MerPAS by TEKRAN

*Mer*cury Passive Air Sampler

UNIVERSITY OF TORONTO

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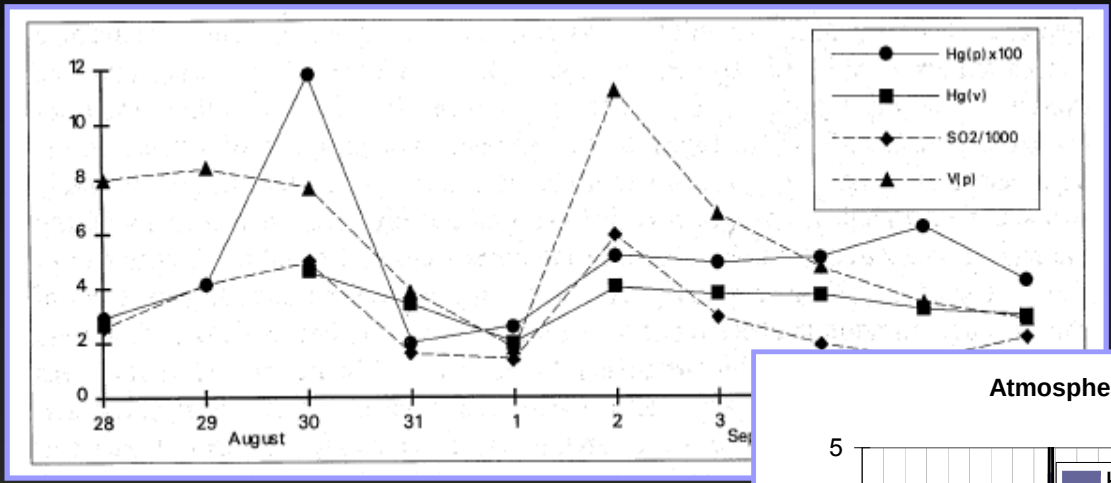
New methods have increase our understanding of atmospheric mercury species behavior



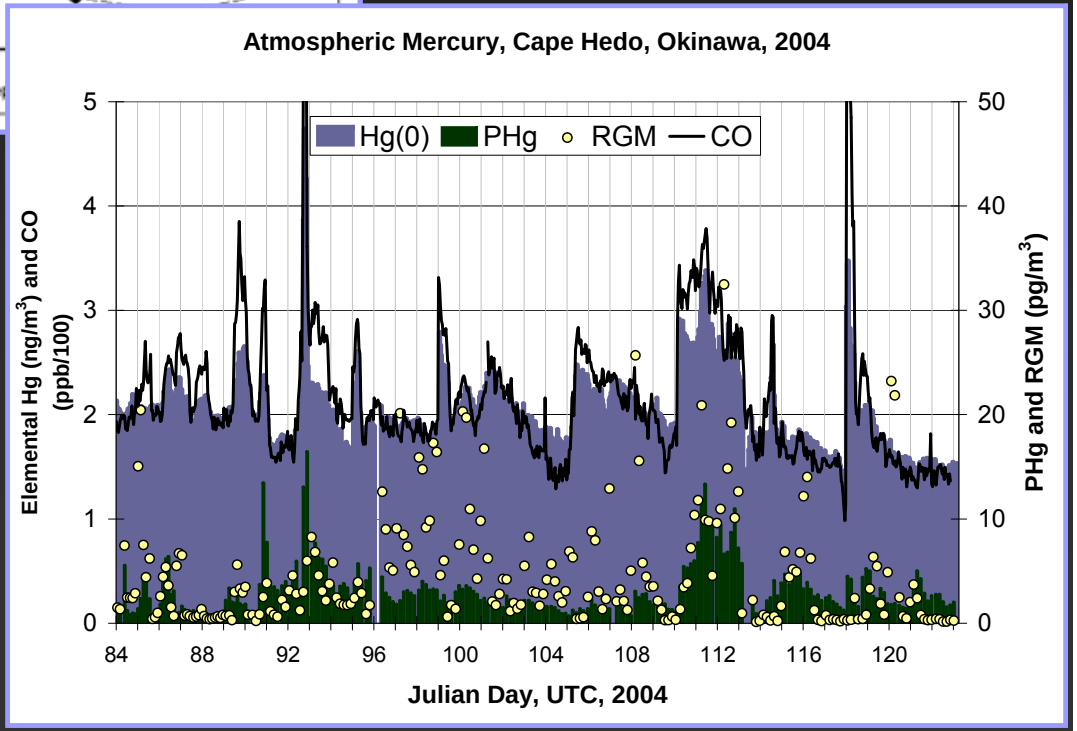
1993

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.*

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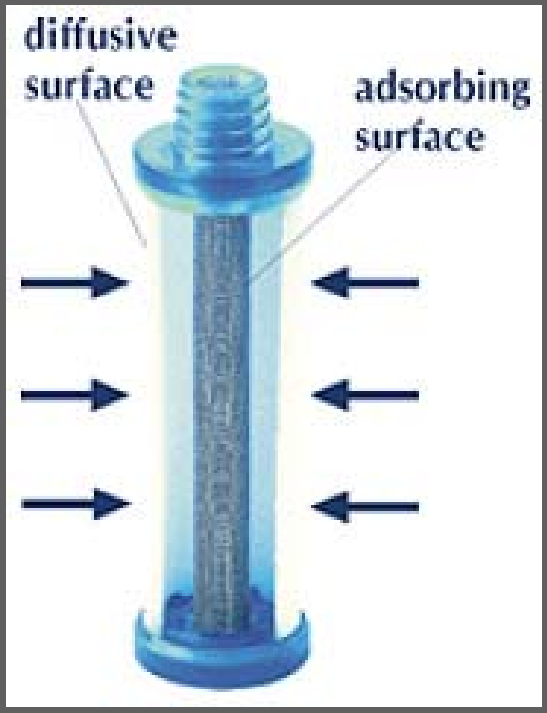
Basics of *Mer*PAS



- 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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*Mer*PAS Development Summary

- 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/m^3). Only passive sampler capable of accurate and precise ambient air measurements.
- Study completed (in press) to quantify annual emissions at a former mercury mine (max 6.7 ug/m^3)
- Further studies underway for performance in indoor air and extreme concentrations (up to mg/m^3)
- Tekran is commercializing sampler through licensing agreement with U. Toronto and scientists

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MerPAS Studies
U. of Toronto

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

A High-Precision Passive Air Sampler for Gaseous Mercury

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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
Open Access
EGU

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

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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

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

Atmospheric Chemistry and Physics
Open Access
EGU

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

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Received: 23 December 2017 – Discussion started: 8 February 2018
Revised: 10 April 2018 – Accepted: 12 April 2018 – Published: 26 April 2018

Spectrochimica Acta Part B 133 (2017) 60–62
Contents lists available at ScienceDirect
Spectrochimica Acta Part B
journal homepage: www.elsevier.com/locate/sab

Technical note

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

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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)*
- Relatively immune to wind and temperature effects
- Uses well known Radiello diffusive barrier
- Highly tested and characterized

* See specifics in subsequent slide

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Select Applications

- Remote sites – no power
- Artisanal gold mining
- Identifying and mapping hot spots
- Community exposure monitoring
- Contaminated site cleanup monitoring
- Indoor spill cleanup and monitoring

Vertical profile industry site

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

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

using the Tekran 2537 at 20 sites

- Global ambient air study – sensitive, precise, accurate
- From McLagan et al., (https://doi.org/10.5194/acp-18-5905-2018)

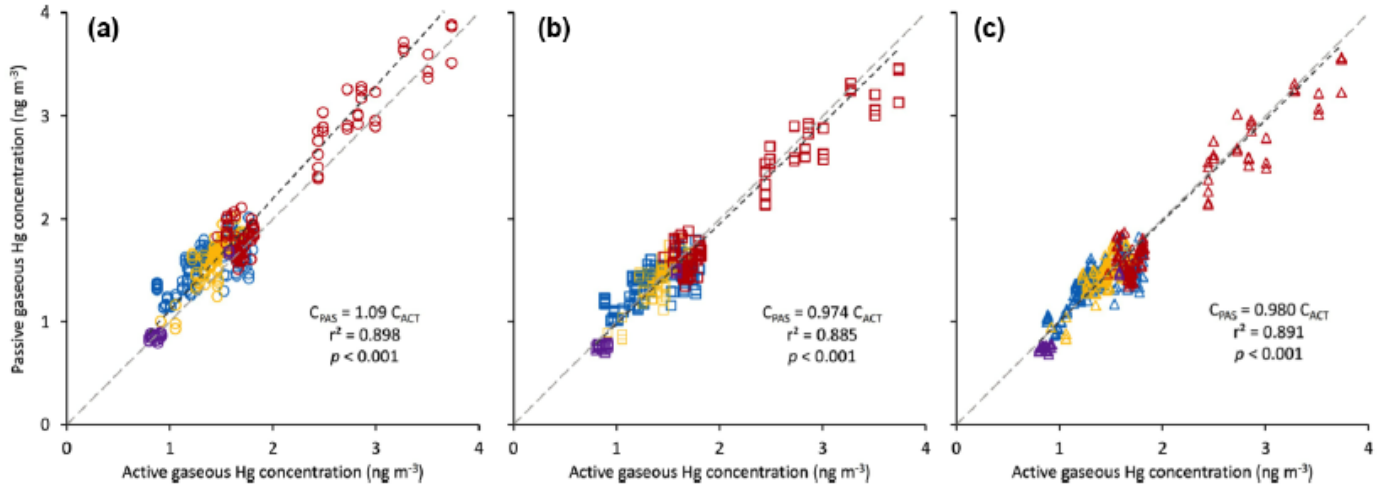

Figure 3. Comparison of active (C_{ACT}; x axis) and passive (C_{PAS}; y axis) gaseous Hg concentrations derived from the original sampling rate (SR; circles in **a**), recalibrated SR (squares in **b**), and adjusted SR (triangles in **c**). Dotted lines represent the trend line for each dataset. Grey dashed line is the 1 : 1 relationship. Markers are coloured according to site type: red – urban sites; blue – rural sites; purple – high-altitude sites; and yellow – northern/Arctic sites. Fitted relationships are for all data combined.

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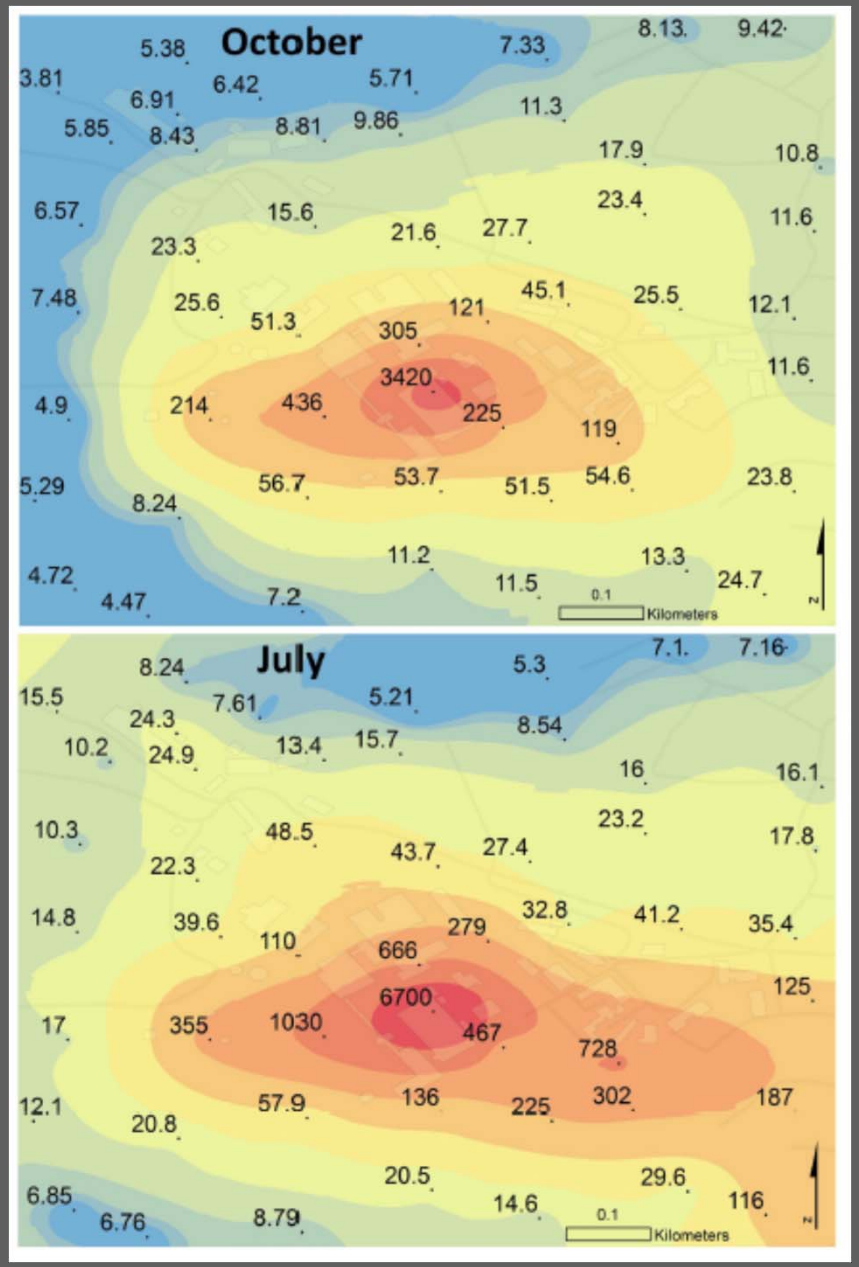
Former Hg Mine Site Mapping

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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*Mer*PAS Analysis

- Analysis must be done in a trace-clean analytical lab by skilled mercury chemists
- Direct thermal analysis is preferr no acid digestion (EPA Method 7473)

Nippon MA-3000

- Multiple instrument vendors ~$40-50K USD
- EPA Method 1631, acid digestion may be required for very high Hg loading (e.g. artisanal gold mining)

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Tekran *Mer*PAS Analysis

- Tekran is offering *Mer*PAS Analysis Service using the direct thermal analysis method (EPA method 7473)
- Our analysis team has over 90 years of experience all focused on mercury measurement
- 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 bicarbonate 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.

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Sample Range and Conditions

- Carbon media capable of adsorbing Hg up to 10% by weight
- Proven for ambient air (~1-20 ng/m^3). Integrated sample time of 1-week minimum up to 1 year maximum.
- Proven for former mercury mine site and surrounding area. Integrated sample time of 1-week for low ug/m^3 levels
- For sites with mean air Hg > 100 ug/m^3
  - Short sample times may be necessary (hours)
  - For longer sample times, analysis will require more analytical runs or may be done using EPA Method 1631E.
  - Depending on project goals, obtaining a representative result may necessitate using multiple *Mer*PAS samplers for each measurement location

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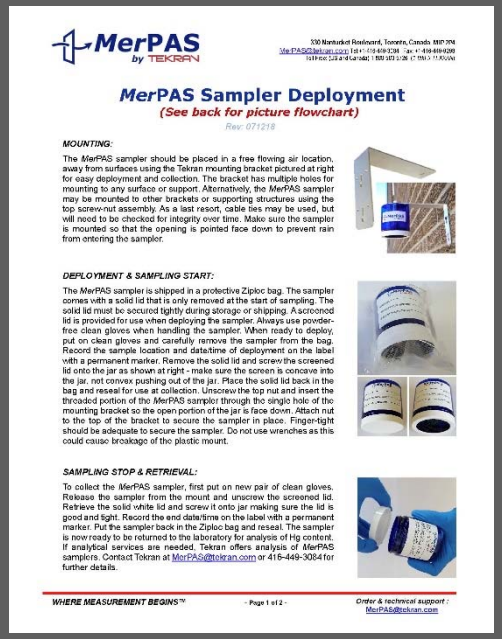
*Mer*PAS Sampling Procedure

- 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



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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.

WHERE MEASUREMENT BEGINS™ - Page 1 of 2 - Order & technical support : MerPAS@tekran.com

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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

SAMPLING STOP & RETREIVAL

9. Attach jar to bracket
10. Proper MerPAS mounting
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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Tekran *Mer*PAS Updates

- Weatherproof plastic label
- Bar Code ID
- More versatile bracket
- Threaded plastic panel mount Radiello and bracket attachment
- Developing electronic tracking to verify sample locations, times & chain of custody

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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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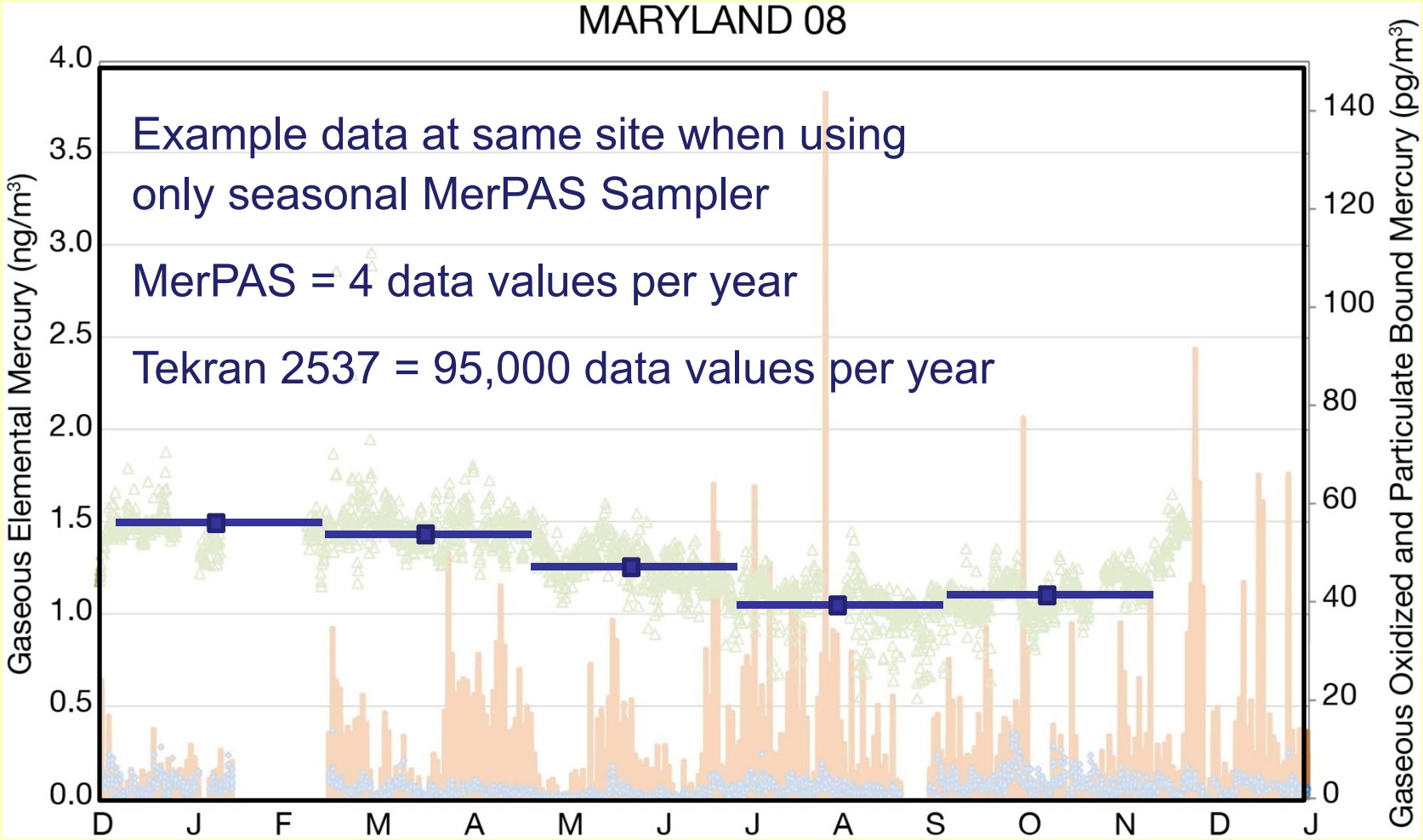
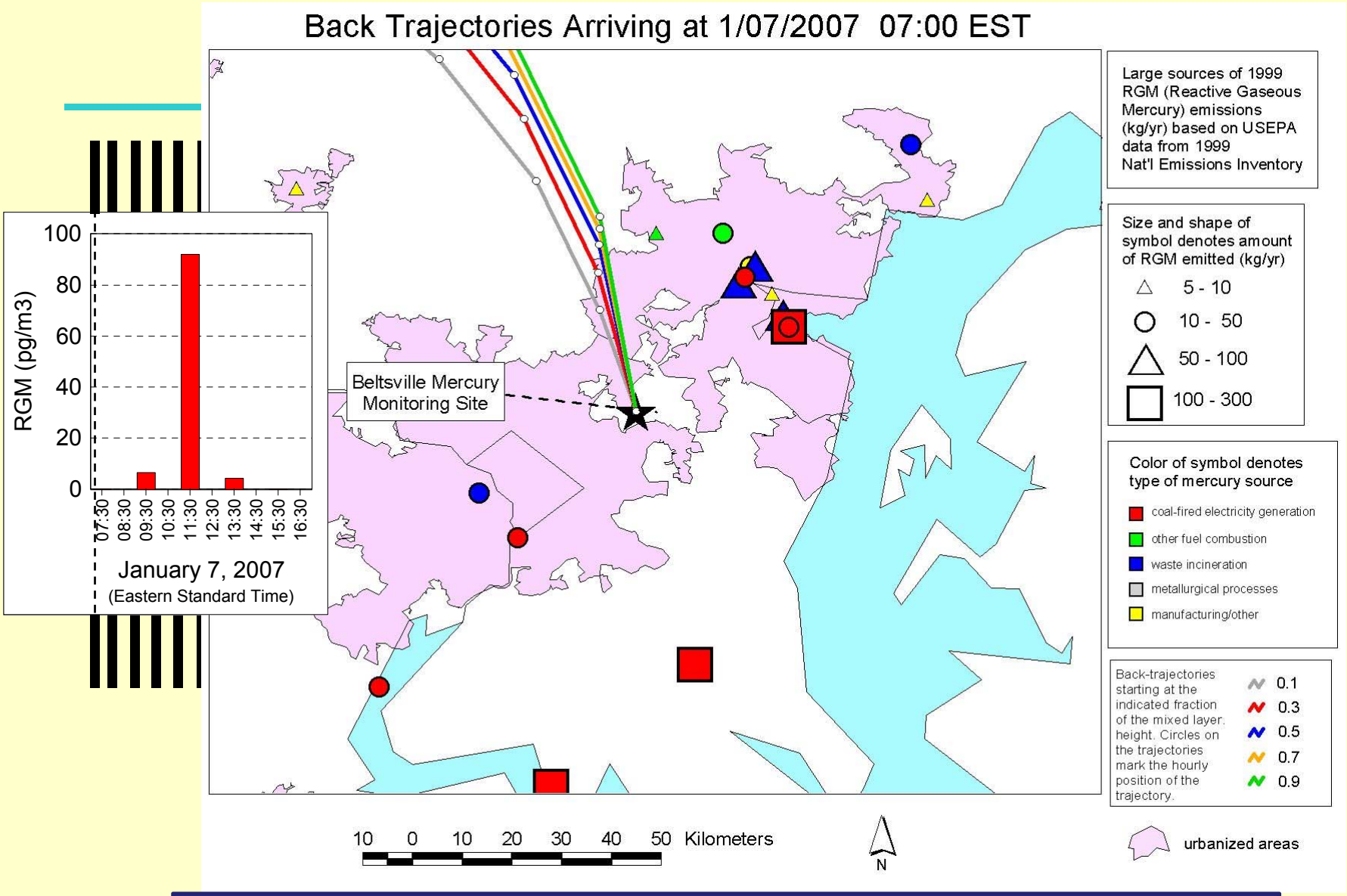
AMNet Rural Site

Close to high emission source region



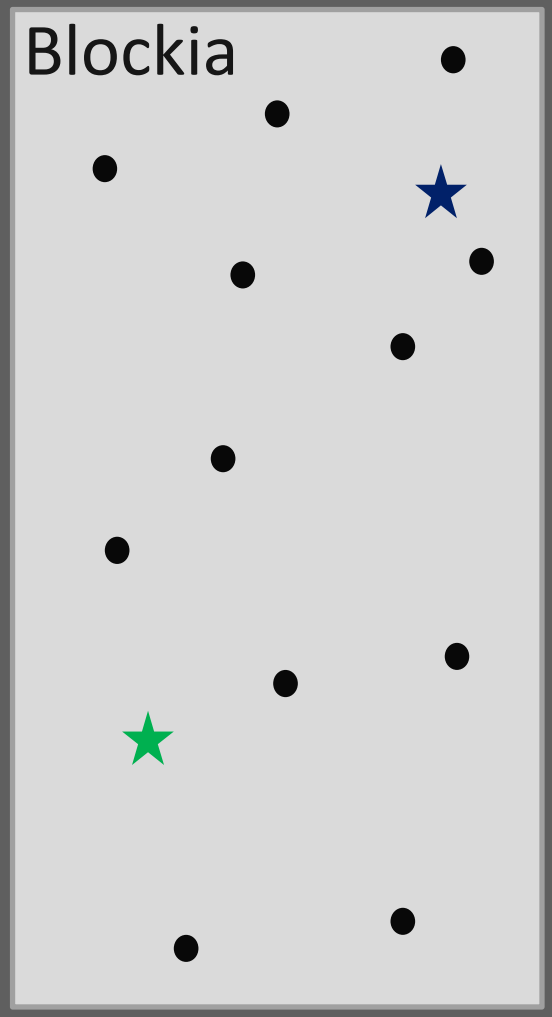
Real-Time Hg Speciation Monitoring Example

Winston Luke & Mark Cohen NOAA-ARL



Sometimes, we see evidence of local and regional "plume" impacts

Blockia Republic National Monitoring Plan



★ Urban Co-Located
MerPAS + Tekran 2537

★ Remote Co-Located
MerPAS + Tekran 2537

● MerPAS Only

Co-Located sites provides both high resolution data and ongoing calibration of the MerPAS method and results

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