Atmospheric Mercury Research at NOAA's Air Resources Laboratory:

Results from the Atmospheric Mercury Network (AMNet)

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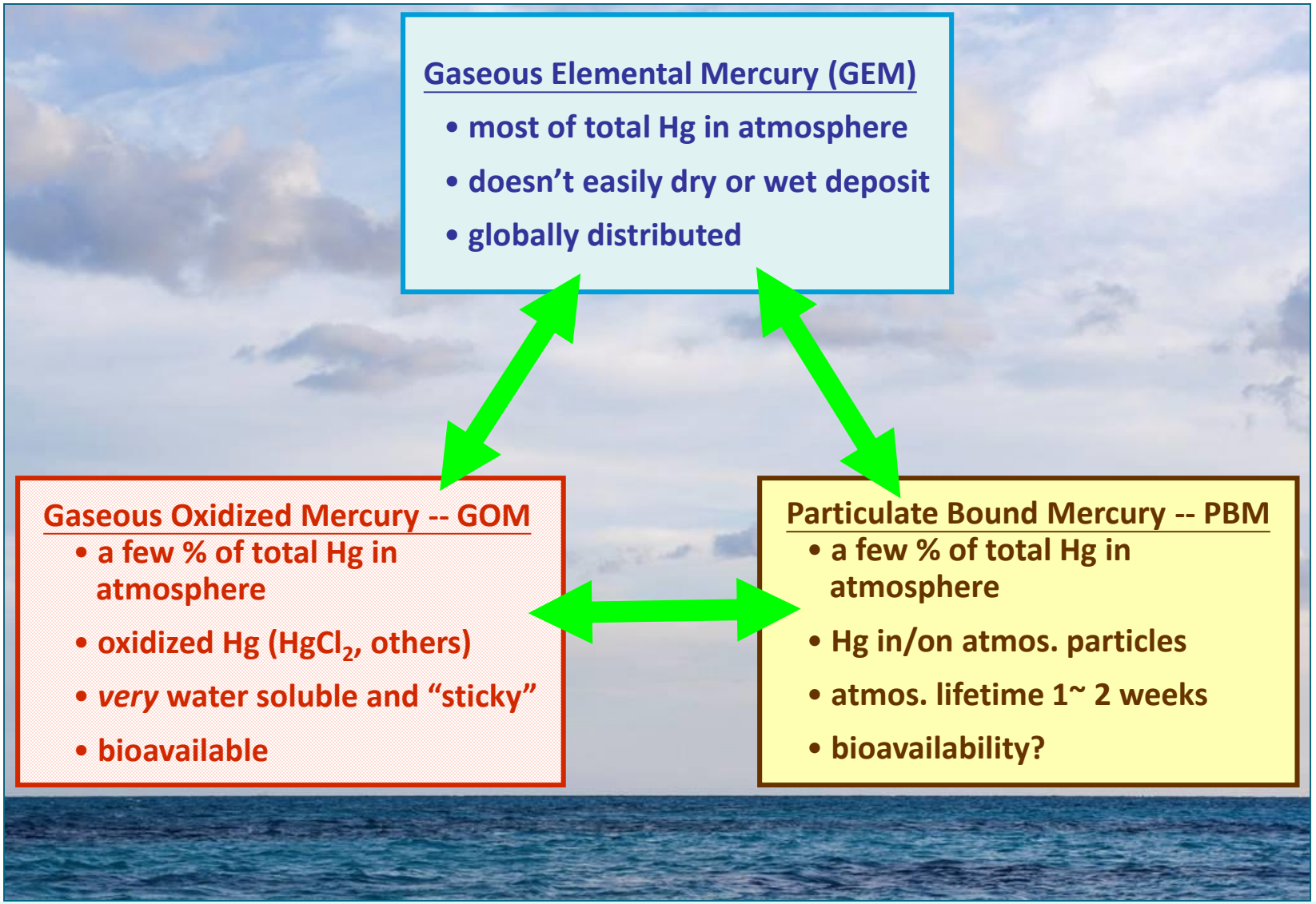
Context

- Mercury exposure via fish consumption is an important public health concern
- Atmospheric emissions and subsequent deposition is a significant pathway through which mercury contamination enters sensitive aquatic ecosystems

Goals

- Provide sound scientific information on the emission, dispersion, transformation, and air-surface exchange of atmospheric mercury compounds
- Measure and understand spatial and temporal trends in air concentrations and air-surface exchange
- Provide robust source-attribution information for atmospheric mercury deposition to sensitive ecosystems, to inform policies to reduce loadings

Different "forms" of mercury in the atmosphere



Measurements – Approaches

- Process Studies / Field Intensives
- Long-Term Monitoring

Process Studies/Field Intensives

- Arctic, Antarctic, Grand Bay, Beltsville, Houston, Ann Arbor, Nevada, …
- Generally large, multi-investigator studies, including method development, inter-comparision and optimization
- Measurements of:
  - Concentrations of different forms of mercury and other key species, at the surface and aloft, using active and passive techniques
  - Air-Surface exchange using micrometeorological and surrogate-surface techniques

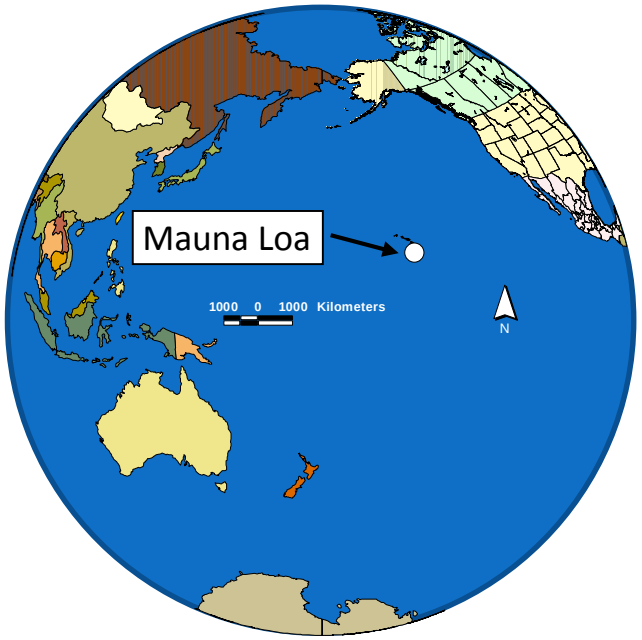
University of Tennessee Space Institute Piper Navajo used for airborne measurements, Grand Bay NERR (MS), July-Aug 2010, April-May 2011

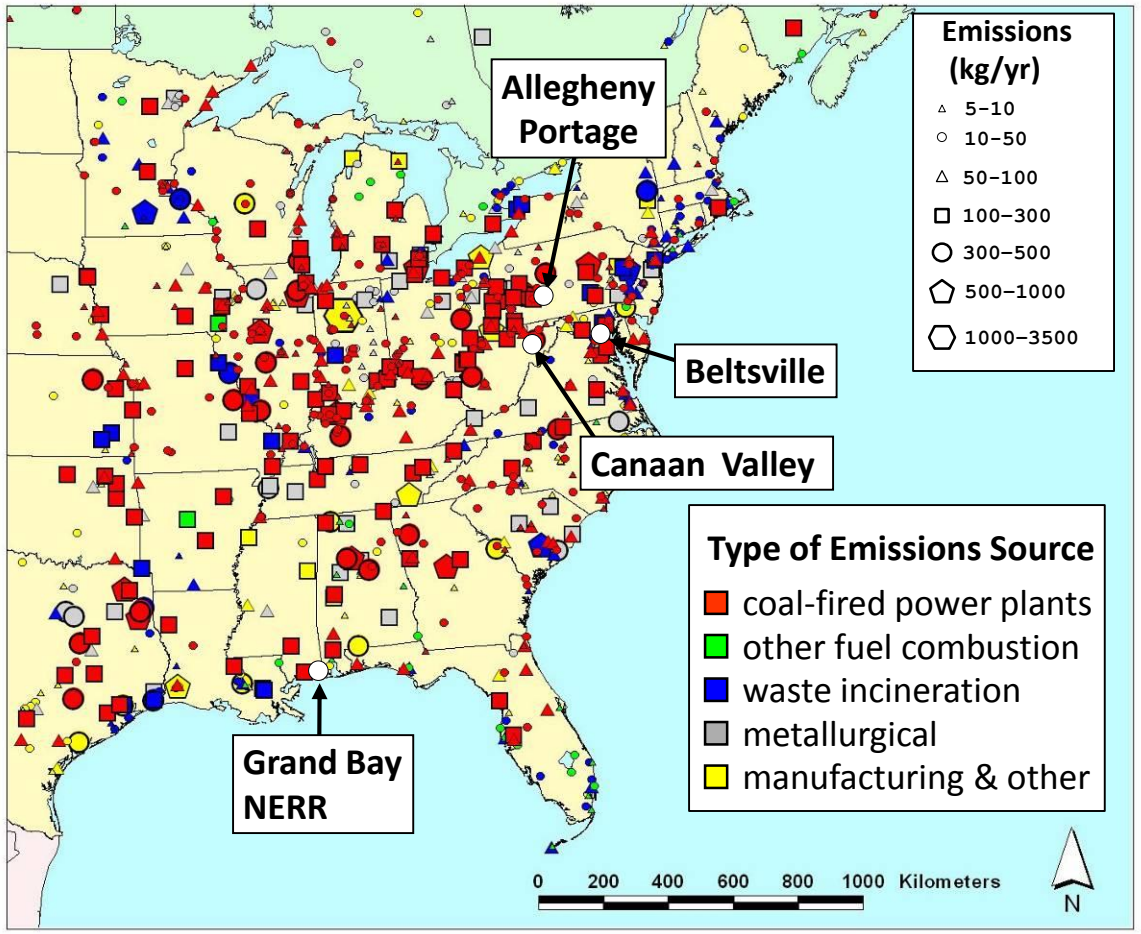
Steve Brooks, NOAA – ARL, Barrow Alaska

Investigating the roles of:

- **halogen chemistry in the marine layer and free troposphere**
- **transport from upper atmosphere**
- **local/regional emissions**
- **Mercury balance and cycling in polar regions**

Long-Term Monitoring





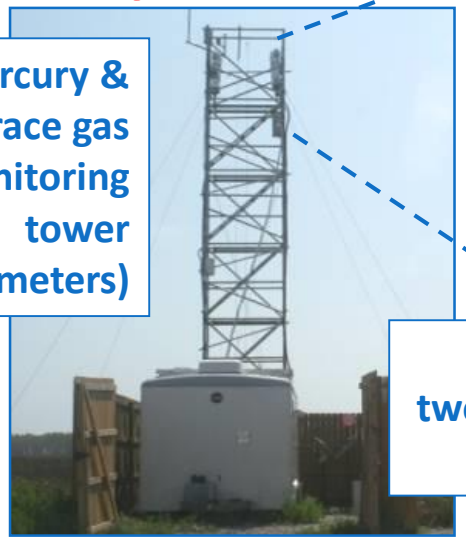
Four ARL long-term mercury measurement sites in the continental U.S., one in Hawaii; 2002 mercury emissions sources based on data from USEPA, Envr. Canada and the CEC

Long-Term Monitoring Examples

Ancillary Measurements of:
- SO_2
- O_3
- CO
- NO/NO_Y
- Black Carbon
- Meteorology
- Solar Radiation

To Address:
- Source attribution and characterization
- Local/Regional emissions
- Air-surface exchange
- Trend analysis
- Model evaluation

Grand Bay NERR



mercury & trace gas monitoring tower (10 meters)

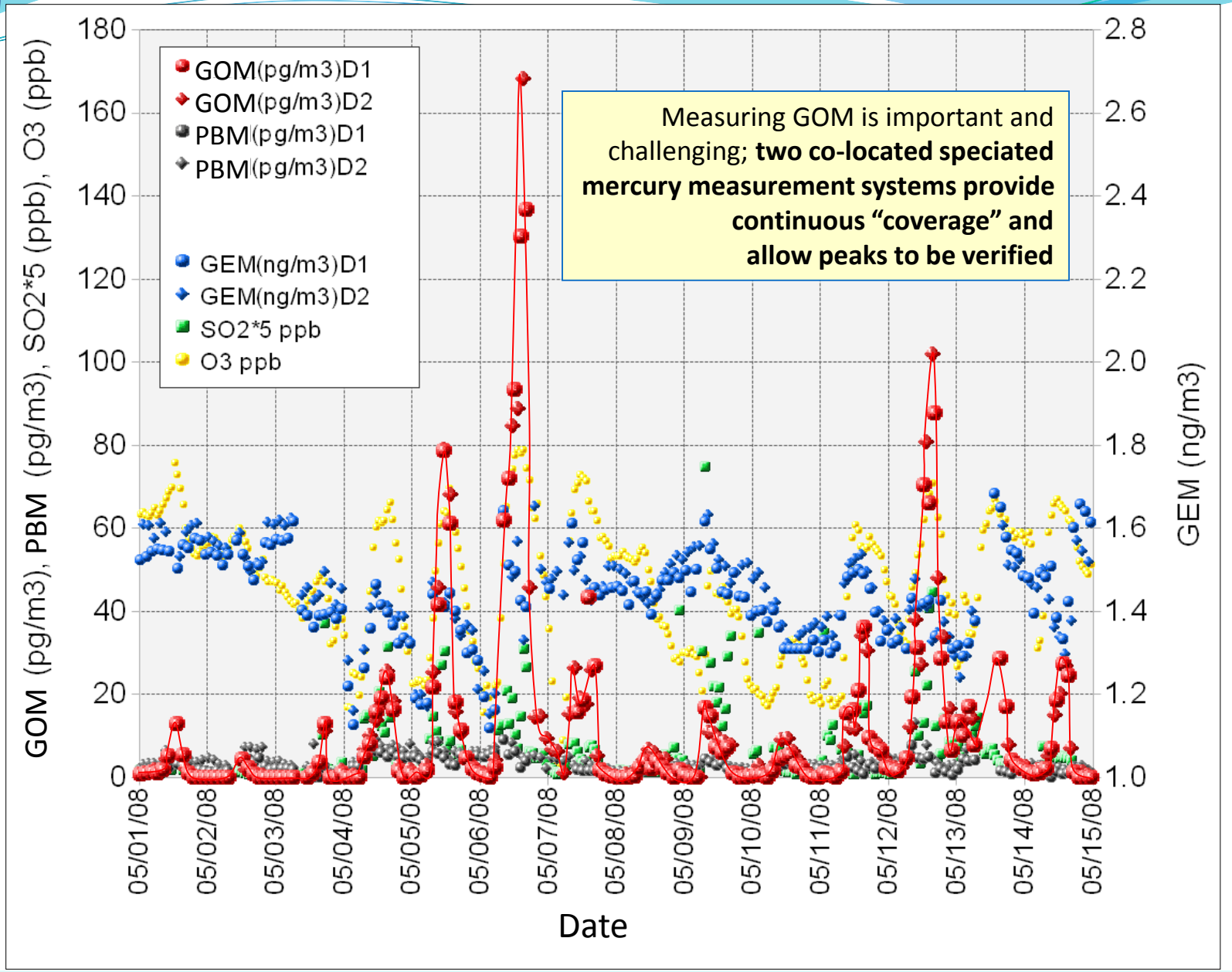
top of tower with two sets of GOM and PBM collectors

precipitation collection

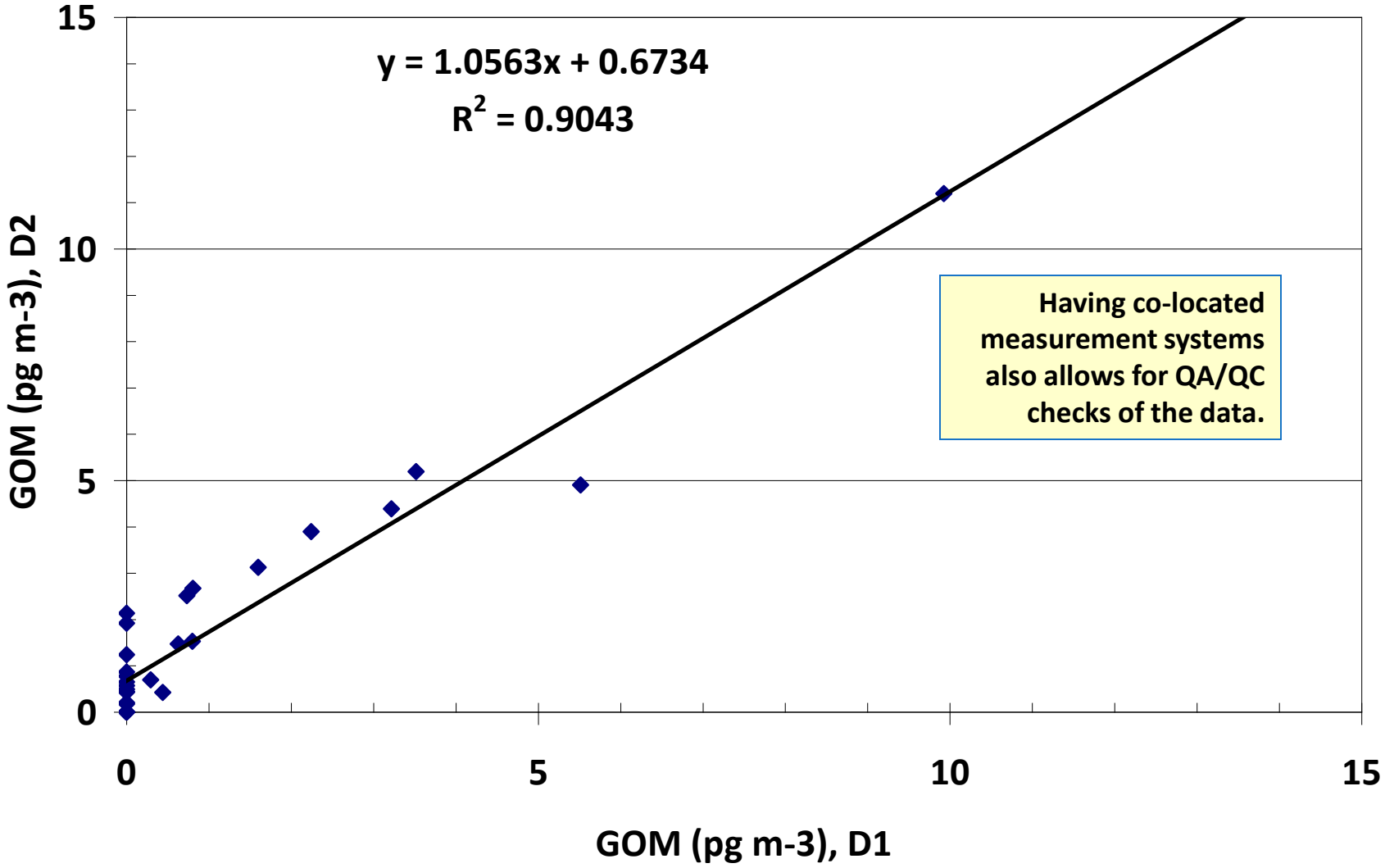
precipitation amount

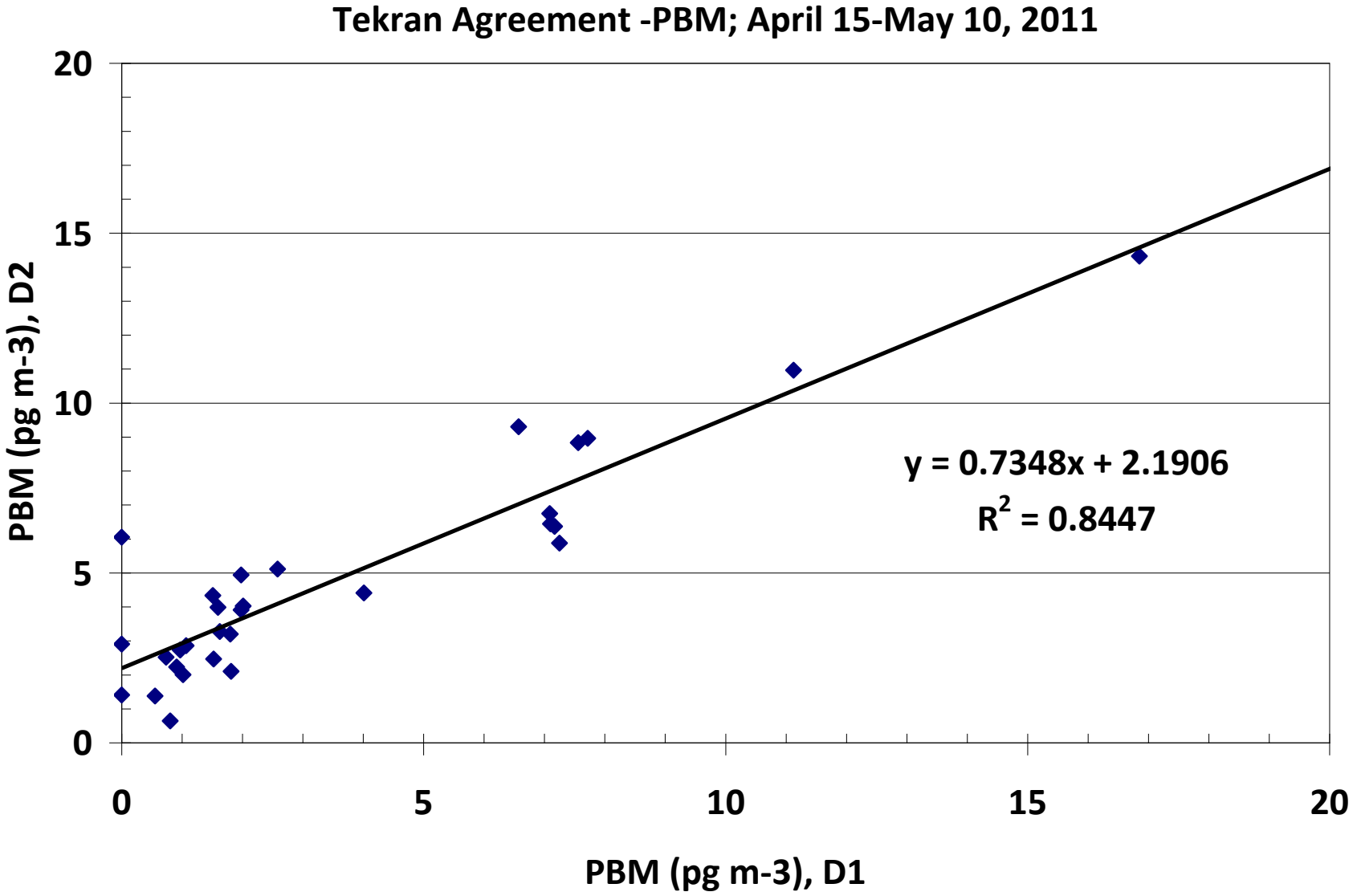
major ions ("acid rain")

Mercury Deposition Network and heavy metals

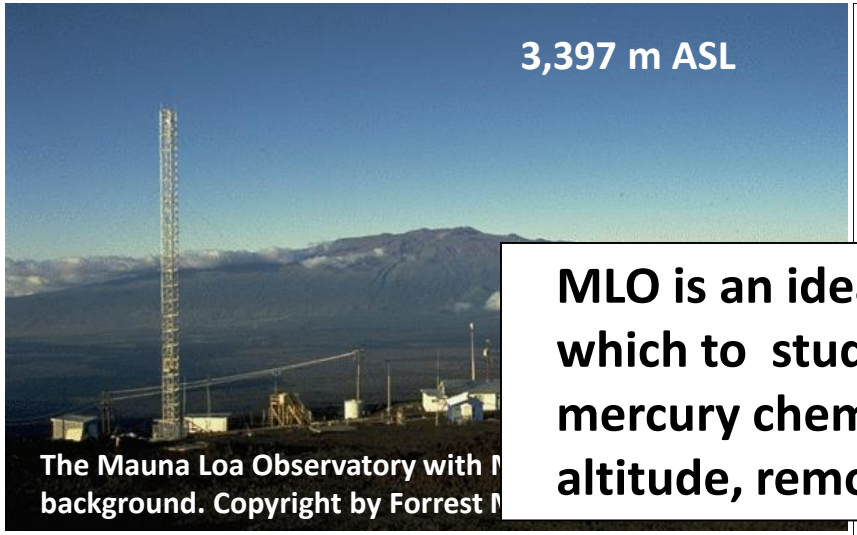

GOM(pg/m3)D1
GOM(pg/m3)D2
PBM(pg/m3)D1
PBM(pg/m3)D2
GEM(ng/m3)D1
GEM(ng/m3)D2
SO2*5 ppb
O3 ppb
Measuring GOM is important and challenging; **two co-located speciated mercury measurement systems provide continuous "coverage" and allow peaks to be verified**
GOM (pg/m3), PBM (pg/m3), SO2*5 (ppb), O3 (ppb)
GEM (ng/m3)
Date
180
160
140
120
100
80
60
40
20
0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
05/01/08
05/02/08
05/03/08
05/04/08
05/05/08
05/06/08
05/07/08
05/08/08
05/09/08
05/10/08
05/11/08
05/12/08
05/13/08
05/14/08
05/15/08

Tekran Agreement -GOM; April 15-May 10, 2011



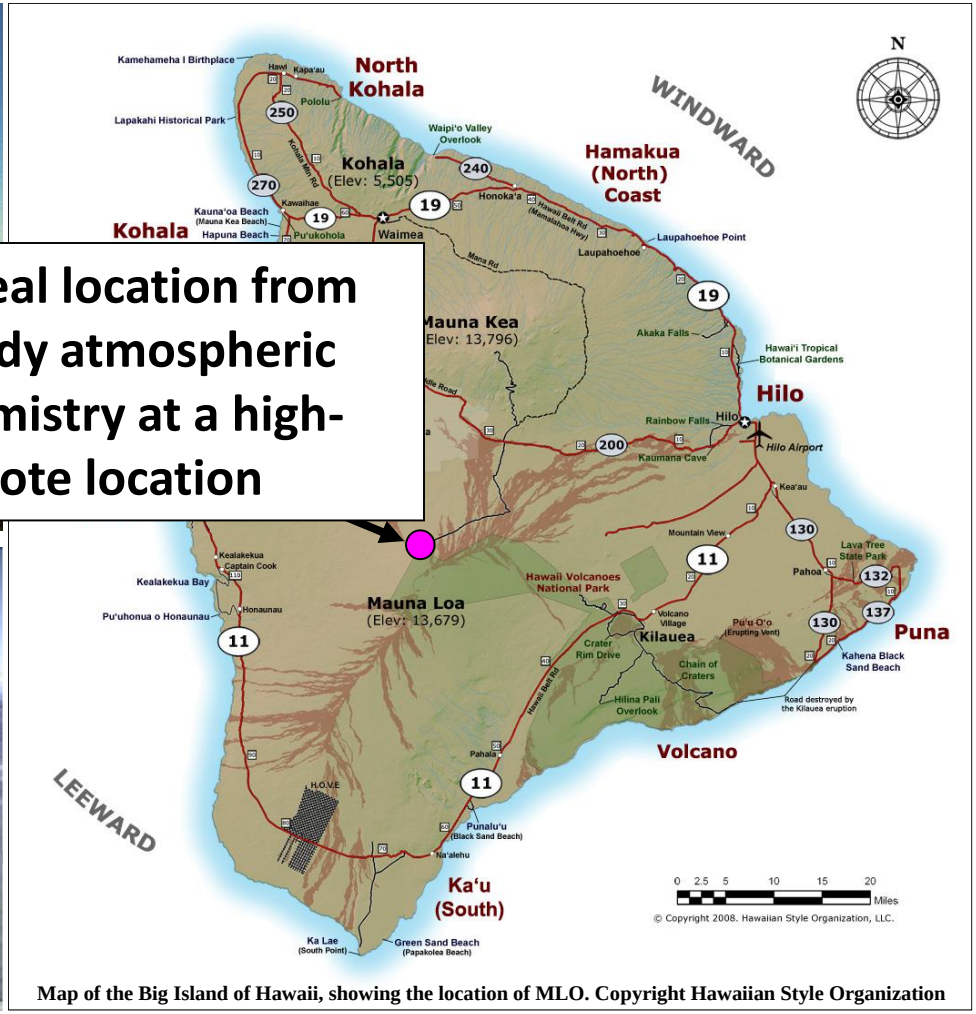

Tekran Agreement -PBM; April 15-May 10, 2011
PBM (pg m-3), D2
PBM (pg m-3), D1
0
5
10
15
20
y = 0.7348x + 2.1906
R2 = 0.8447

Mauna Loa Observatory, Hawaii: *since January 2011*



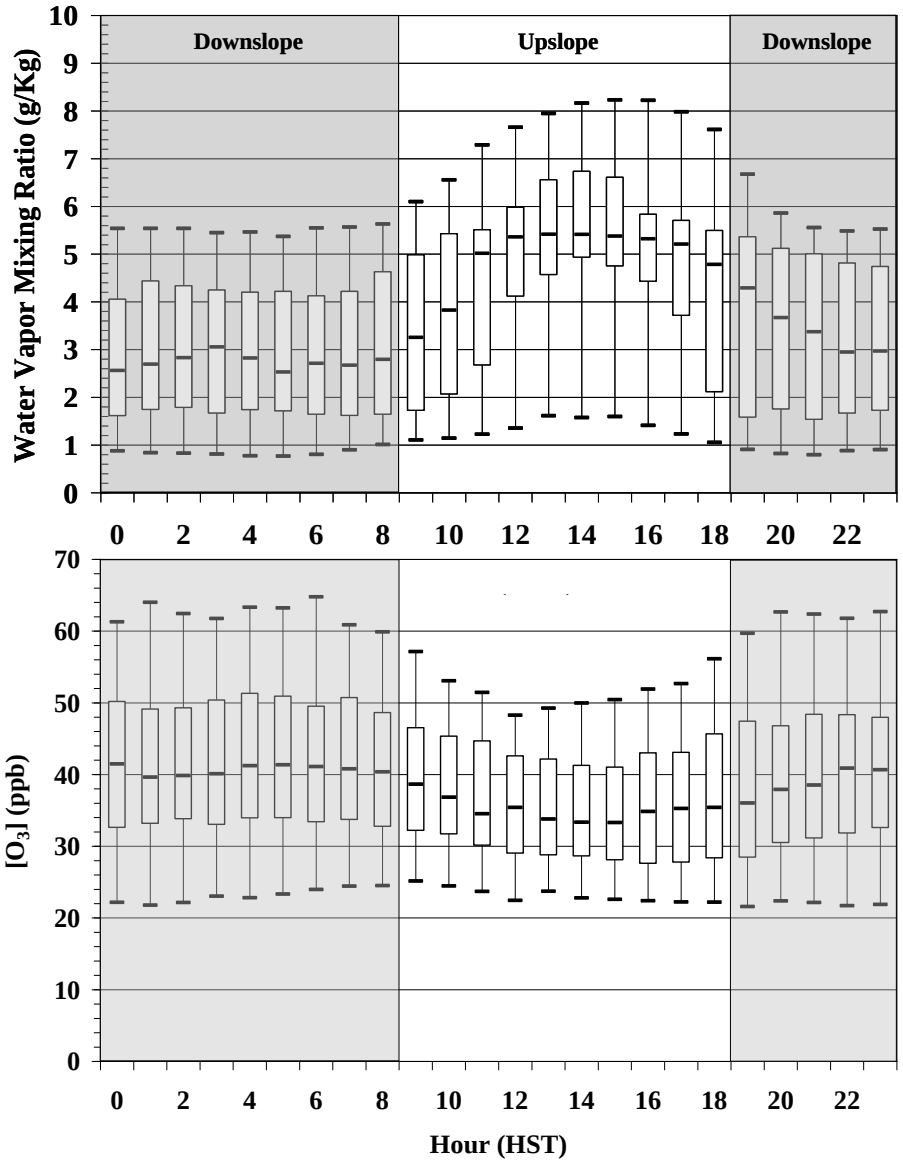
The Mauna Loa Observatory with M
background. Copyright by Forrest M

MLO is an ideal location from which to study atmospheric mercury chemistry at a high-altitude, remote location



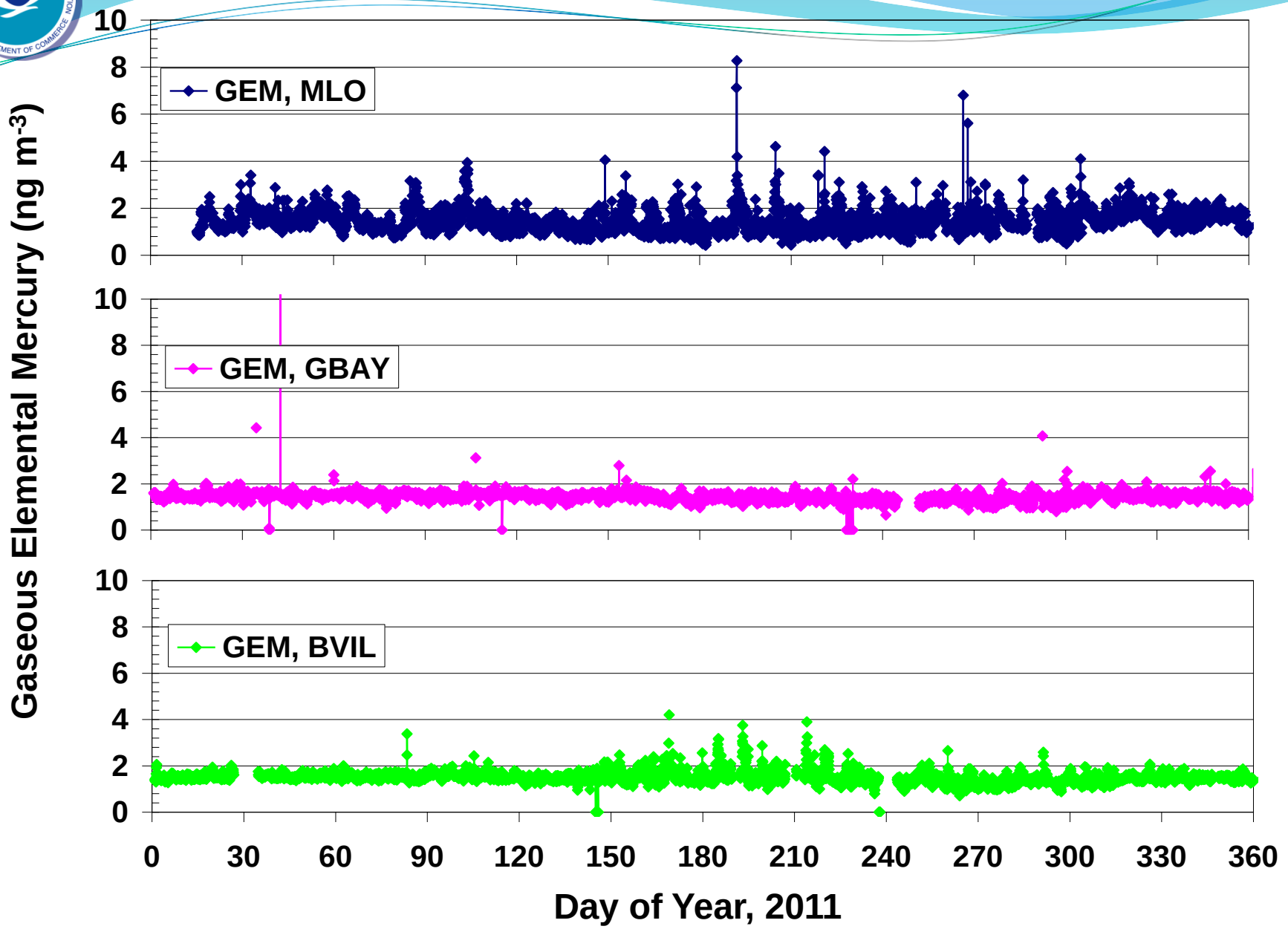
Map of the Big Island of Hawaii, showing the location of MLO. Copyright Hawaiian Style Organization

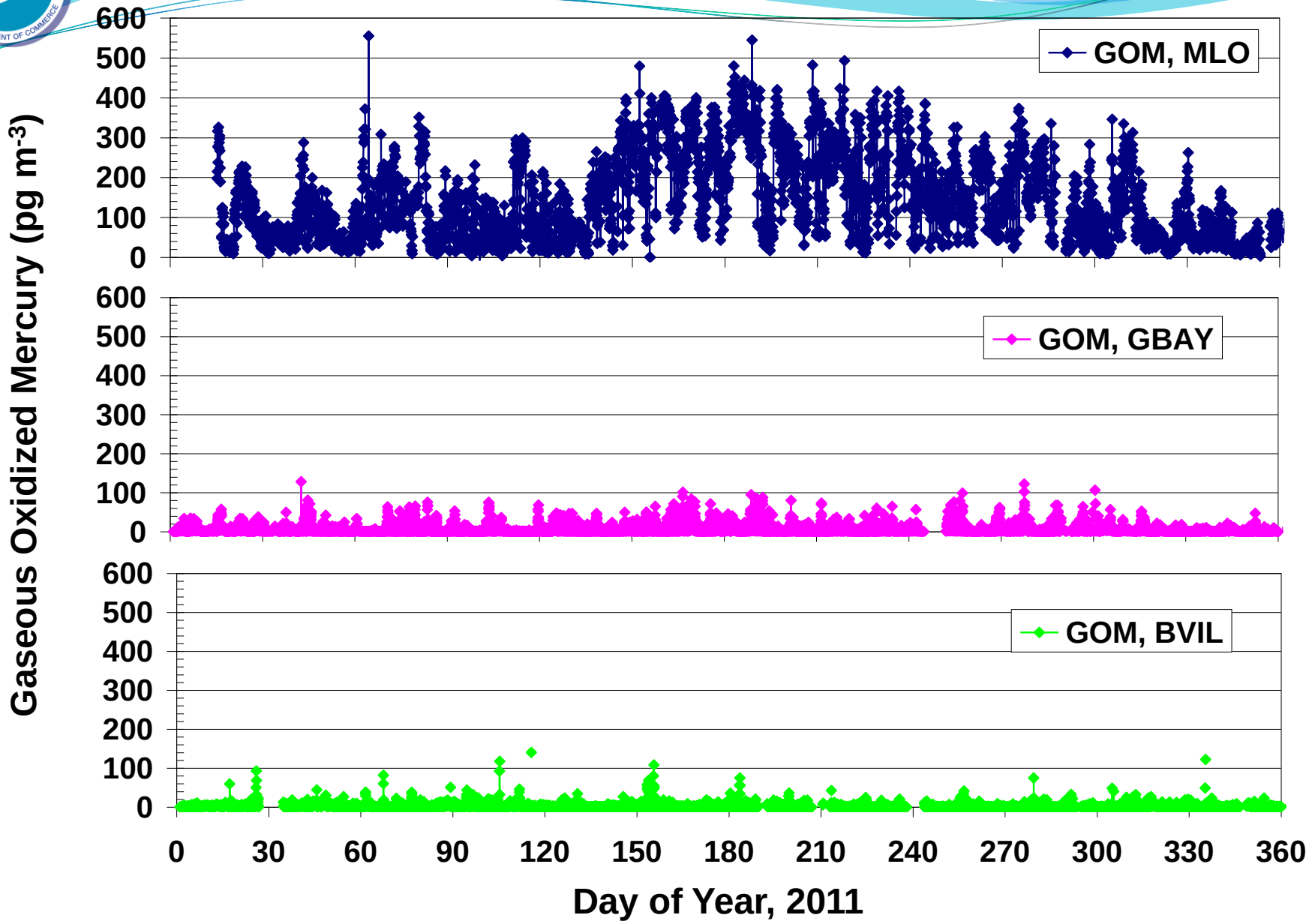
Upslope and Downslope Flow at MLO

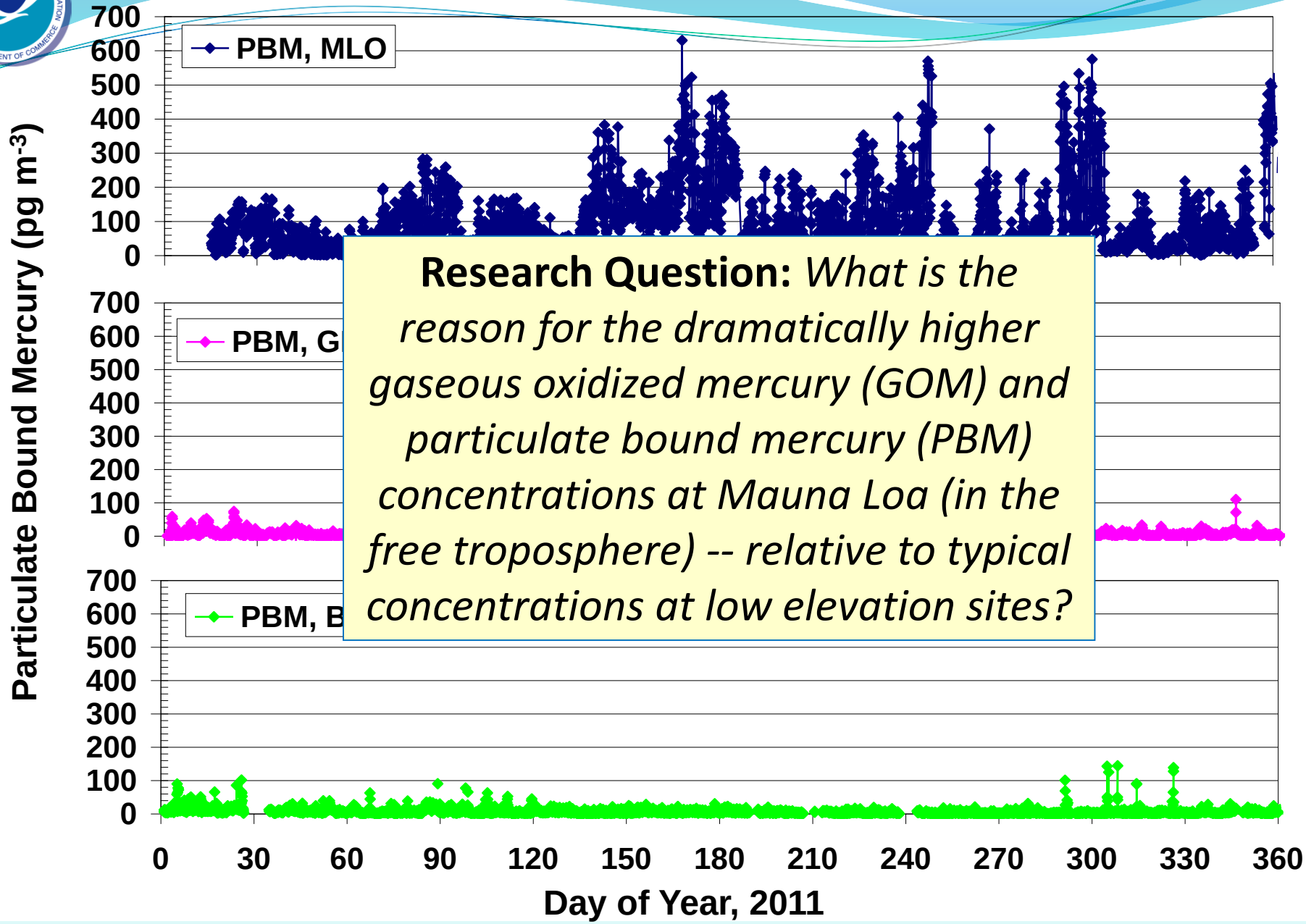


Upslope flow (mainly from the east through northwest) during the day and brings moist, ozone-poor air from lower elevations to the MLO site.

At night, downslope flow (from the southeast through southwest) reverses this transport, and air is often more representative of the free troposphere above.

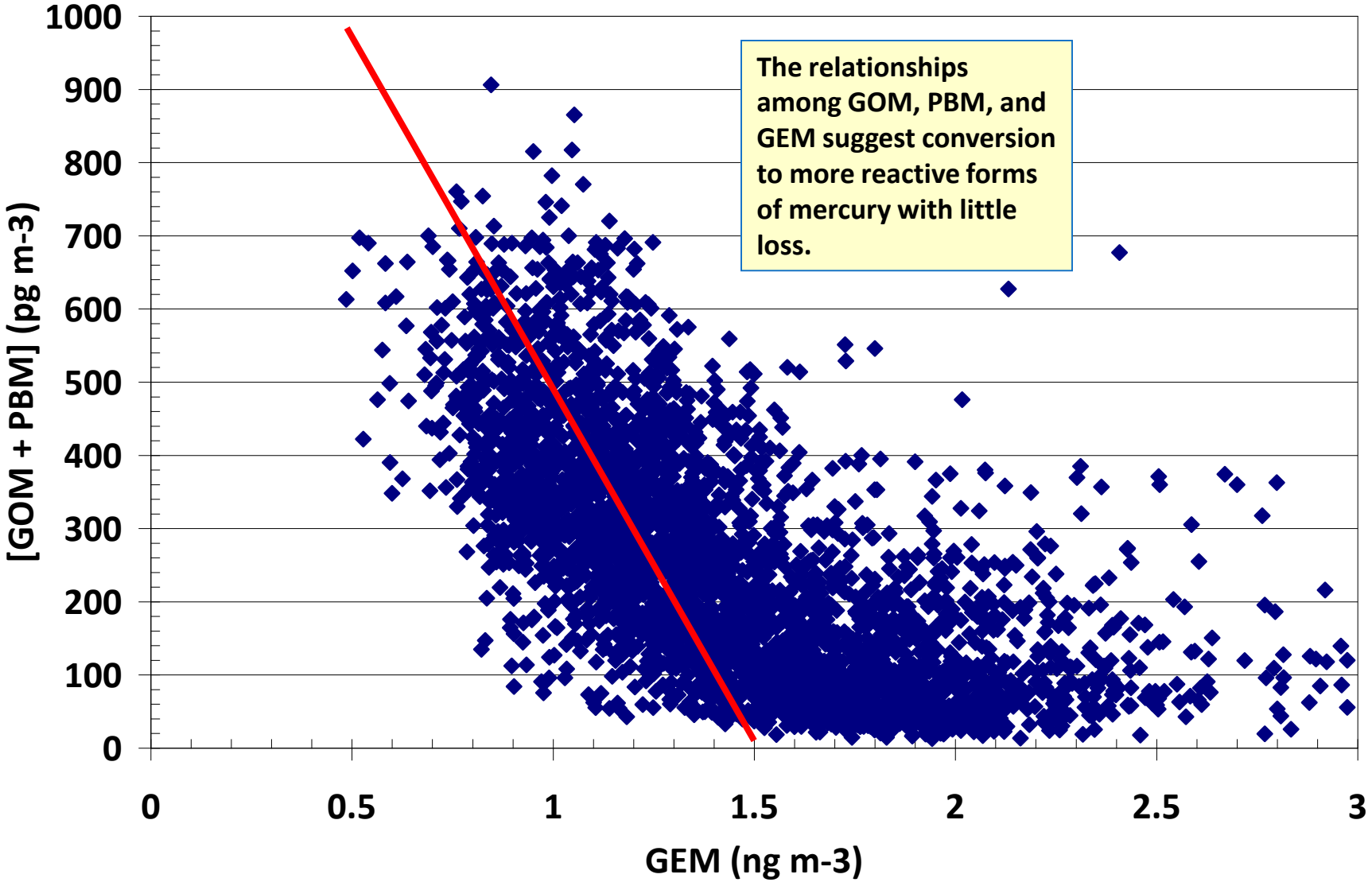

GEM, MLO
GEM, GBAY
GEM, BVIL
Gaseous Elemental Mercury (ng m-3)
Day of Year, 2011
0
2
4
6
8
10
0
30
60
90
120
150
180
210
240
270
300
330
360


Gaseous Oxidized Mercury (pg m-3)
GOM, MLO
GOM, GBAY
GOM, BVIL
600
500
400
300
200
100
0
0
30
60
90
120
150
180
210
240
270
300
330
360
Day of Year, 2011

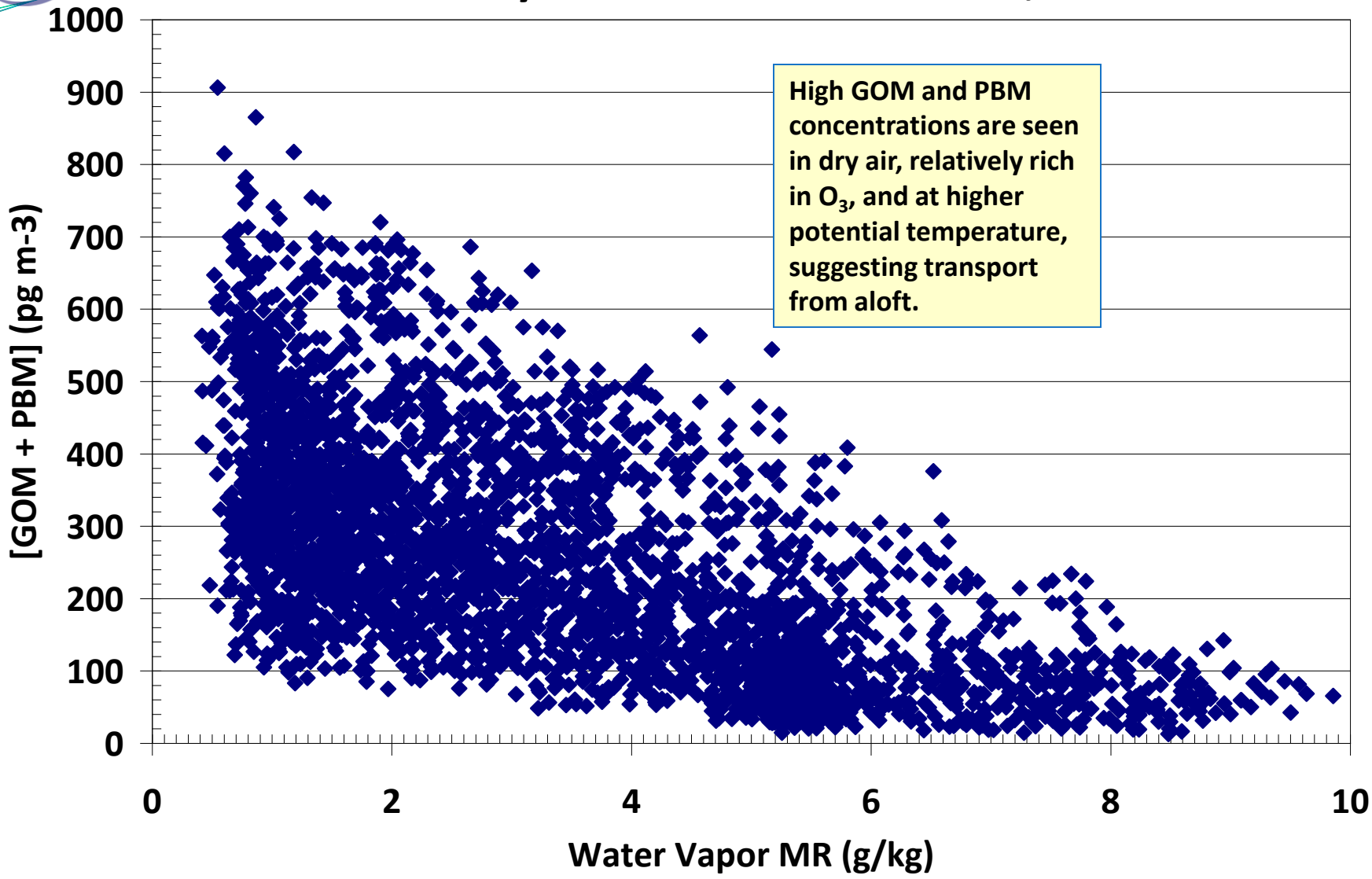


Research Question: *What is the reason for the dramatically higher gaseous oxidized mercury (GOM) and particulate bound mercury (PBM) concentrations at Mauna Loa (in the free troposphere) -- relative to typical concentrations at low elevation sites?*

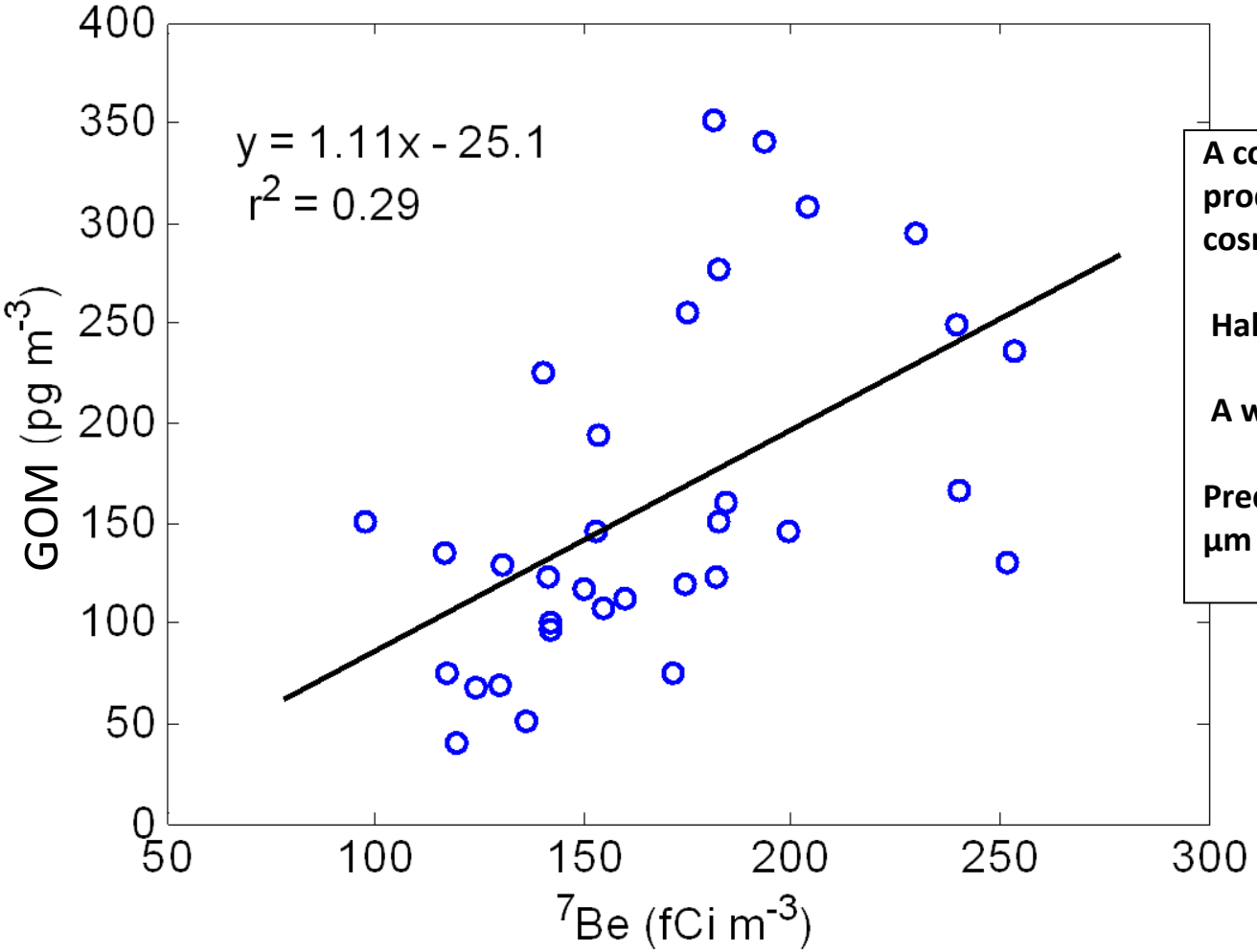
Mercury Measurements at MLO, 2011



Mercury Measurements at MLO, 2011



Mercury Measurements at MLO, 2011



Beryllium-7 (^{7}Be)

A cosmogenic radionuclide produced by spallation reactions of cosmic rays with N2 and O2

Half life: 53.28 days

A well-known stratospheric tracer

Predominantly associated with sub-µm aerosols

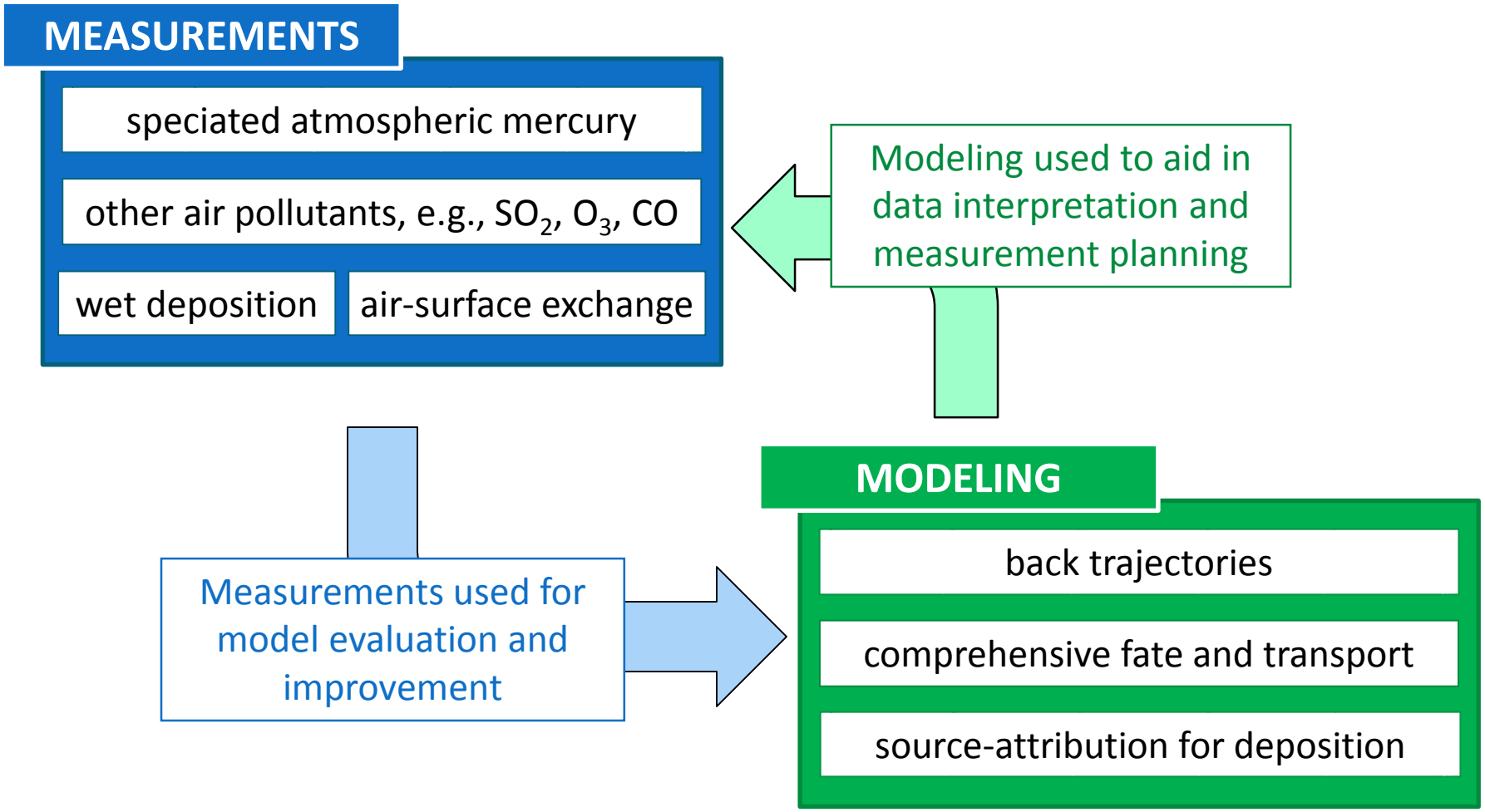
Summary

- GOM measurements at MLO agree broadly with observations at other high elevation sites, but PBM concentrations at MLO are substantially larger. Why?
- Although total mercury remains relatively constant, there is evidence of chemical/physical conversion of GEM to oxidized forms of mercury in the middle to upper troposphere, with minimal losses or removal.
- This suggests that the global pool of oxidized mercury in the free troposphere may be substantial.

Future Directions:

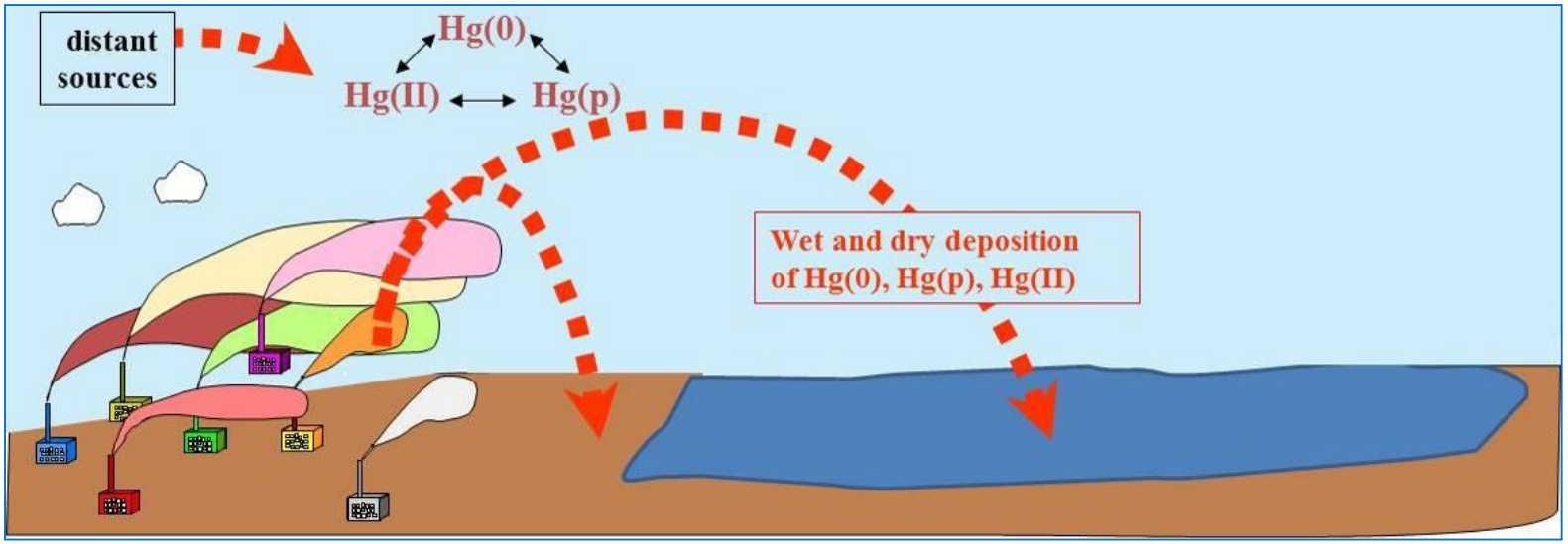
- Trajectory frequency analysis to investigate air mass history and to better understand the role of long-range transport
- Compare data with other high-altitude sites (e.g., Lulin)
- Use of additional ancillary data (CO, soot carbon, etc.) to better understand mercury dynamics

Mercury: Measurements and Modeling



Modeling – Approaches

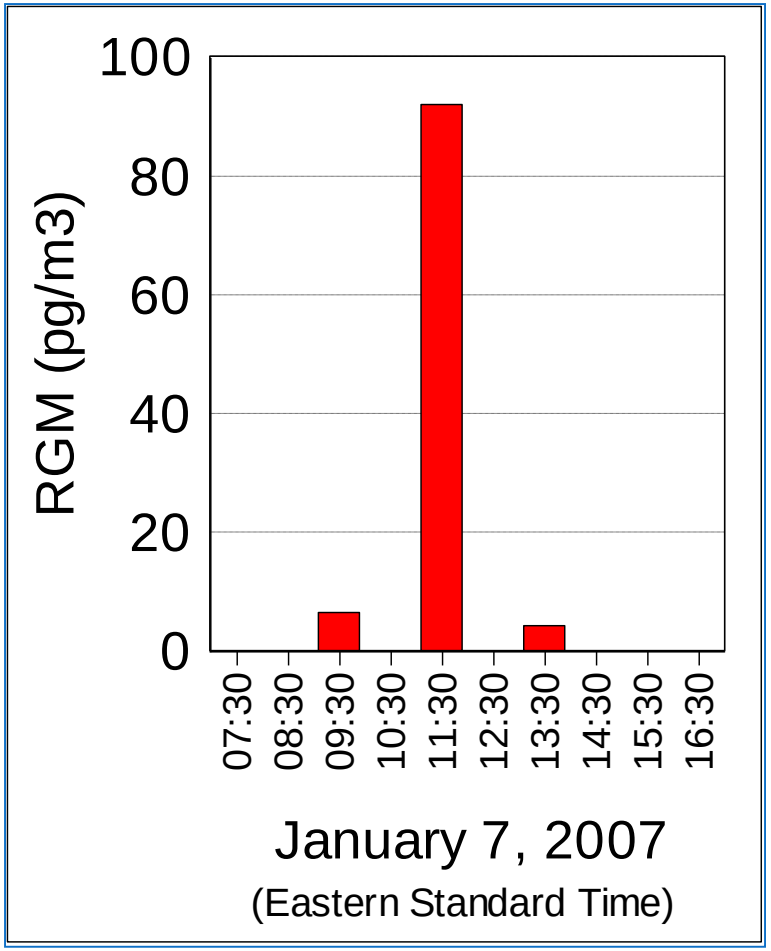
- Back-trajectory analyses with HYSPLIT
- Fate and transport modeling with HYSPLIT-Hg



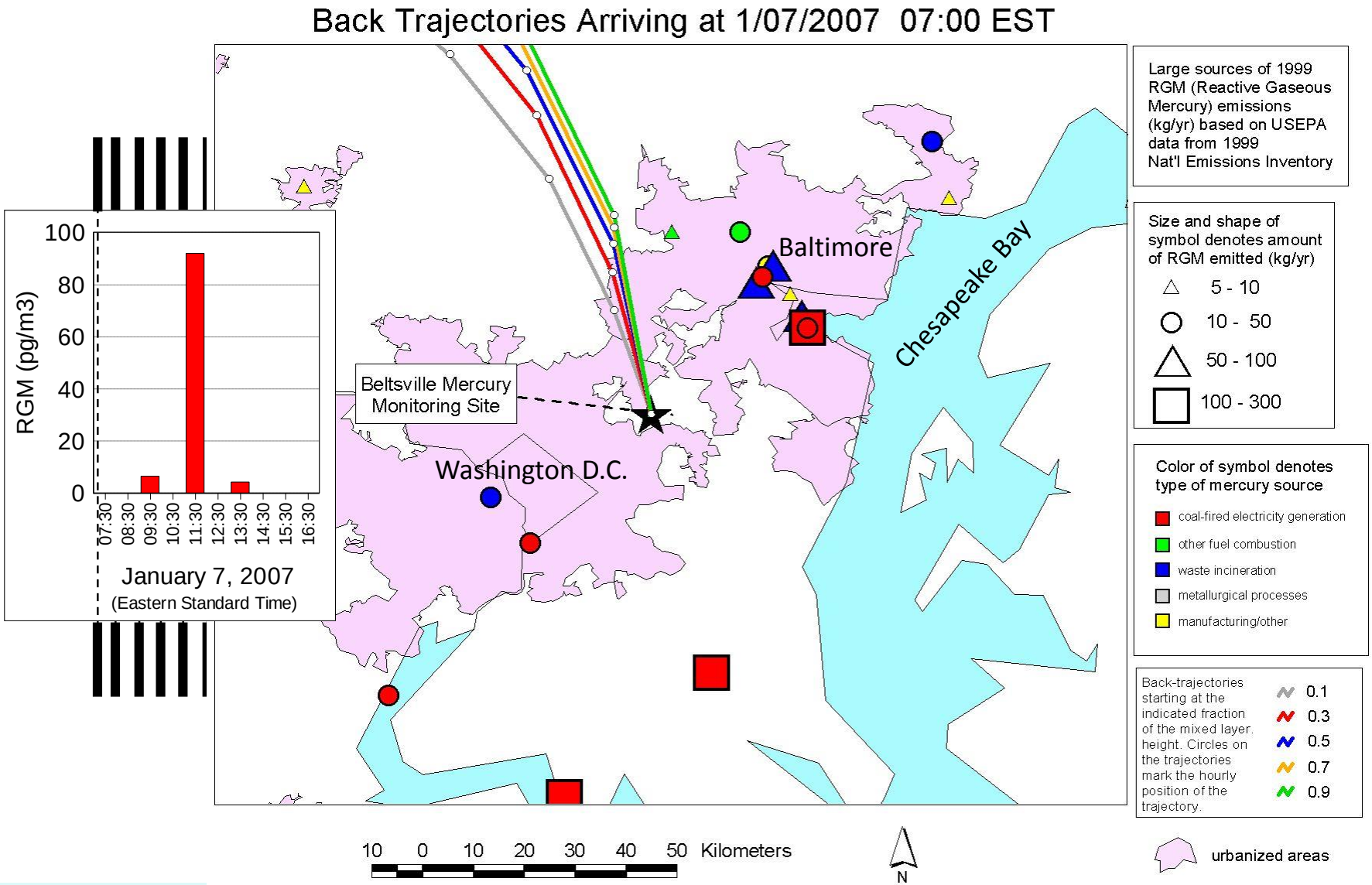
…focus on source-receptor relationships

Back Trajectory Analysis – Episodes

Beltsville, Maryland
mercury site

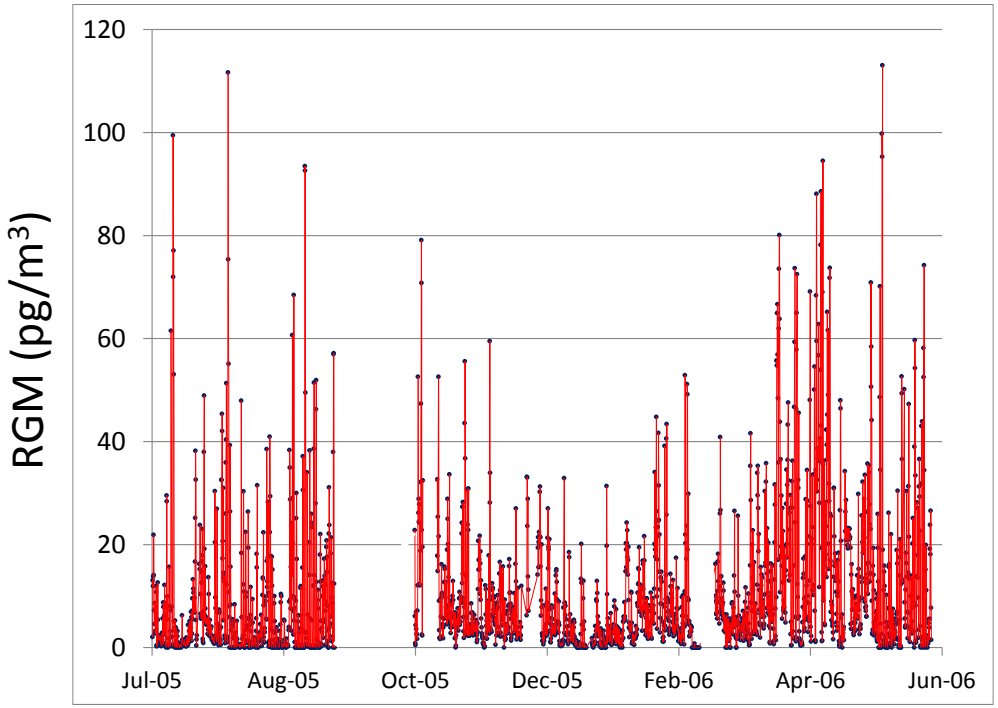


Reactive Gaseous Mercury episode


Back Trajectories Arriving at 1/07/2007 07:00 EST
RGM (pg/m3)
100
80
60
40
20
0
07:30
08:30
09:30
10:30
11:30
12:30
13:30
14:30
15:30
16:30
January 7, 2007
(Eastern Standard Time)
Beltsville Mercury Monitoring Site
Baltimore
Chesapeake Bay
Washington D.C.
Large sources of 1999 RGM (Reactive Gaseous Mercury) emissions (kg/yr) based on USEPA data from 1999 Nat'l Emissions Inventory
Size and shape of symbol denotes amount of RGM emitted (kg/yr)
5 - 10
10 - 50
50 - 100
100 - 300
Color of symbol denotes type of mercury source
coal-fired electricity generation
other fuel combustion
waste incineration
metallurgical processes
manufacturing/other
Back-trajectories starting at the indicated fraction of the mixed layer. height. Circles on the trajectories mark the hourly position of the trajectory.
0.1
0.3
0.5
0.7
0.9
10 0 10 20 30 40 50 Kilometers
N
urbanized areas

Back Trajectory Analysis – "Gridded Trajectory Frequencies"

Instead of single-event analysis, a way to analyze a more extensive data record at a given site



One year of hourly reactive gaseous mercury (RGM) measurements at the Piney Reservoir site in Western Maryland, courtesy of Mark Castro, Univ. of Maryland

- When measured concentrations at a given site are relatively high (or low), where do the air masses arriving at the site tend to come from?
- Are these regions related – or not – to known mercury sources?
- What fraction of trajectories for a given subset of measurements (e.g., top 10% of RGM measurements) pass through each grid square throughout a given domain?
- How does this geographical "trajectory gridded frequency" pattern compare with locations of known mercury air emissions sources?

Modeling – Comprehensive Fate and Transport Simulations

- Start with an emissions inventory
- Use gridded meteorological data
- Simulate the dispersion, chemical transformation, and wet and dry deposition of mercury emitted to the air
- Source-attribution information needed at the end, so optimize modeling system and approach to allow source-receptor information to be captured
- HYSPLIT-Hg developed over the last ~10 years with specialized algorithms for simulation of atmospheric mercury