

The fundamentals, importance and challenges of measuring atmospheric mercury speciation to support dry deposition estimates and models

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Why is mercury speciation and dry deposition important?

- Hg 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, remove rapidly from atmosphere
 - **PBM** (Hg on soot) remove rapidly by wet and dry deposition
- Atmospheric Transport and Deposition Modeling
- Bioaccumulation, Exposure and Risk Assessment

Linkage: Hg Sources to Exposure Measurement and Models are Critical

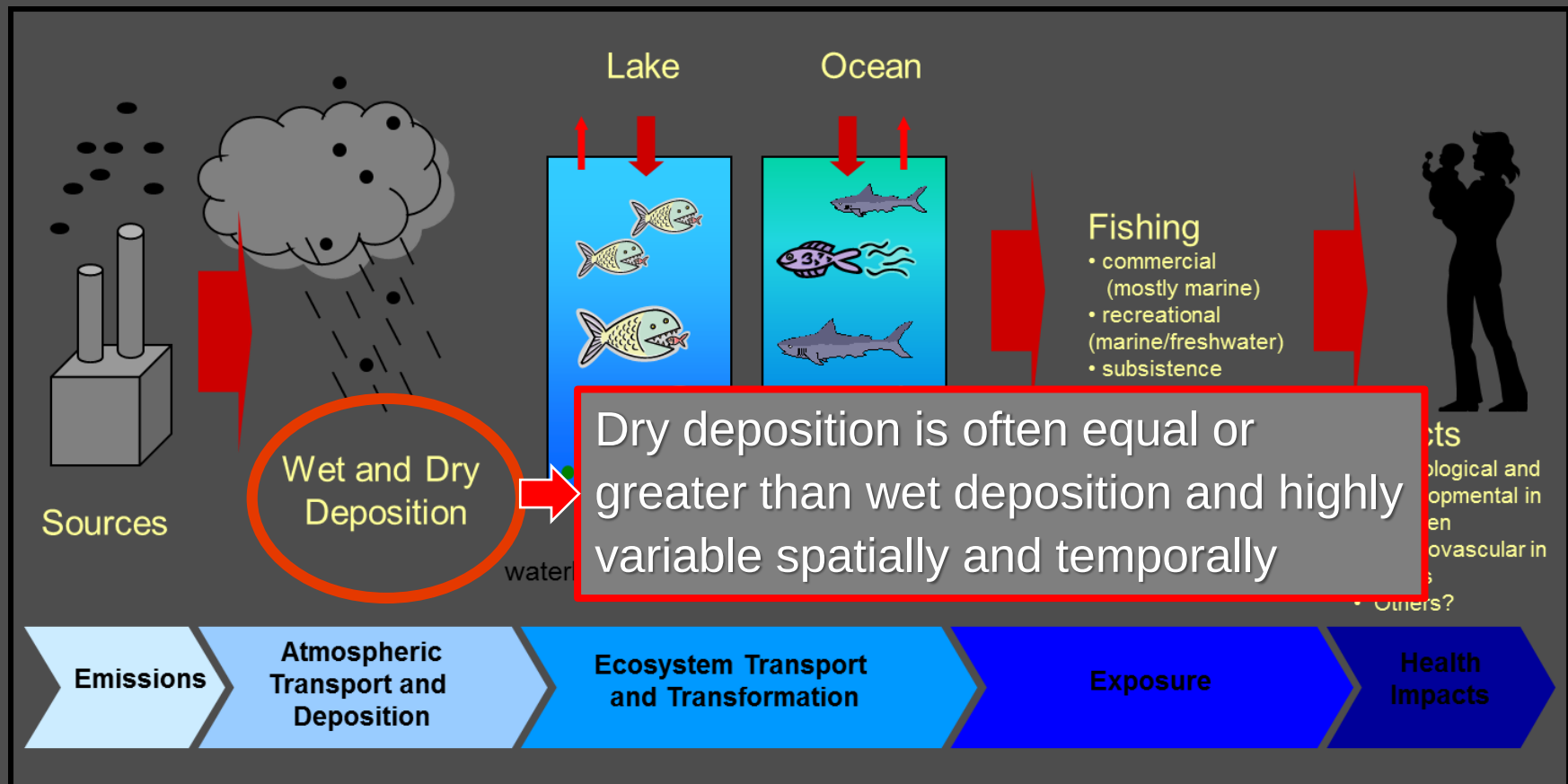
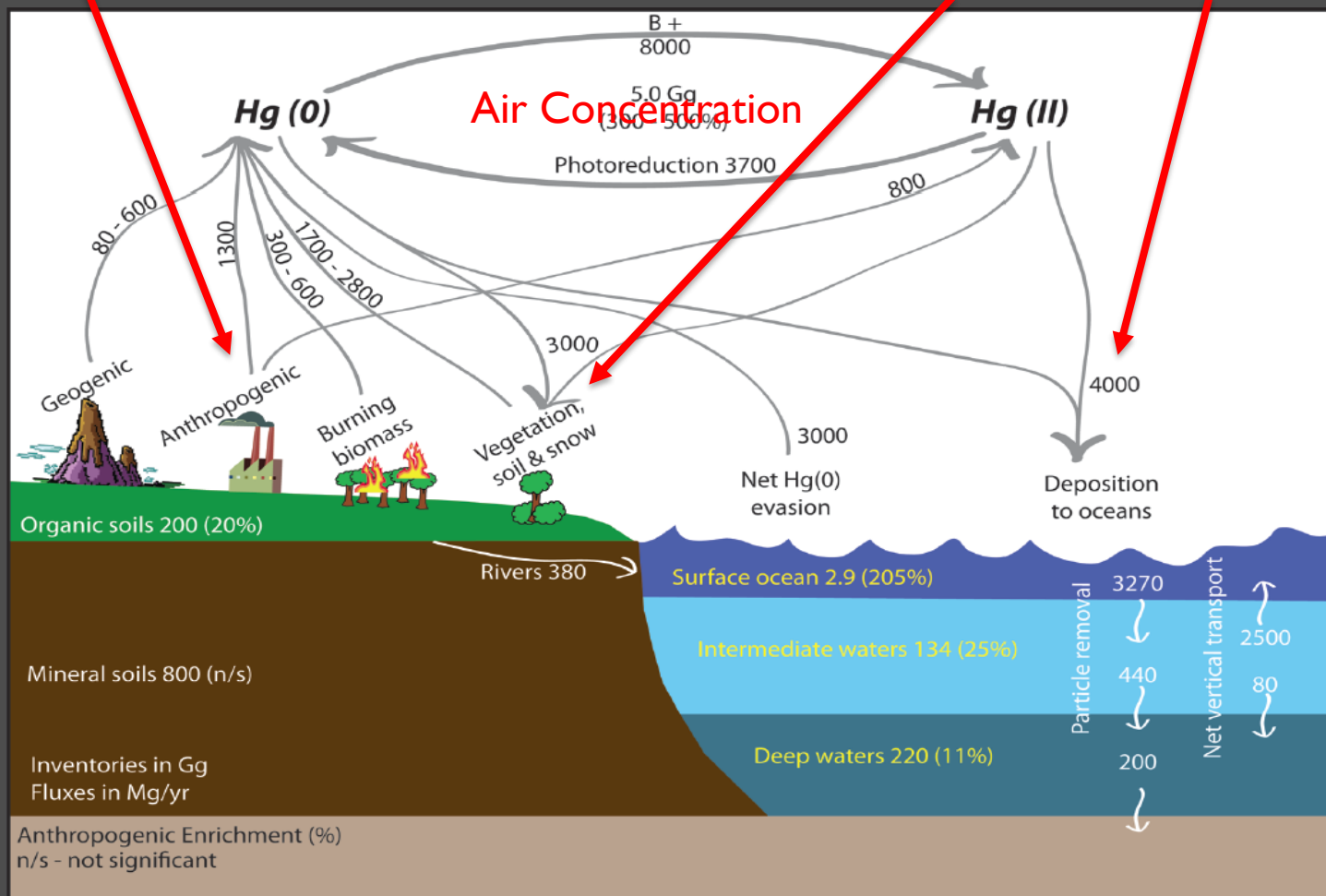


Figure courtesy of USEPA

Sources release mix of Hg chemical species!

Transport, transformation and meteorology produces variable Hg wet & dry deposition rates

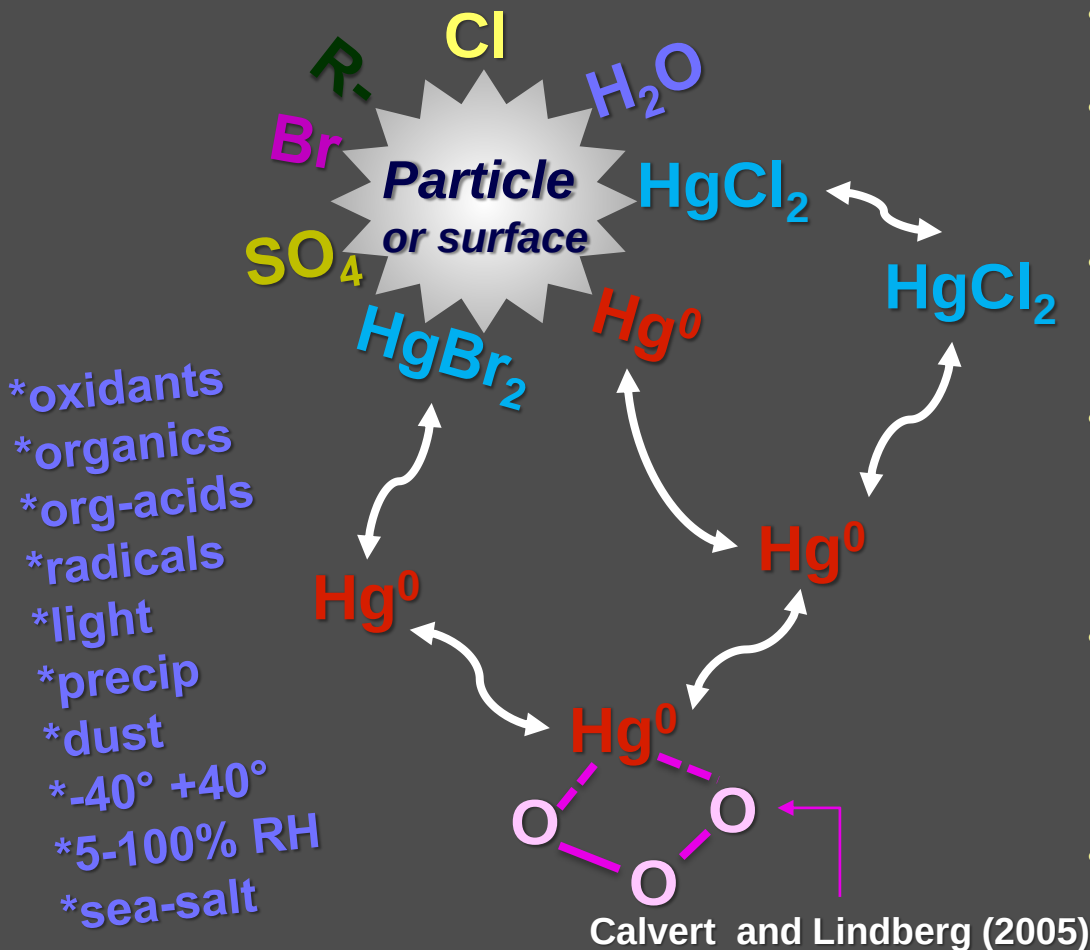


Driscoll, et al., 10.1021/es305071v | Environ. Sci. Technol.

How hard can it be to measure Hg speciation?

GOM & PBM ~ 1 ppqv

GEM ~ 170 ppqv



- What can be expected?
- GOM and PBM typically 1 PPQV (10 pg/m^3) level
- Must use surface collection in operationally defined method
- Surface collection can be challenging due to reactivity of Hg, other gases and PM2.5
- Method must work well in Arctic, urban Asia, tropics, marine, desert, etc.?
- GOM & PBM calibration standards are not available

Requirement for spatial and temporal comparison of Hg concentration and dry deposition data

NADP/AMNet Approved Method & Equipment, Harmonized Operation and Data Validation

Table 1. NADP approved equipment for use in the AMNet.

Equipment	Manufacturer*	Model Number
Continuous Mercury Vapour Analyzer	Tekran	2537A or 2537B
Air Dryer	Tekran	1102
Continuous Oxidized Mercury Speciation Module	Tekran	1130
Continuous Particulate Mercury Module	Tekran	1135

* **Disclaimer:** The use of a trade or manufacturer's name does not constitute an endorsement by the University of Illinois, the Illinois State Water Survey, or the NADP.

NADP AMNet Operations Manual 2011-05
Version 1.0

Table 4. Responsibilities of the Site Operator.

Activity	Frequency
Inspect data	At least twice a week
Inspect site for compliance with siting criteria	Each visit*
Verify operation of the atmospheric mercury equipment	Each visit*
Verify the operation of the meteorological equipment, if applicable	Each visit*
Site Report A <i>Each Visit/Weekly Activities**</i>	Complete: each visit Submit to PO: monthly
Site Report B <i>Glassware Change-out/Monthly Activities**</i>	Complete: as needed Submit to PO: monthly
Site Report C <i>Quarterly Activities**</i>	Complete: as needed Submit to PO: quarterly
Site Report D <i>Annual/As-Needed Activities**</i>	Complete: as needed Submit to PO: when completed
Troubleshoot equipment	As needed
Equipment repairs and maintenance	As needed
Replace/upgrade equipment	As needed
Participate in External Site Performance and Systems Survey	Once every 2 years

* an AMNet site should be visited at least once every two weeks.

** Site Reports A-D are discussed in separate Standard Operating Procedure documents.

Data Validation

As indicated in Figure 2, validation of the Tekran instrument raw data is a three-step process. This process includes:

1. automated quality assurance (QA) checks,
2. manual inspection by the AMNet Site Liaison, and
3. approval by the Site Operator and/or Site Supervisor at each site

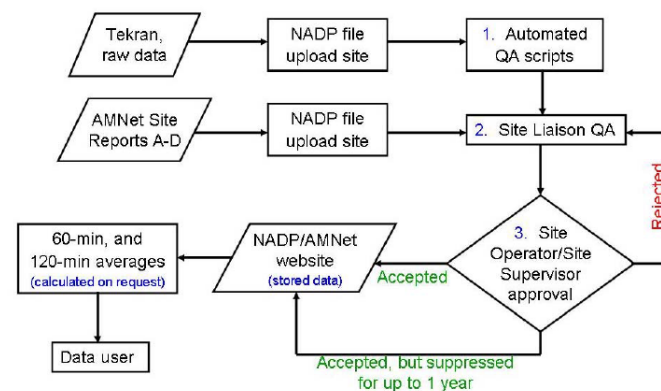


Figure 2. AMNet Quality Assurance and Data Flow Process.

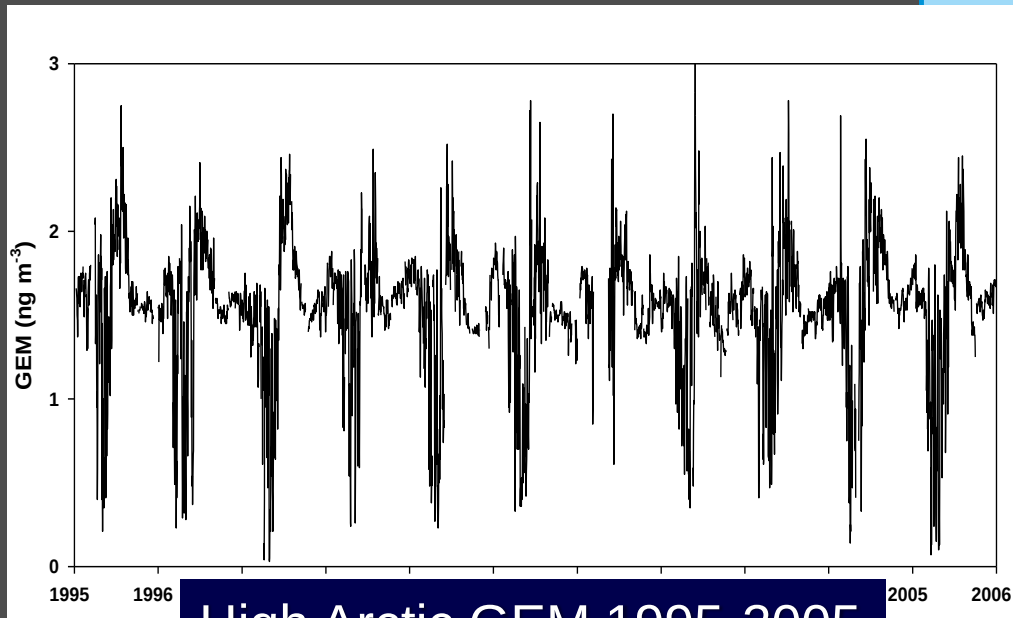
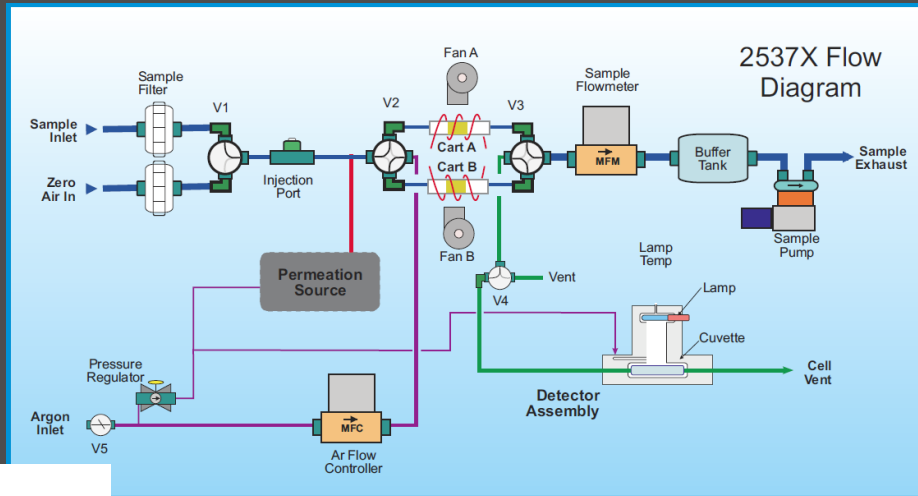
Method of Choice: Cold Vapor Atomic Fluorescence (CVAF)

Ambient Air Gaseous Hg

Automated and Continuous

High time resolution

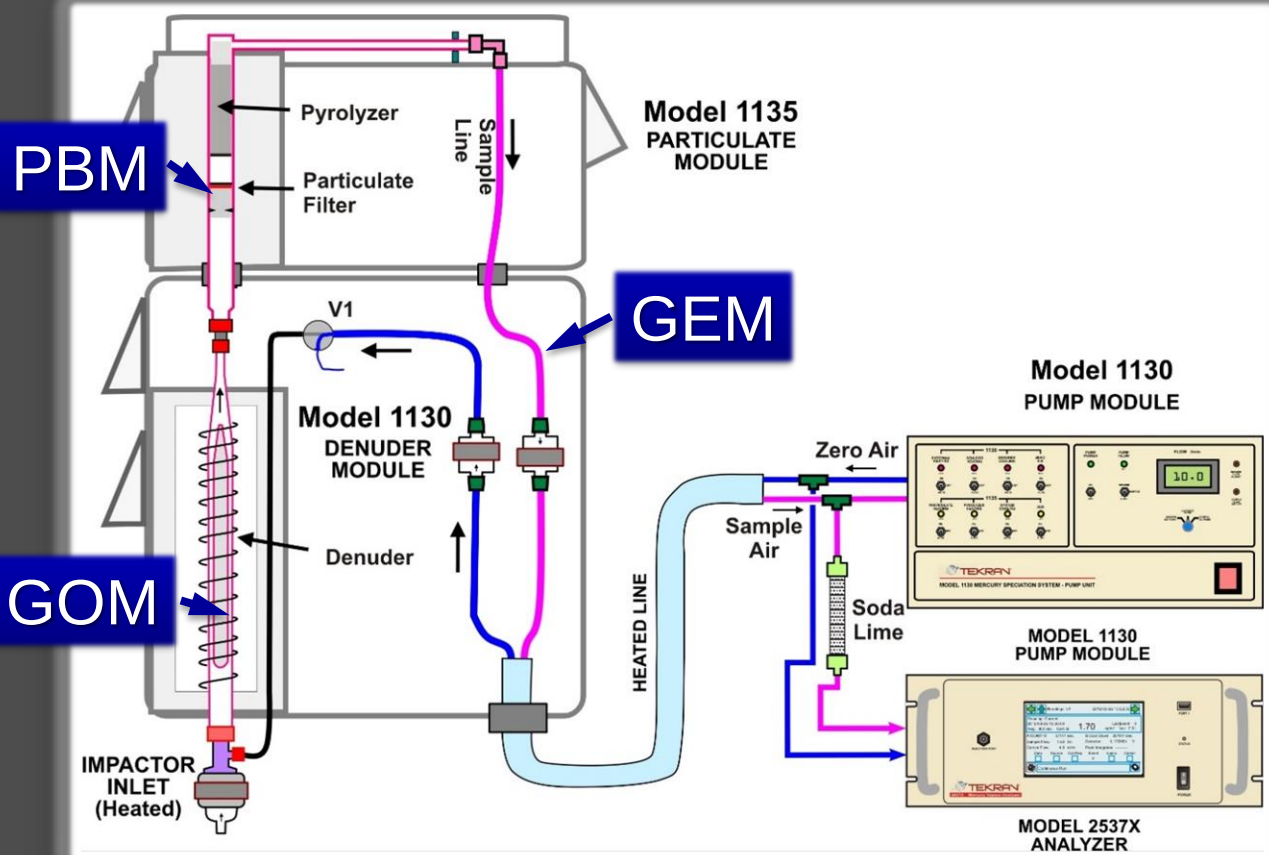
Typical use in AQM Stations



High Arctic GEM 1995-2005



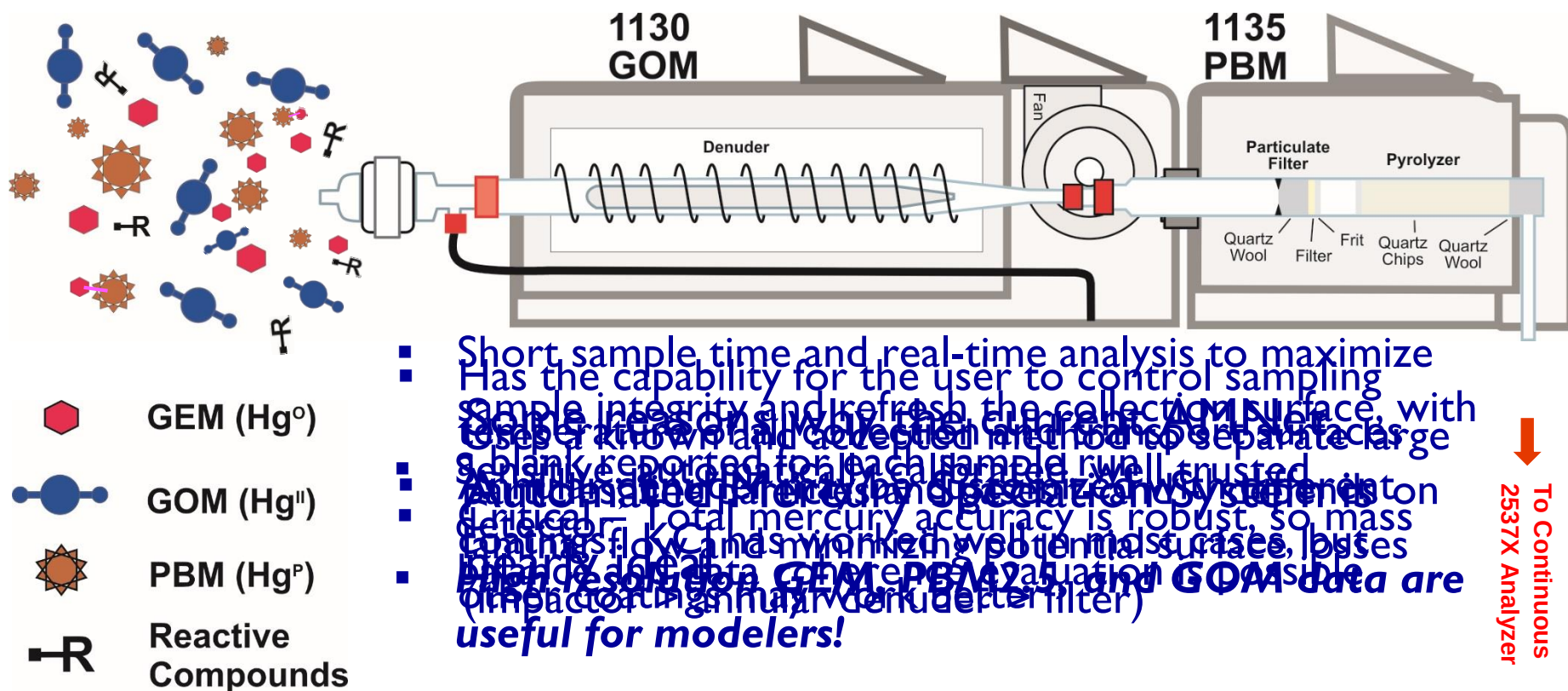
Automated Hg Speciation Method



Method is:

- Lab tested
- Widely published
- QA Challenged
- Adopted by all advanced int'l & national networks
- Improvements ongoing

Automated Mercury Fractionation Method



AMNet Hg species concentration

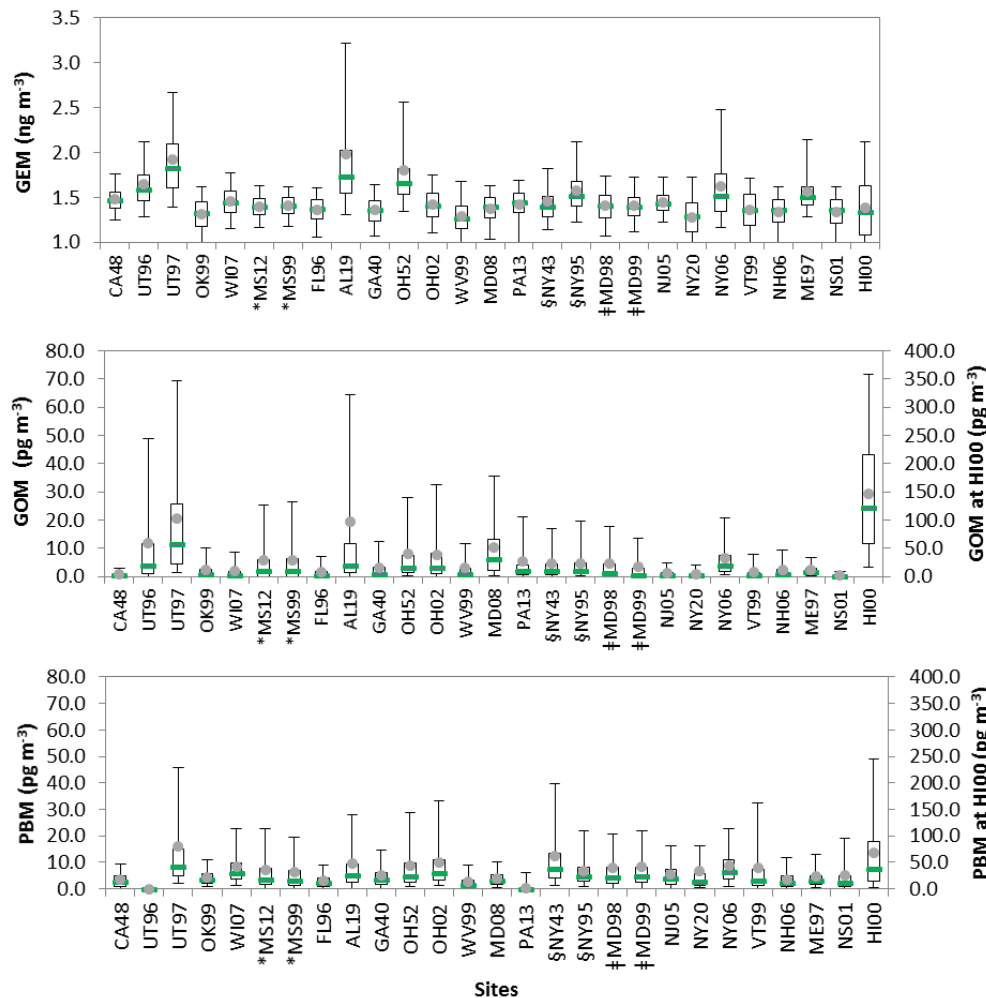
Critical Input for Deposition Models

2009-2014 GEM, GOM, and PBM concentrations

Dots are mean and median values.

Box and whiskers represent the interquartile and 5th-95th% range

Sites are listed west to east.



Six-year Hg dry deposition estimation to multiple land covers types at AMNet monitoring sites

All further slides show model and manuscript of

Leiming Zhang, Environment Canada

Co-Authors - Zhiyong Wu, Irene Cheng,

L. Paige Wright, Mark L. Olson, David A. Gay

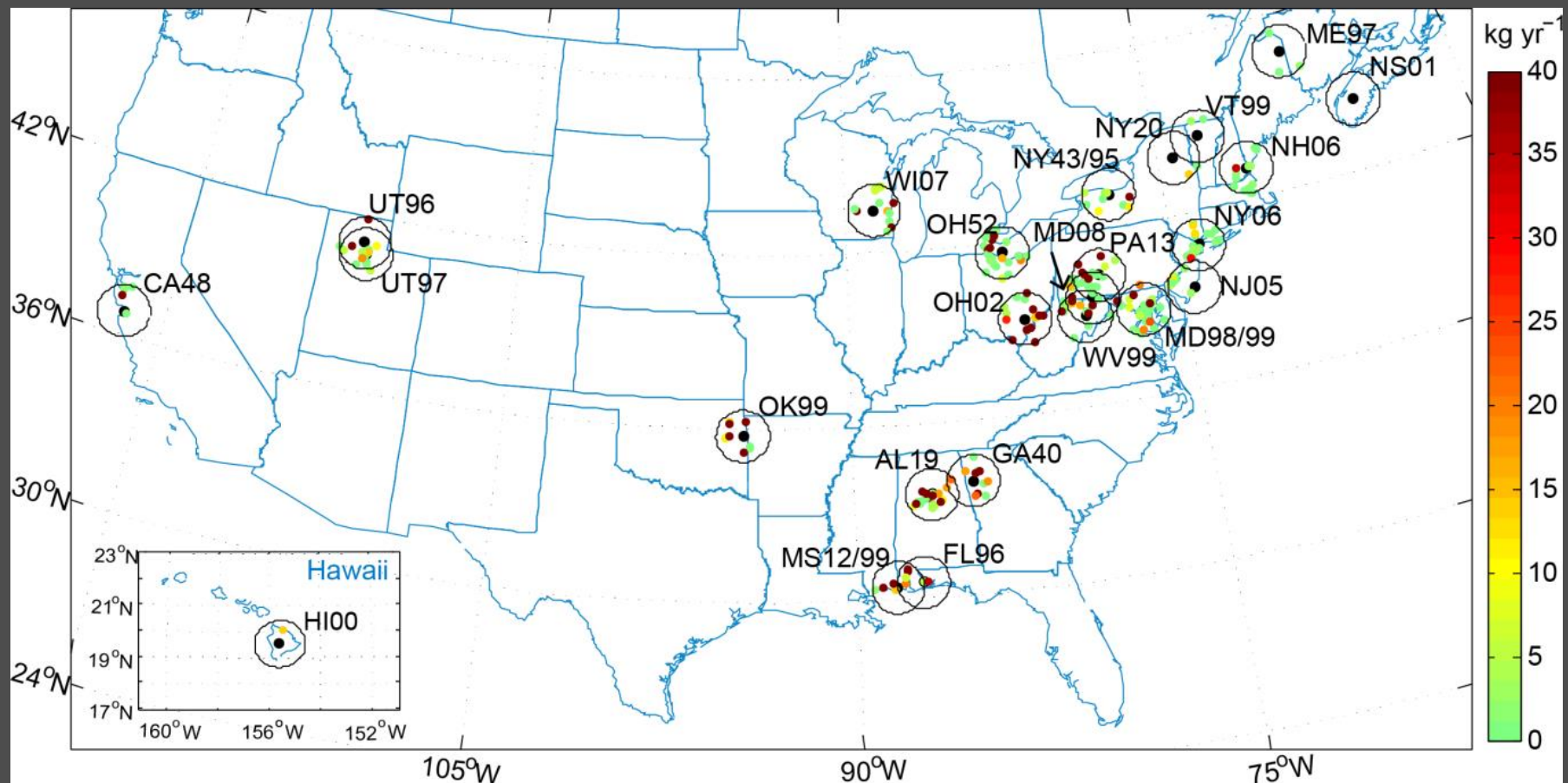
AMNet Dry Deposition Project

- NADP/AMNet goal > use data and model to estimate Hg dry deposition
- NADP approves proposal of Zhang and Gay (2014)
- Used full QA - six-year AMNet data (2009-2014)
- Land cover data extracted from MODIS
- Meteorological data > archived Canadian weather forecast model
- Three peer-reviewed, published algorithms for GOM, PBM and GEM dry deposition used for calculating 2-hourly speciated fluxes.

Hg Dry Deposition Algorithms

- A big-leaf gaseous dry deposition model for GOM (Zhang et al., 2003, 2012)
- A bulk particle dry deposition model for PBM (Zhang and He, 2014)
- A **bi-directional** air-surface exchange model for GEM (Wright and Zhang, 2015)

Map of AMNet sites and mercury air emission sources within a 100 km radius



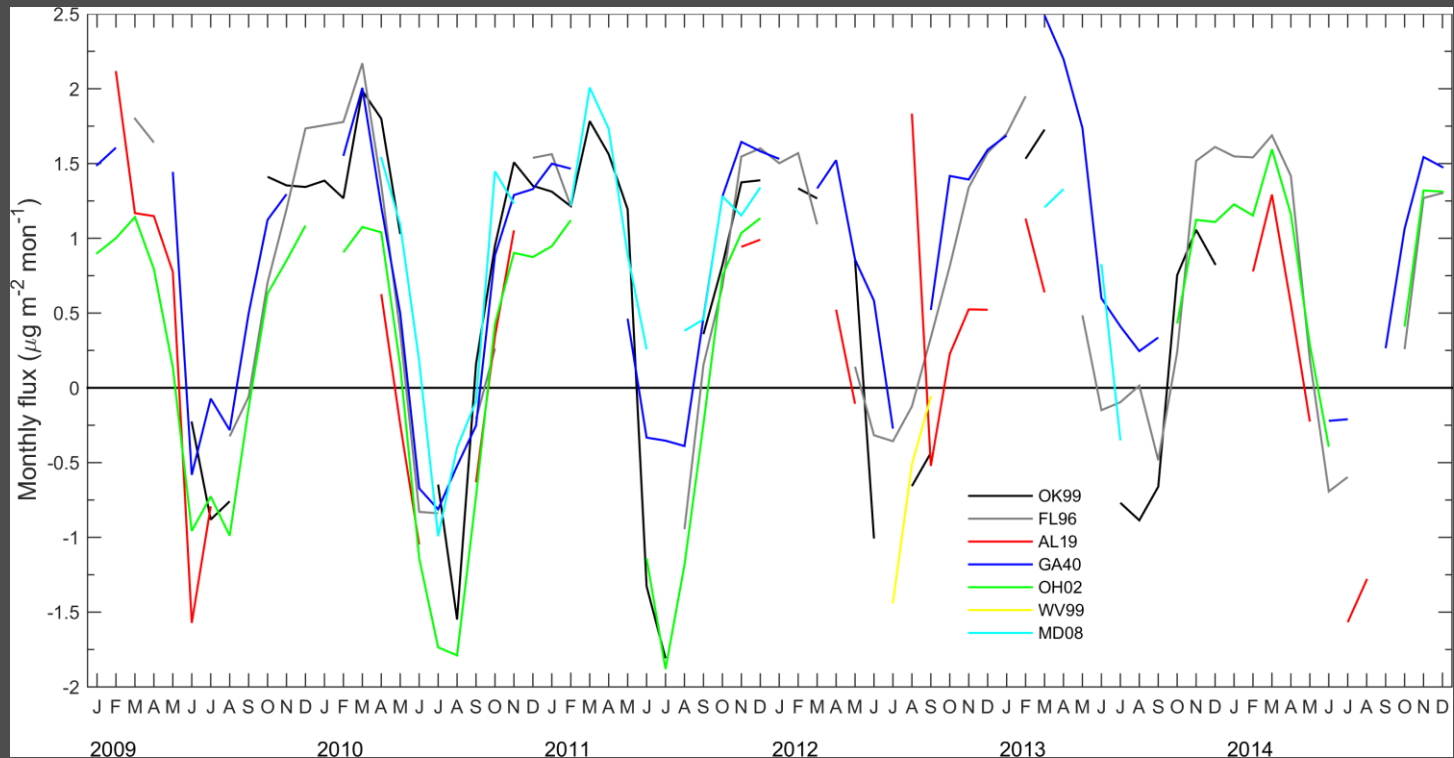
Time series of AMNet Hg Dry Deposition by Site

Land cover area-weighted mercury fluxes from 2009-2014

Net Deposition

$\mu\text{g}/\text{m}^2/\text{month}$

Net Emission

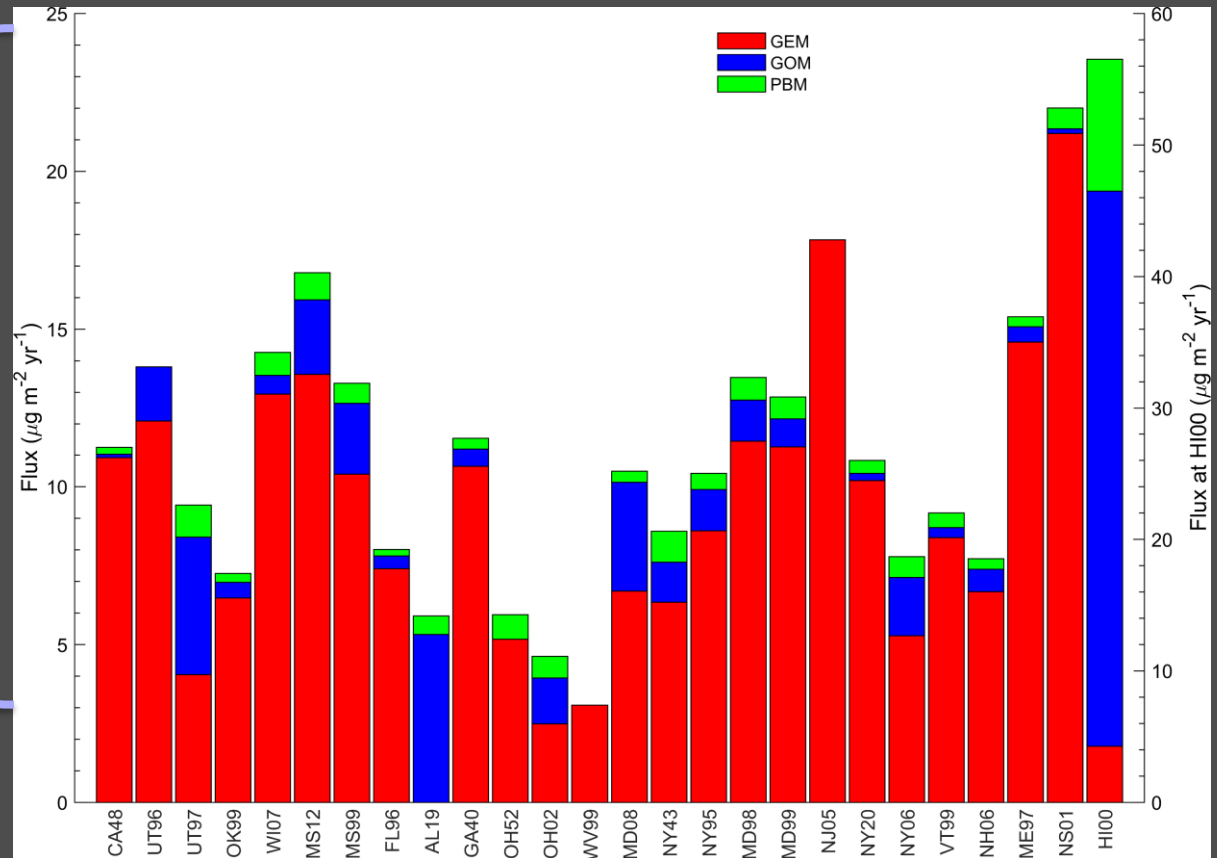


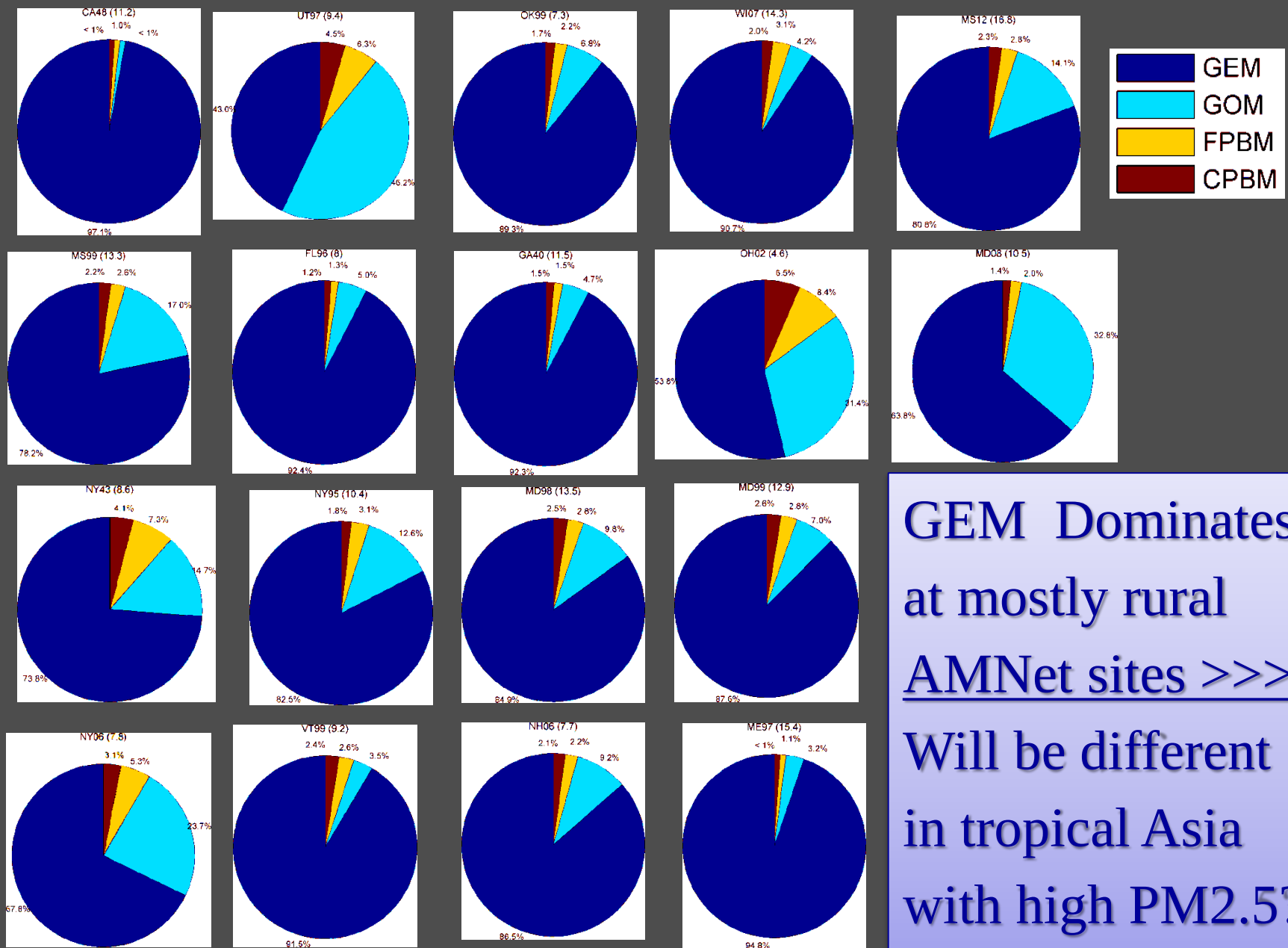
AMNet Hg Dry Deposition by Site

multi-year mean land cover area-weighted (2009-2014)

Range is a factor
of ~7x

3-25 $\mu\text{g}/\text{m}^2/\text{yr}$
range is similar to
wet deposition





GEM Dominates
at mostly rural
AMNet sites >>>
Will be different
in tropical Asia
with high PM2.5?

Conclusions

- Linkage: Hg Sources to Exposure Measurement and Models are Critical
- Air mercury exist in three different forms, with different behavior, thus accurate deposition models require mercury speciation data
- Network method and QA harmonization improves data quality and comparability – **and** – provides support and tools for new sites
- For AMNet, mercury dry deposition is highly variable spatially and temporally, with net flux commonly equal to or greater than wet-deposition.
 - For tropical Asia, do not expect AMNet results to hold true, thus the need for select speciation measurements in this region
 - Even with addition of bi-directional GEM air-surface exchange to the model, GEM is the dominate form driving dry deposition flux at most, but not all AMNet Sites