Atmospheric Fate and Transport of Mercury:
Where does the *mercury* in *mercury deposition* come from?

Dr. Mark Cohen
NOAA Air Resources Laboratory
Silver Spring, Maryland, USA
http://www.arl.noaa.gov/ss/transport/cohen.html

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(revised version, January 2005)

- **Fish consumption is the most important exposure pathway for most humans and wildlife**

- **For many (but not all) aquatic ecosystems, much of the loading comes directly or indirectly through the atmospheric pathway...**

For the atmospheric pathway:

- ❑ **How much of the mercury in atmospheric mercury deposition comes from local, regional, national, continental, and global sources?**

- ❑ **How important are different source types?**

We currently face key policy decisions regarding regulation of Hg emissions:

- **what difference will regulating U.S. coal-fired power plants make?**
- **is emissions trading workable (and ethical)?**
- **how deep should emissions reductions be?**

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")

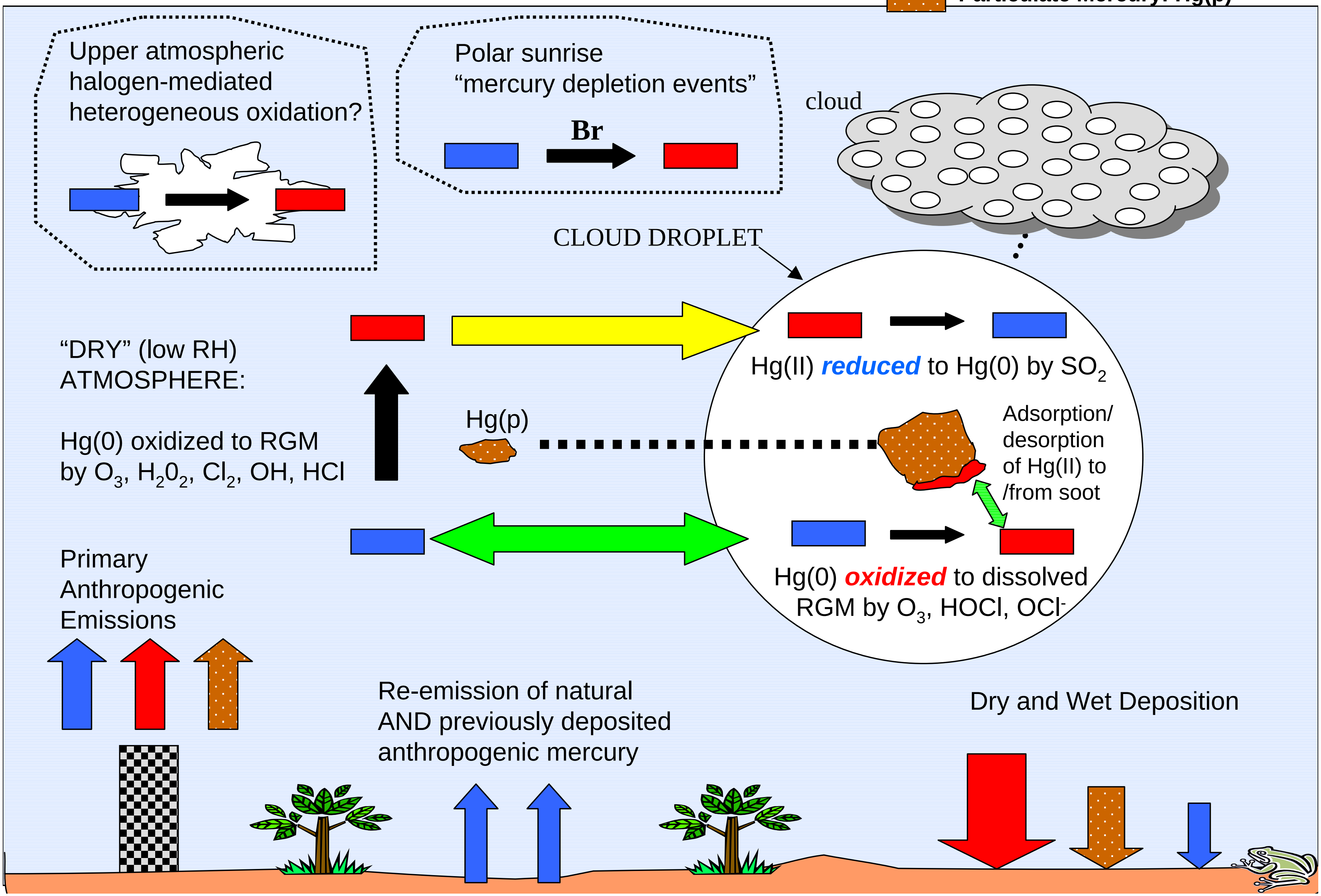
- a few percent of total Hg in atmosphere
- oxidized mercury: Hg(II)
- HgCl2, others species?
- somewhat operationally defined by measurement method
- *very* water soluble
- short atmospheric lifetime (~ 1 week or less);
- more local and regional effects

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 Fate Processes for Hg

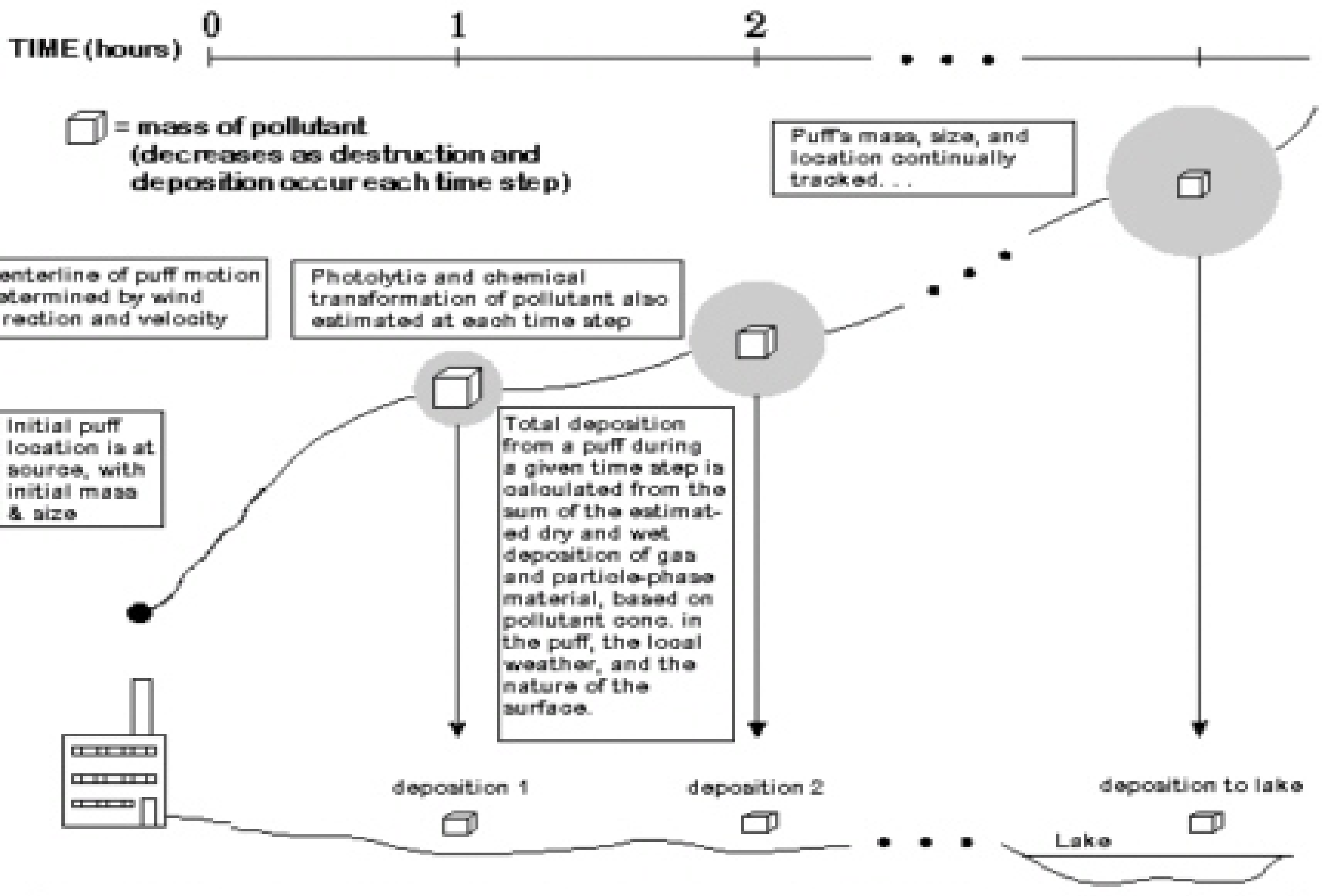
Elemental Mercury: Hg(0)
Reactive Gaseous Mercury: RGM
Particulate Mercury: Hg(p)



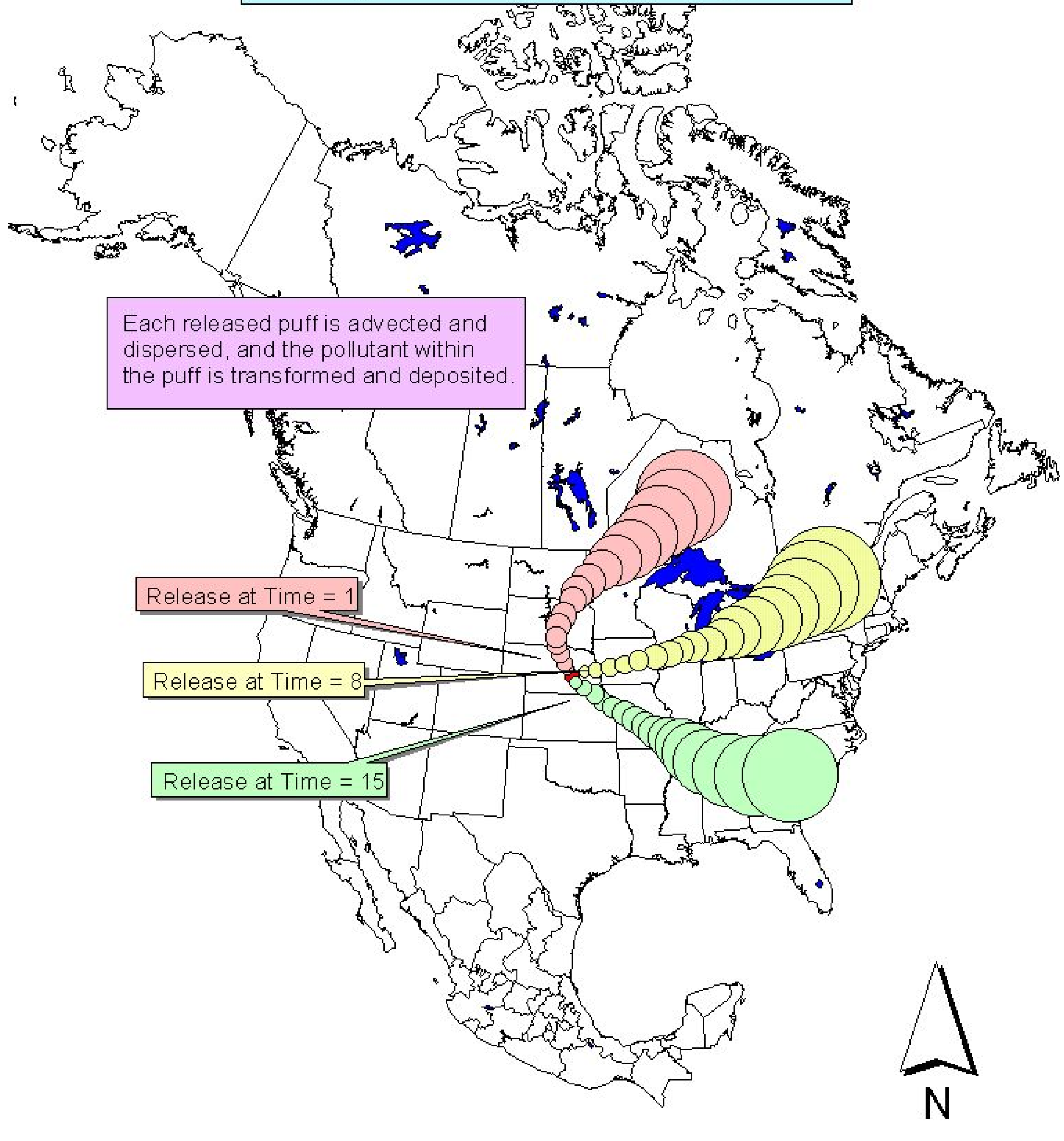
Atmospheric Chemical Reaction Scheme for Mercury

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

Figure 1. Lagrangian Puff Air Transport and Deposition Model

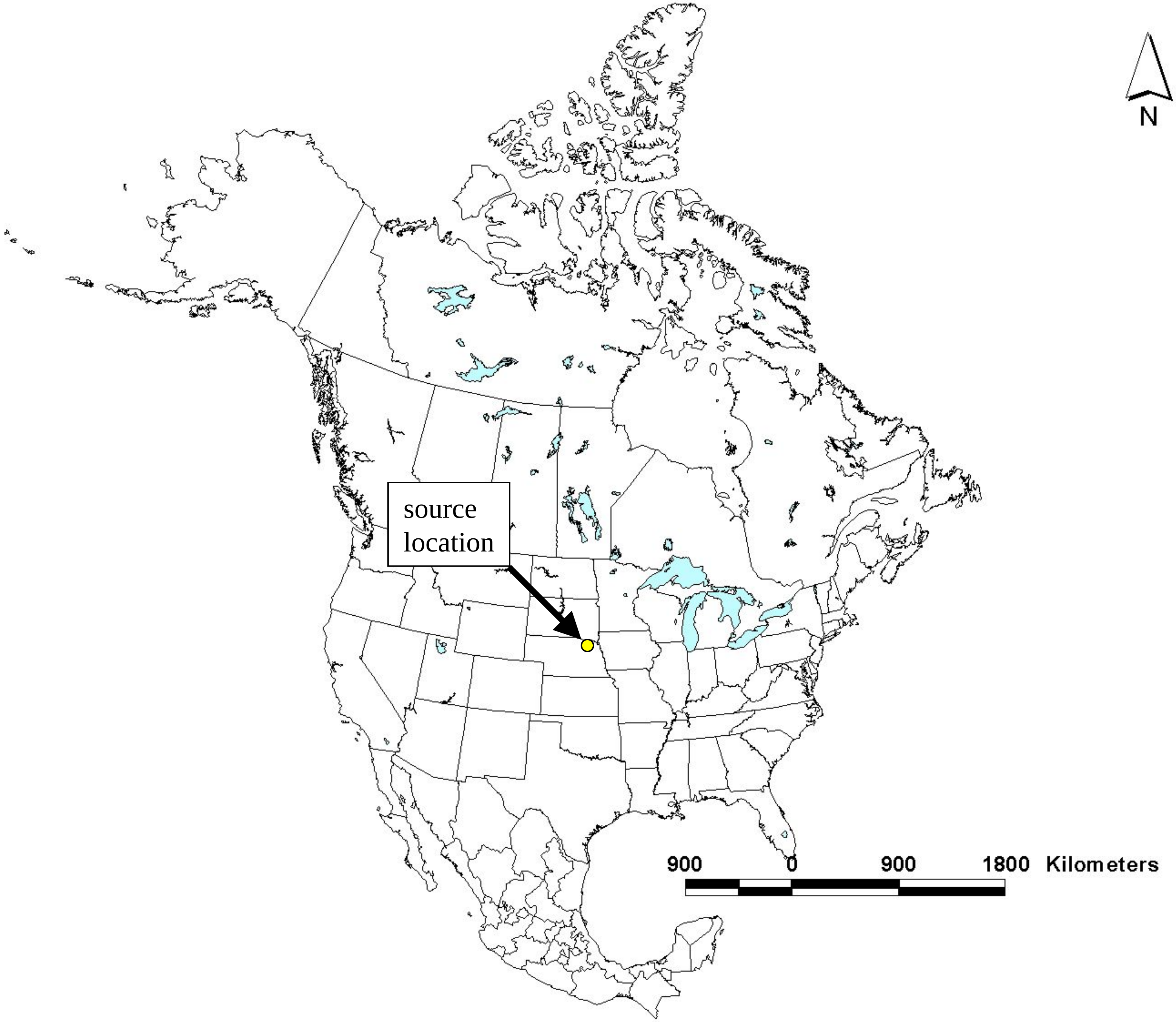


Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).

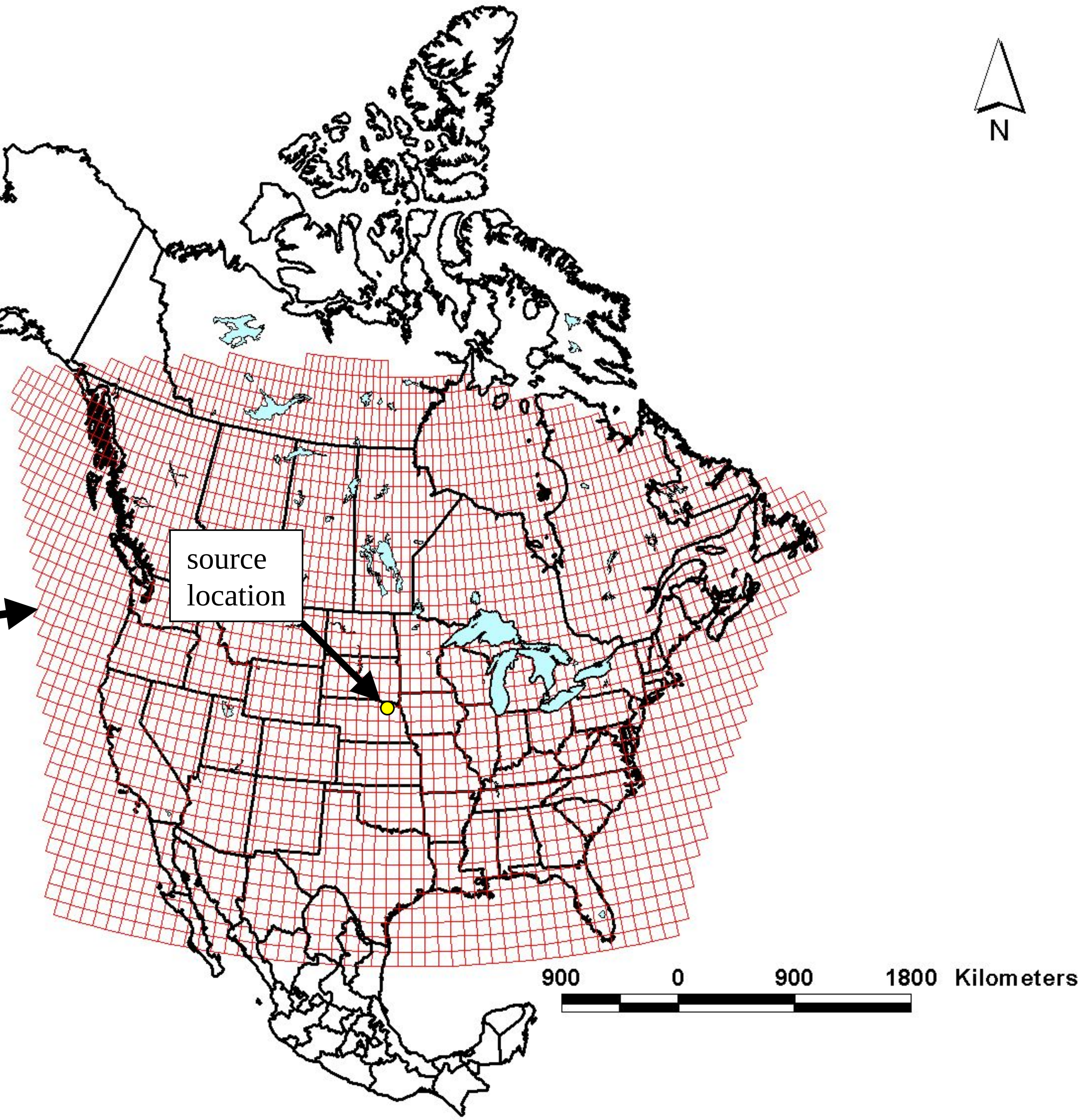


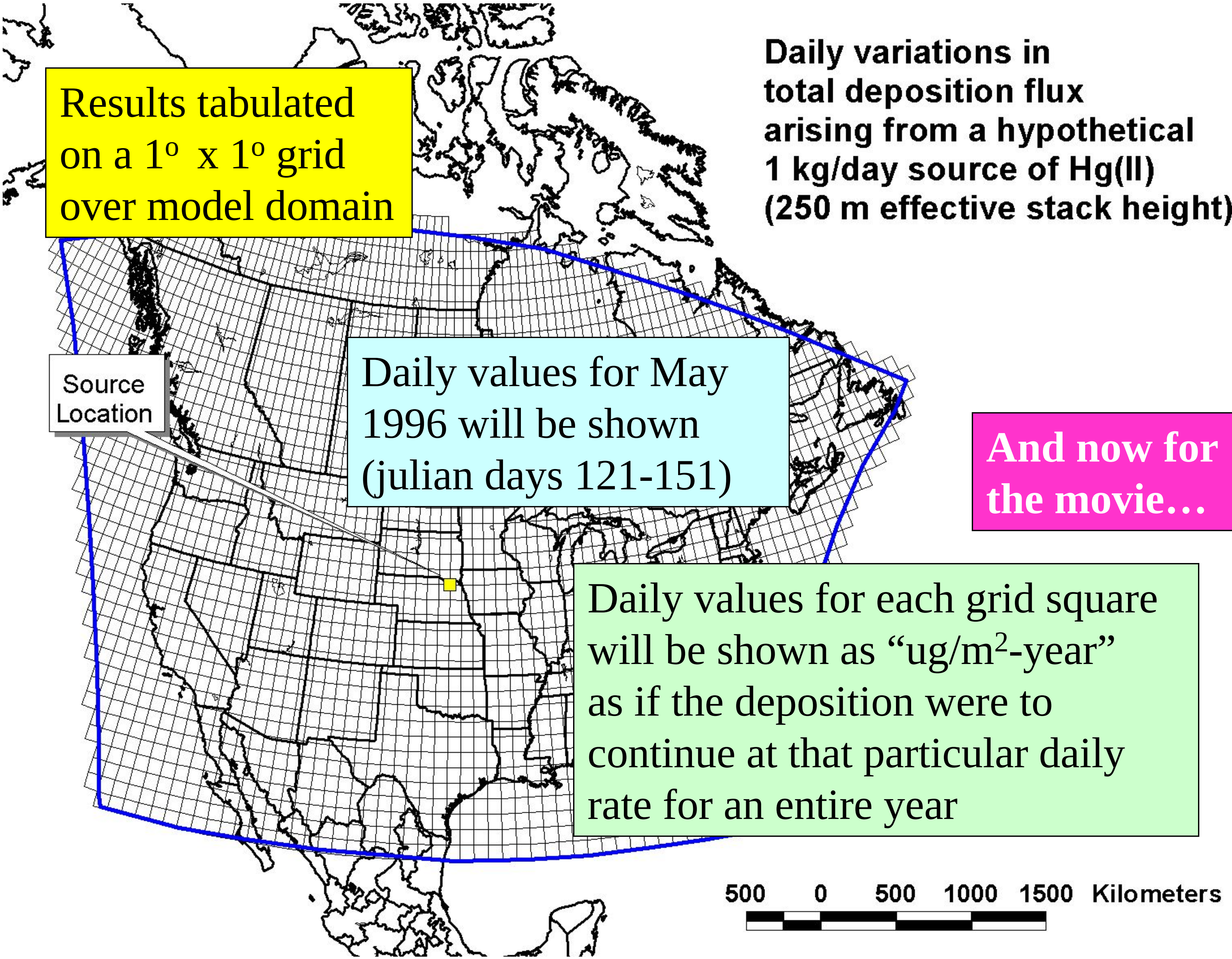
1. The impact of any given mercury emissions source on any receptor is highly variable

- **extreme spatial and temporal variations**
- **Think about the weather and then add all the chemistry and physics of mercury's interactions with the "weather"**


N
source
location
900
0
900
1800
Kilometers

1º x 1º grid over entire modeling domain




Daily variations in
total deposition flux
arising from a hypothetical
1 kg/day source of Hg(II)
(250 m effective stack height)
Results tabulated
on a 1° x 1° grid
over model domain
Source
Location
Daily values for May
1996 will be shown
(julian days 121-151)
And now for
the movie…
Daily values for each grid square
will be shown as "ug/m²-year"
as if the deposition were to
continue at that particular daily
rate for an entire year
500 0 500 1000 1500 Kilometers

2. The impact of any given mercury emissions source on any receptor is highly dependent on the "type" of mercury emitted

- **Elemental mercury - Hg^0 - is not readily dry or wet deposited, and its conversion to ionic Hg or Hg(p) is relatively slow**

- **Particulate mercury – Hg(p) - is moderately susceptible to dry and wet deposition**

- **Ionic mercury – also called Reactive Gaseous Mercury or RGM – is easily dry & wet deposited**

  - ***Current questions regarding conversion of RGM to Hg^0 in plumes...***

Example simulation of the atmospheric fate and transport of mercury emissions:

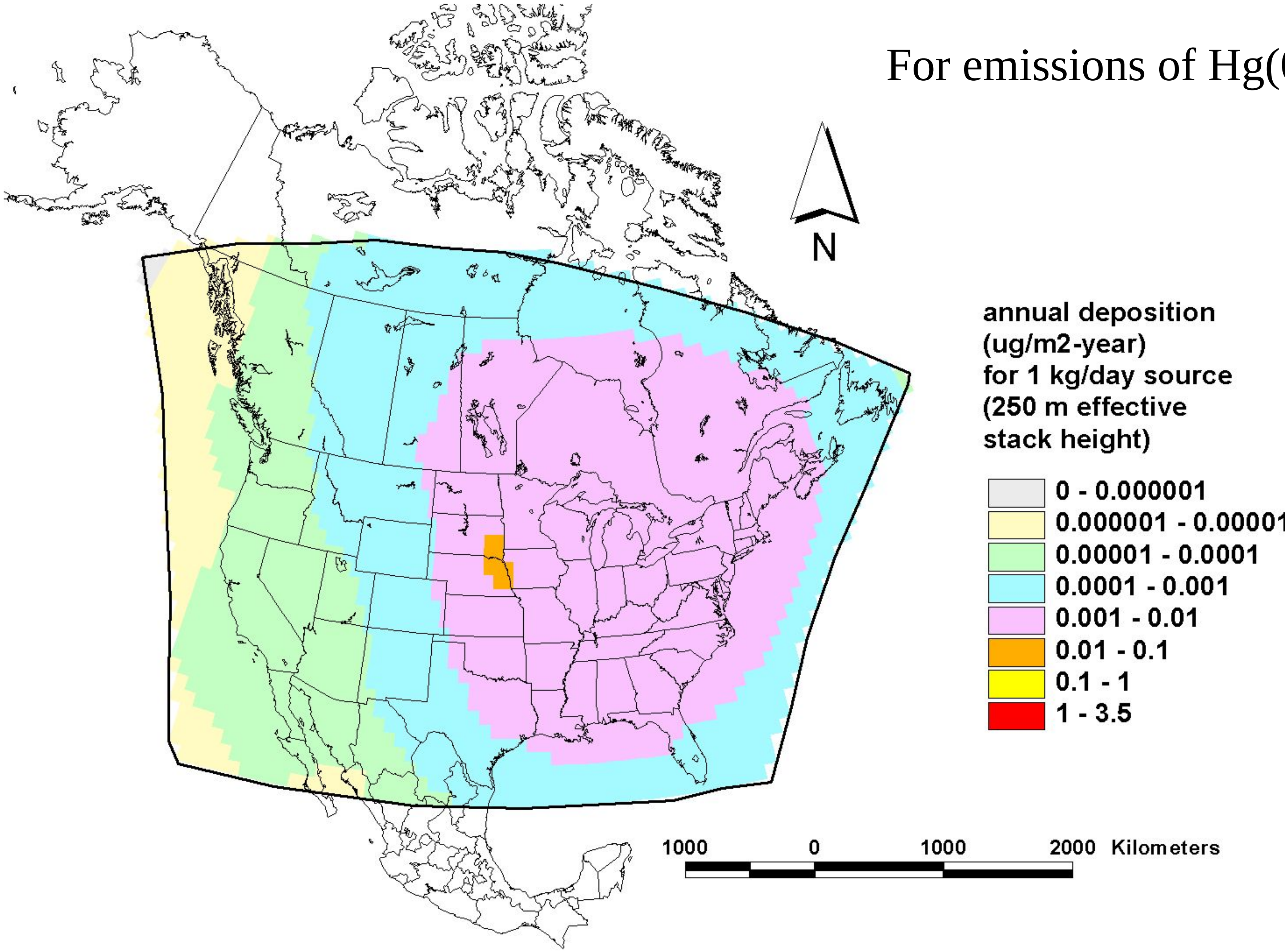
- hypothetical 1 kg/day source of
  RGM, Hg(p) or Hg(0)

- source height 250 meters

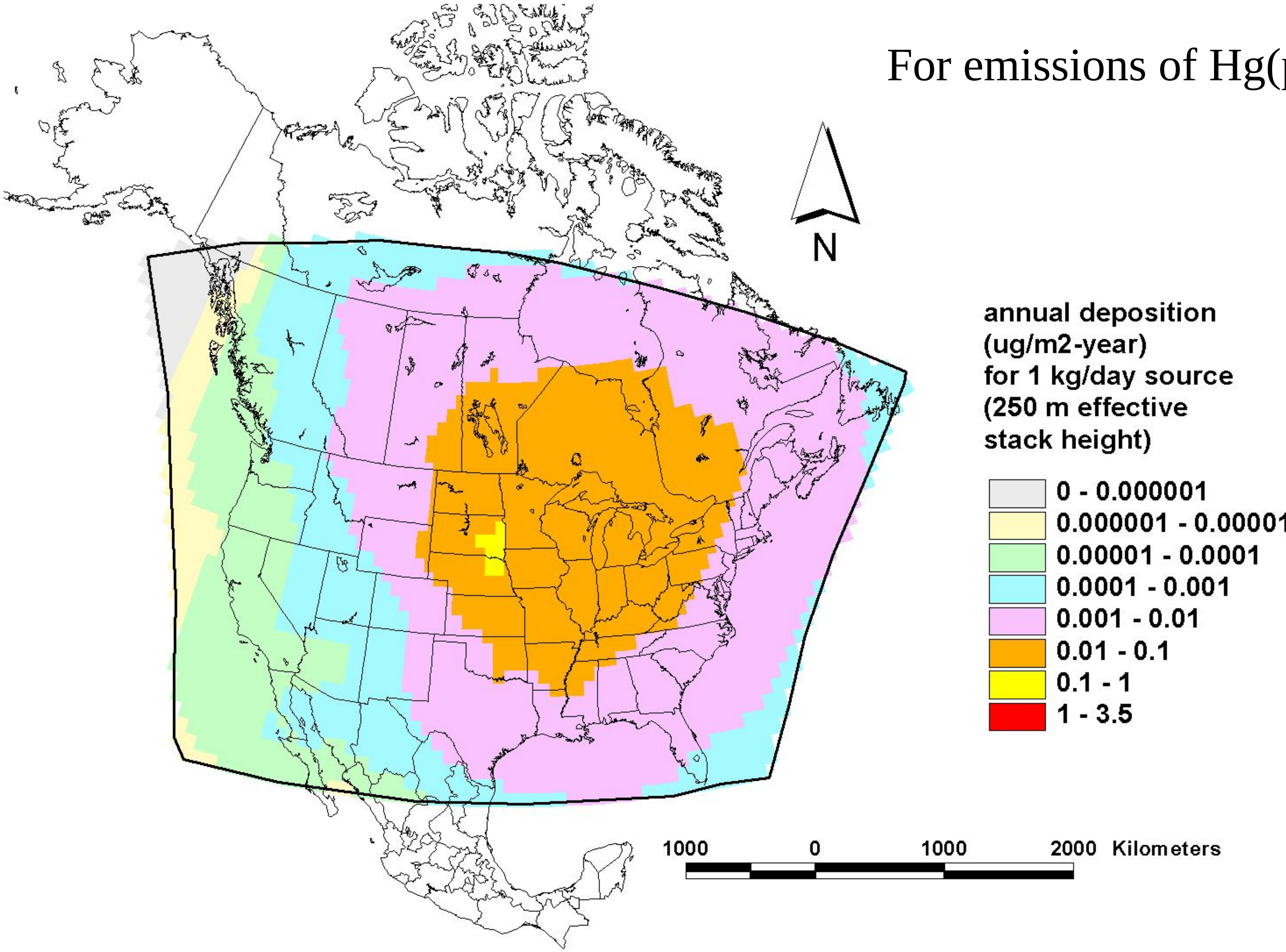
- results tabulated on a 1^{o} x 1^{o} receptor grid

- annual results (1996)

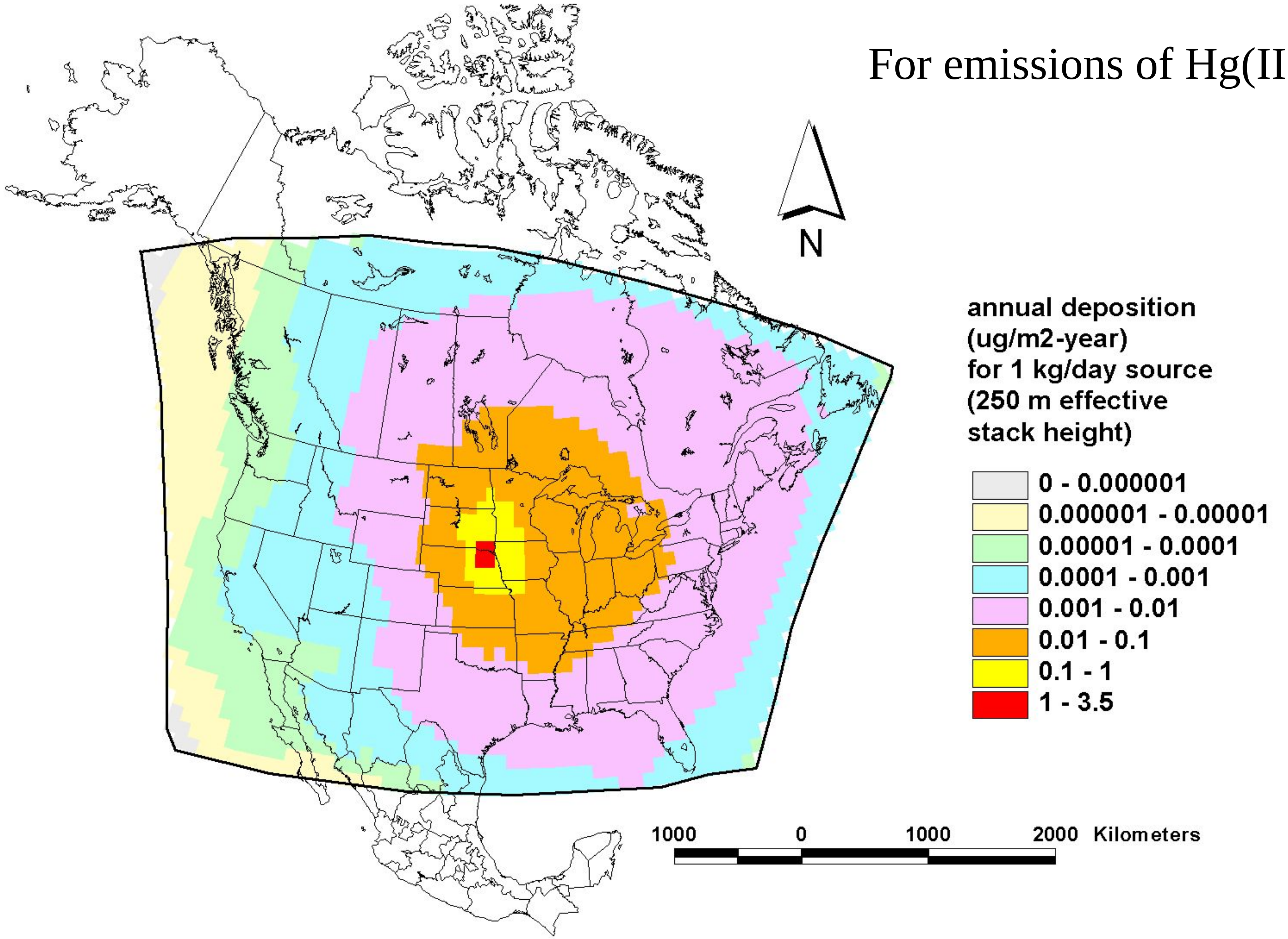
For emissions of Hg(0)



For emissions of Hg(p)

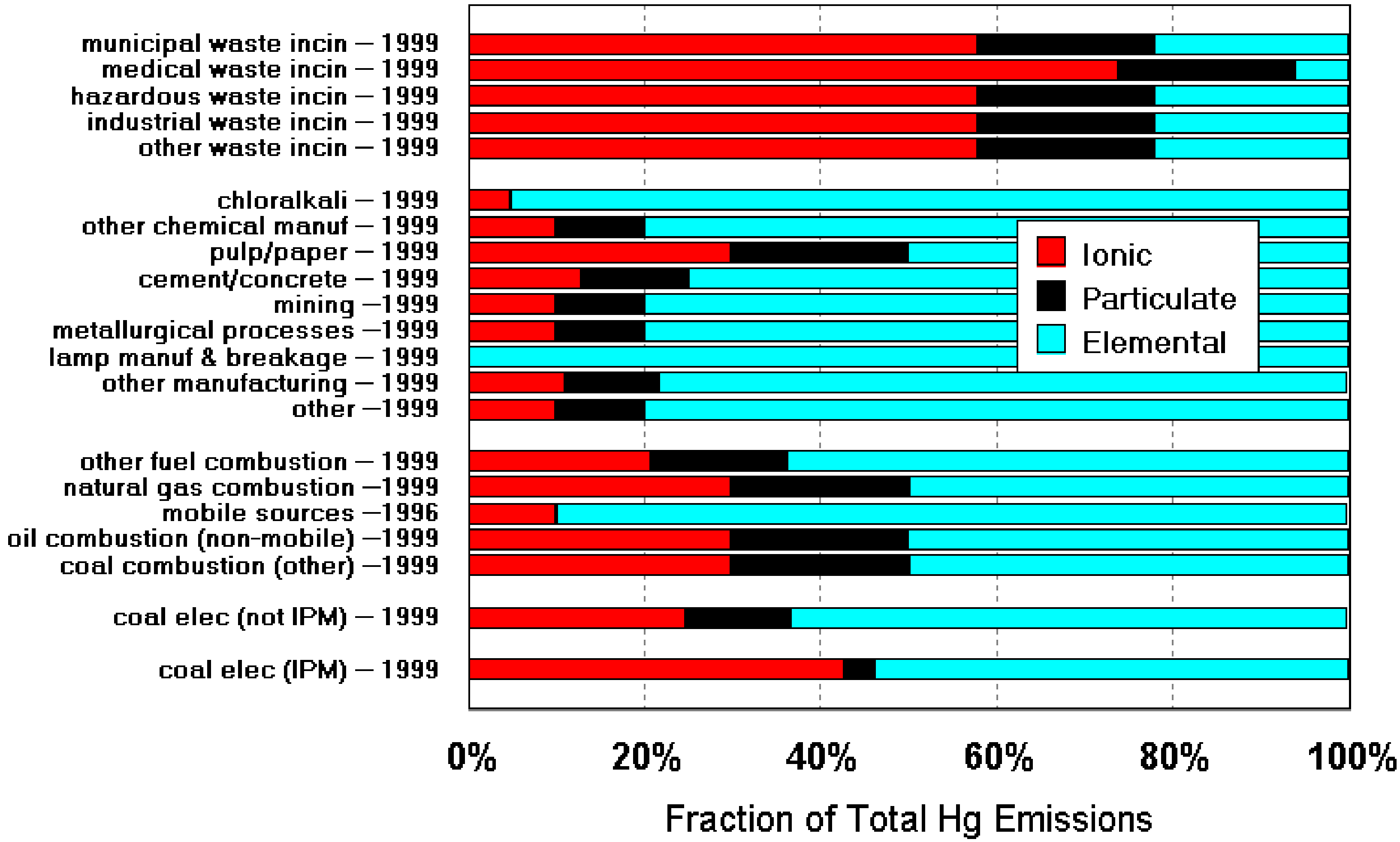


For emissions of Hg(II)

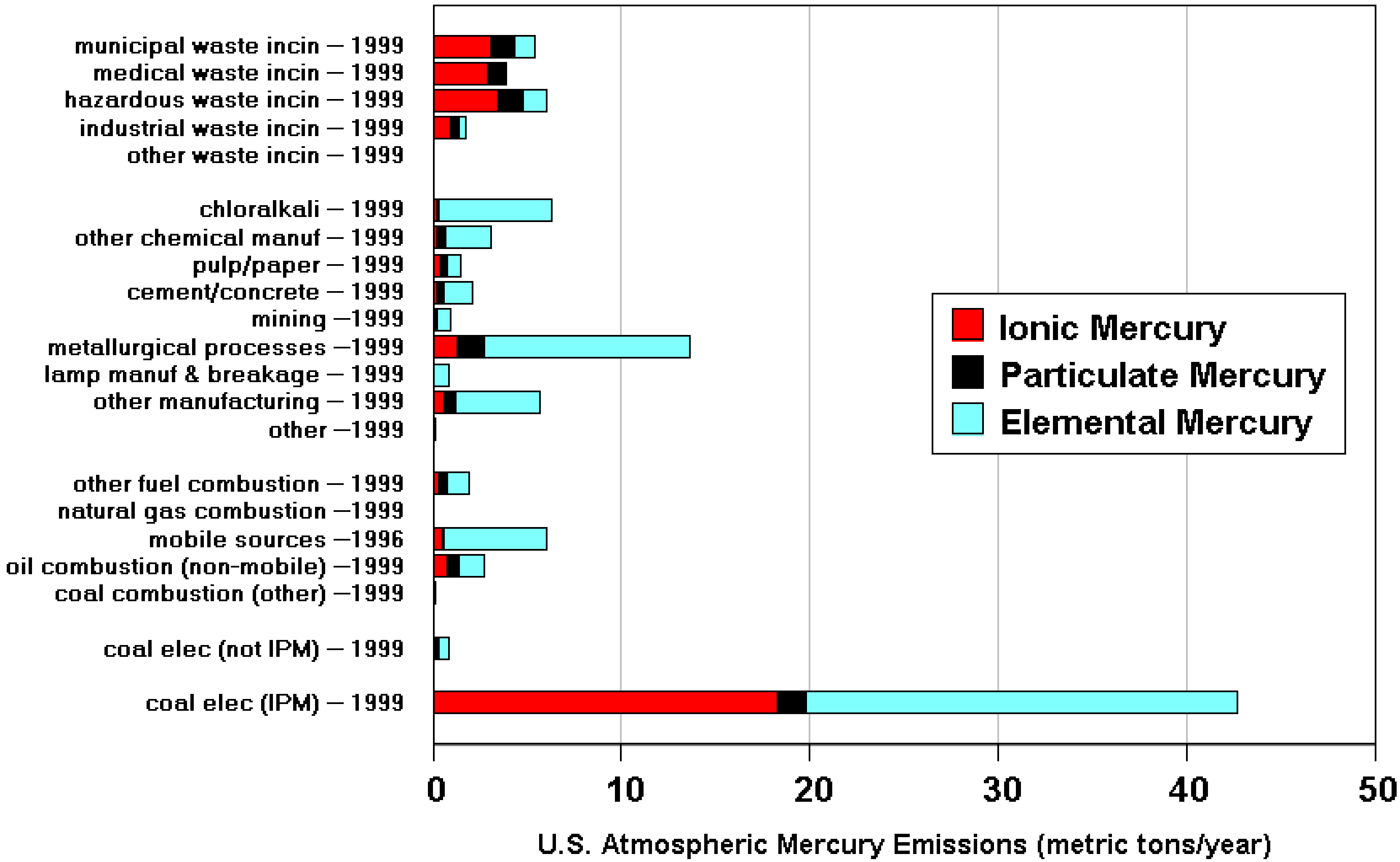


Estimated Speciation Profile for 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

Very uncertain for most sources



Estimated 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

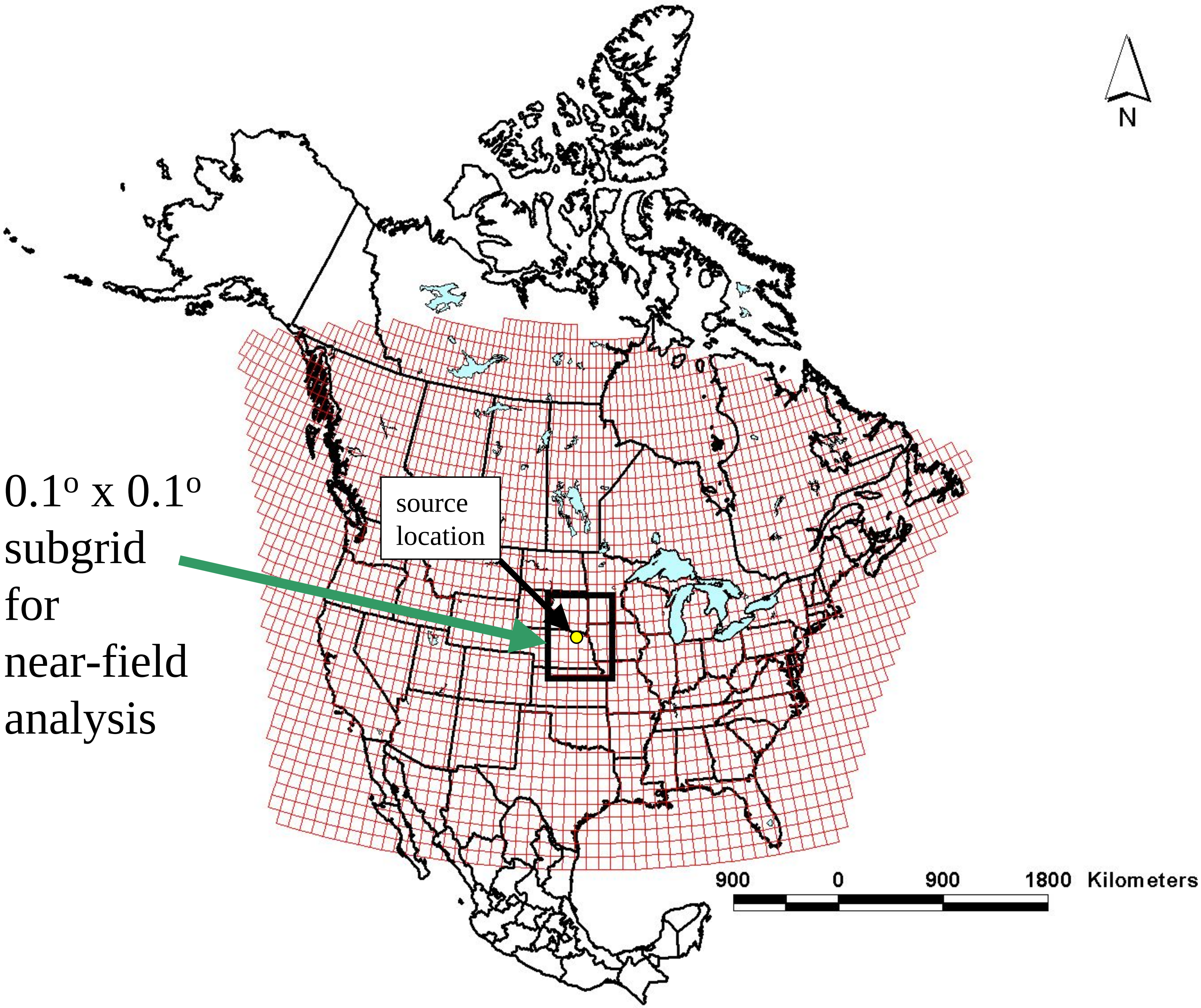


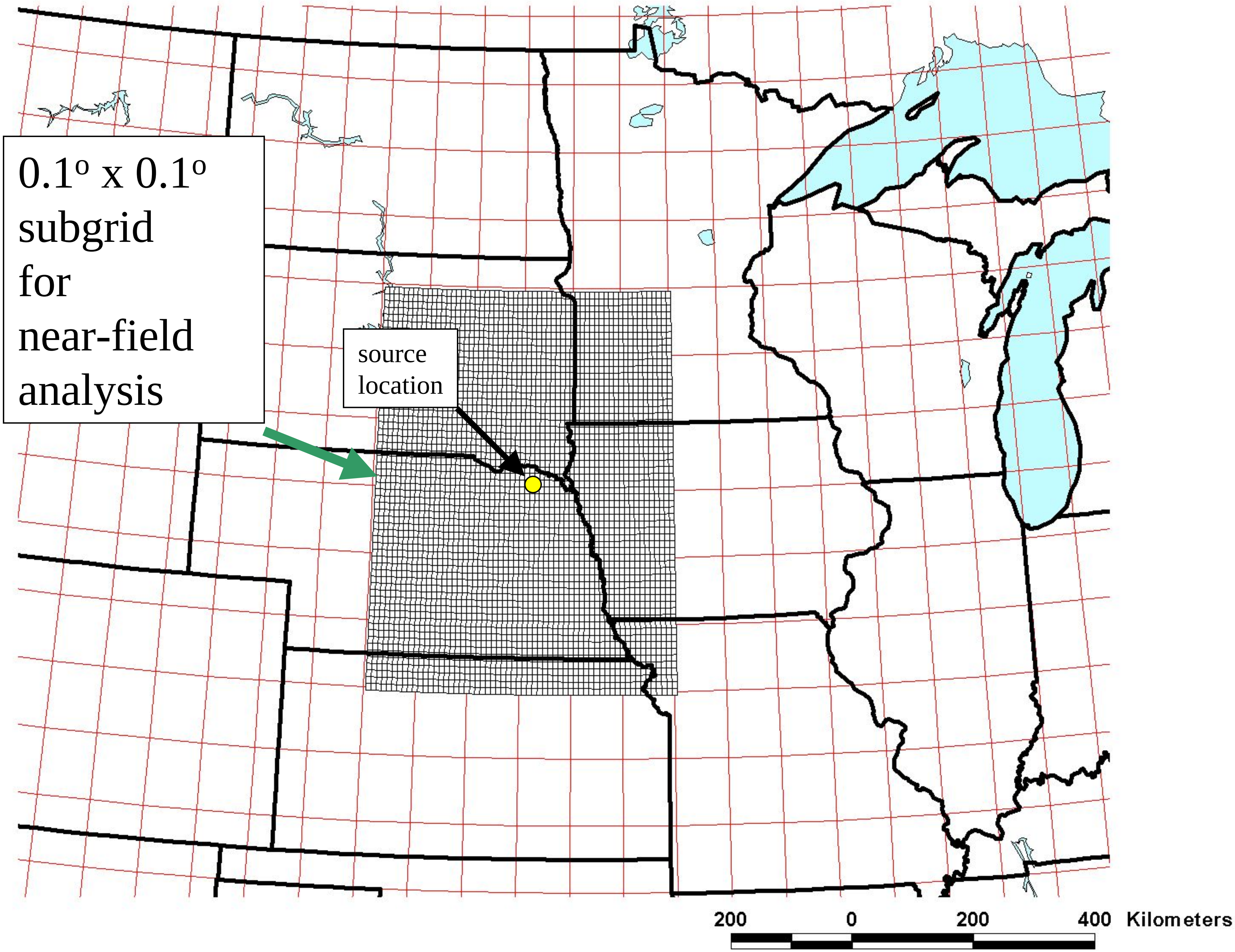
- **Each type of source has a very different emissions speciation profile**

- **Even within a given source type, there can be big differences – depending on process type, fuels and raw materials, pollution control equipment, etc.**

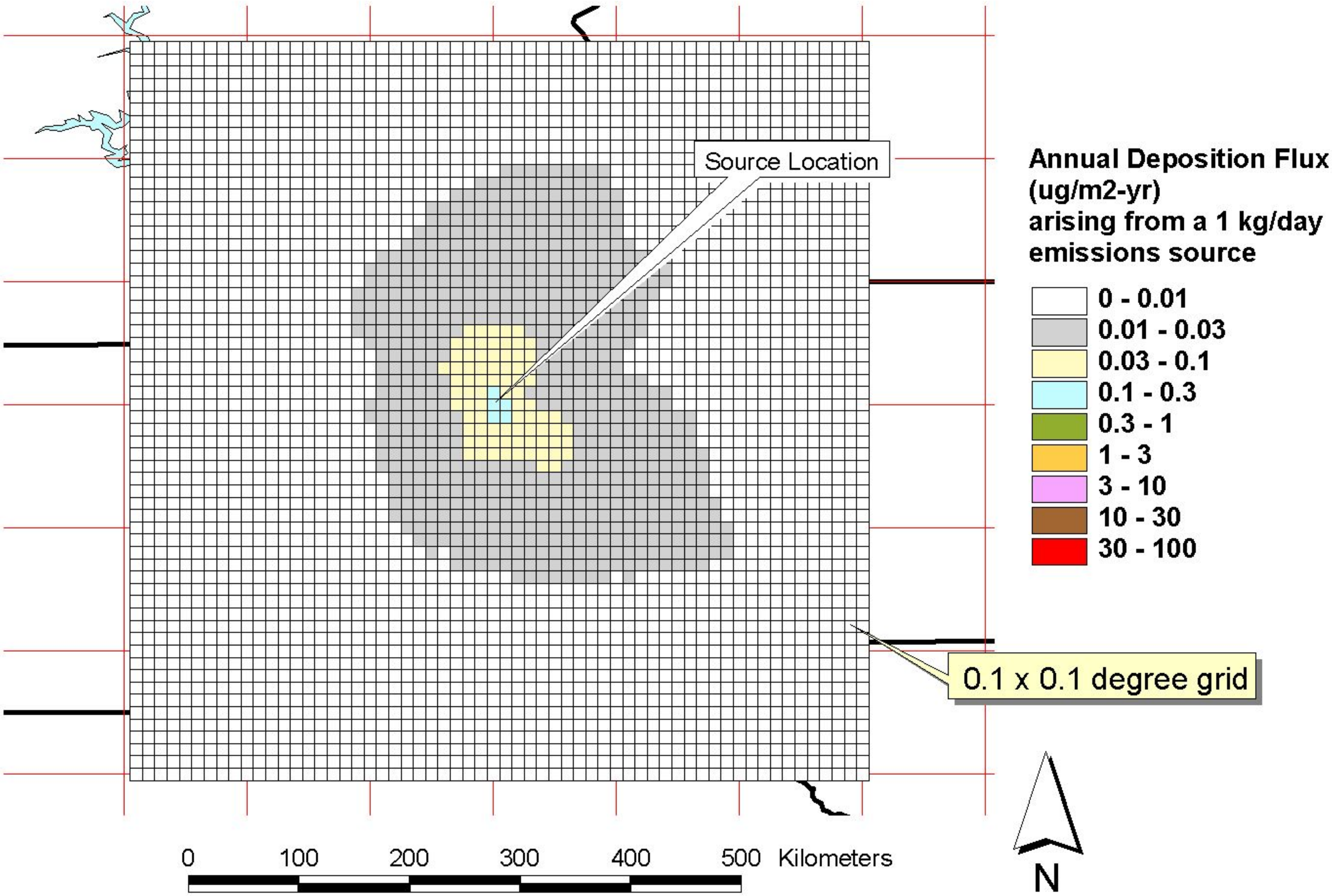
3. There can be large local and regional impacts from any given source

- **same hypothetical 1 kg/day source of RGM**
- **source height 250 meters**
- **exactly the same simulation, but results tabulated on a 0.1^{o} x 0.1^{o} receptor grid**
- **overall results for an entire year (1996)**


0.1° x 0.1° subgrid for near-field analysis
source location
N
900 0 900 1800 Kilometers

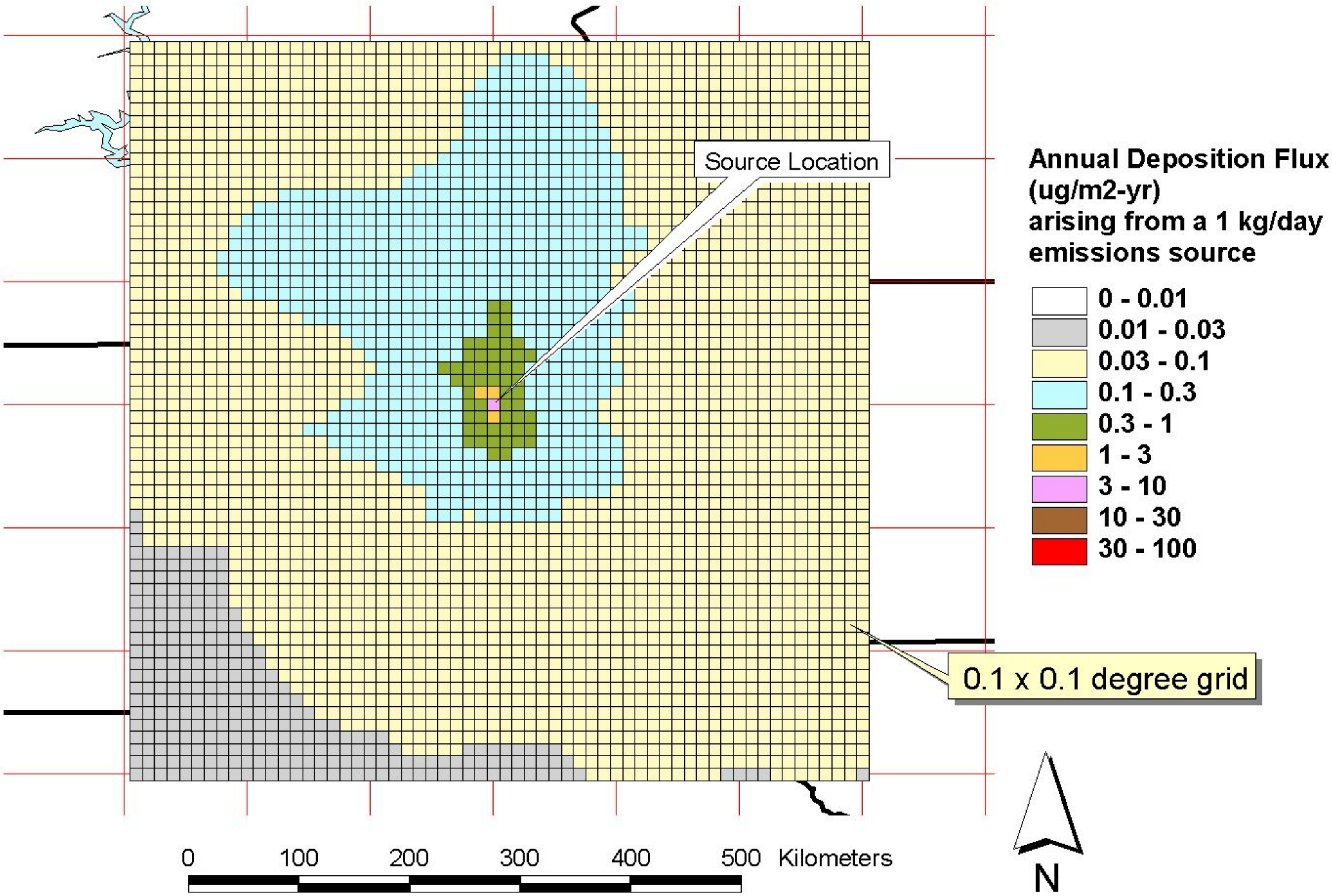

0.1° x 0.1° subgrid for near-field analysis
source location
200
0
200
400 Kilometers

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



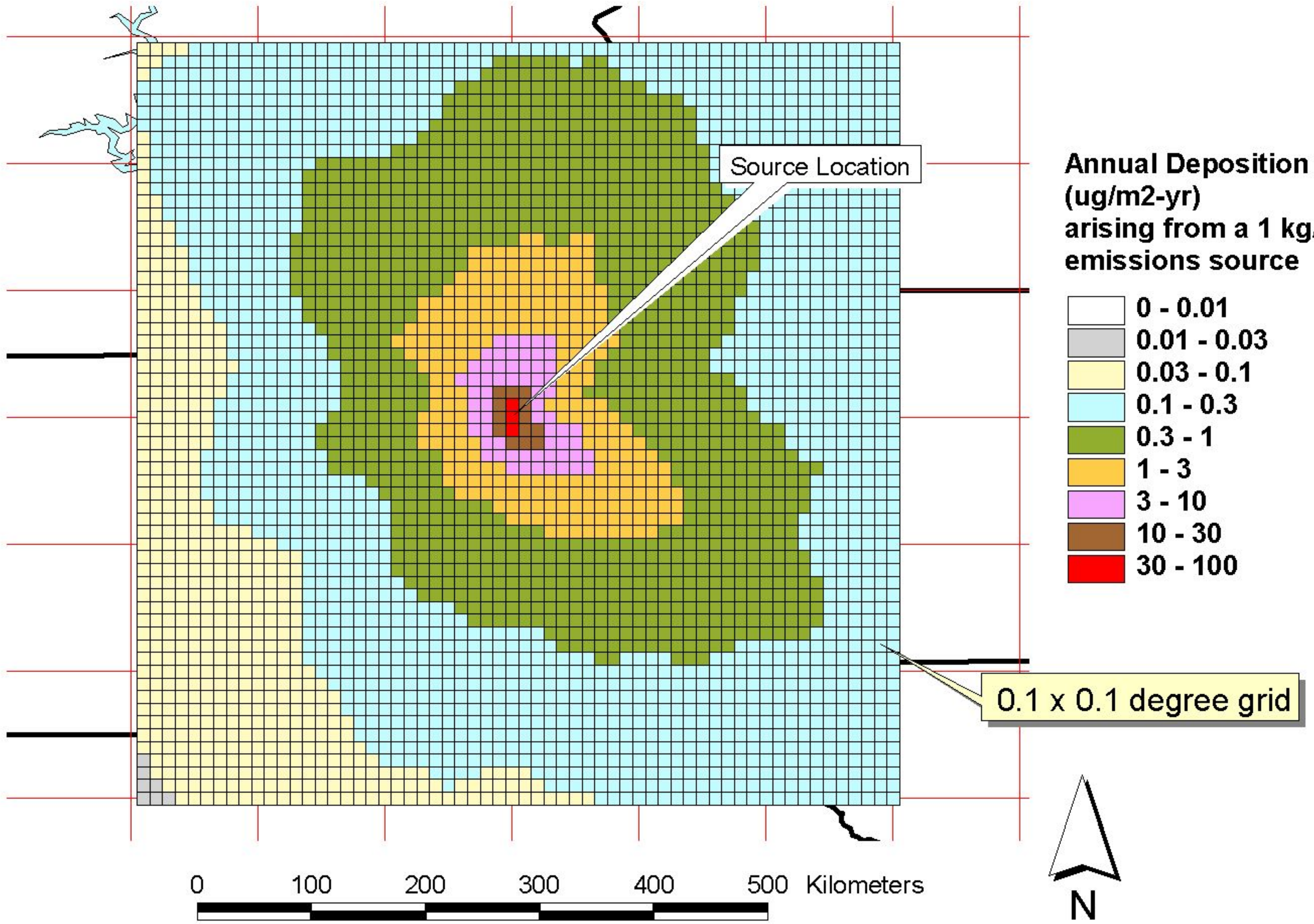
Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

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

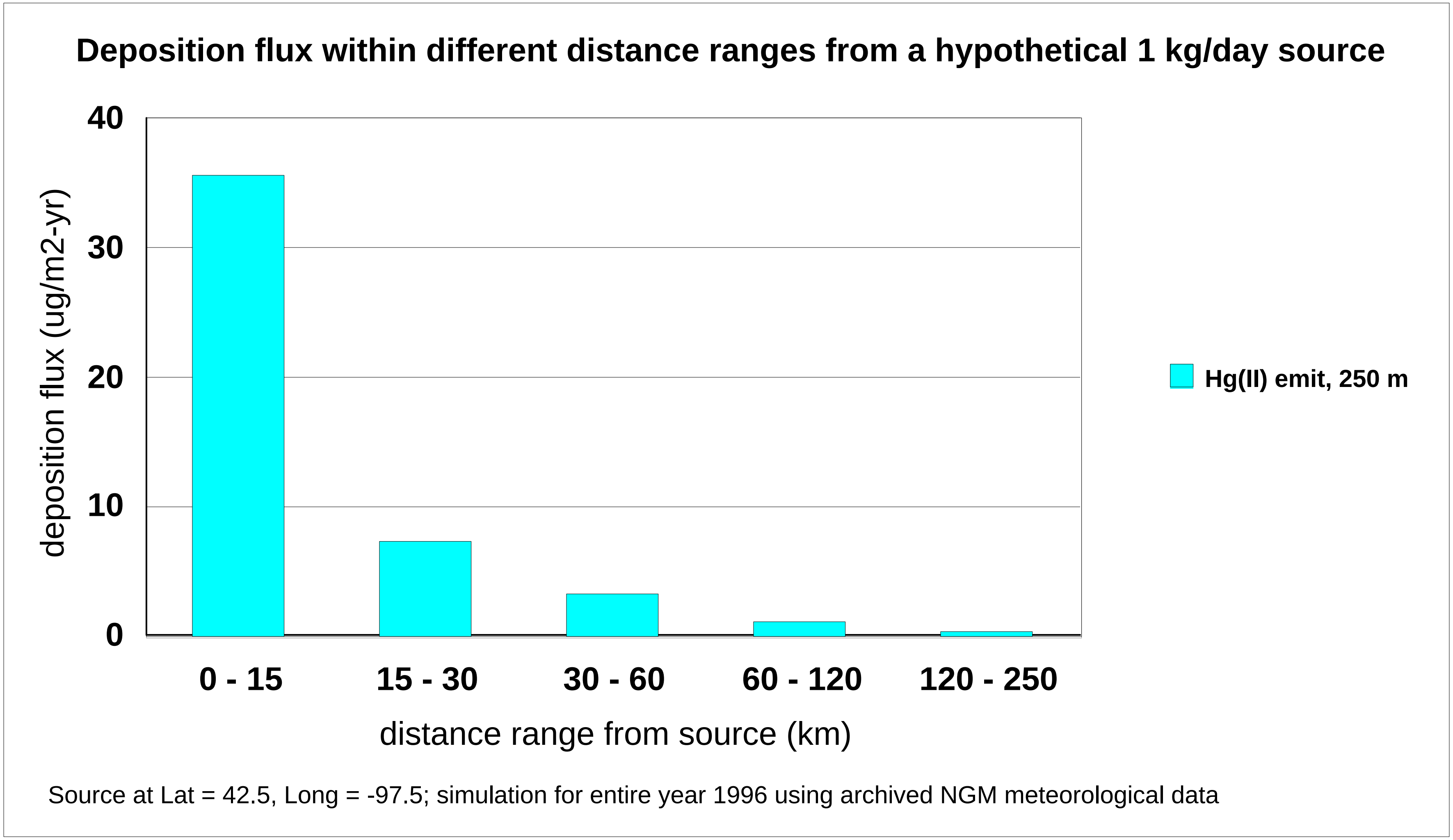


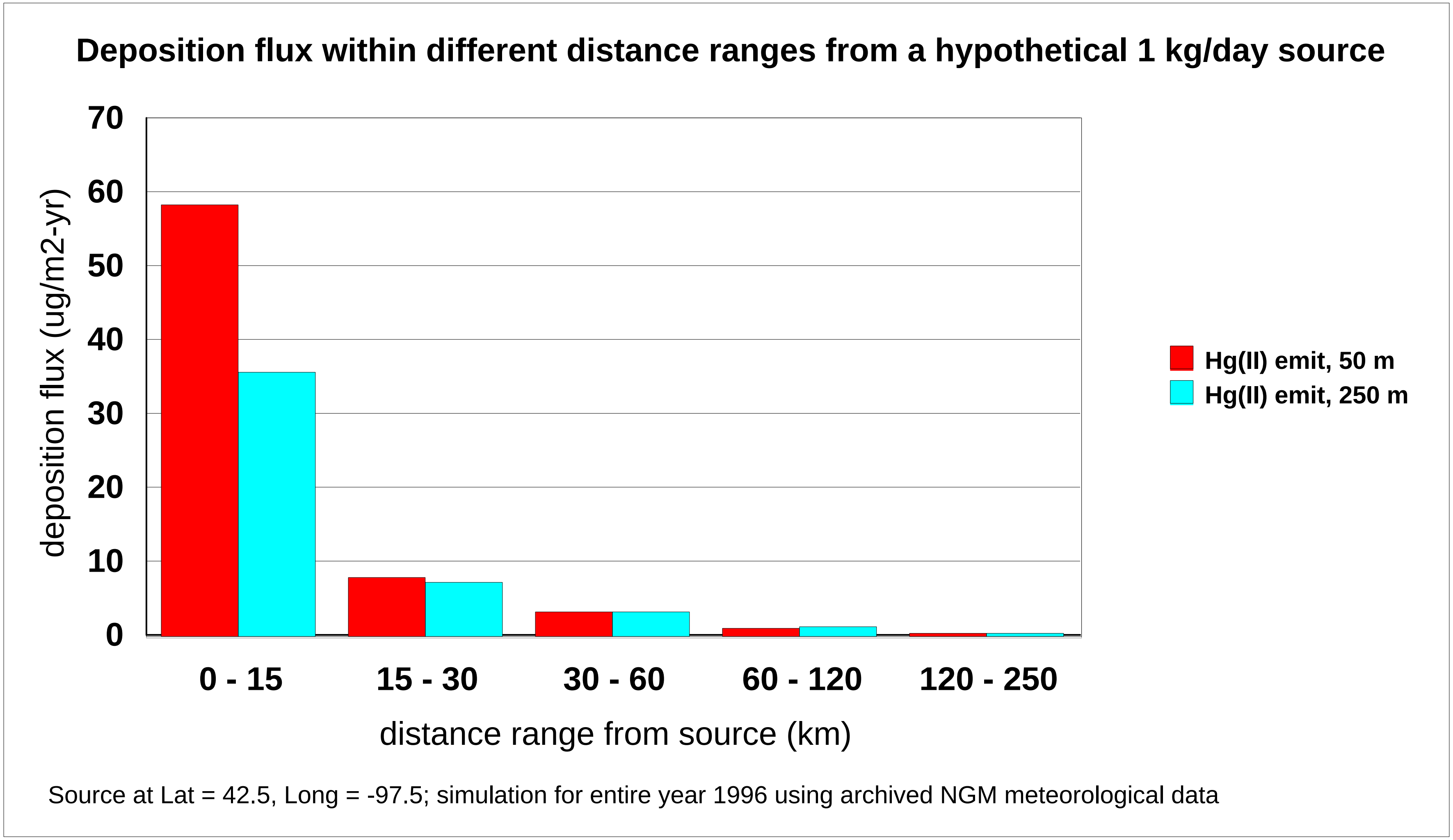
Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

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

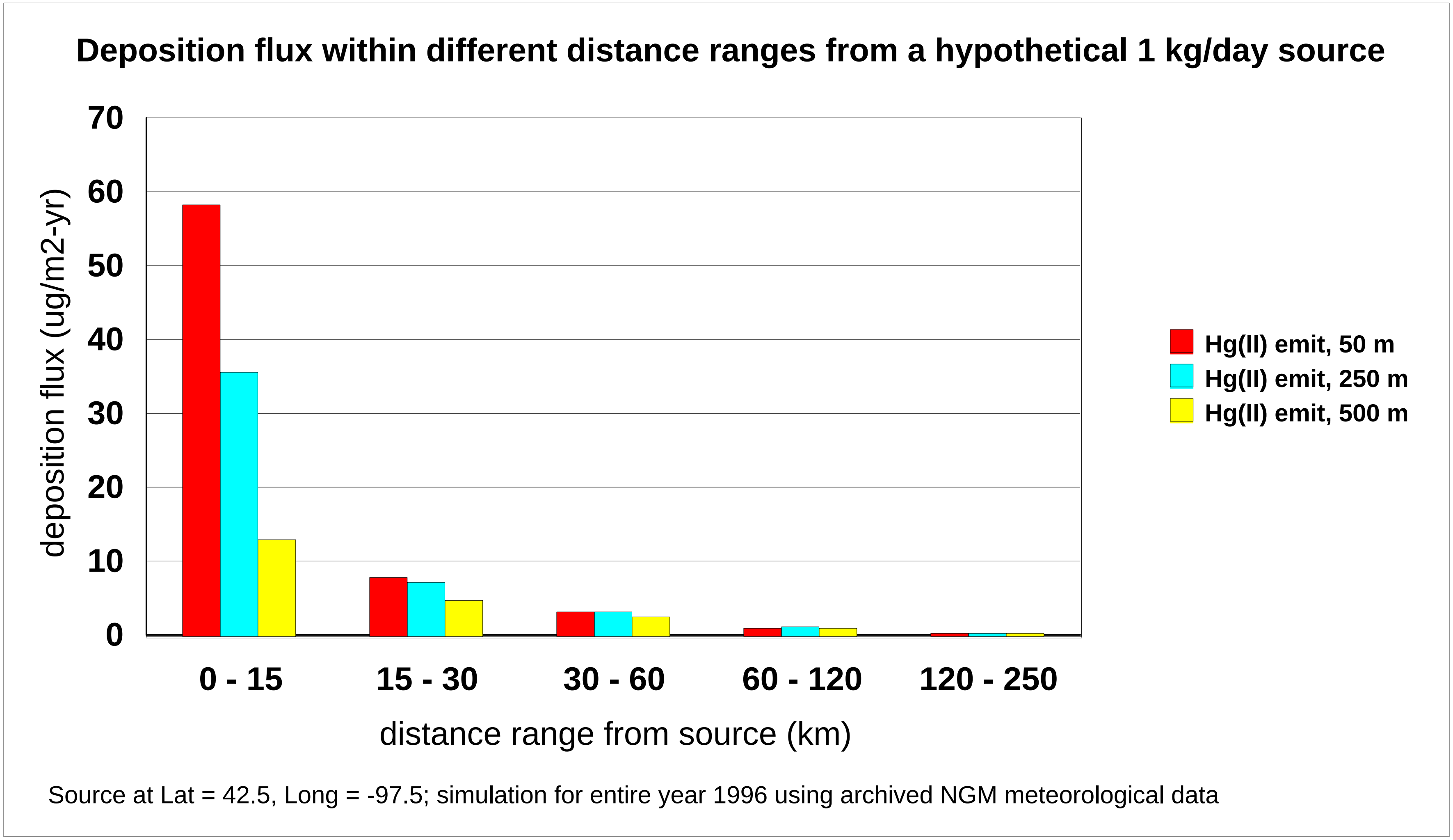


Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

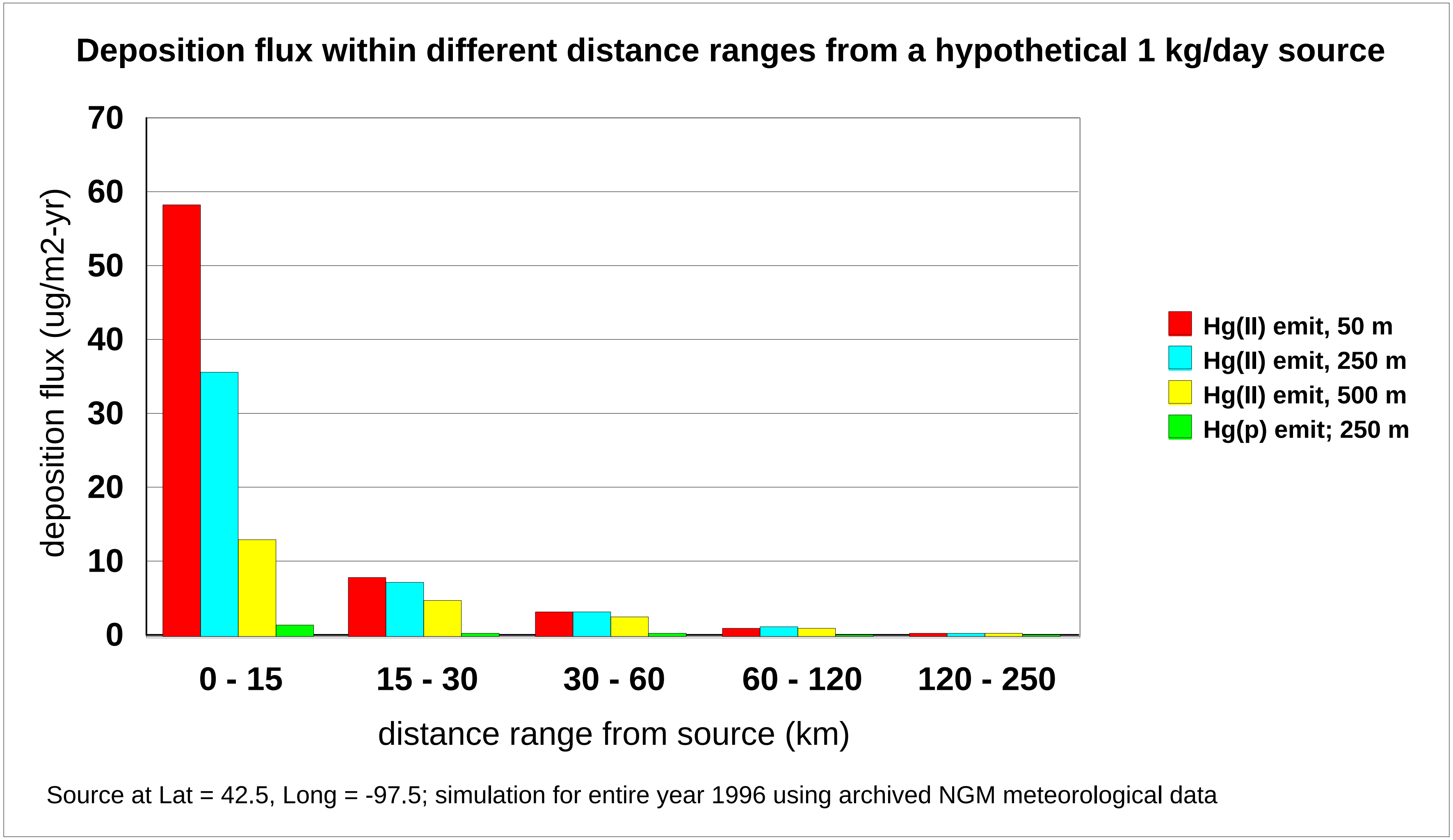

Deposition flux within different distance ranges from a hypothetical 1 kg/day source
40
30
20
10
0
deposition flux (ug/m2-yr)
Hg(II) emit, 250 m
0 - 15
15 - 30
30 - 60
60 - 120
120 - 250
distance range from source (km)
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data



Deposition flux within different distance ranges from a hypothetical 1 kg/day source
deposition flux (ug/m2-yr)
70
60
50
40
30
20
10
0
0 - 15
15 - 30
30 - 60
60 - 120
120 - 250
distance range from source (km)
Hg(II) emit, 50 m
Hg(II) emit, 250 m
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

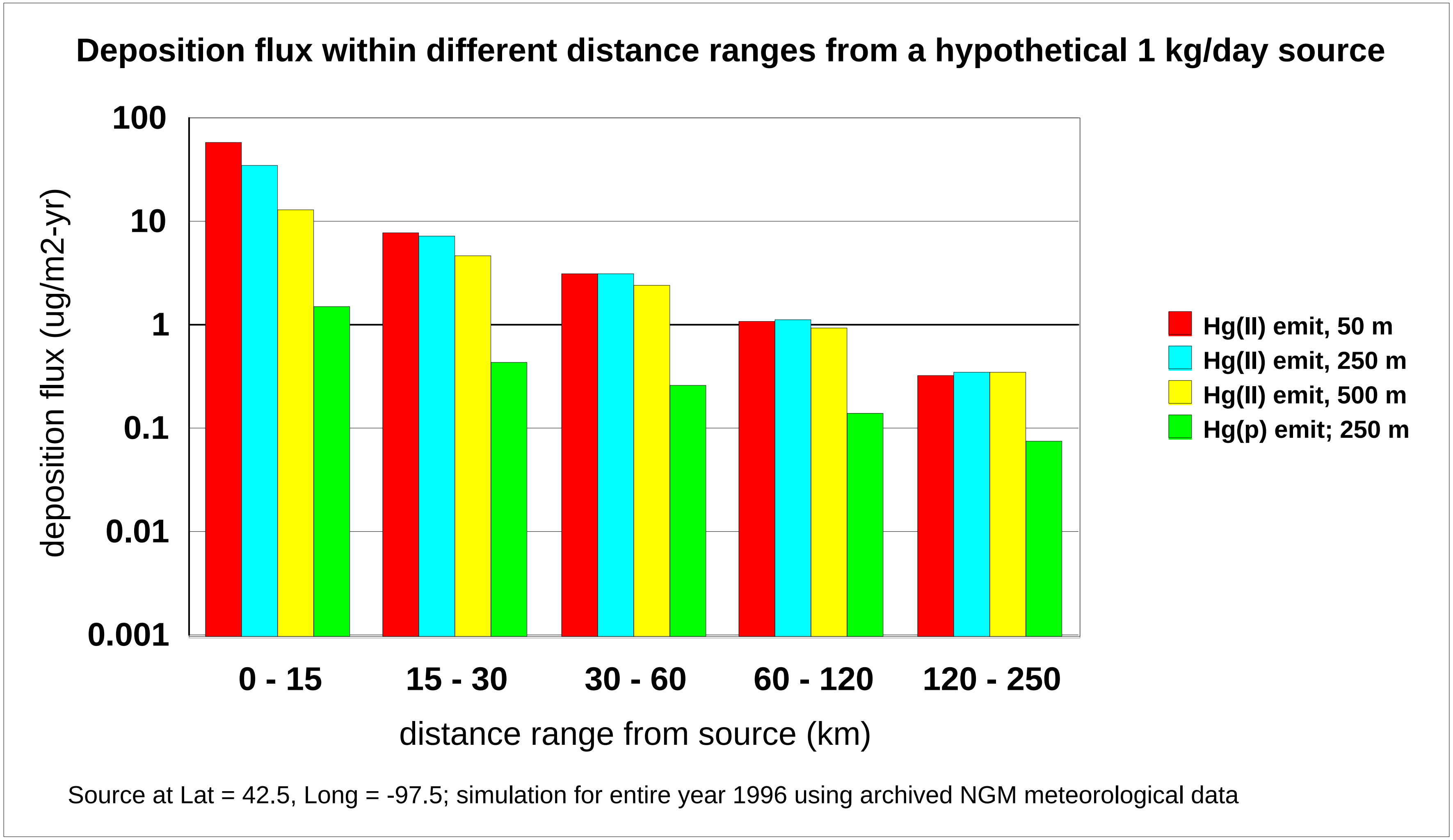


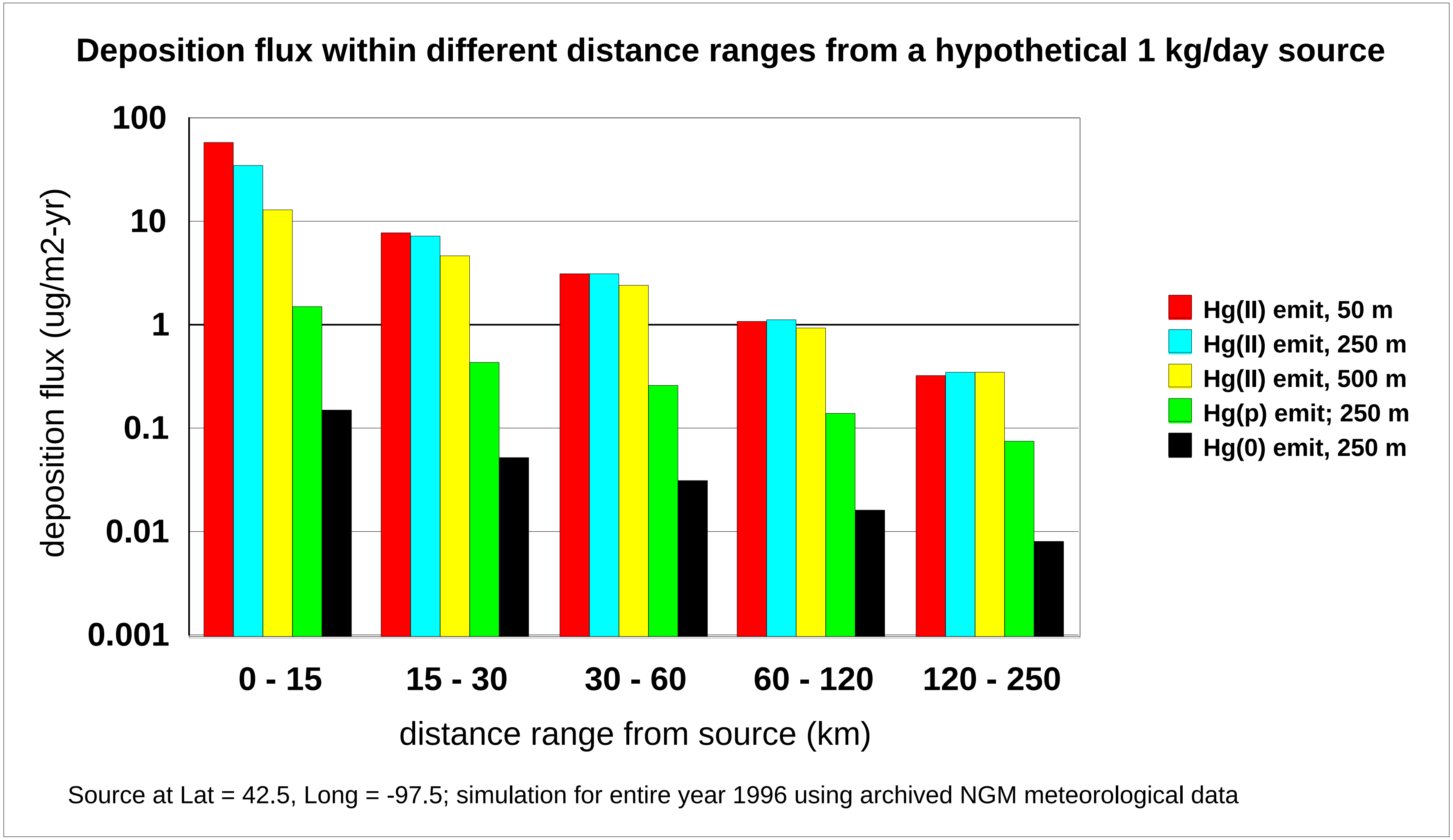
Deposition flux within different distance ranges from a hypothetical 1 kg/day source
deposition flux (ug/m2-yr)
70
60
50
40
30
20
10
0
0 - 15
15 - 30
30 - 60
60 - 120
120 - 250
distance range from source (km)
Hg(II) emit, 50 m
Hg(II) emit, 250 m
Hg(II) emit, 500 m
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data



Deposition flux within different distance ranges from a hypothetical 1 kg/day source
deposition flux (ug/m2-yr)
70
60
50
40
30
20
10
0
0 - 15
15 - 30
30 - 60
60 - 120
120 - 250
distance range from source (km)
Hg(II) emit, 50 m
Hg(II) emit, 250 m
Hg(II) emit, 500 m
Hg(p) emit; 250 m
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

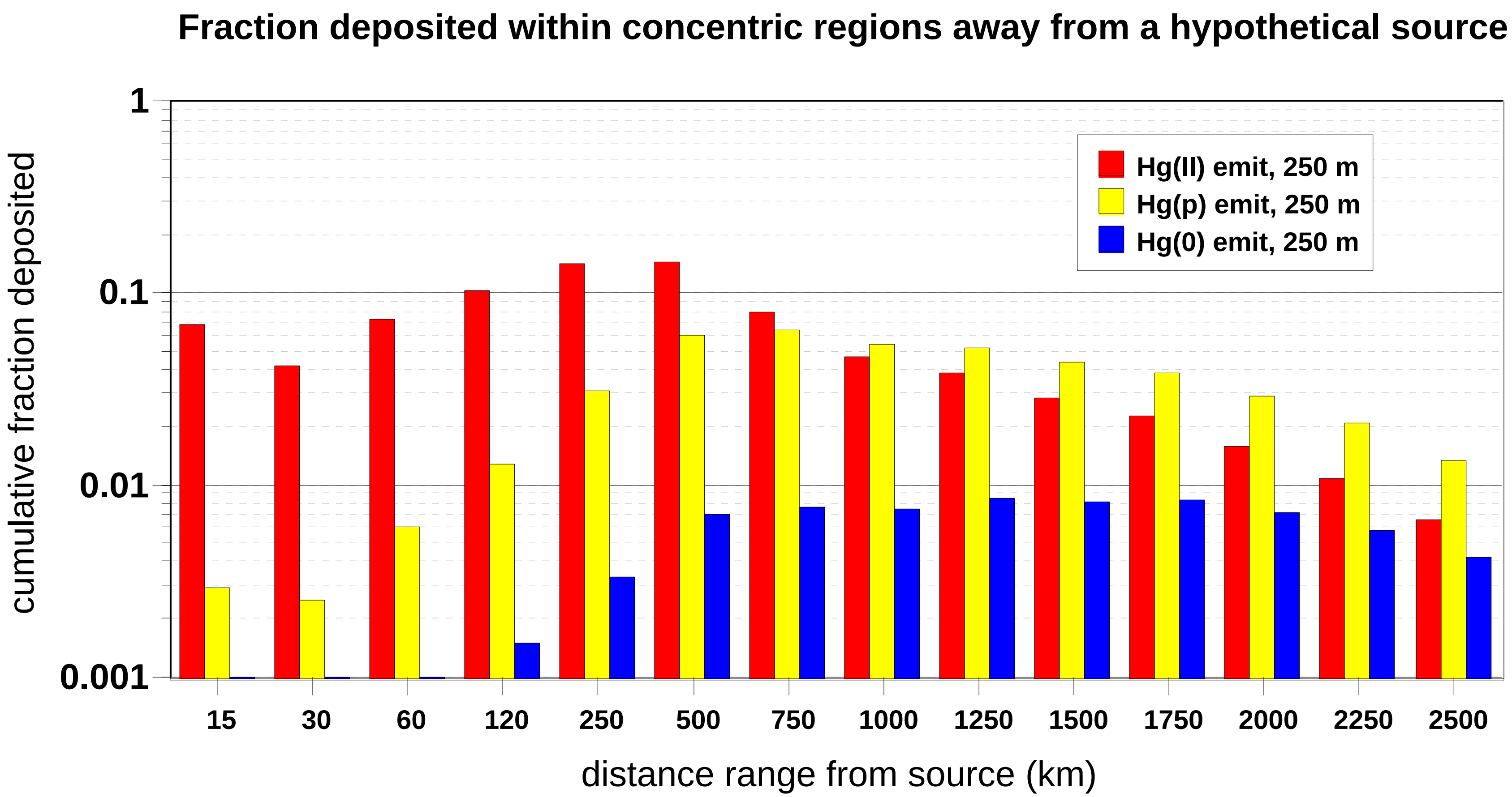
same graph, but with logarithmic scale



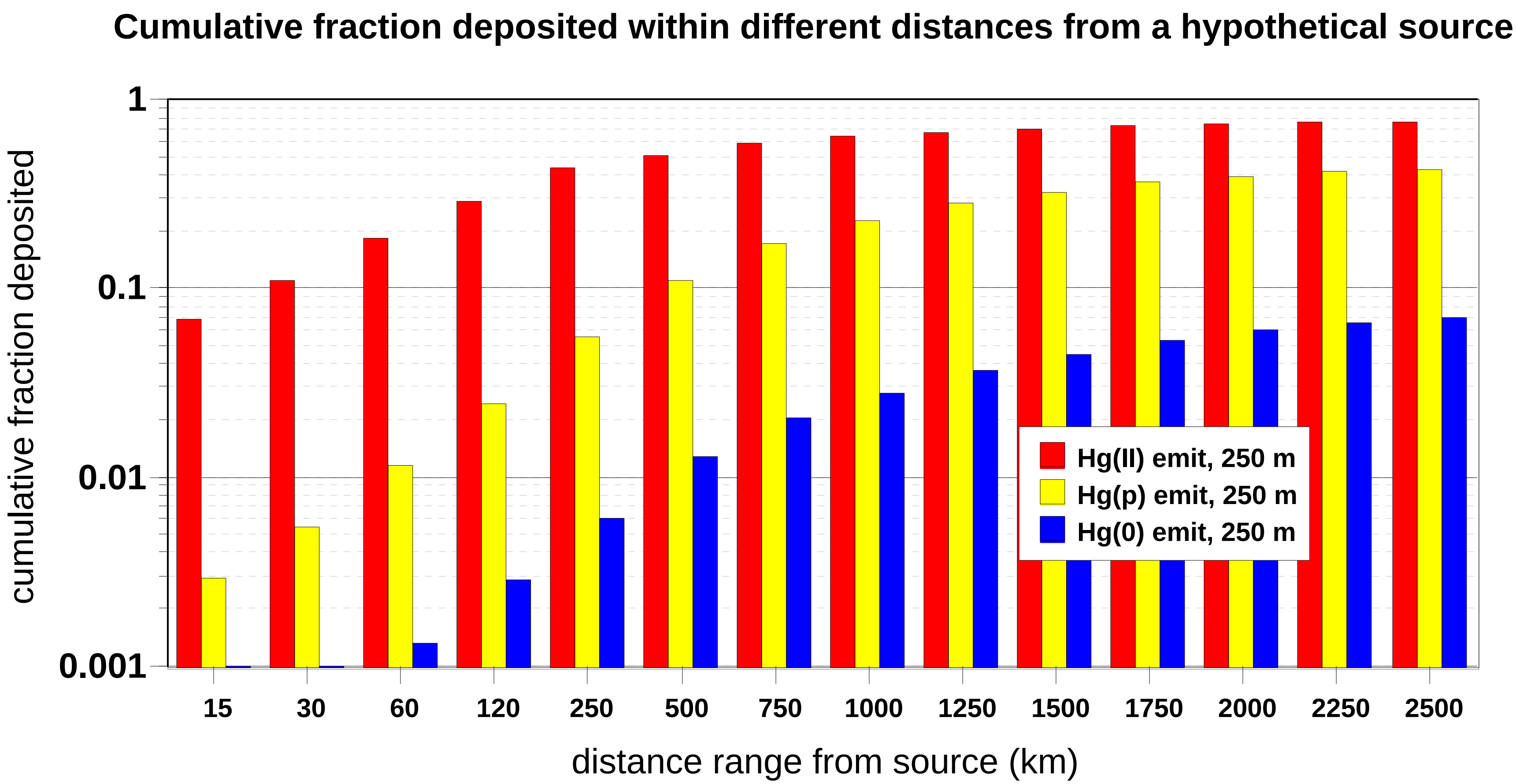


Deposition flux within different distance ranges from a hypothetical 1 kg/day source
deposition flux (ug/m2-yr)
100
10
1
0.1
0.01
0.001
0 - 15
15 - 30
30 - 60
60 - 120
120 - 250
distance range from source (km)
Hg(II) emit, 50 m
Hg(II) emit, 250 m
Hg(II) emit, 500 m
Hg(p) emit; 250 m
Hg(0) emit, 250 m
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

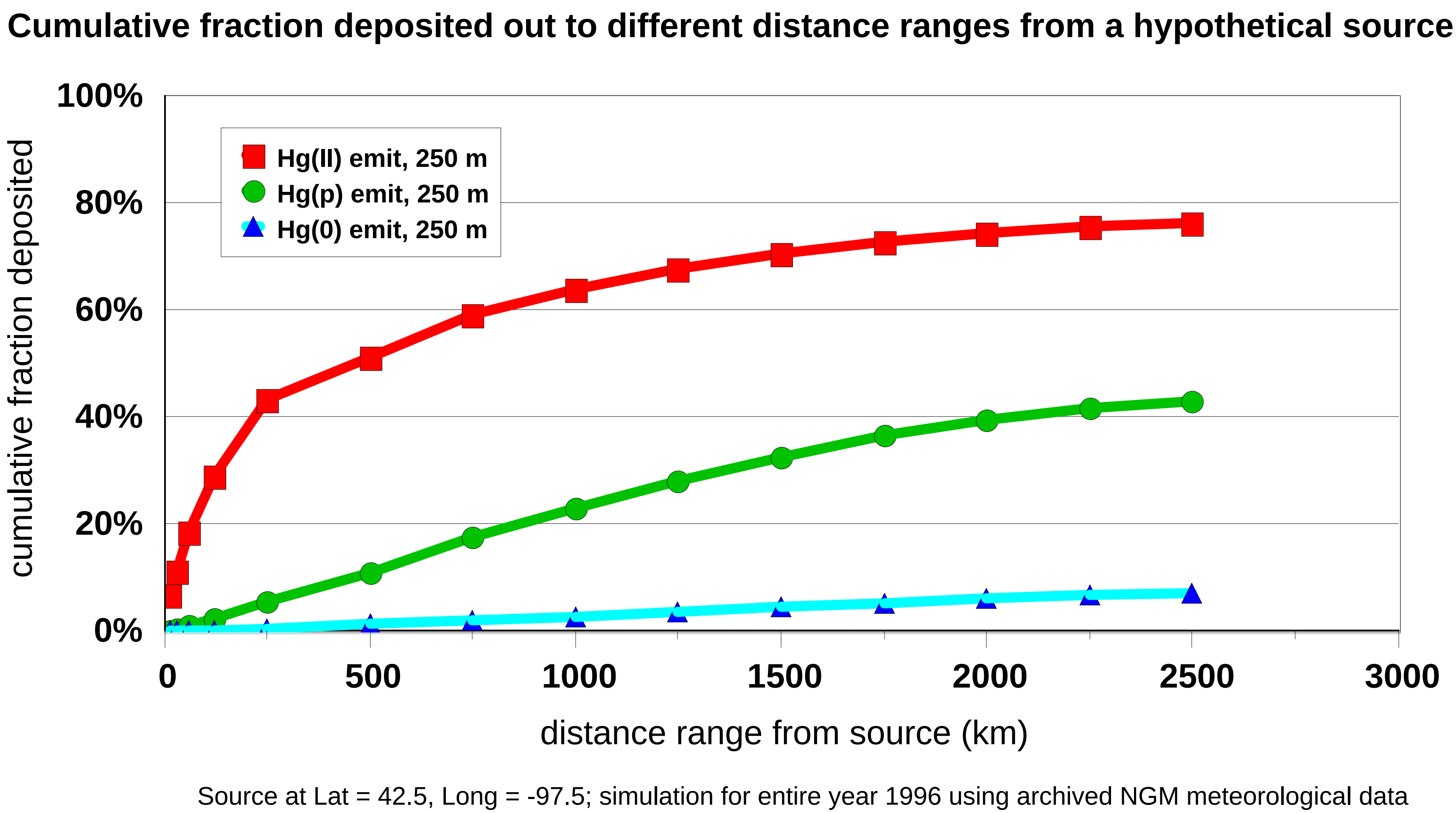
4. At the same time, medium to long range transport can't be ignored



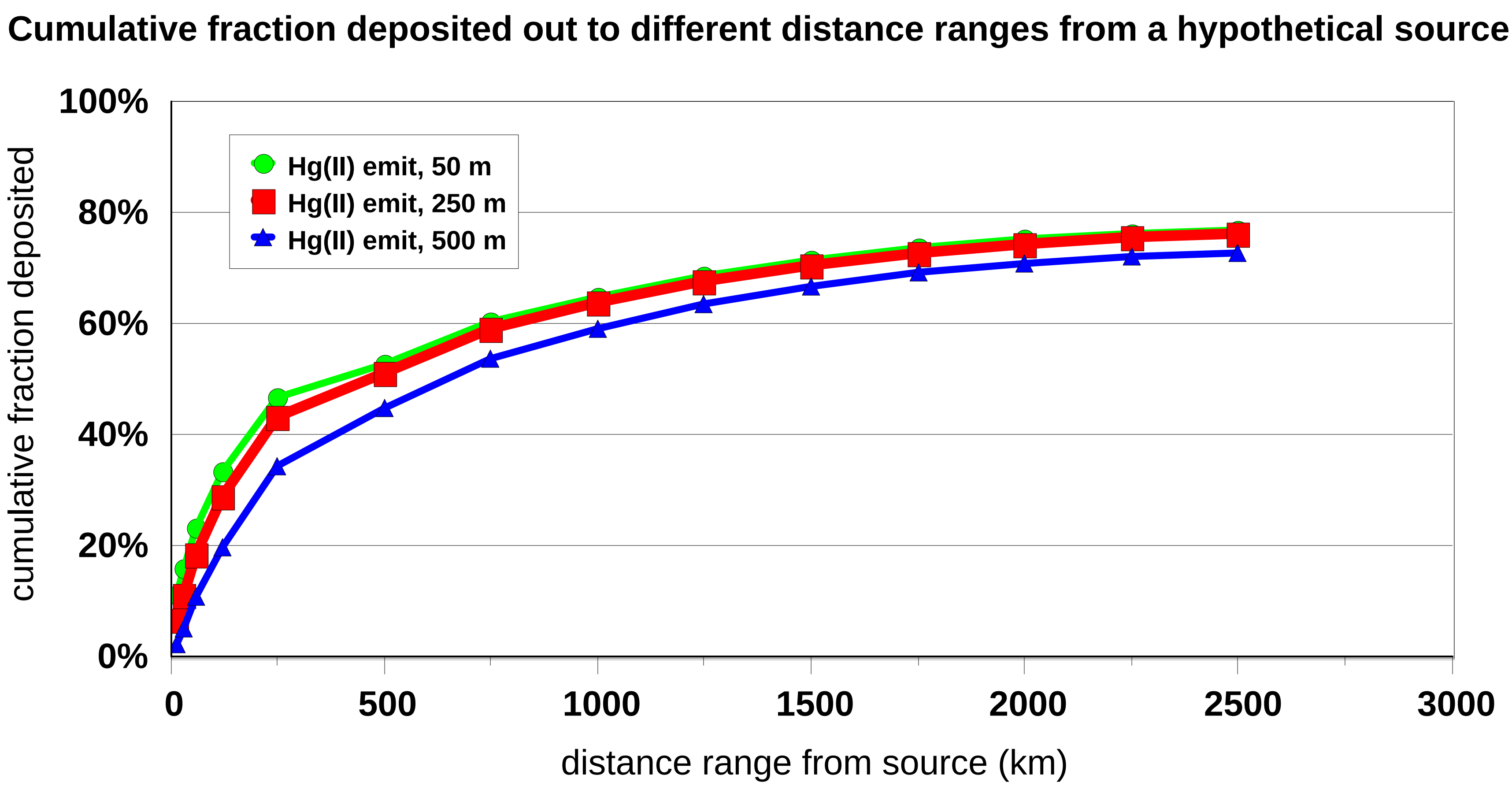
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data



Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

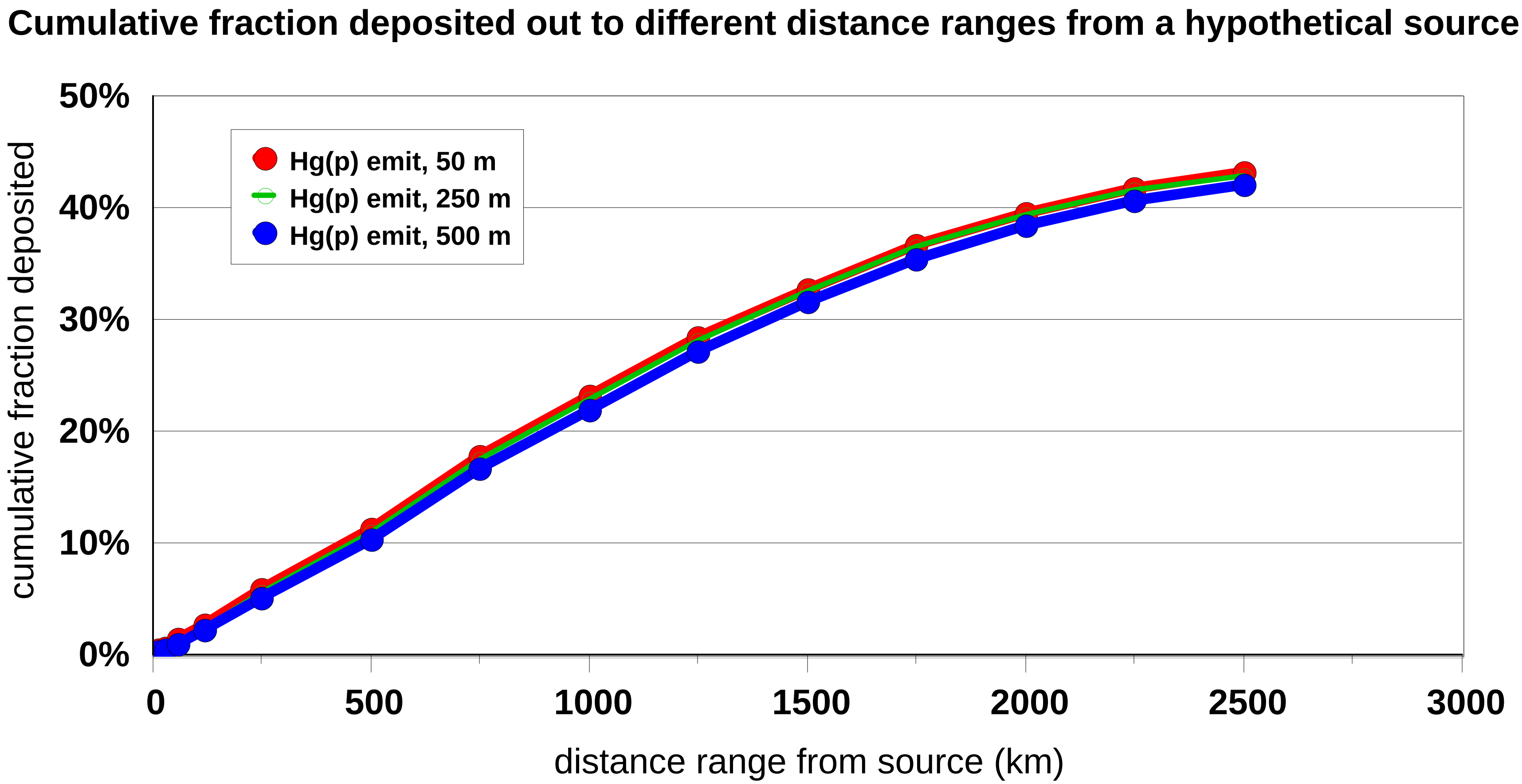

Cumulative fraction deposited out to different distance ranges from a hypothetical source
100%
80%
60%
40%
20%
0%
cumulative fraction deposited
Hg(II) emit, 250 m
Hg(p) emit, 250 m
Hg(0) emit, 250 m
0
500
1000
1500
2000
2500
3000
distance range from source (km)
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

ionic Hg emitted from different source heights



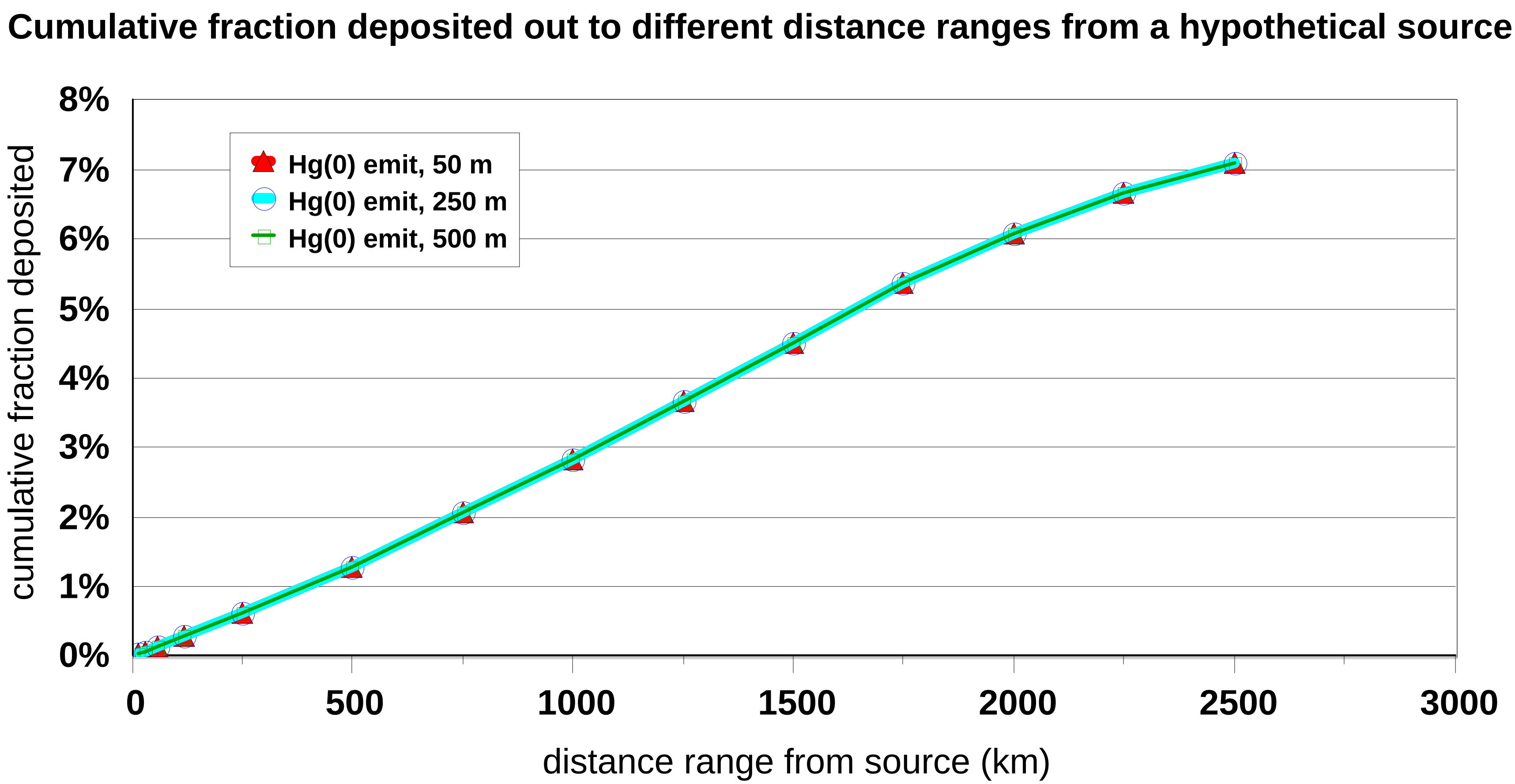
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

Hg(p) emitted from different source heights



Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

Hg(0) emitted from different source heights

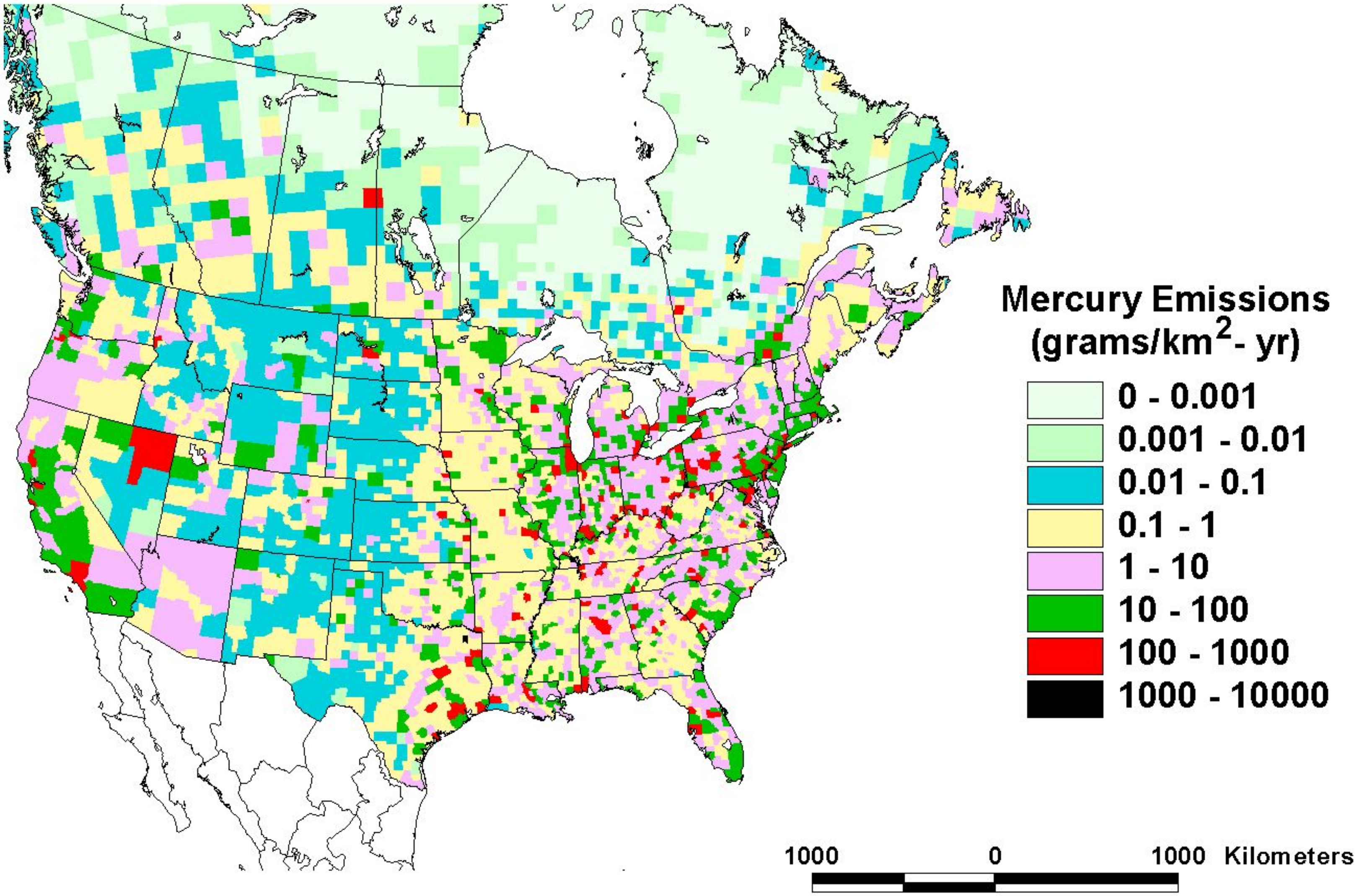


Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

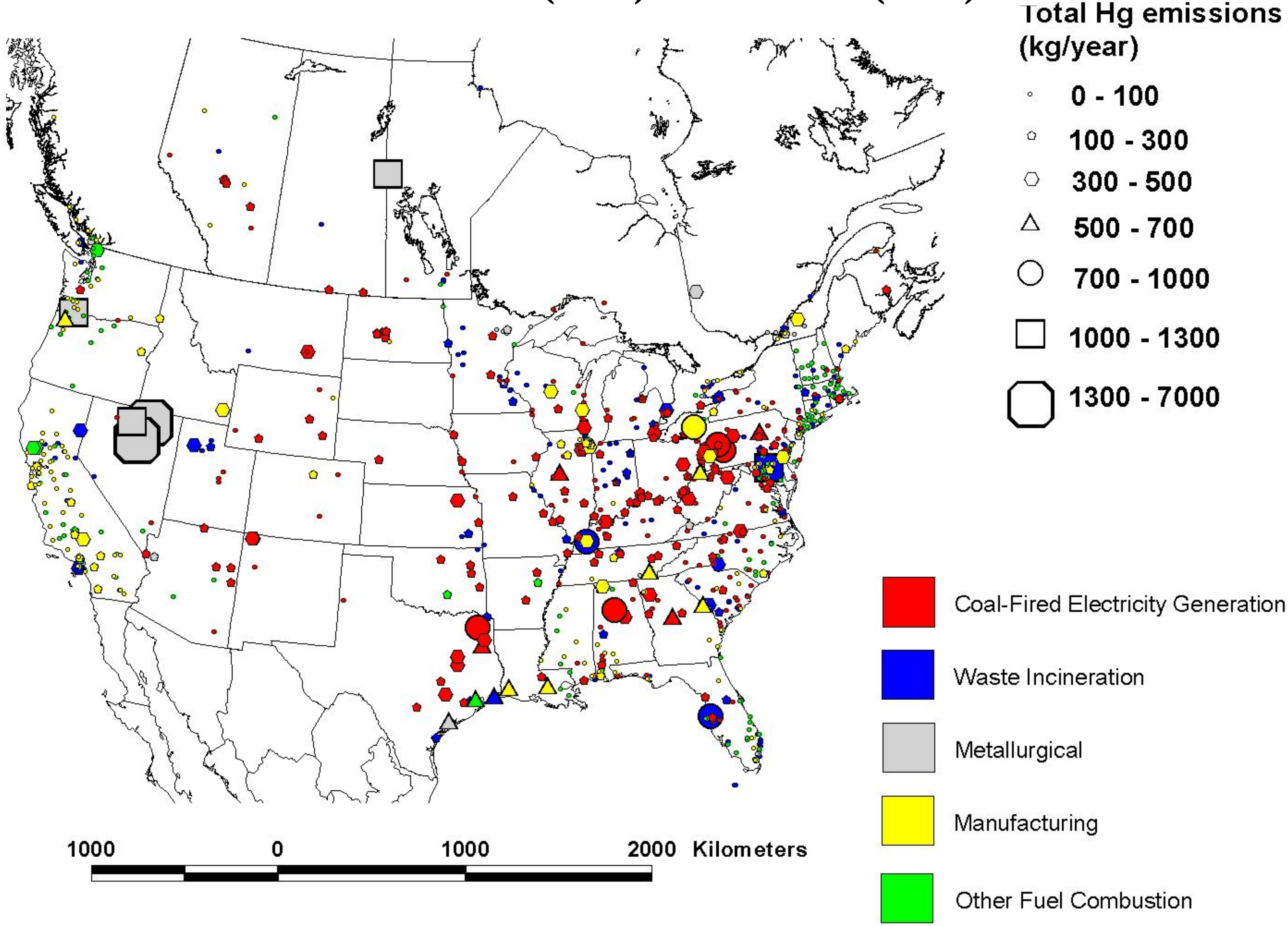
5. There are a lot of sources…

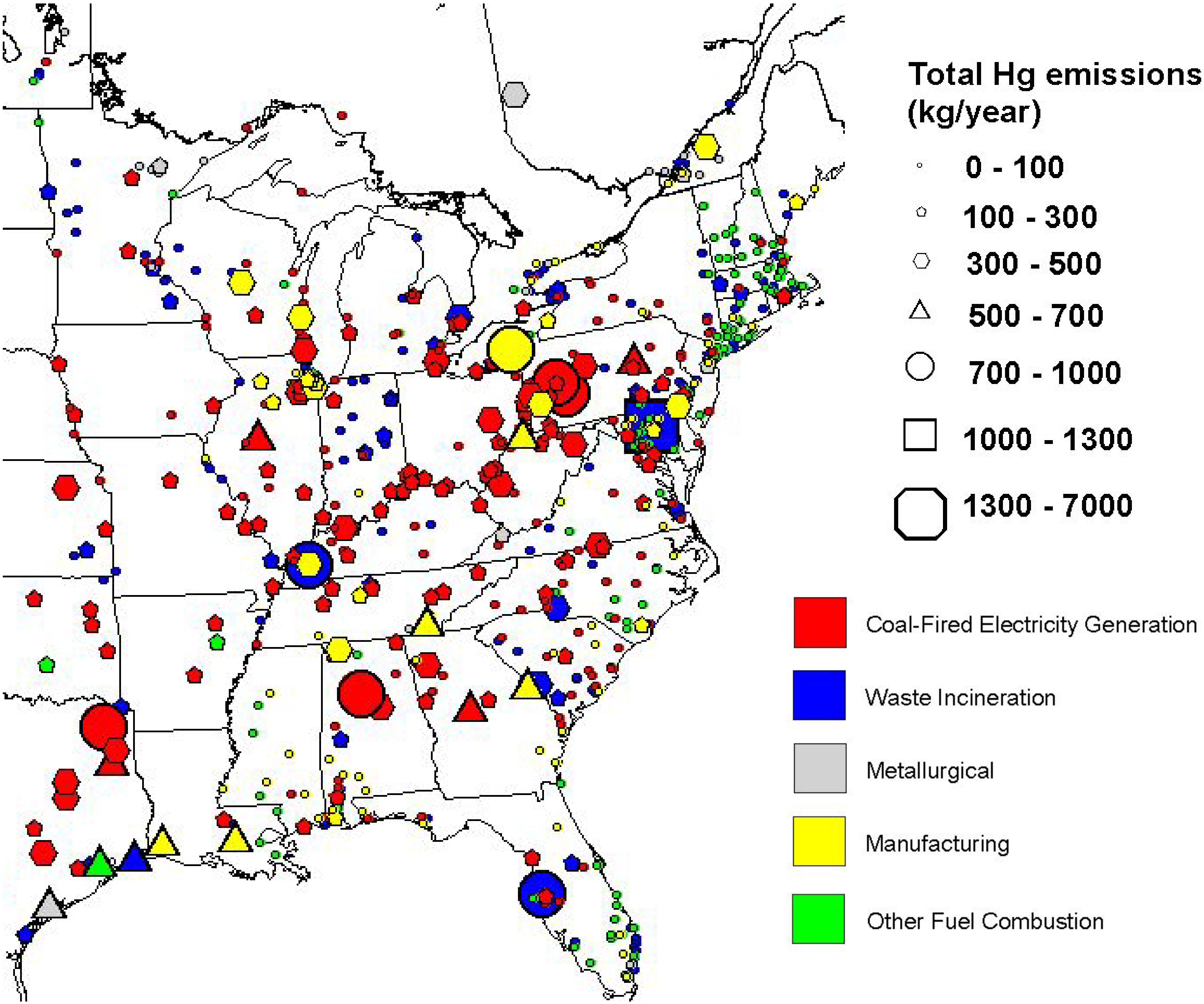
- **Large spatial and temporal variations**
- **Each source emits mercury forms in different proportions**
- **A lot of different sources can contribute significant amounts of mercury through atmospheric deposition to any given receptor**

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



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

6. Getting the source-apportionment information we all need is difficult

- **With measurements alone, generally impossible**
- **Coupling measurements with back-trajectory analyses yields only a little information**
- **Comprehensive fate and transport modeling – “forward” from emissions to deposition – holds the promise of generating detailed source-receptor information**

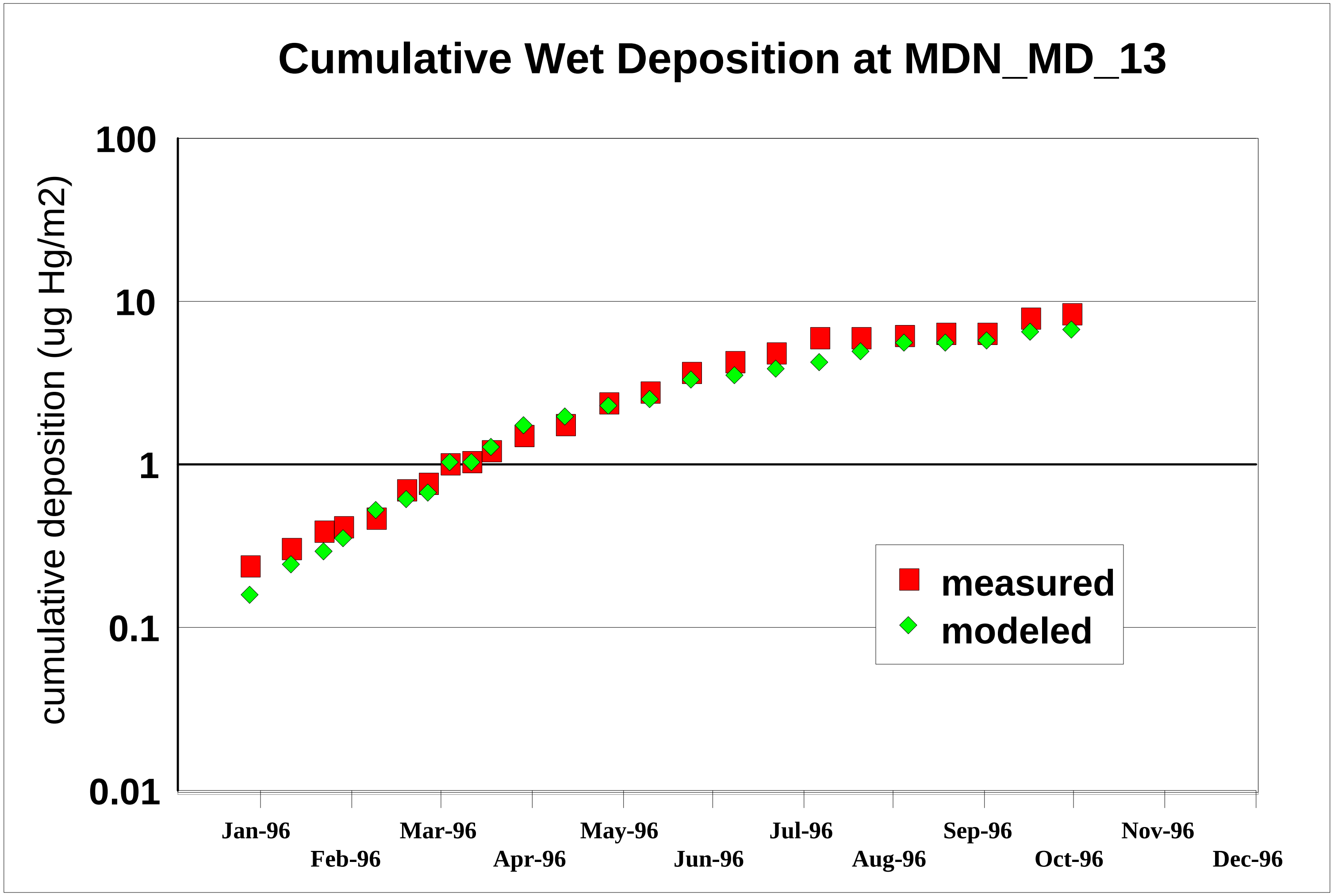
7. There are a lot of uncertainties in current comprehensive fate and transport models

- ❑ **atmospheric chemistry of mercury**
- ❑ **concentrations of key reactants**
- ❑ **meteorological data (e.g., precipitation)**
- ❑ **mercury emissions (amounts & speciation profile)**
- ❑ **data for evaluation are scarce...**

States can play a key role in these

8. Nevertheless, many models seem to be performing reasonably well, i.e., are able to explain a lot of what we see

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



Convention on Long-Range Transboundary Air Pollution

emep

Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe

TECHNICAL REPORT
1/2003 June 2003

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

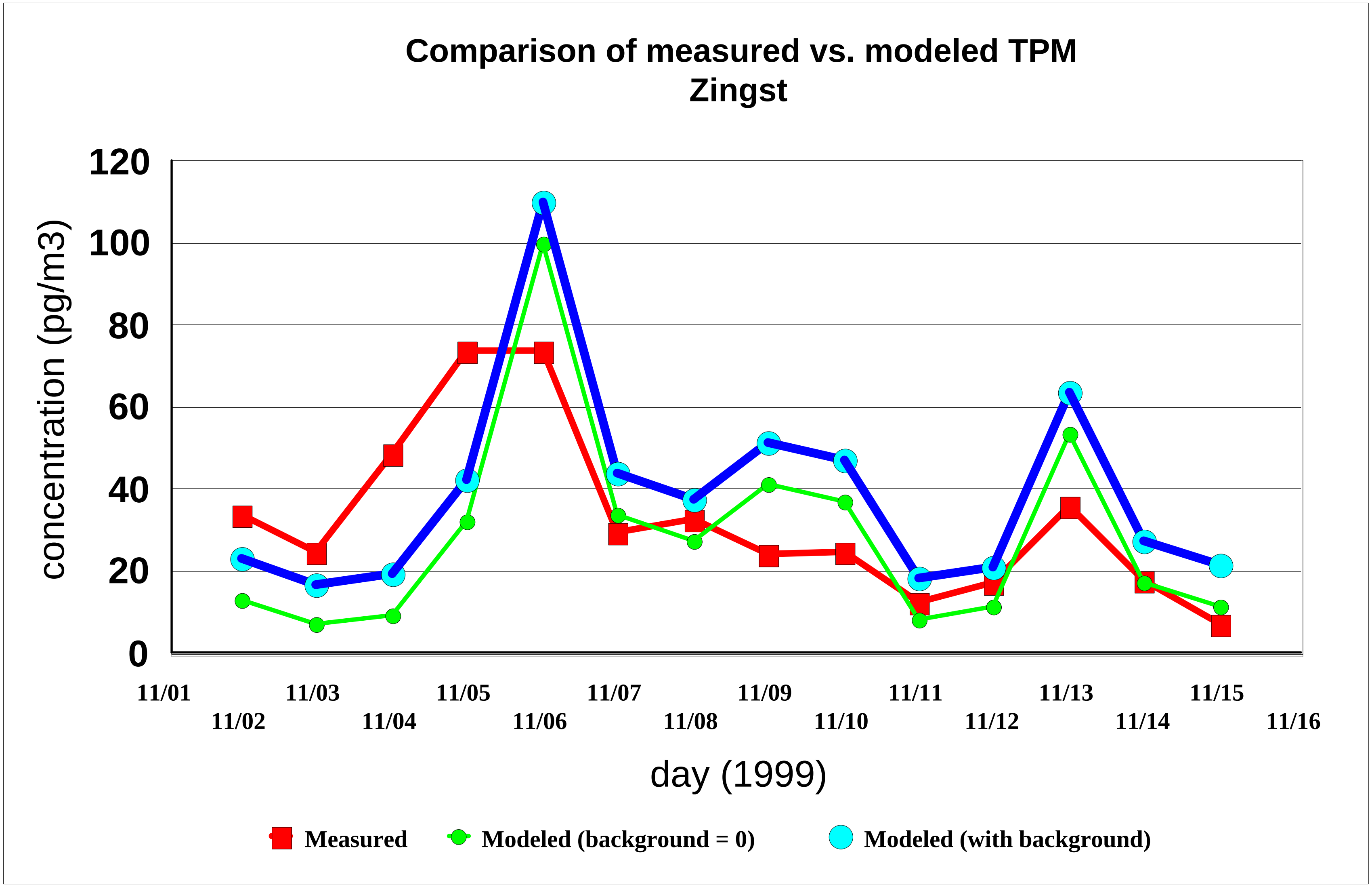
Stage II. Comparison of modeling results with observations obtained during short-term measuring campaigns

Technical Report 1/2003

A. Ryaboshapko, R. Artz,
R. Bullock, J. Christensen,
M. Cohen, A. Dastoor,
D. Davignon, R. Draxler,
R. Ebinghaus, I. Ilyin,
J. Munthe, G. Petersen,
D. Syrakov

msc-e

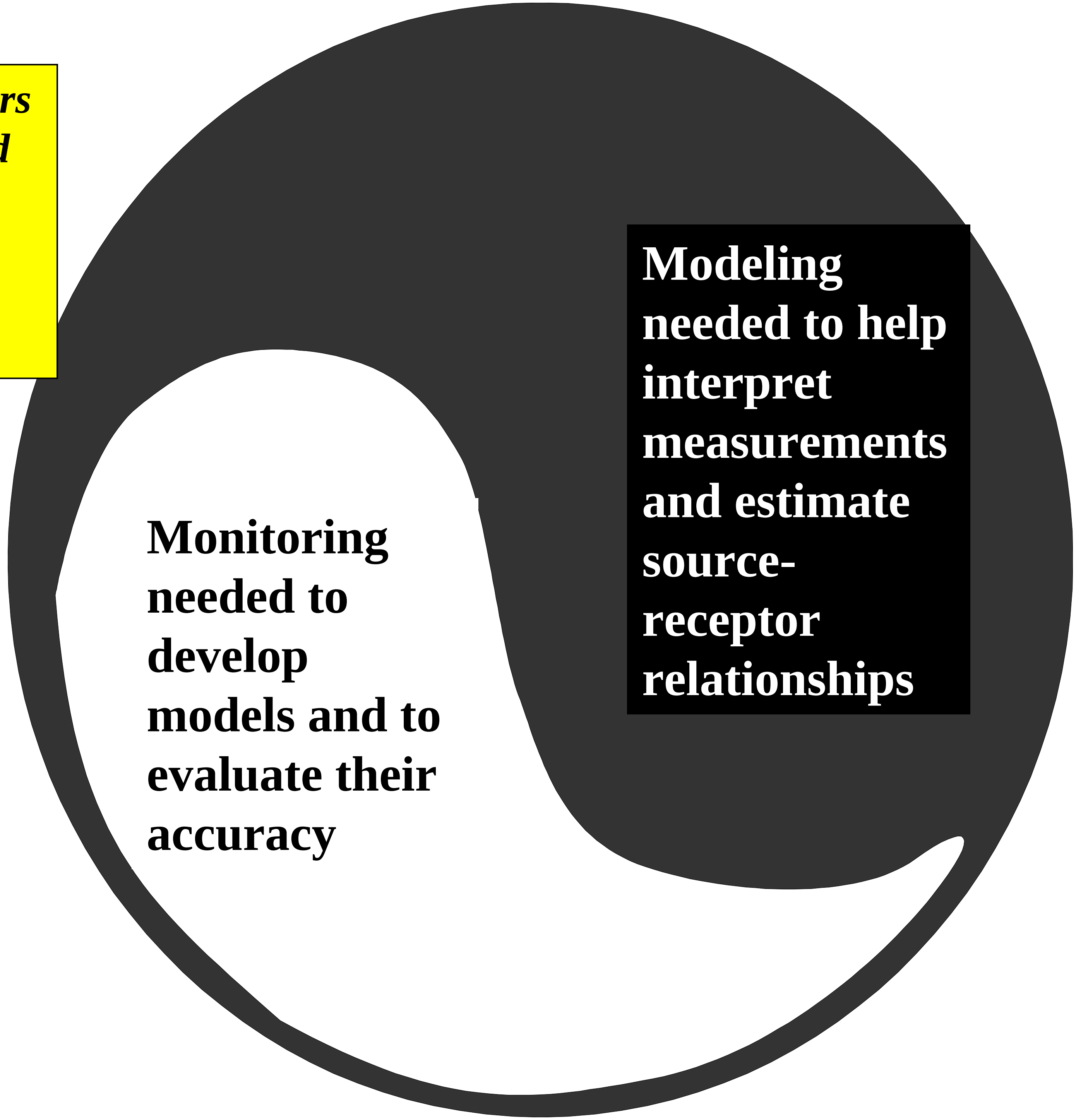
Some HYSPLIT Results from MSC-East Hg Model Intercomparison Study



9. A model does not have to be perfect in order to be useful

- **Often, most decisions just require qualitatively reasonable results**
- **And realistically, most if not all data and information used in decision-making has uncertainties (e.g., public health impacts, economic impacts)**
- **So, we shouldn't demand perfection of models**

10. To get the answers we need, we need to use both monitoring and modeling -- <u>together</u>



11. MDN is GREAT!…but there are some big gaps in atmospheric monitoring – making it very difficult to evaluate and improve models

- **We desperately need national MDN-like network to measure ambient air concentrations of Hg0, Hg(p), and RGM, *with readily available data***
- **What is RGM? What is Hg(p)?**
- **Both "background/regional" *and* near-source measurements needed…**
- **Measurements at different heights in the atmosphere**

Dry Deposition?

- ***Dry deposition is important, and difficult – if not impossible – to measure reliably with current techniques…***
- ***Essentially all dry deposition estimates made currently are made by applying models***
- ***National ambient network of speciated ambient measurements will help to evaluate and improve models of dry deposition***

Source-Apportionment

where does the *mercury* in *mercury deposition* come from?

Source-apportionment answers depend on

- ***where*** **you are, and**
- ***when*** **you are**

(and the effects of deposition will be different in each ecosystem)

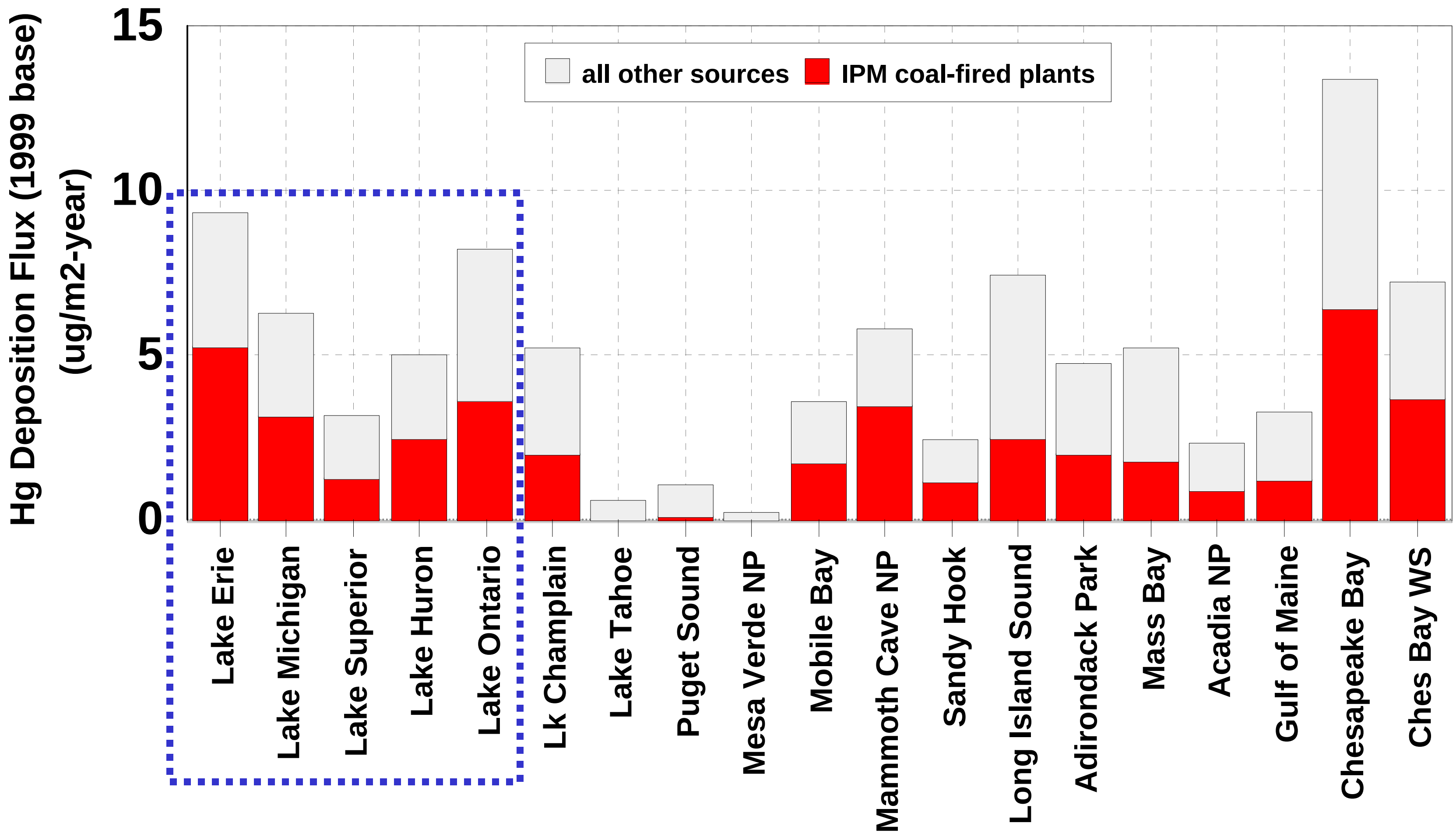
- **For areas *without large emissions sources***

  - **the deposition may be relatively low,**
  - **but what deposition there is may largely come from natural and global sources**

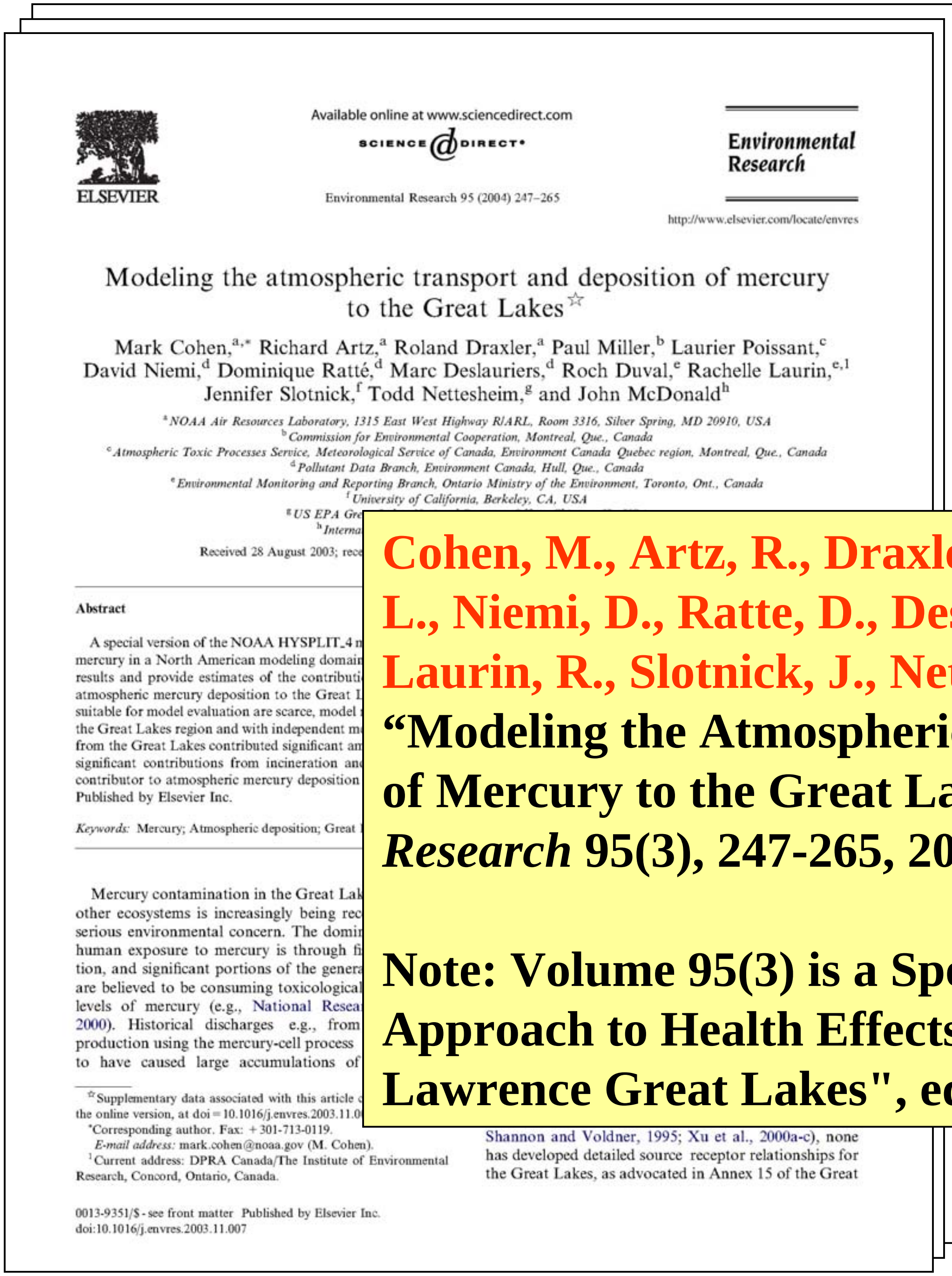
- **For areas *with large emissions sources***

  - **the deposition will be higher**
  - **and be more strongly influenced by these large emissions sources...**

Mercury deposition at selected receptors arising from 1999 base-case emissions from anthropogenic sources in the United States and Canada
(IPM coal fired plants are large coal-fired plants in the U.S. only)



Example of modeling results: Chesapeake Bay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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☆

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

[a] NOAA Air Resources Laboratory, 1315 East West Highway R/ARL, Room 3316, Silver Spring, MD 20910, USA
[b] Commission for Environmental Cooperation, Montreal, Que., Canada
[c] Atmospheric Toxic Processes Service, Meteorological Service of Canada, Environment Canada Quebec region, Montreal, Que., Canada
[d] Pollutant Data Branch, Environment Canada, Hull, Que., Canada
[e] Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, Ont., Canada
[f] University of California, Berkeley, CA, USA
[g] US EPA Gre
[h] Interna

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Abstract

A special version of the NOAA HYSPLIT_4 m
mercury in a North American modeling domai
results and provide estimates of the contributi
atmospheric mercury deposition to the Great L
suitable for model evaluation are scarce, model
the Great Lakes region and with independent m
from the Great Lakes contributed significant am
significant contributions from incineration and
contributor to atmospheric mercury deposition
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Keywords: Mercury; Atmospheric deposition; Great

Mercury contamination in the Great Lak
other ecosystems is increasingly being rec
serious environmental concern. The domi
human exposure to mercury is through fi
tion, and significant portions of the genera
are believed to be consuming toxicological
levels of mercury (e.g., National Resea
2000). Historical discharges e.g., from
production using the mercury-cell process
to have caused large accumulations of

Shannon and Voldner, 1995; Xu et al., 2000a-c), none
has developed detailed source receptor relationships for
the Great Lakes, as advocated in Annex 15 of the Great

☆Supplementary data associated with this article c
the online version, at doi=10.1016/j.envres.2003.11.0
*Corresponding author. Fax: +301-713-0119.
E-mail address: mark.cohen@noaa.gov (M. Cohen).
[1] Current address: DPRA Canada/The Institute of Environmental Research, Concord, Ontario, Canada.

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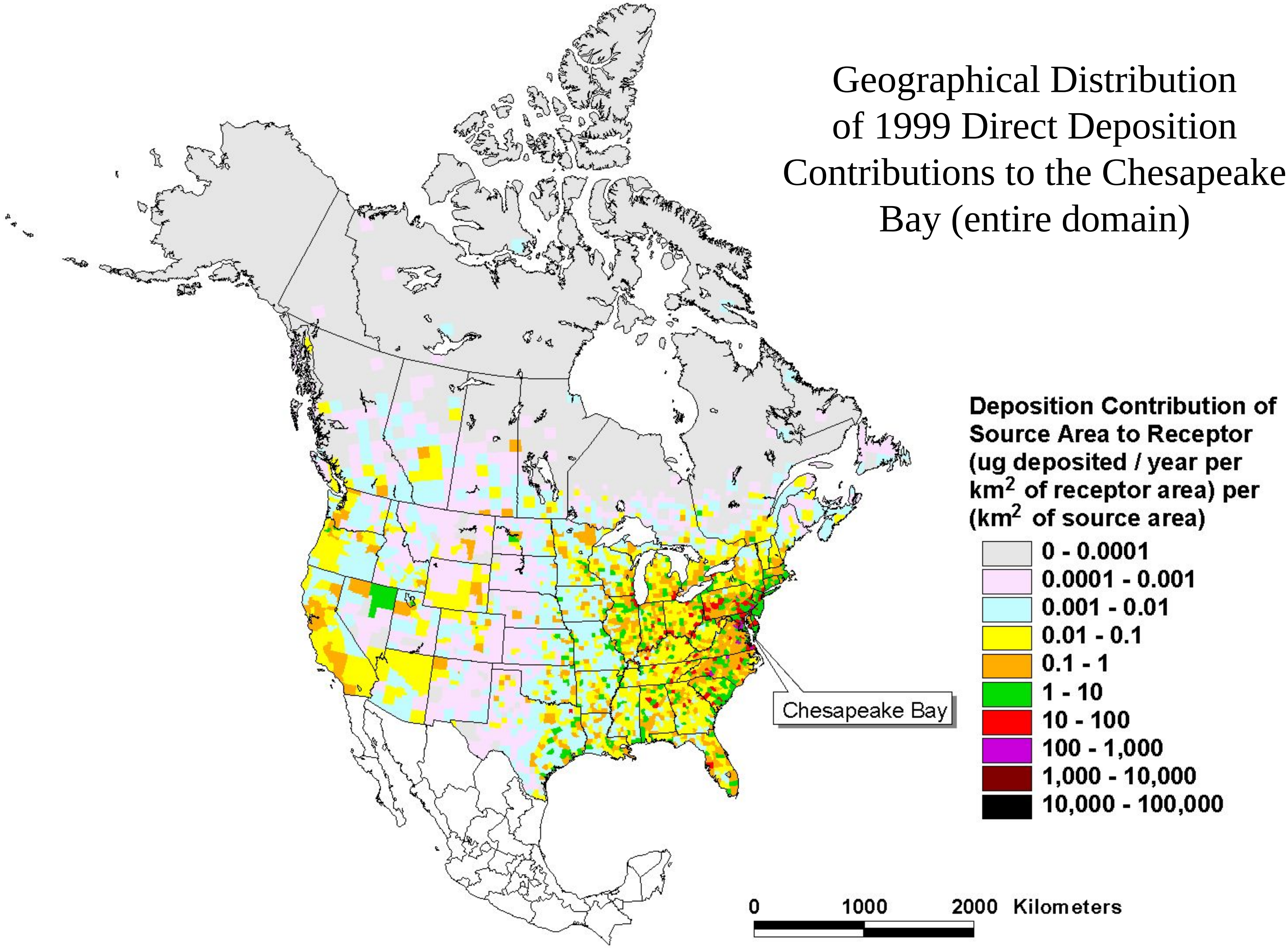
Note: Volume 95(3) is a Special Issue: "An Ecosystem Approach to Health Effects of Mercury in the St. Lawrence Great Lakes", edited by David O. Carpenter.

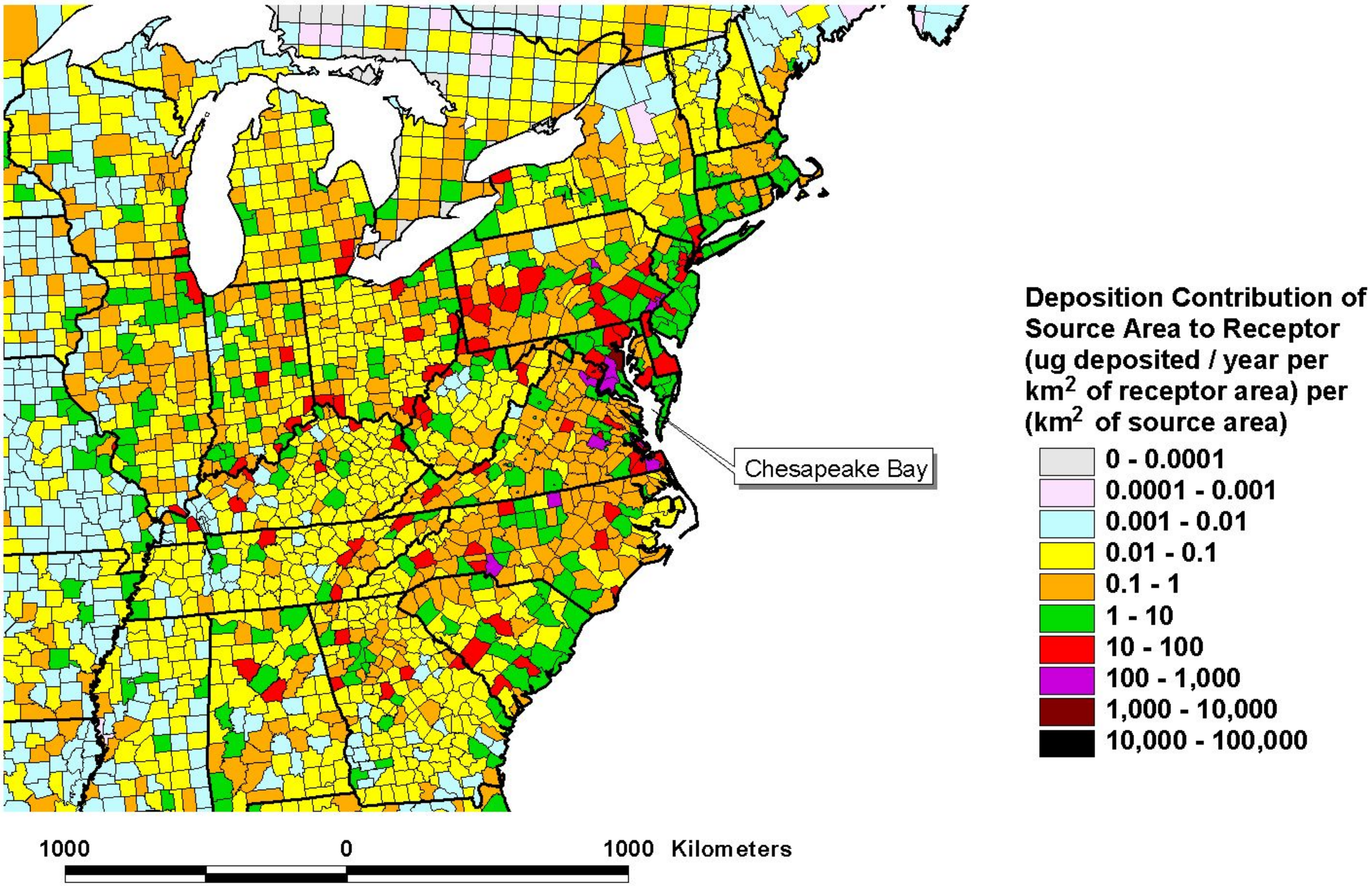
Modeling Methodology

- **Modeling domain: North America**
- **U.S. and Canadian <u>anthropogenic</u> sources**
- **Natural emissions, Re-emissions, & Global sources not included**
- **1996 meterology (180 km horizontal resolution)**
- **Model evaluation: 1996 emissions and 1996 monitoring data**
- **Results: using 1999 emissions**

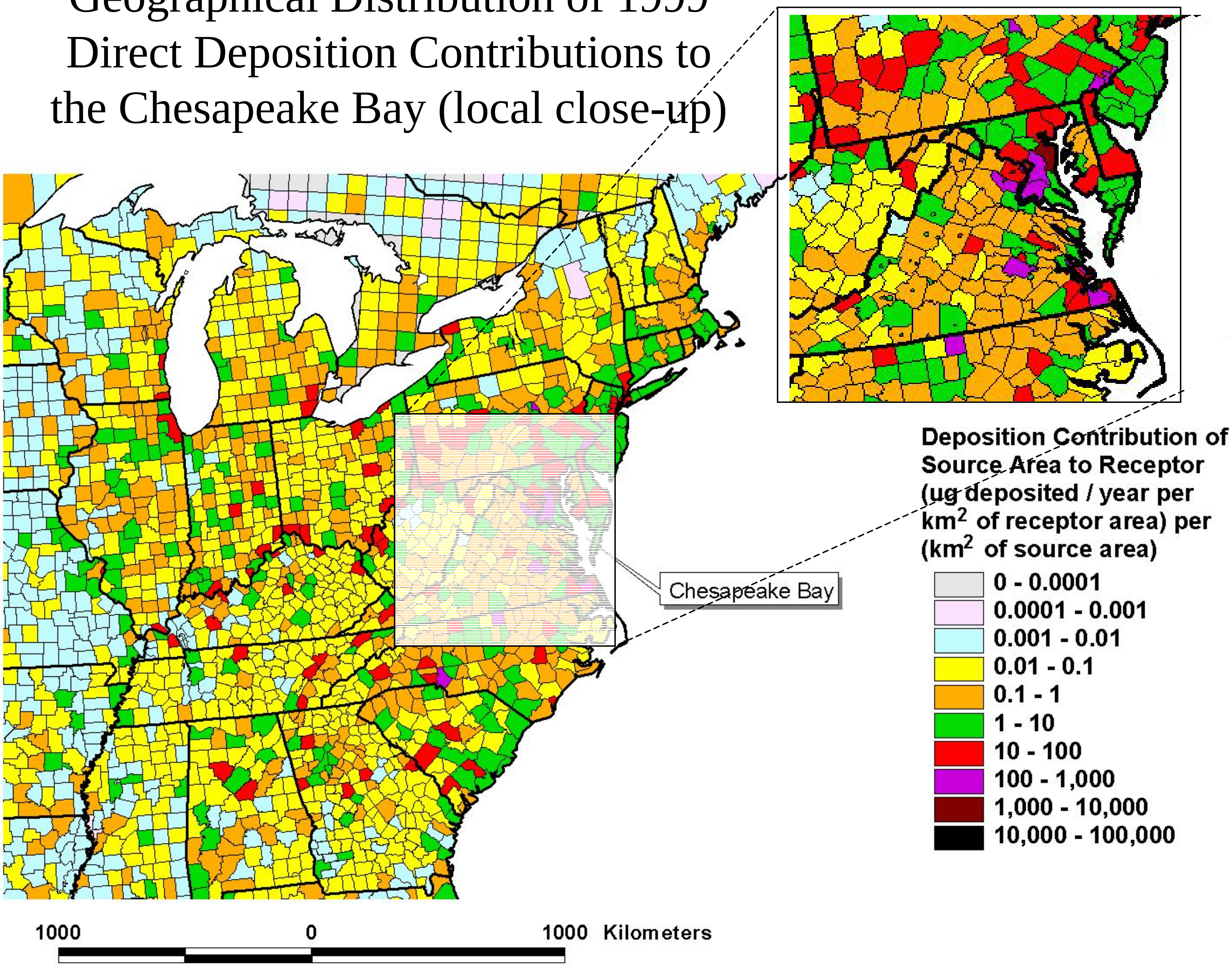
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)



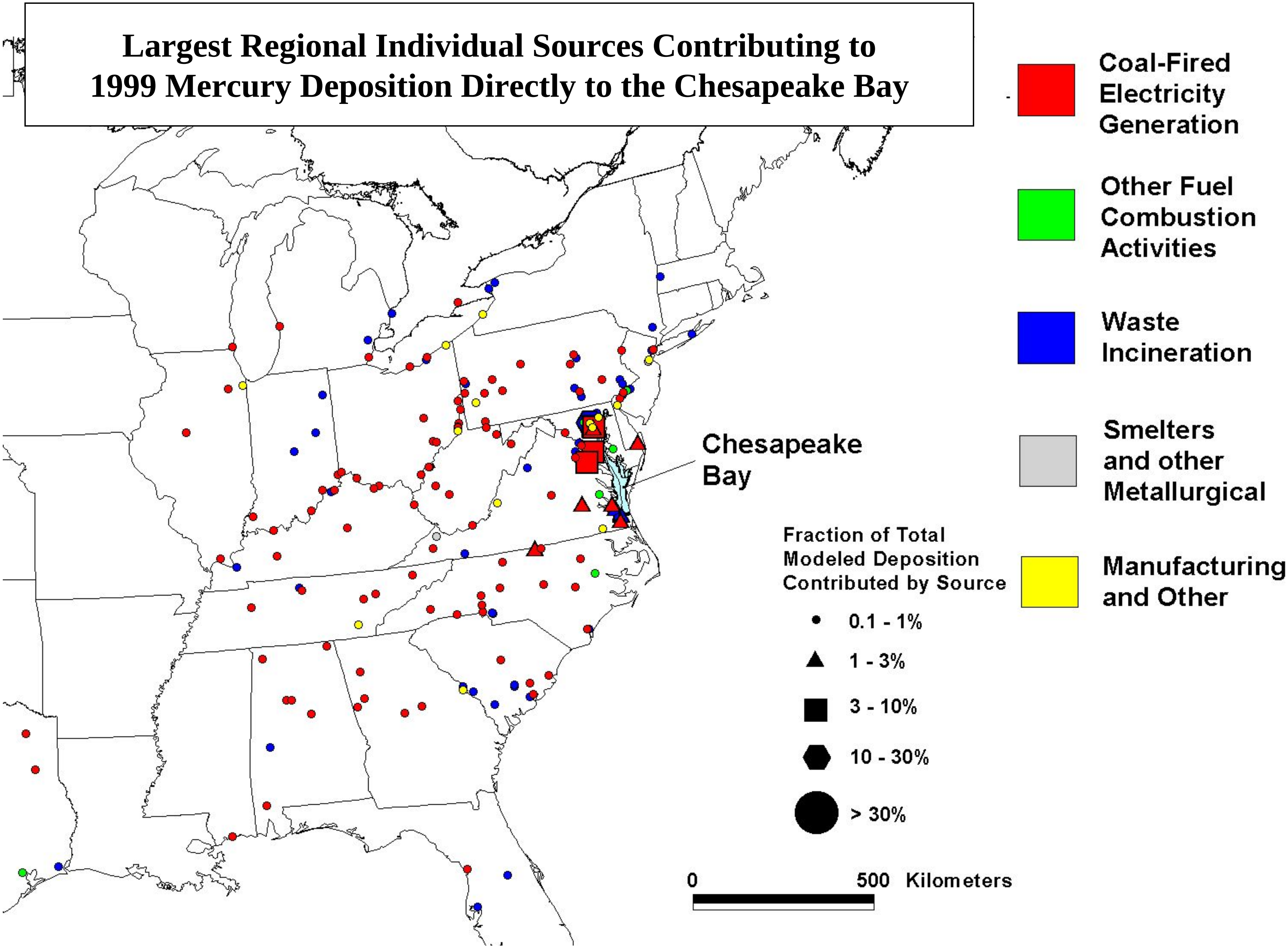
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)



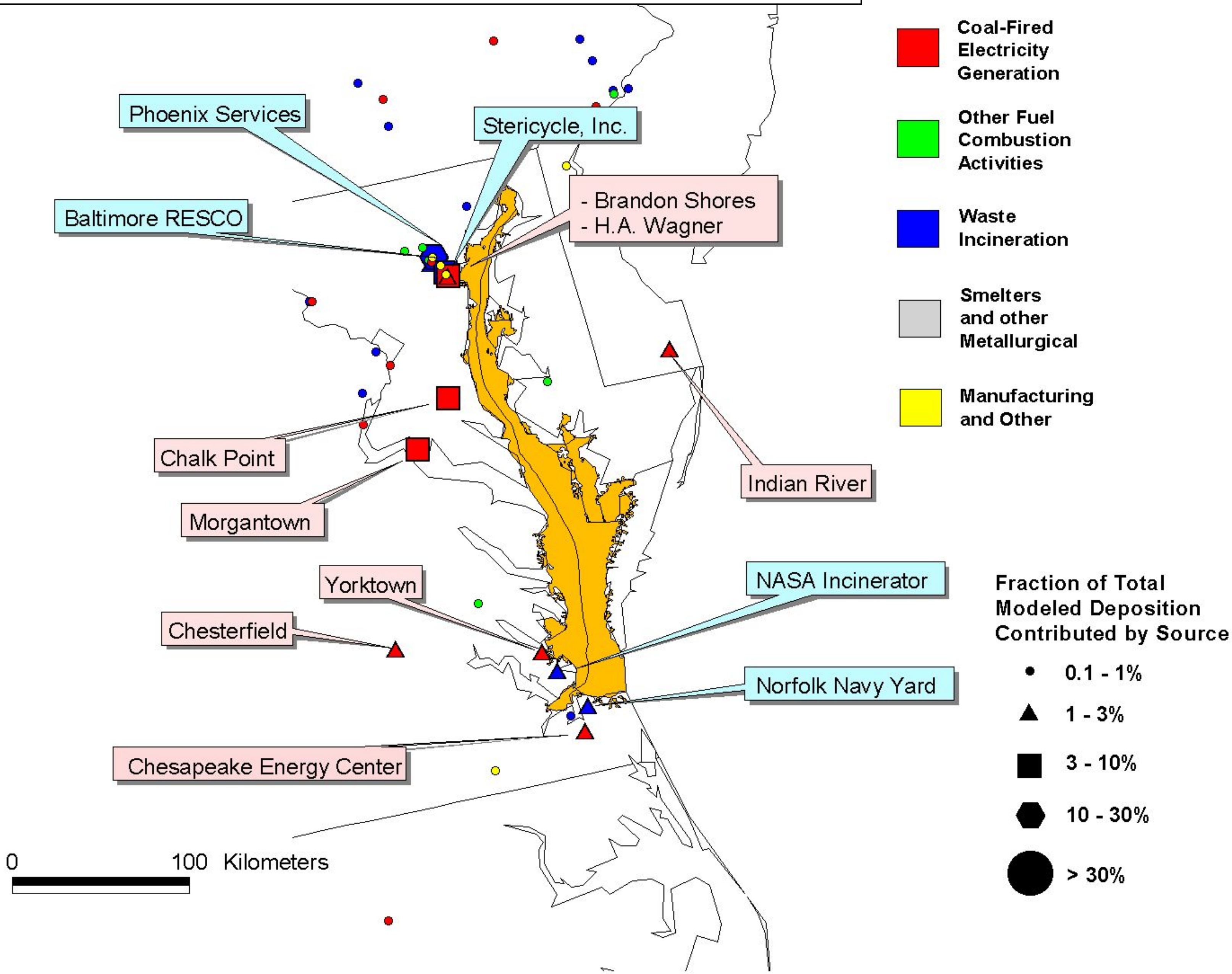
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)



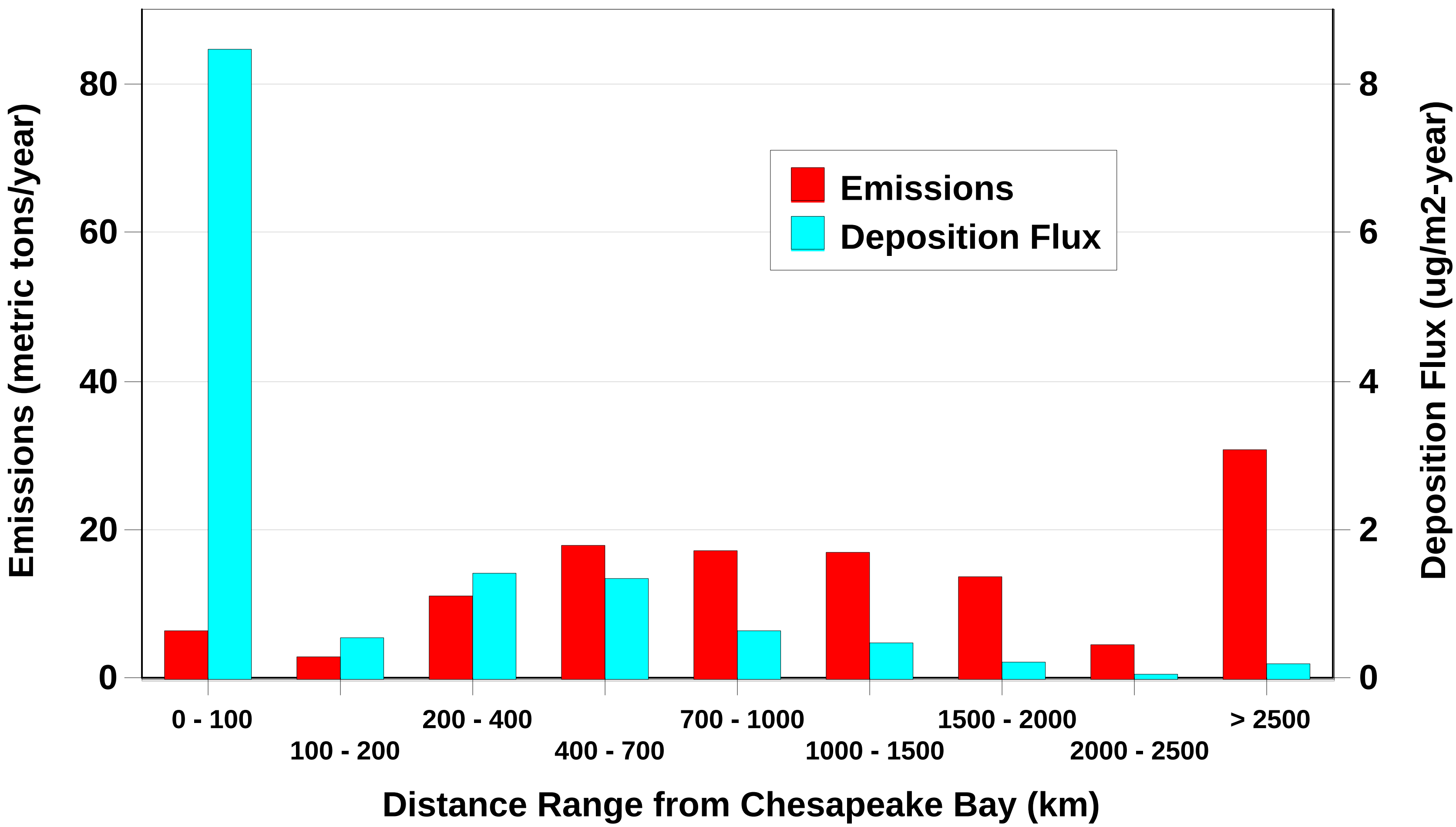
Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

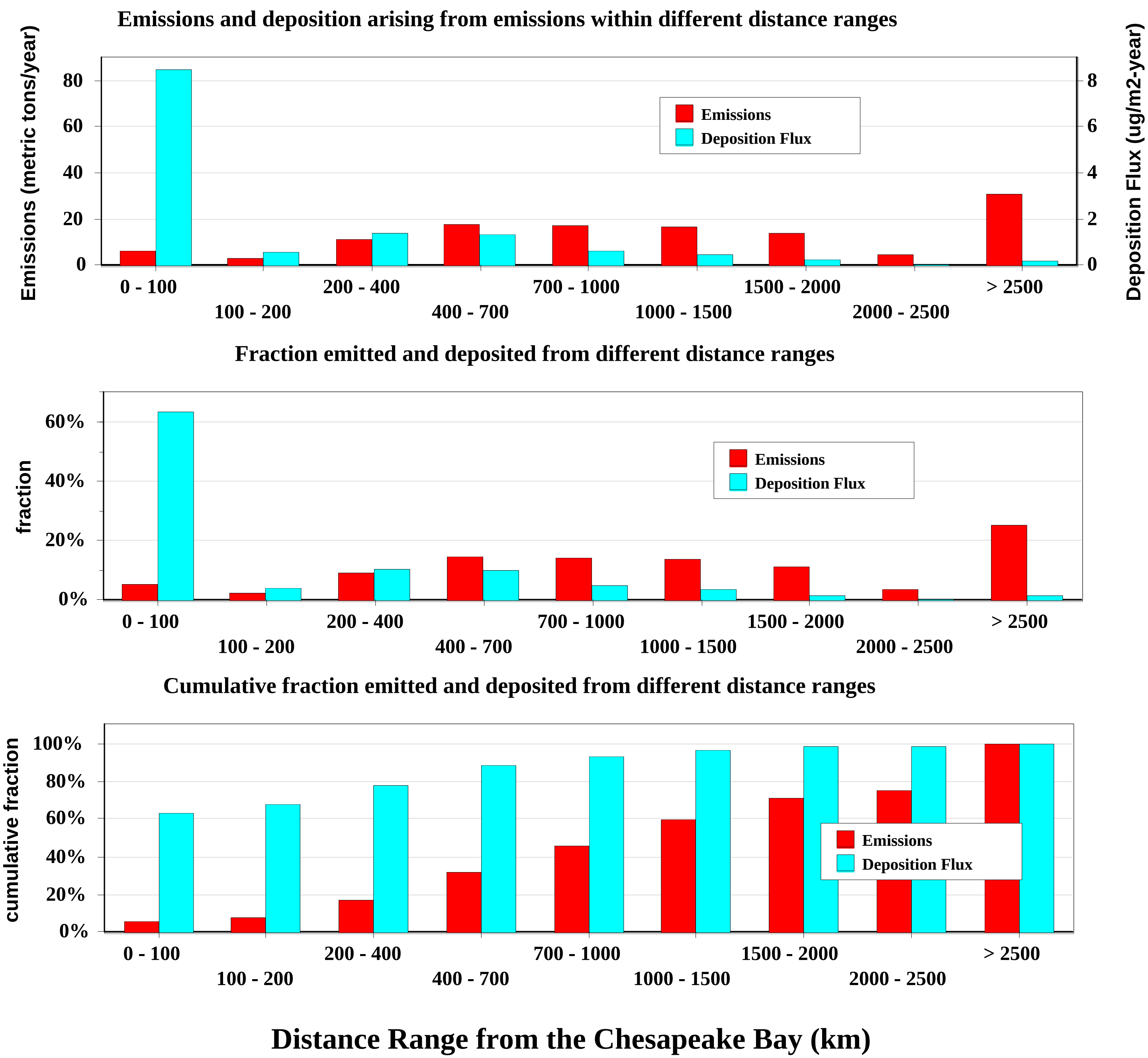


Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

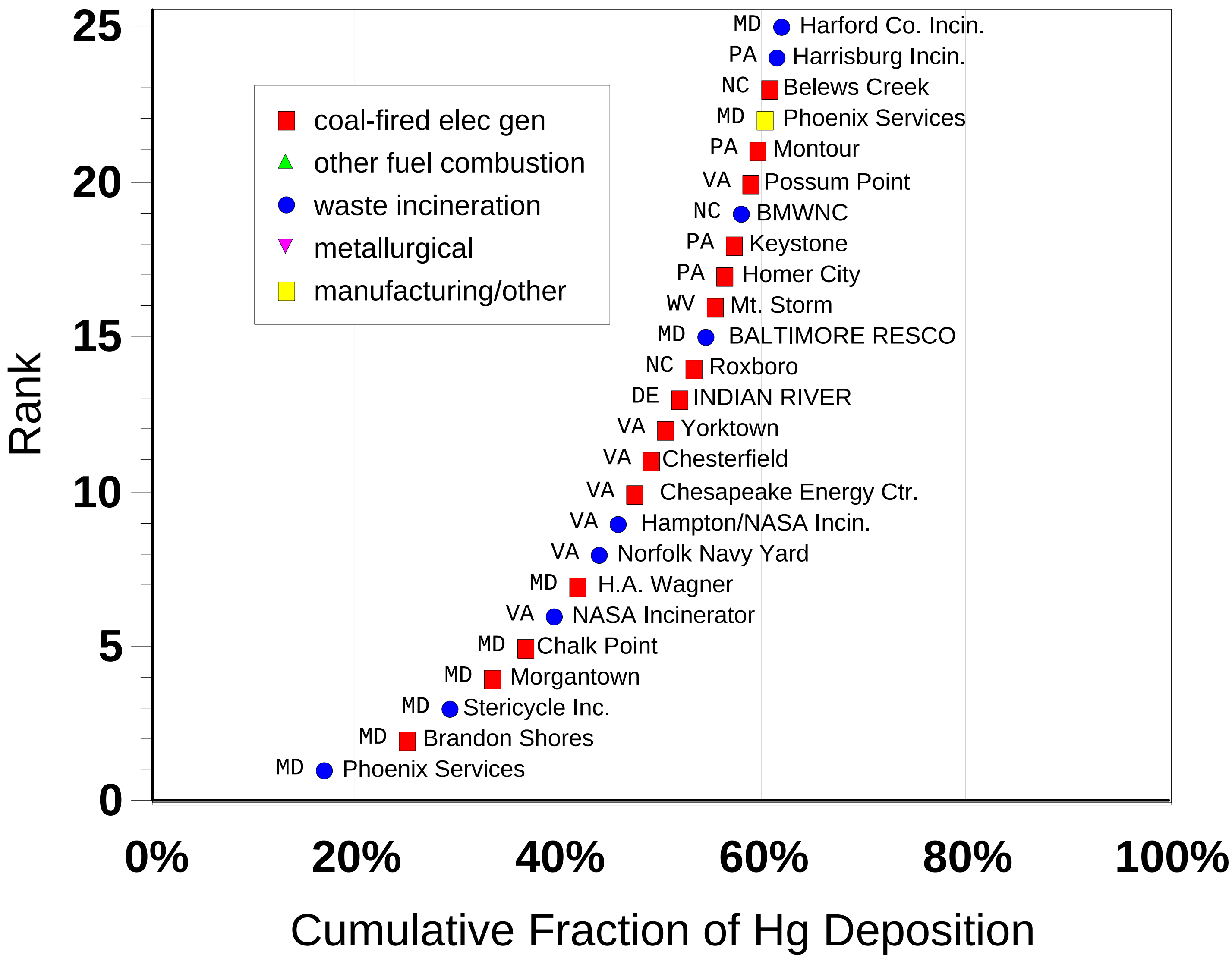


Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay




Emissions and deposition arising from emissions within different distance ranges
Emissions (metric tons/year)
Deposition Flux (ug/m2-year)
0
20
40
60
80
0
2
4
6
8
Emissions
Deposition Flux
0 - 100
100 - 200
200 - 400
400 - 700
700 - 1000
1000 - 1500
1500 - 2000
2000 - 2500
> 2500
Fraction emitted and deposited from different distance ranges
fraction
0%
20%
40%
60%
Emissions
Deposition Flux
0 - 100
100 - 200
200 - 400
400 - 700
700 - 1000
1000 - 1500
1500 - 2000
2000 - 2500
> 2500
Cumulative fraction emitted and deposited from different distance ranges
cumulative fraction
0%
20%
40%
60%
80%
100%
Emissions
Deposition Flux
0 - 100
100 - 200
200 - 400
400 - 700
700 - 1000
1000 - 1500
1500 - 2000
2000 - 2500
> 2500
Distance Range from the Chesapeake Bay (km)

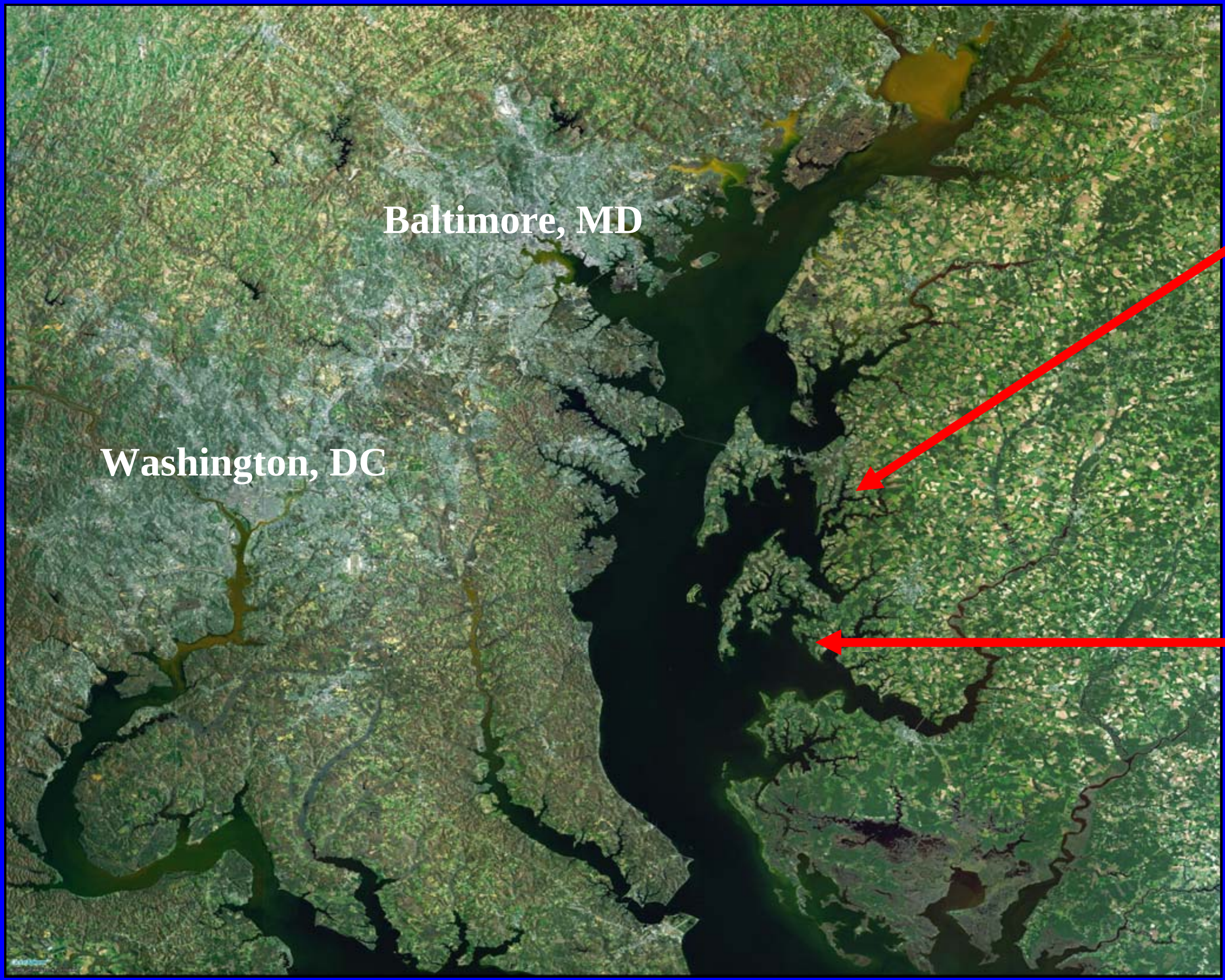
Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay

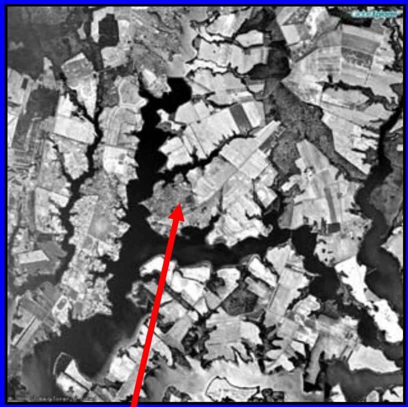


Summer 2004 Chesapeake Bay Atmospheric Hg Study
(June – August 2004)

- 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***

Measurement Sites

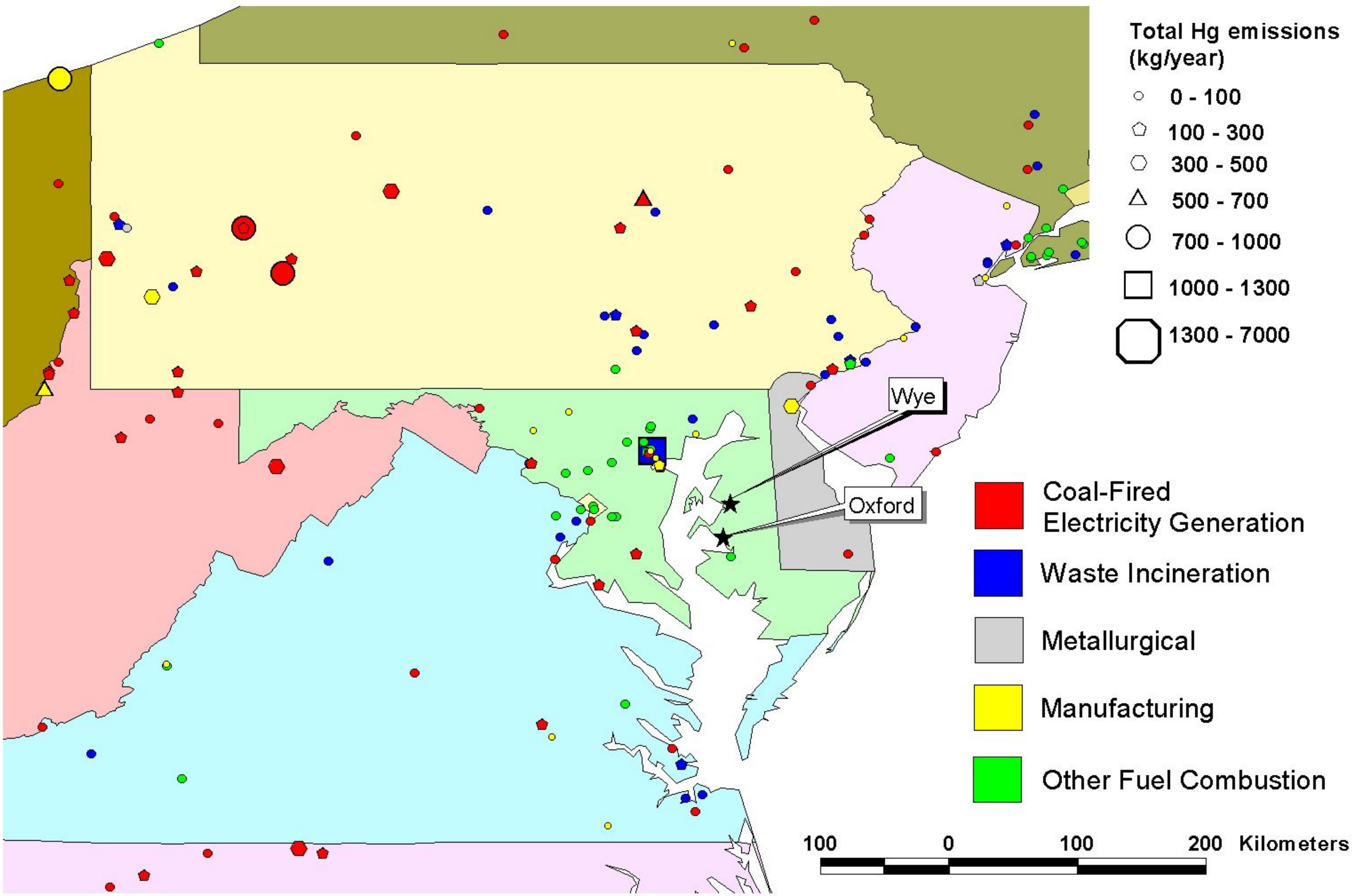




Wye Research and Education Center (38.9131EN, 76.1525EW)

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	✓	✓ (via CASTNet)
Ambient concentration of carbon monoxide	✓	
Meteorology	✓	✓ (via NADP site)
Major ions in precipitation		✓ (via NADP site)

Conclusions

- Source-attribution information is important
- Impacts are episodic & depend on form of mercury emitted
- Modeling needed to get source-attribution information
- (more!) Monitoring for model evaluation & refinement
- Models don't have to be perfect to give useful information
- Many uncertainties but useful model results are emerging
- Many opportunities exist for improvements in modeling/monitoring integrated approaches to develop source-attribution information *(and States can play a key role in developing critical emissions &monitoring information)*

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- CEC (*Paul Miller*)

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- *Roch Duval* (Ontario Ministry of the Environment, Geomatics Service Center)
- *Anne Pope and colleagues* (USEPA OAQPS Emissions Inventory Group)
- *Laurier Poissant* (Environment Canada)
- *John McDonald* (IJC)
- Mercury Deposition Network