Environmental Mercury Measurement: Fundamentals, History, Experience and Current Status in the USA for Research and Monitoring of Air, Emissions and Field Samples

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Symposium on Mercury Pollution Prevention and the International Mercury Convention
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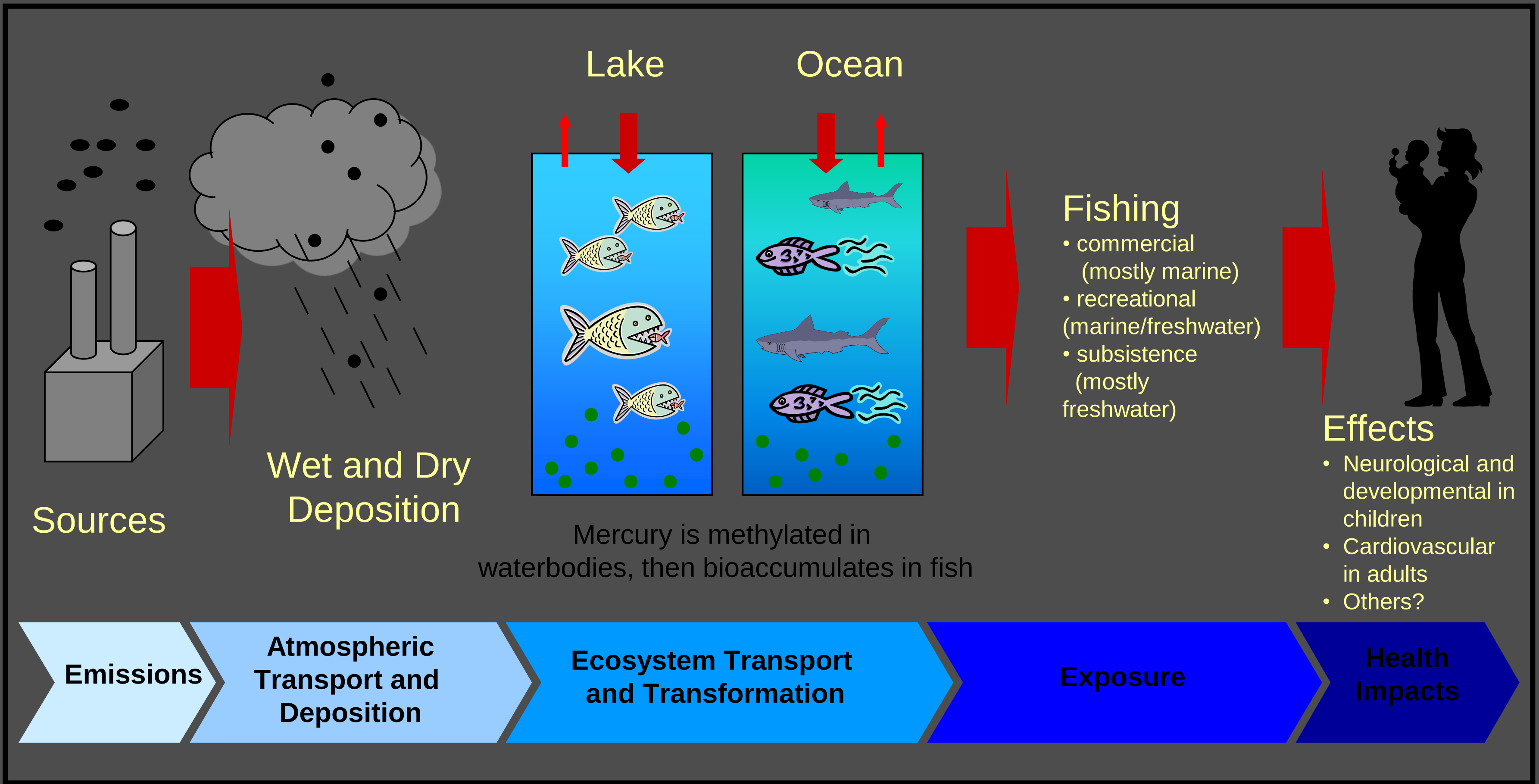
How will the Minimata Convention monitor changes in the mercury biogeochemical cycle?

Part pert trillion concentrations – importance of speciation – matrix challenges – Good data needed for fate and effects models



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Why did Mercury Measurement and Equipment Improve from 1990 to 2010?

1. Many large government funded research studies in Europe, Canada and the USA
2. Mercury Regulation Development and Implementation

- Will the Minimata Convention drive similar investments and improvements in mercury research and monitoring capabilities?

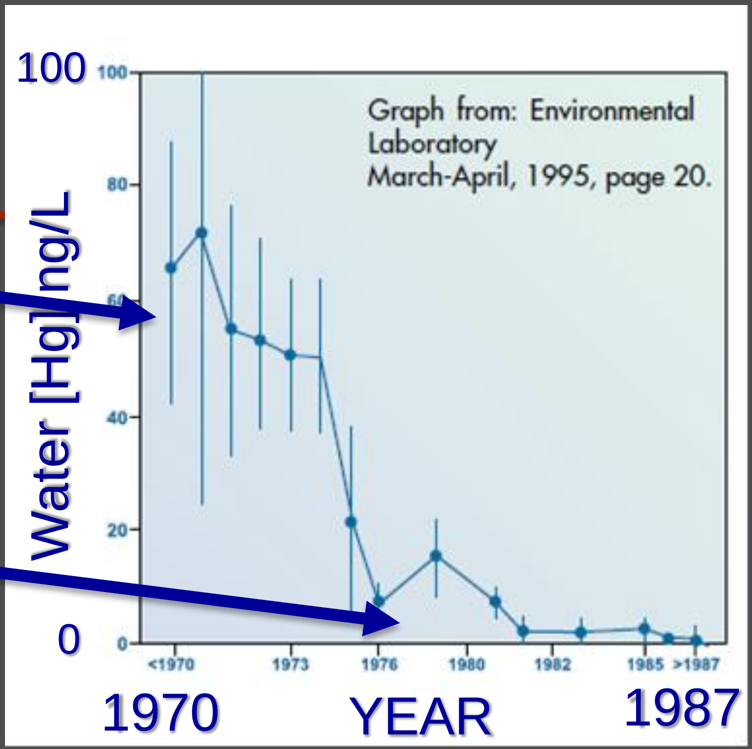
Four Key Developments for Environmental Mercury Measurement in last 25 Years

1. Adoption of trace-metal clean techniques
2. Application of cold-vapor atomic fluorescence spectrometry (CVAFS) for ultra-trace level measurements
3. Methods were developed for mercury speciation in water, air and flue gas emissions
4. Use of automated, continuous speciation analysis systems providing high resolution characterization of mercury in air and flue gas emissions

Development #1 – Trace Metal Clean Techniques for Mercury

Before 1980 - Inaccurate results due to contamination

After 1980 – Accurate results by using trace-clean sampling, handling and measurements techniques (EPA Method 1669)



Very important to discuss and adopt clean-technique standards within the Minimata mercury monitoring process!

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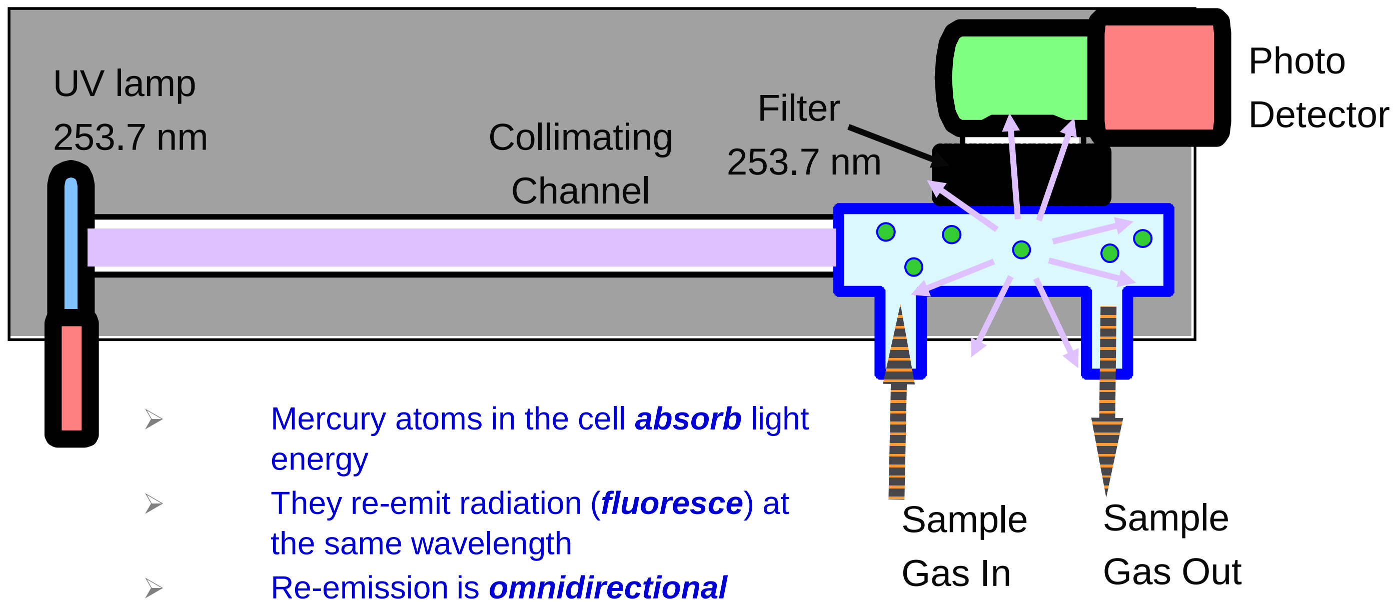
Development #2: Cold Vapor Atomic Fluorescence (CVAF)

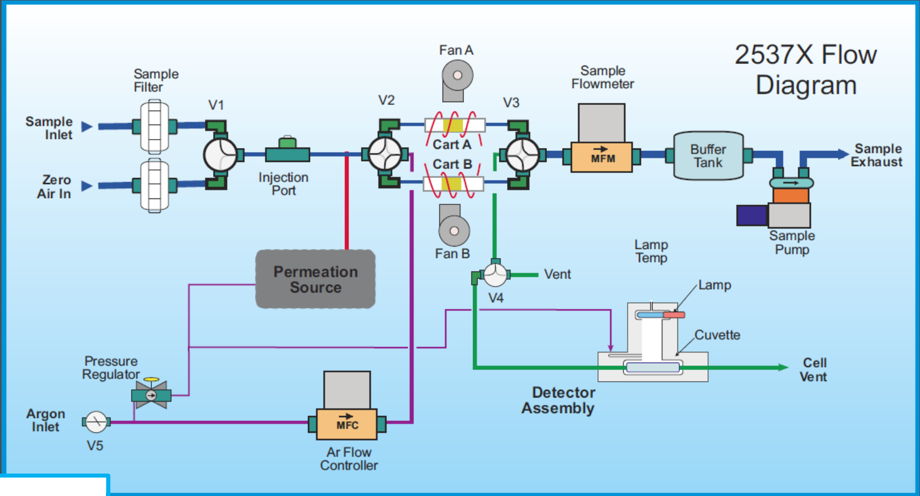
Bloom and Fitzgerald (1988) showed the value of the combination of clean techniques with sensitive and reliable Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS)

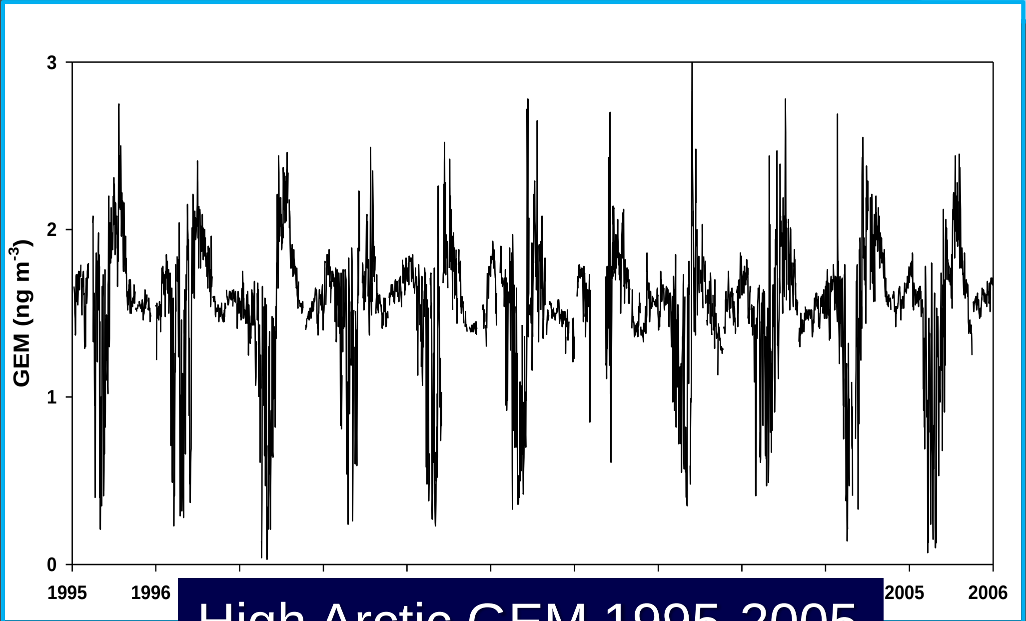


- Mercury atoms in the cell ***absorb*** light energy
- They re-emit radiation (***fluoresce***) at the same wavelength
- Re-emission is ***omnidirectional***
- Photo detector measures ***increase*** in intensity against a dark background

Development #2:
Cold Vapor Atomic Fluorescence (CVAF)

- Ambient Air Gaseous Hg
- Automated and Continuous
- High time resolution
- Typical use in AQM Stations





High Arctic GEM 1995-2005

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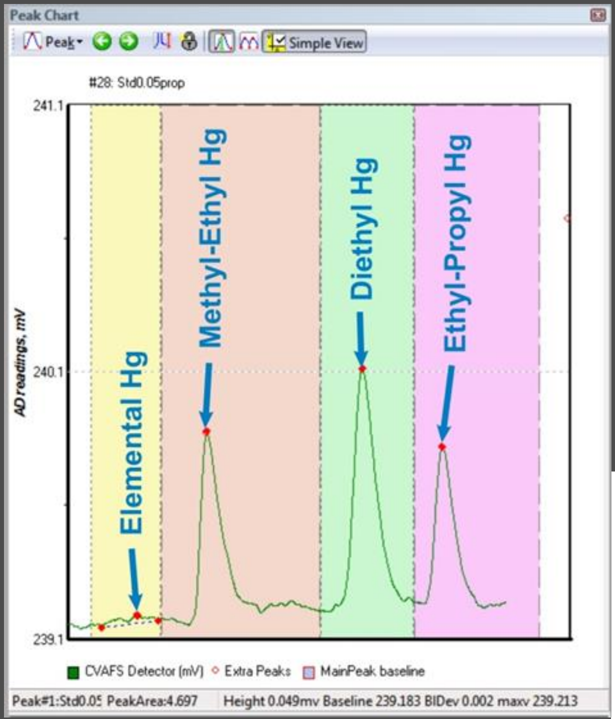
Development #3 Trace-Level Mercury Speciation Methods

Method / Regulation	Matrix	Equipment Example
USEPA Method 1631E Total Mercury	Water, Sediments, Biota, Rainwater	CVAFS – Tekran 2600-IVS
USEPA Method 1630 Methy-Hg, Ethyl-Hg	Water, Sediments, Biota, Rainwater	CVAFS – Tekran 2700
EN 15852:2008 Total Gaseous Mercury	Ambient Air	CVAFS Tekran 2537X
Networks AMNet, GMOS Speciated Mercury	Ambient Air	CVAFS Tekran 2537-1130-1135
USEPA MATS and PC-MACT Total Mercury	Flue Gas Emissions	CVAFS Tekran 3300Xi
Flue Gas Research Speciated Mercury	Flue Gas Emissions	CVAFS Tekran 3300RS

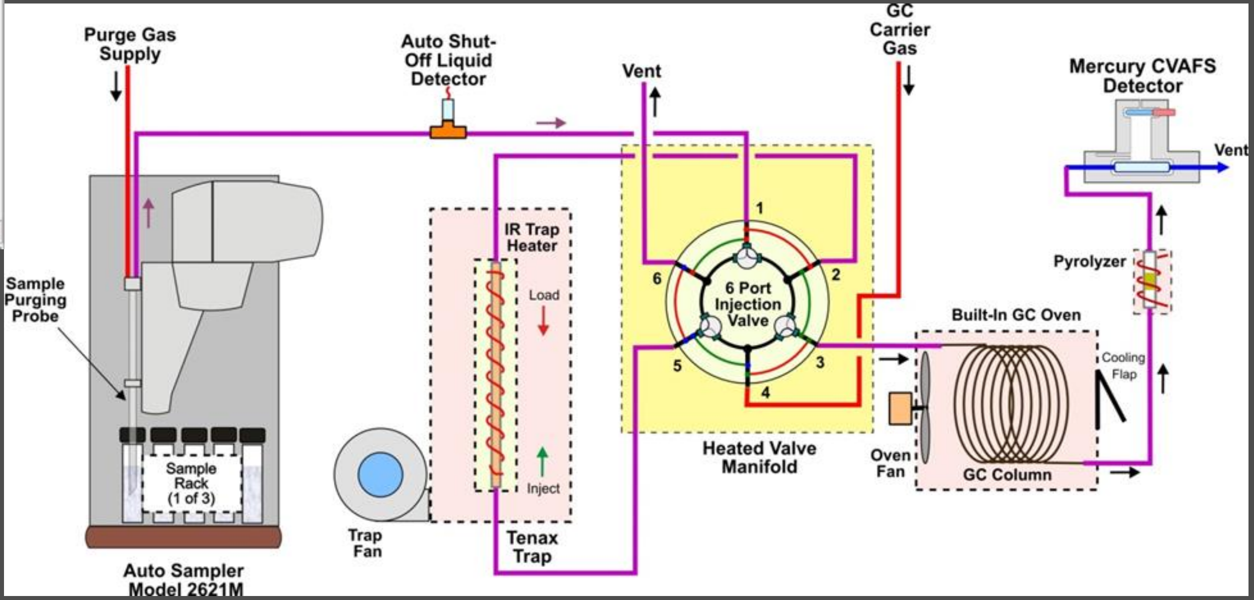
Development #3 Example: Mercury Speciation in Water and Biota



EPA Method 1630

Automated Analysis

All Organo-Hg Species



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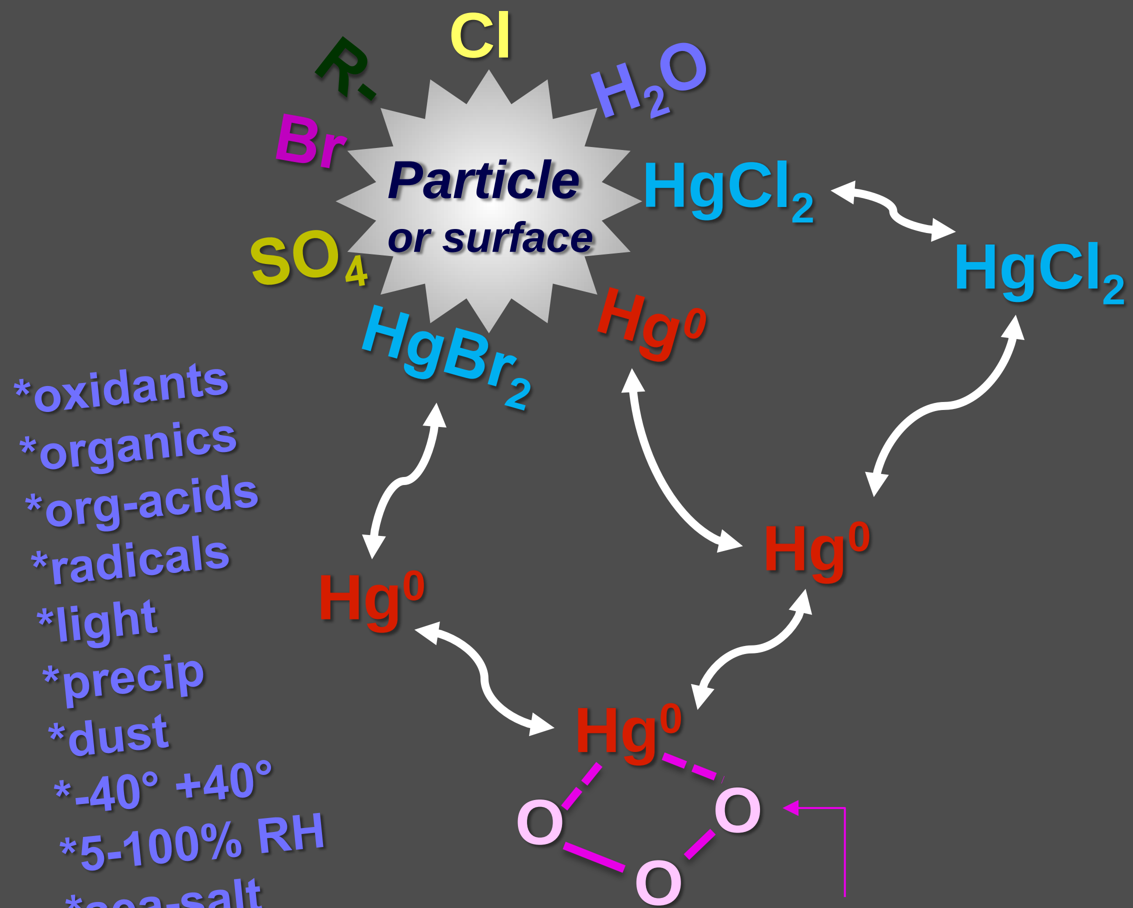
DEVELOPMENT #4
USE OF AUTOMATED, CONTINUOUS SYSTEMS FOR AMBIENT AIR

GEM = **G**aseous **E**lemental **M**ercury
GOM = **G**aseous **O**xidized **M**ercury
PBM = **P**articulate **B**ound **M**ercury

How hard can it be to measure air mercury fractions?

GOM & PBM ~ 1 ppqv

GEM ~ 170 ppqv



Calvert and Lindberg (2005)

- Difficult matrix
- Minimize surface reactions or losses during transport
- Short sample times to maximize species integrity
- Must separate and collect GOM and PBM without capturing any GEM

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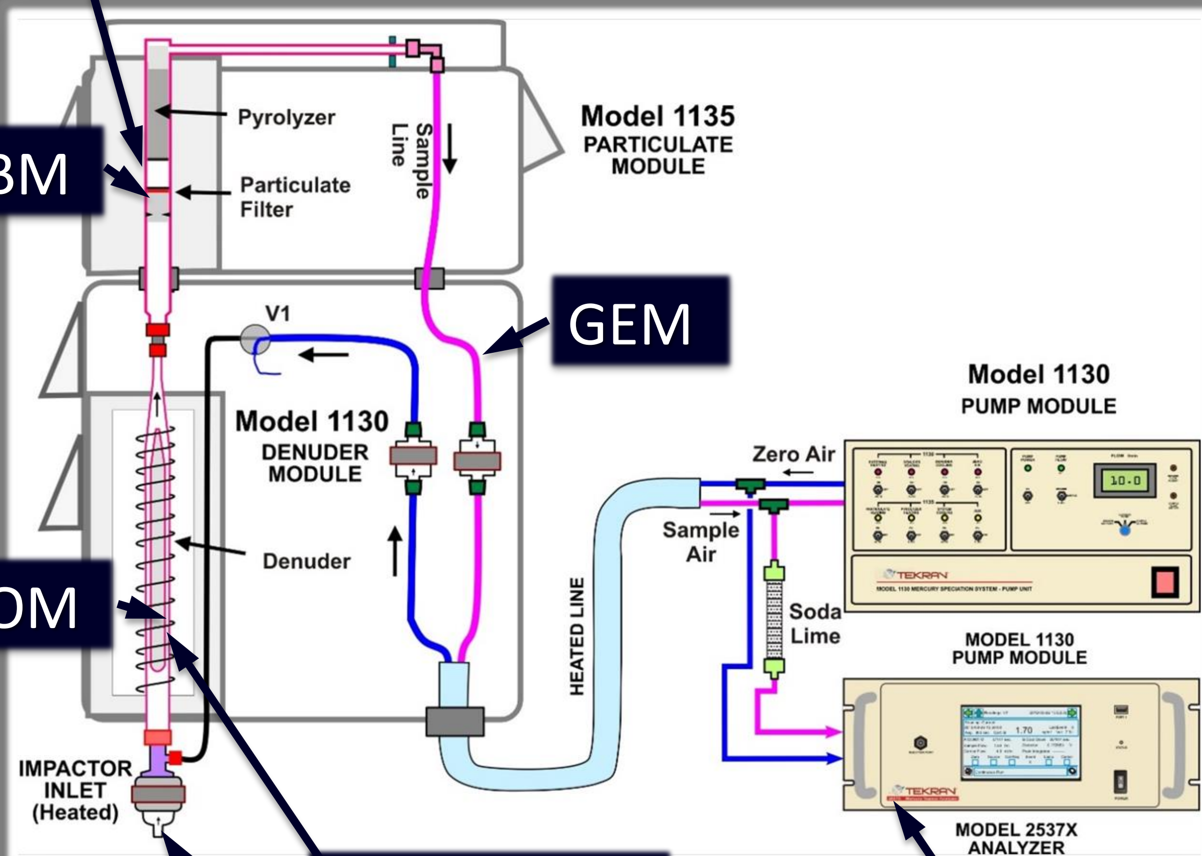
Question: What is the best method for atmospheric mercury fractionation?

- **Criteria:** Continuously measure GEM, $PBM_{2.5}$ and GOM with hourly resolution and DL<5 pg/m^3 (0.5 ppqv) for trends, source-receptor models and impacts of reduced emissions due to regulations.
- **USEPA Initiative and Scientific Consensus:** was to use a 2.5 um inlet > annular denuder > particulate filter > gold-trap CVAFS

USEPA Designed Automated Hg Fractionation Method



Method is:

- Lab tested
- Widely published
- QA Challenged
- Used by all networks
- Designed for research work

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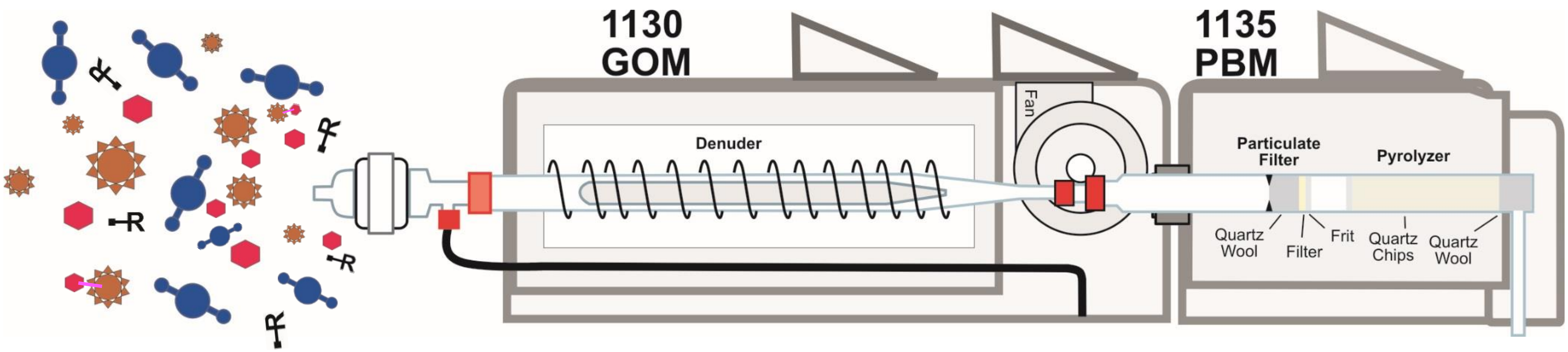
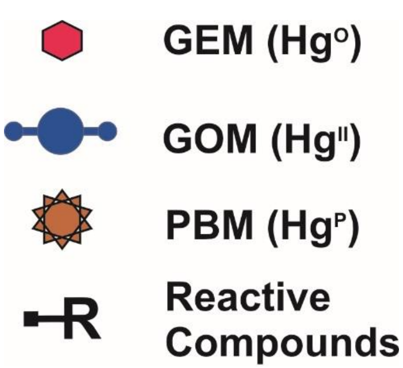
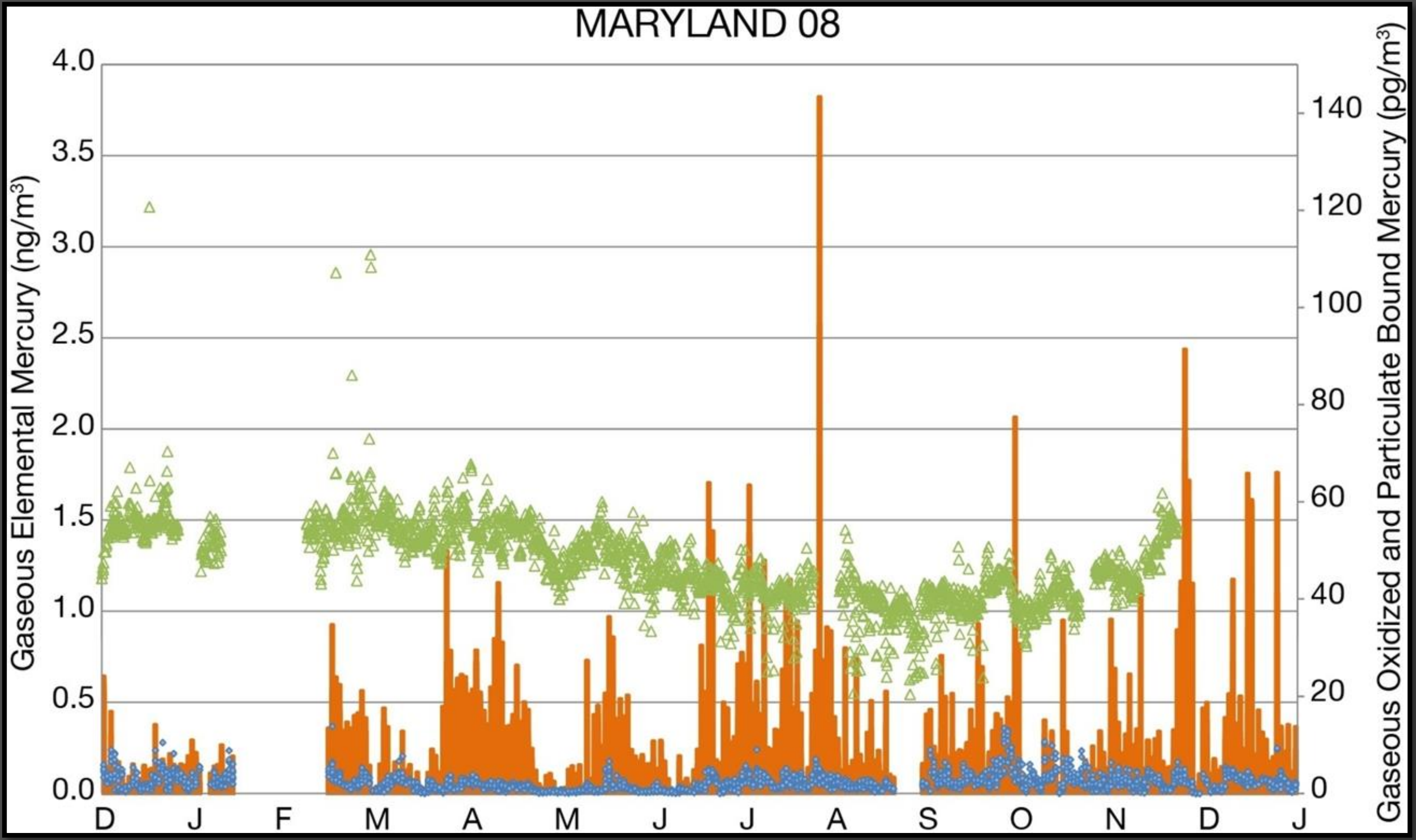
Automated Mercury Fractionation Method using Tekran 2537-1130-1135 Equipment





- Has the capability for the user to control sampling temperature and collection and transport surfaces
- Short sample time and real-time analysis to maximize sample integrity and refresh the collection surface, with a blank reported for each sample run
- Sensitive, automatically calibrated, well-trusted detector
- ***High resolution GEM, PBM2.5, and GOM data are useful for modelers!***
- Critical – Total mercury accuracy is robust, so mass balance and data coherence evaluation is possible

Example Air Mercury Fractionation Data at USA Rural Site Near Emission Sources



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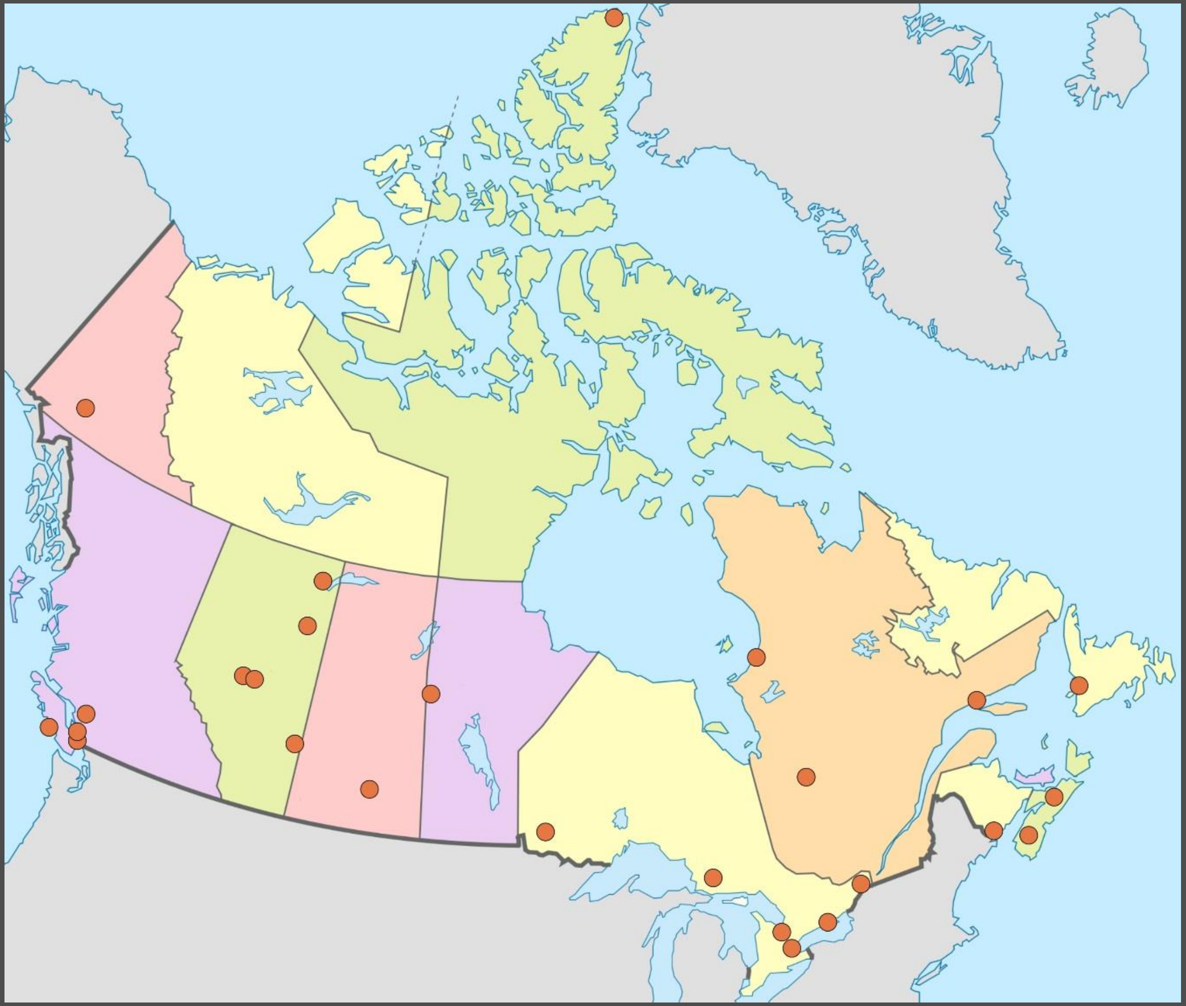
Air Measurement Networks using Tekran Equipment

CANADA Research and Monitoring Sites



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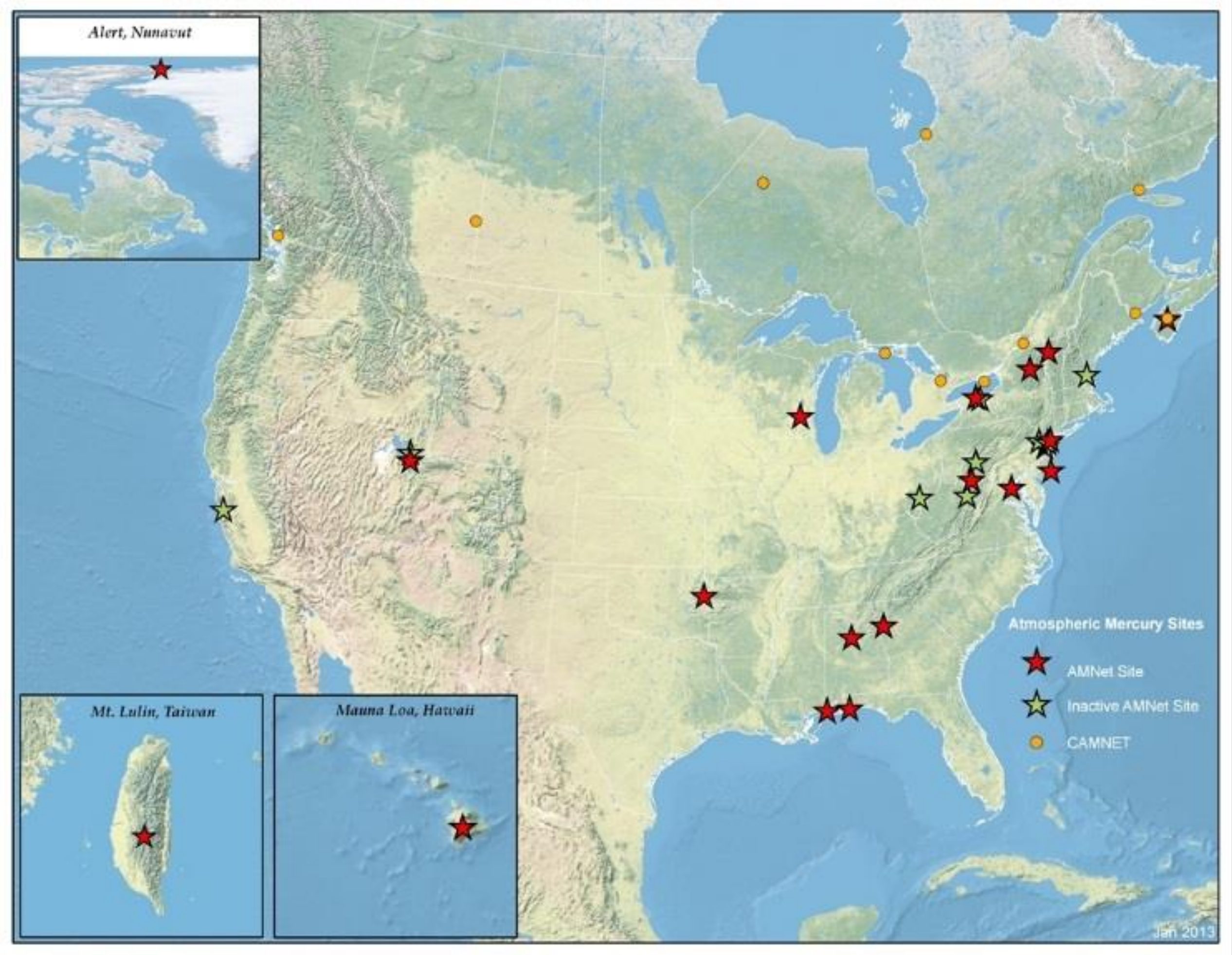
Air Measurement Networks using Tekran Equipment

AMNET – USA * CANADA * ASIA



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CHINA - Research and Monitoring Sites

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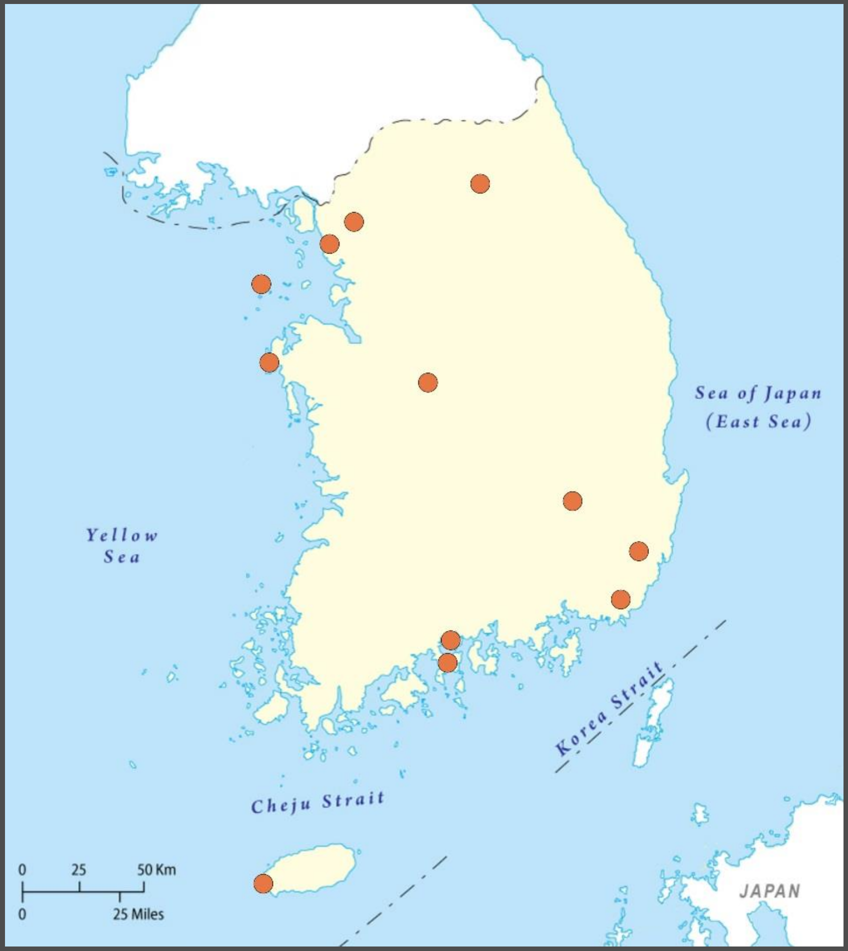
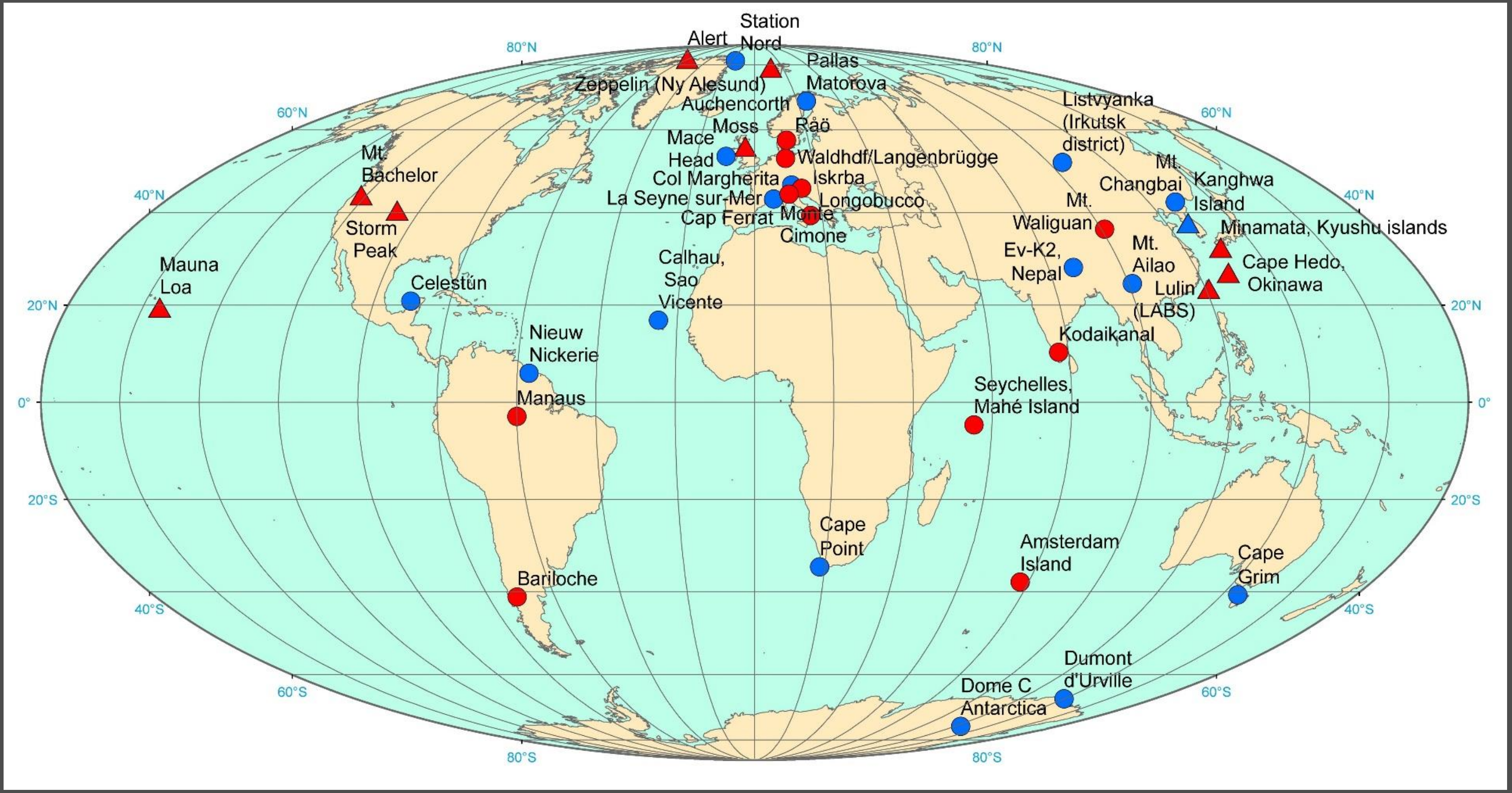
SOUTH KOREA - Monitoring Sites



Air Measurement Networks using Tekran Equipment

GMOS - Global Mercury Observation System



DEVELOPMENT #4
USE OF AUTOMATED, CONTINUOUS SYSTEMS FOR FLUE GAS

U.S. EPA EGU MATS and Cement MACT

Summary – [Hg] must be really low ~ 1.5 ug/m^3 for EGUs

- **EPA Electric Generating Unit Mercury and Air Toxic Standards (MATS) promulgated January 2012**
- **Targeted MATS Pollutants and limits**

Pollutant	Existing Source Std.	New Source Std.
Mercury	1.2 lbs/T-BTU	0.35 lbs/T-BTU
PM	0.03 lbs/M-BTU	
HCl	0.002 lbs/M-BTU	

Deadline for Compliance – April, 2015

- **The EPA Portland Cement MACT**
- **Targeted MACT Pollutants and limits**

Pollutant	Existing Source Std.	New Source Std
Mercury	55 lbs/MM tons clinker	21 lbs/MM tons clinker
THC	24 ppmvd	24 ppmvd
PM	0,07 lbs/ton clinker	0.02 lbs/ton clinker
HCl	3 ppmvd	3 ppmvd
Organic HAP (Alternative to THC)	12 ppmvd	12 ppmvd

Deadline for Compliance – September, 2015

USA - Lessons Learned about HgCEM System Design and Operation

- The coal flue gas **matrix** is very challenging
- **Conversion** of Hg^{2+} to Hg^0 quantitatively with long-term robustness is critical for success
- Quantitative **transport** of Hg species from probe to detector requires:
  - Dilution with dry air
  - High temperatures for Hg^{2+} - no cold spots
  - Inert surface materials

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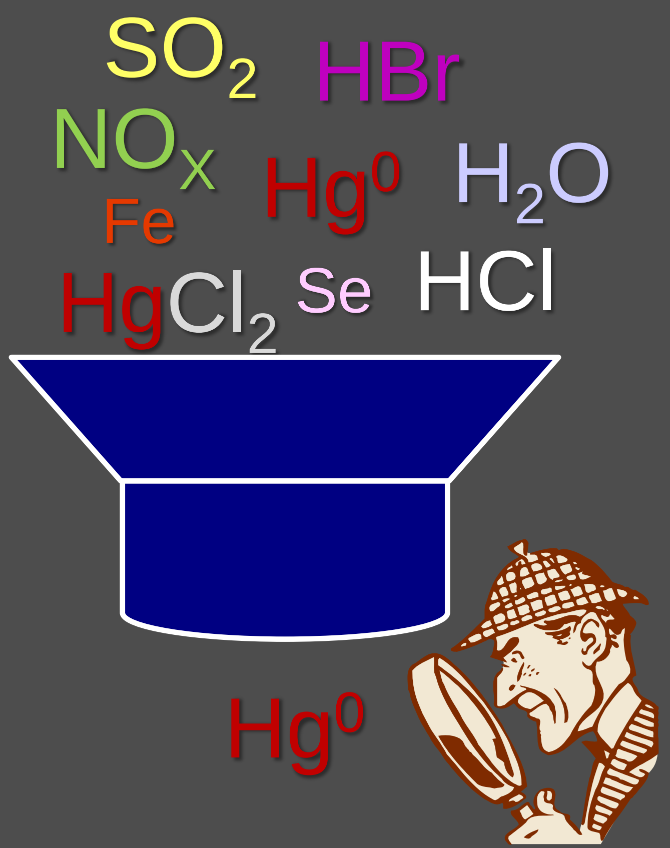
MATRIX: Accurately Measuring pptv* Levels of Mercury in Coal Flue Gas

- 1 µg/m3 Hg = 112 parts per trillion (v/v)
- Accurate measurements requires understanding and managing the many potential mercury redox reactions with halogens, sulfur oxides and water in the gas phase and on surfaces
- Tekran R&D spent 1998 to 2003 understanding flue gas mercury reactions in the laboratory
- Detectors can only measure Hg^0



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CONVERSION: The Challenge of Mercury and Reactive Halogens

- Hg^0 + reactive halogen is our friend and foe:
  - Required for Hg analysis by HgCEMs and direct thermal method for sorbent traps (30B)
  - Helpful for Hg control and used for HgCEM performance checks
- Bi-directional reaction affected by
  - Temperature
  - Catalytic surface reactions
  - Gas and particle matrix

Bi-directional reactions

$$HgCl_2 \rightleftharpoons Hg^0 + Cl_2$$

For analysis, Hg^0 formation must be quantitative with no back reaction

$$Hg^0 + Br_2 \rightleftharpoons HgBr_2$$

For control, HgX_2 formation and capture needs to be quantitative with no back reaction to minimize release of Hg^0

Simplified chemistry for illustration purposes only

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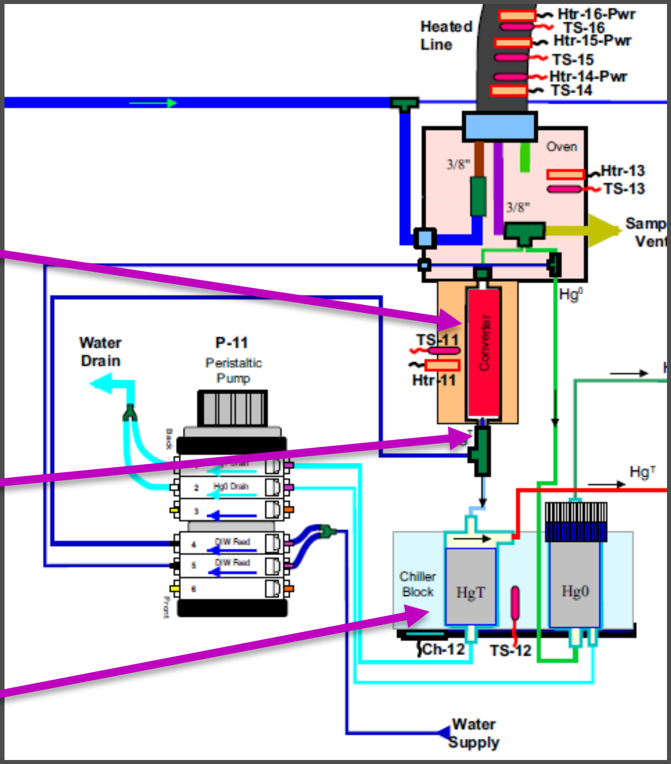
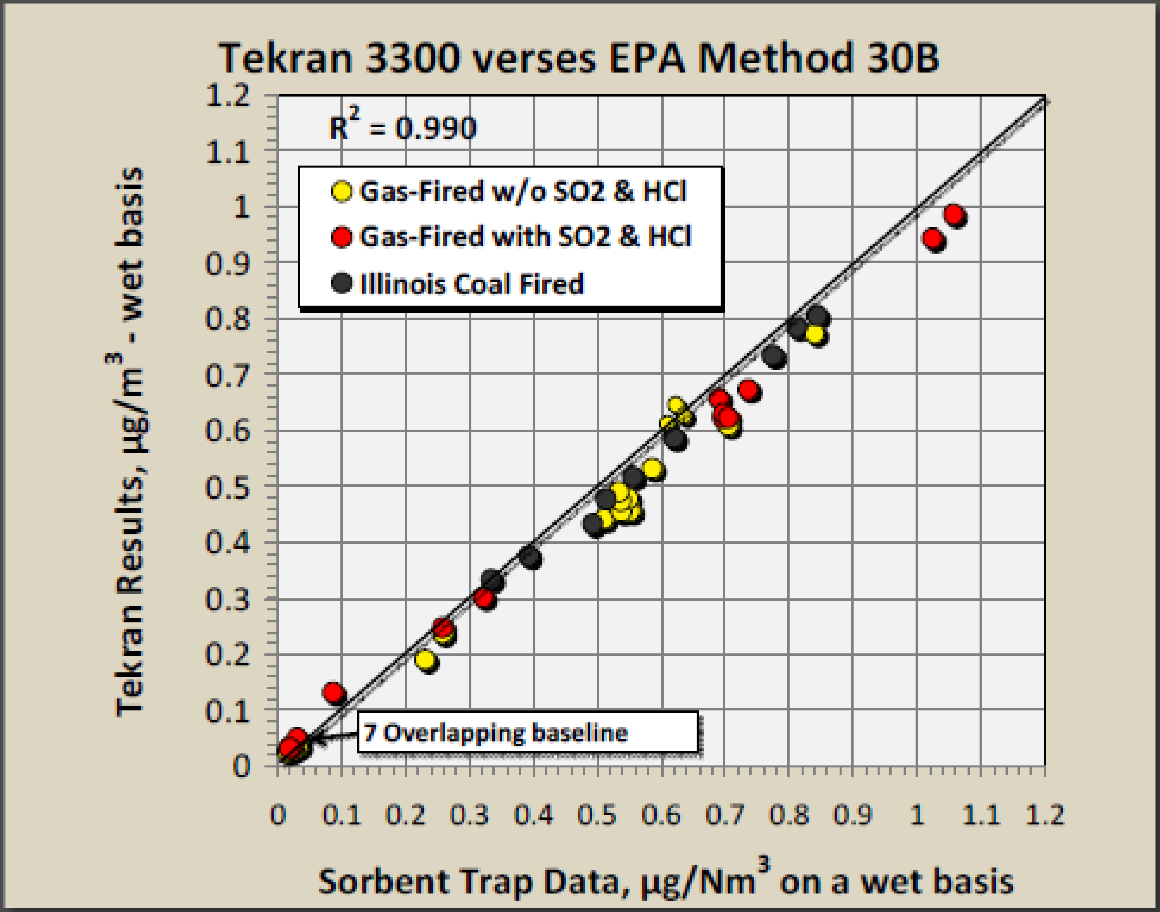
Tekran 3300Xi HgCEM Flue Gas Converter/Conditioner (patented)

- Task: quantitatively convert all Hg^{2+} to Hg^0 with no back reactions in a complex flue gas matrix
- Proprietary thermal converter material set at 700 degrees C
- DI water injected into tail of thermal converter to “fix” Hg^0 from potential back reactions and eliminate interferences
- Gas is rapidly chilled, water condenses and removes reactive compounds. Only Hg^0 remains in clean gas matrix for analyzer



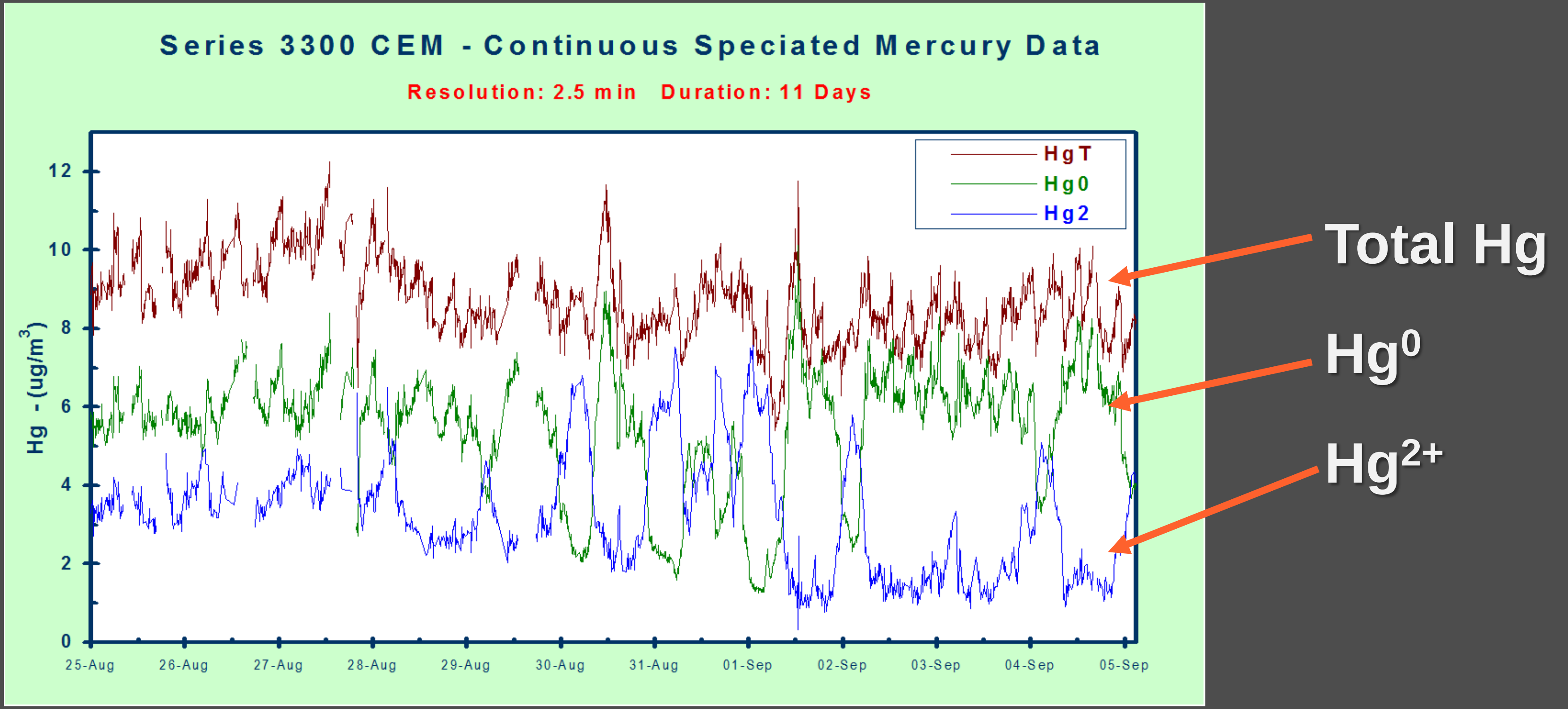
EERC Study Low-Level Measurements
(funded by EPRI, ICCI, CATM in 2010)



One example of many independent field trials done in the USA

Mercury Speciation in Flue Gas

Speciation data in flue gas provides knowledge about control choices and down wind impacts using models



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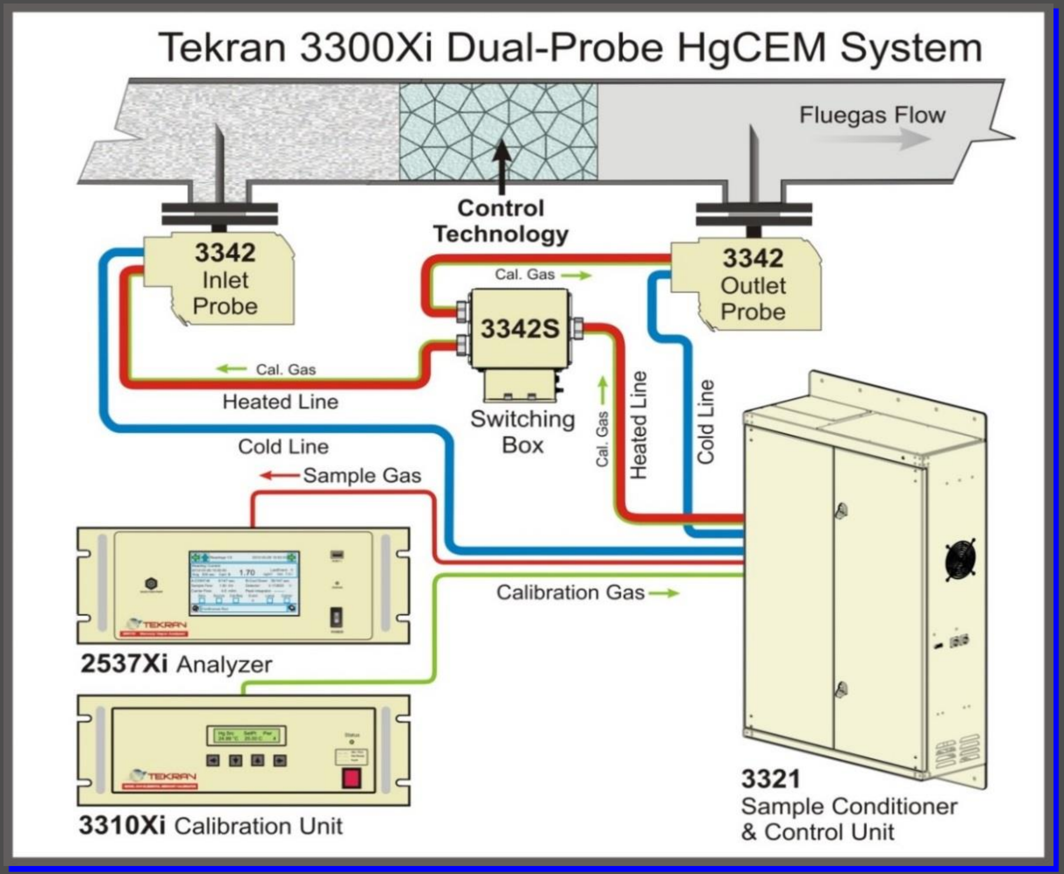
Cabinet-Based Tekran 3300Xi HgCEMS
Configuration for Regulatory Monitory

Interior 3300Xi HgCEMS Cabinet

Cabinet for
HgCEMS

Tekran 3300Xi Dual Port Sampling



Applications:

-Mercury control technology evaluation

-Regulatory monitoring of multiple emissions stacks.

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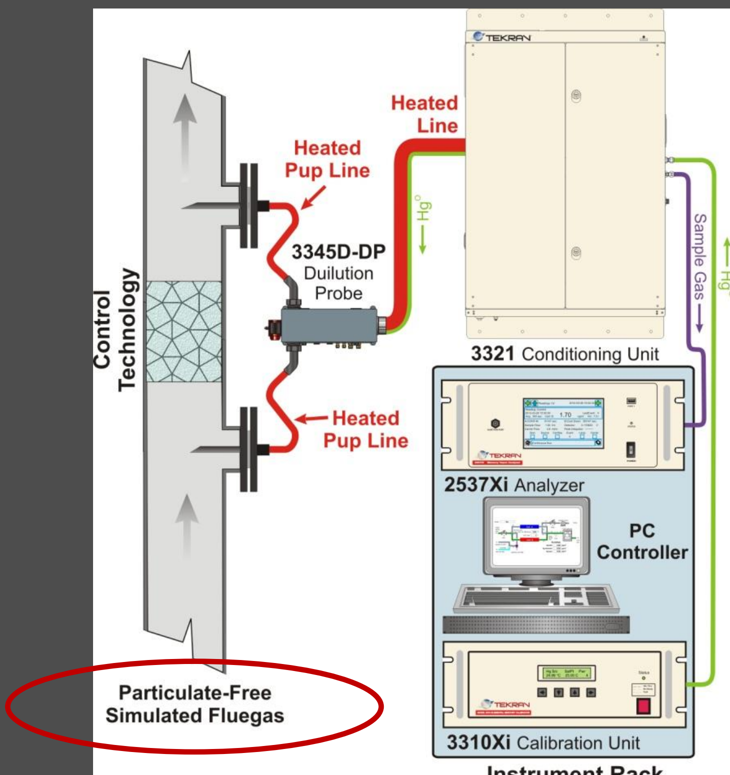
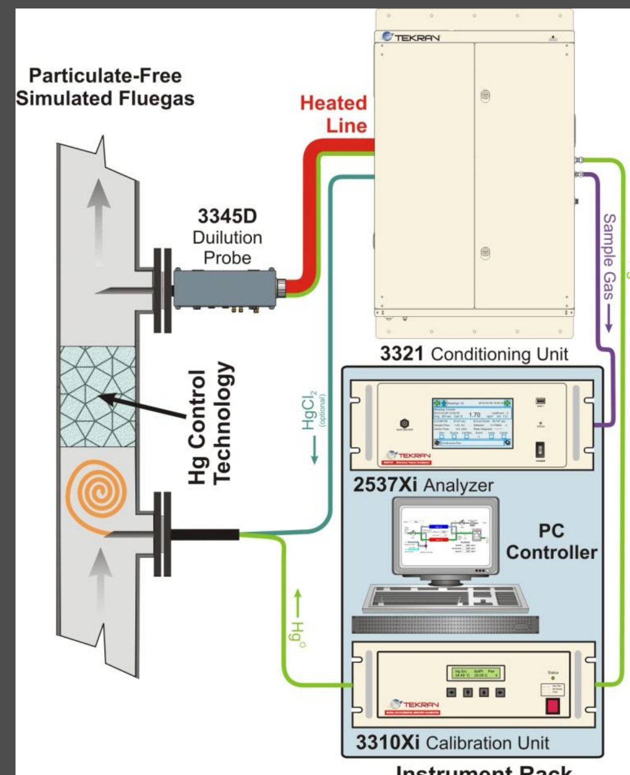
Tekran 3300RS (Research Systems)

3300RS-Dual Probe



3300RS Upstream Injection



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U. of Ningbo-Nottingham Hg Control Technology Configuration with 3300-RS

Slide courtesy of Professor Tao Wu's Research Lab at the U. of Nottingham-Ningbo

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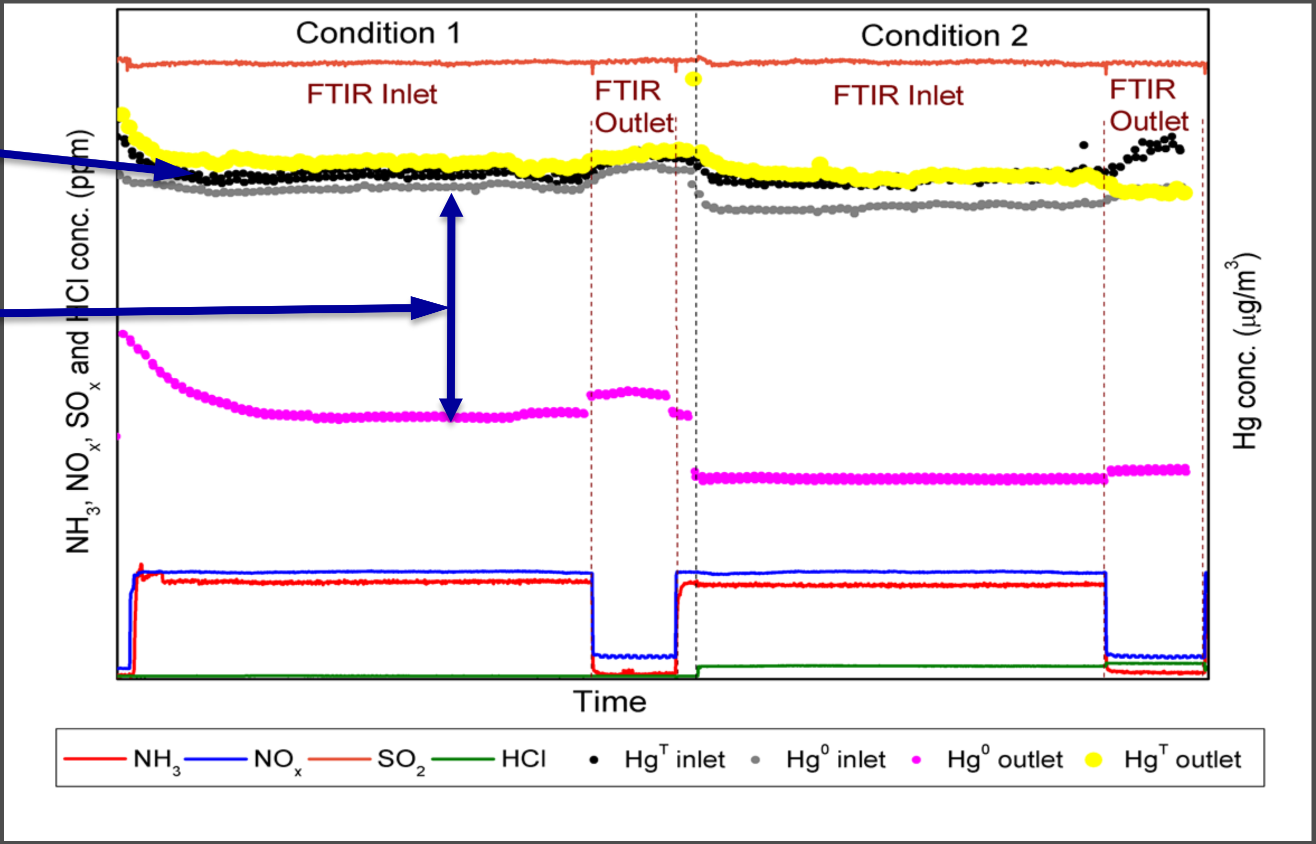
Example data from Johnson Matthey

Conversion of Hg^0 to Hg^{2+} across a catalyst

Simulated flue gas

Good Total Hg Mass Balance at inlet/outlet

Shows Hg^0 to Hg^{2+} conversion across a catalyst



Johnson Matthey

EMISSION CONTROL TECHNOLOGIES

Slide courtesy of Michael Nash at Johnson Matthey

Research Groups Using Tekran 3300 Systems

- **China** – Univ. Nottingham-Ningbo, Jiaotong U., Zhejiang U., Huaneng Clean Energy Institute, Guodian Longyuan, Guodian Nanjing, Huazhong U.
- **USA** – USEPA, Cormatech, Gore, Ablemarle, Coalogix, EERC
- **England** – Johnson Matthey
- **Poland** – CCTW Zabzre

Conclusions

- Require the use of trace metal clean techniques!
- For China – the sooner air, deposition, water and biota monitoring programs begin, the more value they will have as emissions are reduced.
- More government investment needed to improve current measurement methods and technology and to develop new mercury sensors.

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