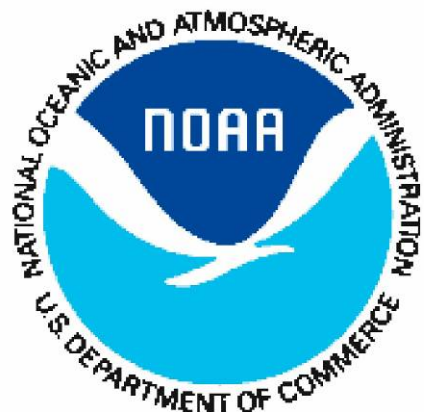


# Simulating the Atmospheric Fate and Transport of Mercury using the NOAA HYSPLIT Model

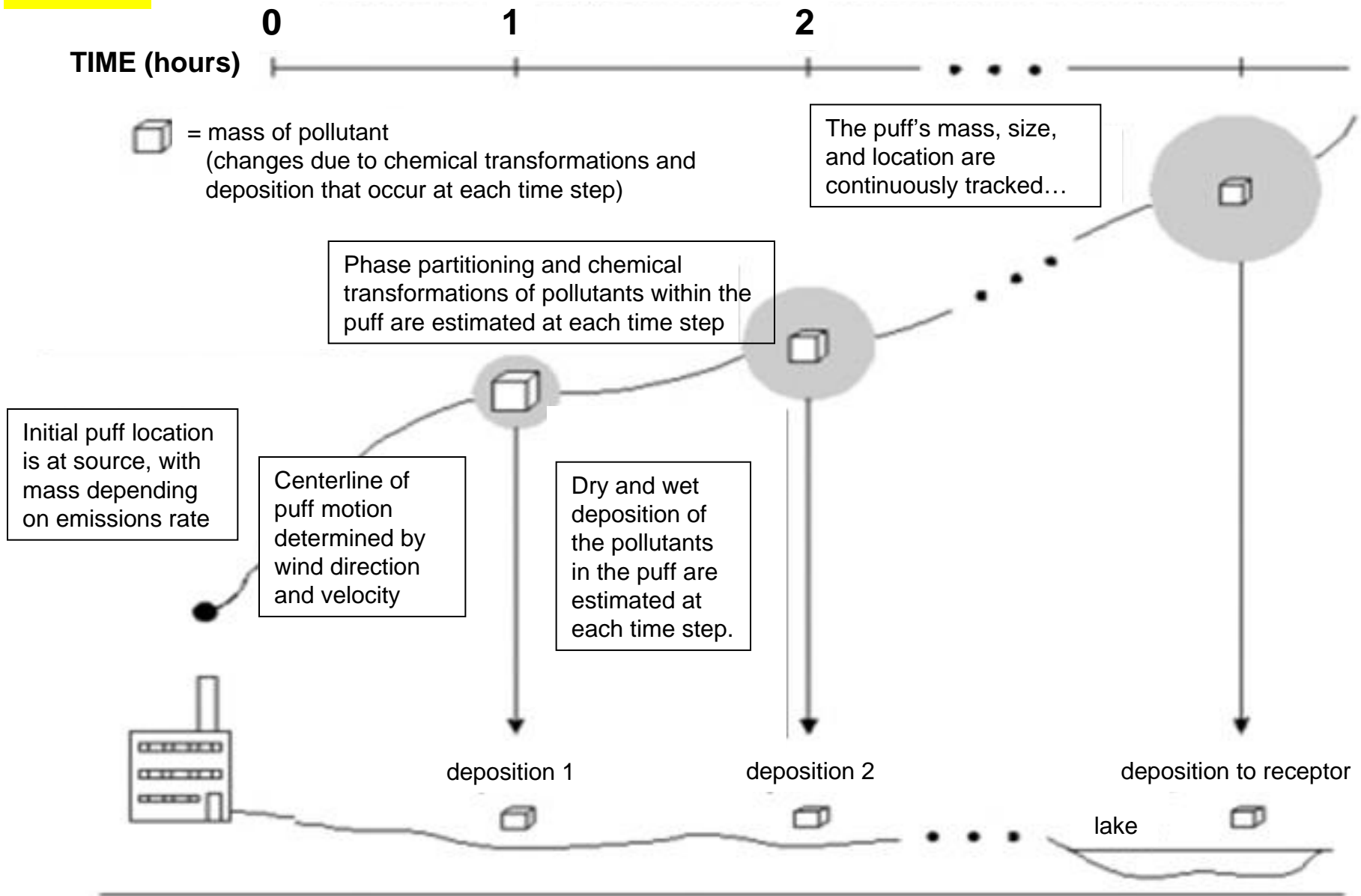
**Mark Cohen, Roland Draxler and Richard Artz**  
**NOAA Air Resources Laboratory**  
**1315 East West Highway,**  
**R/ARL, Room 3316**  
**Silver Spring, Maryland, 20910**



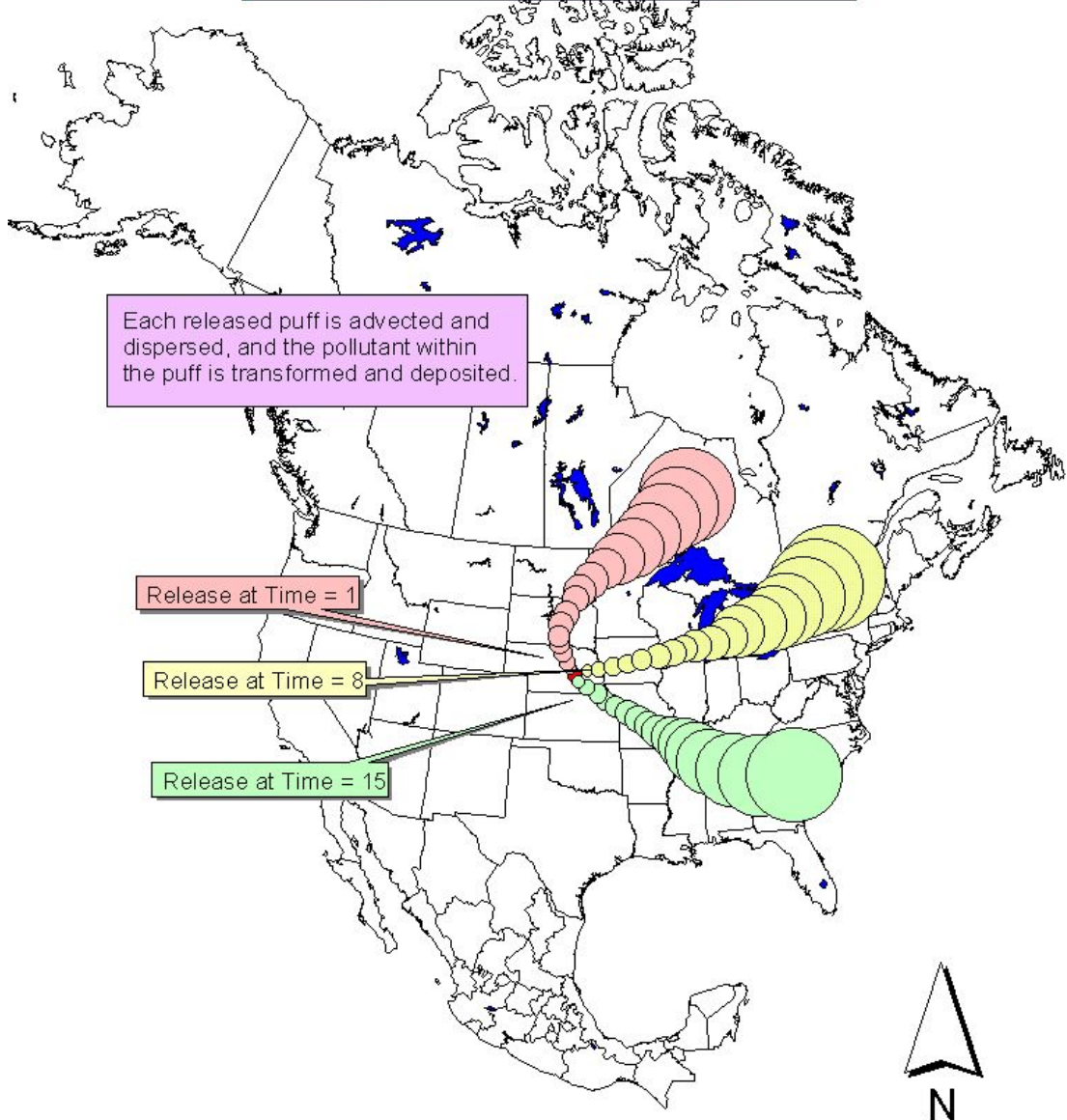
**Presentation at the**  
**NOAA Atmospheric Mercury Meeting**  
**November 14-15, 2006, Silver Spring MD**

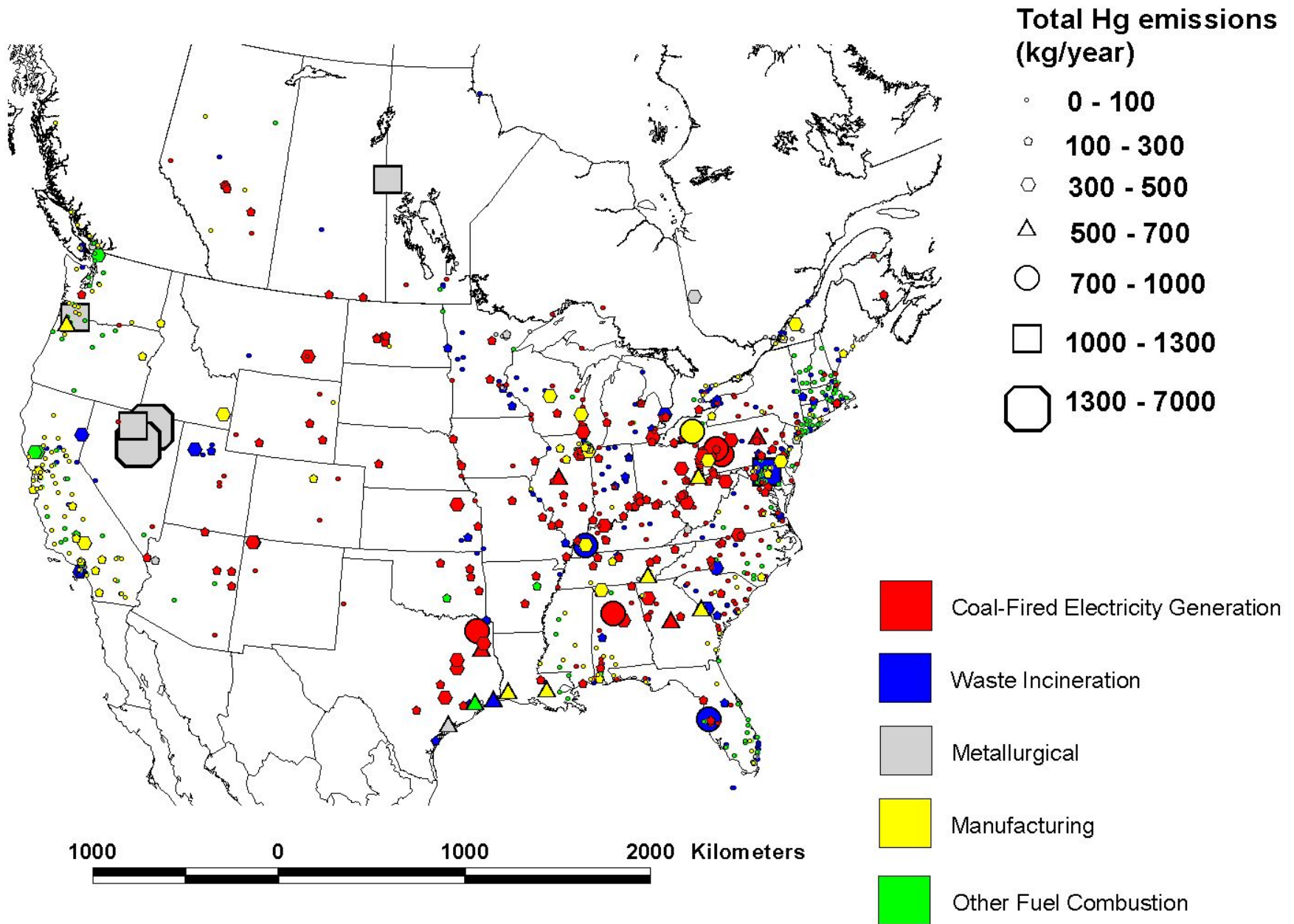
**methodology**

# Lagrangian Puff Atmospheric Fate and Transport Model



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





- **In principle, we need do this for each source in the inventory**
- **But, since there are more than 100,000 sources in the U.S. and Canadian inventory, we need shortcuts...**
- **Shortcuts described in Cohen *et al***  
*Environmental Research* **95**(3), 247-265, 2004



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Environmental Research 95 (2004) 247–265

Environmental Research

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## Modeling the atmospheric transport and deposition of mercury to the Great Lakes<sup>☆</sup>

Mark Cohen,<sup>a,\*</sup> Richard Artz,<sup>a</sup> Roland Draxler,<sup>a</sup> Paul Miller,<sup>b</sup> Laurier Poissant,<sup>c</sup> David Niemi,<sup>d</sup> Dominique Ratté,<sup>d</sup> Marc Deslauriers,<sup>d</sup> Roch Duval,<sup>e</sup> Rachelle Laurin,<sup>e,1</sup> Jennifer Slotnick,<sup>f</sup> Todd Nettesheim,<sup>f</sup> and John McDonald<sup>b</sup>

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<sup>b</sup> Commission for Environmental Cooperation, Montreal, Que., Canada

<sup>c</sup> Atmospheric Toxic Processes Service, Meteorological Service of Canada, Environment Canada—Quebec region, Montreal, Que., Canada

<sup>d</sup> Pollutant Data Branch, Environment Canada Hall, Que., Canada

<sup>e</sup> Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, Ont., Canada

### Abstract

A special version of mercury in a North American Great Lakes region. This paper presents results and provides atmospheric mercury deposition suitable for modeling the Great Lakes region from the Great Lakes. Significant contributions to atmospheric mercury deposition are published by Elsevier.

### Keywords

Mercury contamination of other ecosystems, serious environmental human exposure, and significant levels of mercury (2000). Historic production units to have caused.

<sup>☆</sup> Supplementary material available online at www.sciencedirect.com. Corresponding author. E-mail address: mark.cohen@noaa.gov (M. Cohen).  
<sup>1</sup> Current address: Environmental Research, Concord, Ontario, Canada.

**Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratté, D., Deslauriers, M., Duval, R., Laurin, R., Slotnick, J., Nettesheim, T., McDonald, J.**

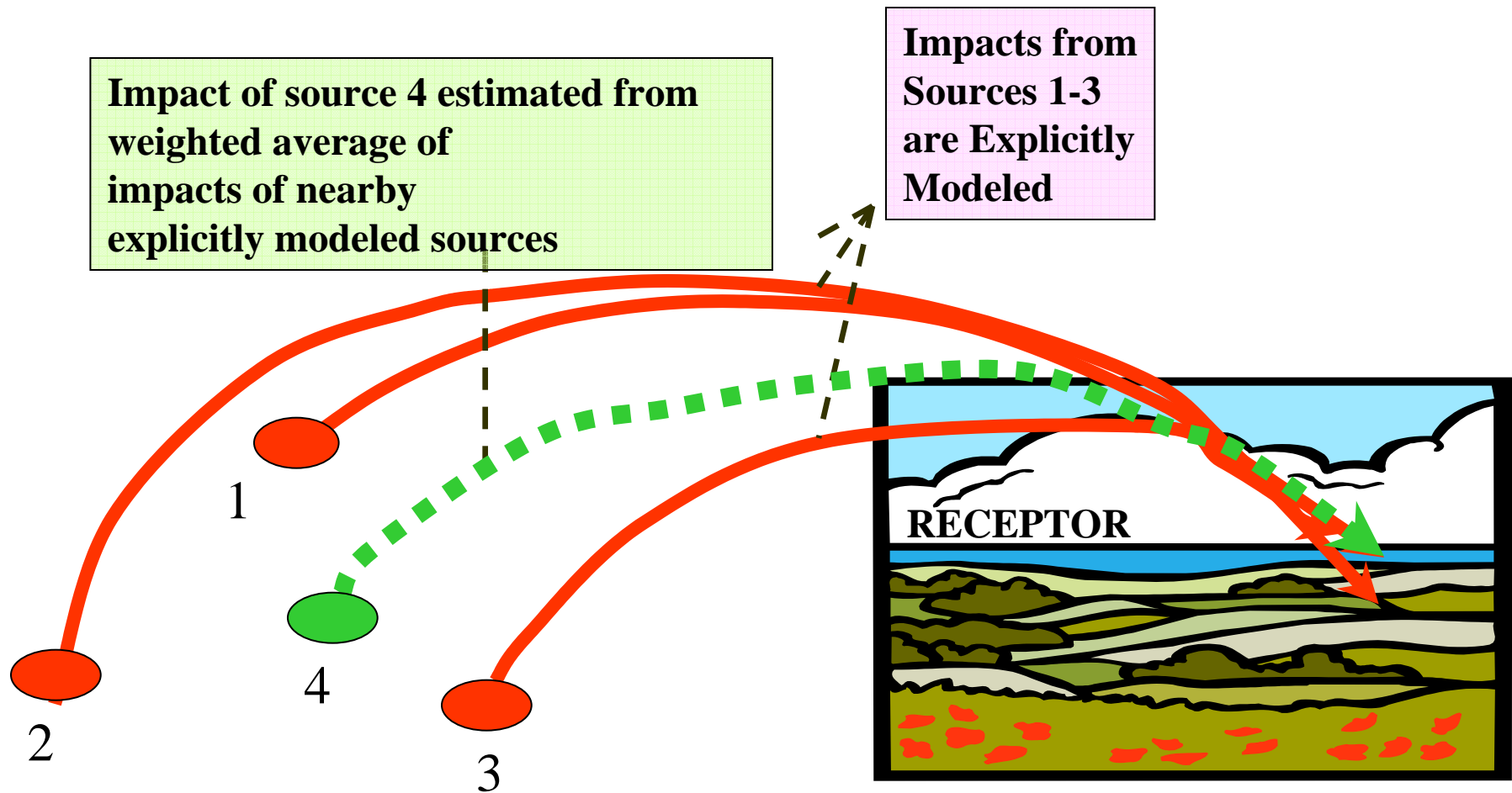
**“Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes.” *Environmental Research* 95(3), 247-265, 2004.**

Note: Volume 95(3) is a Special Issue: "An Ecosystem Approach to Health Effects of Mercury in the St. Lawrence Great Lakes", edited by David O. Carpenter.

- **For each run, simulate fate and transport *everywhere*, but only keep track of impacts on each selected receptor (e.g., Great Lakes, Chesapeake Bay, etc.)**
- **Only run model for a limited number (~100) of hypothetical, individual unit-emissions sources throughout the domain**
- **Use spatial interpolation to estimate impacts from sources at locations not explicitly modeled**



# Spatial interpolation

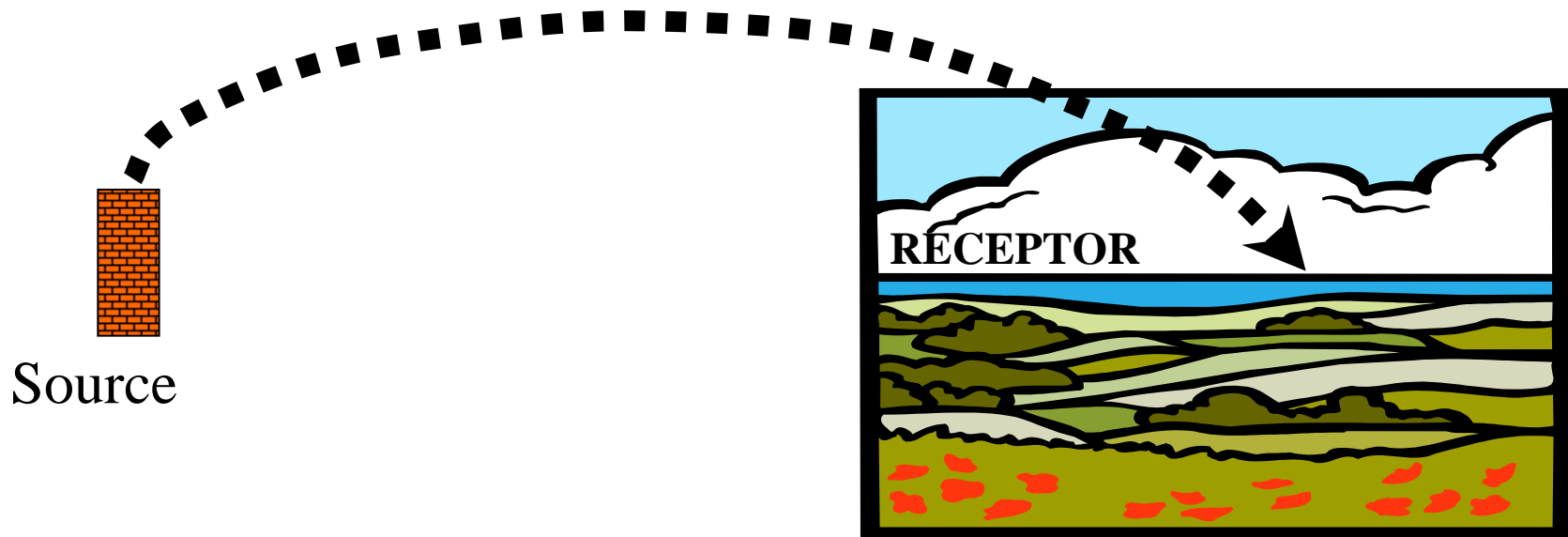


- **Perform separate simulations at each location for emissions of pure Hg(0), Hg(II) and Hg(p)**

*[after emission, simulate transformations between Hg forms]*

- **Impact of emissions mixture taken as a linear combination of impacts of pure component runs on any given receptor**

# “Chemical Interpolation”



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

# What do atmospheric mercury models need?

**Emissions  
Inventories**

**Meteorological  
Data**

**Scientific understanding of  
phase partitioning,  
atmospheric chemistry,  
and deposition processes**

**Ambient data for comprehensive  
model evaluation and improvement**

## **Emissions Inventories**

### **Previous Work**

- **1996, 1999 U.S. NEI**
- **1995, 2000 Canada**

## Emissions Inventories

### Previous Work

- 1996, 1999 U.S. NEI
- 1995, 2000 Canada

### Current Objectives

- 2002 U.S. NEI
- 2002 Canada
- Global – 2000 (Pacyna-NILU)
- Natural sources
- Re-emitted anthropogenic

## Emissions Inventories

<b>Previous Work</b>	<ul style="list-style-type: none"><li>• 1996, 1999 U.S. NEI</li><li>• 1995, 2000 Canada</li></ul>
<b>Current Objectives</b>	<ul style="list-style-type: none"><li>• 2002 U.S. NEI</li><li>• 2002 Canada</li><li>• Global – 2000 (Pacyna-NILU)</li><li>• Natural sources</li><li>• Re-emitted anthropogenic</li></ul>
<b>Challenges and Notes</b>	<ul style="list-style-type: none"><li>• <b>Speciation?</b></li><li>• <b>Short-term variations (e.g. hourly) [CEM's?]</b></li><li>• <b>Longer-term variations (e.g., maintenance)?</b></li><li>• <b>Mobile sources</b></li><li>• <b>Harmonization of source-categories</b></li><li>• <b>Emissions inventories currently only become available many years after the fact; how can we evaluate models using current monitoring data?</b></li></ul>

## **Meteorological Data**

### **Previous Work**

- **For U.S./Canadian modeling, 1996 data from NOAA Nested Grid Model (NGM), 180 km**



## Meteorological Data

### Previous Work

- For U.S./Canadian modeling, 1996 data from NOAA Nested Grid Model (NGM), 180 km

### Current Objectives

- U.S. – NOAA EDAS 40 km, 3 hr
- Global – NOAA GDAS 1° x 1°, 3 hr

## Meteorological Data

<b>Previous Work</b>	<ul style="list-style-type: none"><li>• For U.S./Canadian modeling, 1996 data from NOAA Nested Grid Model (NGM), 180 km</li></ul>
<b>Current Objectives</b>	<ul style="list-style-type: none"><li>• U.S. – NOAA EDAS 40 km, 3 hr</li><li>• Global – NOAA GDAS 1° x 1°, 3 hr</li></ul>
<b>Challenges and Notes</b>	<ul style="list-style-type: none"><li>• <b>Forecast vs. Analysis</b></li><li>• <b>Data assimilation</b></li><li>• <b>Precipitation??</b></li><li>• <b>Difficult to archive NOAA analysis datasets</b></li><li>• <b>Need finer-resolution datasets, especially for near-field analysis and model evaluation</b></li><li>• <b>We have conversion filters (e.g., for MM5), but these data are not readily available</b></li><li>• <b>What is the best way to archive and share data?</b></li></ul>

## Atmospheric Chemistry and Physics

### Previous Work

- Typical chemical mechanism
- Prescribed fields for reactive trace gases (e.g., O<sub>3</sub>, OH, SO<sub>2</sub>) and other necessary constituents (e.g., soot) based on modeled, measured, and/or empirical relationships

# Atmospheric Chemical Reaction Scheme for Mercury

Reaction	Rate	Units	Reference
<b><i>GAS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg(p)}$	3.0E-20	cm <sup>3</sup> /molec-sec	Hall (1995)
$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1.0E-19	cm <sup>3</sup> /molec-sec	Hall and Bloom (1993)
$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg(p)}$	8.5E-19	cm <sup>3</sup> /molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	4.0E-18	cm <sup>3</sup> /molec-sec	Calhoun and Prestbo (2001)
$\text{Hg}^0 + \text{OH}\cdot \rightarrow \text{Hg(p)}$	8.7E-14	cm <sup>3</sup> /molec-sec	Sommar et al. (2001)
<b><i>AQUEOUS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2}$	4.7E+7	(molar-sec) <sup>-1</sup>	Munthe (1992)
$\text{Hg}^0 + \text{OH}\cdot \rightarrow \text{Hg}^{+2}$	2.0E+9	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1997)
$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T * e^{((31.971 * T) - 12595.0) / T}$ sec <sup>-1</sup> [T = temperature (K)]		Van Loon et al. (2002)
$\text{Hg(II)} + \text{HO}_2\cdot \rightarrow \text{Hg}^0$	~ 0	(molar-sec) <sup>-1</sup>	Gardfeldt & Jonnson (2003)
$\text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2}$	2.1E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2}$	2.0E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg(II)} \leftrightarrow \text{Hg(II)}_{(\text{soot})}$	9.0E+2	liters/gram; t = 1/hour	eqnbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$\text{Hg}^{+2} + \text{h}\nu \rightarrow \text{Hg}^0$	6.0E-7	(sec) <sup>-1</sup> (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

## Atmospheric Chemistry and Physics

### Previous Work

- Typical chemical mechanism
- Prescribed fields for reactive trace gases (e.g., O<sub>3</sub>, OH, SO<sub>2</sub>) and other necessary constituents (e.g., soot) based on modeled, measured, and/or empirical relationships

### Current Objectives

- **Include new information on chemistry, e.g., bromine reactions, etc.**
- **Add SO<sub>2</sub> and potentially other compounds into in-situ plume chemistry treatment**
- **Sensitivity analyses**
- **Consider using gridded chemical output from full-chemistry atmospheric model (e.g., CMAQ)**
- **Option - run HYSPLIT in Eulerian mode for chemistry; conduct one-atmosphere simulation**

## Atmospheric Chemistry and Physics

Previous Work	<ul style="list-style-type: none"><li>• Typical chemical mechanism</li><li>• Prescribed fields for reactive trace gases (e.g., O<sub>3</sub>, OH, SO<sub>2</sub>) and other necessary constituents (e.g., soot) based on modeled, measured, and/or empirical relationships</li></ul>
Current Objectives	<ul style="list-style-type: none"><li>• Include new information on chemistry, e.g., Br reactions, etc.</li><li>• Add SO<sub>2</sub> and potentially other compounds into in-situ plume chemistry treatment</li><li>• Sensitivity analyses</li><li>• Consider using gridded chemical output from full-chemistry atmospheric model (e.g., CMAQ)</li><li>• Option - run HYSPLIT in Eulerian mode for chemistry; conduct one-atmosphere simulation</li></ul>
Challenges and Notes	<ul style="list-style-type: none"><li>• <b>What is RGM?</b></li><li>• <b>What is Hg(p)?</b></li><li>• <b>What is solubility of Hg(p)?</b></li><li>• <b>Fate of dissolved Hg(II) when droplet dries out?</b></li><li>• <b>What reactions don't we know about yet?</b></li><li>• <b>What are rates of reactions?</b></li><li>• <b>Uncertainties in wet &amp; dry deposition processes...</b></li></ul>

## Model Evaluation

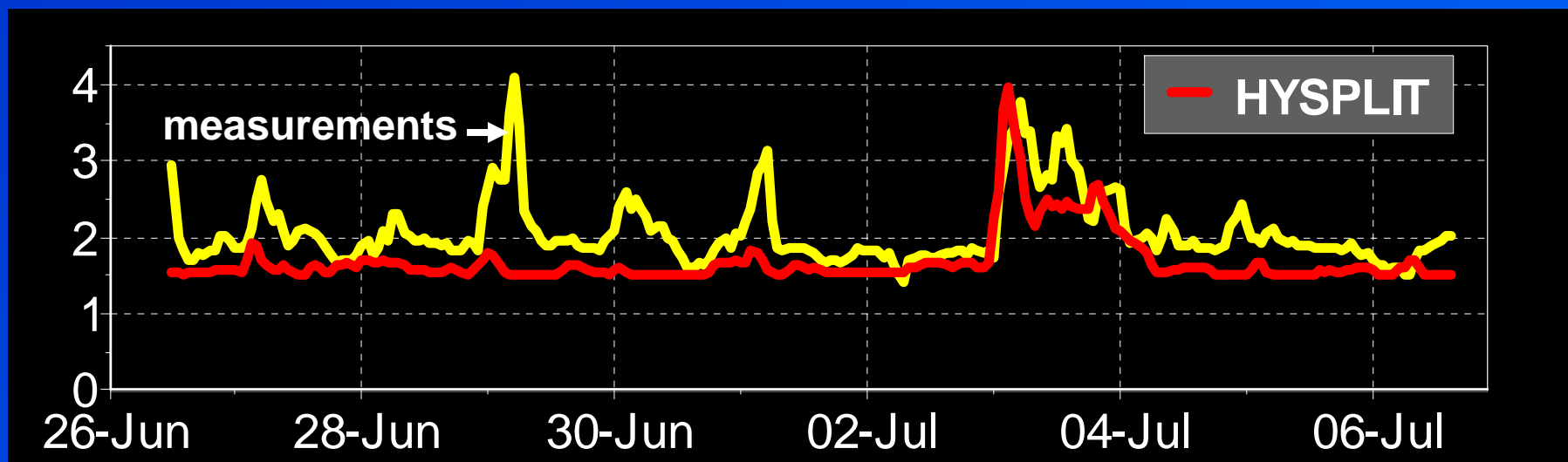
### Previous Work

- **US: 1996 MDN measurements**
- **Europe: 1999 speciated ambient concentrations in short-term episodes, monthly wet deposition**

*EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury*

Intro- duction	Stage I	Stage II			Stage III			Conclu- sions
	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	

**Total Gaseous Mercury (ng/m<sup>3</sup>) at Neuglobsow: June 26 – July 6, 1995**

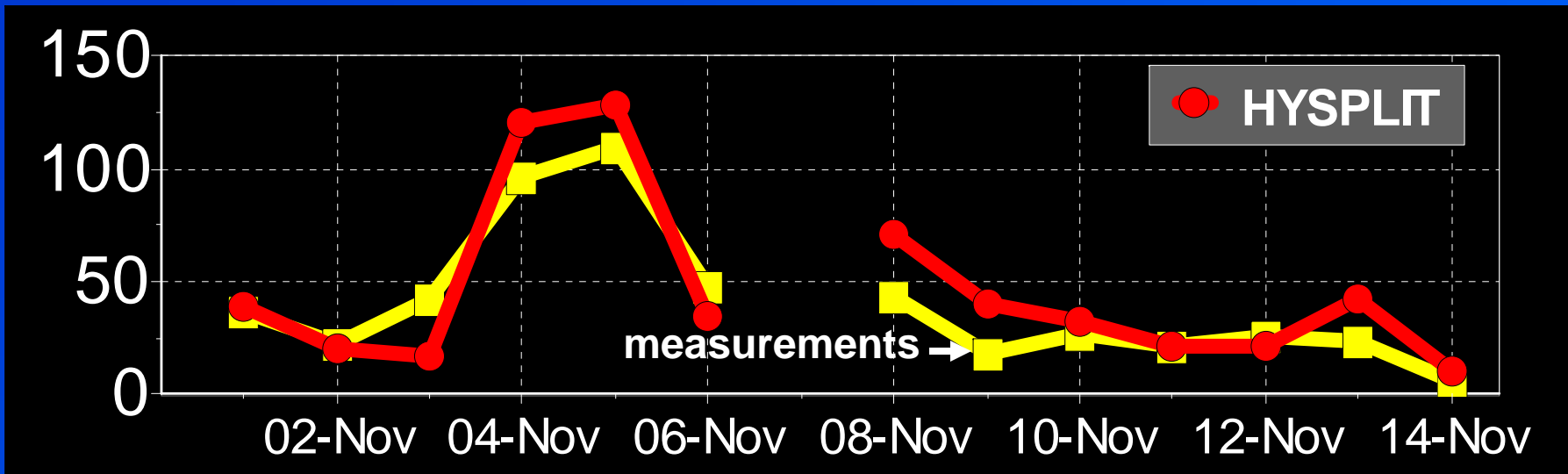




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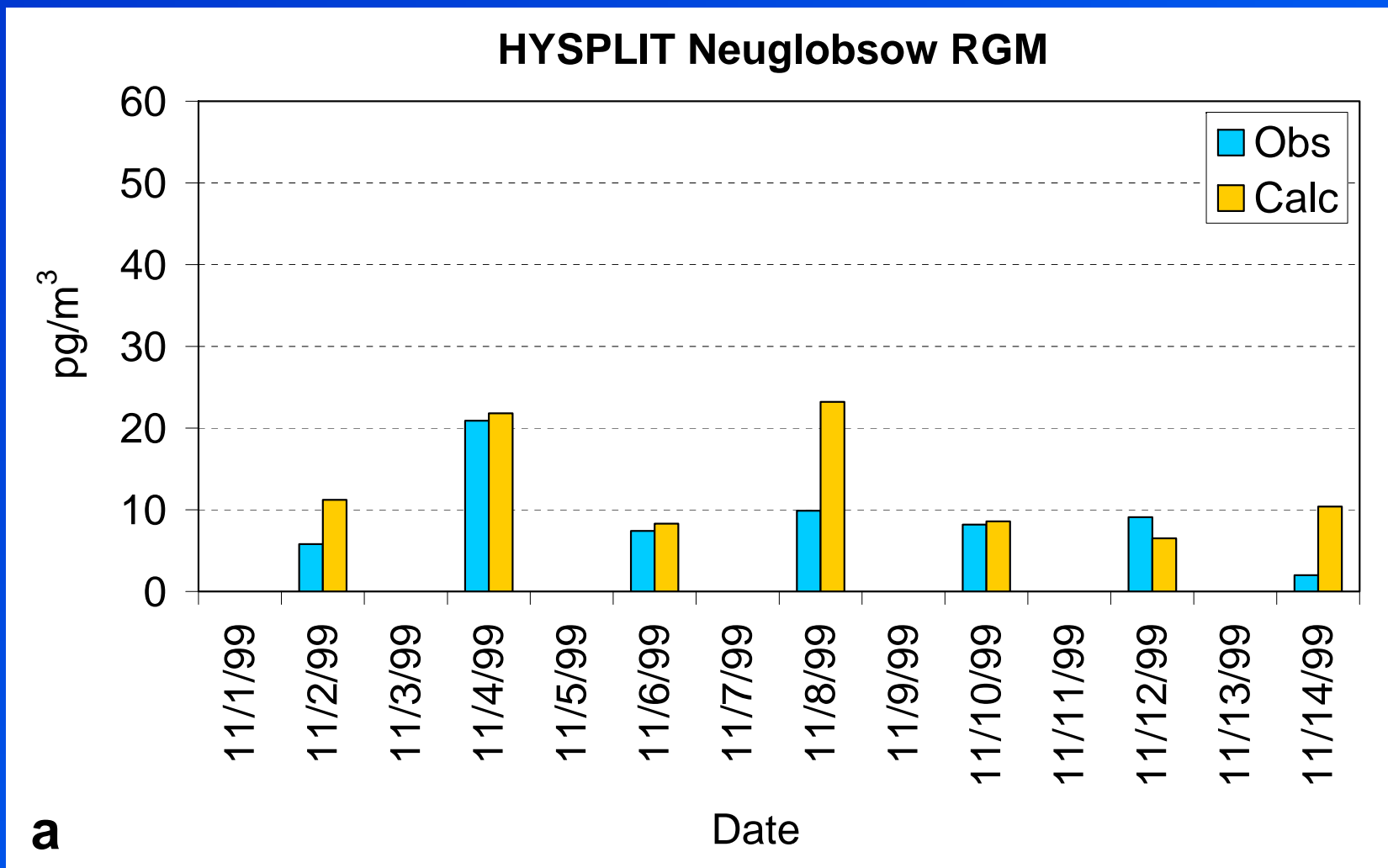
Total **Particulate** Mercury (pg/m<sup>3</sup>) at Neuglobsow, Nov 1-14, 1999



*EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury*

Intro- duction	Stage I	Stage II			Stage III			Conclu- sions
	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	

**Reactive Gaseous Mercury at Neuglobsow, Nov 1-14, 1999**



## Model Evaluation

### Previous Work

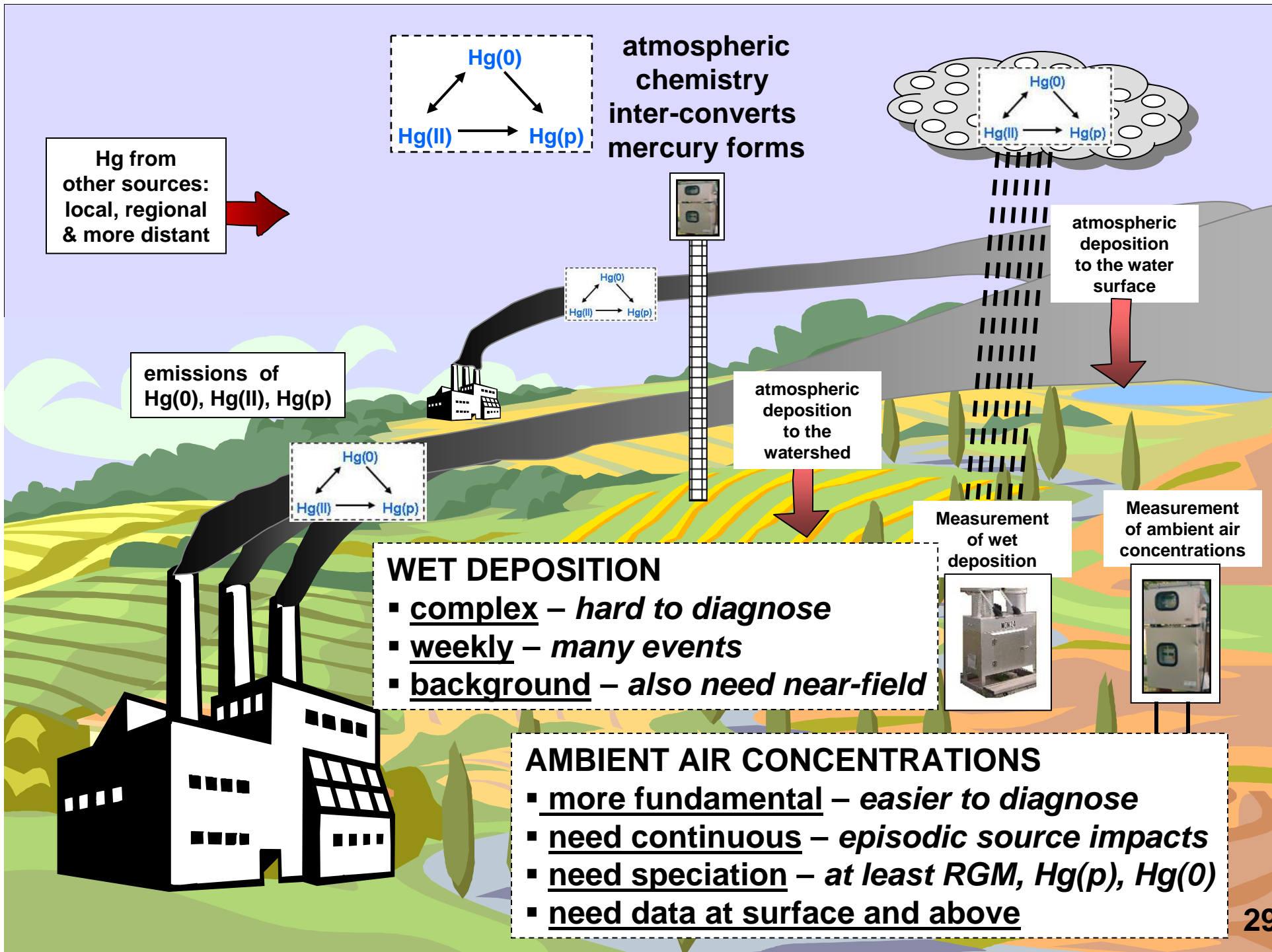
- **US: 1996 MDN measurements**
- **Europe: 1999 speciated ambient concentrations in short-term episodes, monthly wet deposition**

### Current Objectives

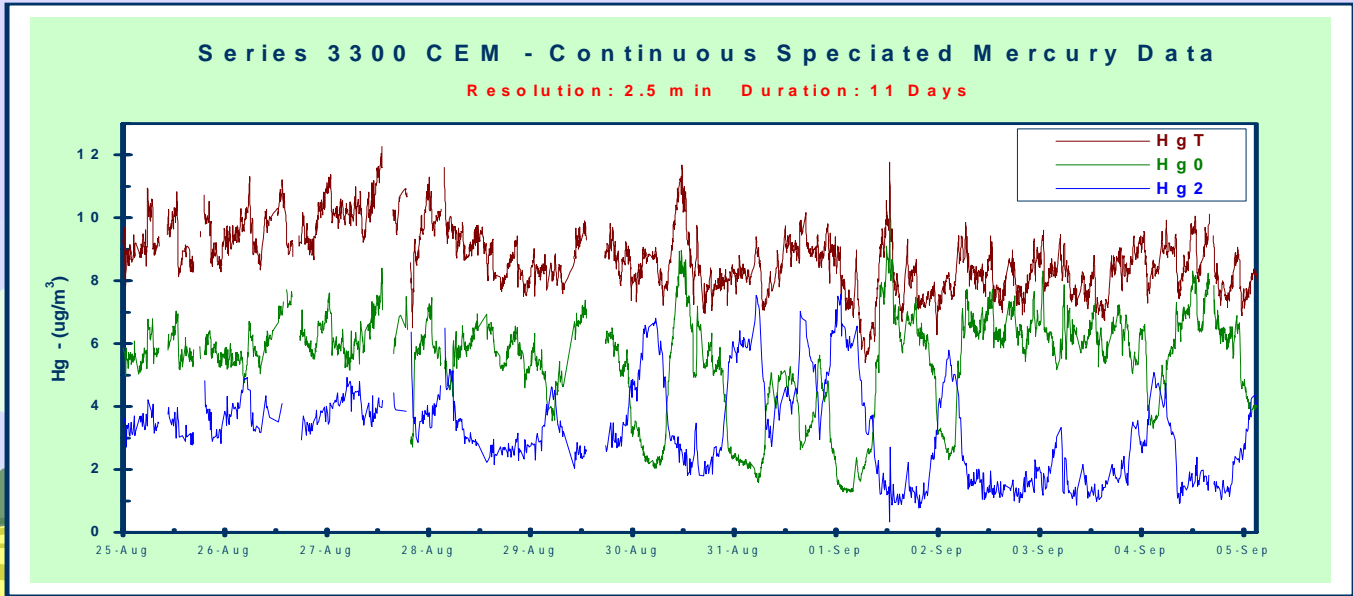
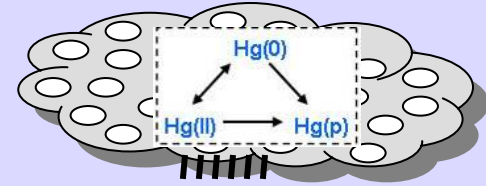
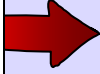
- **Attempt to utilize all available speciated ambient concentrations and wet deposition data from U.S. and other regions**

## Model Evaluation

<b>Previous Work</b>	<ul style="list-style-type: none"><li>• <b>US: 1996 MDN measurements</b></li><li>• <b>Europe: 1999 speciated ambient concentrations in short-term episodes, monthly wet deposition</b></li></ul>
<b>Current Objectives</b>	<ul style="list-style-type: none"><li>• <b>Attempt to utilize all available speciated ambient concentrations and wet deposition data from U.S. and other regions</b></li></ul>
<b>Challenges and Notes</b>	<ul style="list-style-type: none"><li>• <b>Comprehensive evaluation has not been possible due to large gaps in availability of monitoring and process-related data</b></li><li>• <b>Need data for upper atmosphere as well as surface</b></li><li>• <b>Need data for both source-impacted and background sites</b></li><li>• <b>Use of recent monitoring data with EPA 2002 inventory?</b></li><li>• <b>Time-resolved monitoring data vs. non-time-resolved emissions?</b></li><li>• <b>Hard to diagnose differences between models &amp; measurements</b></li><li>• <b>Can we find better ways to share data for model evaluation (and other purposes)? To this end, discussion is beginning on national, cooperative, ambient Hg monitoring network</b></li></ul>



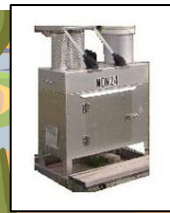
Hg from other sources: local, regional & more distant



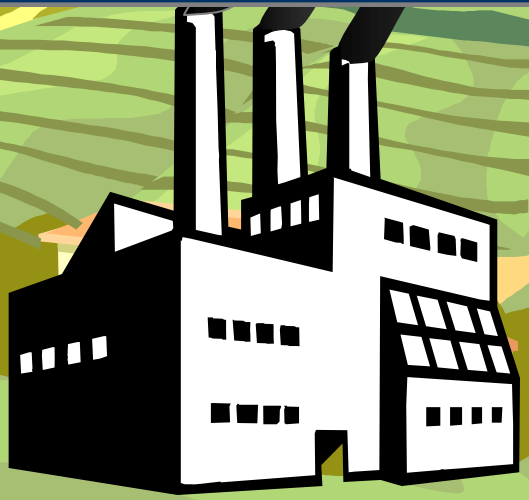
atmospheric deposition to the water surface



Measurement of wet deposition

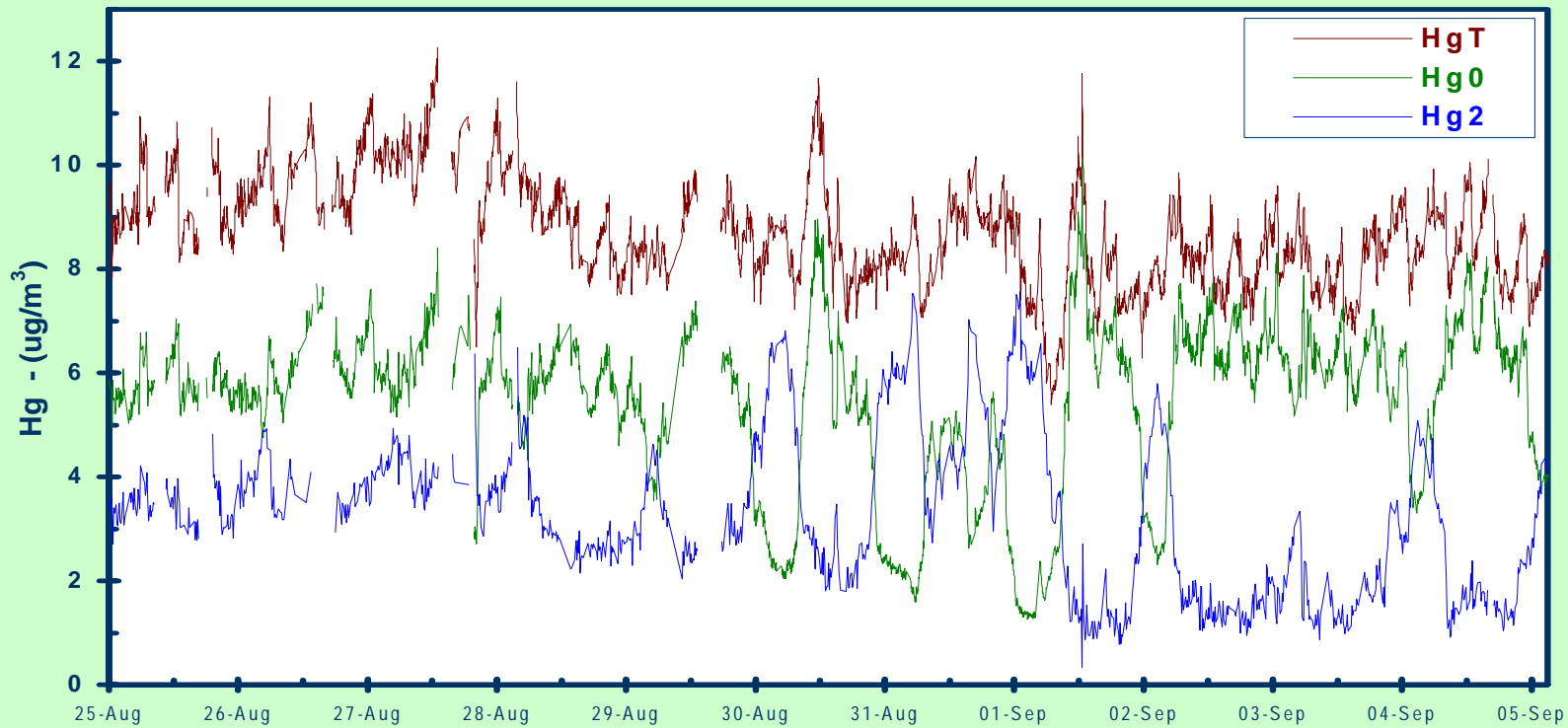


Measurement of ambient air concentrations



## Series 3300 CEM - Continuous Speciated Mercury Data

Resolution: 2.5 min Duration: 11 Days

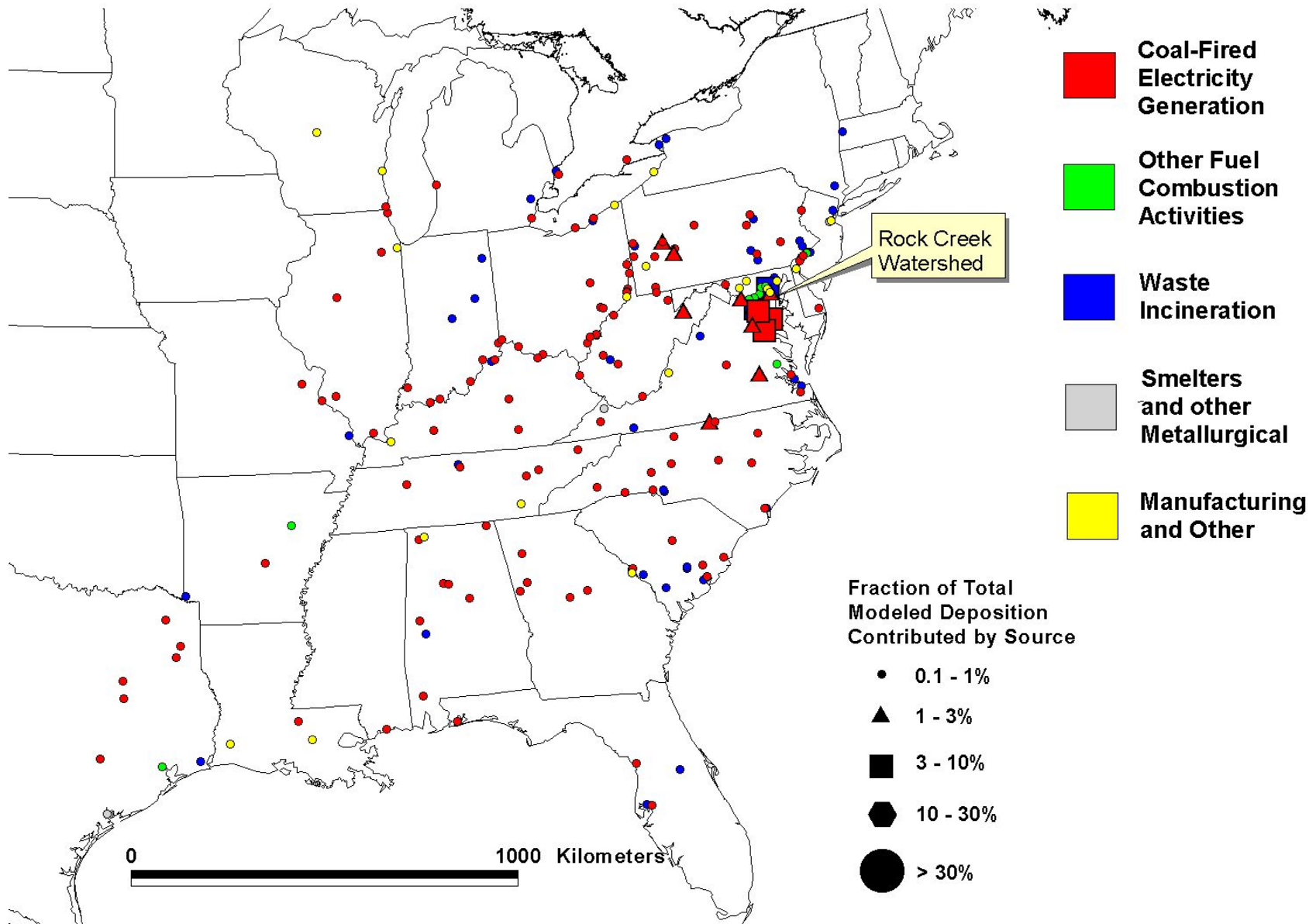


Source: *Tekran Instruments Corporation*

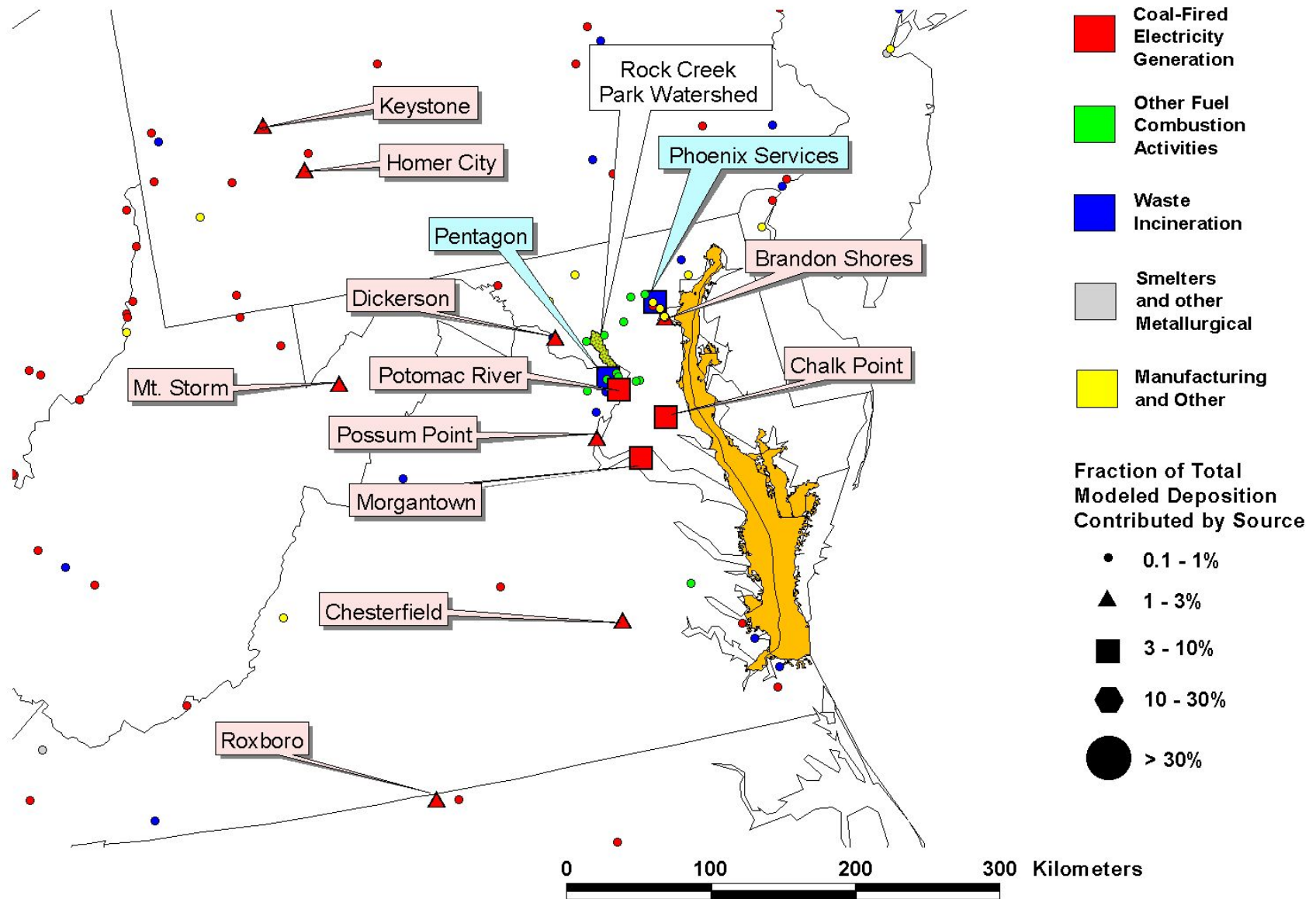
**Example of results:  
Rock Creek Watershed**



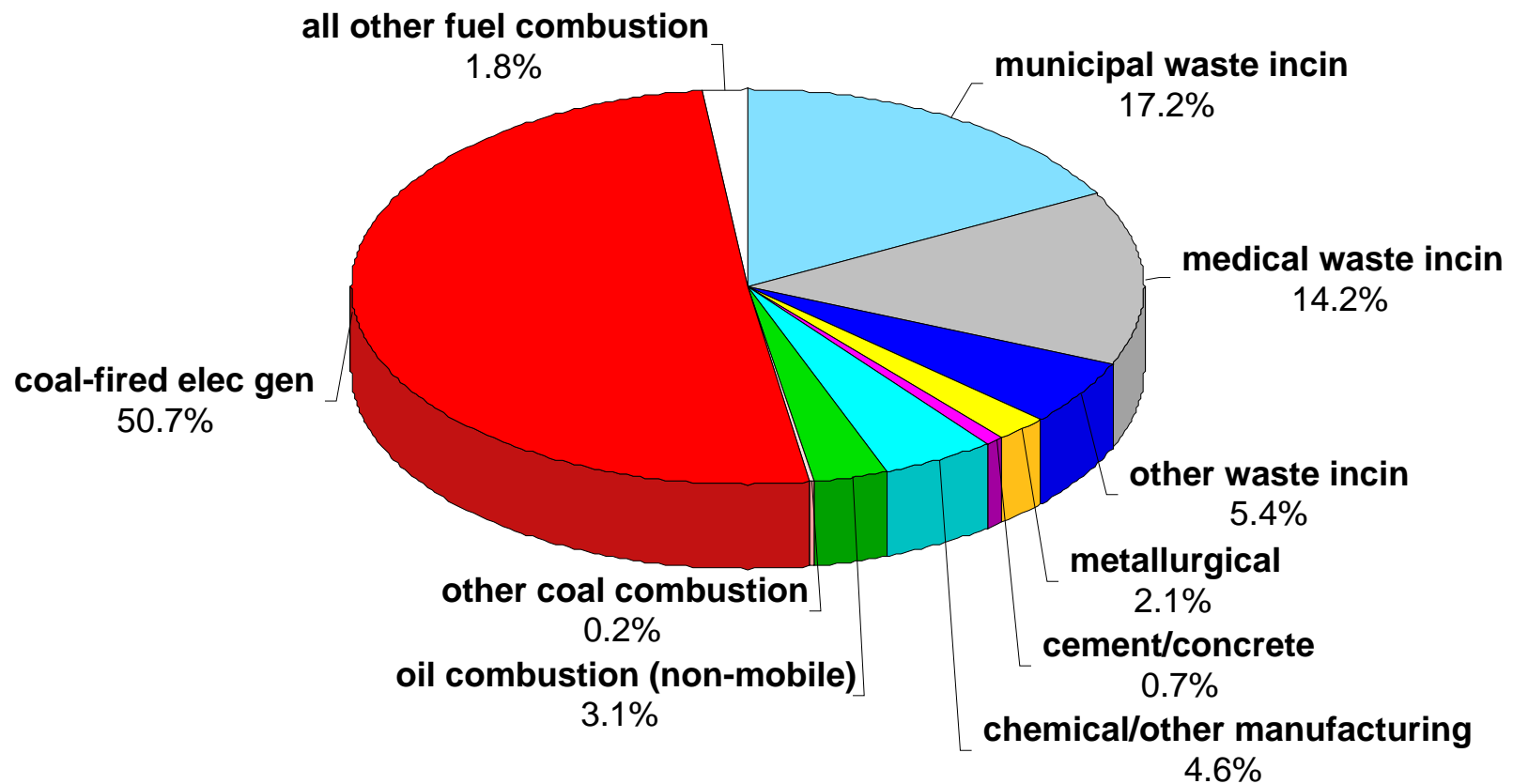
## Largest Model-Estimated U.S./Canada Anthropogenic Contributors to 1999 Mercury Deposition to the Rock Creek Watershed (large region)



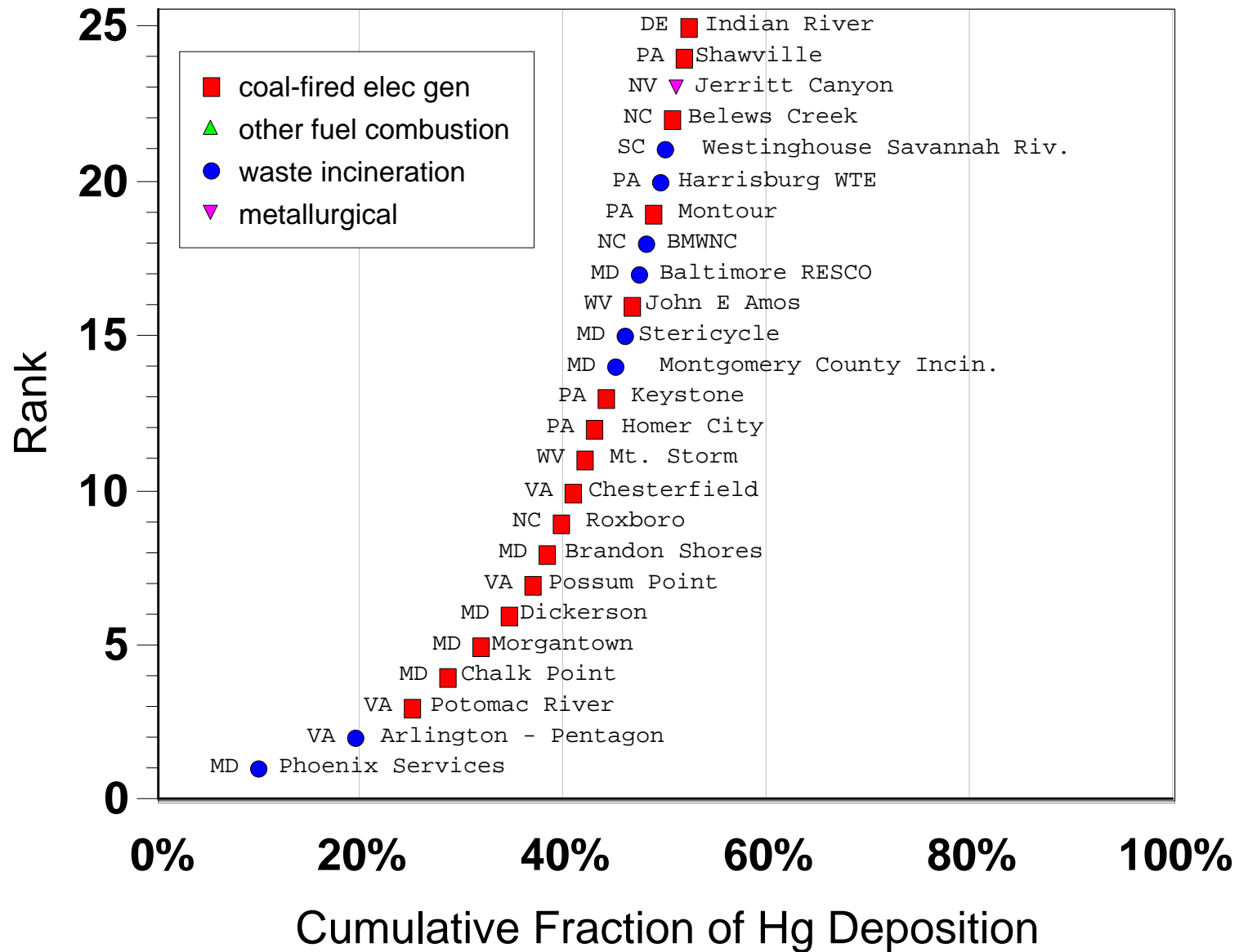
# Largest Model-Estimated U.S./Canada Anthropogenic Contributors to 1999 Mercury Deposition to the Rock Creek Watershed (close up)



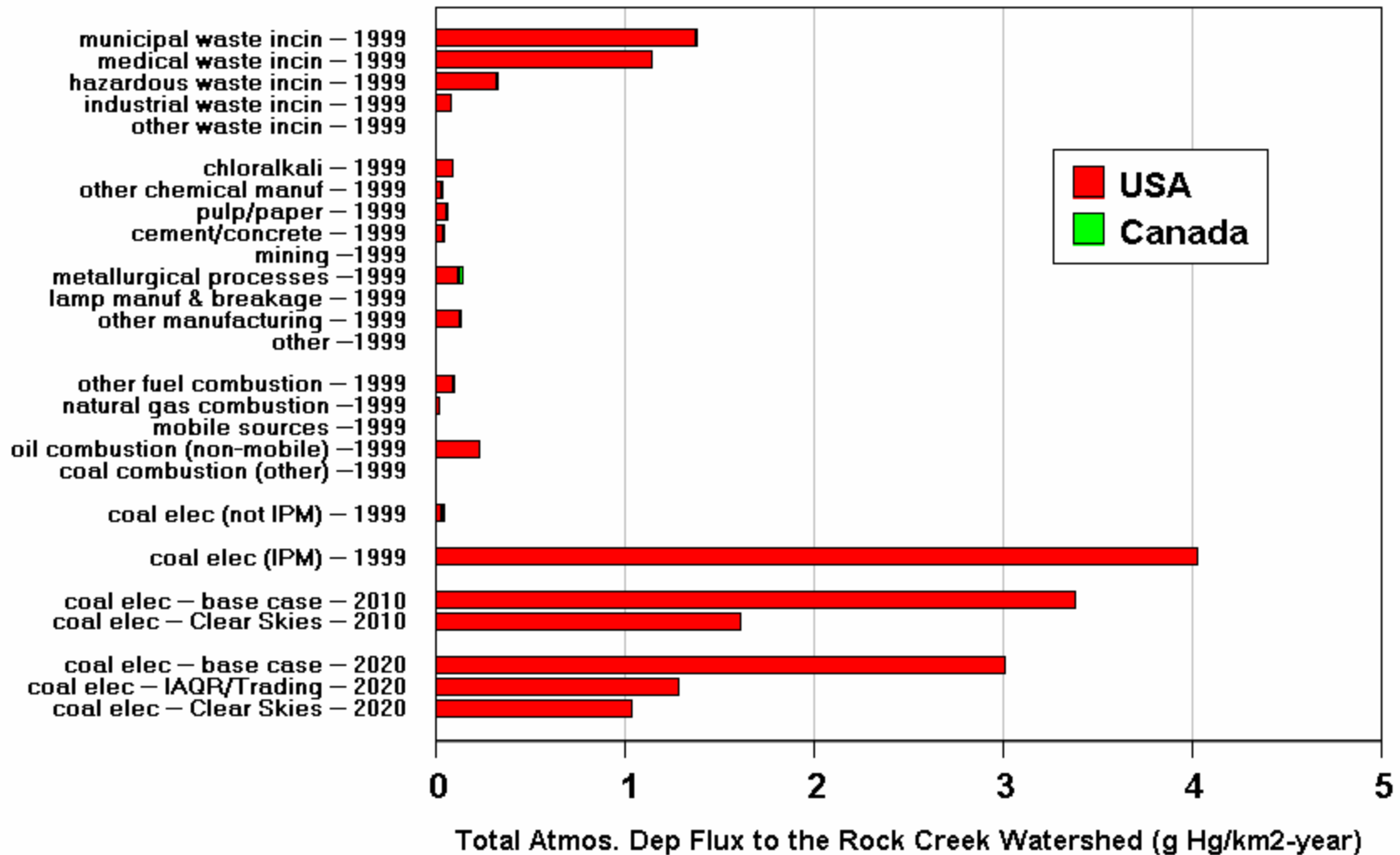
# Proportions of 1999 Model-Estimated Atmospheric Deposition to the Rock Creek Watershed from Different Anthropogenic U.S./Canada Mercury Emissions Source Sectors



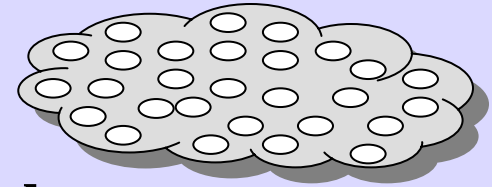
# Top 25 Contributors to Hg Deposition to Rock Creek Watershed



# Atmospheric Deposition Flux to the Rock Creek Watershed from Anthropogenic Mercury Emissions Sources in the U.S. and Canada

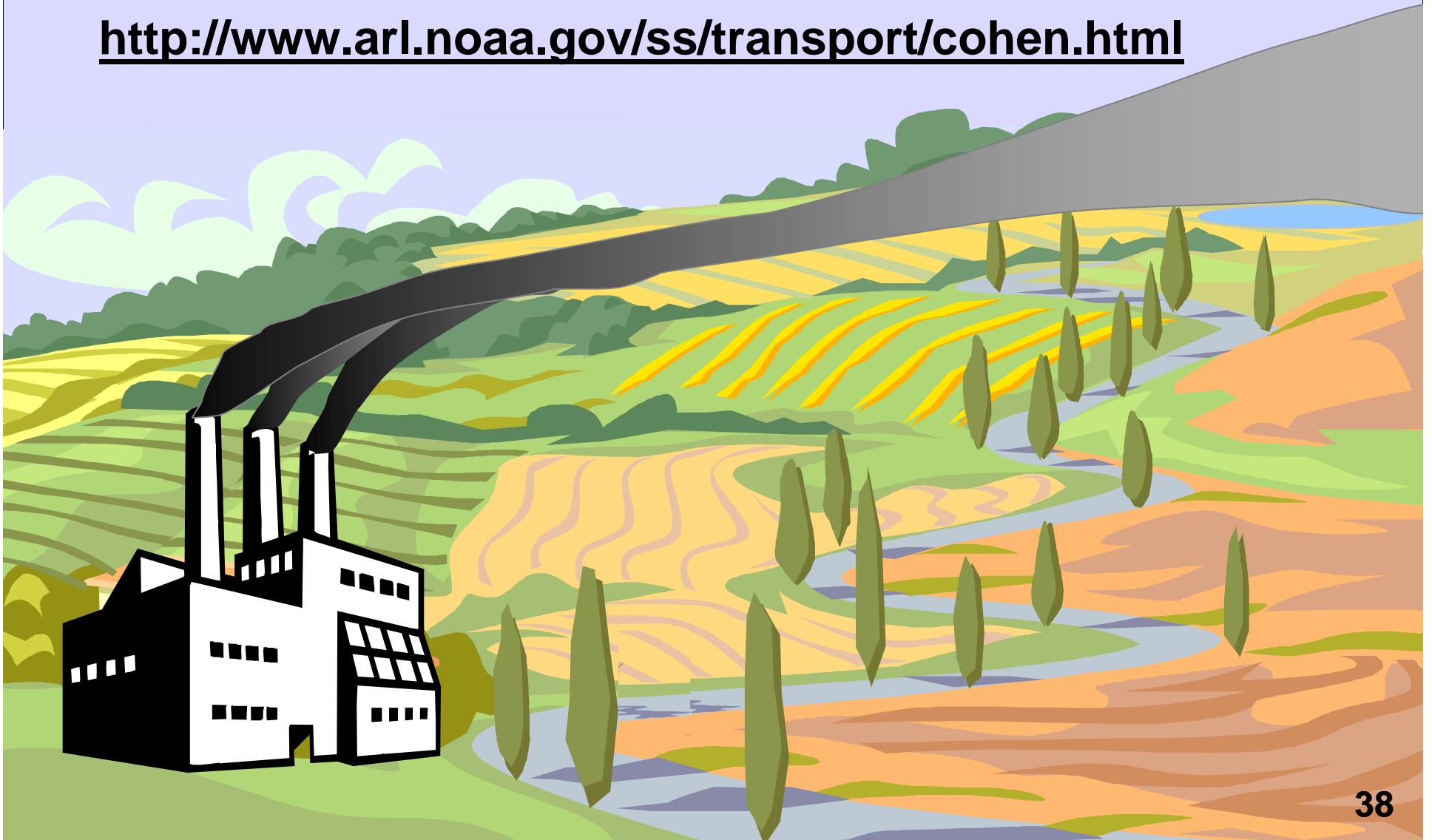


# Thanks!



For more information on this research:

<http://www.arl.noaa.gov/ss/transport/cohen.html>

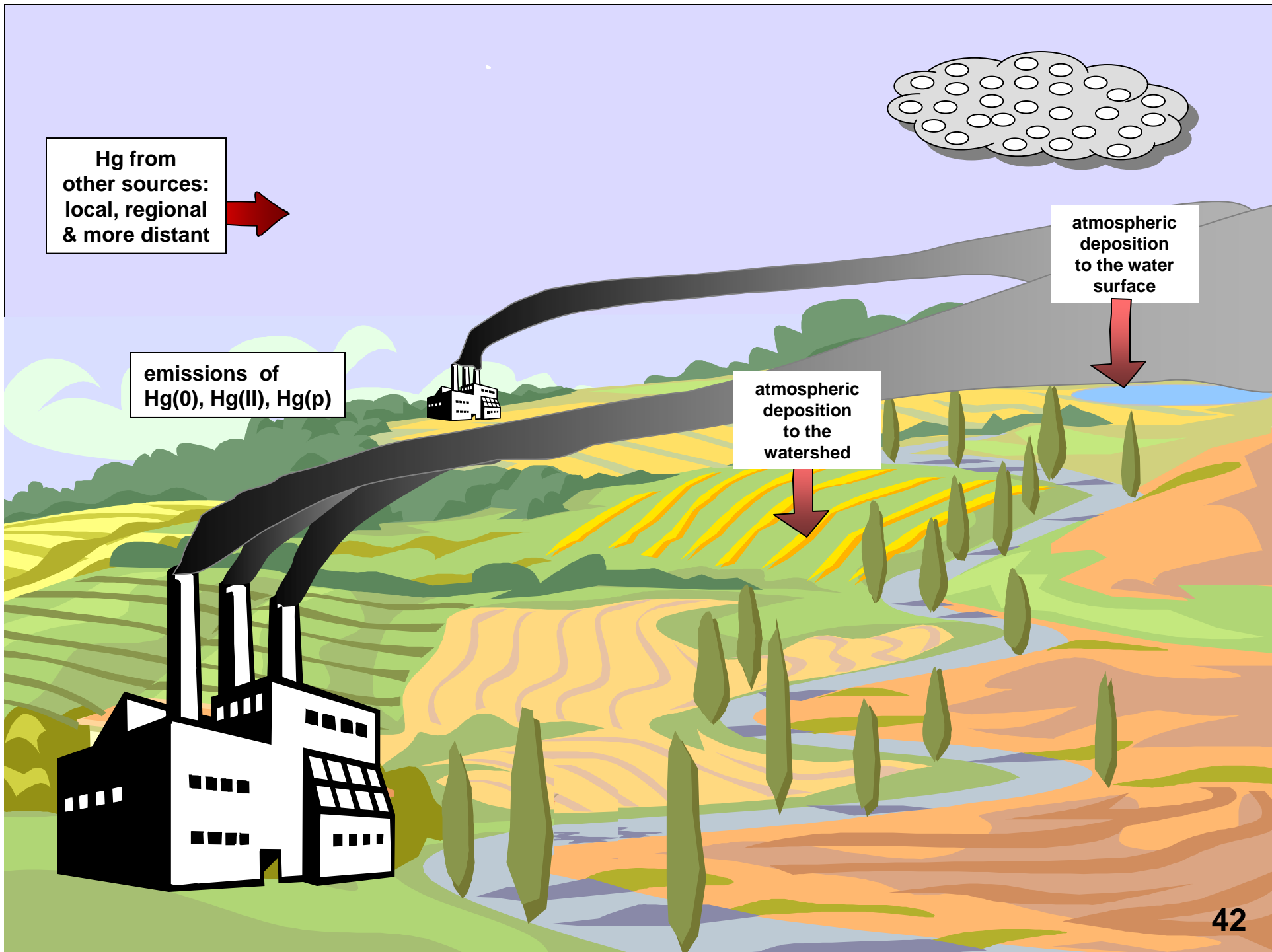




# **Extra Slides**

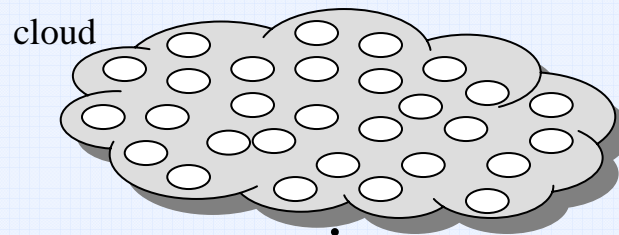
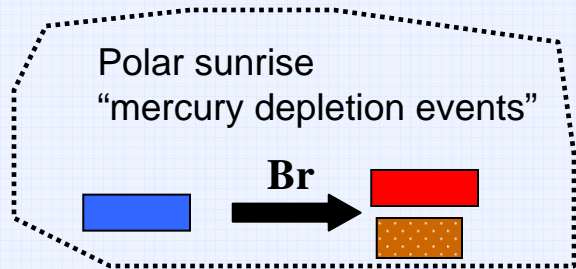
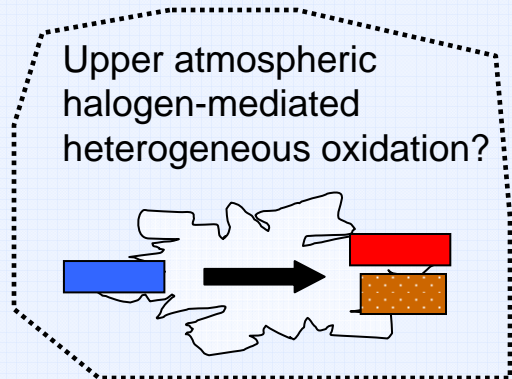


**Context**



# Atmospheric Mercury Fate Processes

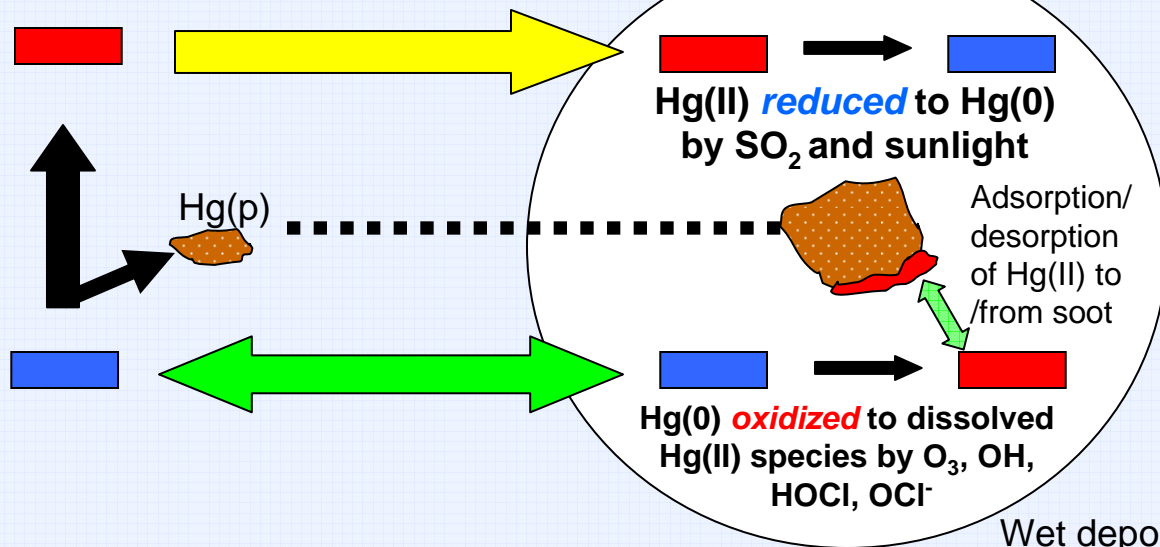
- Elemental Mercury [Hg(0)]
- Hg(II), ionic mercury, RGM
- Particulate Mercury [Hg(p)]



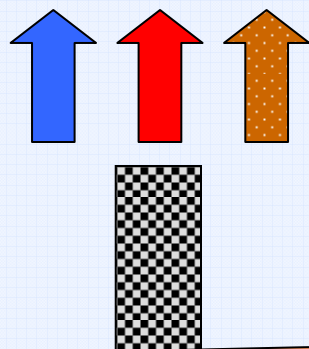
CLOUD DROPLET

Vapor phase:

Hg(0) oxidized to RGM and Hg(p) by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>, OH, HCl



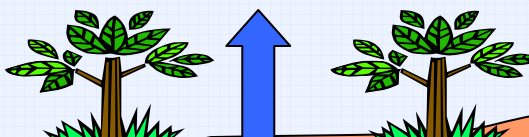
Primary Anthropogenic Emissions



Natural emissions

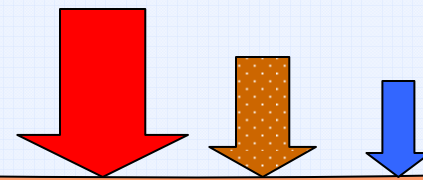


Re-emission of previously deposited anthropogenic and natural mercury



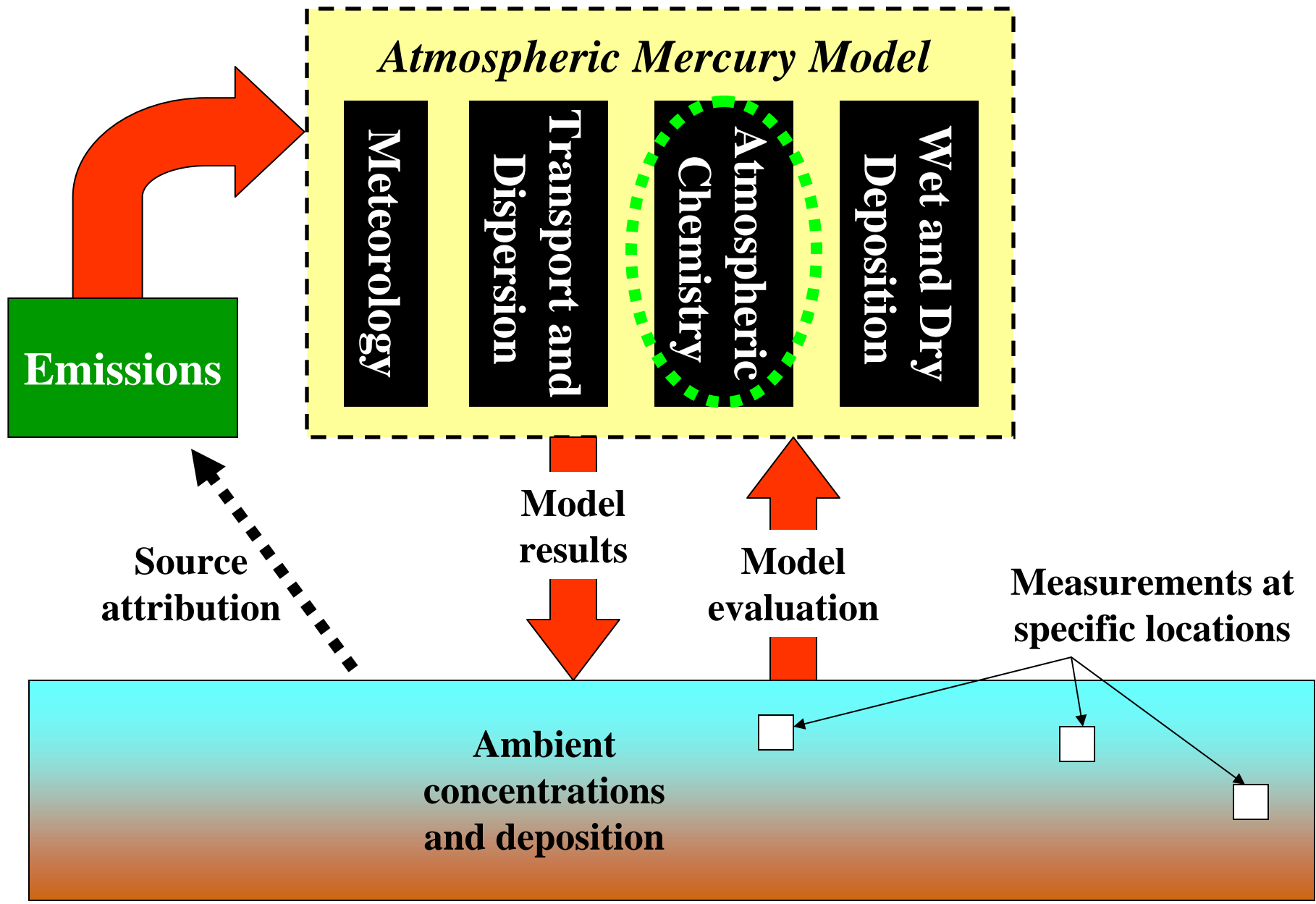
Wet deposition

Dry deposition



- ❑ ***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”**

**methodology**



## Some Current Atmospheric Chemistry Challenges

- ❑ *Plume chemistry*, e.g., rapid reduction of RGM to elemental mercury?
  - ***If significant reduction of RGM to Hg(0) is occurring in power-plant plumes, then much less local/regional deposition***

## RGM reduction in power-plant plumes?

- ❑ *If significant reduction of RGM to Hg(0) is occurring in power-plant plumes, then much less local/regional deposition*
- ❑ No known chemical reaction is capable of causing significant reduction of RGM in plumes – e.g. measured rates of SO<sub>2</sub> reduction can't explain some of the claimed reduction rates
- ❑ Very hard to measure
  - ❑ Aircraft
  - ❑ Static Plume Dilution Chambers (SPDC)
  - ❑ Ground-based measurements



## **RGM reduction in power-plant plumes?**

- Most current state-of-the-science models do not include processes that lead to significant reduction in plumes**
- Recent measurement results show less reduction**
- Significant uncertainties – e.g., mass balance errors comparable to measured effects...**
- Current status – inconclusive... but weight of evidence suggest that while some reduction may be occurring, it may be only a relatively small amount**
- Recent measurements at Steubenville, OH appear to show strong local mercury deposition from coal-fired power plant emissions.**

## Some Current Atmospheric Chemistry Challenges

- ❑ *Plume chemistry*, e.g., rapid reduction of RGM to elemental mercury?
- ❑ *Boundary conditions* for regional models?

# Some Current Atmospheric Chemistry Challenges

- ❑ *Plume chemistry*, e.g., rapid reduction of RGM to elemental mercury?
- ❑ *Boundary conditions* for regional models?
- ❑ ***Oxidation of elemental mercury by  $O_3$  and  $OH^\bullet$  may be over-represented***, leading to overestimation of the contribution of global sources to regional deposition

Calvert, J., and S. Lindberg (2005). Mechanisms of mercury removal by  $O_3$  and  $OH$  in the atmosphere. *Atmospheric Environment* 39: 3355-3367.

# Some Current Atmospheric Chemistry Challenges

- ❑ *Plume chemistry*, e.g., rapid reduction of RGM to elemental mercury?
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- ❑ ***Atmospheric methyl-mercury***: significance? sources? transport? chemistry? deposition?

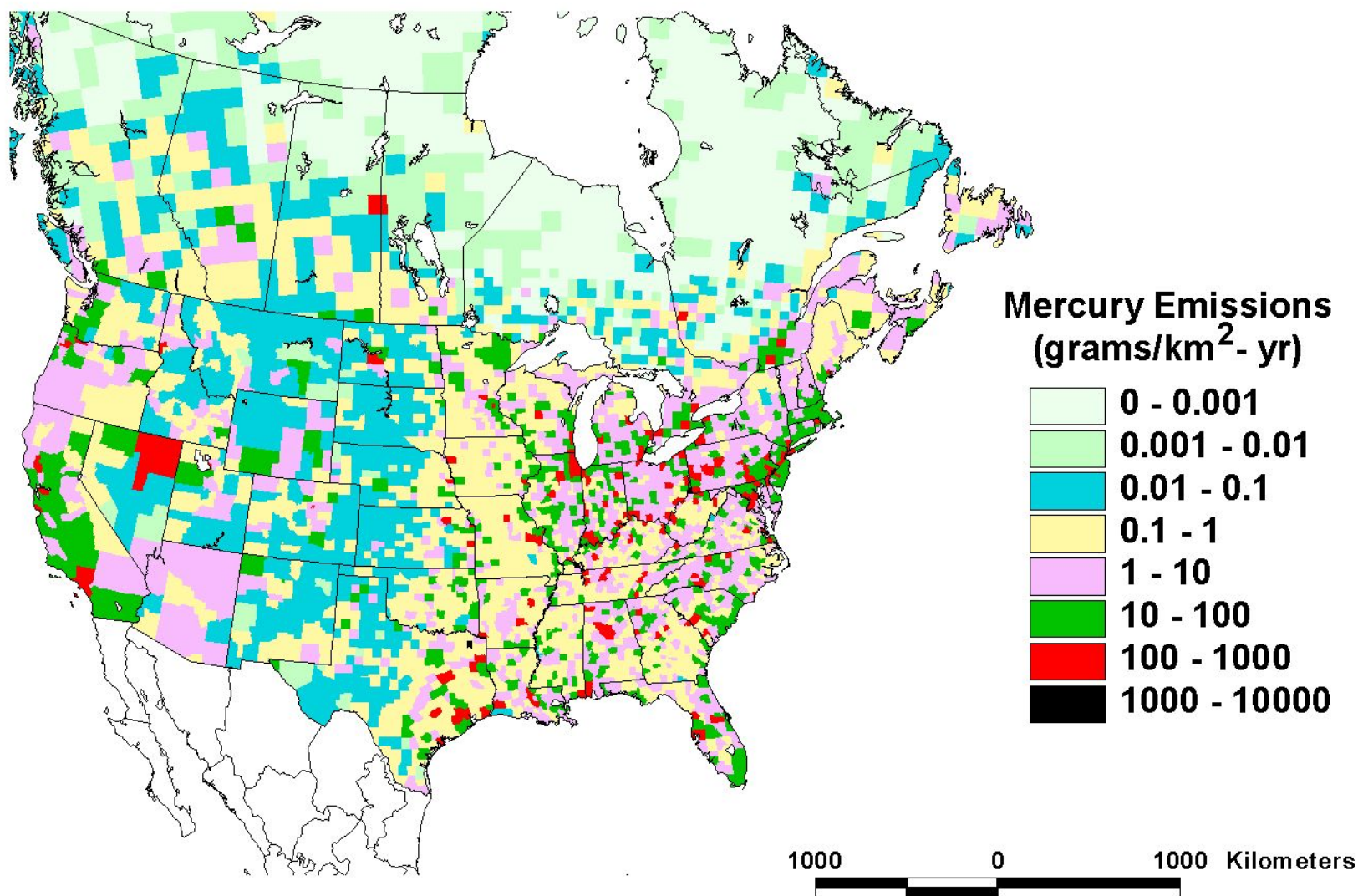
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# Some Current Atmospheric Chemistry Challenges

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e.g., Hall et al. (2005). Methyl and total mercury in precipitation in the Great Lakes region. *Atmospheric Environment* 39: 7557-7569.
- ❑ *Source-Receptor answers influenced by above factors*

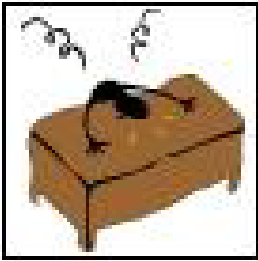
**emissions**

# Geographic Distribution of Estimated Anthropogenic Mercury Emissions in the U.S. (1999) and Canada (2000)

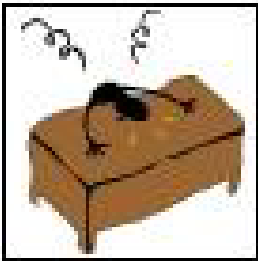


# Temporal Problems with Emissions Inventories

## Variations on time scales of minutes to hours

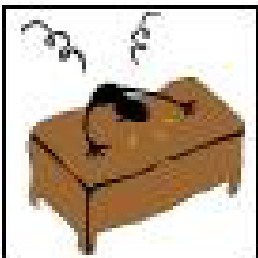


- *CEM's needed – and not just on coal-fired power plants*
- *CEM's must be speciated or of little use in developing critical source-receptor information*
- *Clean Air Mercury Rule only requires ~weekly total-Hg measurements, for purposes of trading*



## 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

$$1000 \text{ MW} \times \$0.10/\text{kw-hr} \\ = \$1,000,000,000 \text{ per year}$$

## Speciation Continuous Emissions Monitor (CEM):

~\$200,000 to purchase/install

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

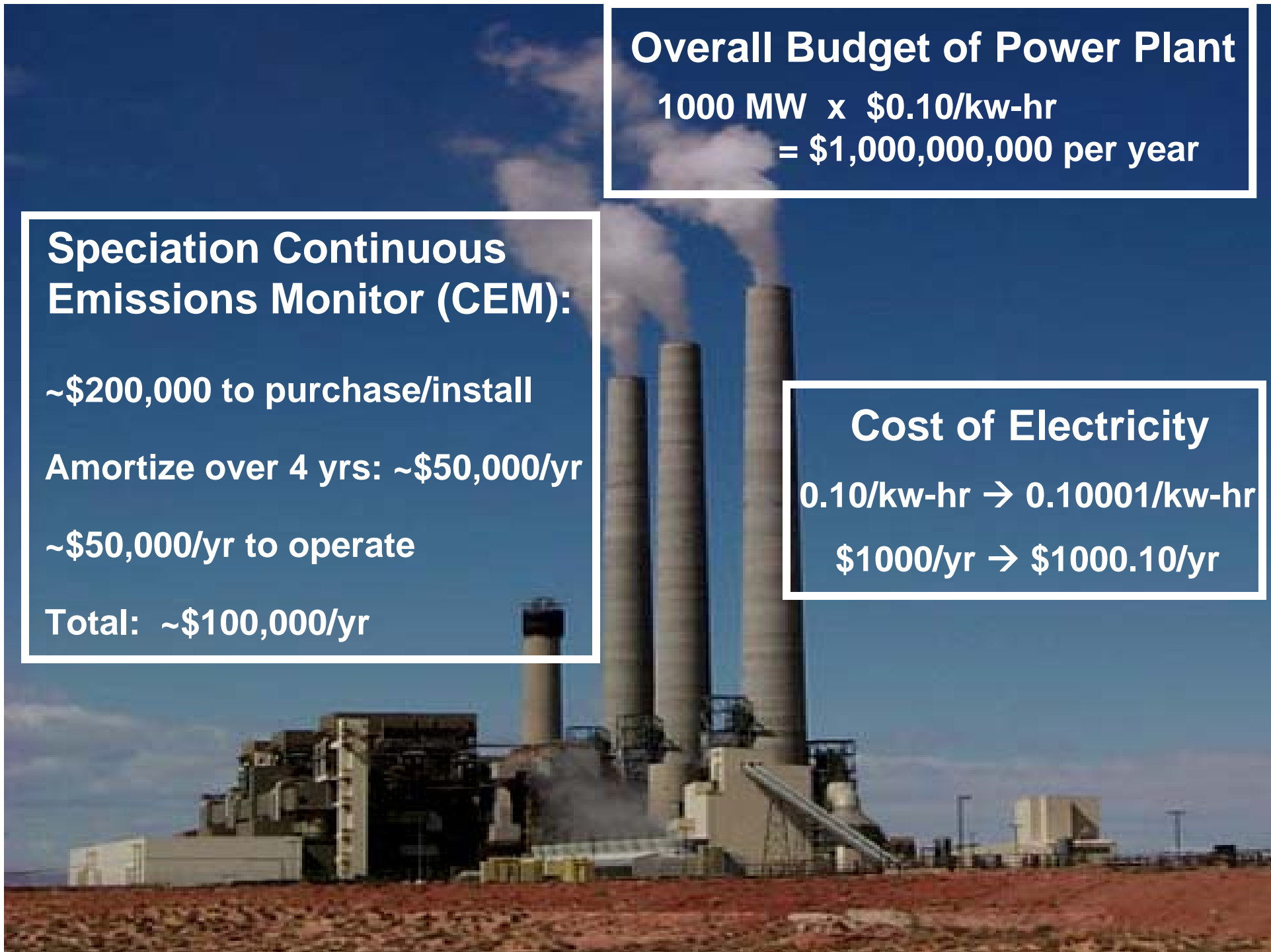
~\$50,000/yr to operate

Total: ~\$100,000/yr

## Cost of Electricity

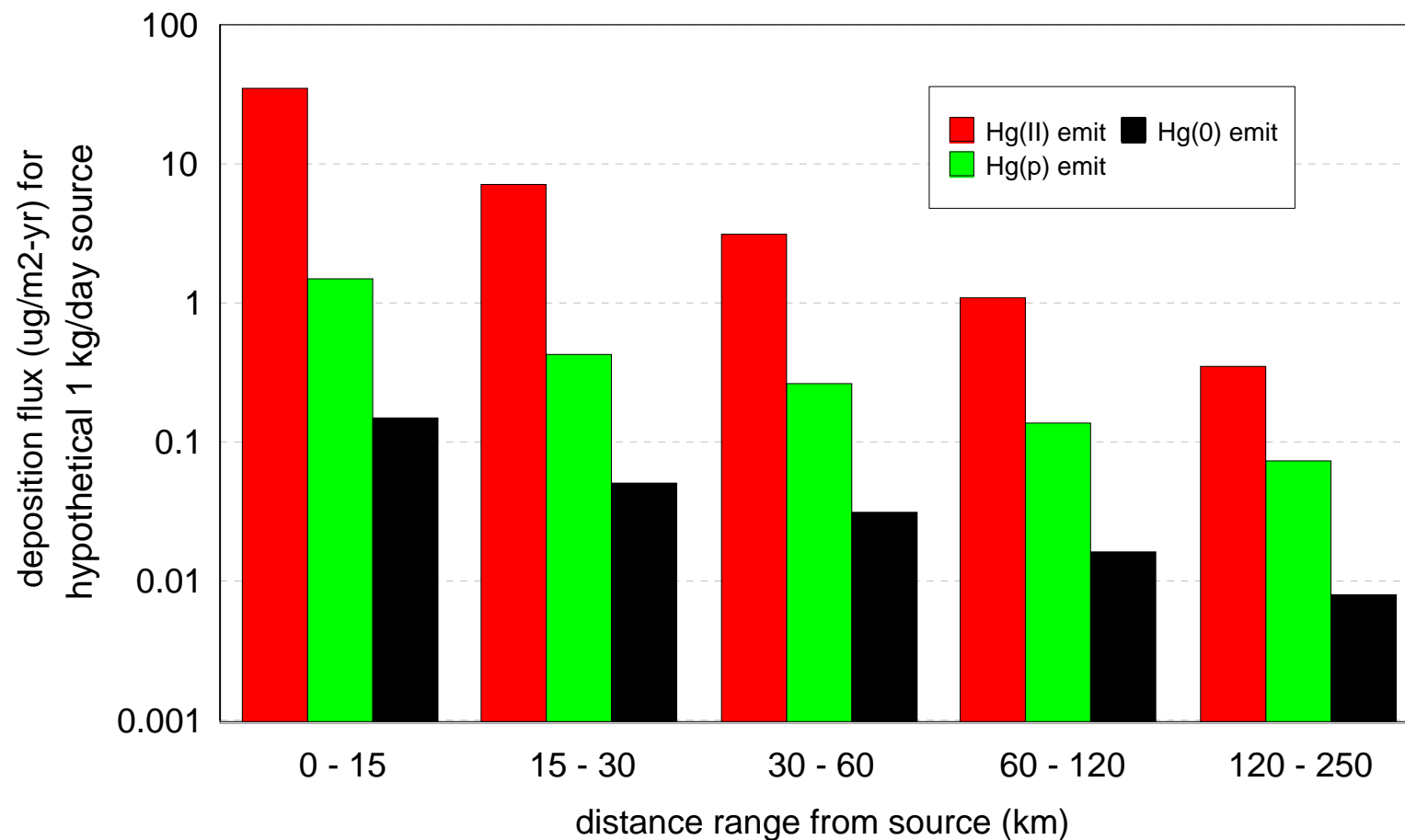
0.10/kw-hr  $\rightarrow$  0.10001/kw-hr

\$1000/yr  $\rightarrow$  \$1000.10/yr



**illustrative  
model  
results**

## Why are emissions speciation data - and potential plume transformations -- critical?



*Logarithmic*

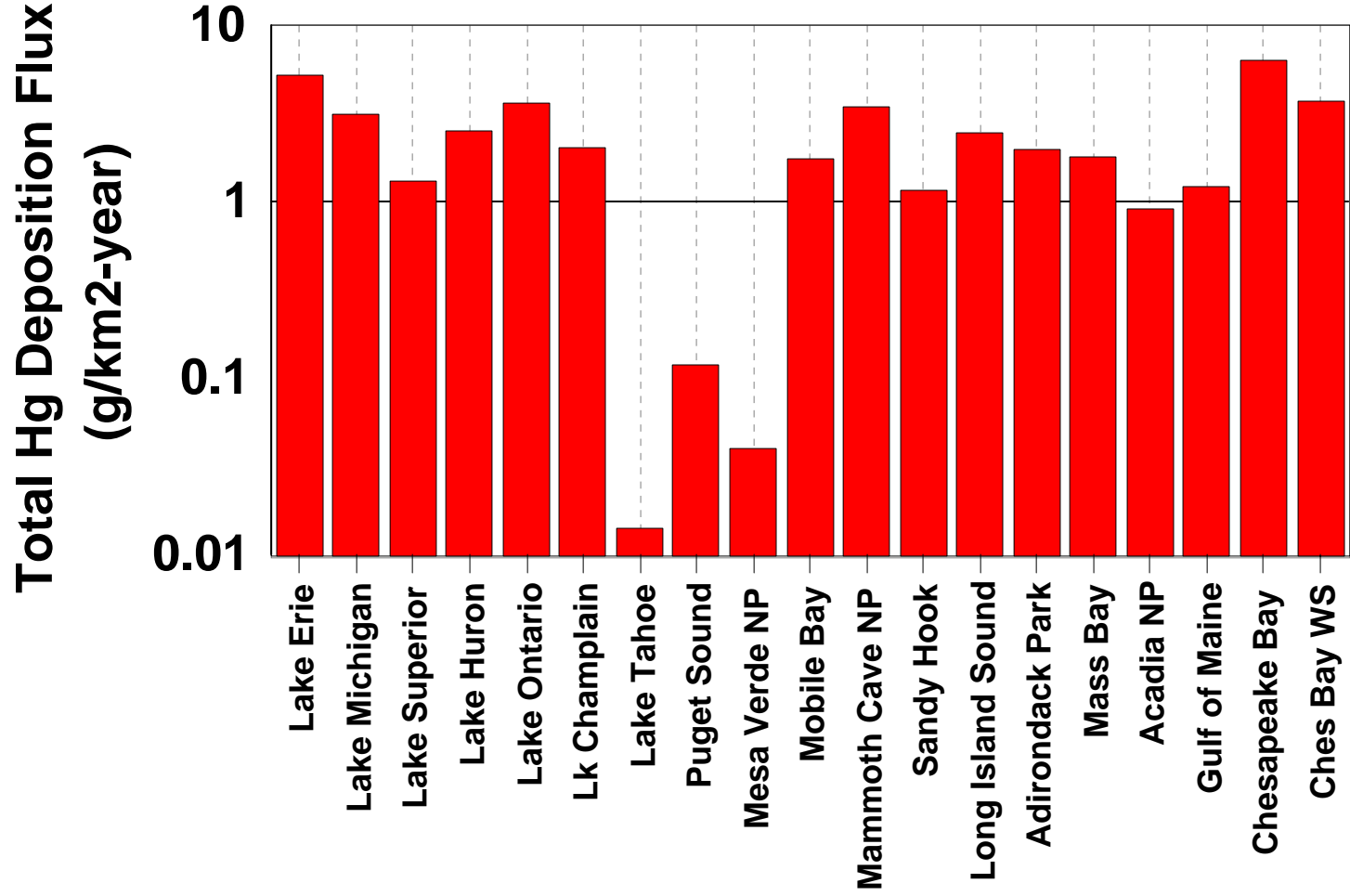
**NOTE: distance results averaged over all directions –  
Some directions will have higher fluxes, some will have lower**

**source-  
receptor  
results**

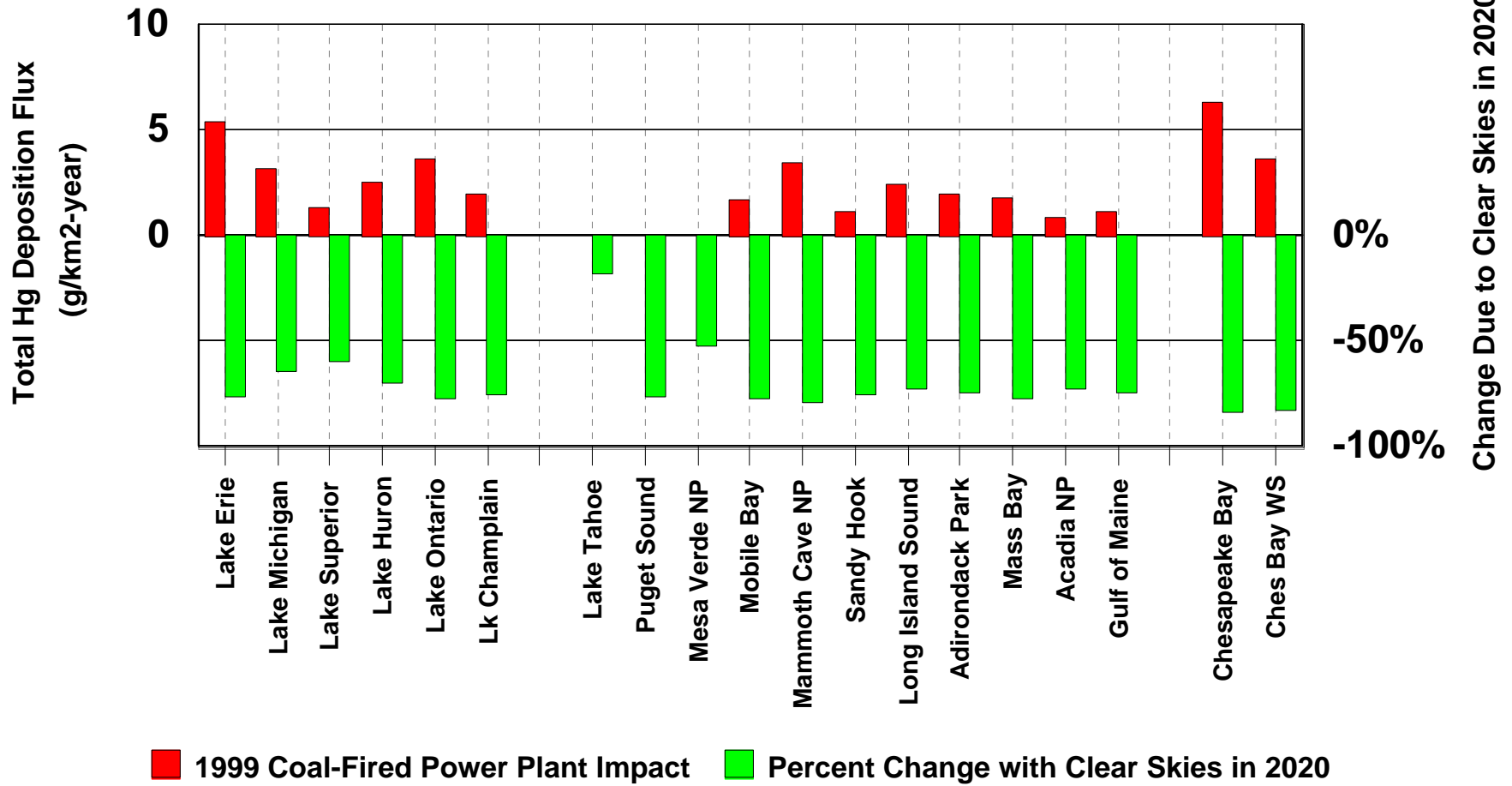
# New Receptors from David Schmeltz, March 2003



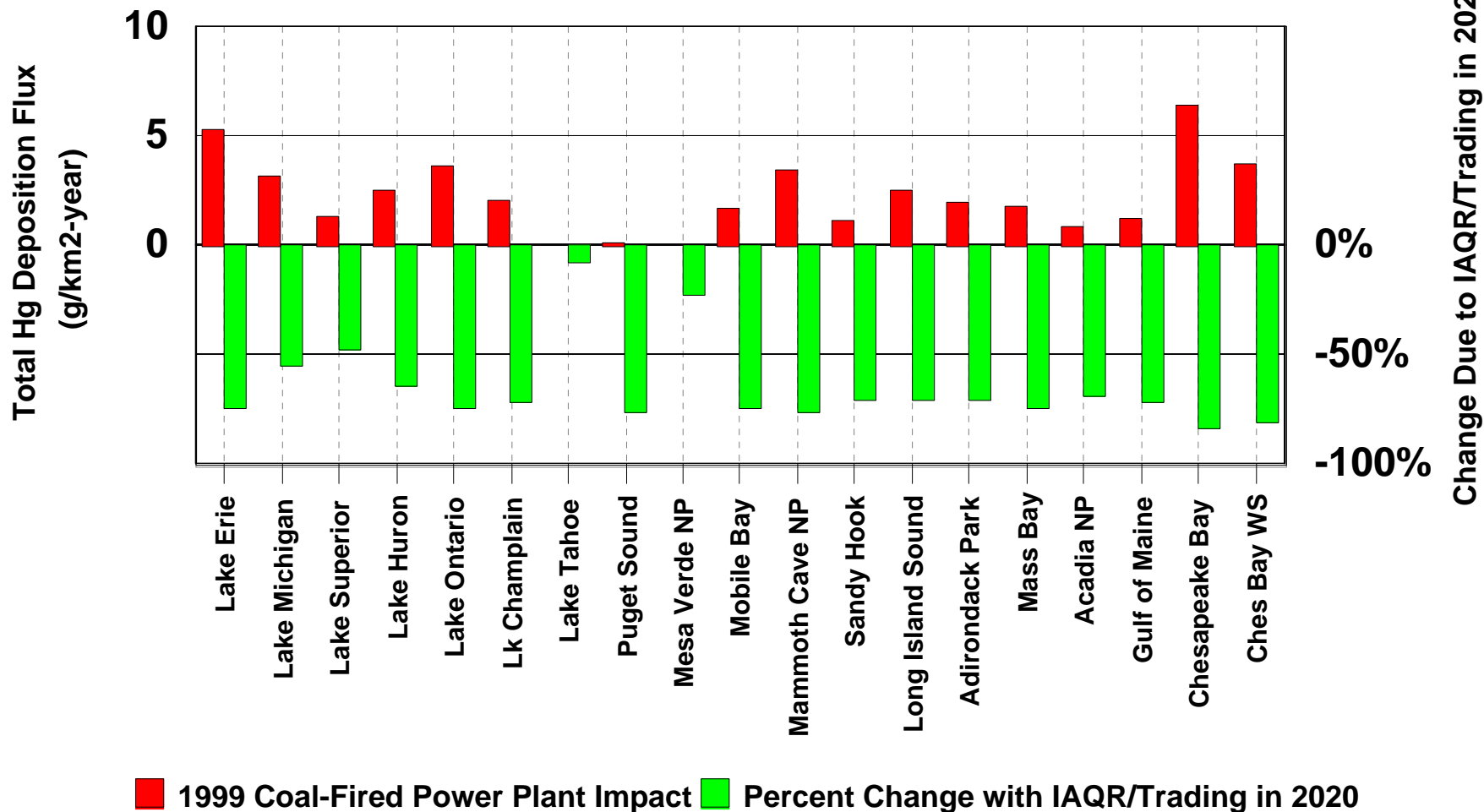
Figure \_\_. Hg Deposition From U.S.  
Coal-Fired Power Plants in 1999



## Hg Deposition from U.S. Coal-Fired Power Plants in 1999 and Percent Change in Impact in 2020 with Clear Skies

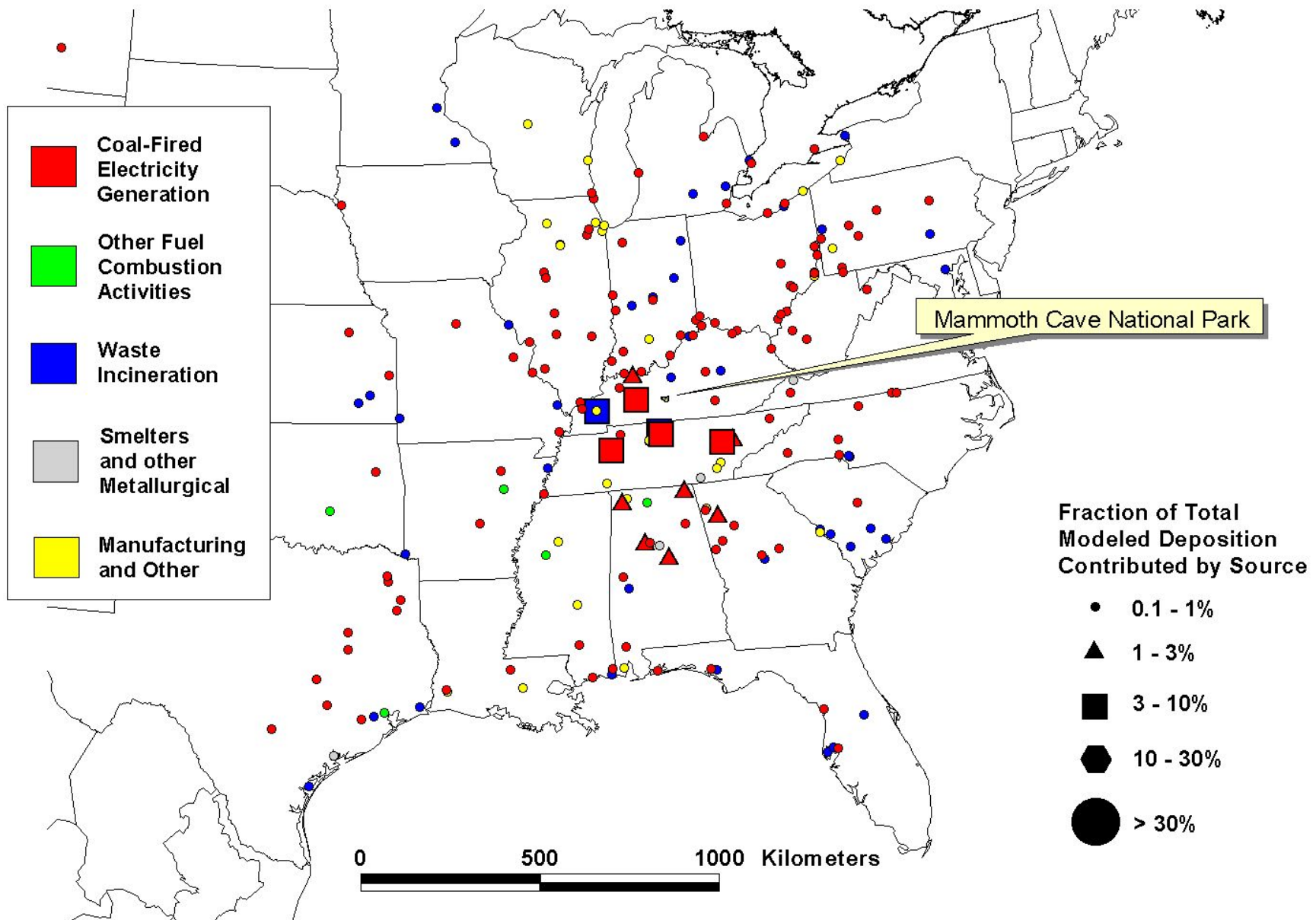


## Hg Deposition from U.S. Coal-Fired Power Plants in 1999 and Percent Change in Impact in 2020 with IAQR/Trading Scenario





**Results for  
Mammoth Cave  
National Park**



Coal-Fired Electricity Generation

Other Fuel Combustion Activities

Waste Incineration

Smelters and other Metallurgical

Manufacturing and Other

Fraction of Total Modeled Deposition Contributed by Source

• 0.1 - 1%

▲ 1 - 3%

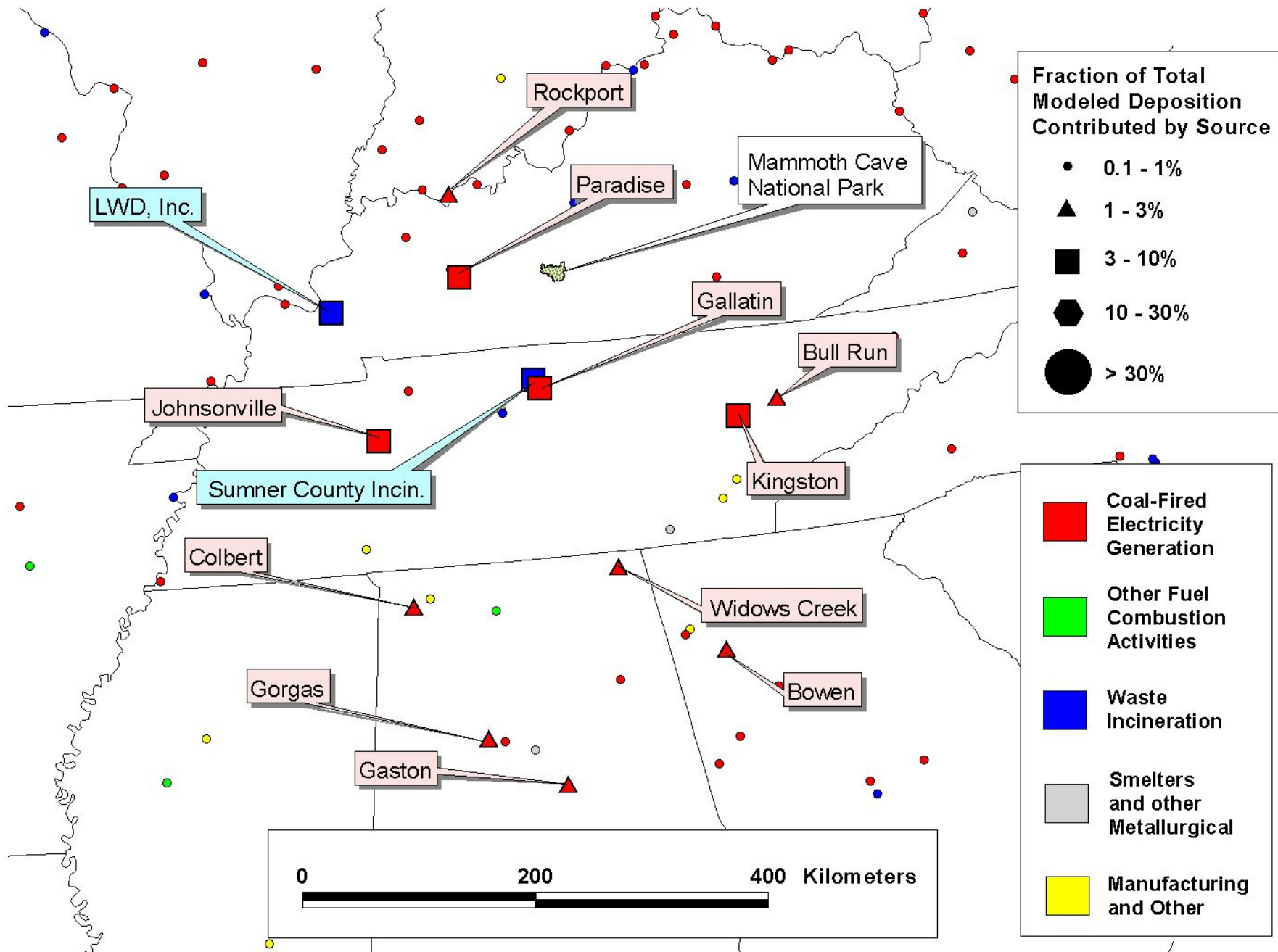
■ 3 - 10%

⬡ 10 - 30%

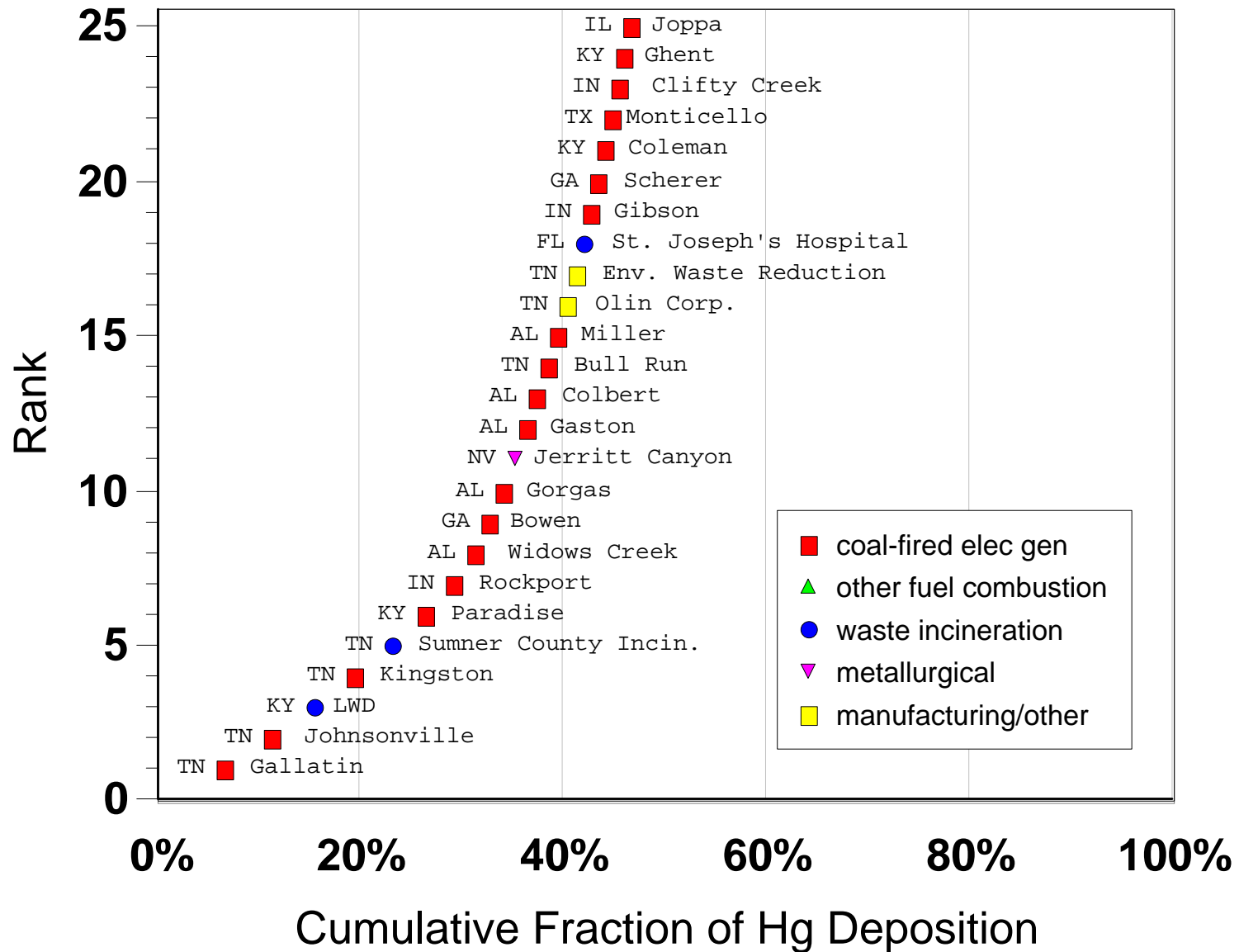
● > 30%

0 500 1000 Kilometers

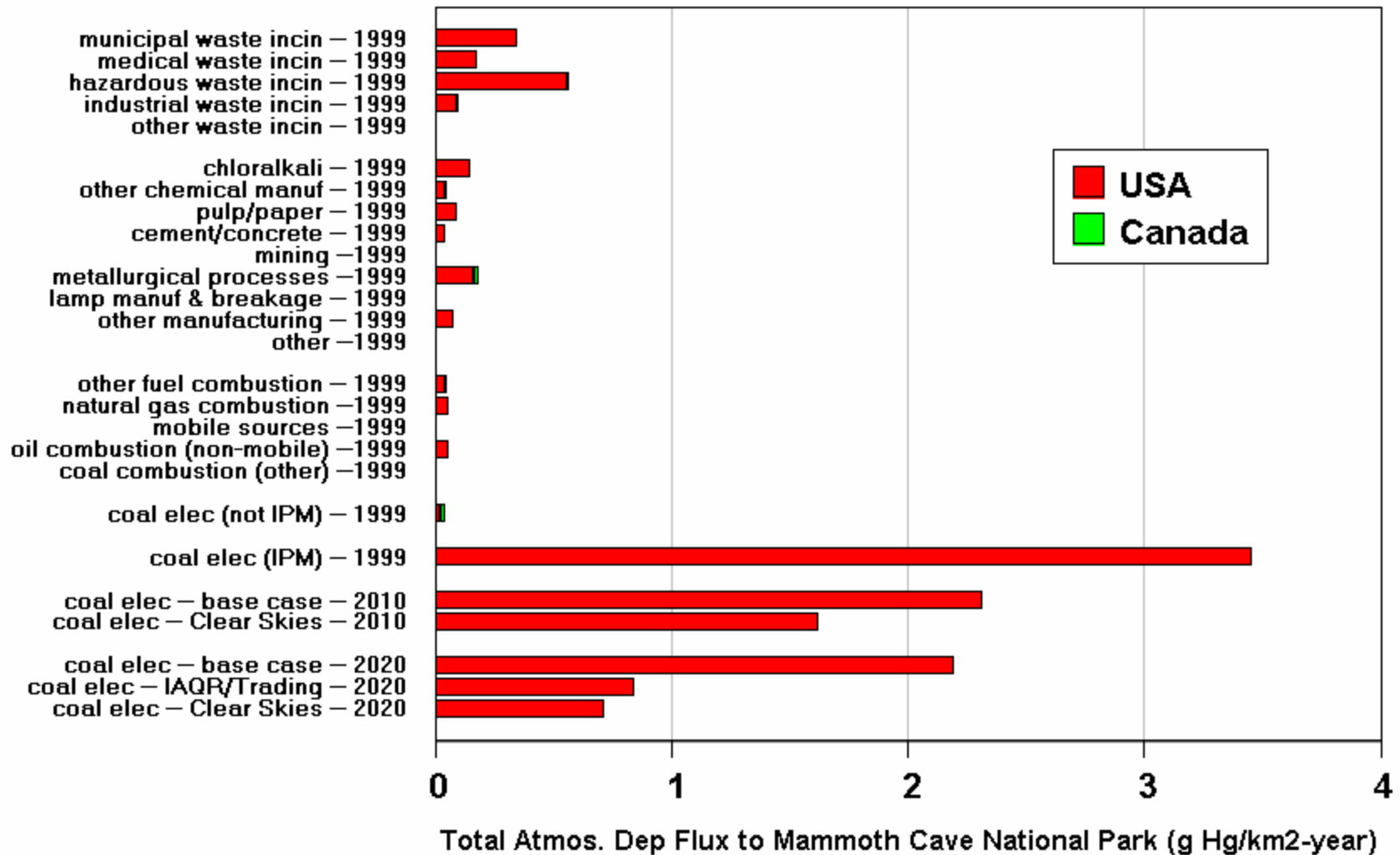
Mammoth Cave National Park



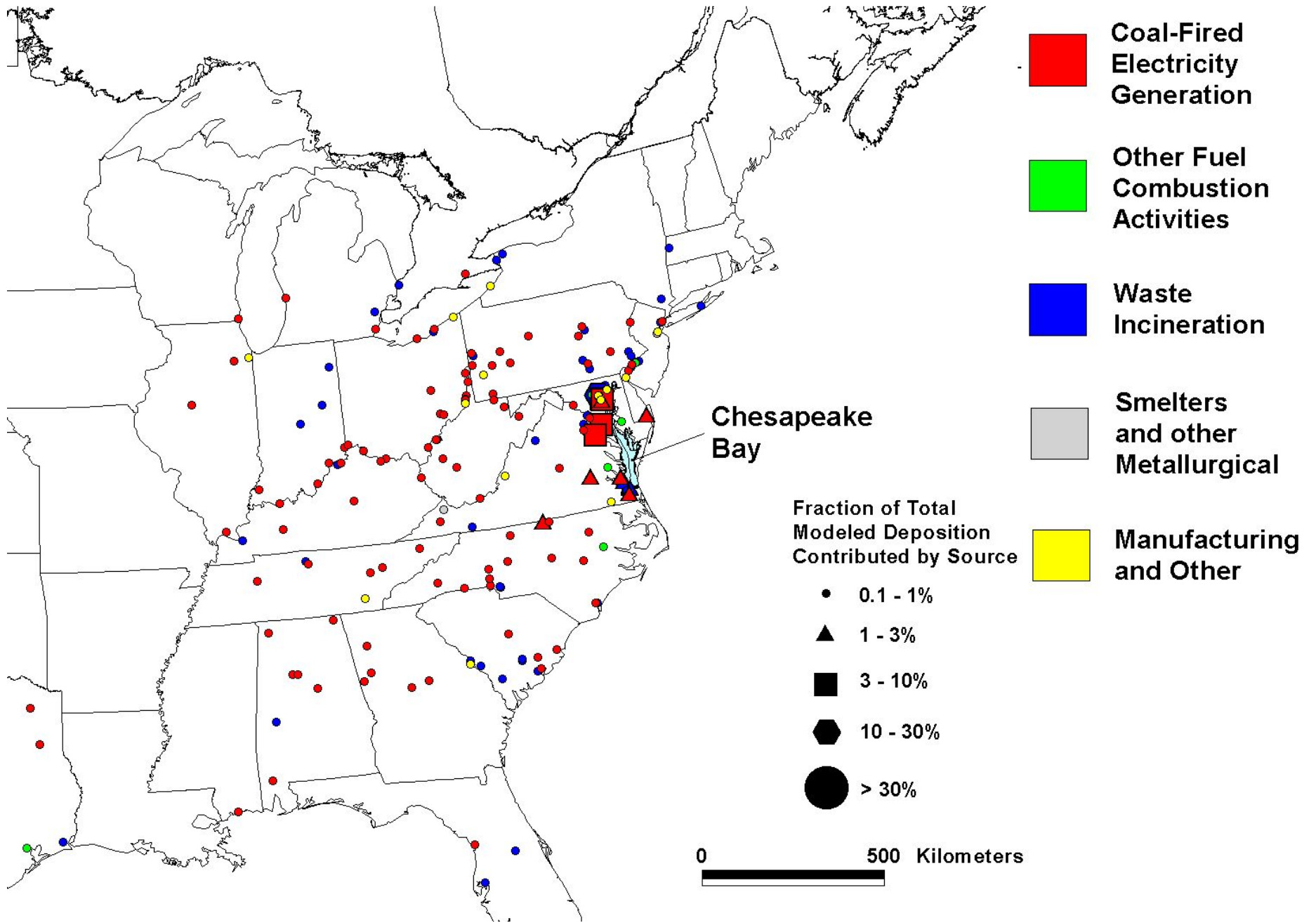
# Top 25 Contributors to Hg Deposition to Mammoth Cave National Park

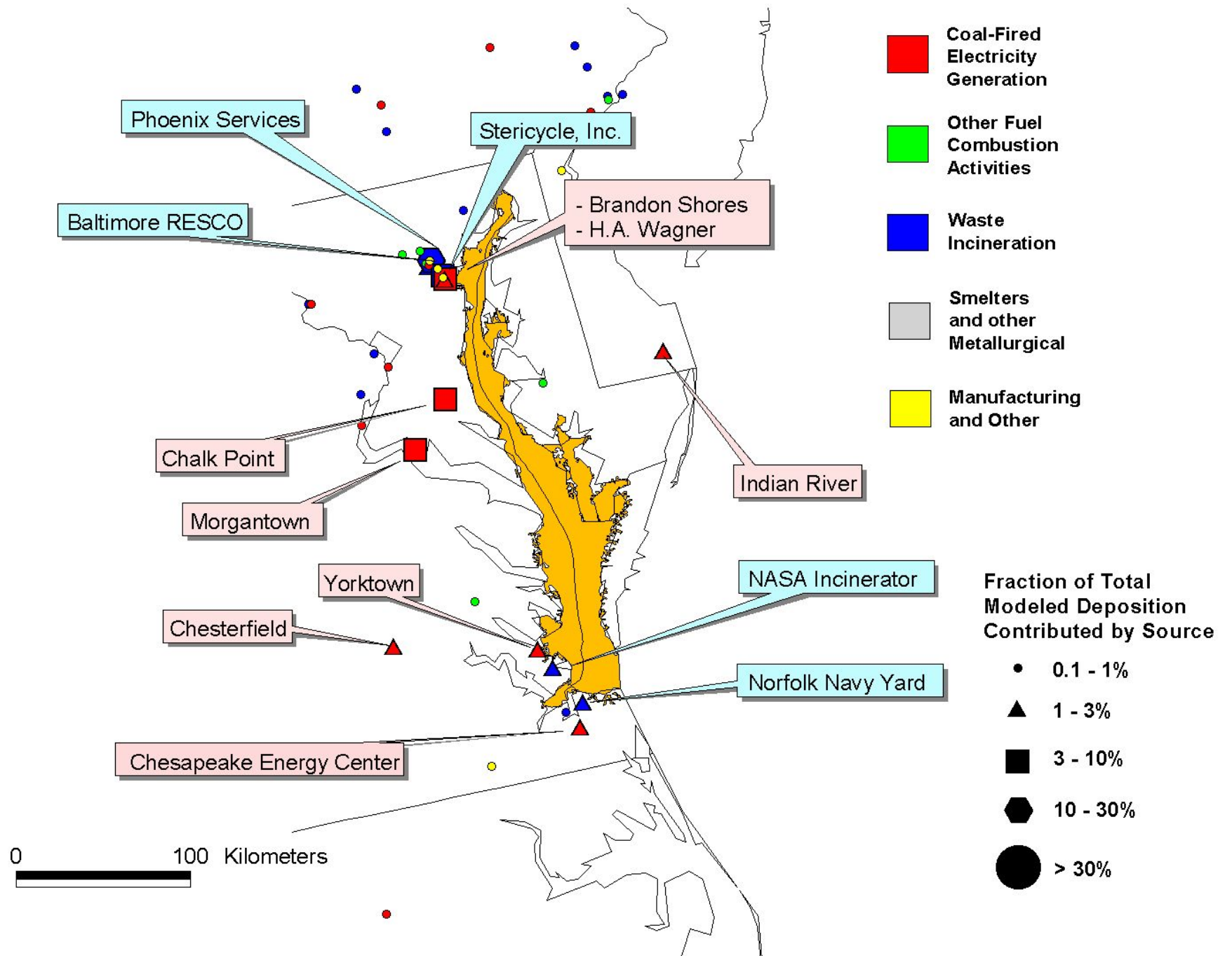


# Atmospheric Deposition Flux to Mammoth Cave National Park from Anthropogenic Mercury Emissions Sources in the U.S. and Canada



# **Results for Chesapeake Bay**

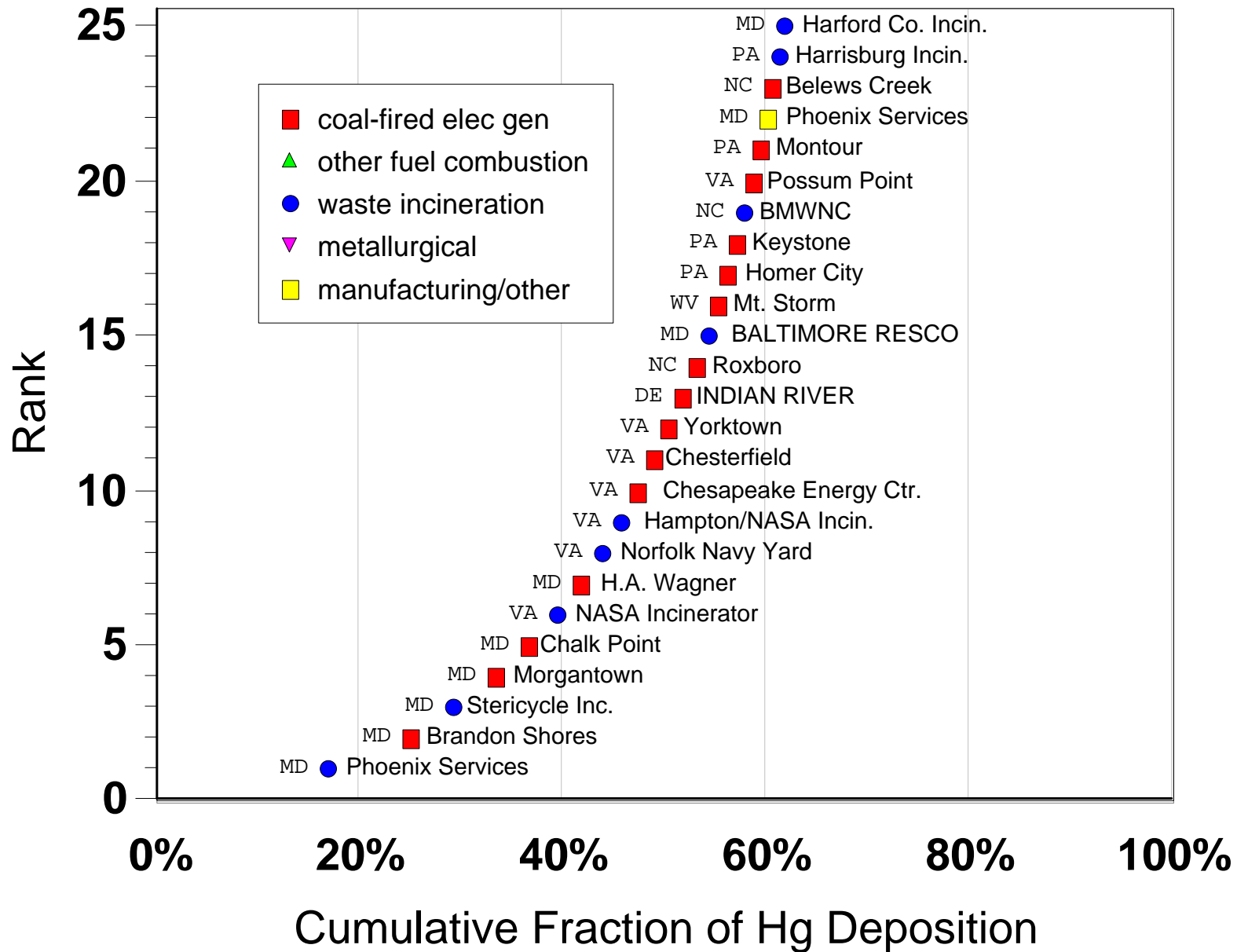




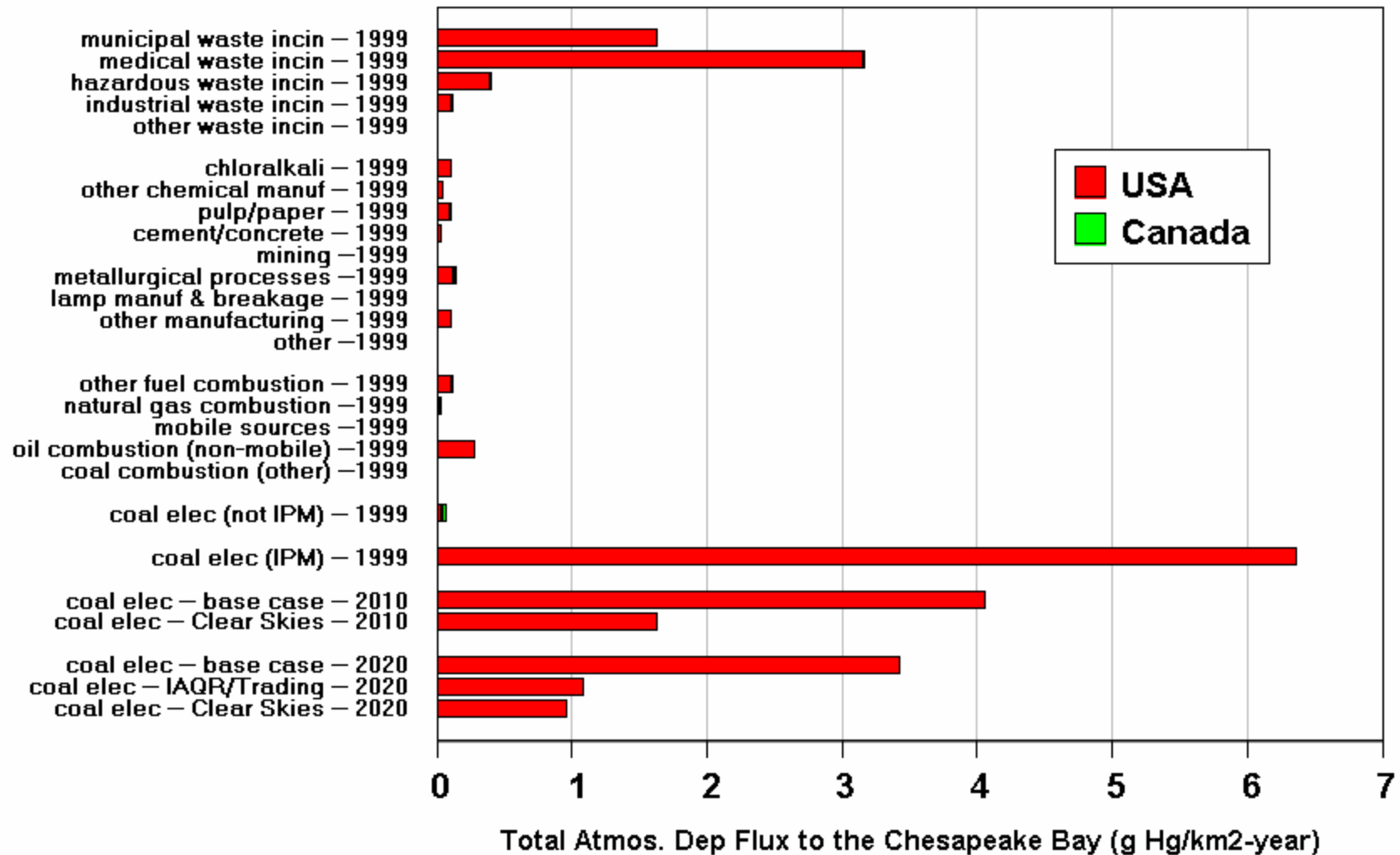
0 100 Kilometers



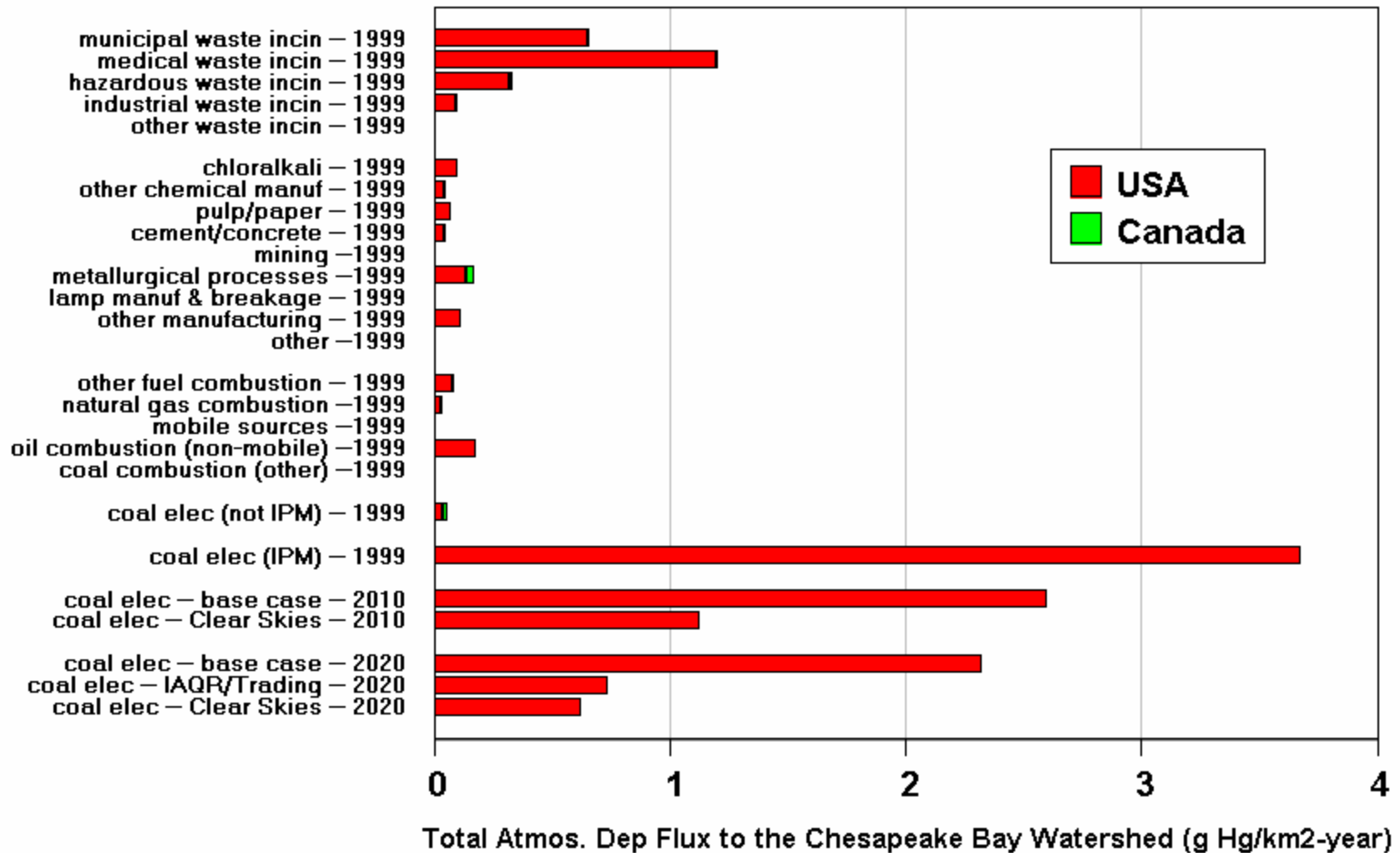
# Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay



# Atmospheric Deposition Flux to the Chesapeake Bay from Anthropogenic Mercury Emissions Sources in the U.S. and Canada



# Atmospheric Deposition Flux to the Chesapeake Bay Watershed from Anthropogenic Mercury Emissions Sources in the U.S. and Canada



# **model evaluation**

# What do atmospheric mercury models need?

**Emissions  
Inventories**

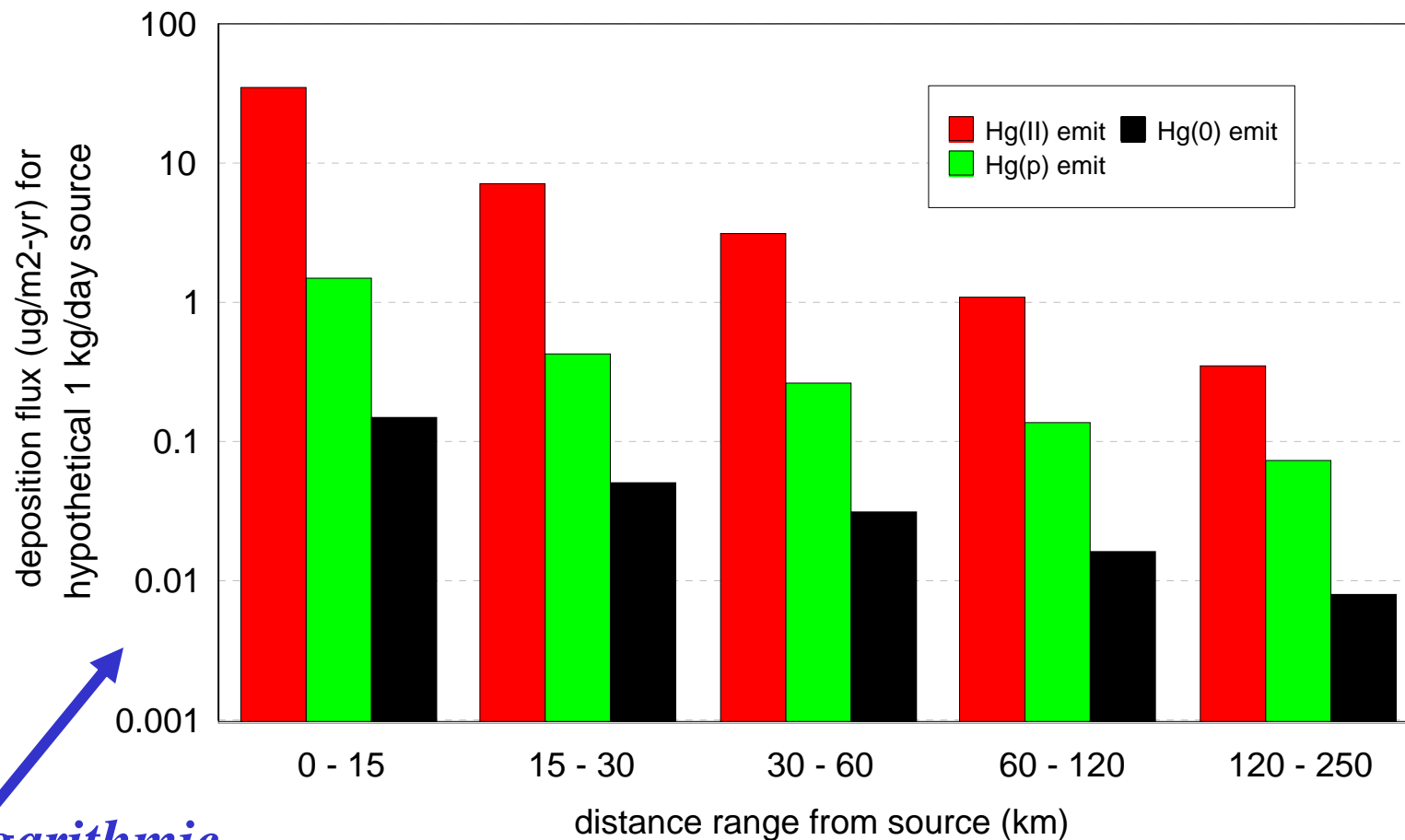
**Meteorological  
Data**

**Scientific understanding of  
phase partitioning,  
atmospheric chemistry,  
and deposition processes**

**Ambient data for comprehensive  
model evaluation and improvement**

	<b>some challenges facing mercury modeling</b>
emissions inventories	<ul style="list-style-type: none"> <li>• need <i>all</i> sources</li> <li>• accurately divided into <i>different Hg forms</i></li> <li>• <b>U.S. 1996, 1999, 2003 / CAN 1995, 2000, 2005</b></li> <li>• <i>temporal</i> variations (e.g. shut downs)</li> </ul>
meteorological data	<ul style="list-style-type: none"> <li>• precipitation not well characterized</li> </ul>
scientific understanding	<ul style="list-style-type: none"> <li>• what is RGM? what is Hg(p)?</li> <li>• accurate info for known reactions?</li> <li>• do we know all significant reactions?</li> <li>• natural emissions, re-emissions?</li> </ul>
ambient data for model evaluation	<ul style="list-style-type: none"> <li>• Mercury Deposition Network (MDN) is great, but:</li> <li>• also need RGM, Hg(p), and Hg(0) concentrations</li> <li>• also need data above the surface (e.g., from aircraft)</li> <li>• also need source-impacted sites (not just background)</li> </ul>

# Why is emissions speciation information critical?



*Logarithmic*

*Hypothesized rapid reduction of Hg(II) in plumes?  
If true, then dramatic impact on modeling results...*

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# Atmospheric Chemical Reaction Scheme for Mercury

Reaction	Rate	Units	Reference
<b><i>GAS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg(p)}$	3.0E-20	cm <sup>3</sup> /molec-sec	Hall (1995)
$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1.0E-19	cm <sup>3</sup> /molec-sec	Hall and Bloom (1993)
$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg(p)}$	8.5E-19	cm <sup>3</sup> /molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	4.0E-18	cm <sup>3</sup> /molec-sec	Calhoun and Prestbo (2001)
$\text{Hg}^0 + \text{OHC} \rightarrow \text{Hg(p)}$	8.7E-14	cm <sup>3</sup> /molec-sec	Sommar et al. (2001)
<b><i>AQUEOUS PHASE REACTIONS</i></b>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2}$	4.7E+7	(molar-sec) <sup>-1</sup>	Munthe (1992)
$\text{Hg}^0 + \text{OHC} \rightarrow \text{Hg}^{+2}$	2.0E+9	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1997)
$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T * e^{((31.971 * T) - 12595.0) / T} \text{ sec}^{-1}$ [T = temperature (K)]		Van Loon et al. (2002)
$\text{Hg(II)} + \text{HO}_2\text{C} \rightarrow \text{Hg}^0$	~ 0	(molar-sec) <sup>-1</sup>	Gardfeldt & Jonnson (2003)
$\text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2}$	2.1E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2}$	2.0E+6	(molar-sec) <sup>-1</sup>	Lin and Pehkonen(1998)
$\text{Hg(II)} \leftrightarrow \text{Hg(II)}_{(\text{soot})}$	9.0E+2	liters/gram; t = 1/hour	eqnbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$\text{Hg}^{+2} + \text{h} \leftrightarrow \text{Hg}^0$	6.0E-7	(sec) <sup>-1</sup> (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

	<b>some challenges facing mercury modeling</b>
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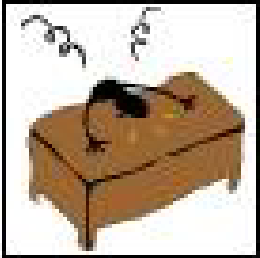
# Some Additional Measurement Issues (from a modeler's perspective)

- **Data availability**
- **Simple vs. Complex Measurements**

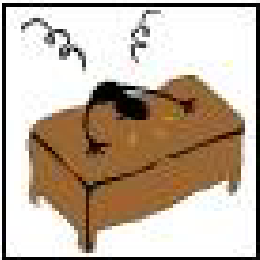
# Some Additional Measurement Issues (from a modeler's perspective)

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- **Simple vs. Complex Measurements**

# Data availability



A major impediment to evaluating and improving atmospheric Hg models has been the lack of speciated Hg air concentration data



There have been very few measurements to date, and these data are rarely made available in a practical way (timely, complete, etc.)



The data being collected at Piney Reservoir could be extremely helpful!

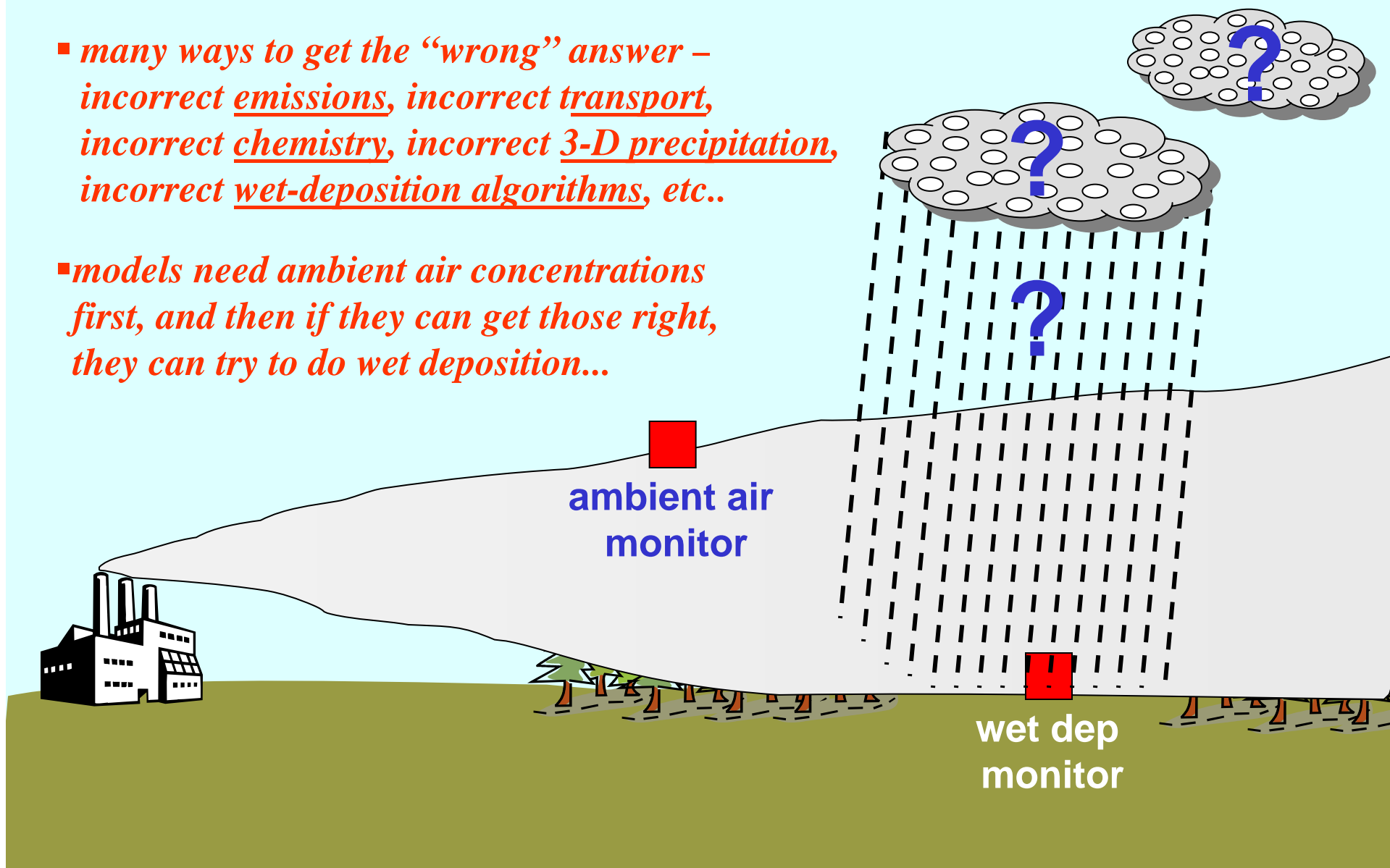
# Some Additional Measurement Issues (from a modeler's perspective)

- **Data availability**
- **Simple vs. Complex Measurements**

## Simple vs. Complex Measurements:

### 1. Wet deposition is a very complicated phenomena...

- *many ways to get the “wrong” answer – incorrect emissions, incorrect transport, incorrect chemistry, incorrect 3-D precipitation, incorrect wet-deposition algorithms, etc..*
- *models need ambient air concentrations first, and then if they can get those right, they can try to do wet deposition...*

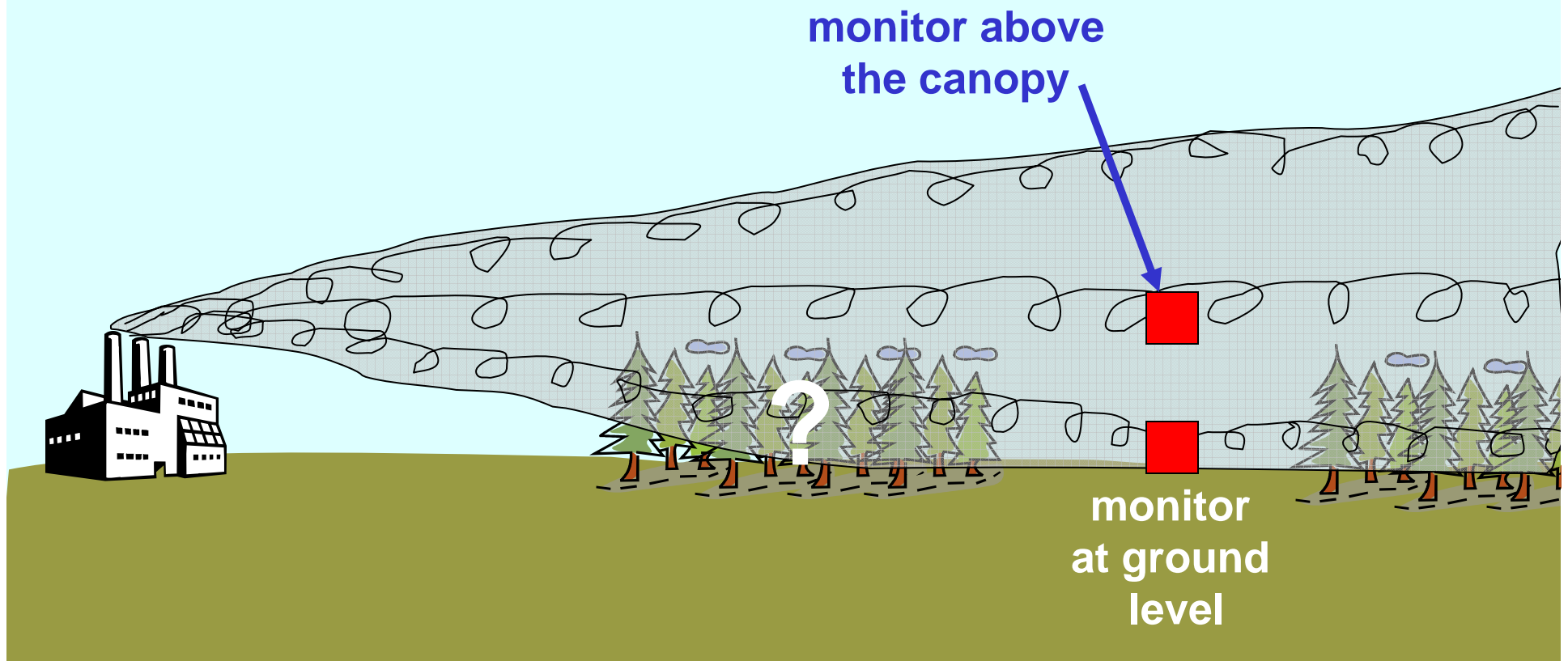




## Simple vs. Complex Measurements:

### 2. Potential complication with ground-level monitors... (“fumigation”, “filtration”, etc.)...

- *atmospheric phenomena are complex and not well understood;*
- *models need “simple” measurements for diagnostic evaluations;*
- *ground-level data for rapidly depositing substances (e.g., RGM) hard to interpret*
- *elevated platforms might be more useful (at present level of understanding)*



### **Simple vs. Complex measurements - 3. Urban areas:**

- a. Emissions inventory poorly known**
- b. Meteorology very complex (flow around buildings)**
- c. So, measurements in urban areas not particularly useful for current large-scale model evaluations**



## Simple vs. Complex Measurements – 4: extreme near-field measurements



- Sampling near intense sources?
- Must get the fine-scale met “perfect”

Ok, if one wants to develop hypotheses regarding *whether or not this is actually a source of the pollutant (and you can't do a stack test for some reason!)*.

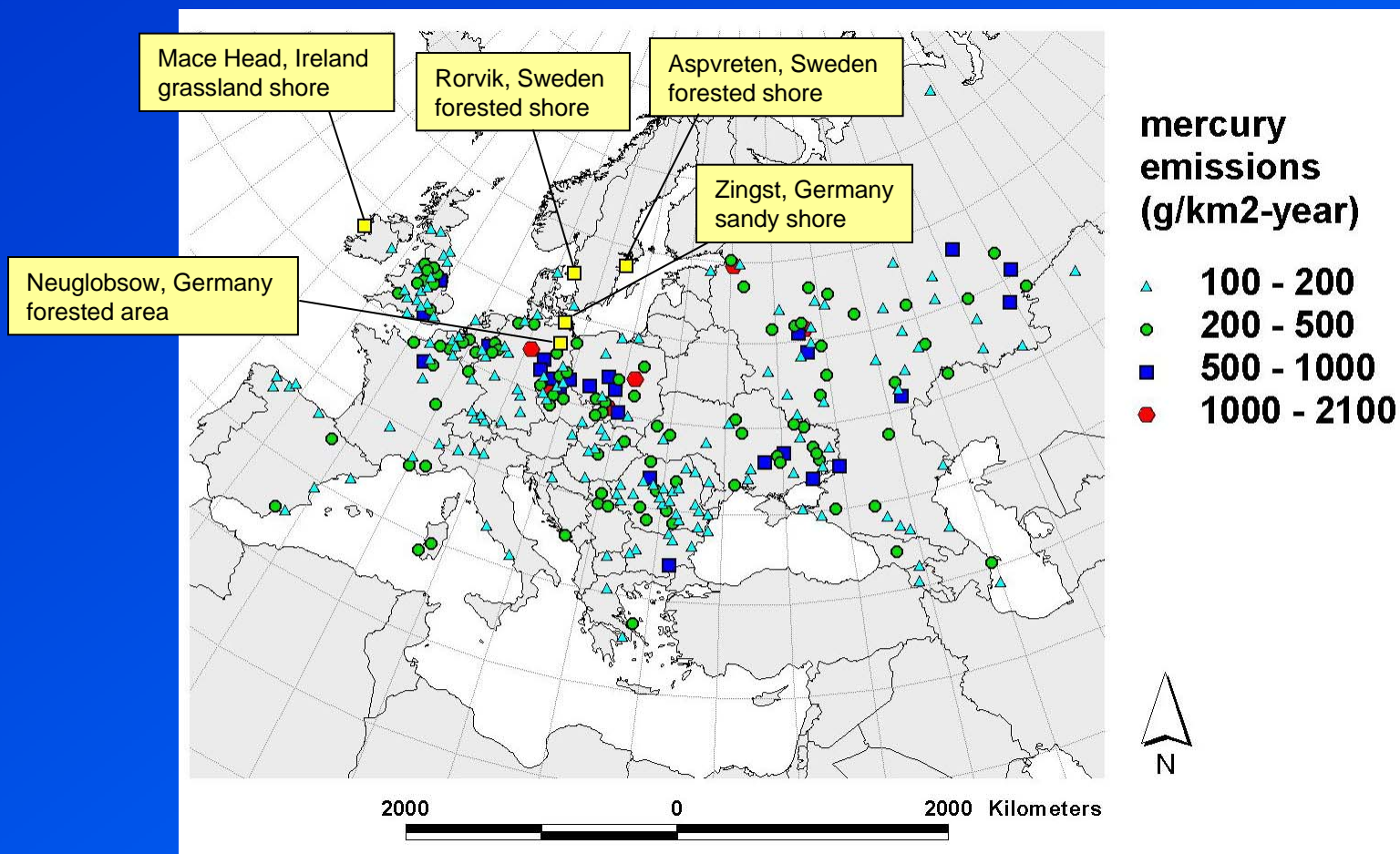
## **Complex vs. Simple Measurements – 5: Need some source impacted measurements**

- **Major questions regarding plume chemistry and near-field impacts (are there “hot spots”?)**
- **Most monitoring sites are designed to be “regional background” sites (e.g., most Mercury Deposition Network sites).**
- **We need some source-impacted sites as well to help resolve near-field questions**
- *But not too close – maybe 20-30 km is ideal (?)*

Intro- duction	Stage I	Stage II			Stage III			Conclu- sions
	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	

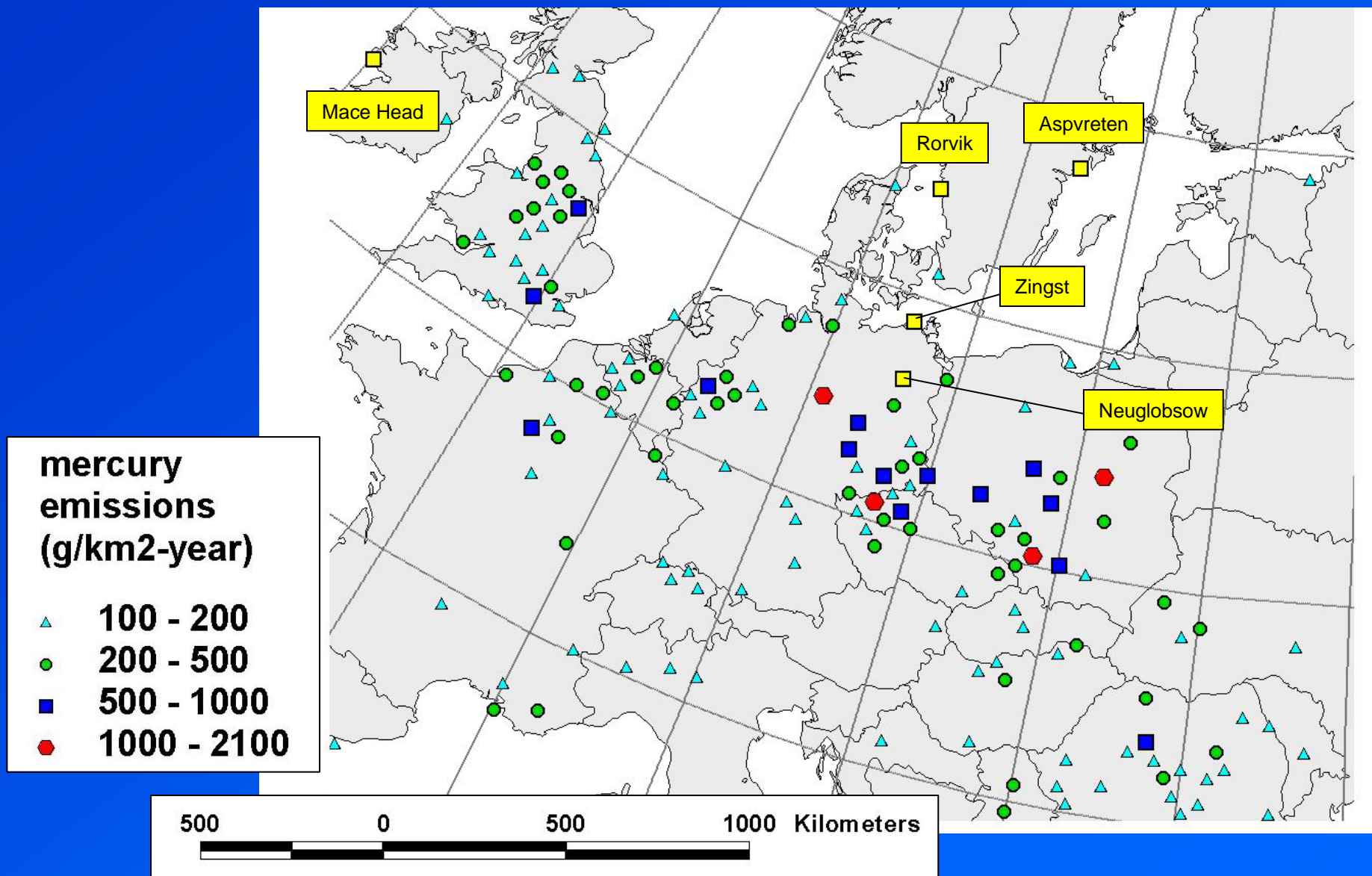
## Anthropogenic Mercury Emissions Inventory and Monitoring Sites for Phase II

(note: only showing largest emitting grid cells)



*EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury*

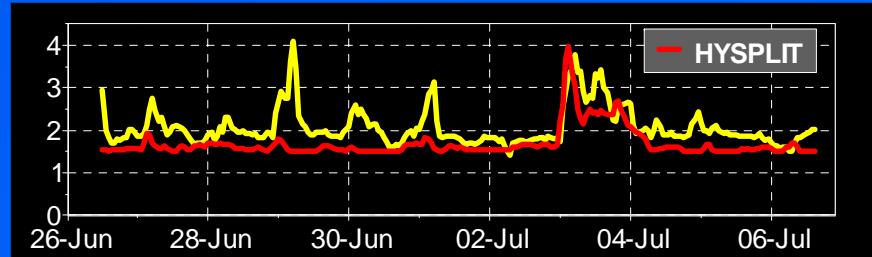
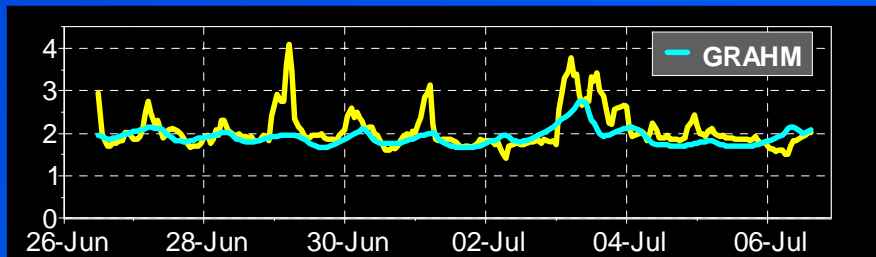
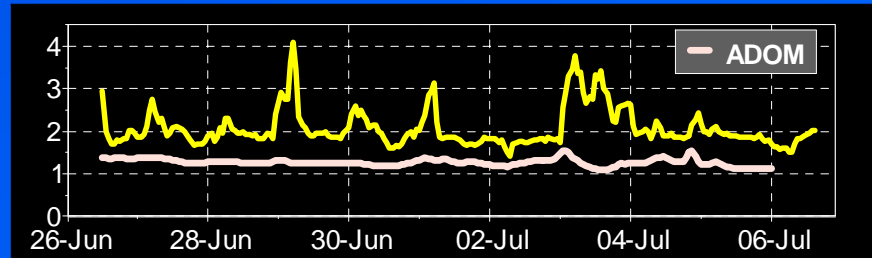
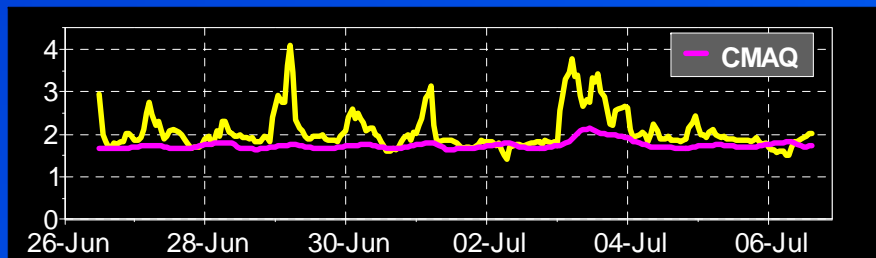
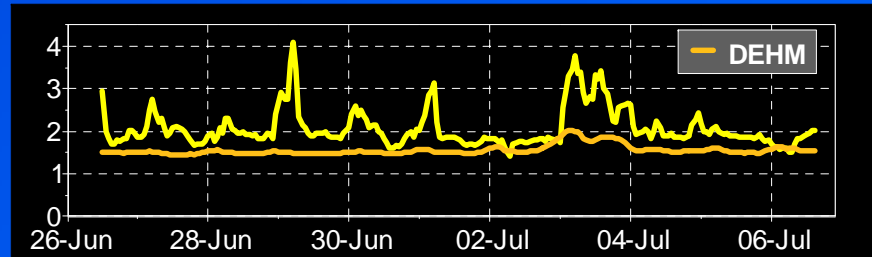
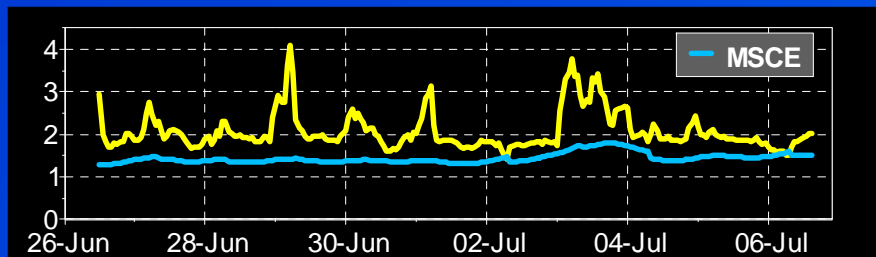
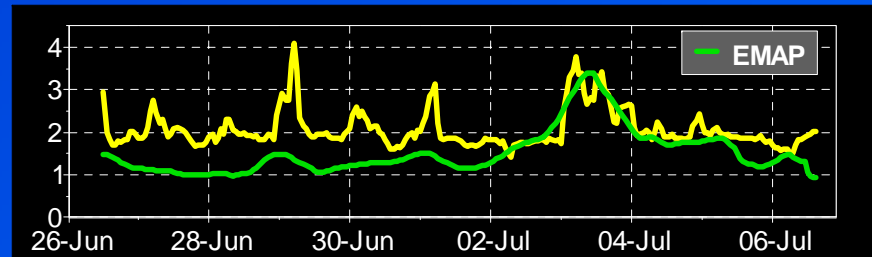
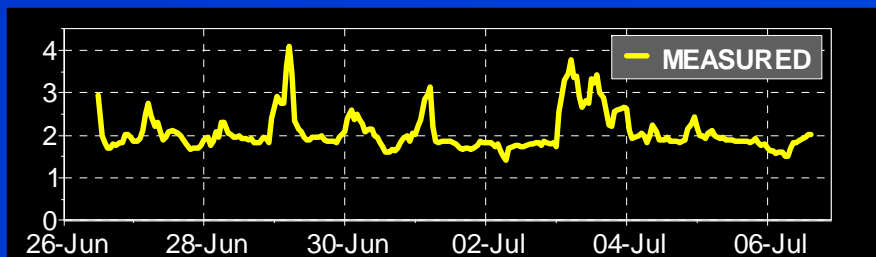
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	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	



*EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury*

Intro- duction	Stage I	Stage II			Stage III			Conclu- sions
	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	

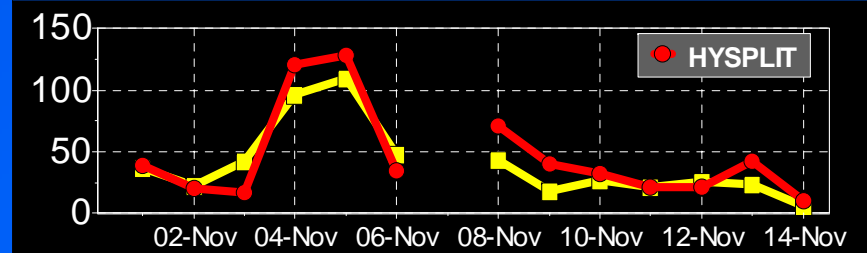
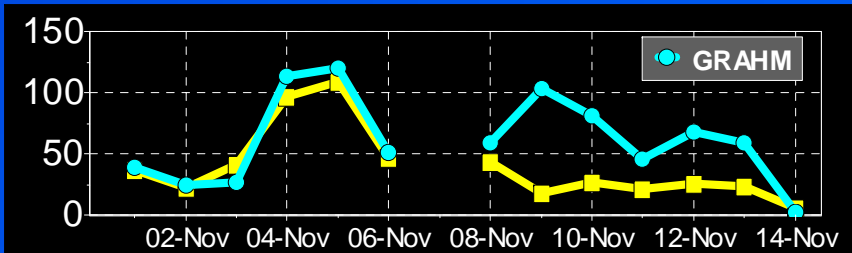
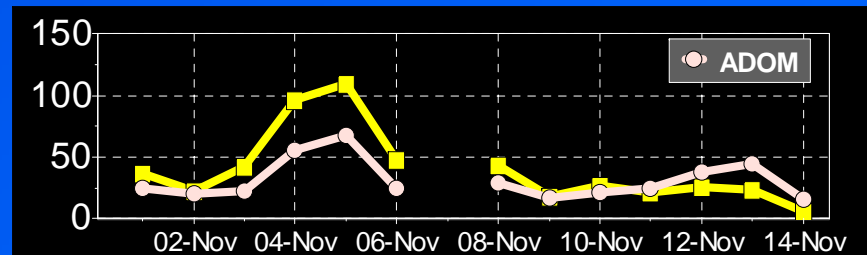
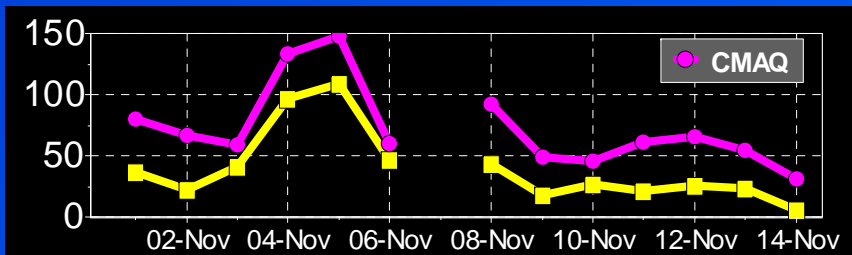
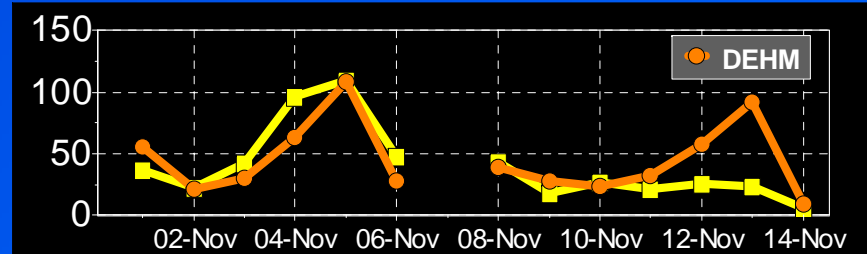
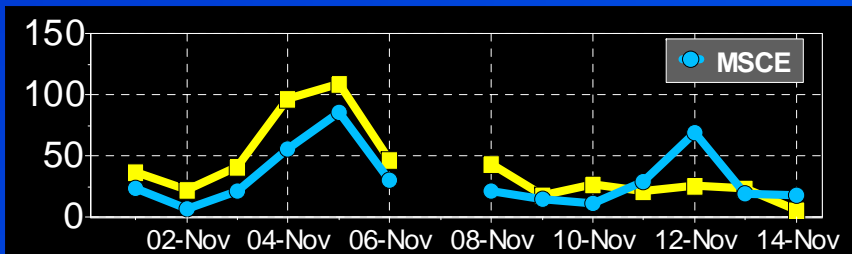
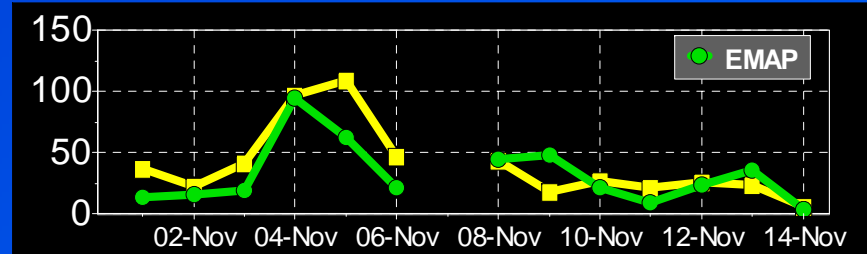
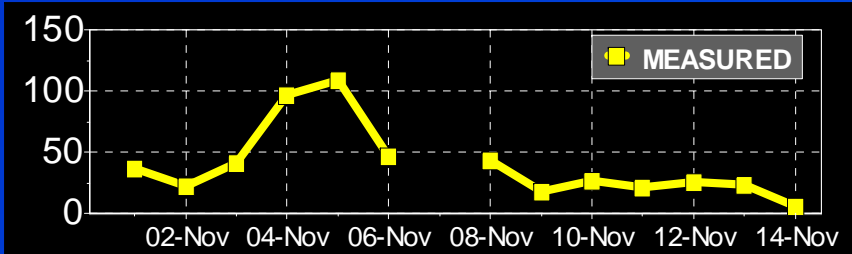
**Total Gaseous Mercury (ng/m<sup>3</sup>) at Neuglobsow: June 26 – July 6, 1995**



*EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury*

Intro- duction	Stage I	Stage II			Stage III			Conclu- sions
	Chemistry	Hg <sup>0</sup>	Hg(p)	RGM	Wet Dep	Dry Dep	Budgets	

**Total *Particulate* Mercury (pg/m<sup>3</sup>) at Neuglobsow, Nov 1-14, 1999**

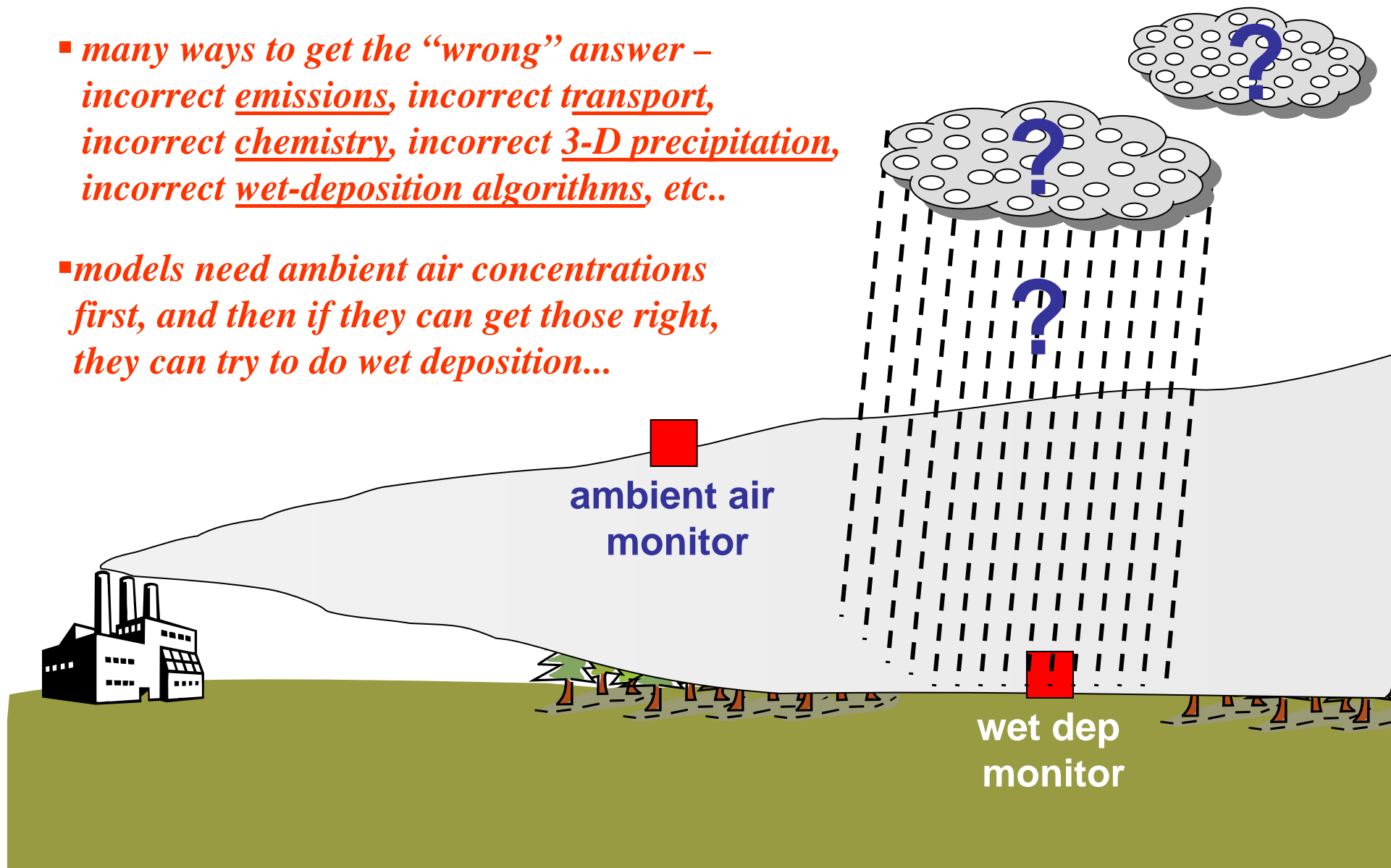


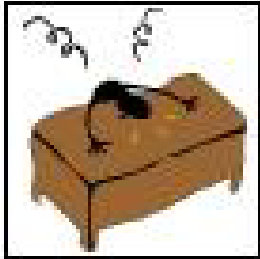


## Simple vs. Complex Measurements:

### 1. Wet deposition is a very complicated phenomena...

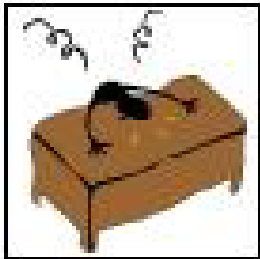
- *many ways to get the “wrong” answer – incorrect emissions, incorrect transport, incorrect chemistry, incorrect 3-D precipitation, incorrect wet-deposition algorithms, etc..*
- *models need ambient air concentrations first, and then if they can get those right, they can try to do wet deposition...*





**speciated ambient concentration data is scarce**

- *few measurement sites at ground level*
- *very few measurements aloft*



**therefore, atmospheric mercury models have not really been comprehensively evaluated yet**

- *we don't really know how good or bad they are*



**collaboration between measurement and modeling community is key**

- *measurers need modelers to help interpret data*
- *modelers need measurements to evaluate models*

**model  
intercomparison**

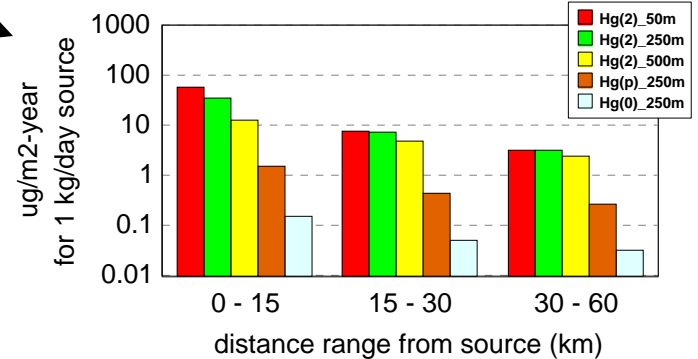
# HYSPLIT 1996



# ISC: 1990-1994

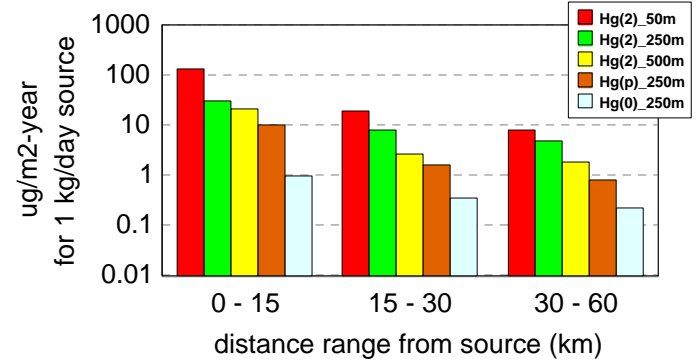


Wet + Dry Deposition: HYSPLIT (Nebraska)  
for emissions of different mercury forms from different stack heights

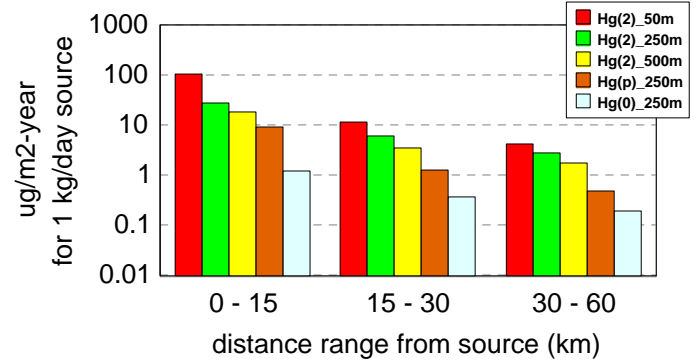


**Different Time Periods and Locations, but Similar Results**

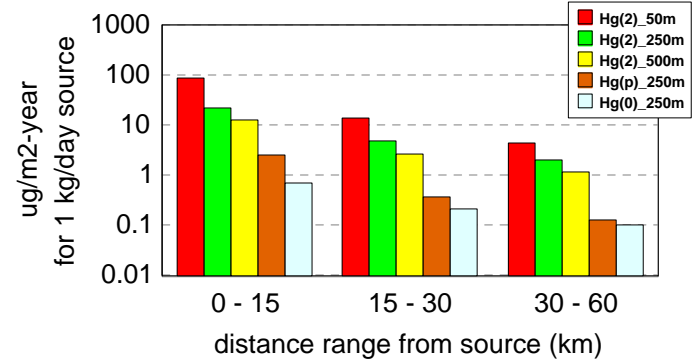
Wet + Dry Deposition: ISC (Kansas City)  
for emissions of different mercury forms from different stack heights



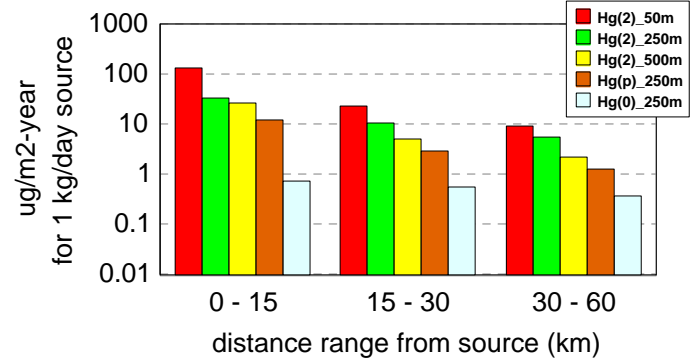
Wet + Dry Deposition: ISC (Tampa)  
for emissions of different mercury forms from different stack heights

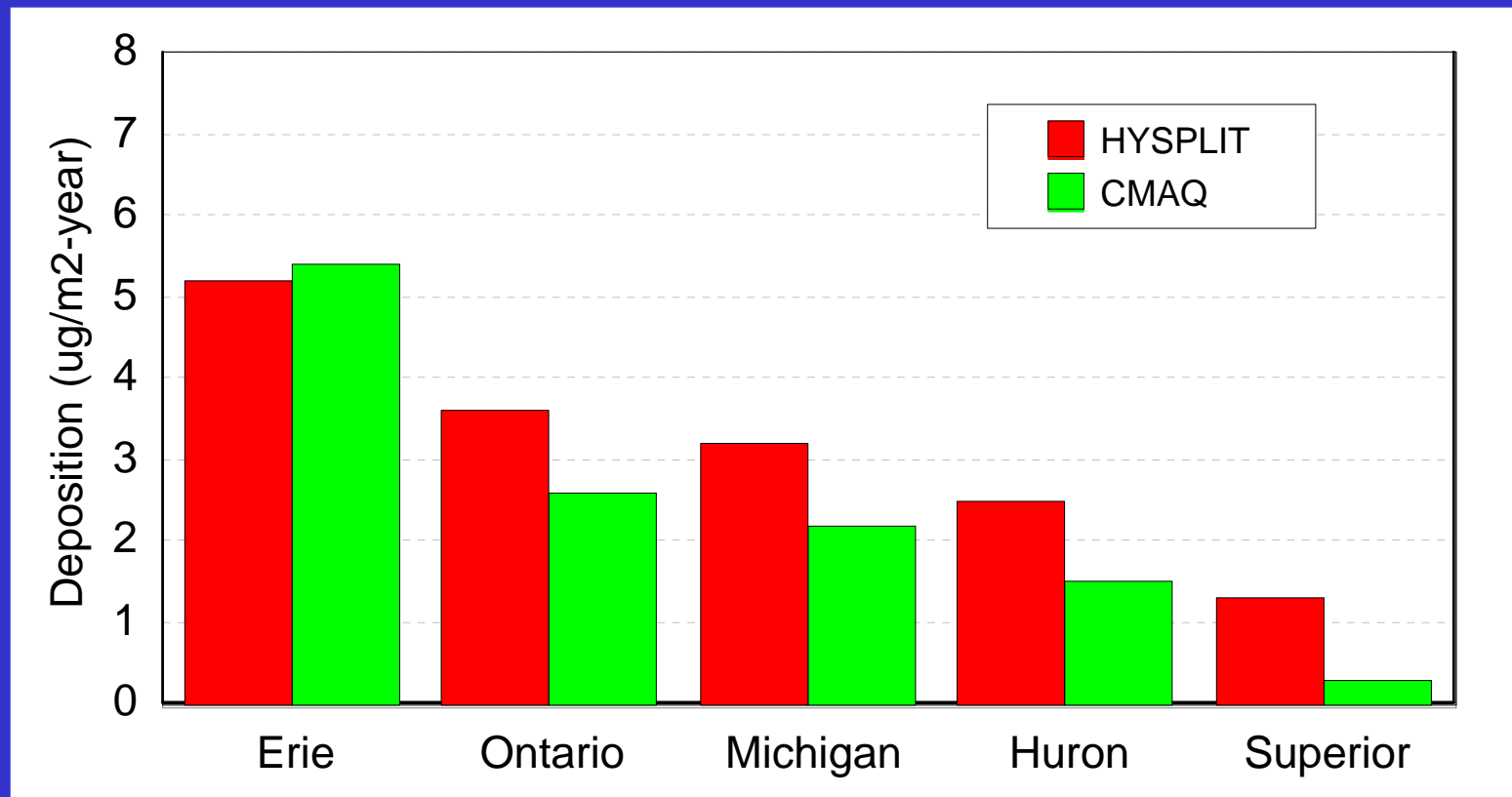


Wet + Dry Deposition: ISC (Phoenix)  
for emissions of different mercury forms from different stack heights

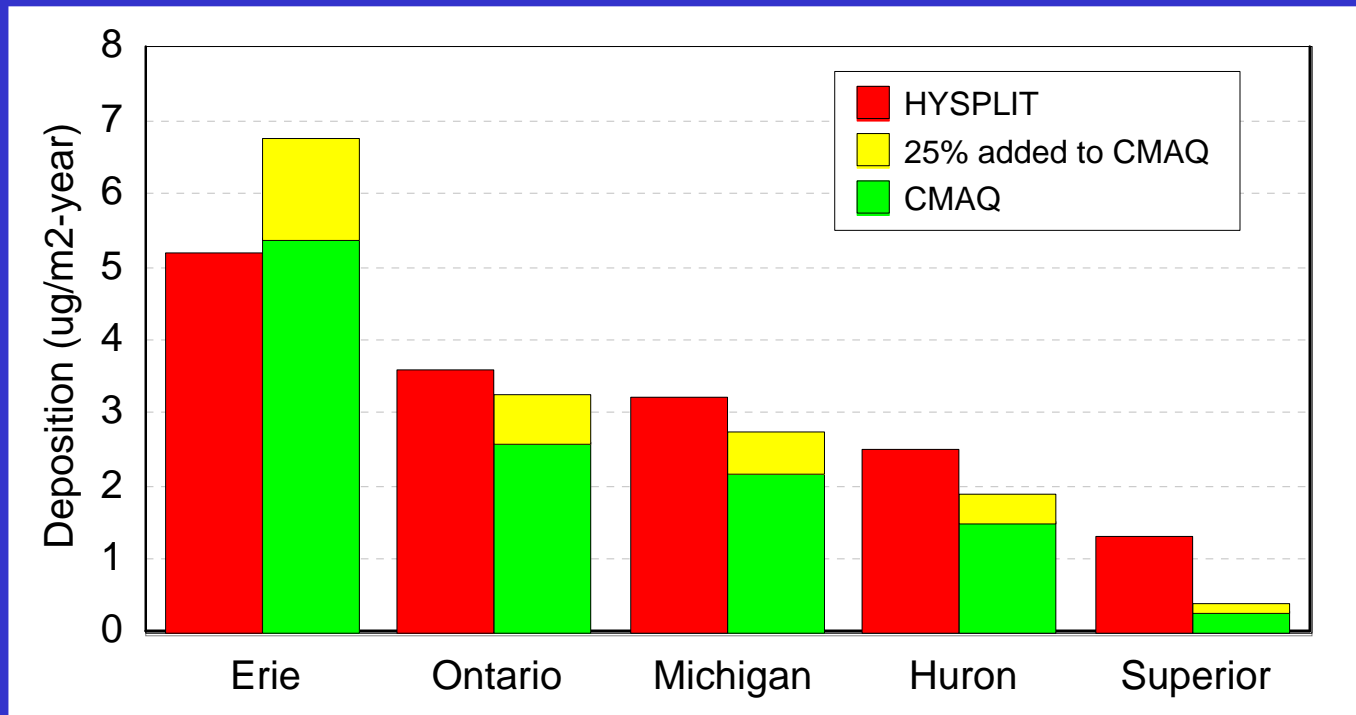


Wet + Dry Deposition: ISC (Indianapolis)  
for emissions of different mercury forms from different stack heights





**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.

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