Atmospheric Mercury Research

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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., SO₂, O₃, CO
- wet deposition
- air-surface exchange

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

Modeling used to aid in data interpretation and measurement planning.
North American mercury sources contribute to atmospheric mercury deposition.

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

Thermocline and local sources contribute to atmospheric mercury deposition.

Regional and global sources contribute to atmospheric mercury deposition.

Mercury from global atmospheric pool entering North America.

Mercury that doesn’t deposit continues its global circulation.

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

Thousands of fish-advisories throughout North America due to mercury contamination.
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)
- Precipitation collection
- Major ions ("acid rain")
- RGM and Hg(p) collectors

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
- Mercury Deposition Network and heavy metals
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
### Site Collaborators

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<td>- <strong>PI = Winston Luke (NOAA)</strong>&lt;br&gt;- EPA Clean Air Markets Division&lt;br&gt;- Univ of Md; Maryland DNR&lt;br&gt;- MACTEC; USGS</td>
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<td>Mauna Loa (HI)</td>
<td>- <strong>PI = Winston Luke (NOAA)</strong>&lt;br&gt;- NOAA ESRL&lt;br&gt;- Many others</td>
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<td>Canaan Valley (WV)</td>
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Measurement Approach – Process Studies / Field Intensives

- Arctic, Antarctic, Grand Bay, Beltsville, Houston, Ann Arbor, Nevada, ...
- Generally large, multi-investigator studies, including method development, inter-comparison 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.
Process Studies / Field Intensives
Grand Bay (MS) Field Intensive
July-Aug 2010, April-May 2011

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
- 2\textsuperscript{nd} phase ongoing now
- see Winston Luke’s poster

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

RGM (pg/m\textsuperscript{3})

SO2 (ppb)

Julian Day 2010
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

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

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

Industry
- TEKRAK
- 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

January 7, 2007
(Eastern Standard Time)

RGM (pg/m³)

07:30 08:30 09:30 10:30 11:30 12:30 13:30 14:30 15:30 16:30
Back Trajectory Analysis – “Gridded Trajectory Frequencies”

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

- 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?

One year of hourly reactive gaseous mercury (RGM) measurements at the Piney Reservoir site in Western Maryland, courtesy of Mark Castro, Univ. of Maryland
Where the air at the Piney Reservoir site tended to come from -- on average -- over the entire year.

Air Emissions

Piney Measurement Site

0.1 degree lat/long regional grid
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
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.

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**
  - red: coal-fired power plants
  - green: other fuel combustion
  - blue: waste incineration
  - gray: metallurgical
  - yellow: manufacturing & other

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

- > 2.5
- 2 – 2.5
- 1.5 - 2
- 1 to 1.5
- 0.5 - 1
- 0 to 0.5
- < -0.5
- -0.5 to 0
- -1 to -0.5
- -1.5 to -1
- -2 to -1.5
- -2.5 to -2
- < -2.5
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
Successful performance in model evaluation and model intercomparison exercises

model intercomparison 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.
Modeling – Accomplishments

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

- municipal waste incin – 1999
- medical waste incin – 1999
- hazardous waste incin – 1999
- industrial waste incin – 1999
- other waste incin – 1999
- chloralkali – 1999
- other chemical manuf – 1999
- pulp/paper – 1999
- cement/concrete – 1999
- mining – 1999
- metallurgical processes – 1999
- lamp manuf & breakage – 1999
- other manufacturing – 1999
- other – 1999
- other fuel combustion – 1999
- natural gas combustion – 1999
- mobile sources – 1996
- oil combustion (non-mobile) – 1999
- coal combustion (other) – 1999
- coal elec (not IPM) – 1999
- coal elec (IPM) – 1999
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)

But these “local” emissions are responsible for a large fraction of the modeled atmospheric deposition.

Only a small fraction of U.S. and Canadian emissions are emitted within 100 km of Lake Michigan.
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...

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

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*
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
Questions?

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