Atmospheric Mercury Research

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Air Resources Laboratory

ARL Laboratory Review
May 3-5, 2011

Context

- Mercury exposure via fish consumption is an important public health concern
- NOAA has a primary stewardship responsibility for the nation's fisheries
- 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

Mercury: Measurements and Modeling

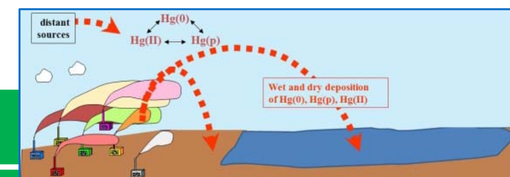
MEASUREMENTS

- speciated atmospheric mercury
- other air pollutants, e.g., SO_2, O_3, CO
- wet deposition
- air-surface exchange

Modeling used to aid in data interpretation and measurement planning

Measurements used for model evaluation and improvement

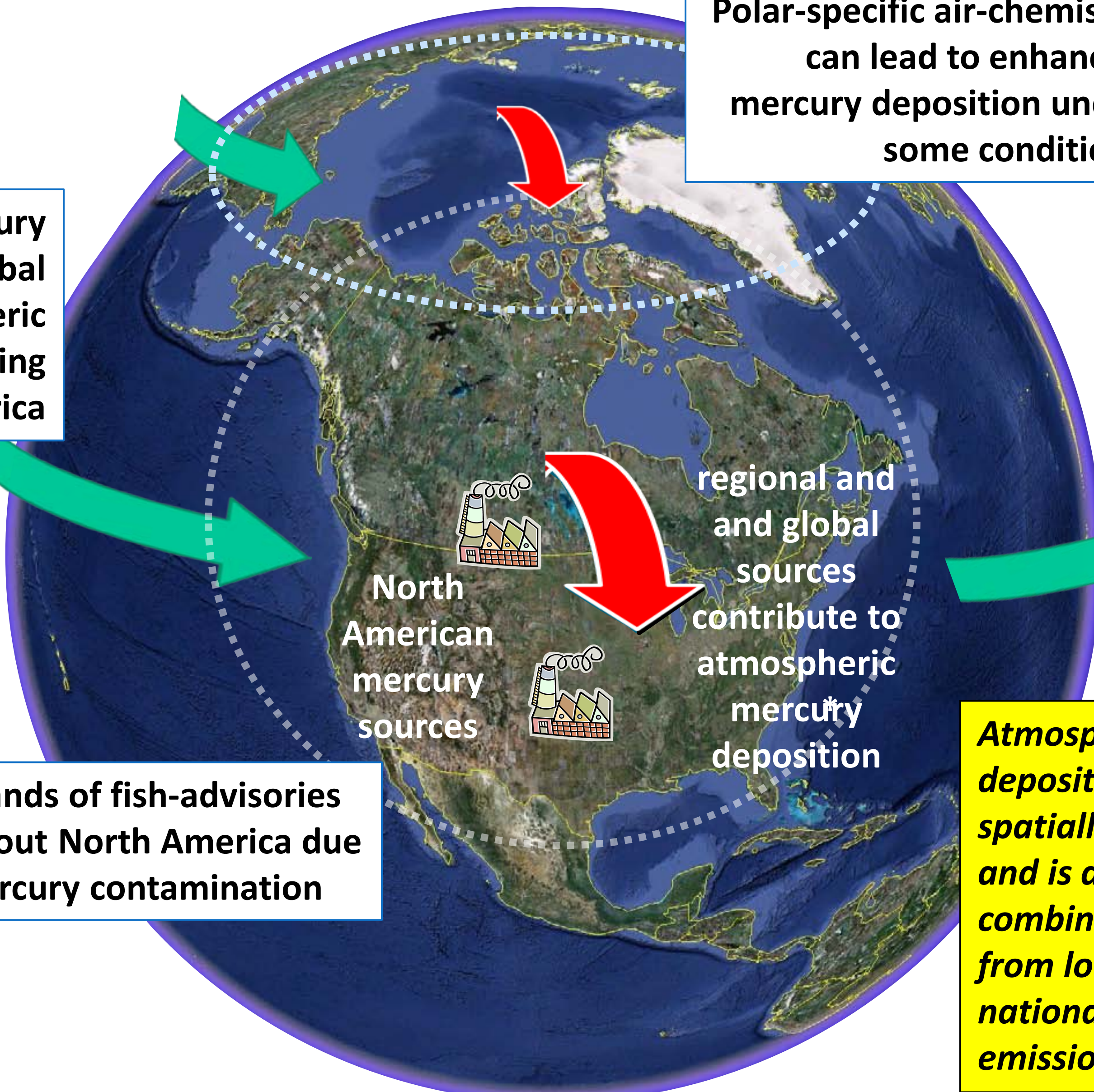
MODELING



- back trajectories
- comprehensive fate and transport
- source-attribution for deposition

mercury from global atmospheric pool entering North America

Polar-specific air-chemistry can lead to enhanced mercury deposition under some conditions



mercury that doesn't deposit continues its global circulation

Thousands of fish-advisories throughout North America due to mercury contamination

Atmospheric mercury deposition varies spatially and temporally, and is always a complex combination of impacts from local, regional, national, and global emissions sources.

Different "forms" of mercury in the atmosphere

Elemental Mercury -- Hg(0)

- most of total Hg in atmosphere
- doesn't easily dry or wet deposit
- globally distributed

?

Reactive Gaseous Mercury -- RGM

- a few % of total atmos. Hg
- oxidized Hg ($HgCl_2$, others)
- *very* water soluble and "sticky"
- bioavailable

?

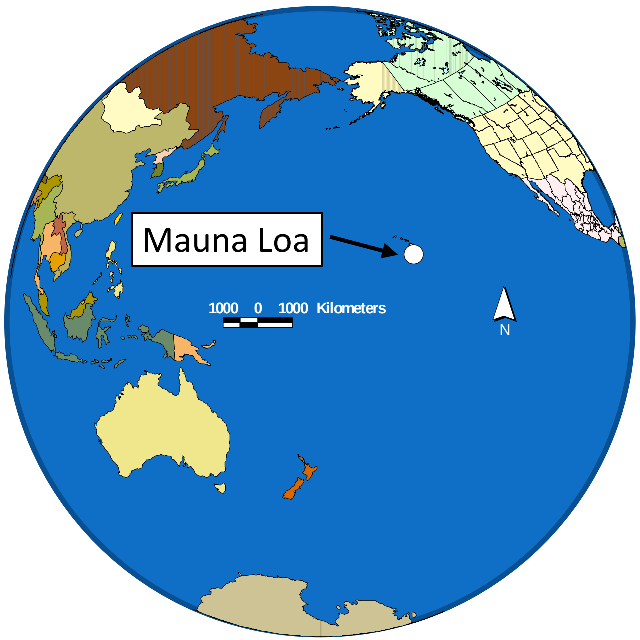
Particulate Mercury -- Hg(p)

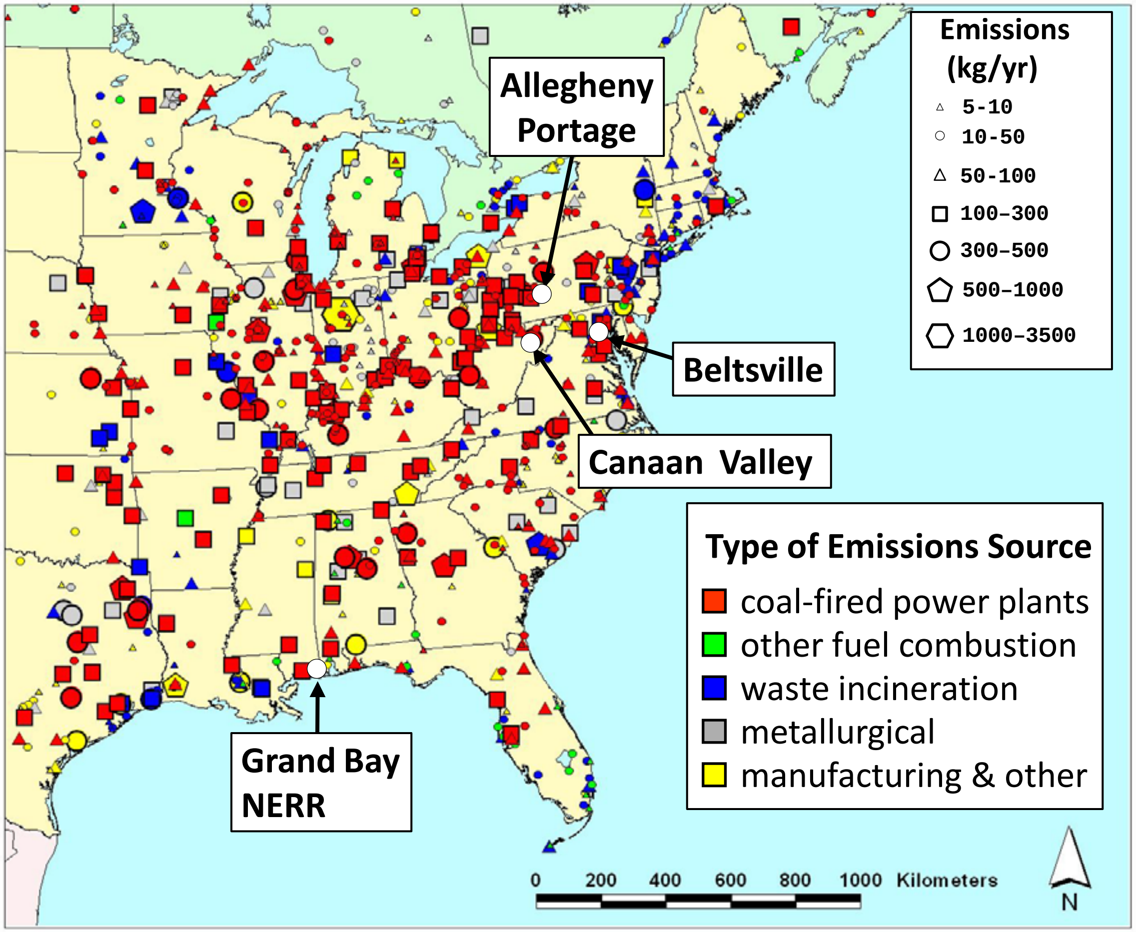
- a few % of total atmos. Hg
- Hg in/on atmos. particles
- atmos. lifetime 1~ 2 weeks
- bioavailability?

Measurements – Approaches

- Long-Term Monitoring
- Process Studies / Field Intensives

Measurement Approach – Long-Term Monitoring

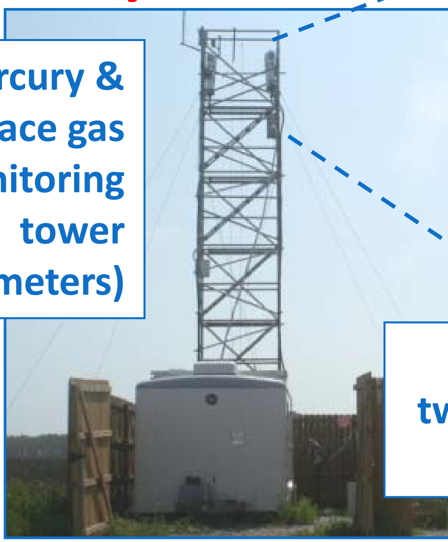




Four ARL long-term mercury measurement sites in the continental U.S., one in Hawaii; 2002 mercury emissions sources based on data from USEPA, Envr. Canada and the CEC

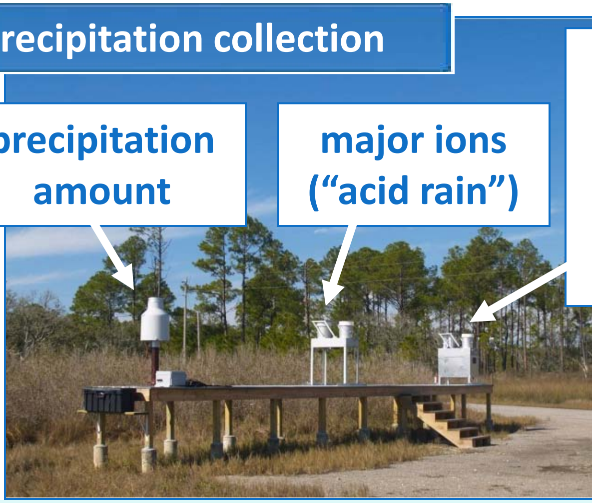
Long-Term Monitoring Examples

Grand Bay NERR



mercury & trace gas monitoring tower (10 meters)

top of tower with two sets of RGM and Hg(p) collectors



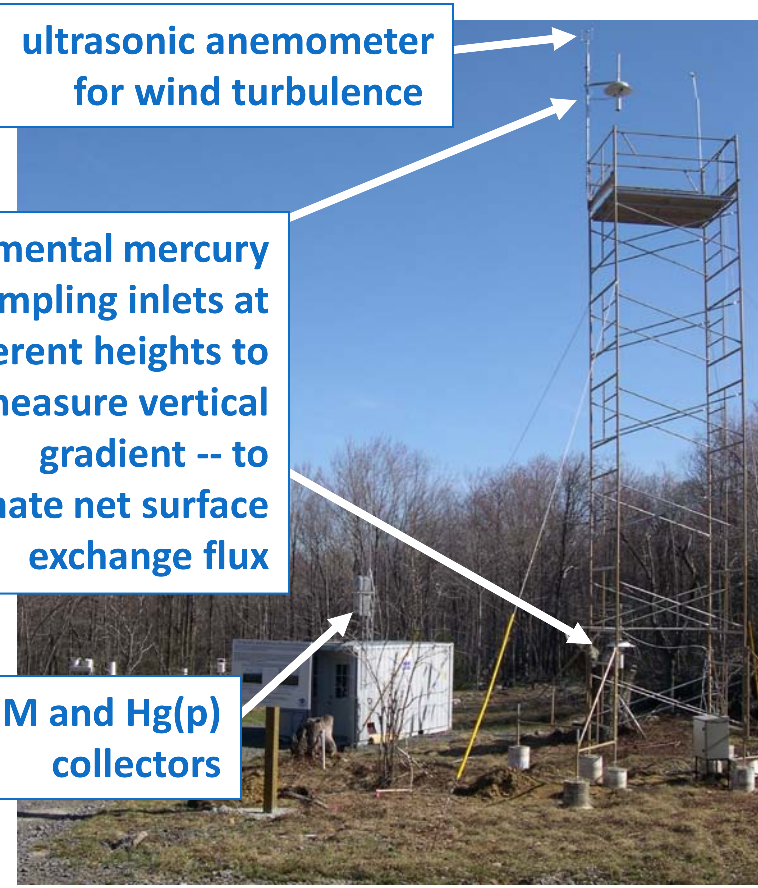
precipitation collection

precipitation amount

major ions ("acid rain")

Mercury Deposition Network and heavy metals

Canaan Valley



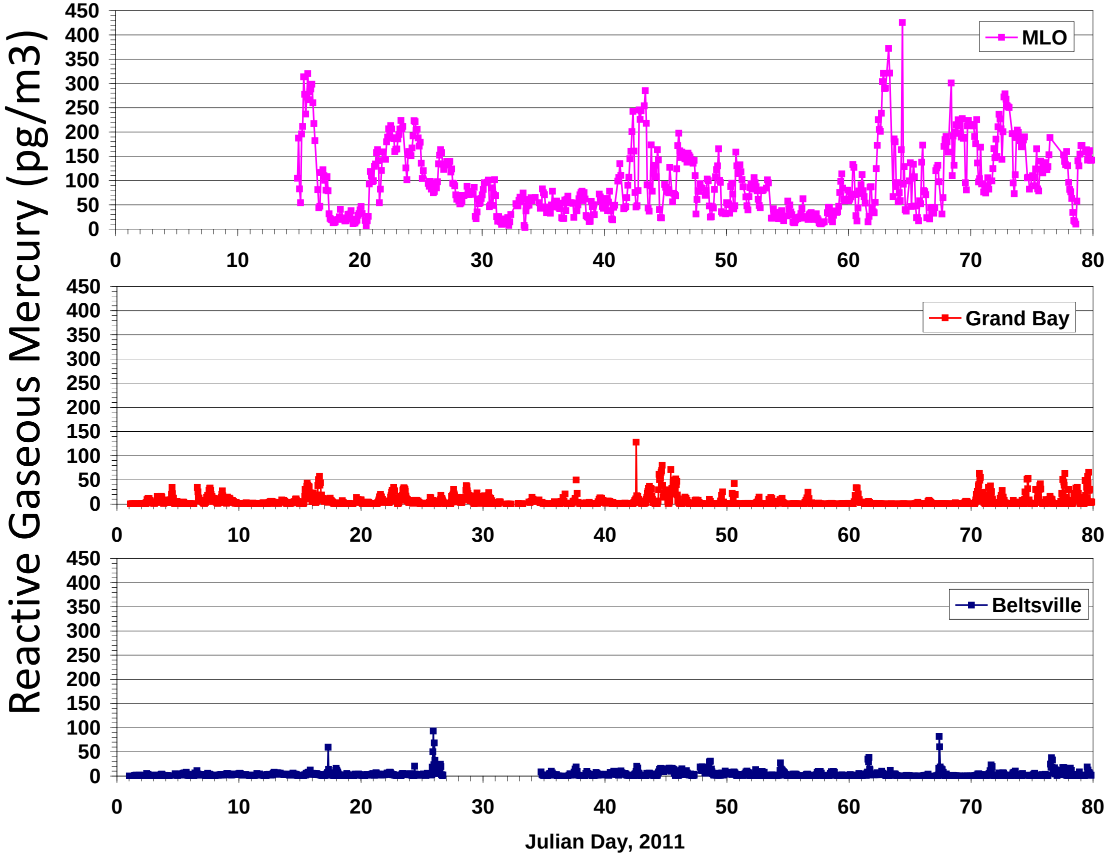
ultrasonic anemometer for wind turbulence

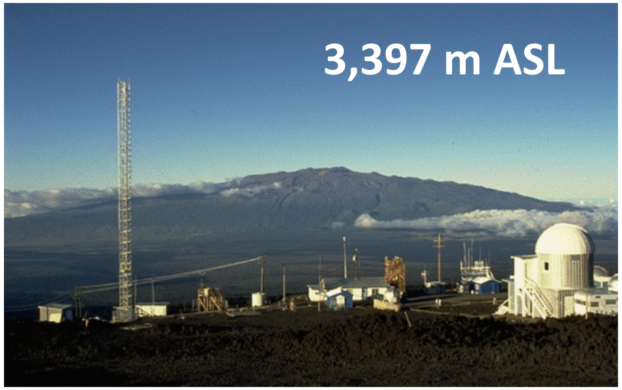
elemental mercury sampling inlets at different heights to measure vertical gradient -- to estimate net surface exchange flux

RGM and Hg(p) collectors

Mauna Loa Observatory, Hawaii: *since January 2011*

Research Question: *What is the reason for the dramatically higher reactive gaseous mercury (RGM) concentrations at Mauna Loa (in the free troposphere) -- relative to typical concentrations at low elevation sites?*





- down-slope flow from the free troposphere at night
- ideal location to study atmospheric mercury chemistry at a high-altitude, remote location

Measurements – Summary

NOAA-led measurement (red dot)
Co-located measurement (green dot)

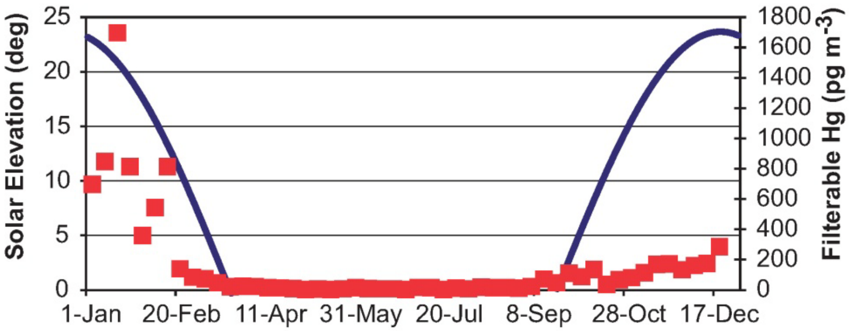
Site	Collaborators	Ambient Air Measurements						Precipitation			Dry Deposition		Other
		Mercury Speciation	SO_2	O_3	NO/NO_y	CO	Carbon black	Major Ions (NTN)	Mercury (MDN)	Trace Metals	Surrogate Surface	Throughfall	Meteor-ology
Beltsville (MD)	*PI = Winston Luke (NOAA)* EPA Clean Air Markets Division Univ of Md; Maryland DNR MACTEC; USGS	NOAA-led, NOAA-led	Co-located	Co-located	Co-located	Co-located		Co-located	Co-located			Co-located	Co-located
Grand Bay (MS)	*PI = Winston Luke (NOAA)* Grand Bay NERR, NOAA-NCCOS MS Dept Envr Quality USEPA, US Fish & Wildlife Service	NOAA-led, NOAA-led	NOAA-led	NOAA-led	NOAA-led	NOAA-led	NOAA-led	Co-located	Co-located	Co-located			NOAA-led
Mauna Loa (HI)	*PI = Winston Luke (NOAA)* NOAA ESRL Many others	NOAA-led	Co-located	Co-located		Co-located	Co-located						Co-located
Canaan Valley (WV)	*PI = Steve Brooks(CVI/NOAA)* Canaan Valley Institute Univ Md Frostburg Lab USGS	NOAA-led		NOAA-led				NOAA-led	NOAA-led		NOAA-led	Co-located	NOAA-led
Allegheny Portage (PA)	*PI = Steve Brooks (CVI/NOAA)* Canaan Valley Institute Pennsylvania DEP National Park Service	NOAA-led						Co-located	Co-located				

Measurement Approach – 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
    - Surface exchange using micrometeorological and surrogate-surface techniques

…the first estimates of the mercury balance and cycling for the Antarctic polar plateau

(see Steve Brooks' poster regarding polar mercury studies)



Weekly averages of filterable Hg (discrete points) and the solar elevation angle at South Pole Station from 2003 to 2006. The peak annual filterable Hg lags the solar maximum by 3–4 weeks.

Steve Brooks, NOAA – ARL, Barrow Alaska

Process Studies / Field Intensives

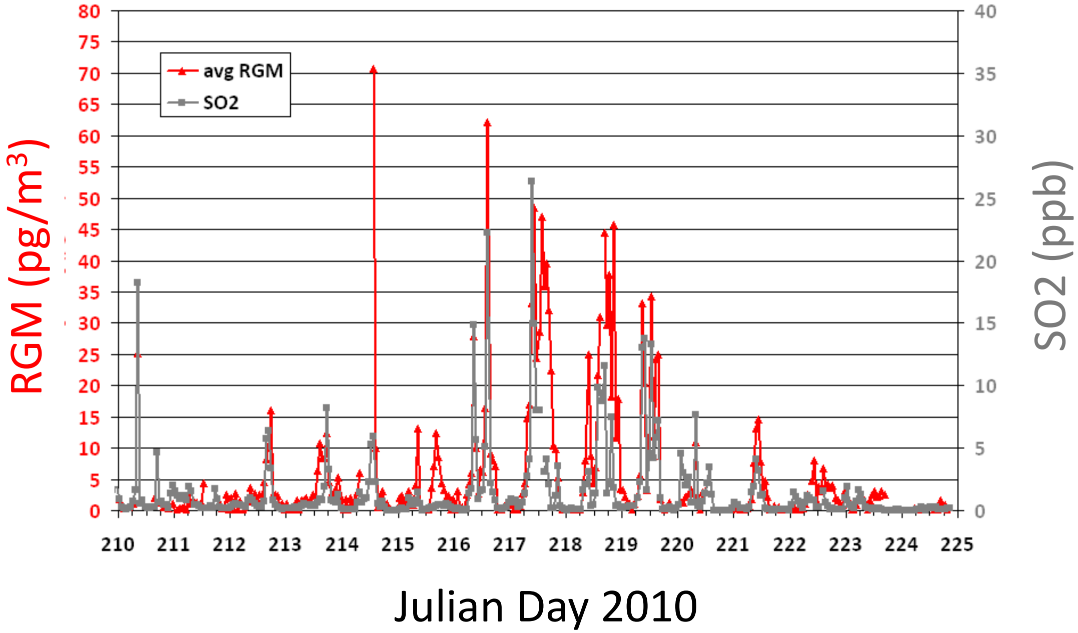
Grand Bay (MS) Field Intensive
July-Aug 2010, April-May 2011

Launching an ozonesonde to collect ozone & meteorological data

Univ. of Tenn. Space Inst. plane for air measurements

- Investigating the roles of:
  - halogen chemistry in the marine layer and free troposphere
  - transport from upper atmos.
  - local/regional emissions
- Measurements at surface and aloft
- 2nd phase ongoing now
- ***see Winston Luke's poster***

Surface RGM and SO2 at the Grand Bay NERR site during the August 2010 intensive

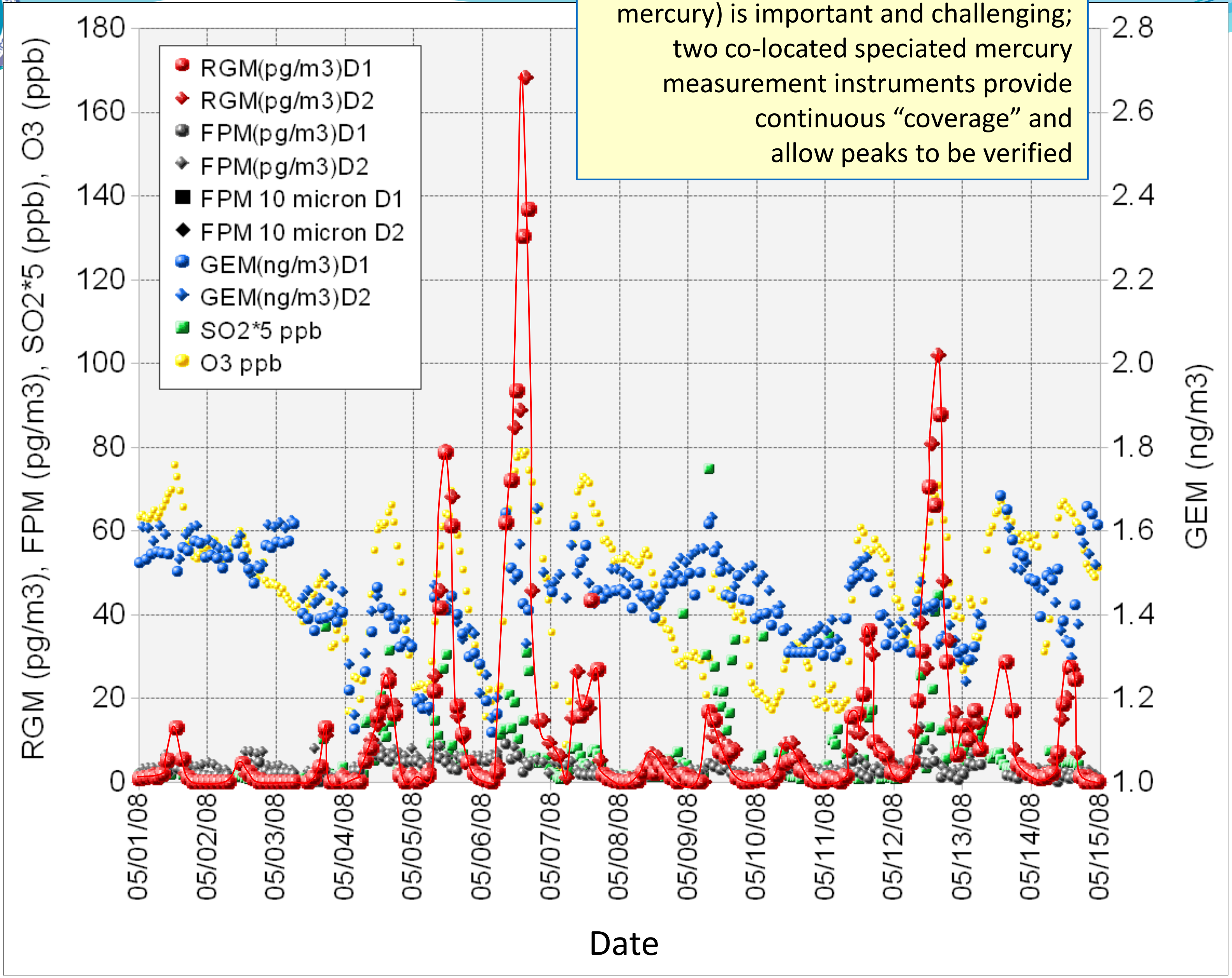


Measurements – Accomplishments

- **long term, high-quality data**
  - atmospheric chemistry
  - trend analysis
  - local vs. long-range transport
  - source-receptor studies
  - model evaluation

Inside the instrument trailer at the Grand Bay NERR long term mercury monitoring site

Measuring RGM (reactive gaseous mercury) is important and challenging; two co-located speciated mercury measurement instruments provide continuous "coverage" and allow peaks to be verified



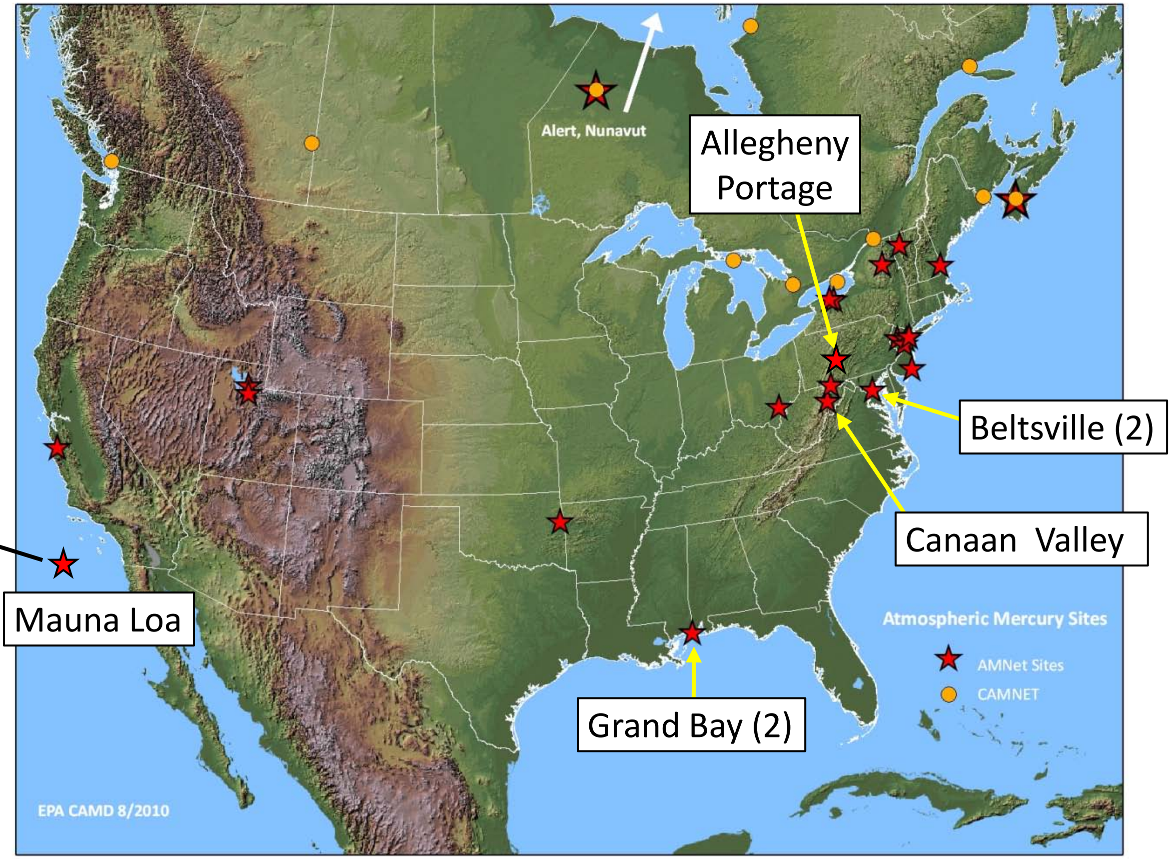
Measurements – Accomplishments

- **long term, high-quality data**
  - atmospheric chemistry
  - trend analysis
  - local vs. long-range transport
  - source-receptor studies
  - model evaluation
- **method development**
  - improved accuracy, operational robustness
  - reduction of sample bias, artifact losses
- **advances in scientific understanding**
  - Polar mercury dynamics
  - dry deposition

Inside the instrument trailer at the Grand Bay NERR long term mercury monitoring site

Measurements – Indicators of Success

- Peer-reviewed publications (e.g., *Atmos. Environ.*, *Geophys. Res. Letters*)
- Funding from other agencies (e.g., EPA, NSF)
- Founding member and key contributor to the Atmospheric Mercury Monitoring Network (AMNet)
    - Data
    - Methods
    - Data analysis



NOAA-ARL sites contributing to the Atmospheric Mercury Monitoring Network (AMNet), an emerging speciated mercury air concentration network

Measurements – Collaborators

NOAA
- Grand Bay National Estuarine Reserve (NERR)
- Nat'l Centers for Coastal & Ocean Science (NCCOS)
- Earth Systems Research Laboratory (ESRL)
- National Weather Service (NWS)
- Sea Grant
- Environmental Research Program (ERP)

Other Federal Agencies
- EPA Clean Air Markets Division (CAMD)
- Fish and Wildlife Service
- Department of Agriculture
- National Park Service
- National Science Foundation
- U.S. Geological Survey

State/Local Governments
- Maryland, Mississippi, Pennsylvania, Texas, Alaska, Virginia, West Virginia

Universities and Institutes
- Canaan Valley Institute
- Florida State University
- University of Houston
- University of Maryland
- University of Tennessee Space Institute
- University of Miami (Florida)
- Georgia Tech University
- Mississippi State University
- Jackson State University
- University of Michigan
- University of Nevada
- University of Illinois
- Valparaiso University

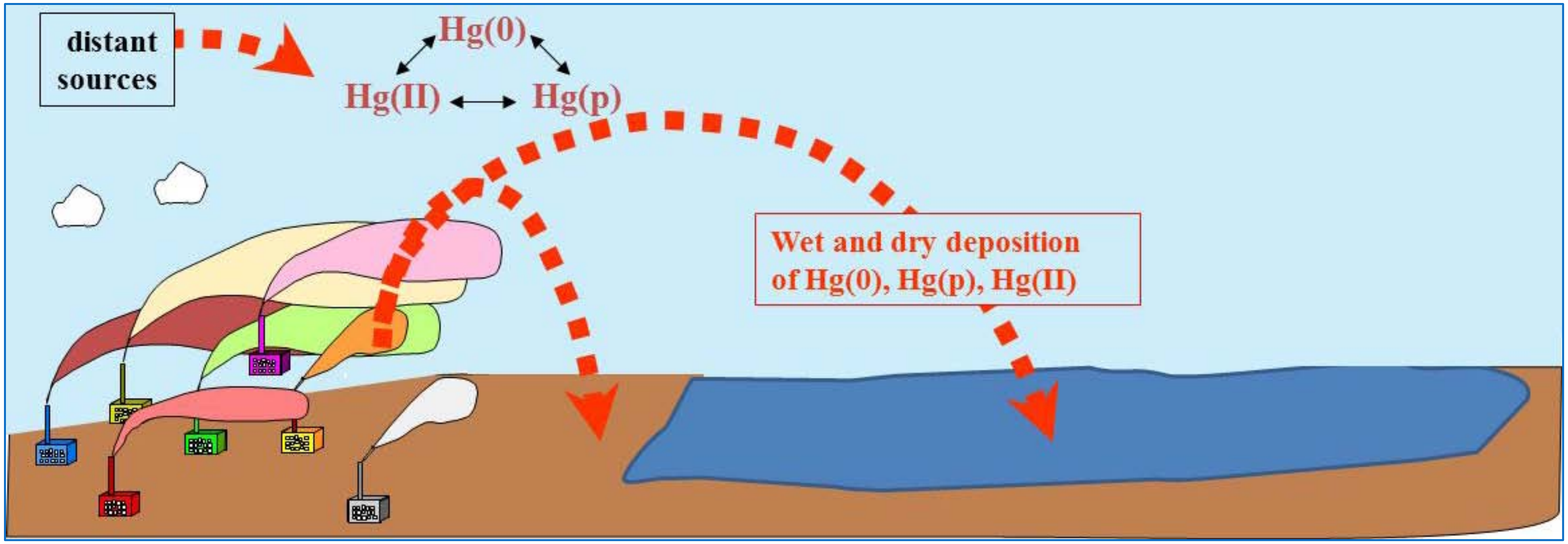
Industry
- TEKRAN
- Electric Power Research Institute
- Southern Company

Measurements – Future Directions

- Optimize existing measurement methods
- Develop new methods, e.g.,
  - laser-based eddy correlation system
  - relaxed-eddy-accumulation (REA) system
  - surrogate surfaces as low cost, simple devices for oxidized mercury concentrations and dry deposition estimates
- Additional measurements at long-term sites
- Publication and additional analysis of datasets
- Field intensives involving process studies to address key uncertainties
- Assess effects of forest fires and floods on ecosystem mercury loads
- Assess the potential impacts of climate change on polar mercury oxidation, deposition, and glacial sequestration

Modeling – Approaches

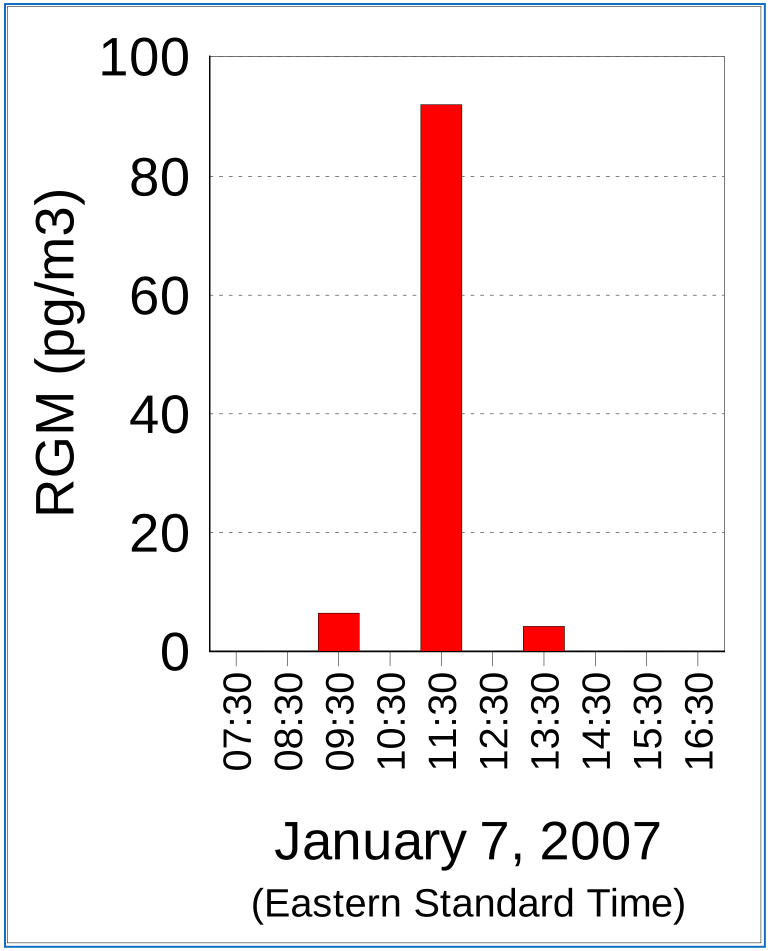
- Back-trajectory analyses with HYSPLIT
- Fate and transport modeling with HYSPLIT-Hg



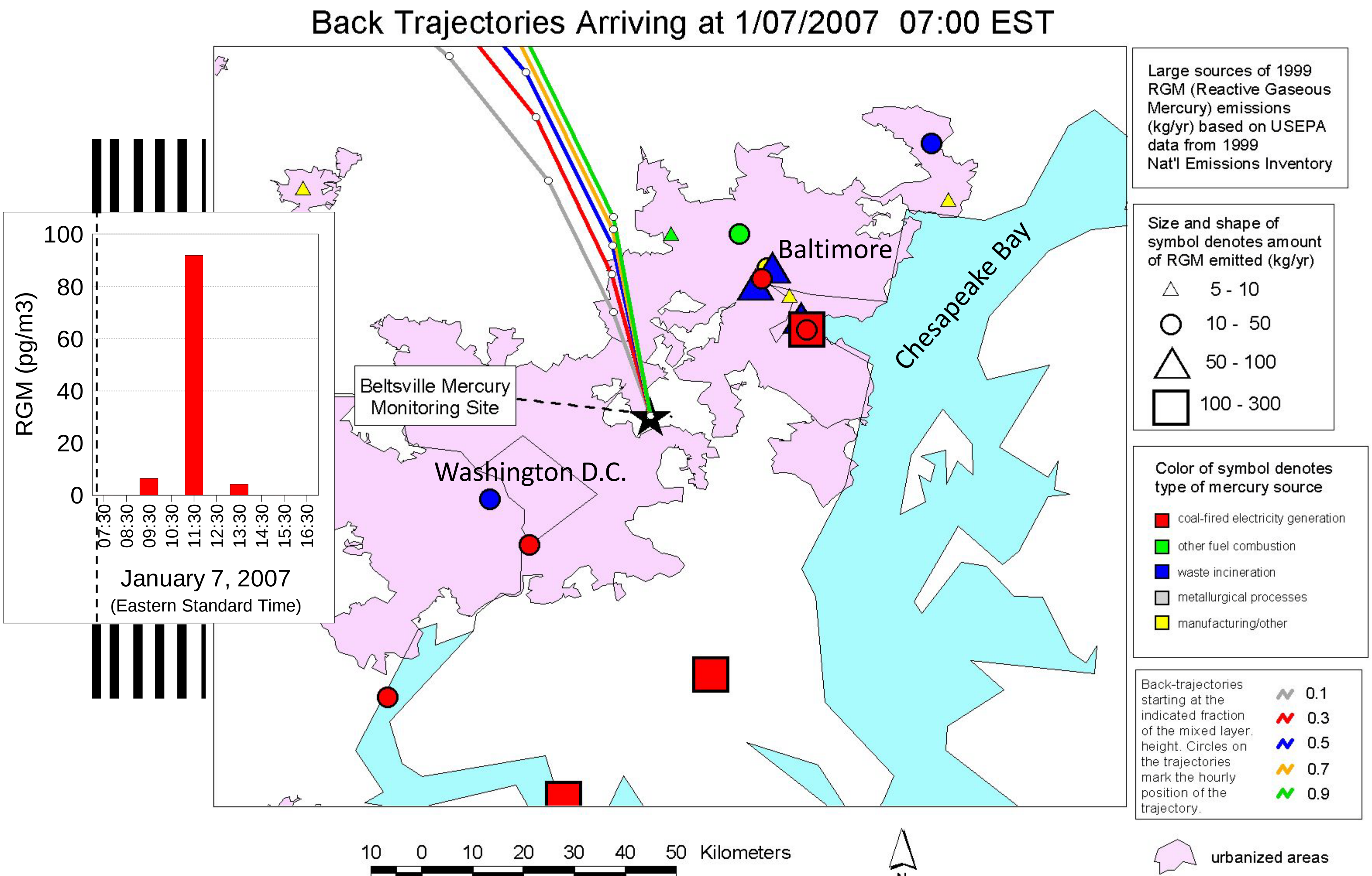
…focus on source-receptor relationships

Back Trajectory Analysis – Episodes

Beltsville, Maryland
mercury site



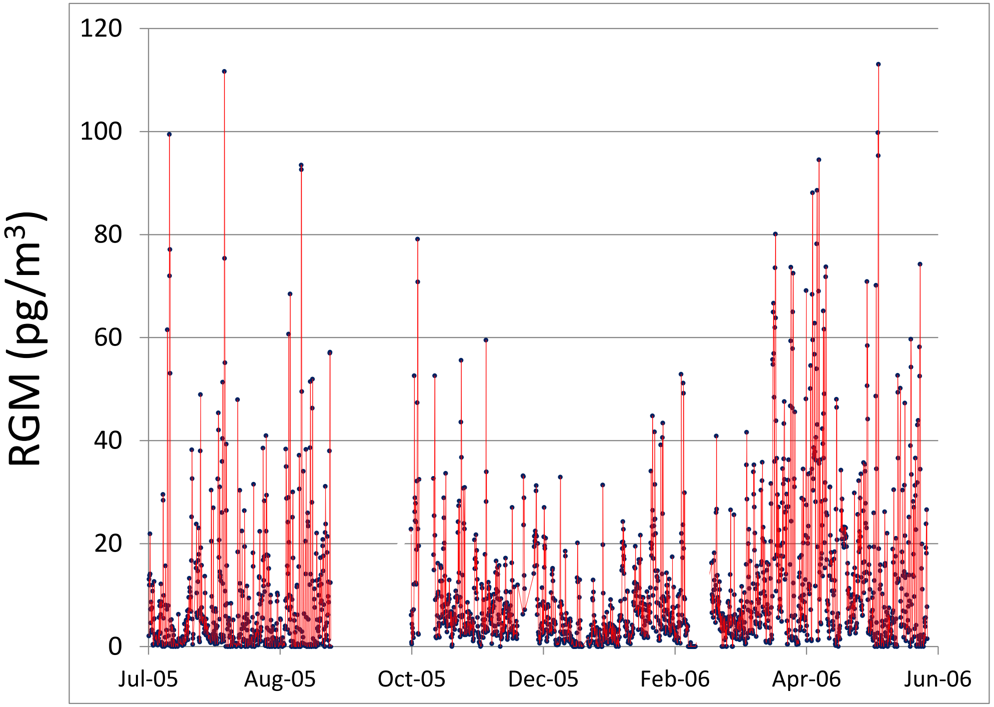
Reactive Gaseous Mercury episode



Back Trajectories Arriving at 1/07/2007 07:00 EST
Baltimore
Chesapeake Bay
Washington D.C.
Beltsville Mercury Monitoring Site
100
80
60
40
20
0
RGM (pg/m3)
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)
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"

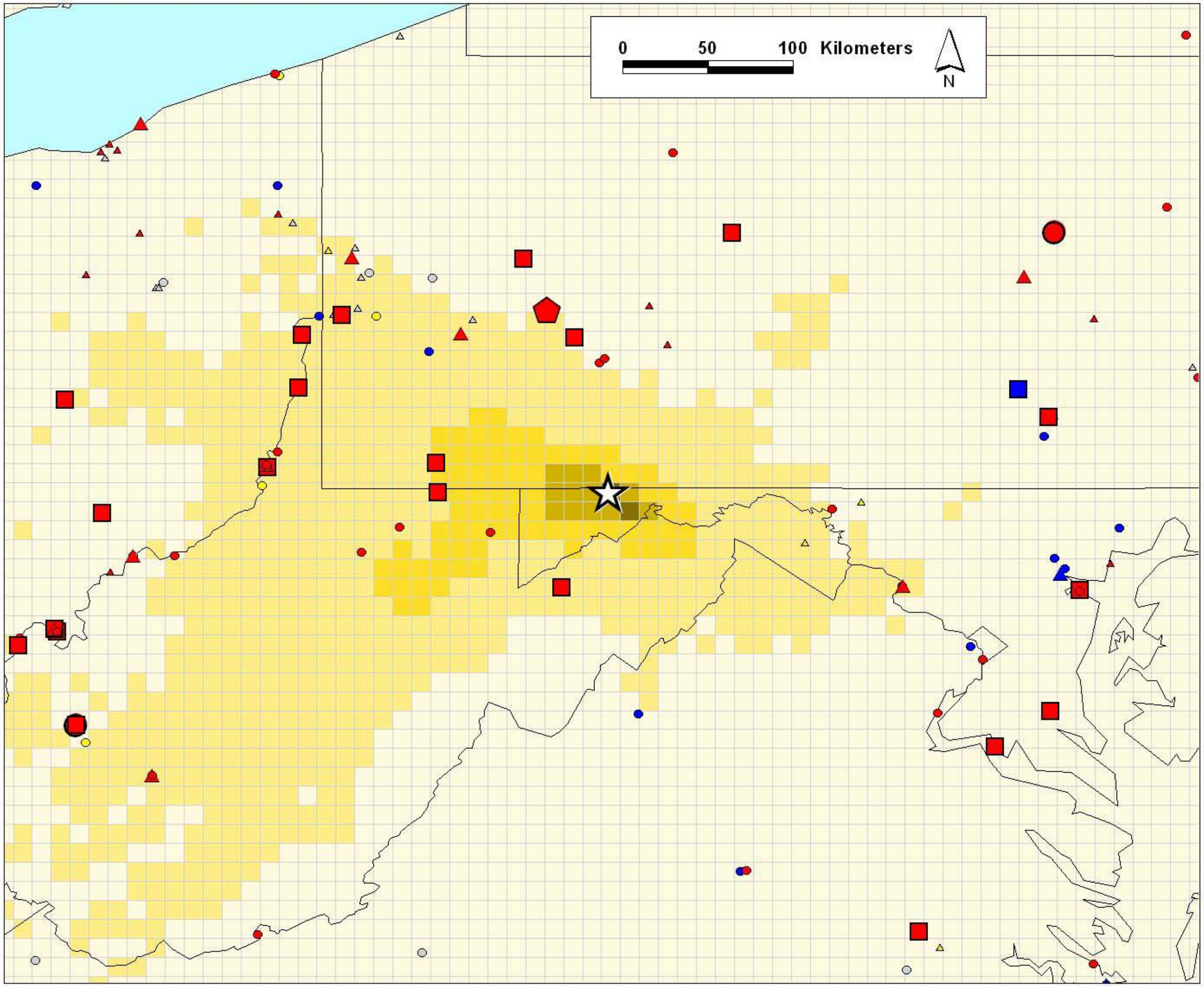
Instead of single-event analysis, a way to analyze a more extensive data record at a given site



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?
- An extension of trajectory cluster analysis
- 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?

Where the air at the Piney Reservoir site tended to come from -- on average -- over the entire year



0.1 degree lat/long regional grid

☆ Piney Measurement Site

Percent of back-trajectories passing through grid square

0 - 1
1- 3
3 - 6
6 – 10
10 - 100

Air Emissions

size/shape of symbol denotes amount of mercury emitted (kg/yr)

5 - 10
10 - 50
50 - 100
100 – 300
300 - 500
500 - 1000
1000 - 3500

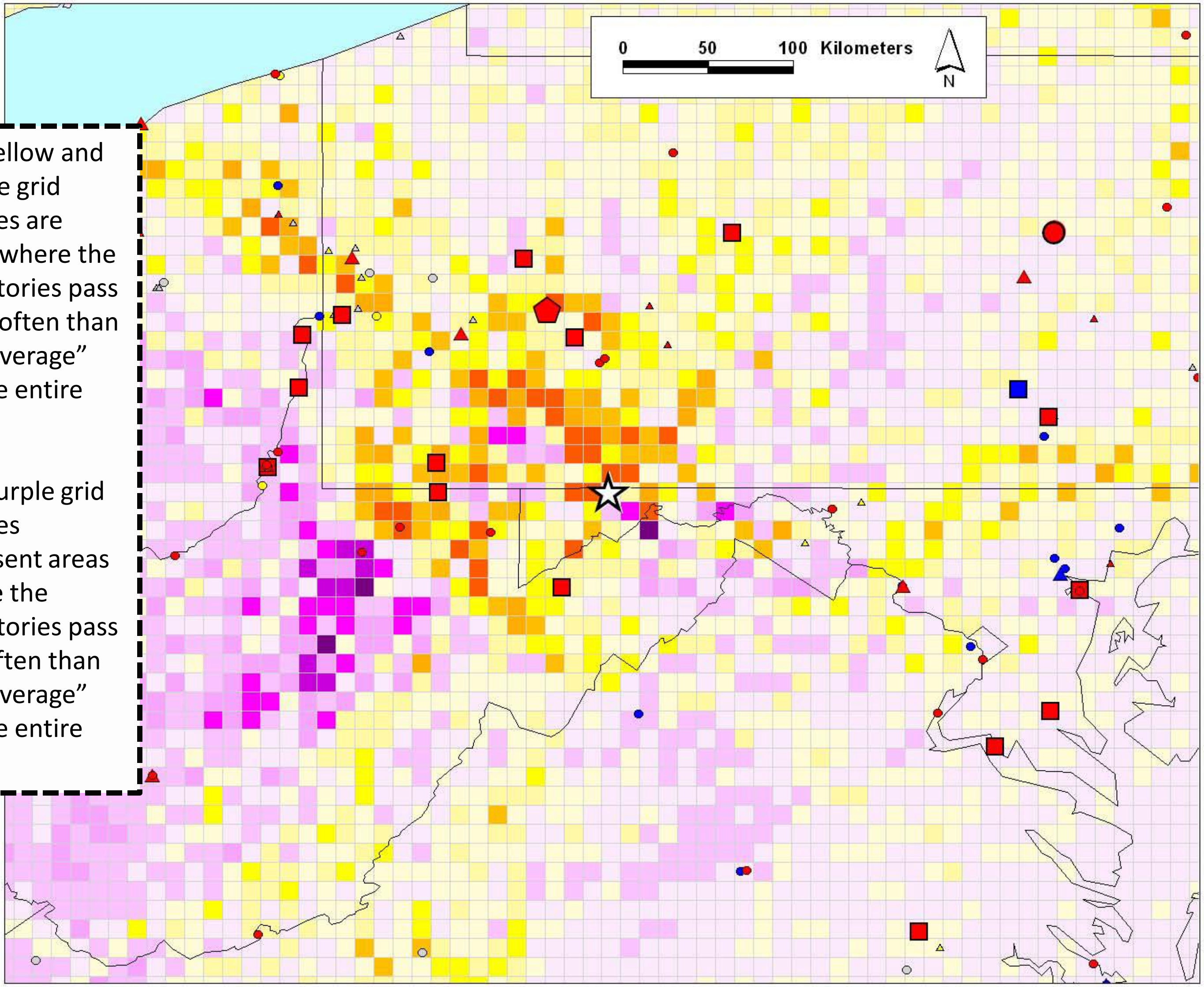
color of symbol denotes type of mercury source

coal-fired power plants
other fuel combustion
waste incineration
metallurgical
manufacturing & other

Where the air tended to come from when the measured RGM at the Piney Reservoir site was HIGH

The yellow and orange grid squares are areas where the trajectories pass more often than the "average" for the entire year

The purple grid squares represent areas where the trajectories pass less often than the "average" for the entire year



0.1 degree lat/long regional grid

☆ Piney Measurement Site

Difference between selected case and total year in percent of back-trajectories passing through grid square

	> 2.5		< -2.5
	2 – 2.5		-2.5 to -2
	1.5 - 2		-2 to -1.5
	1 to 1.5		-1.5 to -1
	0.5 - 1		-1 to -0.5
	0 to 0.5		-0.5 to 0

Air Emissions

size/shape of symbol denotes amount of mercury emitted (kg/yr)

▵	5 - 10
○	10 - 50
△	50 - 100
□	100 – 300
◯	300 - 500
⬠	500 - 1000
⬡	1000 - 3500

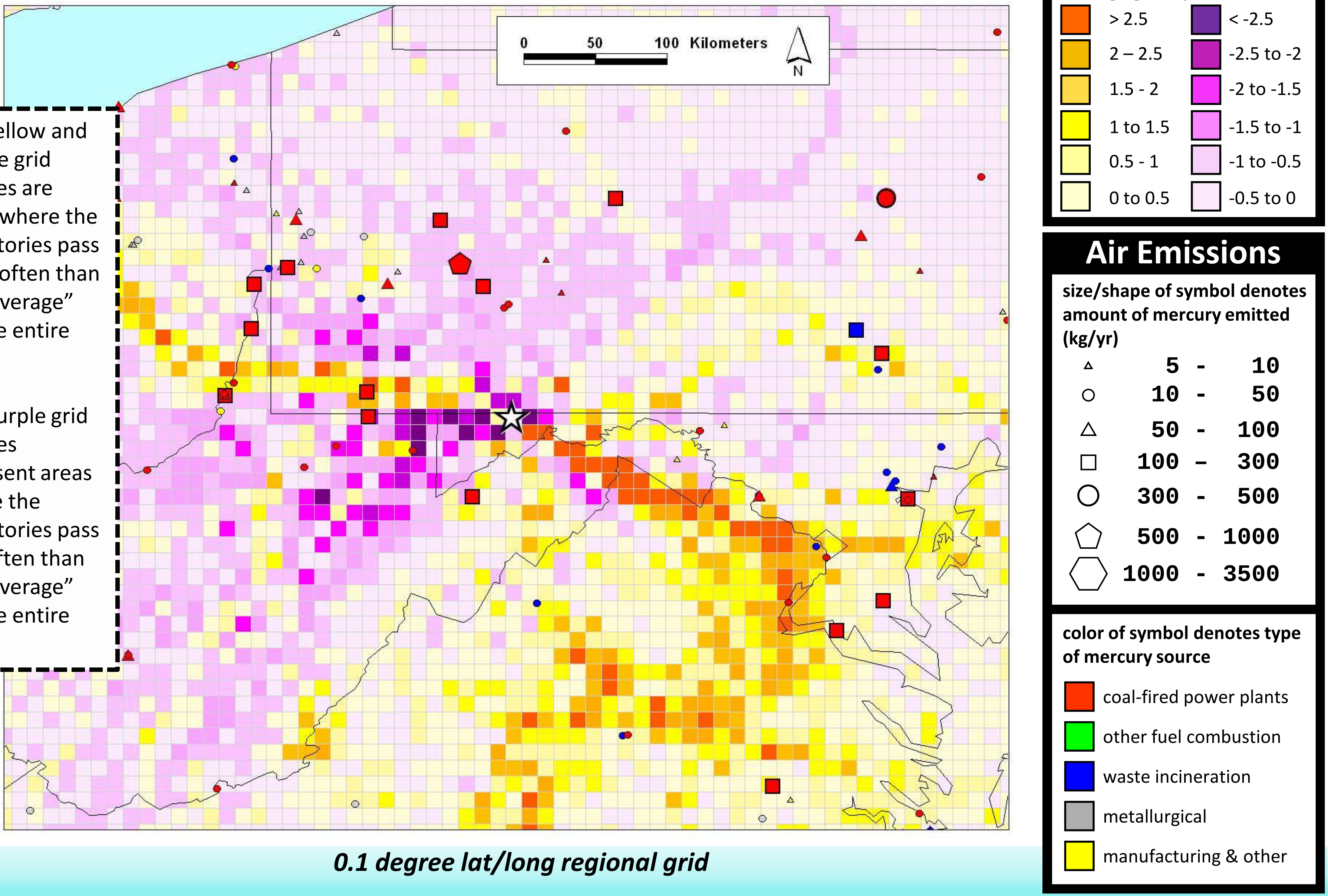
color of symbol denotes type of mercury source

- coal-fired power plants
- other fuel combustion
- waste incineration
- metallurgical
- manufacturing & other

Where the air tended to come from when the measured RGM at the Piney Reservoir site was LOW

The yellow and orange grid squares are areas where the trajectories pass more often than the "average" for the entire year

The purple grid squares represent areas where the trajectories pass less often than the "average" for the entire year



0.1 degree lat/long regional grid

Modeling – Comprehensive Fate and Transport Simulations

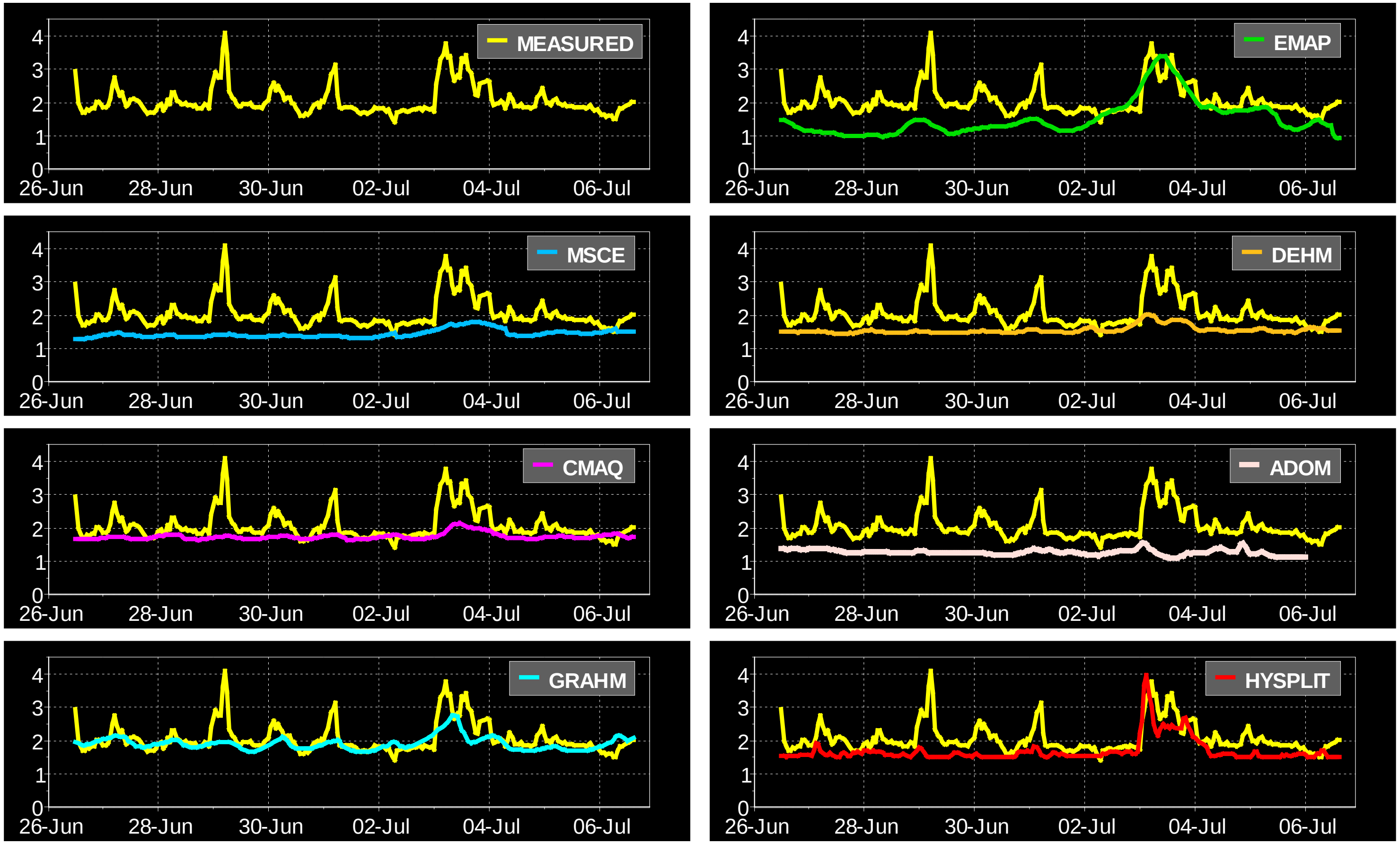
- Start with an emissions inventory
- Use gridded meteorological data
- Simulate the dispersion, chemical transformation, and wet and dry deposition of mercury emitted to the air
- Source-attribution information needed at the end, so optimize modeling system and approach to allow source-receptor information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

Modeling – Accomplishments

Successful performance in model evaluation and model intercomparison exercises

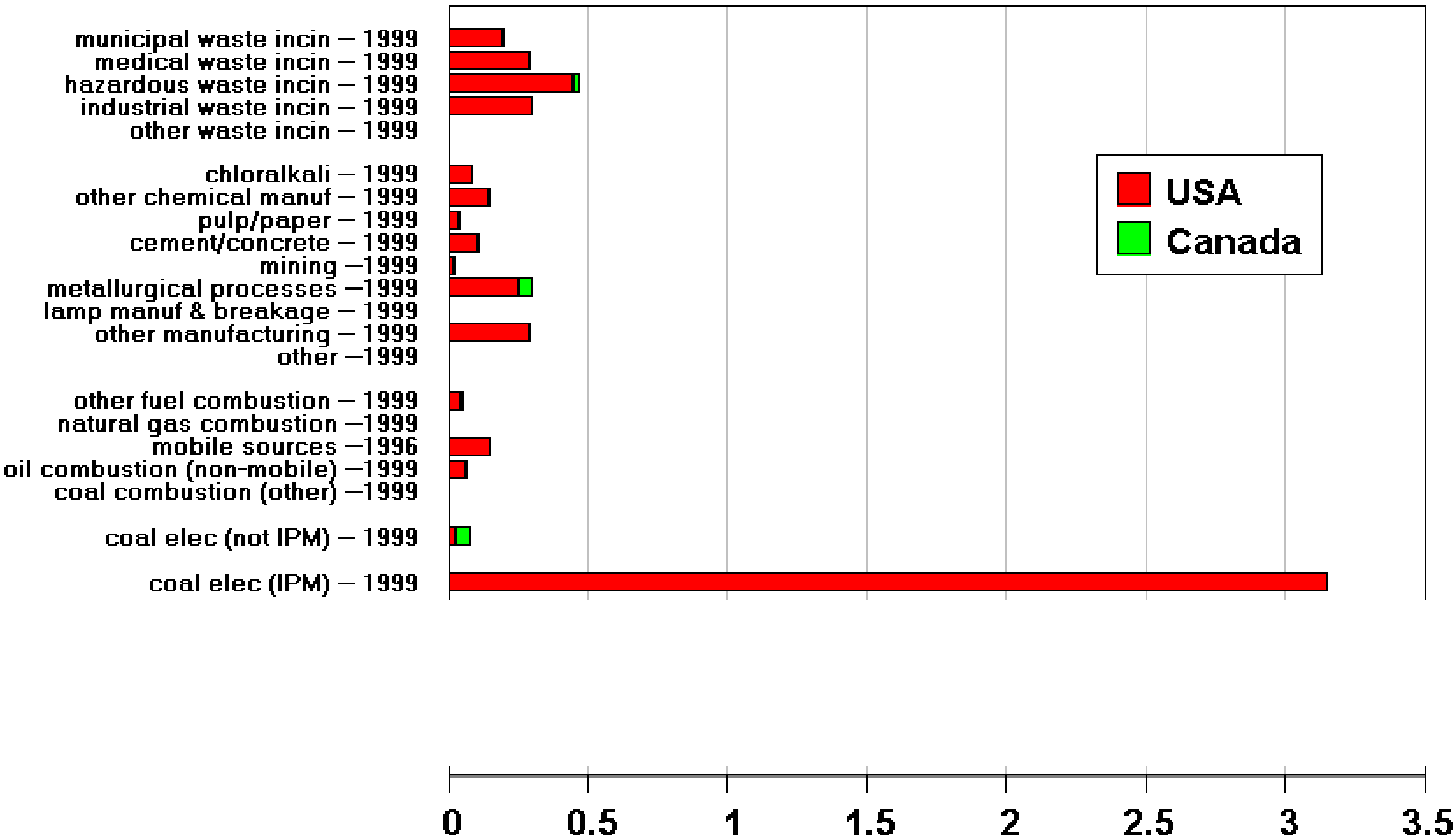
model inter-comparison and evaluation carried out in collaboration with numerous mercury modeling research groups around the world, under the auspices of EMEP (Europe)

Total Gaseous Mercury (ng/m³) at Neuglobsow, Germany, June 26 – July 6, 1995.



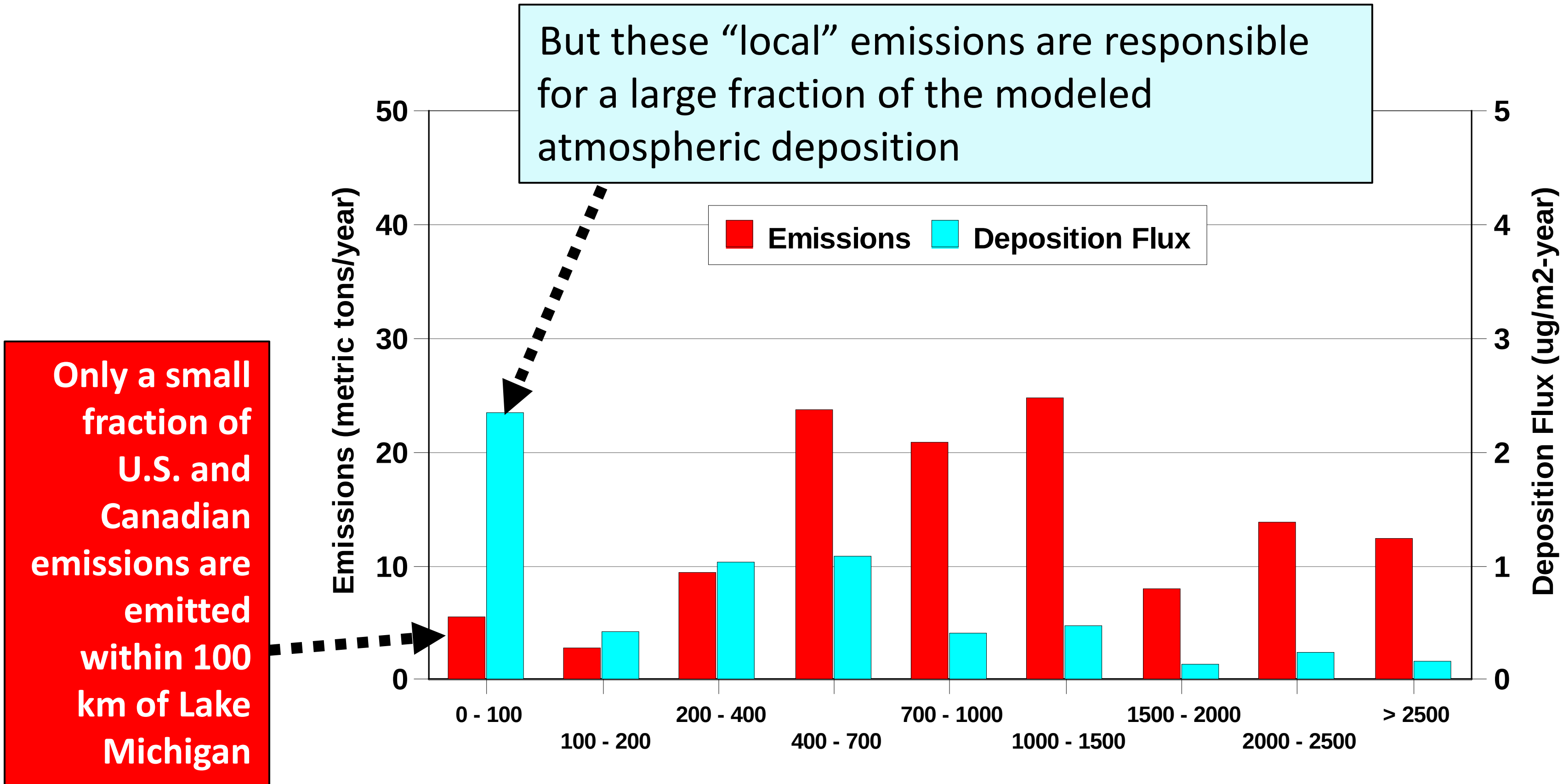
Ryaboshapko et al., **Intercomparison study of atmospheric mercury models: 1. Comparison of models with short-term measurements**. *Science of the Total Environment* **376**, 228-240, **2007**.

Modeling – Accomplishments



Atmospheric Deposition Flux to Lake Michigan from Anthropogenic Mercury Emissions Sources in the U.S. and Canada (g Hg/km2-year)

Modeling – Accomplishments

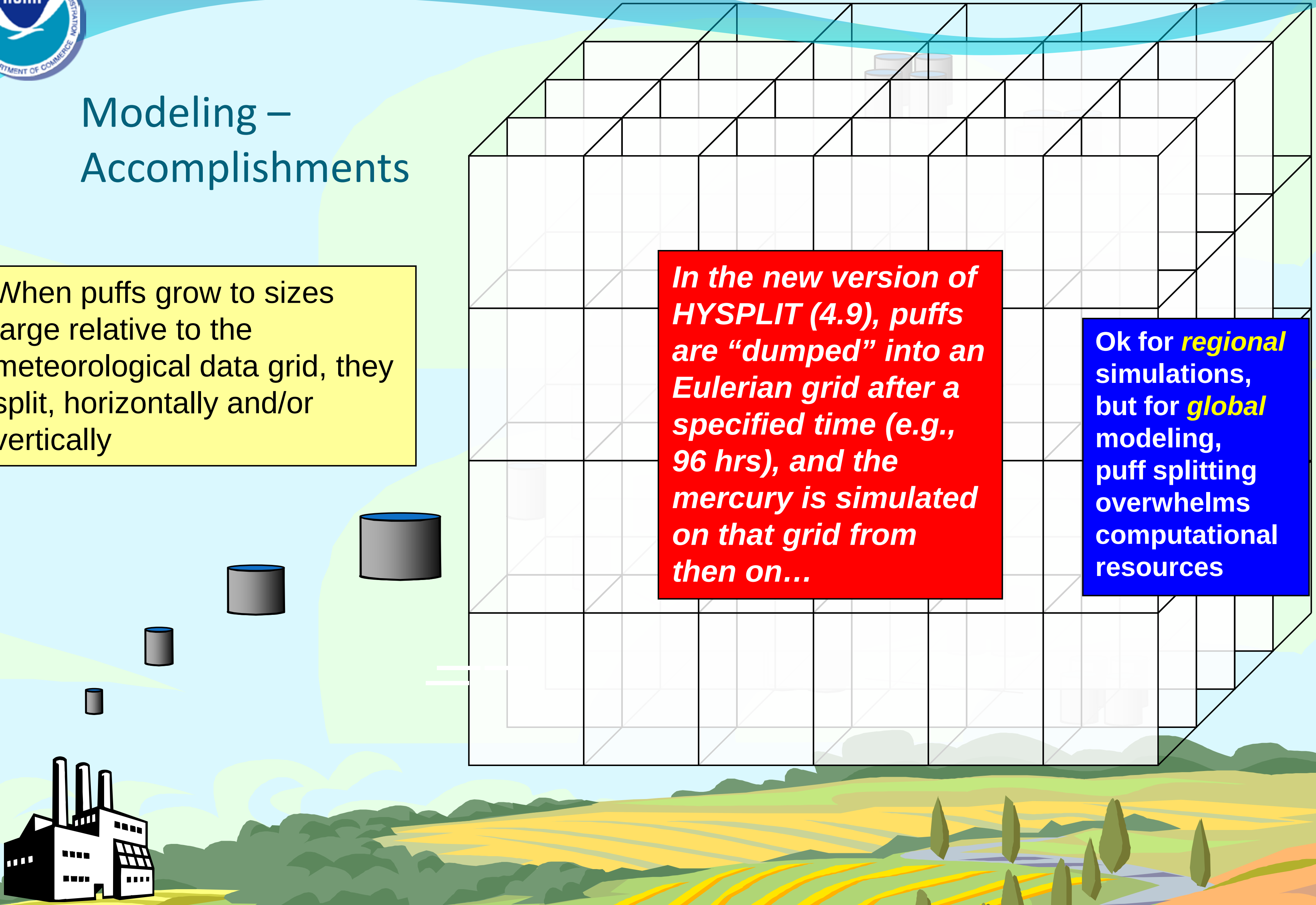


Emissions and deposition to Lake Michigan arising from different distance ranges away from the lake (km)

(based on 1999 anthropogenic emissions in the U.S. and Canada)

Modeling – Accomplishments

When puffs grow to sizes large relative to the meteorological data grid, they split, horizontally and/or vertically

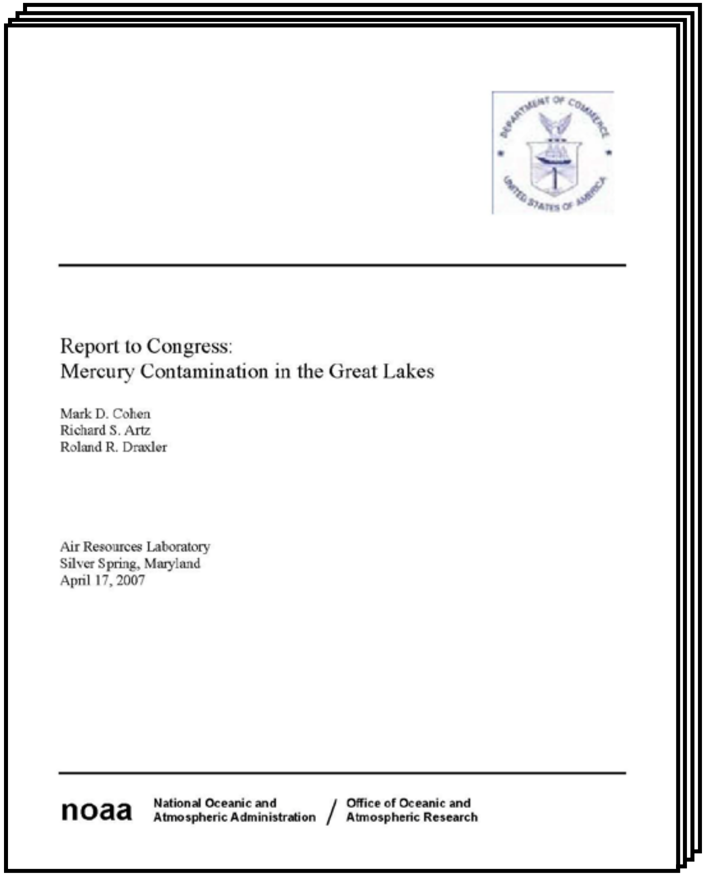


In the new version of HYSPLIT (4.9), puffs are "dumped" into an Eulerian grid after a specified time (e.g., 96 hrs), and the mercury is simulated on that grid from then on…

Ok for *regional* simulations, but for *global* modeling, puff splitting overwhelms computational resources

Modeling – Indicators of Success

- Peer-reviewed publications, e.g., ***NOAA Report to Congress on Mercury Contamination in the Great Lakes***
- Good performance in model intercomparison and model evaluation exercises
- Awarded grants to carry out modeling analysis, e.g., ***Great Lake Restoration Initiative***
- Frequent invitations to provide guidance on regulatory, legislative, and judicial issues
- Examples of impact on decisions include:
  - ***Mercury regulations enacted by Pennsylvania***
  - ***Debate over the Clean Air Mercury Rule (CAMR) related to the "hotspots" issue***


Report to Congress:
Mercury Contamination in the Great Lakes

Mark D. Cohen
Richard S. Artz
Roland R. Draxler

Air Resources Laboratory
Silver Spring, Maryland
April 17, 2007

noaa National Oceanic and Atmospheric Administration / Office of Oceanic and Atmospheric Research

Modeling – Collaborators

NOAA
- National Weather Service (NWS)
- Environmental Modeling Program
- Ecosystem Research Program

Other Federal Agencies and Programs
- EPA Clean Air Markets Division (CAMD)
- Great Lakes Restoration Initiative (GLRI)
- EPA Office of Research and Development
- EPA Great Lakes National Program Office
- US Geological Survey
- National Atmospheric Deposition Program

State/Local Governments
- Pennsylvania, Florida, Mississippi, Maryland
- Gulf of Mexico Alliance (Florida, Texas, Mississippi, Alabama, Louisiana)

Industry
- Electric Power Research Institute
- Southern Company

Universities and Institutes
- University of Maryland
- Jackson State University
- Cornell University
- Syracuse University
- Clarkson University
- Harvard University
- Texas Christian University
- University of Michigan
- University of Washington
- Lake Champlain Research Consortium

International Agencies and Organizations
- International Joint Commission (IJC)
- Commission for Environmental Cooperation (CEC)
- Environment Canada
- Instituto Nacional de Ecología (INE-Mexico)
- Meteorological Synthesizing Centre - East (Russia)
- United Nations Environmental Program (UNEP)
- Arctic Monitoring & Assessment Program (AMAP)
- Norwegian Institute for Air Research (NILU)

Modeling – Future Directions

Policy-Relevant Analysis

- Continue/extend Great Lakes analysis (Great Lakes Restoration Initiative)
- Continue/extend Gulf of Mexico analysis; link with ecosystem model
- Continue/extend numerous collaborations (EPA, State TMDL's, …)

Science

- Improve model physics & chemistry as new info. becomes available
- Further development of global modeling capability
- "particle-mode" dispersion simulation for HYSPLIT-Hg
- Improve treatment of natural sources, surface exchange, and re-emissions
- Multi-media: incorporate surface layers into model

Model Evaluation

- Participate in model intercomparisons
- Episode-focused model evaluation at sites
- Long-term model evaluation at sites

ARL's mercury research represents a rare opportunity to combine modeling, measurements, and meteorological data/modeling

View from the monitoring tower at the Grand Bay NERR long-term mercury monitoring site