A Data Review and Operational Notes: A Year Spent with the Tekran Speciated Ambient Mercury Analyzer at Two Urban Locations in New York State

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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 (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 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 Hg^0, RGM and PHg typically are not found at concentrations considered to be toxic to humans, however:
- Sources emit 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

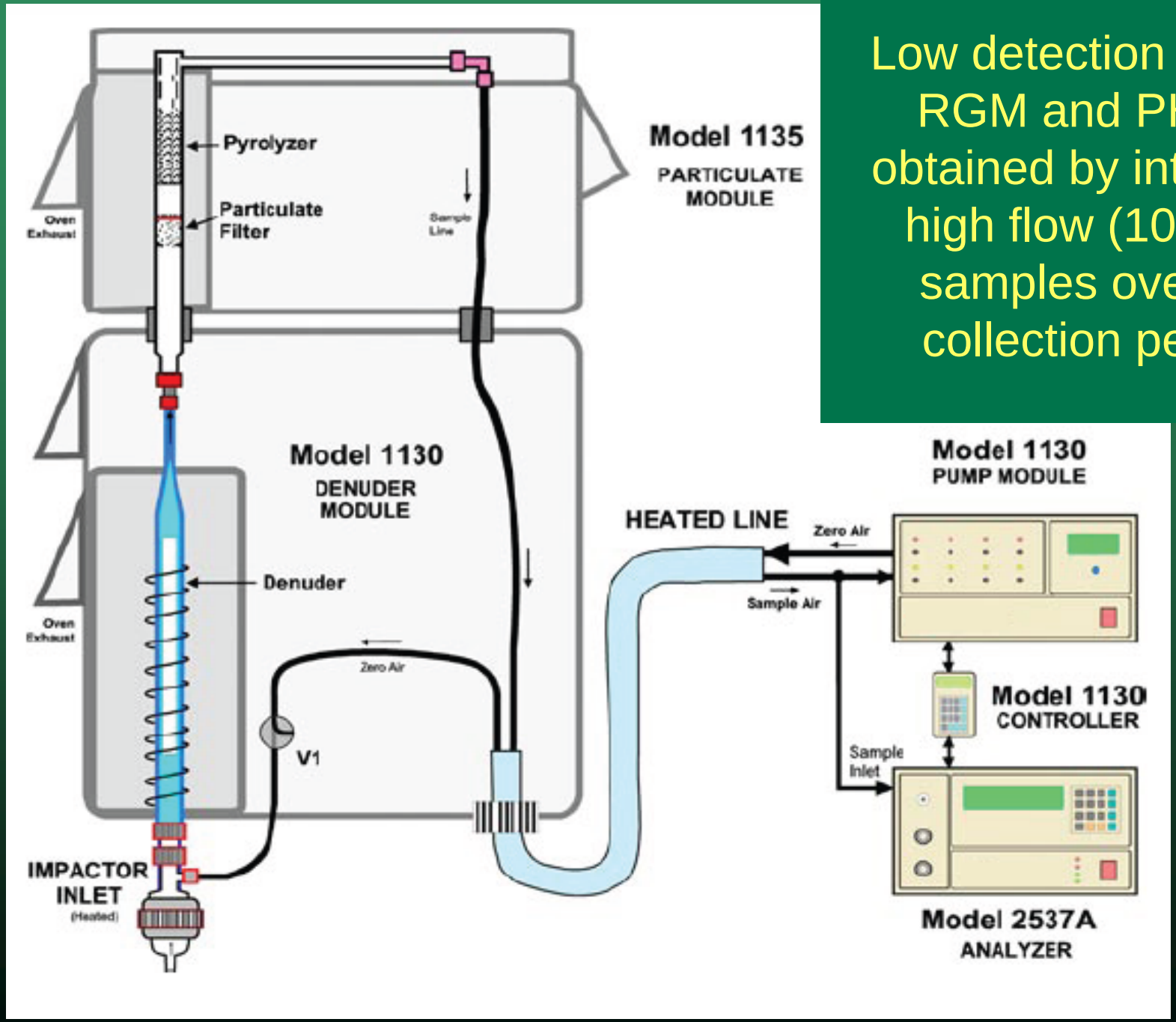
Hg Monitoring Instrumentation

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

Hg Monitoring Instrumentation

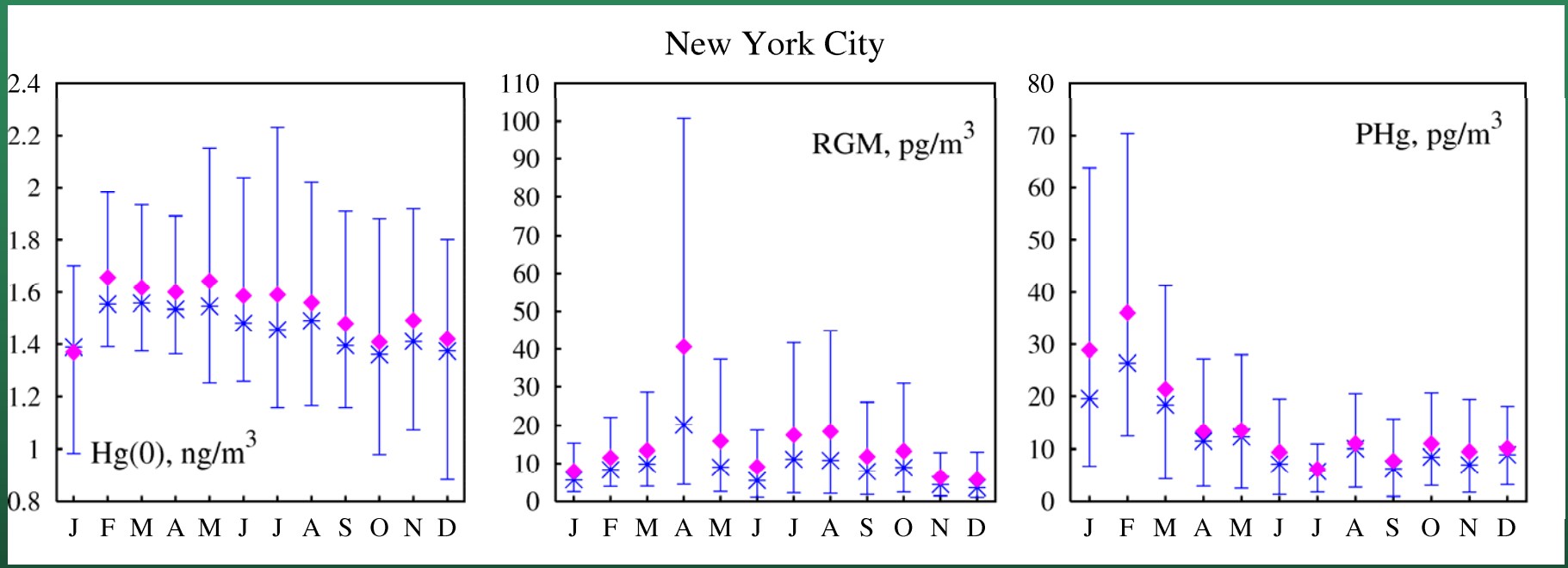
- 1135: PHg is collected for 2-hrs on a filter at 10 L/min. The filter is thermally desorbed at 800 Cº.
- 1130: RGM is collected for 2-hrs on an annular denuder at 10 L/min. The denuder is thermally desorbed at 500 Cº.
- A heated line connects the 1130 & 1135 to the 2537 which analyzes the desorbed PHg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

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



Monthly Averages: NYC

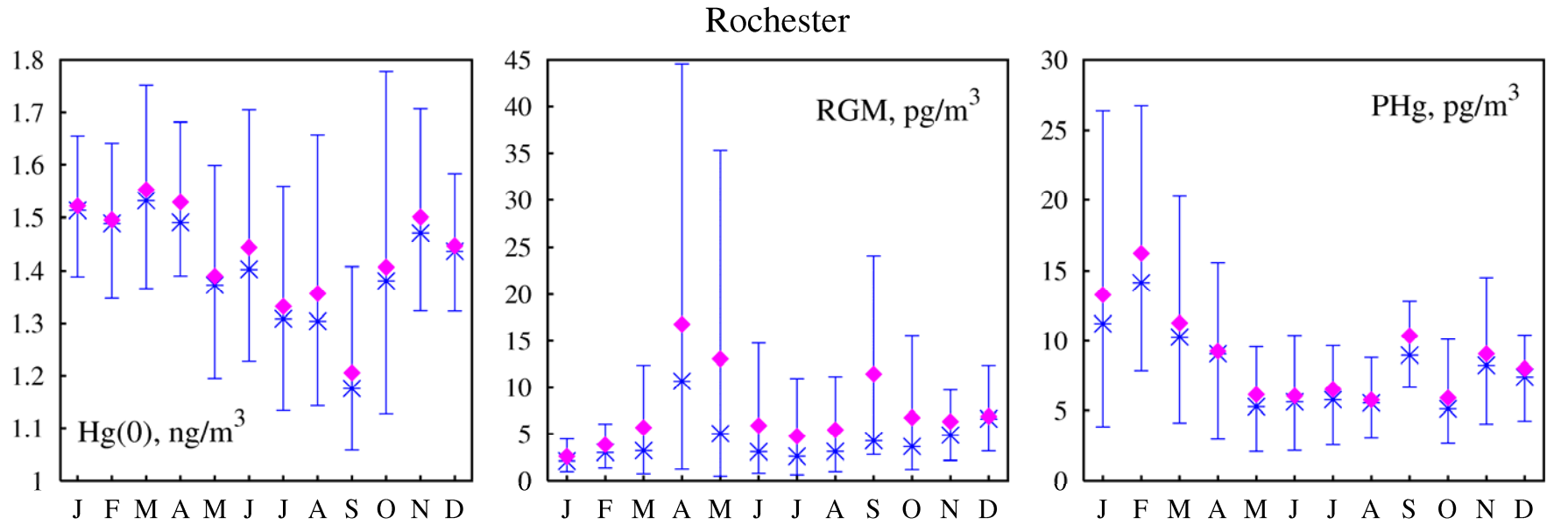
Sept 08’ – Aug 09’



- The Hg^0 is in ng/m^3, the RGM and PHg are in pg/m^3
- The median and 10^{th}, 90^{th} and 50^{th} 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

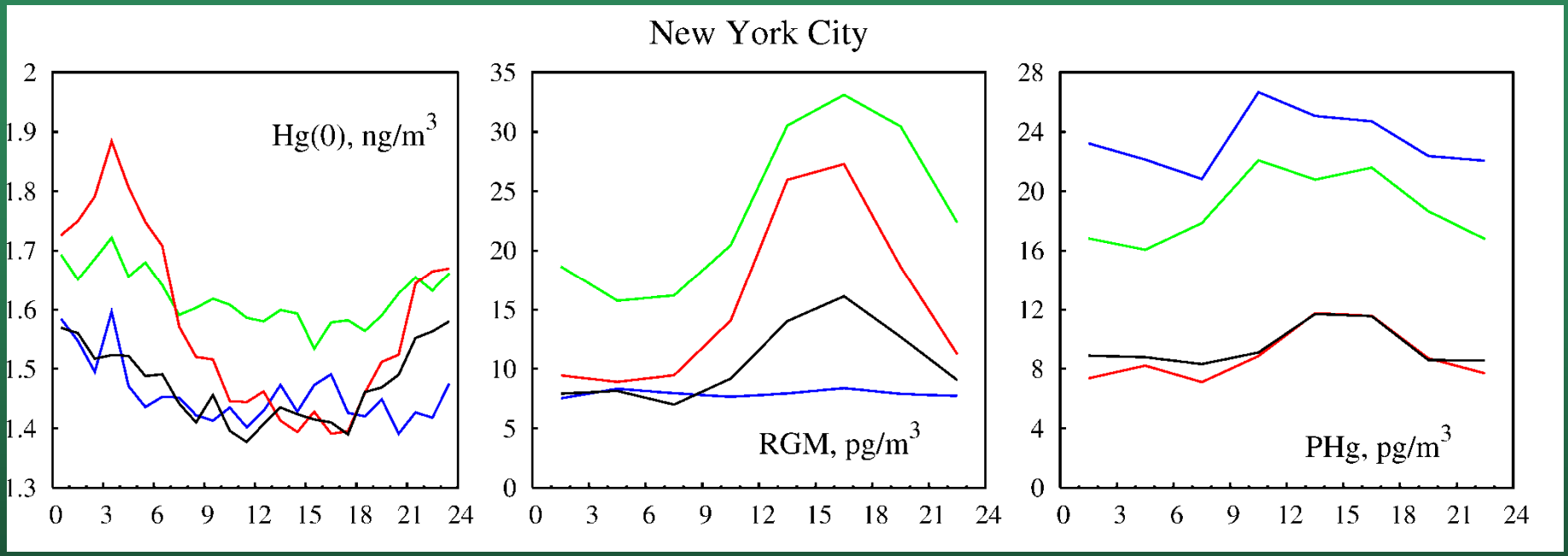
Sept 08' – Aug 09'



- 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

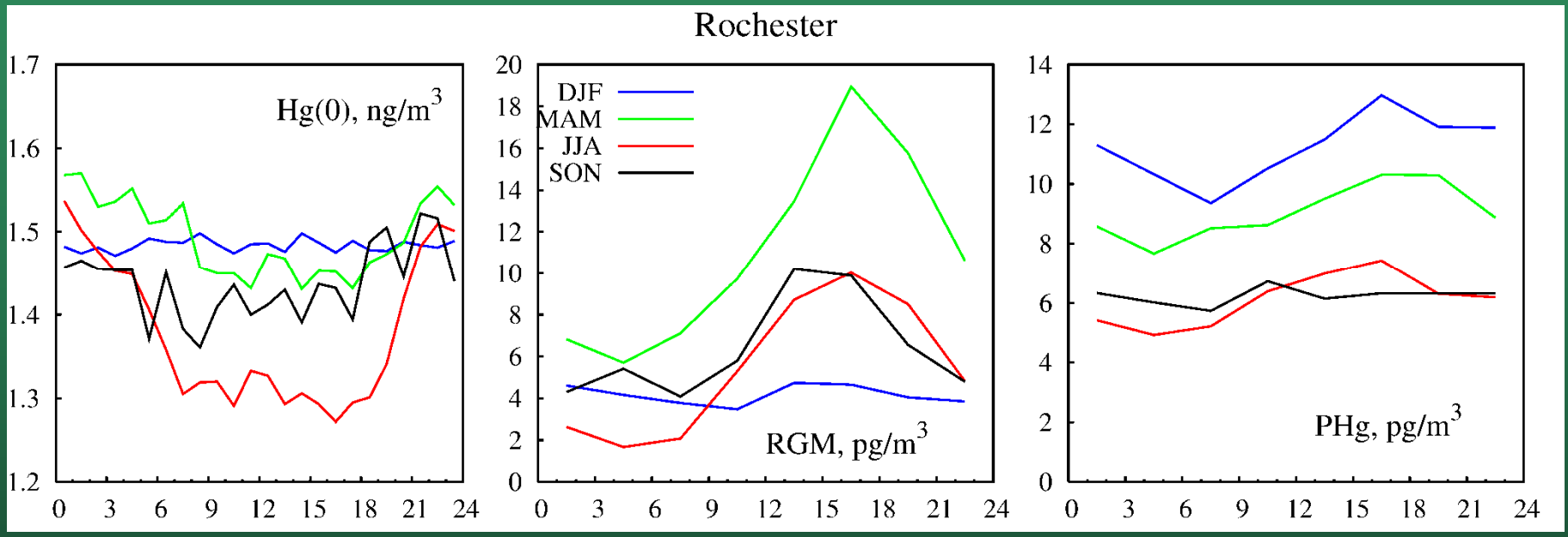
Sept 08' – Aug 09'



- DJF: Dec-Feb, MAM: Mar-May
  JJA: Jun-Aug, SON: Sept-Nov
- The 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

Diurnal Profile: Rochester

Sept 08’ – Aug 09’



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Data Recovery

- NYC: Hg^0 95.0%, RGM 88.2%, PHg 91.3%
- Rochester: Hg^0 96.3%, RGM 86.9%, PHg 79.0%

While this is much better then 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

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 Hg^0 and RGM are quite good.

  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

Hg0, 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)

Is Hg^0, 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.

Conclusions

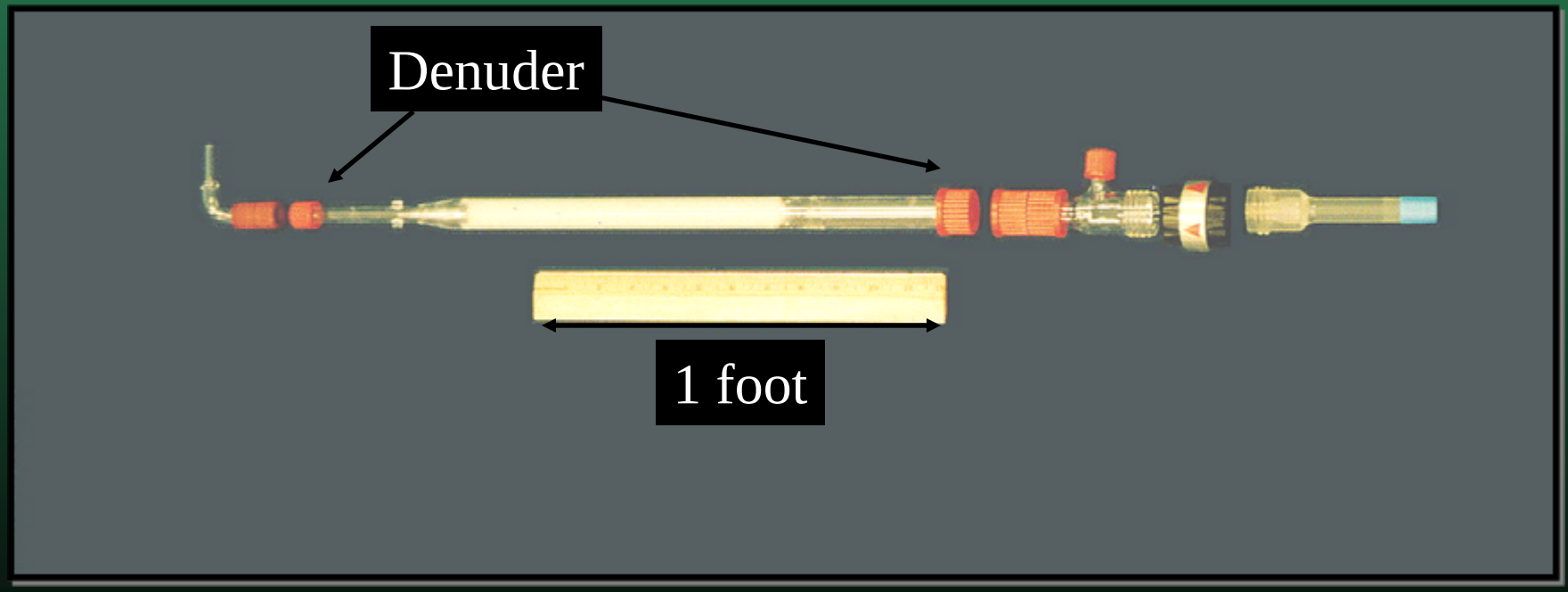
- The Hg^0 and RGM data are reliable, consistent and are useful for the intended monitoring objectives: establishing baselines, providing data for dry deposition estimations, characterizing sources and evaluating source controls
- The PHg data are less useful because the values seem to be extremely sensitive 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.

End of Presentation

The Reactive Gas 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

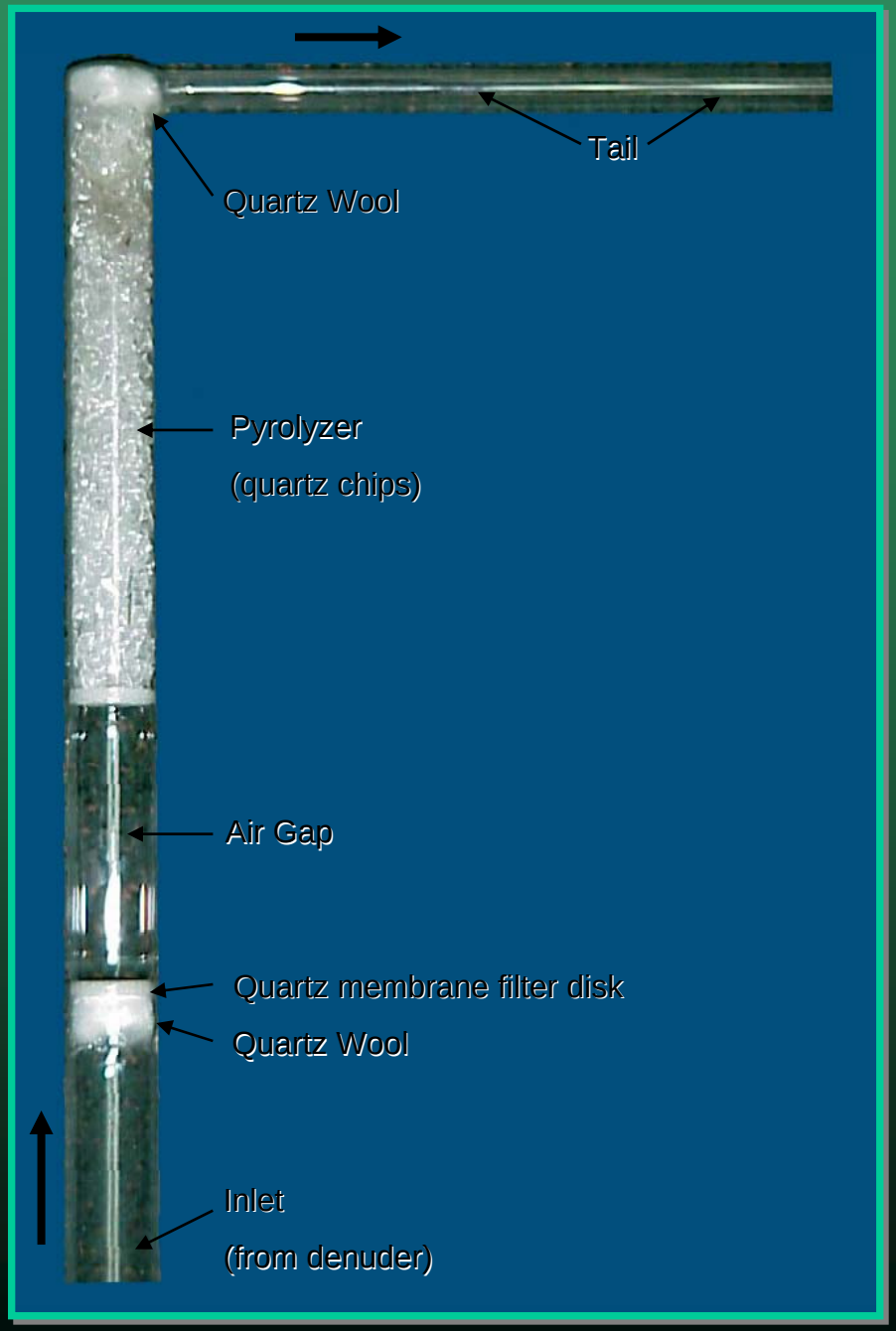


The Pyrolyzer is where the particulate Hg is captured in the 1135.

The Quartz filter and wool must be replaced every 1- 8 weeks depending on which SOP you are reading.

The configuration of the glassware makes the Pyrolyzer very fragile.

The replacement cost is about $825.



NY Toxics Grant: Objectives

Establish a reference baseline for mercury (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.