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# Urban Mercury Monitoring: Data Review and Operational Notes: A Year Spent with the Tekran Speciated Ambient Mercury Analyzer at Two Urban Locations in New York State and an update of the AMNET program

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# NY Toxics Grant: Objectives

- Establish a reference baseline for mercury ( $\text{Hg}^0$ , RGM & PHg) air concentrations and wet deposition in urban areas in New York (The ambient RGM & PHg concentrations are surrogates for dry dep)
- Track the overall progress of mercury reduction strategies for the two largest source categories, municipal waste combustors and coal fired electric utilities.
- Examine if the ratio of elemental to reactive gas mercury is enhanced from atmospheric interactions with the other pollutants prevalent in urban areas.
- Use collocated AMnet wet Hg deposition measurements at the two ambient Hg monitoring sites to attempt to more thoroughly encompass the total mercury loading into the environment.
- Determine if there are significant differences between the Hg wet deposition concentrations found in the predominantly rural MDN network and the 2 urban NY locations.



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## Why Are We So Concerned?

- Long established neurotoxin, slows fetal and child development
- Causes irreversible deficits in brain function
- Sensitive human subpopulation - children in utero, young children
- Methylmercury is a developmental toxicant
- Sensitive animal population - eagles, loons, osprey, mink and otters



# Forms of Atmospheric Mercury

- **Elemental Mercury ( $\text{Hg}^0$ ): approx 99% of Total Hg**

- Mildly reactive gas, sparingly soluble in water

- Long range transport throughout the entire atmosphere

- Global Background Concentration:  $1.5 - 3 \text{ ng/m}^3$

- Atmospheric Lifetime: .5 - 2 Years

- Uptake by vegetation an important deposition pathway

- **Reactive Gaseous Mercury (RGM):**

- Operational term for gaseous Hg compounds

- Water soluble and/or chemically reactive

- Readily deposited to water, soils and vegetation by wet and dry processes

- Atmospheric Lifetime: .5 - 2 Days

- **Particulate Mercury (PHg):**

- Condensed Hg compounds and semi-volatile Hg bound to receptive aerosols

- Atmospheric Lifetime: .5 - 3 Days

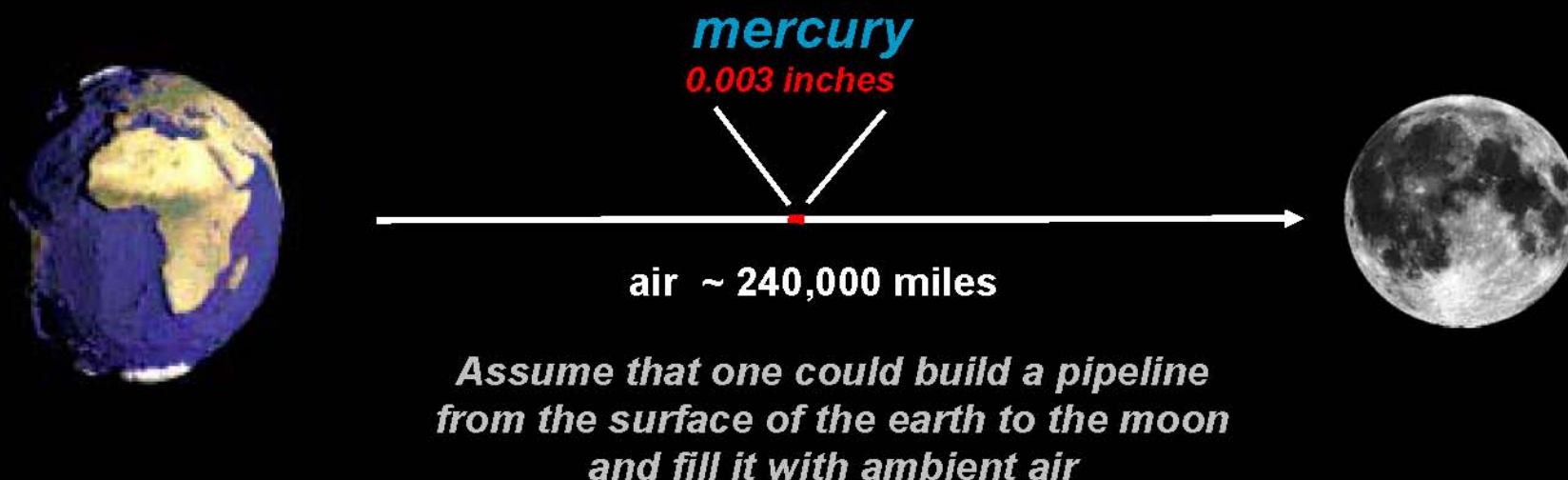


# Is Hg an Air Issue, an Ecosystem Issue or a Water Issue?

- Atmospheric concentrations of  $\text{Hg}^0$ , RGM and PHg typically are not found at concentrations considered to be toxic to humans, however:
- Sources emit  $\text{Hg}^0$  RGM and PHg in different ratios
- Dry and wet deposition of Hg cause soil and water concentrations to be elevated in areas well downwind of sources (RGM and PHg deposit readily)
- Bioaccumulation and Methylation increase the toxicity of Hg in the ecosystem
- RGM and PHg are used to estimate dry deposition



## Just how much mercury are we looking for?



- Ambient air global background level – “Total” Hg
  - Pipeline would be ~ 240,000 miles long
  - Background is ~  $1.7 \text{ ng/m}^3 = 0.2 \text{ ppt (200 ppq) (v/v)}$
  - Approximately **0.003 inches** of the pipeline would be filled with mercury vapor

# Hg Monitoring Instrumentation



- The Tekran 2537B collects  $\text{Hg}^0$  on gold traps.
- Every 5 minutes the traps are thermally desorbed and CVAH is used to determine the concentration of  $\text{Hg}^0$ .
- Argon is used as a carrier gas to increase the instrument sensitivity.
- A controller and 2<sup>nd</sup> pump are used to provide higher flow for the RGM and PHg collectors.





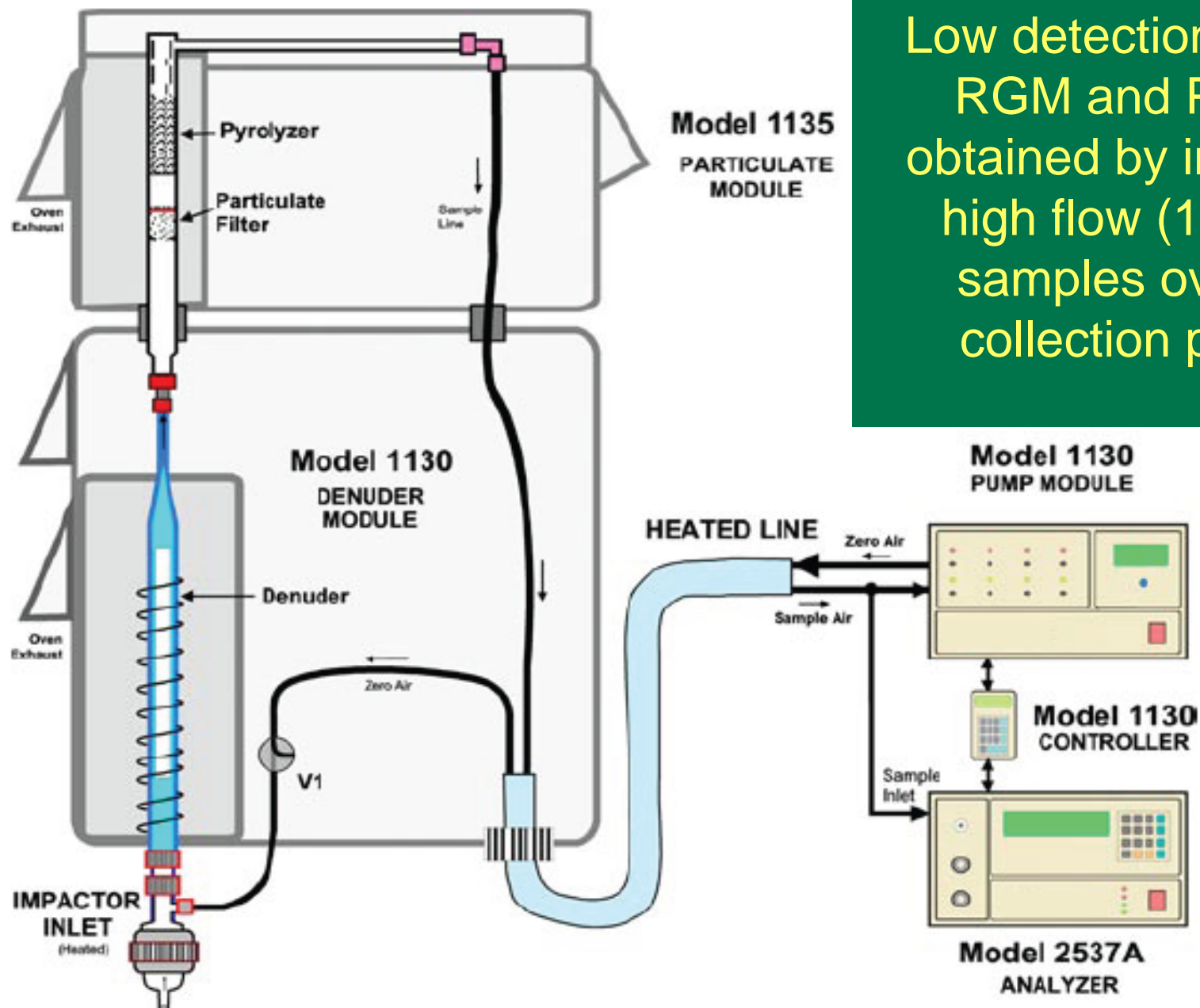
# Hg Monitoring Instrumentation



- 1135: PHg is collected for 2-hrs on a filter at 10 L/min. The filter is thermally desorbed at 800 C°.
- 1130: RGM is collected for 2-hrs on an annular denuder at 10 L/min. The denuder is thermally desorbed at 500 C°.
- A heated line connects the 1130 & 1135 to the 2537 which analyzes the desorbed PHg and RGM







Low detection limits for RGM and PHg are obtained by integrating high flow (10 L/min) samples over 2 Hr collection periods.

# TOPIC 1: Basic sampling, temperature, calibration and thermal desorption settings.

Please be prepared to discuss and come to consensus. Read the notes in blue below for more details summary of responses and consensus level.

## DRAFT NADP-AMI TEKRAN MODEL 1130/1135 CONTROLLER PROGRAM WORKSHEET

Controller S/W revision:

### Description of this Method:

NOTES: 1) Flow rate for near sea-level sites. Sites at higher elevation may adjust to keep volumetric flow at 10 lpm. 2) Desorb zero air flow rate was nominally 5 or 7 lpm. 3) Sample adsorb time was split between 2 and 3 hours - depending on data reduction programming - both may be acceptable, 4) Particulate heat temperature needs discussions and consensus, 5) Current program has primary Pt-Ht on A-Cart and primary RGM-Ht on B-Cart, 6) Auto-recal value needs discussion and consensus, 7) External Heat (heated boot) temperature needs discussion and consensus

### Model 2537A Settings

Cycle Time: (sec)	300
Flow Rate: (L/m)	1.00

### Pump Module Settings

Sample Flow: (L/m):	9.00
Desorb Flow: (L/m)	5.00

### Model 1130 Denuder Module

#### Temperature Settings (deg C)

SP1	Case Heater:	38
SP2	Case Fan:	40
SP1	Heated Line:	50
SP1	Denuder Keep Warm:	50
SP2	Denuder Heat:	500
SP1	Ext. Heat:	75
SP2	Ext Keep Warm:	50

### Model 1135 Particulate Module

#### Temperature Settings (deg C)

SP1	Pyrolyzer Keep Warm:	50
SP2	Pyrolyzer Heat:	850
SP1	Part-Trap Keep Warm:	50
SP2	Part-Trap Heat:	800
SP1	Case Heater:	38
SP2	Case Fan:	40

### Calculated Values

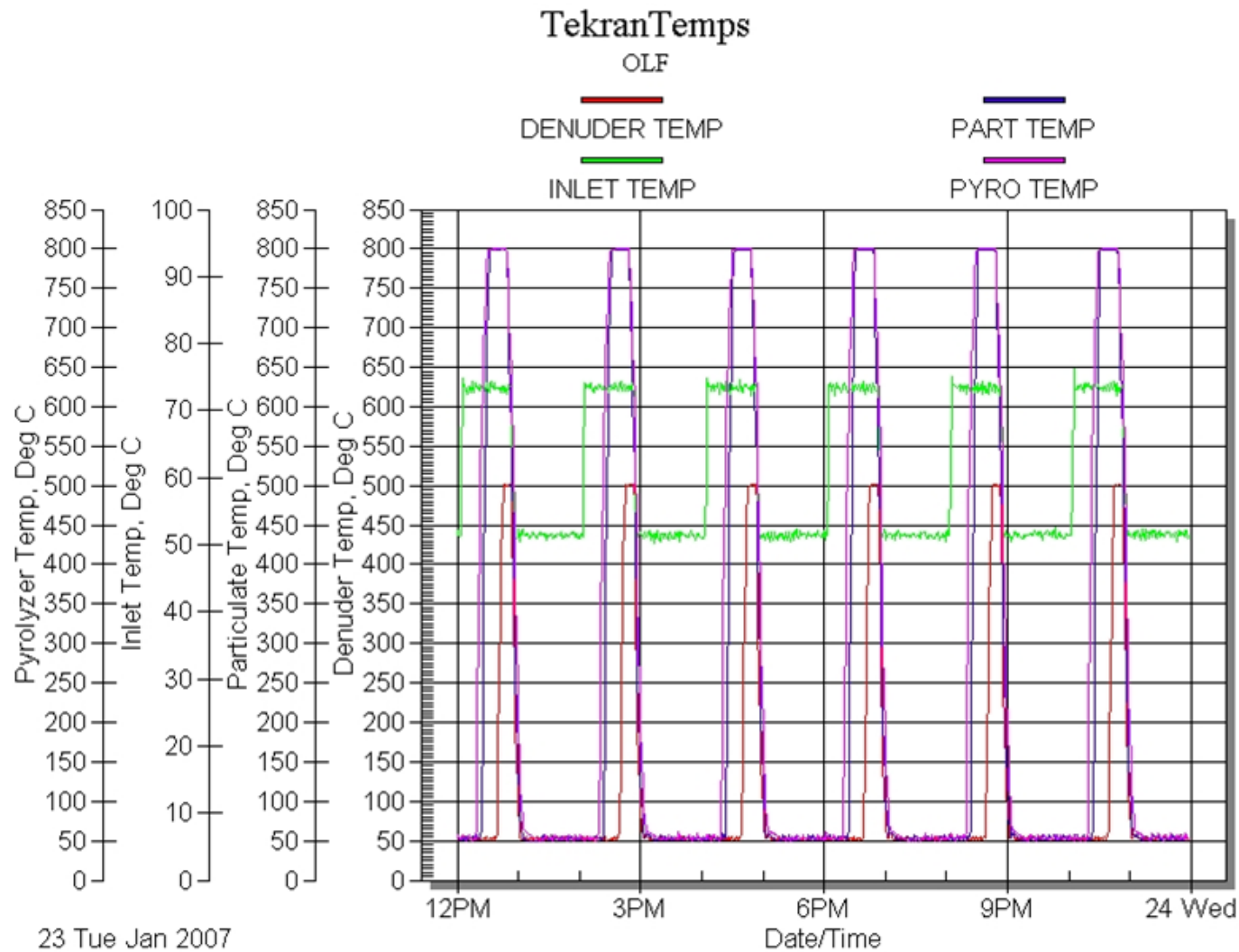
5.00	Model 2537A Sample Volume (L)
10.00	Denuder Flow Rate (L/m)
1,200	Denuder Total Volume (L)
0.00417	Model 2537A Factor (for ng/m3)
4.167	Model 2537A Factor (for pg/m3)
120	Denuder Sample Time (min)
60	Desorb Analysis Time (min)
180	Total Cycle time (min)
30.0	Auto-Recal interval (hours)

Note: Denuder figures above also apply to the particulate trap.

### Au Cartridge Status (RGM & PHg 1st Heat)

Step	Cartridge	Cartridge	Cartridge
1	A	B	A
2	B	-	-
3	A	B	A
4	B	A	
5	B		
6	A	B	-

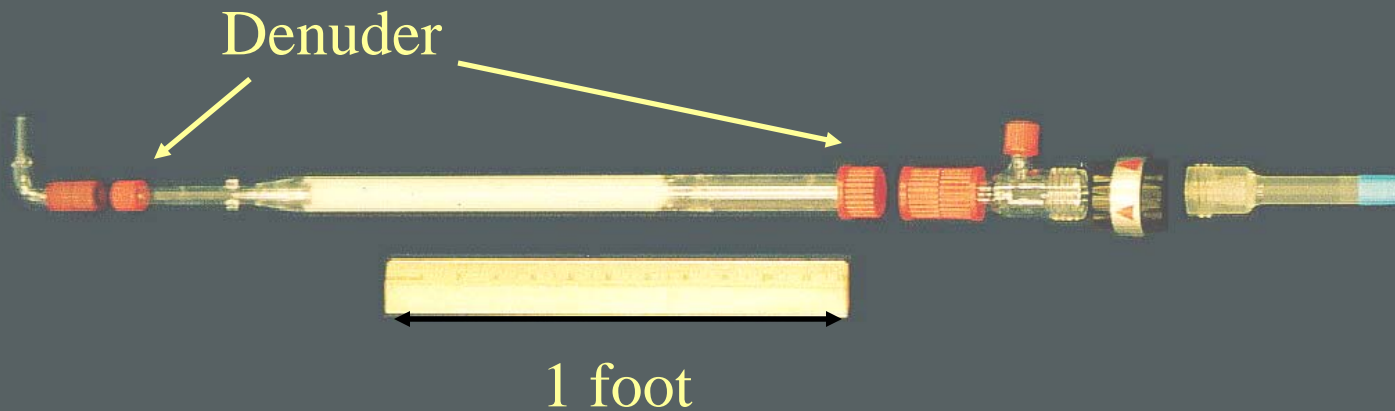
# Tekran Temperature Profiles



**SEARCH**

The RGM Denuder is a thin shell annular design that is coated with KCl. The inner shell is very fragile and subject to breakage during shipping or even installation.

Most of the SOPs recommend recoating every 1 – 2 weeks because the crystals get “smoother” which reduces the capture efficiency.



The denuder replacement cost is about \$625

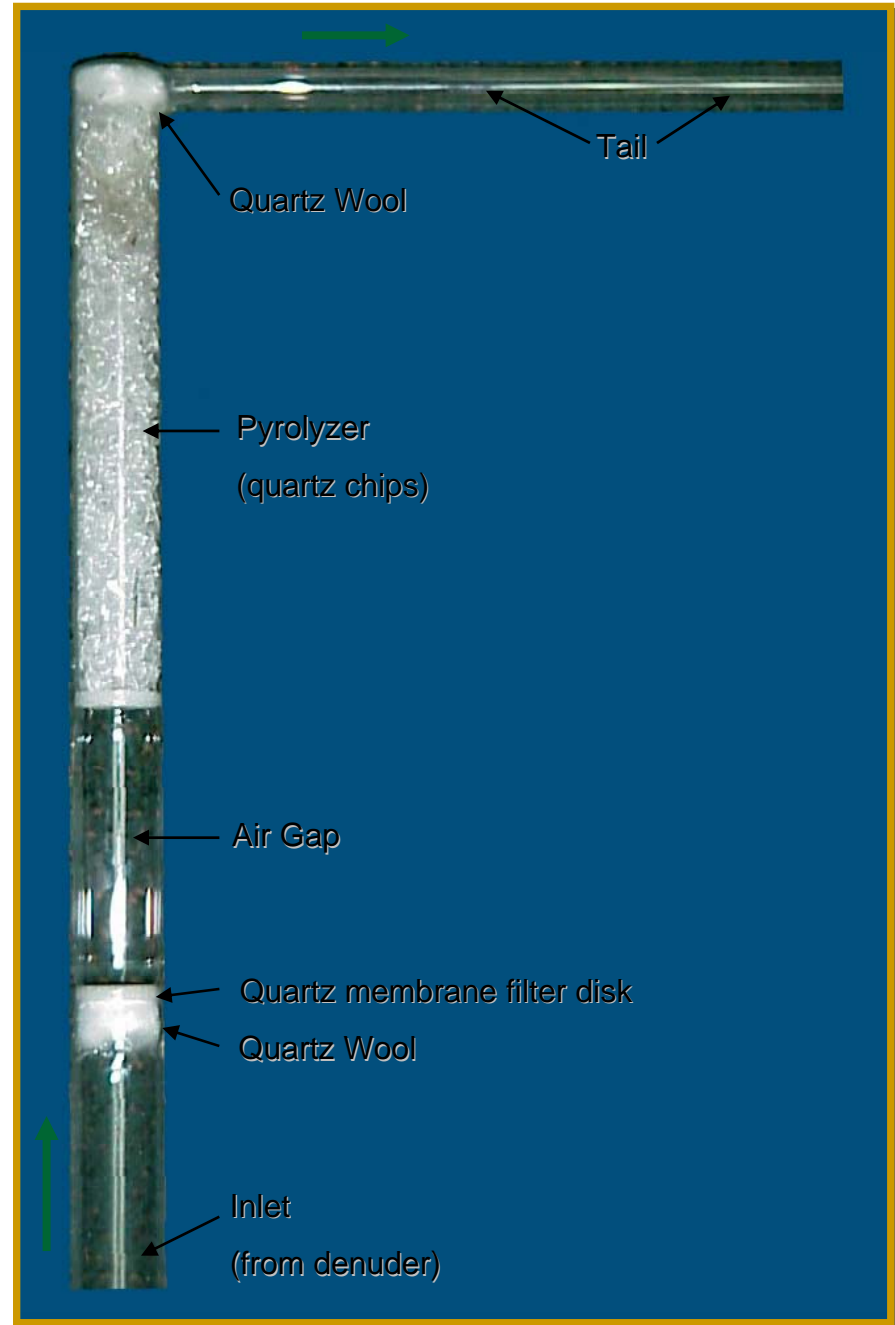
The Pyrolyzer (RPF) is where the particulate Hg is captured in the 1135.

The Quartz filter and wool must be replaced every 2- 8 weeks depending on which SOP you are reading.

The RPF is made out of Quartz in order to withstand repeated heating to 800<sup>0</sup> C.

The configuration and installation procedures makes it too easy to break the RPF.

The RPF is about \$750.



# Hg Wet Deposition Collector

MDN 00-125-2 Automatic Precipitation  
Sampler  
N-CON Systems Company, Inc.  
Crawford, GA

The system minimizes contamination  
by opening the  
collection bottle only when  
precipitation is detected by  
the infrared sensor.

The sample train is glass and is  
exchanged after each weekly sample  
pick-up.





# Hg Wet Deposition Gauge

ETI NOAH IV Total Precipitation Measurement  
System

ETI Instrument Systems, Inc.

Fort Collins, CO

The Gauge weighs all types of precipitation in the  
collector or clinging to the sides.

The infrared onset detection system provides a time  
stamp for each precipitation event.

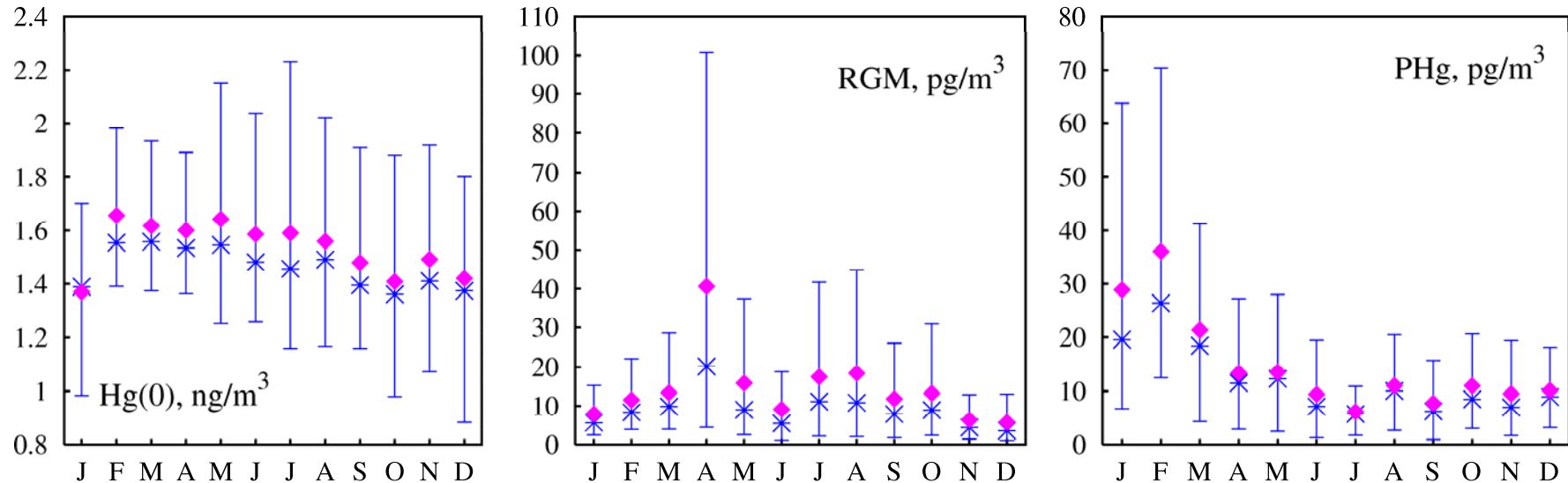
The Bluetooth enabled data logger also records  
event data from the Hg collector.



# Monthly Averages: NYC

Sept 08' – Aug 09'

## New York City

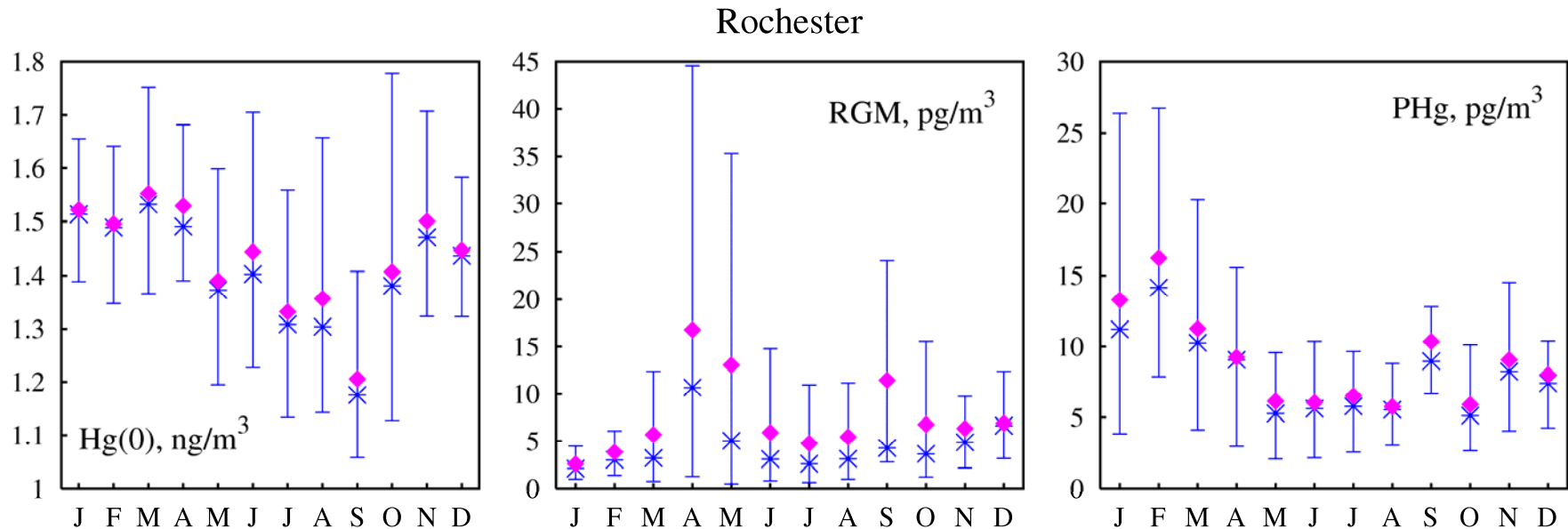


- The Hg<sup>0</sup> is in ng/m<sup>3</sup>, the RGM and PHg are in pg/m<sup>3</sup>
- The median and 10<sup>th</sup>, 90<sup>th</sup> and 50<sup>th</sup> percentiles are shown
- The large peak in RGM in April coincided with the first Ozone episode in 2009, PHg peaks in the winter.



# Monthly Averages: Rochester

Sept 08' –  
Aug 09'



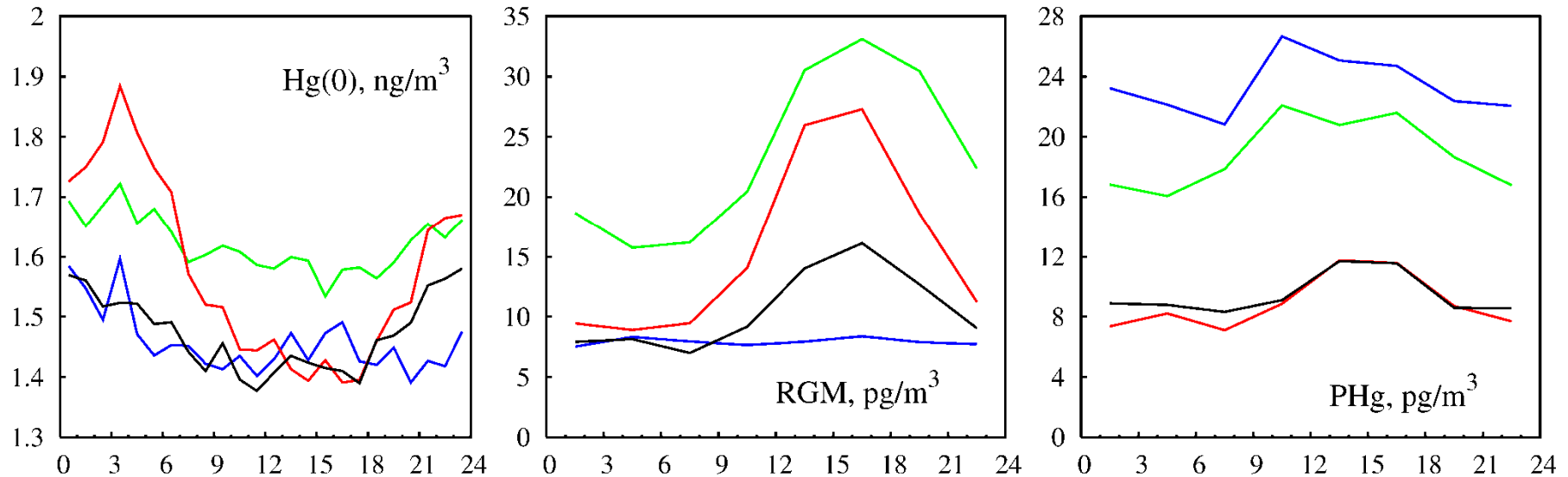
- The concentrations are lower than in NYC but the peaks occur at about the same time. Data from both sites follow patterns found in other studies: Mid-Atlantic and Gulf Coast
- The large peak in RGM in April coincided with the first Ozone episode in 2009, PHg peaks in the winter.



# Diurnal Profile: NYC

Sept 08' – Aug 09'

## New York City



- DJF: Dec-Feb, MAM: Mar-May Aug, SON: Sept-Nov
- The  $\text{Hg}^0$  peak at 3 am in the summer was unexpected
- The Mar-May RGM is driven by one episode in April
- RGM has a similar profile to Ozone

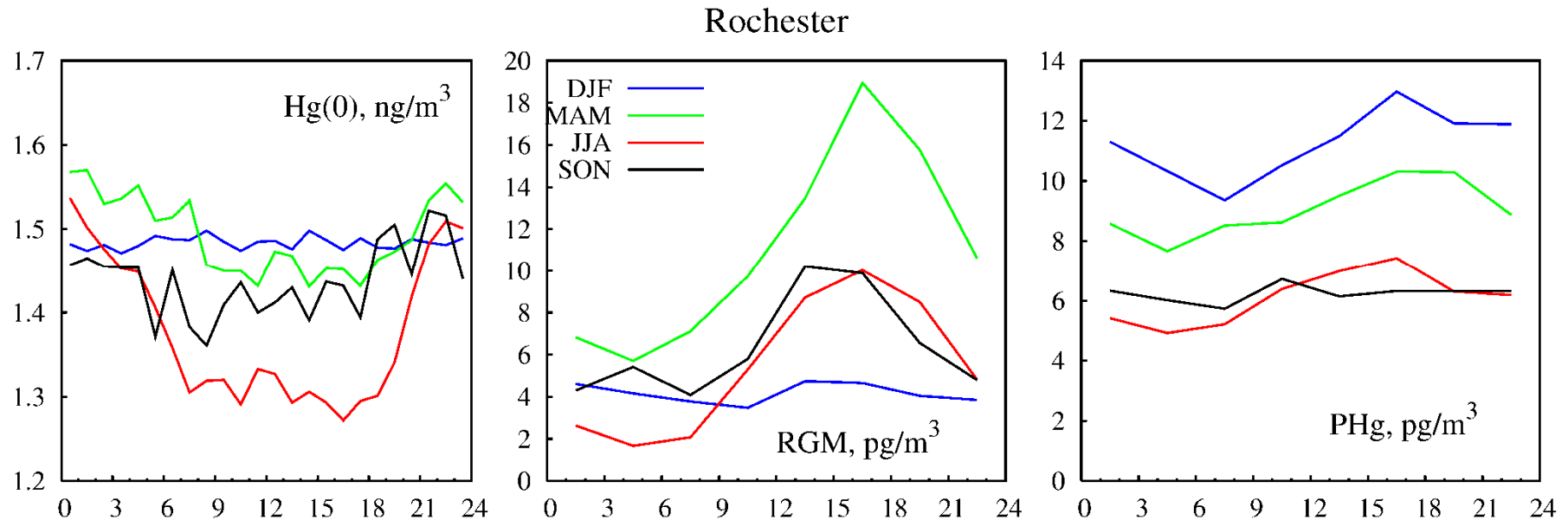
DJF —  
MAM —  
JJA —  
SON —

JJA: Jun-



# Diurnal Profile: Rochester

Sept 08' – Aug 09'



- DJF: Dec-Feb, MAM: Mar-May  
Aug, SON: Sept-Nov
- The Mar-May RGM is driven by one episode in April
- RGM has a similar profile to Ozone

JJA: Jun-



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## Data Recovery

- NYC: Hg<sup>0</sup> 95.0%, RGM 88.2%, PHg 91.3%
- Rochester: Hg<sup>0</sup> 96.3%, RGM 86.9%, PHg 79.0%

While this is much better than expected:

- The data are lightly validated. Future national (AMnet) data handling procedures may reduce the percentage of data that are validated.
- The instruments spent 8 months in the lab prior to deployment where many problems and operational issues were resolved





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## Quality Assurance

- The 2537 is calibrated every 24 or 72 hrs via an automated sequence using an internal permeation source. The perm source is audited with an external source by injection twice a year.
- Instrument checks every 2 weeks include:
  - 2537 Response factor and trap bias check
  - Glassware, soda lime trap and filter exchange
  - Inlet and 2537 flow rate check
  - Leak check (Hg trap: zero method)
  - Hg lamp driver voltage check
- The DataCom option provides sub-minute logging of inlet flow and all regulated temperatures.



## Method Precision: Tekran Collocation



- The NYSDEC collocated with Clarkson at the Rochester monitoring site
- Collocated results for  $\text{Hg}^0$  and RGM are quite good.  
 $\text{Hg}^0$  Slope = 0.86  $R^2 = 0.90$   
RGM Slope = 0.93  $R^2 = 0.99$
- PHg results to date have been less promising but this is likely due to unequal siting, inlet preparation and possibly due to differences in glassware preparation



## Hg<sup>0</sup>, RGM and PHg Monitoring Needs

- Tekran 2537B, 1130, 1135
- 1102 Air Dryer (with active purge upgrade)
- On-site computer to collect Serial data stream
- 2505 Hg permeation calibrator
- Lab facility to clean and re-coat denuder (KCl)
- Site with interior and roof/tower access
  - 1130 and 1135 should be > 2m above roof and away from obstructions and wetted surfaces
- Three 120 v circuits
- A 1-20 L/min flow std (vol and std conditions)



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## Is Hg<sup>0</sup>, RGM and PHg Monitoring for You?

- The cost to purchase a system with other needed equipment is approx: \$110K. The out of country (Canada) purchase and service can also complicate matters.
- Factory training and interaction with the AMnet program is recommended. Many operational issues such as denuder, scrubber and dryer performance are not intuitive and operational recommendations periodically change.
- Field visits and lab work both require about (2-3 hrs every two weeks not incl. travel) Additional time is required to review and validate the data.



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## Atmospheric Mercury Network (AMNet)

- Initiative Started in 2006
- NADP Network Status 2009
- Currently 22 sites
- Dry Deposition of Mercury Species
- Real time Data – No Central Lab
- Near Real Time Quality Assurance
- Web Accessible Data



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# Atmospheric Mercury Network (AMNet)

- Homogenize Methods
- Field Standard Operating Procedure (SOP)
- Data Management SOP
- QA Program Plan
- Annual Site Audits
- Loaner Program (dropped)





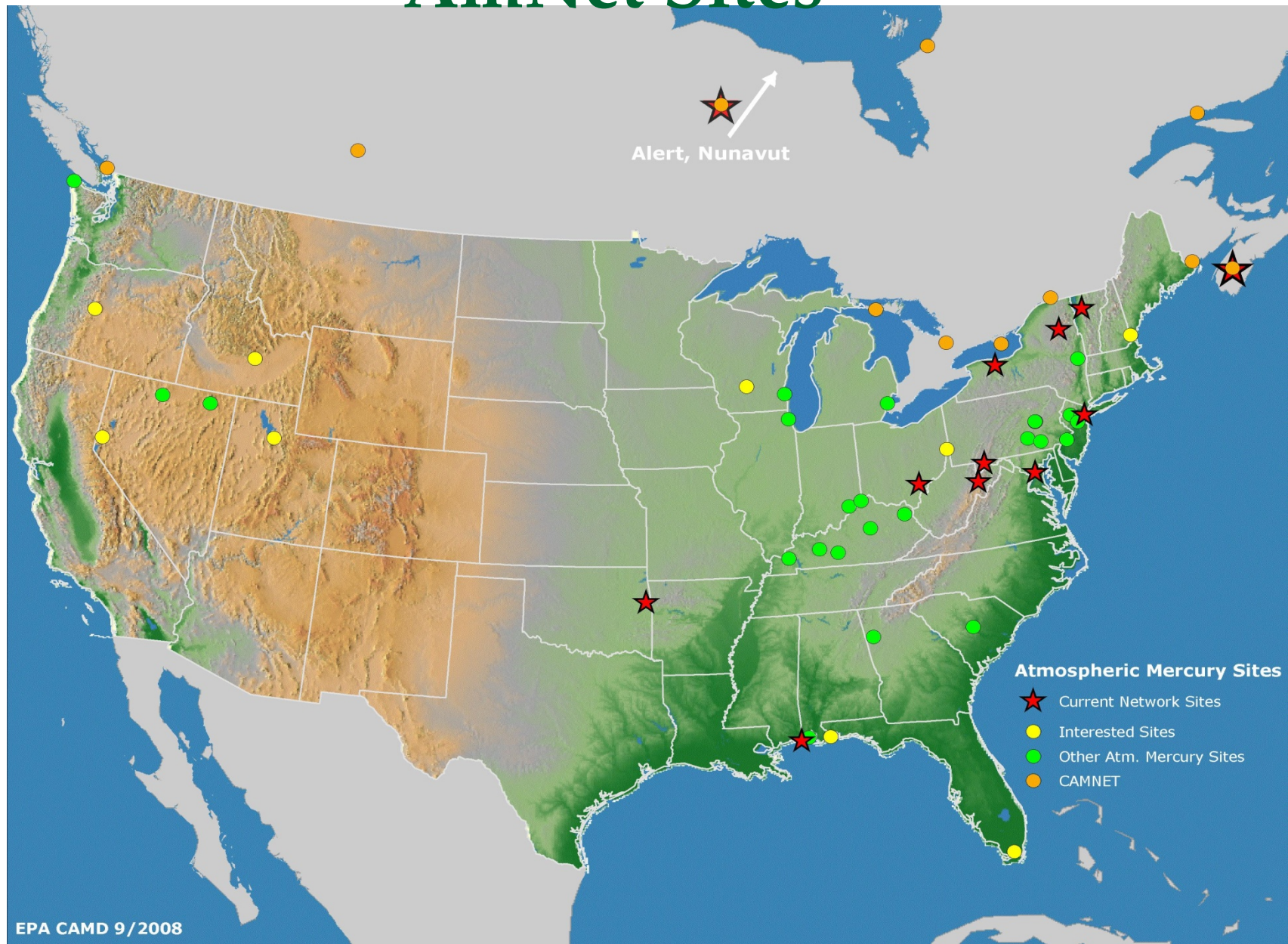
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# AMNet Site Liaison

- Mark Olson (USGS)
- Mercury in Water since 1995
- Managed USGS Hg Lab 1995 - 2007
- Developed Stable Isotope Hg Methods
- Mobile Atm Hg Trailer #1 in 2002, #2 in 2005
- Operated Four Tekran Speciation units



# AmNet Sites



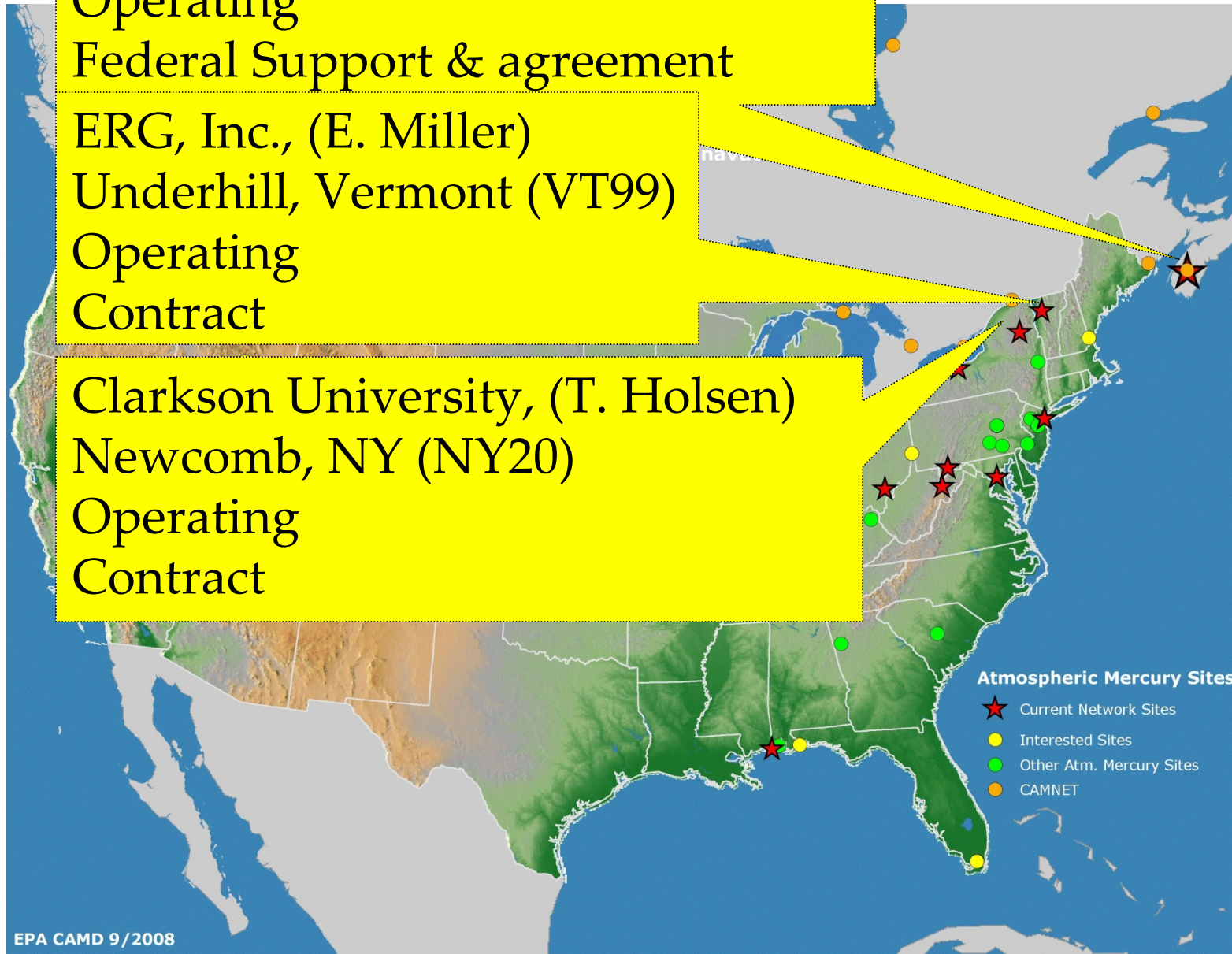


# Network Sites

Environment Canada (R. Tordon)  
Nova Scotia, Canada (NS01),  
Operating  
Federal Support & agreement

ERG, Inc., (E. Miller)  
Underhill, Vermont (VT99)  
Operating  
Contract

Clarkson University, (T. Holsen)  
Newcomb, NY (NY20)  
Operating  
Contract



## Network Sites

New York DEC/Clarkson U  
(T. Holsen/D. Felton)

Rochester, NY (NY43)

Operating  
State Supported

New York DEC (D. Felton)

Bronx, NY

Operating  
State Supported & agreement

University of Maryland (M. Castro)

Frostburg, MD (MD08)

Operating  
Contracted

NOAA ARL/EPA CAMD  
(W.Luke/D.Schmeltz)

Beltsville, MD (MD99)

Operating (multiple instruments)  
Federal Support





## Network Sites

Ohio University (Crist, Conley)  
Athens, OH (OH02)  
Operating  
Contracted

Canaan Valley Inst/NOAA-ARL  
(S. Brooks/R. Artz)  
Davis, WV (WV99)  
Operating Federal Support

Cherokee Nation (R. Callison)  
Stilwell, OK (OK99)  
Elemental operating  
Contracted

NOAA ARL (Luke, Brooks, Artz)  
Grand Bay, MS  
Operating (until the hurricane)  
Federal Support



## Other Sites

Environment Canada (Steffen)  
Alert, Nunavut  
5 years of historical, speciated data

ARA, Inc. Sites (E. Edgerton)  
Multiple sites in the Southeast  
Heavily involved since the beginning

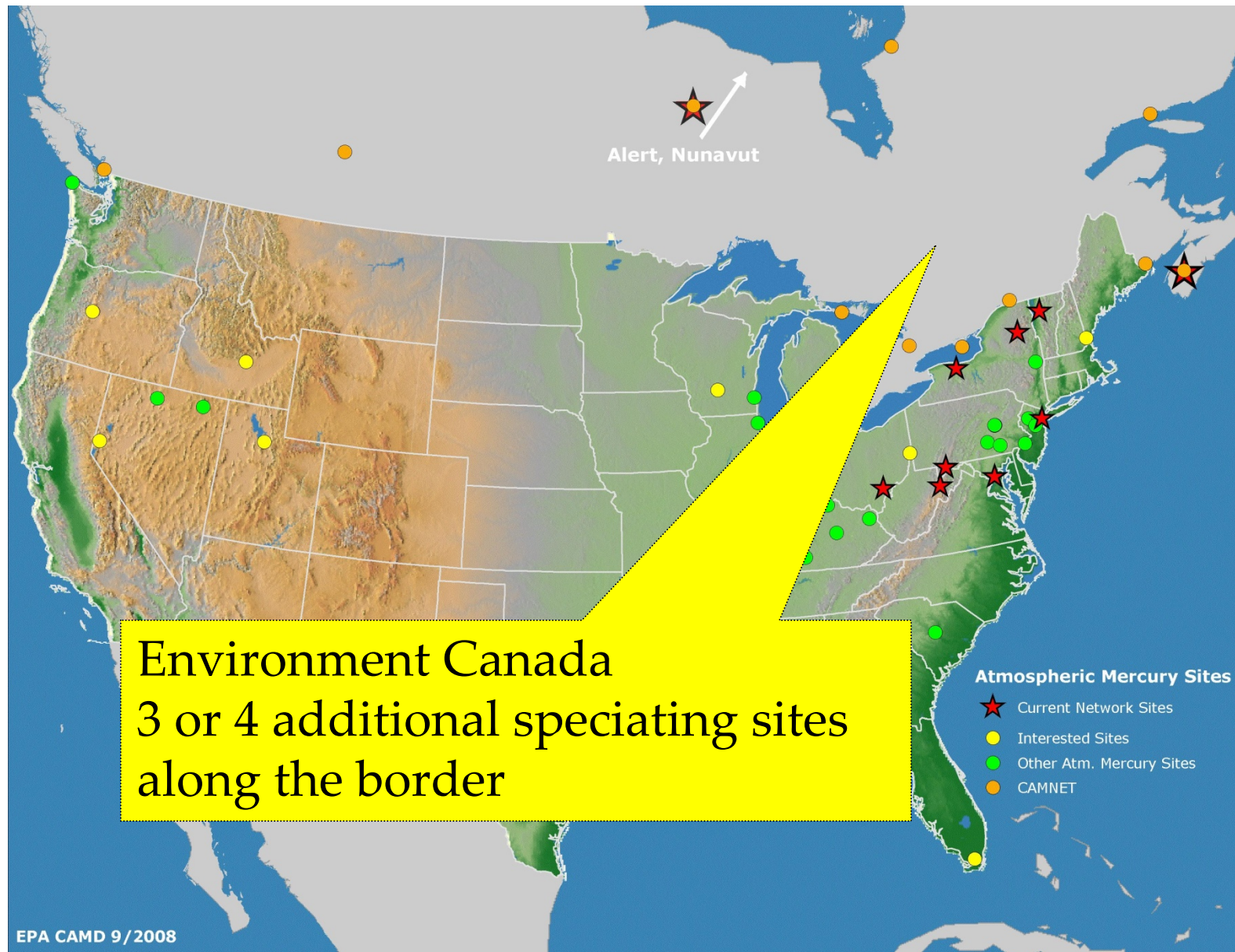
Mt. Bachelor, Oregon (D. Jaffe)  
Has agreed to provide data

### Atmospheric Mercury Sites

- ★ Current Network Sites
- Interested Sites
- Other Atm. Mercury Sites
- CAMNET



# Future Sites?



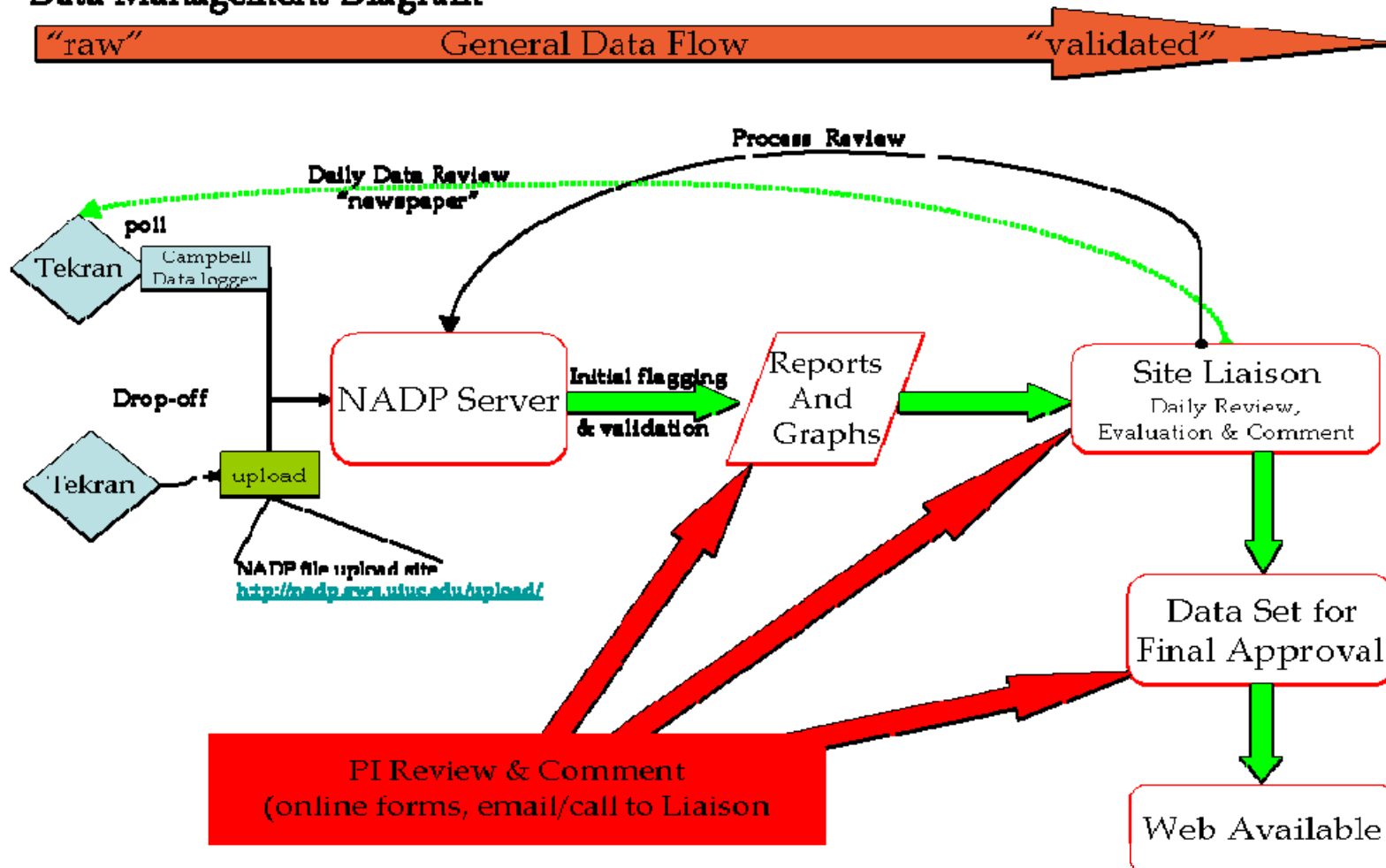
# AmNet's Automated QA Program

## Automated Flags (FLAG1)

Flags	Flag	Description	Conditions for activation	Range	Val/Inv	Color	Data
none		Good Data	Meets following criteria	Extent of flag coverage	V	Green	All
A1	Ambient	Ambient Air Trap Bias	10% Difference over 24 hour period	24-hour means of each trap	V	Yellow	GEM
A2	Ambient	Ambient Air Trap Bias	15% Difference over 24 hour period	24-hour means of each trap	I	Red	GEM
B1	Baseline	Baseline Voltage	Baseline <0.050 or >0.150	Each observation	V	Yellow	All
B2	Baseline	Baseline Voltage Change	Change >0.010 from previous obs.	Compare prev. vs. current obs.	V	Yellow	All
B3	Baseline	High Baseline Deviation	5 consecutive deviations > 0.100	Compare prev. 5 in a row obs.	V	Yellow	All
B5	Baseline	High Baseline Deviation	Baseline deviation >0.200	Each observation	I	Red	All
B0	Baseline	Low Baseline Voltage	Baseline Voltage <0.010	Each observation	I	Red	All
M2	Readout	Multiple Peaks Detected	Status = M2	Each observation	V	Yellow	All
M3	Readout	Multiple Peaks Detected	Status > M2	Each observation	I	Red	All
OL	Readout	Detector Overload	Status = OL	Each observation	V	Yellow	All
NP	Readout	No Peak Detected	Status = NP	Each observation	I	Red	GEM

# AmNet's QA Program: Data Flow

Data Management Diagram



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# Site Liason's Data Quick Look Report

- Baseline Voltage and Deviation over 3 days
- Calibration – RF's and Zero's over 14 days
- Trap comparison – A vs. B and A/B Ratio
- Desorb Cleans A & B, and Blank C
- Post Desorb GEM Passivation Index
- Data Comm Option Temps and Flows
- GEM, GOM, and PBM2.5 Concentrations



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## AmNet Program: Parts Depot

- Site Liaison keeps most parts in stock for troubleshooting and repair purposes
- Multiple parts can be shipped for troubleshooting
- Next day delivery
- Operator replenishes depot
- USEPA PO (01/2010) for NADP specific parts



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## AmNet Program: On Site Audits

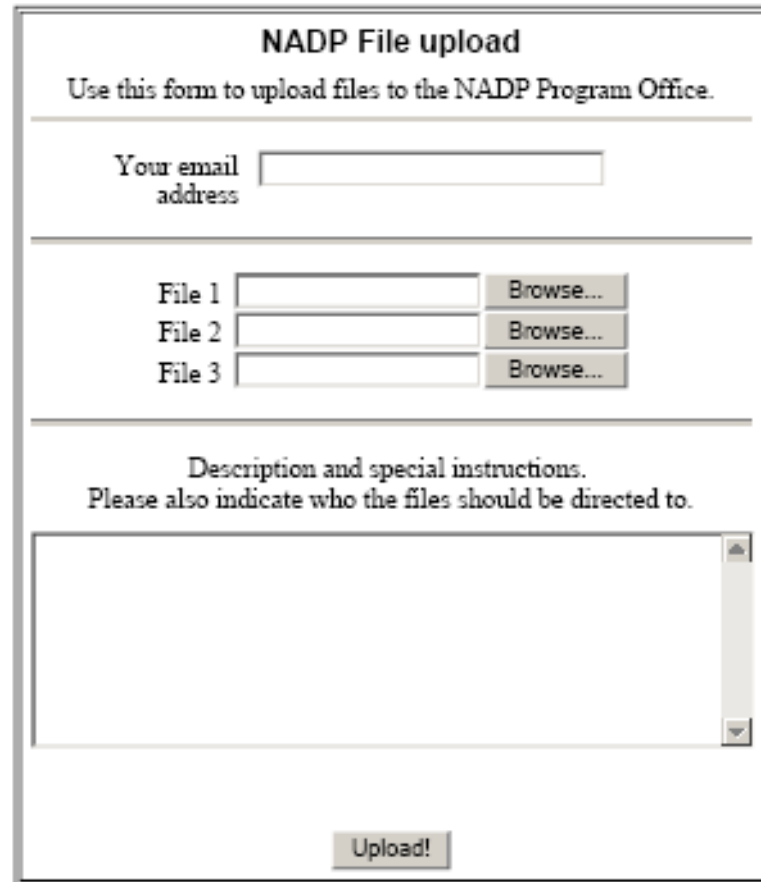
- Operator, site and instrument information
- Independent flow and calibration checks
- Check instrument operation and repair
- Instrument upgrades (DVM for Lamp, 1102 Dryer)
- Annual maintenance
- Training
- Completed 15 sites in FY09



# AmNet Data Acquisition

AmNet would like to have automatic data uploading via the internet (if possible) This provides the best feedback on instrument issues.

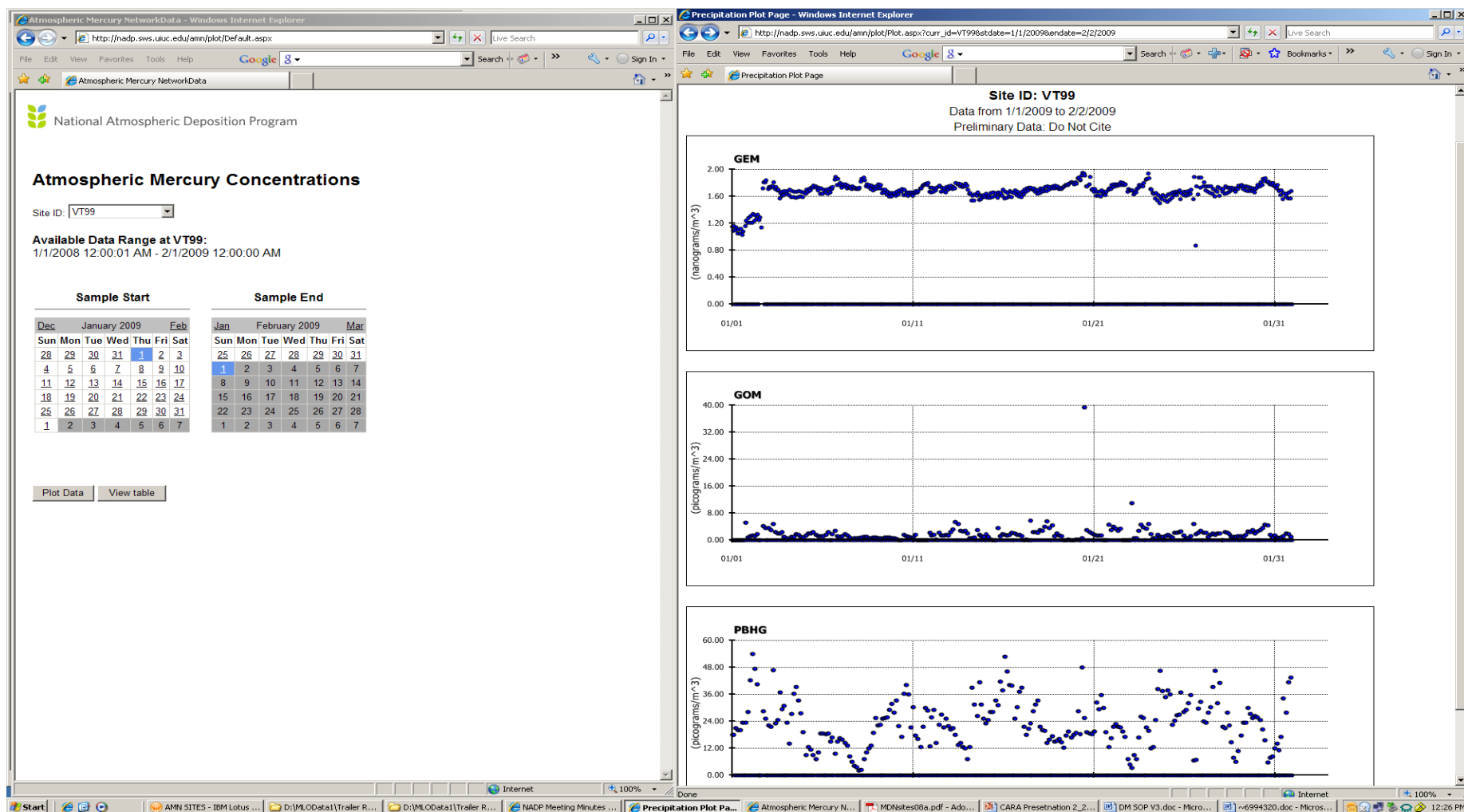
If that is not possible data can be manually uploaded.



The image shows a web form titled "NADP File upload". Below the title is a subtitle: "Use this form to upload files to the NADP Program Office." The form is divided into several sections. The first section contains a label "Your email address" followed by a text input field. The second section contains three rows, each with a label "File 1", "File 2", and "File 3" respectively, followed by a text input field and a "Browse..." button. The third section contains a label "Description and special instructions. Please also indicate who the files should be directed to." followed by a large text area with a vertical scrollbar. At the bottom of the form is a button labeled "Upload!".



# AmNet: Web Site Graphics





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## Conclusions

- The Instruments are expensive and require significant effort to operate
- The Hg<sup>0</sup> and RGM data are reliable, consistent and are useful for the intended monitoring objectives: establishing baselines, providing data for dry deposition estimations, characterizing sources and evaluating source controls
- The PHg data are less useful because the values seem to be extremely sensitive to siting and instrument issues. More work needs to be done to isolate the cause of the collocated bias and determine if the issues can be resolved.

