Atmospheric Mercury Measurements, Speciation and Discoveries

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Presentation Outline

- How do networks and researchers measure atmospheric mercury?
- Why is air mercury speciation important and how does it work?
- What discoveries have occurred due to air mercury monitoring

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Atmospheric Mercury Nomenclature

- GEM = Gaseous elemental mercury = Hg^0
- GOM = Gaseous oxidized mercury = Hg(II)
  - also known as Reactive Gaseous Mercury (RGM)
- $PBM_{2.5}$ = Particulate-bound mercury = $Hg_{p(2.5)}$

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Mercury detection – the challenges
Reality Check: What should we expect?

- GEM = 1.7 ng/m^3
  - Equals 0.2 parts per trillion (v)
  - 5 x 10^6 molec/cm^3
- GOM and PBM = 10 pg/m^3
  - Equals 1.1 parts per quadrillion (v)
  - 2.7 x 10^4 molec/cm^3
- Mercury compounds act like semi-volatile organics

Mercury detection - the challenges

- ***Sensitivity***
  - Mercury is present in the low pptv to ppqv range
- ***Selectivity***
  - Potential interferents are present at ***1000's of times*** higher concentration than mercury
    - O_3
    - SO_2
    - NO_X
    - HCl

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Options for measuring ambient total mercury

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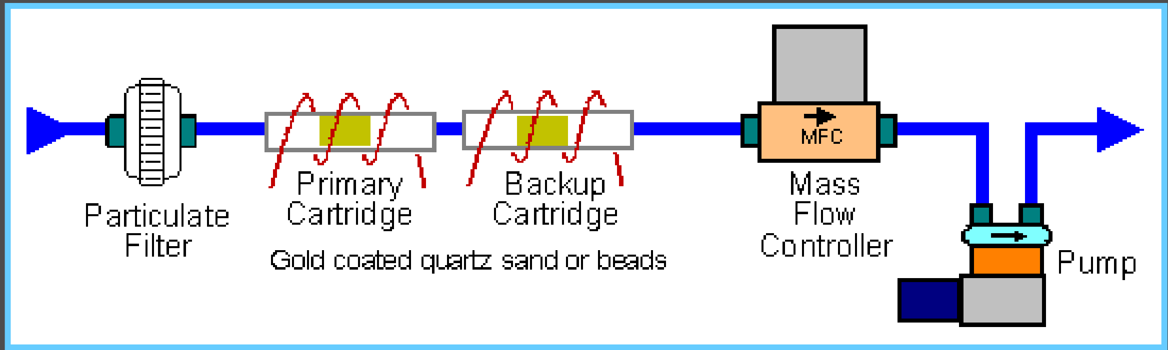
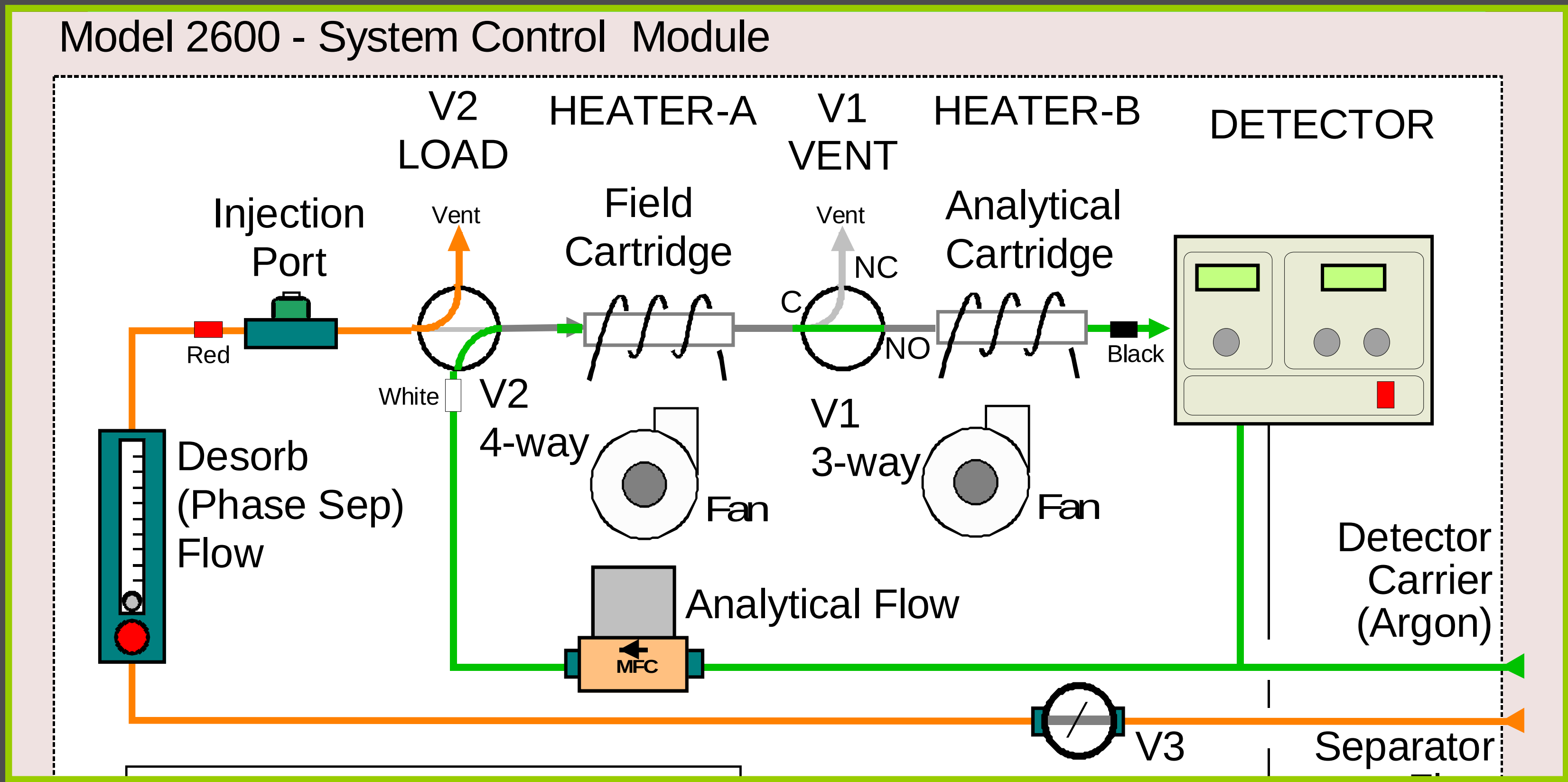
Manual Total Gaseous Mercury Monitoring

- Manual method developed in late 1980's
  - Developed and used by researchers
  - Eventually documented by US EPA as IO-5



  - Gold-coated quartz adsorbent trap & backup trap
  - MFC and pump to measure sample volume
  - Typical exposure time required: ***6-24 hours***

Manual Cartridge Analysis



- Dual stage thermal desorption
- ***Atomic Fluorescence*** (AF) detection

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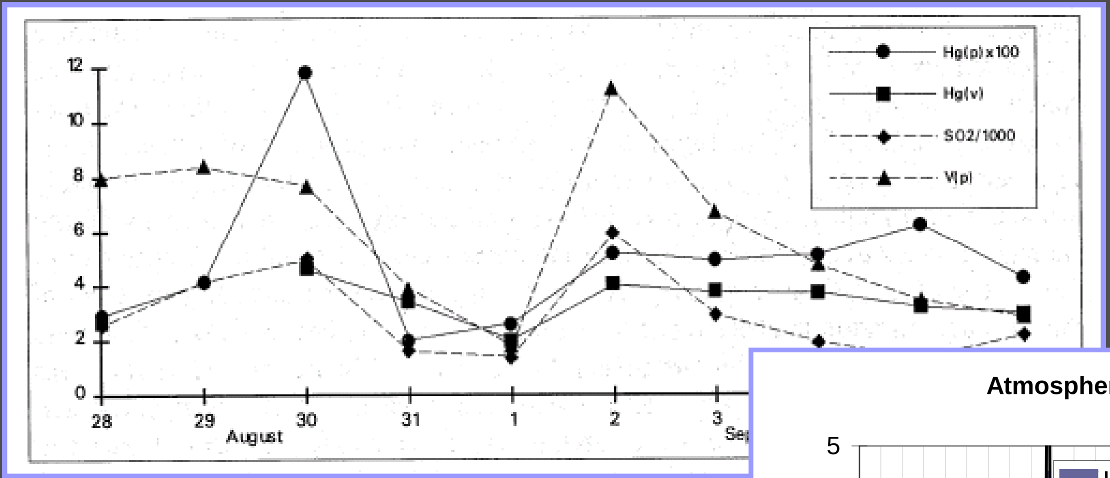
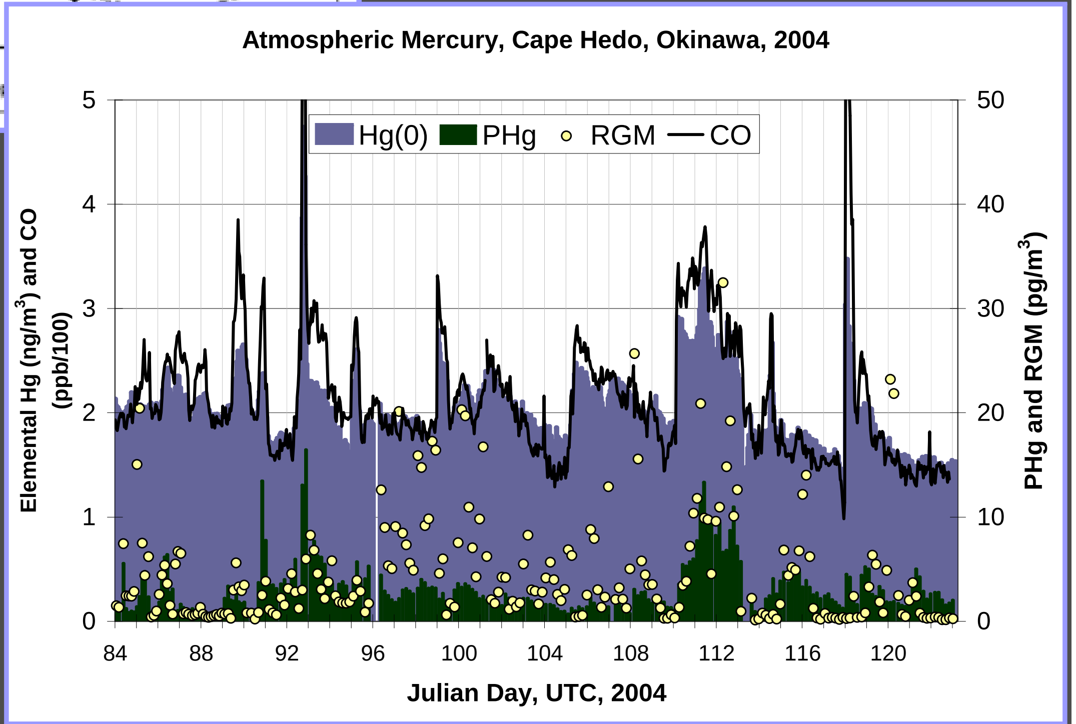
Example of the benefits of automated, high resolution mercury monitoring



1993

24 hour manual method for TGM and Hg_p



2004

5-min automated for GEM & 3-hours for GOM & PBM

Use of and improvement in ancillary measurements has also been important

Adapted from Dvonch et al., 1995 *WASP* and Jaffe et al., 2005 *Atm. Env.*

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Mercury Detection Techniques

- Two spectroscopic techniques used for analysis
  - Atomic Absorption (***AA***)
  - Atomic Fluorescence (***AF***)
- ***Why?***
  - Mercury has a particularly strong absorption/emission line at 253.7 nm
  - Mercury is present in vapor phase at room temperatures

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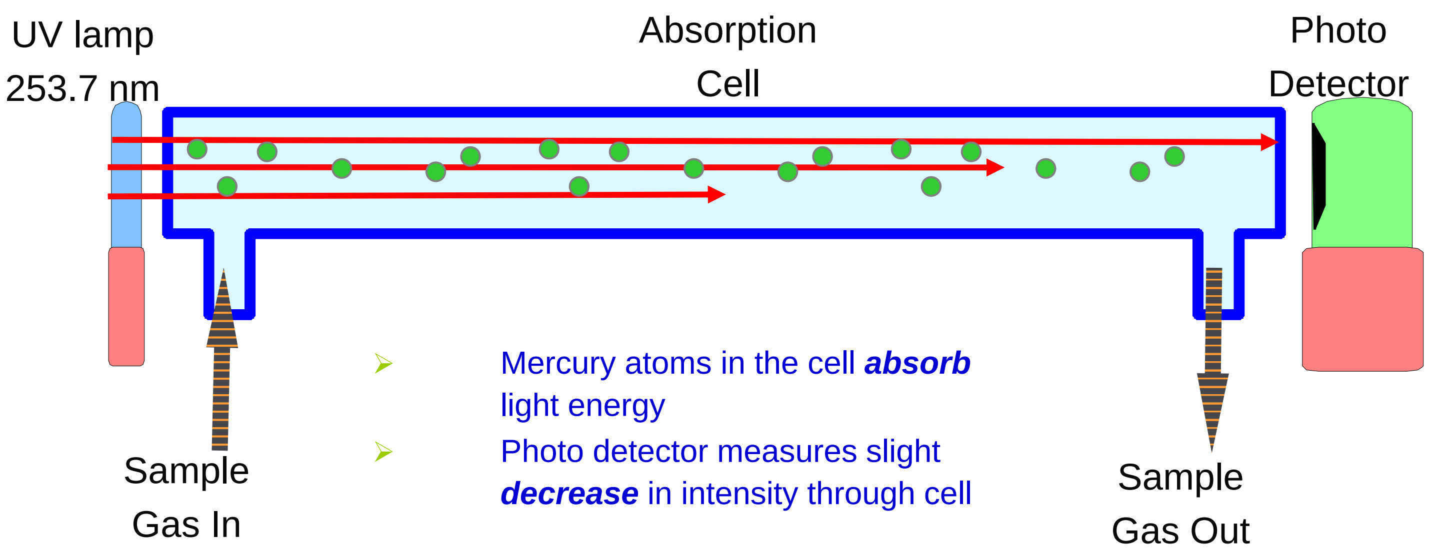
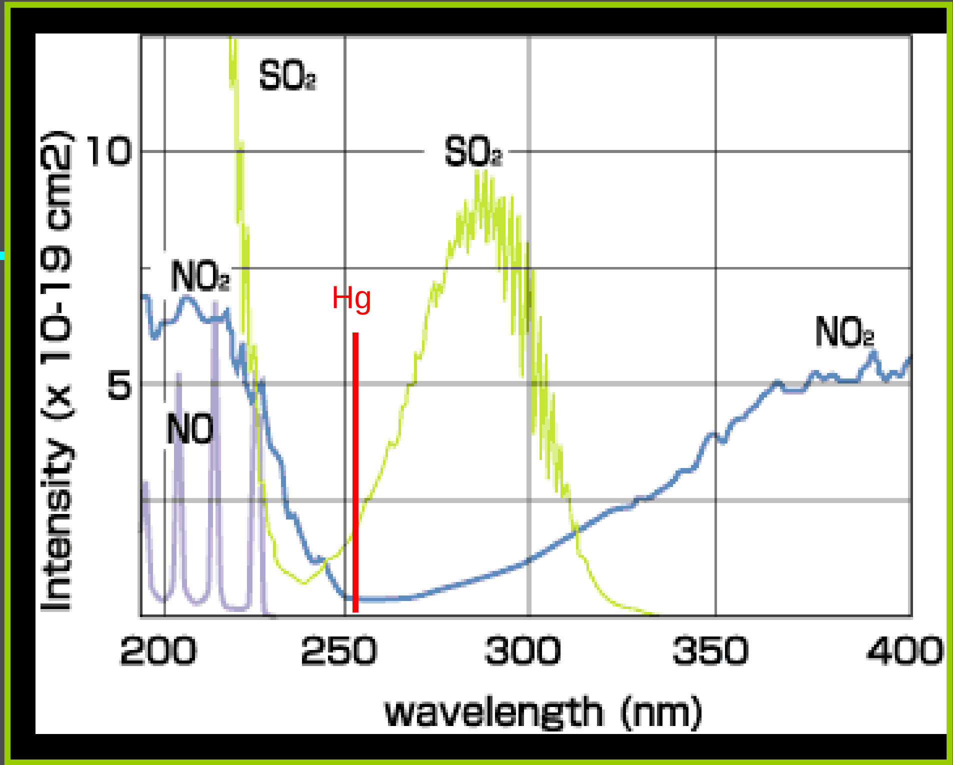
Atomic Absorption (AA) Detector



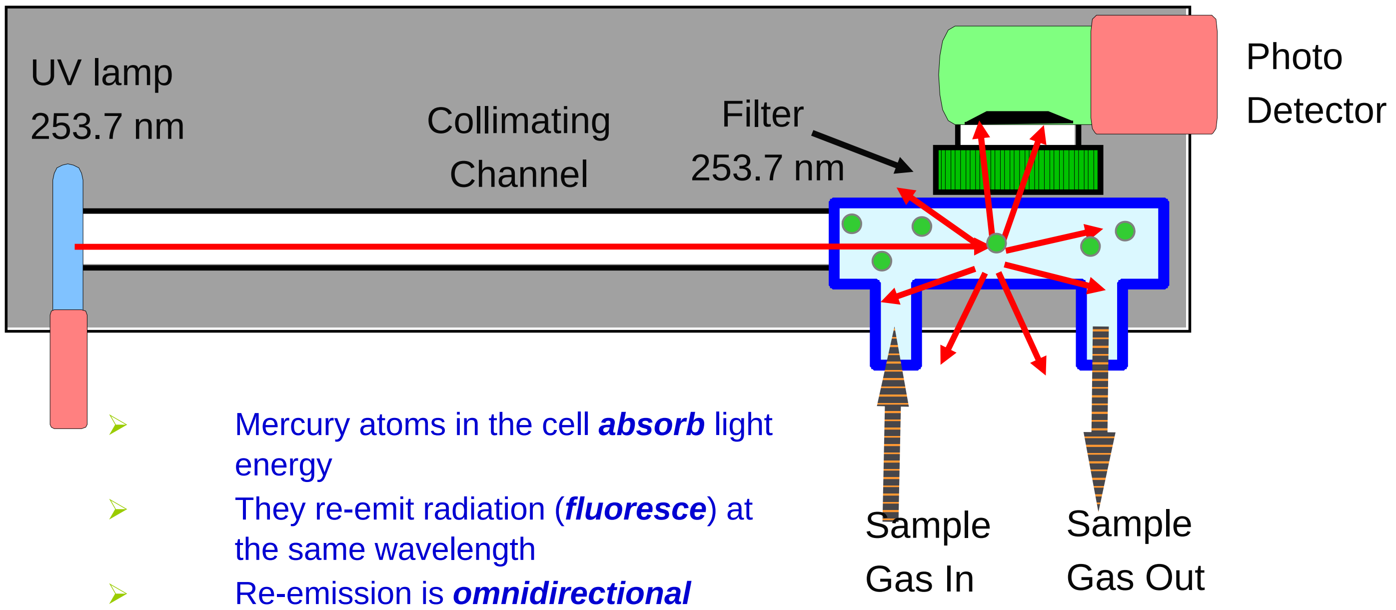
- Mercury atoms in the cell ***absorb*** light energy
- Photo detector measures slight ***decrease*** in intensity through cell

Why not AA?



- Amount of absorption is set by Beer's law
  - Logarithmic response
  - Limited dynamic range
  - USEPA has required 5 point linearity checks
- Not particularly sensitive
  - Looking for very small decreases in a bright background lamp signal
  - It's like trying to find and count one or two individuals as they leave a crowded football stadium with 100,000 people in the stands
- Inherently cross sensitive to any molecular species that absorbs in the UV at 253.7 nm
  - There are lots ! Organics, SO_2, O_3, NO_2 to name but a few

Atomic Fluorescence (AF) Detector



- Mercury atoms in the cell ***absorb*** light energy
- They re-emit radiation (***fluoresce***) at the same wavelength
- Re-emission is ***omnidirectional***
- Photo detector measures ***increase*** in intensity against a dark background

Why Atomic Fluorescence?

- Much more sensitive than atomic adsorption
  - MDL < 0.1 pg absolute
  - It's like finding one or two individuals as they arrive in the stands of an *empty* football stadium
- Not subject to interferences
  - Unlike AA, does not require any sort of compensation/correction scheme
  - Interfering compounds (e.g. SO_2, O_3, organics) often present in concentrations *thousands* of times higher than Hg
  - Analyte must both absorb and reradiate at the subject wavelength
- Inherently linear
  - Detector linear over >5 orders of magnitude
- Simple and rugged
  - Capable of continuous field operation

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Requirements for using AF ?

- The detector and all components must be very high quality to take advantage of AF selectivity and sensitivity
- *Disadvantage of AF*
  - Fluorescence is quenched by any molecular species present
  - Quenching eliminated by using *gold* adsorbent and transfer of mercury into an inert carrier gas stream, normally argon

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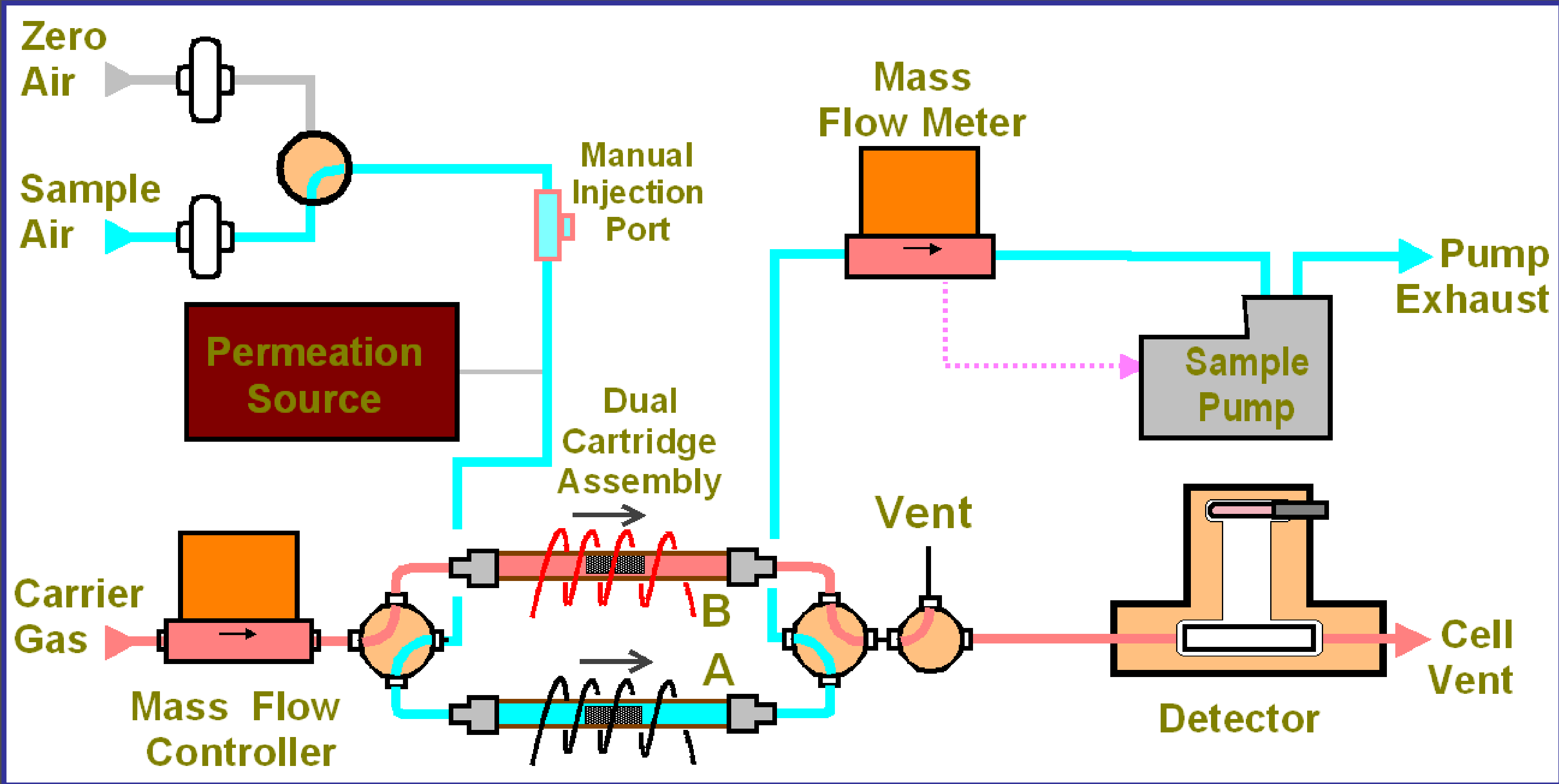
Flow Diagram of Tekran Model 2537 Automated Mercury Analyzer



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The New Tekran 2537X

- **Highlighted Features**
- 100% backwards compatibility
- Network enabled
- Touch screen interface
- Local data storage
- Front panel USB port data retrieval and update
- Improved accessibility of routine maintenance components
- Remote instrument login and control
- Digital control of all devices
- 4U (7 inch high) rack mounted

Automated Total Mercury Analyzer

- Automated implementation of gold-trap AFS method
- Provides continuous total gaseous mercury (TGM) readings with update rate as low as ***2.5*** minutes
- Detection limit **< *0.1 ng/m³*** *(5 minute, 7.5 liter samples)*
- Automatic recalibration with internal Hg^0 permeation source
- Capable of unattended operation for extended periods
- Two cartridges are used to alternately sample and desorb
  - No gaps in data stream

Why Speciate Mercury?

- Species Have Very Different Behaviors
  - **GEM** (Hg^0) is not water soluble, slow to react, transported long distances
  - **GOM** (e.g. $HgCl_2$) is very water soluble, removed rapidly at the surface
  - **PBM** (Hg on soot) removed rapidly by wet and dry deposition
- Atmospheric Transport and Deposition Modeling
- Bioaccumulation, Exposure & Risk Assessment

How can we measure ambient speciated mercury?

…

Challenges of Measuring GOM

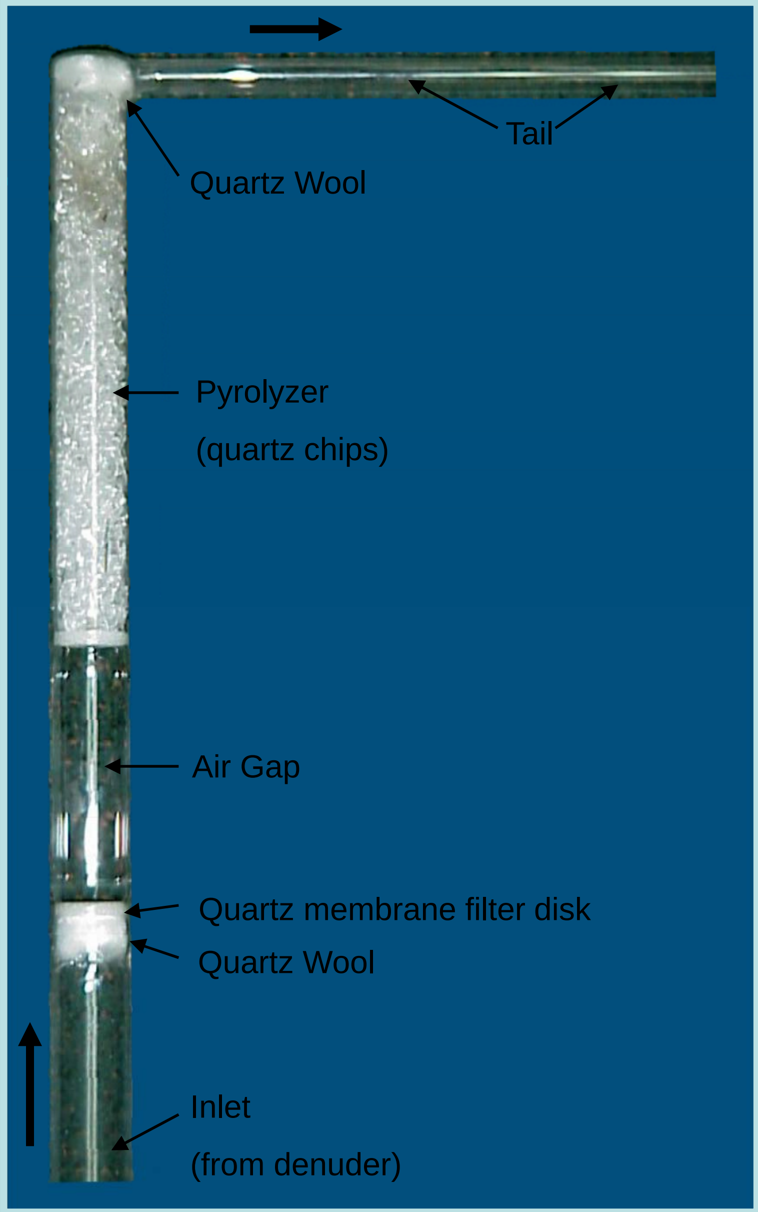
- Method must be *1-2 orders of magnitude more sensitive* than total mercury methods
- Must reject much larger *elemental* component
- Must exclude *particulate* bound mercury, however, conventional particulate filters cannot pass ***GOM***
- Apparatus must pass ***GOM*** to the collector quantitatively. *(GOM is extremely “sticky”)*
  - Sampling components must be located ***out of doors***

GOM Monitoring
Principles of Operation

- Automated GOM monitoring instrumentation now exists
  - Quartz, KCl coated annular denuder is thermally desorbed and regenerated
  - Sampling Phase
    - Absorbs GOM while passing all elemental and particulate Hg
    - Model 2537 reads ***Hg^0*** during this phase
  - Desorption/Analysis Phase
    - Denuder heated to 500 °C
    - GOM released as ***elemental*** mercury

$PBM_{2.5}$ - RPF

- Quartz wool captures bulk of particulate matter
- Quartz filter membrane provides sharp cut-off (<0.1 um)
- Built in pyrolyzer section converts desorbed species to Hg^0
- Carbon based particulate matter on the filter is oxidized to CO_2 during desorption cycle
- Tail provides cooling



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Part 3:
Sampling & Analysis Animation
Model 1130 and Model 1135

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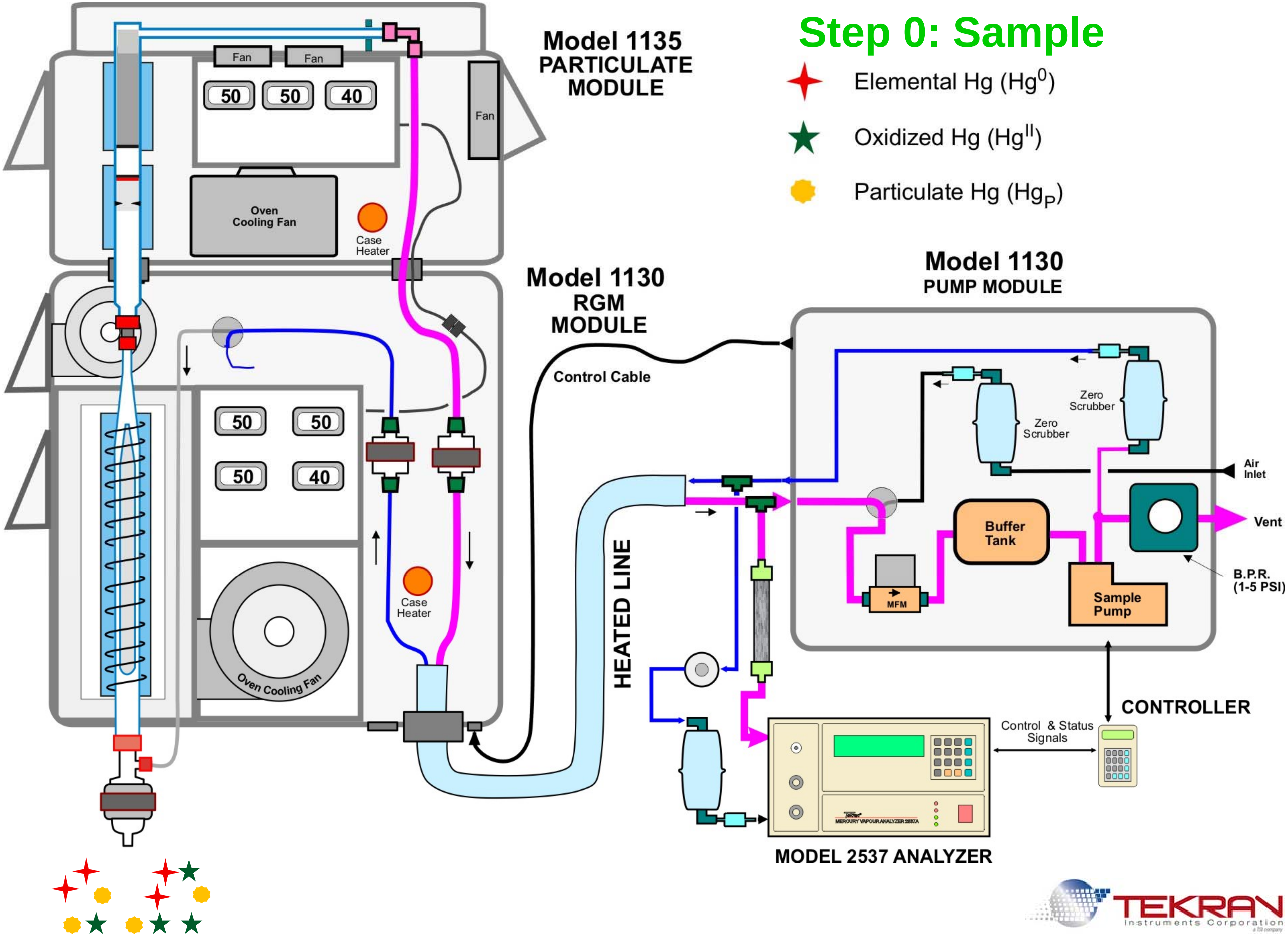
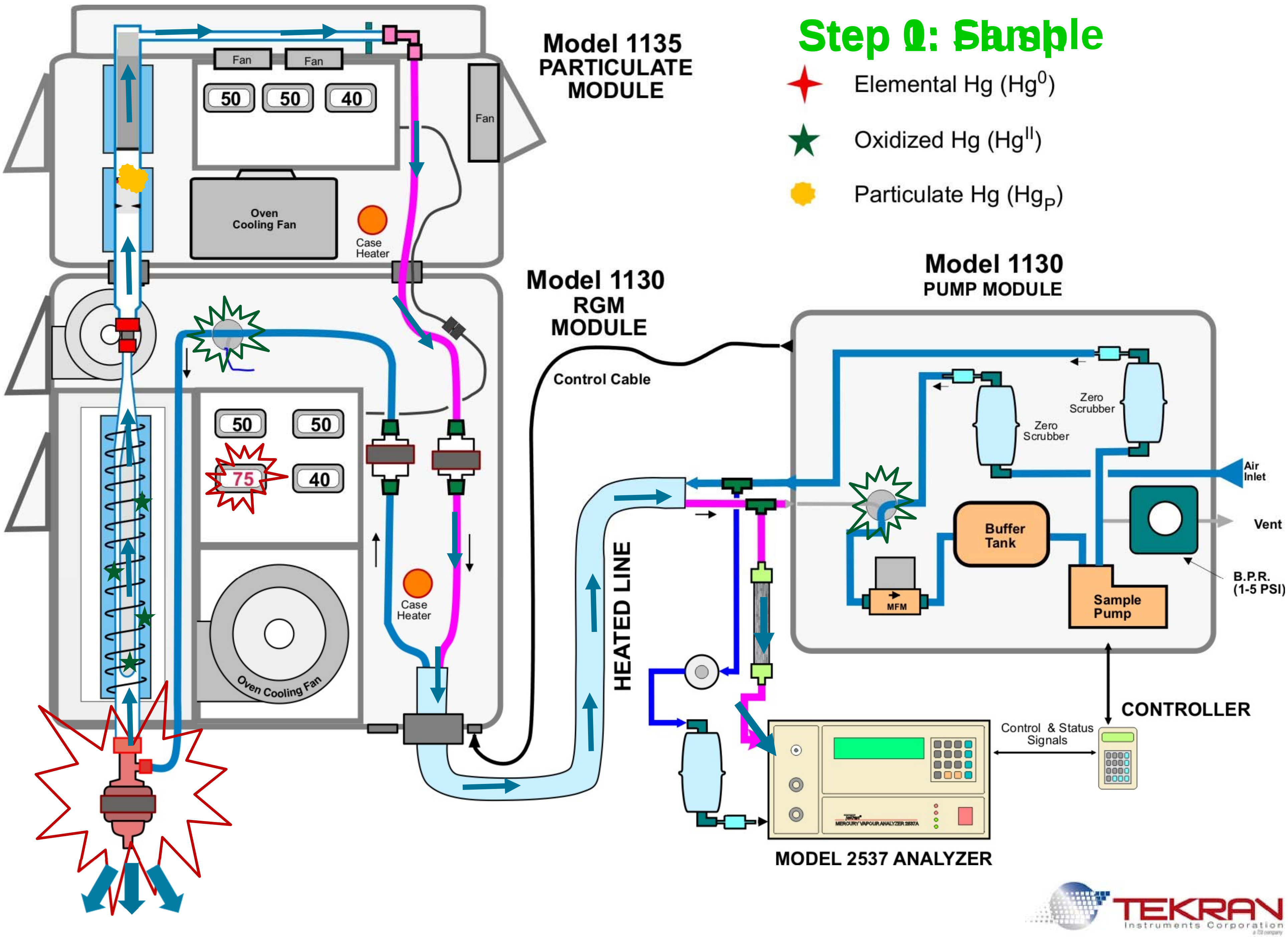
Lucas Hawkins

Rev: 1.0 January 2010

Step 0: Sample





Step 0: Sample
Elemental Hg (Hg^0)
Oxidized Hg (Hg^{II})
Particulate Hg (Hg_P)
Model 1135
PARTICULATE
MODULE
Fan
Fan
Fan
50
50
40
Oven
Cooling Fan
Case
Heater
Model 1130
RGM
MODULE
50
50
75
40
Case
Heater
Oven Cooling Fan
Control Cable
HEATED LINE
Model 1130
PUMP MODULE
Zero
Scrubber
Zero
Scrubber
Air
Inlet
Buffer
Tank
Vent
MFM
Sample
Pump
B.P.R.
(1-5 PSI)
CONTROLLER
Control & Status
Signals
MODEL 2537 ANALYZER
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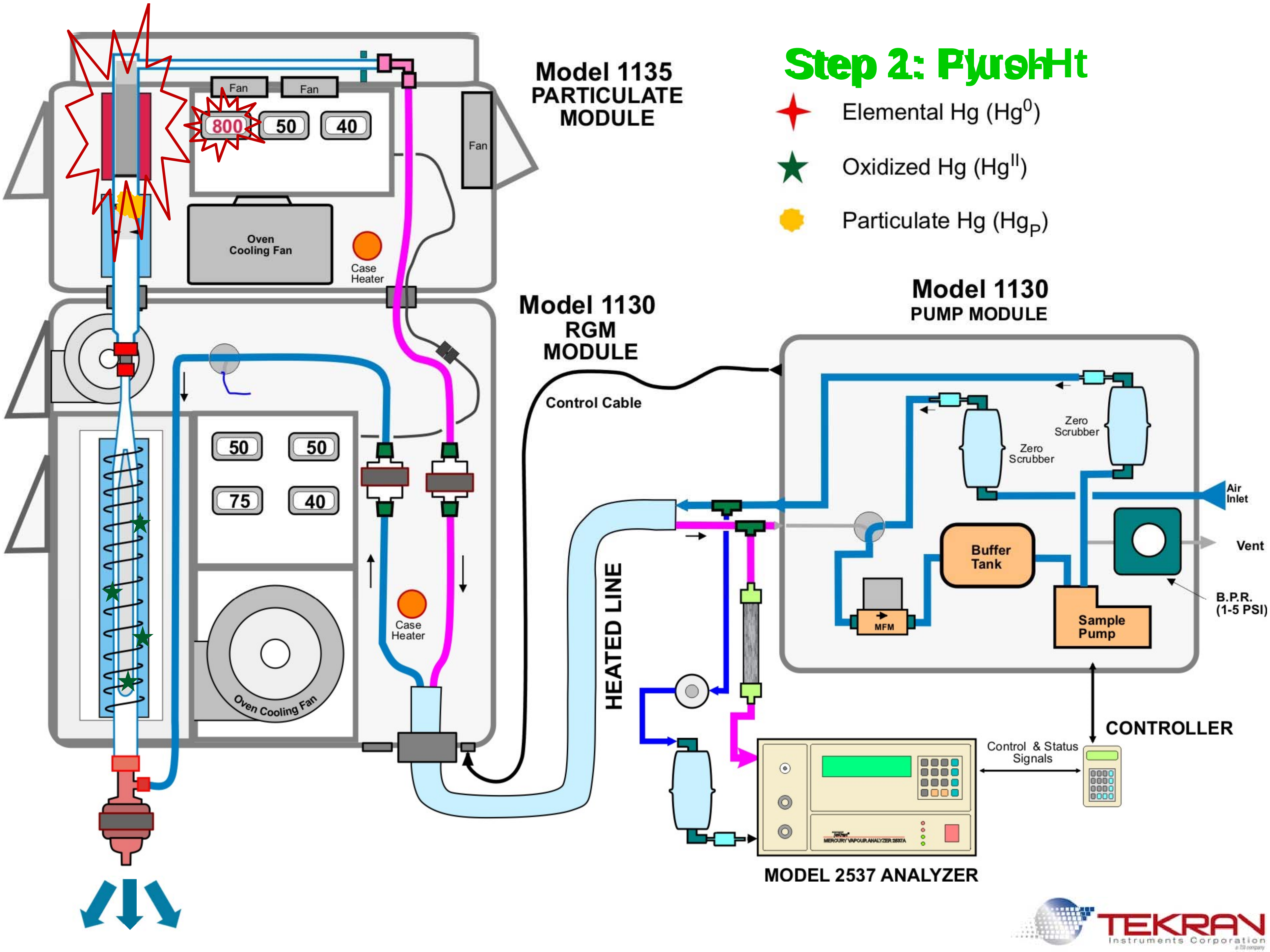

Step 2: PyrushHt
Elemental Hg (Hg^0)
Oxidized Hg (Hg^{II})
Particulate Hg (Hg_P)
Model 1135
PARTICULATE
MODULE
Fan
Fan
Fan
800
50
40
Oven
Cooling Fan
Case
Heater
Model 1130
RGM
MODULE
Control Cable
50
50
75
40
Case
Heater
Oven Cooling Fan
HEATED LINE
Model 1130
PUMP MODULE
Zero
Scrubber
Zero
Scrubber
Air
Inlet
Vent
Buffer
Tank
MFM
Sample
Pump
B.P.R.
(1-5 PSI)
CONTROLLER
Control & Status
Signals
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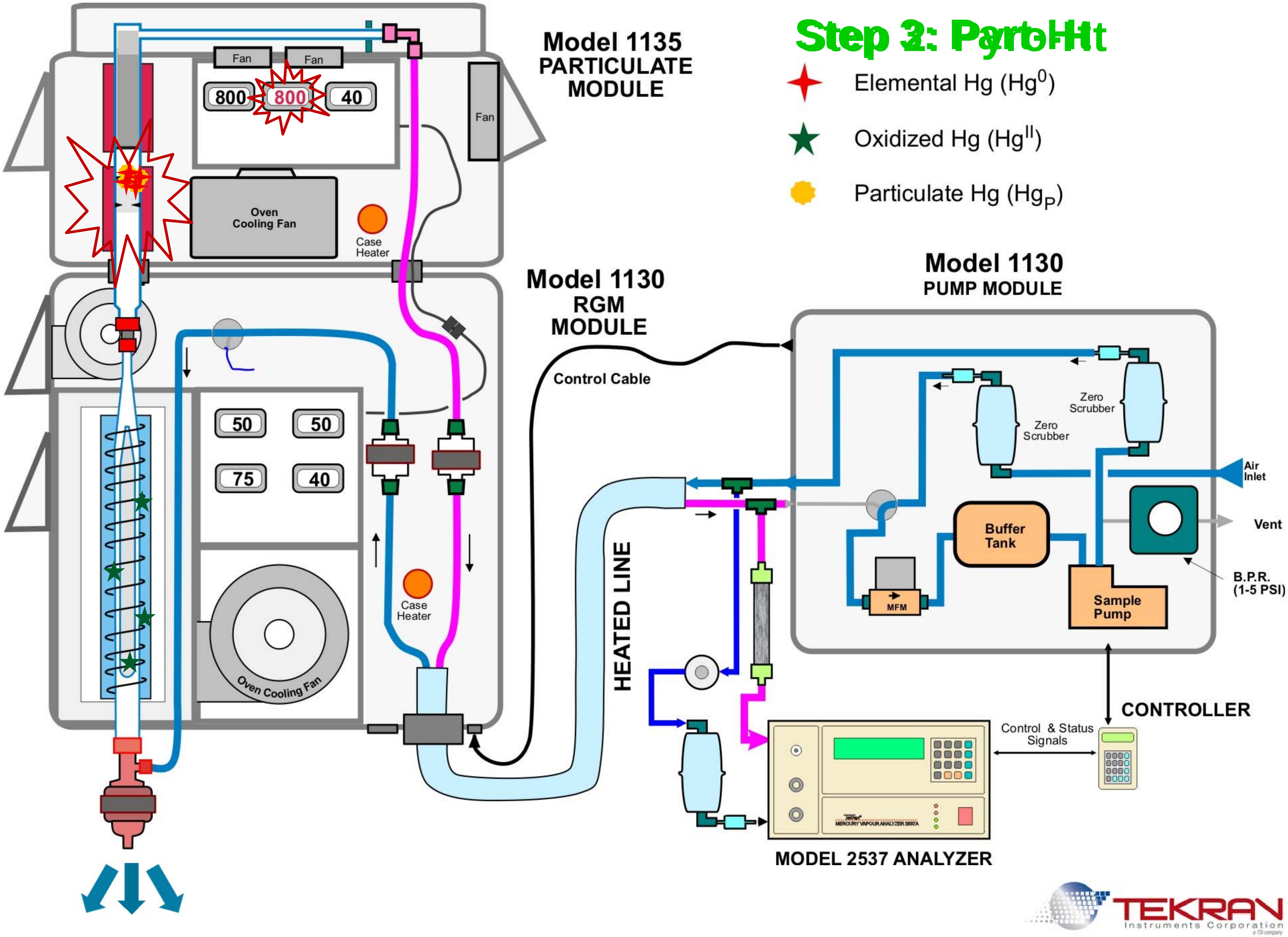
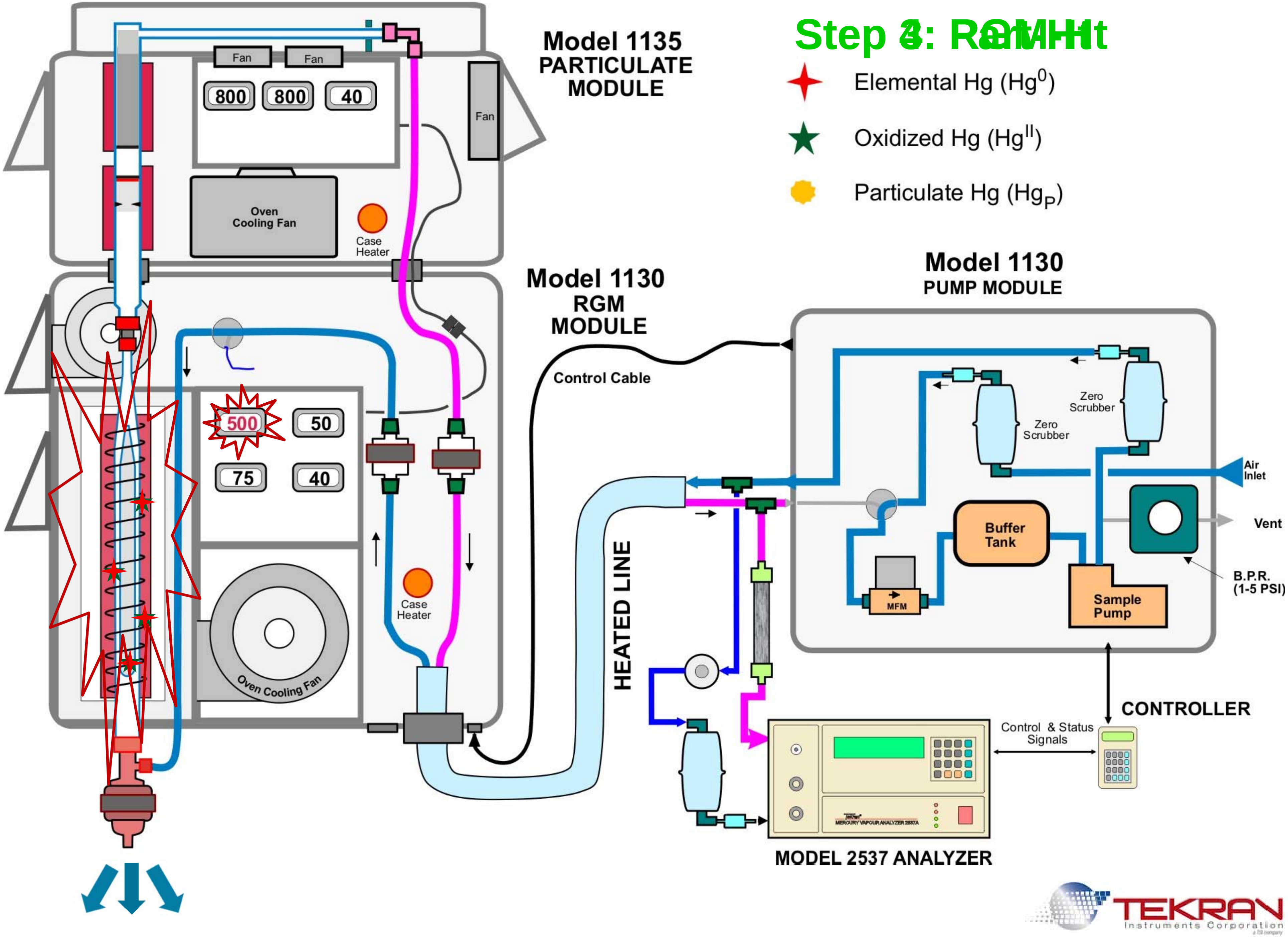
Step 2: Part-Ht / Step 3: Pyro-Ht



Step 3: RGM Ht



Elemental Hg (Hg^0)
Oxidized Hg (Hg^{II})
Particulate Hg (Hg_P)
Model 1135
PARTICULATE
MODULE
Fan
Fan
Fan
800
800
40
Oven
Cooling Fan
Case
Heater
Model 1130
RGM
MODULE
500
50
75
40
Case
Heater
Oven Cooling Fan
Control Cable
HEATED LINE
Model 1130
PUMP MODULE
Zero
Scrubber
Zero
Scrubber
Air
Inlet
Vent
Buffer
Tank
MFM
Sample
Pump
B.P.R.
(1-5 PSI)
CONTROLLER
Control & Status
Signals
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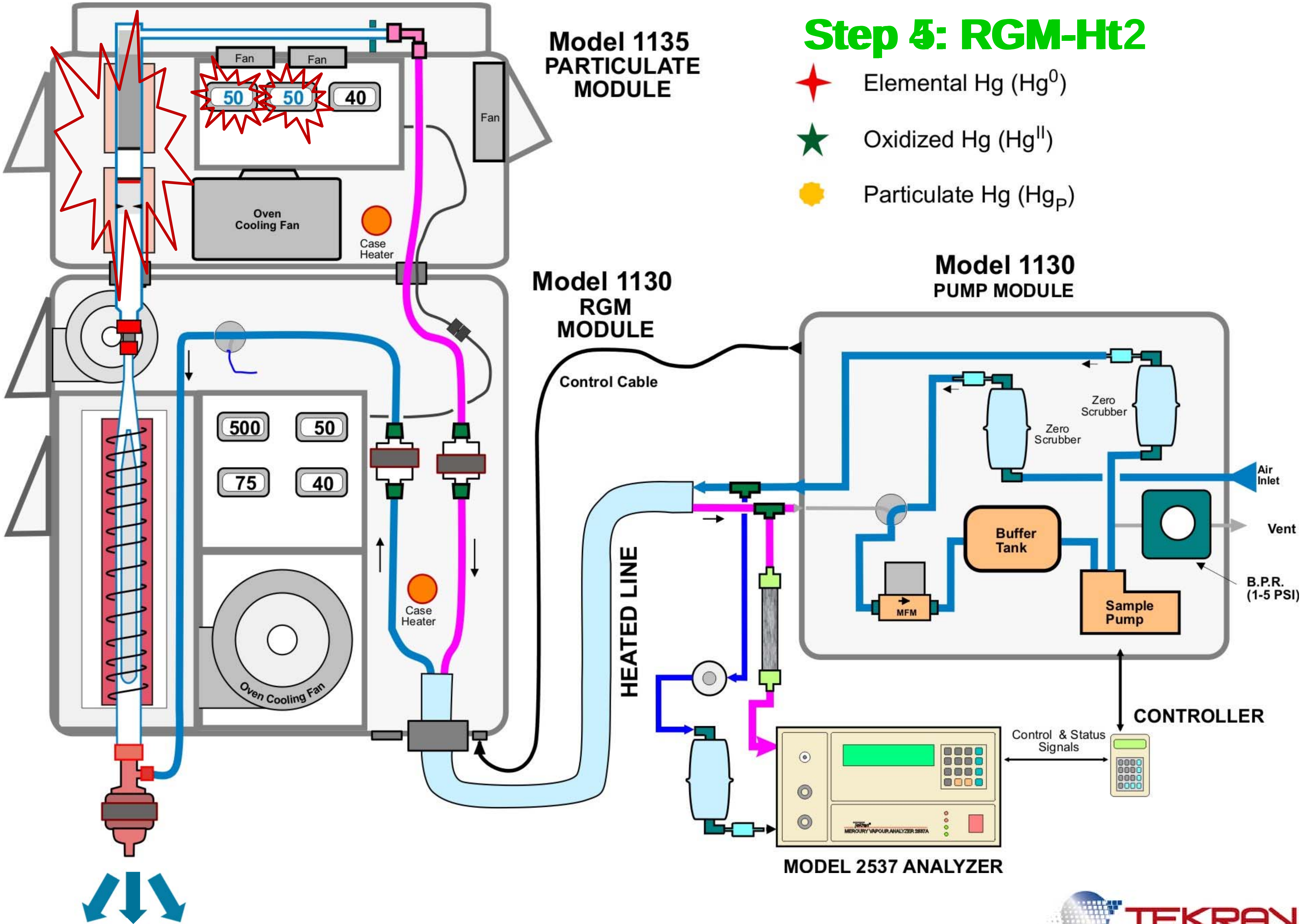
Step 5: RGM-Ht2



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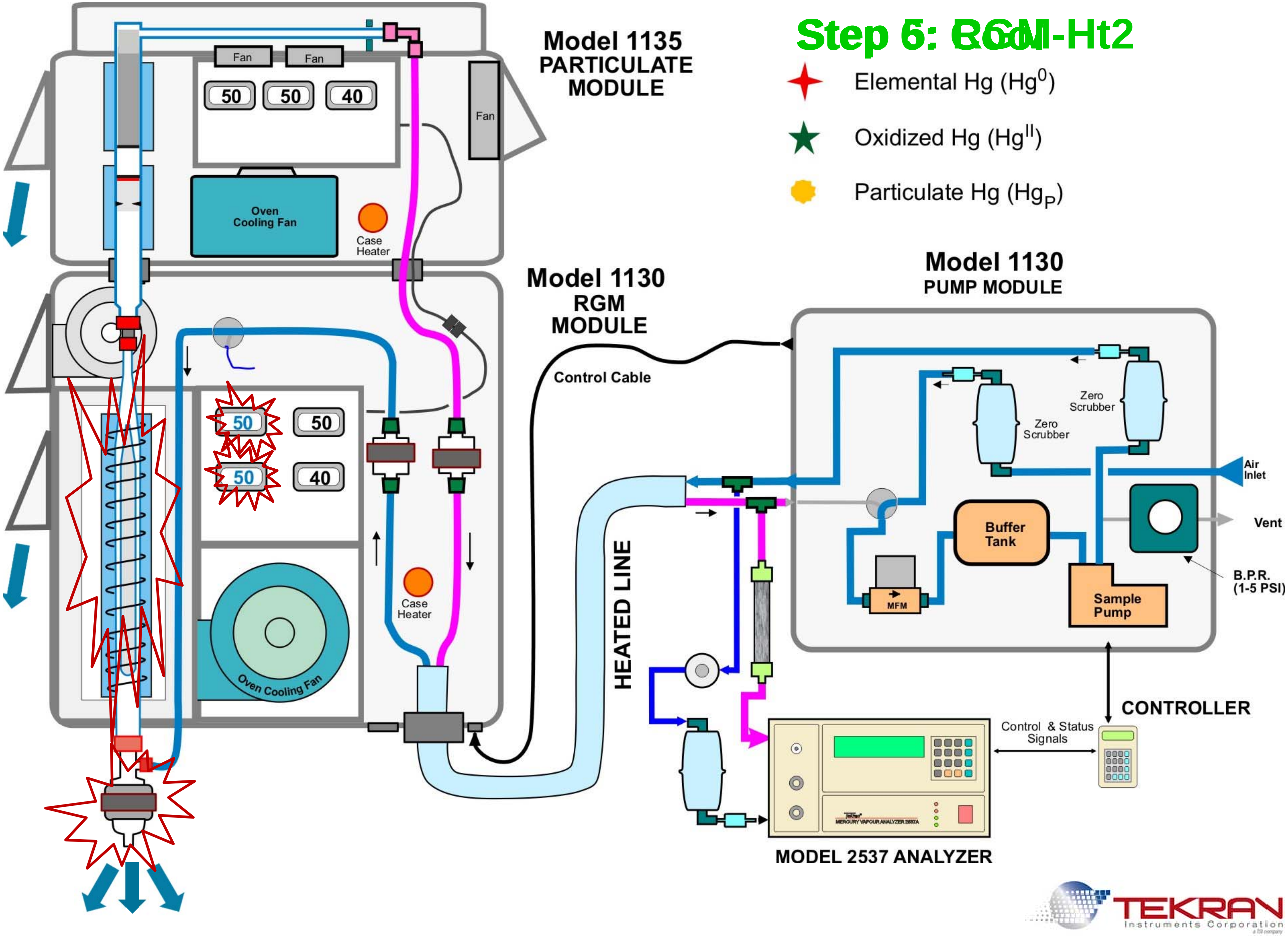
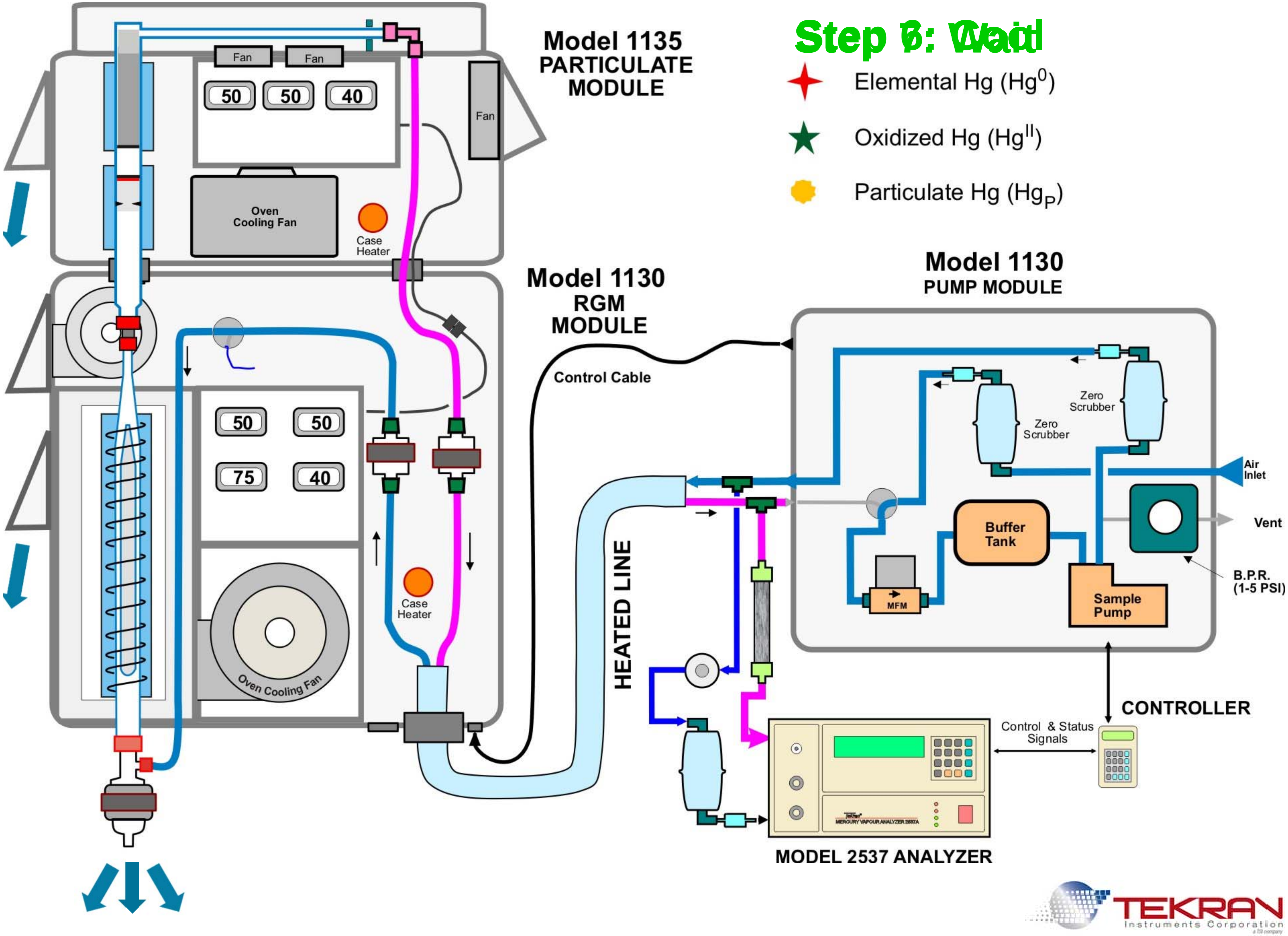
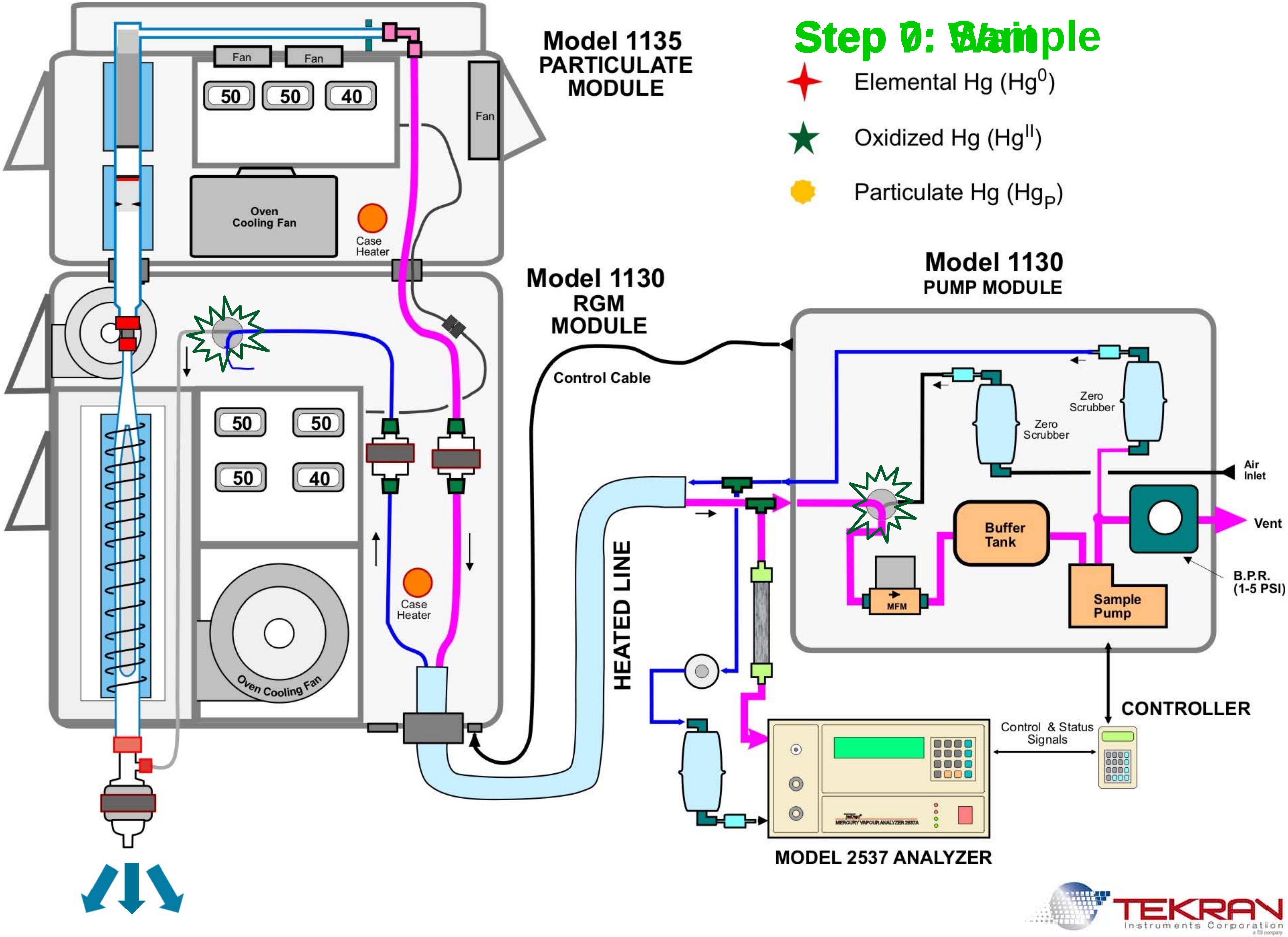
Step 6: RGM-Ht2



Step 6: Wait
Step 7: Cool




Step 0: Wait
Step 1: Sample
Elemental Hg (Hg^0)
Oxidized Hg (Hg^{II})
Particulate Hg (Hg_P)
Model 1135
PARTICULATE
MODULE
Fan
Fan
Fan
50
50
40
Oven
Cooling Fan
Case
Heater
Model 1130
RGM
MODULE
50
50
50
40
Case
Heater
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Control Cable
HEATED LINE
Model 1130
PUMP MODULE
Zero
Scrubber
Zero
Scrubber
Air
Inlet
Buffer
Tank
Vent
MFM
Sample
Pump
B.P.R.
(1-5 PSI)
CONTROLLER
Control & Status
Signals
MODEL 2537 ANALYZER
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Atmospheric Mercury Speciation Field Sites

Cape Hedo, Okinawa
U. of Washington & NIES

Waldof, Germany
UBA & GKSS

New York, USA
Clarkson U. & NYDEC

South Africa

Barrow, Alaska, Env. Canada

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Observations and Discoveries as a result of Mercury Speciation Measurements

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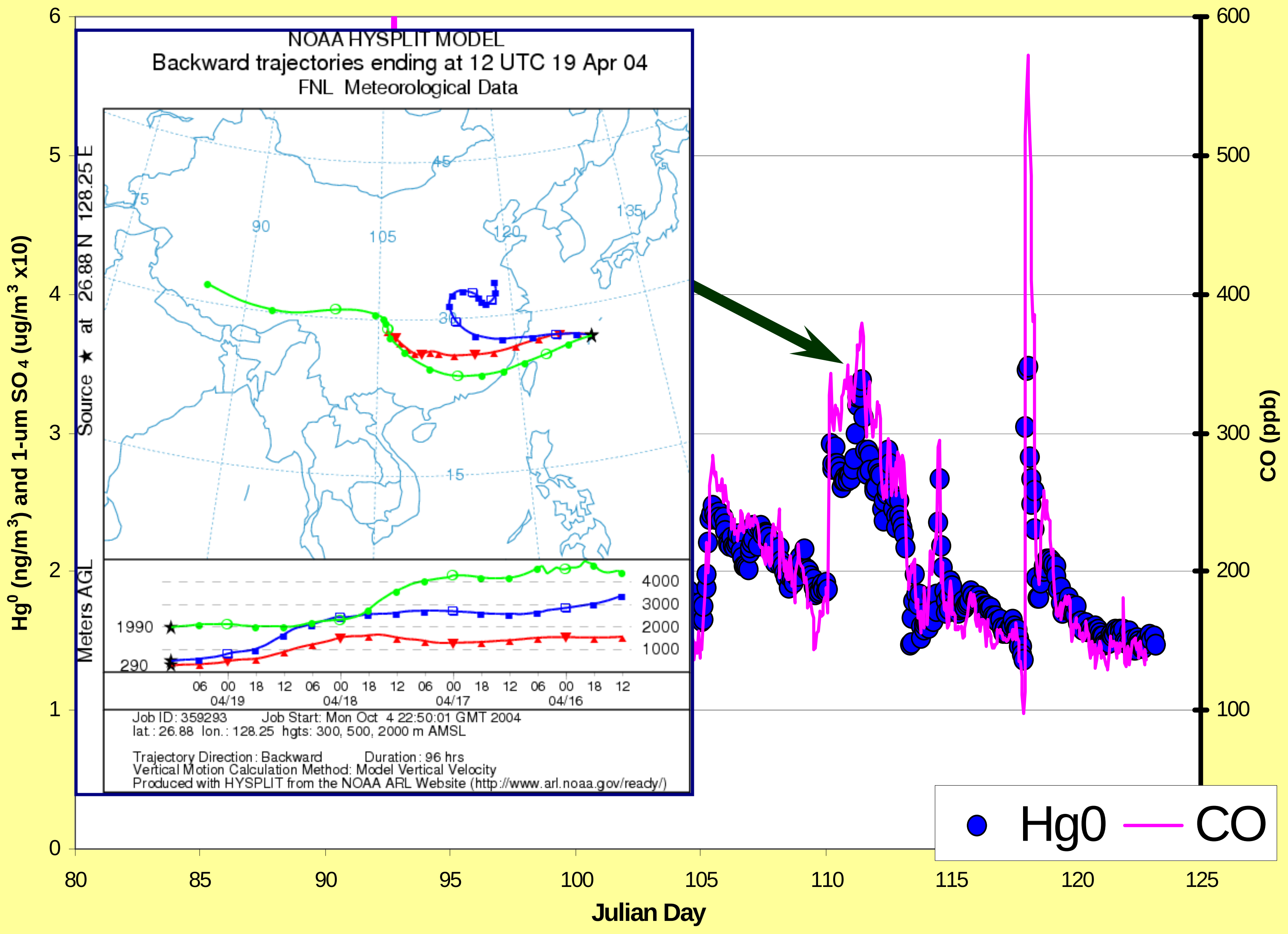
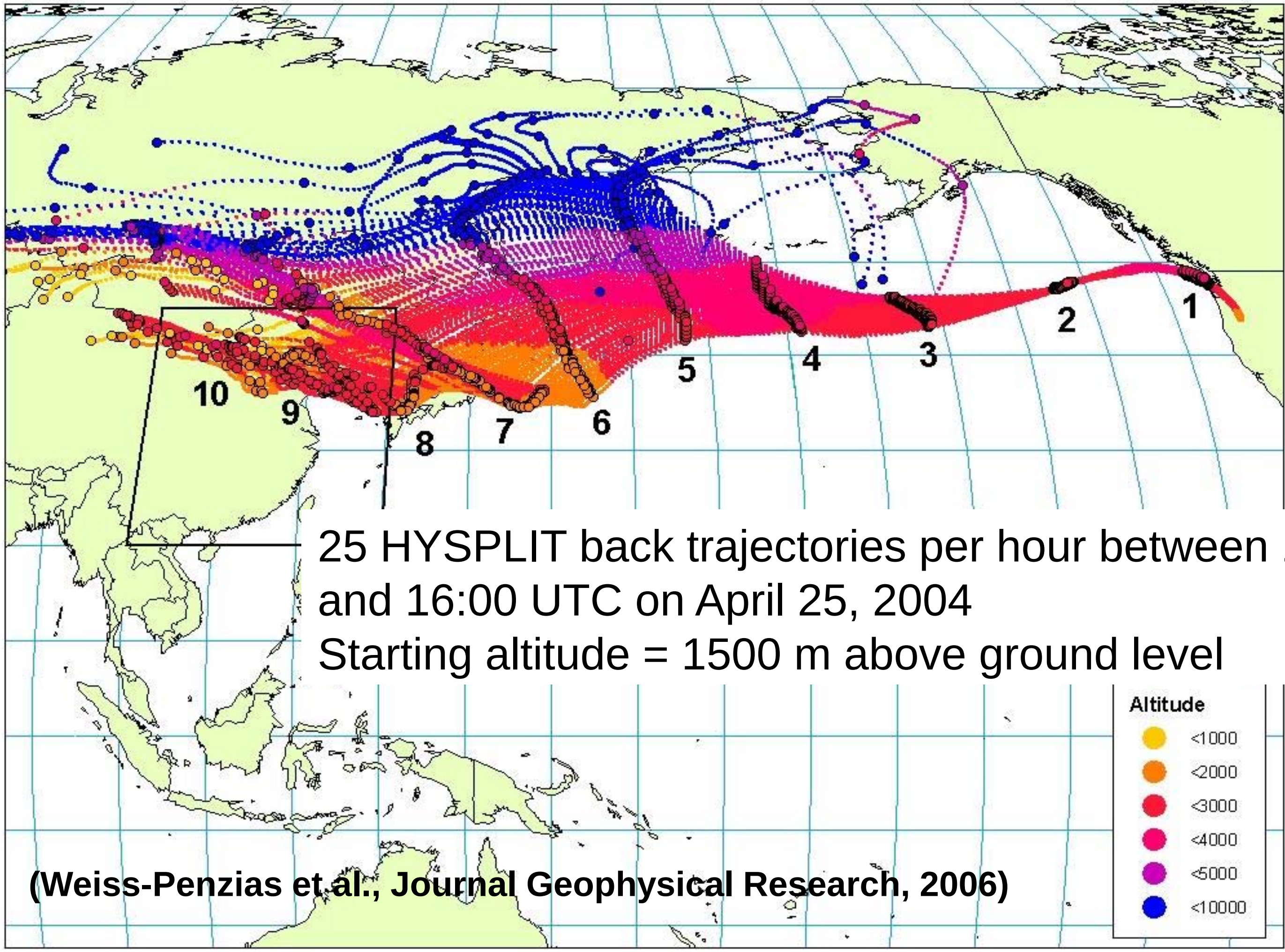
Eleven distinct anthropogenic plumes were observed at Cape HEDO in the spring of 2004



Asian Long-Range Transport (ALRT) of Mercury Plumes to Mt. Bachelor, USA

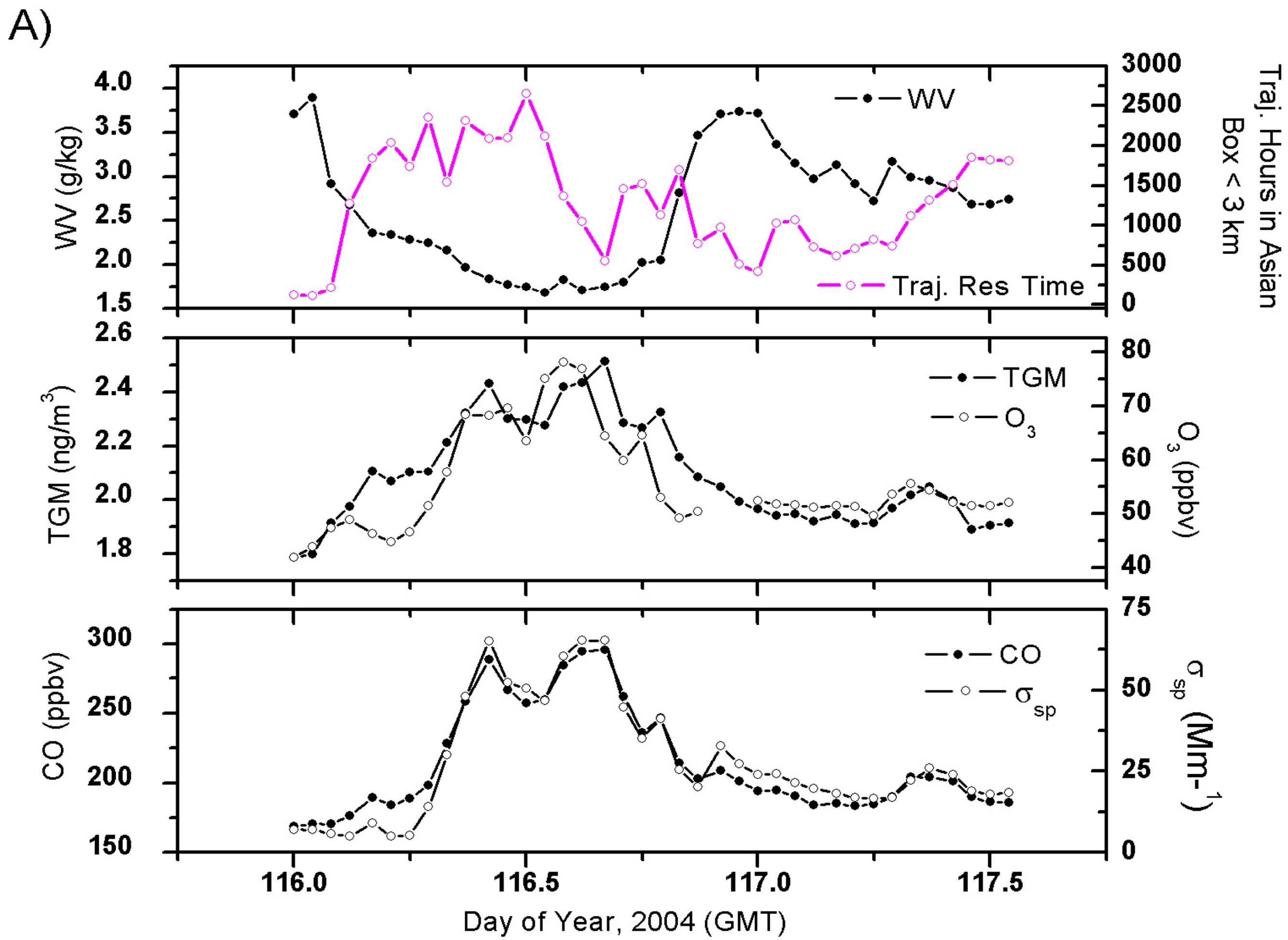


25 HYSPLIT back trajectories per hour between 10:00 and 16:00 UTC on April 25, 2004
Starting altitude = 1500 m above ground level

(Weiss-Penzias et al., Journal Geophysical Research, 2006)

April 25, 2004 ALRT pollution event

Trajectory residence time is total # of trajectory hours in Asian box below 3 km from starting points at MBO of 1500, 1600, 1700, 1800, and 1900 m agl.

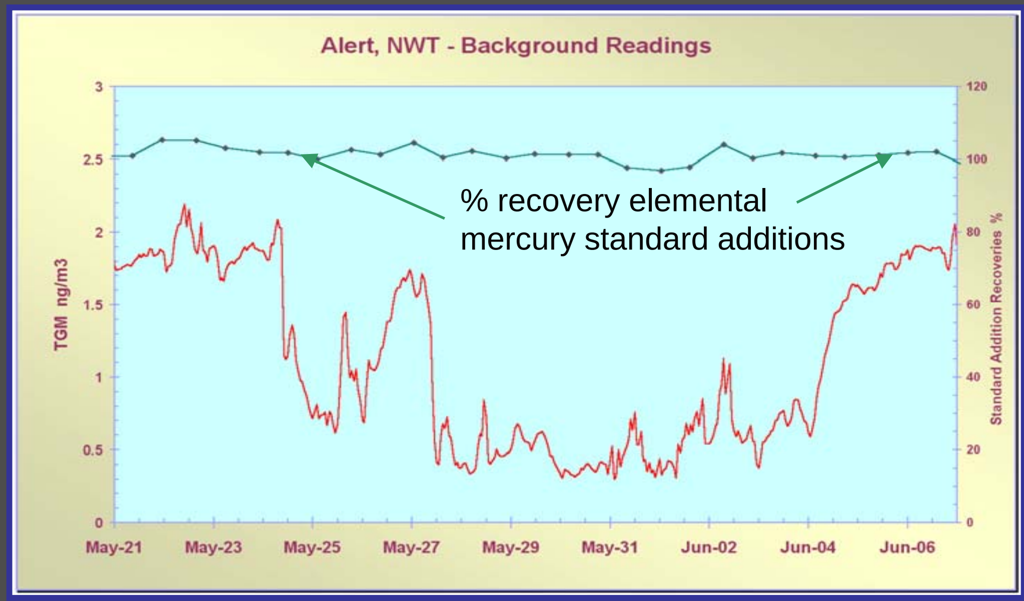


(Weiss-Penzias et al., Journal Geophysical Research, 2006)

Depletions of Elemental Mercury in Alert, Nunavut (Canada)

- Mercury Depletion Events (MDE) discovered in Alert, Canada in early 1990's

- Confirmation studies used Tekran automated equipment



- MDE observed in ***all*** polar regions

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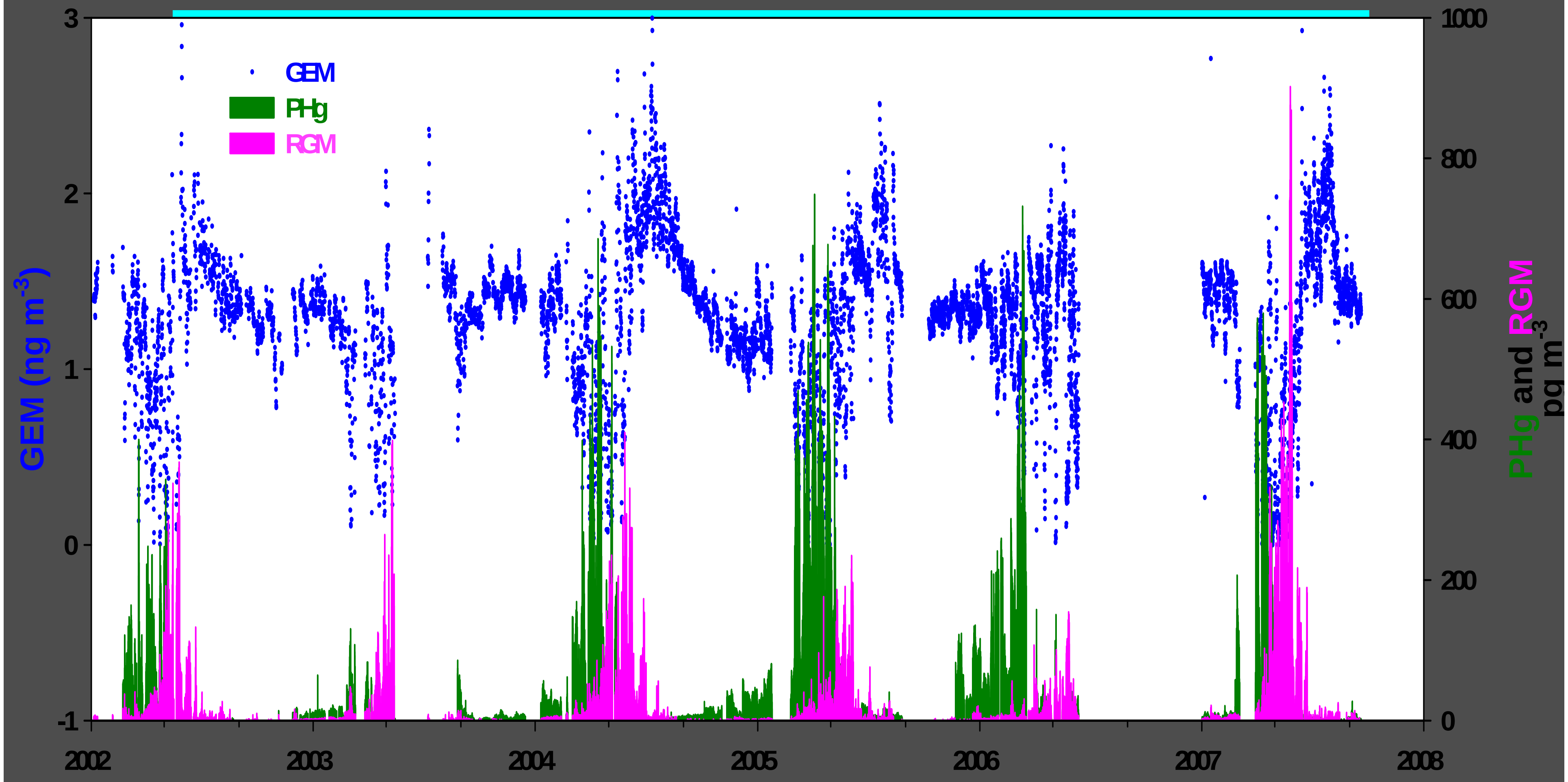
Atmospheric speciation measurements at Alert, Nunavut

Courtesy of Sandy Steffen, Env. Canada



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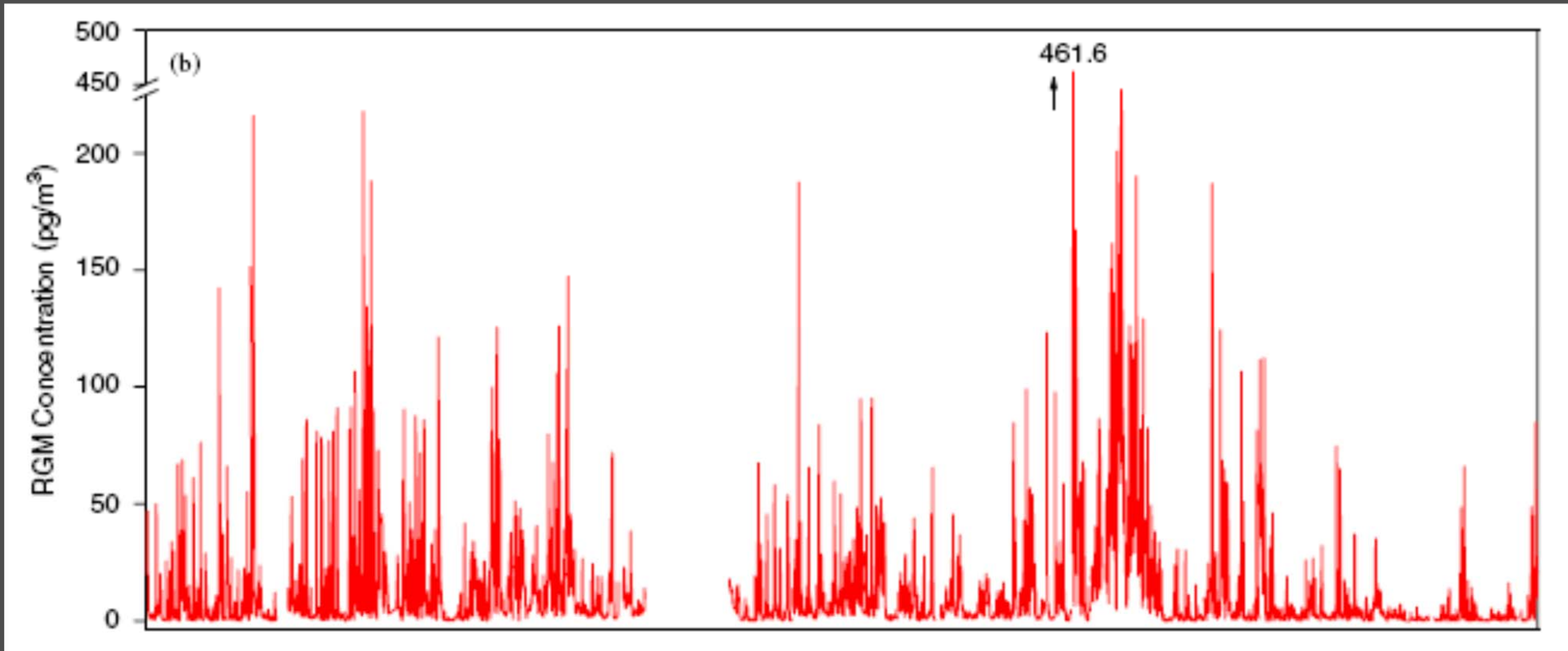
High GOM events due to emissions sources in Ohio (Yatavelli et al., 2006 Atm. Env).



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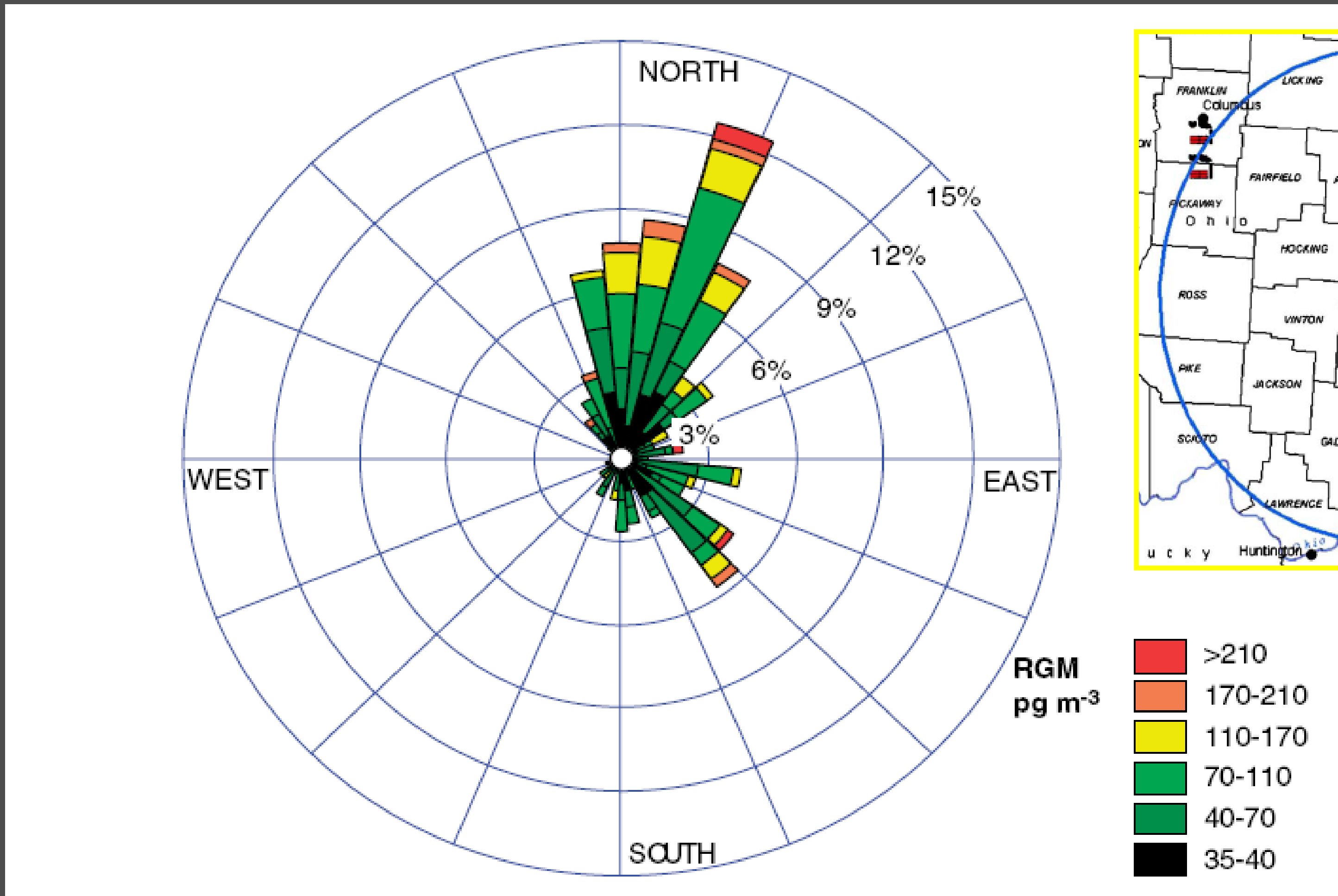
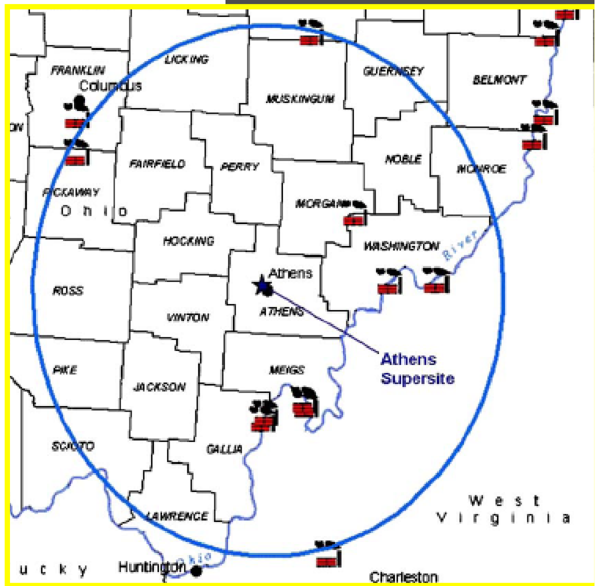
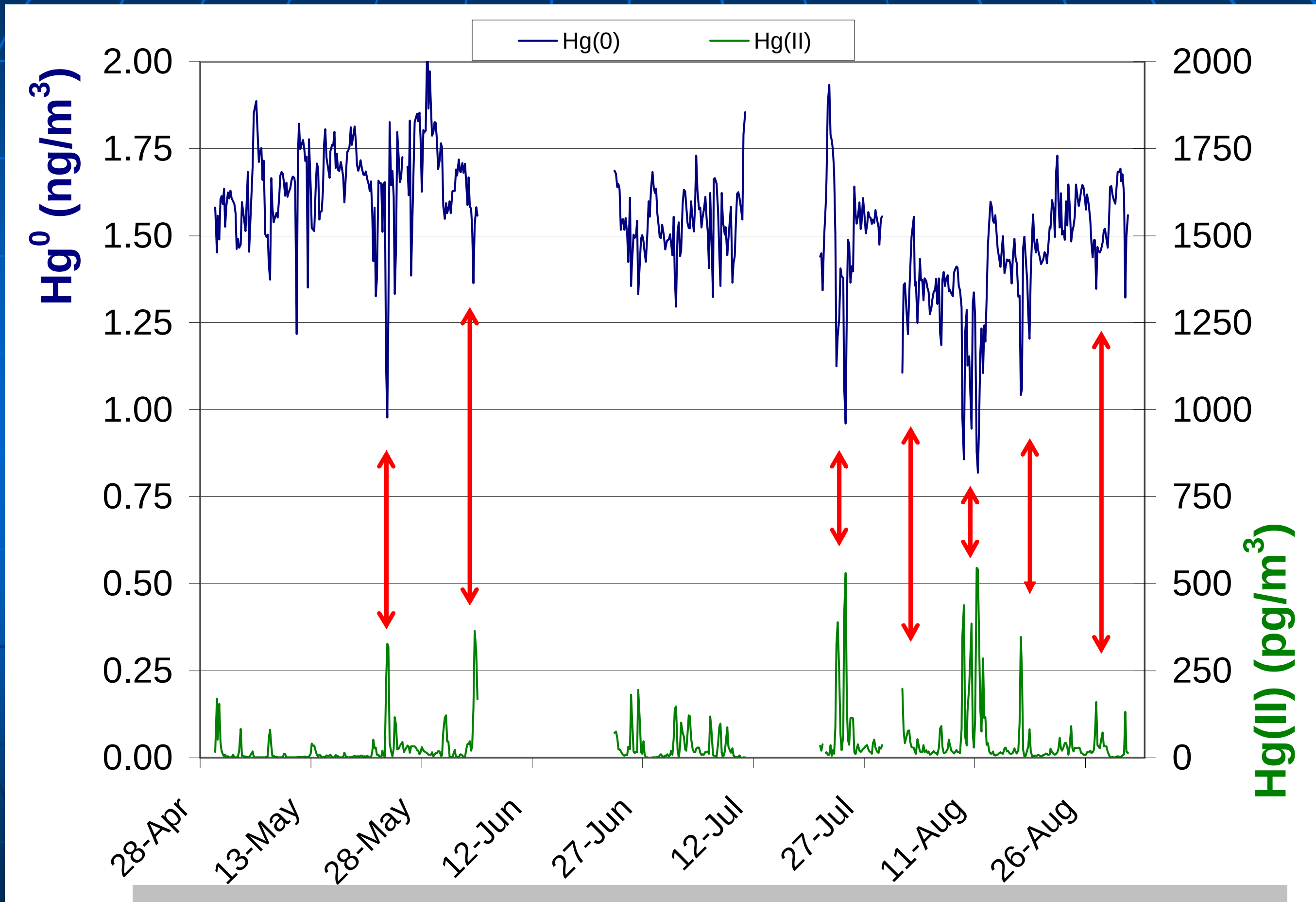
High GOM events from emission sources in Ohio (Yatavelli et al., 2006 Atm. Env.)





Observation and discovery of high GOM in the free-troposphere

May-Aug 2005: Hg^0 and Hg(II)



Mt. Bachelor Data – Swartzendruber et al., 2006 *JGR*,

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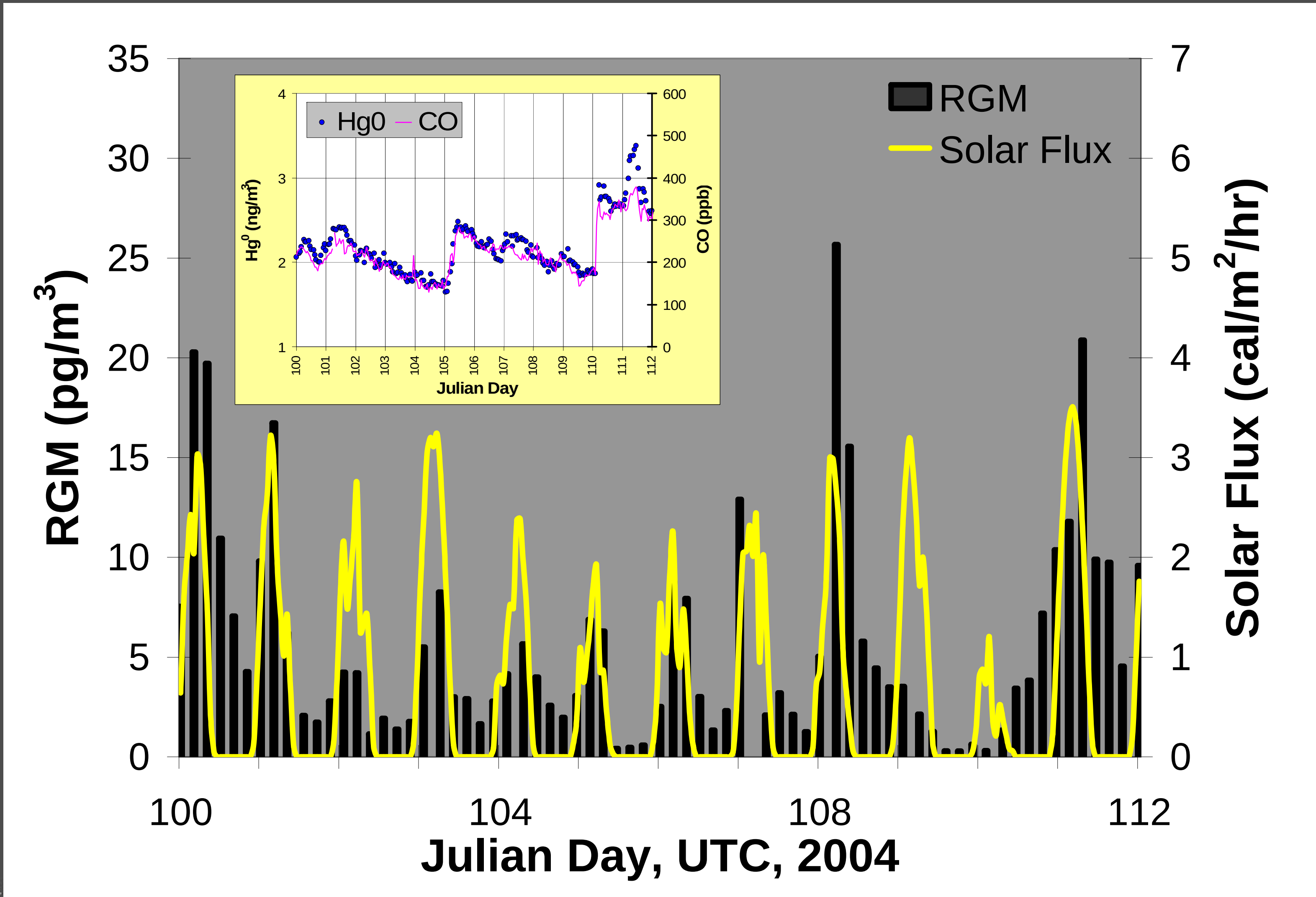
GOM Production in the Marine Boundary Layer



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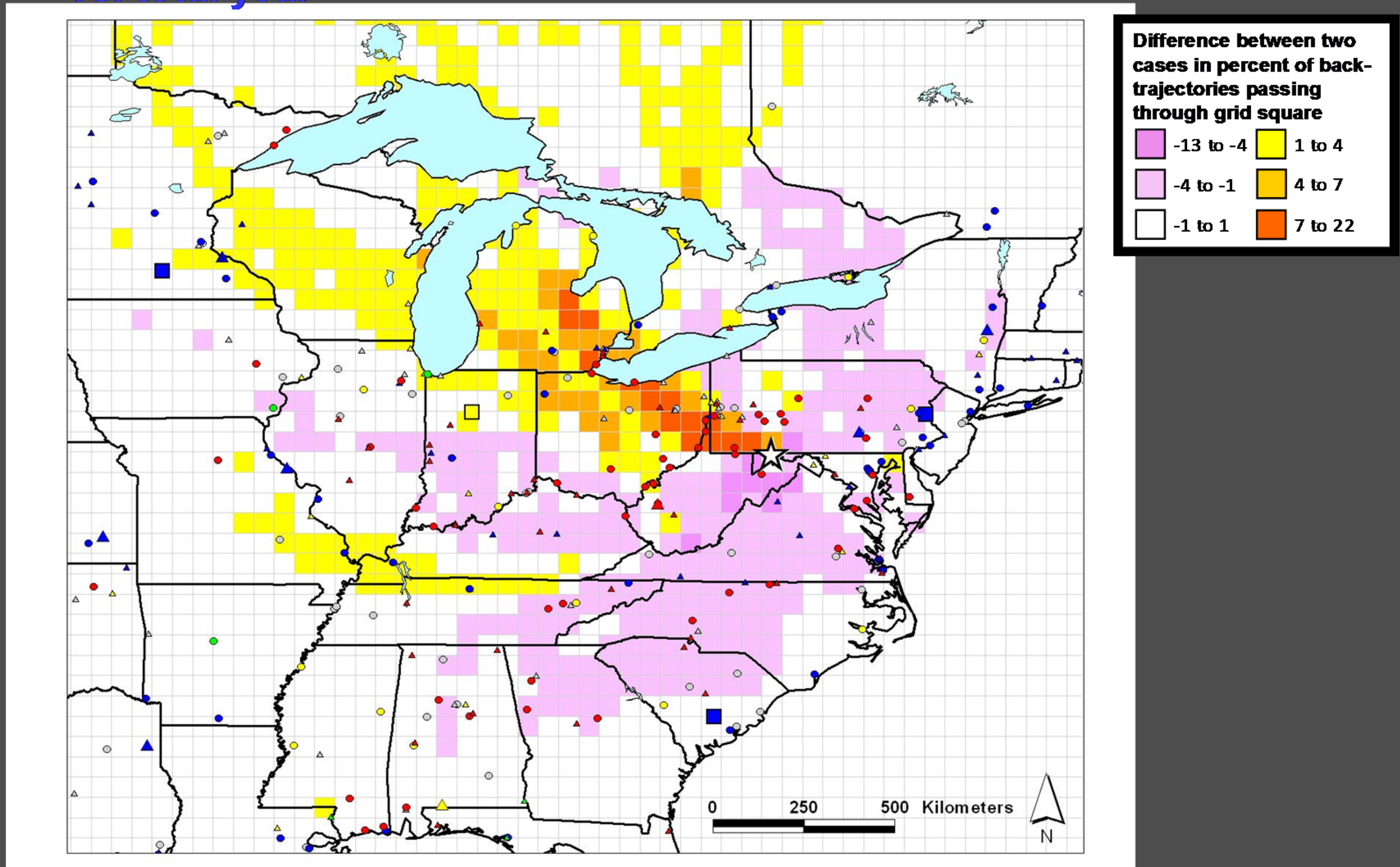
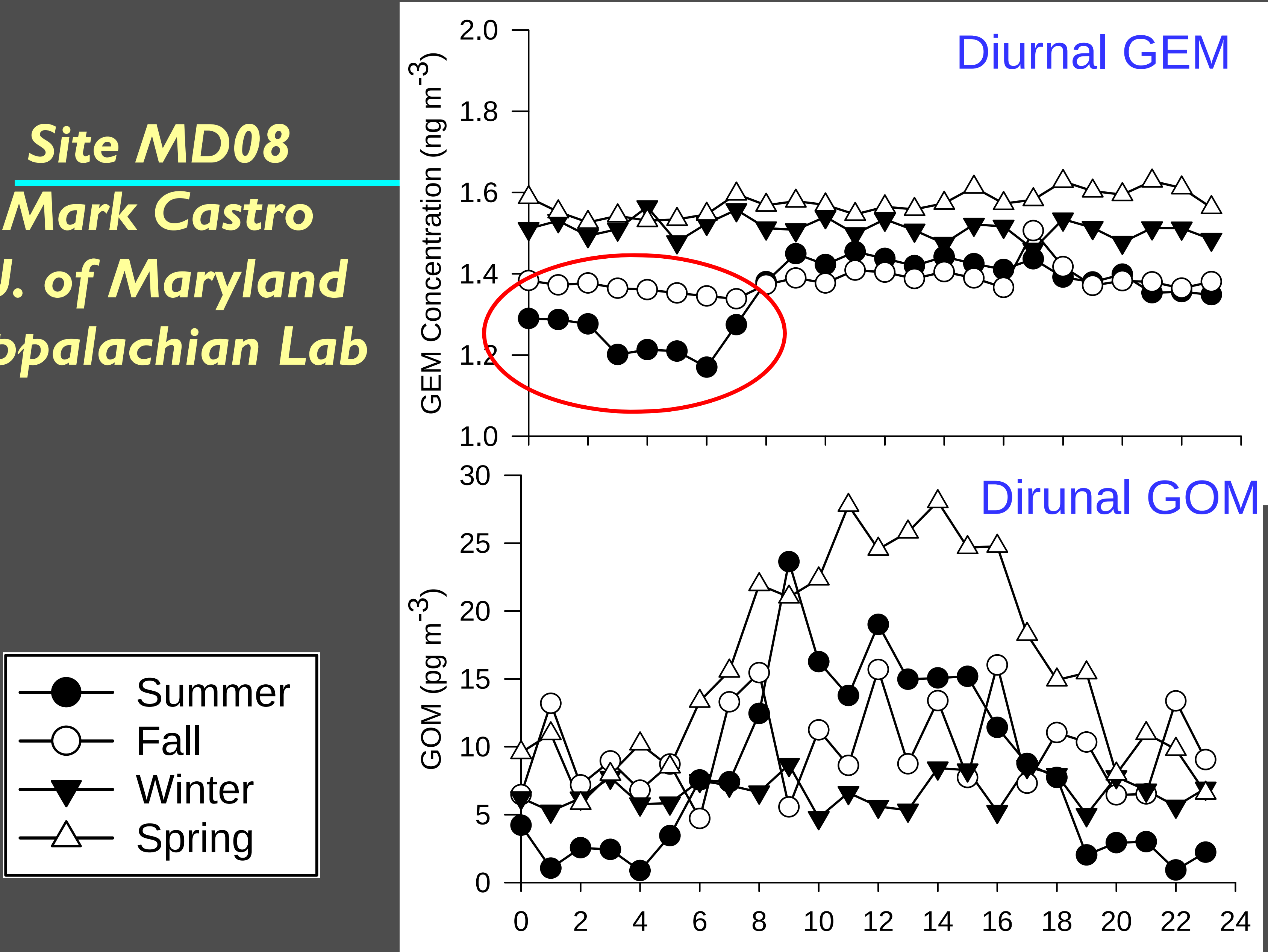
Mark Castro - U. of Maryland
Mark Cohen – NOAA-ARL

Hourly trajectory endpoint frequencies for top 10% of $PBM_{2.5}$ vs. total year



Site MD08

Mark Castro
U. of Maryland
Appalachian Lab



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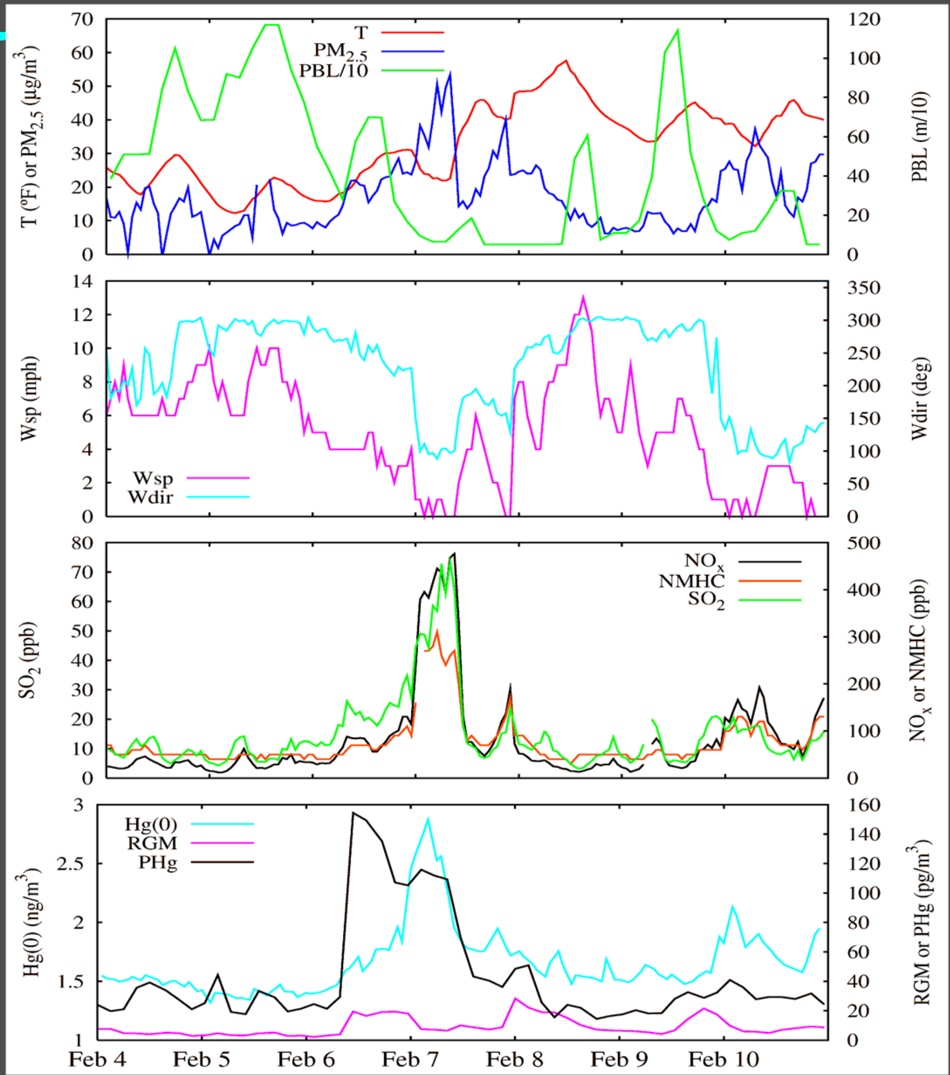
Felton and Civerolo, NYDEC

- Stagnation event in New York City

Wind Speed, Direction

SO2, NOx, NMHC

Mercury Species



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Conclusions

- Networks and research scientists have determined that automated gold-trap pre-concentration and atomic fluorescence spectroscopy (AFS) detection is the preferred method for air mercury monitoring
- Automated atmospheric speciation is possible using the Tekran 2537-1130-1135 system
- Critical new discoveries have been made because of the capability to measure air mercury speciation
  - GOM emissions impact deposition locally
  - GOM is emitted from sources AND made in-situ
  - Monitoring at high resolution with high sensitivity provides needed tool for better understanding mercury

The New Tekran 2537X

Highlights

- 100% backwards compatibility with prior 2537 units and 1130/1135 systems
- Network enabled – No PC needed
- High resolution touch screen interface
- Local data storage and front panel USB port retrieval and update
- Improved accessibility of routine maintenance components

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2537X Data Input / Output

Data Handling & Communication

- On-board storage of sample data with front panel USB retrieval (no PC needed)
- Connectable via serial port, network port, or USB port
- Data logging of multiple instrument parameters
- Built-in data review screens
- Remote instrument login and control
- Digital controls of all devices (PMT, Perm Source, Lamp, etc.)
- RS-485 allows communication with external devices

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2537X Hardware Improvements

What's New Inside the 2537X

- Faster cool down time with independent high-velocity channeled fans
- Main serviceable components located on top deck for ease of access
- New lamp stabilizer and detector electronics
- Lower dead volume permeation chamber
- New valves with reduced dead-volume and better performance
- Reduced height from 5U (8.75") to 4U (7")

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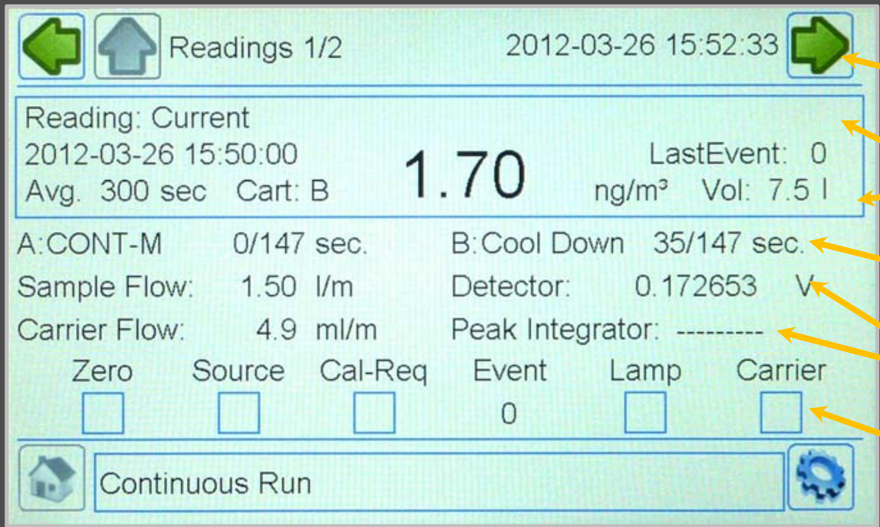
More Hardware Improvements!

What's New Inside the 2537X

- Constant power heater control delivers consistent heating of gold cartridges
- Direct access to cuvette without opening detector block
- Improved gold cartridge mounts for ease of maintenance
- Integrated injection port with flared needle entry point
- Sample Pump located on top panel for easy access
- Protected power switch eliminates accidental instrument power interruption

2537 Information Screens



Home Screen

Page Navigation Button

Last Analysis Summary

Current Analytical Step (Both Cartridges)

Instrumental Parameters

Status Indicators

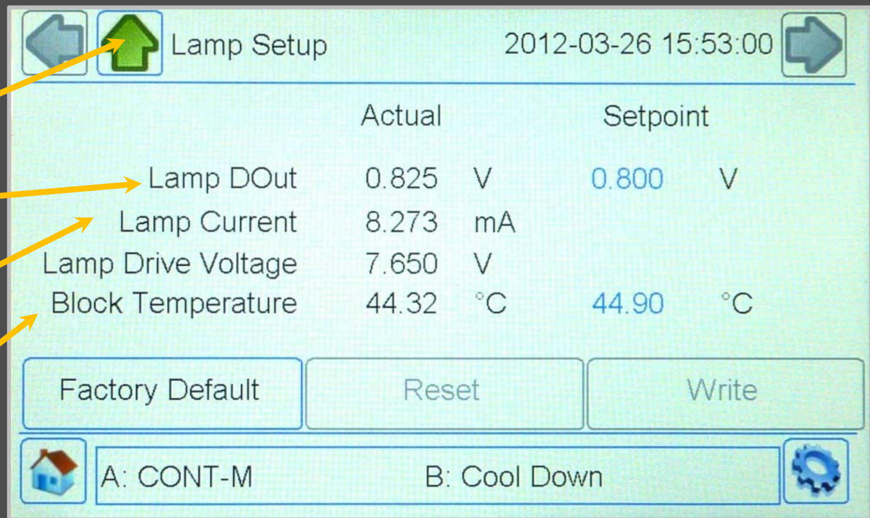
Lamp Adjustment Screen

Page Navigation Buttons

Lamp Emission Setpoint

Current Lamp Driver Values

Lamp Temperature Setpoint



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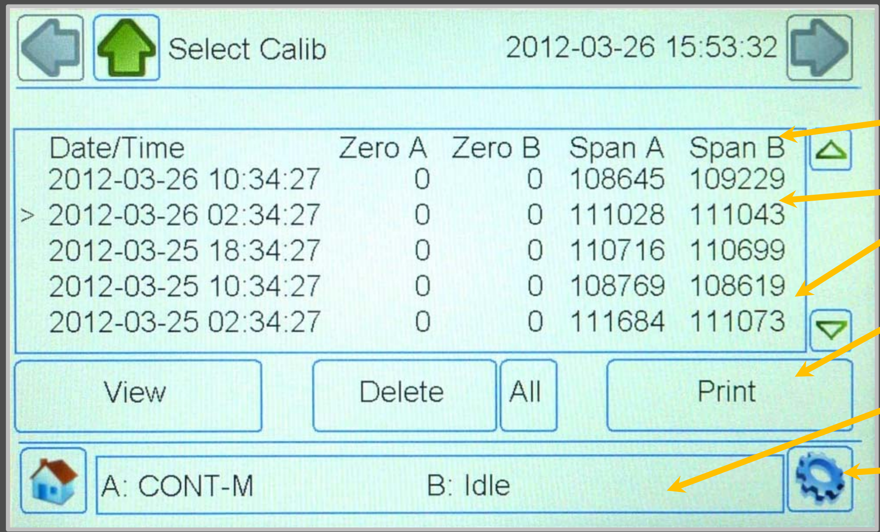
2537 Information Screens



Calibration Review Screen

Calibration Summary Table

Viewable Calibration Files

Calibration Data Control Buttons

Current Run Status

Setup Screen

USB Drive Screen

Data Dump Button

Instrument Plugin Installation Button

Update 2537X Firmware

Download Current Settings (for Backup)

Home Screen