction vs. Observations Wet Deposition Data Averaged by State



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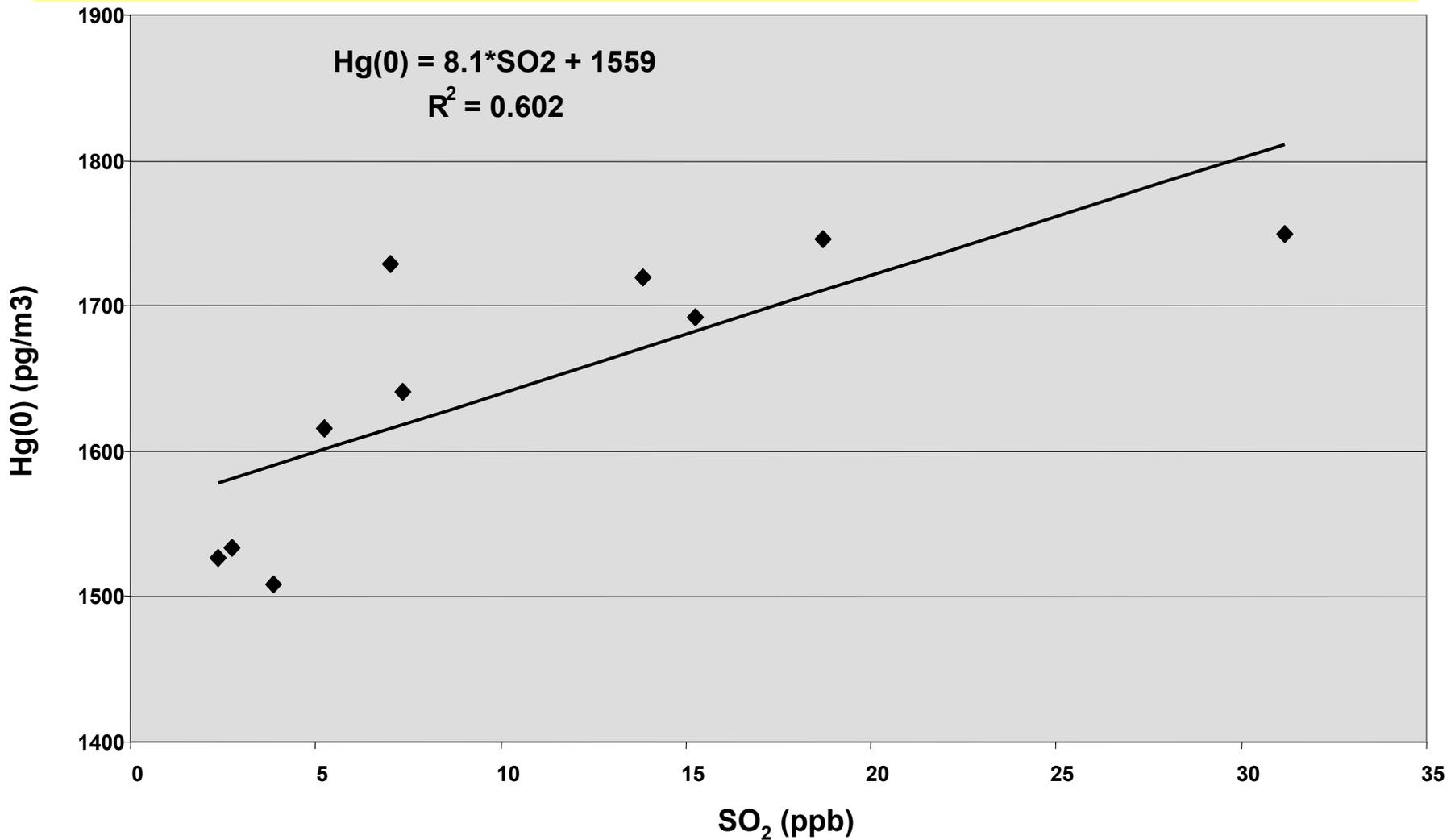
**– FIELD MEASUREMENTS,  
SOURCE vs. SAMPLER  
SPECIATION**

# Simulations vs. Measurements, Plant Bowen to Yorkville Ground Station

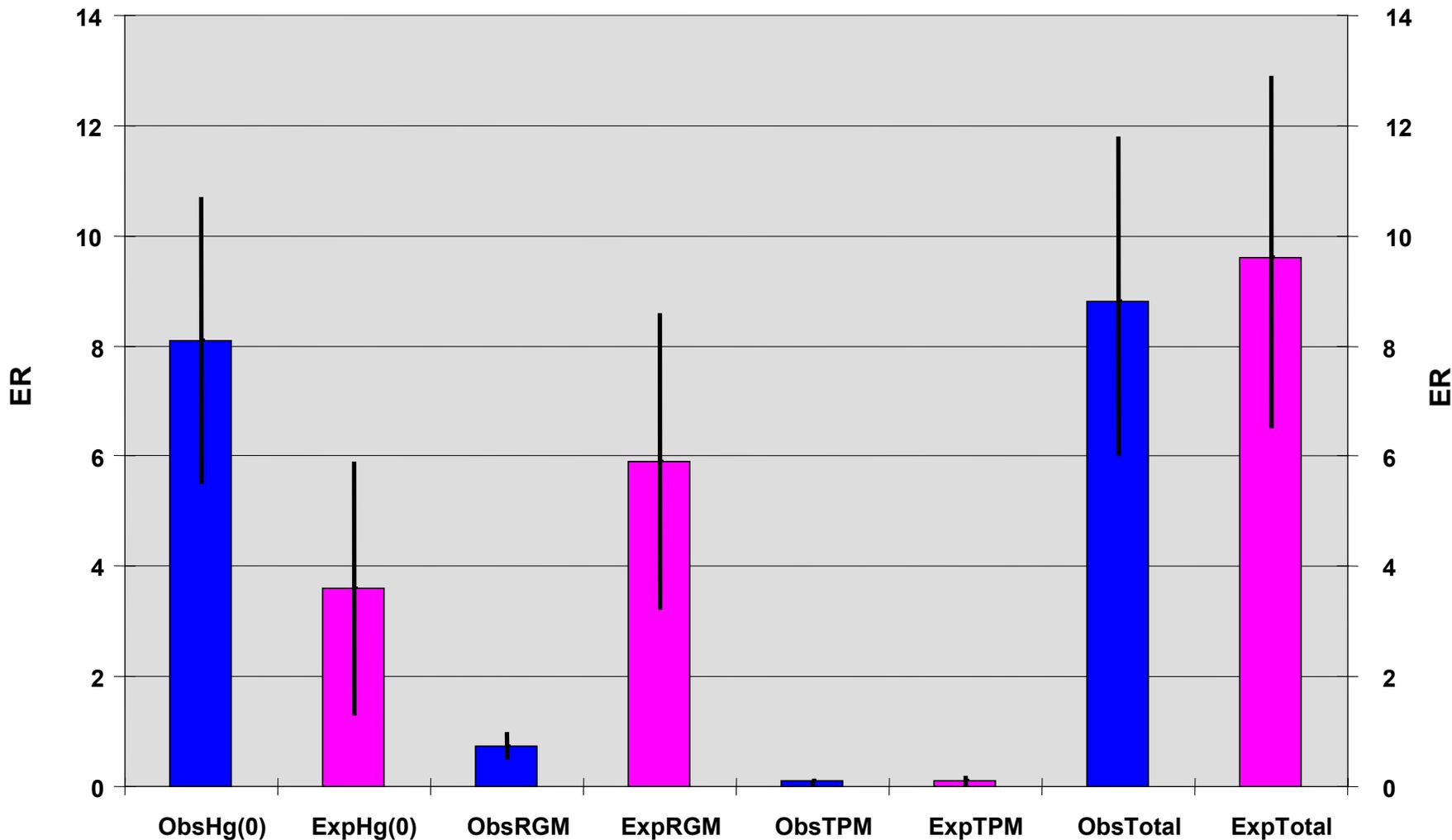
	<u>Emissions</u>	<u>Ambient measurements</u>	<u>TEAM simulations</u>	
			<u>without clouds</u>	<u>with clouds (a)</u>
<b>SO<sub>2</sub>/NO<sub>y</sub></b>	<b>3.2</b>	<b>3.5</b>	<b>3.1</b>	<b>2.9</b>
<b>SO<sub>2</sub>/Hg (x10<sup>5</sup>)</b>	<b>8.2</b>	<b>6.4</b>	<b>7.8</b>	<b>7.3</b>
<b>Hg(0)/Hg<sub>TOT</sub></b>	<b>0.40</b>	<b>0.94</b>	<b>0.41</b>	<b>0.42</b>
<b>Hg(II)/Hg<sub>TOT</sub></b>	<b>0.60</b>	<b>0.06</b>	<b>0.59</b>	<b>0.58</b>

(a) *Clouds placed between 450 m and 2000 m above ground level*

# Hg(0) vs. SO<sub>2</sub> – July 20, 2001 Event, Bowen Plume Impingement at Yorkville Station



# Observed vs. Expected Emission Ratios ( $\text{pg}/\text{m}^3$ per ppb) – July 20, 2001 Event, Bowen Plume Impingement at Yorkville Station

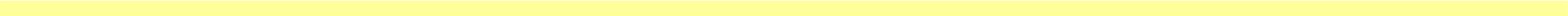




# EXPERIMENTAL PLAN

# WORKING HYPOTHESES

- $\text{Hg(II)}/\text{Hg}_{\text{TOT}}$ : [stack gases]>[aircraft]>[ground station]
- From plume dilution experiments: look for rapid, high-ratio chemical reduction in buoyancy segment of plume out to dilution ratio of hundreds to one.
- Ideally:
  - Steady, unidirectional winds < 15 m/s; low turbulence BL
  - Aircraft sampling of upwind background (free of other major sources), several downwind transects (each with multiple passes), far downwind dispersion
  - Aircraft multiple passes through plume rise portion just above stack
- Reality: a lot more difficult (approach to stack; steady-state conditions;
- Additional goal: method evaluation, plume dilution methods



# MEASUREMENTS AT PLANT BOWEN



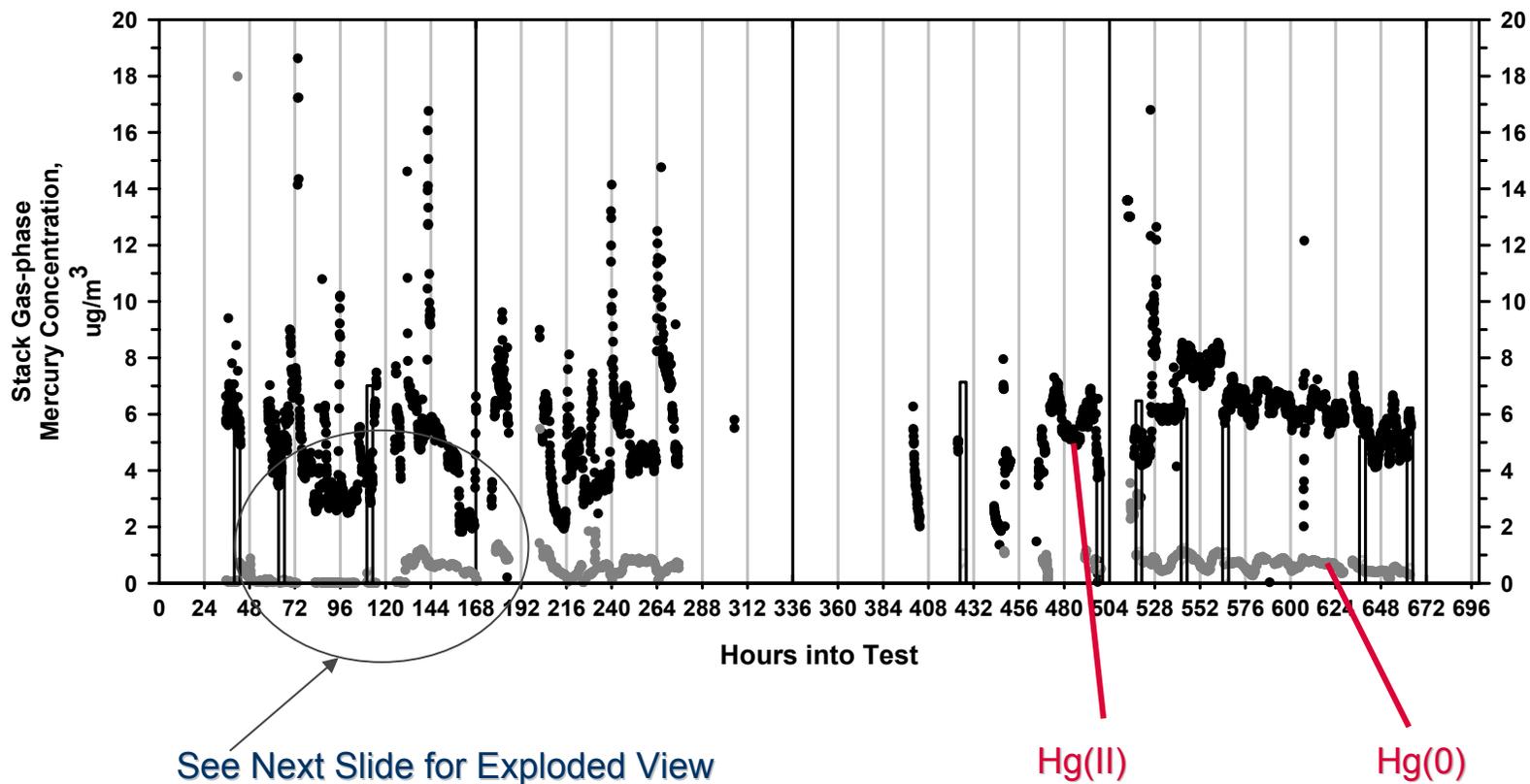
# Plant Bowen

- **Located NW of Atlanta, gently rolling terrain, plateau to SSW (location of ground station)**
- **Twin stacks, 300+ m ht, each venting 2 units through single duct within RC structure**
- **Units 1, 2, 4 operating; Unit 1 had operating SCR**
- **Coordinated measurements: stack OH, stack SPDC Tekran, aircraft Tekrans, ground supersite Tekrans**

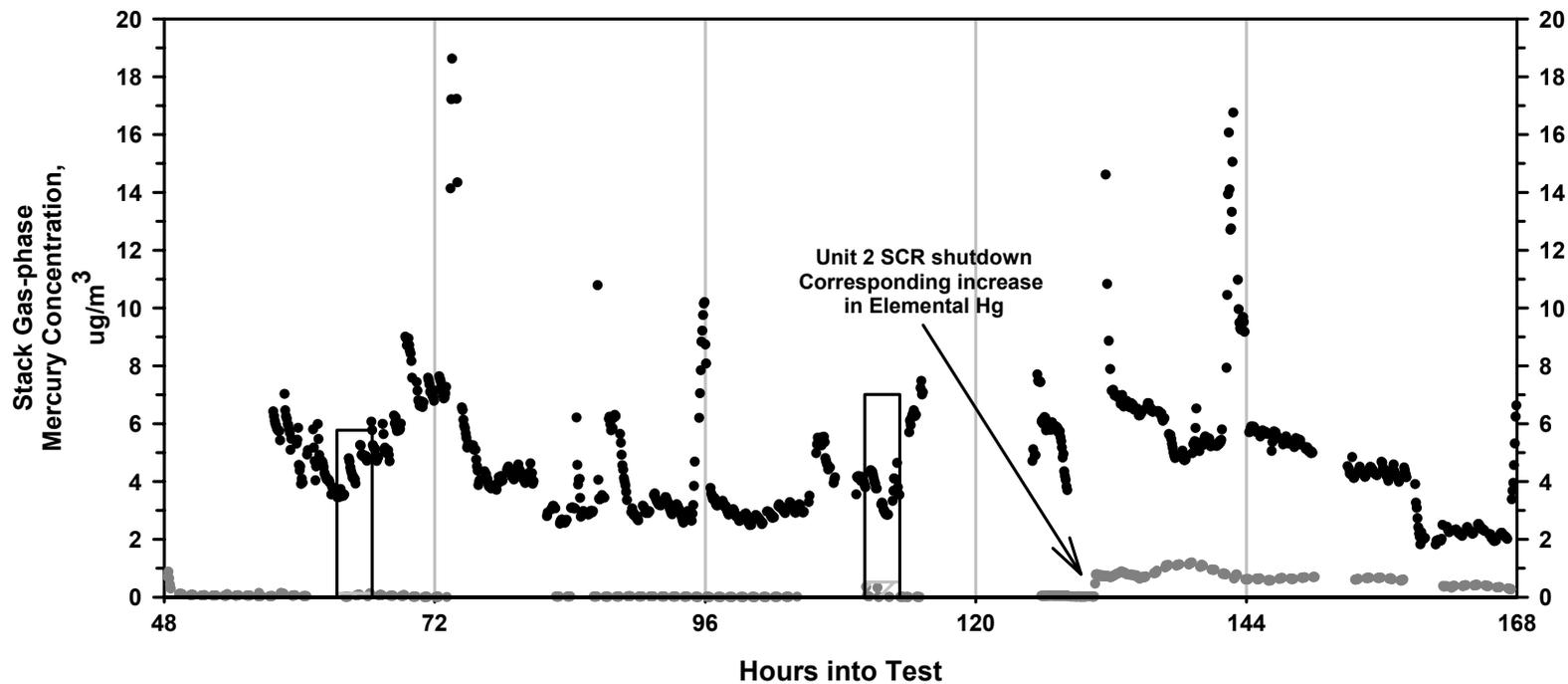




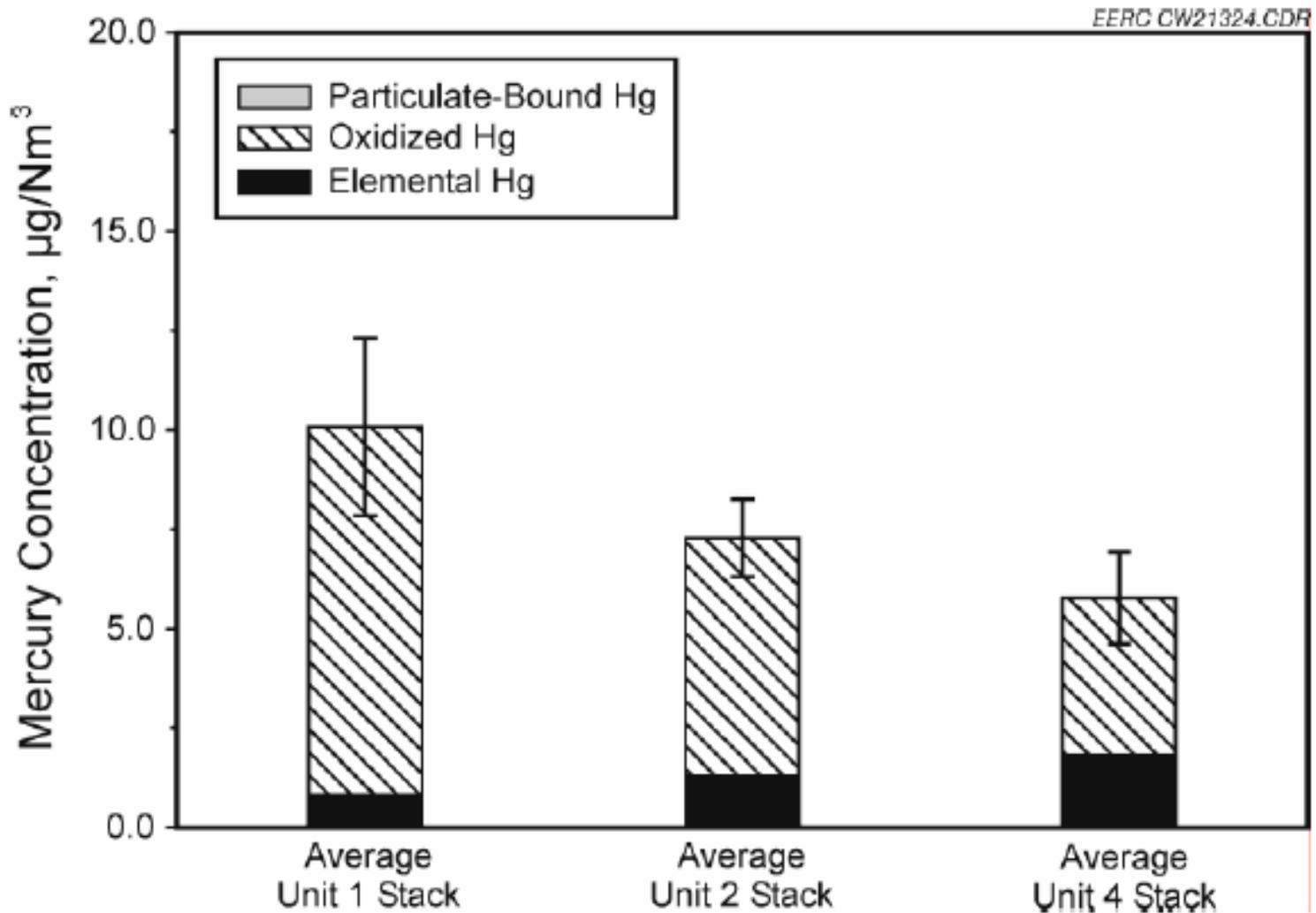
## Bowen Unit 2 Stack Data



## Bowen Unit 2 Stack CMM Data



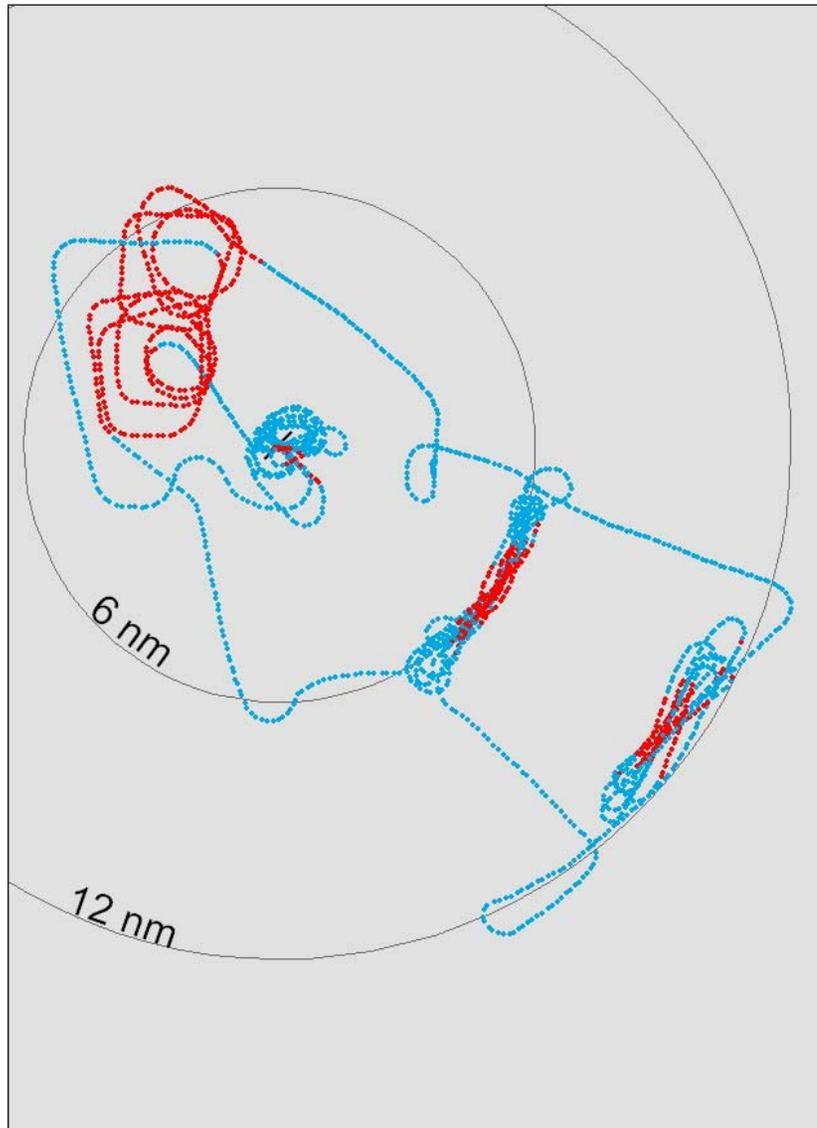
# Plant Bowen Stack Data



# Aircraft Plume Sampling

- **Annular denuders used to capture RGM**
- **Hg(0) captured by the Tekran gold trap**
- **Particulate-bound mercury is captured by a filter, then desorbed to the analyzer**
- **Plume eddy/boundary detection using a NO<sub>x</sub> analyzer**

# Typical Bowen Flight Track



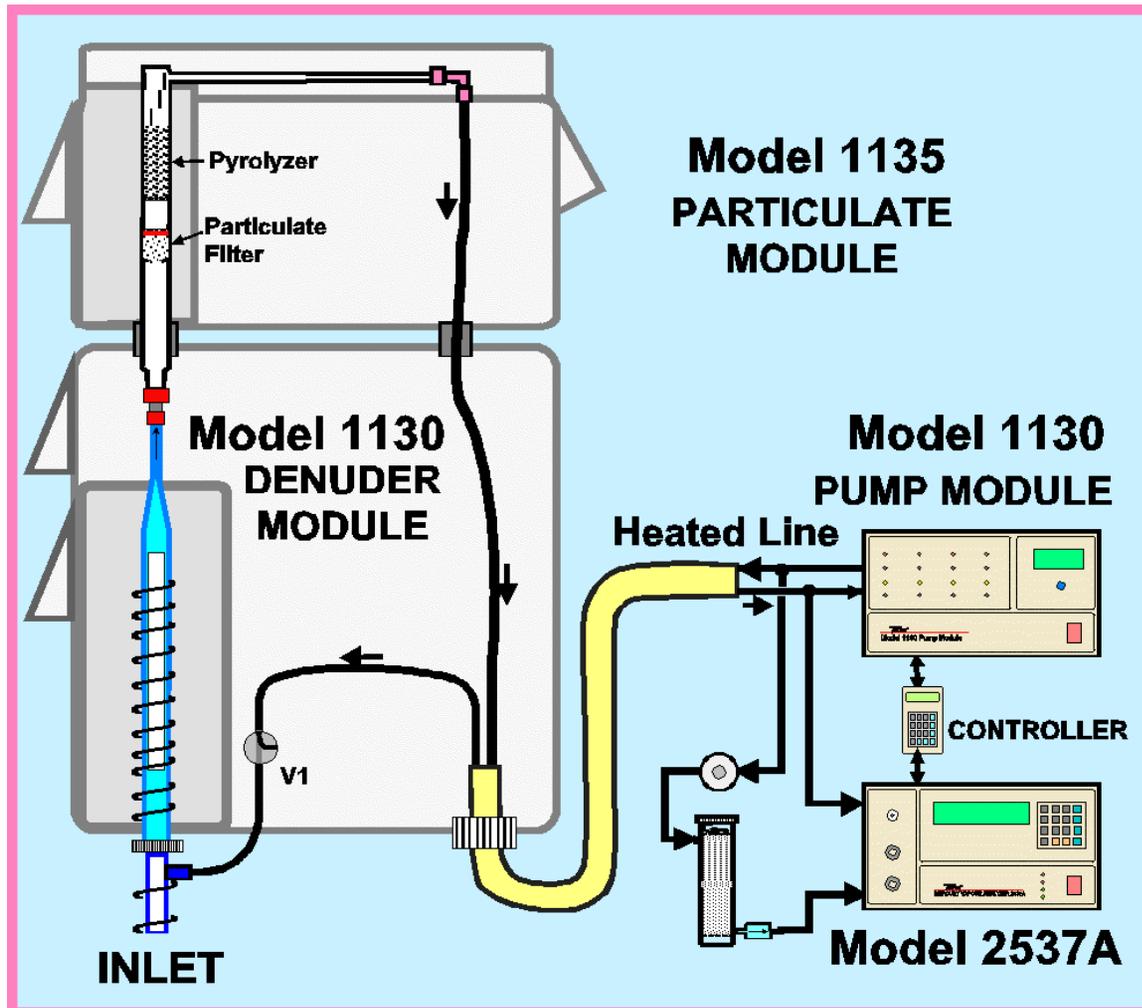
**Flight 6**

**October 17, 2002**

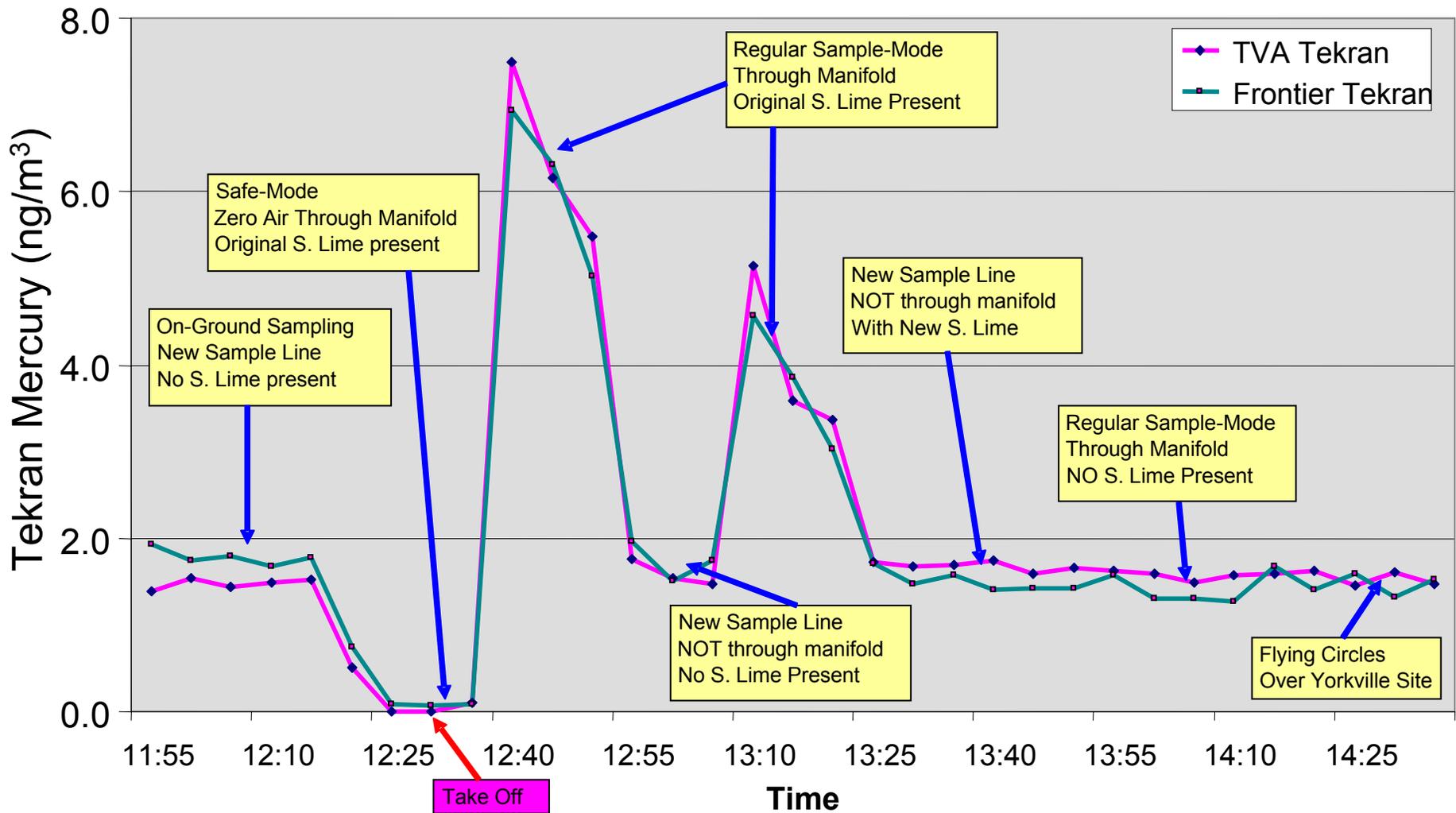
**1245h-1541h**

(segments in red denote  
Tekran capture of ambient  
samples)

# Tekran Automated Hg Analyzer



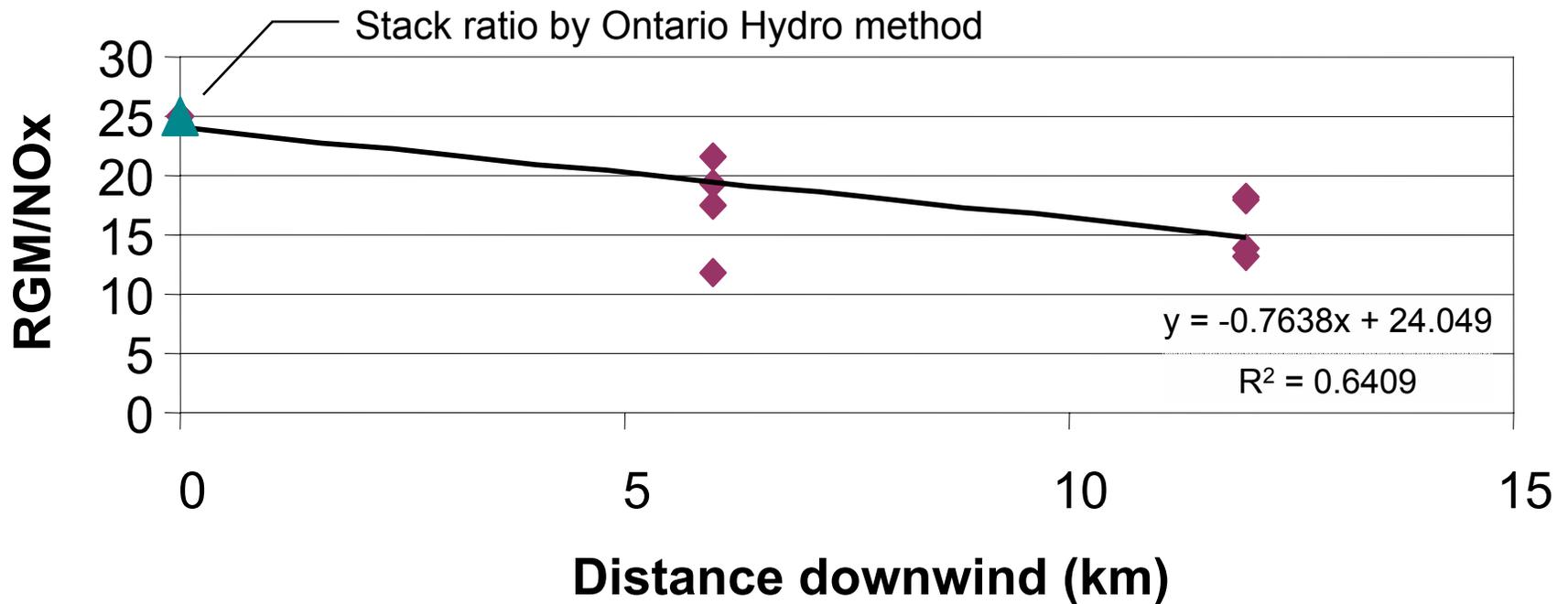
# Tekran Intercomparison During Aircraft Sampling



# RGM and particle mercury concentrations (pg/m<sup>3</sup>) for 4 Bowen sampling flights

Flight Number		0 nm	6 nm	12 nm
2	Dilution Factor	2103	3629	16443
	RGM	1206	616	152
	Particle	n.d.	n.d.	25
4	Dilution Factor	654	11436	24545
	RGM	407	359	296
	Particle	33	12	8
6	Dilution Factor	219	11273	11340
	RGM	9054	327	299
	Particle	1177	5	4
7	Dilution Factor	407	6614	9072
	RGM	5663	648	374
	Particle	43	13	11

# RGM/NOx vs Downwind Distance, 4 Sampling Flights



**HINT OF A MECHANISM????**

# Yusuf et al., 2003

- “Homogeneous and heterogeneous reactions of atmospheric mercury(II) with sulfur(IV),” Huda Yusuf, Nazafarin Lahoutifard, Kirsty Maunder, and Susannah L. Scott (presented at: XII International Conference on Heavy Metals in the Environment”, Grenoble, France, May 26-30, 2003)
  - *Abstract.* Atmospheric models suggest that the reduction of Hg(II) to Hg(0) by S(IV) prolongs the residence time of mercury. The redox reaction was investigated both in the aqueous phase (where the reductant is sulfite) and on particulate matter (where the reductant is SO<sub>2</sub>(g)). In both cases, one of the ultimate products is HgS. A mechanism is proposed involving formation of Hg(0) followed by mercury-induced disproportionation of SO<sub>2</sub> [for SO<sub>2</sub> ~ Hg]
- Proposes  $\text{HgO(s)} + \text{SO}_2\text{(g)} \rightarrow \text{Hg(0)(g)} + \text{SO}_3\text{(g)}$  for  $\text{SO}_2 \gg \text{Hg}$

# Research team, EPRI program on mercury reactions in power plant plumes

- **ARA**
- **Atmospheric and Environmental Research, Inc.**
- **Energy & Environmental Research Ctr, University of North Dakota**
- **Frontier Geosciences**
- **National Energy Technology Laboratory, U.S. DOE**
- **State of Florida**
- **State of Wisconsin Department of Natural Resources**
- **State of Wisconsin Division of Energy**
- **Southern Company**
- **Tennessee Valley Authority**
- **U.S. Environmental Protection Agency**
- **University of Alabama at Huntsville**
- **University of North Dakota**
- **We Energies**
- **Wisconsin Focus on Energy**
- **Many others: Allegheny Power, American Electric Power, Constellation Energy, Detroit Edison, Duke Energy, MEAG, Oglethorpe Power, TXU**

# Global inventory (1995 datum)

Pacyna et al., “Mapping 1995 global anthropogenic emissions of mercury,”  
*Atmosph. Env.*, 2003

Global emissions of total mercury from major anthropogenic sources in 1995 (in tonnes)

Continent	Stationary combustion	Non-ferrous metal production	Pig iron and steel production	Cement production	Waste disposal	Total
Europe	185.5	15.4	10.2	26.2	12.4	249.7
Africa	197.0	7.9	0.5	5.2		210.6
Asia	860.4	87.4	12.1	81.8	32.6	1074.3
North America	104.8	25.1	4.6	12.9	66.1	213.5
South America	26.9	25.4	1.4	5.5		59.2
Australia & Oceania	99.9	4.4	0.3	0.8	0.1	105.5
Total	1474.5	165.6	29.1	132.4	111.2	1912.8 <sup>a</sup>

<sup>a</sup>In addition, emission of about 514 tonnes of Hg was estimated for chlor-alkali plants, gold production, and the use of mercury for various purposes (primary battery production, production of measuring and control instruments, production of electrical lighting, wiring devices, and electrical switches) in 1995.



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