Atmospheric Fate and Transport of Mercury

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Lake Ontario Contaminant Monitoring & Research Workshop
Planning for the 2008 Cooperative Monitoring Year
- Contaminants Component –
Grand Island Holiday Inn, Grand Island, New York
March 27 & 28, 2007

Thanks, John!

To

John McDonald

from your
Great Lakes Multi-Compartment
Mercury Project colleagues,
with deep appreciation and respect.
Our heartfelt thanks for your leadership,
contributions, enthusiasm, and inspiration.
March 2007

Standing (from left): Eric Uram, Gary Foley, John McDonald, Greg Mierle, Sheng-Wei Wang;

Kneeling (from left): Chris Knightes, Elsie Sunderland, Wolfgang Scheider, Mark Cohen

At the *Lake Ontario Contaminant Monitoring, Modeling & Research Workshop*, Grand Island, NY, March 27-28, 2007

MANY THANKS TO:

- **Gary Foley, J. David Mobley, Elsie Sunderland, Chris Knightes (EPA); Panos Georgopolous and Sheng-Wei Wang (EOSHI Rutgers Univ); John McDonald (IJC):** *funding and collaboration on multimedia Hg modeling*

- **David Schmeltz, Gary Lear, John Schakenbach, Scott Hedges, Rey Forte (EPA):** *funding and collaboration on Hg models and /measurements, including new EPA-NOAA Hg monitoring site at Beltsville, MD.*

- **David Ruple, Mark Woodrey (Grand Bay NERR), Susan White , Gary Matlock, Russell Callender, Jawed Hameedi (NOAA), and Durwin Carter (U.S. Fish and Wildlife Service):** *collaboration at NOAA Grand Bay NERR atmospheric monitoring site*

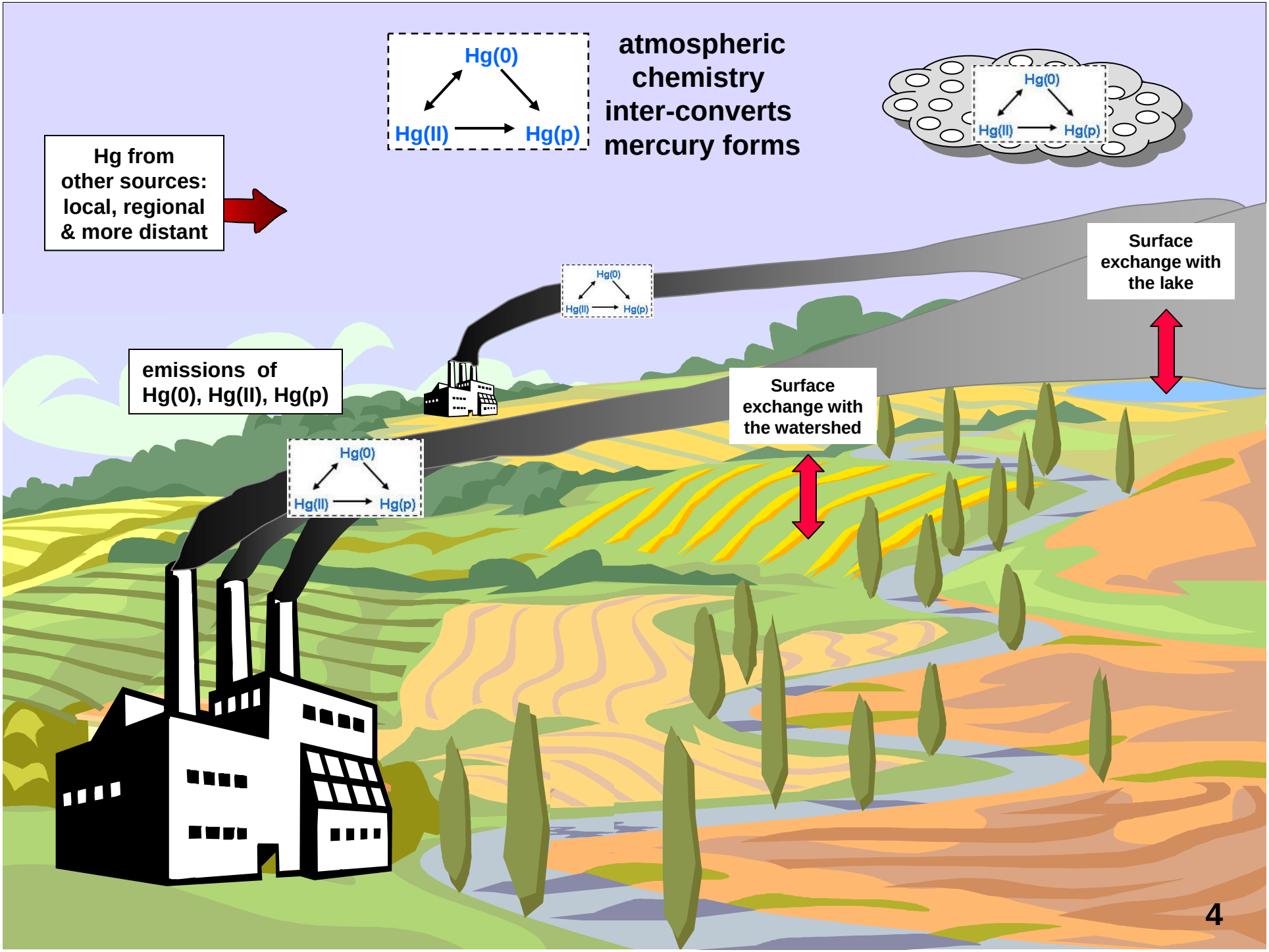
- **Anne Pope and colleagues (EPA):** *U.S. mercury emissions inventory*

- **David Niemi, Dominique Ratte, Marc Deslauriers (Environment Canada):** *Canadian mercury emissions inventory data*

- **Mark Castro (Univ. Md, Frostburg), Fabien Laurier (Univ Md Ches Biol Lab), Rob Mason (Univ CT), Laurier Poissant (Envr Can):** *ambient Hg data for model evaluation*

- **Roland Draxler, Glenn Rolph, Rick Artz (NOAA):** *HYSPLIT model and met data*

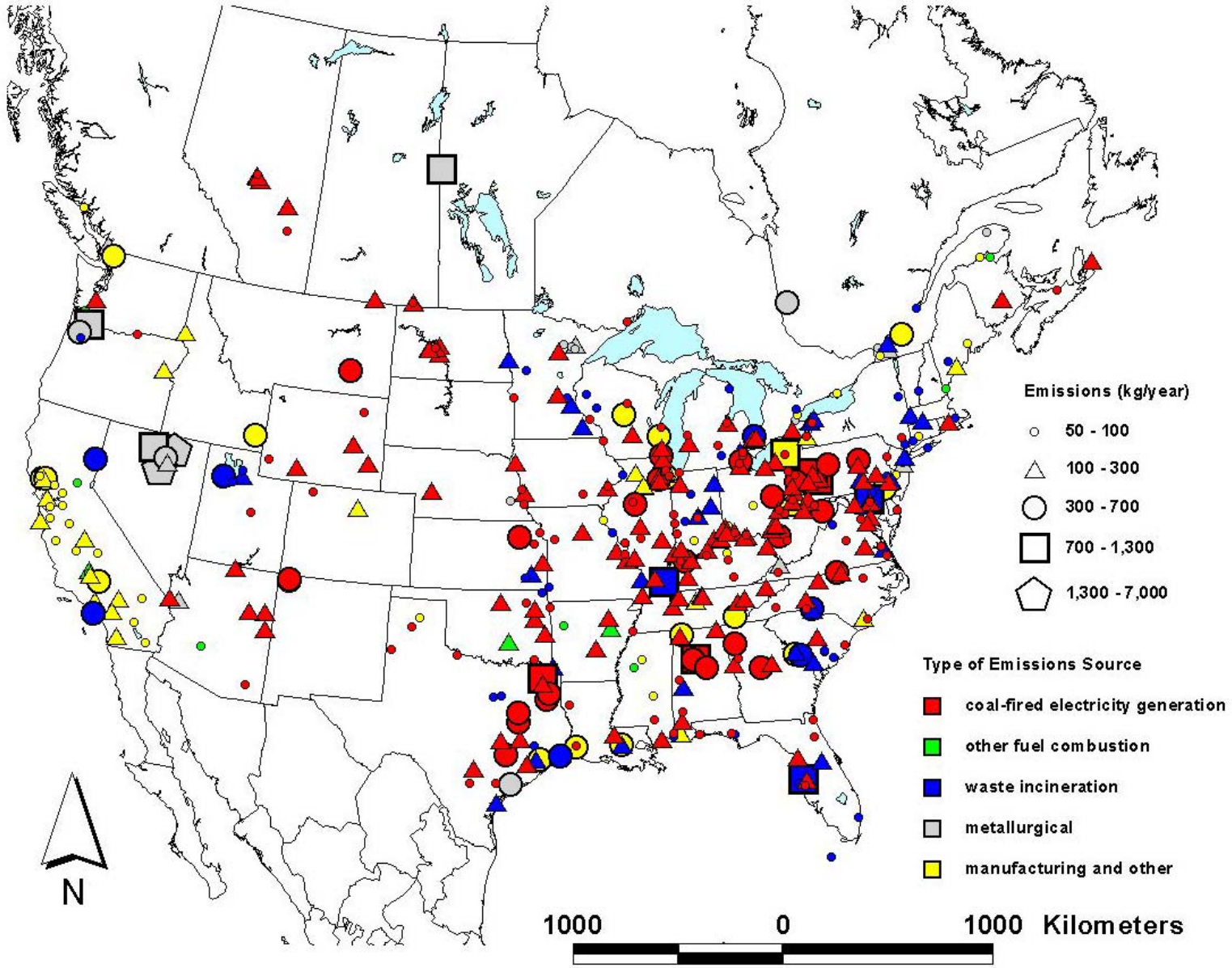
- **Steve Brooks, Winston Luke, Paul Kelley (NOAA) :** *ambient Hg data*


Hg(0)
Hg(II)
Hg(p)
atmospheric chemistry inter-converts mercury forms
Hg from other sources: local, regional & more distant
emissions of Hg(0), Hg(II), Hg(p)
Surface exchange with the lake
Surface exchange with the watershed

Objectives and Rationale of Atmospheric Modeling in Conjunction with Great Lake Multi-Compartment Mercury Modeling Project

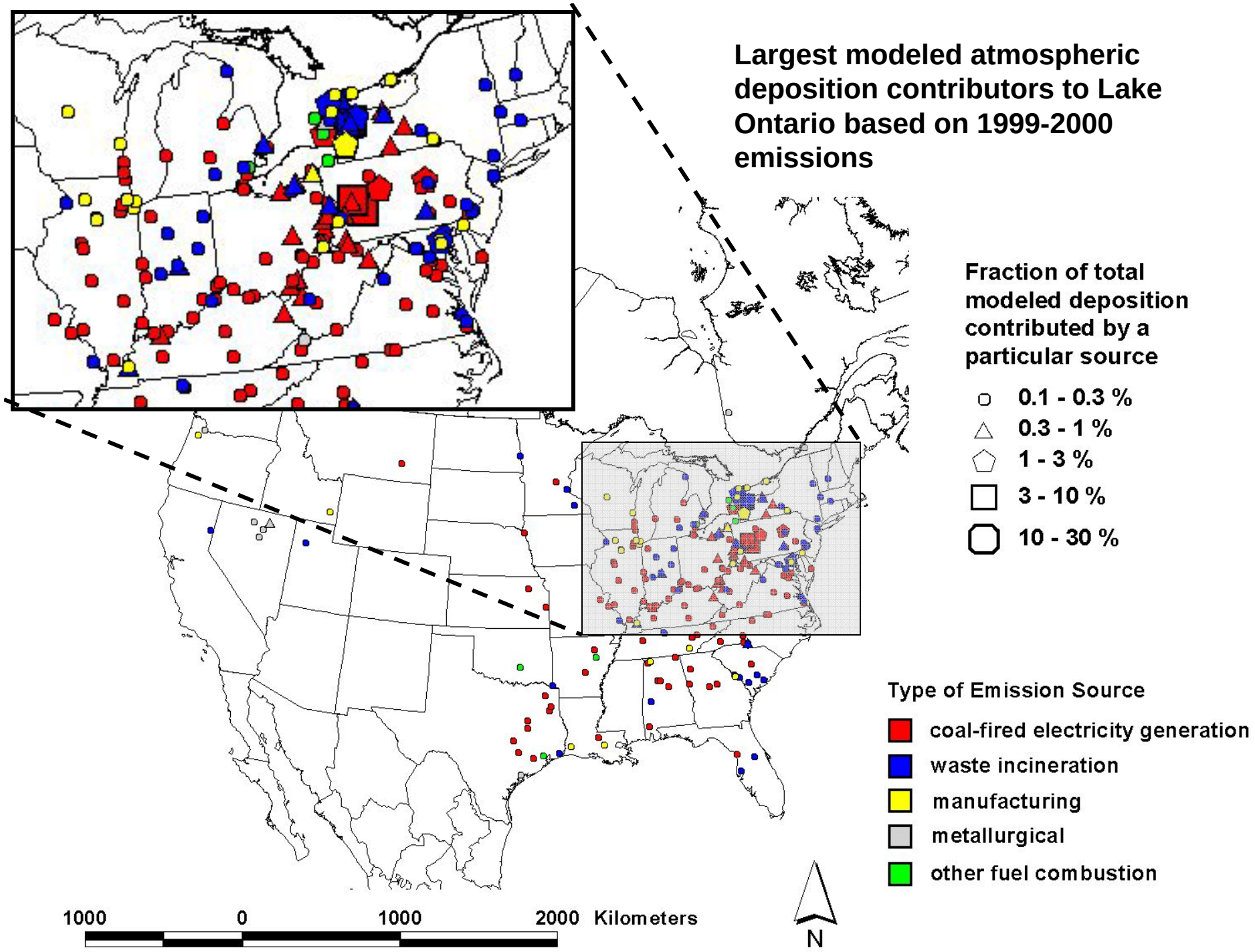
- **Estimate *deposition amount* of different mercury species and/or forms to different regions of Lake Ontario lake surface and watershed, for use in ecological assessment and modeling**
  - **dry deposition generally estimated with models**
  - **modeling can help fill in spatial gaps between measurement sites**
  - **modeling can help estimate deposition for other times**
    - **past**
    - **future (for different emissions scenarios)**
- **Estimate *source attribution* for deposition of different mercury species and/or forms to different regions of Lake Ontario lake surface and watershed, including estimation of the relative importance of:**
  - **different source regions (local, regional, national, continental, global)**
  - **different jurisdictions (different states and provinces)**
  - **anthropogenic vs. natural emissions**
  - **different anthropogenic source types (power plants, waste incin., etc)**

Largest mercury sources in U.S. and Canadian air emissions inventories (~1999-2000)

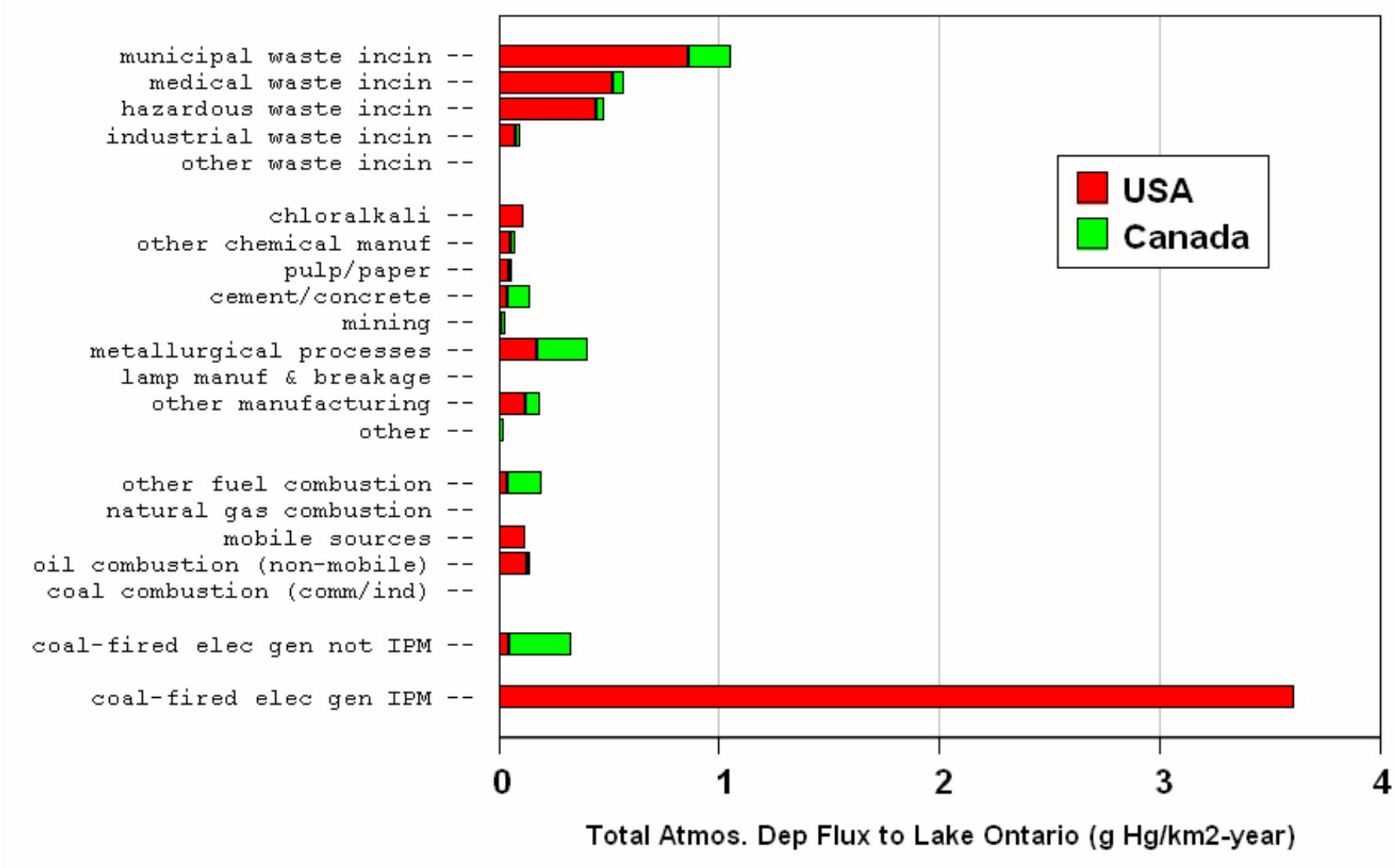


Source of emissions data: U.S. EPA and Environment Canada

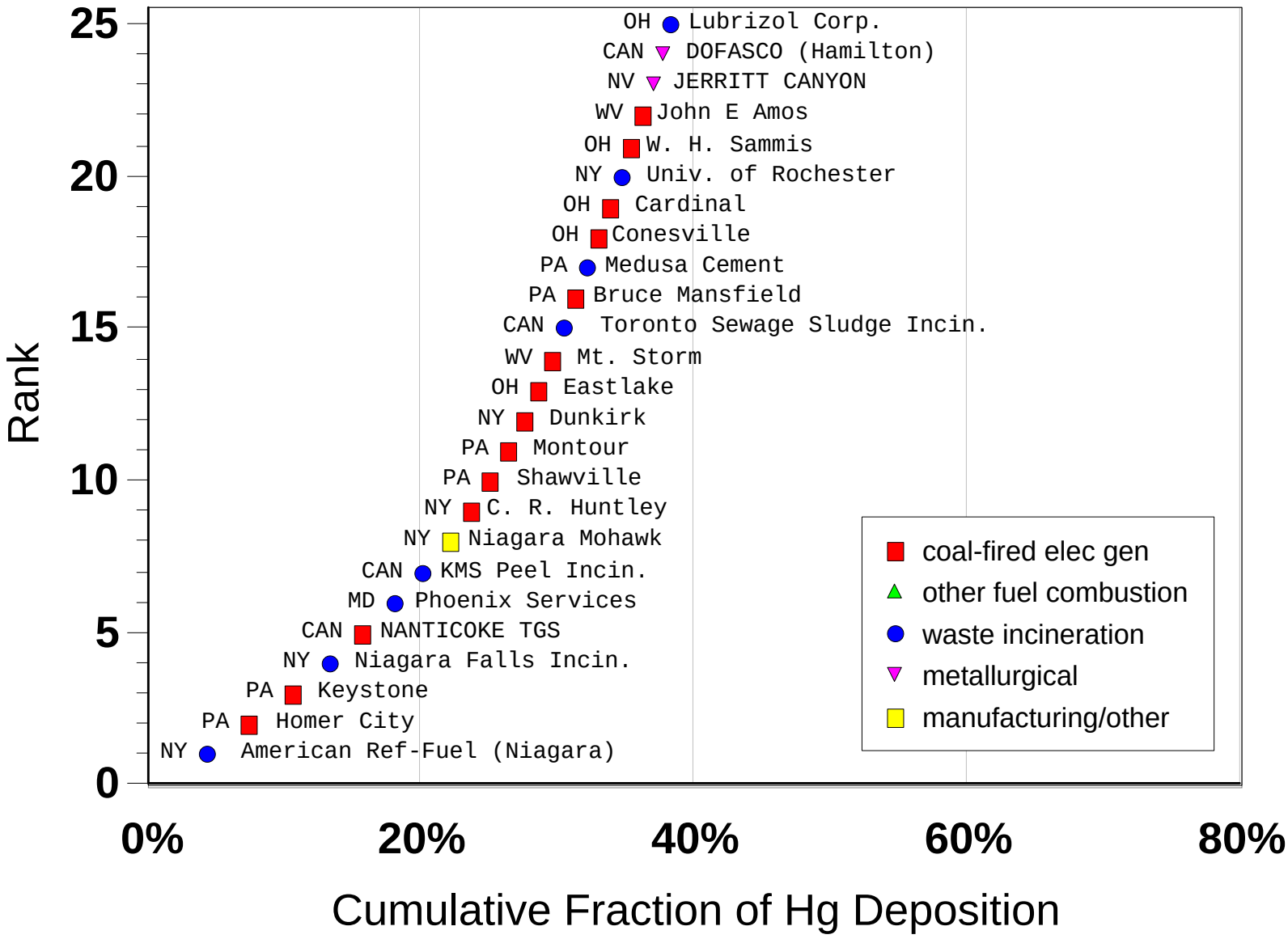
Some preliminary results for the atmospheric deposition impact of U.S. and Canadian anthropogenic mercury air emissions sources on Lake Ontario


Largest modeled atmospheric deposition contributors to Lake Ontario based on 1999-2000 emissions
Fraction of total modeled deposition contributed by a particular source
0.1 - 0.3 %
0.3 - 1 %
1 - 3 %
3 - 10 %
10 - 30 %
Type of Emission Source
coal-fired electricity generation
waste incineration
manufacturing
metallurgical
other fuel combustion
1000 0 1000 2000 Kilometers
N

Modeled atmospheric mercury deposition to Lake Ontario from U.S. and Canadian source sectors based on 1999-2000 emissions

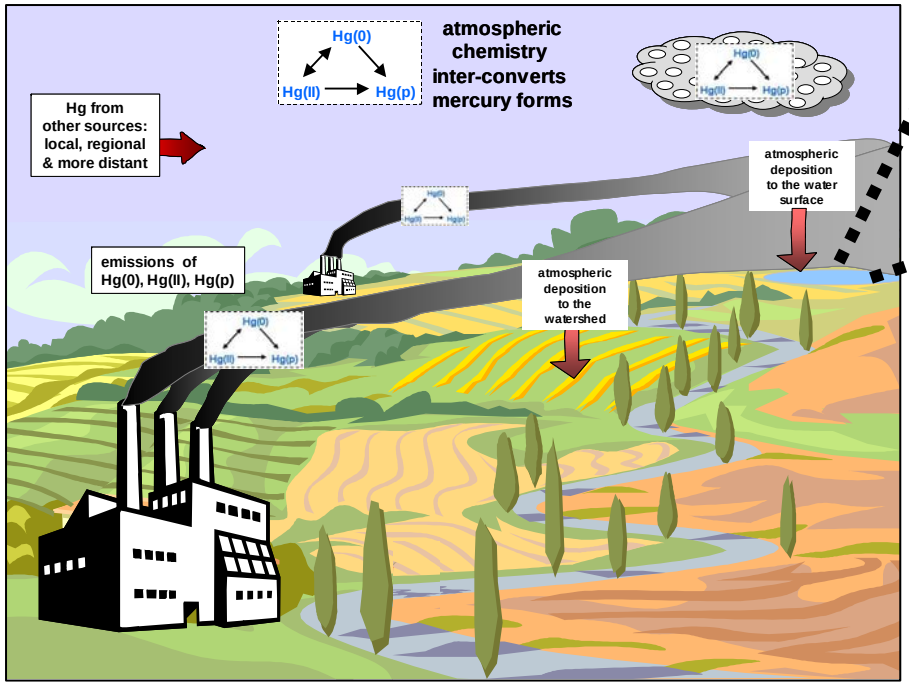


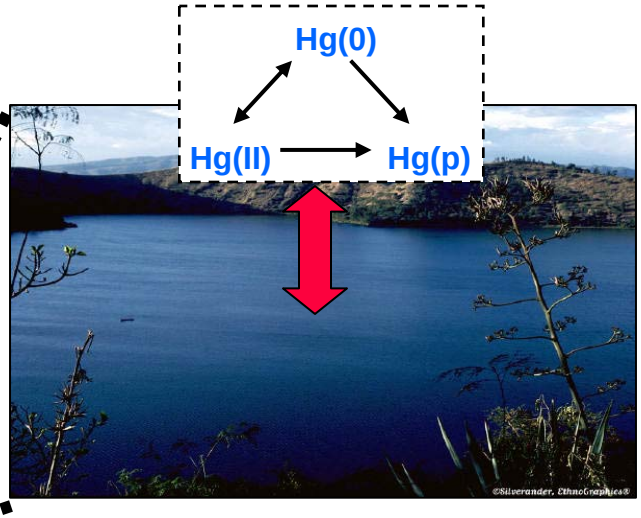
Top 25 Contributors to 1999 Hg Deposition Directly to Lake Ontario



Many uncertainties in these earlier results…

How to refine modeling and link with other models in a multi-media framework?

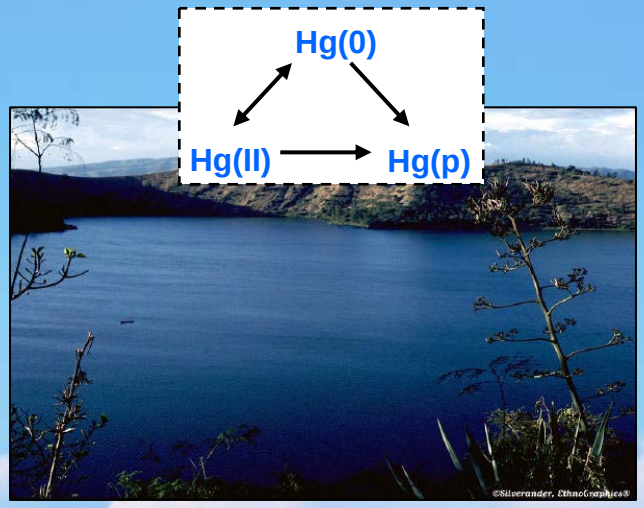




For Lake Ontario:

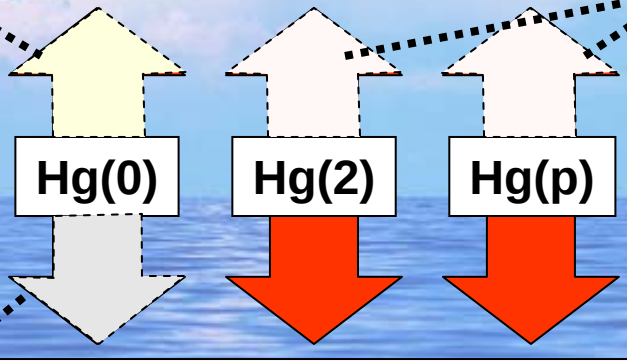
How to link the atmospheric model and the aquatic fate/cycling model?

Surface exchange of Hg(0) from Lake Ontario *may* not have large impact on overall atmospheric Hg fate-transport (?)

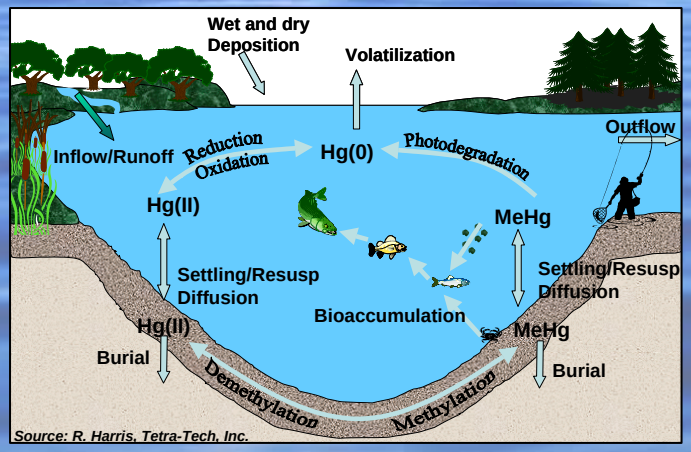


It may turn out that dynamic, *run-time* linkage between lake and atmosphere is not critical for Hg (?) (we will see…)

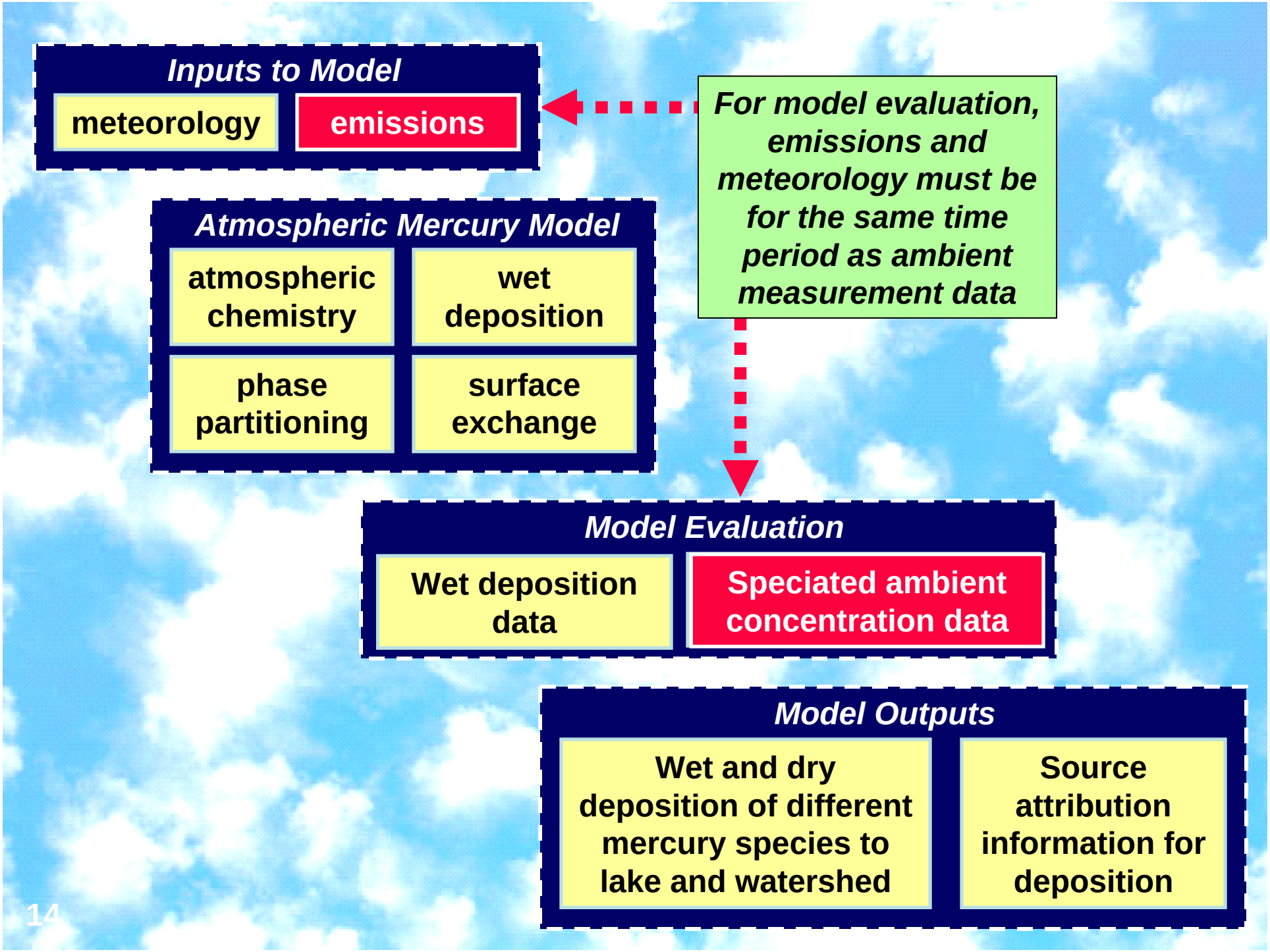
Air-Water Interface – at the boundary between the atmospheric model (over the lake) and the lake fate and cycling model

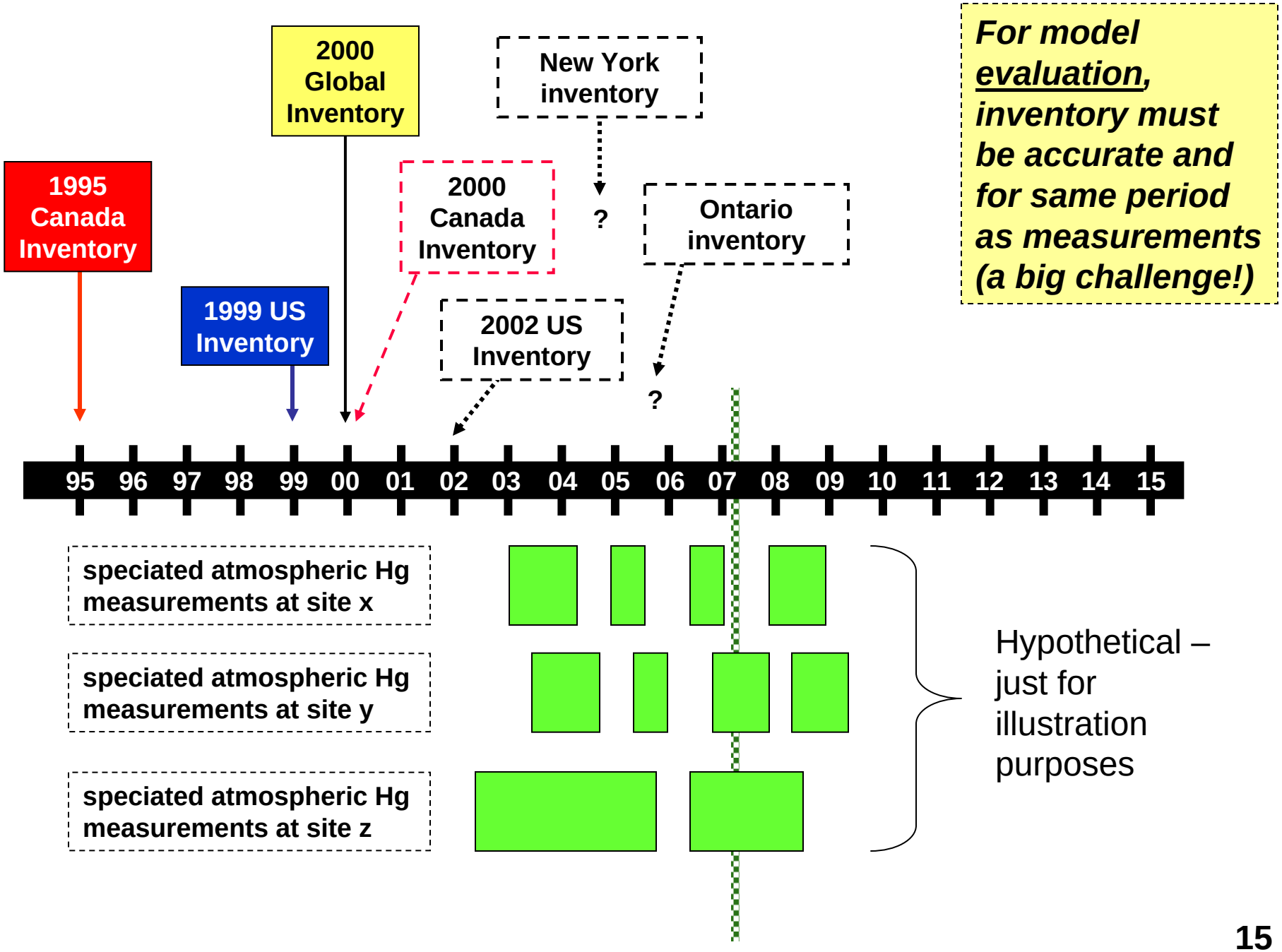


Upward Flux of Hg(2) and Hg(p) is probably small



The precise specification of surface exchange of Hg(0) *may* not have large impact on methyl-mercury production (???)

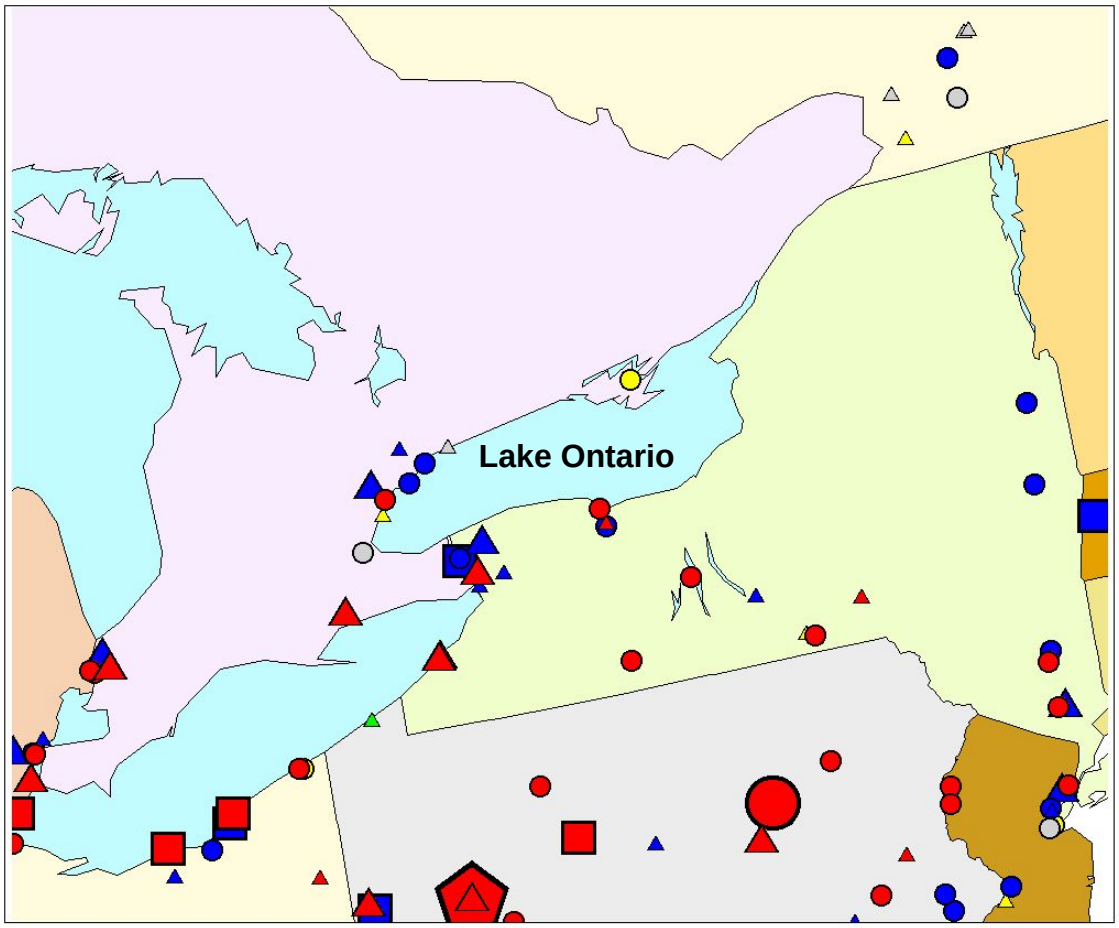

Inputs to Model
meteorology
emissions
For model evaluation, emissions and meteorology must be for the same time period as ambient measurement data
Atmospheric Mercury Model
atmospheric chemistry
wet deposition
phase partitioning
surface exchange
Model Evaluation
Wet deposition data
Speciated ambient concentration data
Model Outputs
Wet and dry deposition of different mercury species to lake and watershed
Source attribution information for deposition



For model <u>evaluation</u>, inventory must be accurate and for same period as measurements (a big challenge!)

RGM emissions (~1999) in the Lake Ontario region

"RGM" = Reactive Gaseous Mercury, the form of atmospheric mercury most readily deposited



size/shape of symbol indicates estimated magnitude of RGM emissions (kg RGM/yr)

- 5 - 10
- 10 - 50
- 50 -100
- 100 -300
- 300 - 500
- 500 - 700

color of symbol indicates type of source

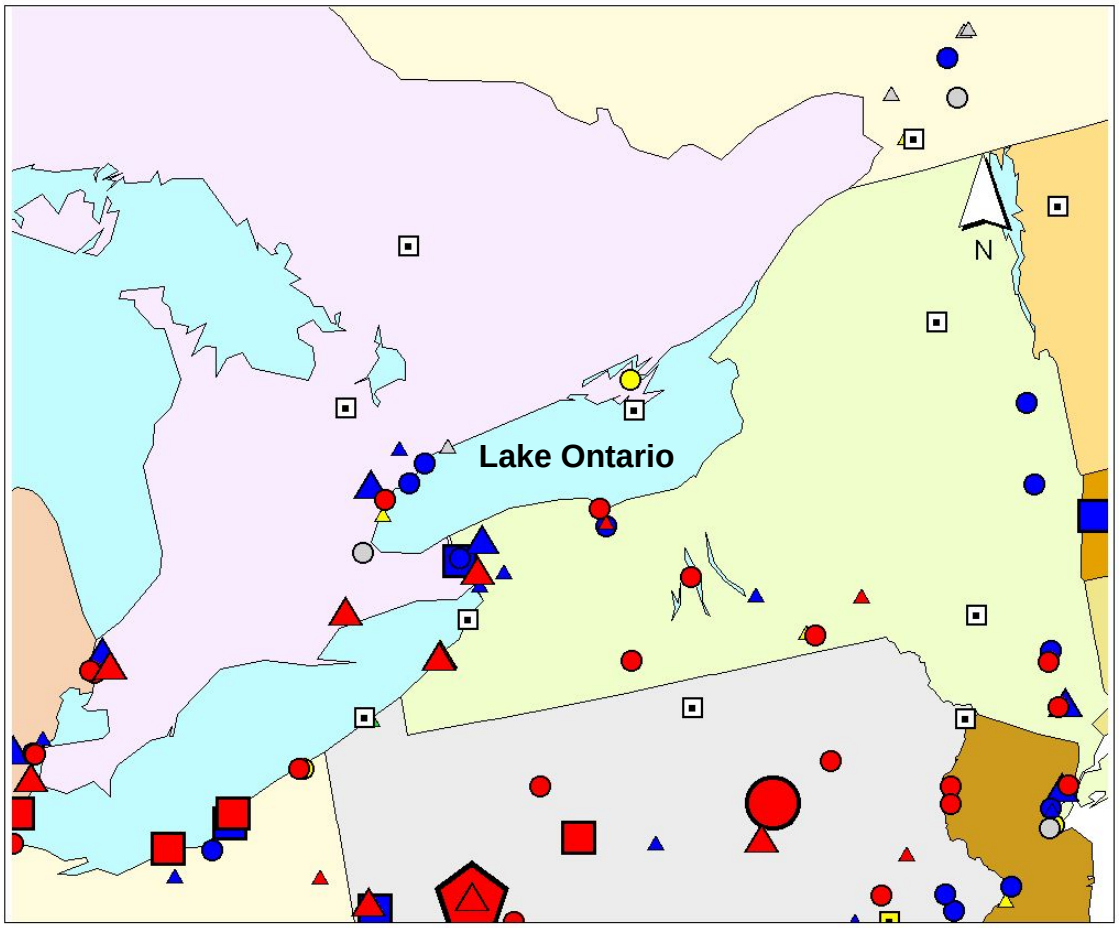
- coal fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical
- manufacting / other

N

100 0 100 200 300 400 500 Kilometers

Source of emissions data: U.S. EPA and Environment Canada

RGM emissions (~1999) in the Lake Ontario region, and Mercury Deposition Network (MDN) sites



Mercury Deposition Network (MDN), Wet Deposition Measurement Site

size/shape of symbol indicates estimated magnitude of RGM emissions (kg RGM/yr)

- 5 - 10
- 10 - 50
- 50 -100
- 100 -300
- 300 - 500
- 500 - 700

color of symbol indicates type of source

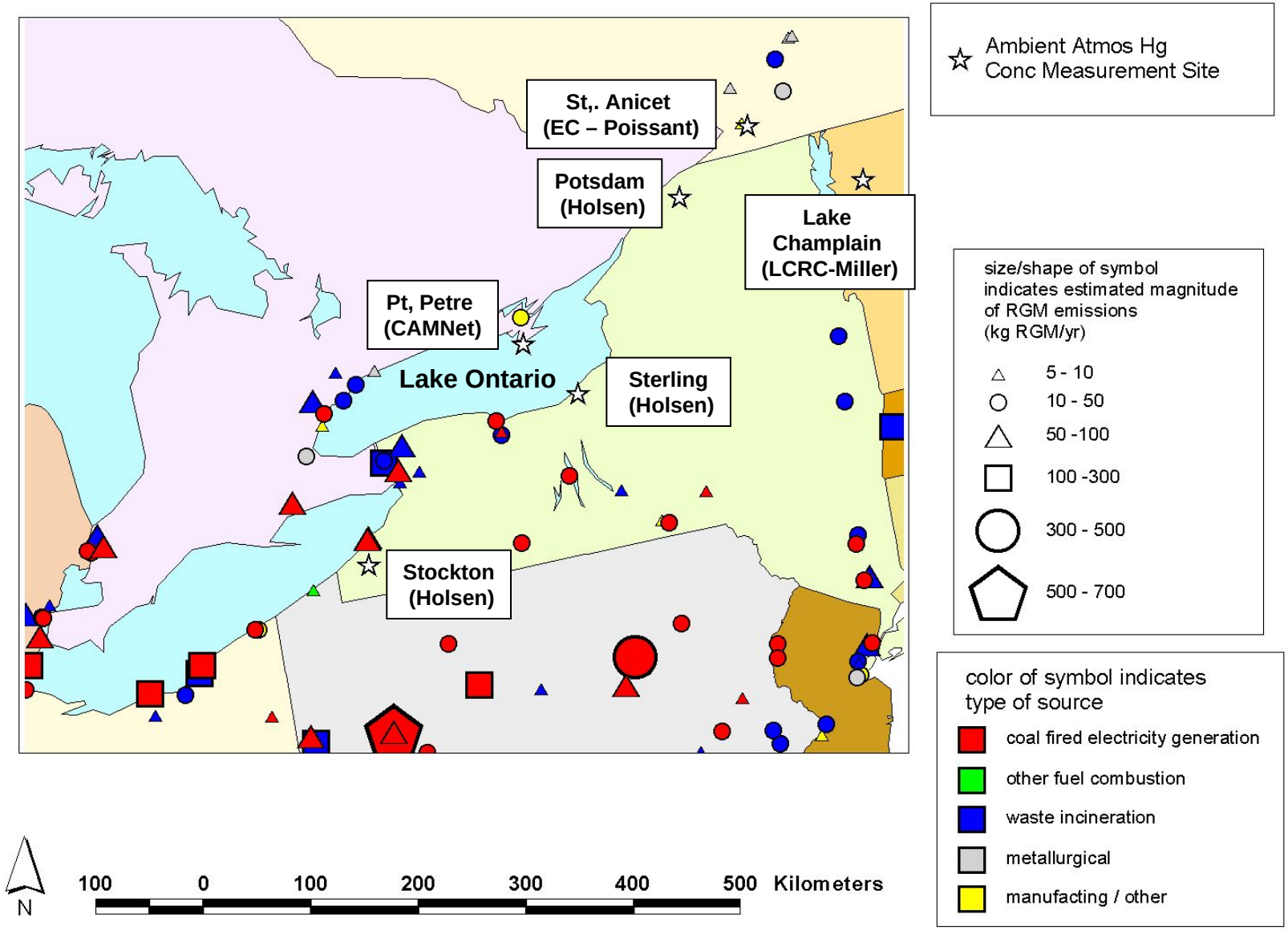
- coal fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical
- manufacting / other

N

100 0 100 200 300 400 500 Kilometers

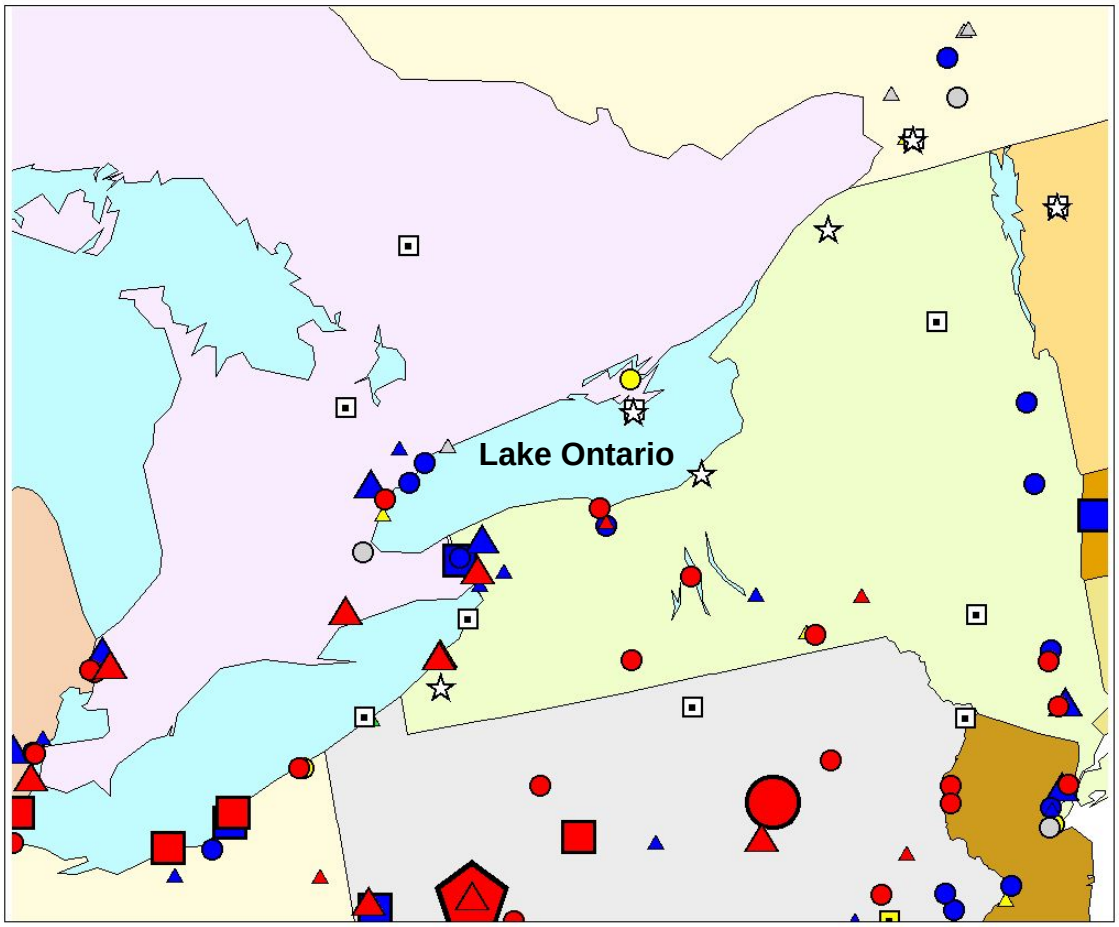
Source of emissions data: U.S. EPA and Environment Canada

RGM emissions (~1999) in the Lake Ontario region, and (some of the) sites where speciated concentrations of atmospheric Hg have been measured



Source of emissions data: U.S. EPA and Environment Canada

RGM emissions (~1999) in the Lake Ontario region, along with MDN and ambient concentration sites



Ambient Atmos Hg Conc Measurement Site

Mercury Deposition Network (MDN), Wet Deposition Measurement Site

size/shape of symbol indicates estimated magnitude of RGM emissions (kg RGM/yr)

- 5 - 10
- 10 - 50
- 50 -100
- 100 -300
- 300 - 500
- 500 - 700

color of symbol indicates type of source

- coal fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical
- manufacting / other

N

100 0 100 200 300 400 500 Kilometers

Source of emissions data: U.S. EPA and Environment Canada

Atmospheric models can potentially provide valuable deposition and source-attribution information.

But… models have not been adequately evaluated, so we don't really know very well how good or bad they are…

… air pollution model or error pollution model?

Challenges / critical data needs for model evaluation:

Ambient Monitoring Data

- ❑ speciated ambient concentrations
  (need RGM and Hg(p), not just total gaseous mercury)
- ❑ wet deposition

Emissions inventories

- ❑ complete
- ❑ "accurate"
- ❑ speciated
- ❑ up-to-date (or at least for the same period as measurements)
- ❑ temporal resolution better than annual (e.g., shut-downs, etc)

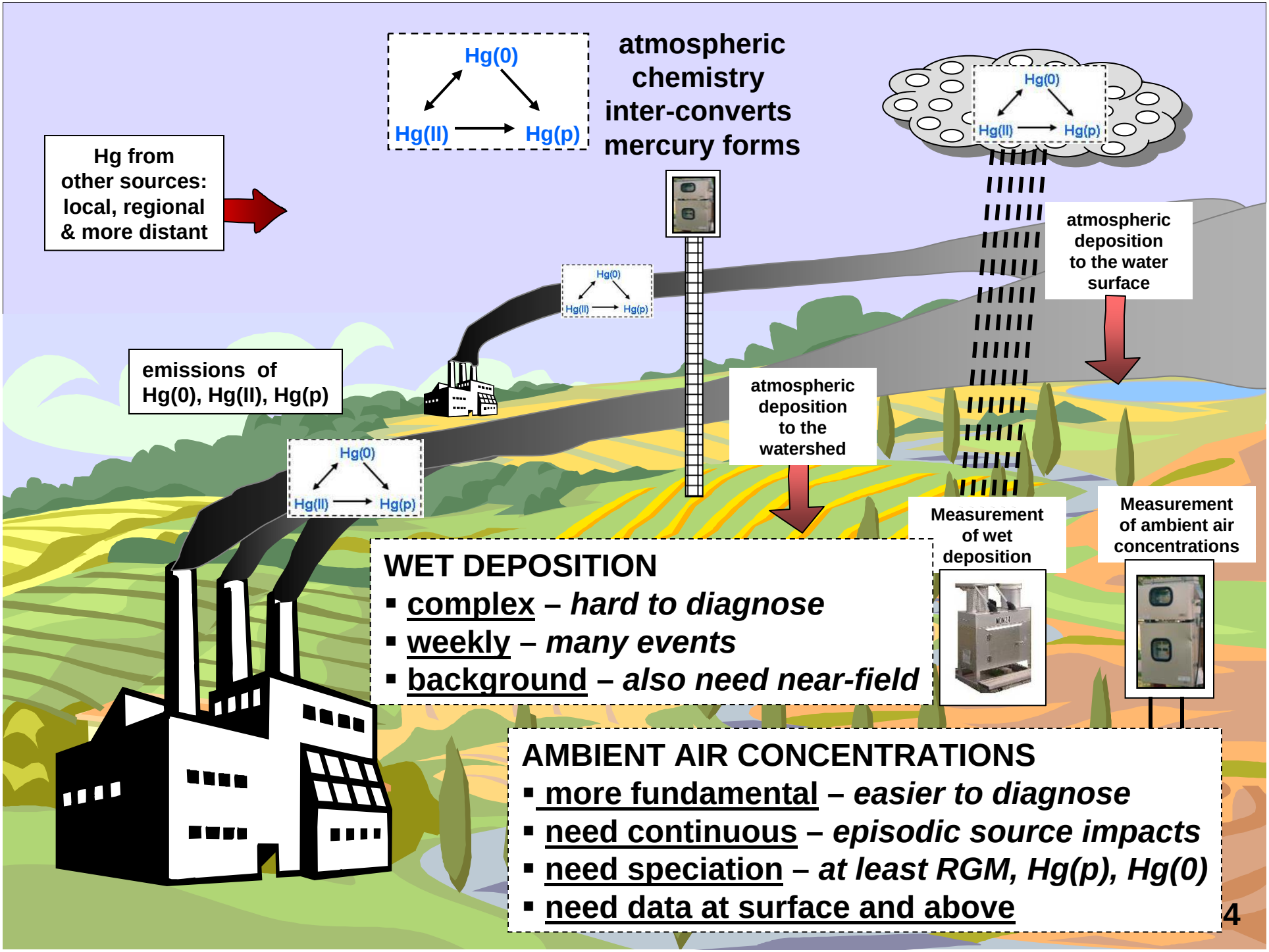
Thanks!

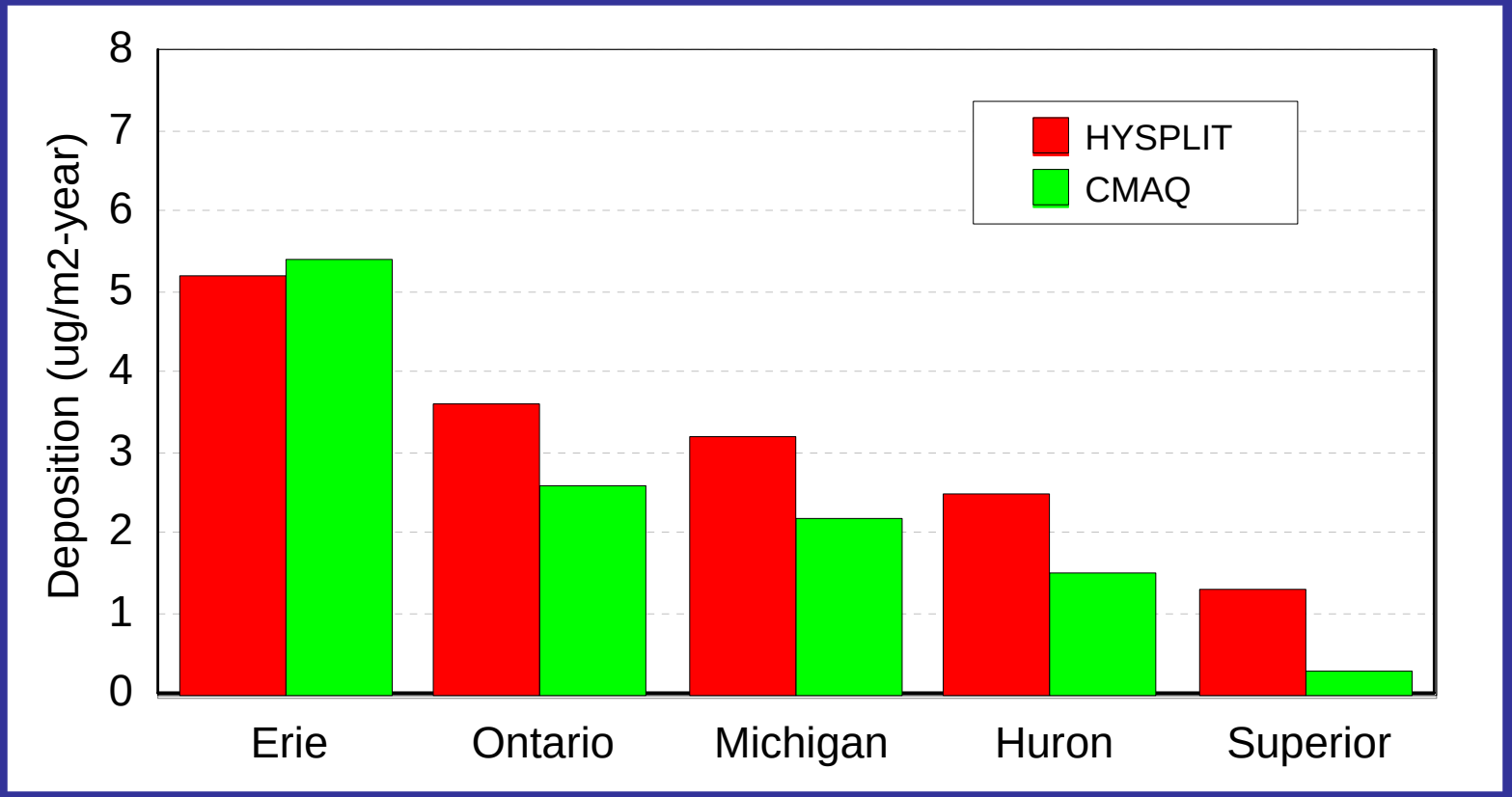
Extra Slides

- ***policy development*** **requires:**
  - **source-attribution (*source-receptor* info)**
  - **estimated impacts of alternative future scenarios**

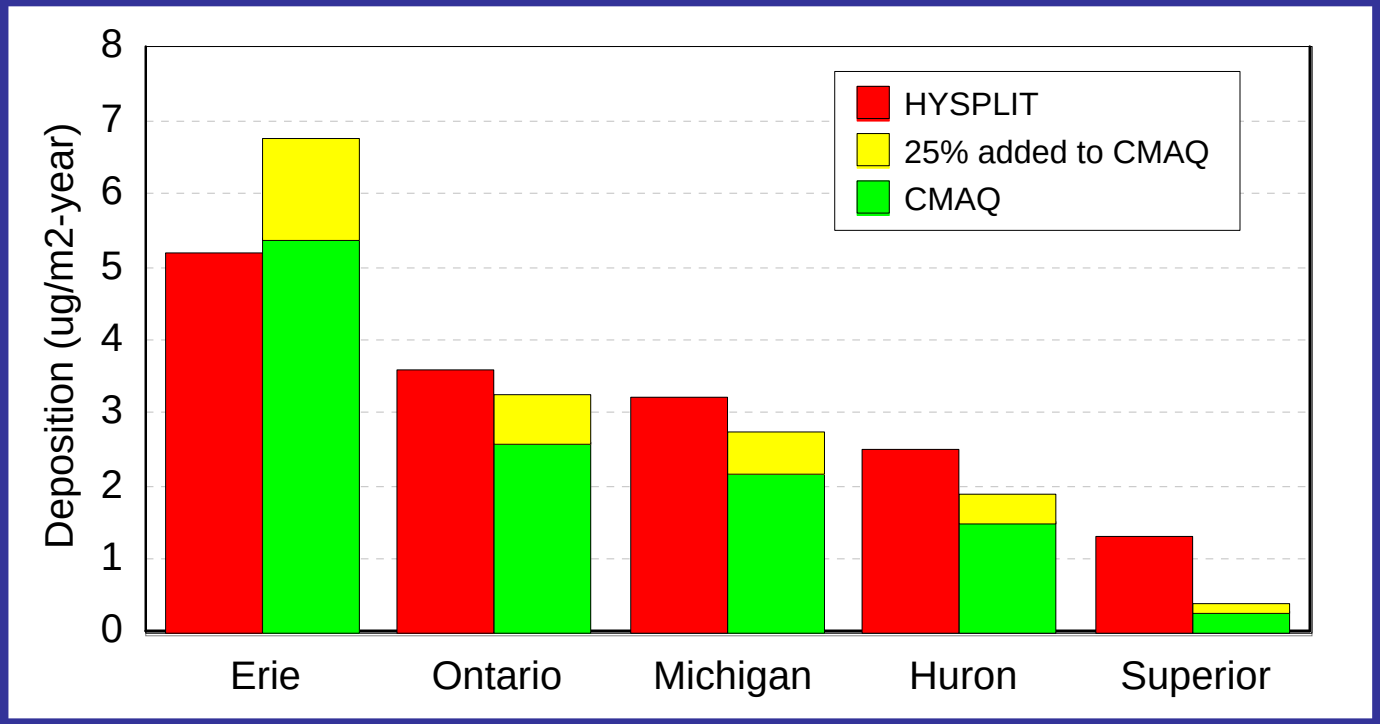
- **estimation of *source-attribution* & *future impacts* requires atmospheric models**

- ***atmospheric models*** **require:**
  - **knowledge of atmospheric chemistry & fate**
  - **emissions data**
  - **ambient data for “ground-truthing”**


Hg(0)
Hg(II)
Hg(p)
atmospheric chemistry inter-converts mercury forms
Hg from other sources: local, regional & more distant
emissions of Hg(0), Hg(II), Hg(p)
atmospheric deposition to the water surface
atmospheric deposition to the watershed
Measurement of wet deposition
Measurement of ambient air concentrations
WET DEPOSITION
▪ complex – hard to diagnose
▪ weekly – many events
▪ background – also need near-field
AMBIENT AIR CONCENTRATIONS
▪ more fundamental – easier to diagnose
▪ need continuous – episodic source impacts
▪ need speciation – at least RGM, Hg(p), Hg(0)
▪ need data at surface and above

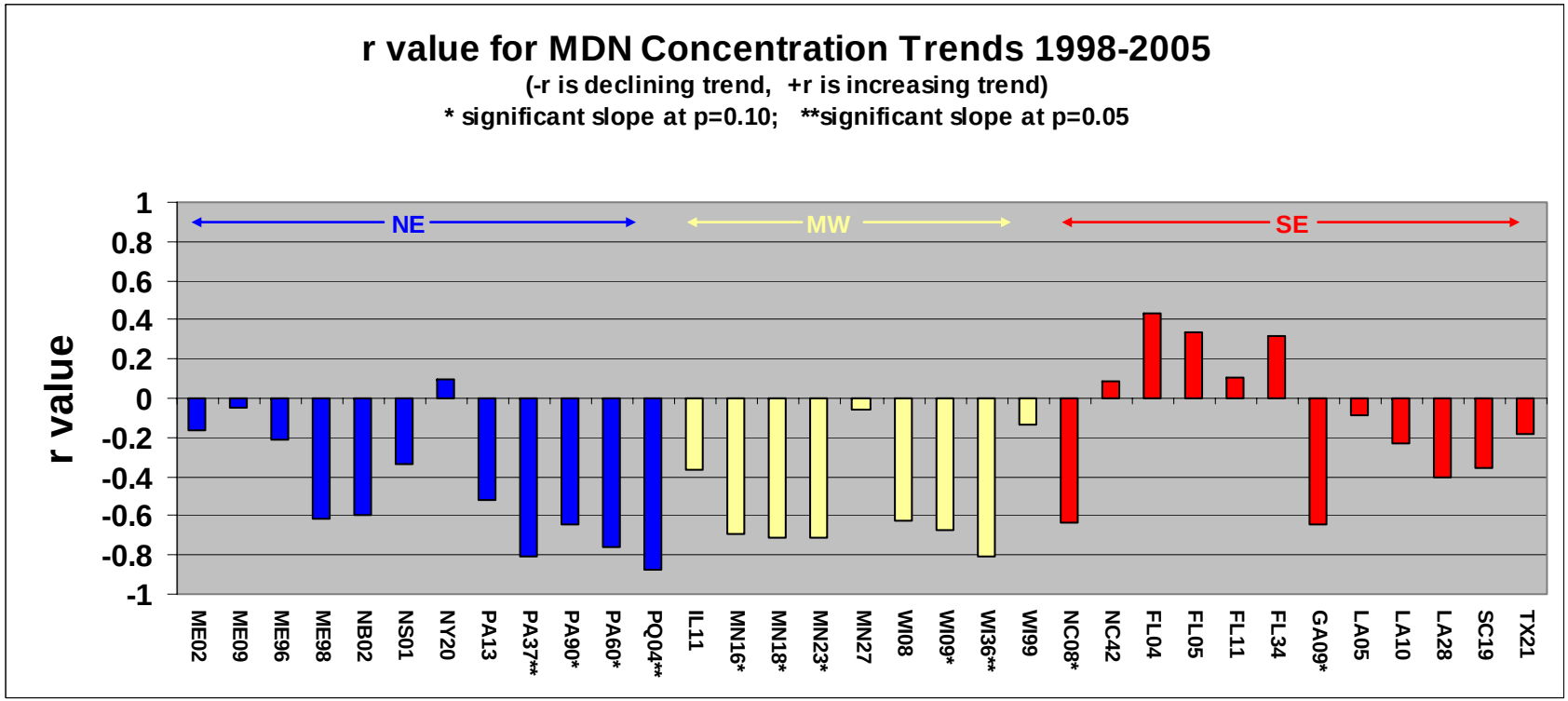


Model-estimated U.S. utility atmospheric mercury deposition contribution to the Great Lakes: HYSPLIT-Hg (1996 meteorology, 1999 emissions) vs. CMAQ-HG (2001 meteorology, 2001 emissions).



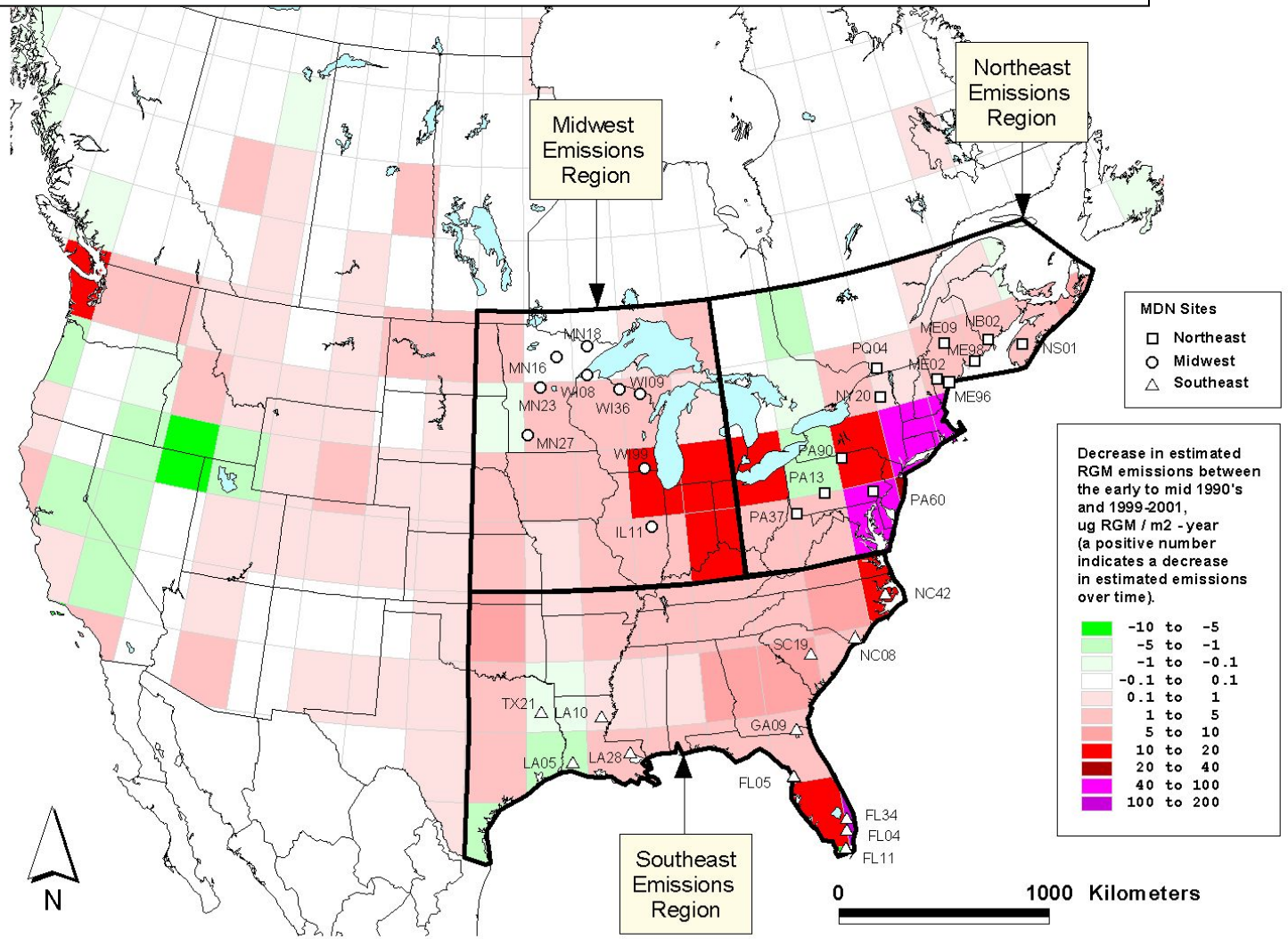
- Model-estimated U.S. utility atmospheric mercury deposition contribution to the Great Lakes: HYSPLIT-Hg (1996 meteorology, 1999 emissions) vs. CMAQ-Hg (2001 meteorology, 2001 emissions).

- This figure also shows an added component of the CMAQ-Hg estimates -- corresponding to 30% of the CMAQ-Hg results – in an attempt to adjust the CMAQ-Hg results to account for the deposition underprediction found in the CMAQ-Hg model evaluation.



Source: Regional Precipitation Mercury Trends in the Eastern USA, 1998-2005: Declines in the Northeast and Midwest, but No Change in the Southeast. Thomas J. Butler, Mark Cohen, Gene E. Likens and Francoise M. Vermeylen, David Schmeltz and Richard Artz. In preparation, 2007.

Reactive Gaseous Mercury (RGM) emissions flux changes between 1990-1996 and 1999-2001



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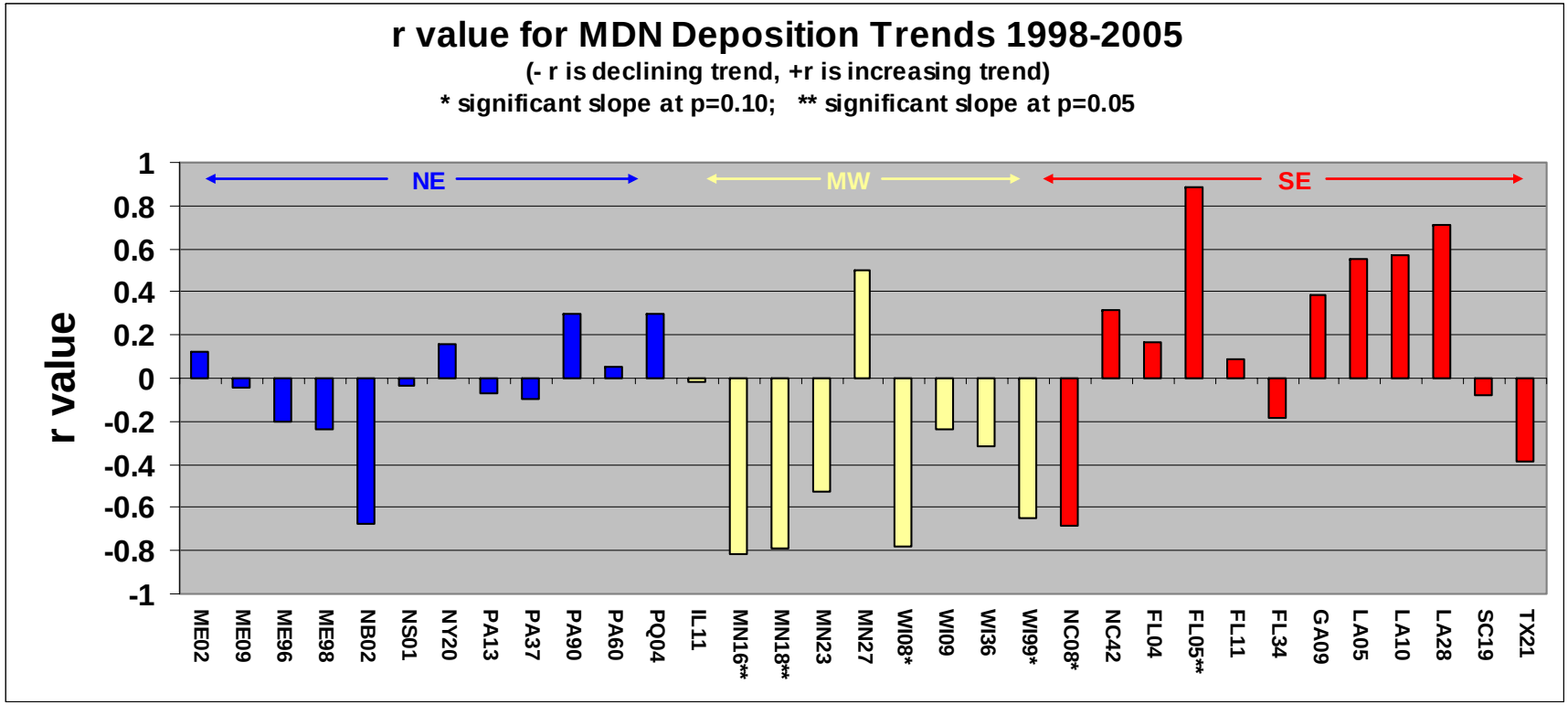

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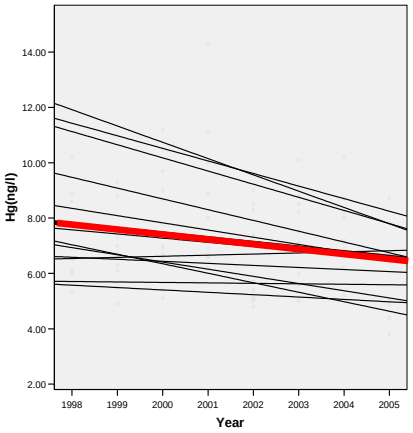
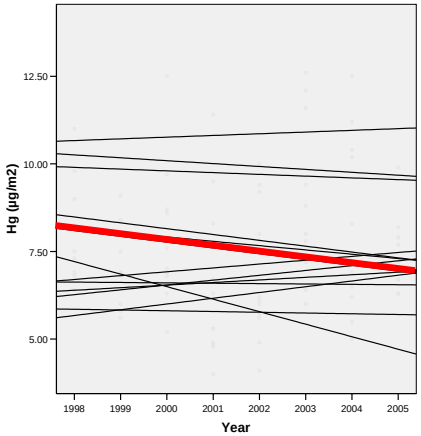
Random Coefficient Model results for Northeastern and Midwestern annual mercury concentration and deposition for 1998 to 2005.

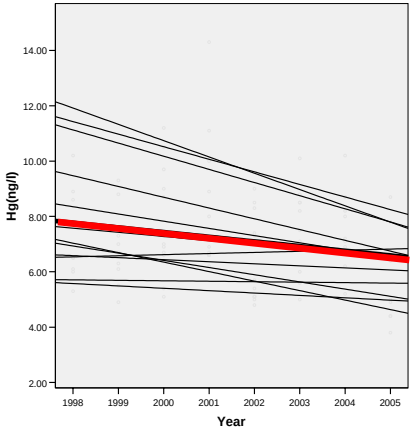
NE Concentration



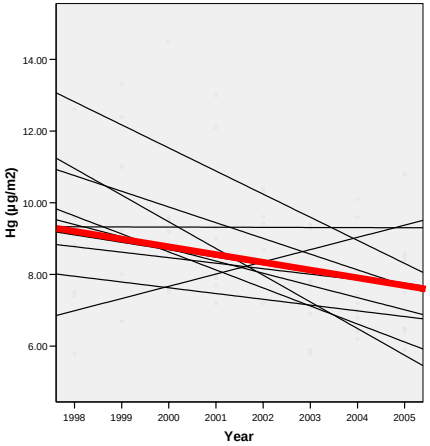
NE Deposition



MW Concentration



MW Deposition



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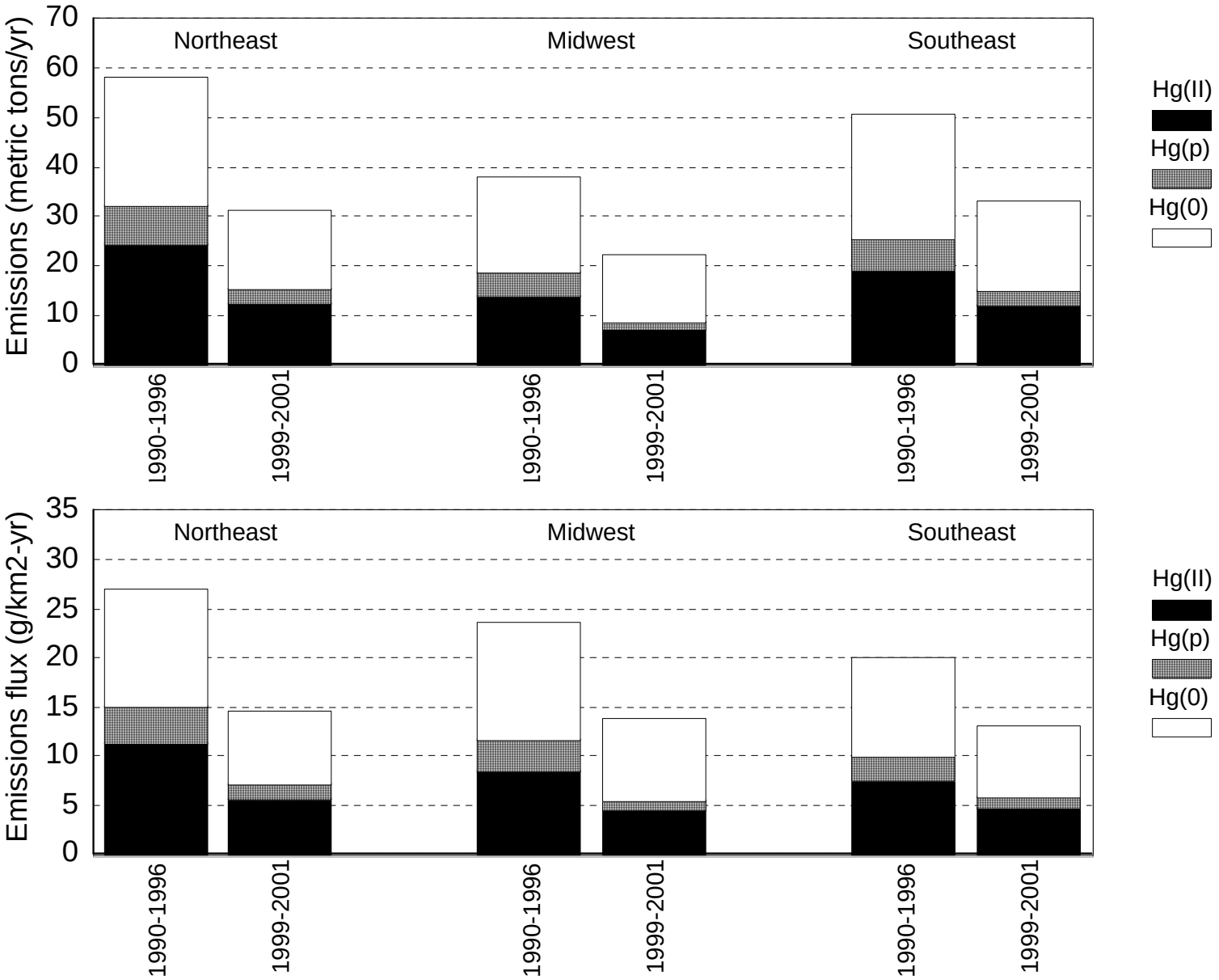

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In some states, there is a statewide mercury-related fish consumption advisory for lakes (L) and/or rivers (R), and in other cases, advisories have been issued for specific waterbodies. In the case of statewide advisories, the year the advisory was established is given. It is noted that Pennsylvania's statewide advisory was established for a number of pollutants, including mercury, and is not necessarily considered to be only a mercury-specific statewide consumption advisory. Mercury-related advisories for specific fish species have also been established by one or more states and provinces for each of the Great Lakes. Sources of information for this figure: Illinois Department of Public Health (2006); Indiana State Department of Public Health et al. (2006); Michigan Department of Community Health (2006); Minnesota Department of Health (2006); New York State Department of Health (2006); Ohio EPA Division of Surface Water (2006); Ontario Ministry of the Environment (2006a); Pennsylvania Department of Environmental Protection (2006); USEPA (2005f); and Wisconsin Department of Natural Resources (2006).

Figure 2. Summary of mercury-related fish consumption advisories in the Great Lakes region.

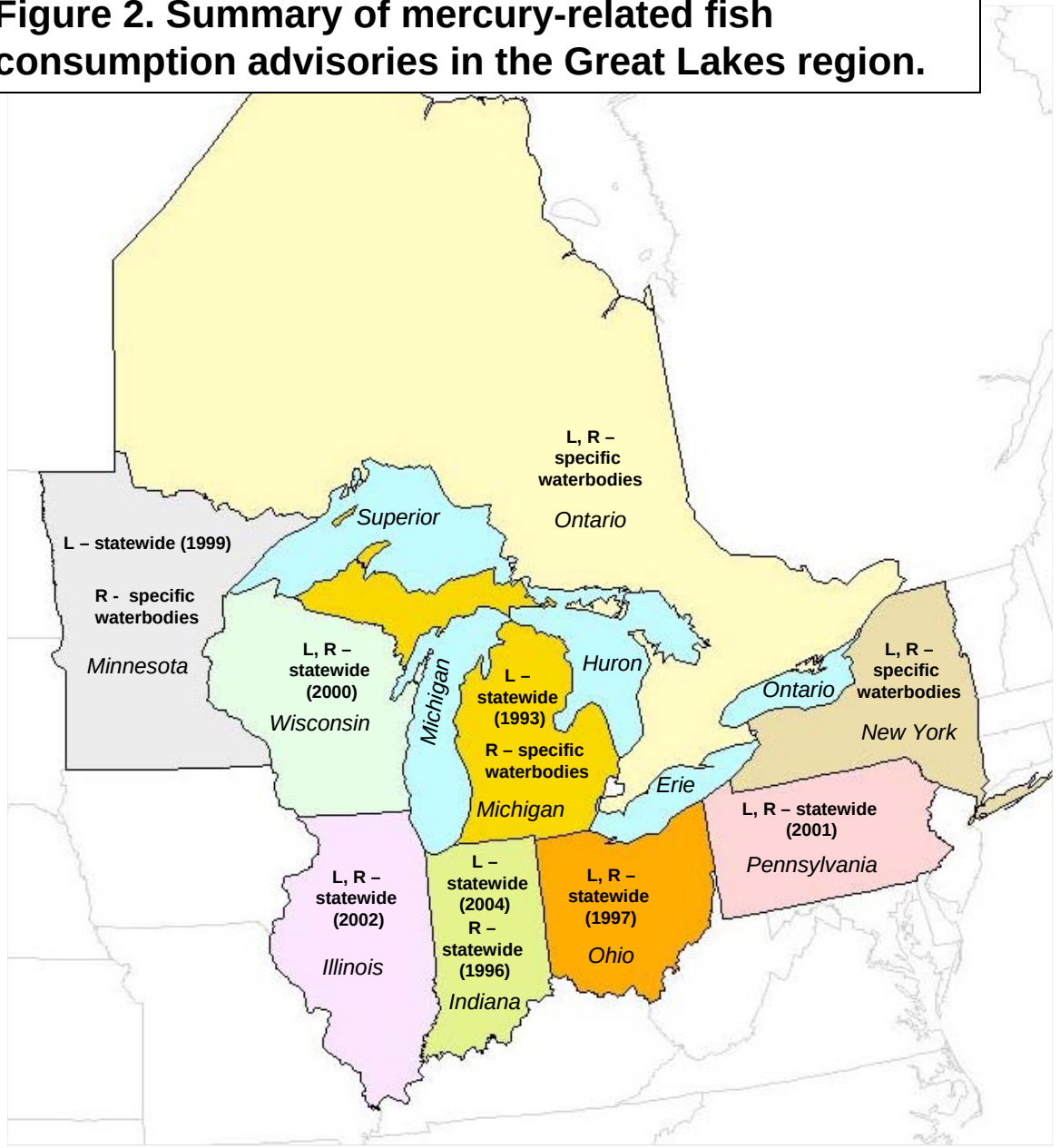
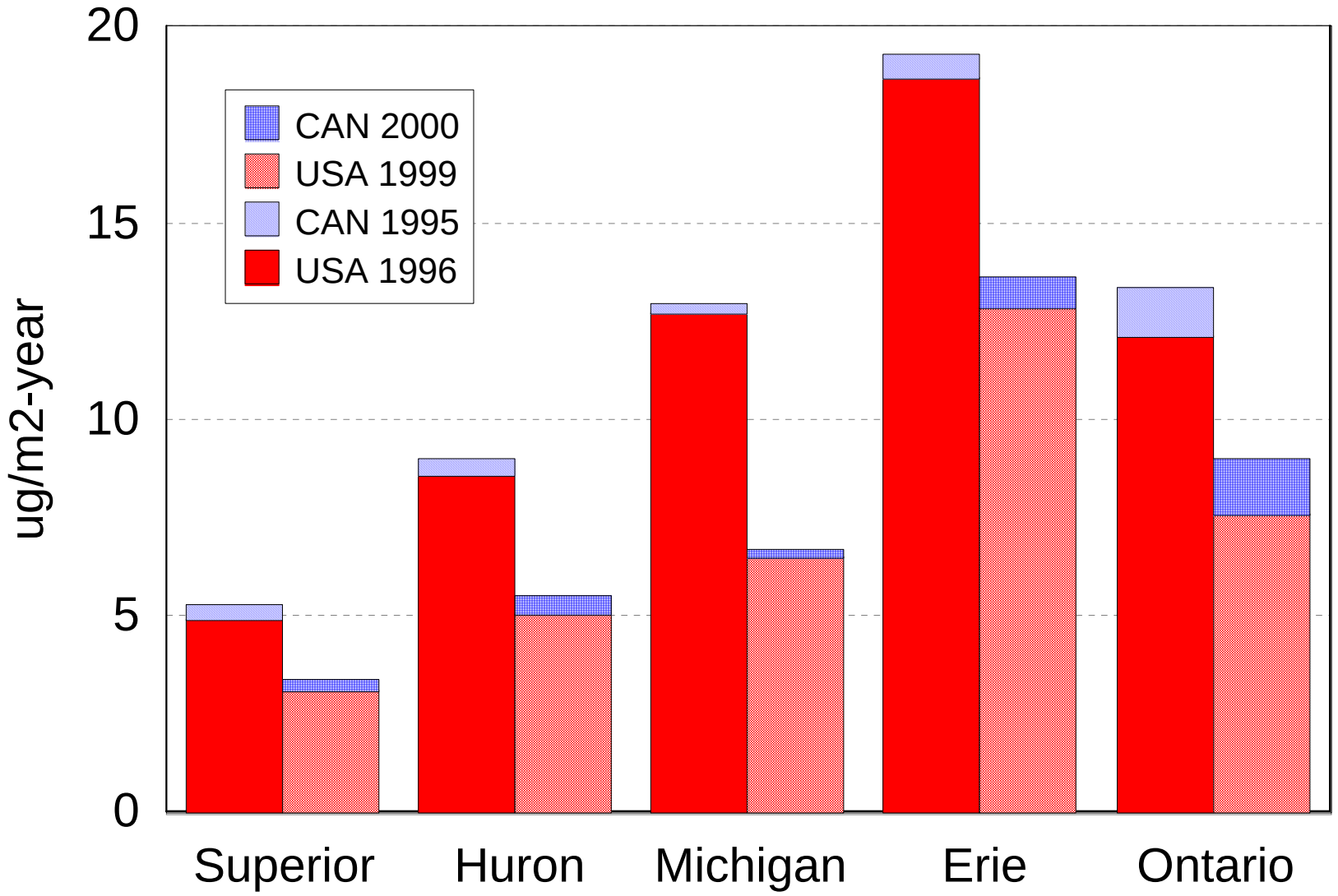
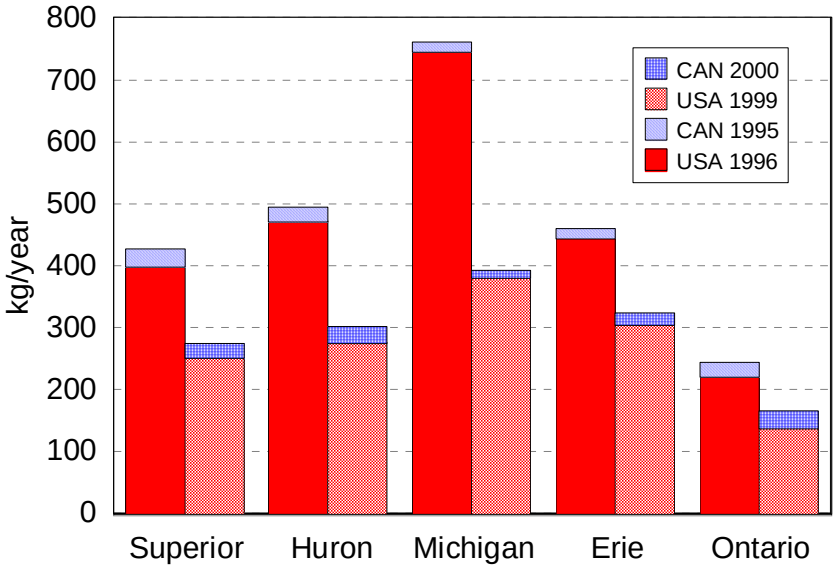


Figure 92. Modeled mercury flux to the Great Lakes (1995-1996 vs. 1999-2001), arising from anthropogenic mercury air emissions sources in the United States and Canada

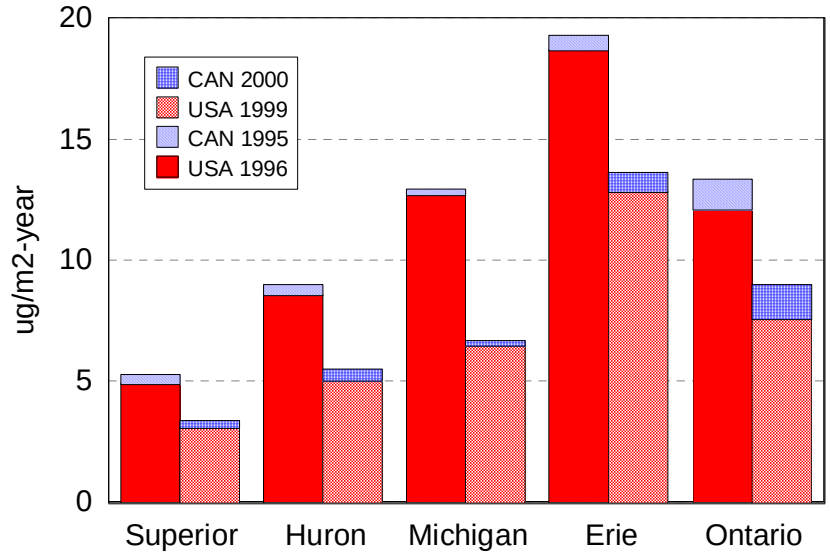




Modeled mercury deposition (kg/year) to the Great Lakes (1995-1996 vs. 1999-2000), arising from anthropogenic mercury air emissions sources in the U.S. and Canada

Model results for atmospheric deposition show that:

- **U.S. contributes much more than Canada**
- **Significant decrease between 1996 and 1999 (primarily due to decreased emissions from waste incineration)**



Modeled mercury flux (ug/m2-yr) to the Great Lakes (1995-1996 vs. 1999-2000), arising from anthropogenic mercury air emissions sources in the U.S. and Canada

Figure 101. Mercury concentration trends Great Lakes Walleye. Total mercury concentrations (ppm or ug Hg/g).

Sources of data: Ontario Ministry of the Environment (2006b), for 45-cm Walleye data, and Environment Canada (2006), for data on Lake Erie Walleye ages 4-6.

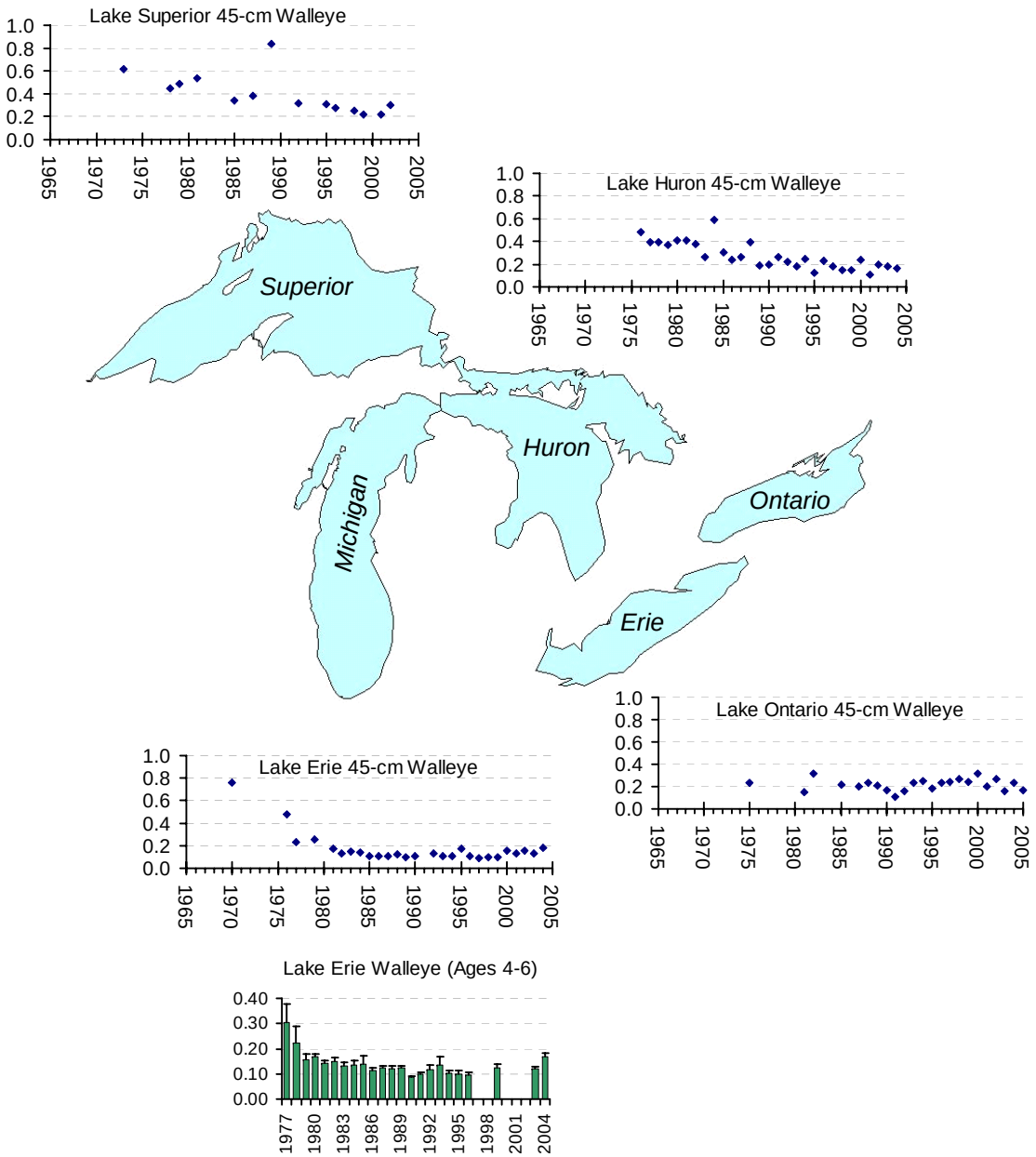
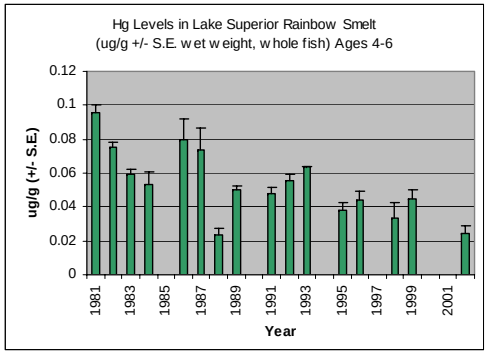
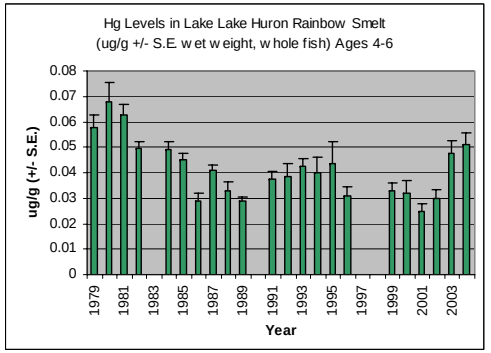
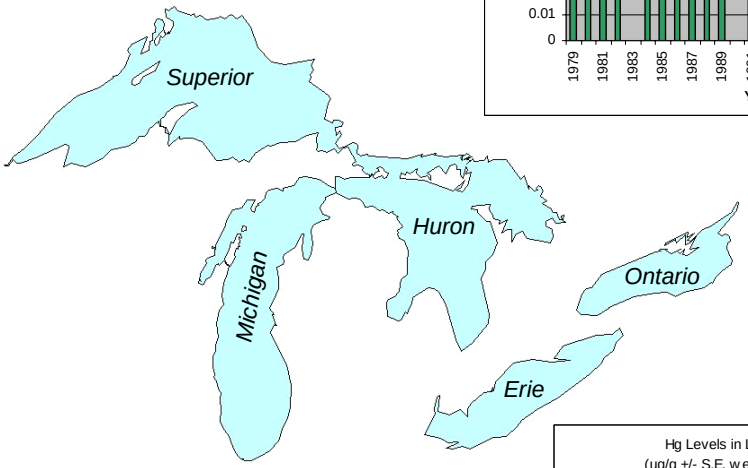


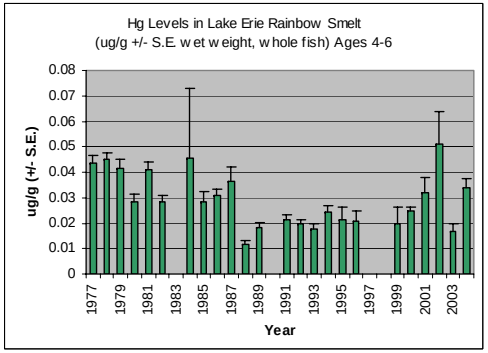
Figure 102. Total mercury levels in Great Lakes Rainbow Smelt, 1977-2004.

Source of data: Environment Canada (2006). Note that the scales for the lakes are different.









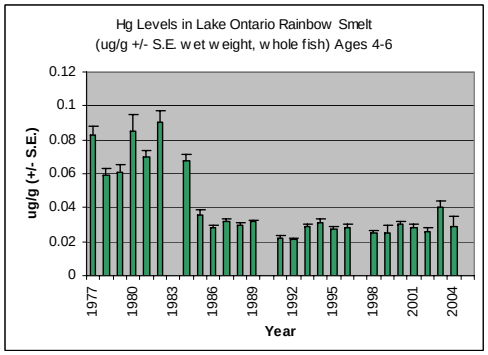
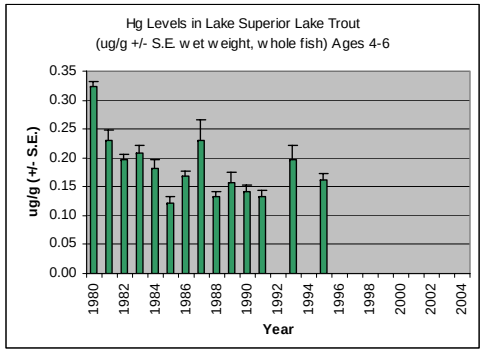
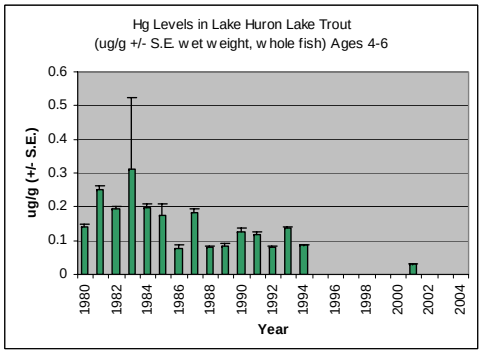
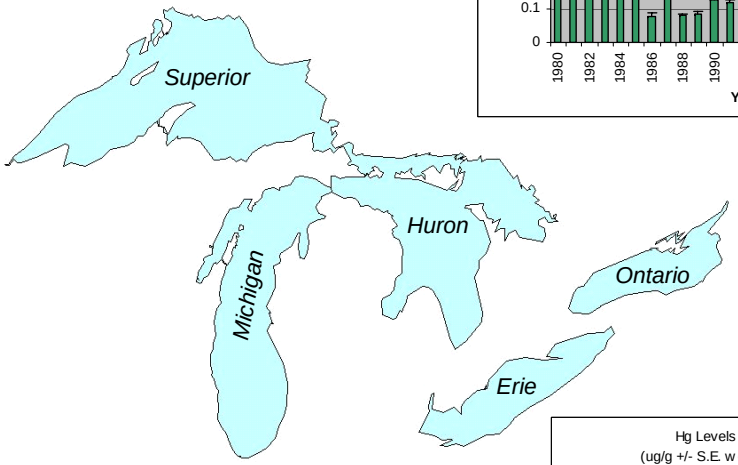


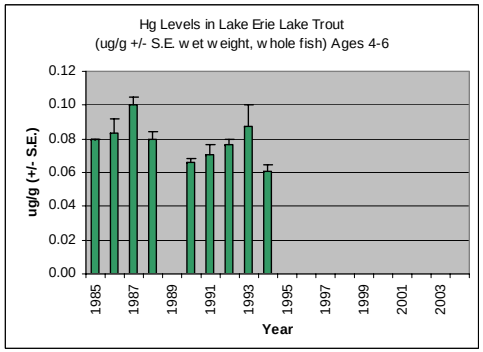
Figure 103. Mercury concentration trends in Lake Trout in the Great Lakes.

Data from Environment Canada (2006). Note that for Lake Huron, there was an average of 25 fish sampled each year from 1980 to 1994, but that the data shown for 2001 represents only 1 fish.









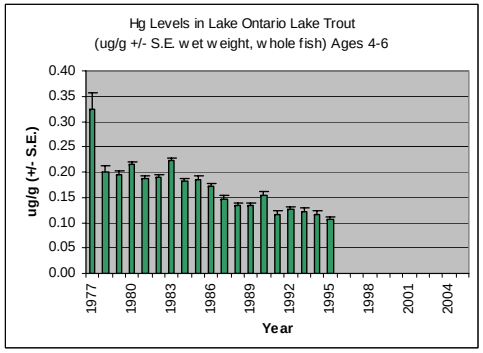


Figure 106. Trends in Herring Gull Egg Hg concentrations.

Source of data – Canadian Wildlife Service. Total mercury concentrations in eggs from colonies in the Great Lakes region expressed in units of ug Hg/g (wet weight).

From 1971 – 1985, analysis was generally conducted on individual eggs (~10) from a given colony, and the standard deviation in concentrations is shown on the graphs.

From 1986 to the present, analysis was generally conducted on a composite sample for a given colony.

The trend lines shown are for illustration purposes only; they were created by fitting the data to a function of the form y = cxb.

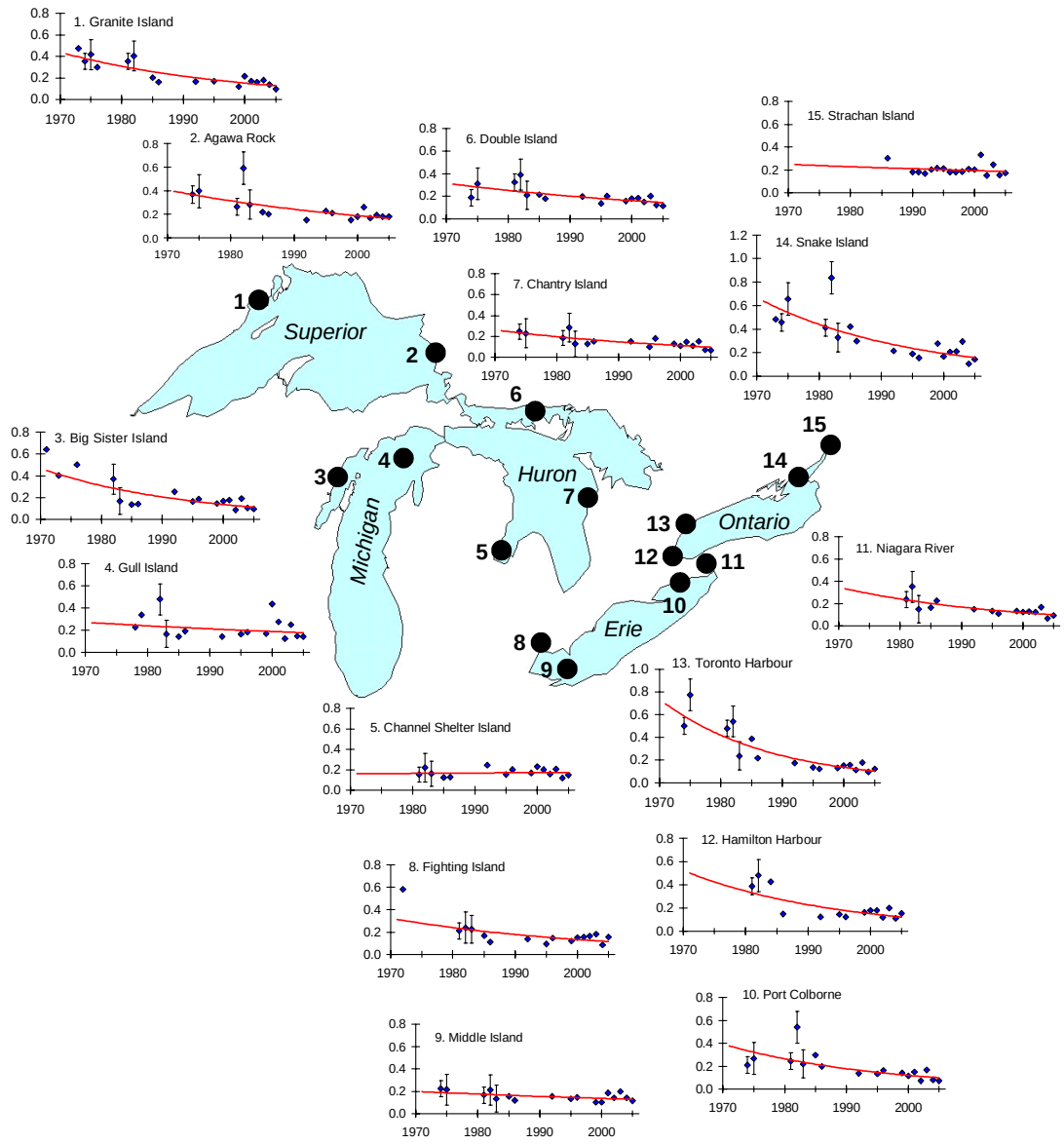
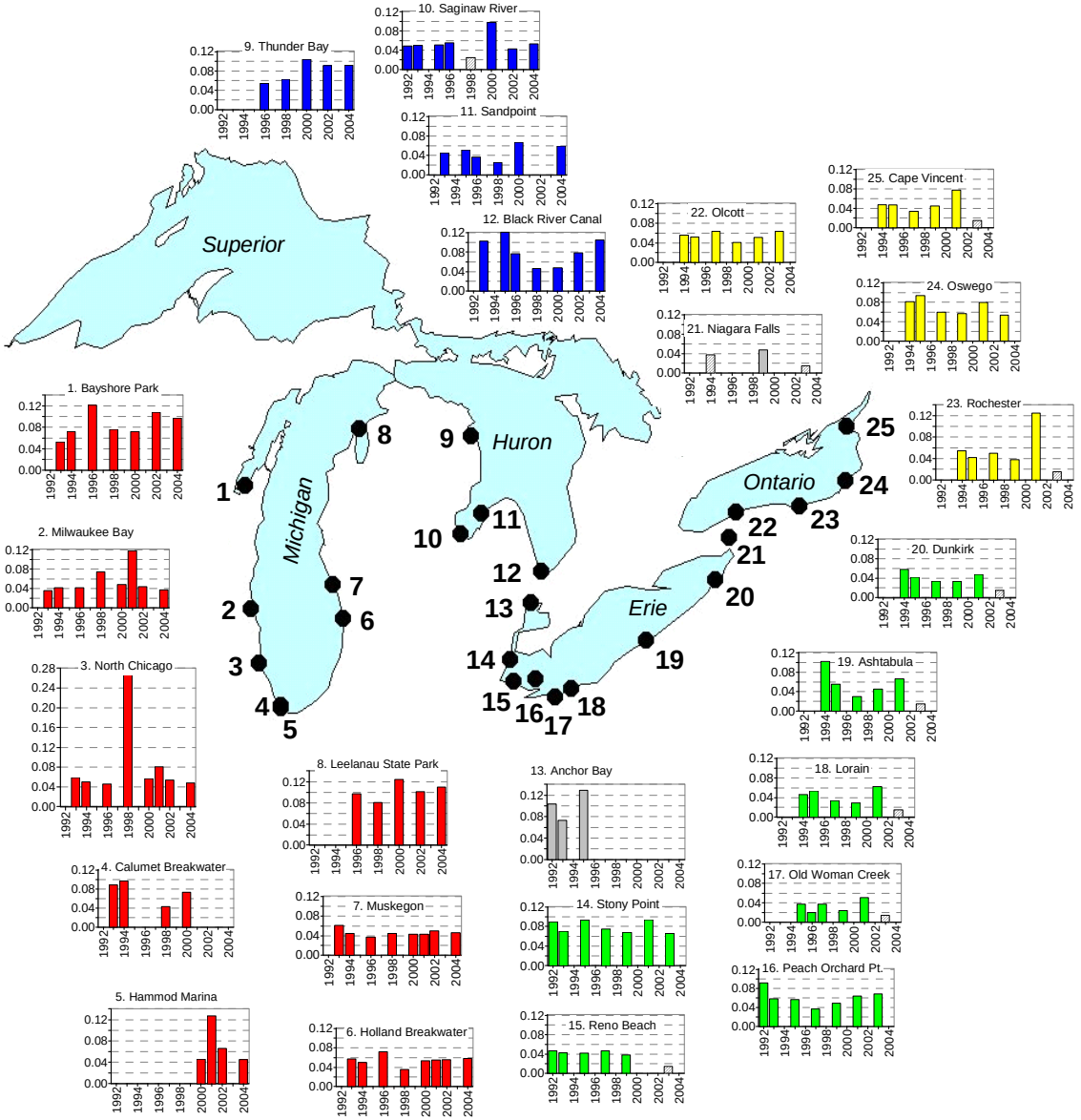
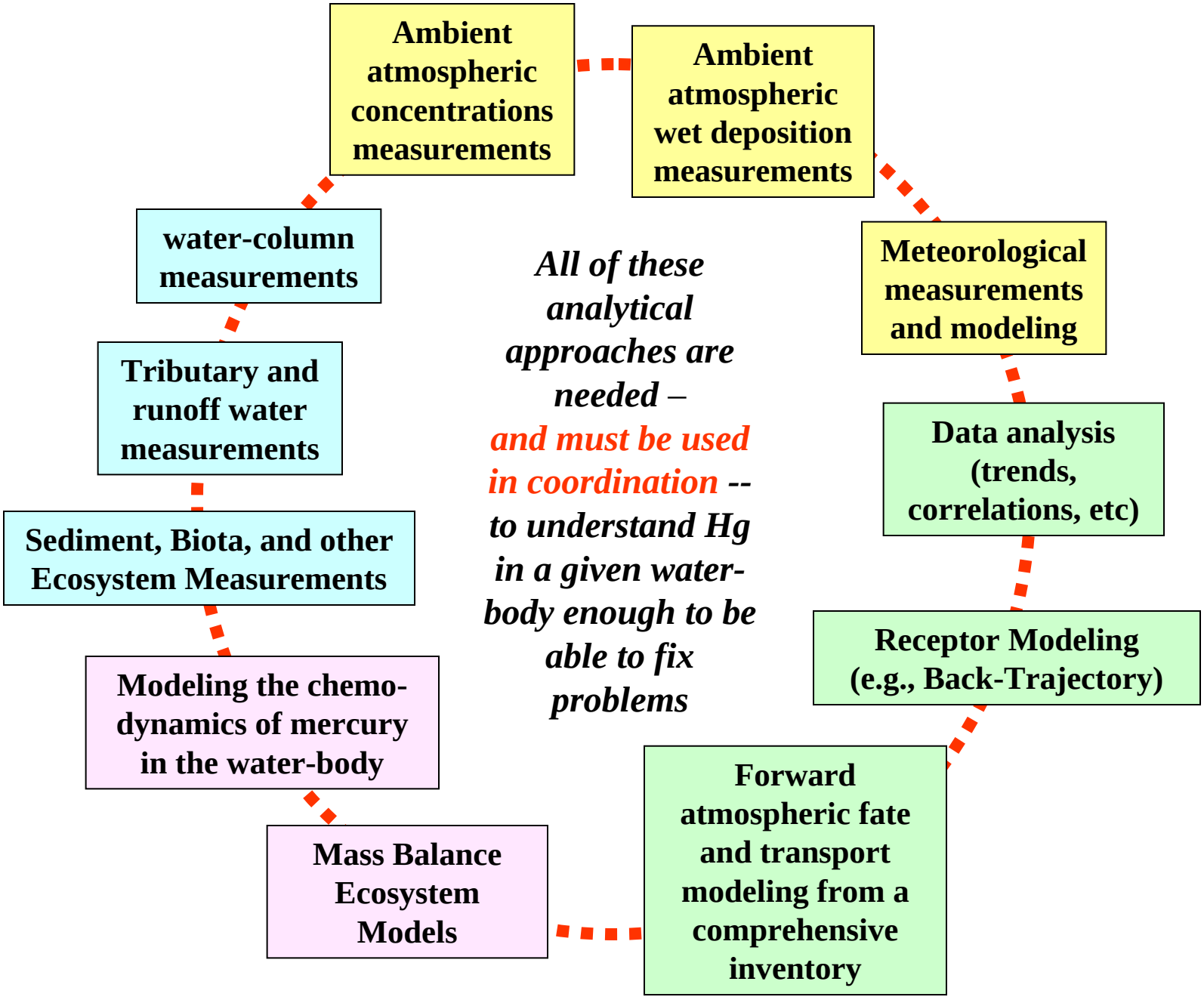


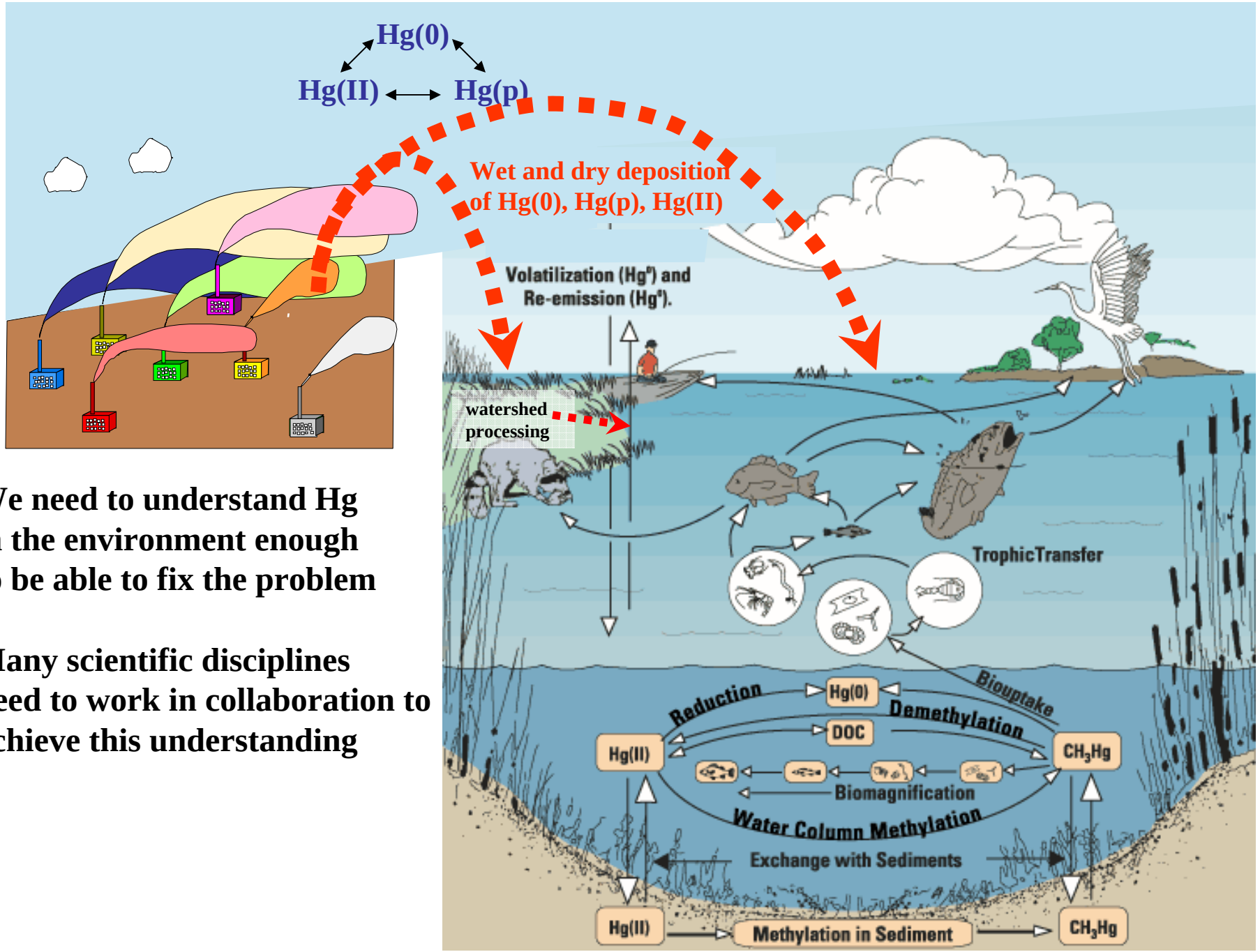
Figure 107. Mercury concentration in Great Lakes region mussels (1992-2004). Total mercury in mussels (ug/g, on a dry weight basis).

In a few cases (e.g. for several sites in 2003), mercury concentrations were below the detection limit. In these cases the concentrations are shown with a white cross-hatched bar at a value of one-half the detection limit; in reality, the mercury concentration could have been anywhere between zero and the detection limit.

Source of data: NOAA Center for Coastal Monitoring and Assessment (CCMA) (2006) and "Monitoring Data - Mussel Watch" website: http://www8.nos.noaa.gov/cit/nsandt/download/mw_monitoring.aspx



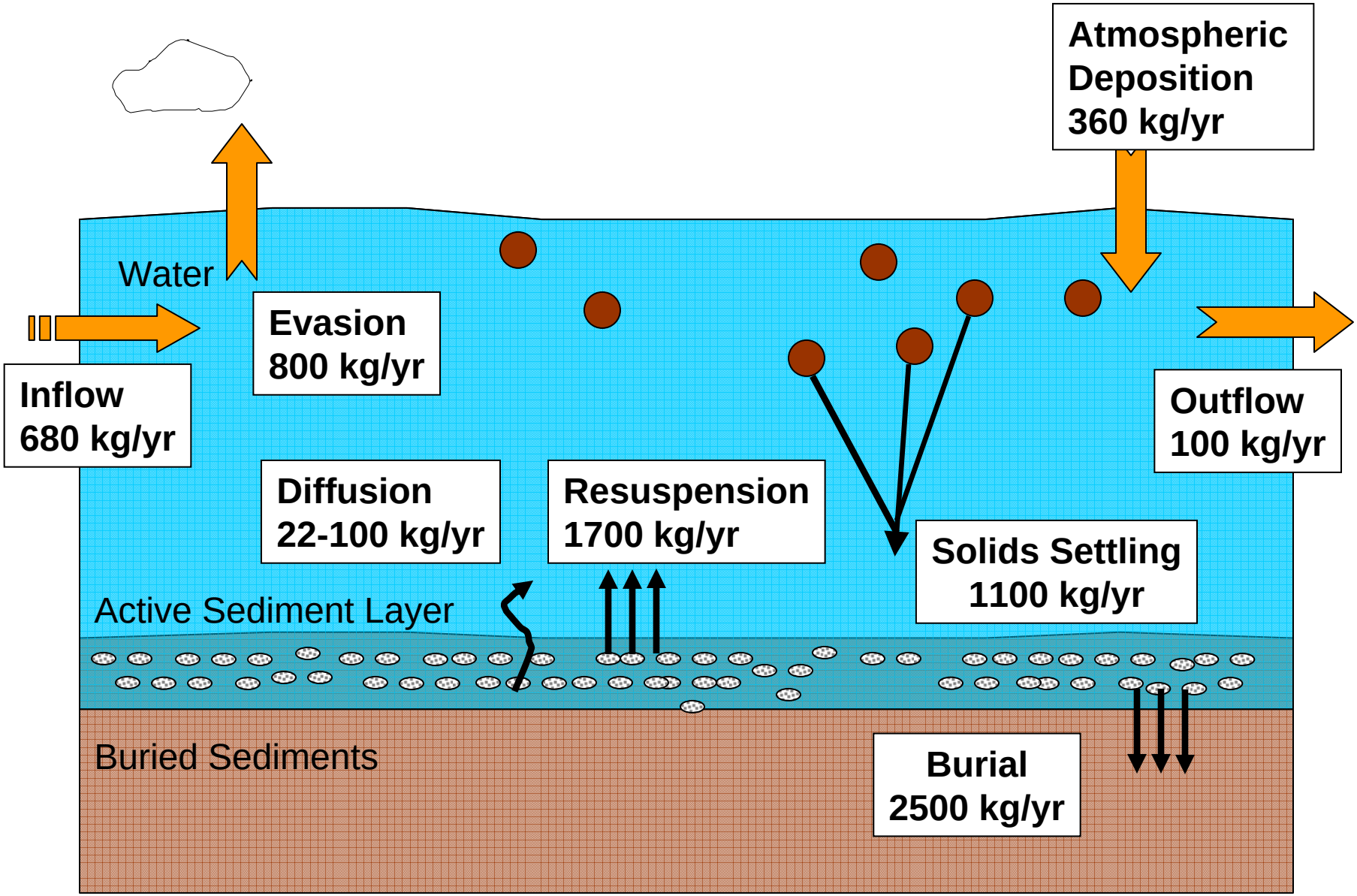

Ambient atmospheric concentrations measurements
Ambient atmospheric wet deposition measurements
water-column measurements
Meteorological measurements and modeling
Tributary and runoff water measurements
Data analysis (trends, correlations, etc)
Sediment, Biota, and other Ecosystem Measurements
Receptor Modeling (e.g., Back-Trajectory)
Modeling the chemo-dynamics of mercury in the water-body
Forward atmospheric fate and transport modeling from a comprehensive inventory
Mass Balance Ecosystem Models
All of these analytical approaches are needed – and must be used in coordination -- to understand Hg in a given water-body enough to be able to fix problems



We need to understand Hg in the environment enough to be able to fix the problem

Many scientific disciplines need to work in collaboration to achieve this understanding

Total Mercury Fluxes Lake Ontario

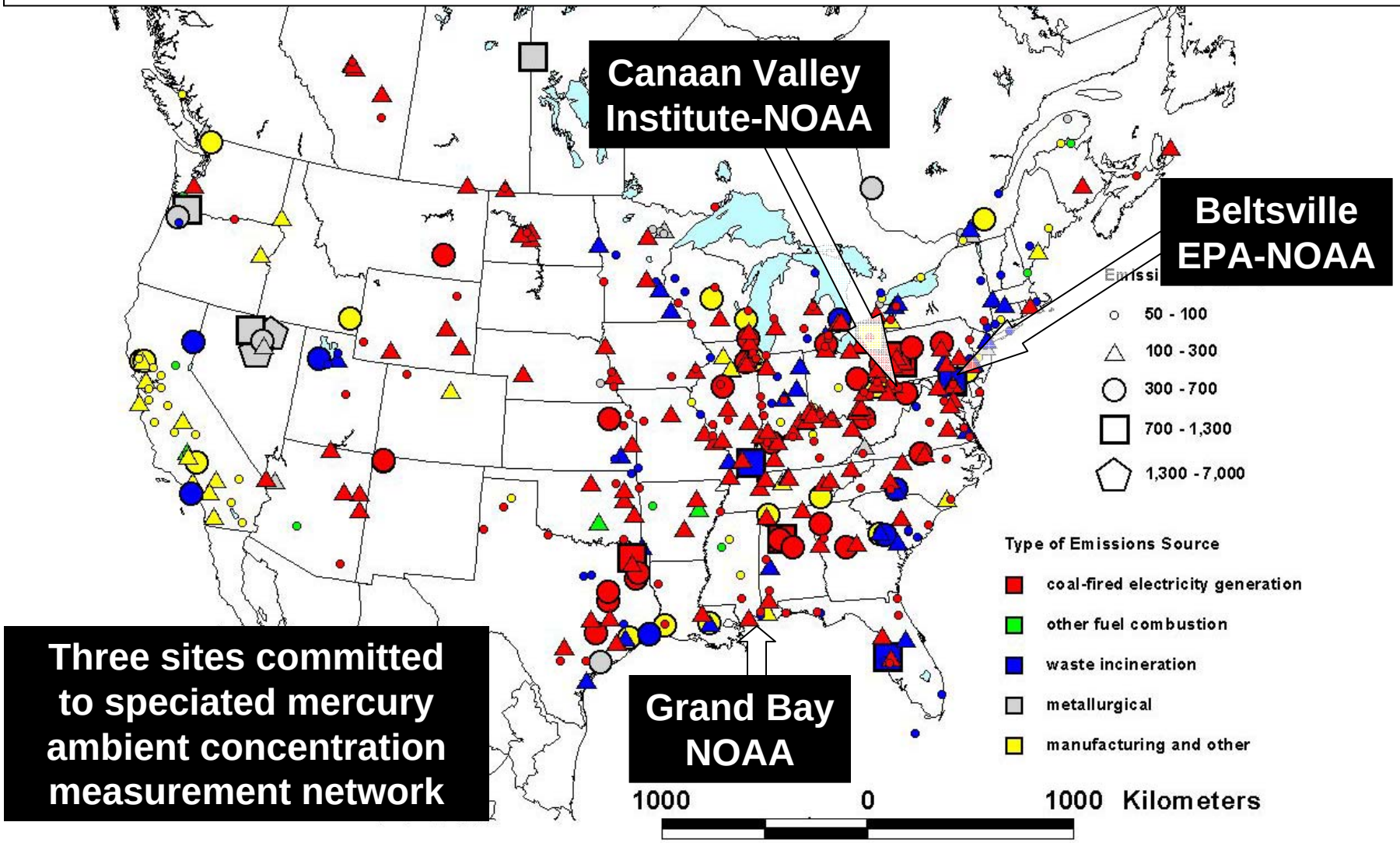


slide courtesy of Elsie Sunderland, USEPA

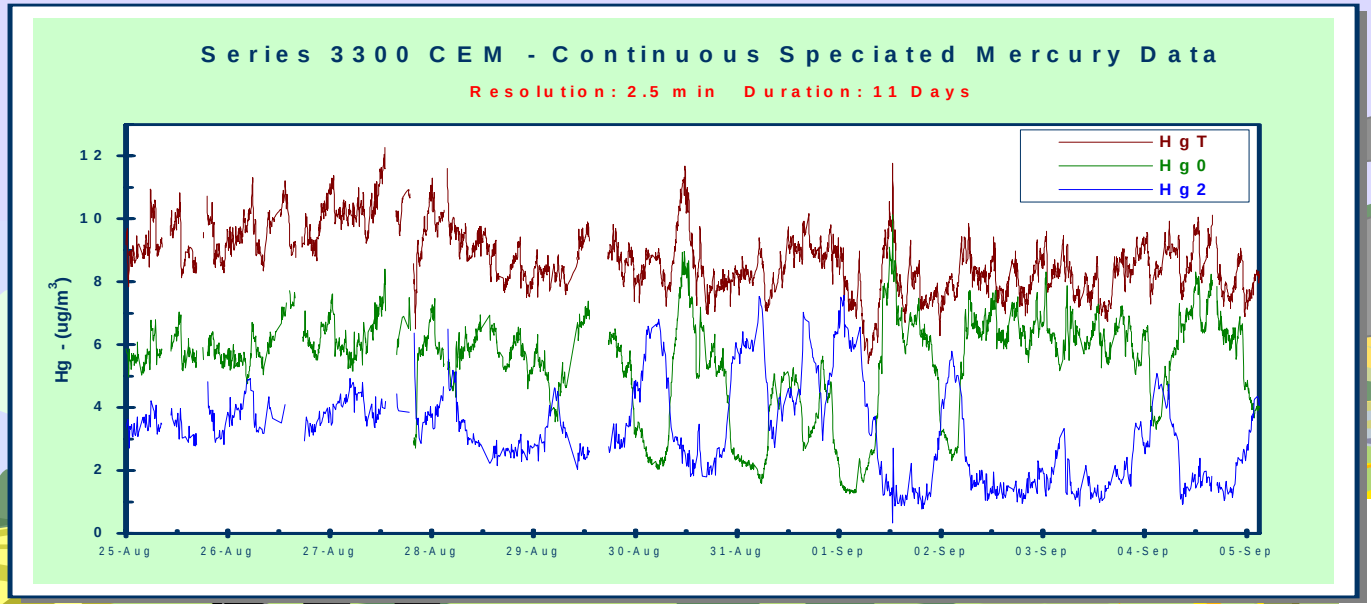
Table 4. Summary of U.S. anthropogenic mercury emissions inventories

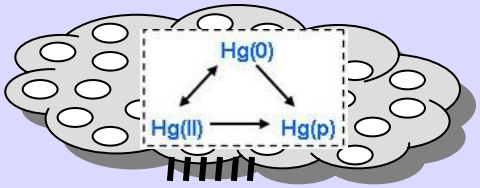
Inventory	Avail-able for this study	Geo-graphical resolution	Nominal Time period for inventory	Total U.S. direct anthro-pogenic emissions (tons/yr)	Notes and/or References
1990 Cumulative Outdoor Exposure Study	no	point and area sources	1990	266	Rosenbaum et al., 1999ab.
1990 National Toxics Inventory (NTI)	yes	national totals only	1990	220	EPA (2005a, 2006). These data are based on the 1990 National Toxics Inventory. We have not been able to find any detailed documentation for this inventory.
Mercury Study Report to Congress (MSRTC, Vol. 2)	yes	point and area sources	1994-95*	158	The geographically resolved version of this inventory was used as input to the RELMAP atmospheric fate and transport model (MSTRC, Vol. 3), EPA, 1997. It does not include gold mining, estimated in later inventories to be on the order of 13 tons/year
1996 National Toxics Inventory (NTI)	no	point sources and county-level area sources	1996	195	This inventory has been withdrawn by the EPA due to data quality concerns. The 195 ton total value was obtained from EPA (2006).
hybrid “1996” inventory	yes	point sources and county-level area sources	1996	162	used in NOAA atmospheric mercury simulations with the HYSPLIT-Hg model (Cohen et al, 2004). It contains elements of the MSRTC inventory (for municipal and medical waste incinerators and commerical/industrial boilers), 1999 estimates for coal-fired power plants, and the 1996 NTI for other point and area sources.
1999 National Emissions Inventory (NEI)	yes	point sources and county-level area sources	1999	113	some of the incinerator emission reductions may not have occured till 2000-2001
2002 National Emissions Inventory (NEI)	no	point sources and county-level area sources	2002	?	We have been unable to obtain summary or detailed information from this inventory, as of December 2006.
2005 National Emissions Inventory (NEI)	no	point sources and county-level area sources (?)	2005	?	This inventory will be released in the future. The EPA reports that it will represent a reduced level of effort, to allow additional resources to be devoted to developing a re-engineered 2008 inventory. Earlier announced plans called for the inventory to be released in Dec 2006, but it does not appear to be available at this time.

Largest sources of total mercury emissions to the air in the U.S. and Canada, based on the U.S. EPA 1999 National Emissions Inventory and 1995-2000 data from Environment Canada



Hg from other sources: local, regional & more distant

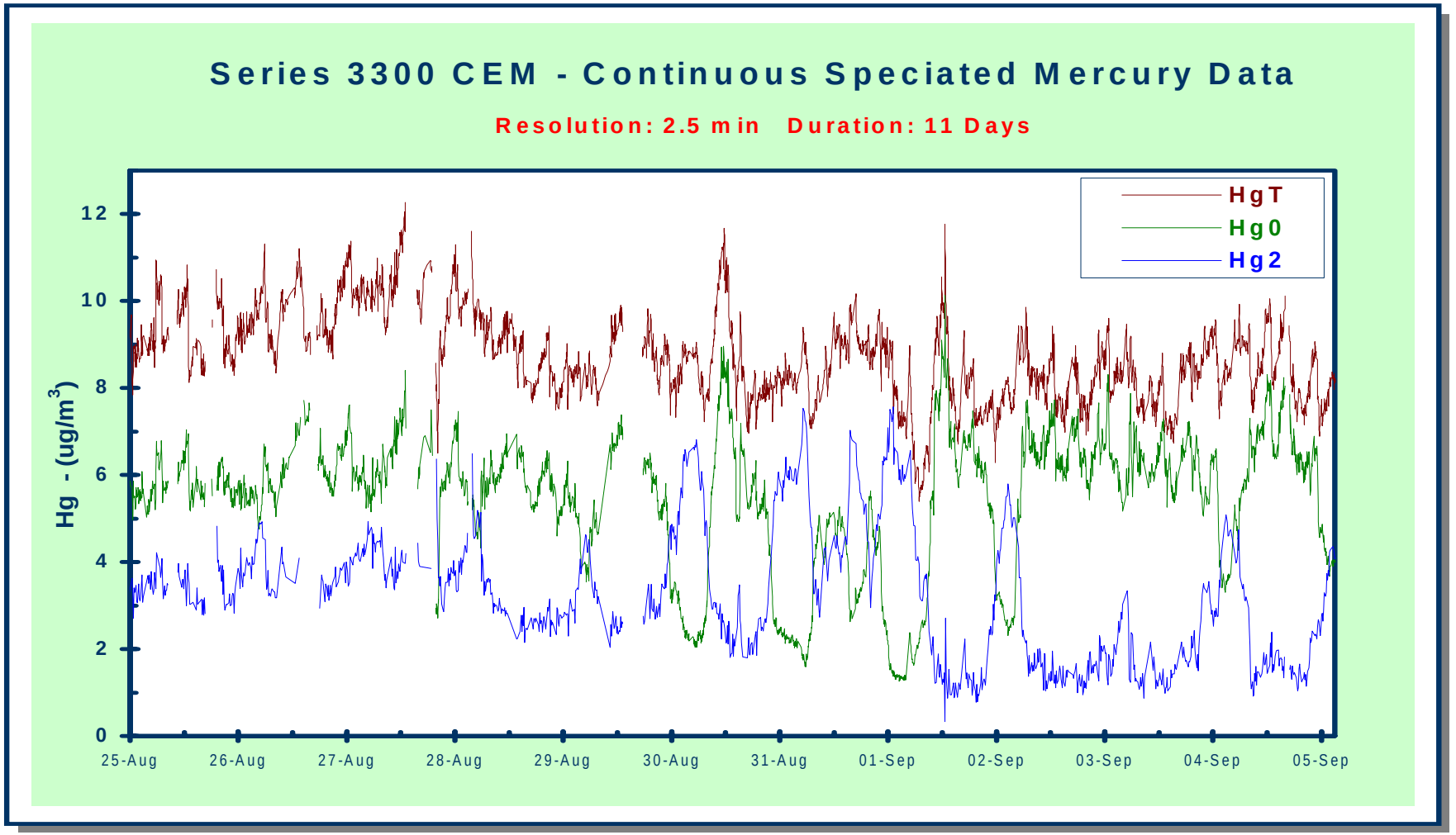




atmospheric deposition to the water surface

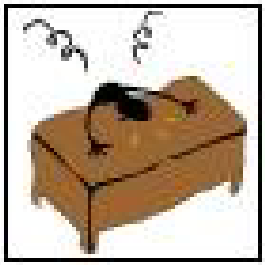
Measurement of wet deposition

Measurement of ambient air concentrations



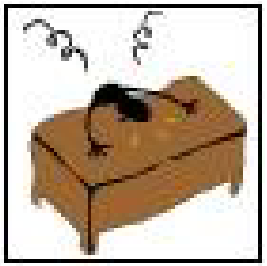
Thanks to **Marty Keller, Senior Applications Engineer, Tekran Instruments Corporation, *for providing this graph!***

Temporal Problems with Emissions Inventories



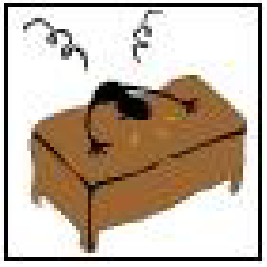
Variations on time scales of minutes to hours

- *CEM's needed – and not just on coal-fired power plants*
- *CEM's must be speciated or of little use in developing critical source-receptor information*
- *Clean Air Mercury Rule only requires ~weekly total-Hg measurements, for purposes of trading*



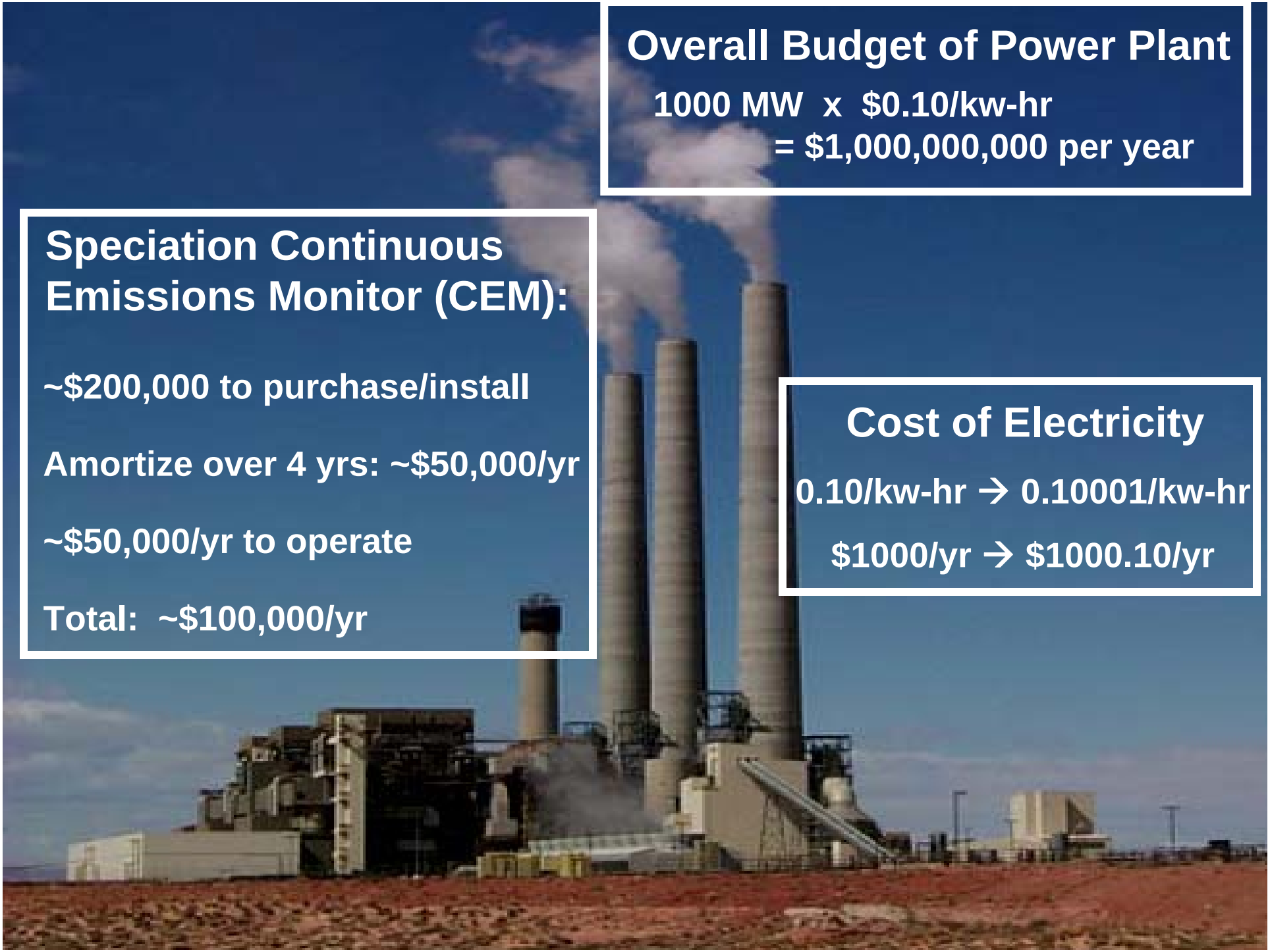
We don't have information about major events

- *e.g., maintenance or permanent closures, installation of new pollution control devices, process changes*
- *Therefore, difficult to interpret trends in ambient data*



Long delay before inventories released

- *2002 inventory is being released this year in U.S.; till now, the latest available inventory was for 1999*
- *How can we use new measurement data?*



Overall Budget of Power Plant

1000 MW x $0.10/kw-hr
= $1,000,000,000 per year

Speciation Continuous Emissions Monitor (CEM):

~$200,000 to purchase/install

Amortize over 4 yrs: ~$50,000/yr

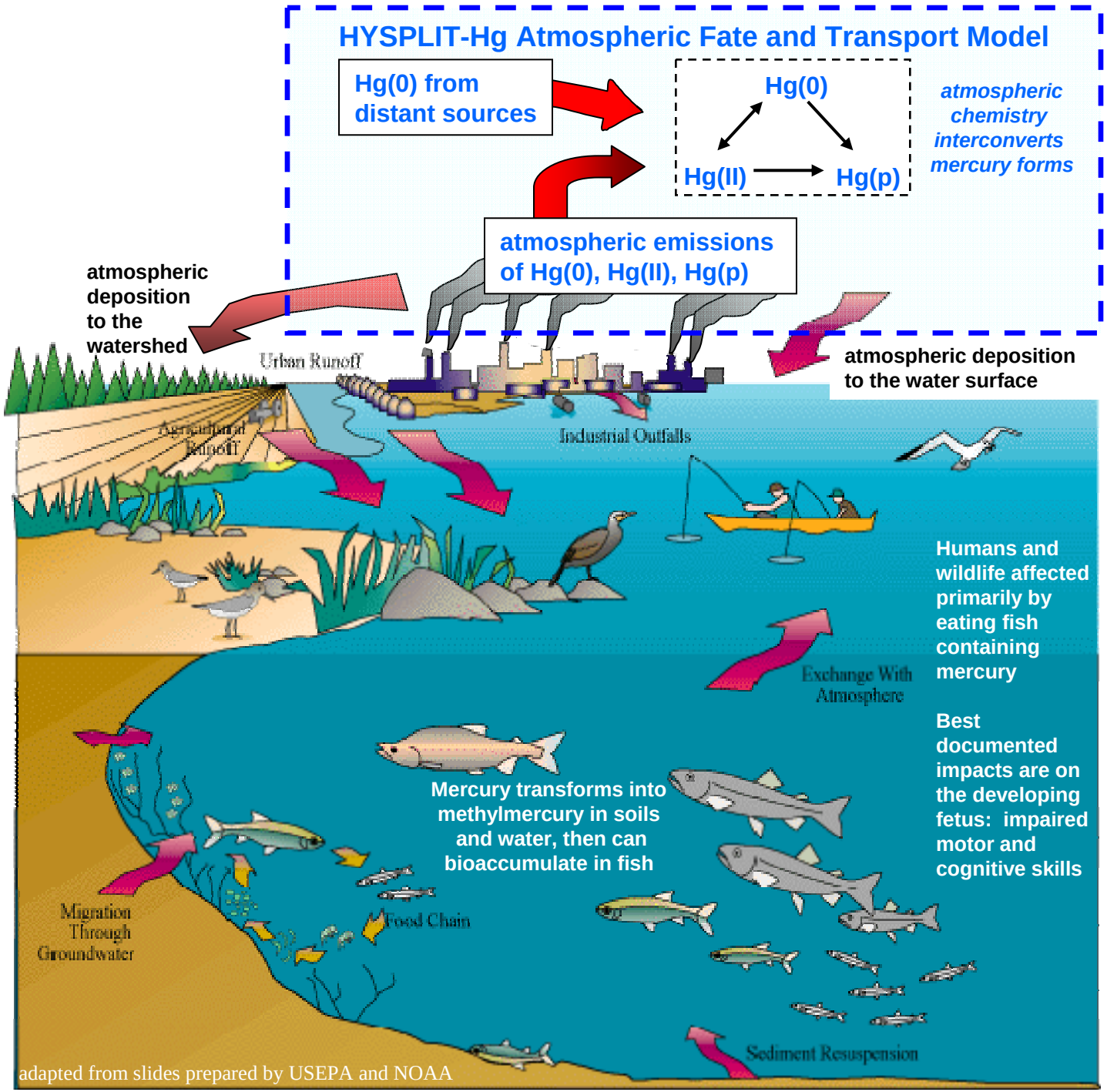
~$50,000/yr to operate

Total: ~$100,000/yr

Cost of Electricity

0.10/kw-hr → 0.10001/kw-hr

$1000/yr → $1000.10/yr



Where does the mercury come from that is depositing to any given waterbody or watershed?

- How much from local/regional sources?
- How much from global sources?
- Monitoring alone cannot give us the answer
- atmospheric models required, "ground-truthed" by atmospheric monitoring