# Is it Possible to Accurately Measure Ambient Air Mercury at the Low Part Per Quadrillion Level Using Passive Samplers

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*NADP Fall Symposium 2018*

UNIVERSITY OF TORONTO


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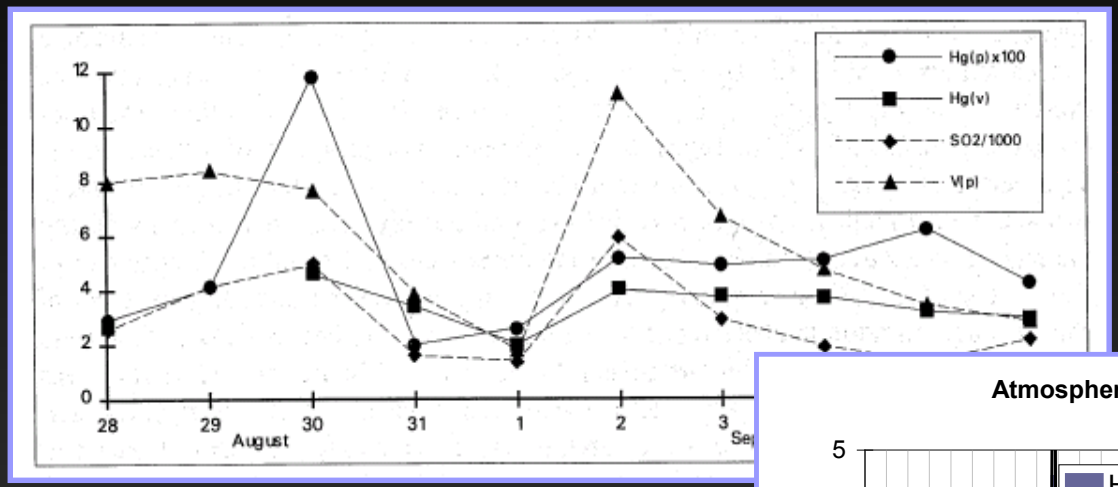
# New methods have increase our understanding of atmospheric mercury species behavior



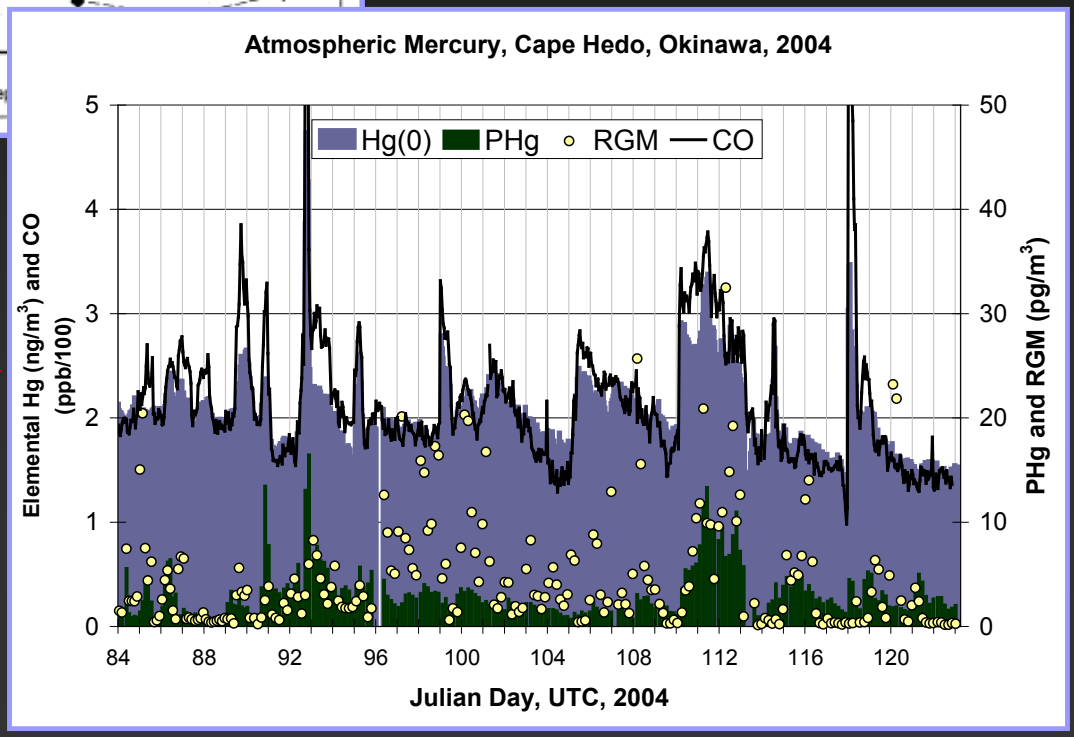

**1993**

24 hour manual method for TGM and $Hg_p$

**2004**

5-min automated for $Hg^0$; hours for RGM & $Hg_p$

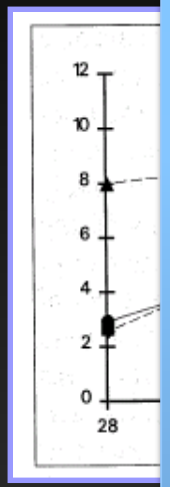
Use of and improvement in ancillary measurements has also been important




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

TEKRAN Instruments Corporation

# New methods have increase our understanding of atmospheric mercury species behavior




Using passive samplers and lab analysis appears to be taking a step backwards for ambient air monitoring at first thought. But now with Minimata compliance, low-tech air mercury monitoring is needed and necessary to compliment electronic high resolution air mercury fate & effects measurements.

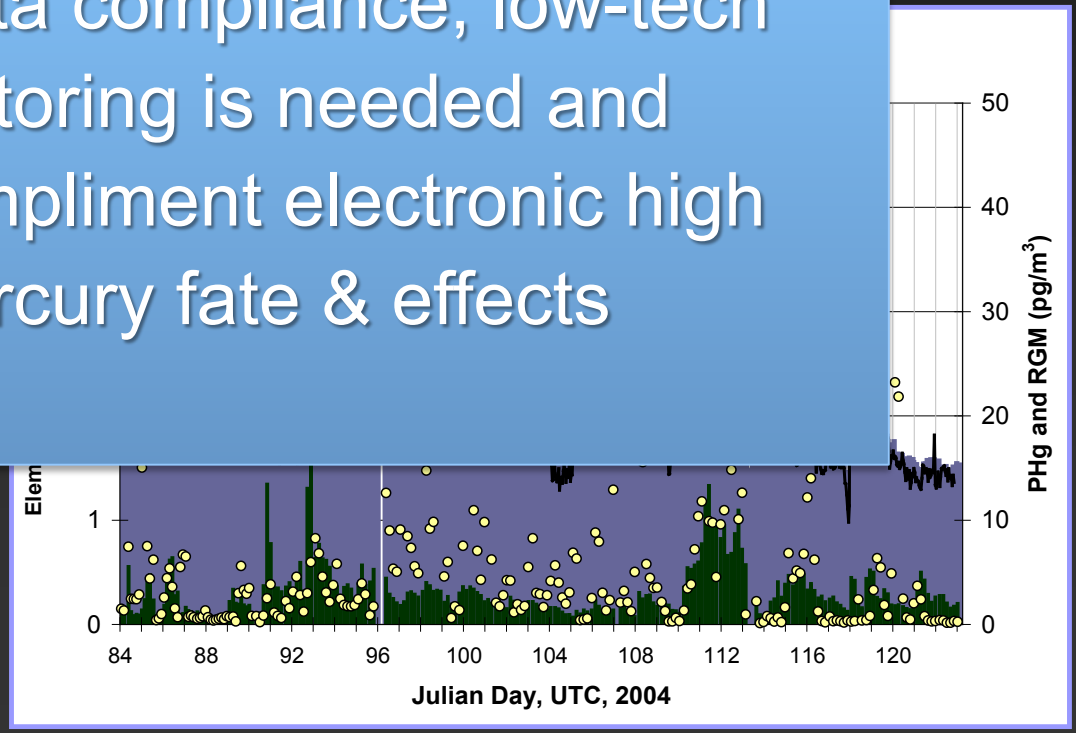
ethod

**200**

5-min

hours

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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# *Mer*PAS Development Summary

- Developed at U. of Toronto by David McLagan, Frank Wania and Carl Mitchell
- U. of Toronto global study documented that MerPAS is capable of accurate and precise background ambient air measurements (1-3 ng/m$^3$ = 100-350 ppqv).
- On-going studies for contaminated sites and indoor air
- Tekran is commercializing sampler through licensing agreement with U. of Toronto and scientists

# MerPAS Studies
# U. of Toronto

ENVIRONMENTAL Science & Technology LETTERS
Letter
pubs.acs.org/journal/estlcu

## A High-Precision Passive Air Sampler for Gaseous Mercury

David S. McLagan,[†] Carl P. J. Mitchell,[†] Haiyong Huang,[†] Ying Duan Lei,[†] Amanda S. Cole,[‡] Alexandra Steffen,[‡] Hayley Hung,[‡] and Frank Wania*[,†]

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Supporting Information

ABSTRACT: Passive air samplers (PASs) provide an opportunity to improve the spatial range and resolution of gaseous mercury (Hg) measurements. Here, we propose a sampler design that combines a sulfur-impregnated activated carbon sorbent, a Radiello diffusive barrier, and a protective shield for outdoor deployments. The amount of gaseous Hg taken up by the sampler increased linearly with time for both an 11-week indoor ($r^2$ = 0.990) and 12-month outdoor ($r^2$ = 0.996) deployment, yielding sampling rates of 0.158 ± 0.008 $m^3$ $day^{-1}$ indoors and 0.121 ± 0.005 $m^3$ $day^{-1}$ outdoors. These sampling rates are close to modeled estimates of 0.166 $m^3$ $day^{-1}$ indoors and 0.129 $m^3$ $day^{-1}$ outdoors. Replicate precision is better than for all previous PASs for gaseous Hg, especially during outdoor deployments (2 ± 1.3%). Such precision is essential for discriminating the relatively small concentration variations occurring at background sites. Deployment times for obtaining reliable time-averaged atmospheric gaseous Hg concentrations range from a week to at least one year.


Atmos. Meas. Tech., 10, 3651–3660, 2017
https://doi.org/10.5194/amt-10-3651-2017


Atmospheric Measurement Techniques
EGU Open Access

## The effects of meteorological parameters and diffusive barrier reuse on the sampling rate of a passive air sampler for gaseous mercury

**David S. McLagan, Carl P. J. Mitchell, Haiyong Huang, Batual Abdul Hussain, Ying Duan Lei, and Frank Wania**

Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1065 Military Trail, M1C 1A4, Toronto, Ontario, Canada

*Correspondence to:* Frank Wania (frank.wania@utoronto.ca)

Received: 15 March 2017 – Discussion started: 2 May 2017
Revised: 4 September 2017 – Accepted: 5 September 2017 – Published: 5 October 2017

## Characterization and Quantification of Atmospheric Mercury Sources Using Passive Air Samplers

David S. McLagan,[1] Fabrizio Monaci,[2,*] Haiyong Huang,[1] Ying Duan Lei,[1] Carl P. J. Mitchell,[1] and Frank Wania[1,*]

[1] *University of Toronto Scarborough, Department of Physical and Environmental Sciences 1065 Military Trail, Toronto, Ontario, Canada M1C 1A4*

[2] *Università di Siena, Department of Life Sciences, via Mattioli 4, 53100 Siena, Italy*

Atmos. Chem. Phys., 18, 5905–5919, 2018
https://doi.org/10.5194/acp-18-5905-2018


Atmospheric Chemistry and Physics
EGU Open Access

## Global evaluation and calibration of a passive air sampler for gaseous mercury

**David S. McLagan[1], Carl P. J. Mitchell[1], Alexandra Steffen[2], Hayley Hung[2], Cecilia Shin[2], Geoff W. Stupple[2], Mark L. Olson[3], Winston T. Luke[4], Paul Kelley[4], Dean Howard[5], Grant C. Edwards[5], Peter F. Nelson[5], Hang Xiao[6], Guey-Rong Sheu[7], Annekatrin Dreyer[8], Haiyong Huang[1], Batual Abdul Hussain[1], Ying D. Lei[1], Ilana Tavshunsky[1], and Frank Wania[1]**

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Technical note

## Application of sodium carbonate prevents sulphur poisoning of catalysts in automated total mercury analysis

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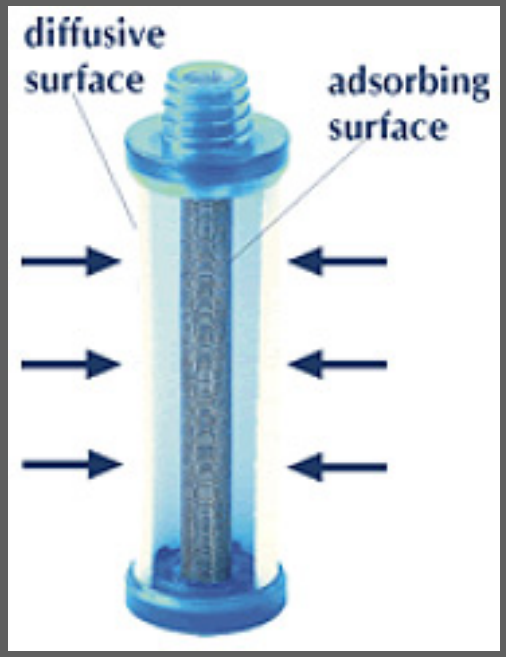
*Department of Physical & Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, ON M1C 1A4, Canada*

# Basics of *Mer*PAS


*High sulfur carbon media in stainless steel screen insert*




- Design resulted in precise, stable, robust **S**ampling **R**ate (**SR**)
- Jar provides protection, eliminates wind effects and used as a container for transport
- SR determined using the Tekran 2537 Hg Monitor

**Concentration derivation equation:**

gaseous Hg concentration (ng $m^{-3}$) — sampling rate ($m^3$ $day^{-1}$)

$$C = m / (SR * t)$$

mass of sorbed Hg (ng) — deployment time (days)

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# Challenges for Passive Measurement of Ambient Air Gaseous Elemental Mercury (GEM)

- Range of background GEM is 100-350 parts per quadrillion (ppqv)
- Passive samplers need a high level of accuracy and precision similar to active Tekran 2537 samples (e.g. uncertainty of 5-10%)
- Variability in sampling rate (SR = $m^3$/day) results in a loss of accuracy and precision
- Potential sources of SR variability
  - Changes in meteorology
  - Sorbent degradation
  - Low sorbent uptake capacity
  - Reactions of adsorbed analyte
  - Poor analytical sensitivity
  - Poor analytical blank control
  - Interfering compounds or particles

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# Global Study Sampling Locations


- All samplers deployed in triplicate for precision
- All sites have active Tekran 2537 GEM measurements
- Temperature and wind speed measured at each site
- Site colors indicated *Mer*PAS sample frequency

From McLagan et al., (https://doi.org/10.5194/acp-18-5905-2018)

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# Objectives

- Test previous calibrated SR (**0.121 $m^3$/day**) under variable meteorological and mercury levels at active monitoring sites
- Recalibrate SR using a greater pool of data
- Assess effectiveness of SR adjustment factors for T & WS established in McLagan et al. (2017)

# Methods & Calculations

**Analysis:**

thermal decomposition, amalgamation, & AAS (USEPA Method 7473) using a AMA254 (Leco)

**Concentration derivation equation:**

gaseous Hg concentration (ng $m^{-3}$) — sampling rate ($m^3$ $day^{-1}$)

$$C = m / (SR * t)$$

mass of sorbed Hg (ng) — deployment time (days)

**Sampling rate adjustment equation:** [6]

Adjusted sampling rate ($m^3$ $day^{-1}$) — Avg. temperature from experimental deployment (°C) — Temperature adjustment factor ($m^3$ $day^{-1}$ $°C^{-1}$) — Wind speed adjustment factor ($m^2$ s $day^{-1}$)

$$SR_{adj} = SR_{cal} + (T_{exp} - 10.0°C)*\mathbf{0.0009} + (WS_{exp} - 3.3\ m\ s^{-1})*\mathbf{0.0028}$$

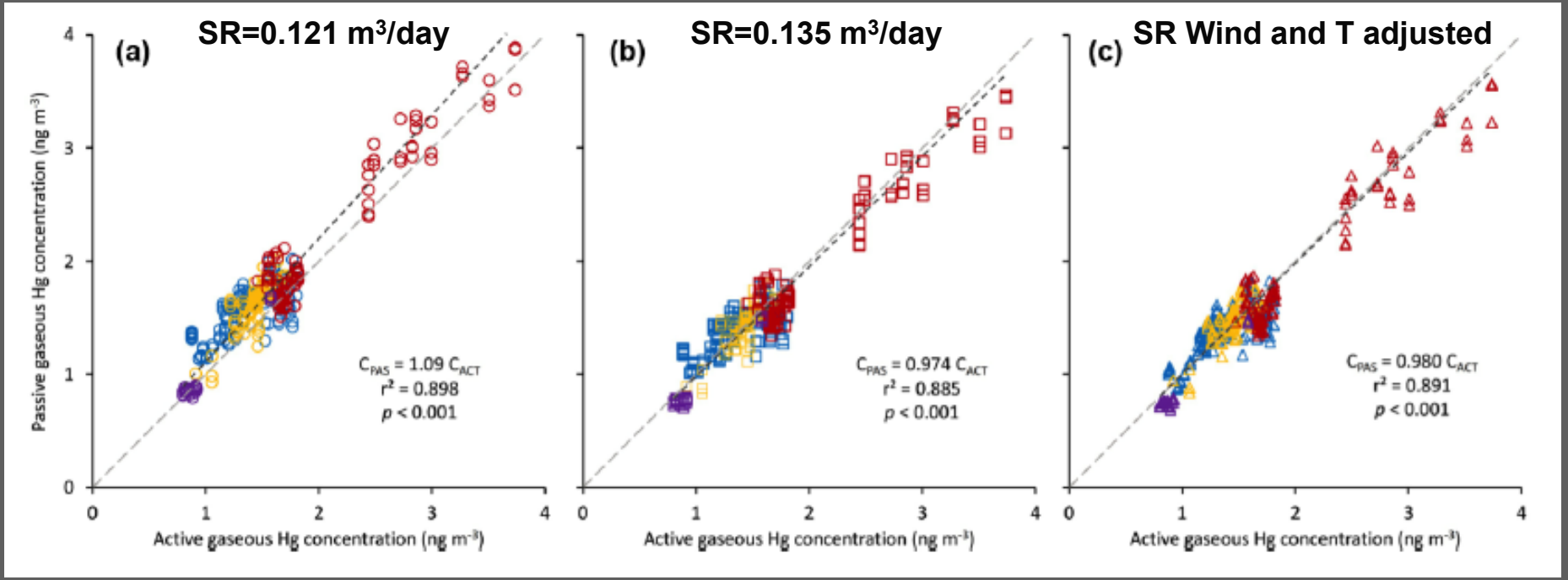
Previously calibrated sampling rate ($m^3$ $day^{-1}$) [2] — Avg. temperature from all calibration experiments – this study (°C) — Avg. wind speed from experimental deployment (m $s^{-1}$) — Avg. wind speed from all calibration experiments – this study (m $s^{-1}$)

From McLagan et al., (https://doi.org/10.5194/acp-18-5905-2018)

# *Mer*PAS Sample Rate Calibration ($m^3$/day)

Global ambient air study with "active" Tekran 2537 at 20 sites

- Range 1-4 ng/$m^3$ [GEM]  X-Axis Active  Y-Axis Passive
- Replicate Precision (RSD) = 3 ± 3 % (n=396)
- Accuracy Improved RPD 14 ±11% > 9 ± 8% > 8 ± 6% $m^3$/day




From McLagan et al., (https://doi.org/10.5194/acp-18-5905-2018)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# *Mer*PAS Features


- No power required
- Simple to deploy & retrieve
- Low entry cost – low temporal resolution
- Range likely unlimited (1 ng/m$^3$ to 10 mg/m$^3$)*
- Confirmed linear SR to ug/m$^3$ levels
- Relatively immune to WS and T effects
- Uses well known Radiello diffusive barrier

* See specifics in subsequent slide

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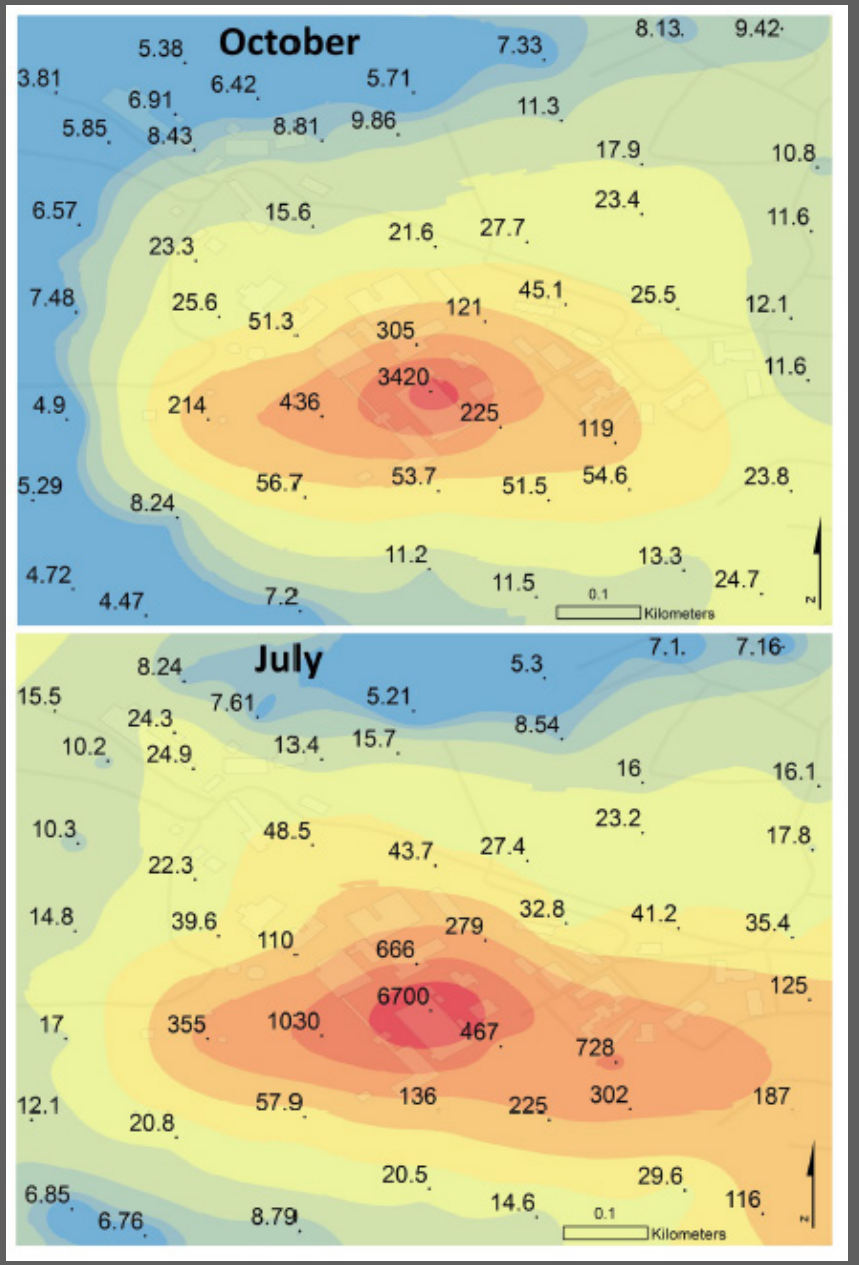
# Former Hg Mine Site Mapping

McLagan et al., 2018 (submitted)

- Values in ng/m$^3$
- Area of ~0.6 km$^2$
- Survey around mine site buildings
- 1-week sample deployment
- Seasonal differences

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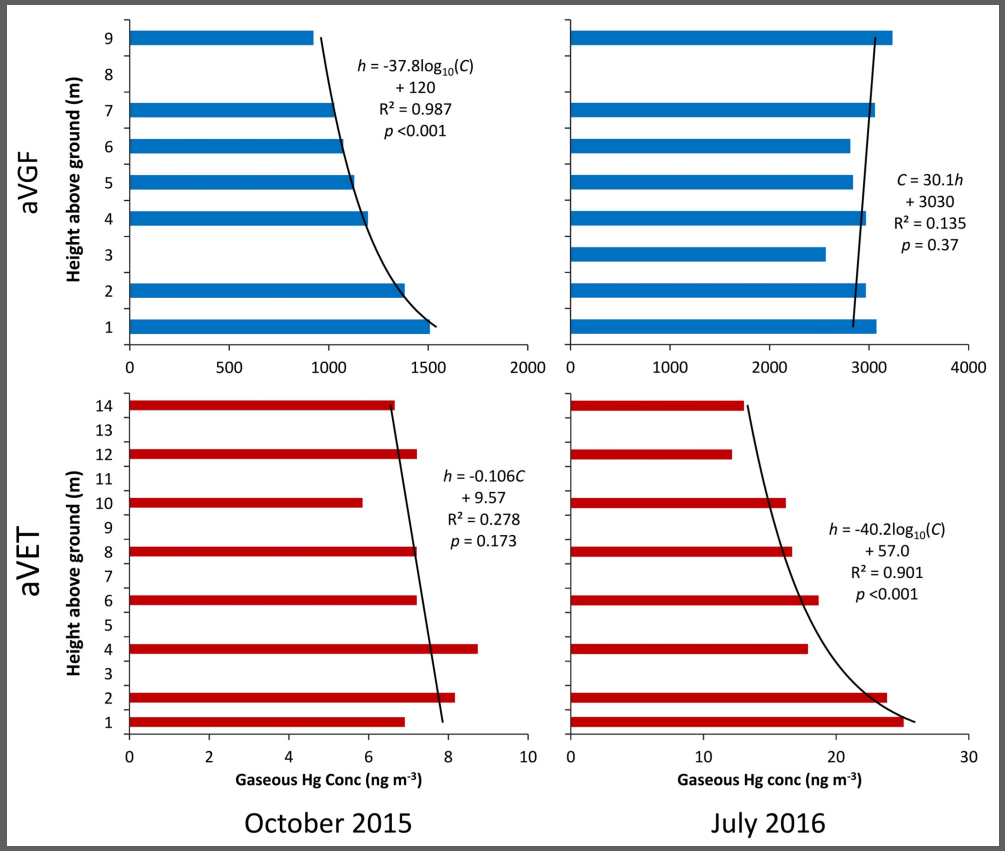
# Former Hg Mine Site Mapping

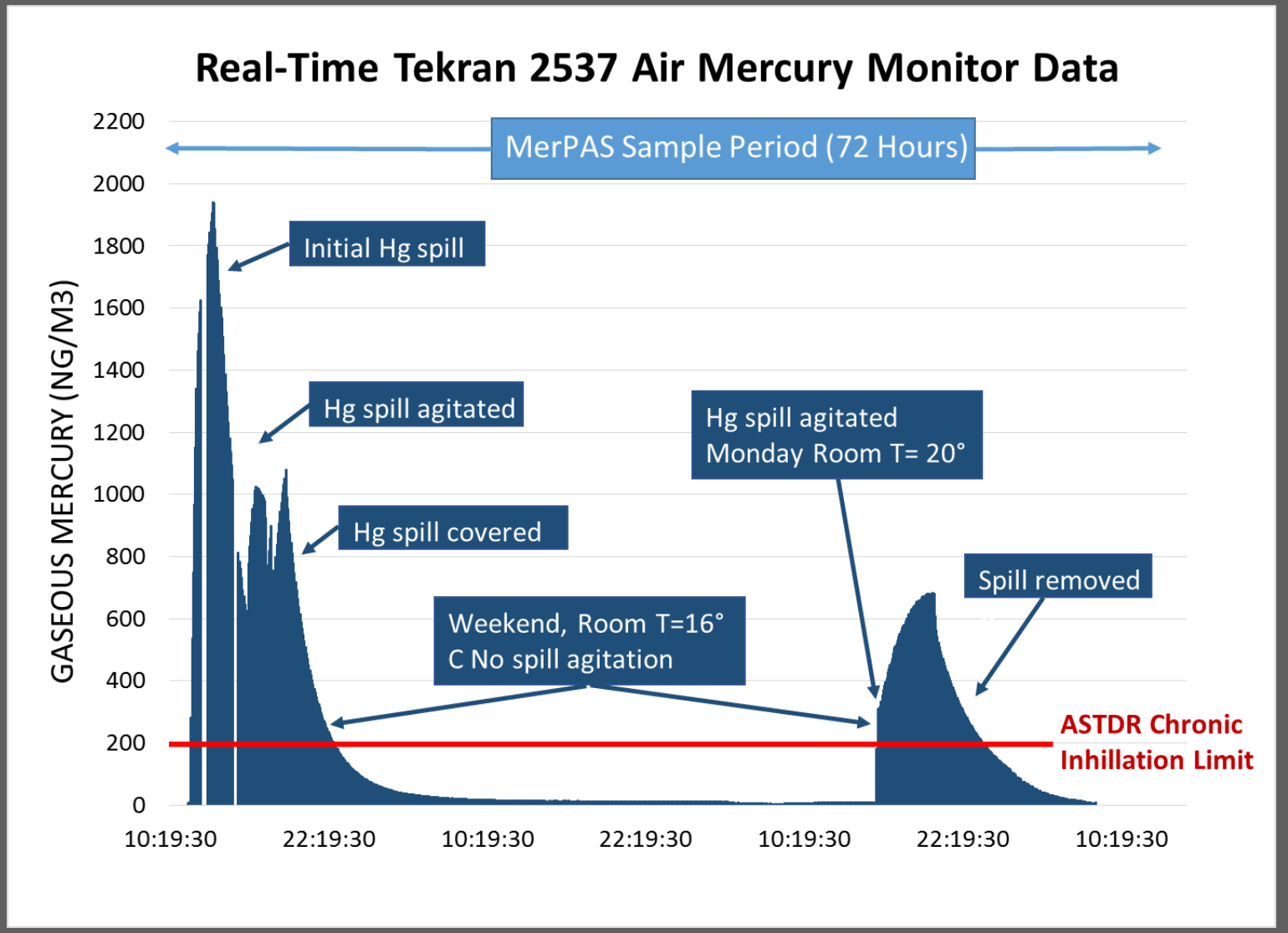
McLagan et al., 2018 (submitted)

- Emissions estimated at 80±40 and 150±75 kg/yr for October and July, respectively

*MerPAS Measured Vertical Gradients at former Hg Mine Site*



# MerPAS Example: Indoor Mercury Spill

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# MerPAS Example: Indoor Mercury Spill

Mercury Spill

*Mer*PAS Samplers

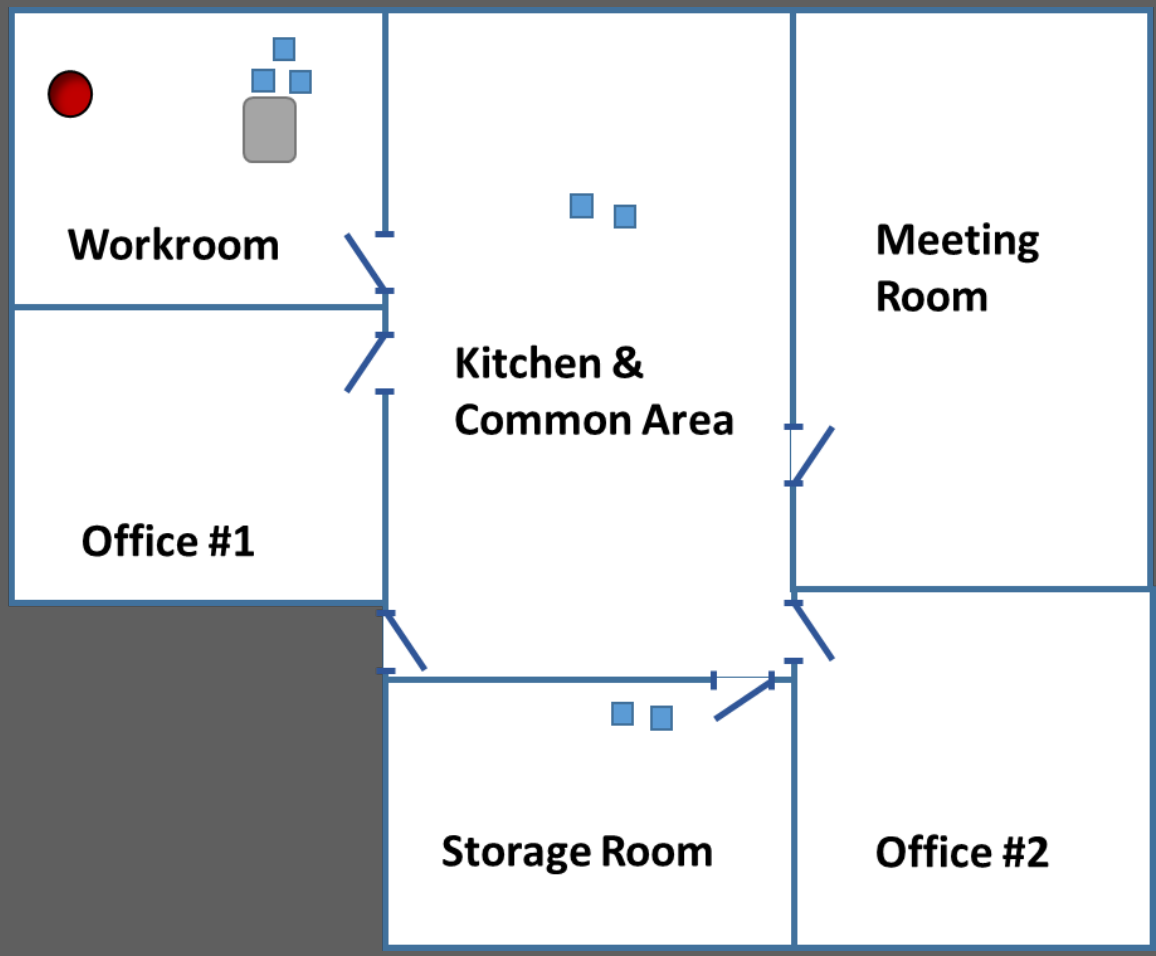
Tekran Monitor

Work Room *Mer*PAS = 200 ng/m$^3$

Work Room Tekran = 192 ng/m$^3$

Kitchen *Mer*PAS = 51.4 ng/m$^3$

Storage Room *Mer*PAS = 46.9 ng/m$^3$

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# *Mer*PAS Analysis

- Analysis must be done in a trace-clean analytical lab by skilled mercury chemists
- Direct thermal analysis is preferred, no acid digestion (EPA Method 7473)
- Multiple instrument vendors
- EPA Method 1631, acid digestion may be required for very high Hg loading (e.g. artisanal gold mining)


Nippon MA-3000

# Tekran *Mer*PAS Analysis

- Tekran is offering *Mer*PAS Analysis Service using the direct thermal analysis method (EPA method 7473)
- Tekran will offer to be an independent reference laboratory for national and international networks

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# *Mer*PAS Analysis Challenges - I

- The sulfur rich carbon sorbent is a tough matrix that can cause low bias, catalyst failure and gold trap degradation
- Matrix issues are mitigated with addition of sodium carbonate and limiting amount of sorbent for each analytical run
- Typical ambient air sample split into 2 or more runs of sorbent
- Many quality assurance samples must be run to maintain high quality results

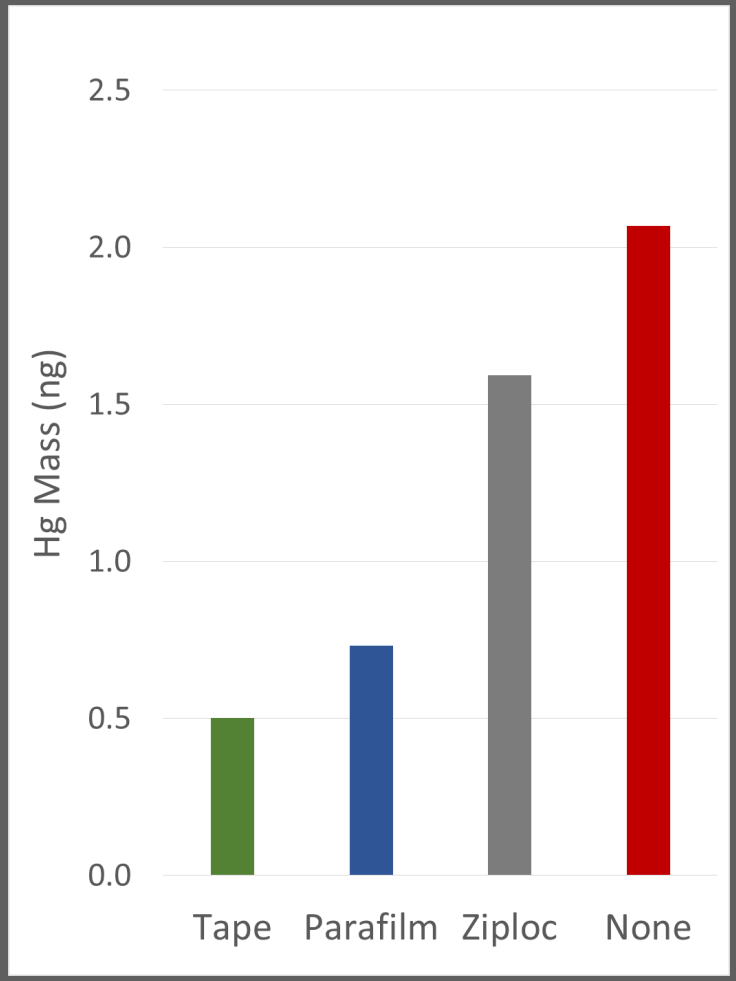
# *Mer*PAS Analysis Challenges - II

- Direct thermal analysis is destructive
  - Must transfer 100% of sorbent to analysis boat for accurate results
  - Easy to spill sorbent during preparation, weighing and transfer – loss of results can cause large data gaps
  - Easy for analytical run to go bad >> data gaps
- Blank control
  - Field blanks, trips blanks and material blanks are necessary to evaluate accuracy and performance of the site operator, shipping/storage and analyst.

# Blanks: Exposure to High Hg Levels

## Should tape be added to the jar lid seal?

- High Hg = 500-3000 ng/m$^3$
- ~9 days of blank exposure
- 2 separate tests
- Test B included carbon sorbent packet added to Ziploc bag
- Study lacks comparison to non-exposed preparation blanks
- Raw MerPAS carbon is ~0.04 ng per sample

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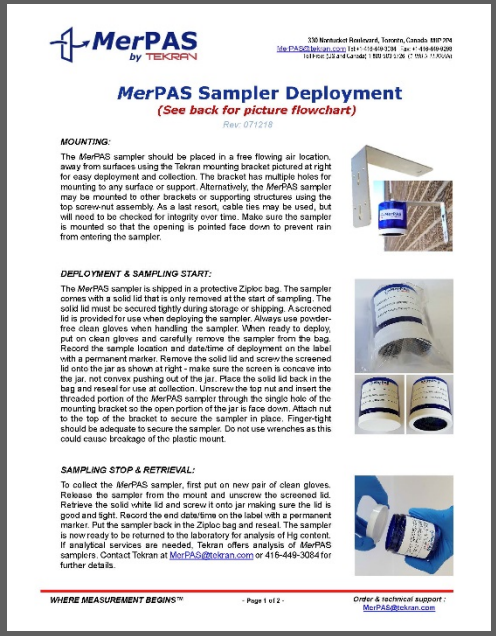
# *Mer*PAS Sampling Procedure

- Can include clean hands sampling kit
- Multiple mounting options
- Handwritten sample info or bar code may be used
- Sample location, blanks and replicates should be considered



MerPAS by TEKRAN

**MerPAS Sampler Deployment**

*(See back for picture flowchart)*

Rev: 071218

***MOUNTING:***

The MerPAS sampler should be placed in a free flowing air location, away from surfaces using the Tekran mounting bracket pictured at right for easy deployment and collection. The bracket has multiple holes for mounting to any surface or support. Alternatively, the MerPAS sampler may be mounted to other brackets or supporting structures using the top screw-nut assembly. As a last resort, cable ties may be used, but will need to be checked for integrity over time. Make sure the sampler is mounted so that the opening is pointed face down to prevent rain from entering the sampler.

***DEPLOYMENT & SAMPLING START:***

The MerPAS sampler is shipped in a protective Ziploc bag. The sampler comes with a solid lid that is only removed at the start of sampling. The solid lid must be secured tightly during storage or shipping. A screened lid is provided for use when deploying the sampler. Always use powder-free clean gloves when handling the sampler. When ready to deploy, put on clean gloves and carefully remove the sampler from the bag. Record the sample location and date/time of deployment on the label with a permanent marker. Remove the solid lid and screw the screened lid onto the jar as shown at right - make sure the screen is concave into the jar, not convex pushing out of the jar. Place the solid lid back in the bag and reseal for use at collection. Unscrew the top nut and insert the threaded portion of the MerPAS sampler through the single hole of the mounting bracket so the open portion of the jar is face down. Attach nut to the top of the bracket to secure the sampler in place. Finger-tight should be adequate to secure the sampler. Do not use wrenches as this could cause breakage of the plastic mount.

***SAMPLING STOP & RETRIEVAL:***

To collect the MerPAS sampler, first put on new pair of clean gloves. Release the sampler from the mount and unscrew the screened lid. Retrieve the solid white lid and screw it onto jar making sure the lid is good and tight. Record the end date/time on the label with a permanent marker. Put the sampler back in the Ziploc bag and reseal. The sampler is now ready to be returned to the laboratory for analysis of Hg content. If analytical services are needed, Tekran offers analysis of MerPAS samplers. Contact Tekran at MerPAS@tekran.com or 416-449-3084 for further details.

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MerPAS by TEKRAN

DEPLOYMENT & SAMPLING START

1. Open bag - use gloves!
2. Remove lid and sample
3. Remove solid lid & put in bag
4. Attach screened lid to jar
5. Good concave screen shape
6. Bad convex screen shape
7. Label sample with date/time
8. Unscrew top nut
9. Attach jar to bracket
10. Proper MerPAS mounting

SAMPLING STOP & RETREIVAL

11. To collect, remove top nut
12. Removed screened lid
13. Retrieve solid lid
14. Screw on solid lid TIGHTLY!
15. Record sample end time
16. Seal in Bag

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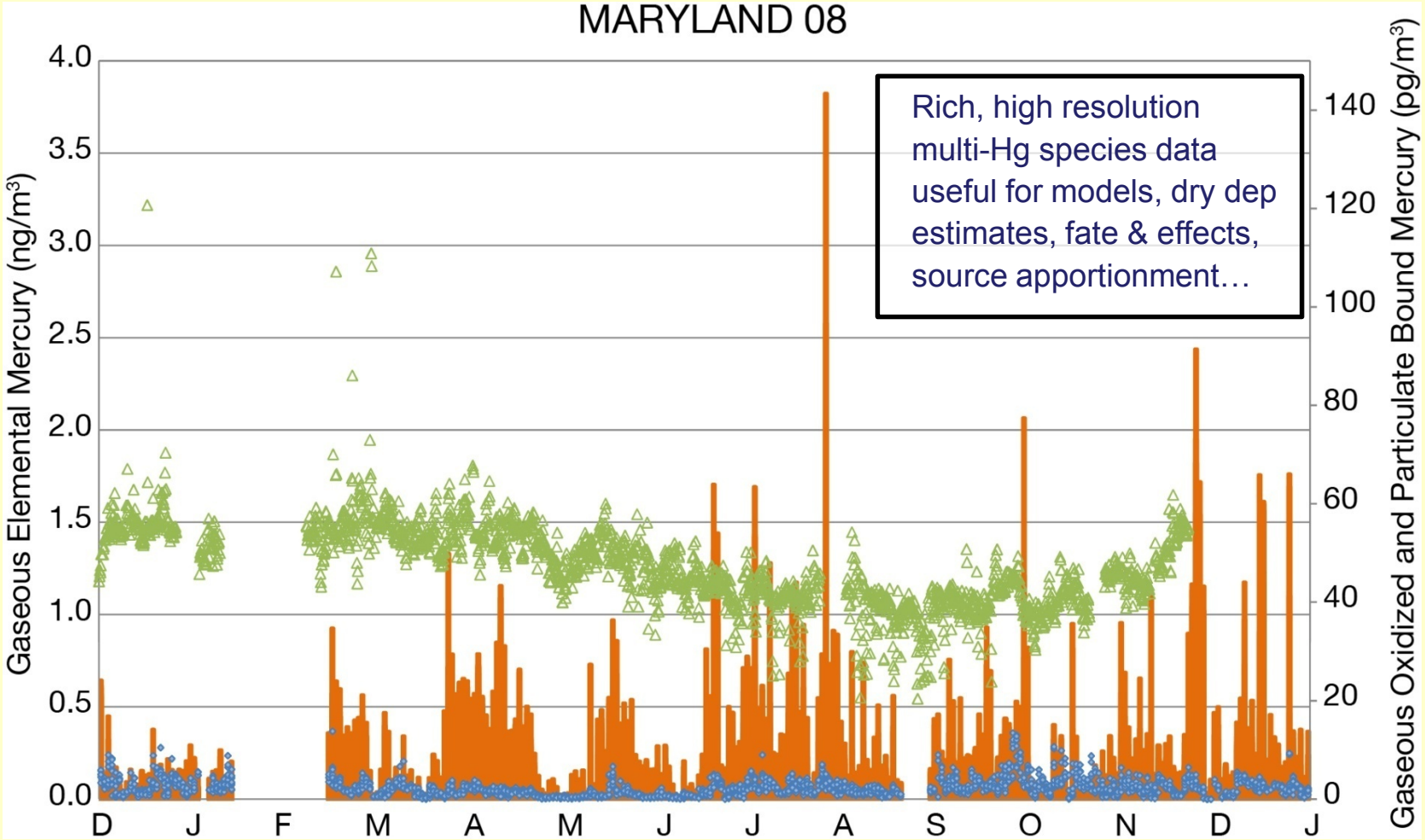
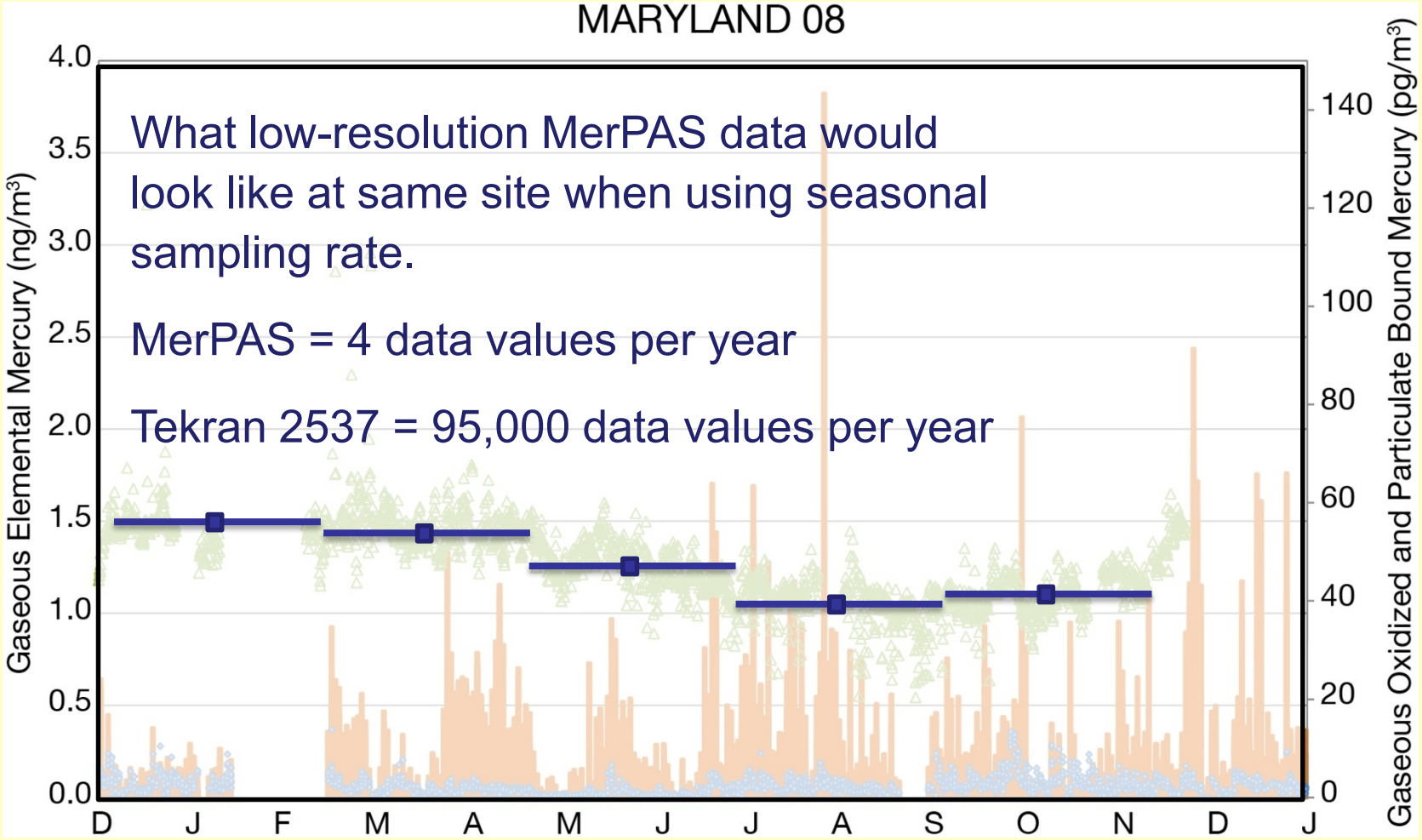
# AMNet Rural Site

## Close to high emission source region



# AMNet Rural Site

## Close to high emission source region



# Select Applications for Minimata & Exposure

*Vertical profile industry site*

- Artisanal gold mining
- Identifying and mapping hot spots
- Community exposure monitoring
- Contaminated site cleanup monitoring
- Indoor spill cleanup and monitoring

- Personal exposure industry, schools, workplace & homes
- Area source emission estimates (high spatial resolution and vertical gradients)

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# Select Applications for Fate & Effects

- Remote Sites – No Power
  - National Parks & Federal Lands
  - High Elevation Sites
  - Industrial Fence Line (e.g. gold smelters)
  - Agriculture Land Use Studies
  - Gradient and Canopy Studies
- NADP MDN and Litterfall Sites
- AMNet - SR confirmation
- GAPS Global Atm. Passive Sampling Network
  (ECCC, Sandy Steffen Initiative)


*Remote Canopy Deployment*

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# Why Use *Mer*PAS

- Radial diffusive surface has better performance than 2-D badge type passive air samplers
- Proven to be highly accurate and precise
- Media has low consistent blanks and massive uptake capacity
- Robust packaging and simple to deploy
- Direct thermal analysis can be faster, easier and lower cost compared to liquid acid digestion and analysis

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