ELECTRIC POWER RESEARCH INSTITUTE

In-Plume Redox of Mercury: Lab, Field, and Mechanistic Studies

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DOE/NETL Mercury Control Technology R&D Program Review
Pittsburgh
July 12, 2005

Issue: Are There Rapid Mercury Oxidation and/or Reduction Reactions Occurring in Plumes Associated with Coal-Fired Power Plants?

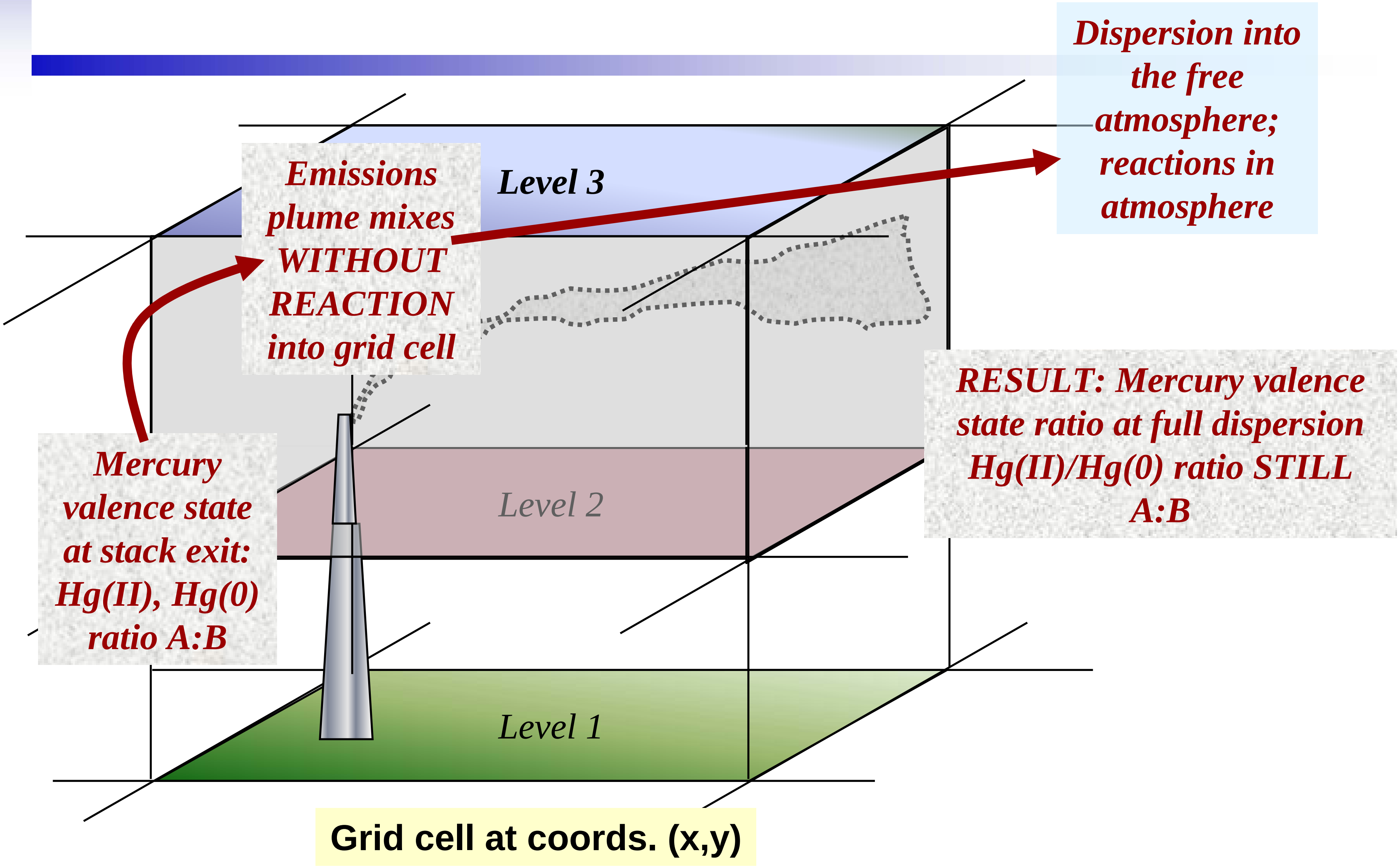
- Evidence
  - Rapid Hg(II)→Hg(0) in 0.5-1 m^3 static dilution chamber experiments
    - Measurements using pilot, full-scale PP flue gases
    - No reduction with waste combustor flue gases
  - Divalent fraction of measured total mercury = 1/10 expected, 25 km from coal-fired plant
  - Large-scale match of measured vs. modeled Hg(II) downwind of Ohio R. valley improved by reduction rxns
- Objections
  - No fundamental chemical mechanism to date
  - ??Wall-effect reaction rate changes in chambers
  - Deposition, other sources, unmeasured stack ratios in field measurements

Implications of Possible Mercury Redox Reactions (If It's the "Re..." Part)

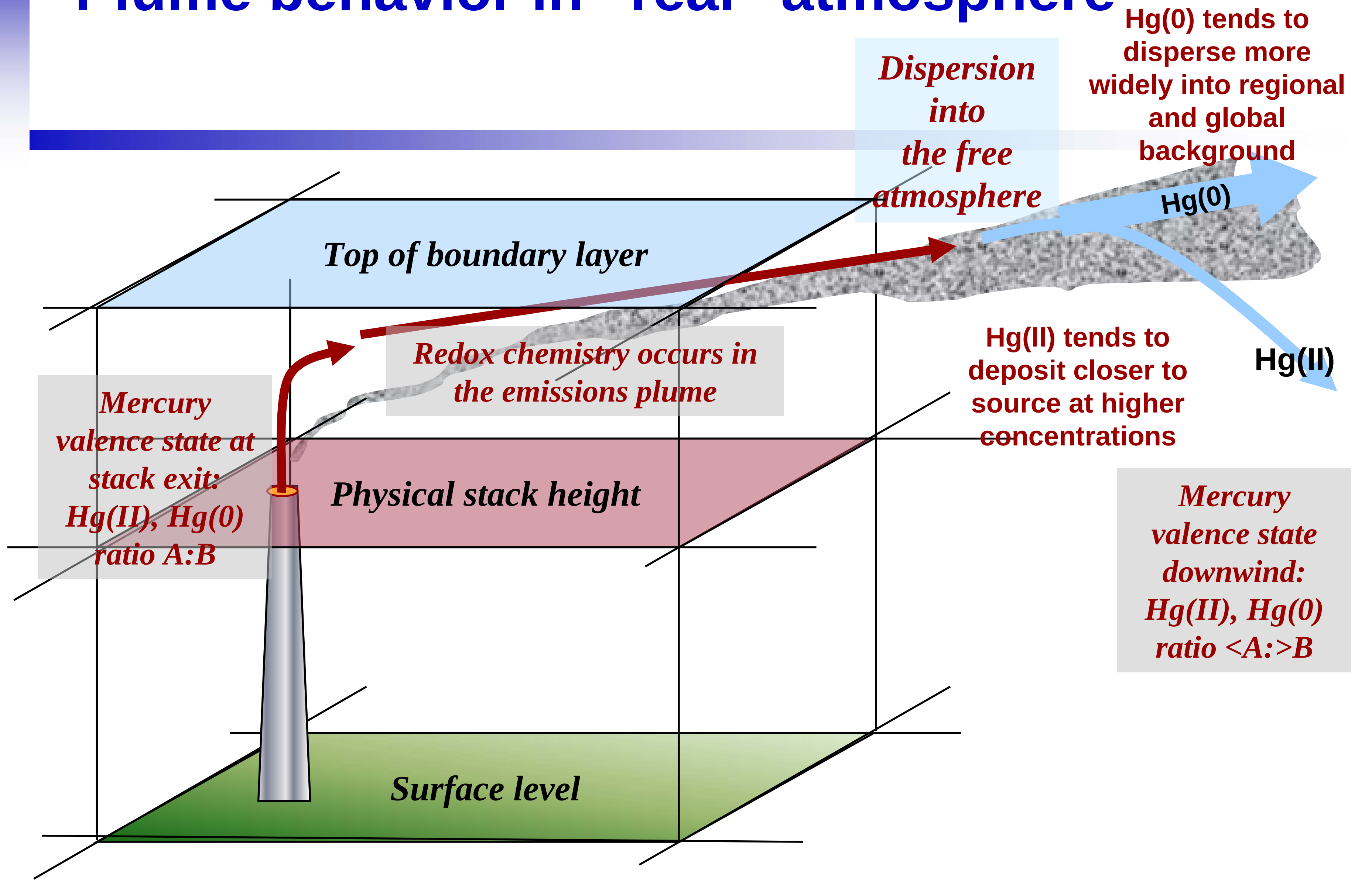
- Deposition
  - Marginally lower (but observable) deposition downwind of such sources
  - Less overlap between sources=critical source targeting for management
  - More long-range transport
- Global balance
  - An additional "source" term with too few sinks
  - Need for more and more rapid removal

CURRENT MODELING OF MERCURY IN PLUMES

Plume behavior in model atmosphere

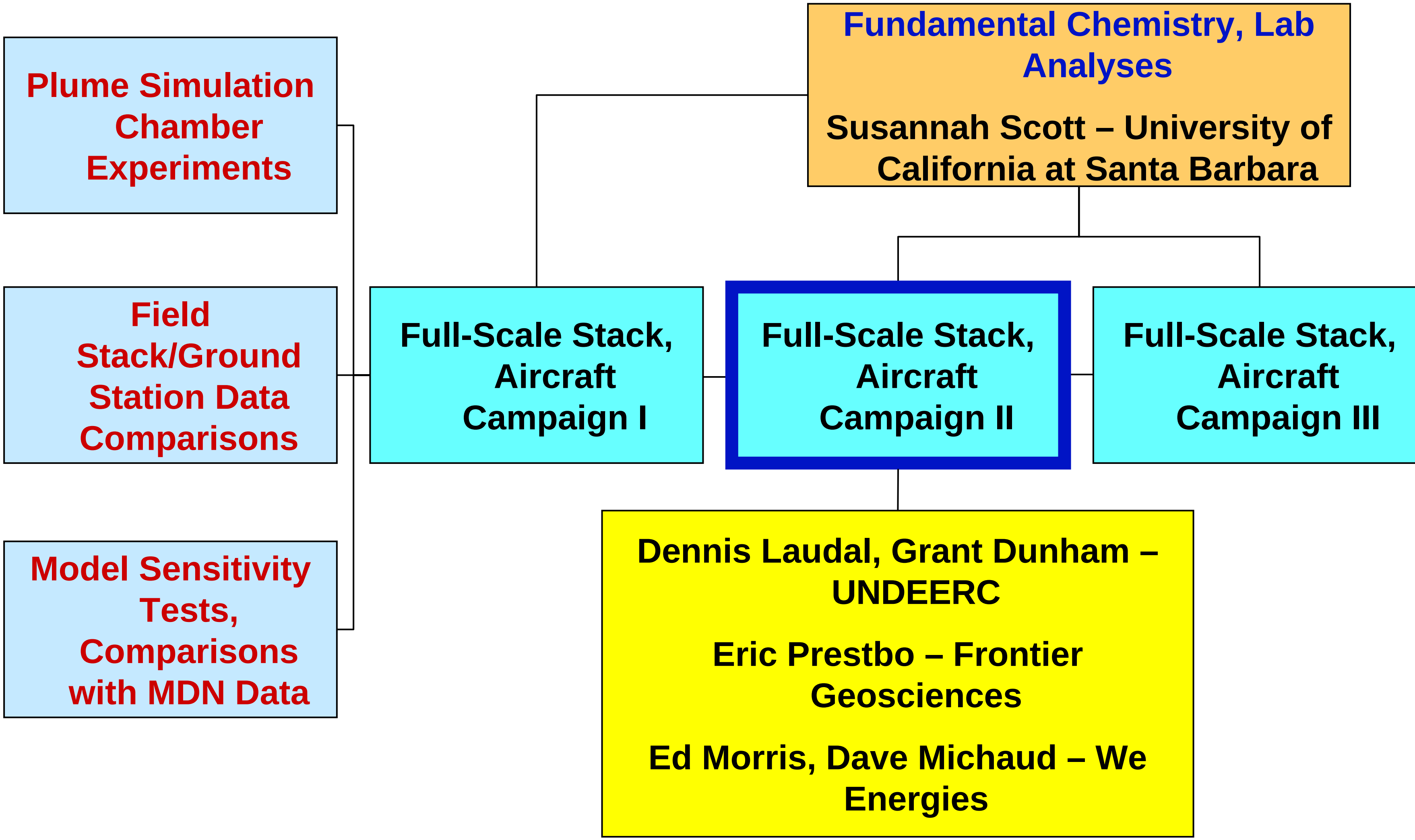


Plume behavior in “real” atmosphere



EPRI Plume Mercury Chemistry Program

Plume Mercury Chemistry Research Program

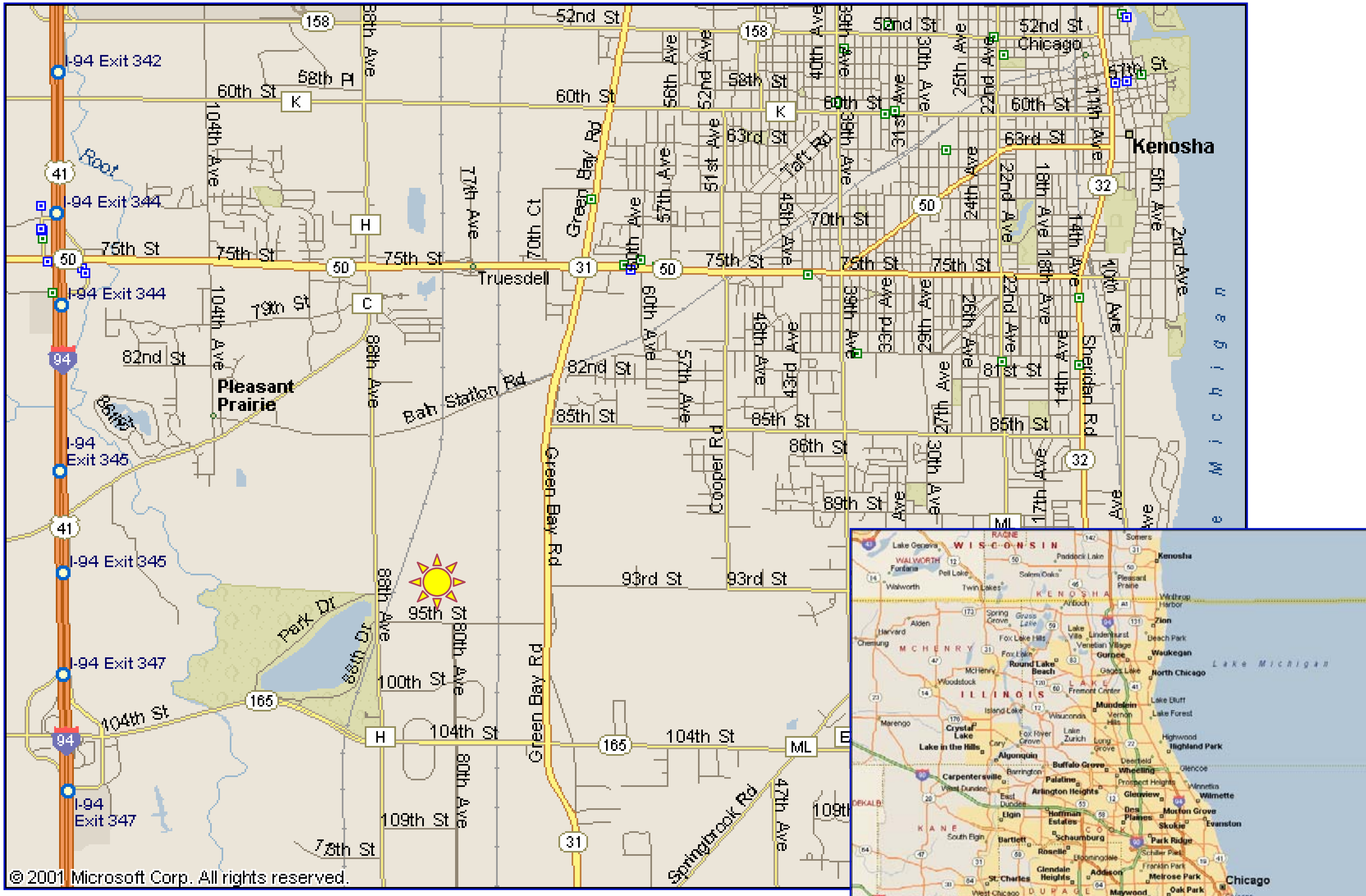


Comparison of Plants I and II

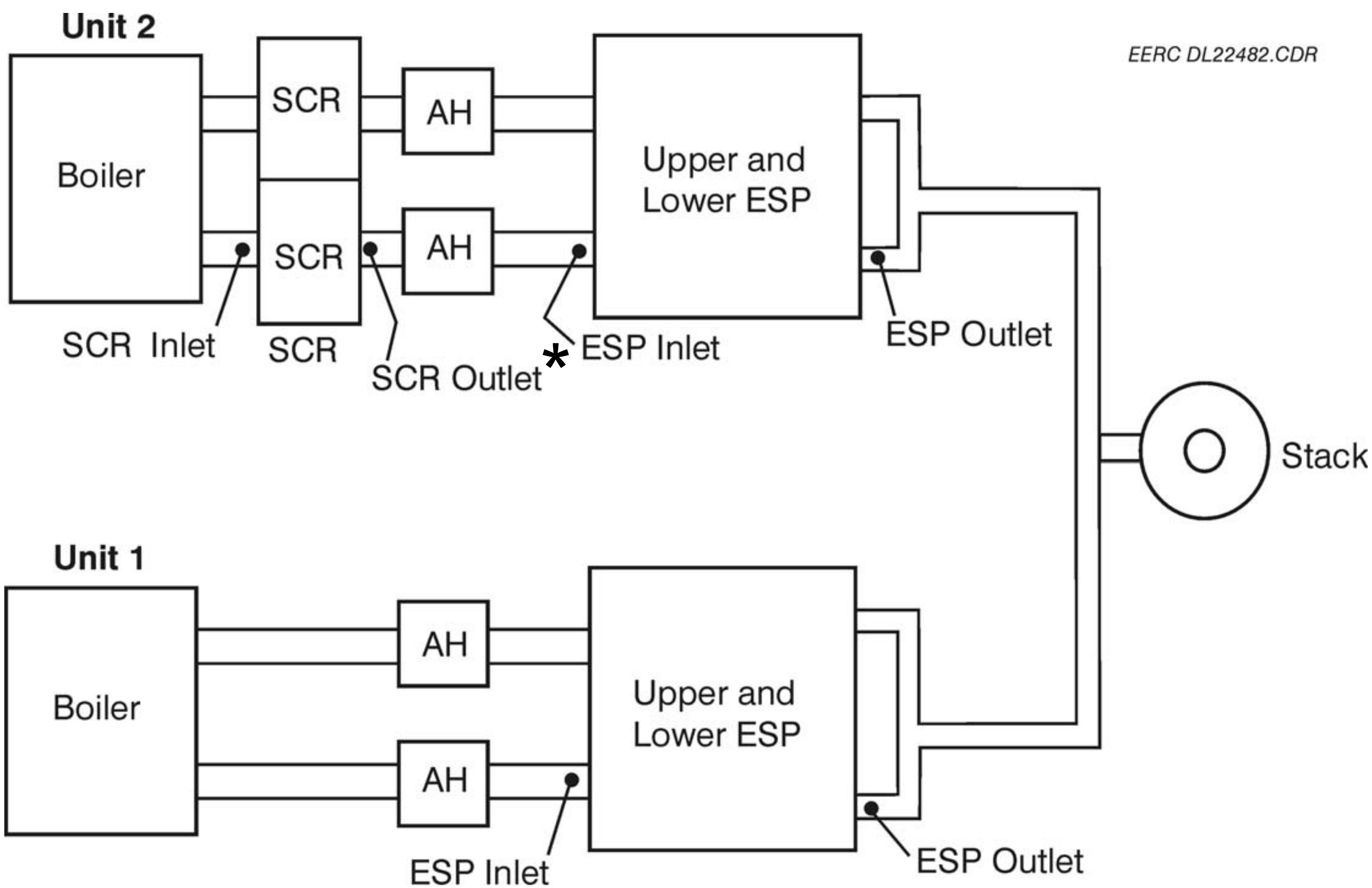
Power Plant Site	*Hg_T, g/s*	*Hg^{II}, g/s*	*Fraction Divalent*	*Coal Cl (ppm)*	*Coal S (ppm)*
Plant Bowen, Georgia	1.2×10^{-3}	2.1×10^{-3}	0.61	1,094	0.96
Pleasant Prairie Power Plant, Wisconsin	1.1×10^{-2}	1.7×10^{-3}	0.14	14	0.44

From ICR database

Pleasant Prairie Power Plant, Pleasant Prairie, Wisconsin

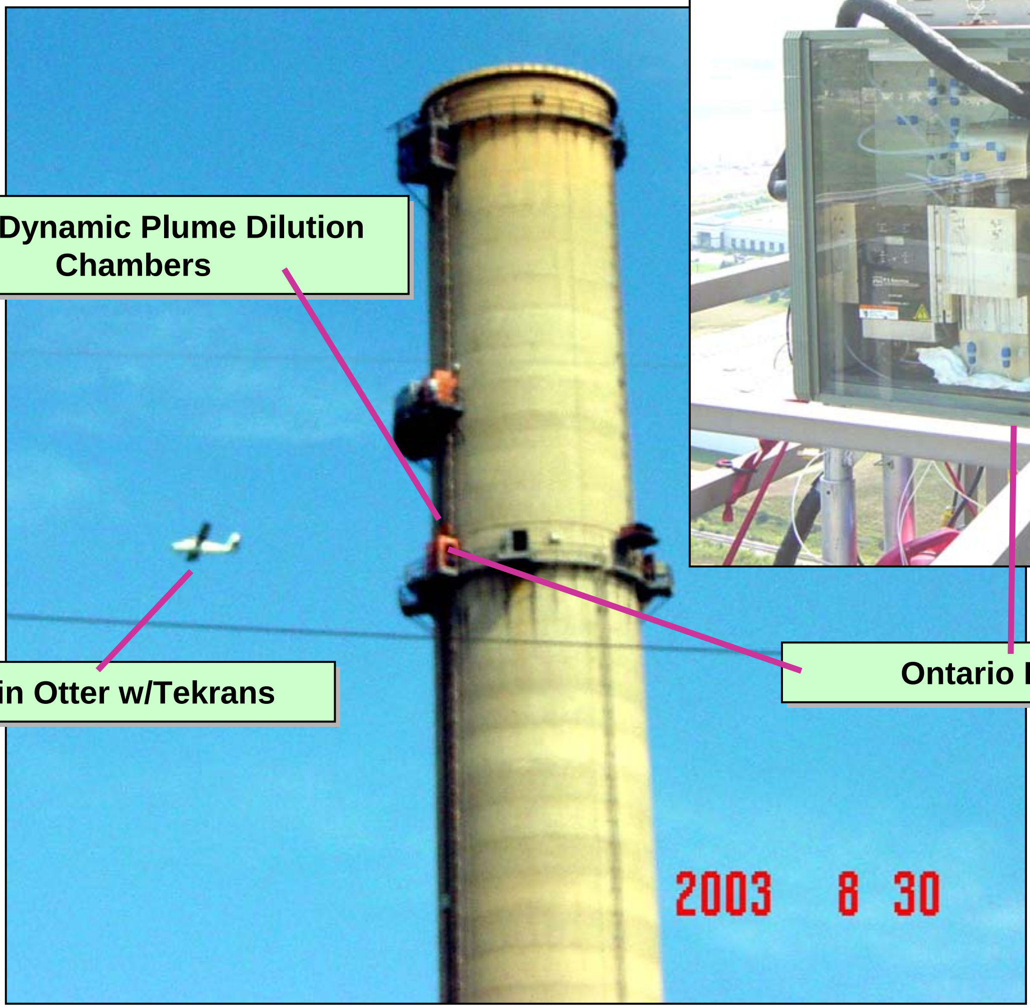


Schematic of Pleasant Prairie Power Plant Operating Configuration at Time of Campaign



*indicates mercury measurement location

Plume mercury chemistry: Pleasant Prairie Experiment



Static/Dynamic Plume Dilution Chambers

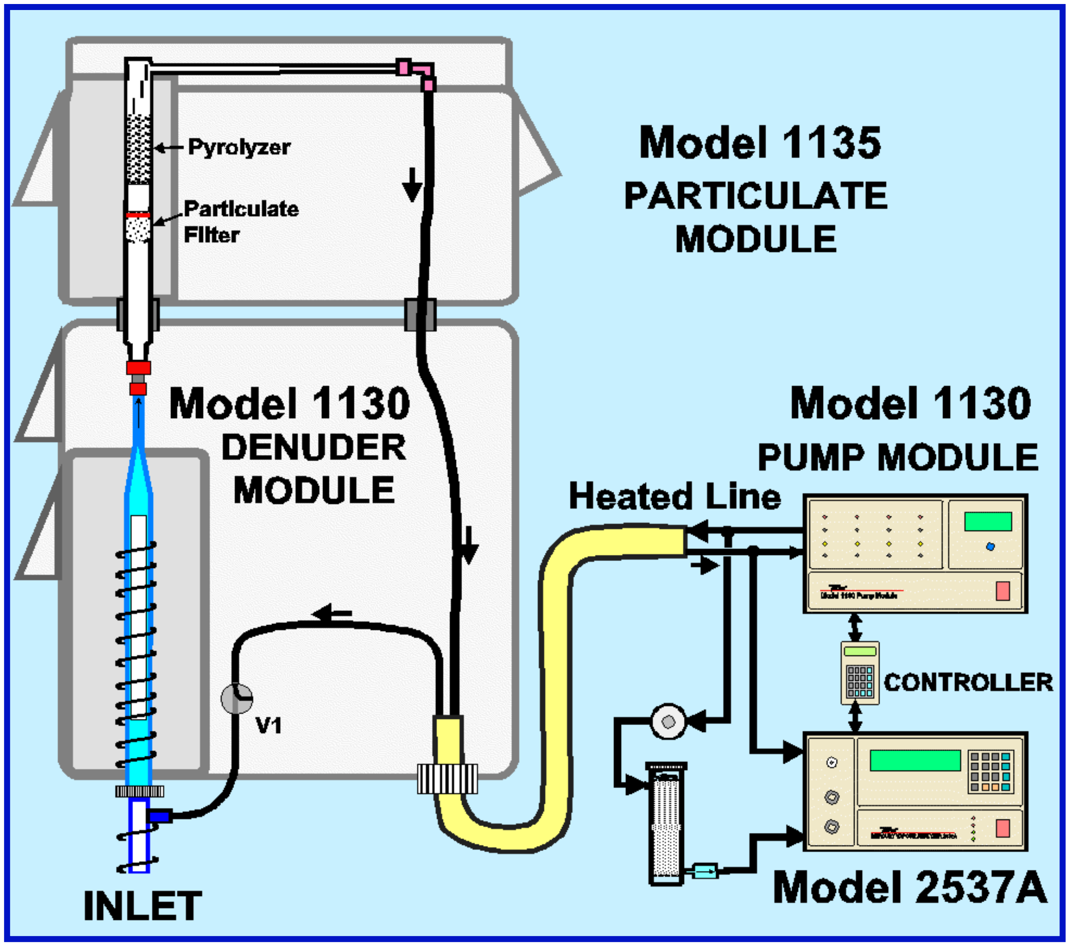
Twin Otter w/Tekrans

Ontario Hydro/CEMs

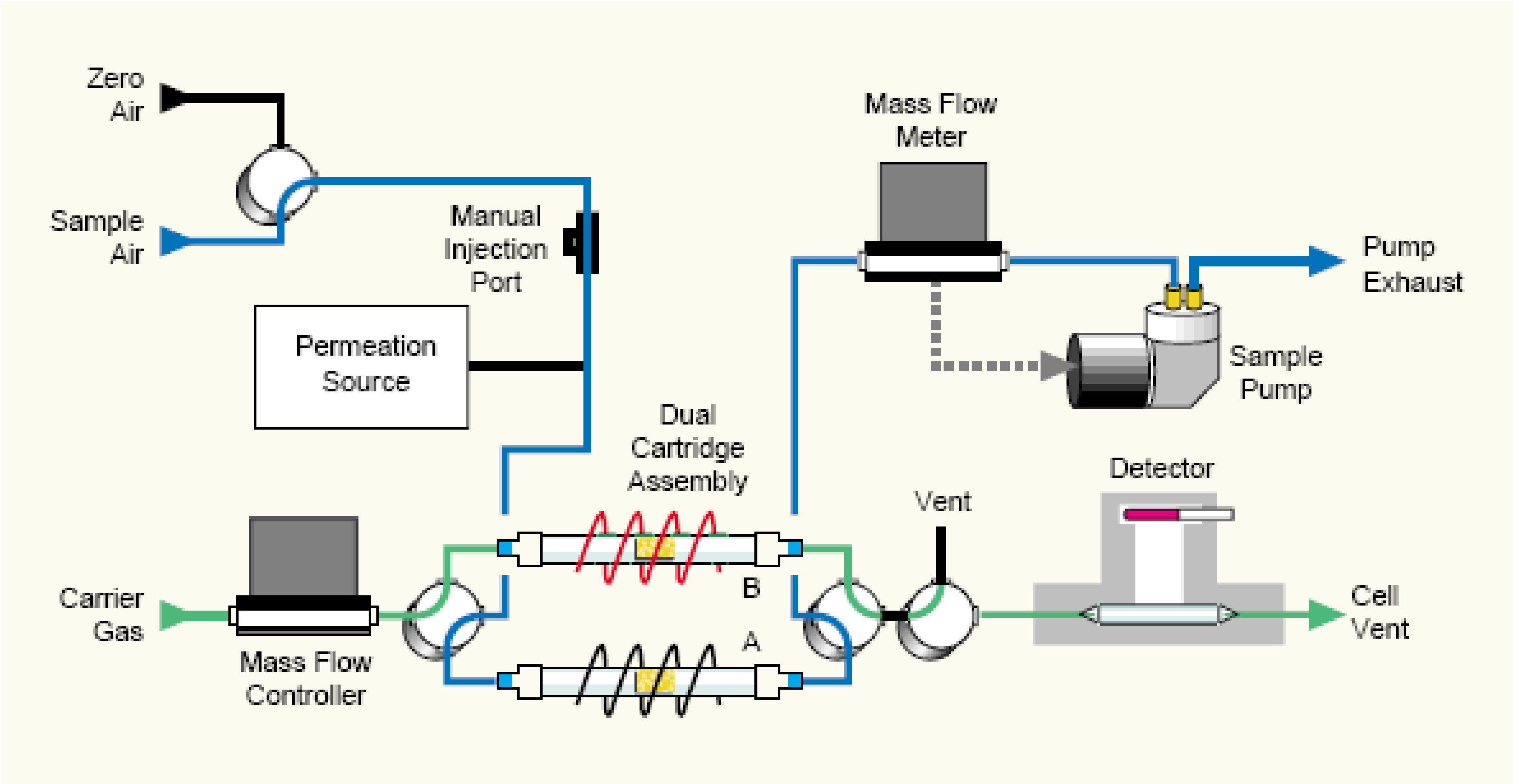
P4 Plume from Air and Ground

EERC DL23732.CDR

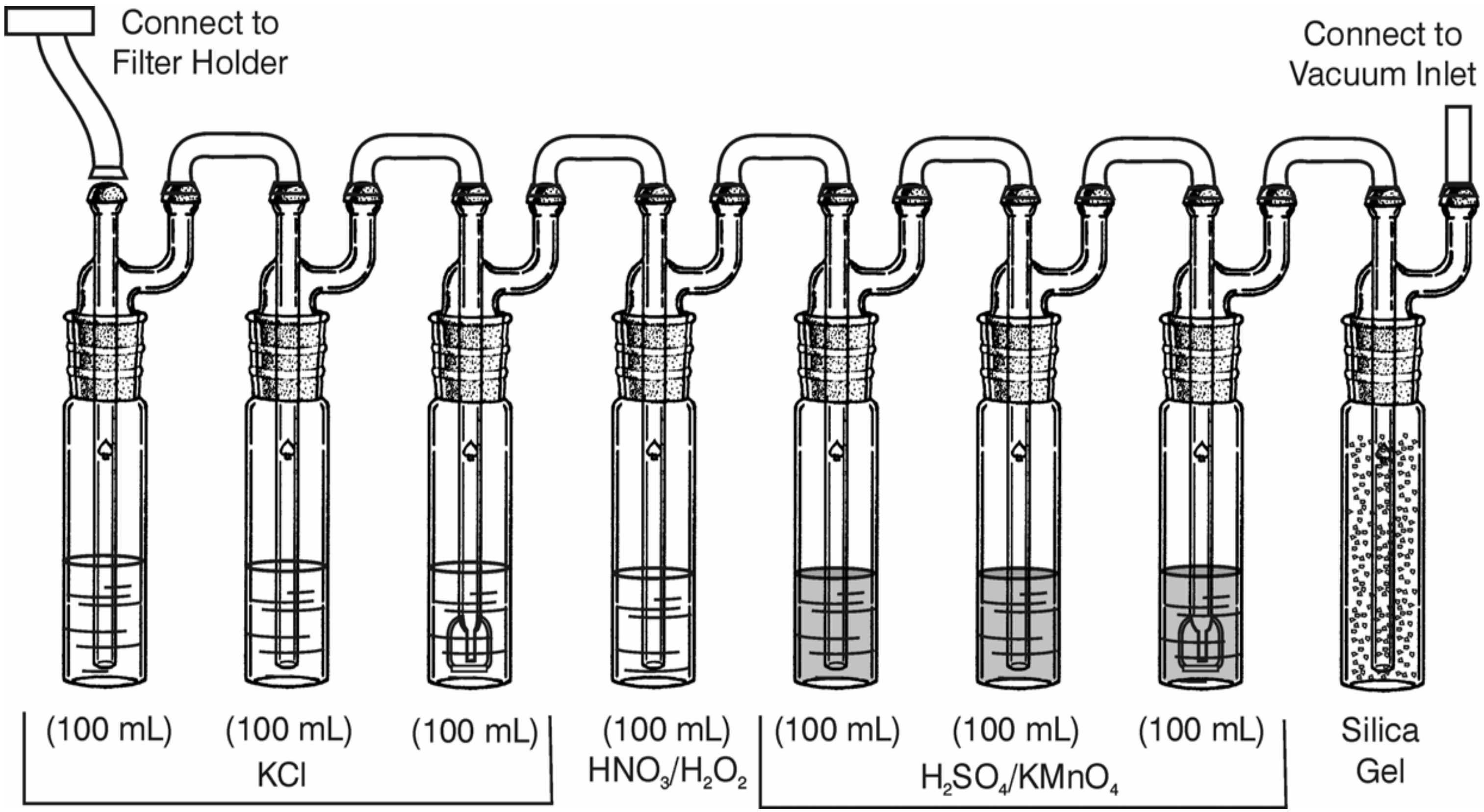
Diagram of the Tekran Automated Hg Analyzer



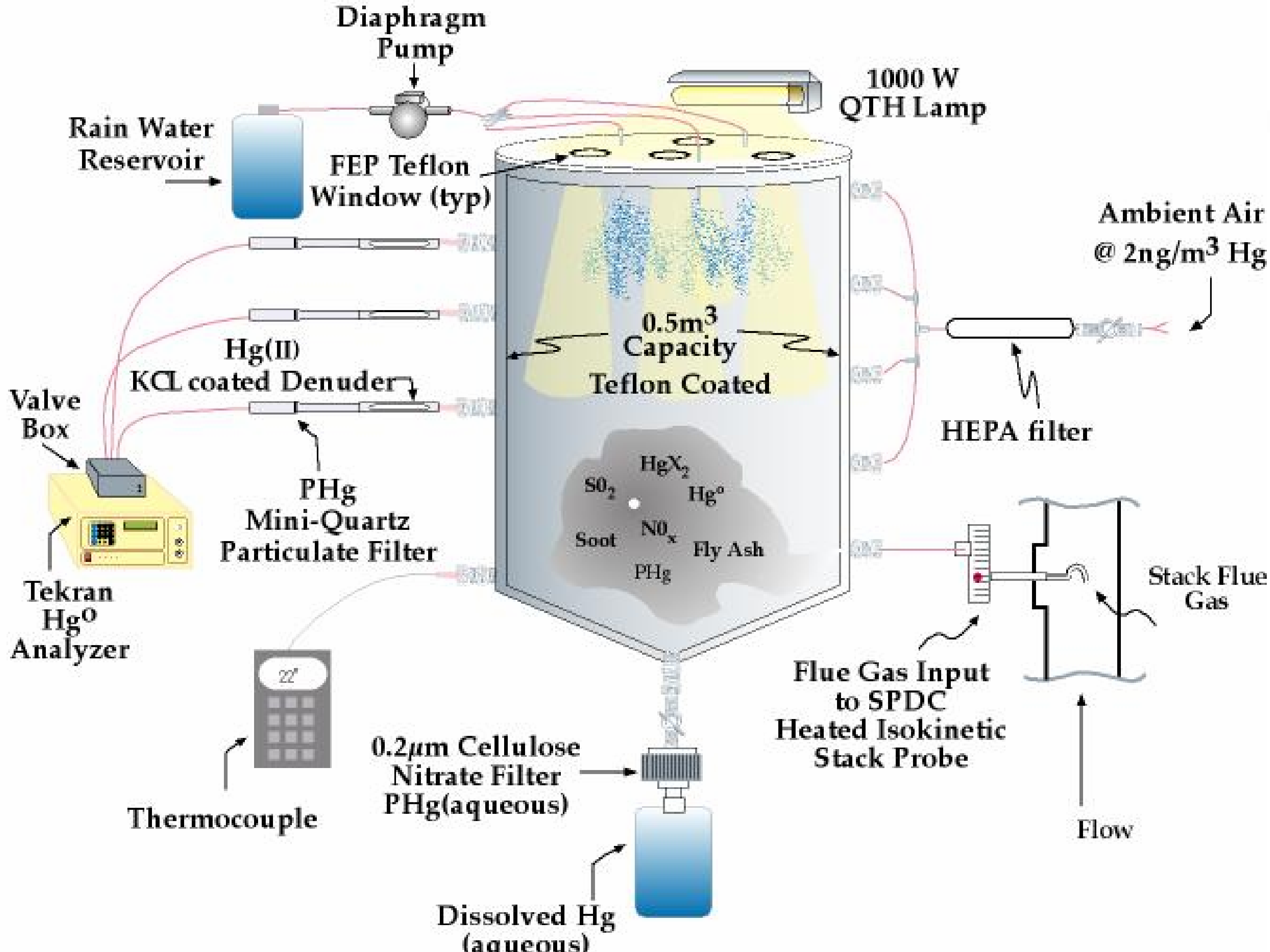
Tekran Sample Flow Diagram



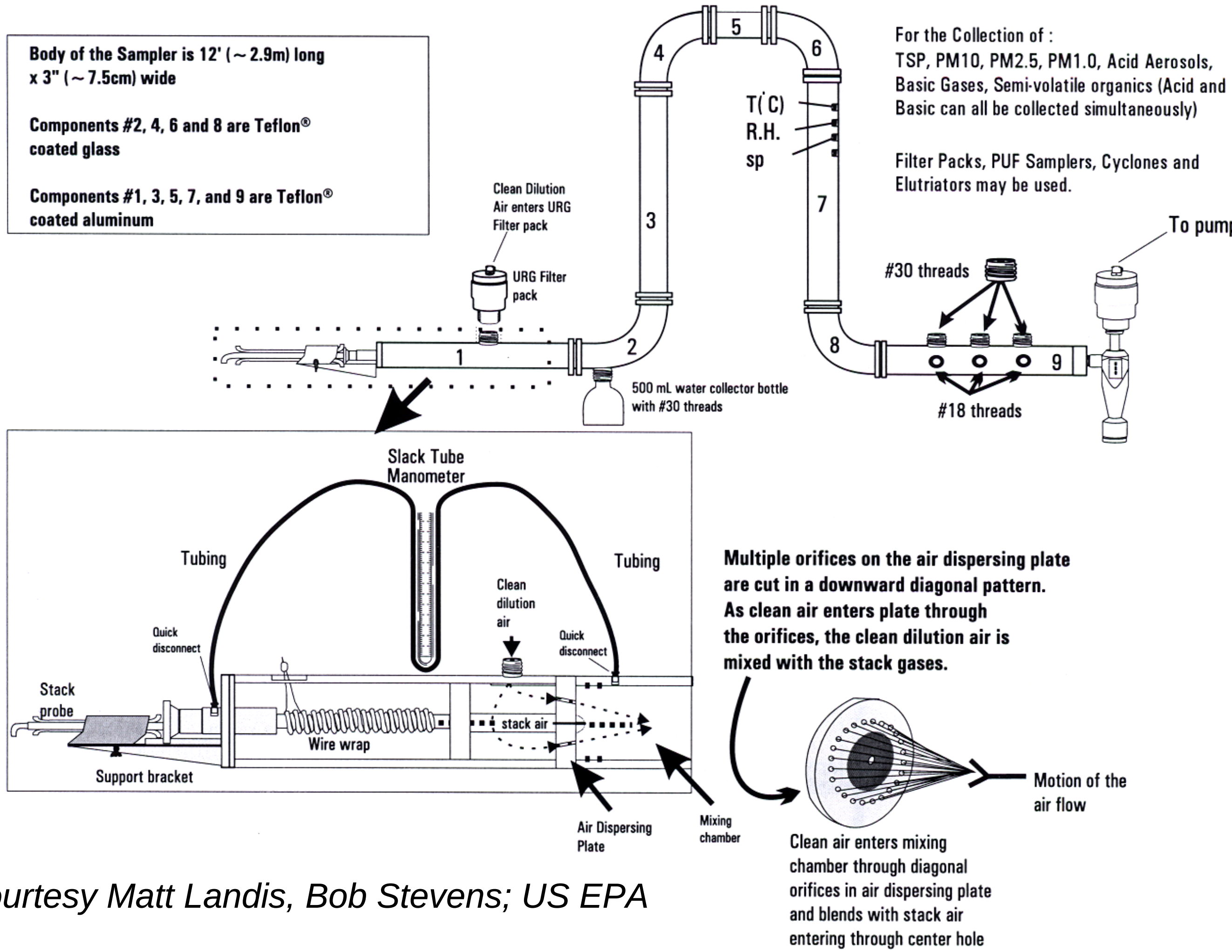
Sample Train, Ontario Hydro Method



Static Plume Dilution Chamber (SPDC) Schematic



Dynamic Plume Dilution Stream



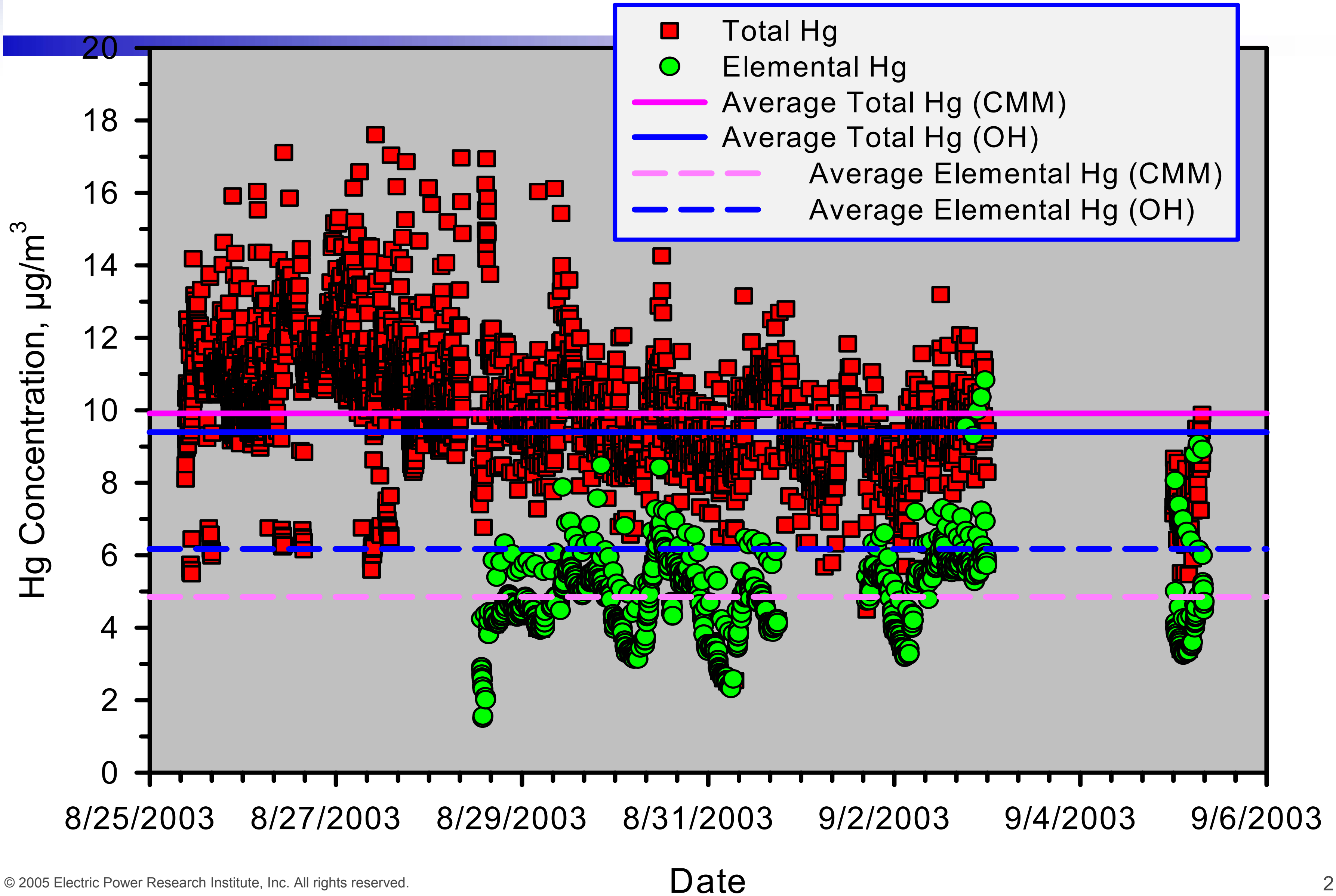
Instrumentation Courtesy Matt Landis, Bob Stevens; US EPA

PLEASANT PRAIRIE POWER PLANT FIELD CAMPAIGN

Stack Sampling

- Mercury SCEM at the stack inlet, measuring mercury continuously during each flight.
- Three Ontario Hydro samples were taken at the stack when the Hg SCEM was set up.
- One additional Ontario Hydro sample was taken each flight day.

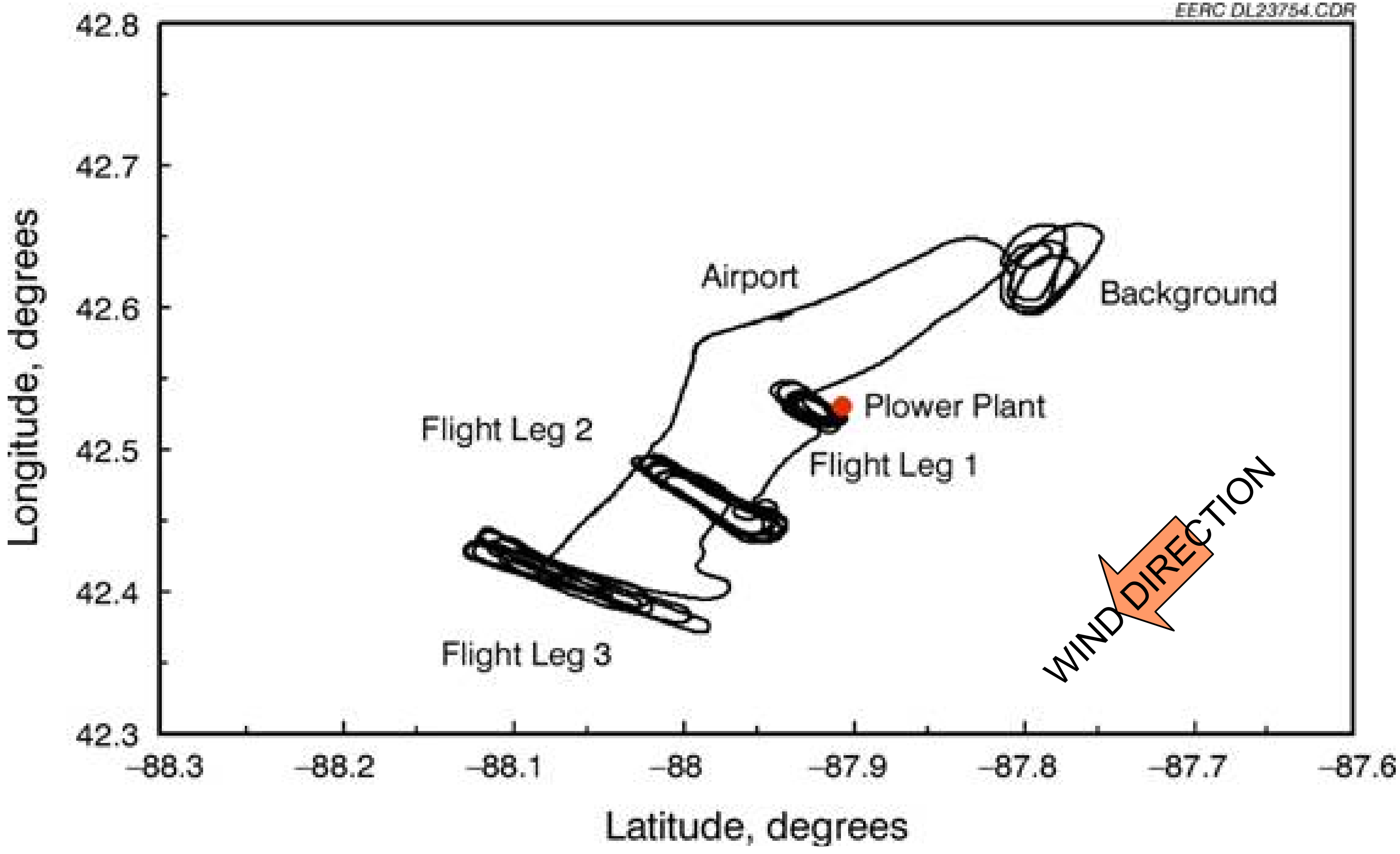
Pleasant Prairie Hg Emissions



Plume Sampling Aloft

- Background racetrack ~5 miles upwind
- Sample at plume tipover (effective stack height), ~5 miles downwind, ~10 miles downwind 25 minutes each
- Background concentrations (27 August 2003)
  - Hg^0=2.0 ng/Nm^3 (N= 1 atm and 0°C)
  - Hg(p)=7.5 pg/Nm^3
  - RGM=9.8 pg/Nm^3
- Plume demarcation is NOx excursion, background flight used to set trigger point for sampling
- Short plume eddy transects suppressed
- Lag time about 0.1 sec

Sample flight track, August 27, 2003



Calculation of Dilution Ratios

$$DR = \frac{(\text{stack } NO_x - \text{background } NO_x)}{(\text{plume } NO_x - \text{background } NO_x)}$$

Hg^0 vs. Distance, Average of 4 Runs

	Hg_p, µg/Nm³	Hg^0, µg/Nm³	RGM, µg/Nm³	Total Hg, µg/Nm³	% Hg^0
Stack					
Average	0.00	3.2	6.2	9.4	66
Std. Dev.	0.00	0.5	0.7	0.7	5.1
0 Miles					
Average	0.06	10.4	2.0	12.4	84
Std. Dev.	0.04	3.1	0.5	3.2	5.0
5 Miles					
Average	0.10	15.7	1.7	17.5	89
Std. Dev.	0.06	8.7	0.8	9.3	4.0
10 Miles					
Average	0.09	12.4	1.6	14.1	88
Std. Dev.	0.08	4.8	0.7	5.4	2.6

* All concentrations are based on normal (N) conditions defined as 1 atmosphere pressure, 20°C, and 3% O_2. – background concentrations removed

Results

- The fraction of RGM in the plume is lower than that in the stack at each of the in-plume measurement locations aloft
- RGM dropped by 38% on average from in-stack measurement to effective stack height
- RGM dropped by a total of 47% on average from in-stack measurement to the 5-mile sampling location
- No further drop in RGM was observed between 5 and 10 mile locations

IS THERE A SUPPORTABLE MECHANISM?

Hints Of A Mechanism

- "Homogeneous and heterogeneous reactions of atmospheric mercury(II) with sulfur(IV)," Yusuf, Lahoutifard, Maunder, Scott (presented at: XII ICHMET, Grenoble, France, May 26-30, 2003)
  - Atmospheric models suggest reduction of Hg(II) to Hg(0) by S(IV)
  - Reaction investigated in aqueous phase (reductant = sulfite) and on particulate surfaces (reductant = SO_2(g))
- Both → HgS for $SO_2 \approx$ Hg
- Propose HgO(s) + SO_2(g) → Hg(0)(g) + SO_3(g) for $SO_2 \gg$ Hg

Reaction Mechanism Studies

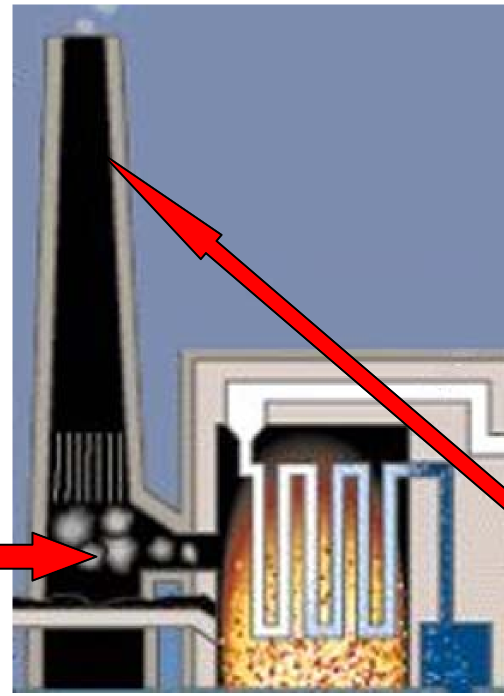
Speciation due to redox is *dynamic* in power plant stacks and plumes.

Some elemental mercury formed during combustion may be *oxidized* in the stack to Hg(II):

$Hg^0 + ½\,O_2 \rightarrow HgO$

$Hg^0 + Cl_2 \rightarrow HgCl_2$

$2\,Hg^0 + HOCl \rightarrow HgCl_2 + H_2O$



A fraction of the oxidized mercury may be spontaneously *reduced* to the elemental form, which is not readily trapped or deposited.

One reduction reaction for Hg(II) is known:

$HgSO_3 + H_2O \rightarrow Hg^0 + H_2SO_4$

Several *new* candidate reactions are being studied:

simple reduction

$HgCl_2 + H_2 \rightarrow Hg^0 + 2\,HCl$

$HgCl_2 + 2\,HO\bullet \rightarrow Hg^0 + 2\,HOCl$

coupled reduction

$Hg(NO_3)_2 + SO_2 \rightarrow Hg^0 + SO_3 + N_2O_5$

Kinetic Studies of Mercury Reduction Rates

More precise plume modeling requires accurate rate constants, measured under controlled laboratory conditions

Gas-phase chemistry

- H_2 produced by water-gas shift reaction over fly ash:

$$HgCl_2 + H_2 \rightarrow Hg^0 + 2\ HCl$$

- rate of HCl formation monitored by *in situ* gas phase IR spectroscopy

Photochemistry

- photolysis of CH_3NO_2 generates HO•

$$HgCl_2 + 2\ HO\bullet \rightarrow Hg^0 + 2\ HOCl$$

- rate of reaction of reference hydrocarbon reports on the reaction with $HgCl_2$

Coupled redox reactions

- the overall thermodynamics is affected by incorporating ligand chemistry:

$$Hg(NO_3)_2 + SO_2 \rightarrow Hg^0 + SO_3 + N_2O_5$$

$$HgSO_3 + HO\bullet \rightarrow Hg^0 + HSO_4$$

Conclusions

- Aircraft measurements at Pleasant Prairie support close-in, rapid chemical reduction of Hg^{II} to Hg^{0} in the plume
- Simultaneous measurements of P4 flue gas reactions in static test chamber do not support this conclusion
- Changes in Hg^{II} proportionation have now been observed at two power plants with aircraft measurements
- Range in coal and plume contents of Cl (7:1) and S (2:1) may encompass range of reaction inputs allowed
- Further proof-of-method for chamber surrogate method is required
- Establishing feasible mechanism is required
- More full-scale tests are required

Acknowledgements

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