

# Modeling the Atmospheric Transport and Deposition of Mercury

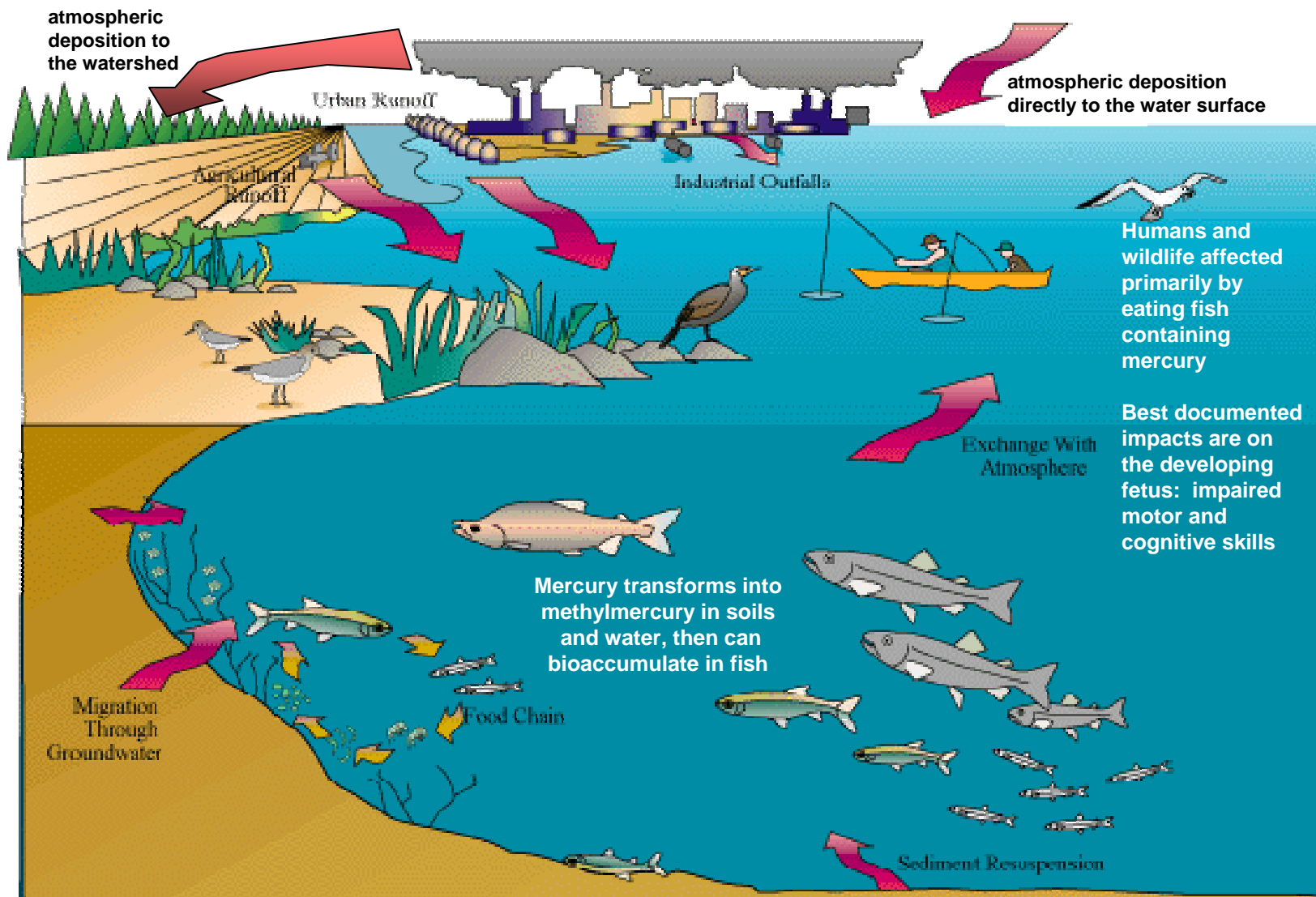


**Dr. Mark Cohen**  
**NOAA Air Resources Laboratory**  
**Silver Spring, Maryland**



**Materials assembled for a discussion with**  
**Maryland Department of the Environment,**  
**Baltimore MD, August 25, 2005**

**There are many ways in which mercury is introduced into a given aquatic ecosystem... atmospheric deposition can be a very significant pathway**



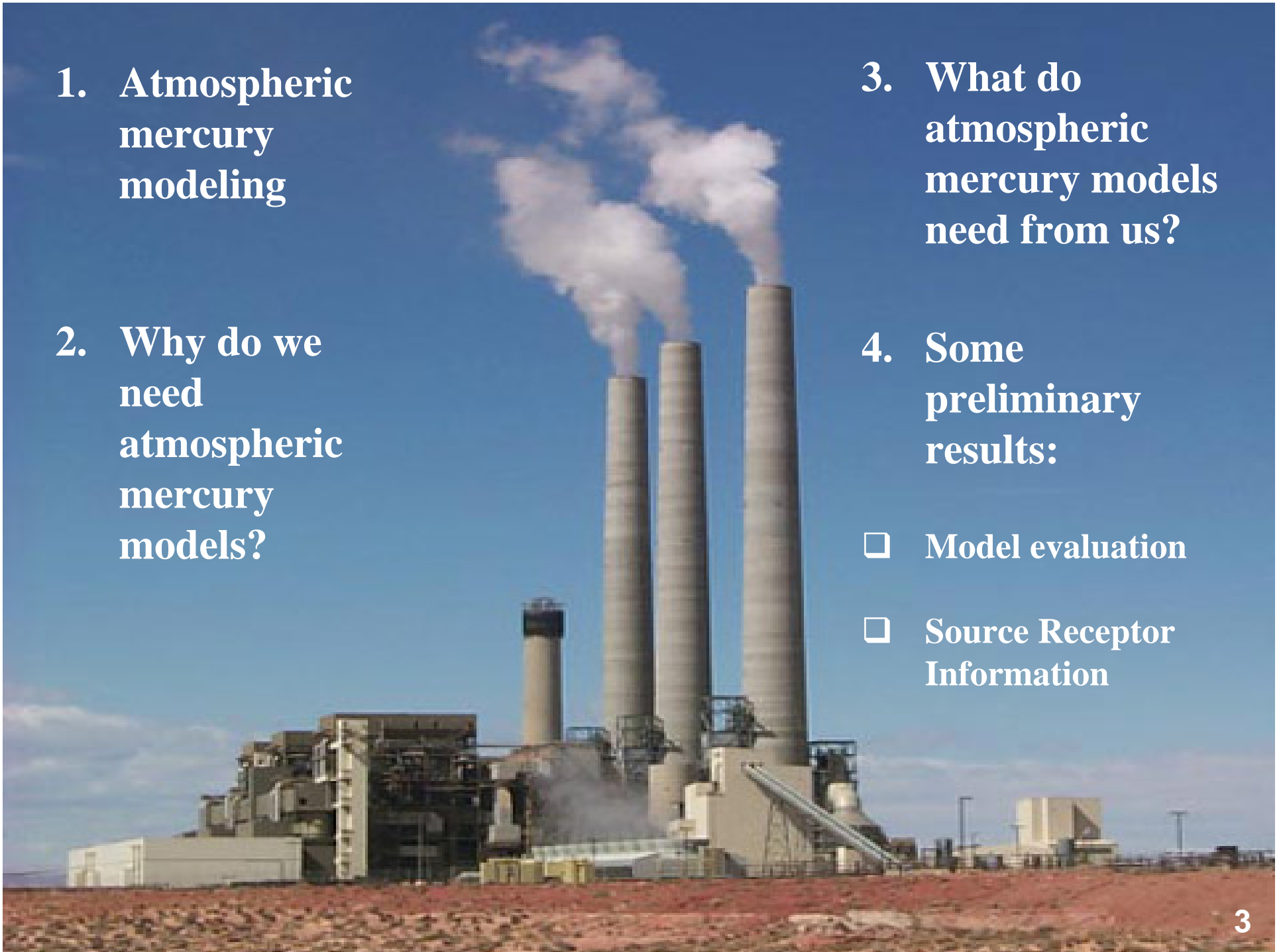
**1. Atmospheric mercury modeling**

**2. Why do we need atmospheric mercury models?**

**3. What do atmospheric mercury models need from us?**

**4. Some preliminary results:**

- Model evaluation
- Source Receptor Information



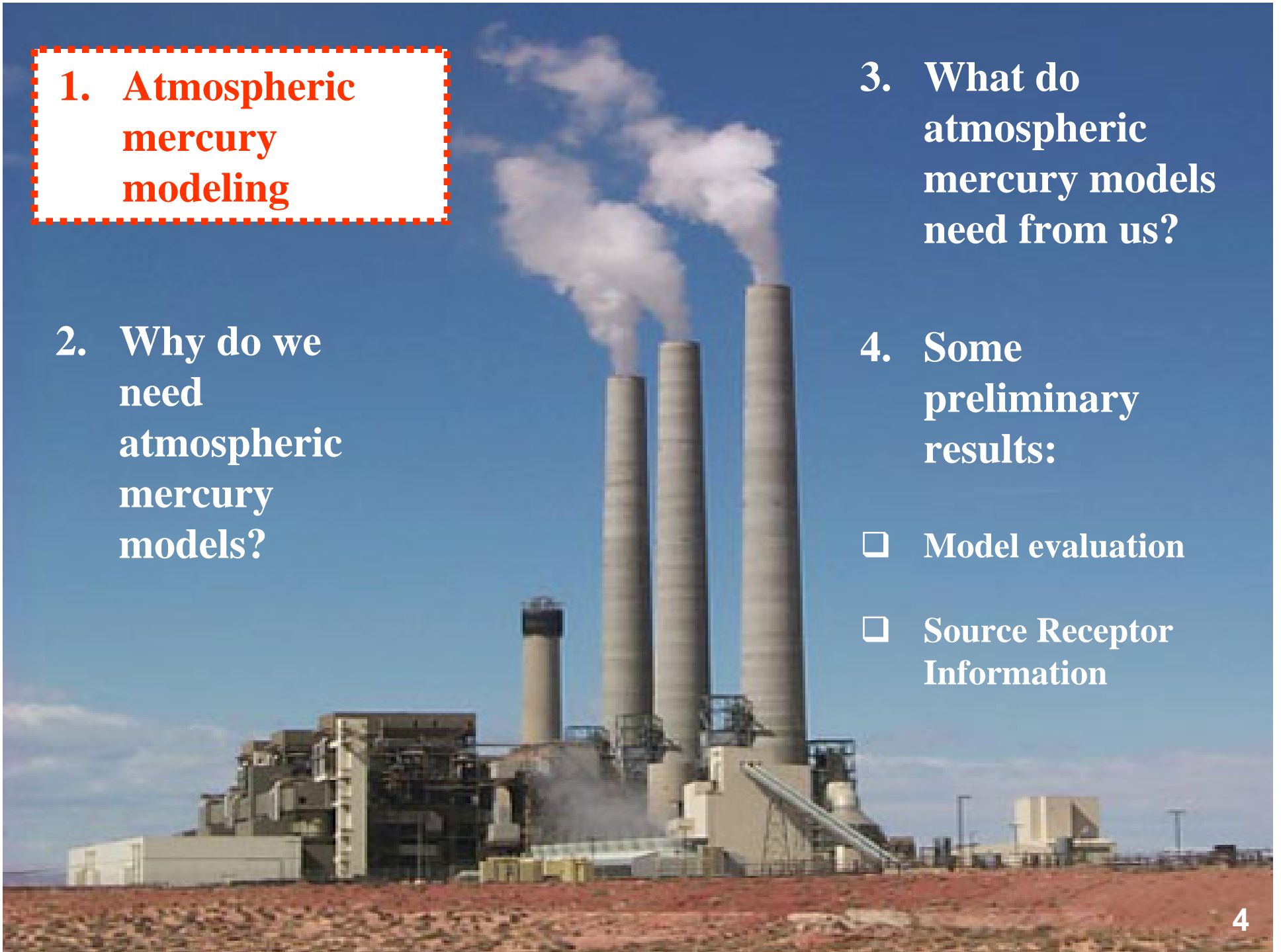
# 1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results:

- Model evaluation
- Source Receptor Information



# Three “forms” of atmospheric mercury



## Elemental Mercury: Hg(0)

- ~ 95% of total Hg in atmosphere
- *not* very water soluble
- long atmospheric lifetime (~ 0.5 - 1 yr); globally distributed



## Reactive Gaseous Mercury (“RGM”)

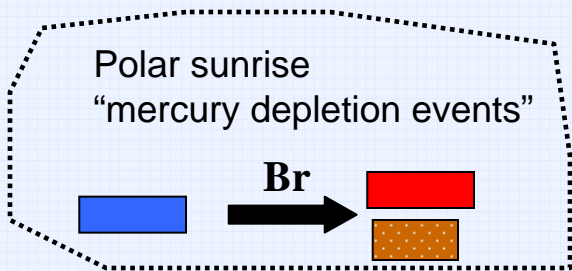
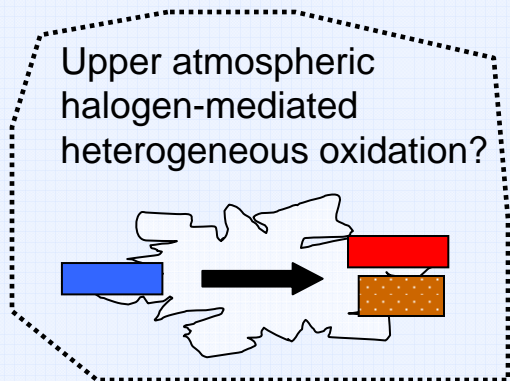
- a few percent of total Hg in atmosphere
- oxidized mercury: Hg(II)
- HgCl<sub>2</sub>, others species?
- somewhat operationally defined by measurement method
- *very* water soluble
- short atmospheric lifetime (~ 1 week or less);
- more local and regional effects



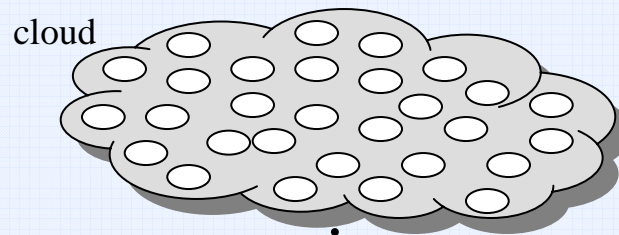
## Particulate Mercury (Hg(p))

- a few percent of total Hg in atmosphere
- not pure particles of mercury...  
(Hg compounds associated with atmospheric particulate)
- species largely unknown (in some cases, may be HgO?)
- moderate atmospheric lifetime (perhaps 1~ 2 weeks)
- local and regional effects
- bioavailability?

# Atmospheric Mercury Fate Processes



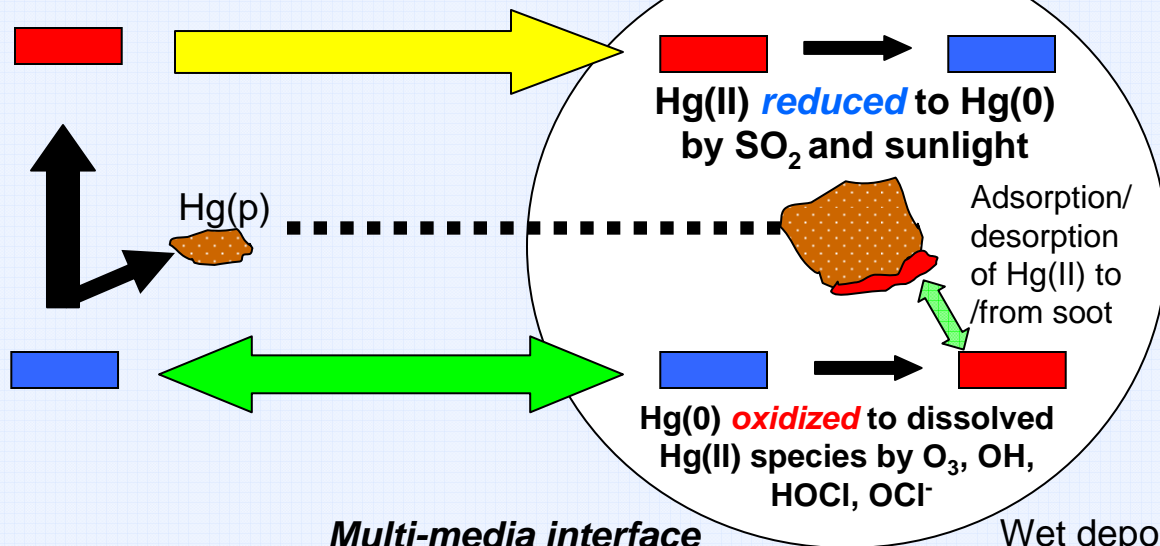
- Elemental Mercury [Hg(0)]
- Hg(II), ionic mercury, RGM
- Particulate Mercury [Hg(p)]



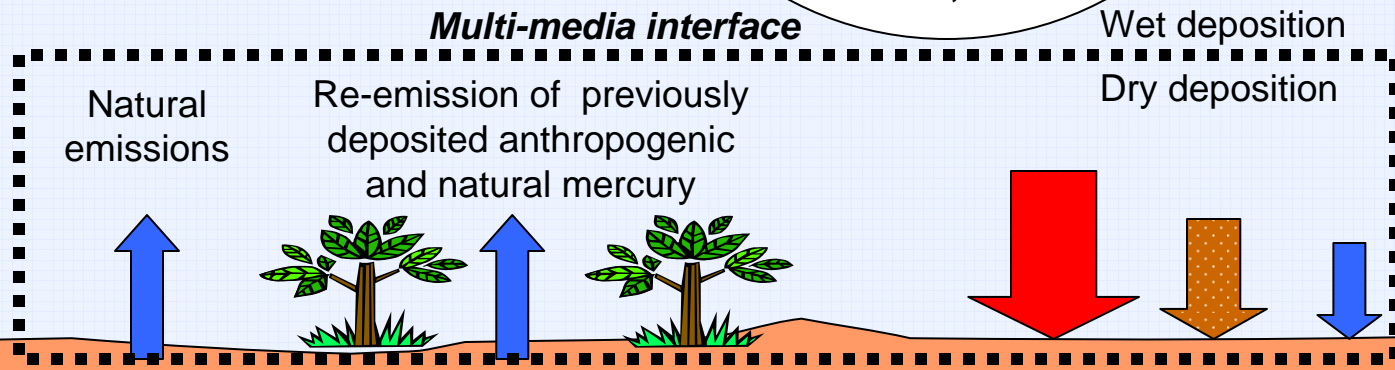
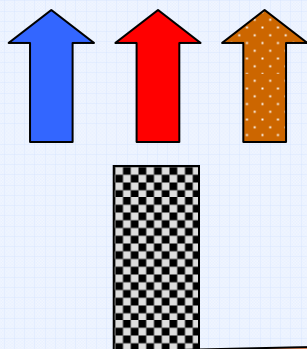
CLOUD DROPLET

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

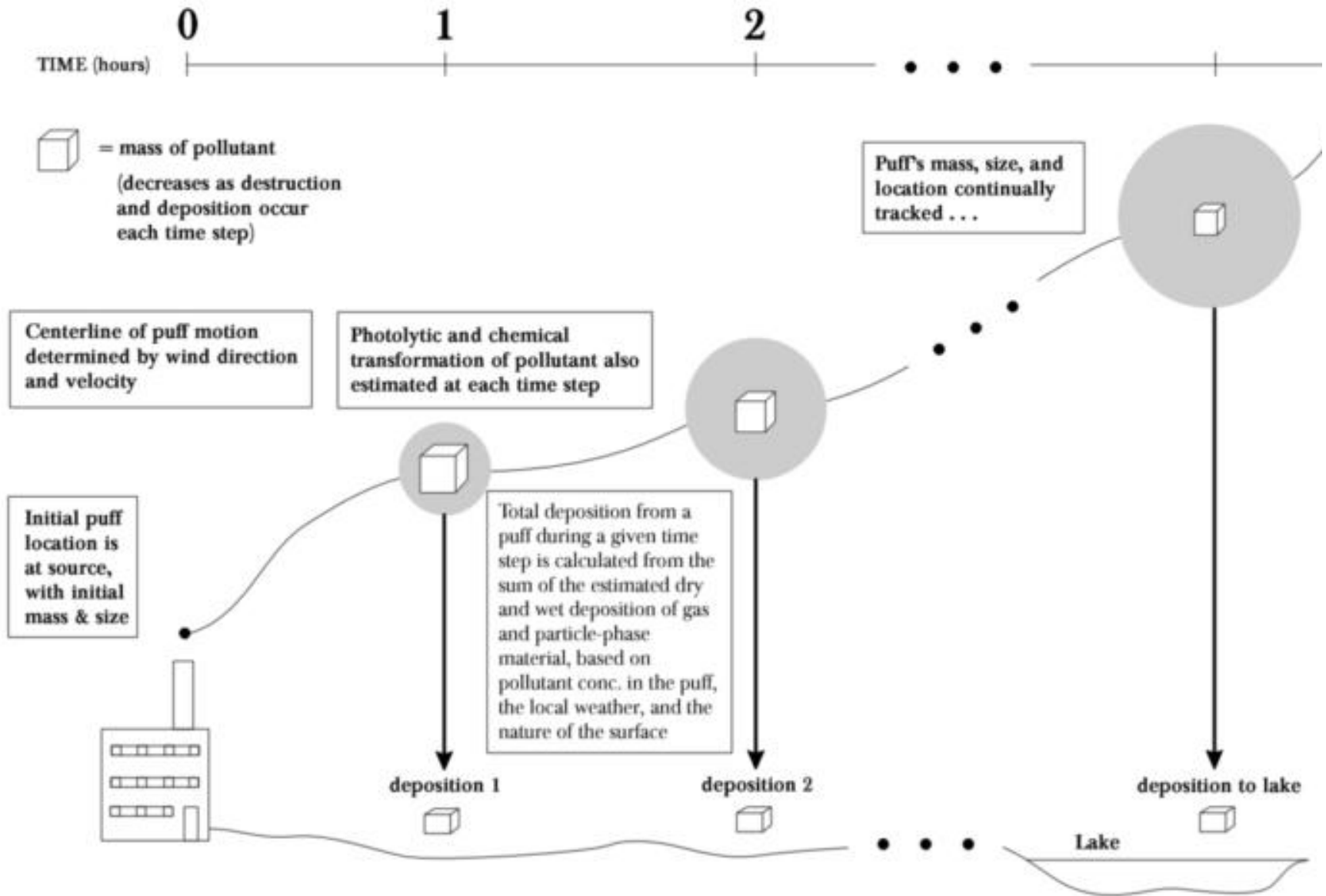


# Atmospheric Chemical Reaction Scheme for Mercury

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)
$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T^*e^{((31.971*T)-12595.0)/T}$ sec <sup>-1</sup> [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	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$\text{Hg}^{+2} + \text{h}^- \rightarrow \text{Hg}^0$	6.0E-7	(sec) <sup>-1</sup> (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

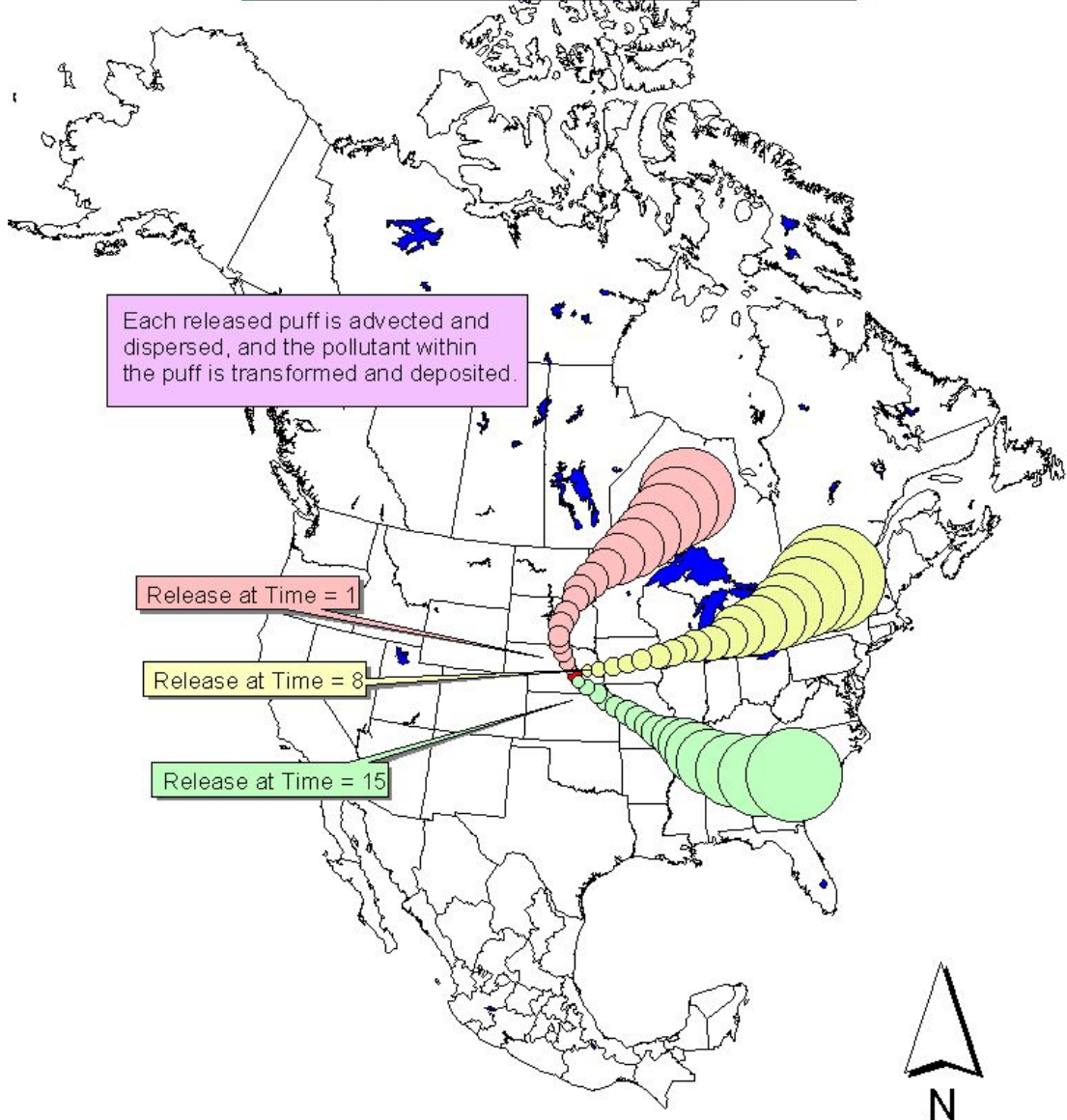
# NOAA HYSPLIT MODEL

## Lagrangian Puff Air Transport and Deposition Model

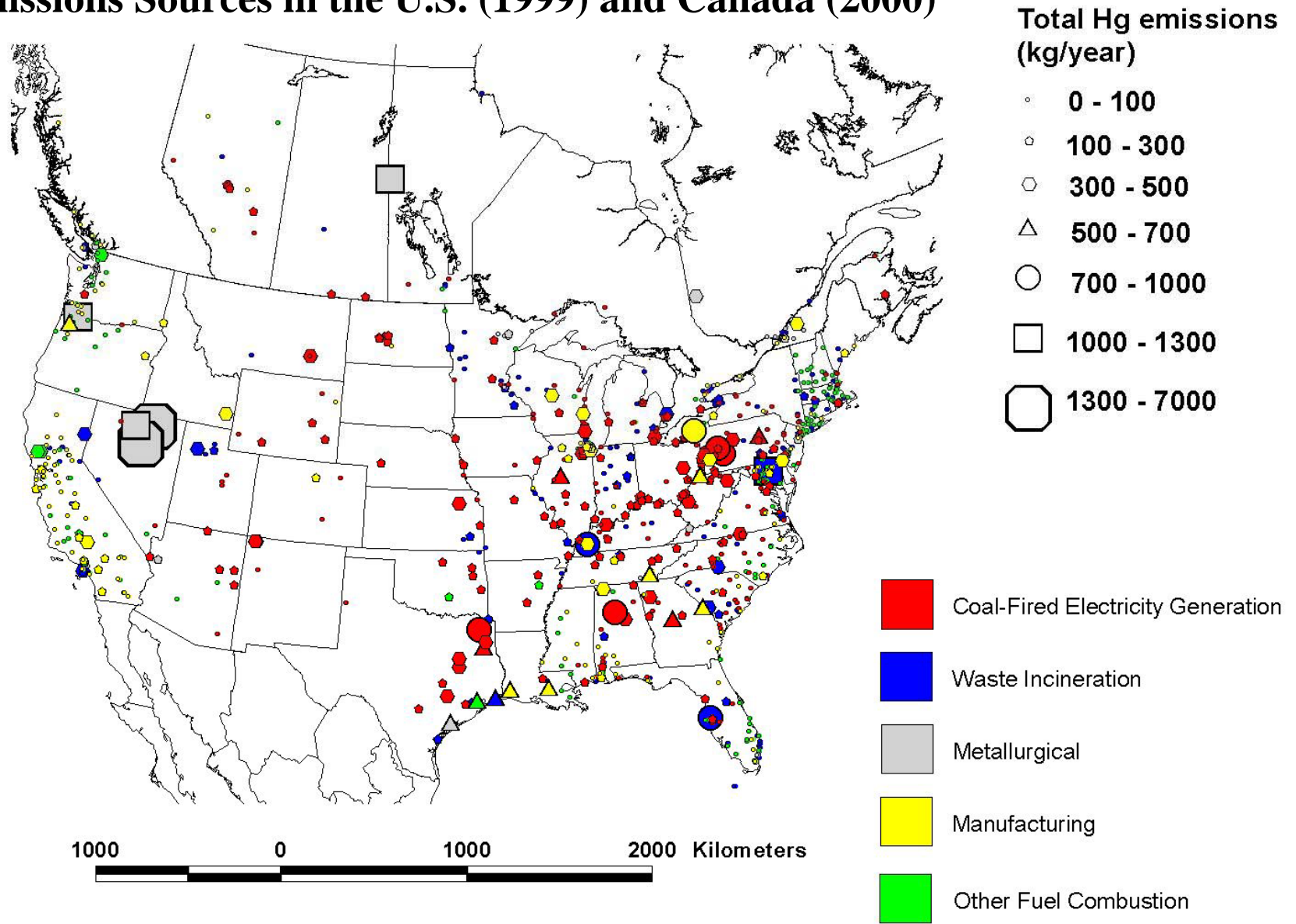


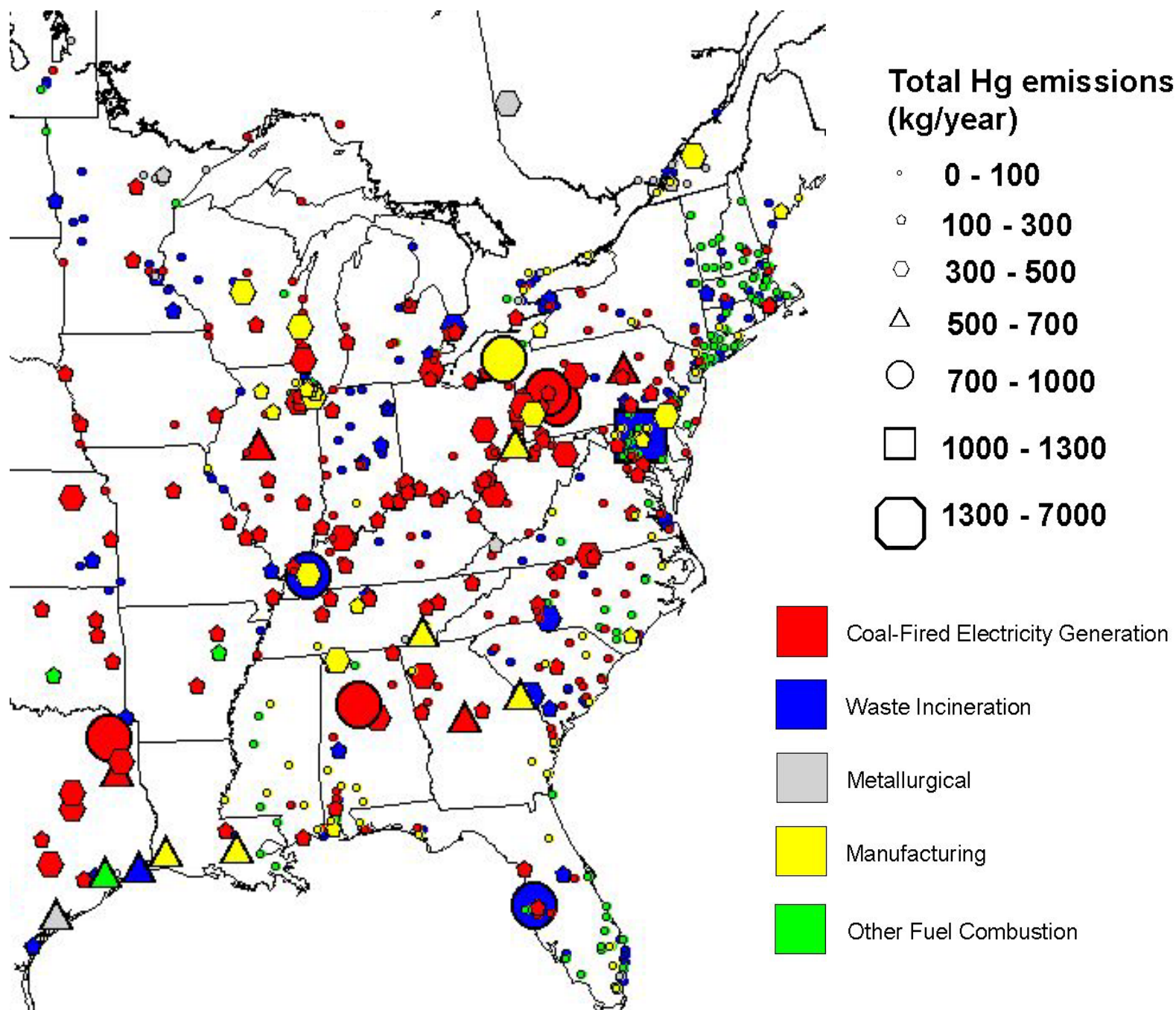


Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).



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





- **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**



## 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,d</sup> Jennifer Slotnick,<sup>f</sup> Todd Nettesheim,<sup>g</sup> and John McDonald<sup>h</sup>

<sup>a</sup> NOAA Air Resources Laboratory, 1315 East West Highway, BART, Room 316, Silver Spring, MD 20910, USA

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

<sup>c</sup> Atmospheric Toxicology and Health Division, Health Canada, Ottawa, Ontario, Canada

<sup>d</sup> Health Canada, Ottawa, 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.

### Abstract

A special version of mercury in a North American region and provide estimates of atmospheric mercury available for model evaluation in the Great Lakes region from the Great Lakes. Significant contribution to atmospheric mercury is published by Elsevier.

**Keywords:** Mercury; Atmospheric transport; Deposition; Great Lakes; Modeling

Mercury contamination of other ecosystems is a serious environmental problem. Human exposure to mercury, and significant levels of mercury (2000). Historical production using the to have caused in

<sup>☆</sup> Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.envres.2003.11.007](http://doi.org/10.1016/j.envres.2003.11.007).

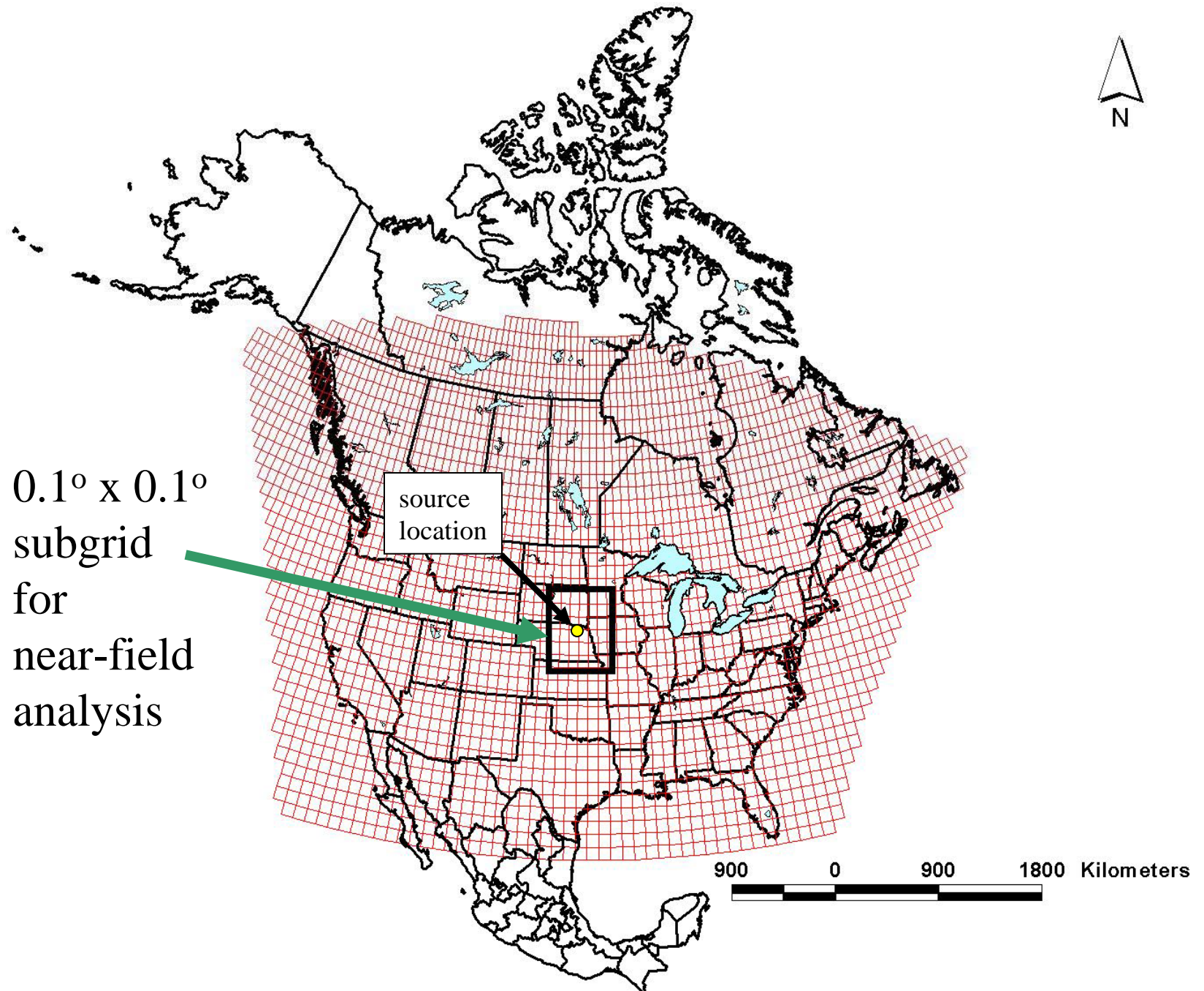
\* Corresponding author.

E-mail address: [mark.cohen@noaa.gov](mailto:mark.cohen@noaa.gov) (M. Cohen).

<sup>c</sup> Current address: IPRAC, Canada, The Institute of Environmental Research, Concord, Ontario, Canada

has developed detailed source-receptor relationships for the Great Lakes, as advocated in Annex 15 of the Great Lakes Action Plan.

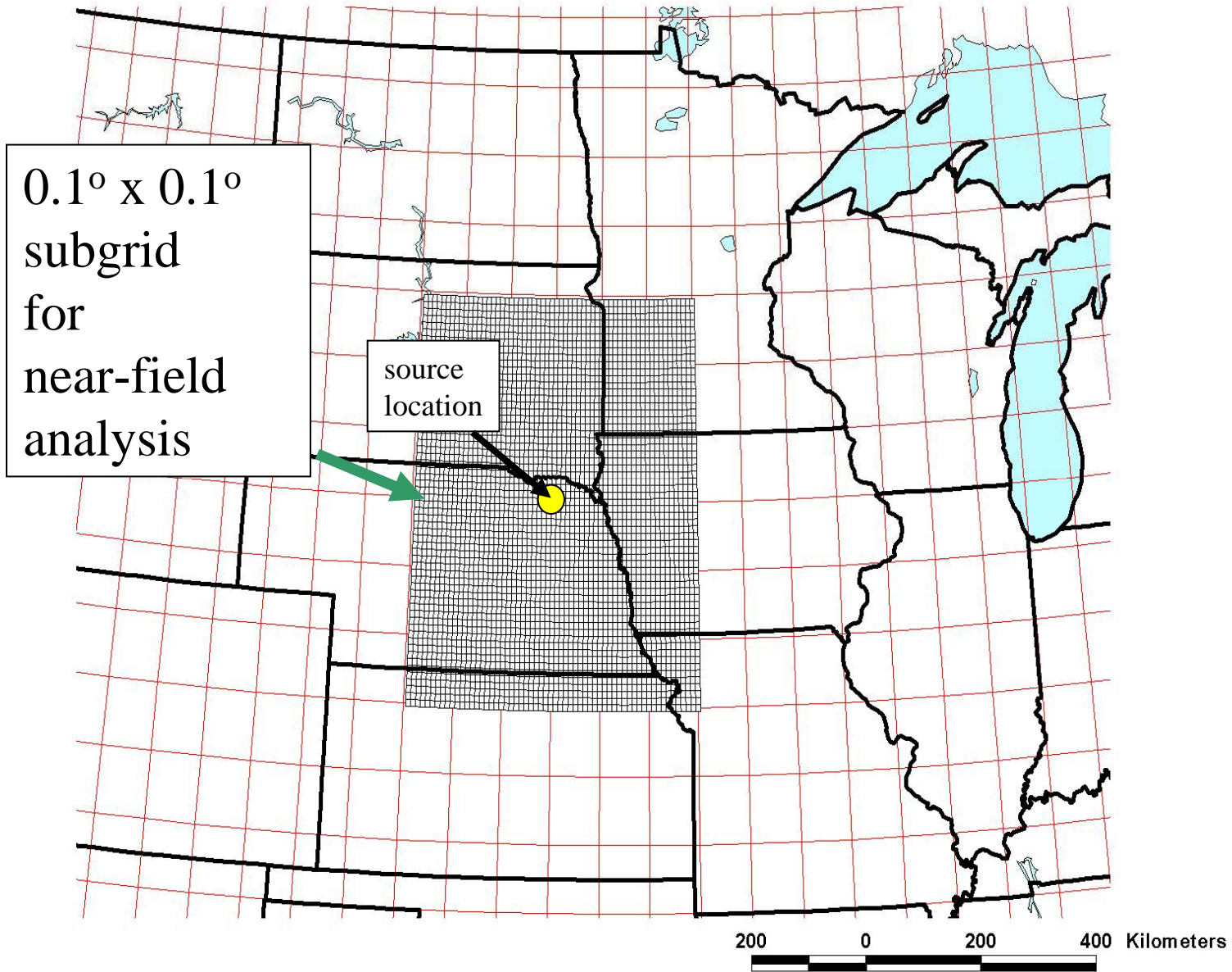
- **For each run, simulate fate and transport *everywhere*, but only keep track of impacts on each selected receptor (e.g., Great Lakes, Chesapeake Bay, etc.)**
- **Only run model for a limited number (~100) of hypothetical, individual unit-emissions sources throughout the domain**
- **Use spatial interpolation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



0.1° x 0.1°  
subgrid  
for  
near-field  
analysis

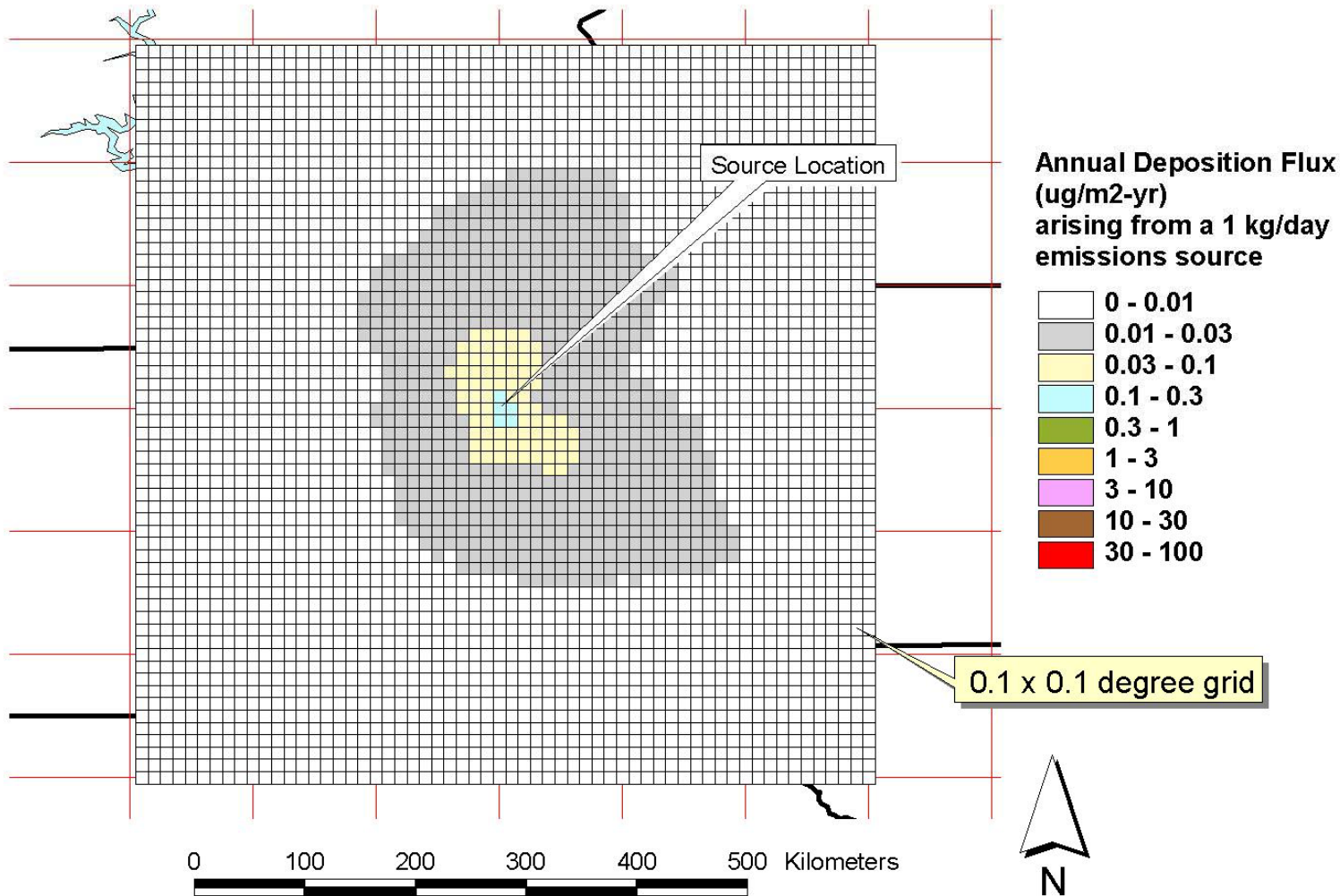
source  
location

900 0 900 1800 Kilometers



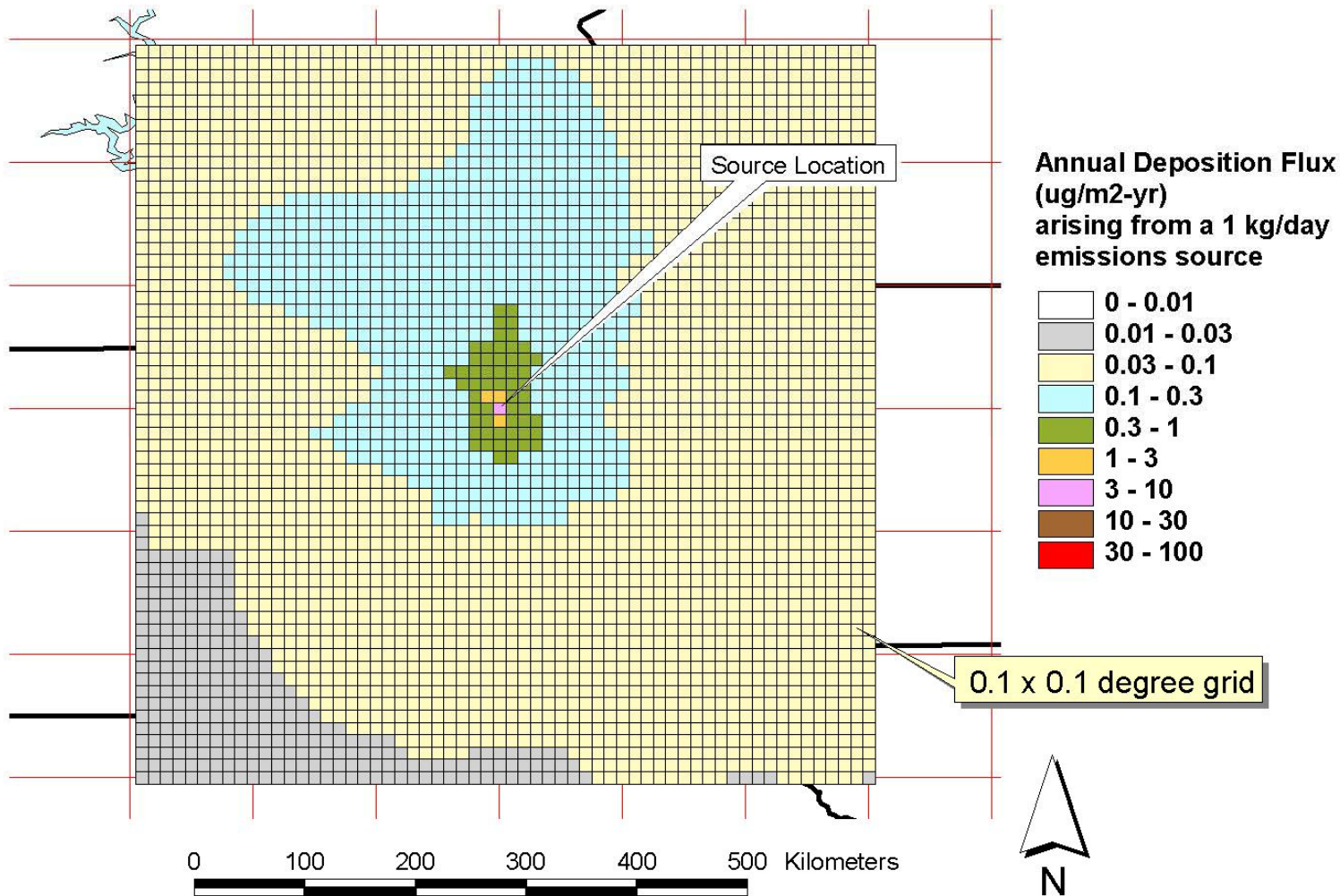


# Annual deposition summary for emissions of elemental Hg from a 250 meter high source



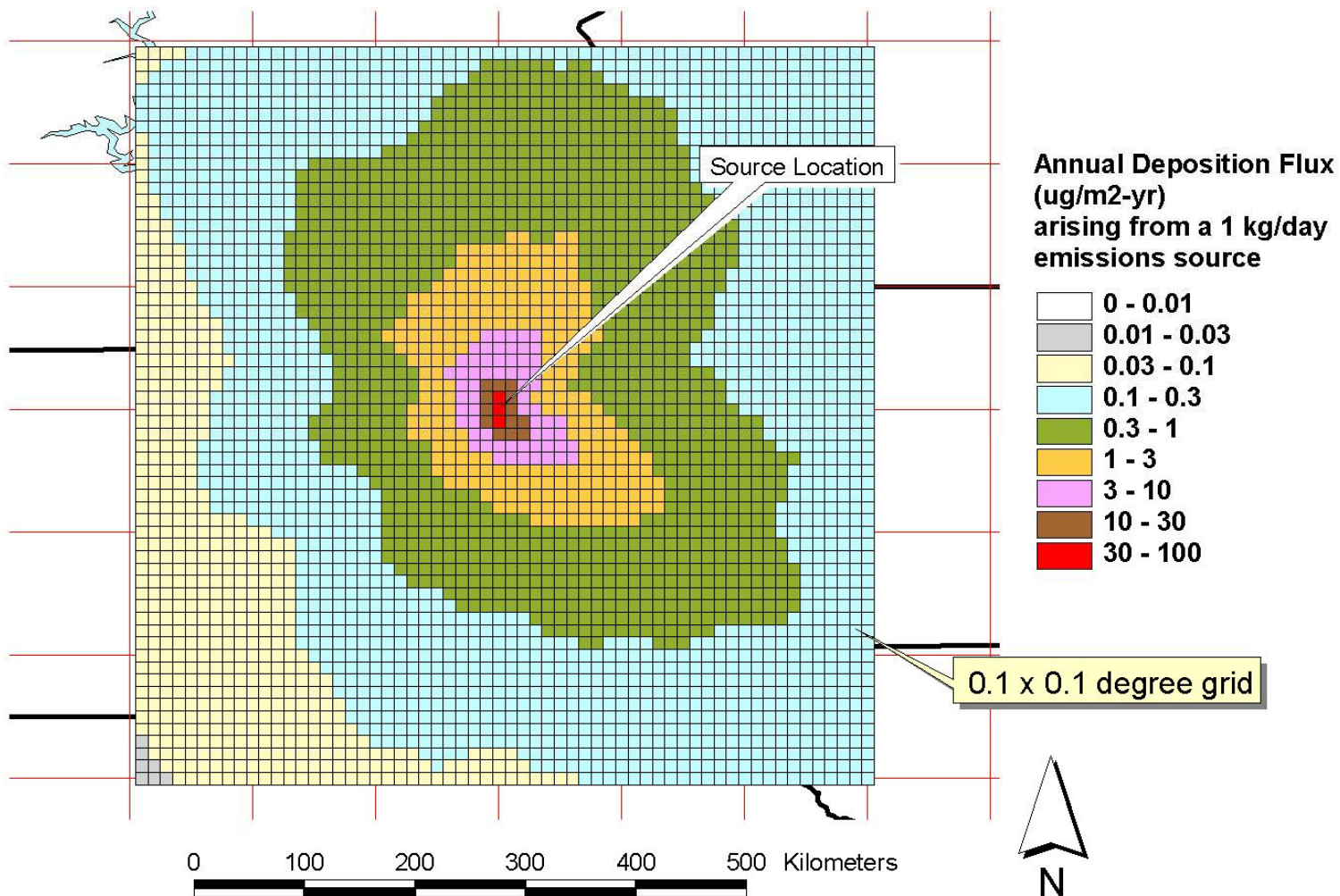
Hypothetical emissions source at lat = 42.5, long = -97.5;  
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

# Annual deposition summary for emissions of particulate Hg from a 250 meter high source



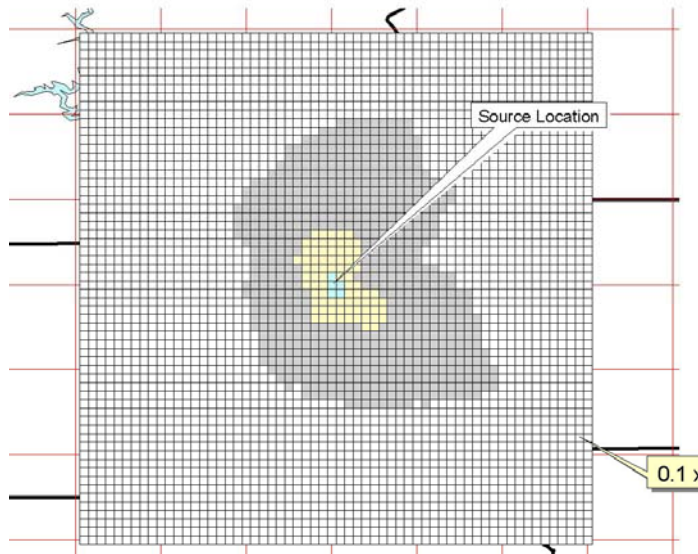
Hypothetical emissions source at lat = 42.5, long = -97.5;  
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

# Annual deposition summary for emissions of ionic Hg from a 250 meter high source

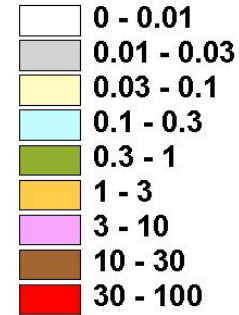


Hypothetical emissions source at lat = 42.5, long = -97.5;  
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

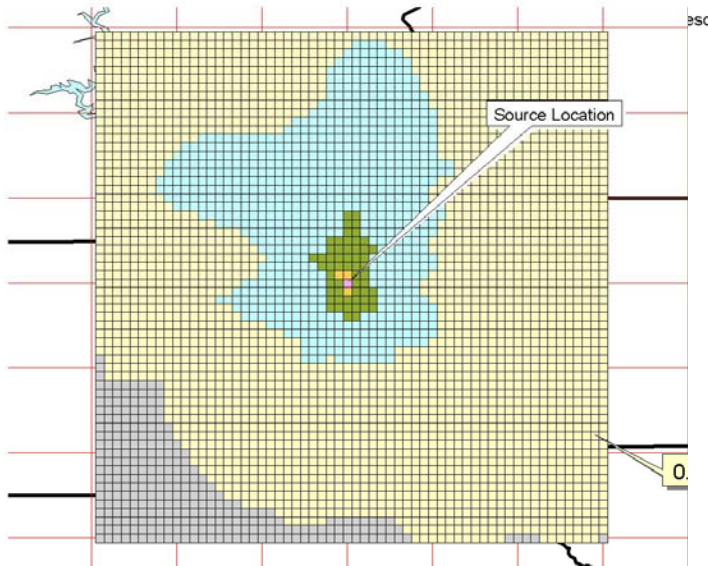
**Annual deposition summary for emissions of elemental Hg from a 250 meter high source**



**Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source**



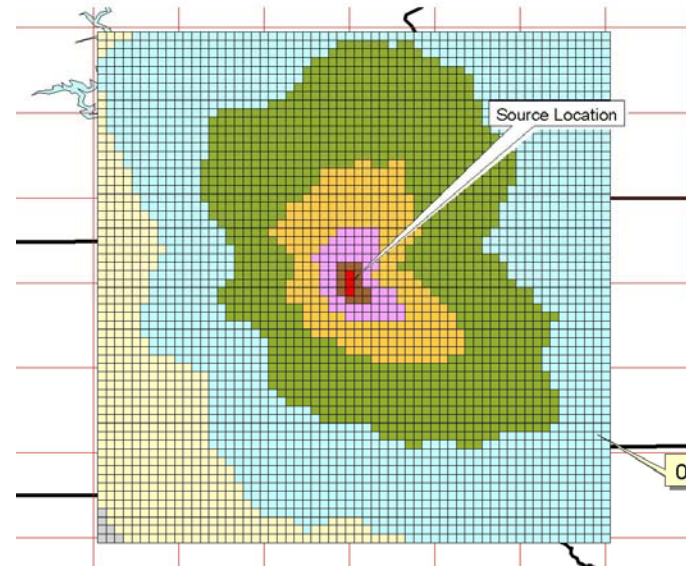
**Annual deposition summary for emissions of particulate Hg from a 250 meter high source**



0 100 200 300 400 500 Kilometers

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km r

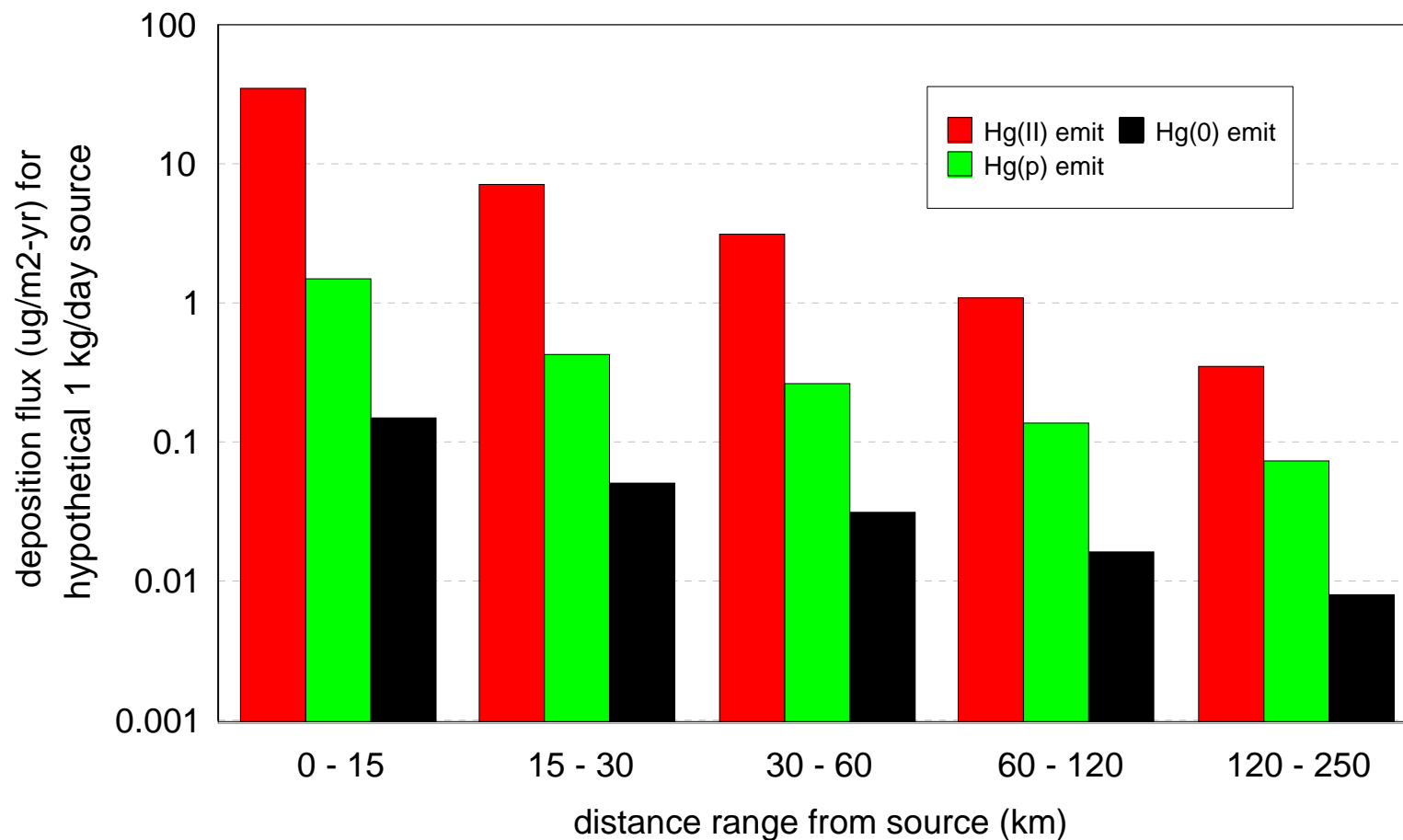
**Annual deposition summary for emissions of ionic Hg from a 250 meter high source**



0 100 200 300 400 500 Kilometers

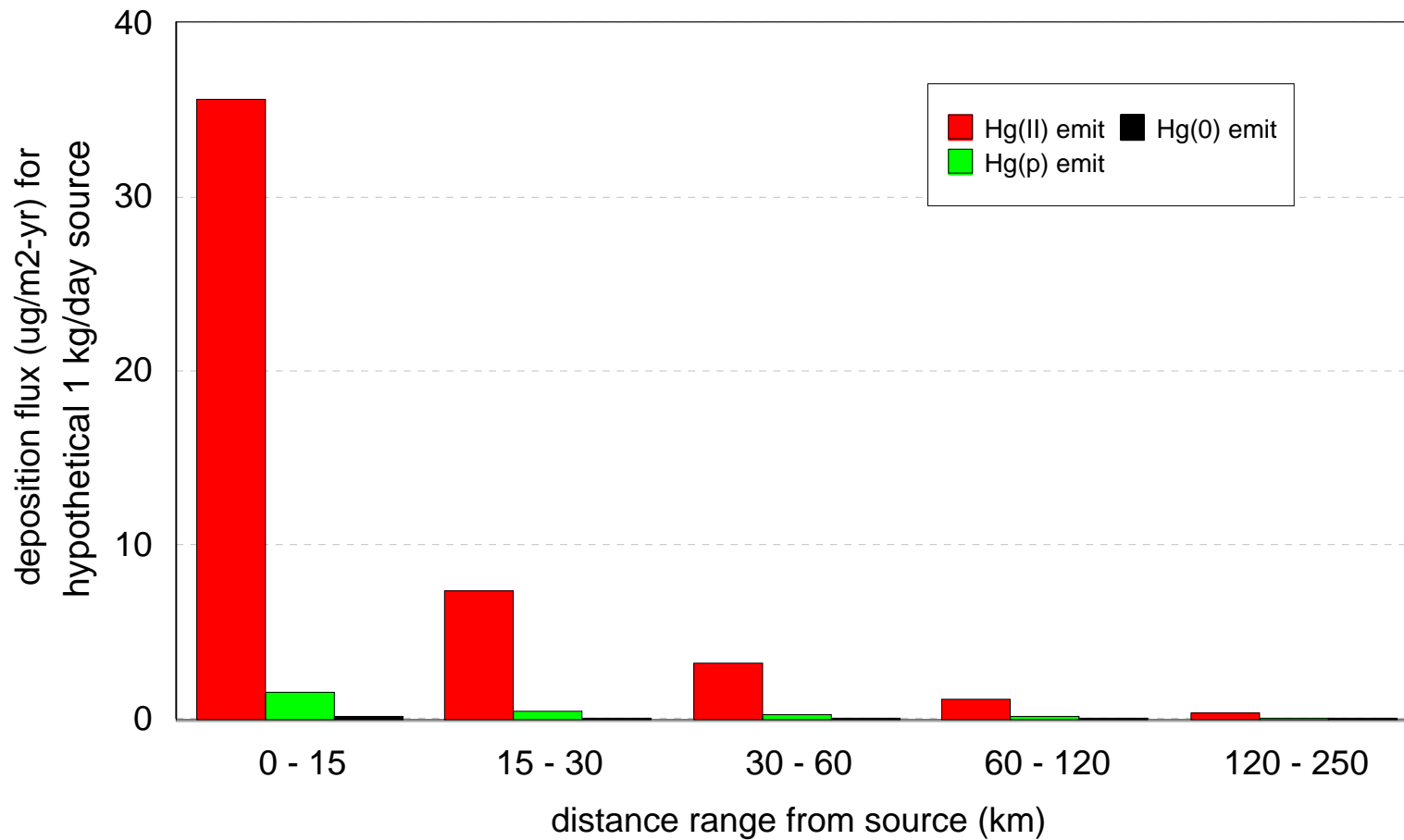
Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km r

# Why is emissions speciation information critical?



*Logarithmic*

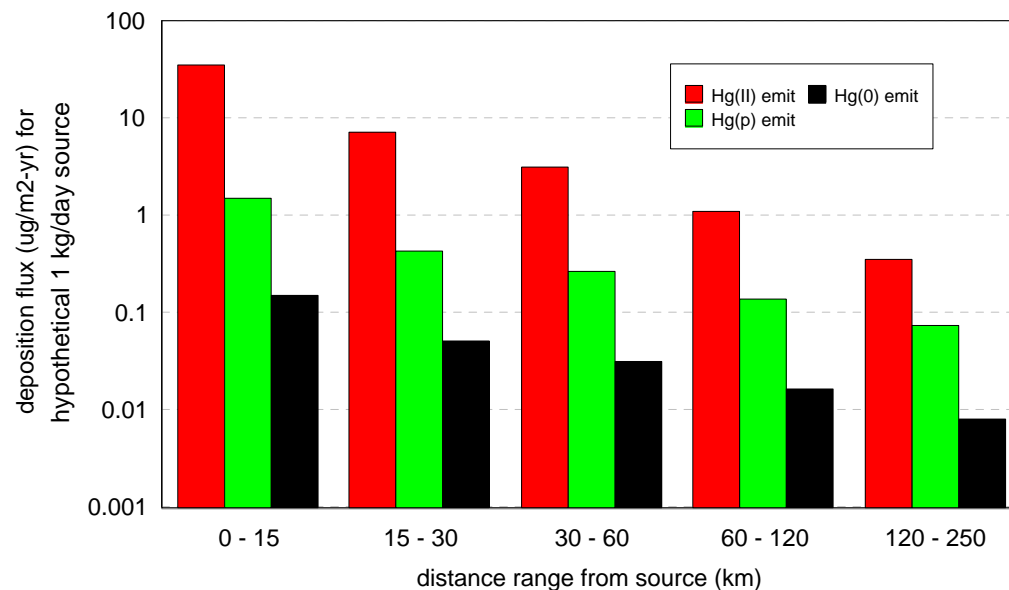
# Why is emissions speciation information critical?



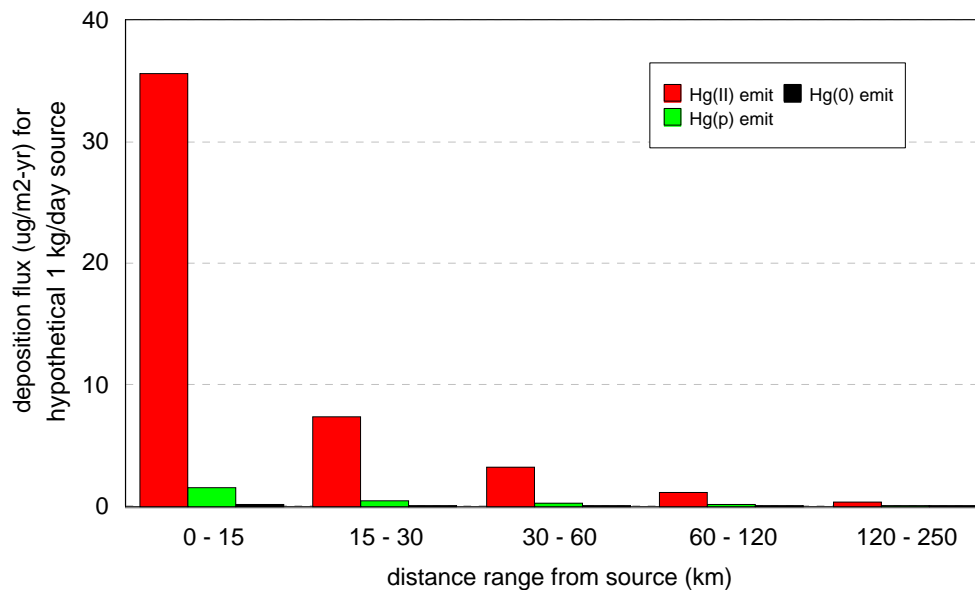
*Linear*

# Why is emissions speciation information critical?

*Logarithmic*



*Linear*



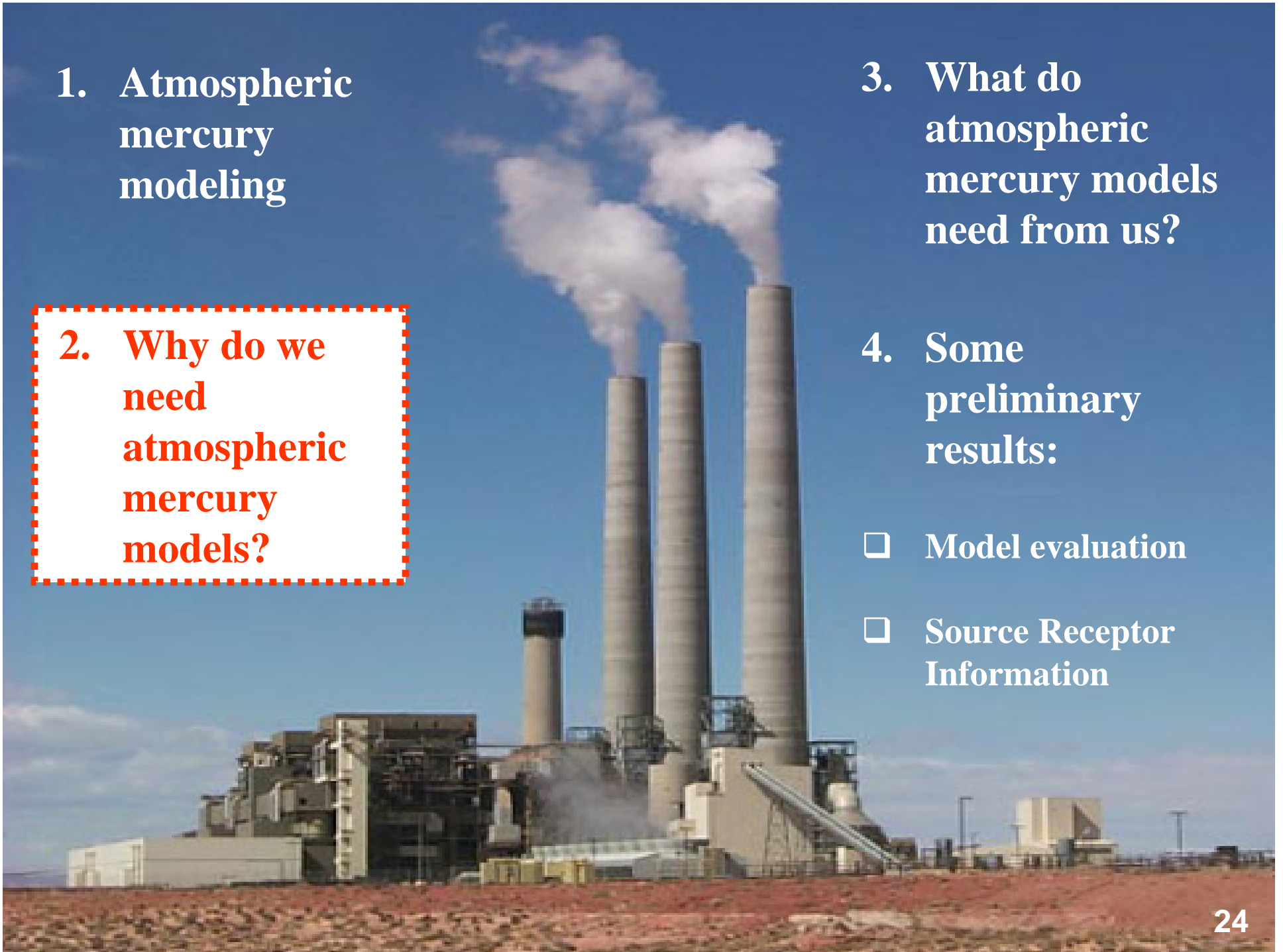
1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results:

- Model evaluation
- Source Receptor Information





## Why do we need atmospheric mercury models?

- to get *comprehensive source attribution* information ---  
**we don't just want to know how much is depositing at any given location, we also want to know where it came from...**
- to estimate *deposition over large regions*,  
...because deposition fields are highly spatially variable,  
and one can't measure everywhere all the time...
- to estimate *dry deposition*
- to evaluate *potential consequences* of alternative future emissions scenarios

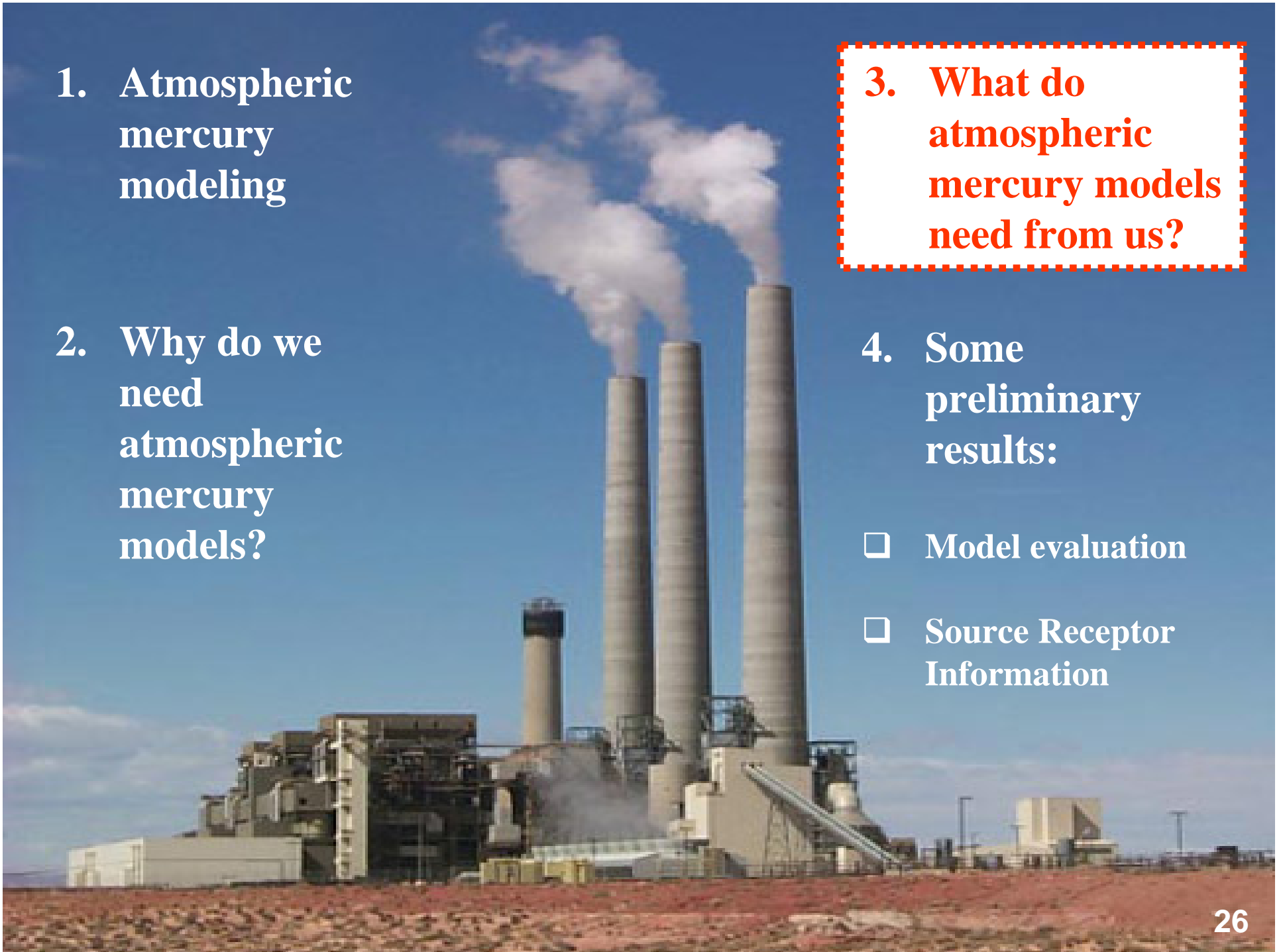
1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results:

- Model evaluation
- Source Receptor Information



# What do atmospheric mercury models need?

**Emissions  
Inventories**

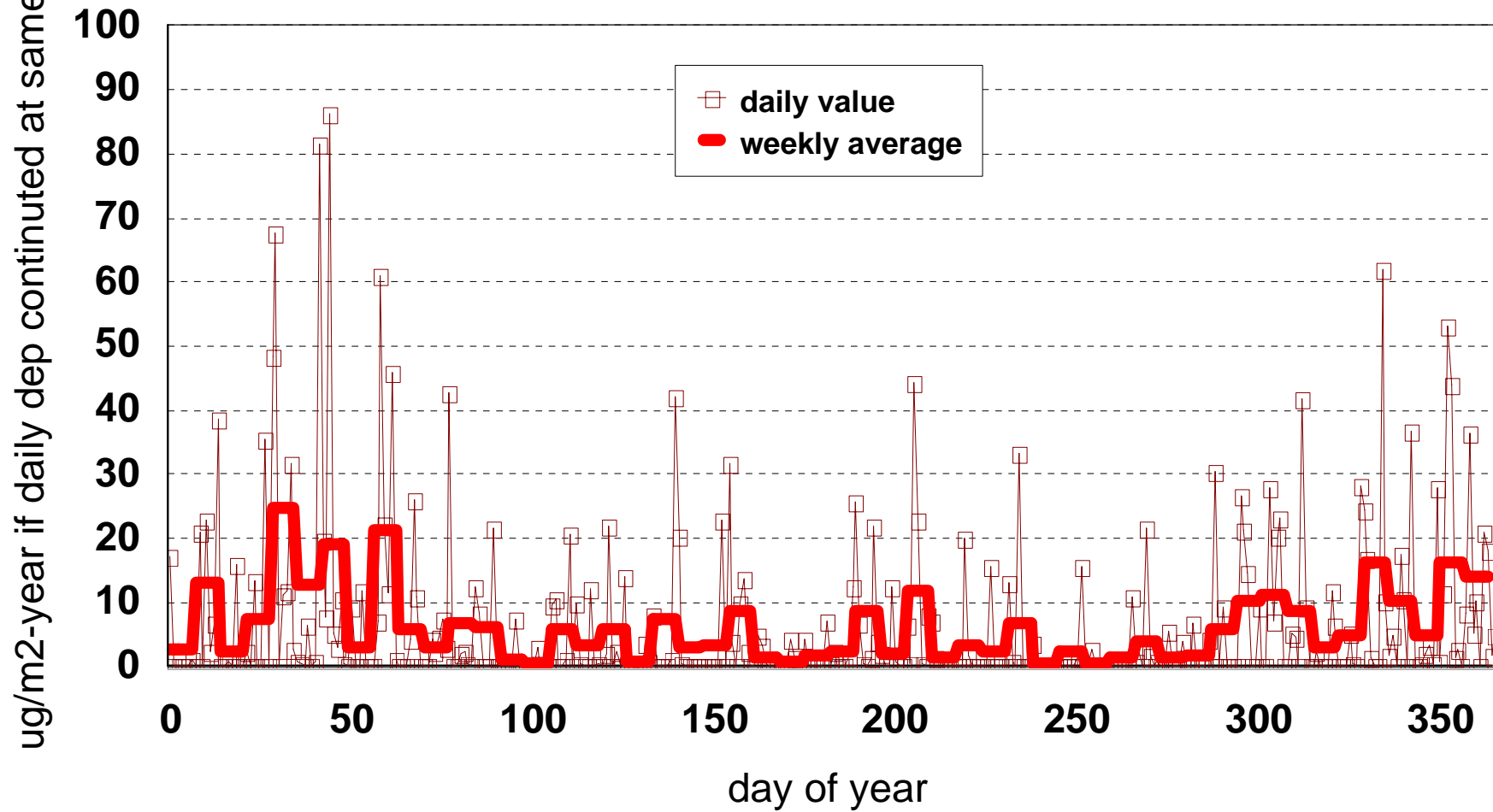
**Meteorological  
Data**

**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>

Illustrative example of total deposition at a location  
~40 km "downwind" of a 1 kg/day RGM source



	<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>
<b>meteorological data</b>	<ul style="list-style-type: none"> <li>• <b>precipitation not well characterized</b></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>

	<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>

	<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>



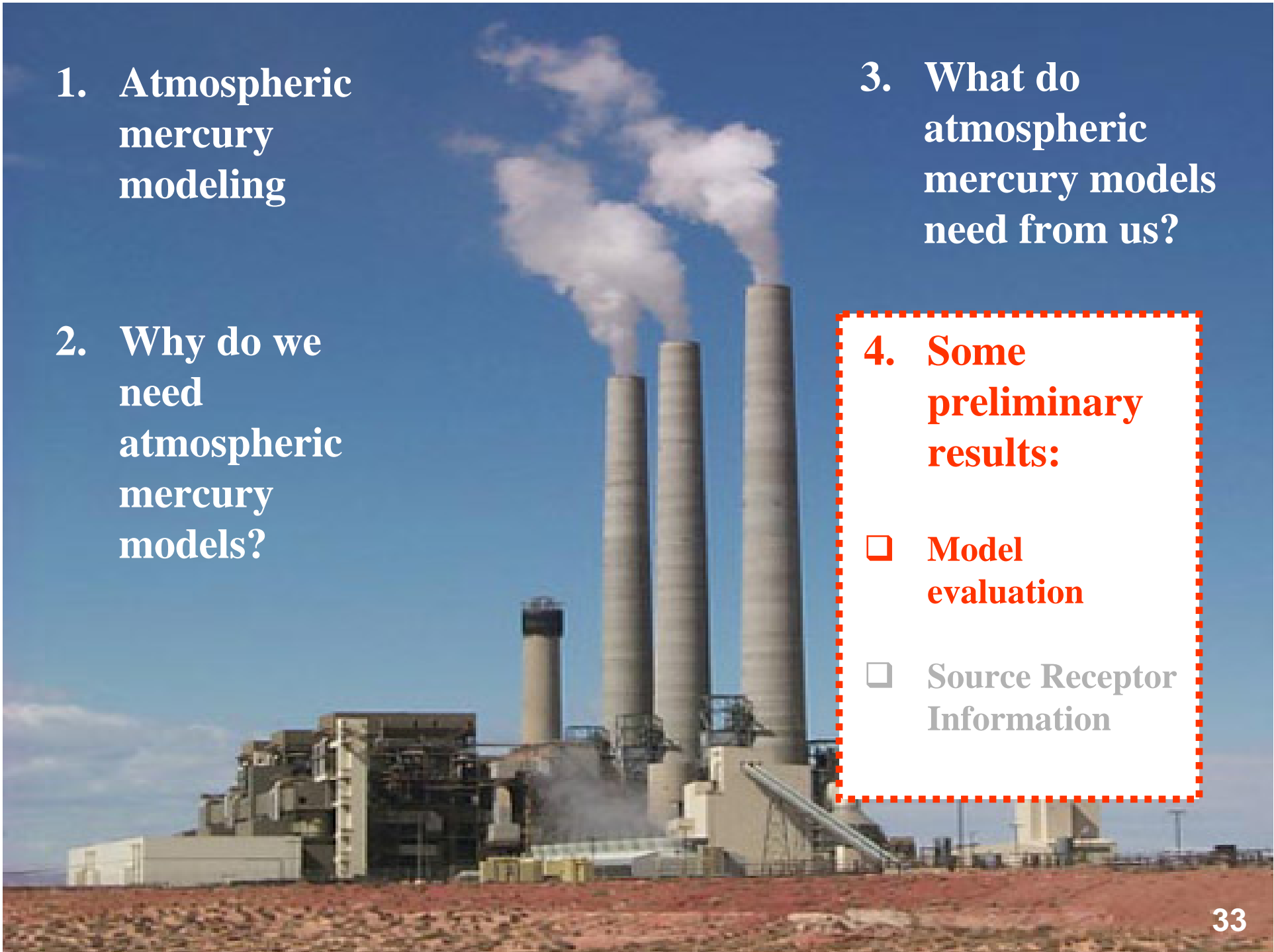
1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

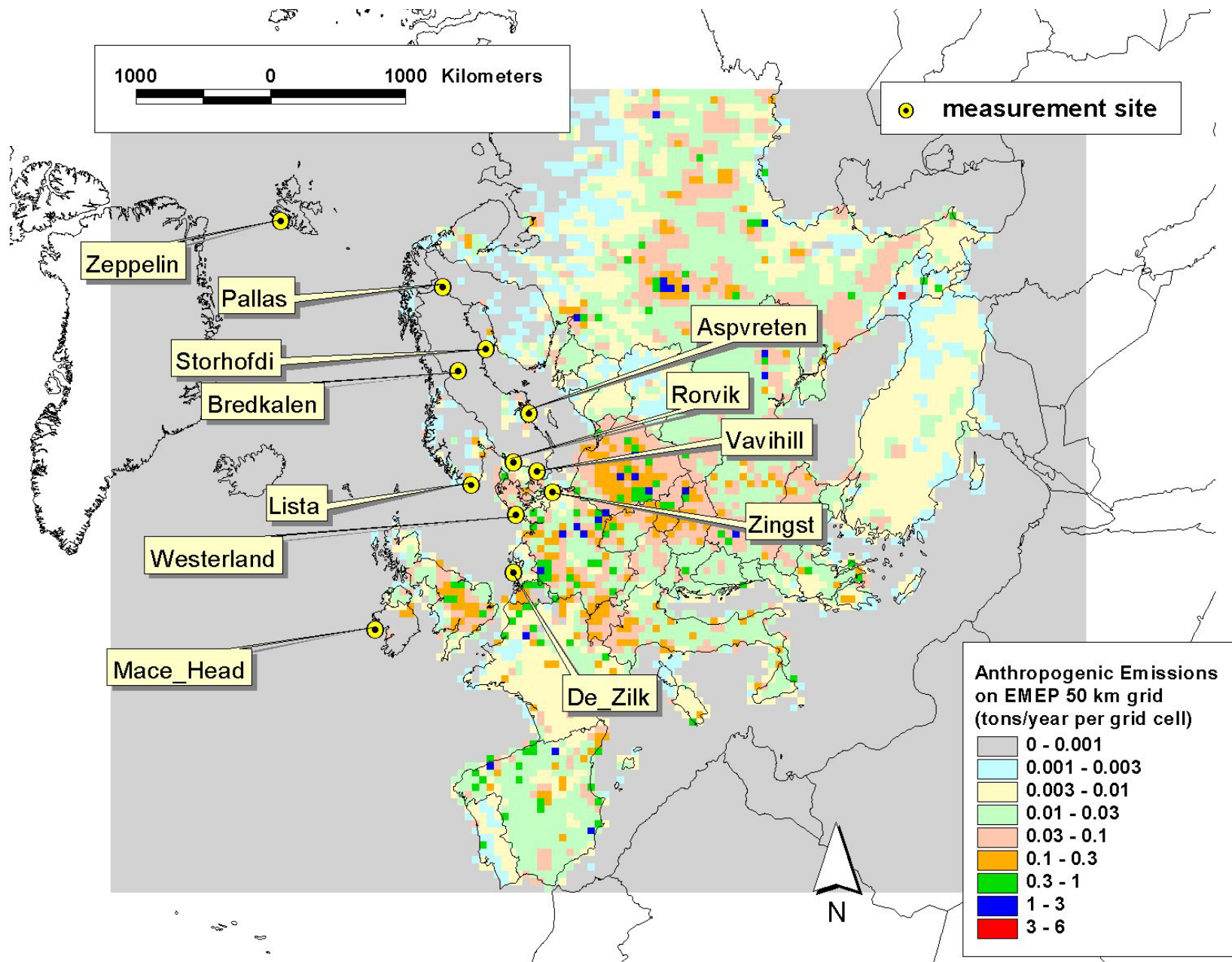
4. **Some preliminary results:**

- Model evaluation**
- Source Receptor Information**

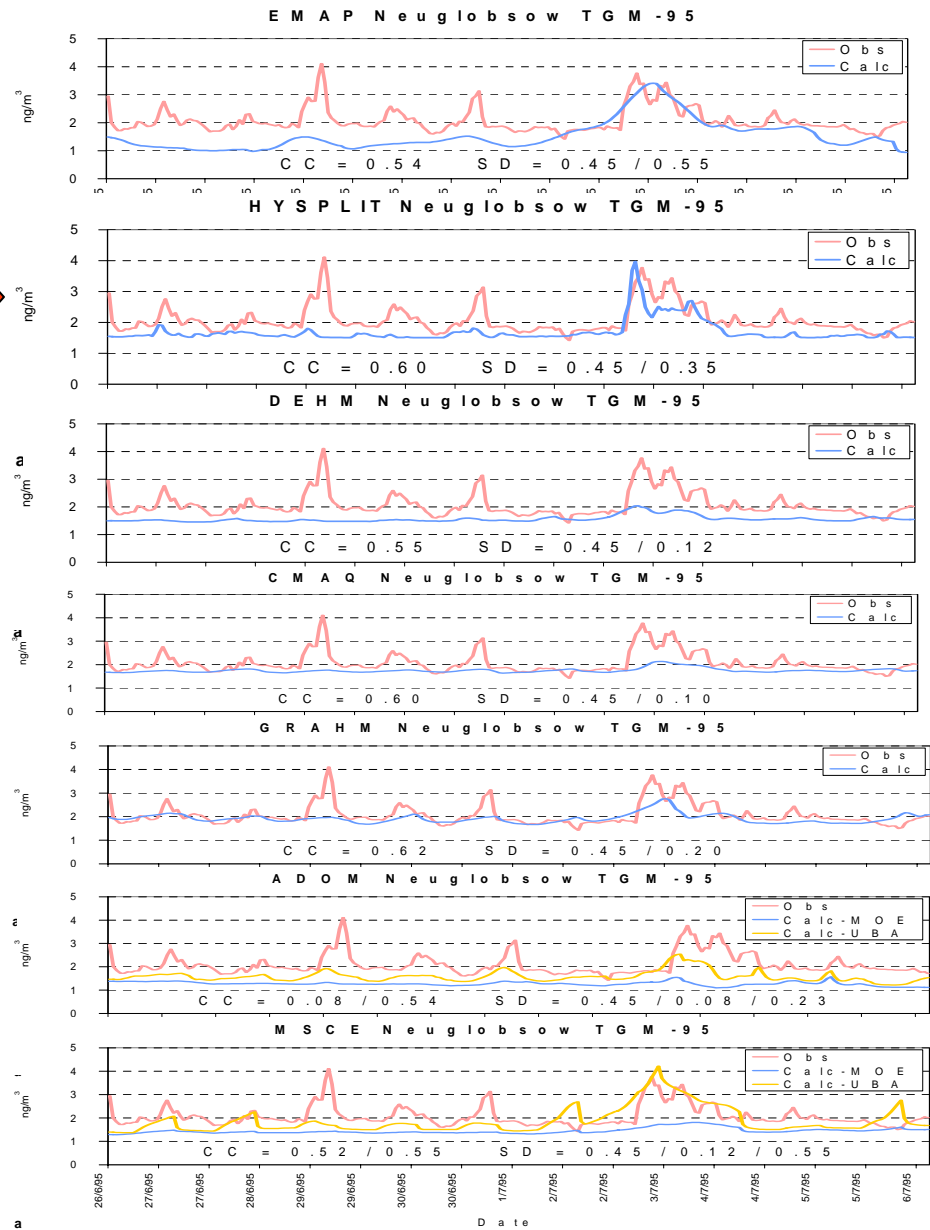
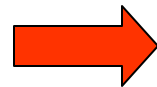


- EMEP Model Intercomparison
  - Phase II – ambient concentrations
  - Phase III – wet and dry deposition
  
- Chesapeake Bay region

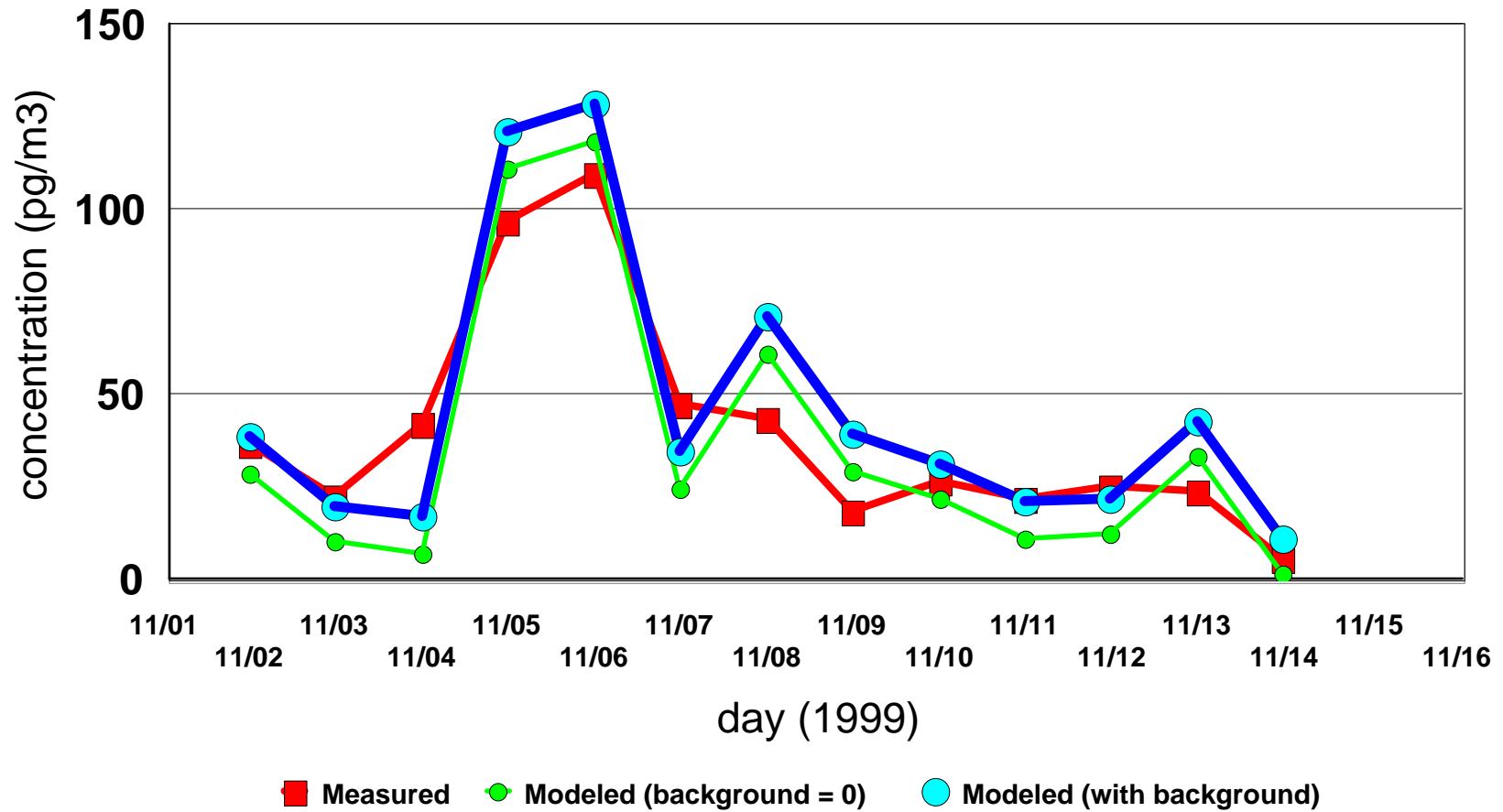
- EMEP Model Intercomparison
  - Phase II – ambient concentrations
  - Phase III – wet and dry deposition
  
- Chesapeake Bay region



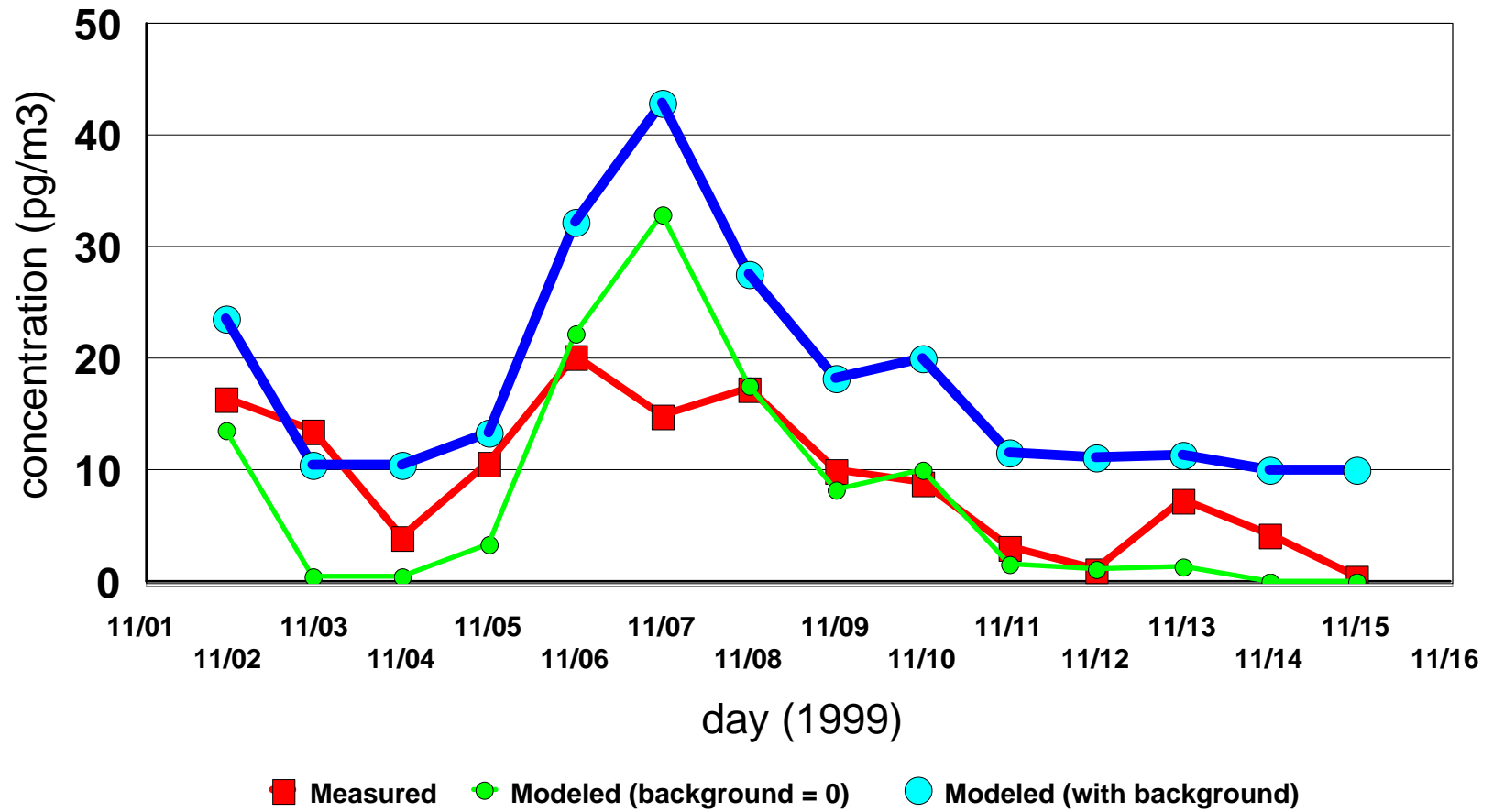
# Measured and Simulated Total Gaseous Mercury at Neuglobsow during the 1995 episode



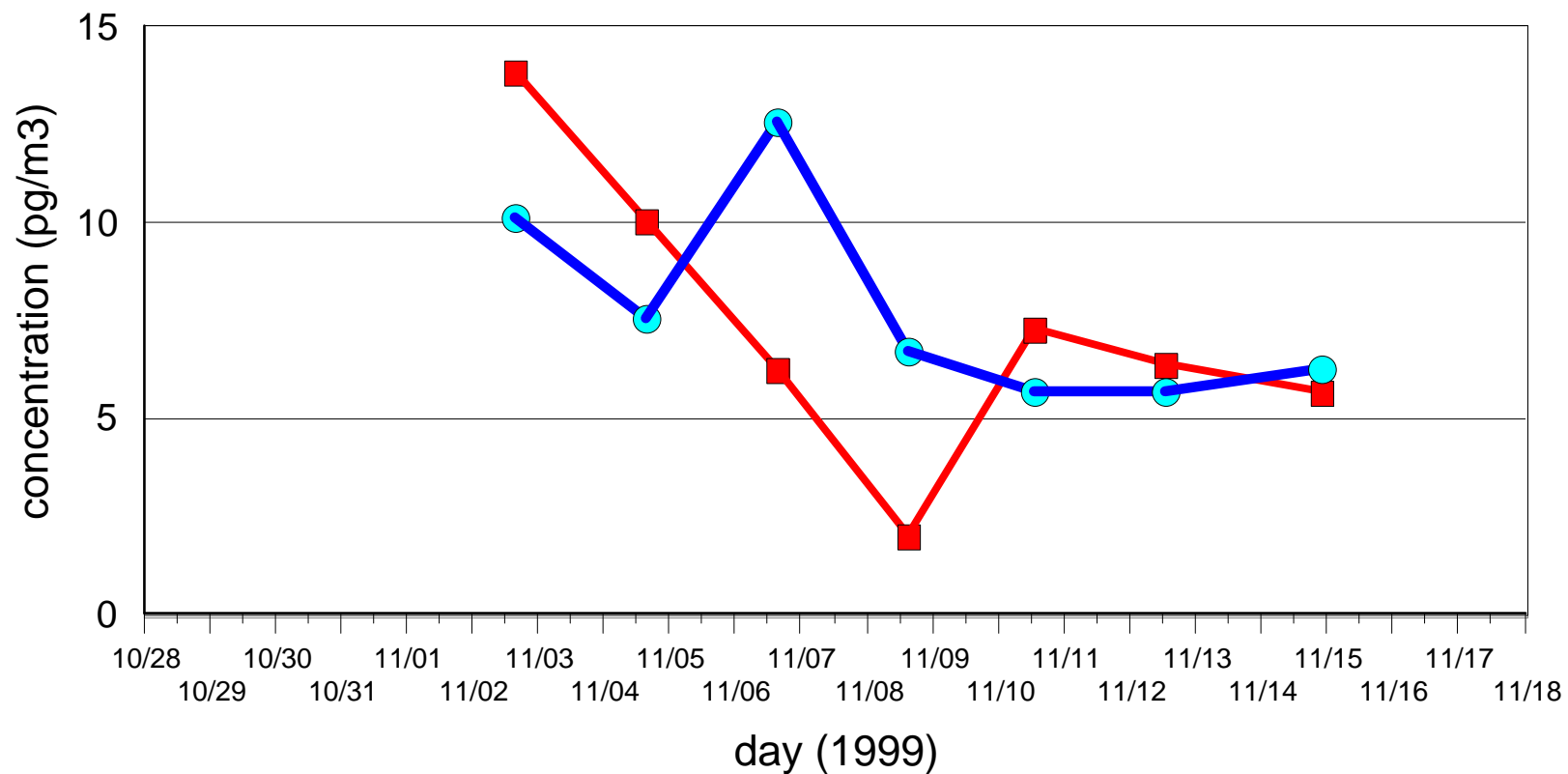
Comparison of measured vs. modeled TPM  
Neuglobsow



Comparison of measured vs. modeled TPM  
Aspvreten



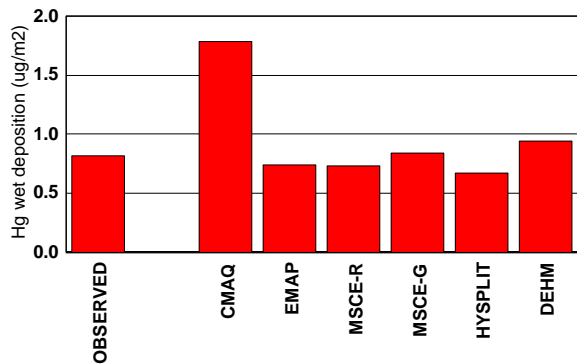
**Comparison of measured vs. modeled RGM  
(comparison for measurement periods only)**



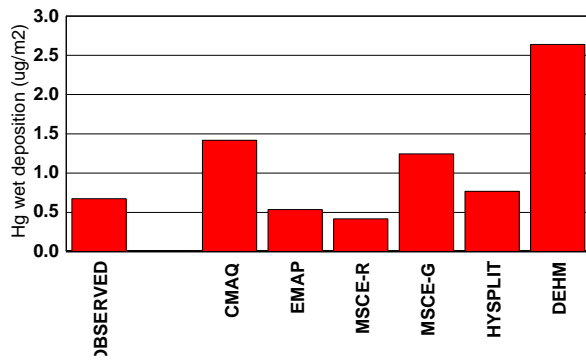
**■ Rorvik measured RGM      ● Rorvik modeled RGM**



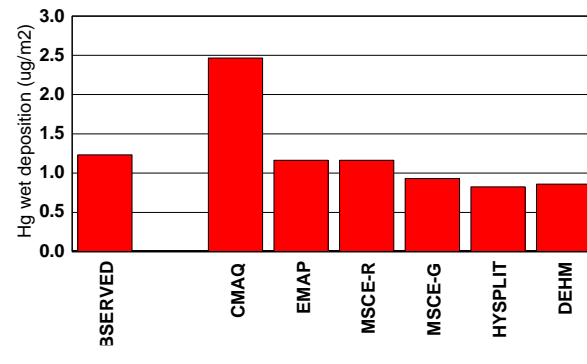
August Wet Deposition at DE01



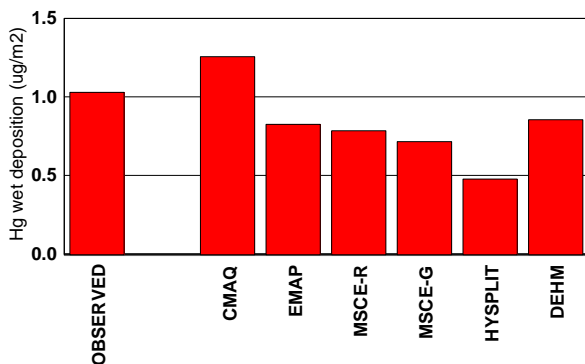
August Wet Deposition at DE09



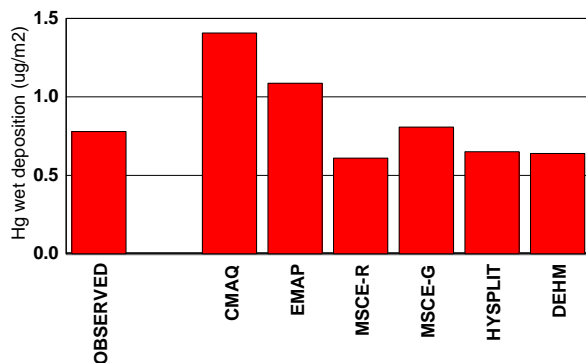
August Wet Deposition at NL91



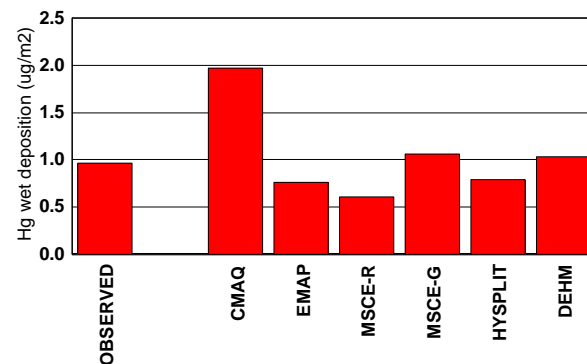
August Wet Deposition at NO99



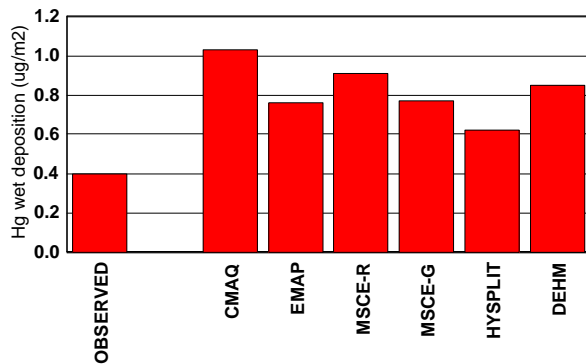
August Wet Deposition at SE02



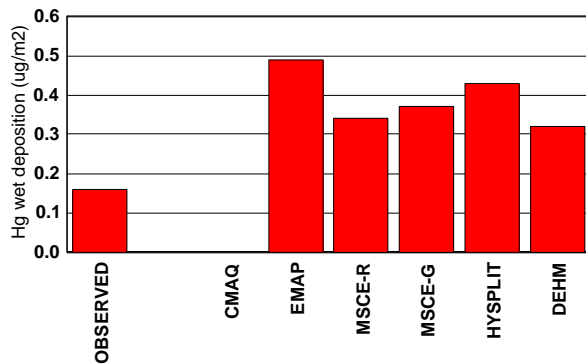
August Wet Deposition at SE11



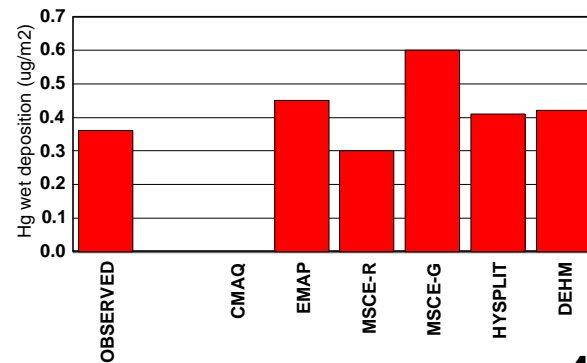
August Wet Deposition at SE12



August Wet Deposition at SE05

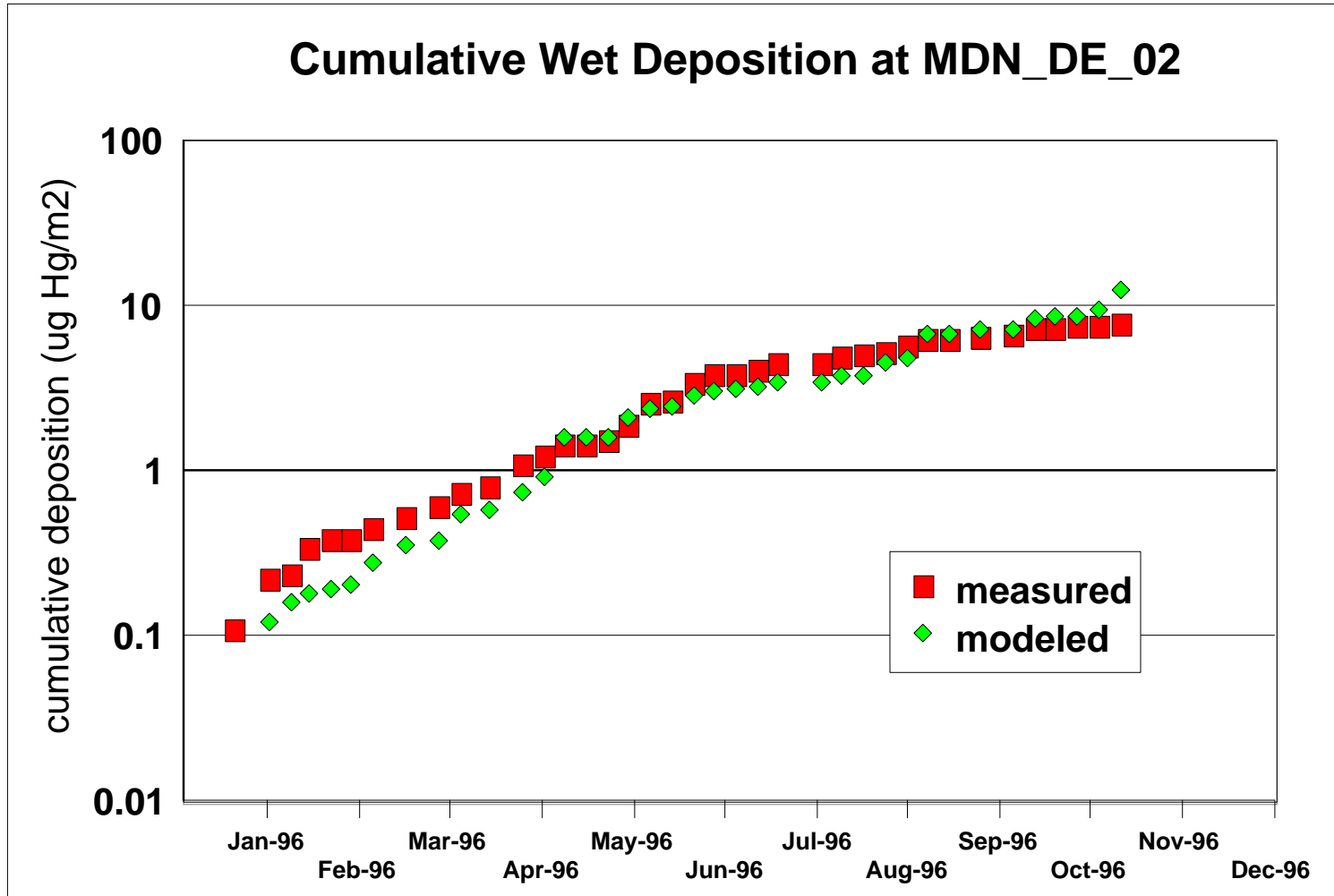


August Wet Deposition at FI96

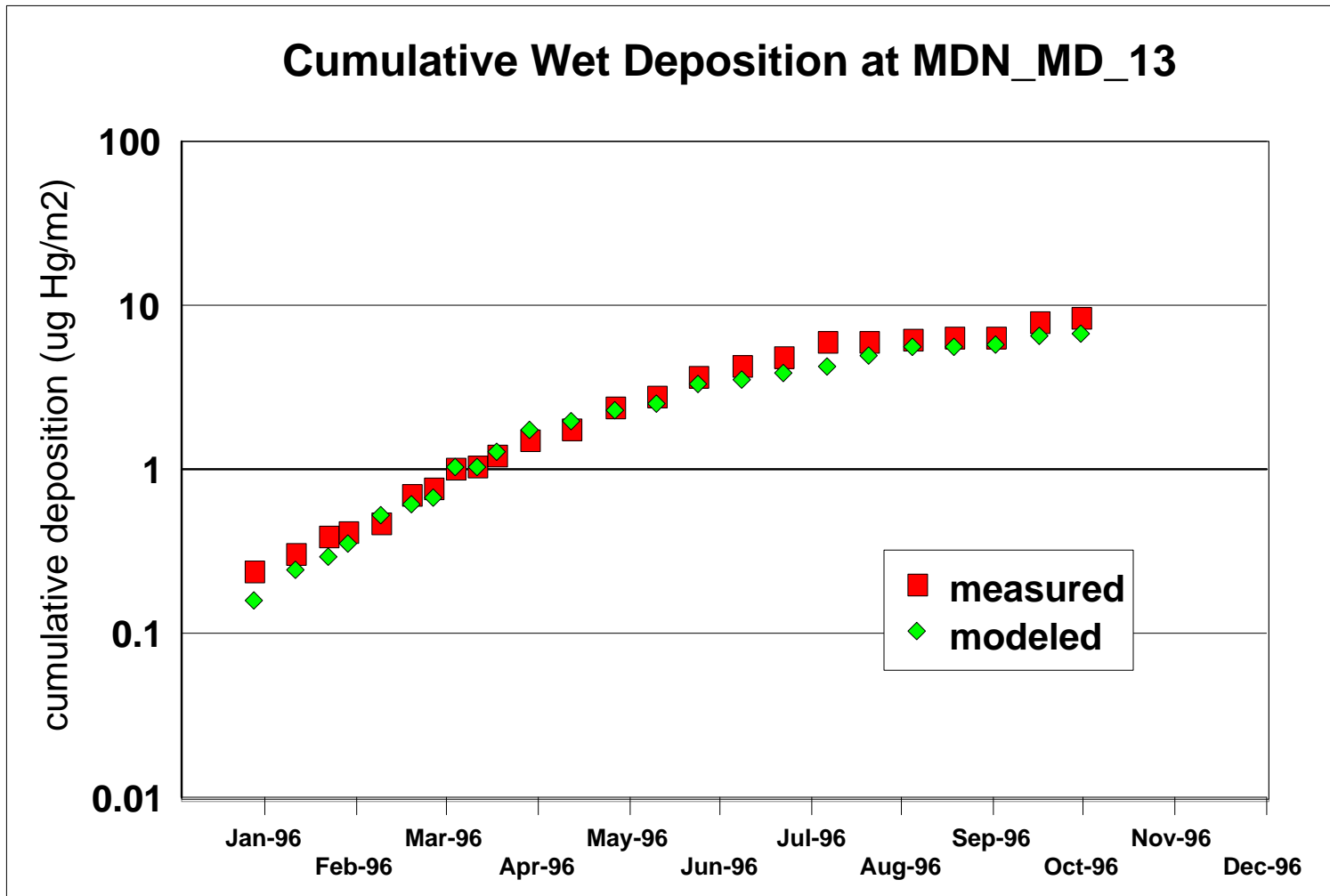


- EMEP Model Intercomparison
  - Phase II – ambient concentrations
  - Phase III – wet and dry deposition
  
- Chesapeake Bay region

## Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE\_02 during 1996



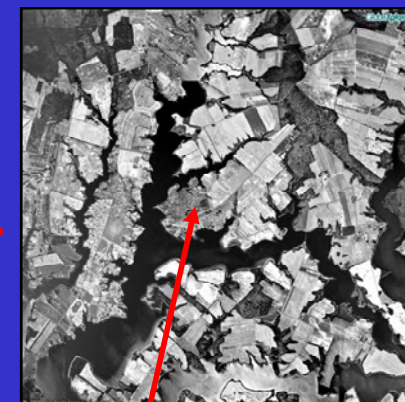
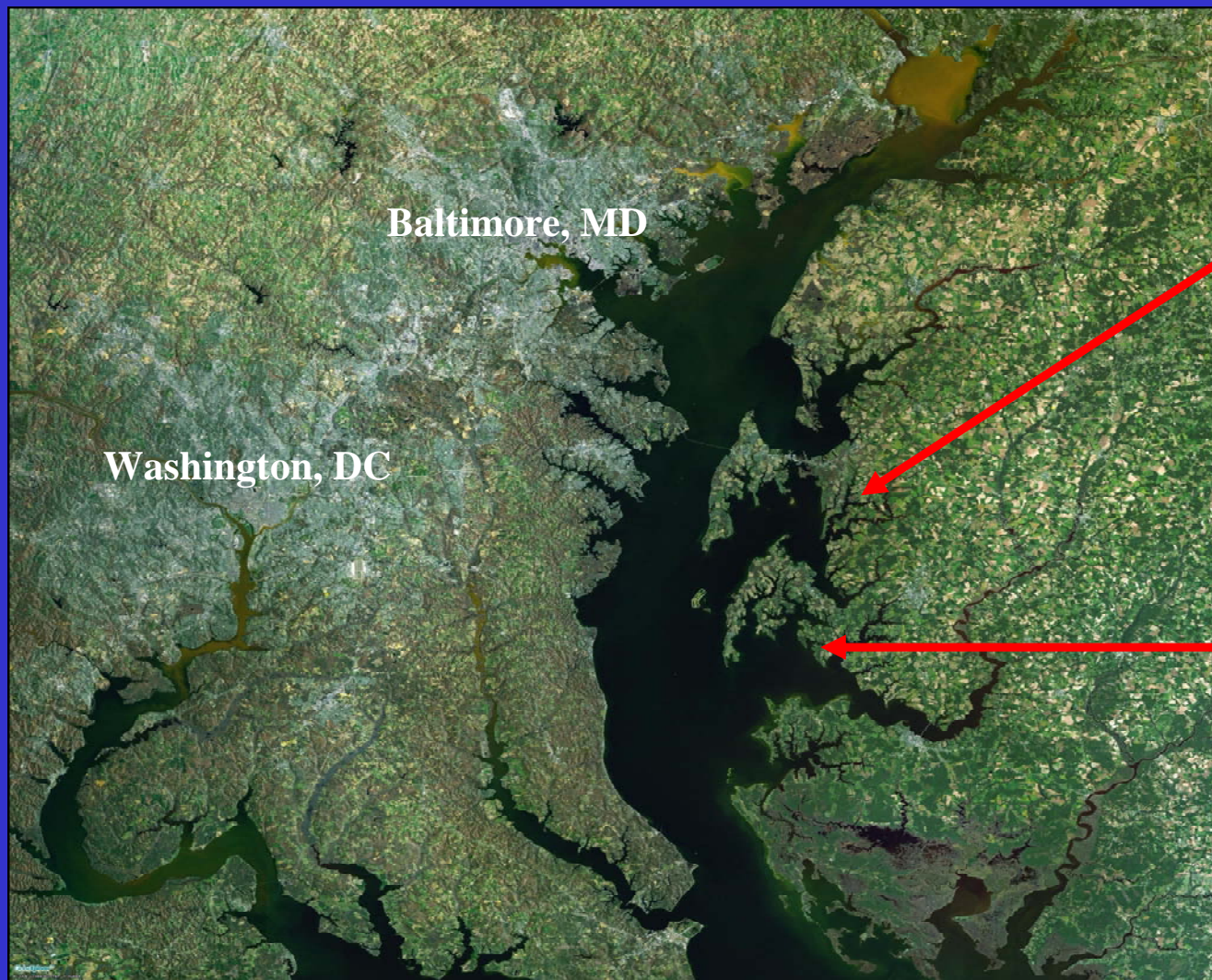
## Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD\_13 during 1996



## **Summer 2004 Chesapeake Bay Atmospheric Hg Study (June – August 2004)**

- NOAA Cooperative Oxford Lab: *Bob Wood*
- NOAA Air Resources Lab Atmospheric Turbulence and Diffusion Division (ATDD): *Steve Brooks*
- NOAA Air Resources Lab HQ Division: *Winston Luke, Paul Kelley, Mark Cohen, Richard Artz*
- NOAA Chesapeake Bay Office: *Maggie Kerchner*
- Frontier GeoSciences: *Bob Brunette, Gerard van der Jagt, Eric Prestbo*
- Univ. of MD Wye Res. and Educ. Center: *Mike Newall*

# Summer 2004 Measurement Sites

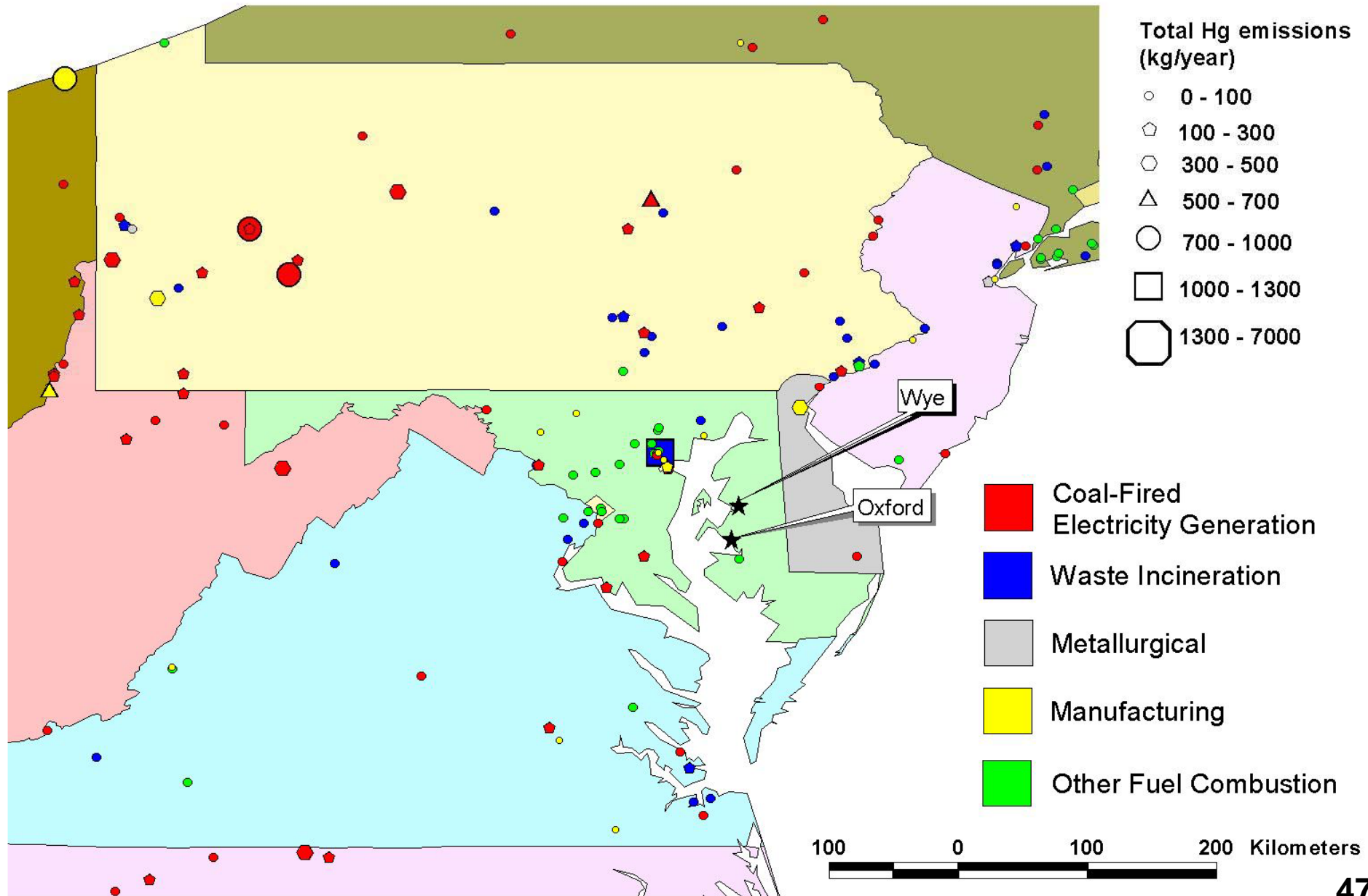


Wye Research and  
Education Center  
(38.9131EN, 76.1525EW)



Cooperative Oxford Lab  
(38.678EN, 76.173EW)

# regional emissions (1999) and sampling sites for summer 2004 Ches Bay Hg study



## Summer 2004 Chesapeake Bay Atmospheric Hg Study (June – August 2004)

	<b>Oxford</b>	<b>Wye</b>
Event-based precipitation samples analyzed for Hg	✓	✓
Speciated Hg concentrations in ambient air (RGM, Hg(p), Hg <sup>0</sup> )	✓	✓
Ambient concentration of ozone and sulfur dioxide	✓ (continuous)	✓ (weekly via AirMON Dry)
Ambient concentration of carbon monoxide	✓	
Meteorology	✓	✓ (via NADP/NTN site)
Major ions in precipitation		✓ (via NADP/NTN site)



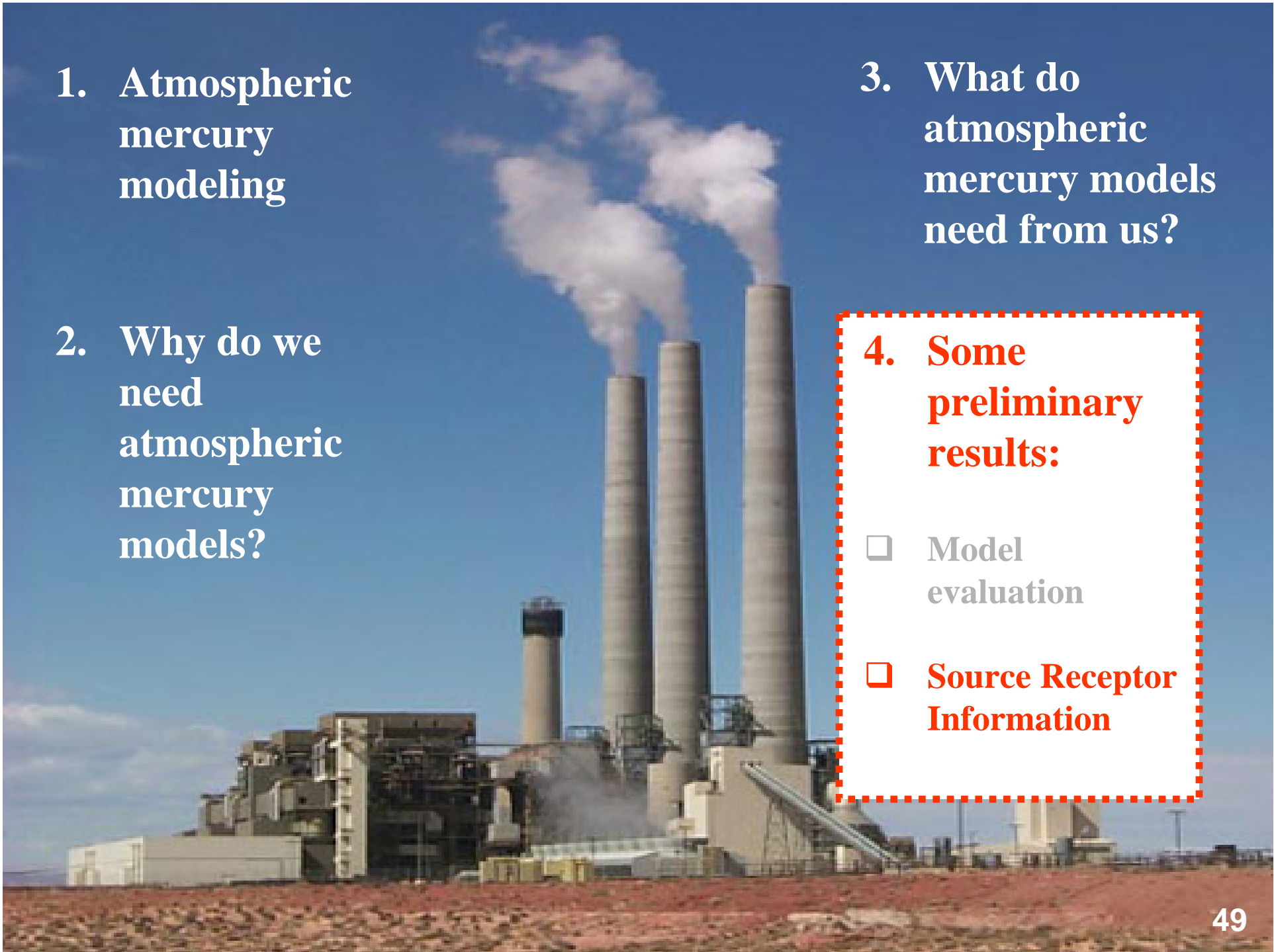
1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

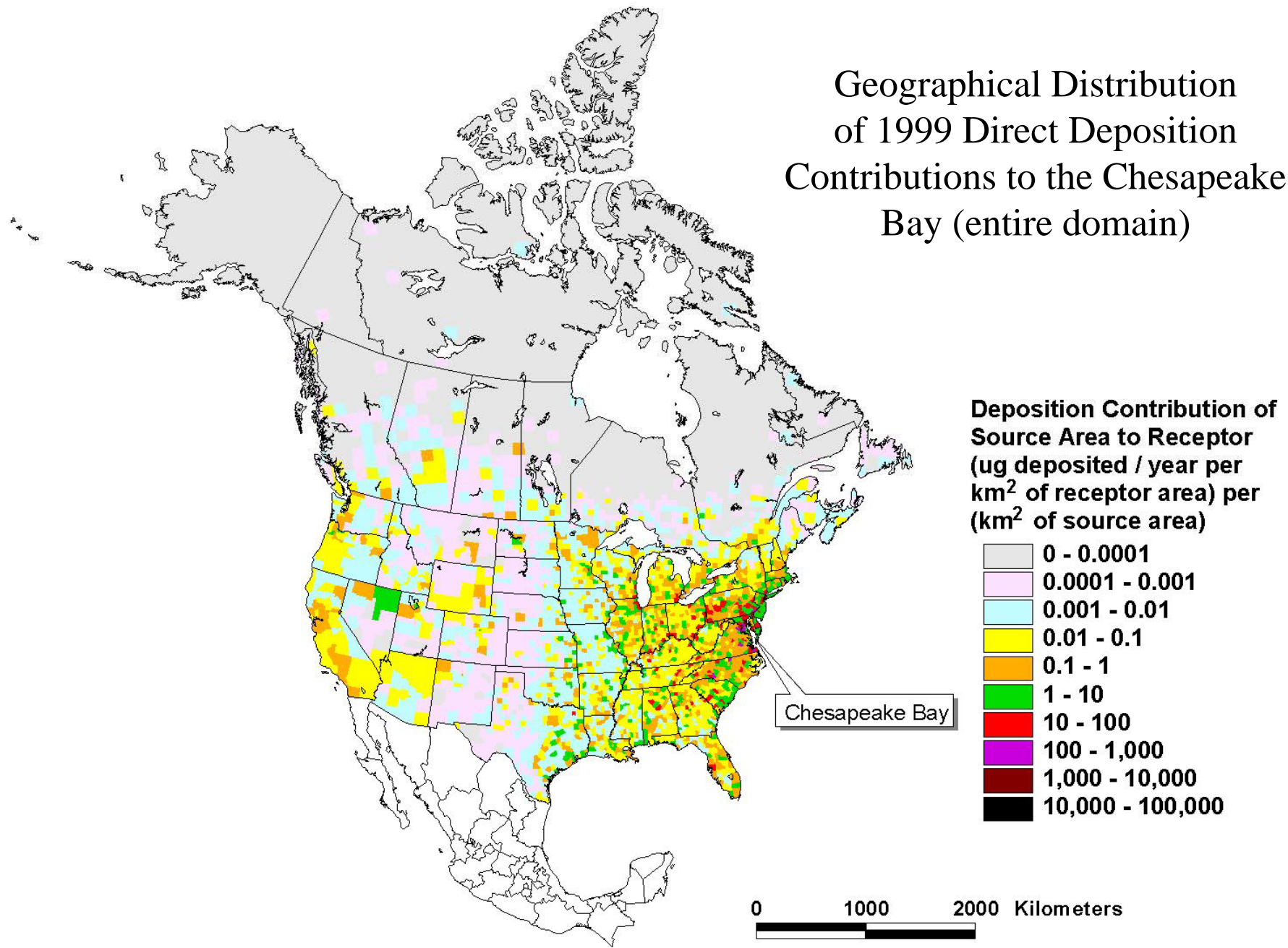
4. **Some preliminary results:**

- Model evaluation
- Source Receptor Information**

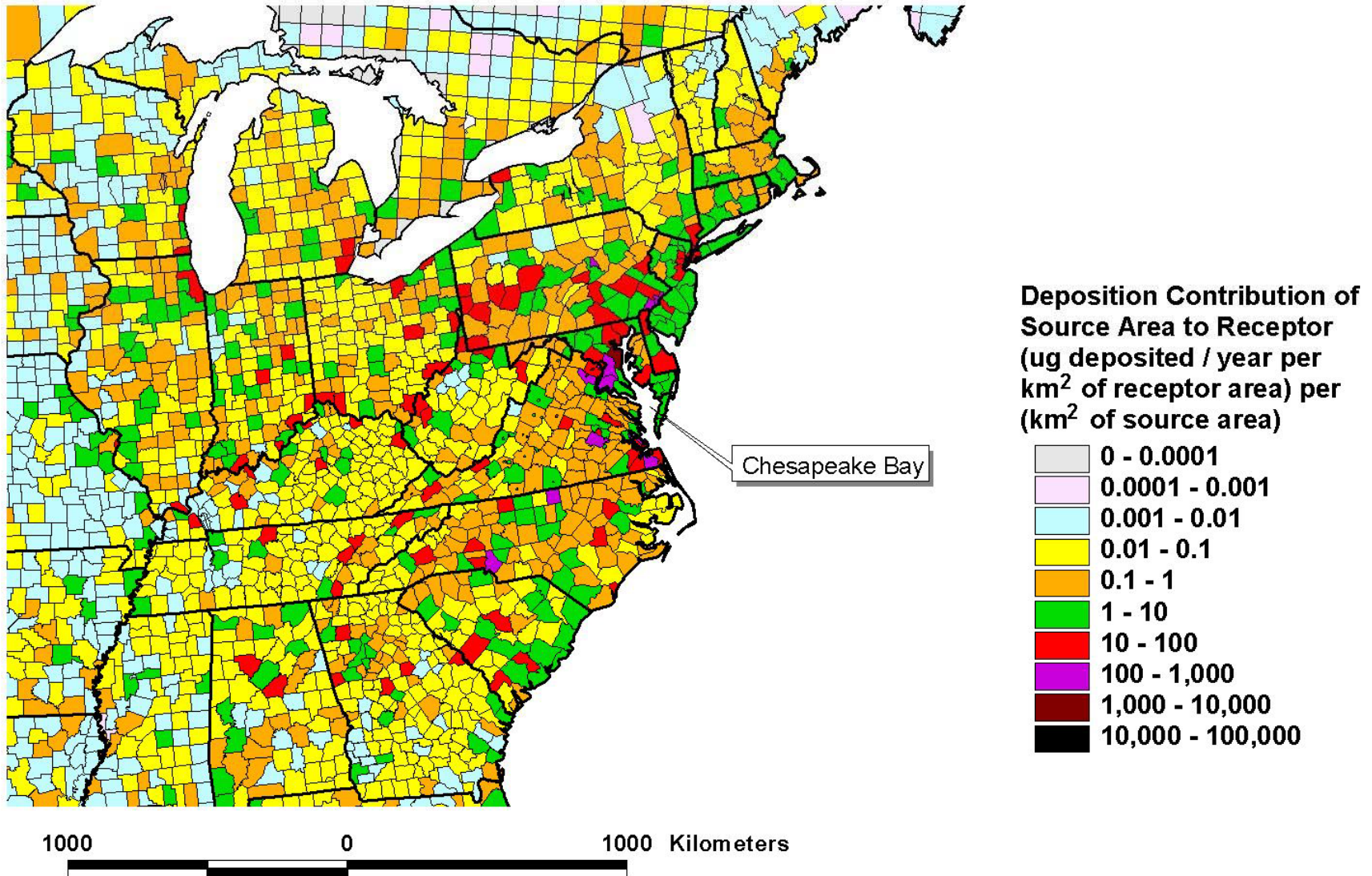


**Example of  
Detailed Results:  
1999 Results for  
Chesapeake Bay**

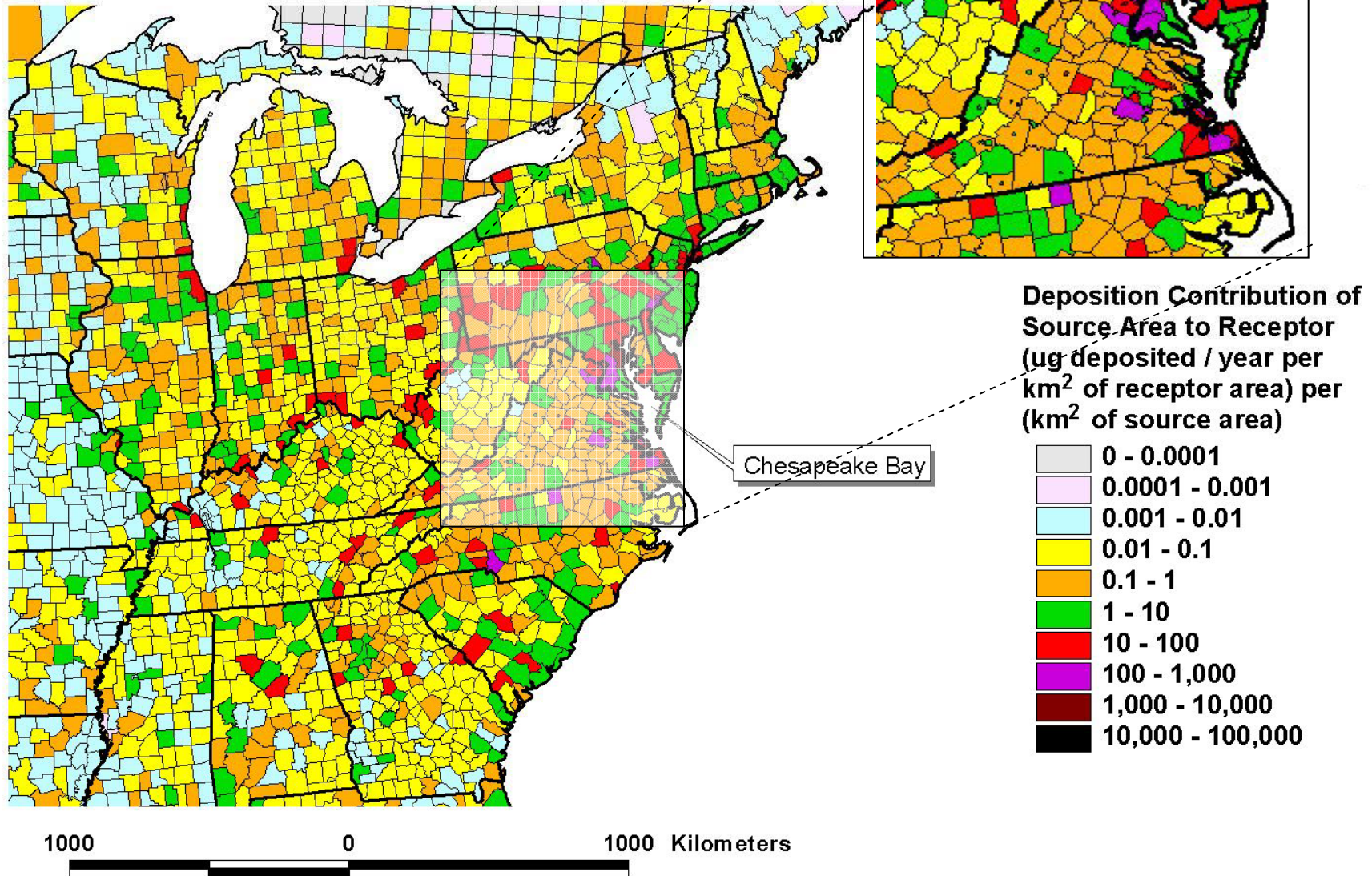
# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)



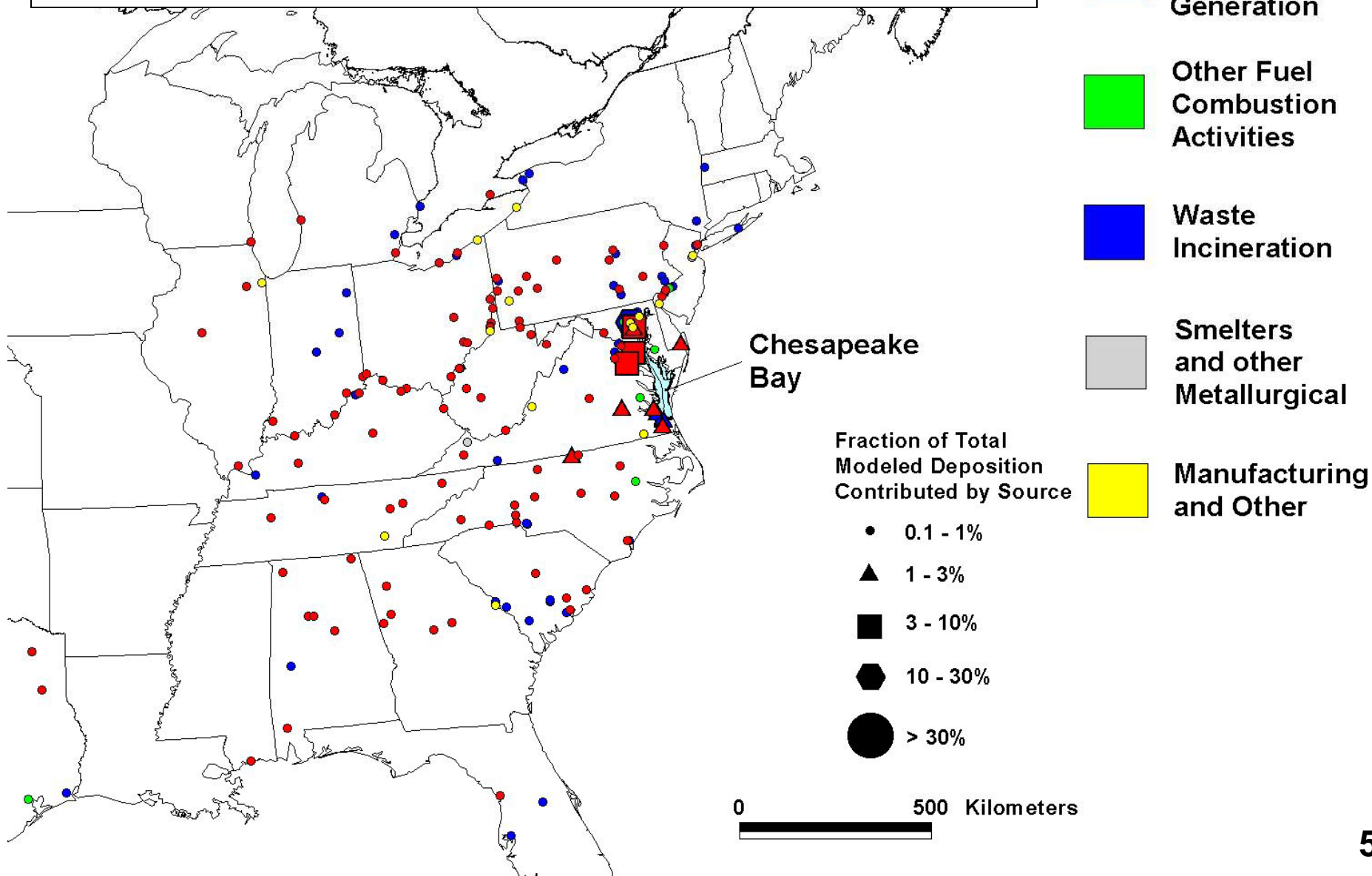
# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)



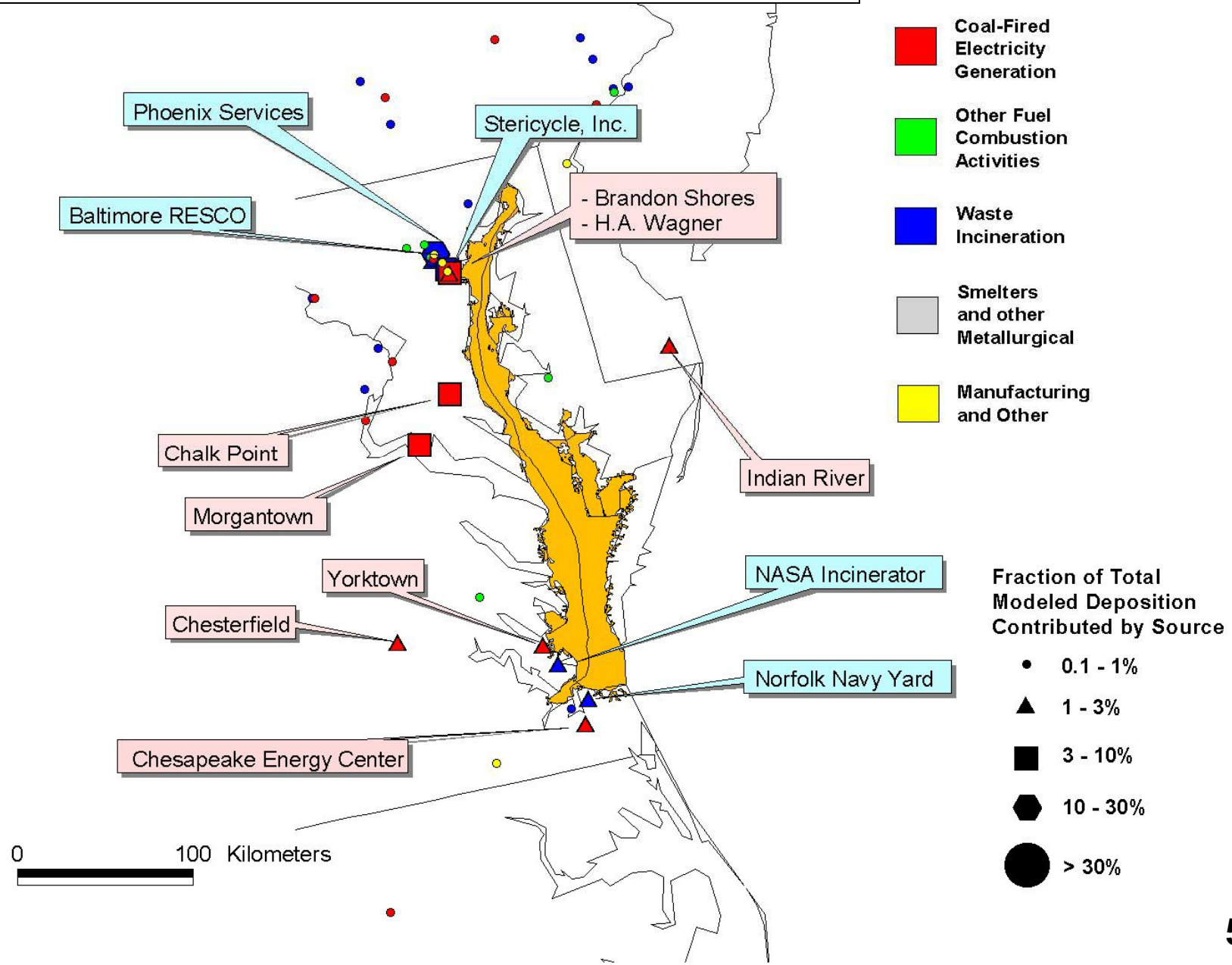
# Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)



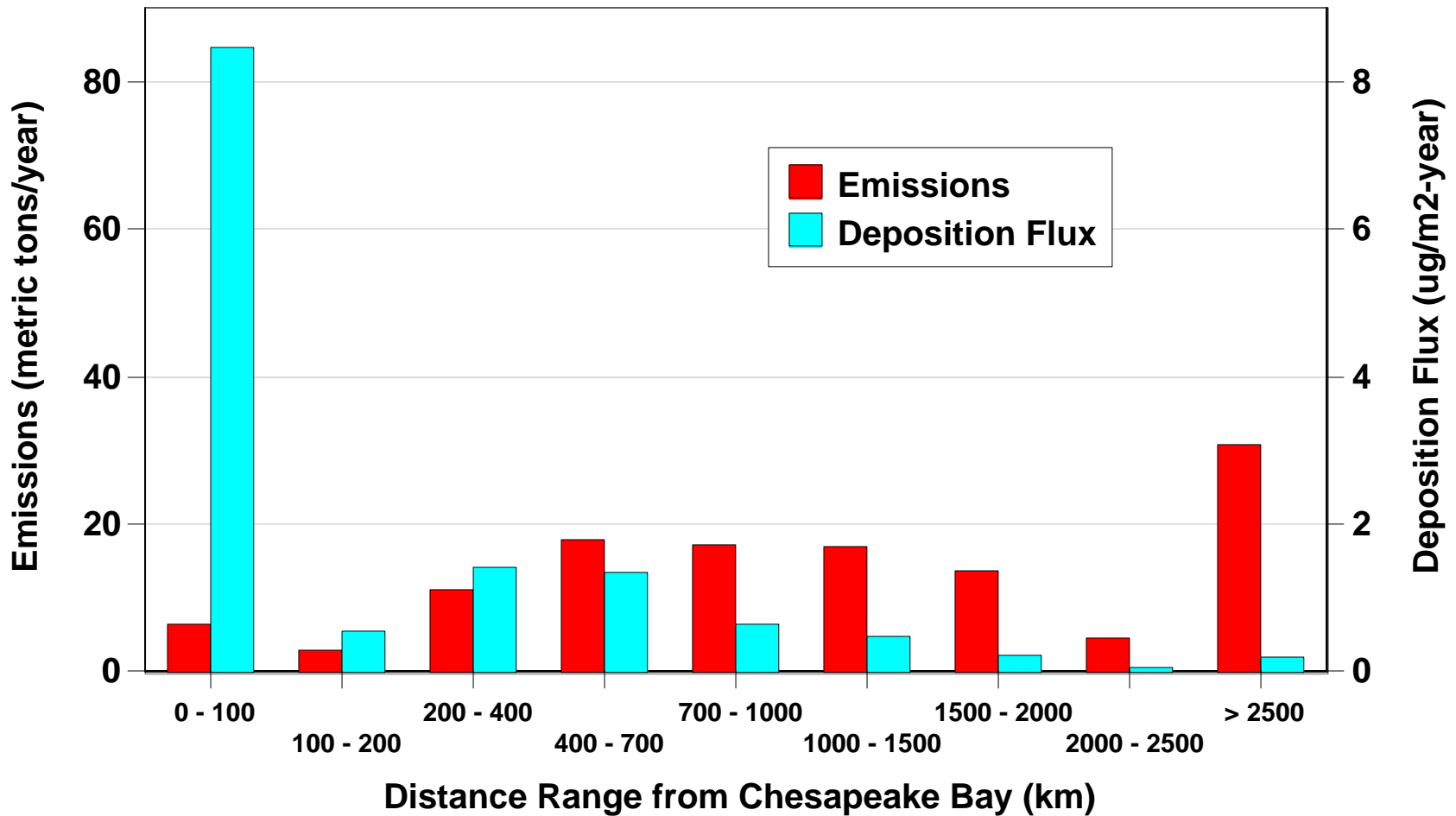
# Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



# Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

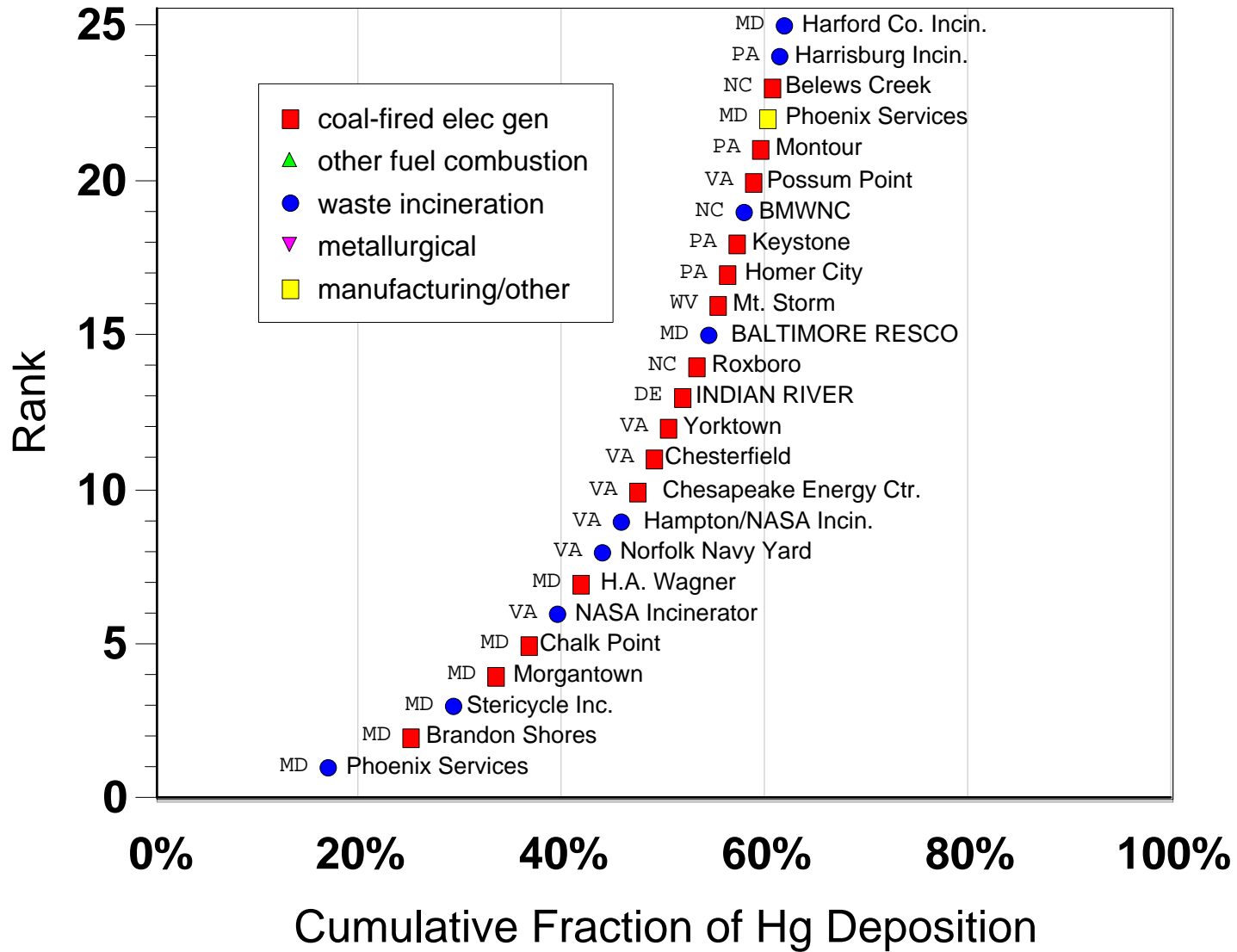


# Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay



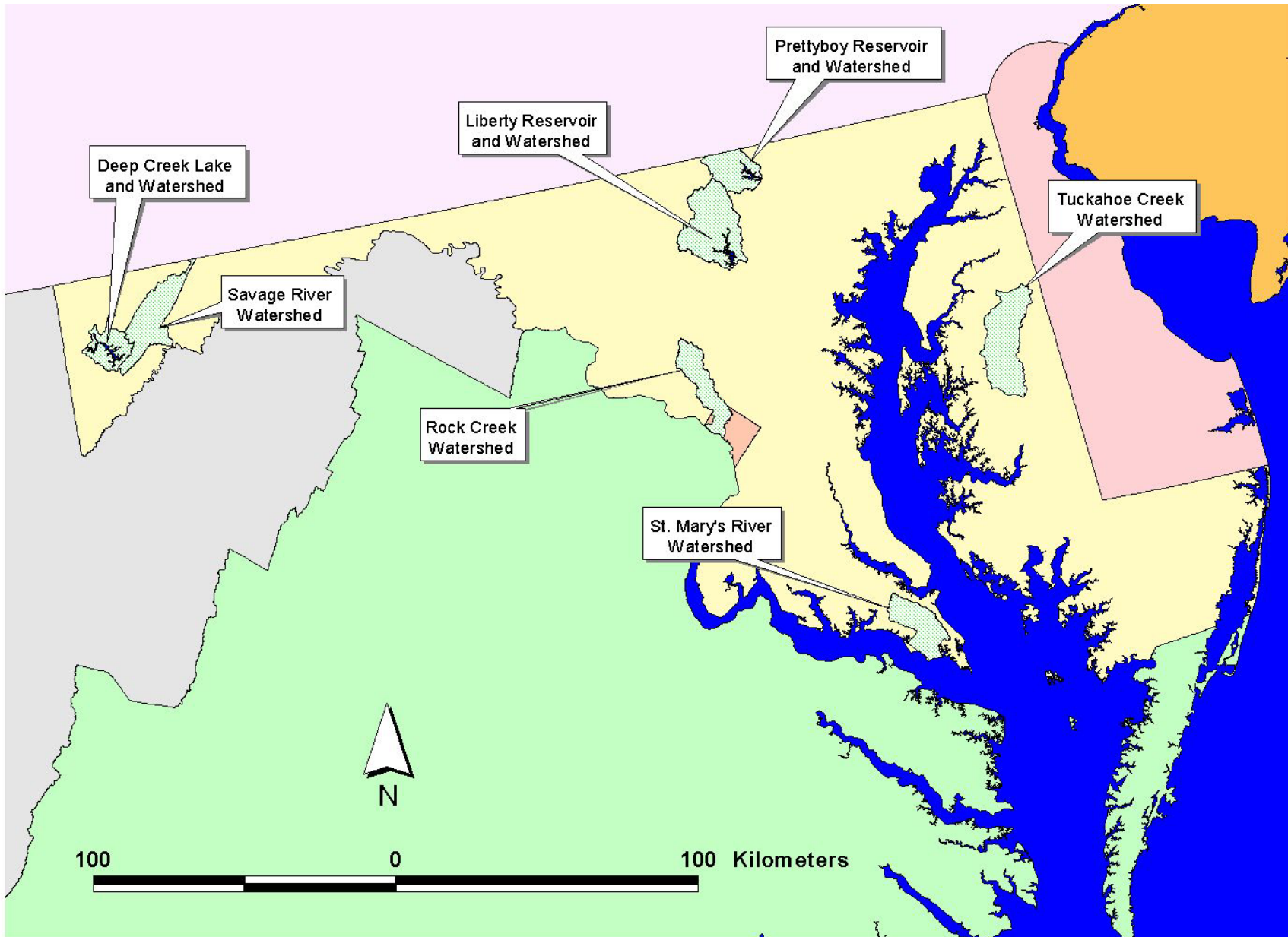


# Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay

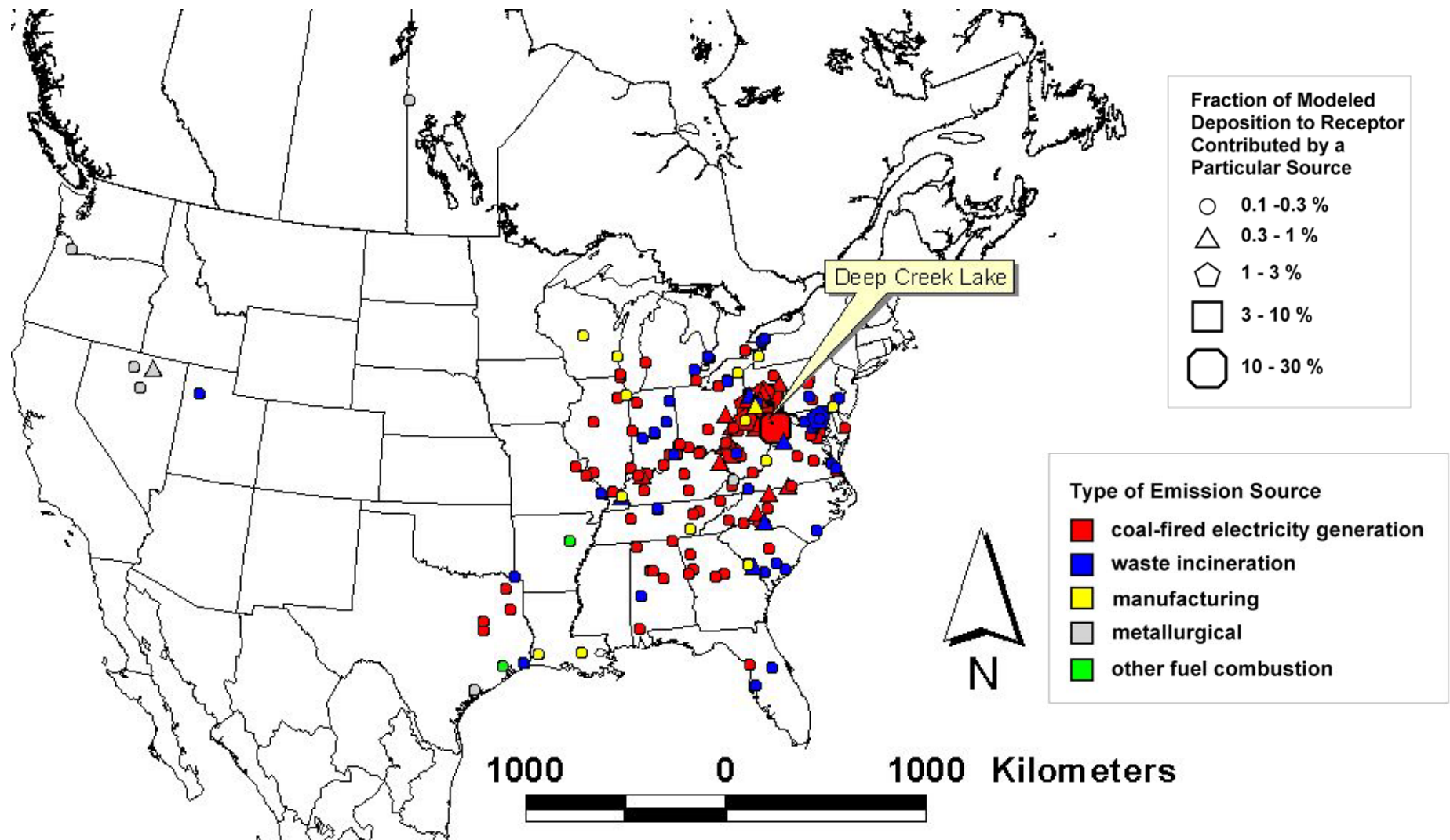


# **Preliminary Results for other Maryland Receptors**

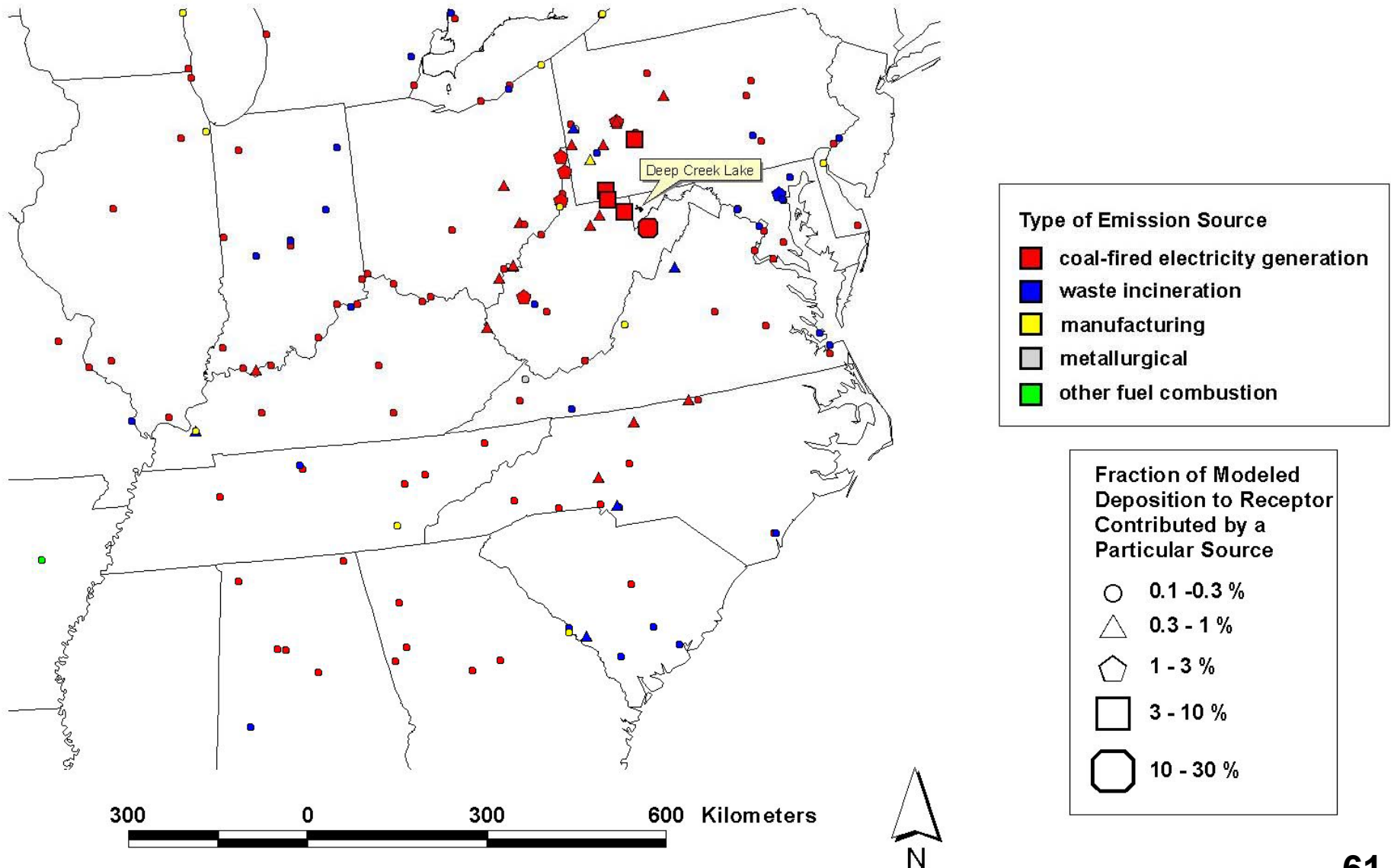
# Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling (*but modeling was not optimized for these receptors!*)



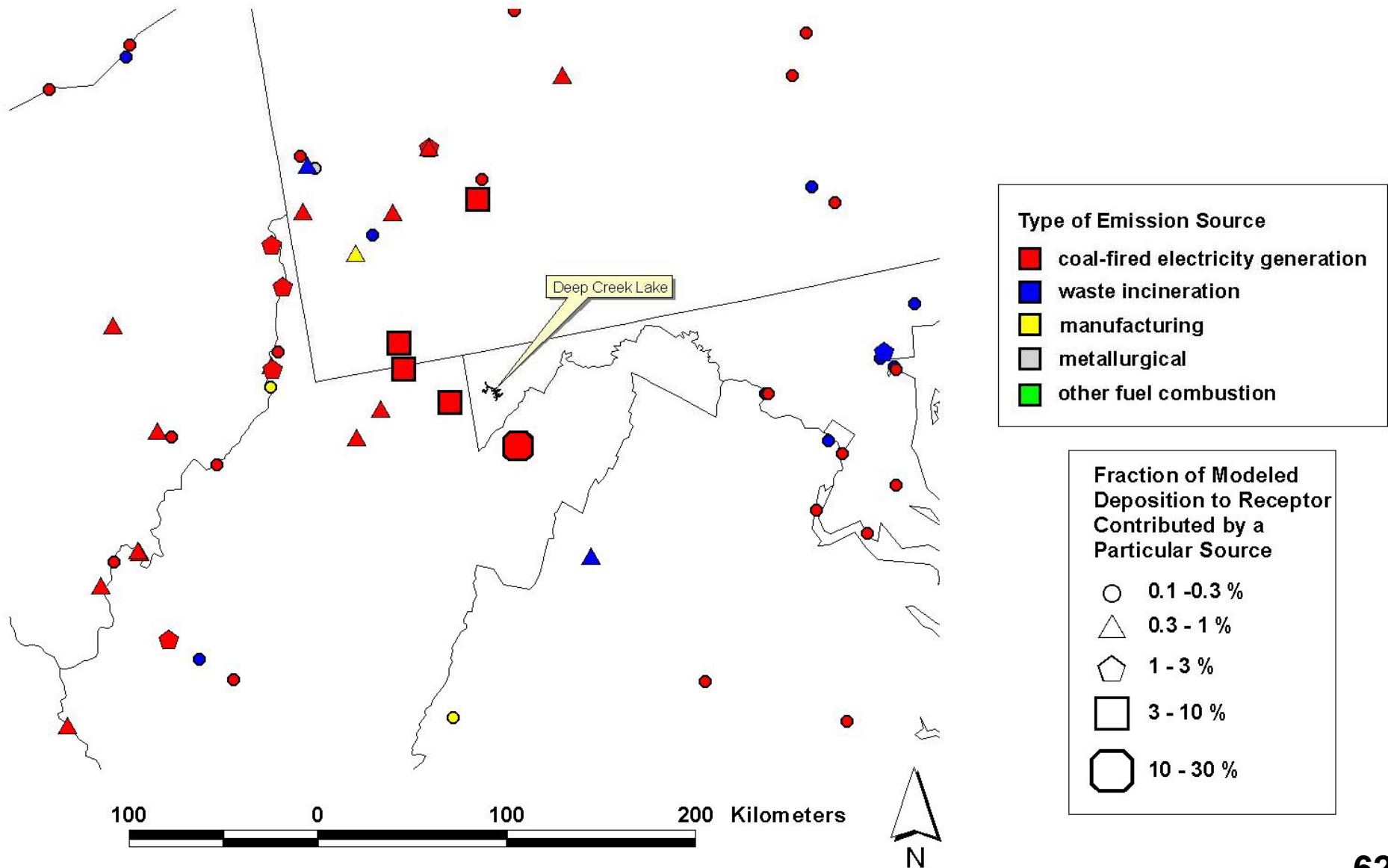
Largest Modeled Atmospheric Deposition Contributors Directly to  
Deep Creek Lake based on 1999 USEPA Emissions Inventory  
(national view)



# Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (regional view)









# Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (close-up view)



# Some Next Steps

- Use more highly resolved meteorological data grid
- Expand model domain to include global sources
- Simulate natural emissions and re-emissions of previously deposited Hg
- Additional model evaluation exercises ... more sites, more time periods, more variables [*Measurements in Chesapeake Bay region*]
- Sensitivity analyses and examination of atmospheric Hg chemistry (e.g. marine boundary layer, upper atmosphere)
- Dynamic linkage with ecosystem cycling models

# Conclusions

-  **Source-attribution information is important**
-  **Impacts are episodic & depend on form of mercury emitted**
-  **Modeling needed to get source-attribution information**
-  **Not enough monitoring data to evaluate and improve models**
-  **Many uncertainties but useful model results are emerging**
-  **Models don't have to be perfect to give useful information**

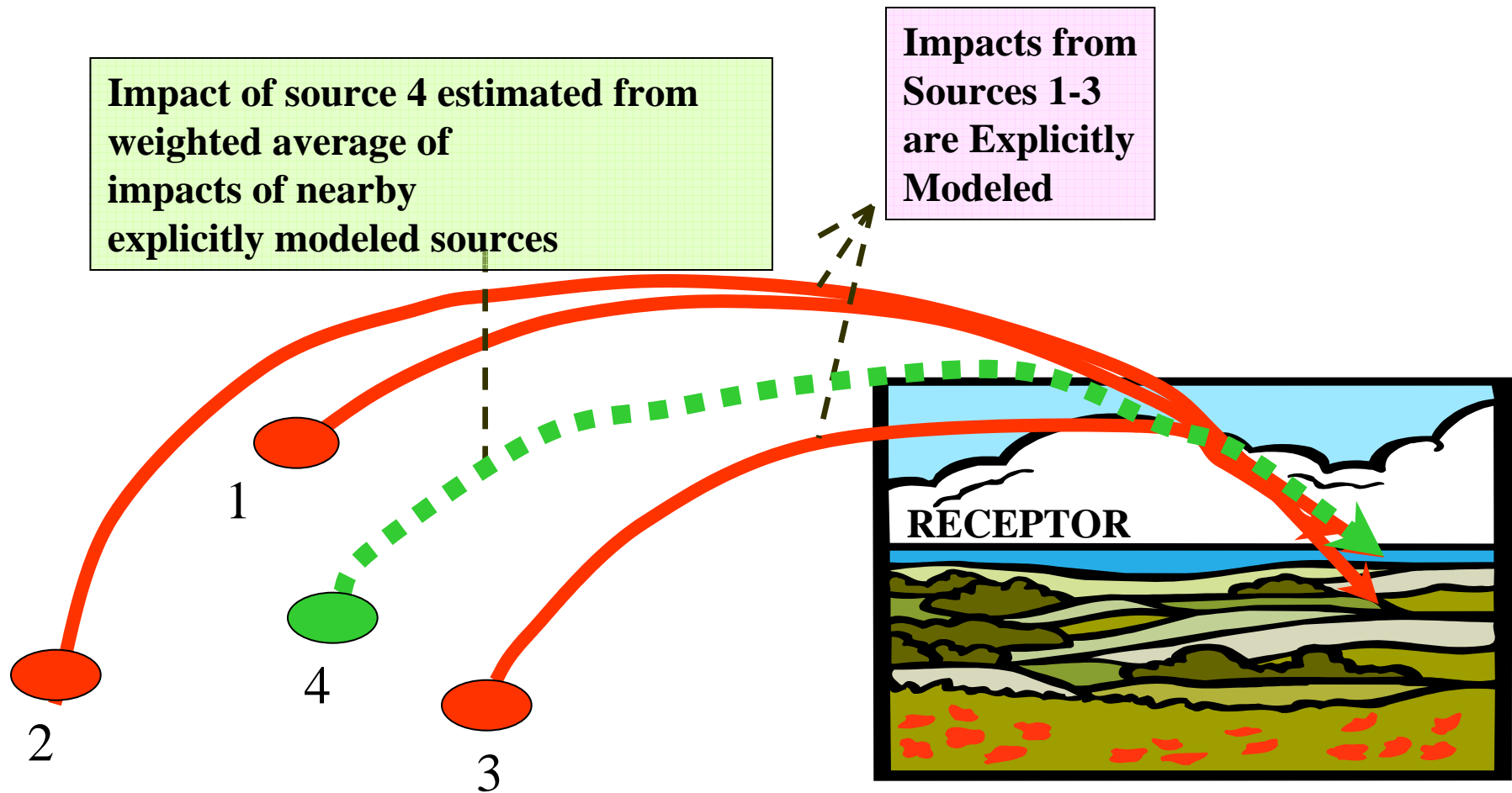


# EXTRA SLIDES

## Why might the atmospheric fate of mercury emissions be essentially linearly independent?

- Hg is present at extremely trace levels in the atmosphere
- Hg won't affect meteorology (can simulate meteorology independently, and provide results to drive model)
- Most species that complex or react with Hg are generally present at *much* higher concentrations than Hg
- Other species (e.g. OH) generally react with many other compounds than Hg, so while present in trace quantities, their concentrations cannot be strongly influenced by Hg
- Wet and dry deposition processes are generally 1<sup>st</sup> order with respect to Hg
- The current “consensus” chemical mechanism (equilibrium + reactions) does not contain any equations that are not 1<sup>st</sup> order in Hg

# Spatial interpolation

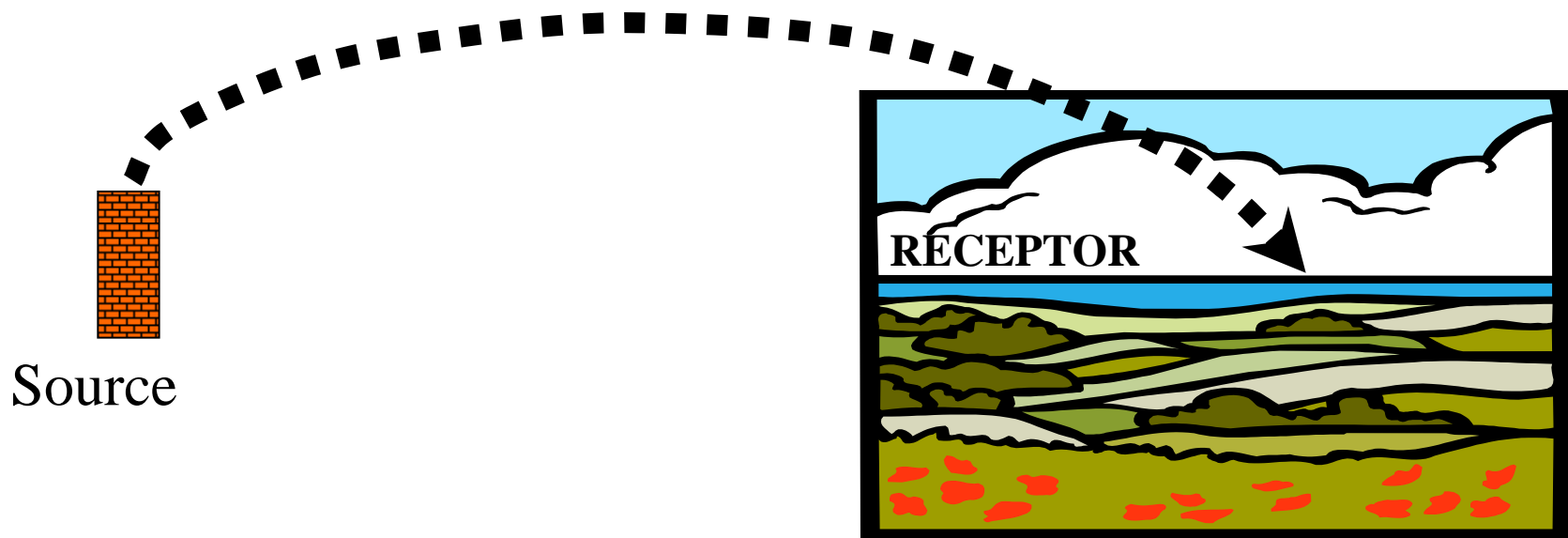


- **Perform separate simulations at each location for emissions of pure Hg(0), Hg(II) and Hg(p)**

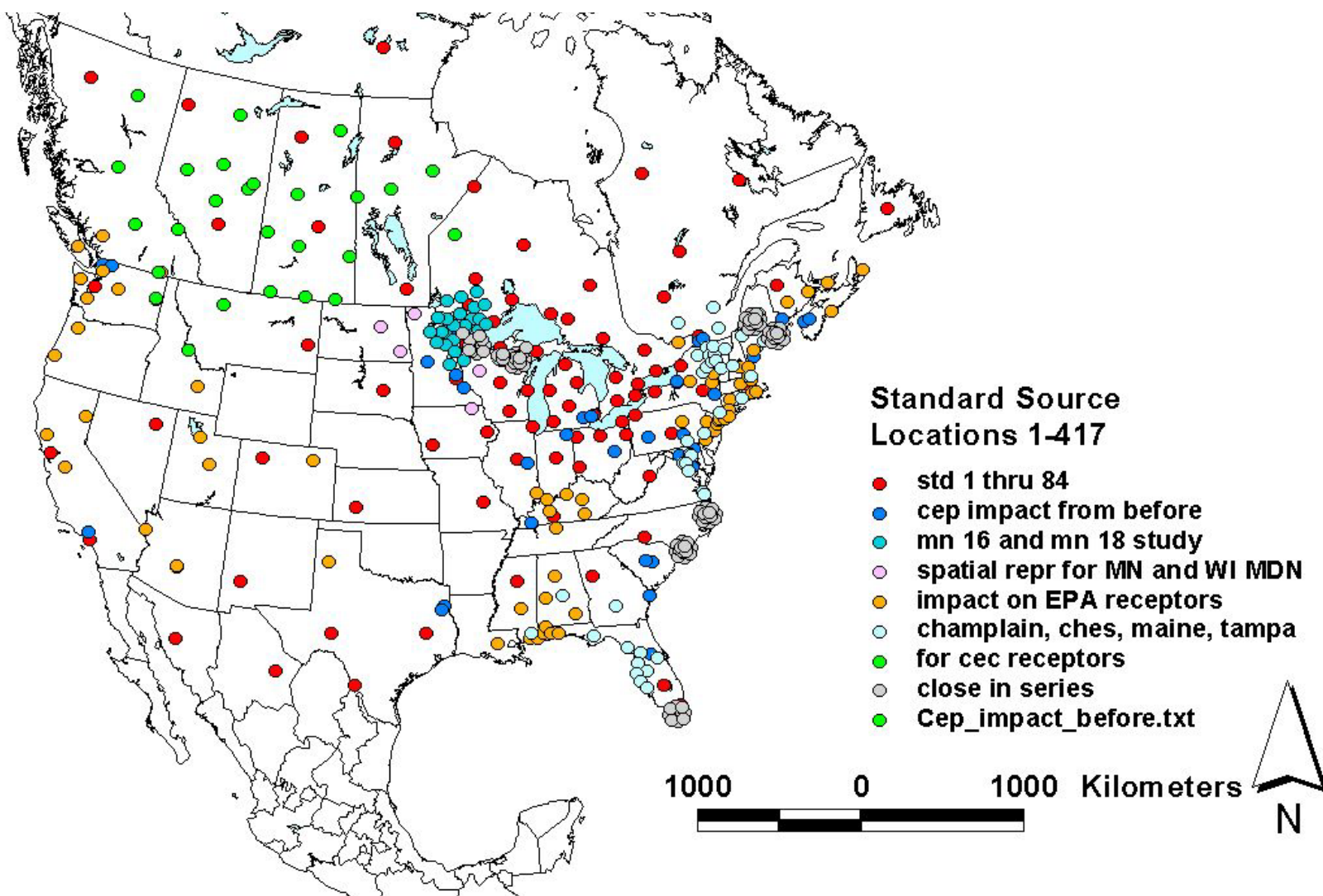
*[after emission, simulate transformations between Hg forms]*

- **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>



# Standard Source Locations in Maryland region during recent simulation

