Modeling the Atmospheric Transport and Deposition of Mercury

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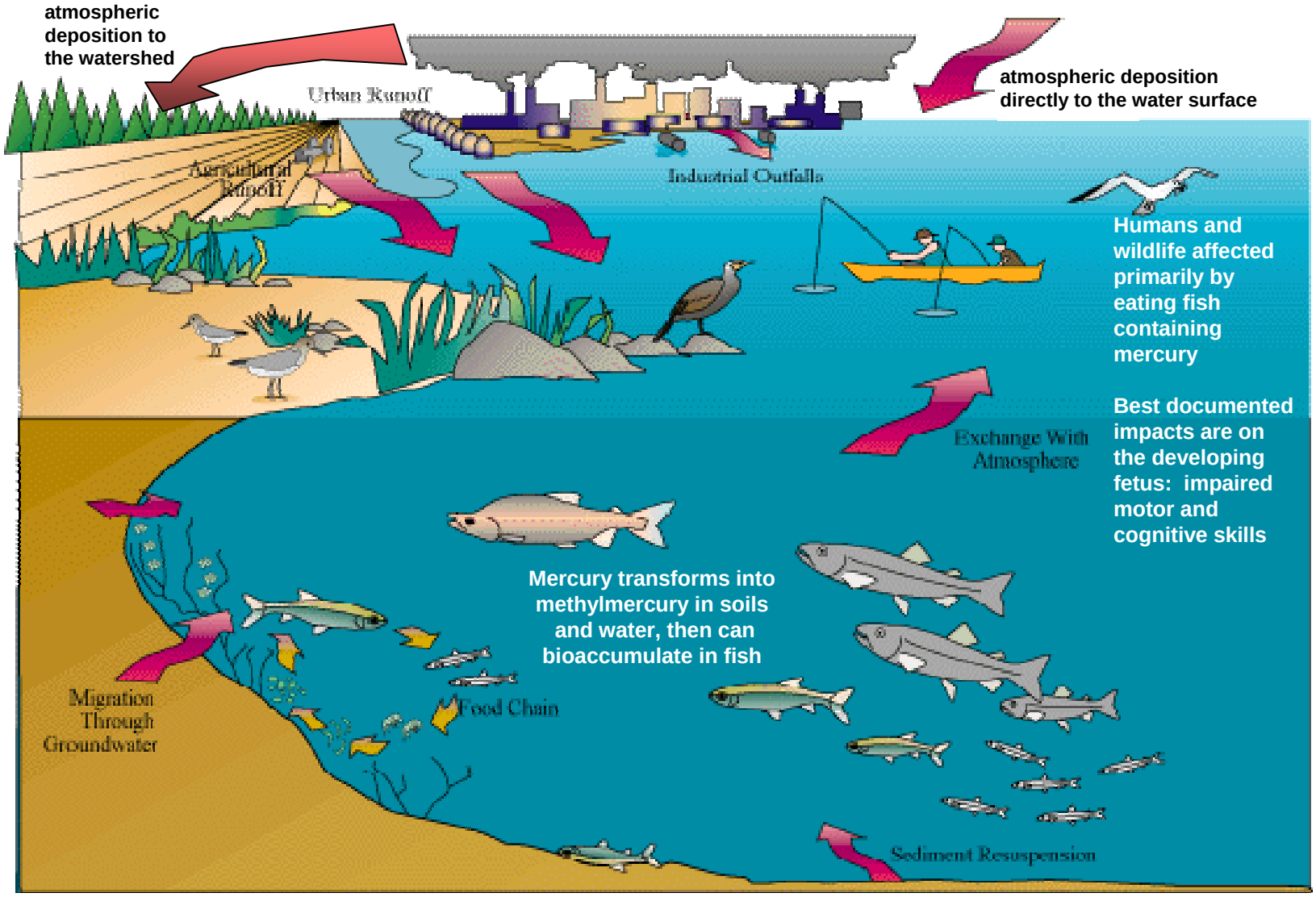
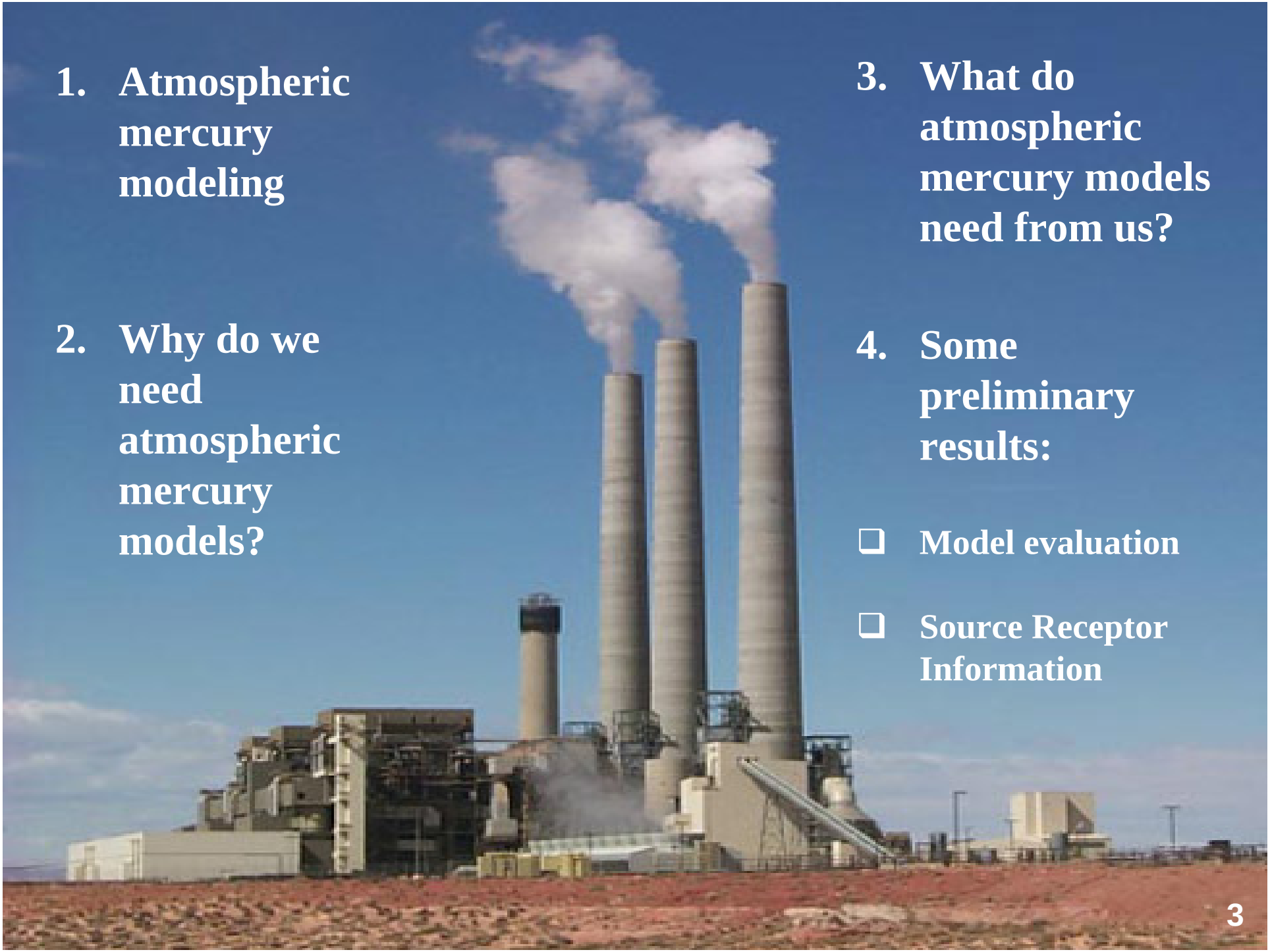
Silver Spring, Maryland

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





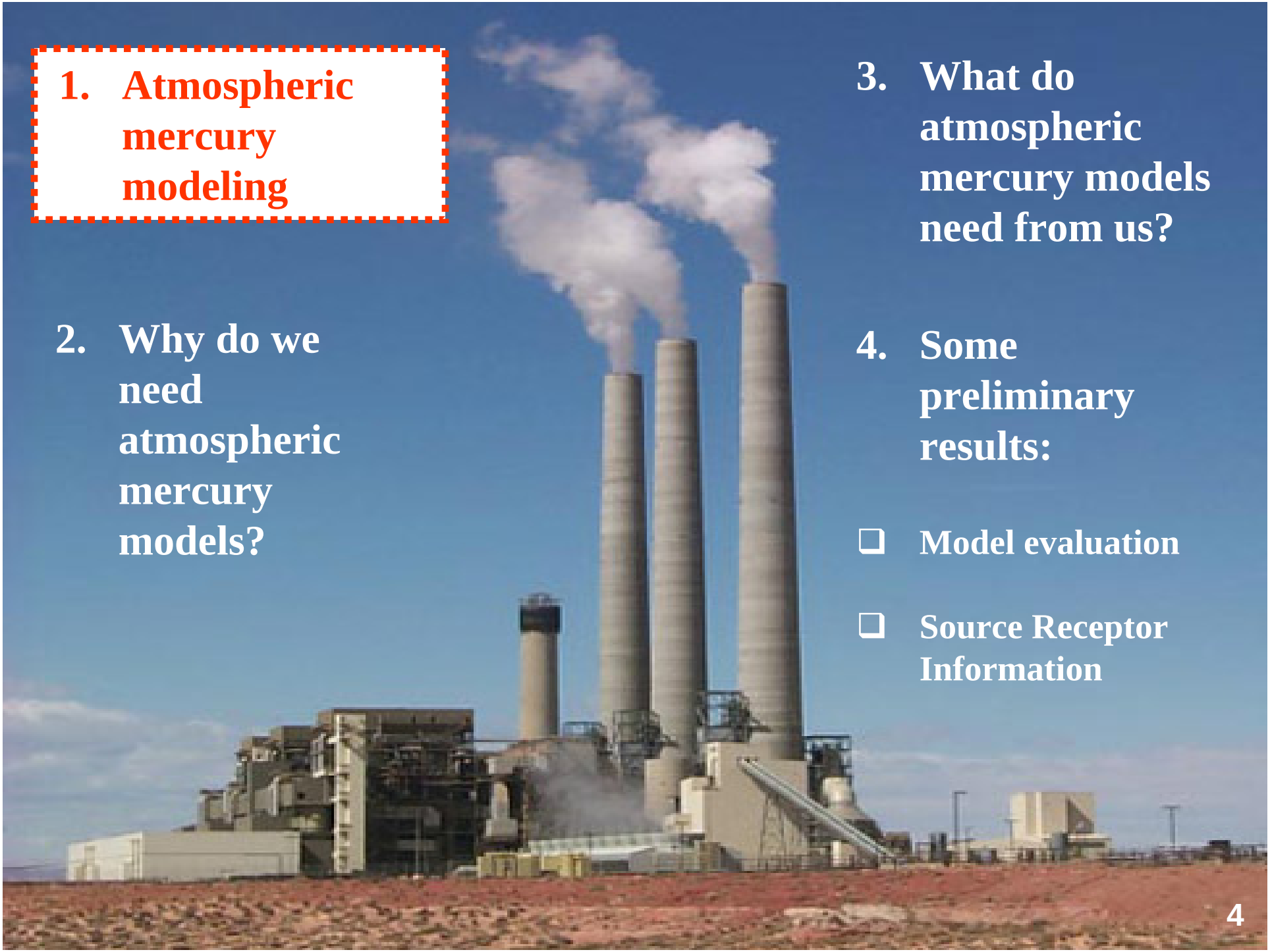
1. **Atmospheric mercury modeling**

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**



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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**

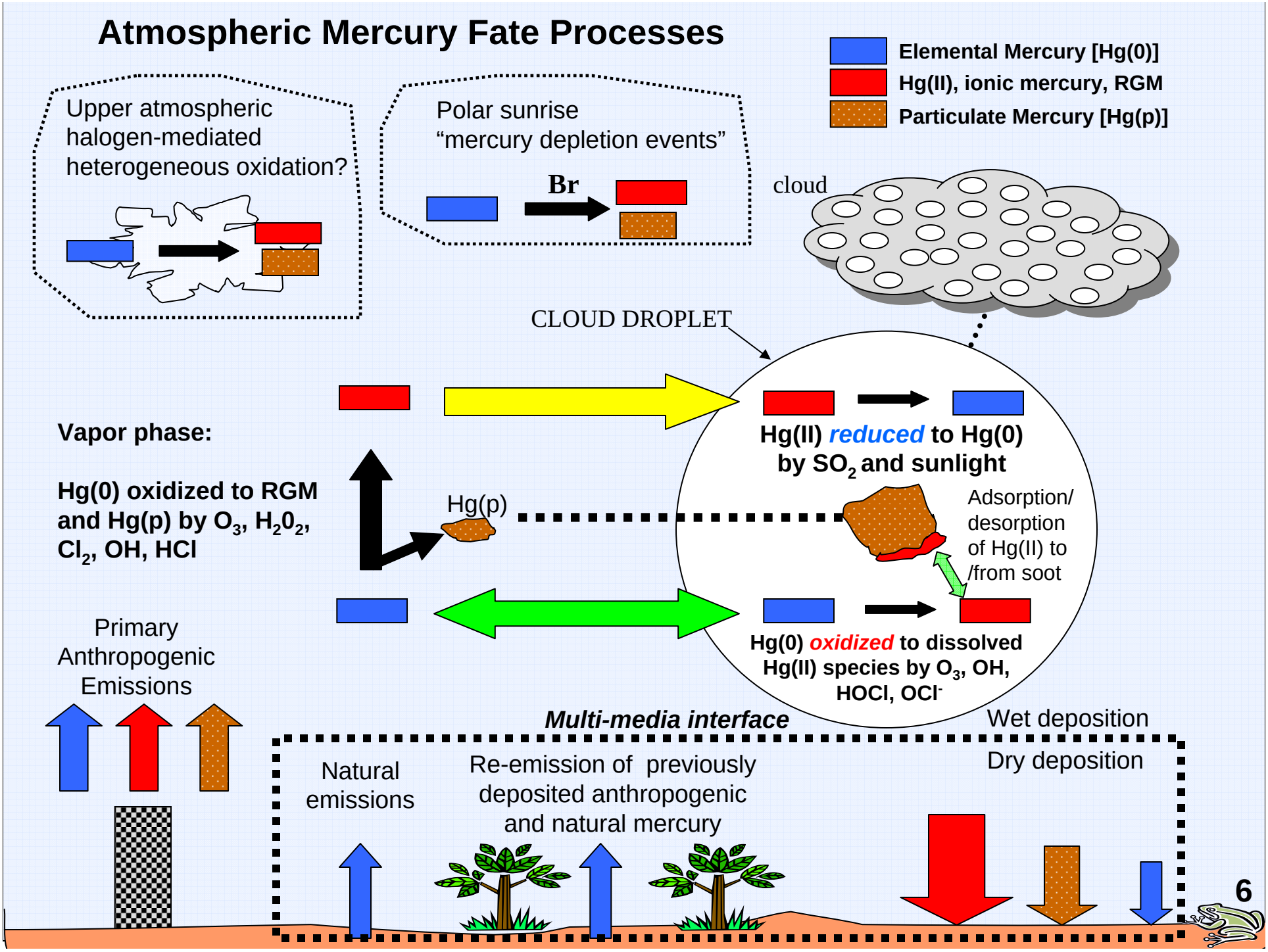
Reactive Gaseous Mercury (“RGM”)

- **a few percent of total Hg in atmosphere**
- **oxidized mercury: Hg(II)**
- **HgCl2, 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

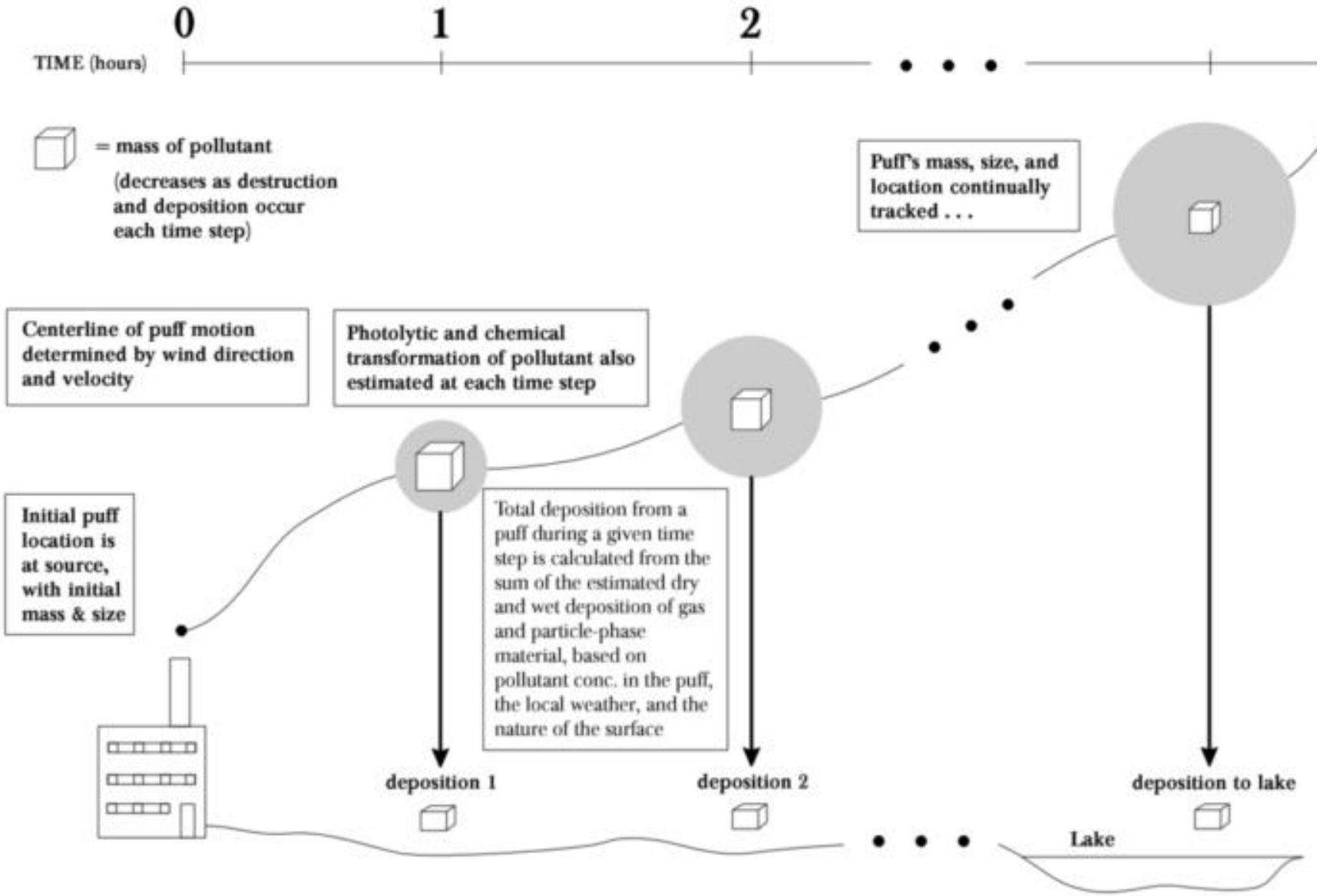


Atmospheric Chemical Reaction Scheme for Mercury

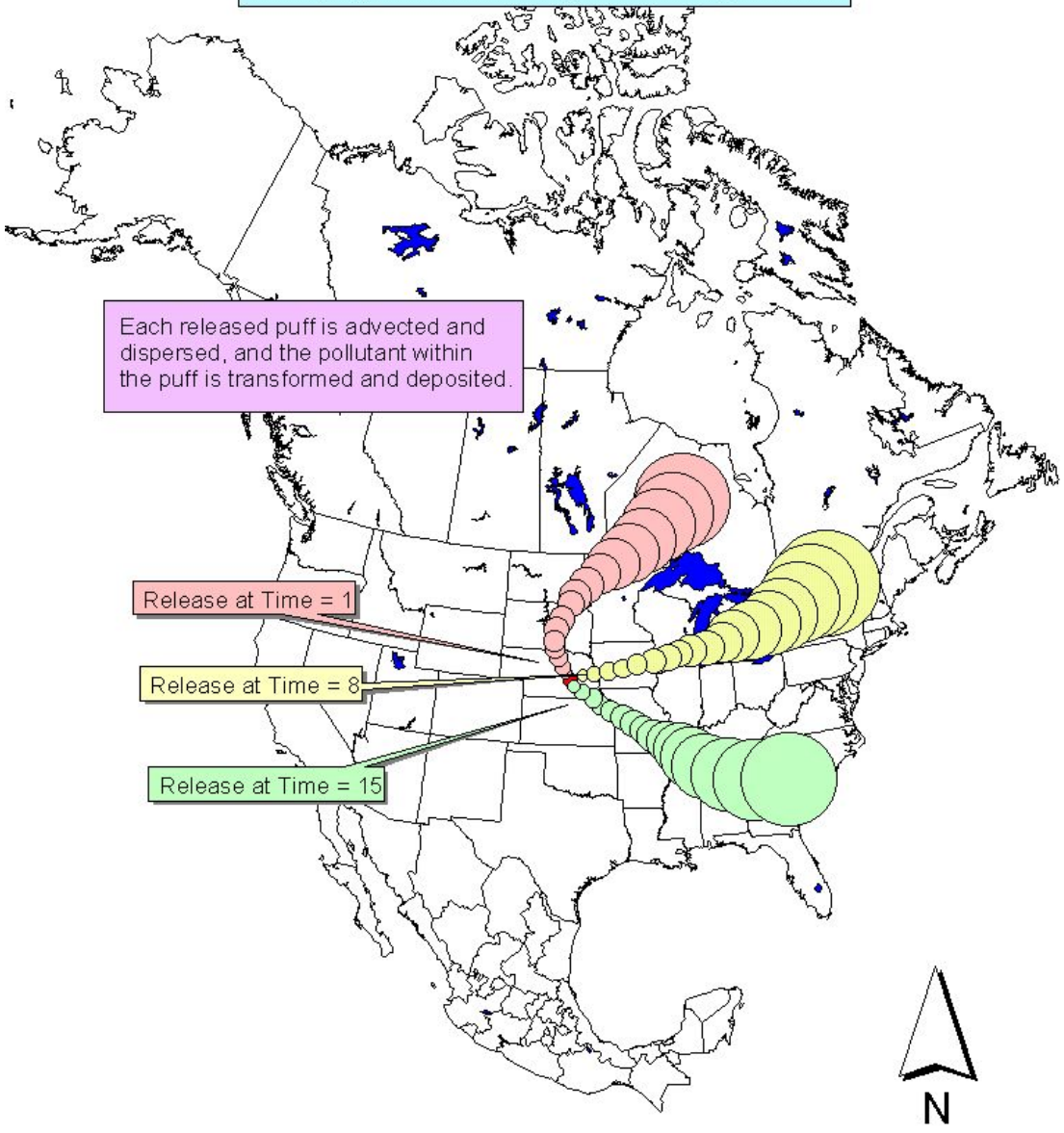
Reaction	Rate	Units	Reference
GAS PHASE REACTIONS			
$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm^3/molec-sec	Hall (1995)
$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm^3/molec-sec	Calhoun and Prestbo (2001)
$Hg^0 + OHC \rightarrow Hg(p)$	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
AQUEOUS PHASE REACTIONS			
$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(molar\text{-}sec)^{-1}$	Munthe (1992)
$Hg^0 + OHC \rightarrow Hg^{+2}$	2.0E+9	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1997)
$HgSO_3 \rightarrow Hg^0$	$T*e^{((31.971*T)-12595.0)/T)}$ sec^{-1} [T = temperature (K)]		Van Loon et al. (2002)
$Hg(II) + HO_2C \rightarrow Hg^0$	~ 0	$(molar\text{-}sec)^{-1}$	Gardfeldt & Jonnson (2003)
$Hg^0 + HOCl \rightarrow Hg^{+2}$	2.1E+6	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1998)
$Hg^0 + OCl^{-1} \rightarrow Hg^{+2}$	2.0E+6	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1998)
$Hg(II) \leftrightarrow Hg(II)_{(soot)}$	9.0E+2	liters/gram; t = 1/hour	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$Hg^{+2} + h< \rightarrow Hg^0$	6.0E-7	$(sec)^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

NOAA HYSPLIT MODEL

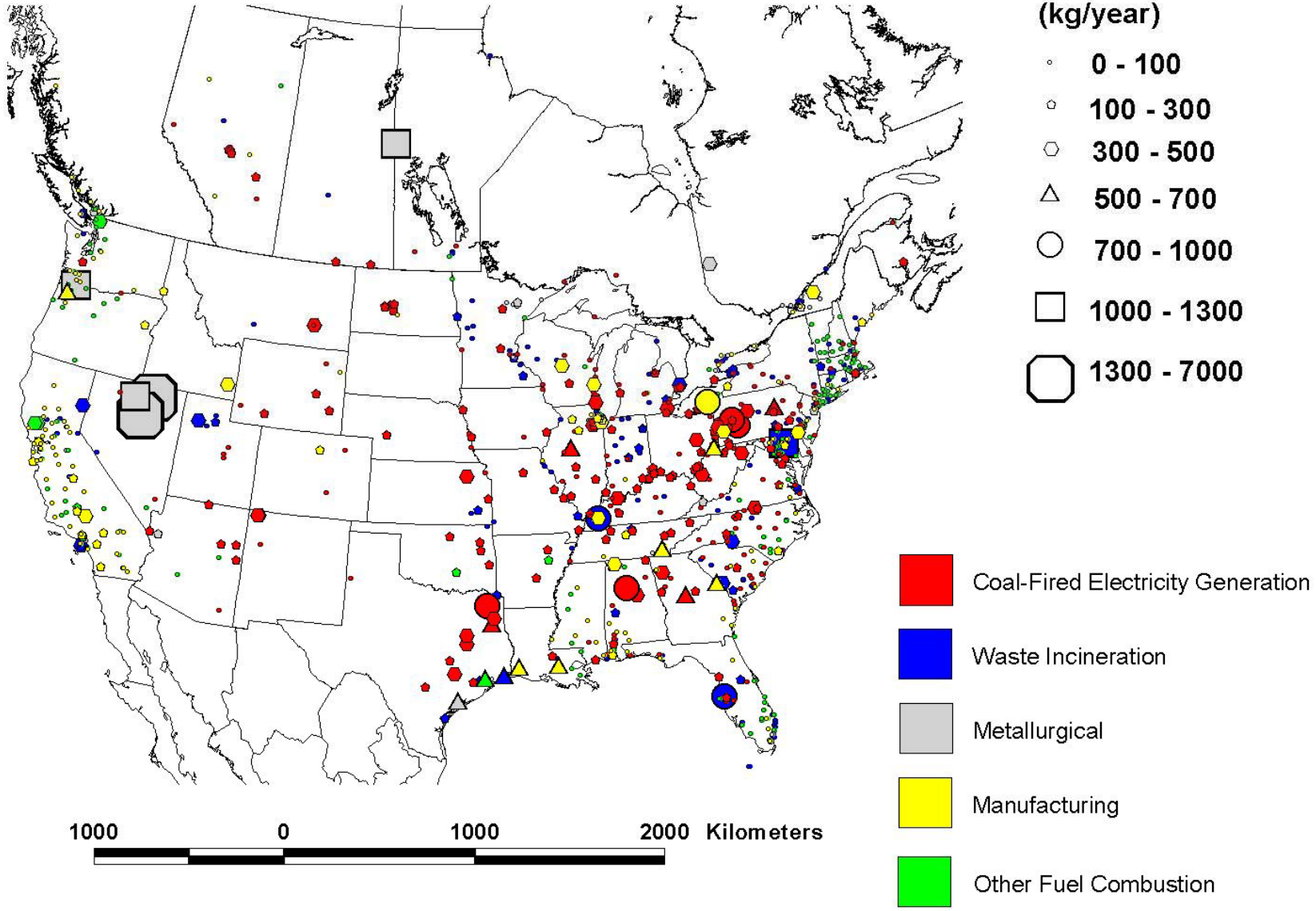
Lagrangian Puff Air Transport and Deposition Model

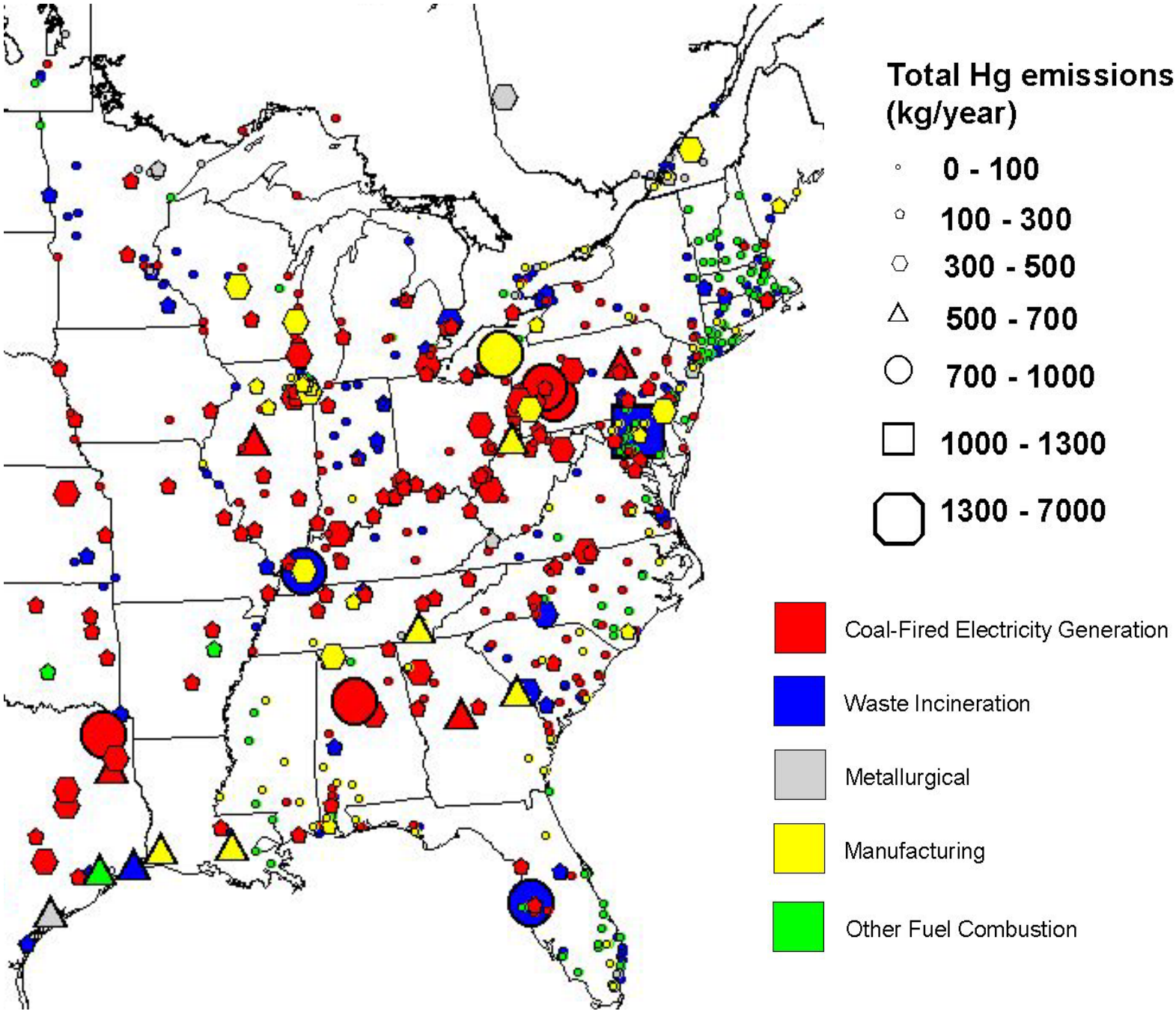


Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).



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

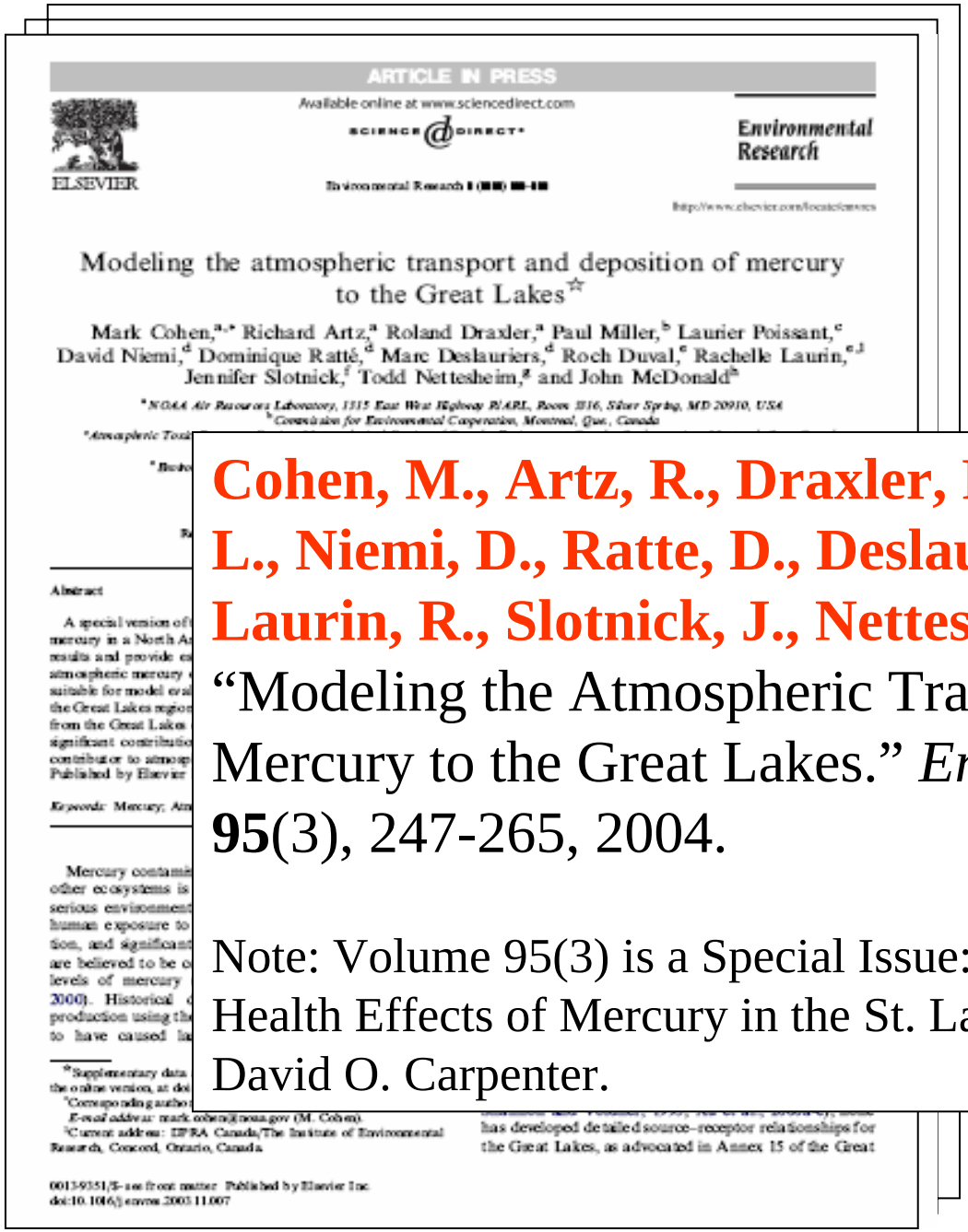



Total Hg emissions
(kg/year)
0 - 100
100 - 300
300 - 500
500 - 700
700 - 1000
1000 - 1300
1300 - 7000
Coal-Fired Electricity Generation
Waste Incineration
Metallurgical
Manufacturing
Other Fuel Combustion

- **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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Modeling the atmospheric transport and deposition of mercury to the Great Lakes☆

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[b] Commission for Environmental Cooperation, Montreal, Que., Canada

Abstract

Keywords: Mercury; Atm

Mercury contami
other ecosystems is
serious environment
human exposure to
tion, and significant
are believed to be c
levels of mercury
2000). Historical
production using th
to have caused la

☆Supplementary data
the online version, at do

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has developed detailed source–receptor relationships for the Great Lakes, as advocated in Annex 15 of the Great

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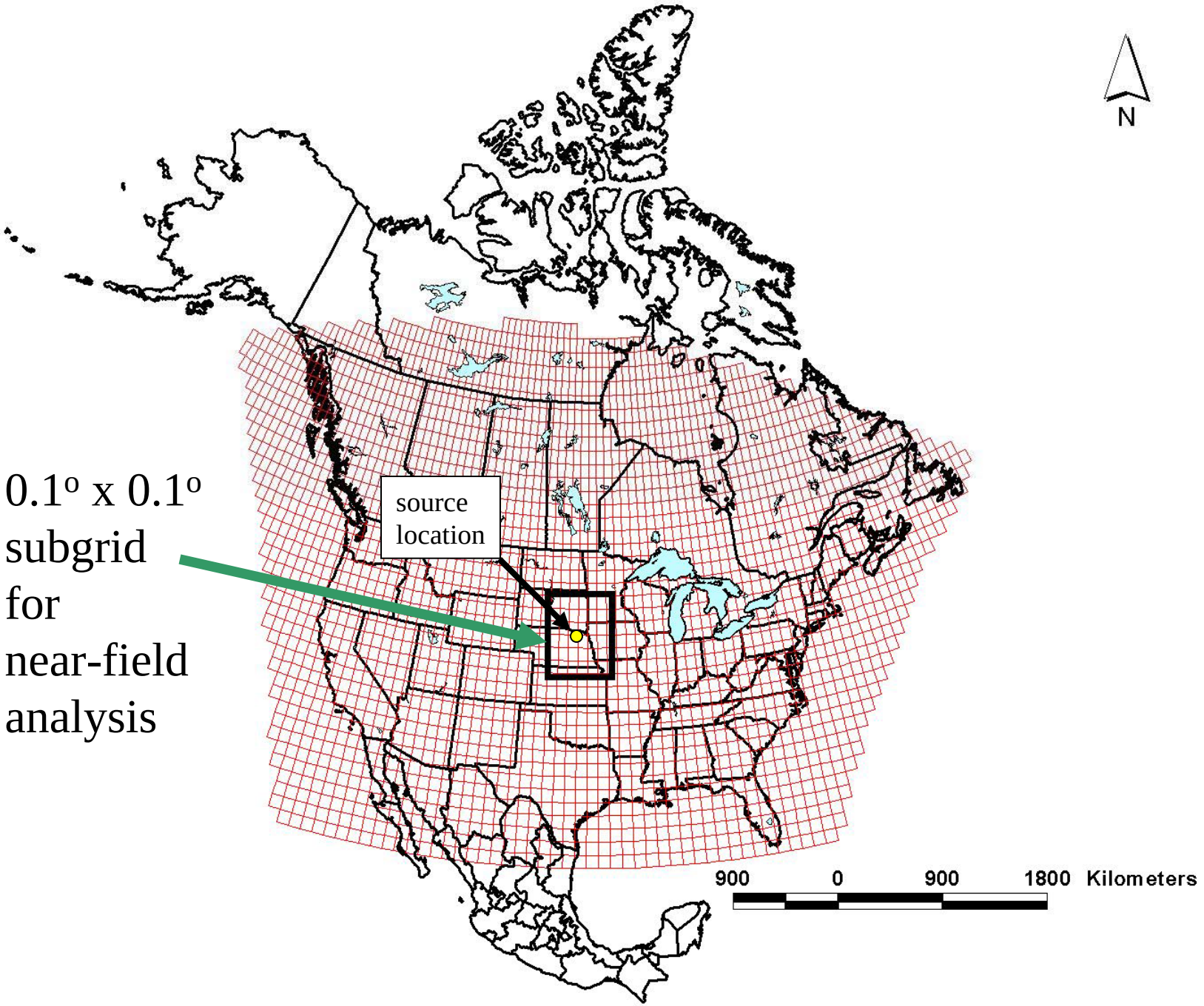
Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratte, D., Deslauriers, M., Duval, R., Laurin, R., Slotnick, J., Nettesheim, T., McDonald, J. "Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes." *Environmental Research* **95**(3), 247-265, 2004.

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.

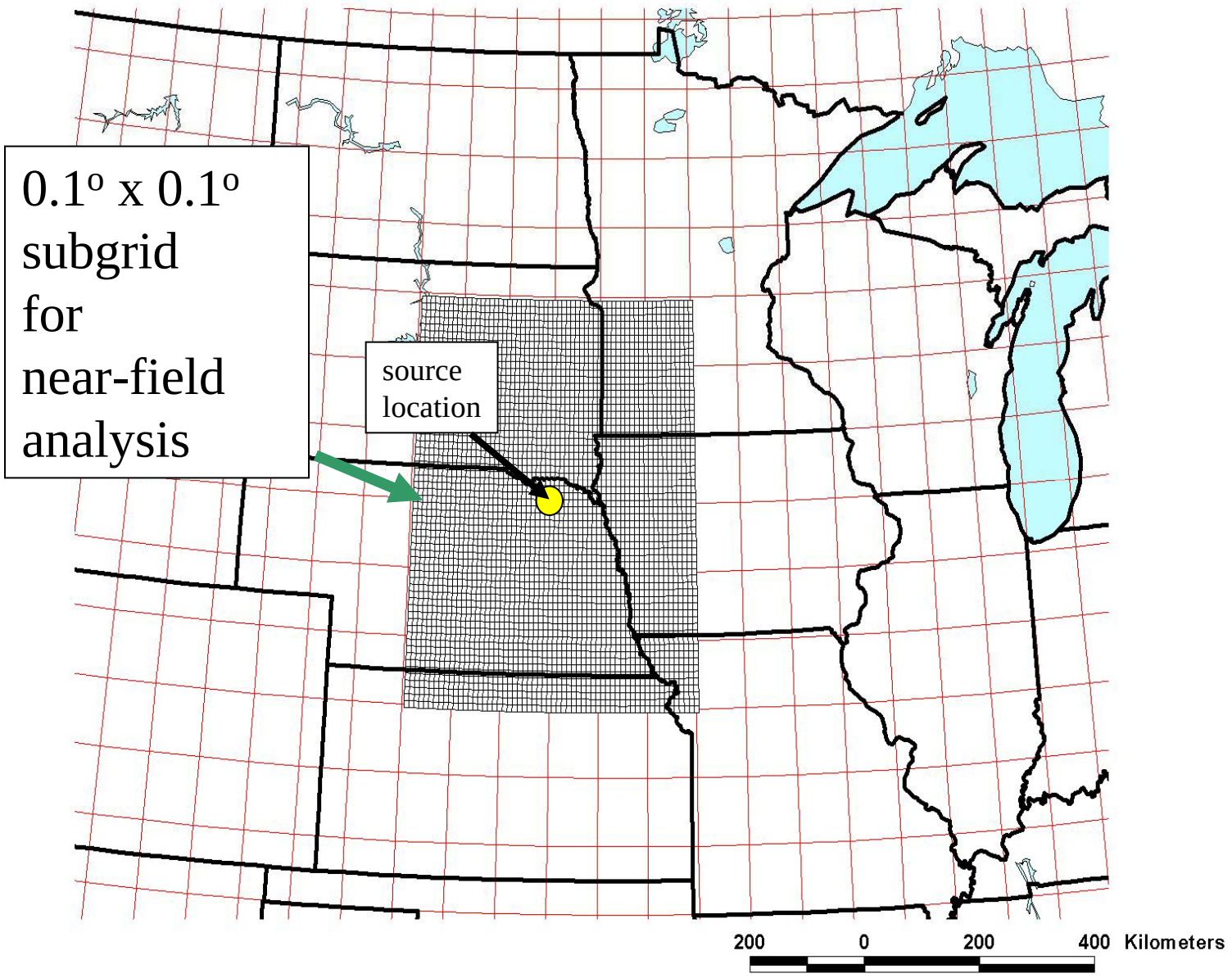
- **For each run, simulate fate and transport *everywhere*, but only keep track of impacts on each selected receptor (e.g., Great Lakes, Chesapeake Bay, etc.)**

- **Only run model for a limited number (~100) of hypothetical, individual unit-emissions sources throughout the domain**

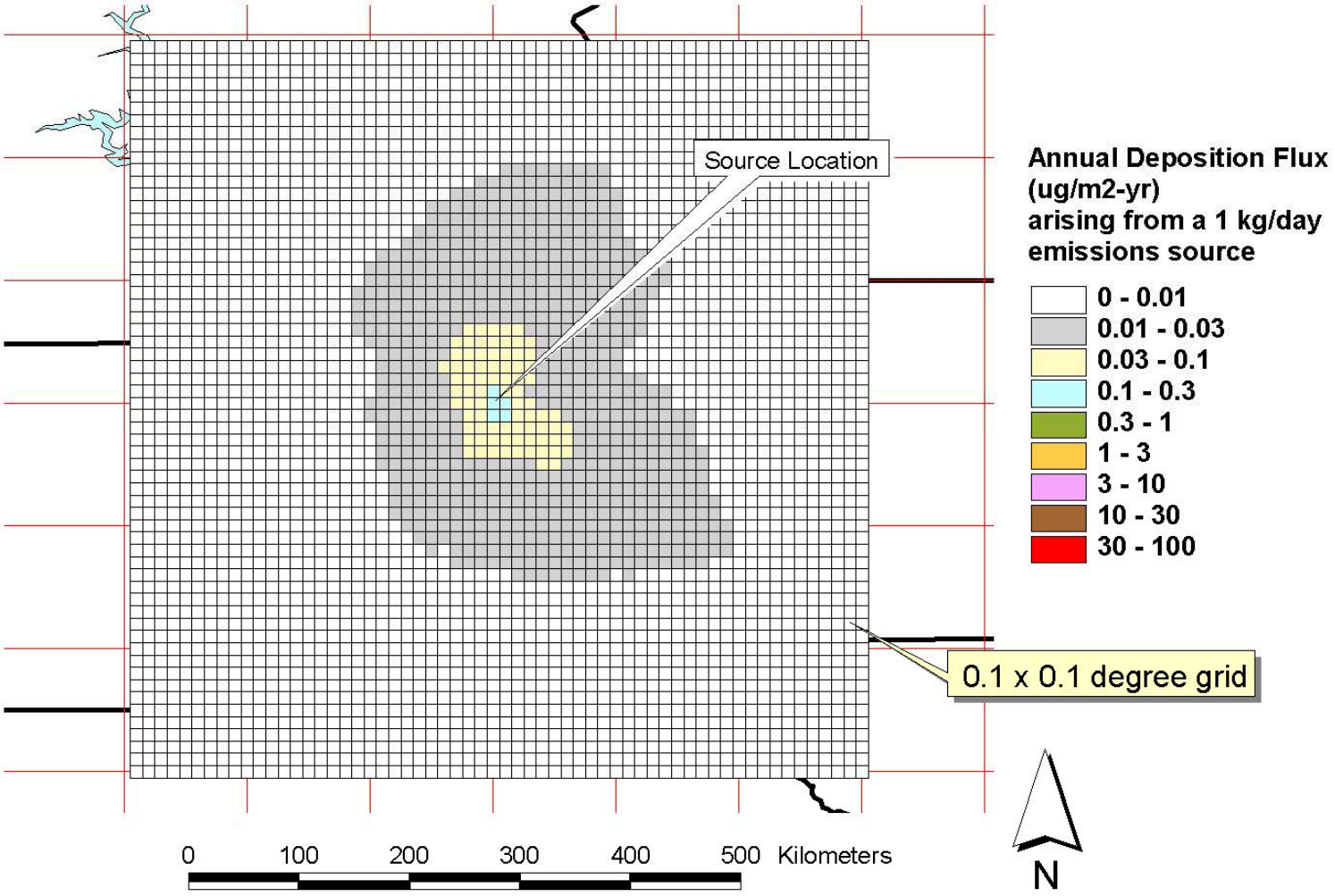
- **Use spatial interpolation to estimate impacts from sources at locations not explicitly modeled**



0.1^{o} x 0.1^{o} subgrid for near-field analysis


0.1° x 0.1° subgrid for near-field analysis
source location
200 0 200 400 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)

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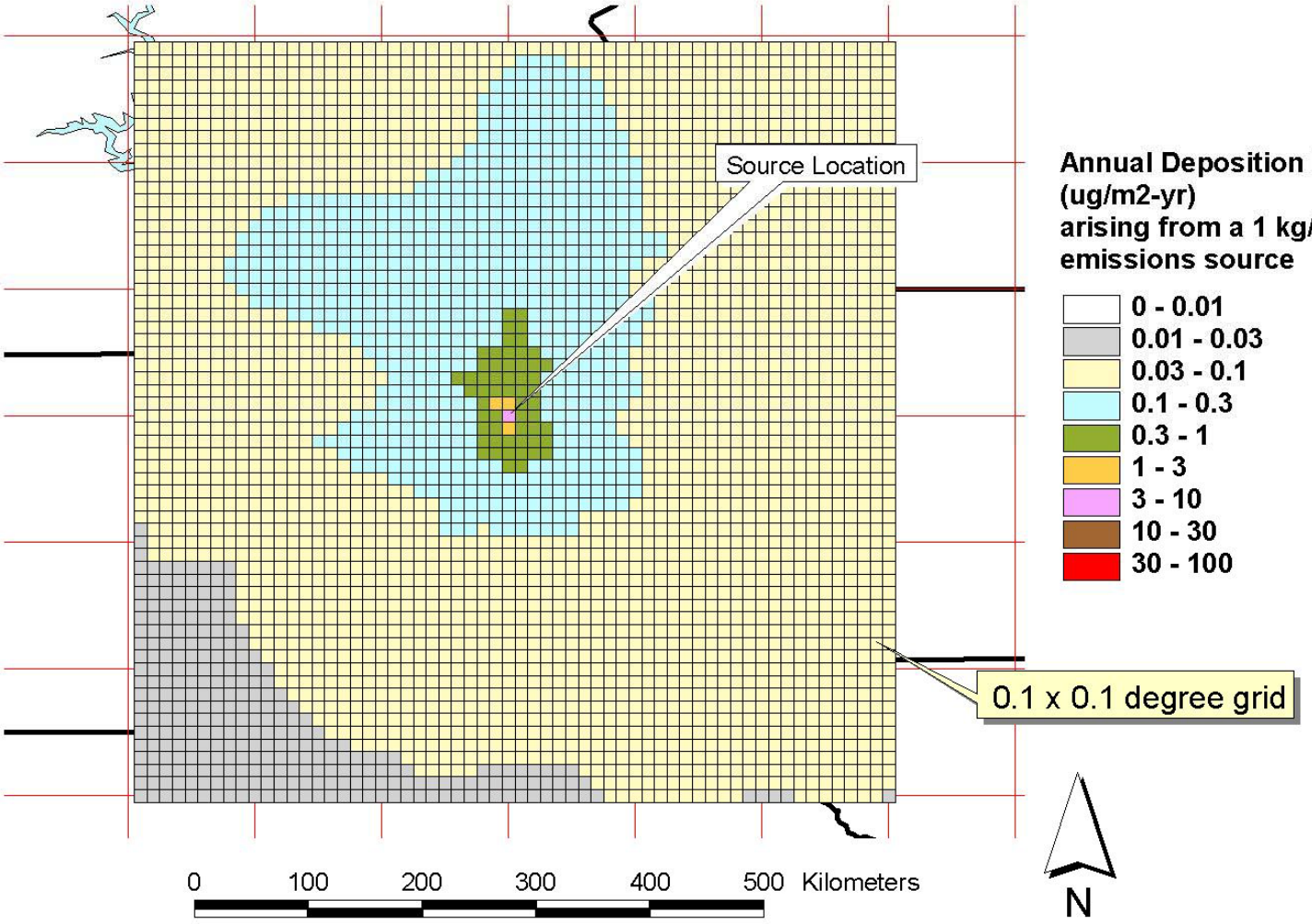

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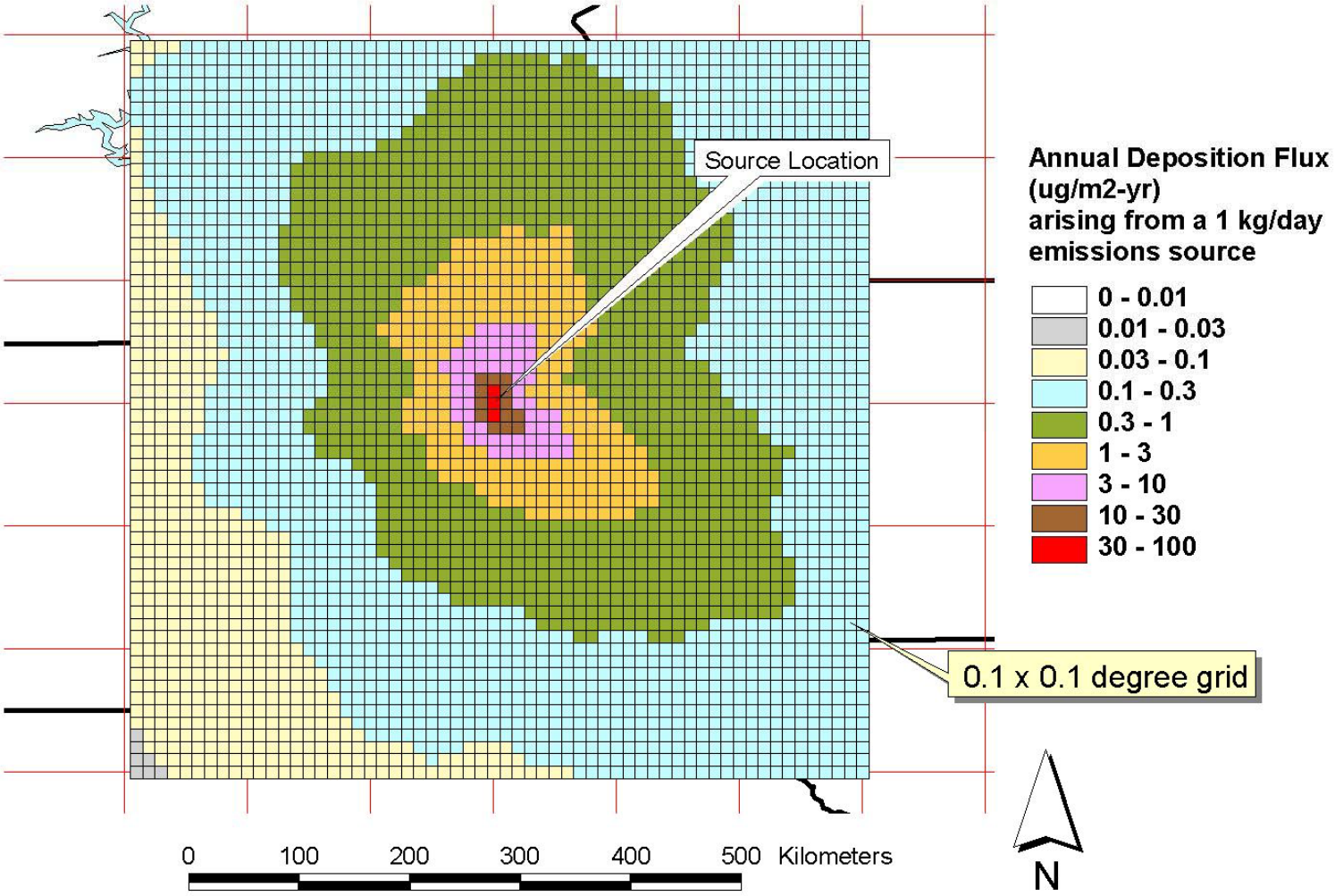

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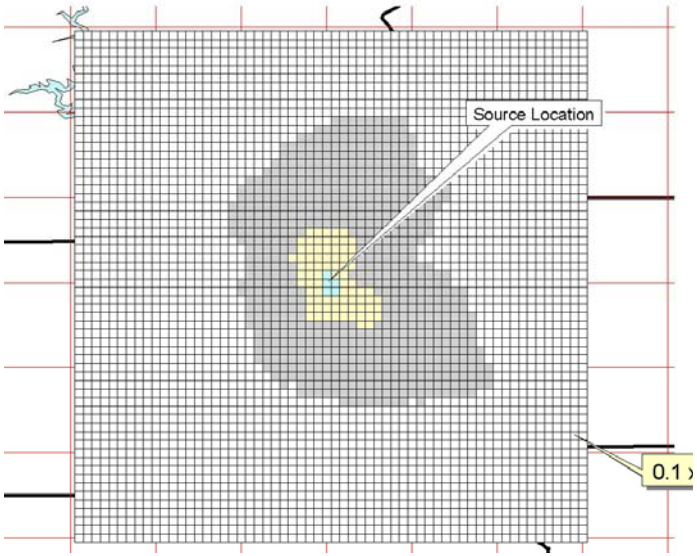

Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source

- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

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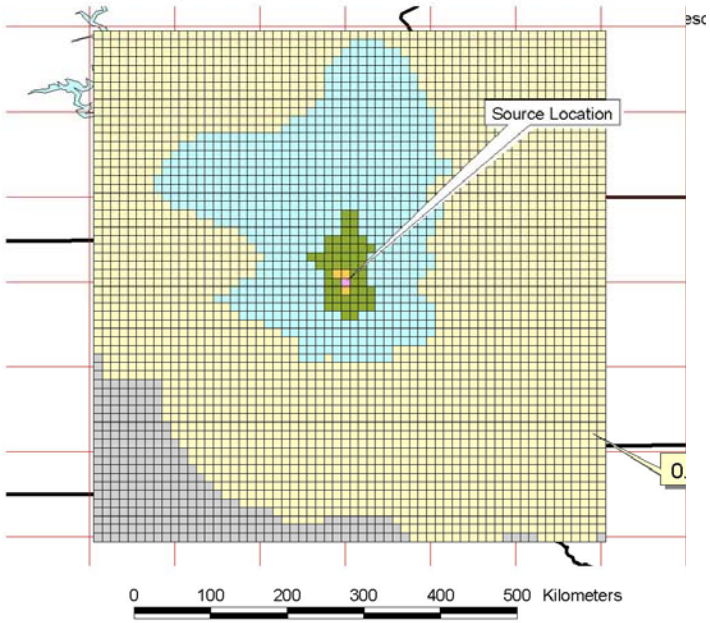

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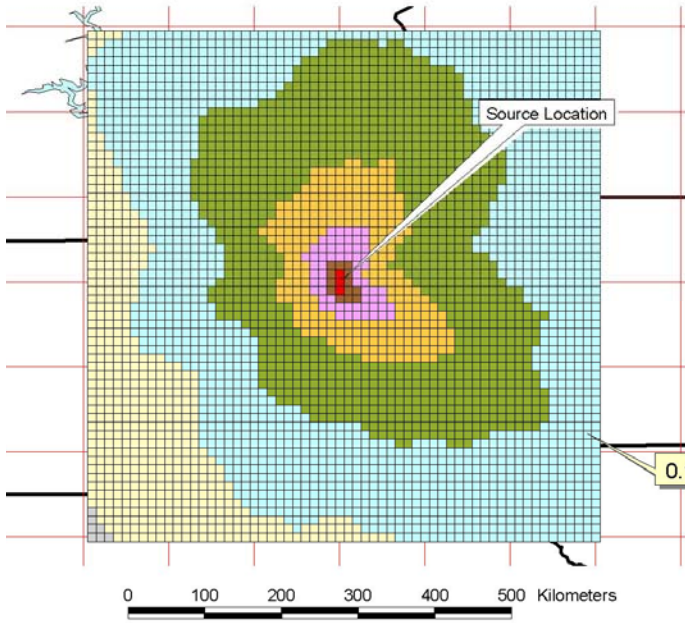

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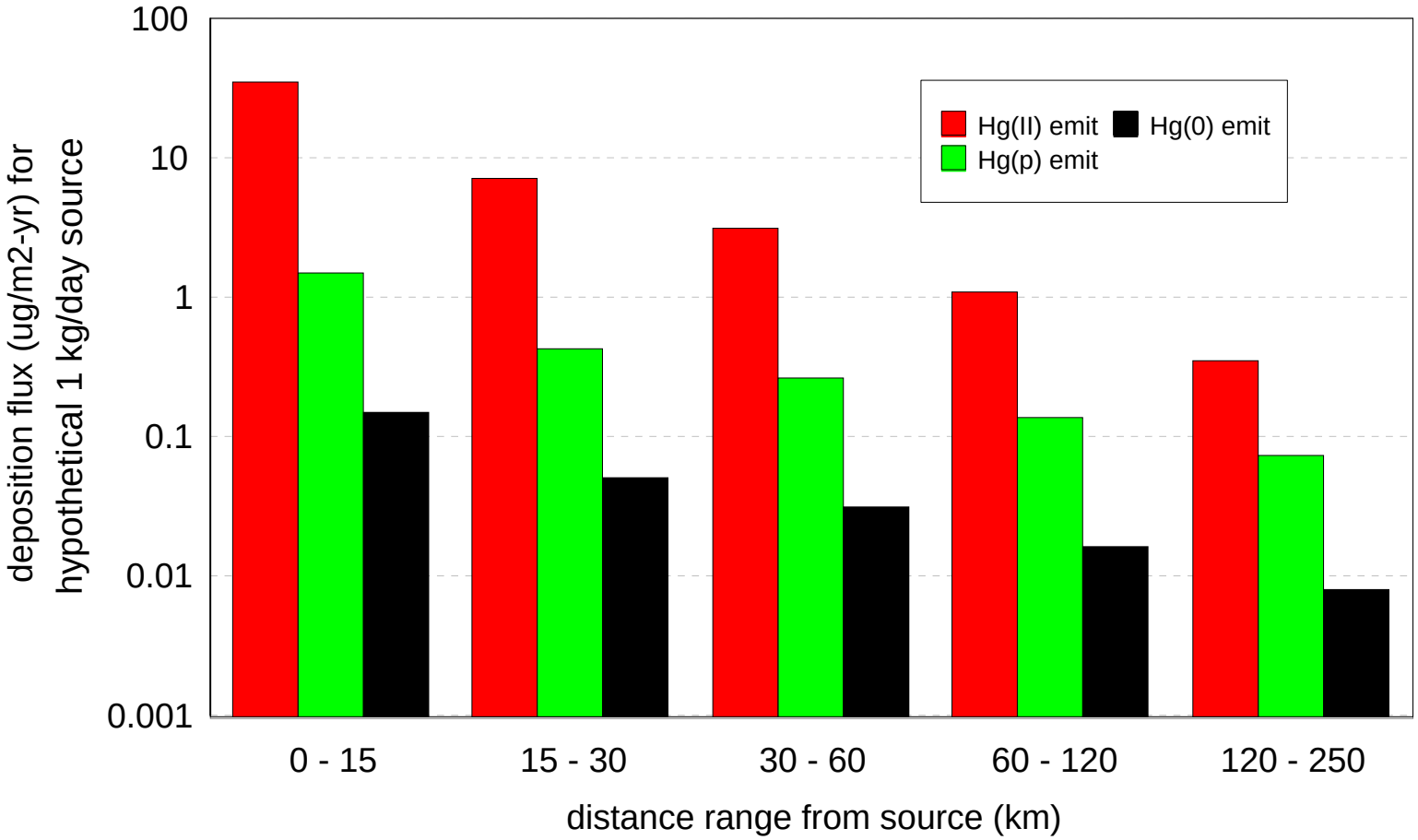
Why is emissions speciation information critical?



Logarithmic

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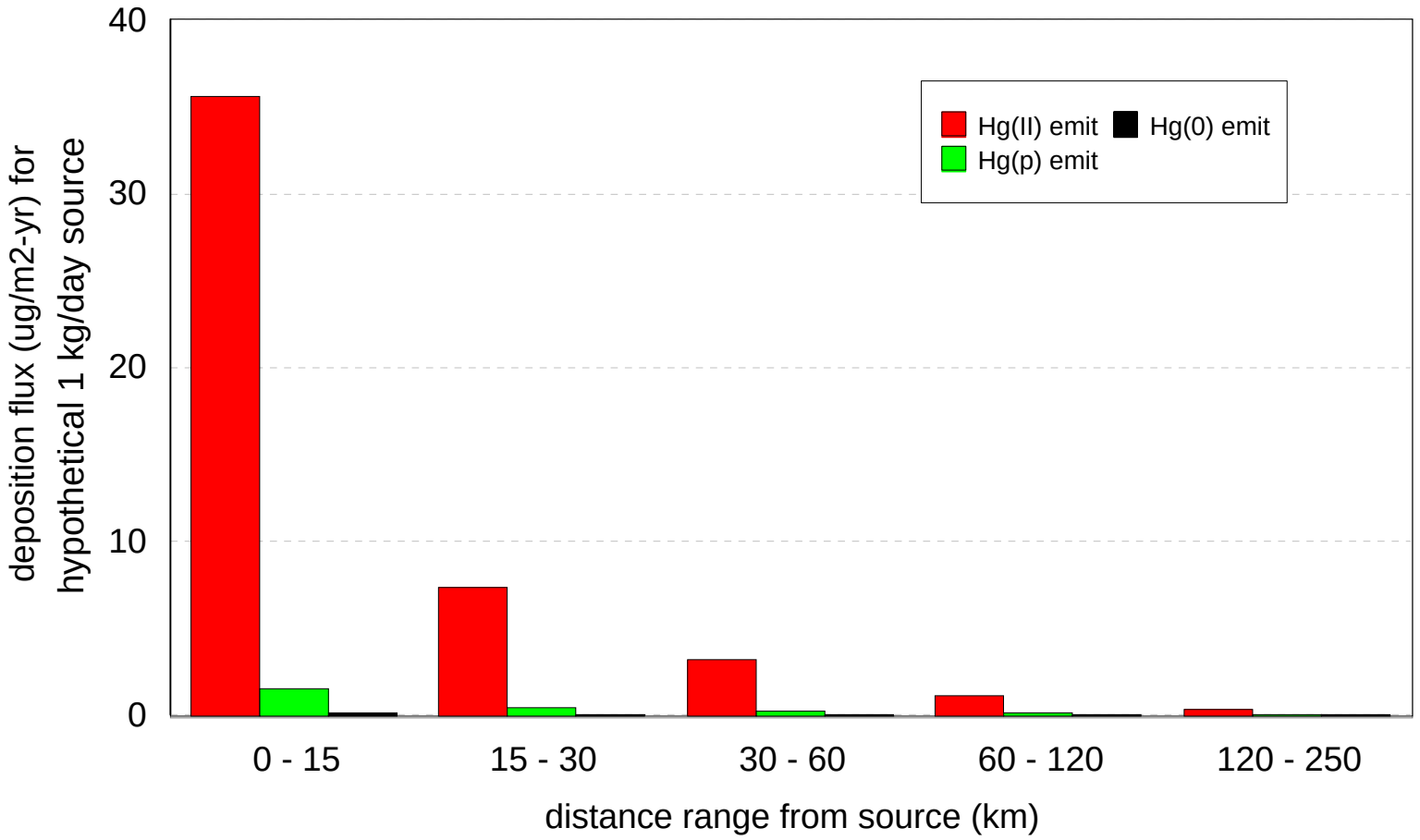

Linear

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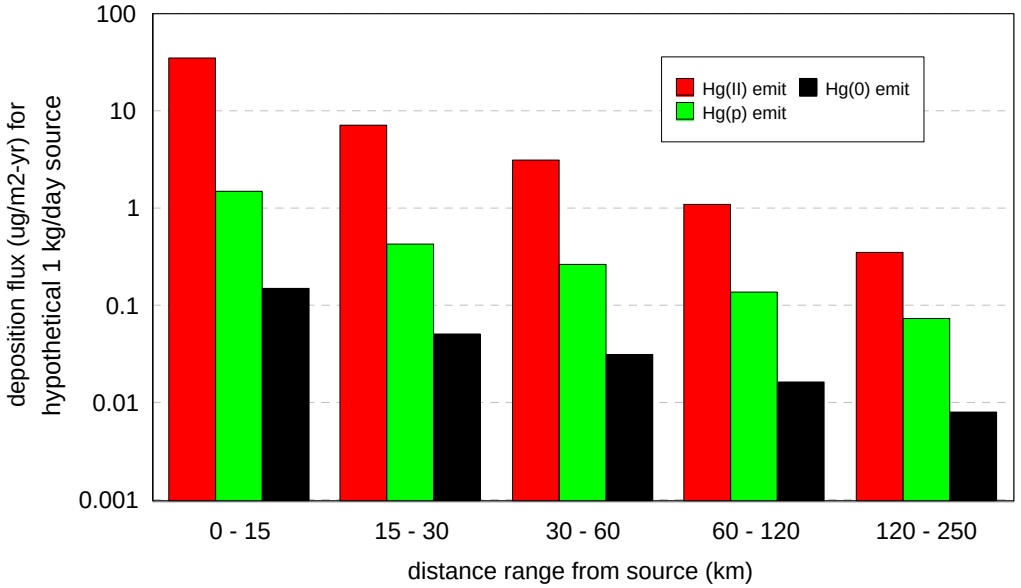
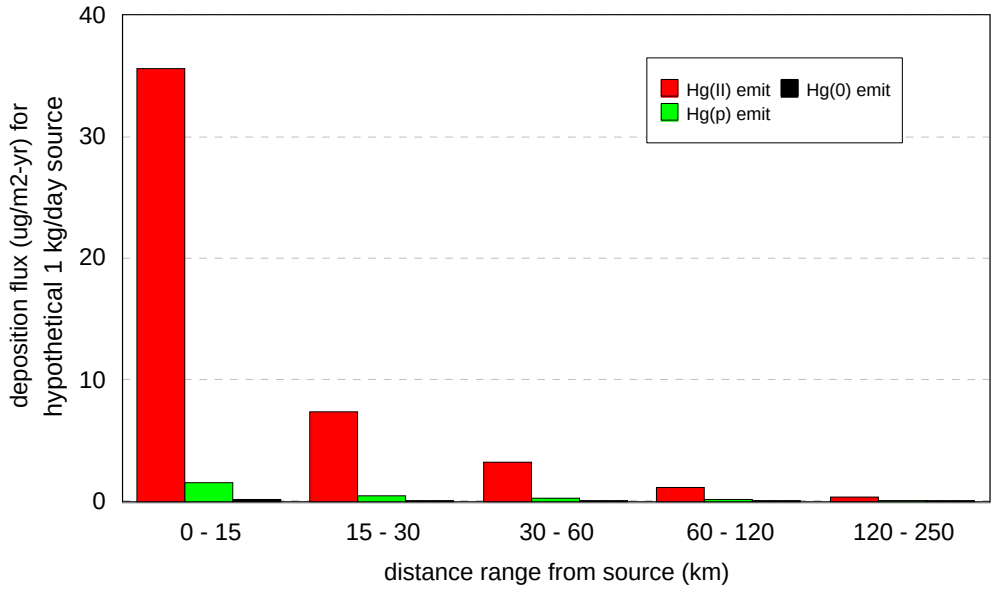
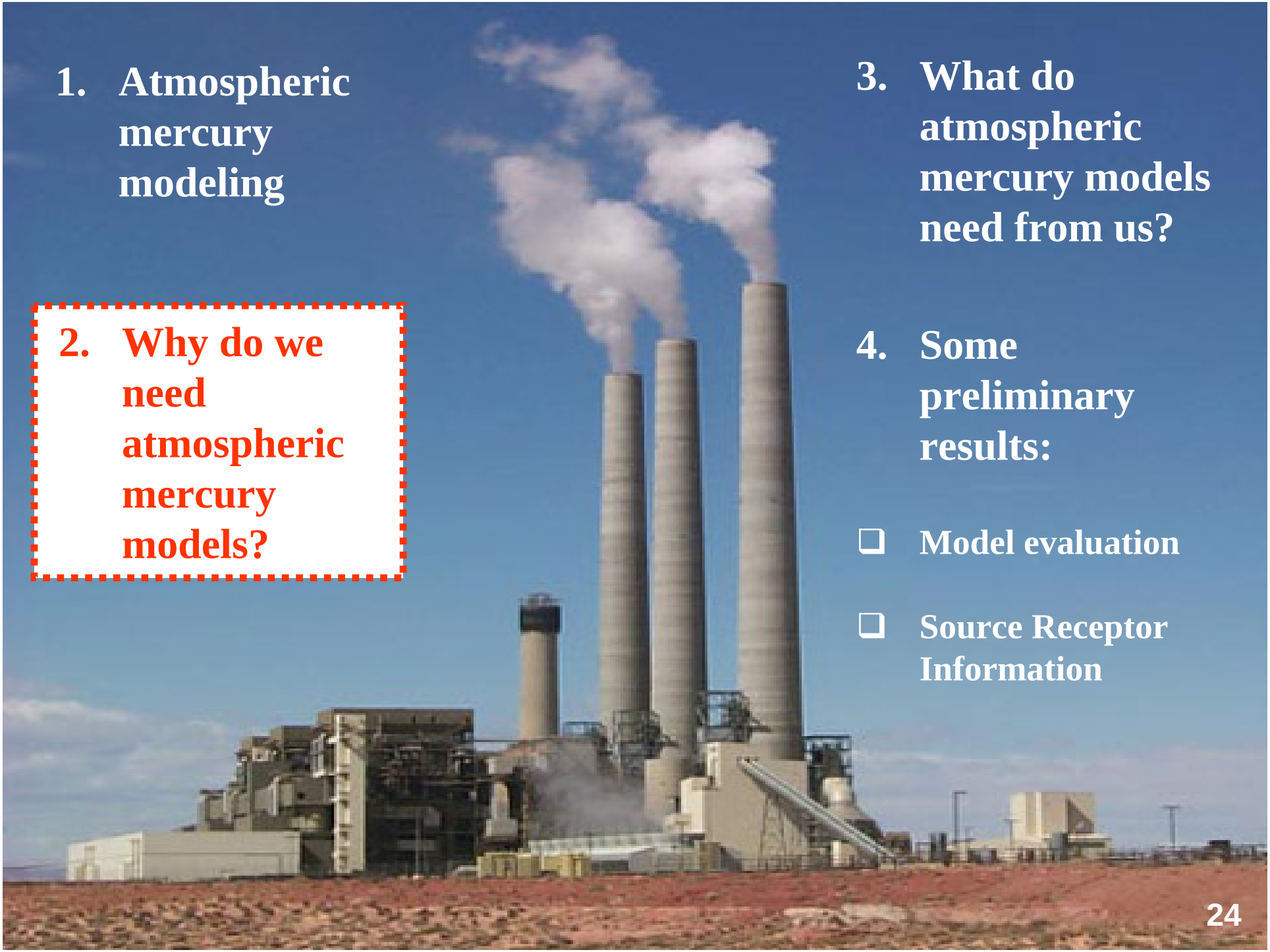
Logarithmic



Linear





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4. Some preliminary results:

- ❑ Model evaluation
- ❑ Source Receptor Information

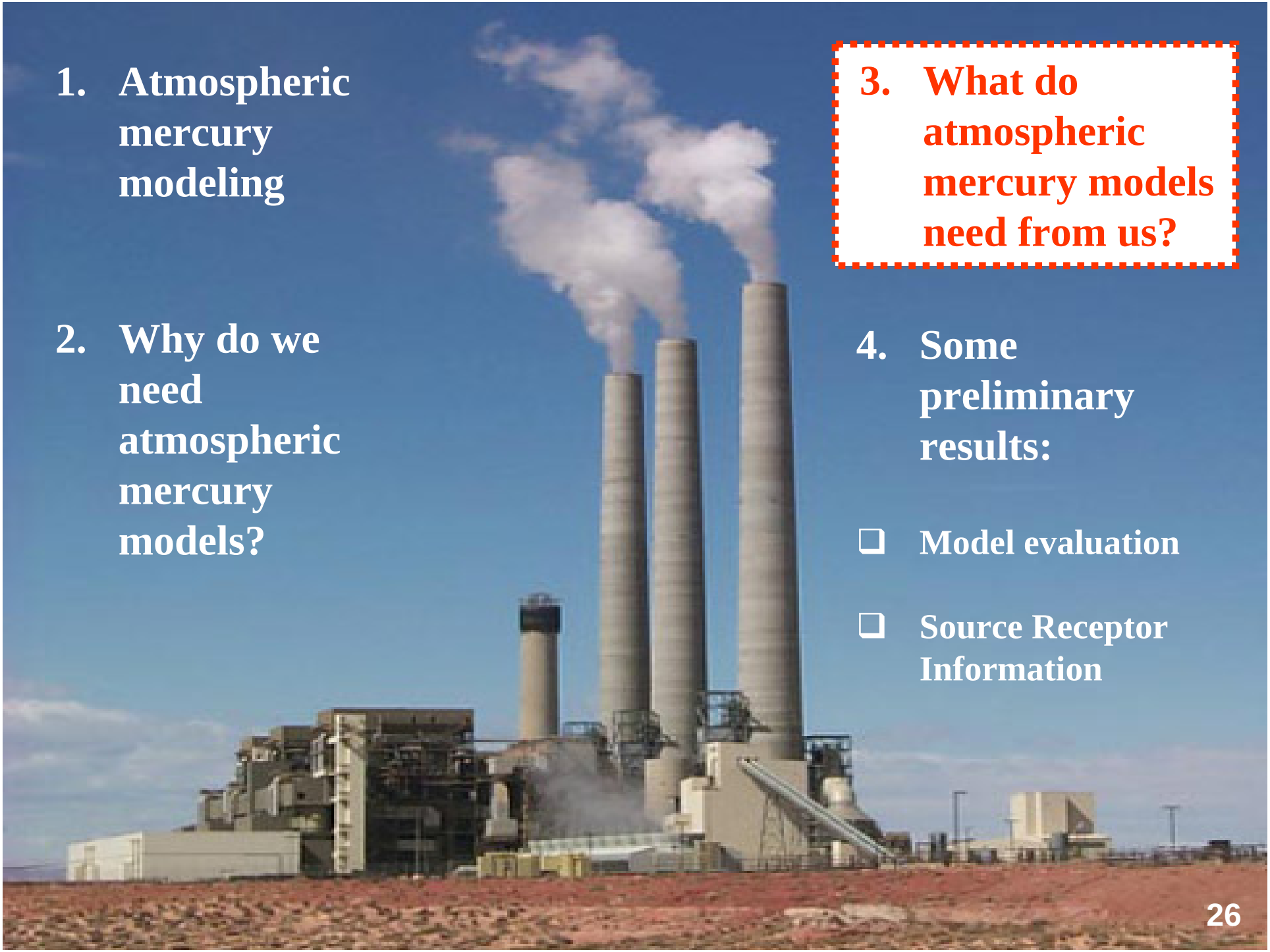
Why do we need atmospheric mercury models?

- 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



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What do atmospheric mercury models need?

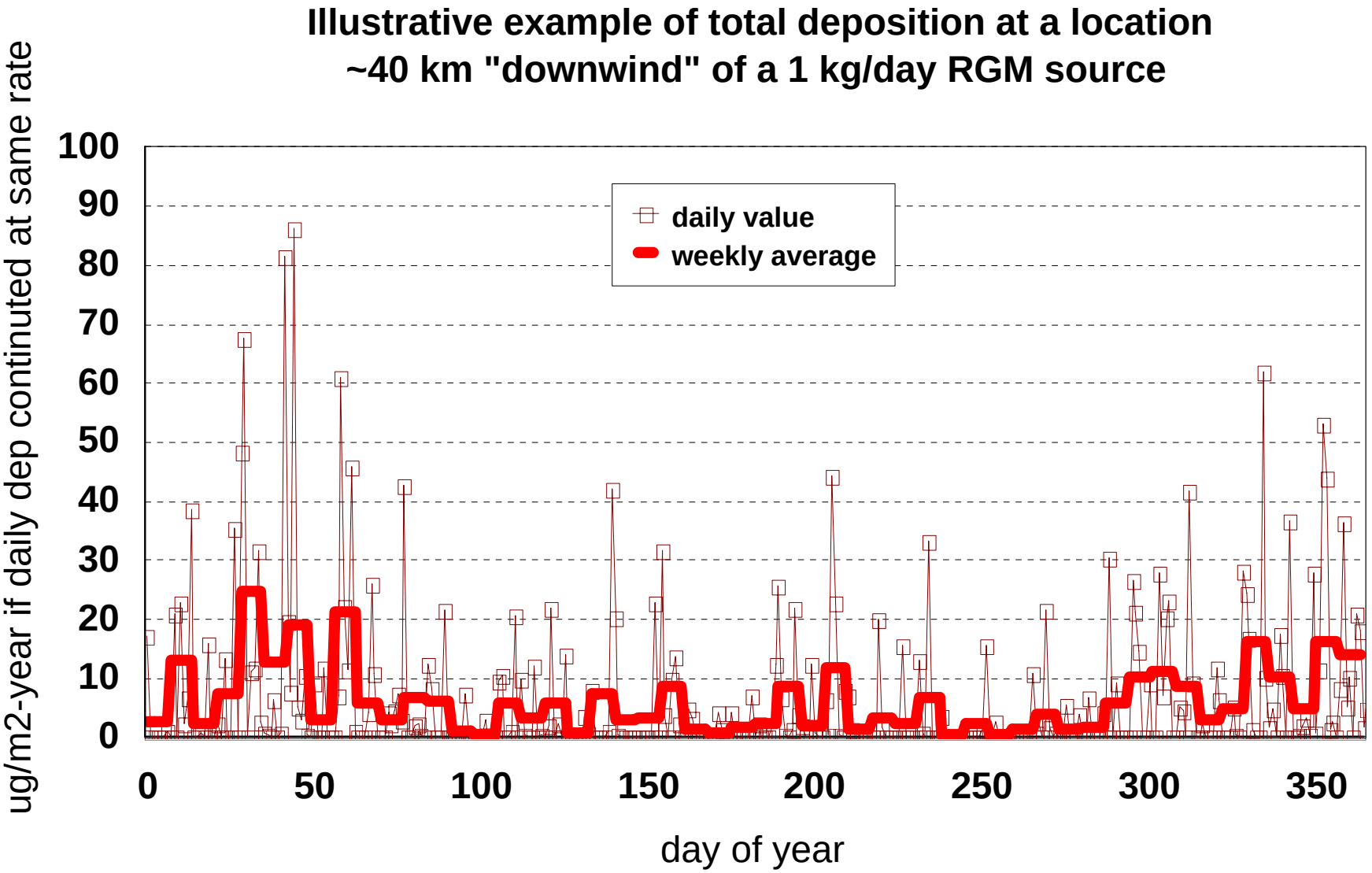
Emissions Inventories

Meteorological Data

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

Ambient data for comprehensive model evaluation and improvement

	some challenges facing mercury modeling
emissions inventories	• need *all* sources • accurately divided into *different Hg forms* • **U.S. 1996, 1999, 2003 / CAN 1995, 2000, 2005** • *temporal* variations (e.g. shut downs)
meteorological data	• precipitation not well characterized
scientific understanding	• what is RGM? what is Hg(p)? • accurate info for known reactions? • do we know all significant reactions? • natural emissions, re-emissions?
ambient data for model evaluation	• Mercury Deposition Network (MDN) is great, but: • also need RGM, Hg(p), and Hg(0) concentrations • also need data above the surface (e.g., from aircraft) • also need source-impacted sites (not just background)


Illustrative example of total deposition at a location
~40 km "downwind" of a 1 kg/day RGM source
ug/m2-year if daily dep continuted at same rate
100
90
80
70
60
50
40
30
20
10
0
daily value
weekly average
0
50
100
150
200
250
300
350
day of year

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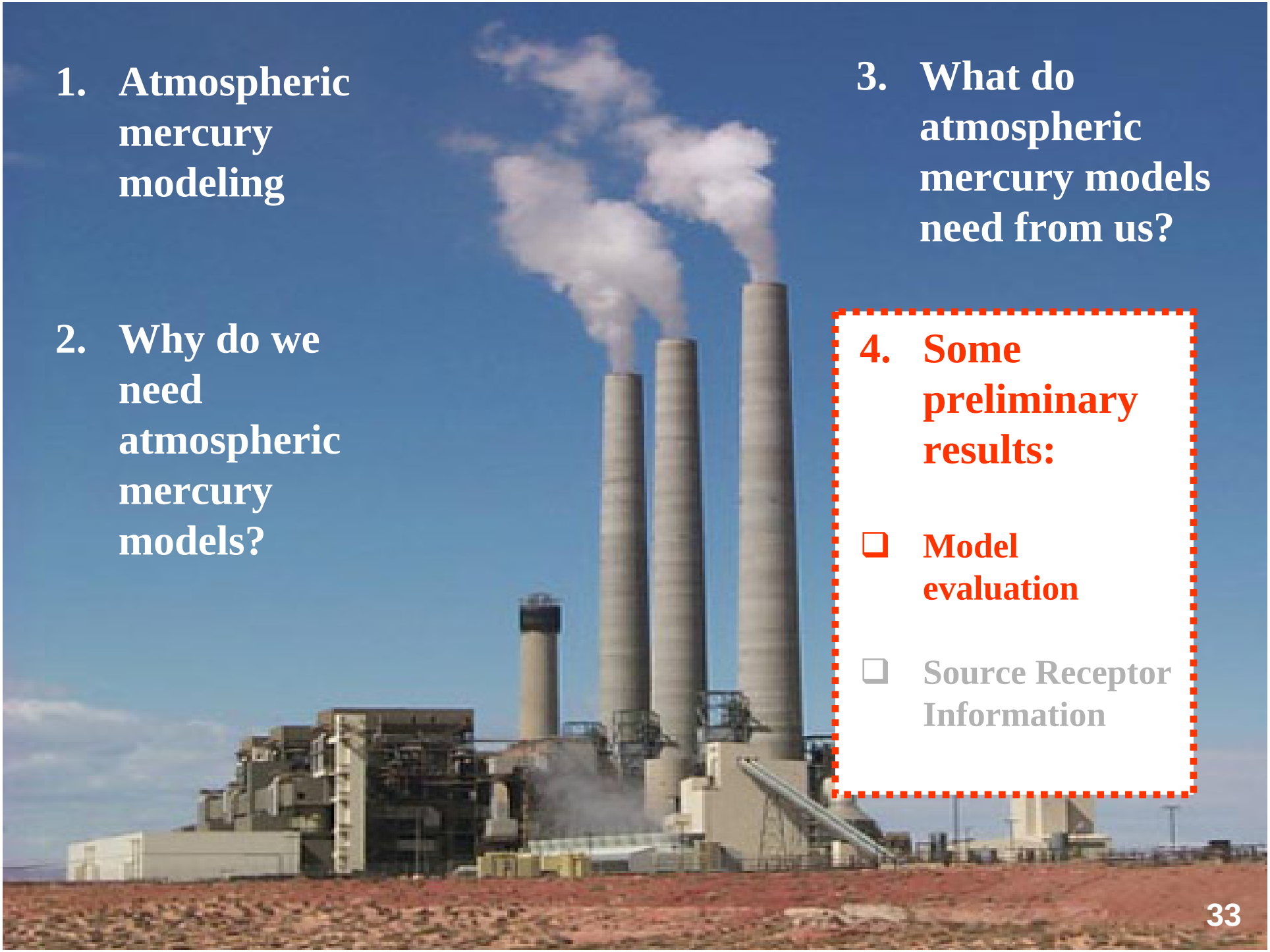

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  - Phase II – ambient concentrations
  - Phase III – wet and dry deposition
- Chesapeake Bay region

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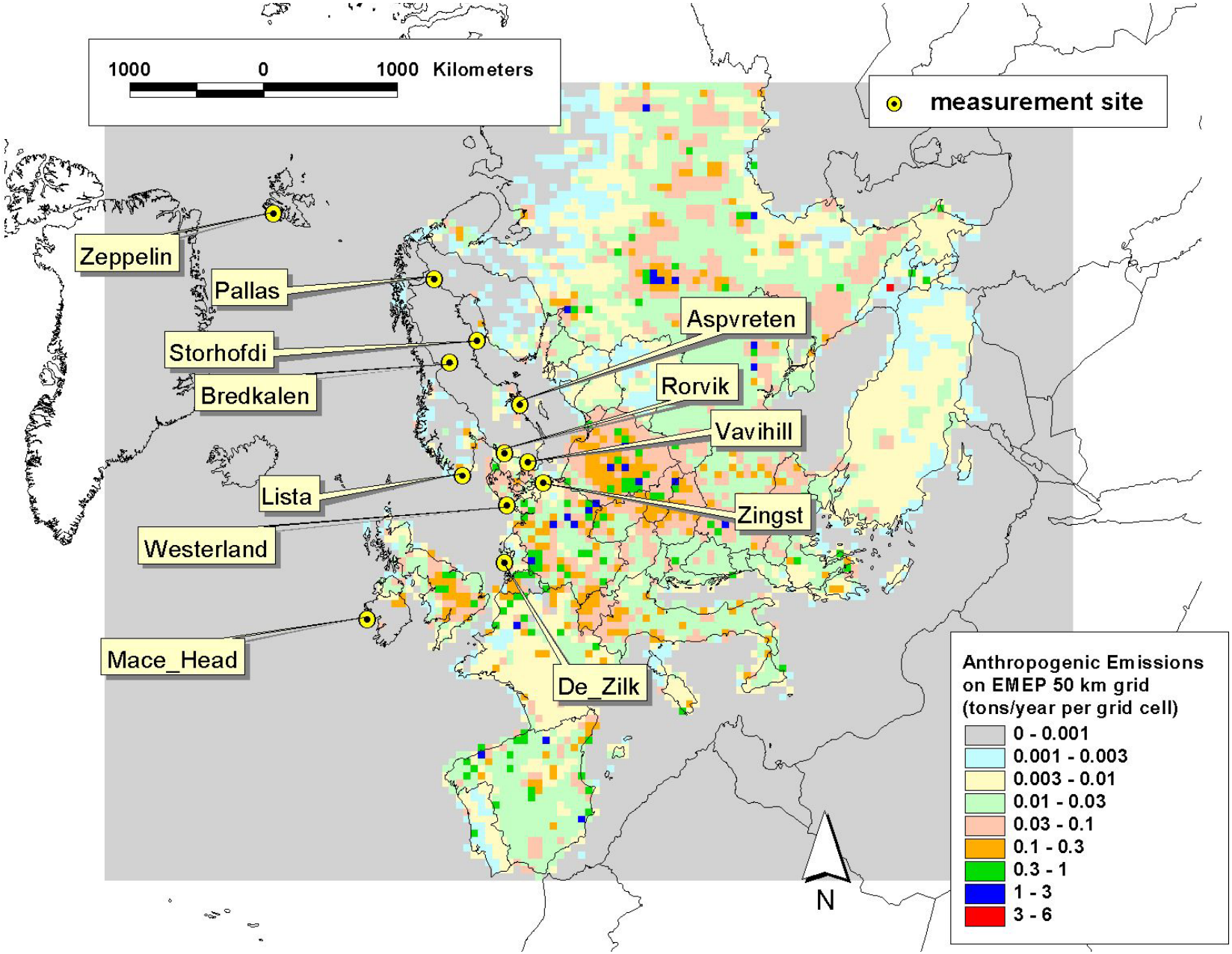
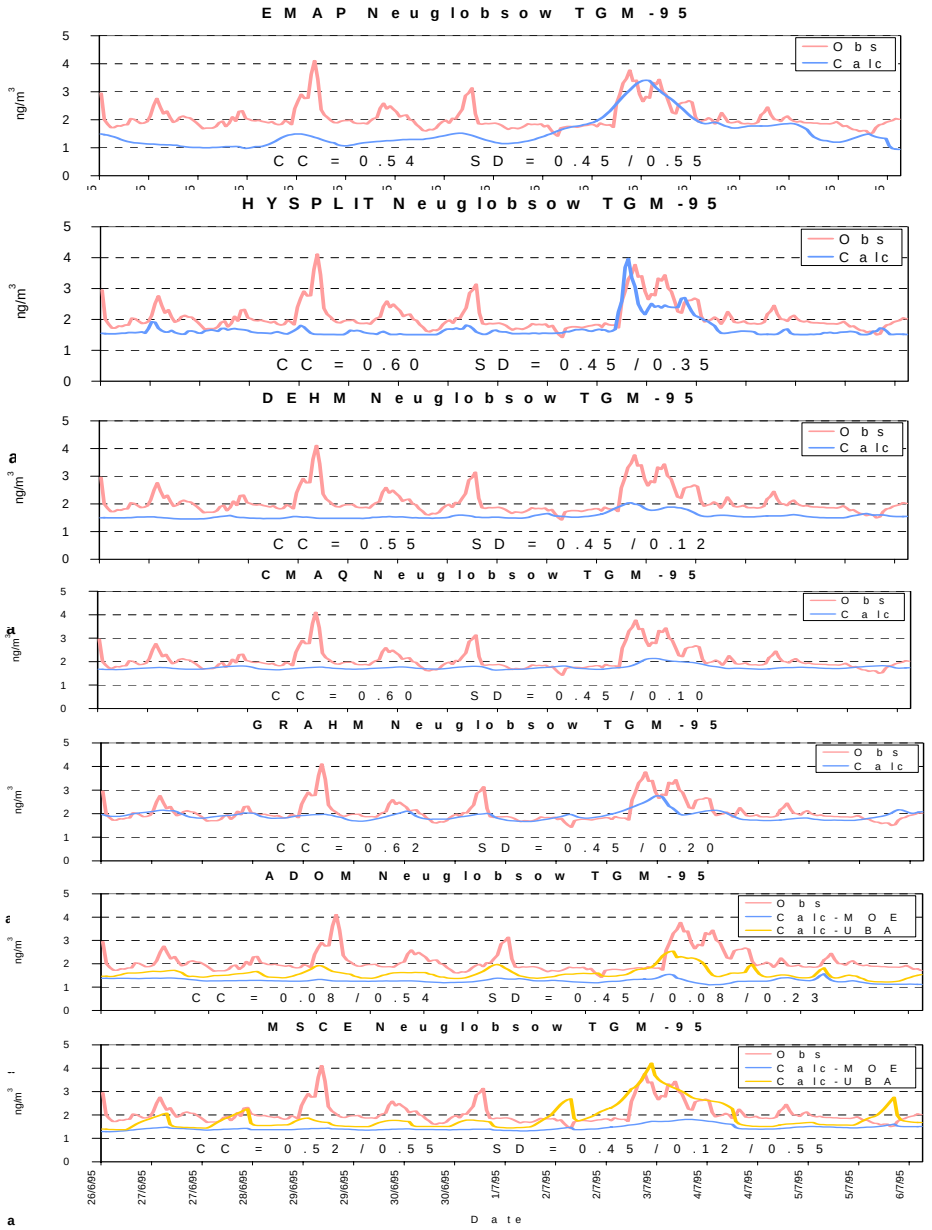
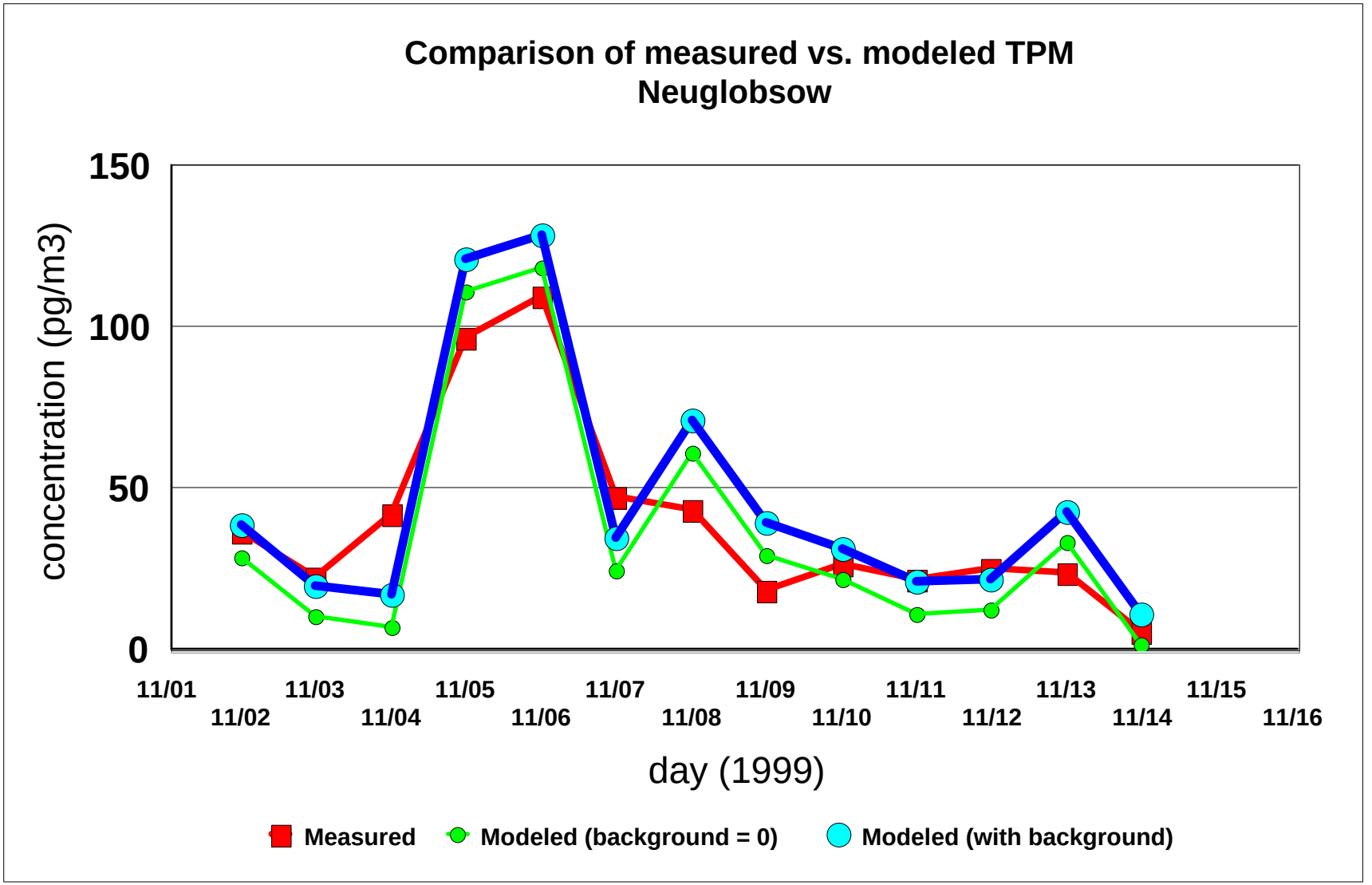
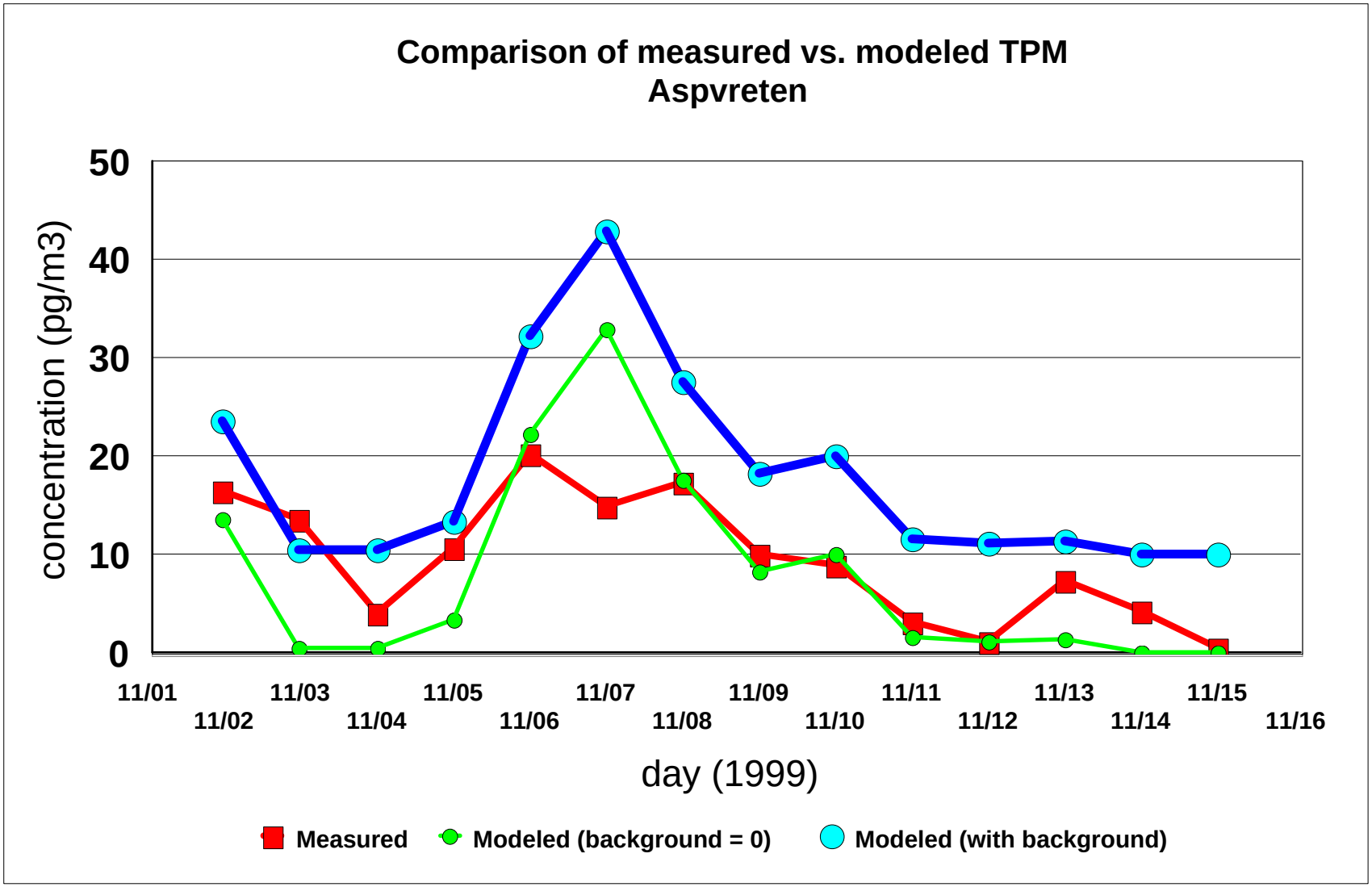
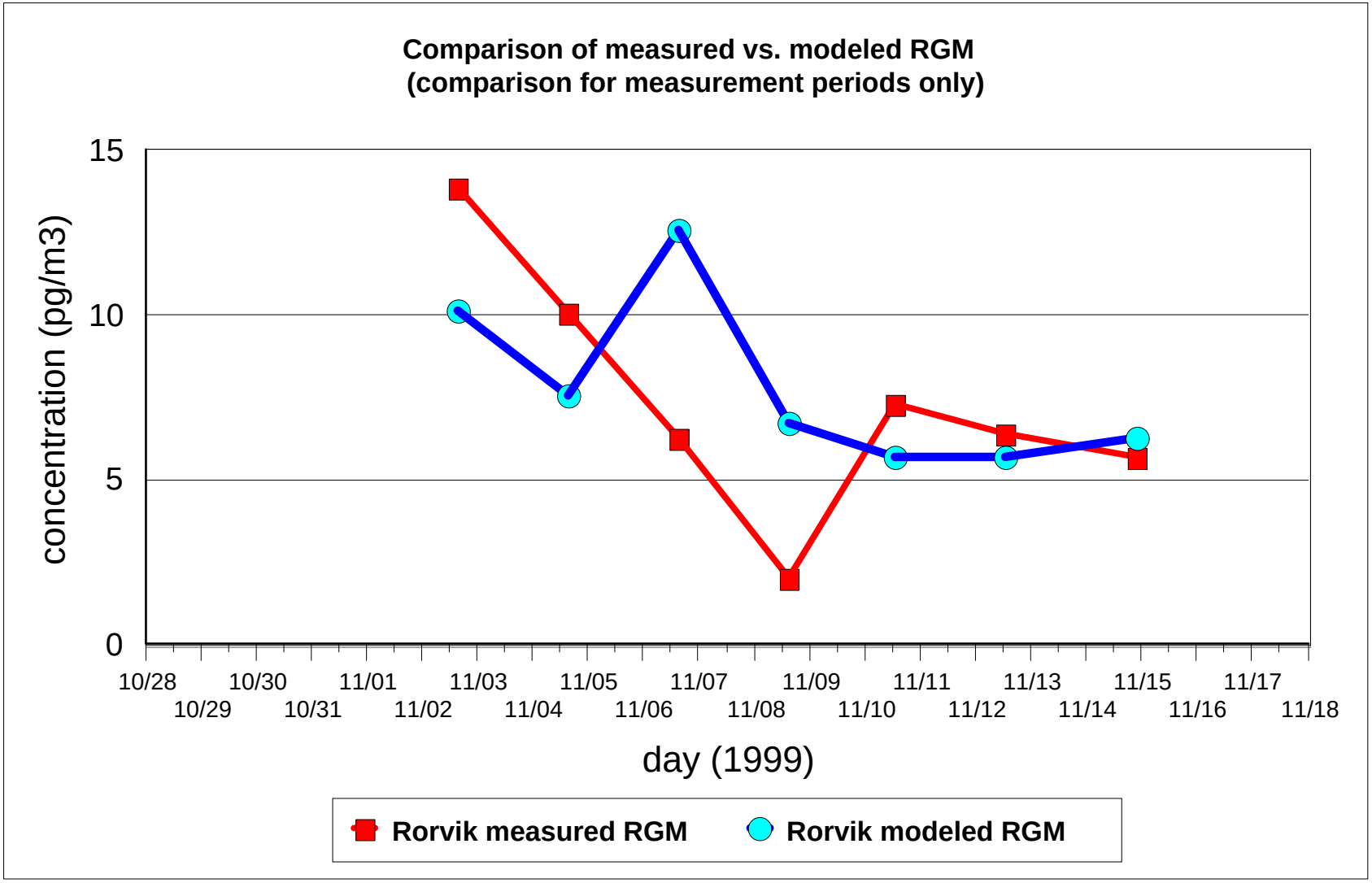

1000 0 1000 Kilometers
measurement site
Zeppelin
Pallas
Storhofdi
Bredkalen
Aspvreten
Rorvik
Vavihill
Lista
Zingst
Westerland
Mace_Head
De_Zilk
N
Anthropogenic Emissions on EMEP 50 km grid (tons/year per grid cell)
0 - 0.001
0.001 - 0.003
0.003 - 0.01
0.01 - 0.03
0.03 - 0.1
0.1 - 0.3
0.3 - 1
1 - 3
3 - 6

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

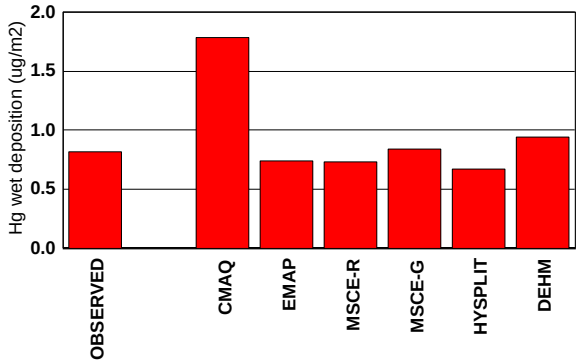



Comparison of measured vs. modeled TPM
Neuglobsow
150
100
50
0
concentration (pg/m3)
11/01
11/02
11/03
11/04
11/05
11/06
11/07
11/08
11/09
11/10
11/11
11/12
11/13
11/14
11/15
11/16
day (1999)
Measured
Modeled (background = 0)
Modeled (with background)

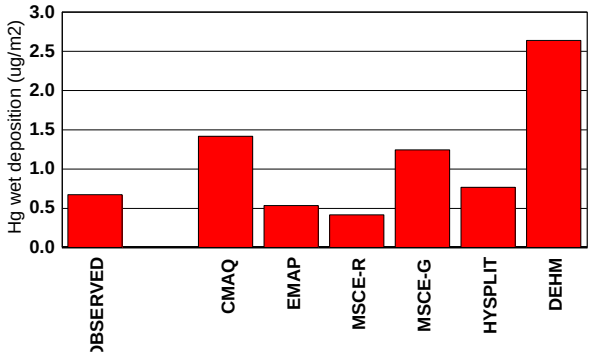

Comparison of measured vs. modeled TPM
Aspvreten
concentration (pg/m3)
50
40
30
20
10
0
11/01
11/02
11/03
11/04
11/05
11/06
11/07
11/08
11/09
11/10
11/11
11/12
11/13
11/14
11/15
11/16
day (1999)
Measured
Modeled (background = 0)
Modeled (with background)


Comparison of measured vs. modeled RGM
(comparison for measurement periods only)
concentration (pg/m3)
15
10
5
0
10/28
10/29
10/30
10/31
11/01
11/02
11/03
11/04
11/05
11/06
11/07
11/08
11/09
11/10
11/11
11/12
11/13
11/14
11/15
11/16
11/17
11/18
day (1999)
Rorvik measured RGM
Rorvik modeled RGM

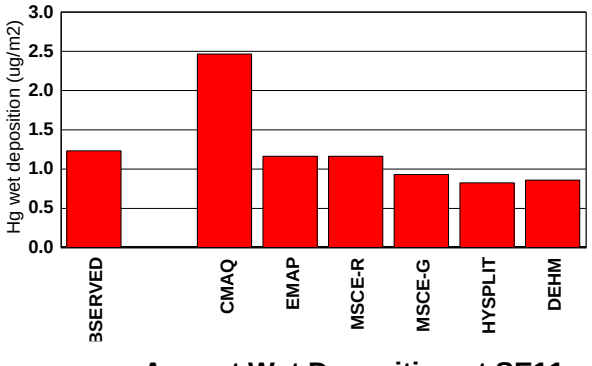
August Wet Deposition at DE01



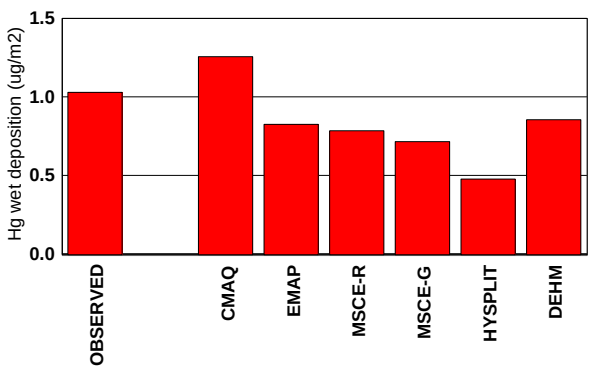
August Wet Deposition at DE09



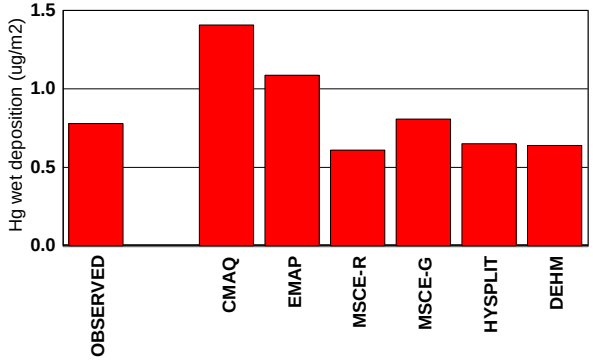
August Wet Deposition at NL91



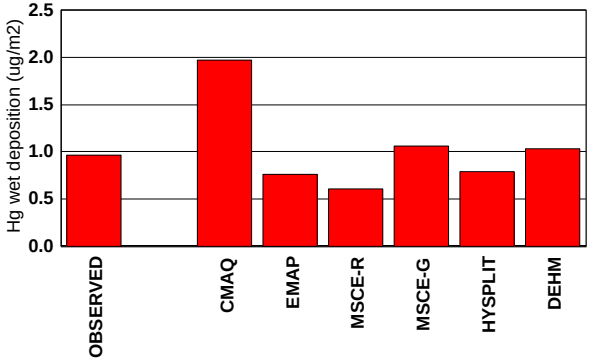
August Wet Deposition at NO99



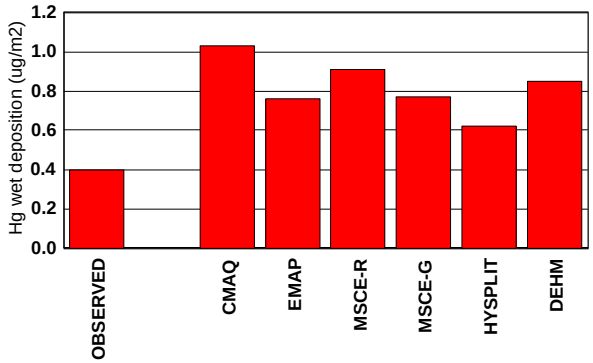
August Wet Deposition at SE02



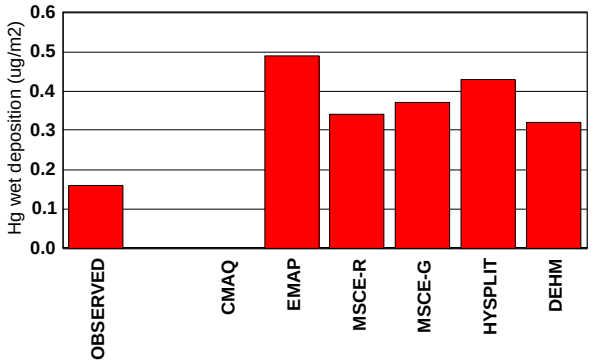
August Wet Deposition at SE11



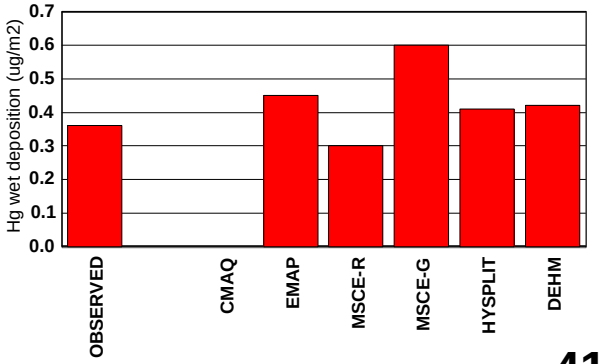
August Wet Deposition at SE12



August Wet Deposition at SE05

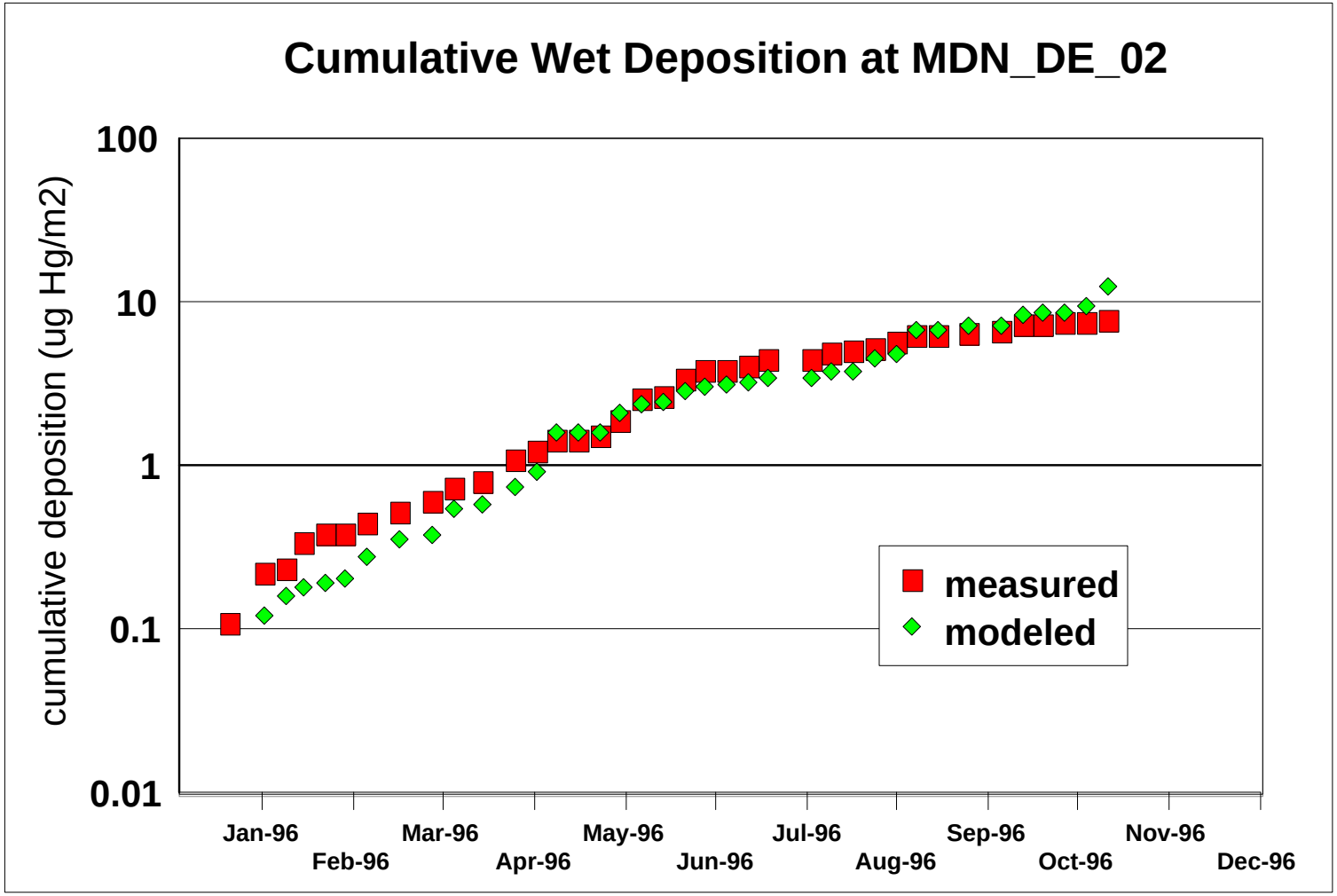


August Wet Deposition at FI96

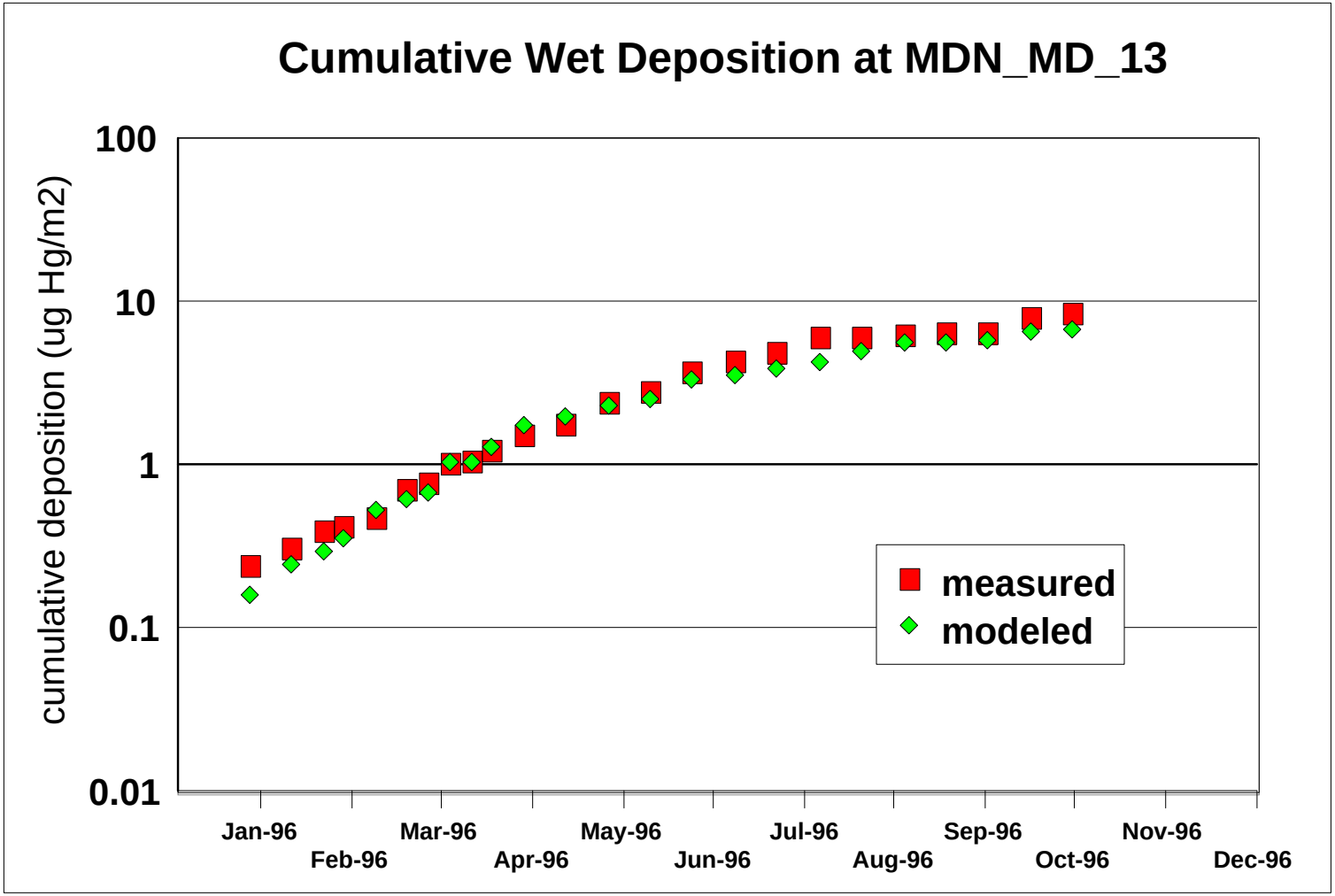


- EMEP Model Intercomparison
  - Phase II – ambient concentrations
  - Phase III – wet and dry deposition
- Chesapeake Bay region

Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE_02 during 1996



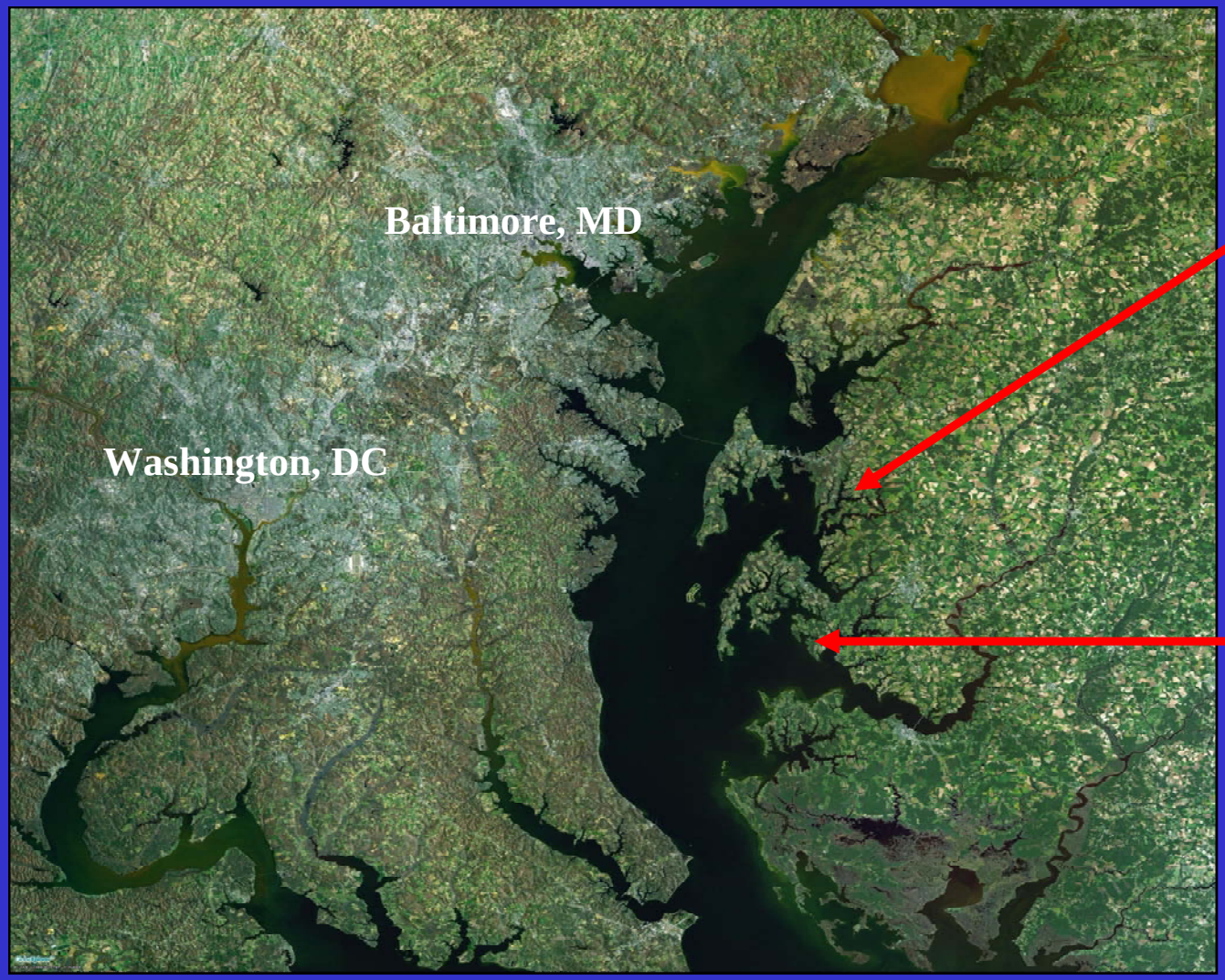
Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD_13 during 1996

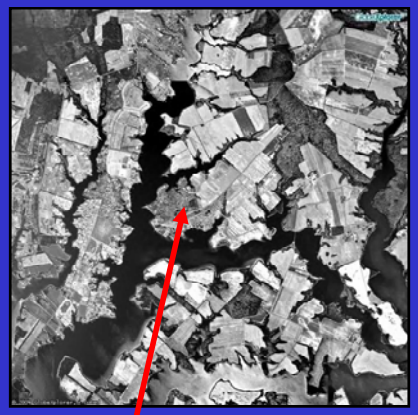


Summer 2004 Chesapeake Bay Atmospheric Hg Study (June – August 2004)

- 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

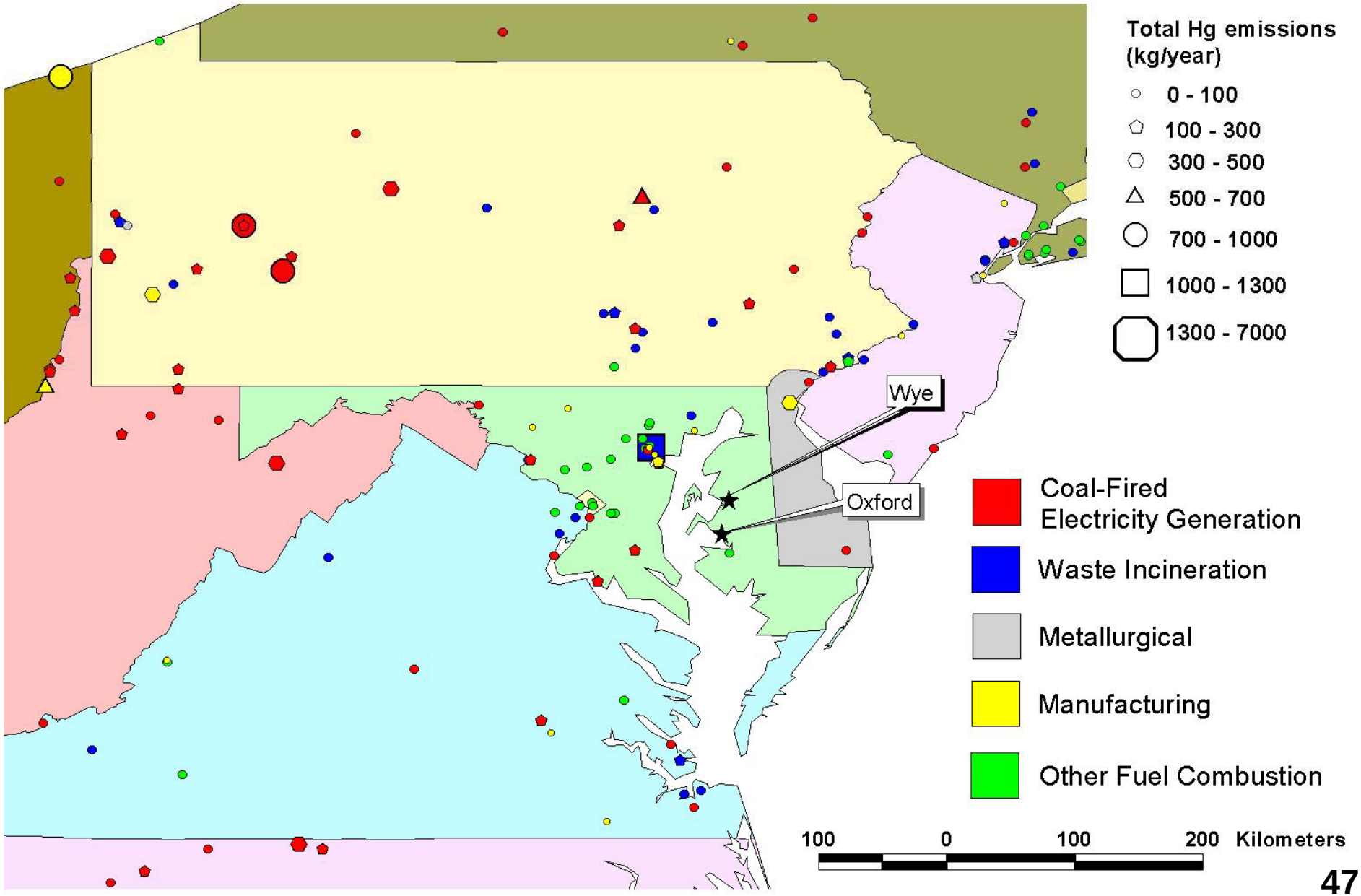




Wye Research and
Education Center
(38.9131EN, 76.1525EW)

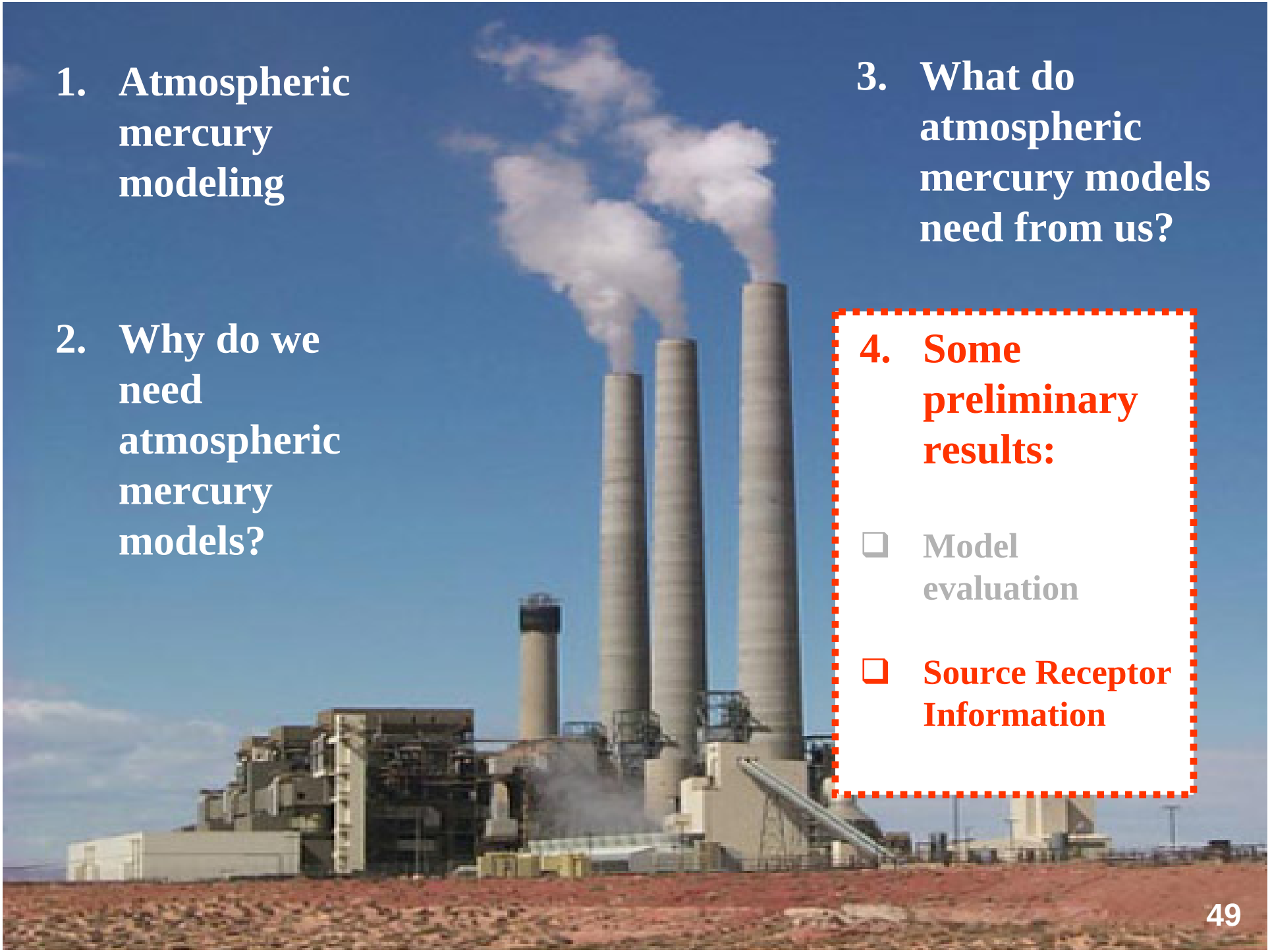
Cooperative Oxford Lab
(38.678EN, 76.173EW)

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



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

	Oxford	Wye
Event-based precipitation samples analyzed for Hg	✓	✓
Speciated Hg concentrations in ambient air (RGM, Hg(p), Hg^0)	✓	✓
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?

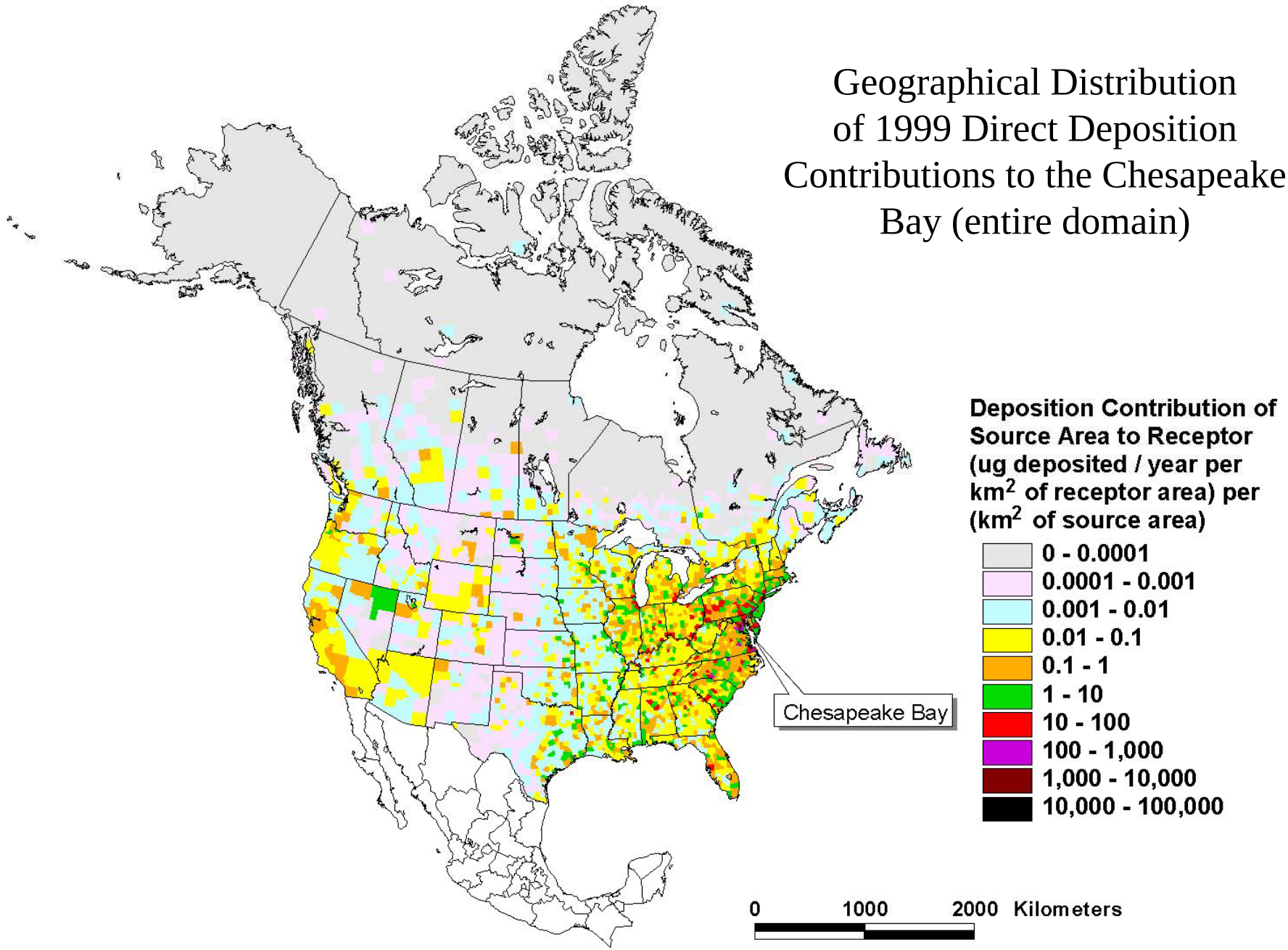
3. What do atmospheric mercury models need from us?

4. Some preliminary results:

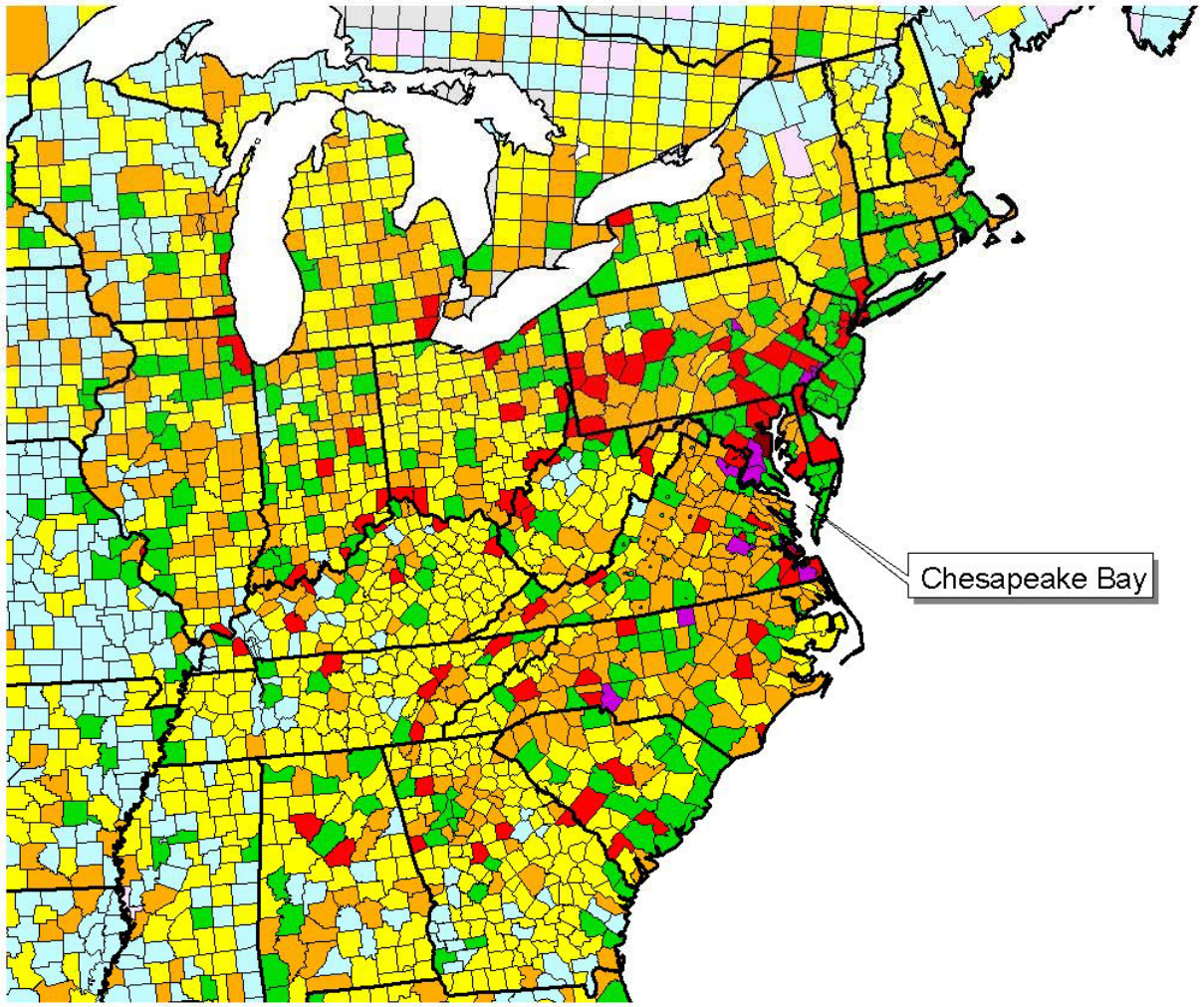
- ❑ Model evaluation
- ❑ Source Receptor Information

Example of Detailed Results: 1999 Results for Chesapeake Bay

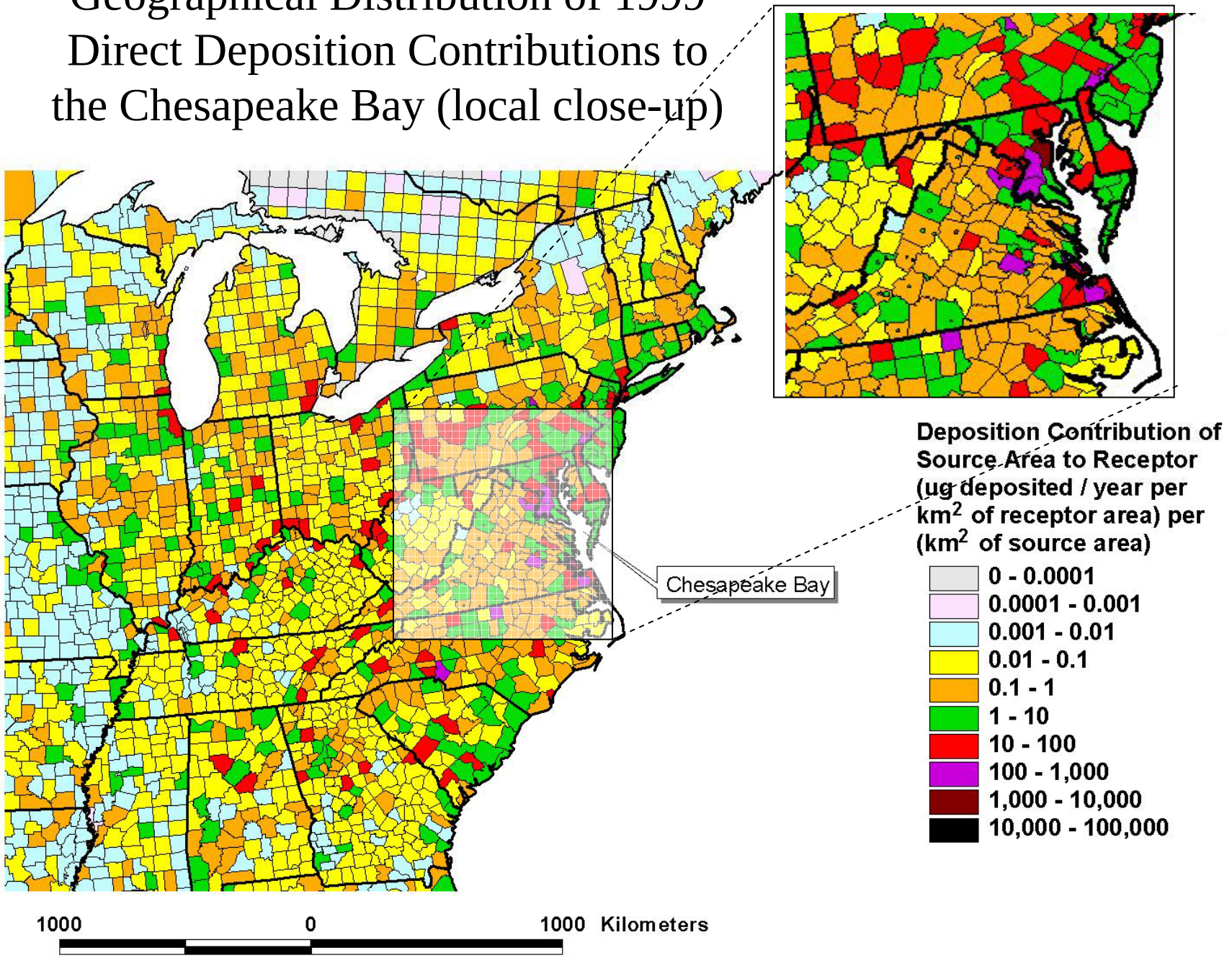
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)



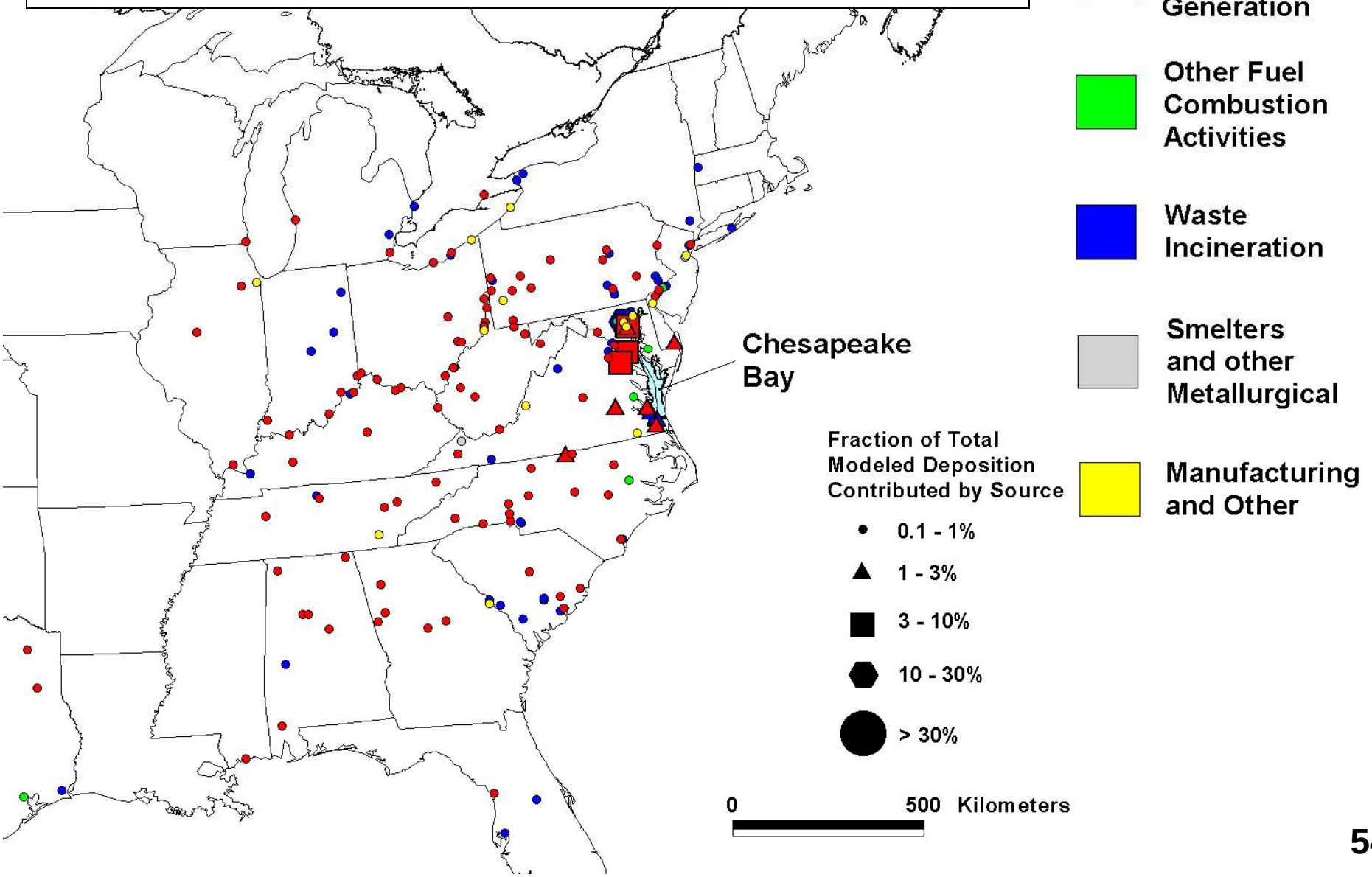
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)



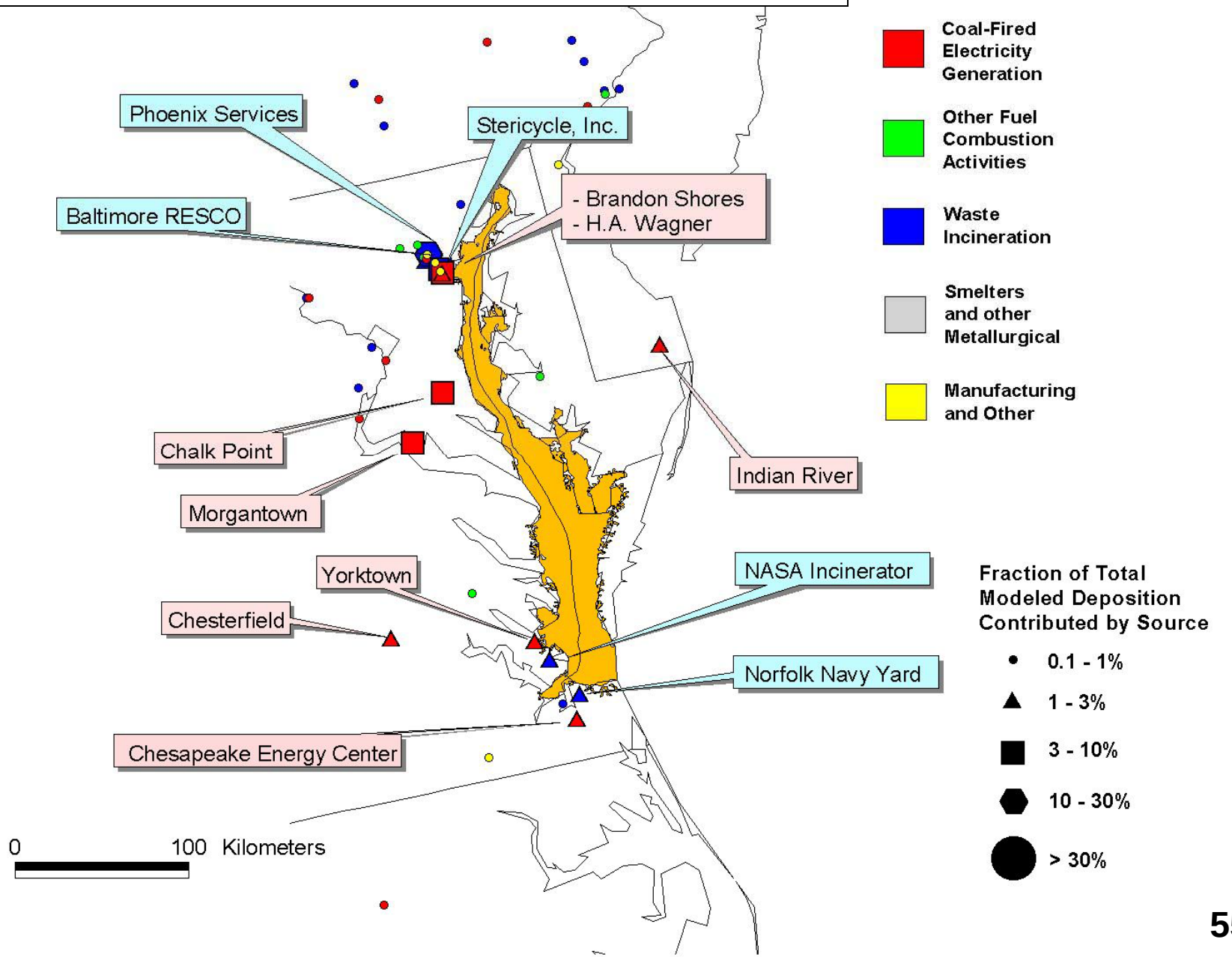
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)



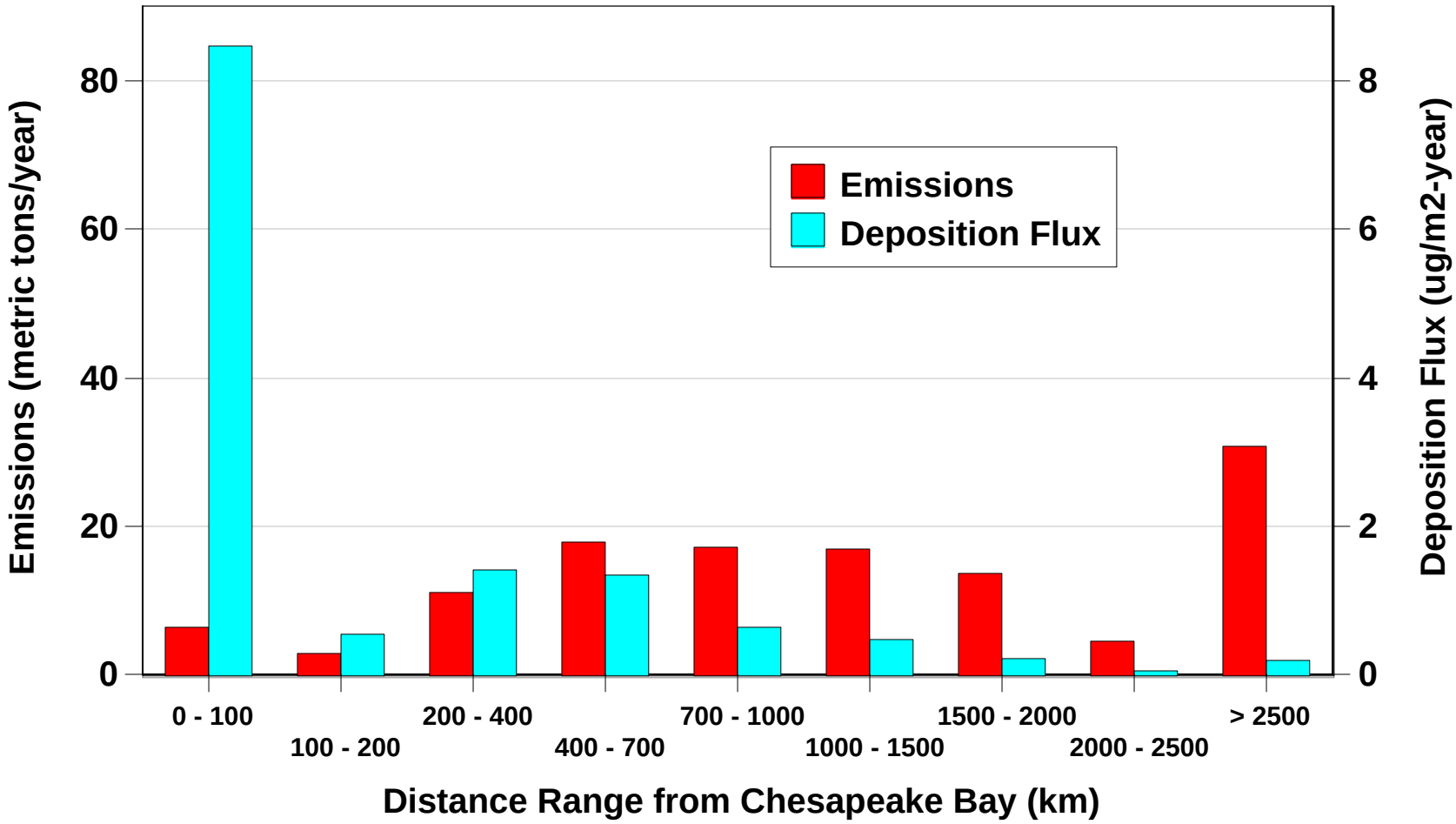
Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



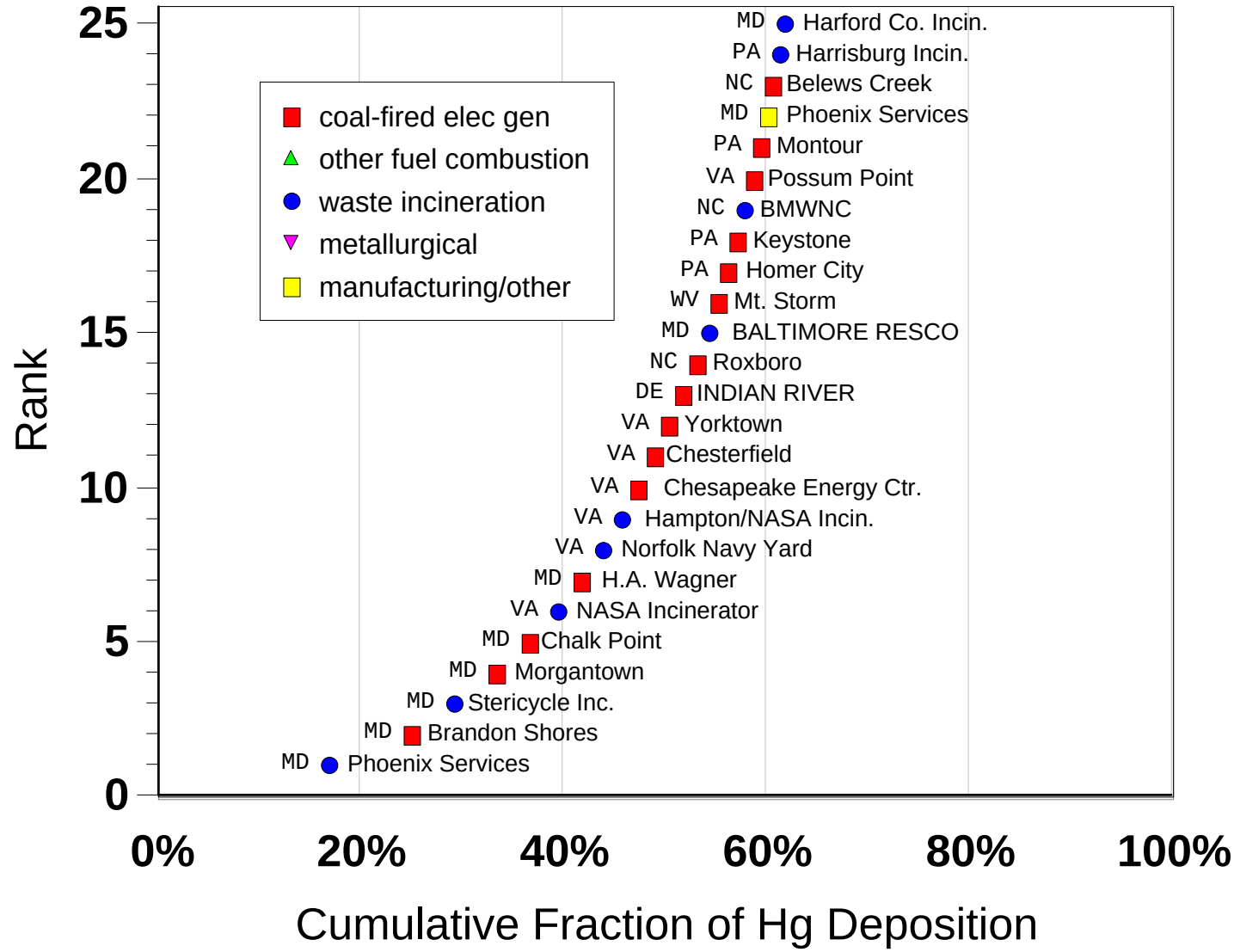
Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



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

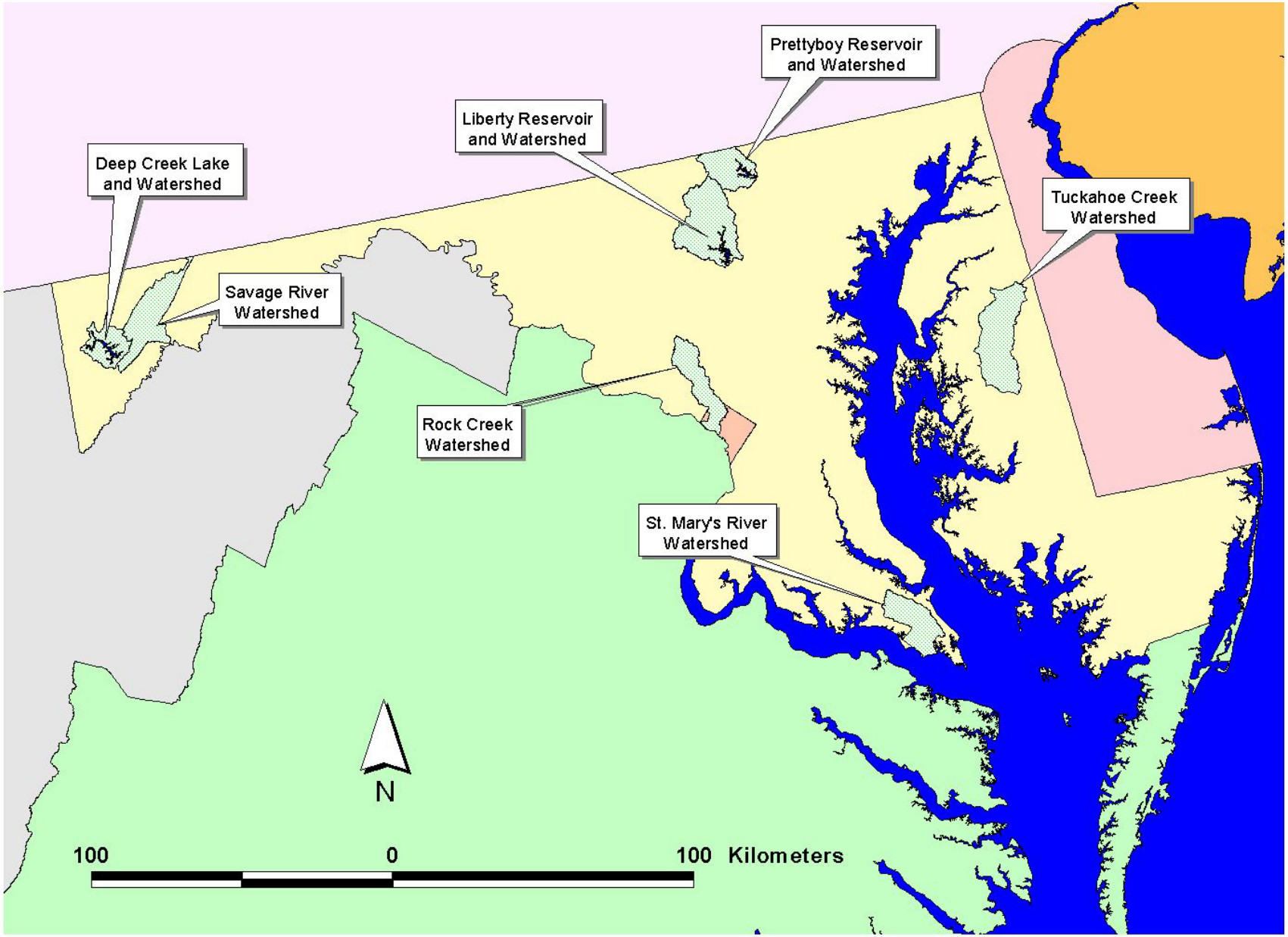


Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay

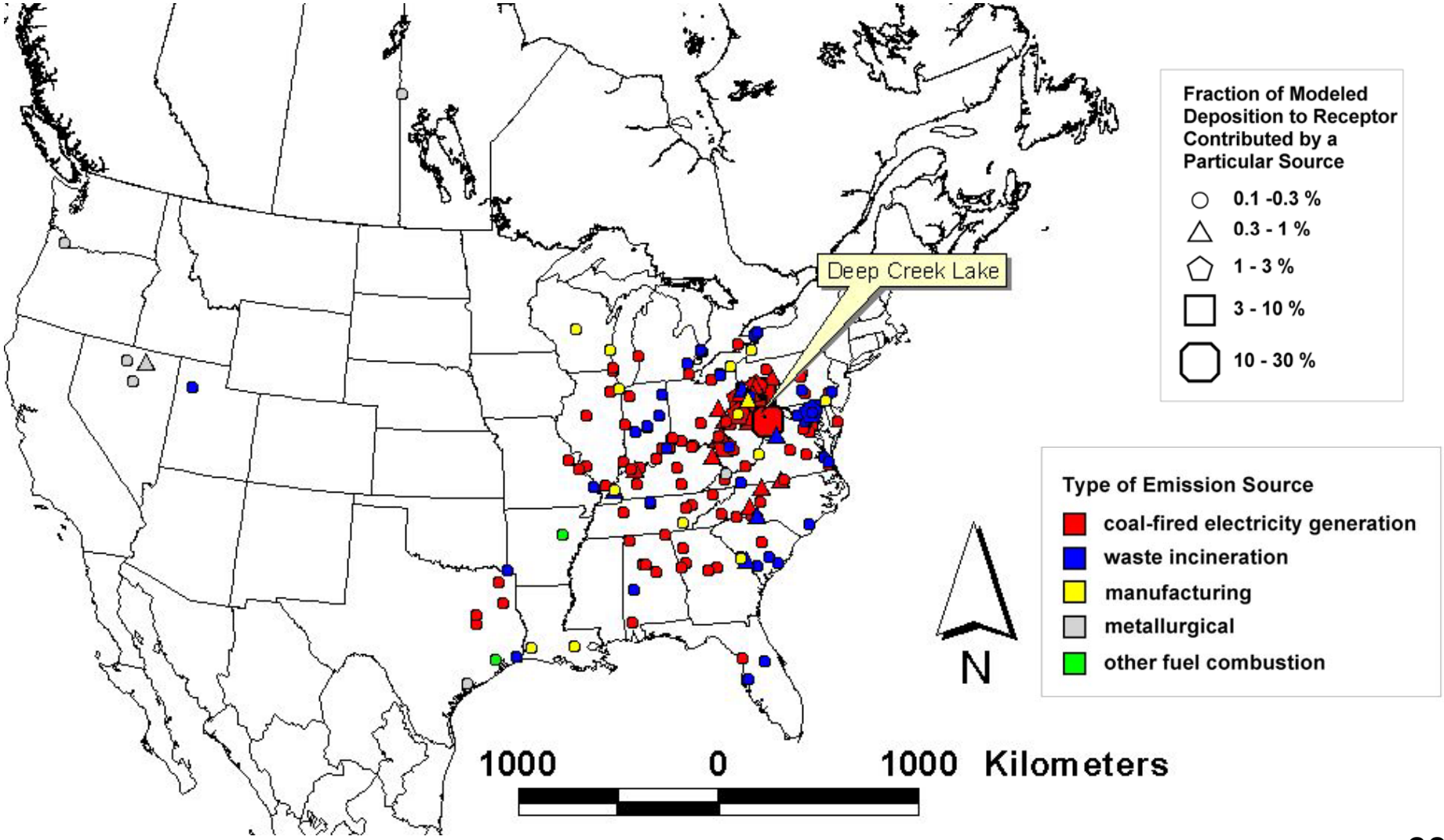


Preliminary Results for other Maryland Receptors

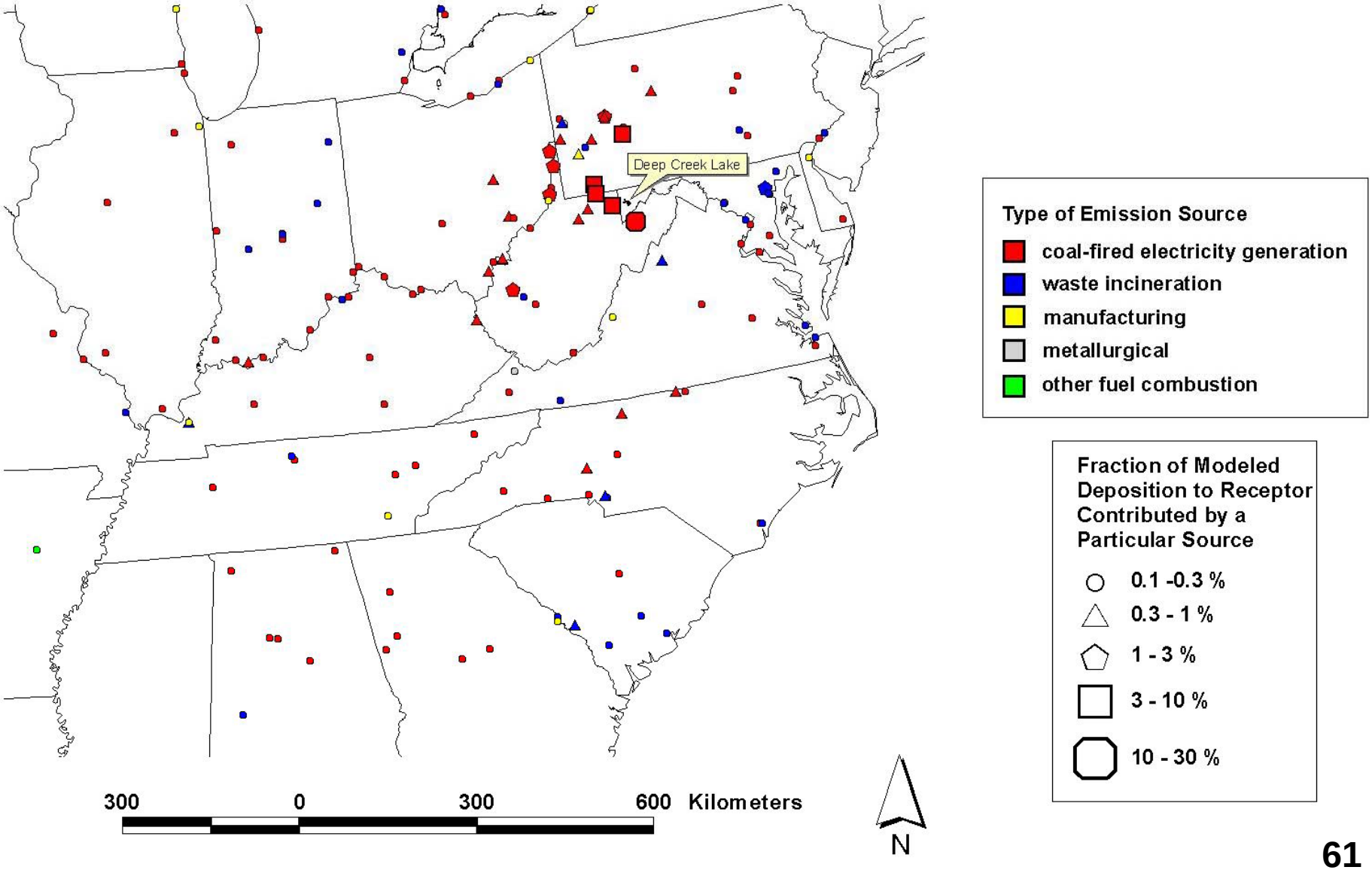
Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling *(but modeling was not optimized for these receptors!)*



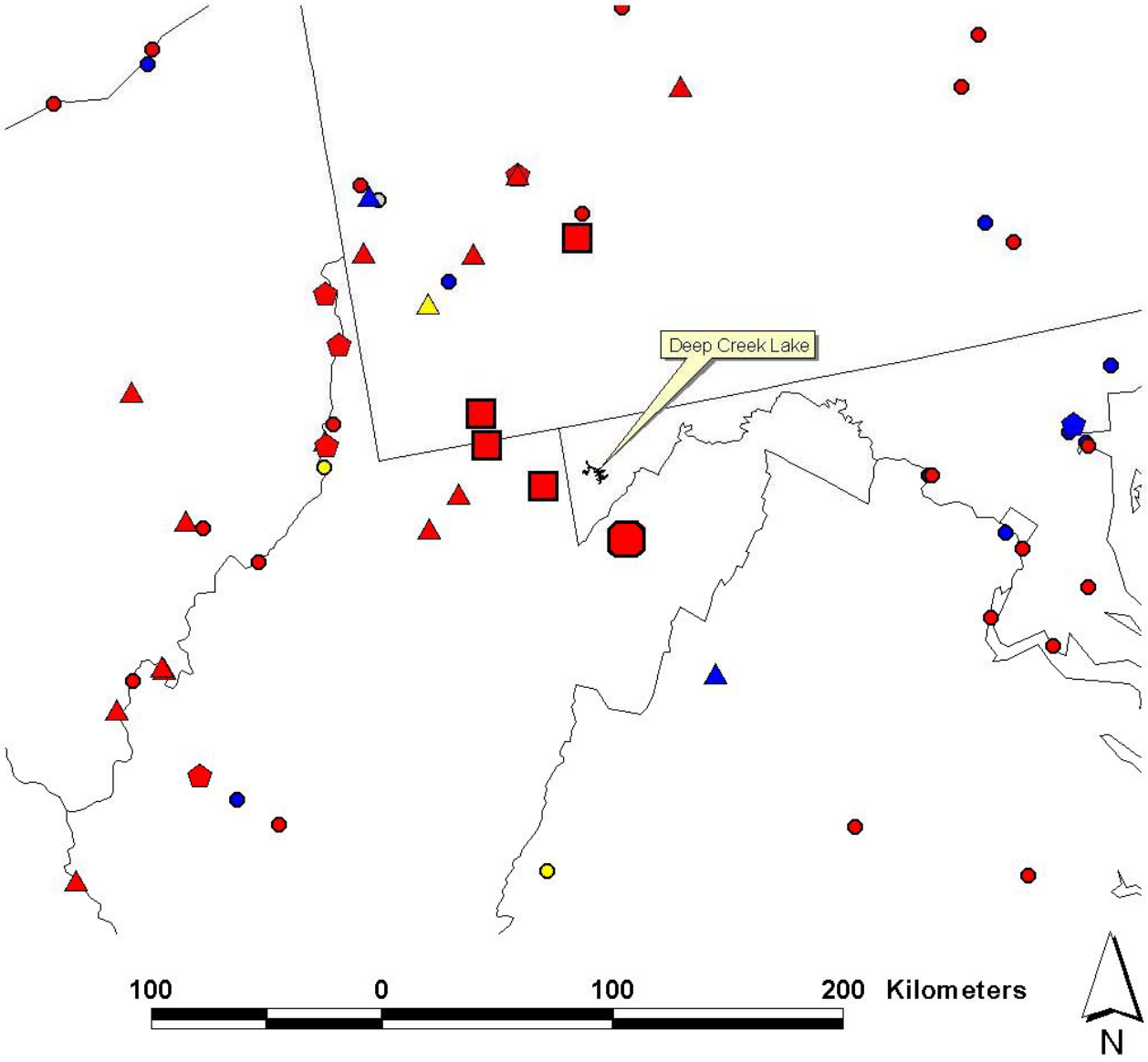
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (national view)



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)



Type of Emission Source

- coal-fired electricity generation
- waste incineration
- manufacturing
- metallurgical
- other fuel combustion

Fraction of Modeled Deposition to Receptor Contributed by a Particular Source

- 0.1 -0.3 %
- 0.3 - 1 %
- 1 - 3 %
- 3 - 10 %
- 10 - 30 %

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

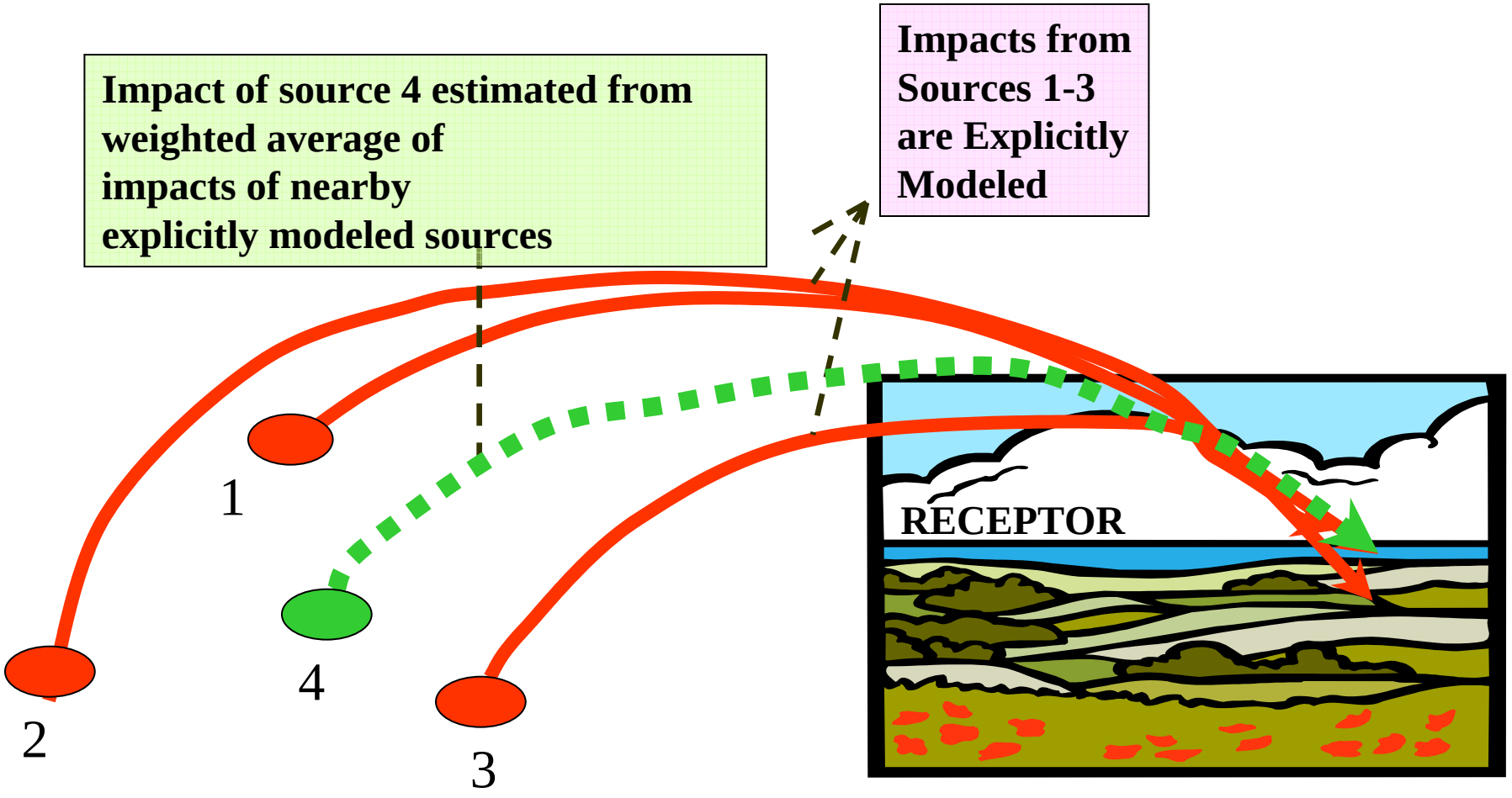
- Source-attribution information is important
- Impacts are episodic & depend on form of mercury emitted
- Modeling needed to get source-attribution information
- Not enough monitoring data to evaluate and improve models
- Many uncertainties but useful model results are emerging
- Models don’t have to 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 1st order with respect to Hg**
- **The current "consensus" chemical mechanism (equilibrium + reactions) does not contain any equations that are not 1st order in Hg**

Spatial interpolation

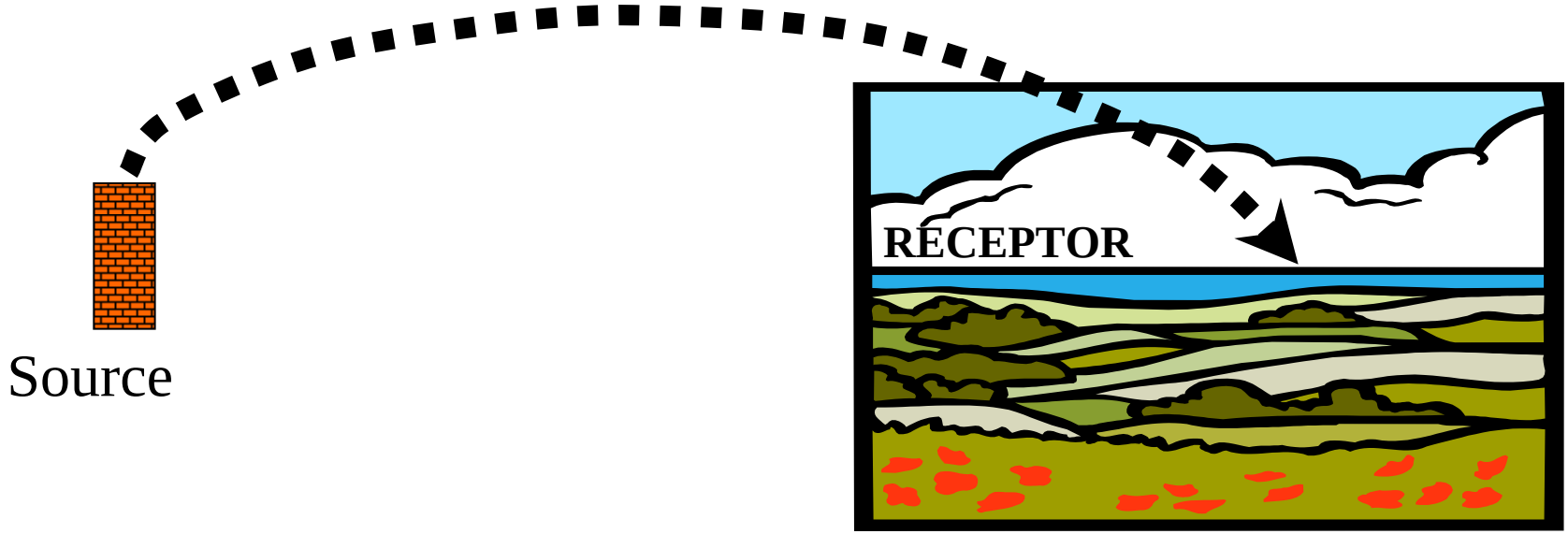


- **Perform separate simulations at each location for emissions of pure Hg(0), Hg(II) and Hg(p)**

  [*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”



Impact of Source Emitting
30% Hg(0)
50% Hg(II)
20% Hg(p)

=

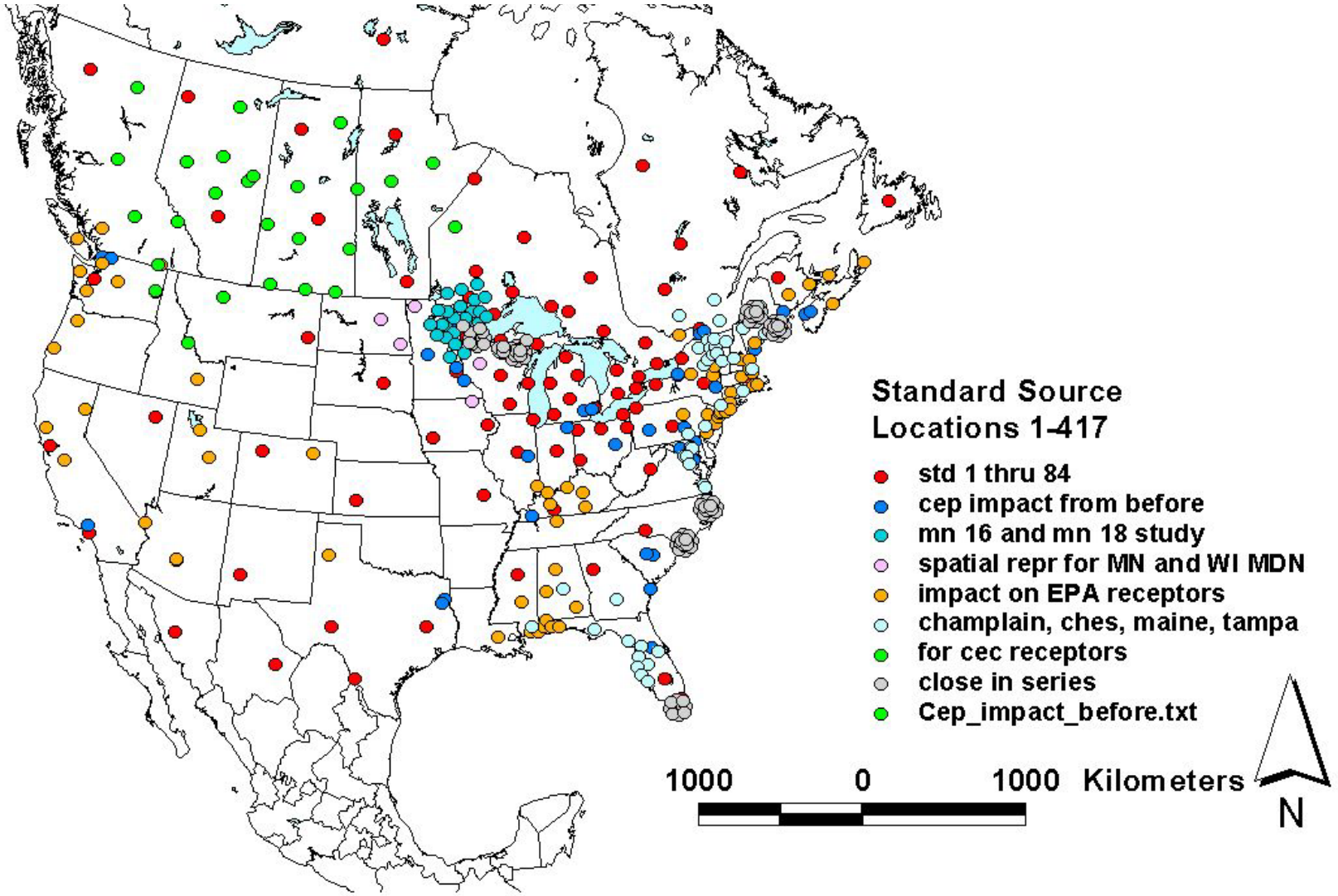
0.3 x **Impact of Source Emitting Pure Hg(0)**

+

0.5 x **Impact of Source Emitting Pure Hg(II)**

+

0.2 x **Impact of Source Emitting Pure Hg(p)**


Standard Source
Locations 1-417
std 1 thru 84
cep impact from before
mn 16 and mn 18 study
spatial repr for MN and WI MDN
impact on EPA receptors
champlain, ches, maine, tampa
for cec receptors
close in series
Cep_impact_before.txt
1000
0
1000 Kilometers
N

Standard Source Locations in Maryland region during recent simulation