

A North American Perspective: Regulatory Compliance Mercury Emission Monitoring below 100 pptv and Tools to Evaluate the Benefits of Lower Mercury Emissions in Ambient Air

presented by

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Measuring Mercury Emissions is challenging

- There are at least 3 forms, Hg^0 , HgCl_2 and particle-bound Hg:
Must convert to Hg^0 to measure
- $1 \text{ ug/m}^3 = 112 \text{ parts per trillion by volume (pptv)}$
- Concentrations of SO_2 , NO_x , HCl , H_2O and other interferences are up to 10^6 greater
- Rule of Thumb: Measurement cost inversely proportional to concentration
- Development of traceable Hg^0 emission gas standards not available until recently

U.S. EPA EGU MATS and Cement MACT

U.S. EPA Mercury Regulation	Existing Source Standard	New Source Standard	Deadline for Compliance
Electric Generator Unit MATS	1.2 lbs./T-BTU	0.35 lbs./T-BTU	April 2015
Portland Cement MACT	55 lbs./MM tons clinker	21 lbs./MM tons clinker	September 2015

- Summary – for EGUs, mercury concentration must be really low at ~ 170 parts per trillion (v/v) = $1.5 \mu\text{g}/\text{m}^3$ for EGUs

Yes – possible to control and measure mercury from point sources below 1 $\mu\text{g}/\text{m}^3$

- Over 200 units of the Tekran 3300 Series HgCEM System have been sold in the USA to comply with State Regulations and the US EPA MATS and MACT emission regulations
- Many Tekran 3300 HgCEM Systems have been operating continuously since 2010
- Typical coal flue gas Hg values are below 1 $\mu\text{g}/\text{m}^3$ or ~ 100 pptv

Sounds simple – NO - It was a long, difficult development process by industry, vendors and the US EPA

Impact of US EPA Regulations

- New Air Pollution Control Strategies
- New or Improved Monitoring Technologies
- Proof of Performance of 1 & 2
- Compliance Monitoring and Reporting
- Control Systems Performance Monitoring and Optimization

In the USA, HgCEM Equipment Trials in Real Flue Gas Determines Acceptance

- Because U.S EPA Regulations are based on performance standards, there is no need to have an equivalent MCERTS or TUV certification required in the USA for HgCEM equipment. Instead there are:
 - EPA Field Trials in 2004-2005
 - Independent Research Group Performance Testing
 - Field Trials by Power and Cement Companies
 - High frequency QA checks, NIST traceable standards protocol and annual Relative Accuracy Tests (RATA)

U.S. EPA Trials 2005 - Summary



EPA RATA Testing Trials

Company / Instrument	Trial A - Round 1		Trial B - Round 1		Trial B - Round 2	
	Mean Difference (µg/dscm)	Relative Accuracy	Mean Difference (µg/dscm)	Relative Accuracy	Mean Difference (µg/dscm)	Relative Accuracy
Tekran / Gold+AFS	0.26	10.5%	0.50	18.4%	0.30	18.8%
#2 / Direct AFS	*	*	1.00	37.5%	0.84	94.5%
#3 / AAS	*	*	*	*	-0.63	75.7%
#4 / AAS	*	*	1.30	81.9%	*	*
#5 / AAS	1.57	49.3%	1.60	51.9%	*	*
#6 / AAS	*	*	*	*	0.48	36.2%

* No Data

- Relative Accuracy must be <20%
- Most HgCEMs did poorly, except Tekran and Thermo. Only the Tekran 3300 CEM was able to pass **all** USEPA Trial performance measurements.

Field Trials: 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

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 reactions



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



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

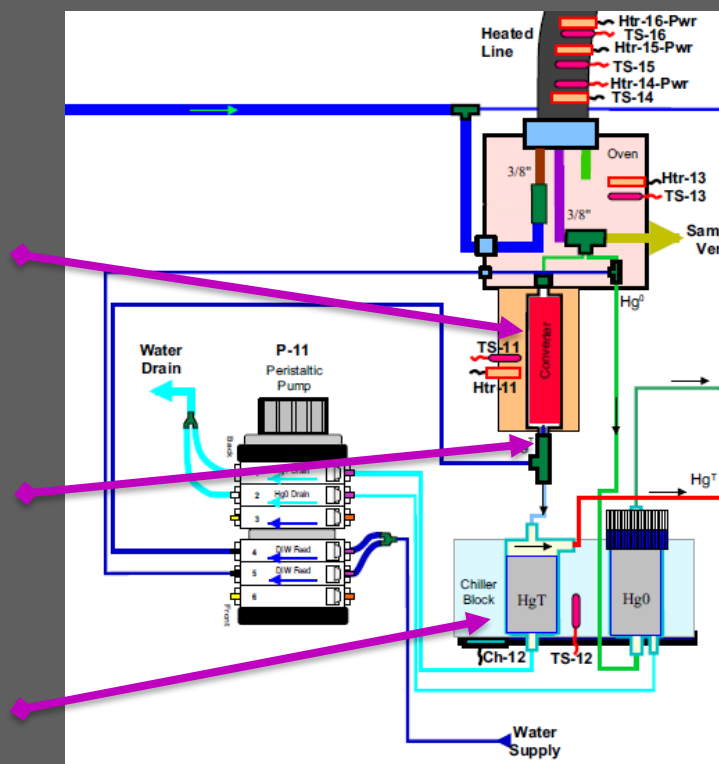
- Bi-directional reaction affected by

- Temperature
- Catalytic surface reactions
- Gas and particle matrix

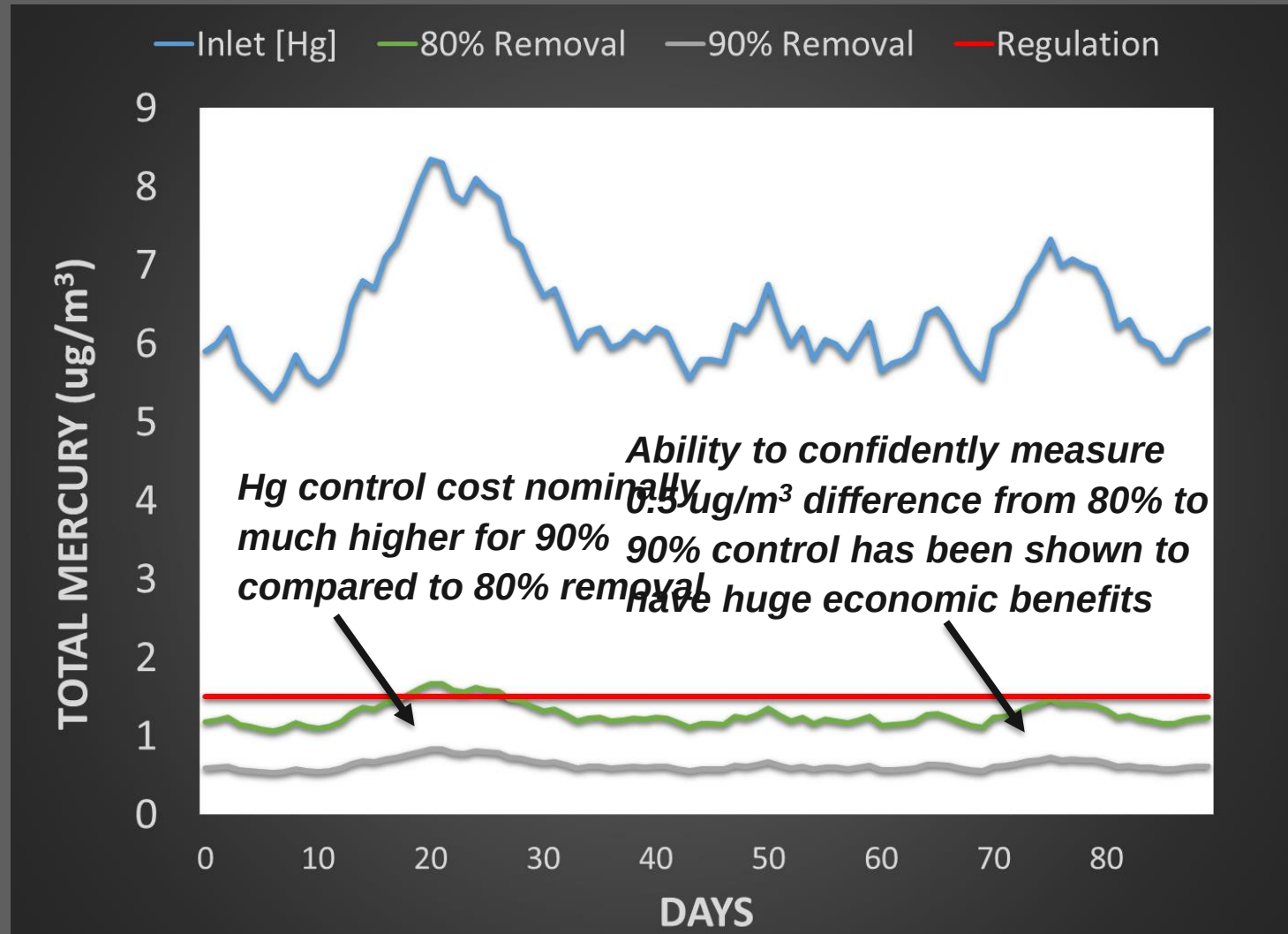
Simplified chemistry for illustration purposes only

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

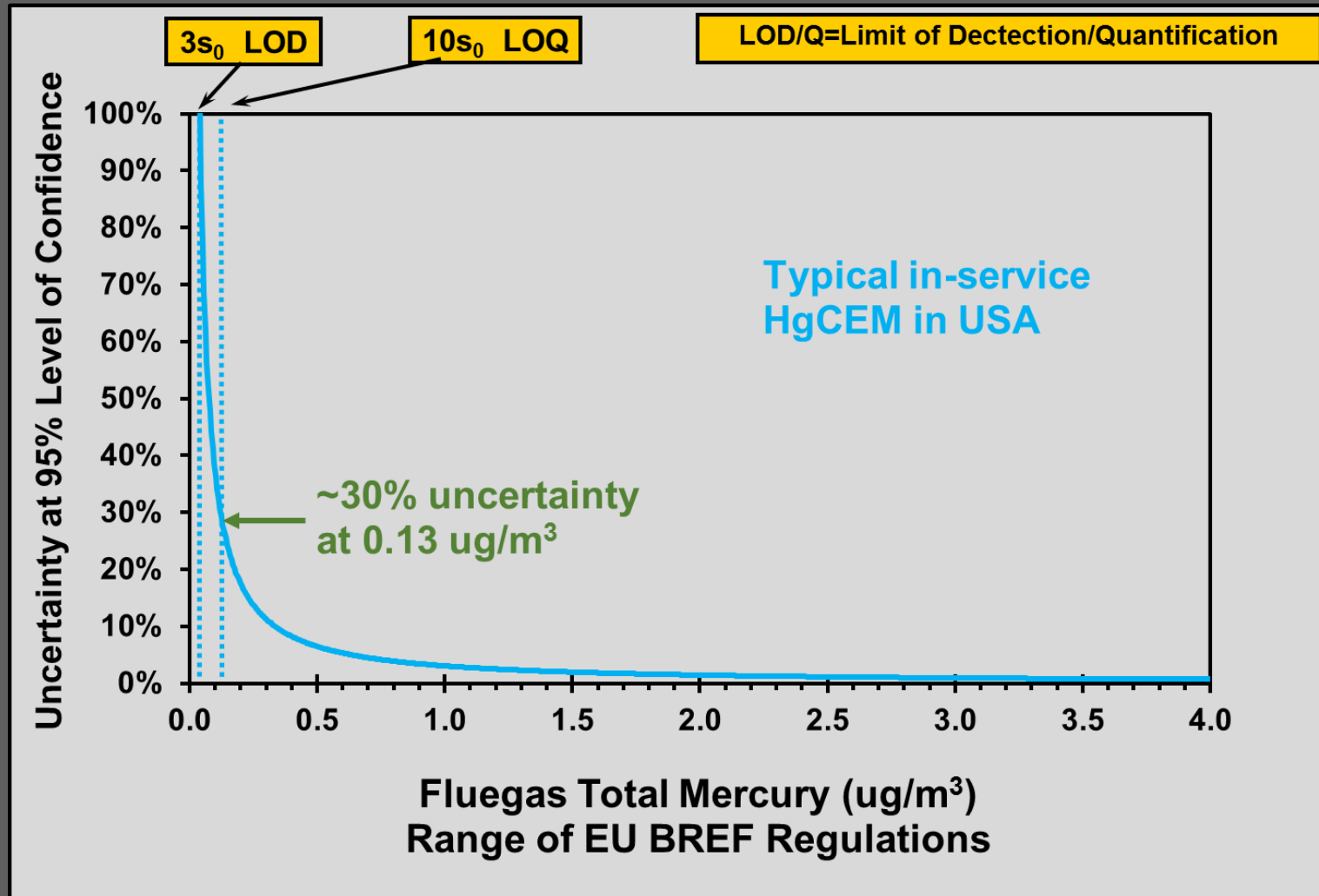
- Task: quantitatively convert all Hg^{2+} to Hg^0 with no back reactions in a complex flue gas matrix at the low pptv level
- Proprietary thermal converter material set at 700 degrees C
- DI water injected into tail of thermal converter to “fix” Hg^0 from potential back reactions and eliminate interferences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



Typical USA Power Plant Emission Target



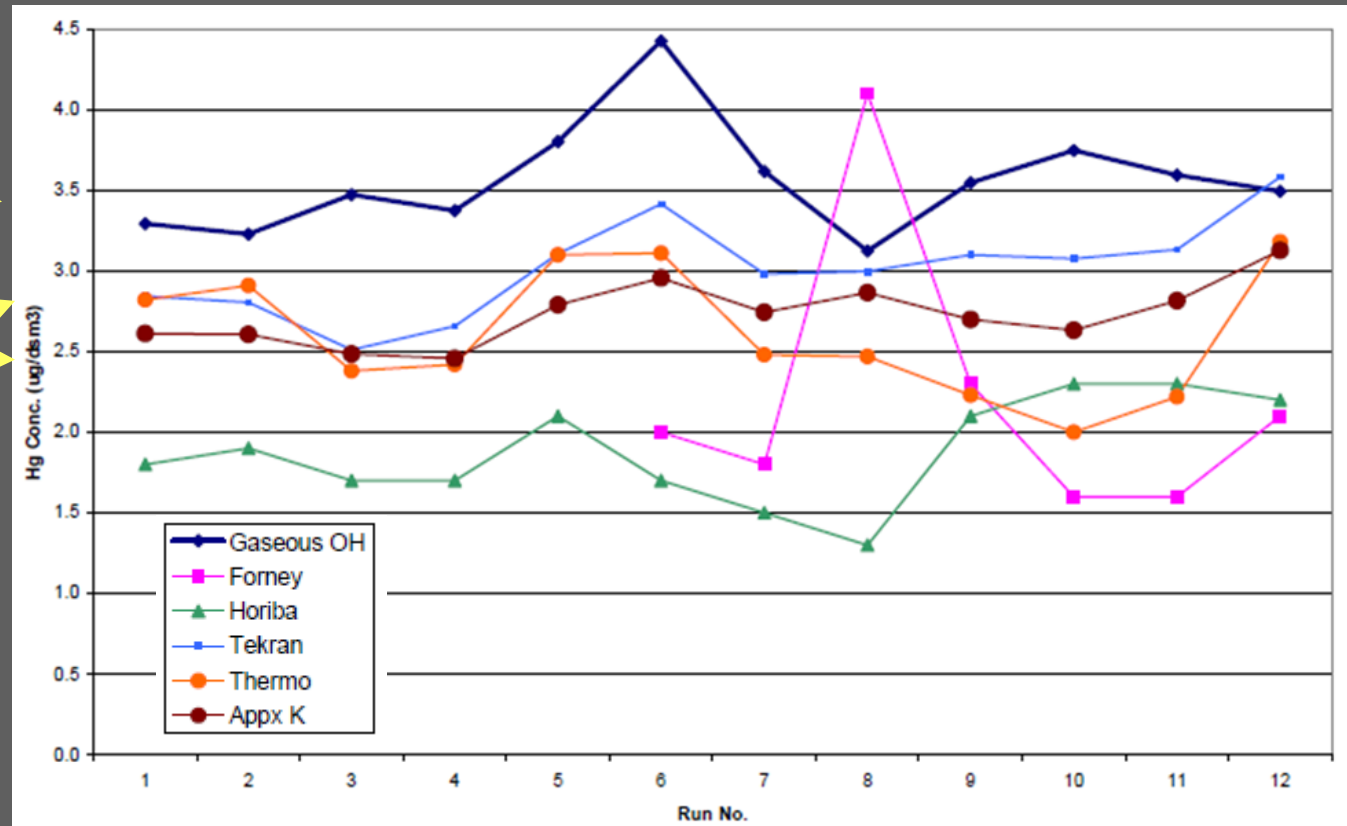
Confidence in HgCEM data below 1 $\mu\text{g}/\text{m}^3$ requires a very low detection limit



EPA trials and many other studies showed the limitations of wet-impinger methods as a reference standard

Wet-Impinger →

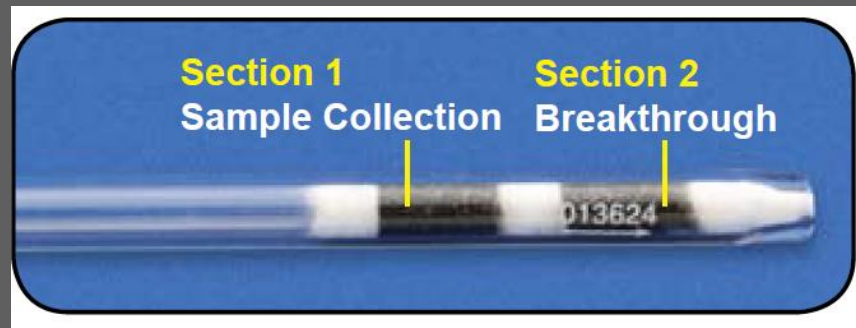
Tekran, Thermo &
Sorbent Trap →



Relative Accuracy Testing - EPA Method 30B

Improved capability to validate low HgCEM values

- Method is only intended for use for low particulate conditions (e.g., sampling after all pollution control devices)
- Method designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{2+})
- Sorbent Traps have:
 - mineral wool section (intended for PM),
 - primary capture section,
 - secondary (breakthrough) capture section
 - final mineral wool section
- Particulate Hg that is captured in the trap is included in the analysis

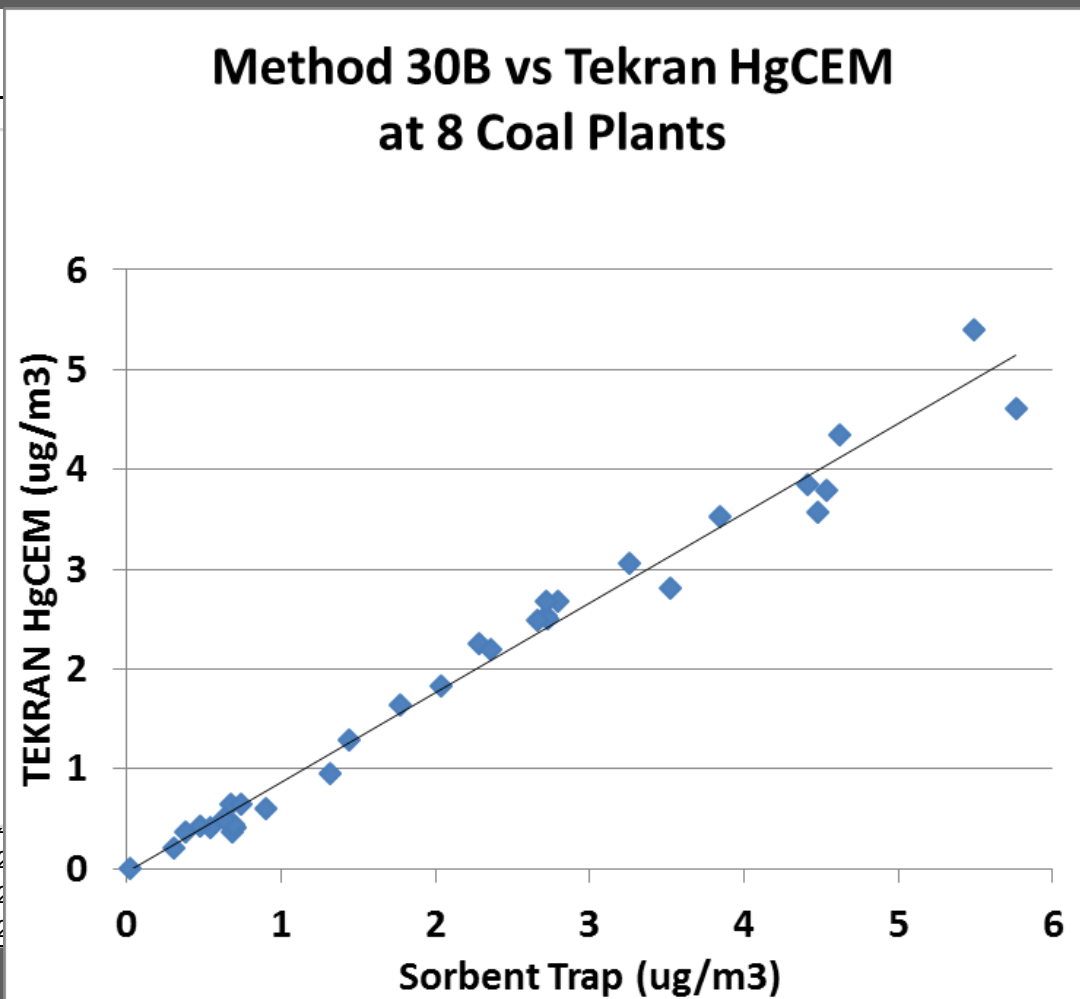


Tekran HgCEM RATA Results

Parameter: HGT
 Effective Date/Time: 05/28/2014 08:55
 Monitoring System ID: 05/28/2014 10:09
 Test Reason: QA
 Overall RA: 4.8
 CEMS Time Offset :
 Test Comment:

Operating Level: Normal
 Mean CEMS: 5.611
 Mean Reference: 5.789
 Mean Difference: 0.178

Run	Started	
1	05/28/2014 08:55	0
2	05/28/2014 10:09	0
3	05/28/2014 11:05	0
4	05/28/2014 11:58	0
5	05/28/2014 12:45	0
6	05/28/2014 13:29	0
7	05/28/2014 14:12	0
8	05/28/2014 15:00	05/28/2
9	05/28/2014 15:44	05/28/2
10	05/28/2014 16:27	05/28/2



Port in EDR: N
 Use BAF: Y
 Use Method: 30B

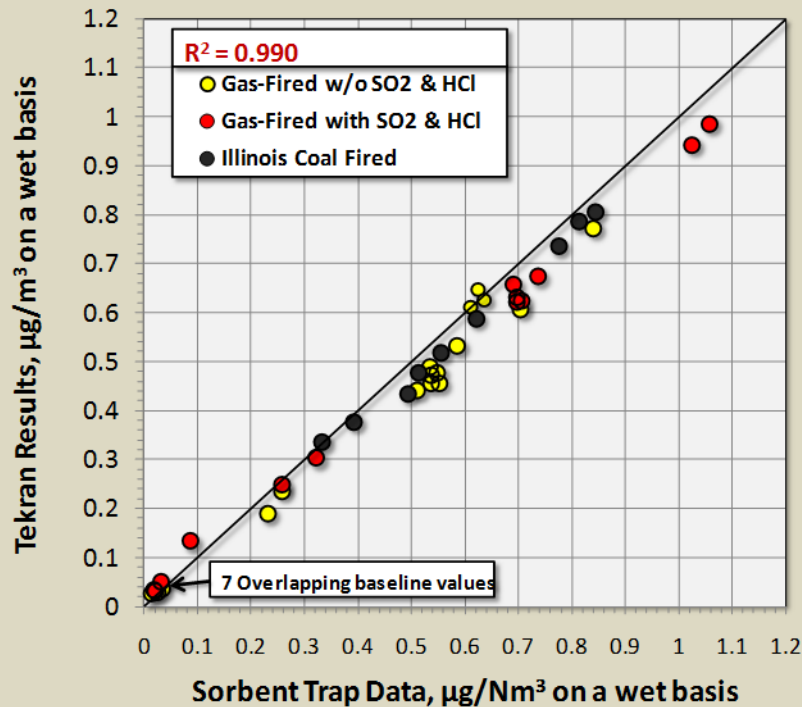
	Use
198	
198	Y
198	Y
198	Y
196	Y
195	Y
195	Y
195	Y
195	Y
195	Y
196	Y

Joint EERC, EPRI & ICCI Project

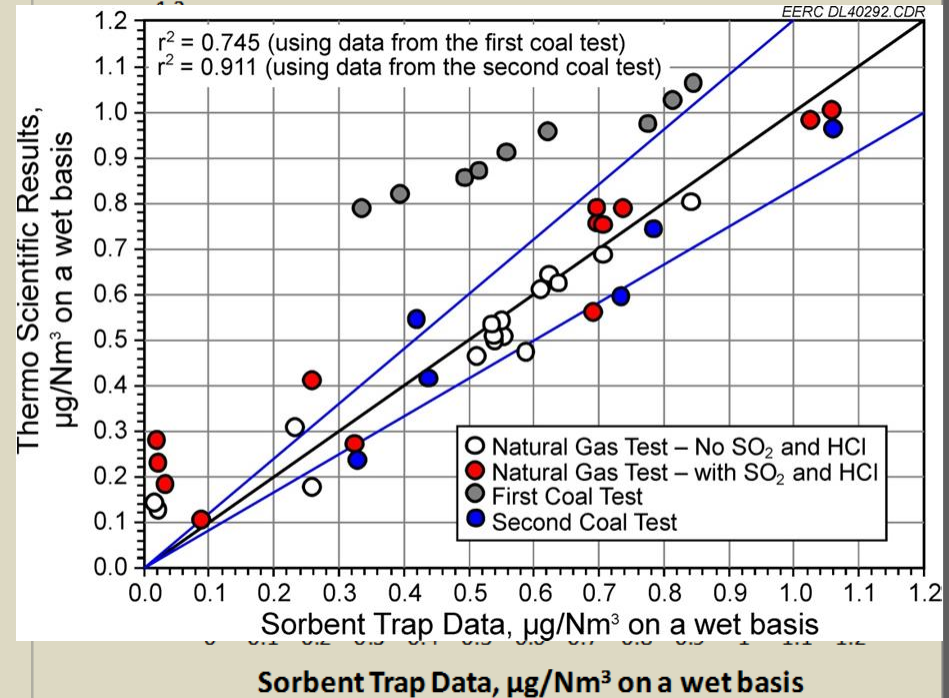
Determining the Accuracy of CMMs at Low Mercury Concentrations

Figures adapted from Laudal et al., 2010

Tekran 3300 versus EPA Method 30B



Thermo Freedom versus EPA Method 30B



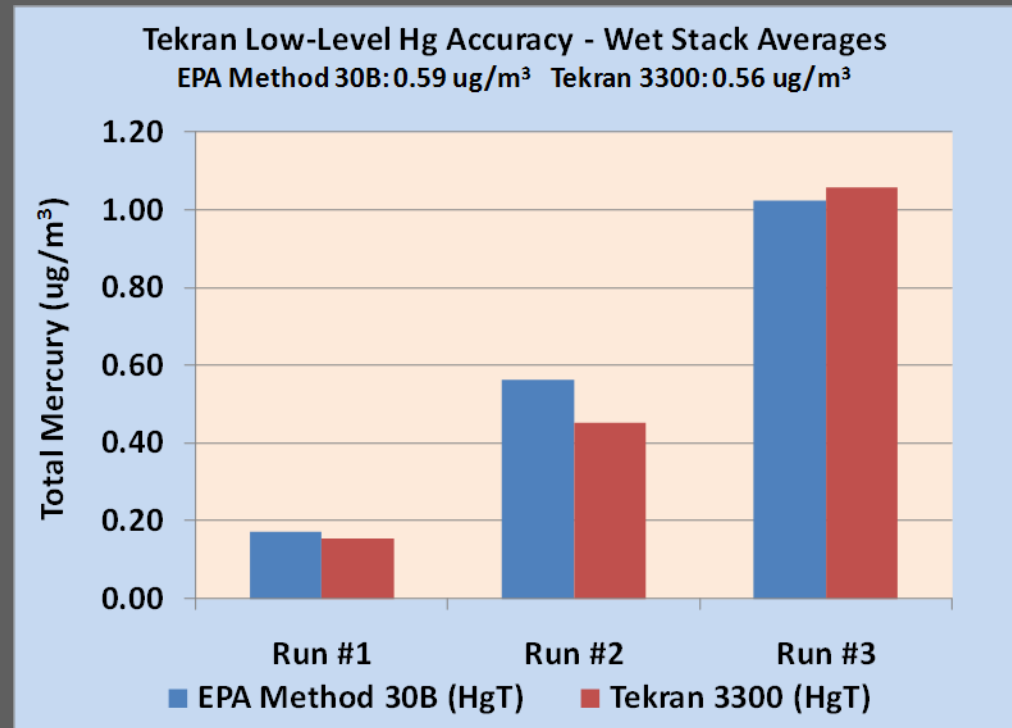
NOTE: The coal result bias for the Thermo Freedom System was resolved on a second test at EERC

Reliant Energy: HgCEM Accuracy - low Hg levels – wet scrubber stack - 2007

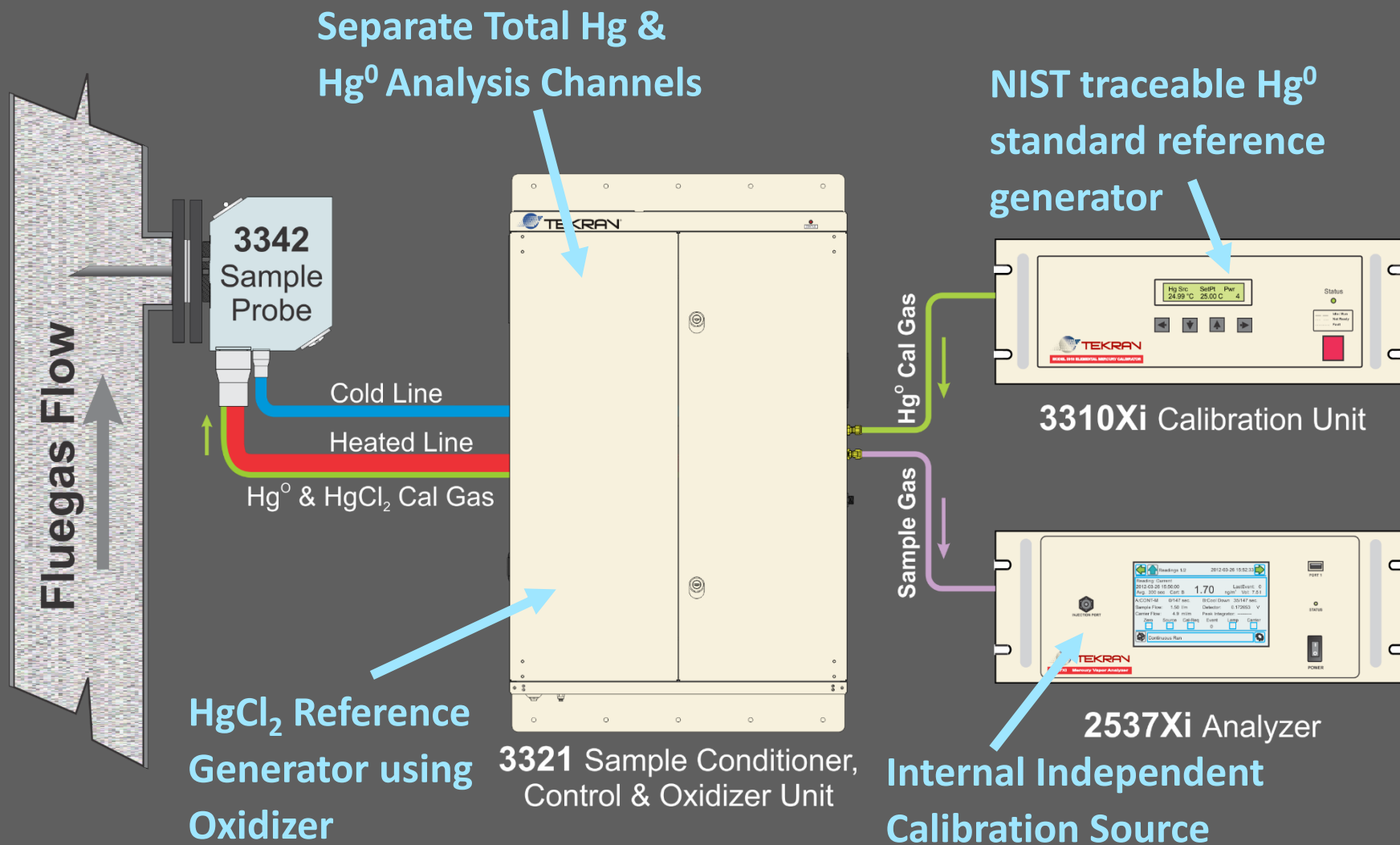
- Sorbent Traps (avg) = 0.59 ug/m^3
- Tekran with M&C (avg) = 0.56 ug/m^3
- Slide courtesy of Eric Roland



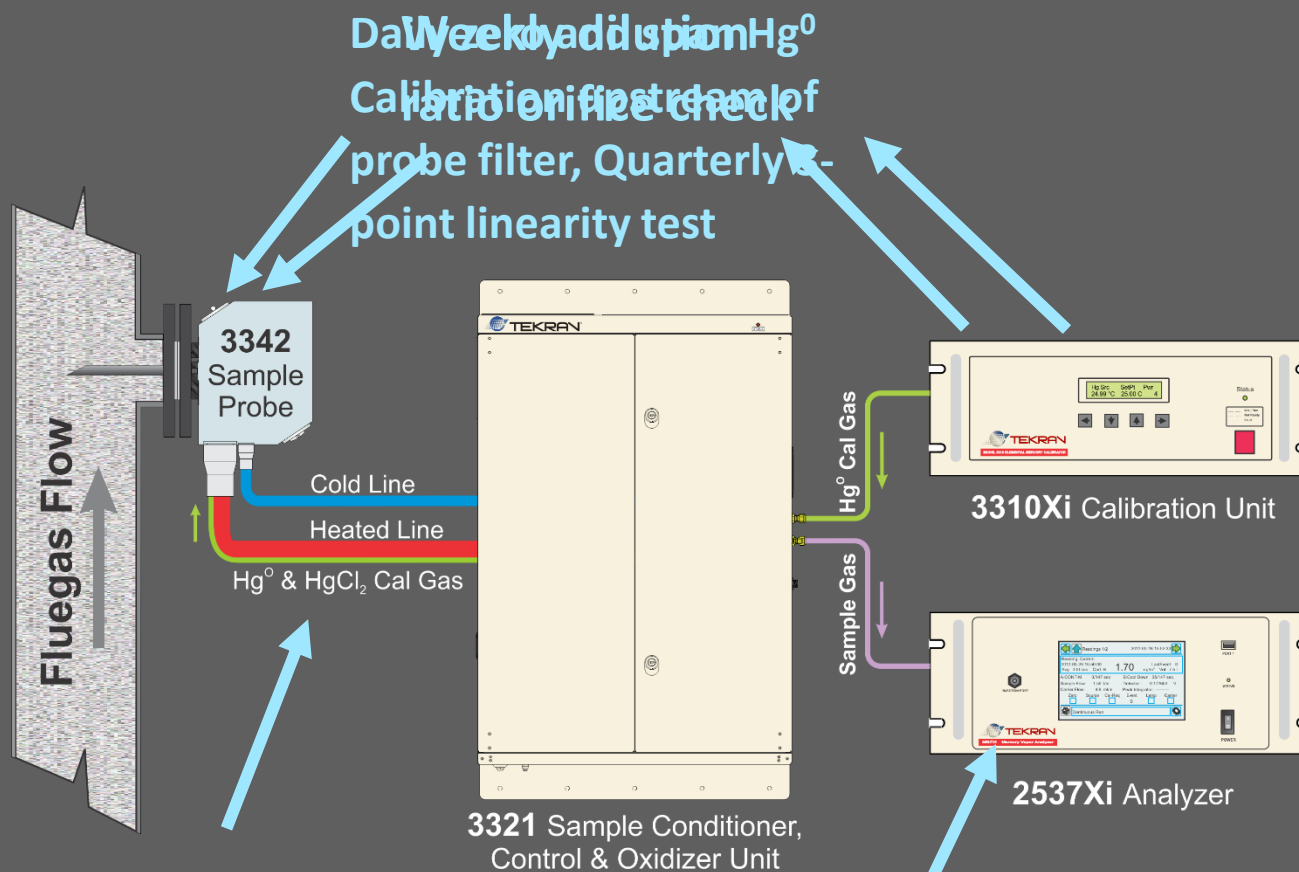
NOTE: Reliant Energy
is now NRG



USA Regulation Required Hardware for accuracy at low $\mu\text{g}/\text{m}^3$



USA Regulation Required Quality Assurance

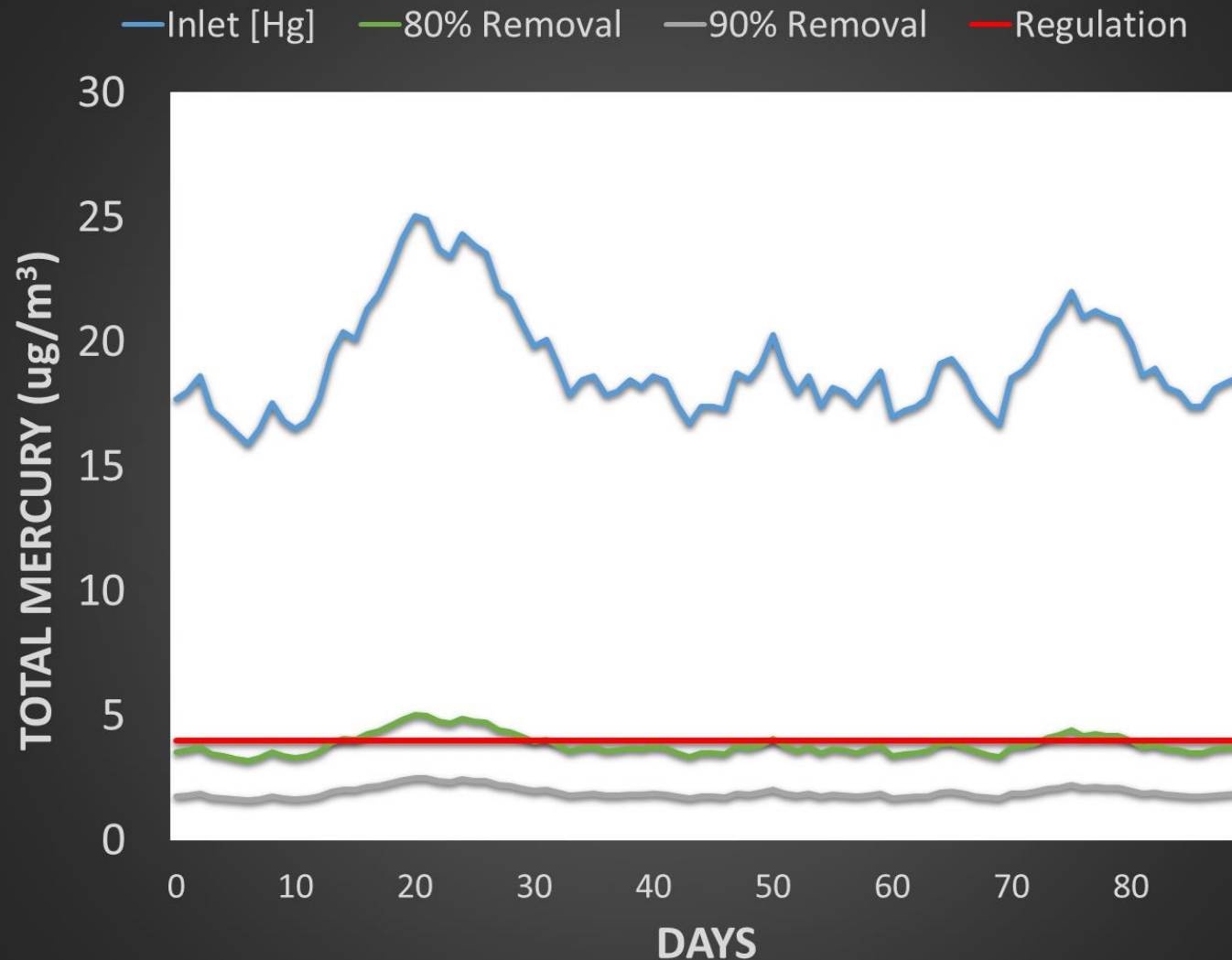


Weekly single point HgCl₂ calibration gas integrity check through probe filter and converter: Measure total Hg, Hg⁰ and Hg(II). 3-Point test done quarterly

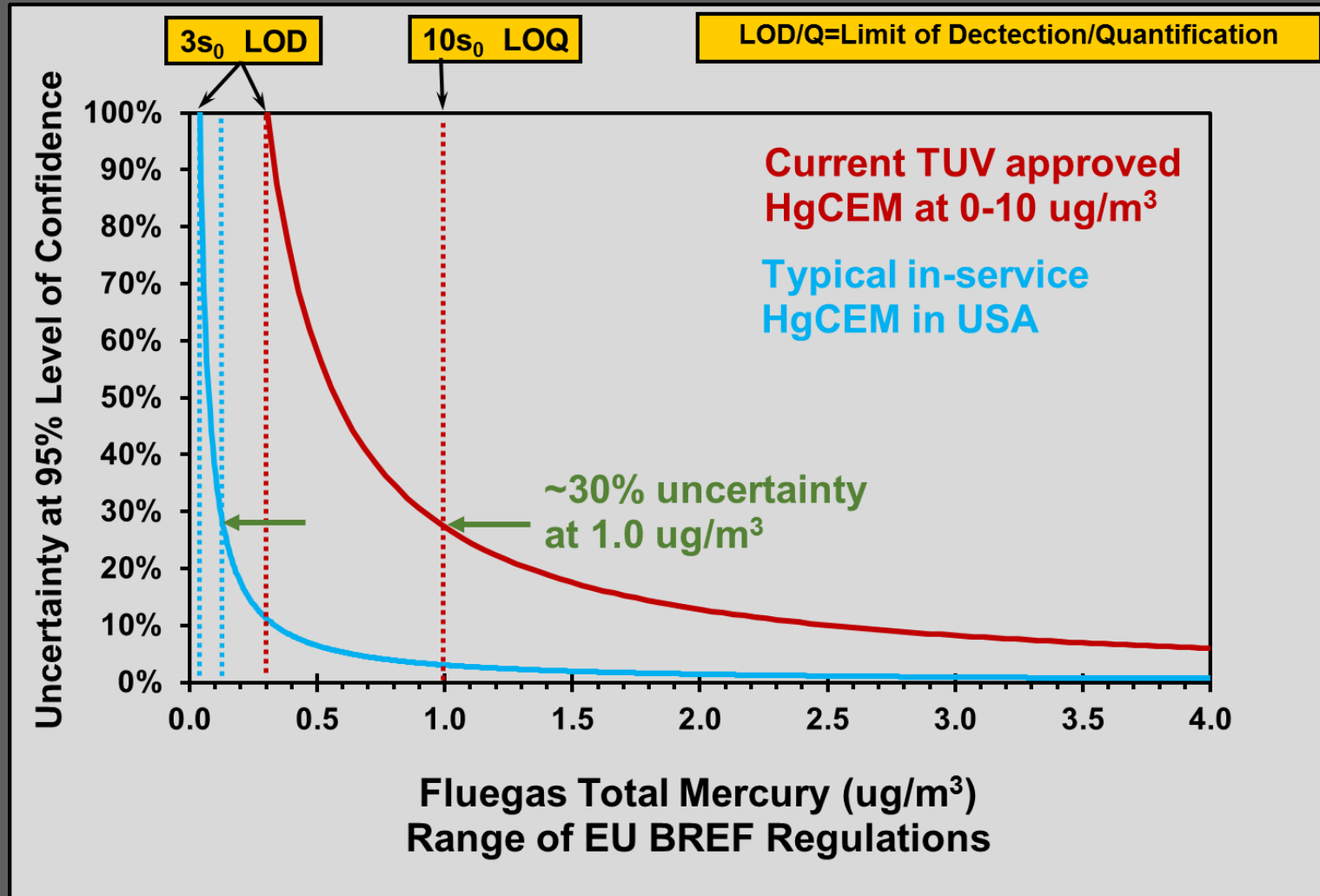
2537Xi Hg⁰ permeation ratio test every 48 hours to monitor stability of Hg⁰ generator. Extends NIST certification frequency

Example New Lignite-Fired EGU

Percent Reduction to Meet EU BREF

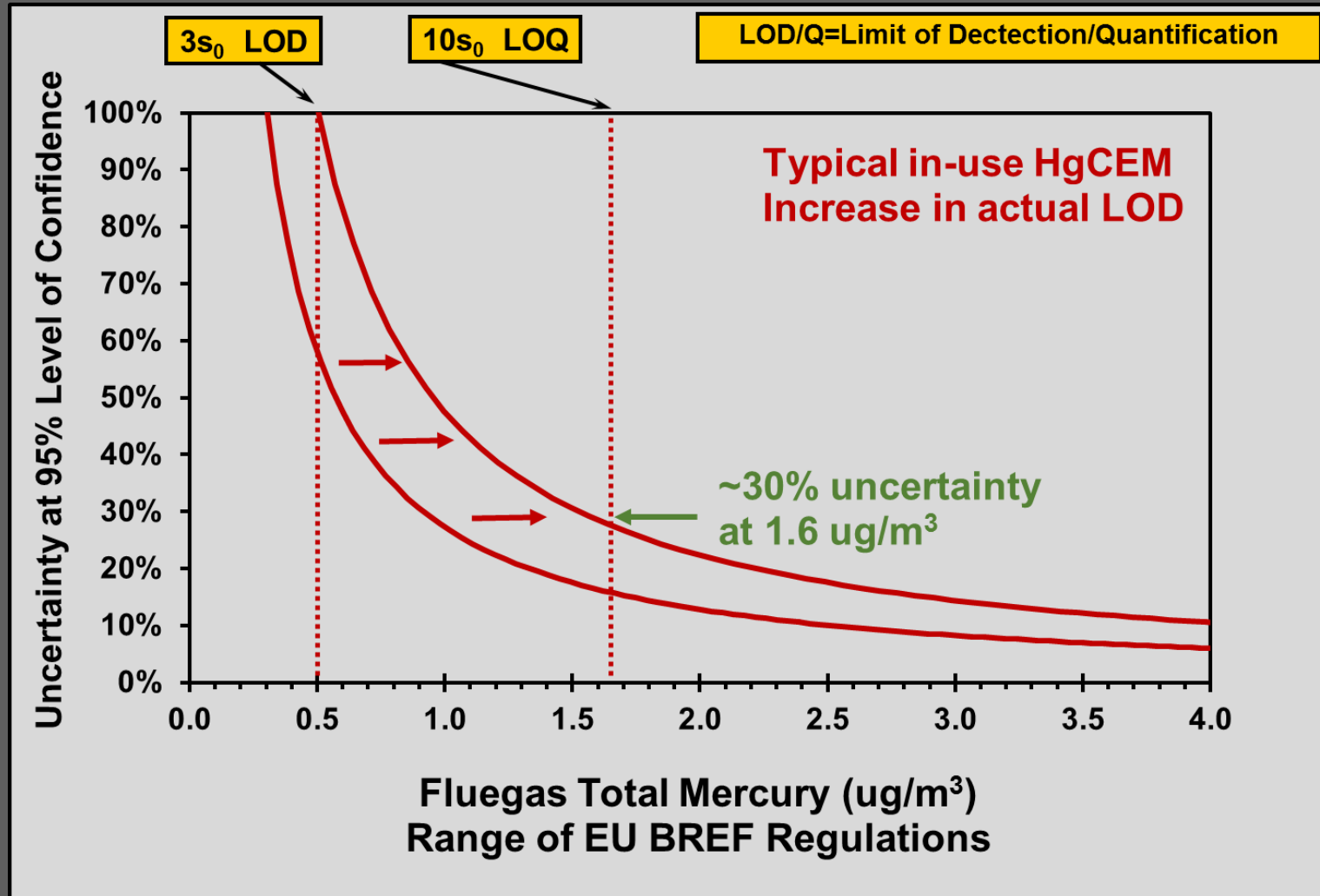


Higher HgCEM detection limit = higher uncertainty at levels important for compliance and control



Higher HgCEM detection limit = higher uncertainty

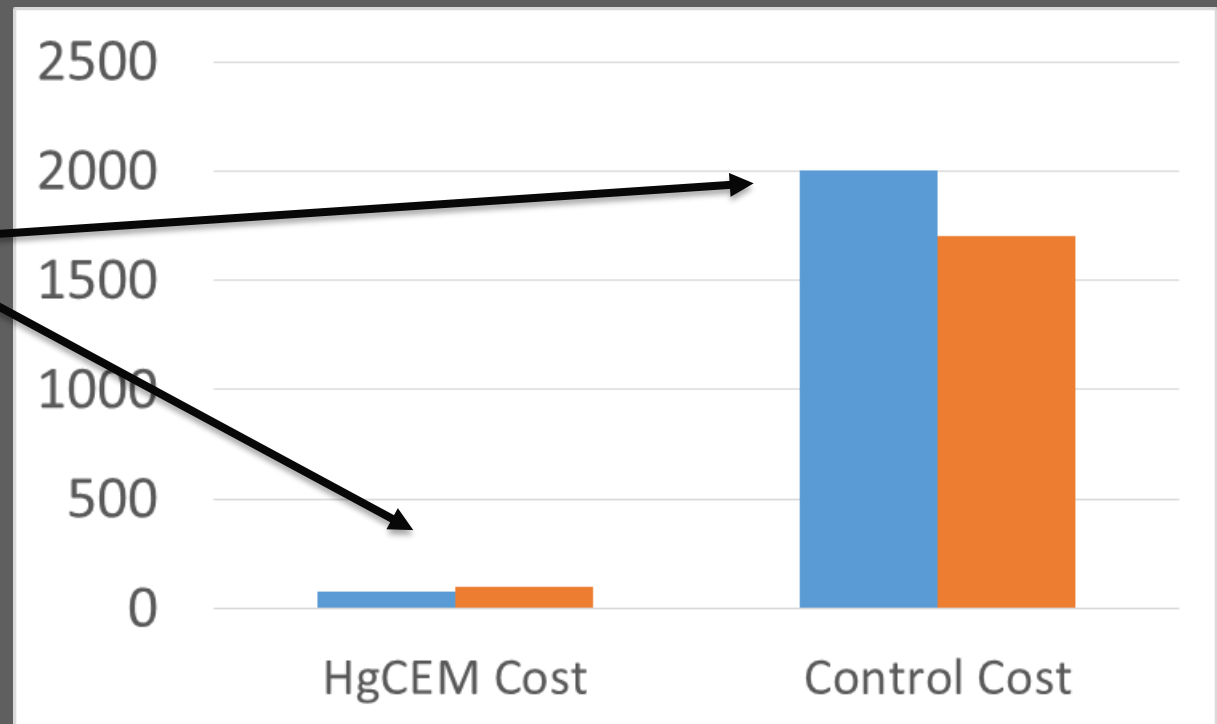
Typical drift in HgCEM sensitivity



HgCEM Cost and Performance

- In the USA, HgCEM performance was often more important than HgCEM system hardware and maintenance cost
- Why? - - because high HgCEM system performance can offer large savings in control technology costs.

Marginal HgCEM cost increase may have large annual control cost benefit



Conclusions

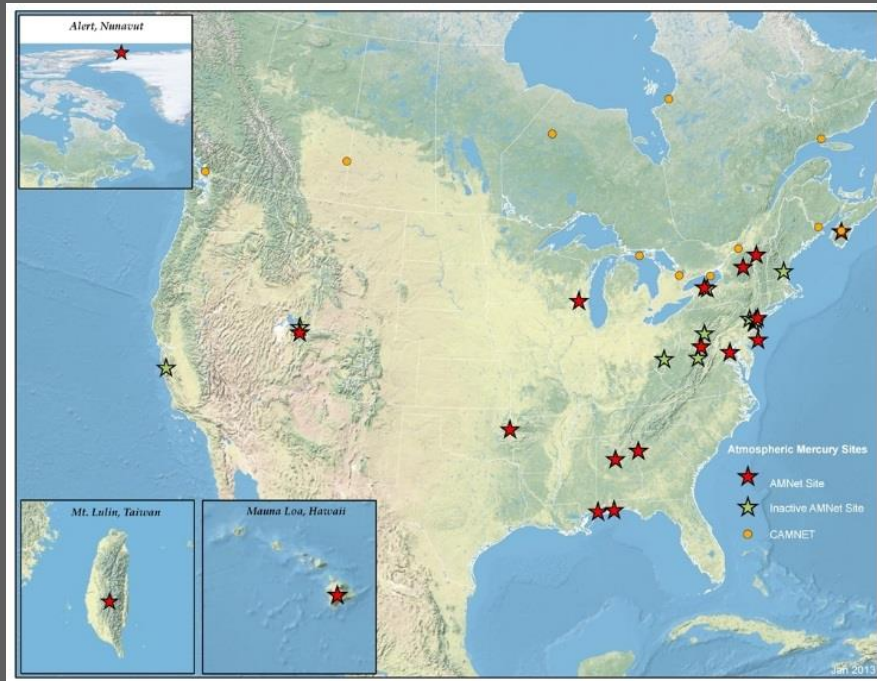
- USA Hg Emission Regulations proved that control and measurement possible at $< 1 \text{ ug/m}^3$ ($\sim 100 \text{ pptv}$)
- Using sorbent trap reference method (EPA 30B) was a big improvement for HgCEM performance studies and validating accuracy at $< 1 \text{ ug/m}^3$ ($\sim 100 \text{ pptv}$)
- Choosing high performance HgCEM equipment for control technology evaluation, process monitoring and regulatory compliance can result in large economic benefits.

Tools to Evaluate the Benefits of Lower Mercury Emissions in Ambient Air

- Coordinated air mercury networks
- New mercury passive sampler capable of measuring background mercury levels (1-2 ng/m³)

Atmospheric Mercury Network (AMNet)

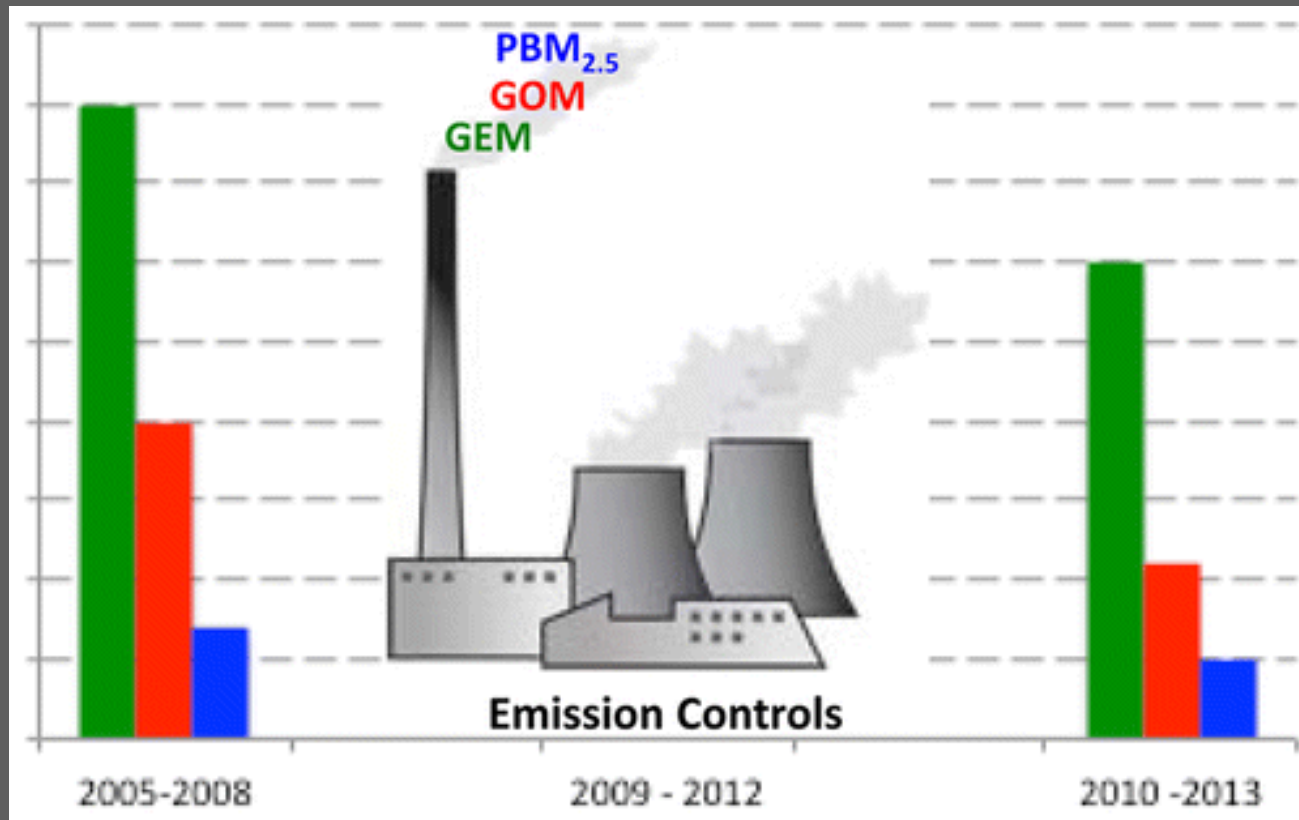
USA * CANADA * ASIA



- Purpose - Establish a mercury speciation network to support:
 - dry deposition estimates
 - emission regulation impacts
 - model evaluation
 - long-term trends
- Required Equipment
 - Tekran Atmospheric Speciation System 2537-1130-1135
- <http://nadp.slh.wisc.edu/AMNet/>

Effectiveness of Mercury Emission Reductions

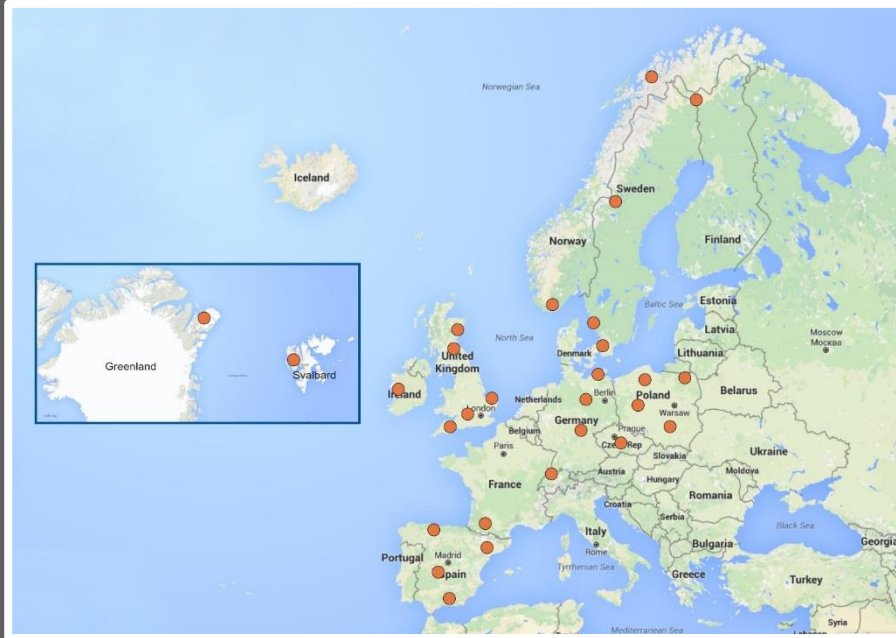
Air Mercury Network (AMNet) shows decrease in Hg levels



Castro & Sherwell, Effectiveness of Emission Controls to Reduce the Atmospheric Concentrations of Mercury, *Environ. Sci. Technol.*, 2015, 49 (24), pp 14000–14007

Coordination of EU Network and Data Management Recommended

EUROPE - Research and Monitoring Sites



Map is only partial listing of all EU sites

- EMEP in Europe – Level 3 sites have Tekran 2537-1130-1135 Systems
- Government Networks and Researchers in Europe use the Tekran 2537 including:
 - Germany, Italy,
 - Poland, Finland,
 - Sweden, Norway,
 - France, Spain,
 - Iceland, Ireland,
 - Great Britain,
 - Austria, Switzerland
 - Czech Republic, Greece,
 - Slovenia, Denmark,
 - Lithuania

MerPAS Development Summary

Mercury Passive Air Sampler

- Developed at U. of Toronto by McLagan, Wania and Mitchell
- Global study showed MerPAS is highly sensitive, accurate and precise for ambient air levels (1-5 ng/m³)
- Study completed (in press) to quantify annual emissions at a former mercury mine (max 6.7 ug/m³)
- Further studies underway for performance in indoor air and extreme concentrations (up to mg/m³)
- Tekran is commercializing sampler through licensing agreement with U. Toronto and scientists

MerPAS Features

- No power required
- No skill needed to deploy & retrieve
- Low cost – low temporal resolution
- Range likely unlimited (1 ng/m³ to 10 mg/m³)*
- Relatively immune to wind and temperature effects
- Uses well known Radiello diffusive barrier
- Highly tested and characterized

* See specifics in subsequent slide



Former Hg Mine Site Mapping

McLagan et al., 2018 (submitted)

- Values in ng/m^3
- Area survey around mine
- 41 km^2
- 3-Month sample deployment
- Range 1.3 to 150 ng/m^3
- Seasonal differences

