

# Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes

Dr. Mark Cohen
NOAA Air Resources Laboratory (ARL)
College Park, MD, USA

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## Acknowledgements

HYSPLIT Development Team at ARL:

Roland Draxler Glenn Rolph Barbara Stunder Ariel Stein Fantine Ngan

Mercury Research Team at ARL: Winston Luke Paul Kelley Steve Brooks Xinrong Ren

IT Team at ARL:

Rick Jiang Yan Huang

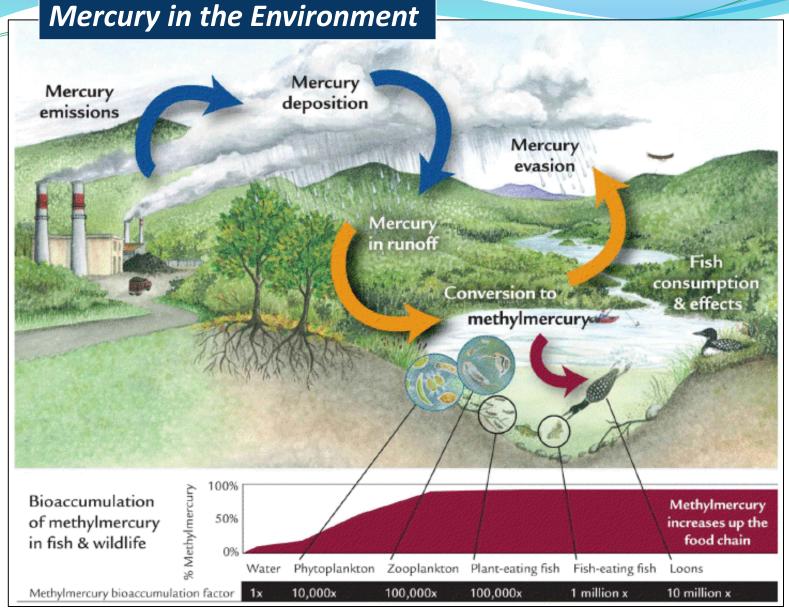
**Funding:** 

**Great Lakes Restoration Initiative,** via Interagency Agreement with USEPA

+ numerous collaborations with external partners involving:

- emissions inventory data for model input, and
- atmospheric measurement data for model evaluation



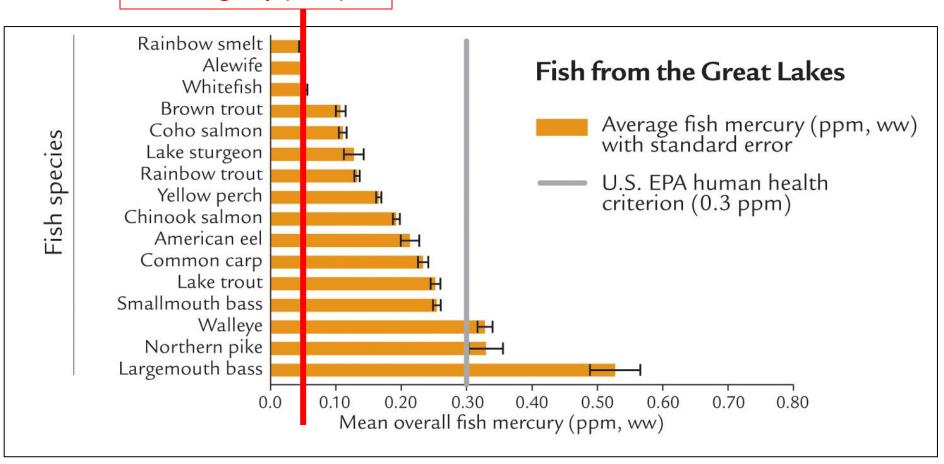


Biodiversity Research Institute (2011):



#### 0.05 ppm level recommended by the Great Lakes Fish Advisory Workgroup (2007)

## Mercury in Great Lakes Fish

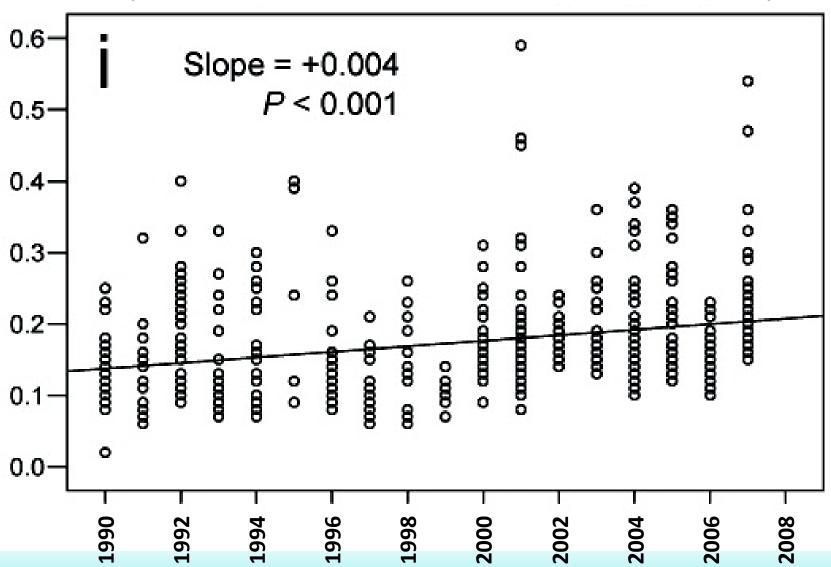


Evers, D.C., et al. (2011). *Great Lakes Mercury Connections: The Extent and Effects of Mercury Pollution in the Great Lakes Region*. Biodiversity Research Institute. Gorham, Maine. Report BRI 2011-18. 44 pages.



#### Temporal trends of mercury in Lake Erie

45-55 cm walleye collected between 1990-2007 (Bhavsar et al., Environ. Sci. Technol. 2010, 44, 3273-3279)



Atmospheric deposition is believed to be the largest current mercury loading pathway to the Great Lakes...

► How much is deposited and where does it come from?

(...this information can only be obtained via modeling...)





# 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**

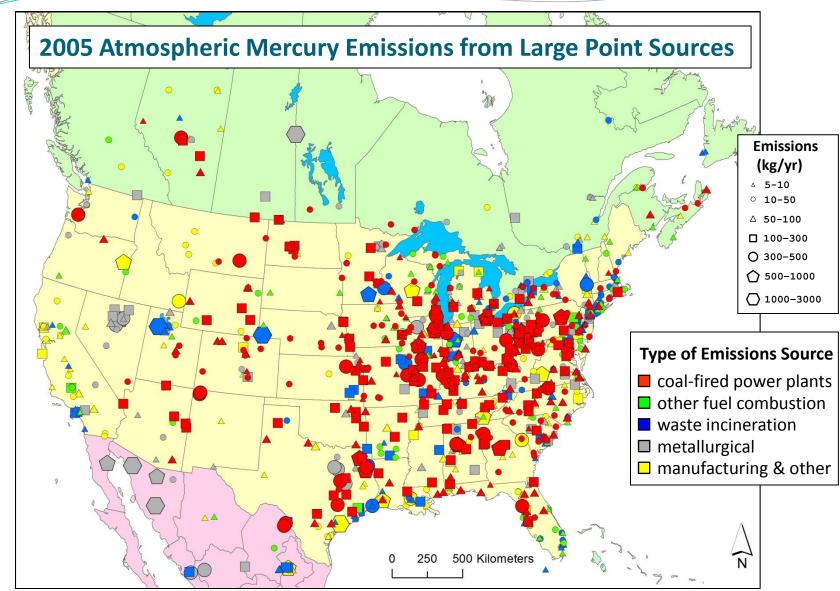
- a few % of total atmos. Hg
- oxidized Hg (HgCl<sub>2</sub>, others)
- very water soluble and "sticky"
- bioavailable

#### Particulate Mercury -- Hg(p)

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

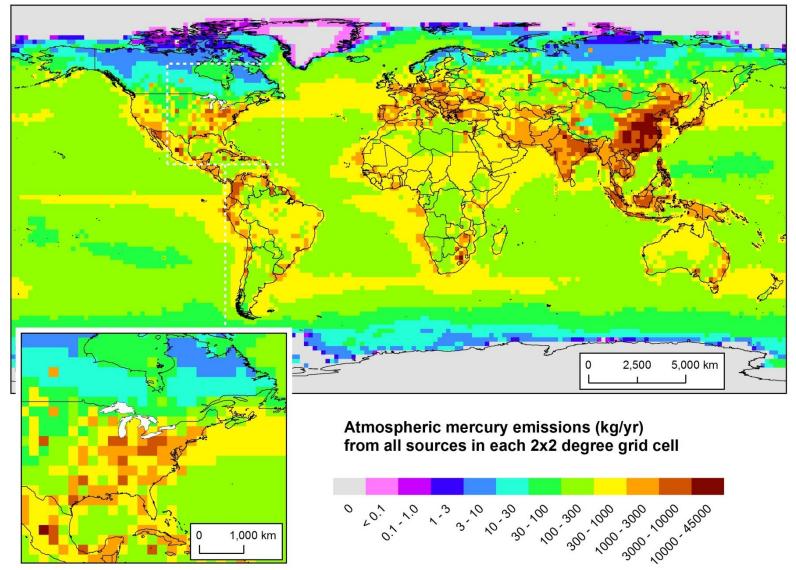


#### Starting point: where is mercury emitted to the air?



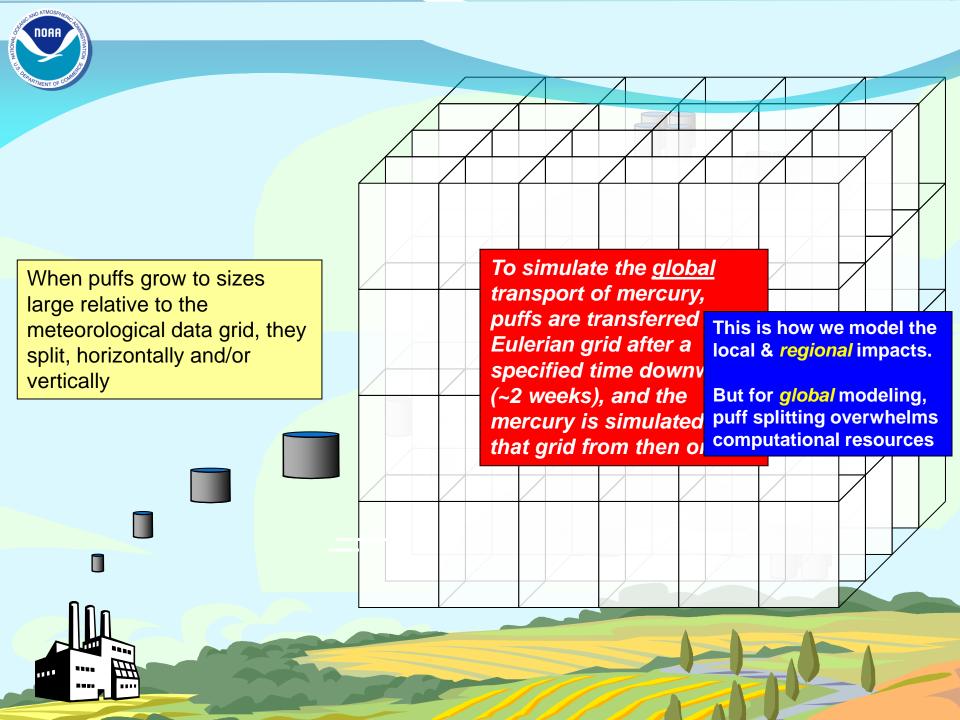


# 2005 Atmospheric Mercury Emissions (Direct Anthropogenic + Re-emit + Natural)



#### *Next step: What happens to the mercury after it is emitted?*

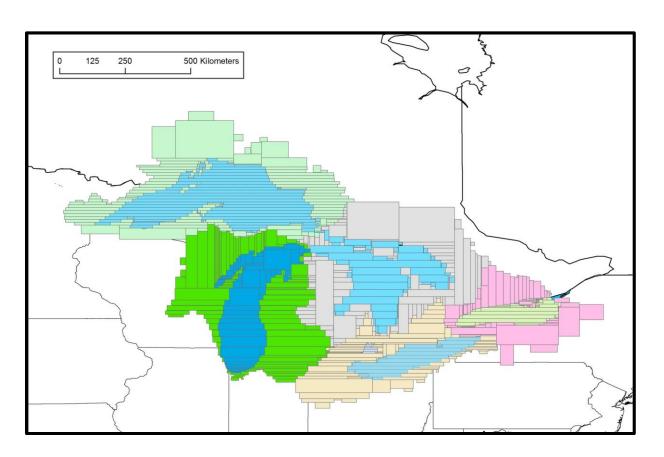
#### **HYSPLIT-Hg Lagrangian Puff Atmospheric Fate and Transport Model** TIME (hours) The puff's mass, size, = mass of pollutant and location are (changes due to chemical transformations and continuously tracked... deposition that occur at each time step) **Uncertainties** Phase partitioning and chemical transformations of pollutants within the puff are estimated at each time step Initial puff location is at source, with Centerline of Dry and wet mass depending puff motion deposition of on emissions rate determined by **Uncertainties** the pollutants wind direction in the puff are and velocity estimated at each time step. **Uncertainties** CHETED deposition 1 deposition 2 deposition to receptor CHITID CHED [] lake





## Deposition explicitly modeled to actual lake/watershed areas

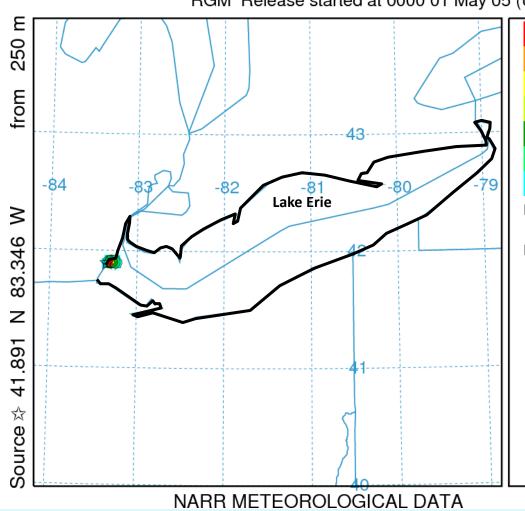
 As opposed to the usual practice of ascribing portions of gridded deposition to these areas in a post-processing step





# Illustrative simulation of reactive gaseous mercury (RGM) emissions from one power plant on the shore of Lake Erie: hourly deposition estimates for the first two weeks in May 2005

Deposition (ng/m2-hr) at ground-level Integrated from 0000 01 May to 0100 01 May 05 (UTC) RGM Release started at 0000 01 May 05 (UTC)



>1.0E+02 ng/m2-hr >3.3E+01 ng/m2-hr >1.0E+01 ng/m2-hr >3.3E+00 ng/m2-hr >1.0E+00 ng/m2-hr >3.3E-01 ng/m2-hr >1.0E-01 ng/m2-hr Maximum: 7.6E+00 (identified as a square) Minimum: 1.6E-03

Results scaled to actual RGM emissions of 43.6 g/hr

1 ng/m2-hr = 8.8 ug/m2-yr (if it persisted the entire year)

Total deposition to Lk Erie is ~20 ug/m2-yr

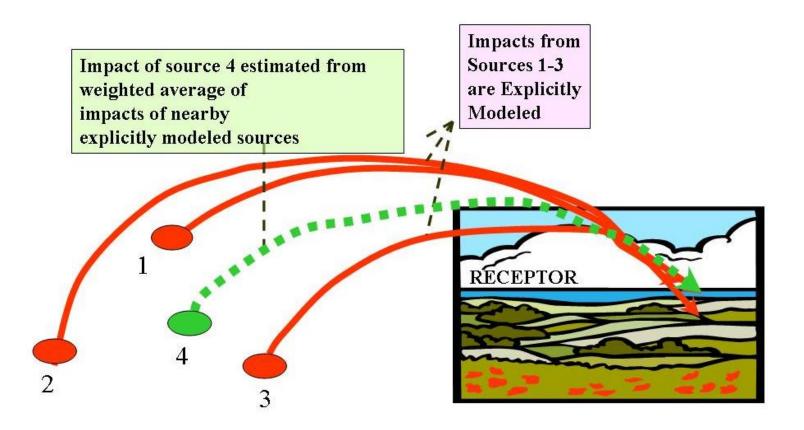


## **Computational Challenge**

- **→** 350,000 sources in global emissions inventory
  - **■** Would like to keep track of each source individually
    - typical one-year simulation takes~96 processor hours
      - ~3800 processor years, if ran explicit simulation for each source
        - ~240 years on 16-processor workstation

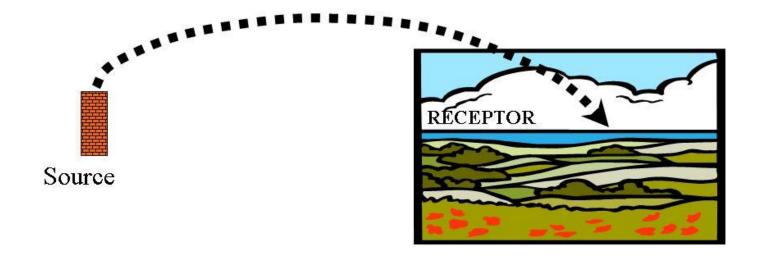


# **Spatial Interpolation**





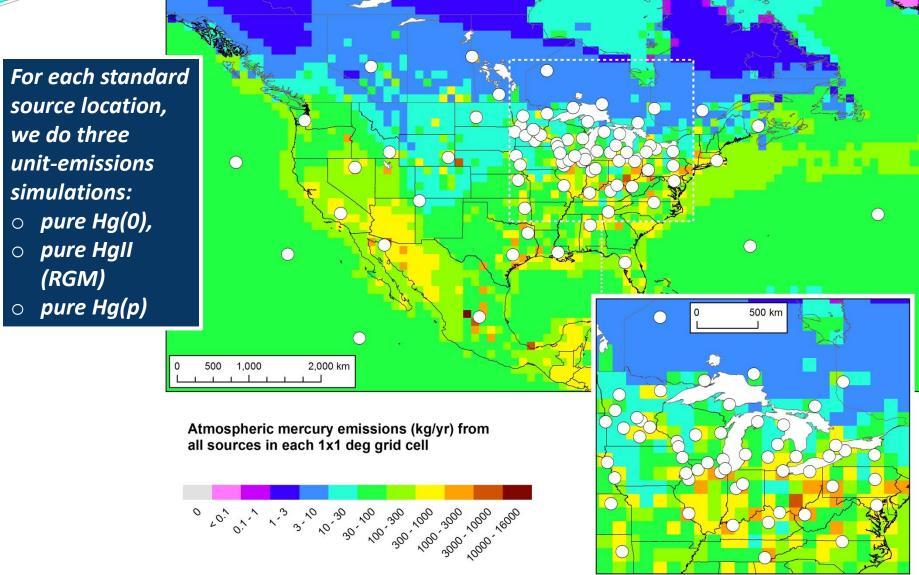
# Chemical Interpolation



		0.3 x	Impact of Source Emitting Pure Hg(0)
Impact of Source Emitting			+
30% Hg(0)	=	0.5 x	Impact of Source Emitting Pure Hg(II)
50% Hg(II)			-
20% Hg(p)		0.2 x	Impact of Source Emitting Pure Hg(p)

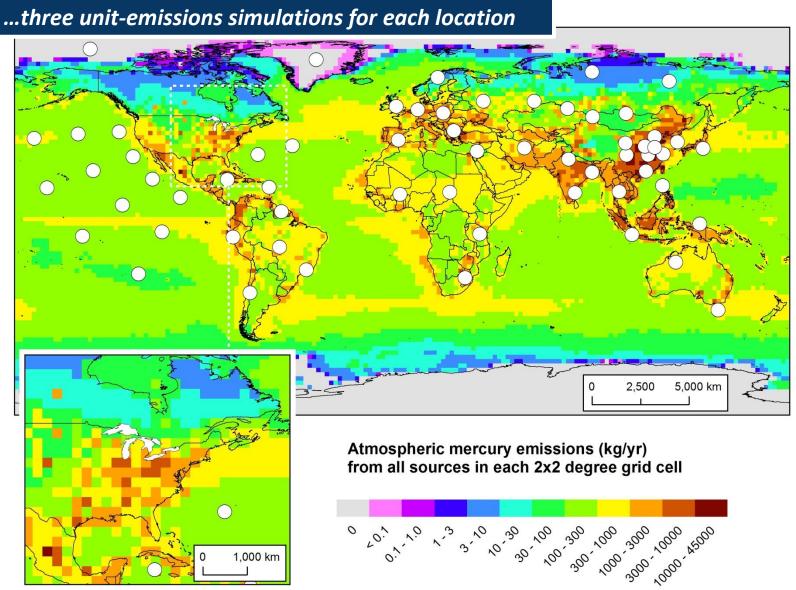


#### Standard Points in North America





#### Standard Points Outside of North America



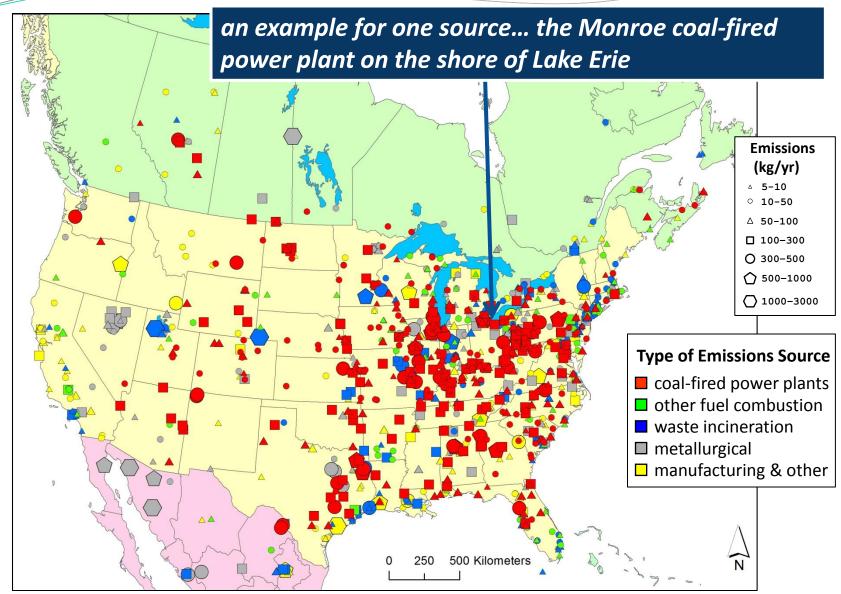


## **Computational Solution**

- This analysis done with 136 standard source locations
  - 3 unit emissions simulations from each location (Hg(0), RGM, and Hg(p)
    - → ~4.5 processor years
      - → ~3.5 months on 16-processor workstation

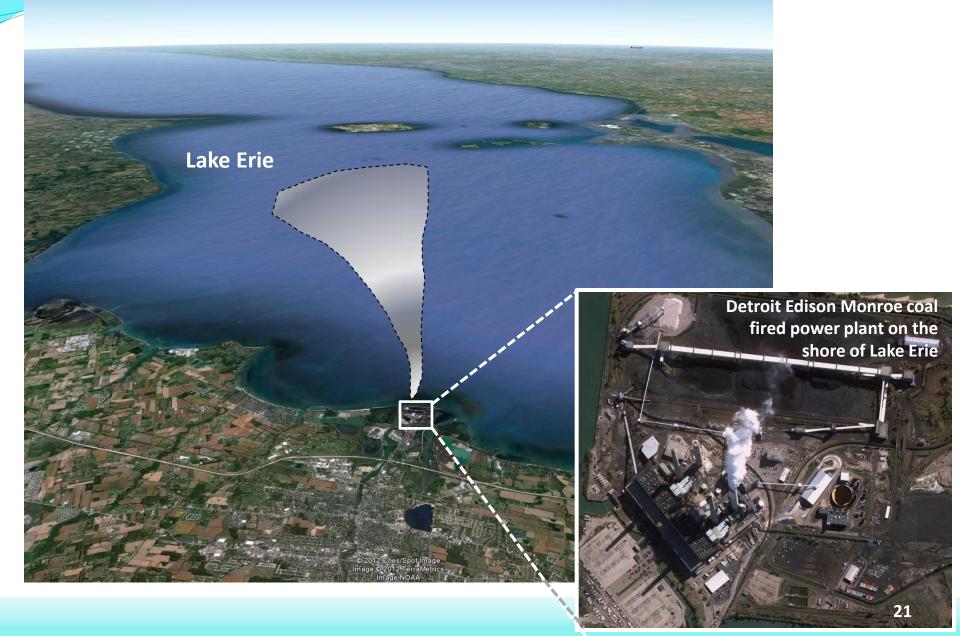
instead of 240 years ... almost 1000x less!







- ➤ Monroe emitted 561 kg of mercury in 2005 (EPA's National Emissions Inventory)
- ➤ How much of this mercury was deposited into Lake Erie and its watershed?





- Monroe emitted 561 kg of mercury in 2005 (EPA's National Emissions Inventory)
- ➤ Modeling results for this specific source:
  - 24 kg (~4%) of this emitted mercury was deposited directly into Lake Erie
  - 107 kg (~19%) of this emitted mercury was deposited in the Lake Erie Watershed
- ➤ We make this same type of estimate for *every source* in the national and global emissions inventories used as model input... *using spatial and chemical interpolation*





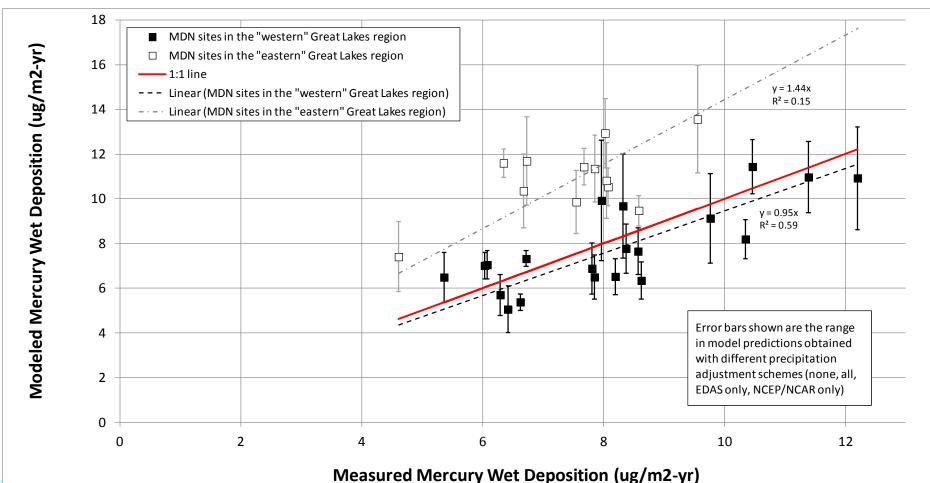
#### **Outline of Modeling Analysis**

- HYSPLIT
- HYSPLIT-Hg (with mercury-specific chemistry, ...)
- Unit Emissions Simulations of Hg(0), Hg(II) and Hg(p)
   from an array of standard source locations
- Emissions Inventory emissions of Hg(0), Hg(II), and Hg(p) from sources at specified latitudes and longitudes
- "Multiplication" of emissions inventory by array of unit emissions simulations using spatial and chemical interpolation
- Evaluate overall model results: compare against ambient measurements
- Source-attribution results for deposition to selected receptors



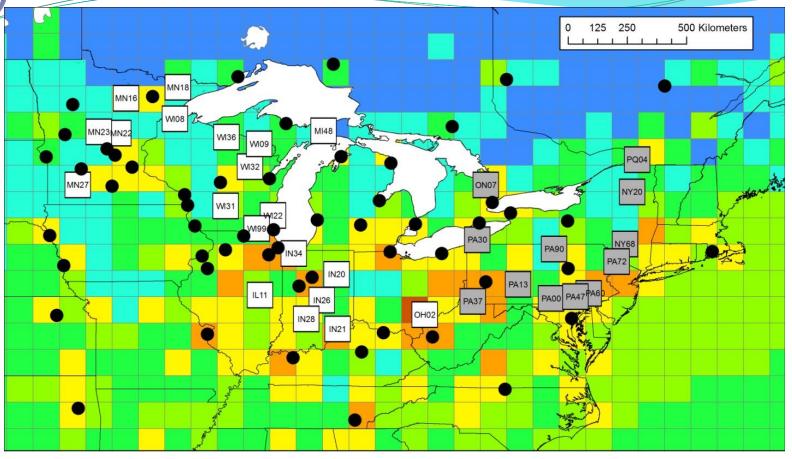
After all the standard source simulations have been run, and the impacts of each of the ~350,000 sources worldwide are estimated using spatial and chemical interpolation, is the model giving reasonable results?

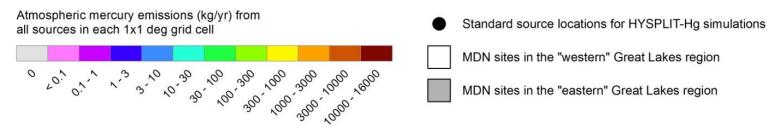
# Modeled vs. Measured Wet Deposition of Mercury at Sites in the Great Lakes Region





#### Standard source locations, MDN sites, and mercury emissions in the Great Lakes region





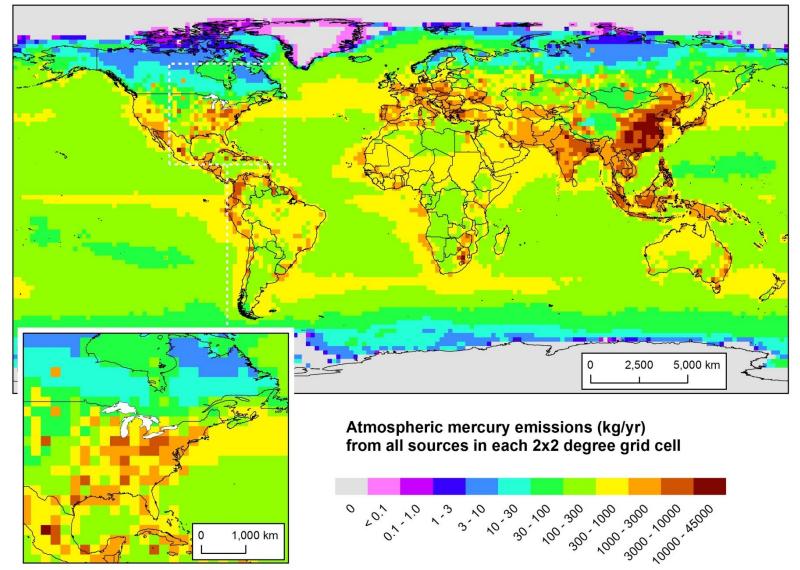


#### **Outline of Modeling Analysis**

- HYSPLIT
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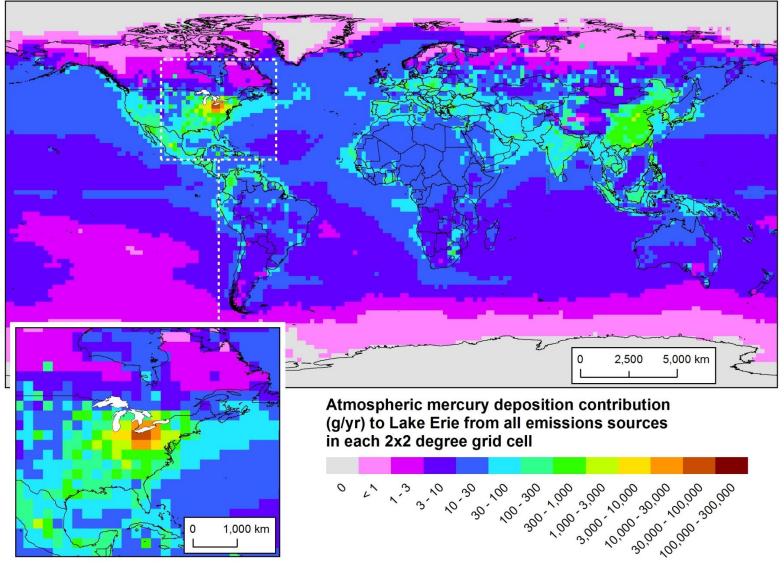


# 2005 Atmospheric Mercury Emissions (Direct Anthropogenic + Re-emit + Natural)





#### Keep track of the contributions from each source, and add them up



**Geographical Distribution of 2005 Atmospheric Mercury Deposition Contributions to Lake Erie** 



■ Emissions from

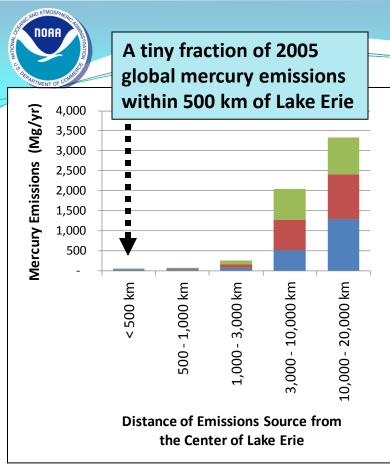
**Emissions** 

Emissions from

Anthropogenic

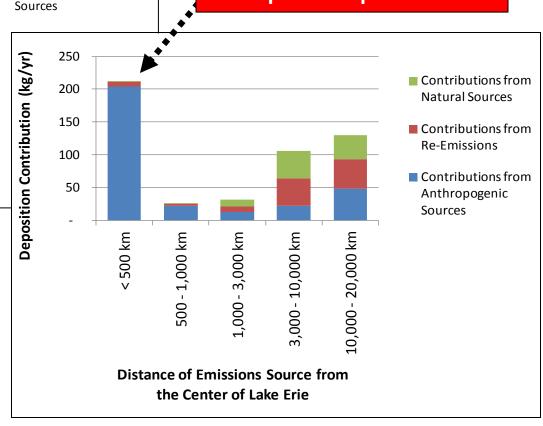
Natural Sources

■ Emissions from Re-

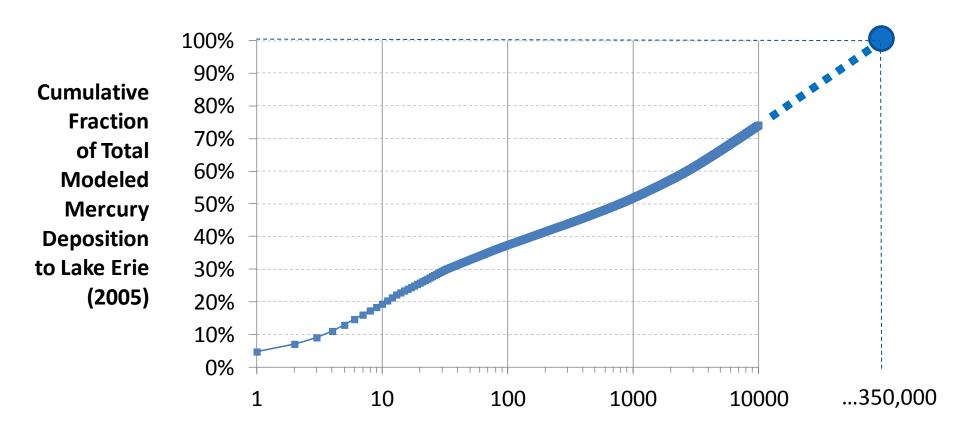


Modeling results show that these "regional" emissions are responsible for a large fraction of the modeled 2005 atmospheric deposition

Important policy implications!



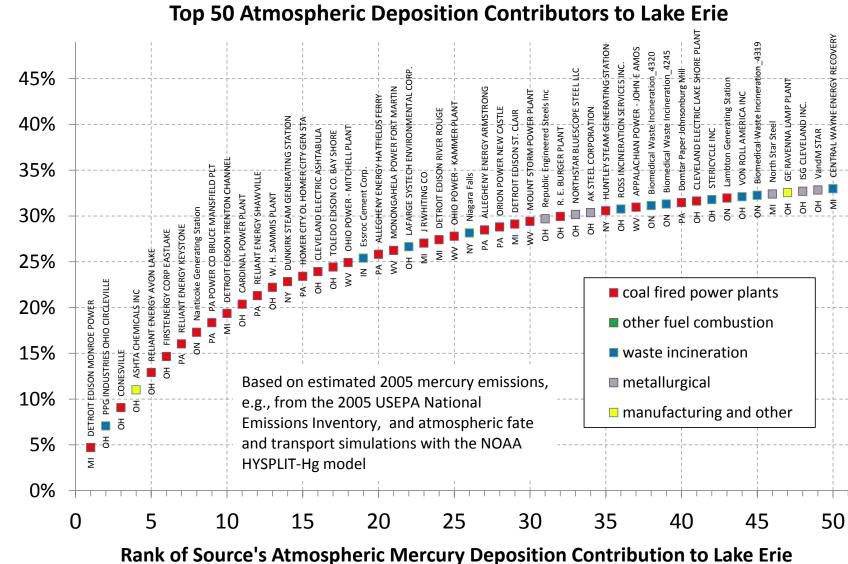




Rank of Source's Atmospheric Mercury Deposition Contribution to Lake Erie

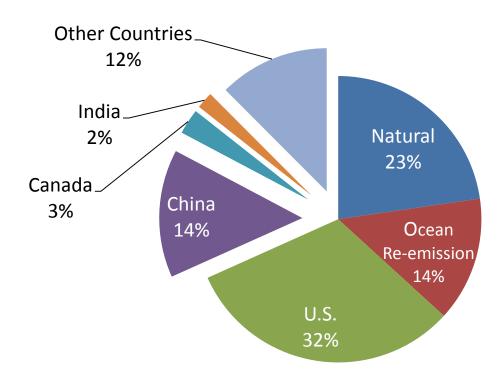


# Cumulative Fraction of Total Modeled Deposition (2005)





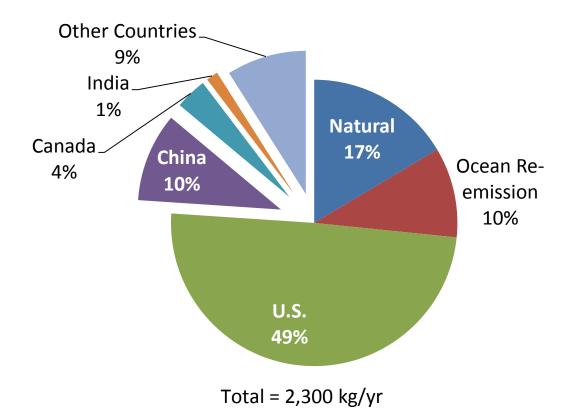
#### Sources of Mercury Deposition to the Great Lakes Basin 2005 Baseline Analysis



Total = 11,300 kg/yr

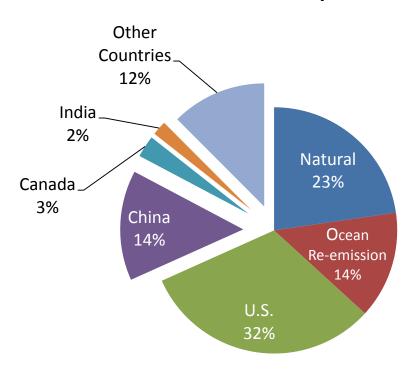


#### Sources of Mercury Deposition to the Lake Erie Basin 2005 Baseline Analysis



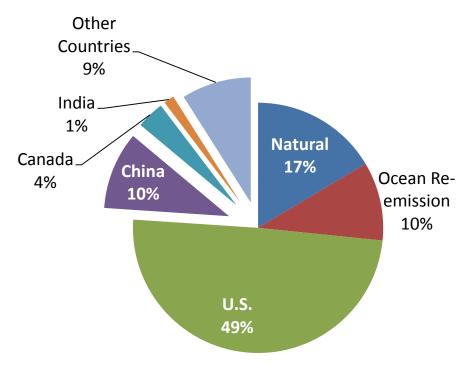


#### Sources of Mercury Deposition to the <u>Great Lakes Basin</u> 2005 Baseline Analysis



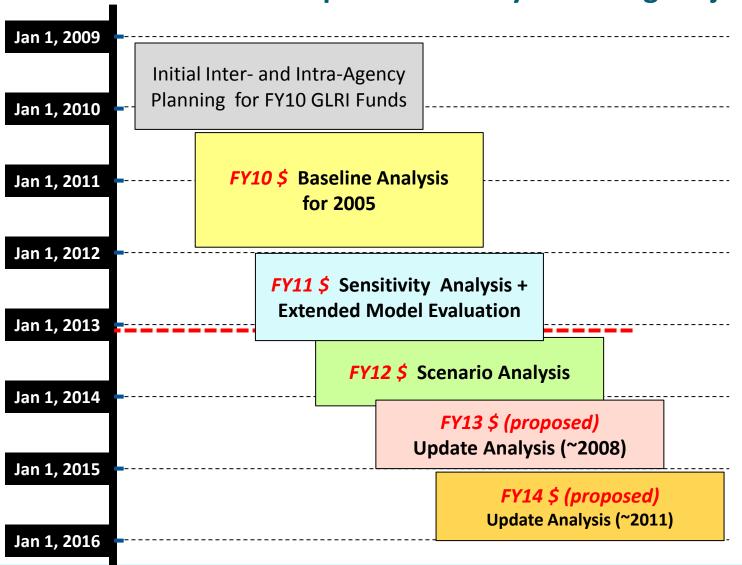
#### Total = 11,300 kg/yr

#### Sources of Mercury Deposition to the <u>Lake Erie Basin</u> 2005 Baseline Analysis



Total = 2,300 kg/yr

## **ARL's GLRI Atmospheric Mercury Modeling Project**





# **Phase 1: Baseline Analysis for 2005**

(Final Report Completed December 2011)

- 2005 was chosen as the analysis year, because 2005 was the latest year for which comprehensive mercury emissions inventory data were available at the start of this project
- Using 2005 meteorological data and emissions, the deposition and source-attribution for this deposition to each Great Lake and its watershed was estimated
- The model results were ground-truthed against 2005
   Mercury Deposition Network data from sites in the
   Great Lakes region



#### Modeling Atmospheric Mercury Deposition to the Great Lakes.

Final Report for work conducted with FY2010 funding from the Great Lakes Restoration Initiative. December 16, 2011. Mark Cohen, Roland Draxler, Richard Artz. NOAA Air Resources Laboratory, Silver Spring, MD, USA. 160 pages.

http://www.arl.noaa.gov/documents/reports/GLRI\_FY2010\_ Atmospheric\_Mercury\_Final\_Report\_2011\_Dec\_16.pdf

http://www.arl.noaa.gov/documents/reports/Figures\_Tables \_GLRI\_NOAA\_Atmos\_Mercury\_Report\_Dec\_16\_2011.pptx

#### One-page summary:

http://www.arl.noaa.gov/documents/reports/ GLRI\_Atmos\_Mercury\_Summary.pdf



## Some Key Features of this Analysis

### Deposition explicitly modeled to actual lake/watershed areas

 As opposed to the usual practice of ascribing portions of gridded deposition to these areas in a post-processing step

### Combination of Lagrangian & Eulerian modeling

 allows accurate and computationally efficient estimates of the fate and transport of atmospheric mercury over all relevant length scales – from "local" to global.

### Uniquely detailed source-attribution information is created

- deposition contribution to each Great Lakes and watersheds from each source in the emissions inventories used is estimated individually
- The level of source discrimination is only limited by the detail in the emissions inventories
- Source-type breakdowns not possible in this 1<sup>st</sup> phase for global sources, because the global emissions inventory available did not have source-type breakdowns for each grid square



## Some Key Findings of this Analysis

- "Single Source" results illustrate source-receptor relationships
  - For example, a "typical" coal-fired power plant near Lake Erie may contribute on the order of 1000x the mercury for the same emissions as a comparable facility in China.
- Regional, national, & global mercury emissions are all important contributors to mercury deposition in the Great Lakes Basin
  - For Lakes Erie and Ontario, the U.S. contribution is at its most significant
  - For Lakes Huron and Superior, the U.S. contribution is less significant.
  - Local & regional sources have a much greater atmospheric deposition contributions than their emissions, as a fraction of total global mercury emissions, would suggest.



## Some Key Findings of this Analysis (...continued)

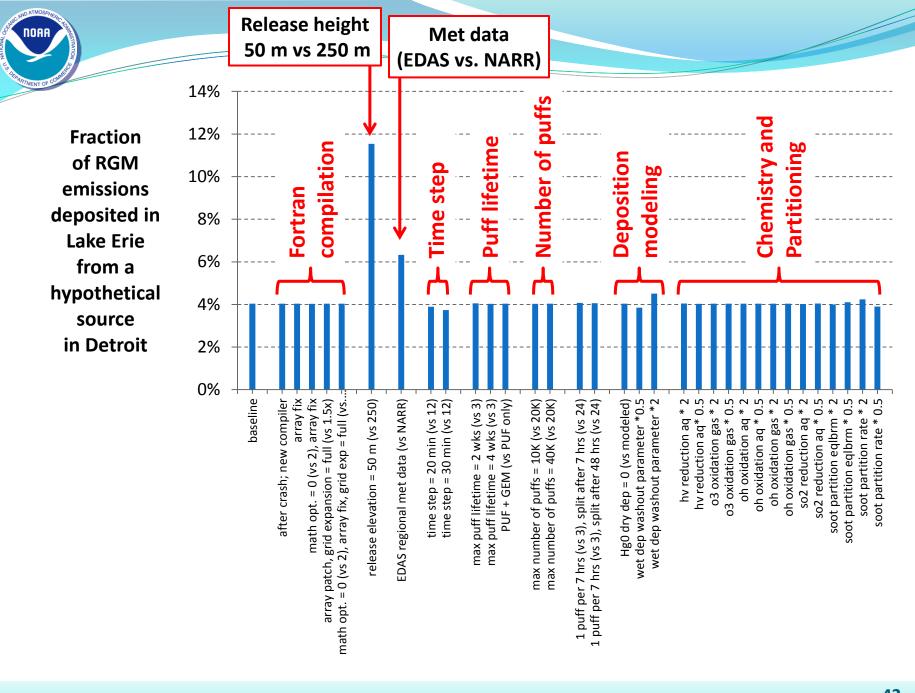
### Reasonable agreement with measurements

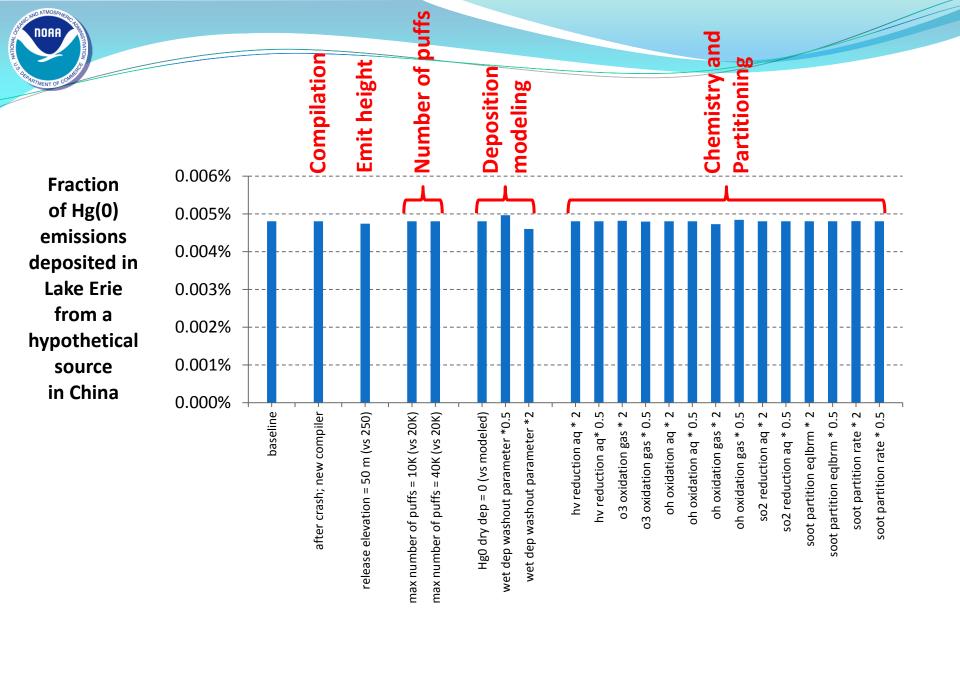
- Despite numerous uncertainties in model input data and other modeling aspects
- Comparison at sites where significant computational resources were expended – corresponding to regions that were the most important for estimating deposition to the Great Lakes and their watersheds – showed good consistency between model predictions and measured quantities.
- For a smaller subset of sites generally downwind of the Great Lakes (in regions not expected to contribute most significantly to Great Lakes atmospheric deposition), less computational resources were expended, and the comparison showed moderate, but understandable, discrepancies.



# Phase 2: Sensitivity Analysis + Extended Model Evaluation (current work, with GLRI FY11 funding)

- Examining the influence of uncertainties on the modeling results, by varying critical model parameters, algorithms, and inputs, and analyzing the resulting differences in results
- Ground-truthing the model against additional ambient monitoring data, e.g., ambient mercury air concentration measurements and wet deposition data not included in the Mercury Deposition Network (MDN)







## **Phase 3: Scenarios**

(next year's work, with GLRI FY12 funding)

- A modeling analyses such as this is the *only* way to quantitatively examine the potential consequences of alternative future emissions scenarios
- We will work with EPA and other Great Lakes Stakeholders to identify and specify the most policy relevant scenarios to examine
- For each scenario, we will estimate the amount of atmospheric deposition to each of the Great Lakes and their watersheds, along with the detailed sourceattribution for this deposition

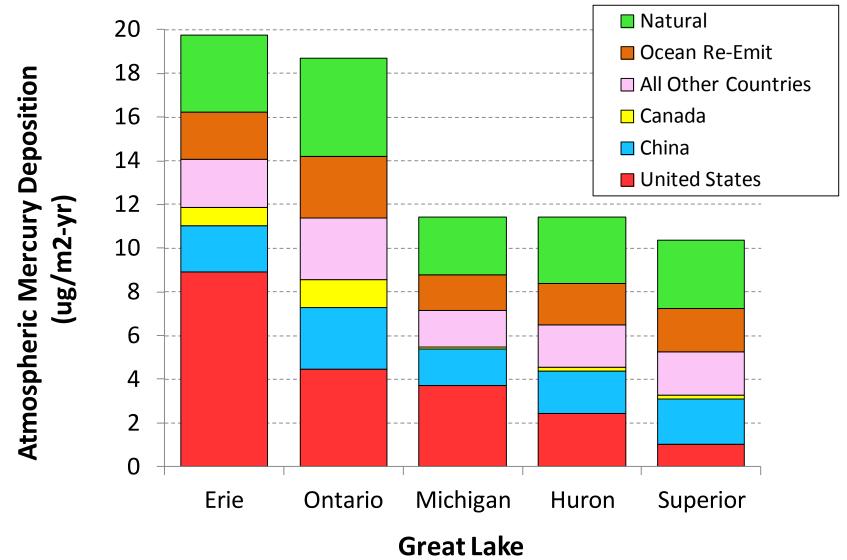


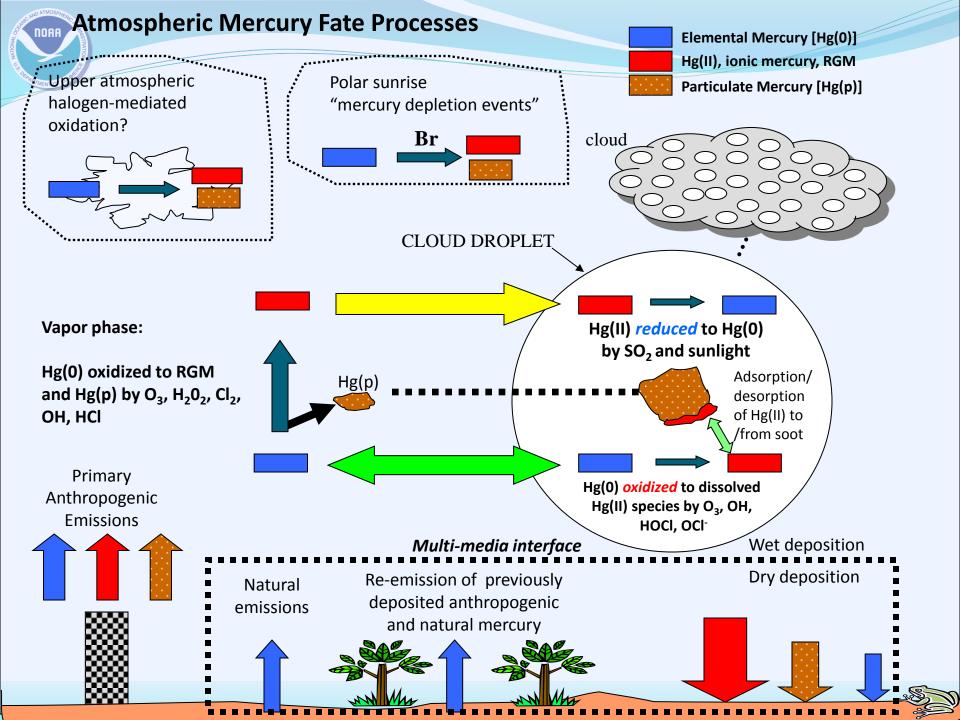




## **EXTRA SLIDES**







%n			
ving) Atmospheric Chen	sical Departion	Cabamafan	N / 0 H
Ming) Atmospheric Cher	ilcai Reaction	Scheme for	wer
3			

HOALO	ving) Atmospheric Chemical Reaction Scheme for Mercury									
OF CO	Reaction	Rate	Units	Reference						
	GAS PHASE REACTIONS									
?	$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm <sup>3</sup> /molec-sec	Hall (1995)						
	$Hg^0 + HCI \rightarrow HgCl_2$	1.0E-19	cm <sup>3</sup> /molec-sec	Hall and Bloom (1993)						
	$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm <sup>3</sup> /molec-sec	Tokos et al. (1998) (upper limit based on experiments)						
	$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm <sup>3</sup> /molec-sec	Calhoun and Prestbo (2001)						
?	$Hg^0 + OH \rightarrow Hg(p)$	8.7E-14	cm <sup>3</sup> /molec-sec	Sommar et al. (2001)						
new	$Hg^0 + Br \rightarrow HgBr_2$									
	AQUEOUS PHASE REA	JEOUS PHASE REACTIONS								
	$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	(molar-sec) <sup>-1</sup>	Munthe (1992)						
	$Hg^0 + OH \rightarrow Hg^{+2}$	2.0E+9	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1997)						
	$HgSO_3 \rightarrow Hg^0$	T*e <sup>((31.971*T)-12595.0)/T)</sup> sec <sup>-1</sup>		Van Loon et al. (2002)						
		[T = tempera	ature (K)]							
?	$Hg(II) + HO_2 \rightarrow Hg^0$	~ 0	(molar-sec) <sup>-1</sup>	Gardfeldt & Jonnson (2003)						
	Hg <sup>0</sup> + HOCl → Hg <sup>+2</sup>	2.1E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)						
	$Hg^0 + OCI^{-1} \rightarrow Hg^{+2}$	2.0E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)						
	Hg(II) ↔ Hg(II) <sub>(soot)</sub>	9.0E+2	liters/gram; t = 1/hour	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).						
	$Hg^{+2} + hv \rightarrow Hg^{0}$	6.0E-7	(sec) <sup>-1</sup> (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)						

### What year to model?



#### Mercury Emissions Inventory

- U.S. anthropogenic emissions inventory
- Canadian anthropogenic emissions inventory
- Mexican anthropogenic emissions inventory
- Global anthropogenic emissions inventory
- Natural emissions inventory
- Re-emissions inventory
- Ambient Data for Model Evaluation
  - Wet deposition (Mercury Deposition Network)
  - "Speciated" Air Concentrations
- Meteorological Data to drive model
  - NCEP/NCAR Global Reanalysis (2.5 deg)
  - NCEP EDAS 40km North American Domain
  - North American Regional Reanalysis (NARR)

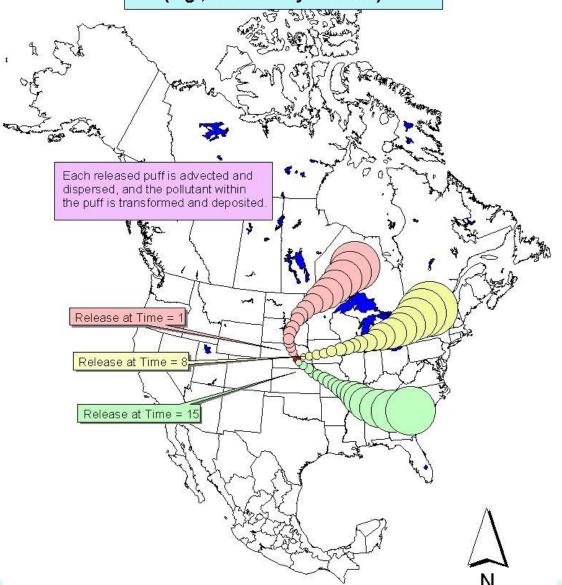
Dataset
Available
for 2005

Need all of these datasets for the same year

2005 chosen for baseline analysis

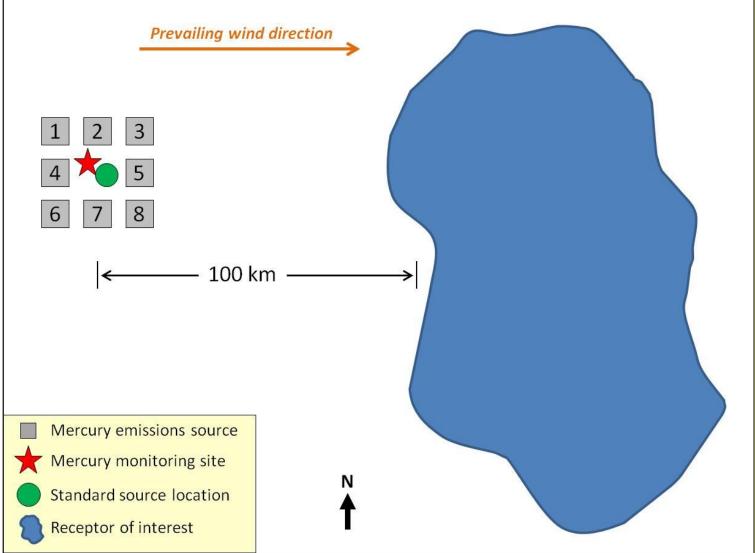


Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).





## Getting good ground-truthing results harder than estimating deposition to the Great Lakes

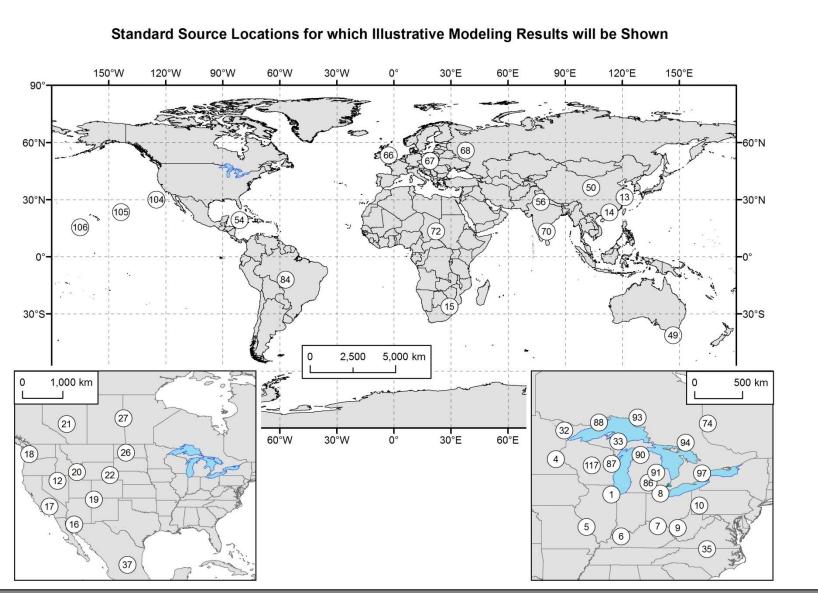


One Standard
Source Location
(green dot)
would do a
decent job of
estimating
deposition to the
receptor, for all
of the
hypothetical,
"actual" source
locations shown
(numbered
boxes)

But the same
Standard Source
Location would
be completely
inadequate to
estimate
deposition and
concentrations at
the monitoring
site (red star)

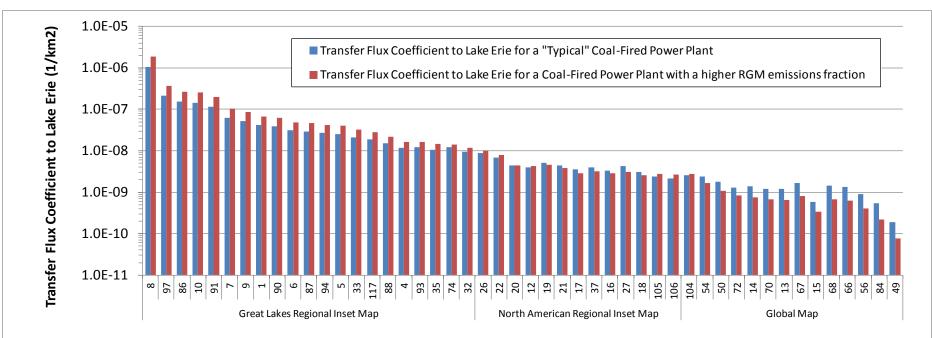


### **Standard Source Locations for Illustrative Modeling Results**





# Lake Erie Transfer Flux Coefficients for two kinds of Generic Coal-Fired Power Plants (logarithmic scale)



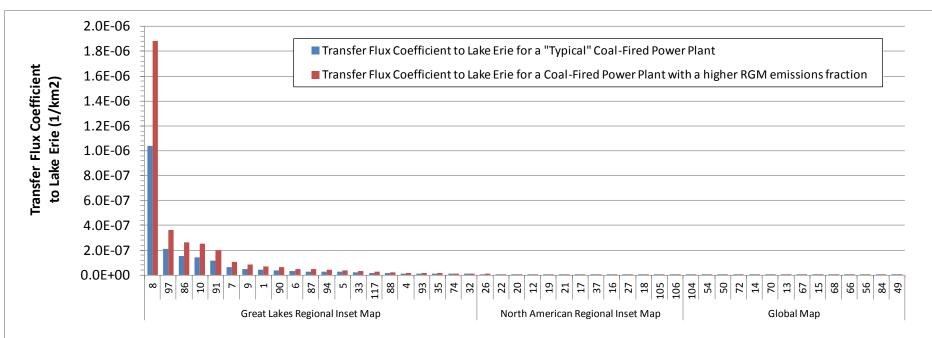
#### **Standard Source Location Number**

The "Transfer Flux Coefficient" is calculated as the atmospheric deposition flux to a given receptor (in this case, Lake Erie) in units of g/km2-yr, divided by the total emissions from the source, in units of g/yr.

With this transfer flux coefficient, if one knows the emissions of the source in the given location, then the atmospheric deposition flux impact of the source on the receptor can be estimated, by simply multiplying the emissions by the transfer flux coefficient.



# Lake Erie Transfer Flux Coefficients for two kinds of Generic Coal-Fired Power Plants (linear scale)



#### **Standard Source Location Number**

The "Transfer Flux Coefficient" is calculated as the atmospheric deposition flux to a given receptor (in this case, Lake Erie) in units of g/km2-yr, divided by the total emissions from the source, in units of g/yr.

With this transfer flux coefficient, if one knows the emissions of the source in the given location, then the atmospheric deposition flux impact of the source on the receptor can be estimated, by simply multiplying the emissions by the transfer flux coefficient.



# In order to conveniently compare different model results, a "transfer flux coefficient" X will be used, defined as the following:

$$X = \begin{array}{c} \frac{deposition\;flux\;rate}{emissions\;rate} &= \frac{\frac{grams\;Hg\;deposited\;per\;year}{km^2\;of\;receptor\;area}}{grams\;Hg\;emitted\;per\;year\;from\;the\;source} \; [=]\;\frac{1}{km^2} \end{array}$$

$$deposition \ flux \ rate = \frac{grams \ Hg \ deposited \ per \ year}{km^2 \ of \ receptor \ area} \left(\frac{g}{km^2 yr}\right)$$

$$= transfer\ flux\ coefficient\ \left(\frac{1}{km^2}\right)* source\ mercury\ emissions\ (\frac{g}{yr})$$

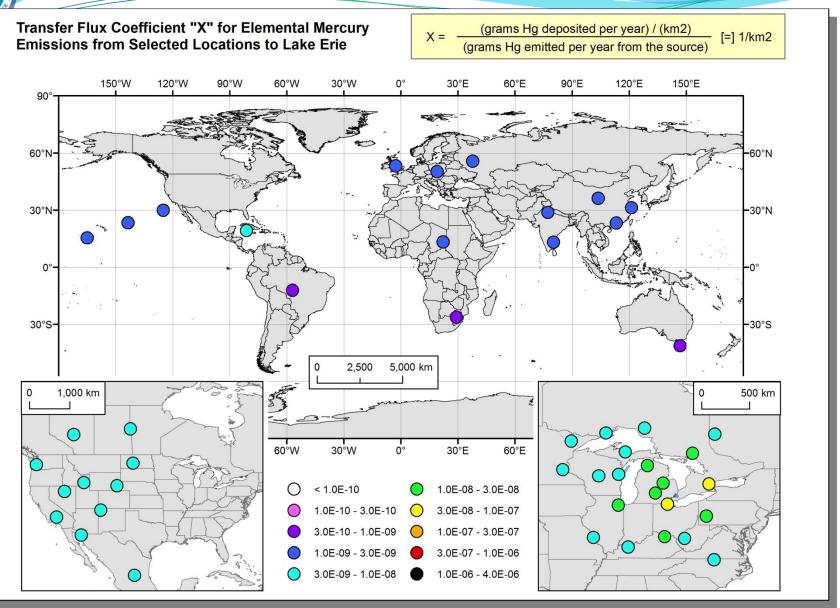


$$deposition \ flux \ rate = \frac{grams \ Hg \ deposited \ per \ year}{km^2 \ of \ receptor \ area} \left(\frac{g}{km^2 yr}\right)$$

= transfer flux coefficient 
$$\left(\frac{1}{km^2}\right)$$
\* source mercury emissions  $\left(\frac{g}{yr}\right)$ 

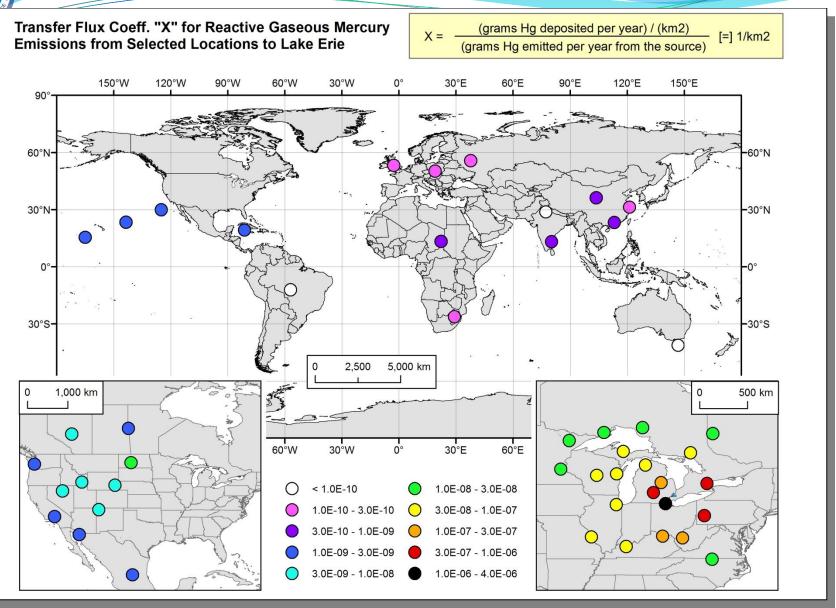
NORA NO ATMOSPHERICAL ROLL STRATE

Transfer Flux Coefficients For Pure Elemental Mercury Emissions at an Illustrative Subset of Standard Source Locations, for Deposition Flux Contributions to Lake Erie



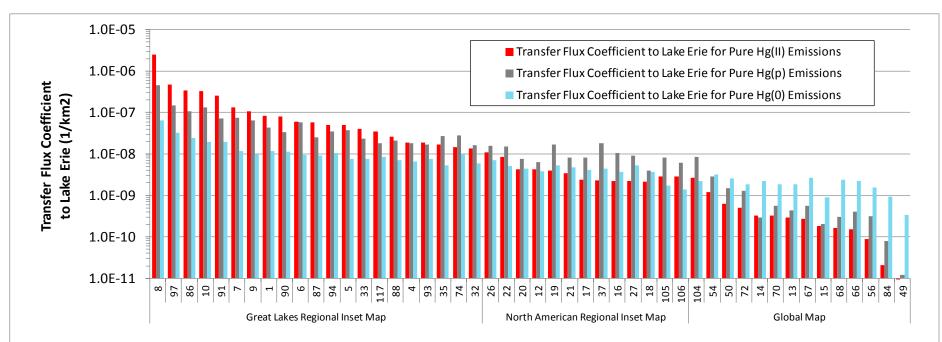


Transfer Flux Coefficients For Pure Reactive Gaseous Mercury Emissions at an Illustrative Subset of Standard Source Locations, for Deposition Flux Contributions to Lake Erie





# Transfer Flux Coefficients For Hg(0), Hg(II), and Hg(p) to Lake Erie (logarithmic scale)



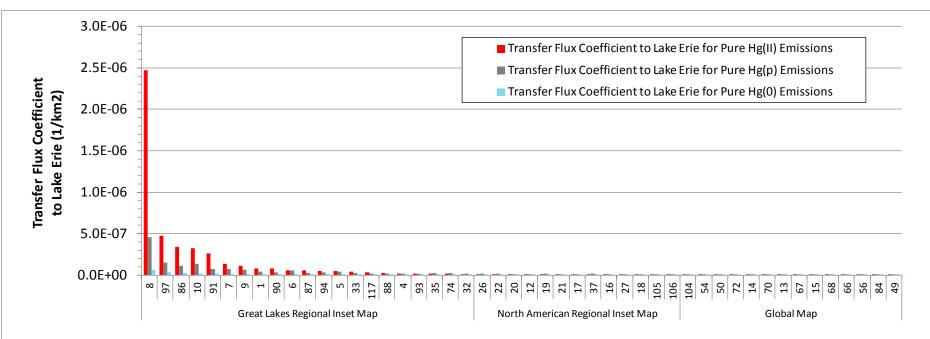
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The "Transfer Flux Coefficient" is calculated as the atmospheric deposition flux to a given receptor (in this case, Lake Erie) in units of g/km2-yr, divided by the total emissions from the source, in units of g/yr.

With this transfer flux coefficient, if one knows the emissions of the source in the given location, then the atmospheric deposition flux impact of the source on the receptor can be estimated, by simply multiplying the emissions by the transfer flux coefficient.



# Transfer Flux Coefficients For Hg(0), Hg(II), and Hg(p) to Lake Erie (linear scale)



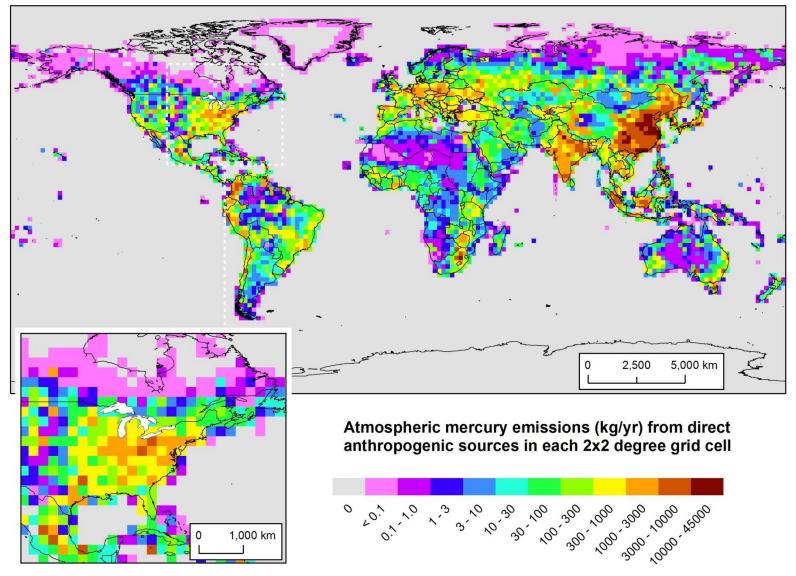
#### **Standard Source Location Number**

The "Transfer Flux Coefficient" is calculated as the atmospheric deposition flux to a given receptor (in this case, Lake Erie) in units of g/km2-yr, divided by the total emissions from the source, in units of g/yr.

With this transfer flux coefficient, if one knows the emissions of the source in the given location, then the atmospheric deposition flux impact of the source on the receptor can be estimated, by simply multiplying the emissions by the transfer flux coefficient.

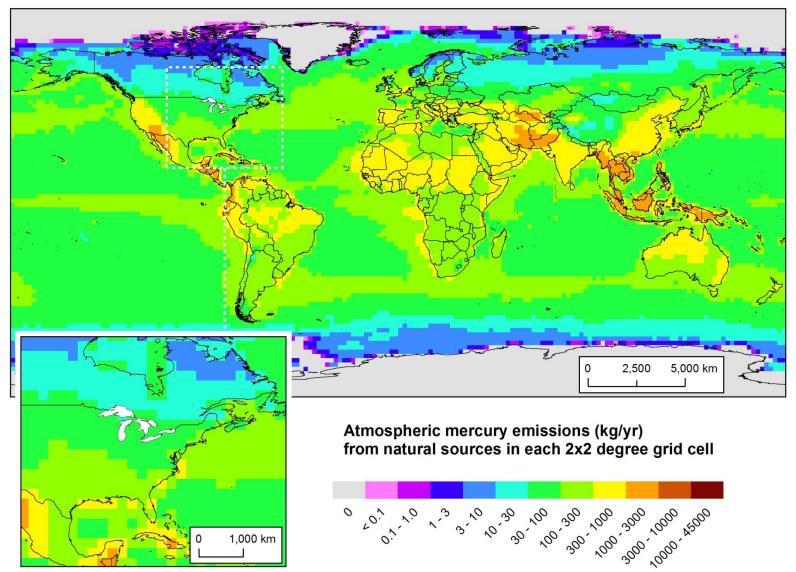


## **Anthropogenic Mercury Emissions (ca. 2005)**



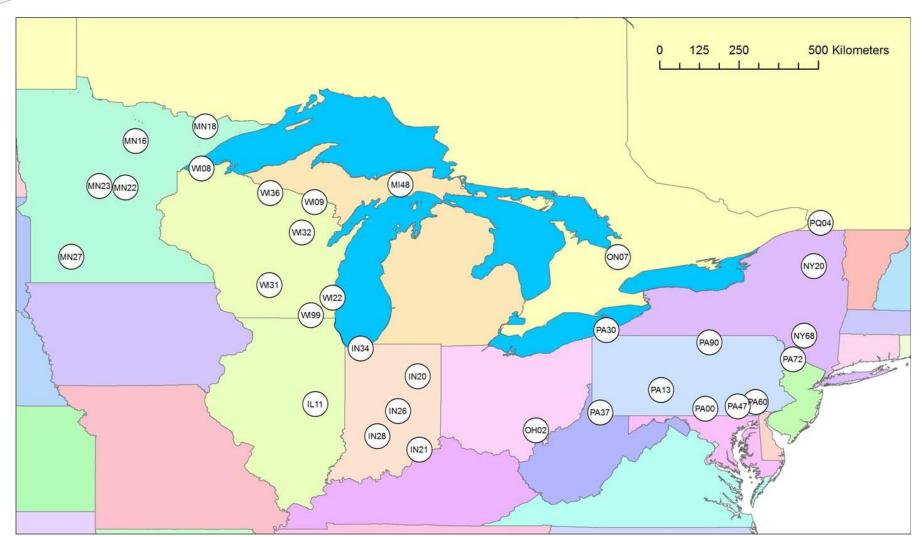


## Natural mercury emissions



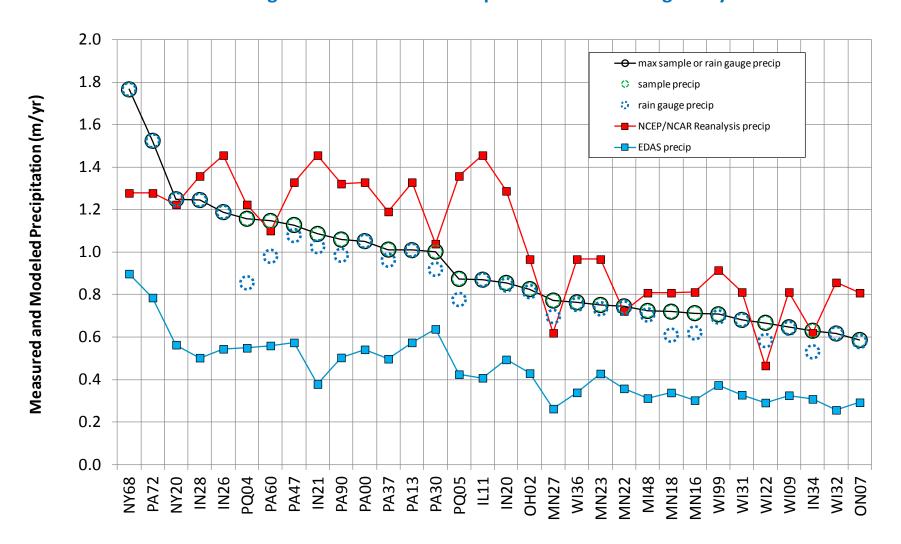


## Figure 55. Mercury Deposition Network Sites in the Great Lakes Region Considered in an Initial Model Evaluation Analysis



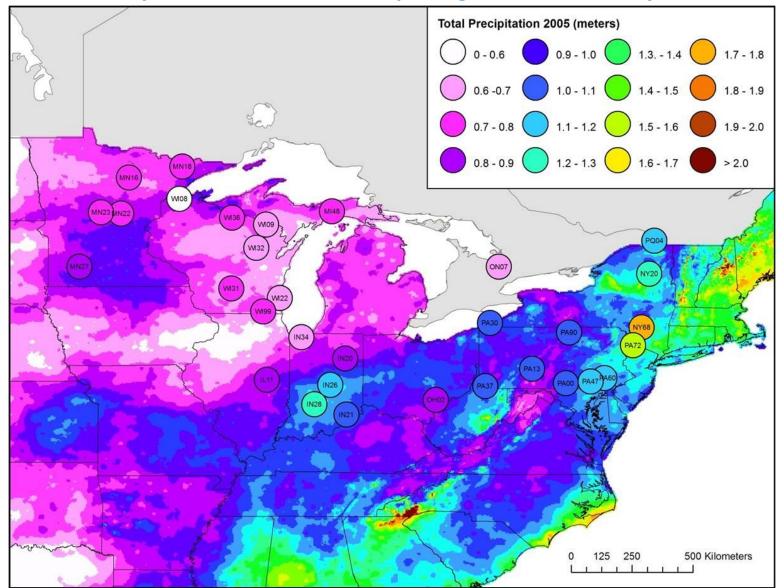


# the Great-Lakes Region MDN Sites with the Precipitation in the Meteorological Datasets Used as Inputs to this Modeling Study



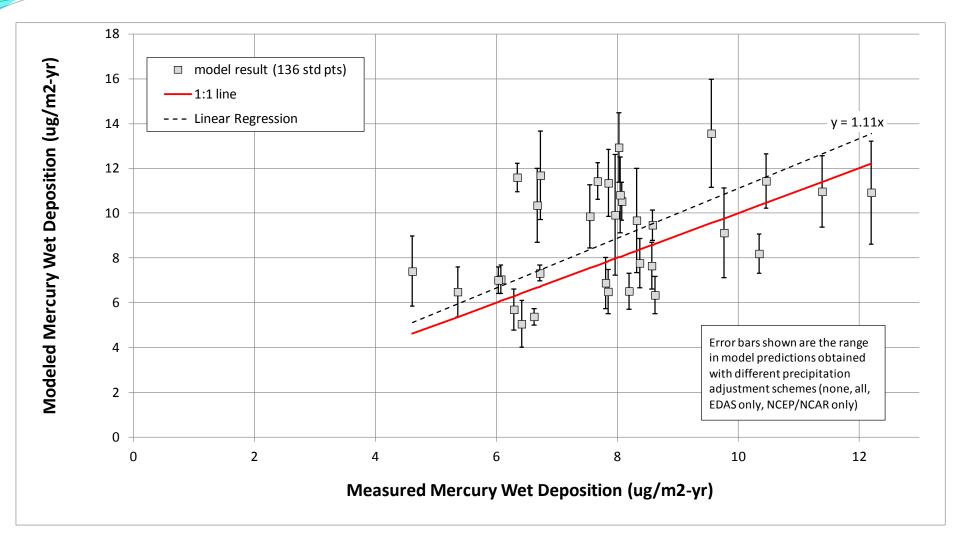


# Comparison of 2005 precipitation total as measured at MDN sites in the Great Lakes region (circles) with precipitation totals assembled by the PRISM Climate Group, Oregon State University



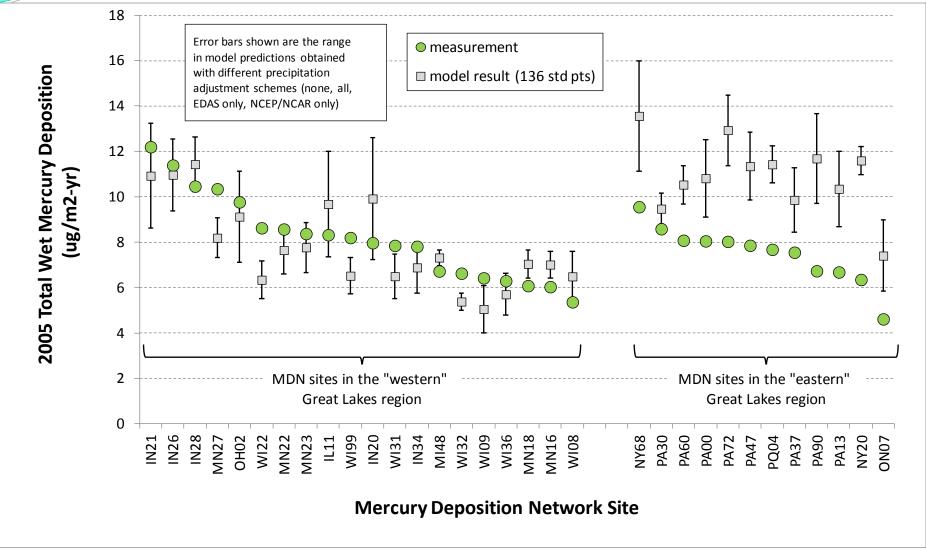


### Modeled vs. Measured Wet Deposition of Mercury at Sites in the Great Lakes Region





#### Modeled vs. Measured Wet Deposition of Mercury at Sites in the Great Lakes Region



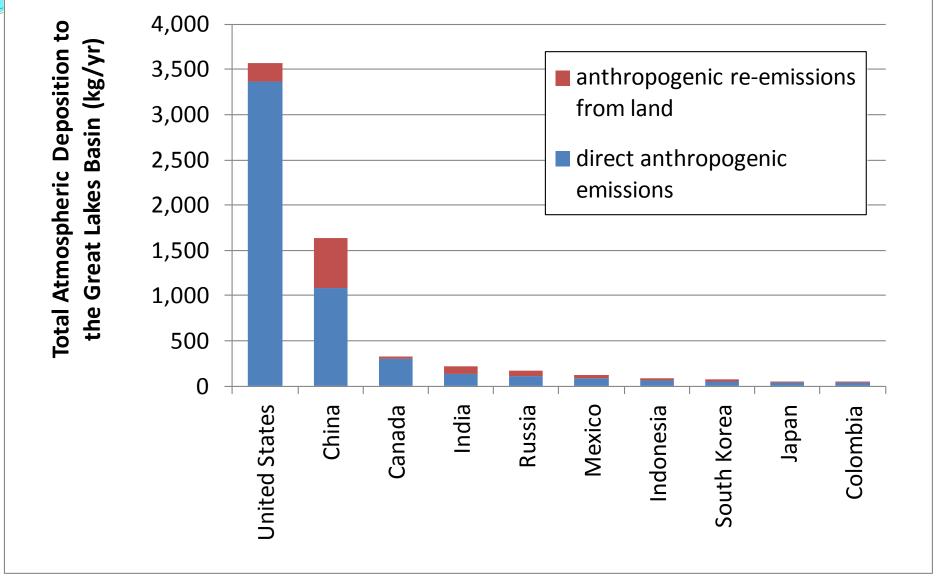


### **Summary of Mercury Emissions Inventories Used in GLRI Analysis**

Inventory	domain	Number of records	Hg(0) emissions (Mg/yr)	RGM emissions (Mg/yr)	Hg(p) emissions (Mg/yr)	Total mercury emissions (Mg/yr)
U.S. Point Sources	United States	19,353	50.6	35.5	9.1	95
U.S. Area Sources	United States	44,848	4.5	1.8	1.1	7.4
Canadian Point Sources	Canada	166	3.0	1.7	0.4	5.1
Canadian Area Sources	Canada	12,372	1.0	0.96	0.42	2.4
Mexican Point Sources	Mexico	268	28	0.81	0.46	29
Mexican Area Sources	Mexico	160	1.25	0.38	0.25	1.9
Global Anthropogenic Sources not in U.S., Canada, or Mexico	Global, except for the U.S., Canada, and Mexico	52,173	1,239	434	113	1,786
Global Re-emissions from Land	Global land (and freshwater) surfaces	129,180	750	0	0	750
Global Re-emissions from the Ocean	Global oceans	43,324	1,250	0	0	1,250
Global Natural Sources	Global	64,800	1,800	0	0	1,800
Total		366,804	5,127	475	125	5,728



## Model-estimated 2005 deposition to the Great Lakes Basin from countries with the highest modeled contribution from direct and re-emitted anthropogenic sources





## Model-estimated per capita 2005 deposition to the Great Lakes Basin from countries with the highest modeled contribution from direct & re-emitted anthropogenic sources

