Modeling the Fate and Transport of Atmospheric Mercury in the Chesapeake Bay Region

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

Presentation at

NOAA Chesapeake Bay Office
May 17, 2004, Annapolis MD

- **Modeling Methodology**
- **Hg Emissions Inventory**
- **Model Evaluation**
- **Some Results for Chesapeake Bay**
- **Some Next Steps**

Modeling Methodology

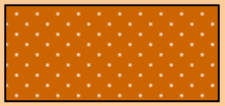
Three “forms” of atmospheric mercury

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”)

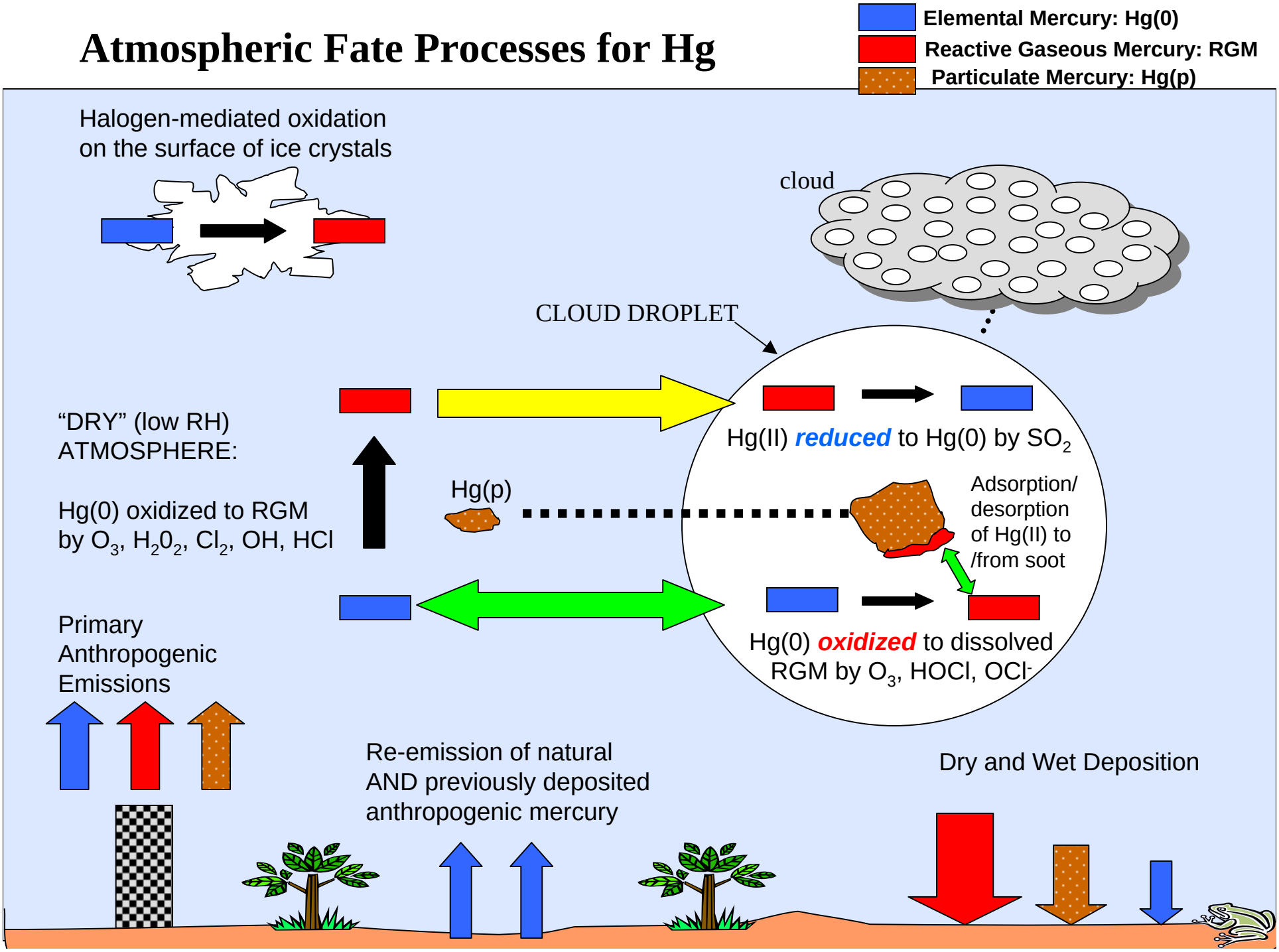
- **a few percent of total Hg in atmosphere**
- **oxidized mercury: Hg(II)**
- **HgCl2, others species?**
- **somewhat operationally defined by measurement method**
- ***very* water soluble**
- **short atmospheric lifetime (~ 1 week or less);**
- **more local and regional effects**



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?**

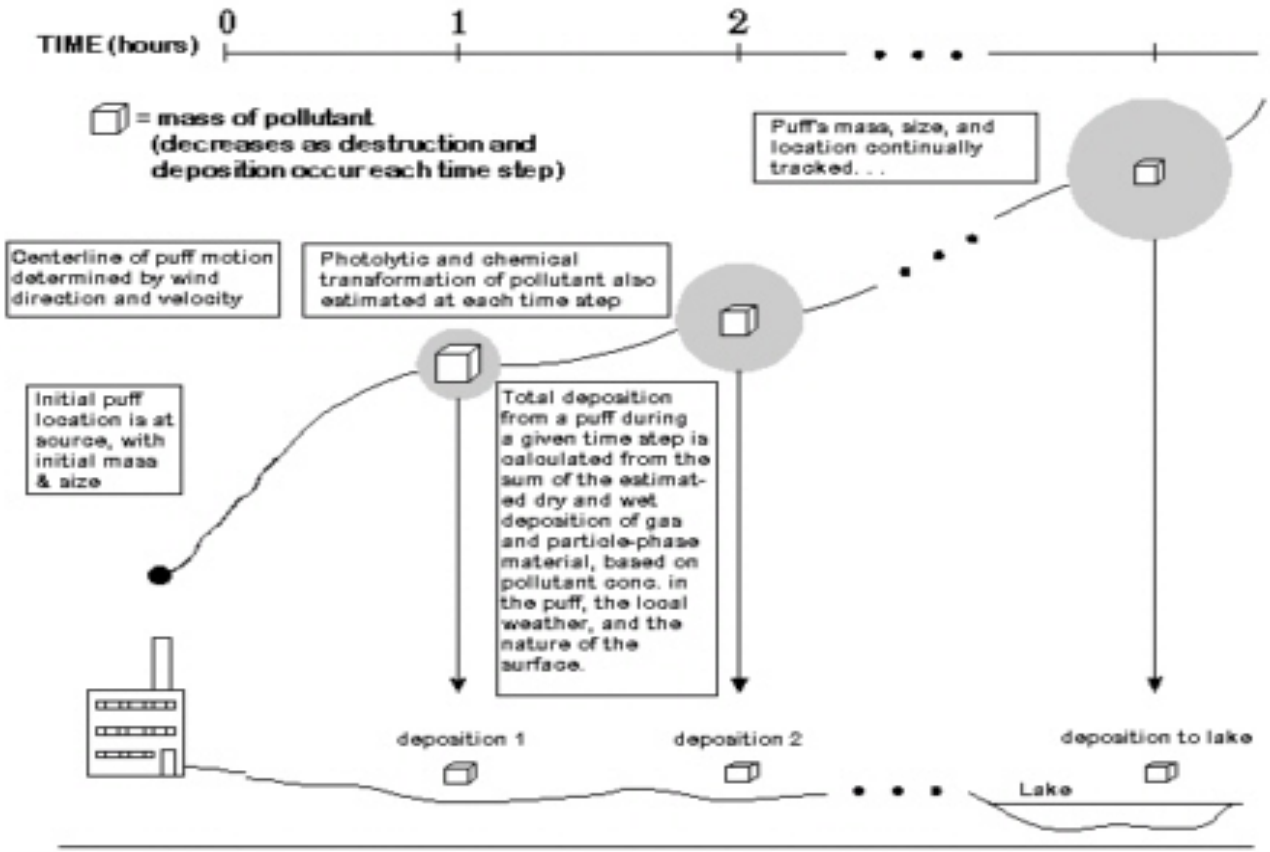
Atmospheric Fate Processes for Hg

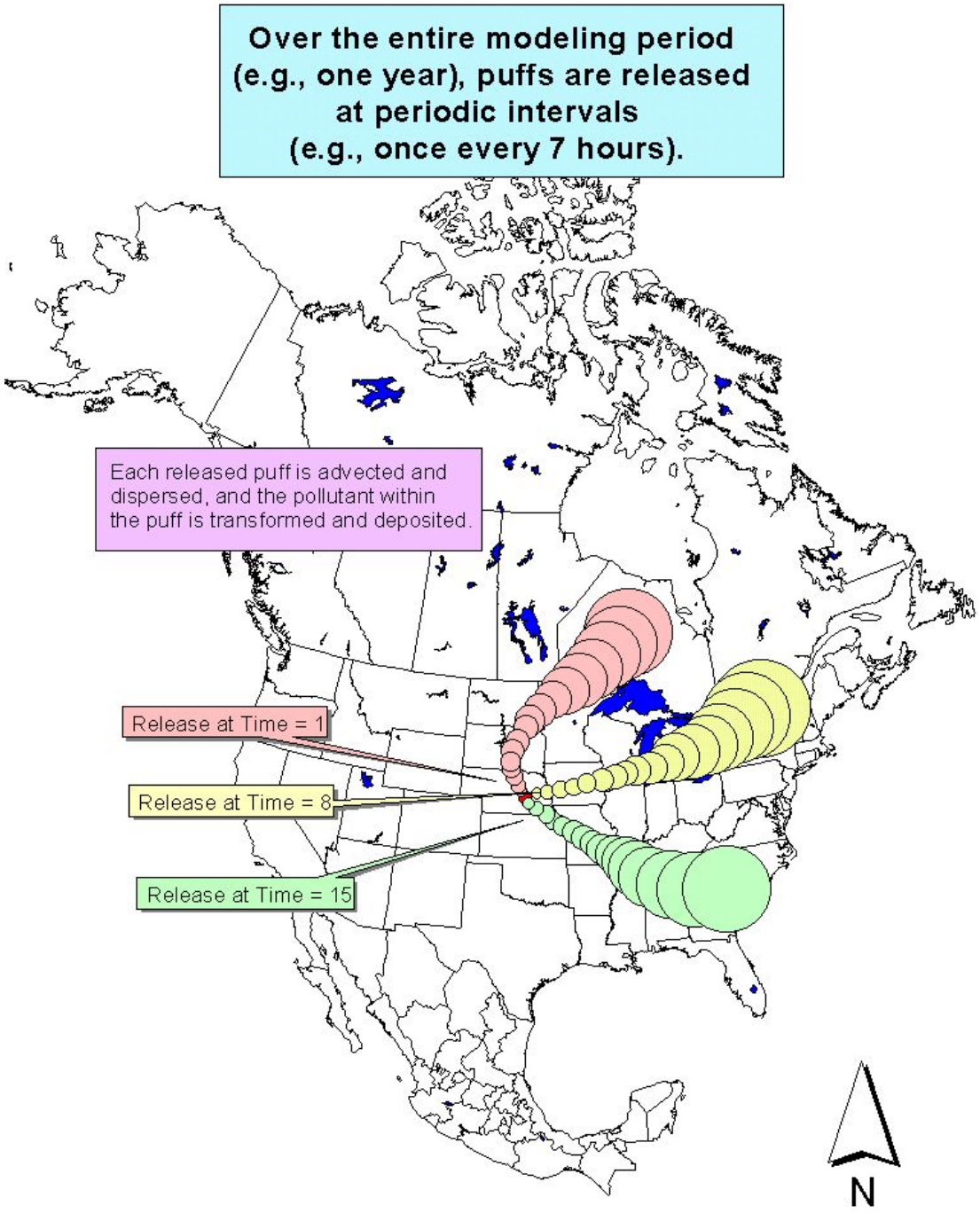


Atmospheric Chemical Reaction Scheme for Mercury

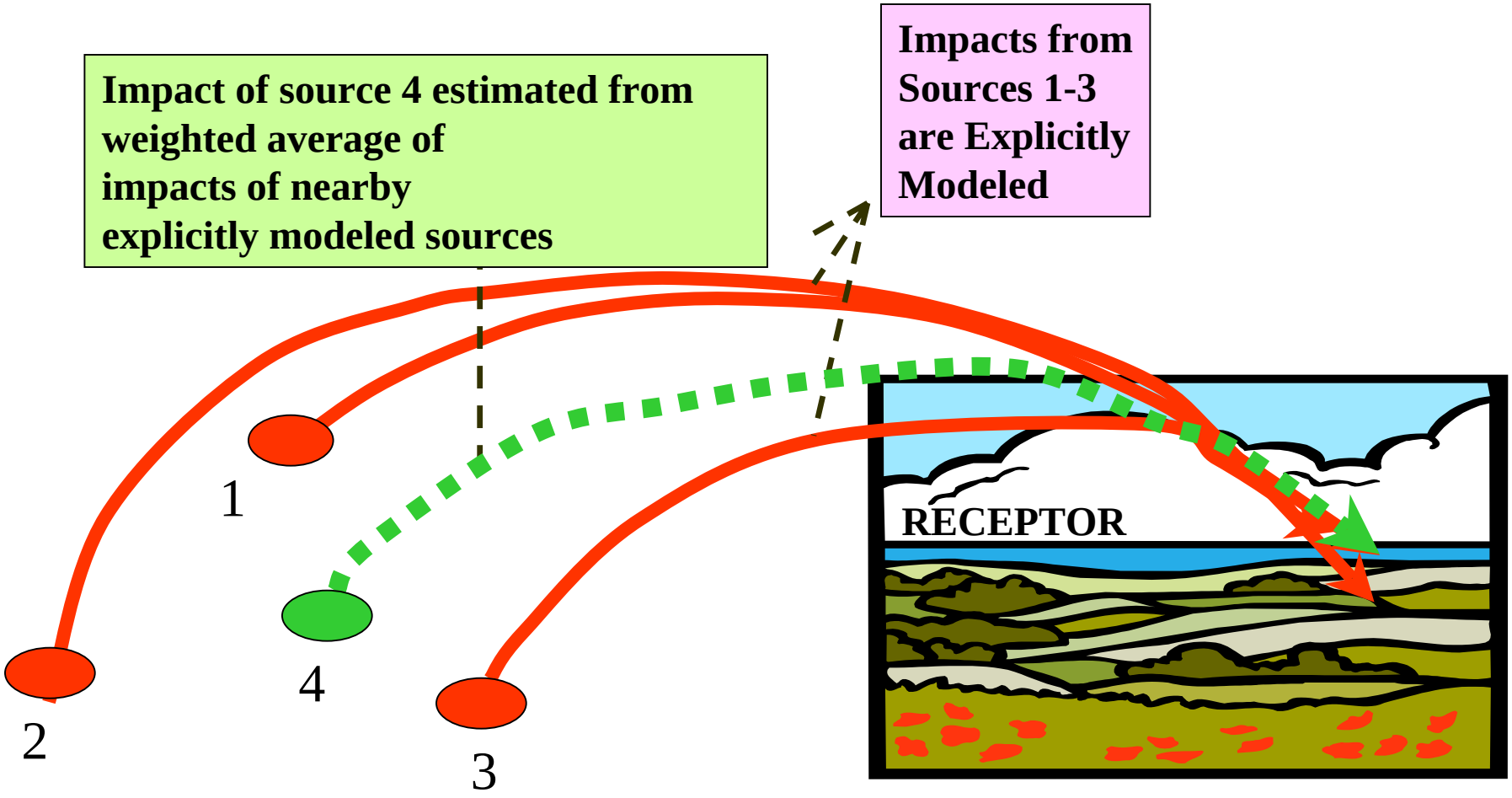
Reaction	Rate	Units	Reference
GAS PHASE REACTIONS			
$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm^3/molec-sec	Hall (1995)
$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$Hg^0 + Cl_2 \rightarrow HgCl_2$	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)

Figure 1. Lagrangian Puff Air Transport and Deposition Model

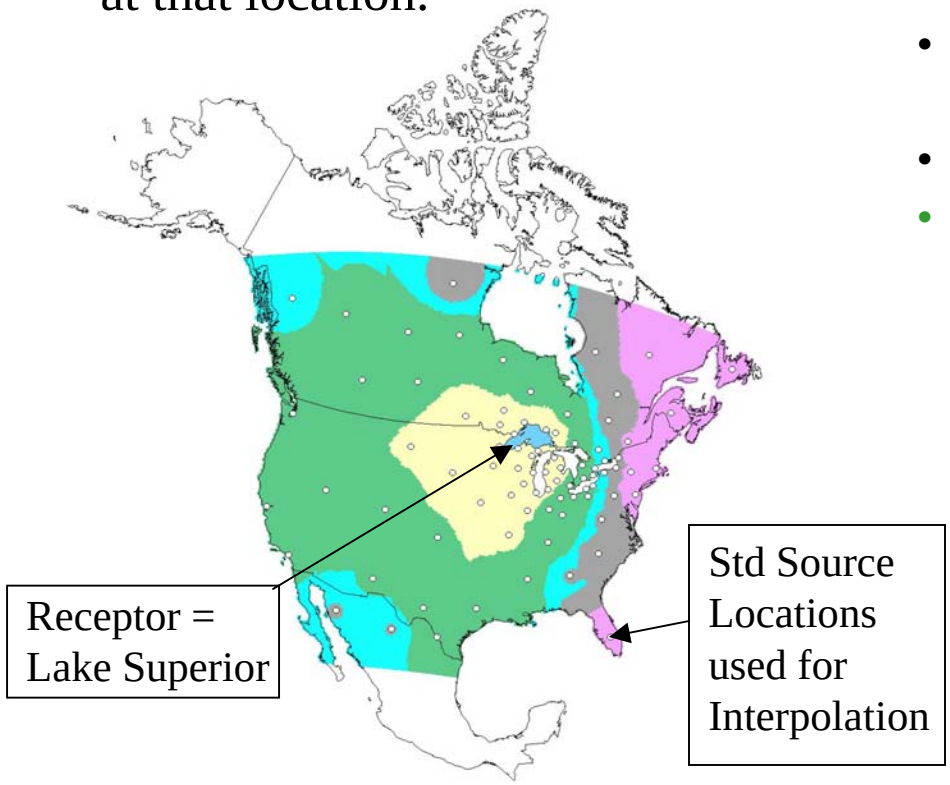



Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).
Each released puff is advected and dispersed, and the pollutant within the puff is transformed and deposited.
Release at Time = 1
Release at Time = 8
Release at Time = 15
N

Spatial interpolation



at any given location,
the ***transfer coefficient***
is defined as the amount
that would be deposited
in the given receptor
(in this case, Lake Superior)
if there were emissions
at that location.

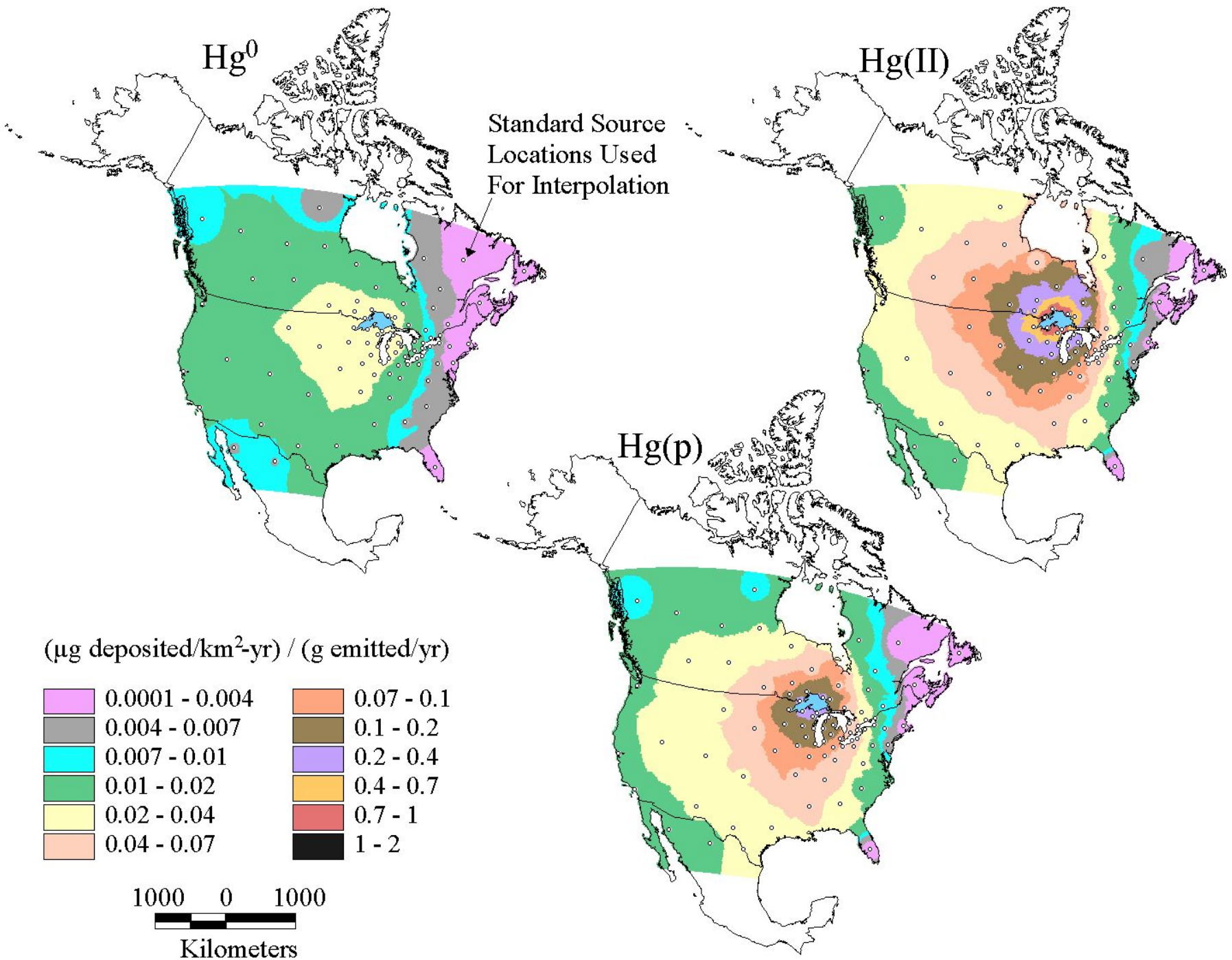


Transfer Coefficients

- **refer to *hypothetical* emissions;**
  [are independent of actual emissions]
- **can be formulated with different units**
  [in this example: total Hg deposition flux (ug/km2-yr) / emissions (g/yr)]
- **will depend on the pollutant**
  [in this example: Hg(0)]
- **will depend on the receptor**
  [in this example: Lake Superior]
- **and the time period being modeled**
- ***[in this example: entire year 1996]***

(μg deposited/km^2-yr) / (g emitted/yr)

0.0001 - 0.004	0.07 - 0.1
0.004 - 0.007	0.1 - 0.2
0.007 - 0.01	0.2 - 0.4
0.01 - 0.02	0.4 - 0.7
0.02 - 0.04	0.7 - 1
0.04 - 0.07	1 - 2


Hg0
Hg(II)
Hg(p)
Standard Source
Locations Used
For Interpolation
(µg deposited/km2-yr) / (g emitted/yr)
0.0001 - 0.004
0.004 - 0.007
0.007 - 0.01
0.01 - 0.02
0.02 - 0.04
0.04 - 0.07
0.07 - 0.1
0.1 - 0.2
0.2 - 0.4
0.4 - 0.7
0.7 - 1
1 - 2
1000 0 1000
Kilometers

ARTICLE IN PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Environmental Research

Environmental Research ■ (■■■■) ■■–■■

http://www.elsevier.com/locate/envres

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 Great Lakes National Program Office, Chicago, IL, USA*
[h] *International Joint Commission, Windsor, Ont., Canada*

Received 28 August 2003; received in revised form 12 November 2003; accepted 19 November 2003

Abstract

A special version of the NOAA HYSPLIT_4 model has been developed and used to estimate the atmospheric fate and transport of mercury in a North American modeling domain. Spatial and chemical interpolation procedures were used to expand the modeling results and provide estimates of the contribution of each source in a 1996 anthropogenic US/Canadian emissions inventory to atmospheric mercury deposition to the Great Lakes. While there are uncertainties in the emissions inventories and ambient data suitable for model evaluation are scarce, model results were found to be reasonably consistent with wet deposition measurements in the Great Lakes region and with independent measurement-based estimates of deposition to Lake Michigan. Sources up to 2000 km from the Great Lakes contributed significant amounts of mercury through atmospheric transport and deposition. While there were significant contributions from incineration and metallurgical sources, coal combustion was generally found to be the largest contributor to atmospheric mercury deposition to the Great Lakes.
Published by Elsevier Inc.

Keywords: Mercury; Atmospheric deposition; Great Lakes; Source–receptor modeling; Emissions

Mercury contamination in the Great Lakes and many other ecosystems is increasingly being recognized as a serious environmental concern. The dominant route of human exposure to mercury is through fish consumption, and significant portions of the general population are believed to be consuming toxicologically significant levels of mercury (e.g., National Research Council, 2000). Historical discharges—e.g., from chlor-alkali production using the mercury-cell process—are believed to have caused large accumulations of mercury in sediments in Lake Erie and Lake Ontario (Marvin et al., 2003). As these discharges have been substantially reduced, atmospheric deposition is now believed to be a more significant loading pathway for these lakes. Mass balance calculations for Lake Michigan (Mason and Sullivan, 1997) and Lake Superior (Dolan et al., 1993) indicate that atmospheric deposition accounts for approximately 75% of the overall mercury loading to these lakes.

While there have been several mercury modeling efforts in North America (Bullock et al., 1998; Bullock and Brehme, 2002; Dvonch et al., 1998; Lin et al., 2001; Pai et al., 1997; Seigneur et al., 2000, 2001, 2003a, b; 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

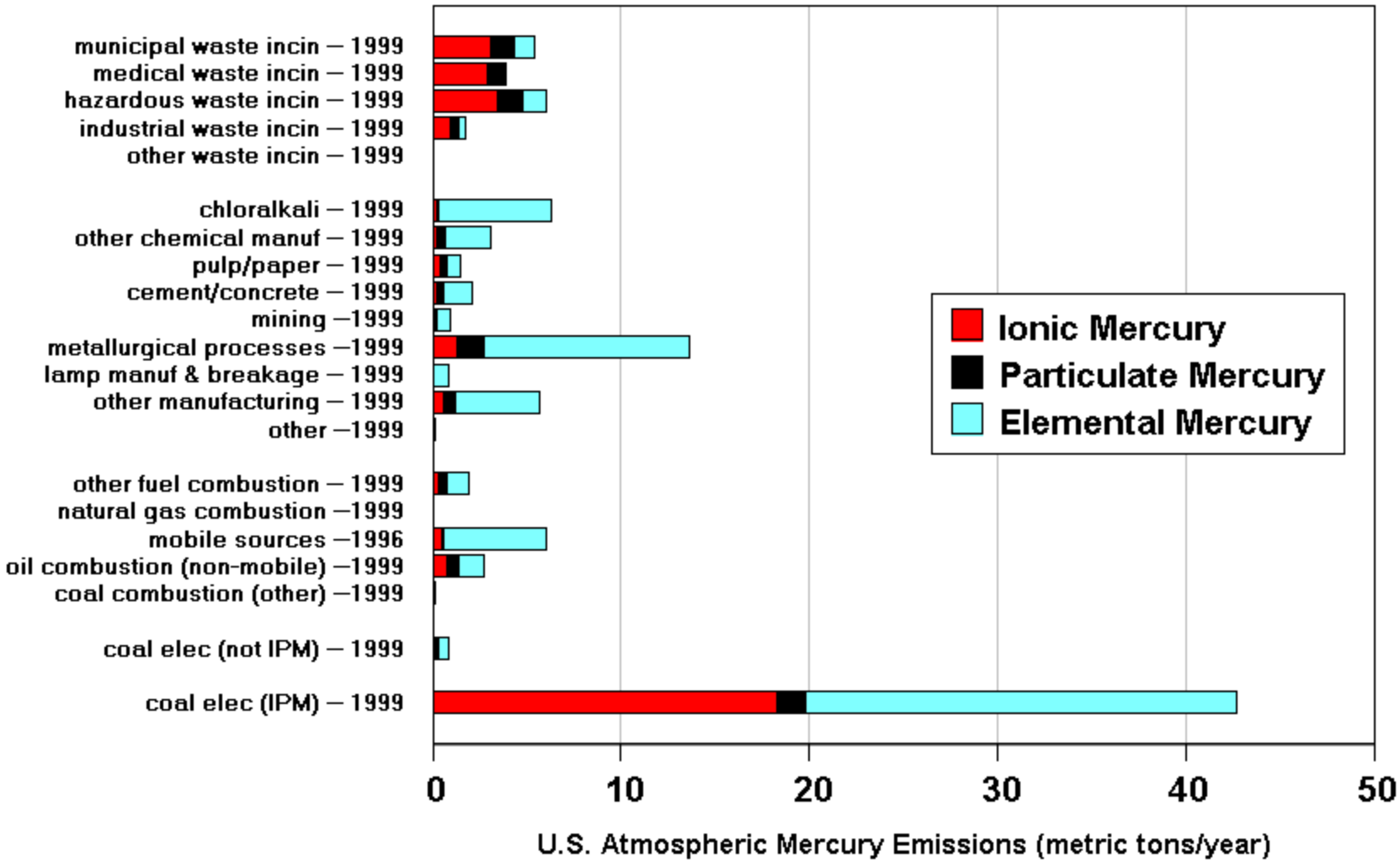
☆Supplementary data associated with this article can be found, in the online version, at doi = 10.1016/j.envres.2003.11.007

*Corresponding author. Fax: +301-713-0119.
E-mail address: mark.cohen@noaa.gov (M. Cohen).
[1] Current address: IPRA Canada/The Institute of Environmental Research, Concord, Ontario, Canada.

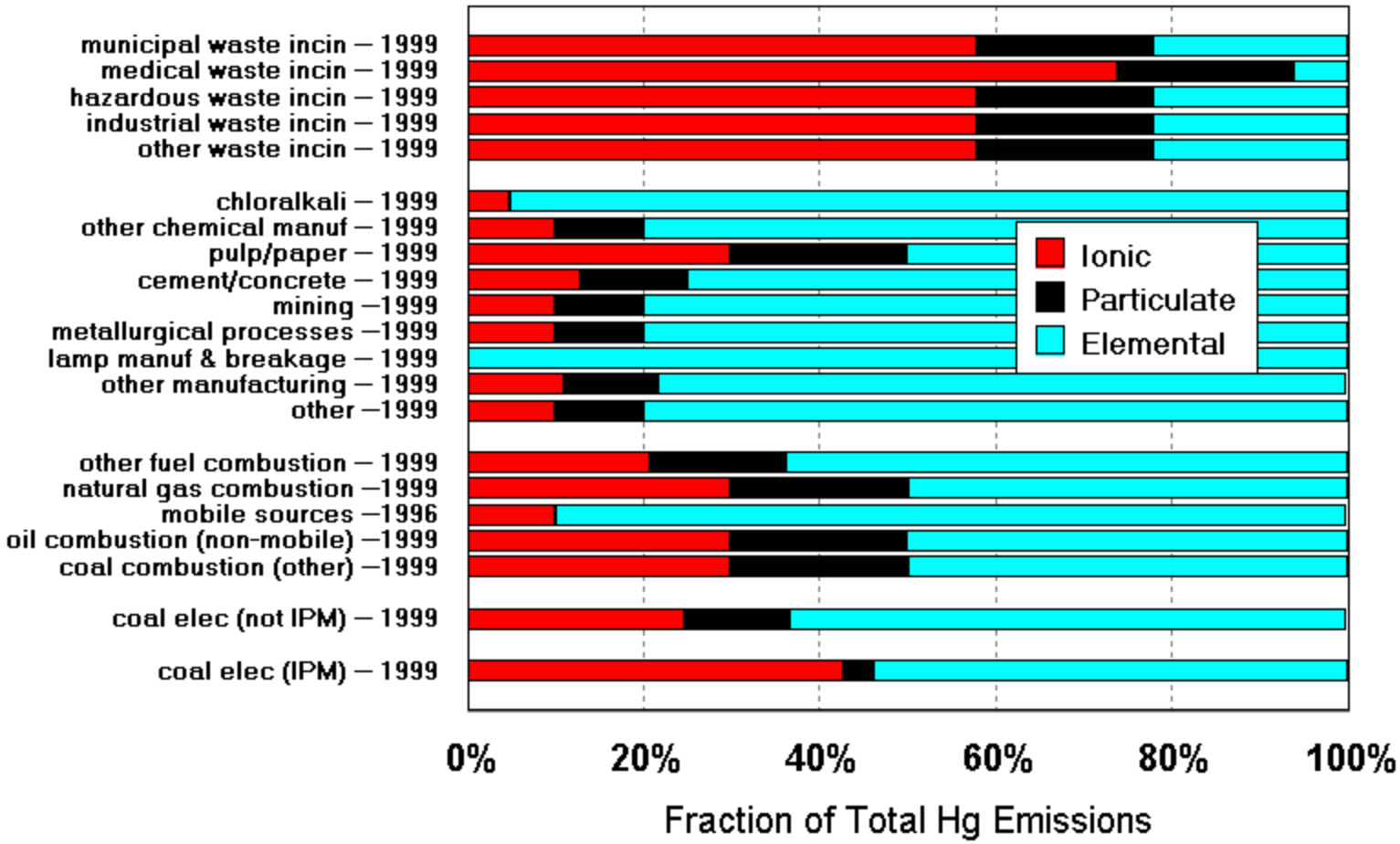
0013-9351/$ - see front matter Published by Elsevier Inc.
doi:10.1016/j.envres.2003.11.007

Mercury Emissions Inventory

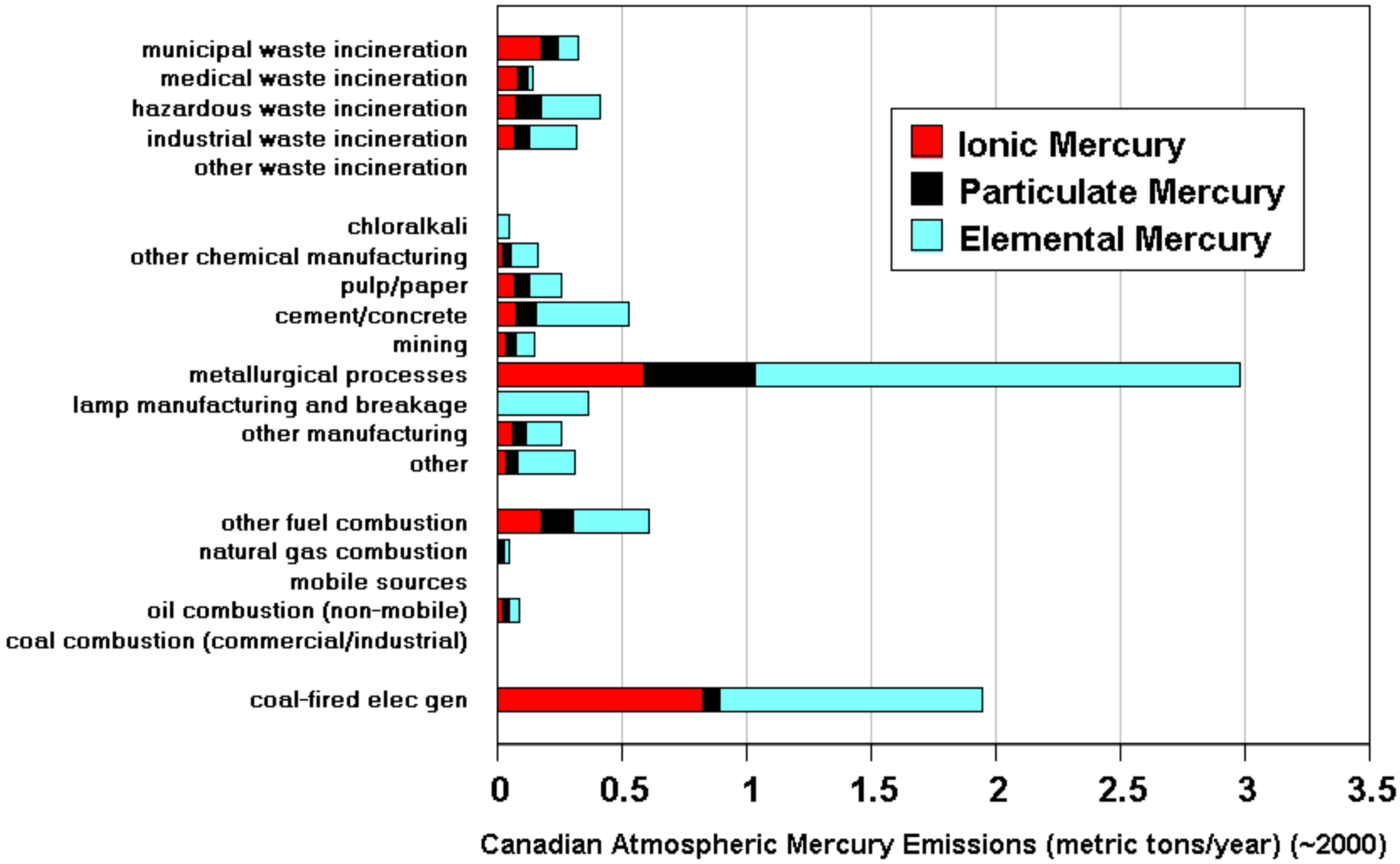
Estimated 1999 U.S. Atmospheric Anthropogenic Mercury Emissions



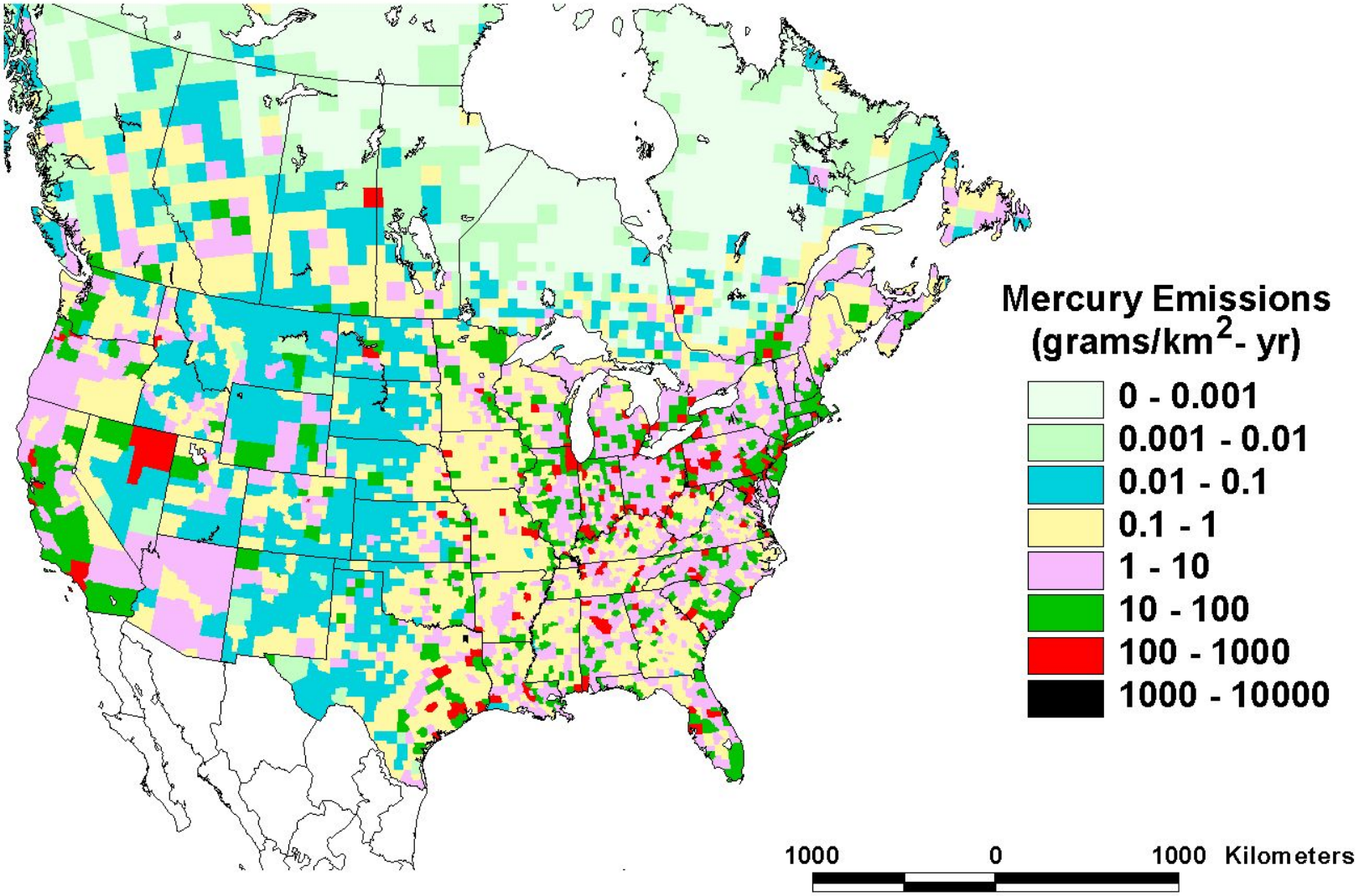
Estimated Speciation Profile for 1999 U.S. Atmospheric Anthropogenic Mercury Emissions

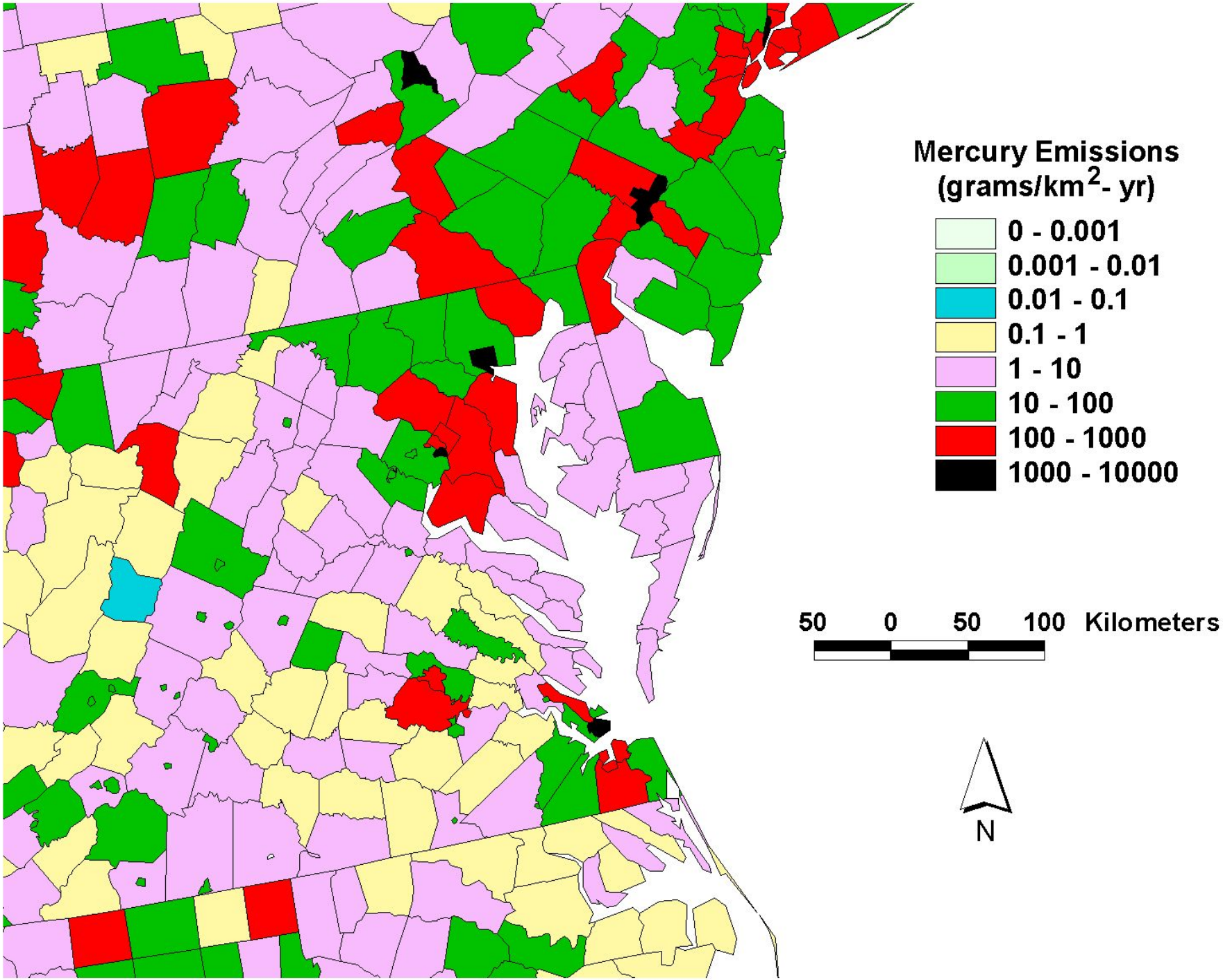


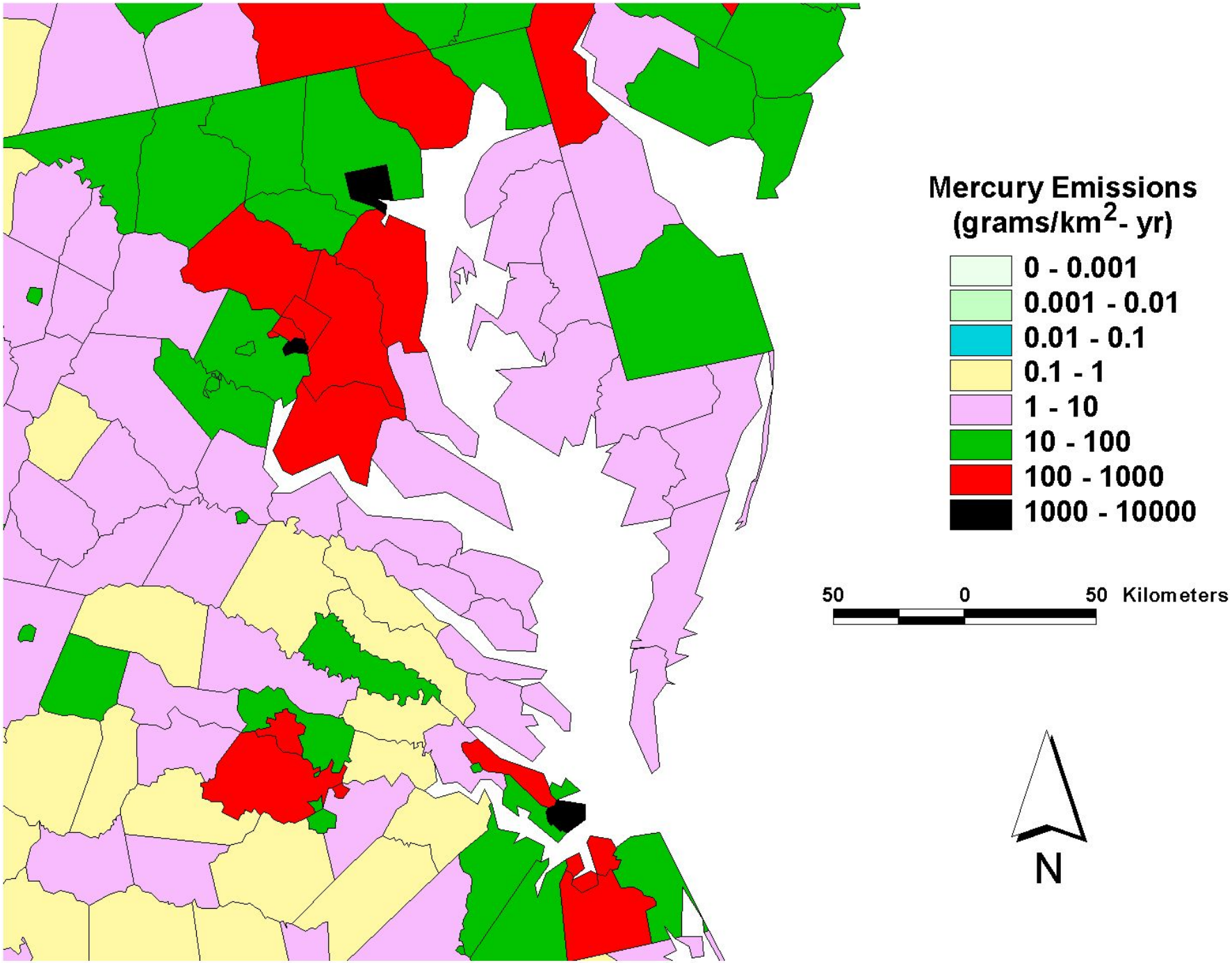
Estimated 2000 Canadian Atmospheric Anthropogenic Mercury Emissions

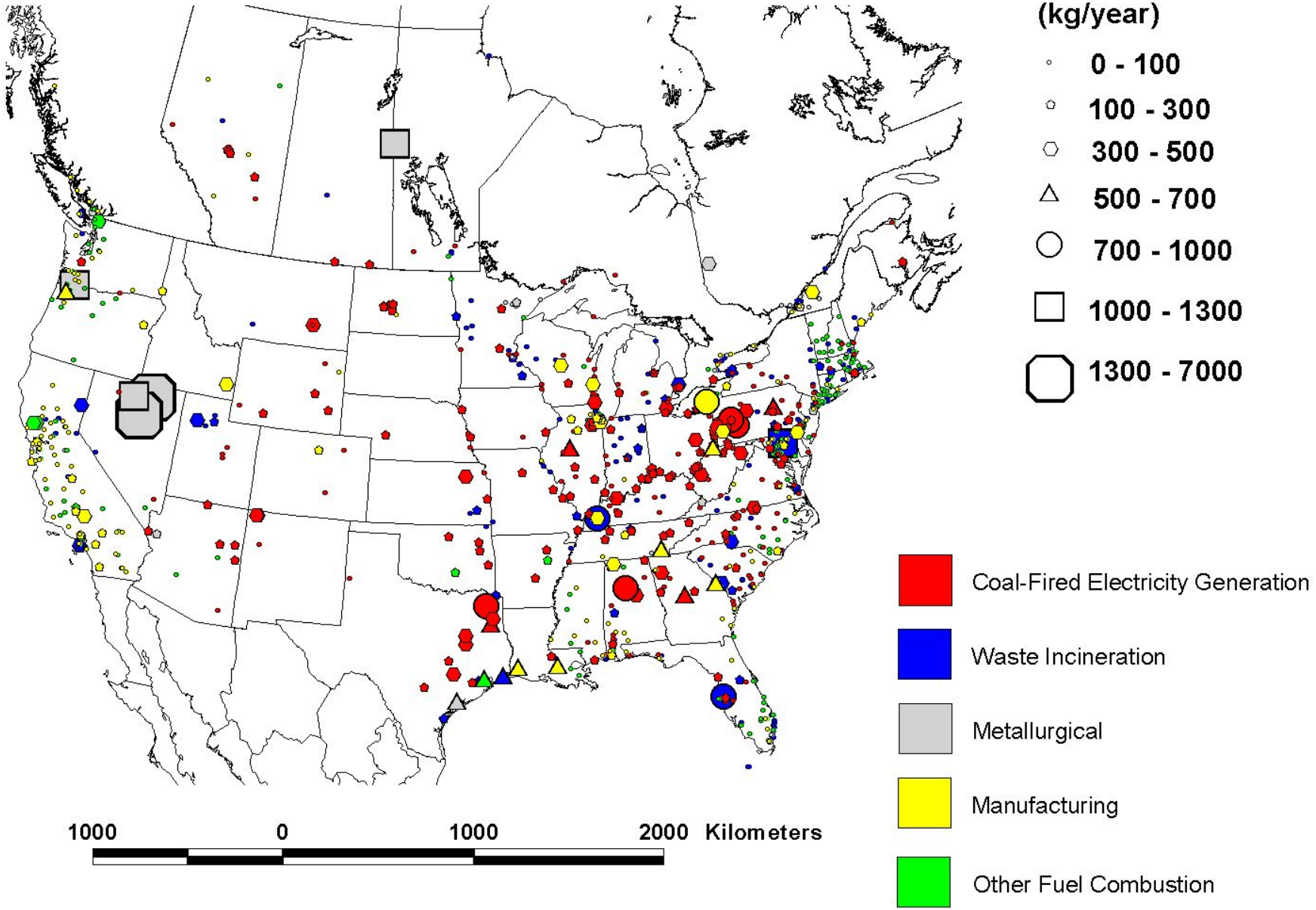


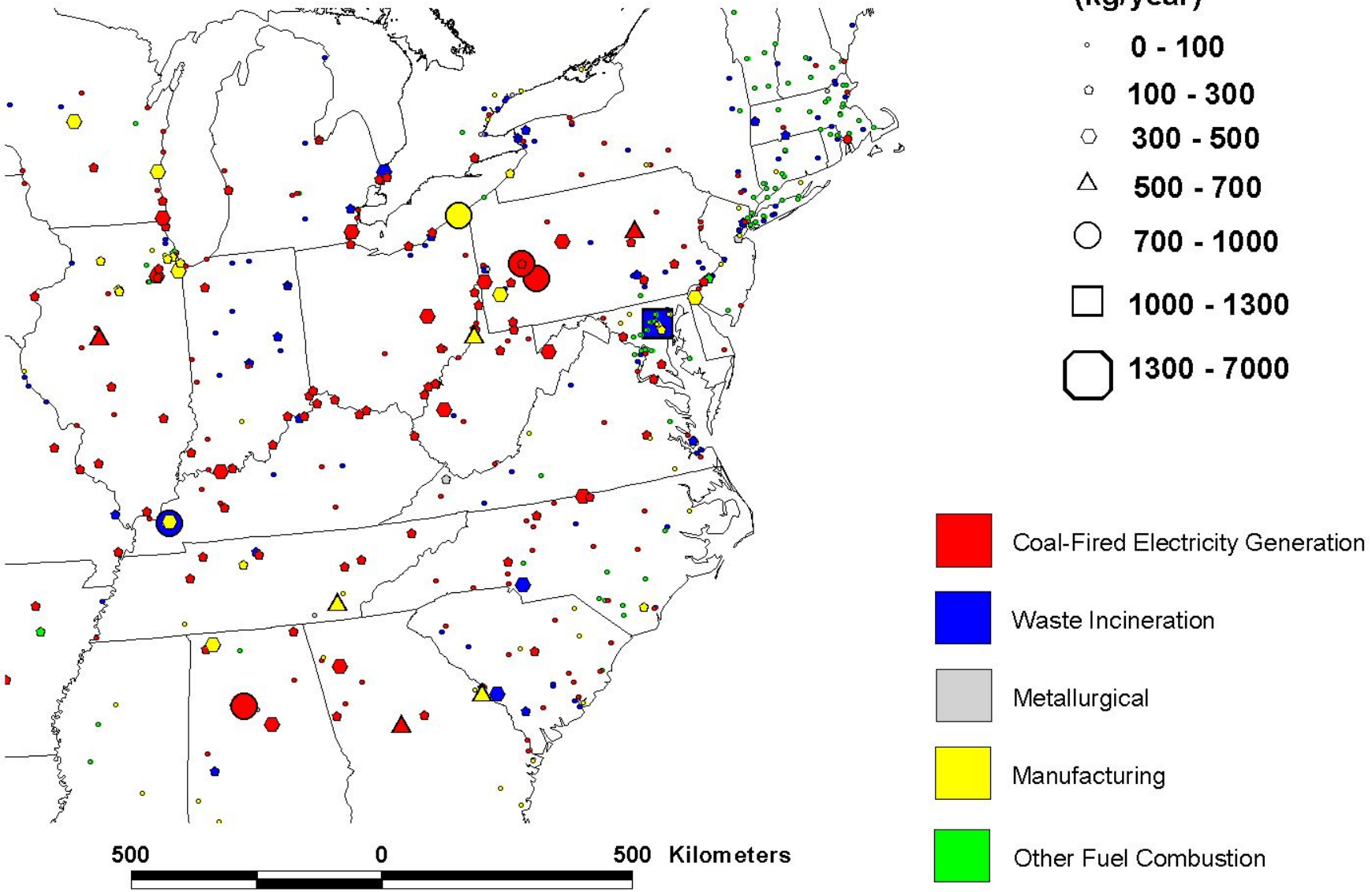
Geographic Distribution of Estimated Anthropogenic Mercury Emissions in the U.S. (1999) and Canada (2000)

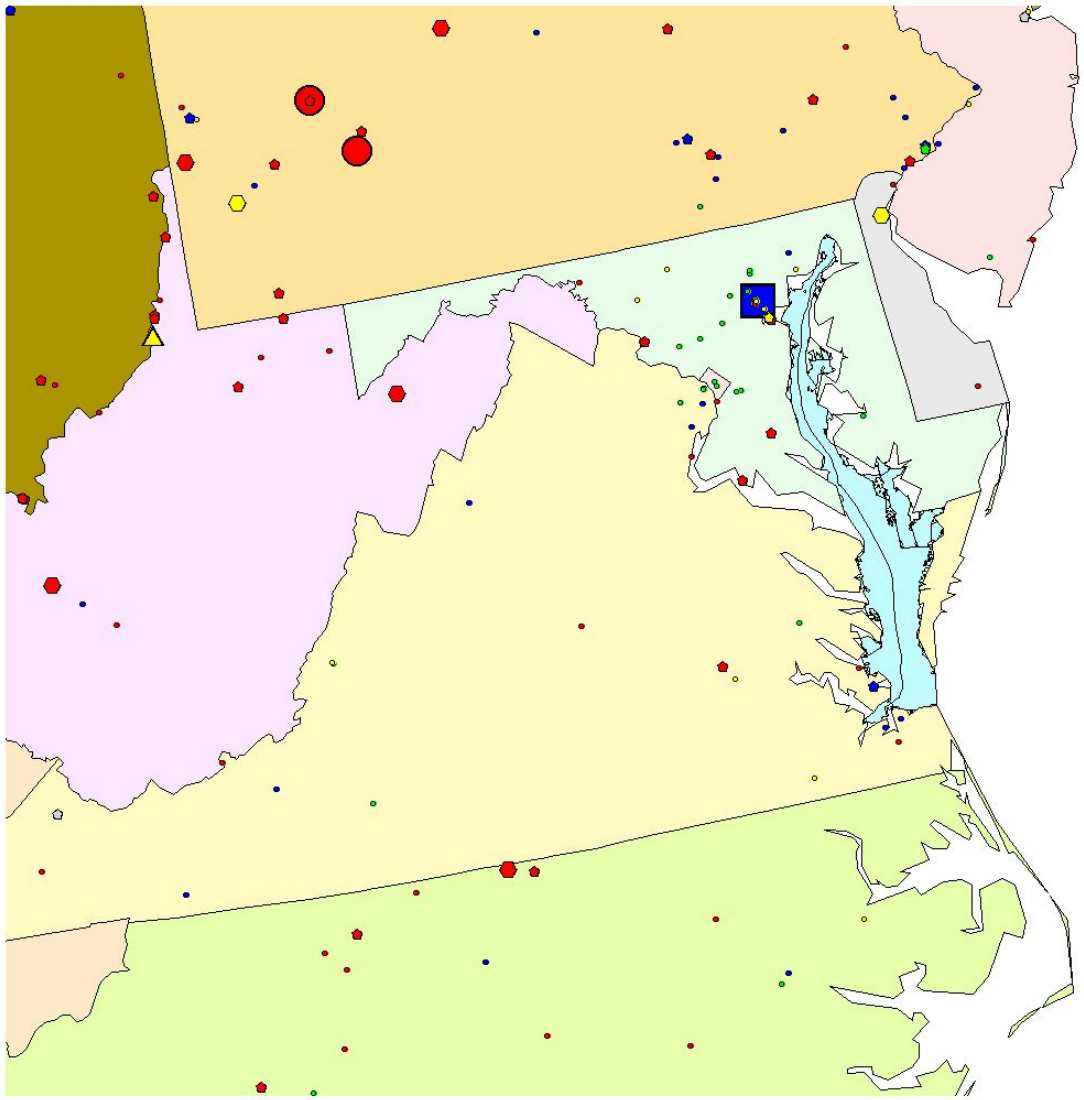



Mercury Emissions
(grams/km2- yr)
0 - 0.001
0.001 - 0.01
0.01 - 0.1
0.1 - 1
1 - 10
10 - 100
100 - 1000
1000 - 10000
50 0 50 100 Kilometers
N


Mercury Emissions
(grams/km2- yr)
0 - 0.001
0.001 - 0.01
0.01 - 0.1
0.1 - 1
1 - 10
10 - 100
100 - 1000
1000 - 10000
50
0
50 Kilometers
N


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
1000
0
1000
2000 Kilometers

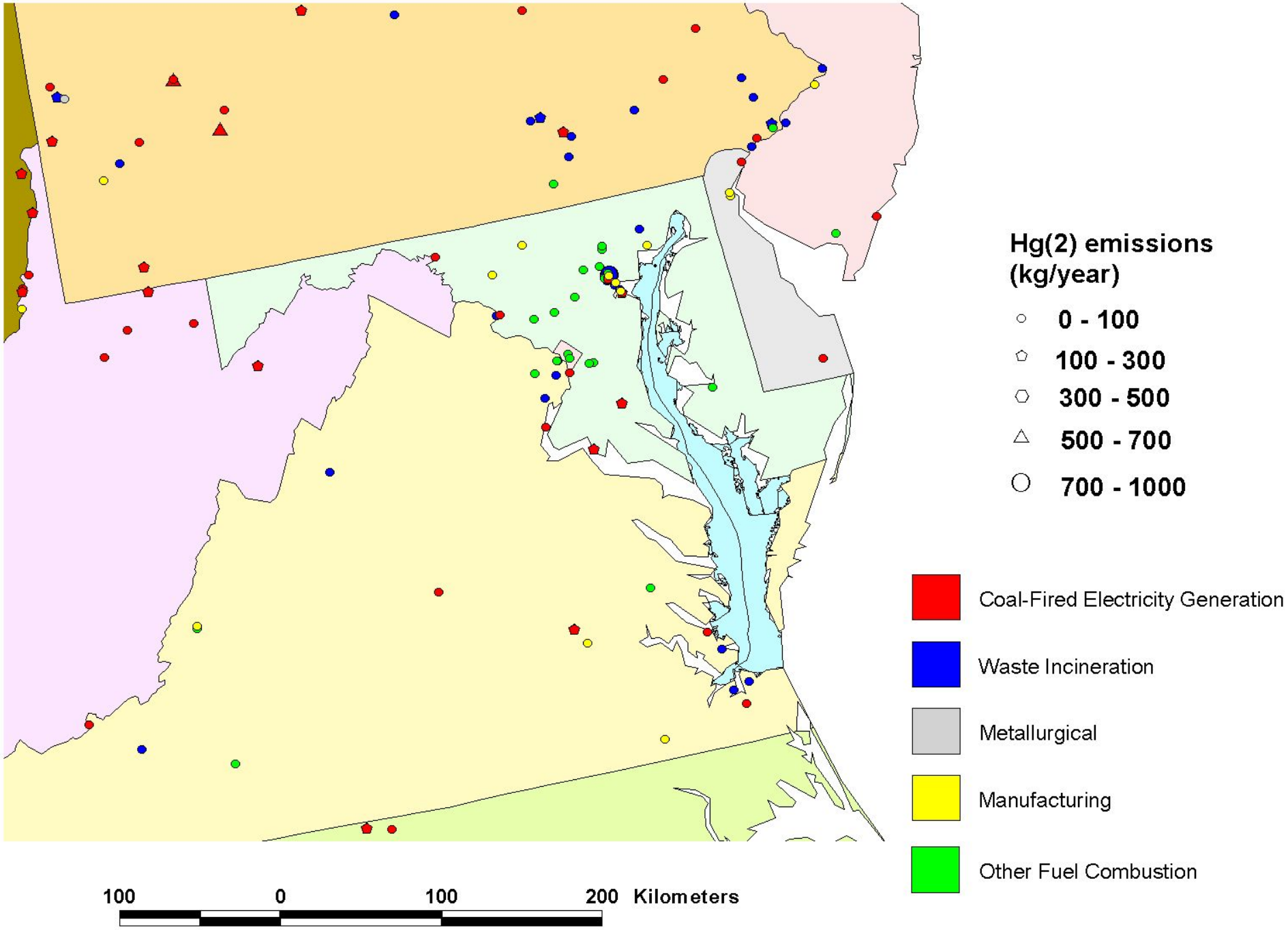

Total Hg emissions
(kg/year)
0 - 100
100 - 300
300 - 500
500 - 700
700 - 1000
1000 - 1300
1300 - 7000
Coal-Fired Electricity Generation
Waste Incineration
Metallurgical
Manufacturing
Other Fuel Combustion
500
0
500 Kilometers



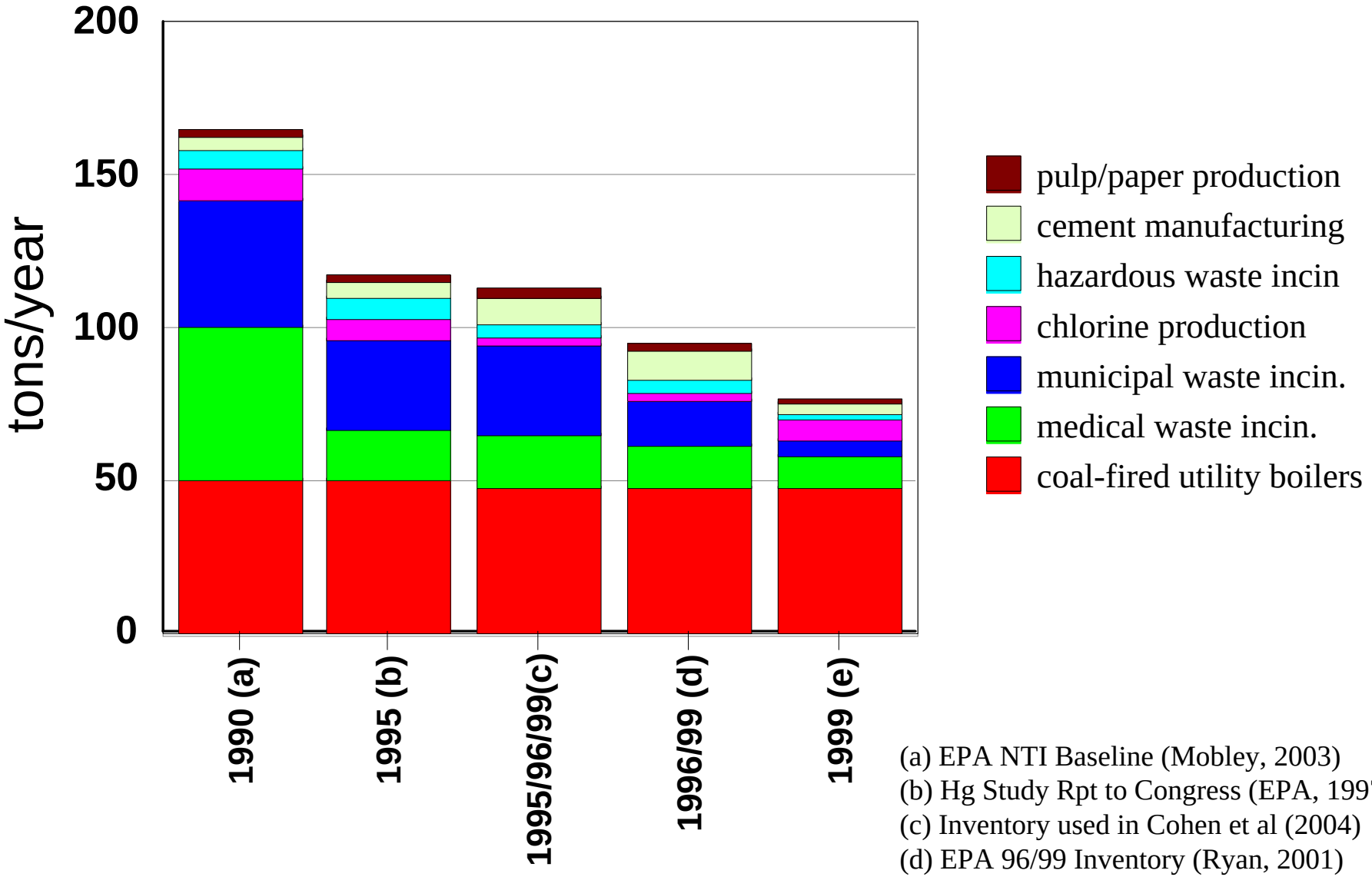
Total Hg emissions (kg/year)

- 0 - 100
- 100 - 300
- 300 - 500
- 500 - 700
- 700 - 1000
- 1000 - 1300
- 1300 - 7000

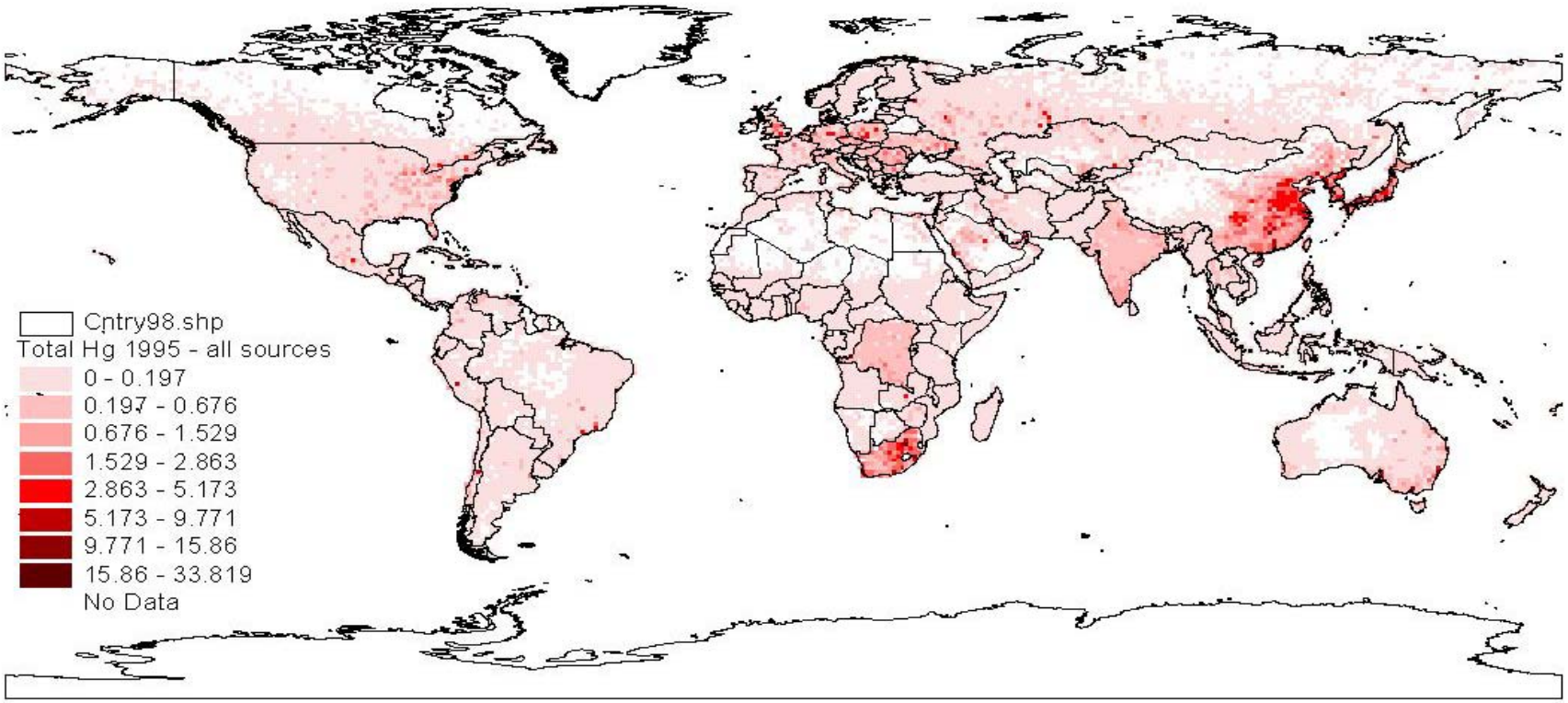
- Coal-Fired Electricity Generation
- Waste Incineration
- Metallurgical
- Manufacturing
- Other Fuel Combustion


Hg(2) emissions
(kg/year)
0 - 100
100 - 300
300 - 500
500 - 700
700 - 1000
Coal-Fired Electricity Generation
Waste Incineration
Metallurgical
Manufacturing
Other Fuel Combustion
100
0
100
200 Kilometers

Reported trends in U.S. atmospheric mercury emissions 1990-1999 (selected source categories)



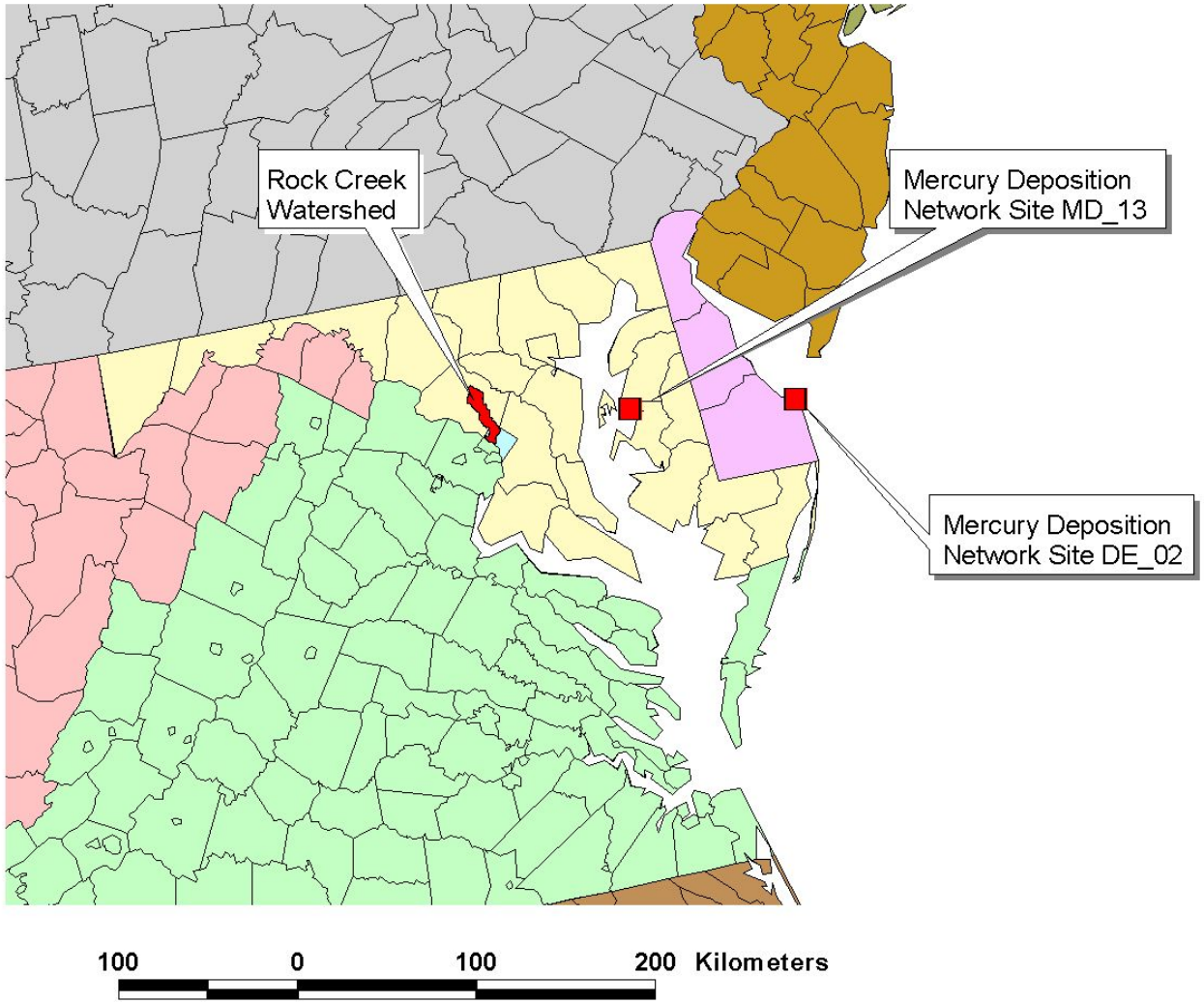
(a) EPA NTI Baseline (Mobley, 2003)
(b) Hg Study Rpt to Congress (EPA, 1997)
(c) Inventory used in Cohen et al (2004)
(d) EPA 96/99 Inventory (Ryan, 2001)
(e) EPA NEI 1999 (draft) (Mobley, 2003)



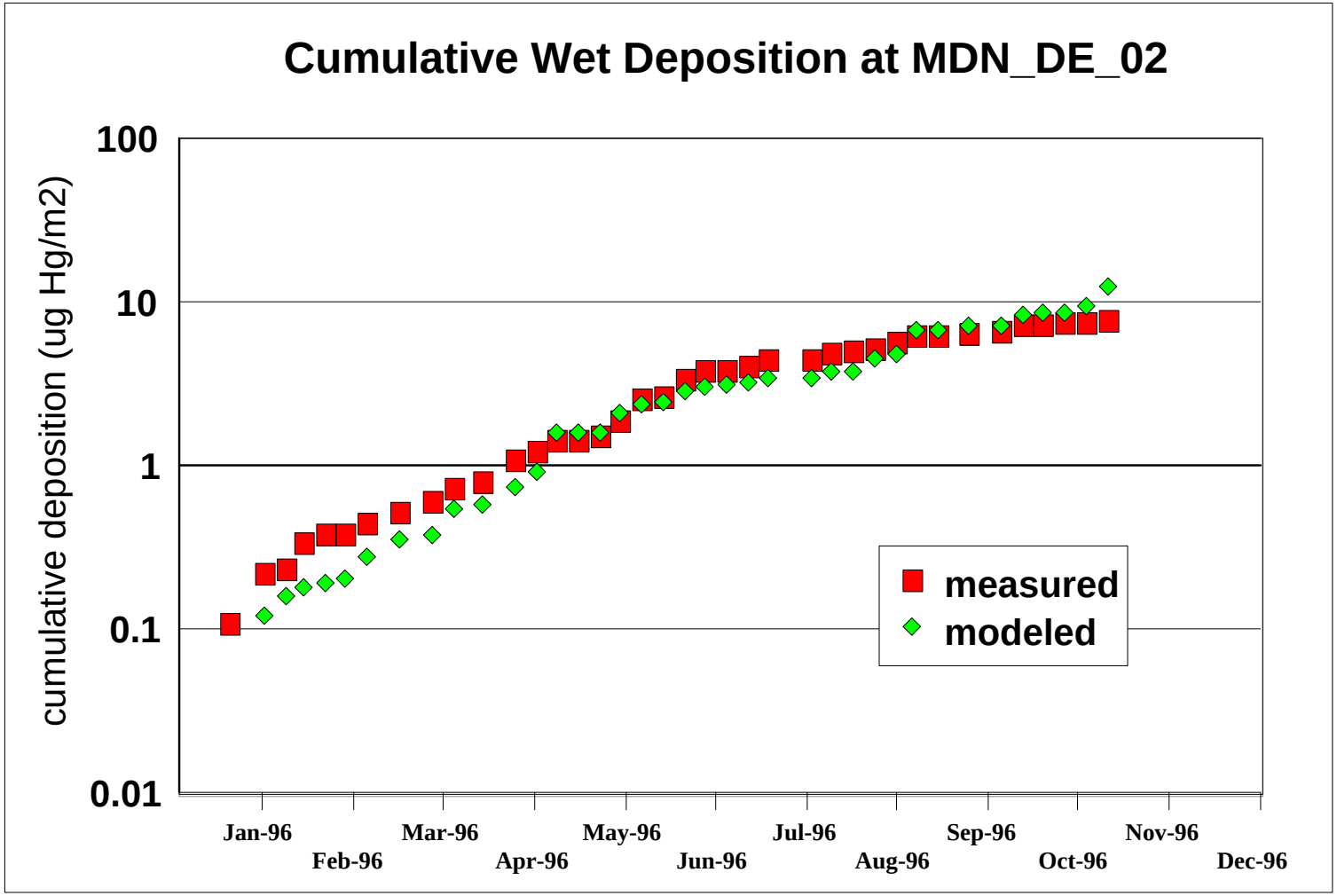
1995 Global Hg Emissions Inventory
Josef Pacyna,NILU, Norway (2001)

Model Evaluation

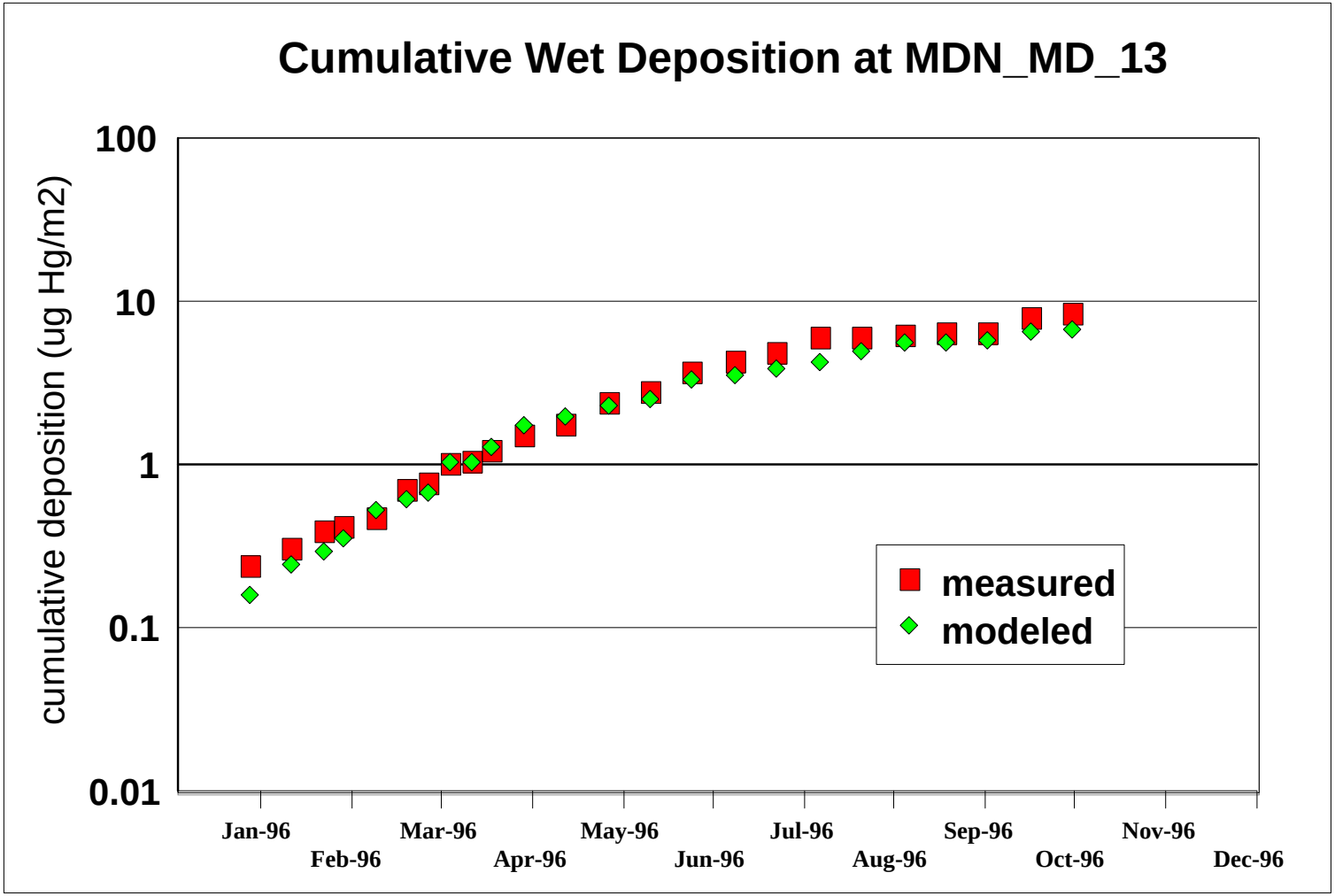
Mercury Deposition Network Sites with 1996 data in the Chesapeake Bay Region



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

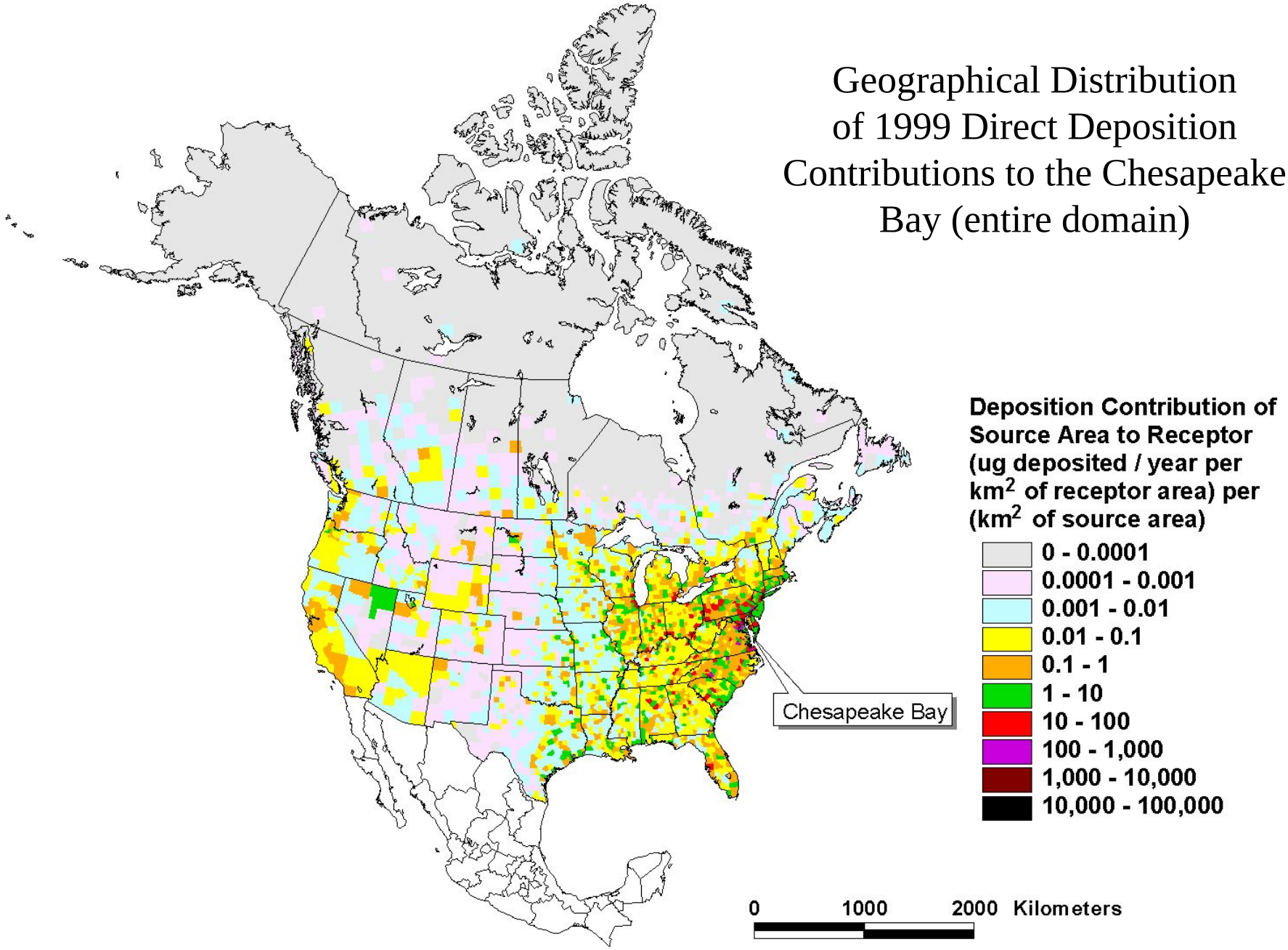


Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site MD_13 during 1996

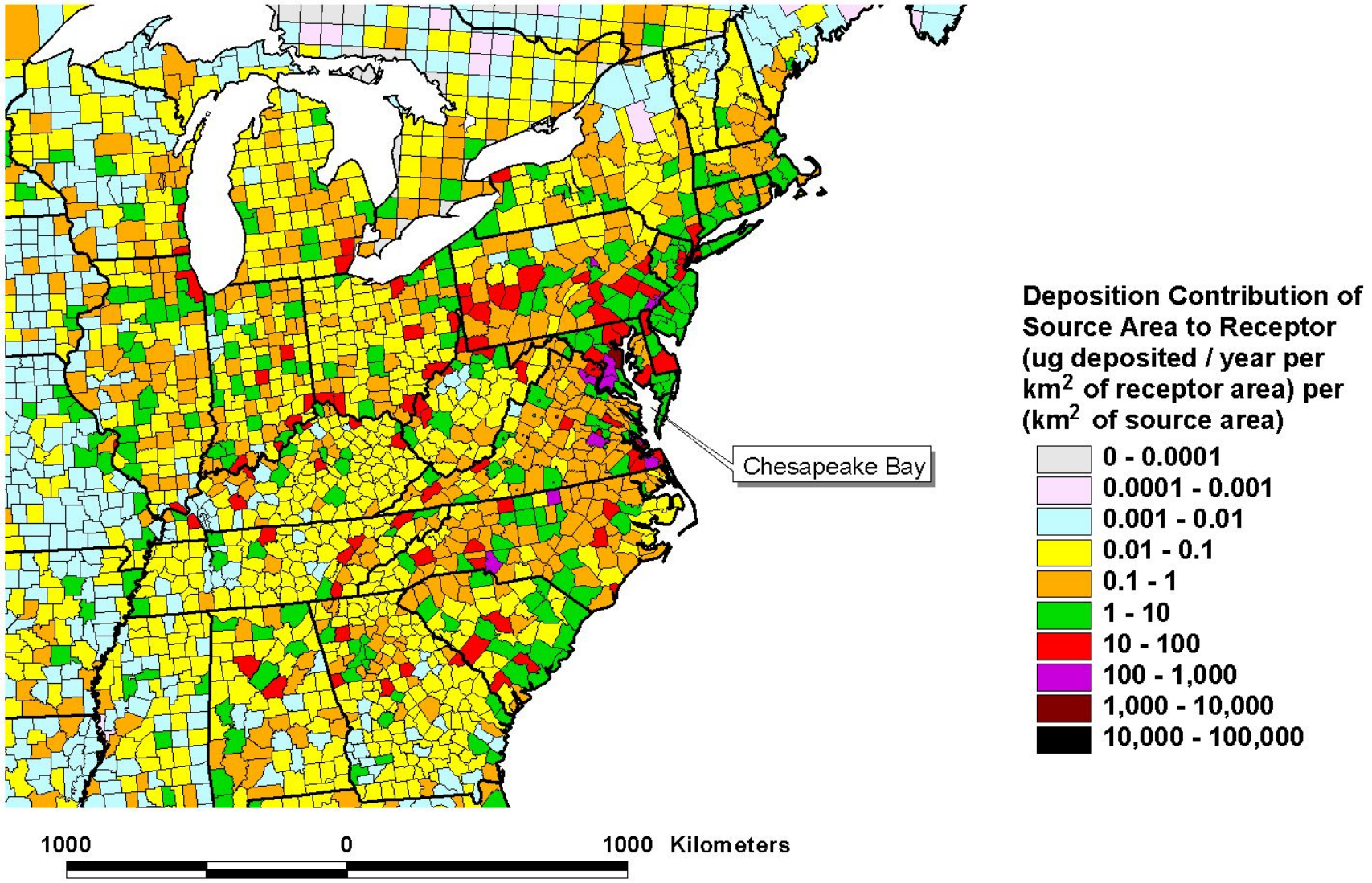


1999 Results for Chesapeake Bay

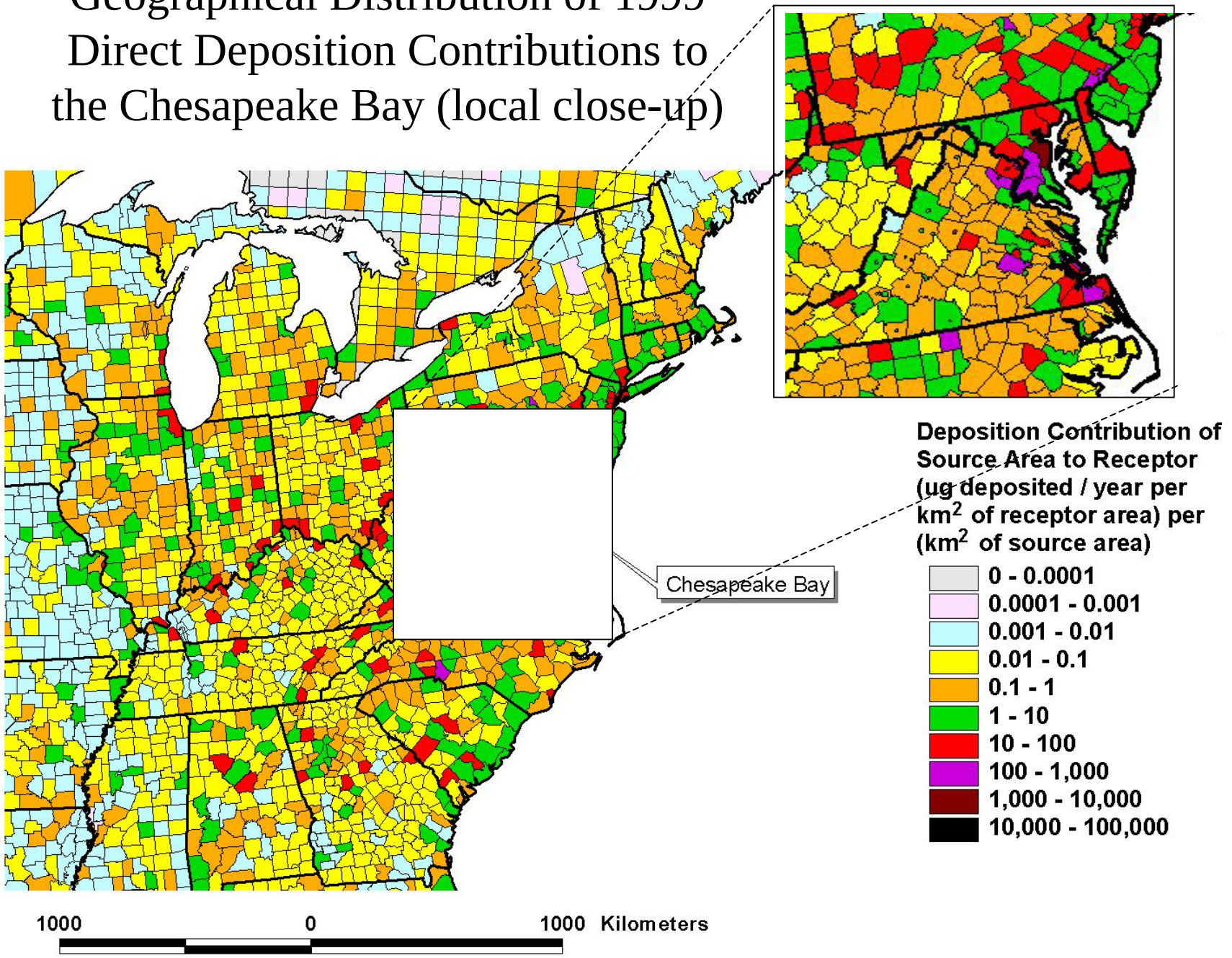
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)



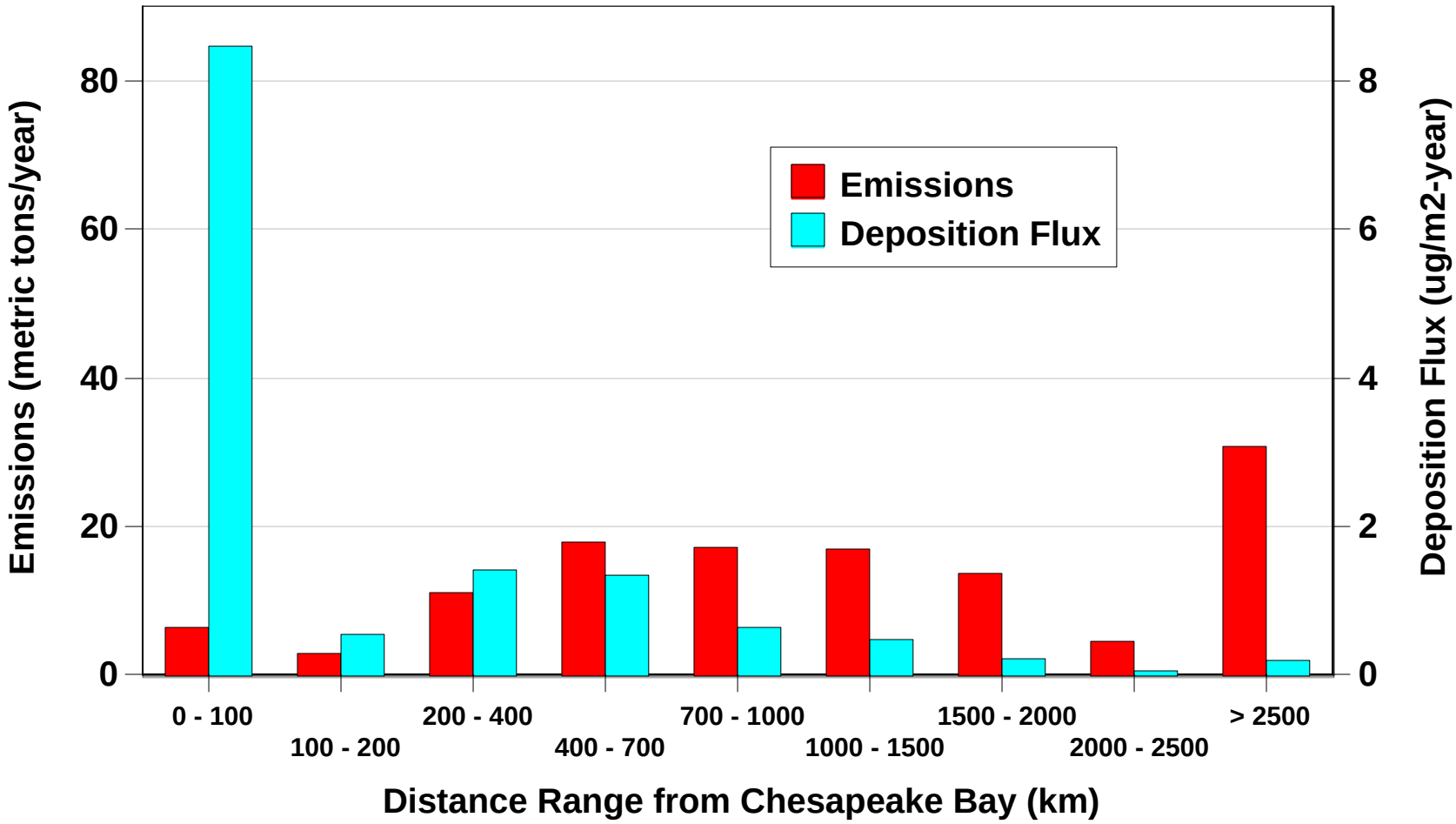
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)



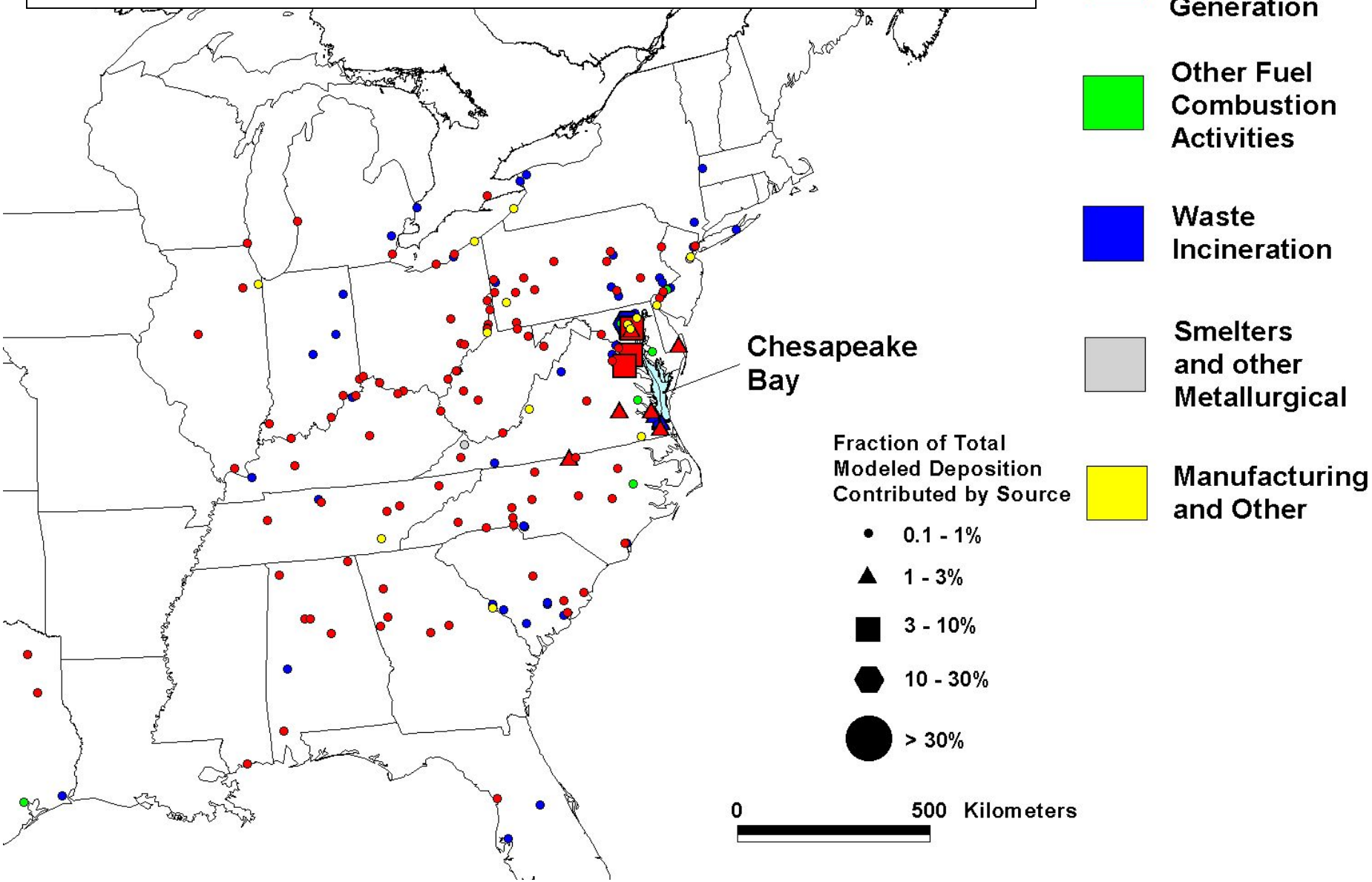
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)



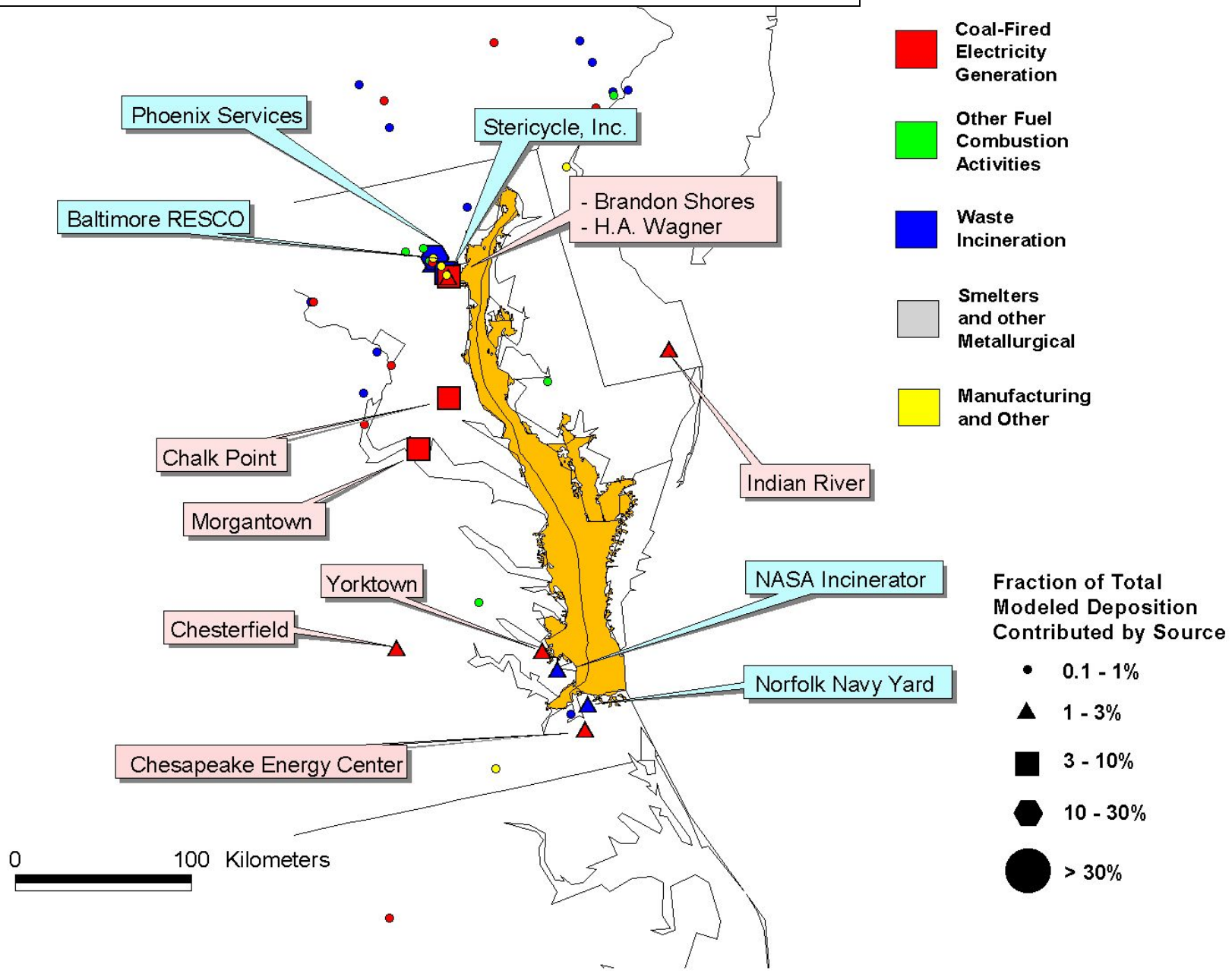
Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay



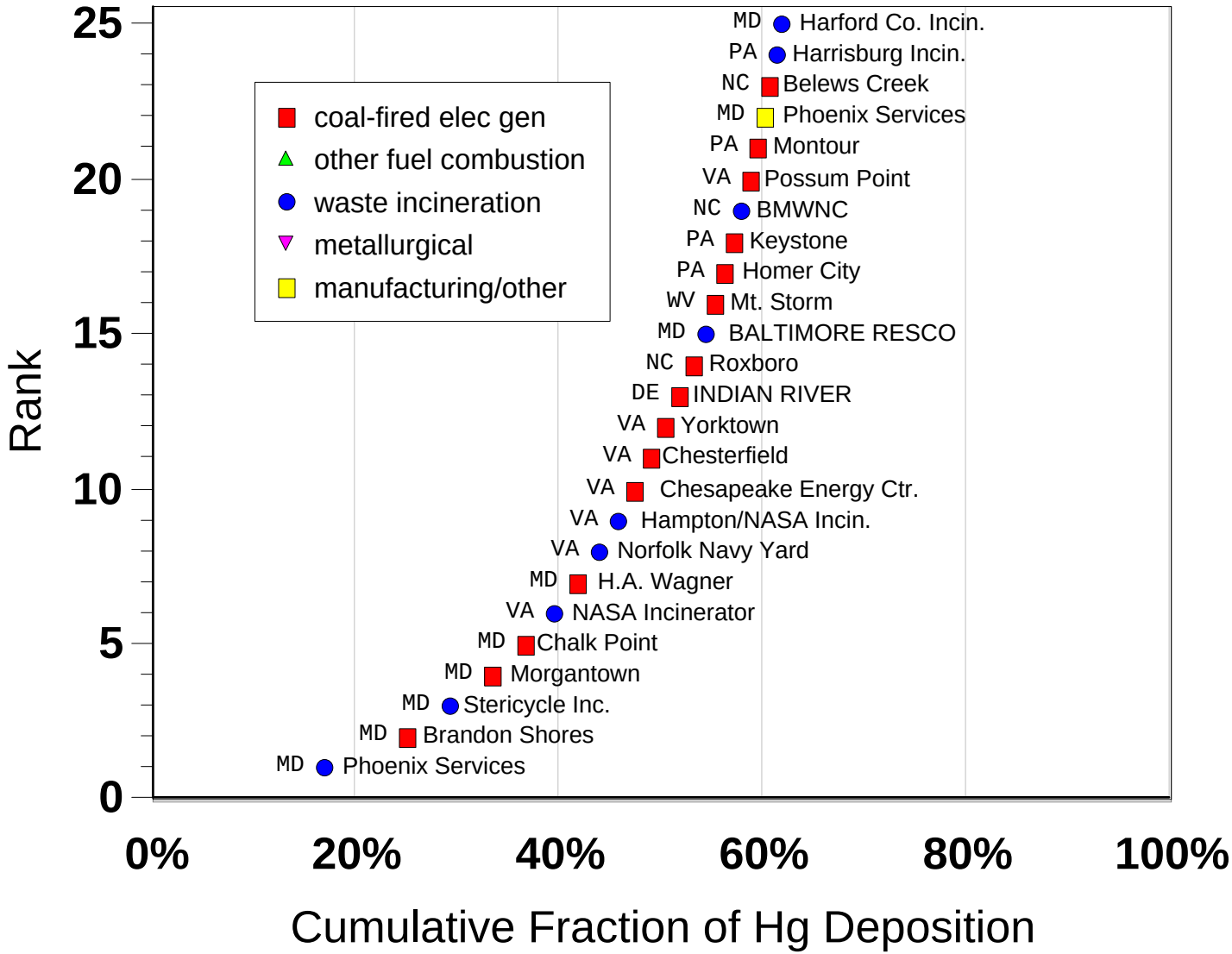
Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



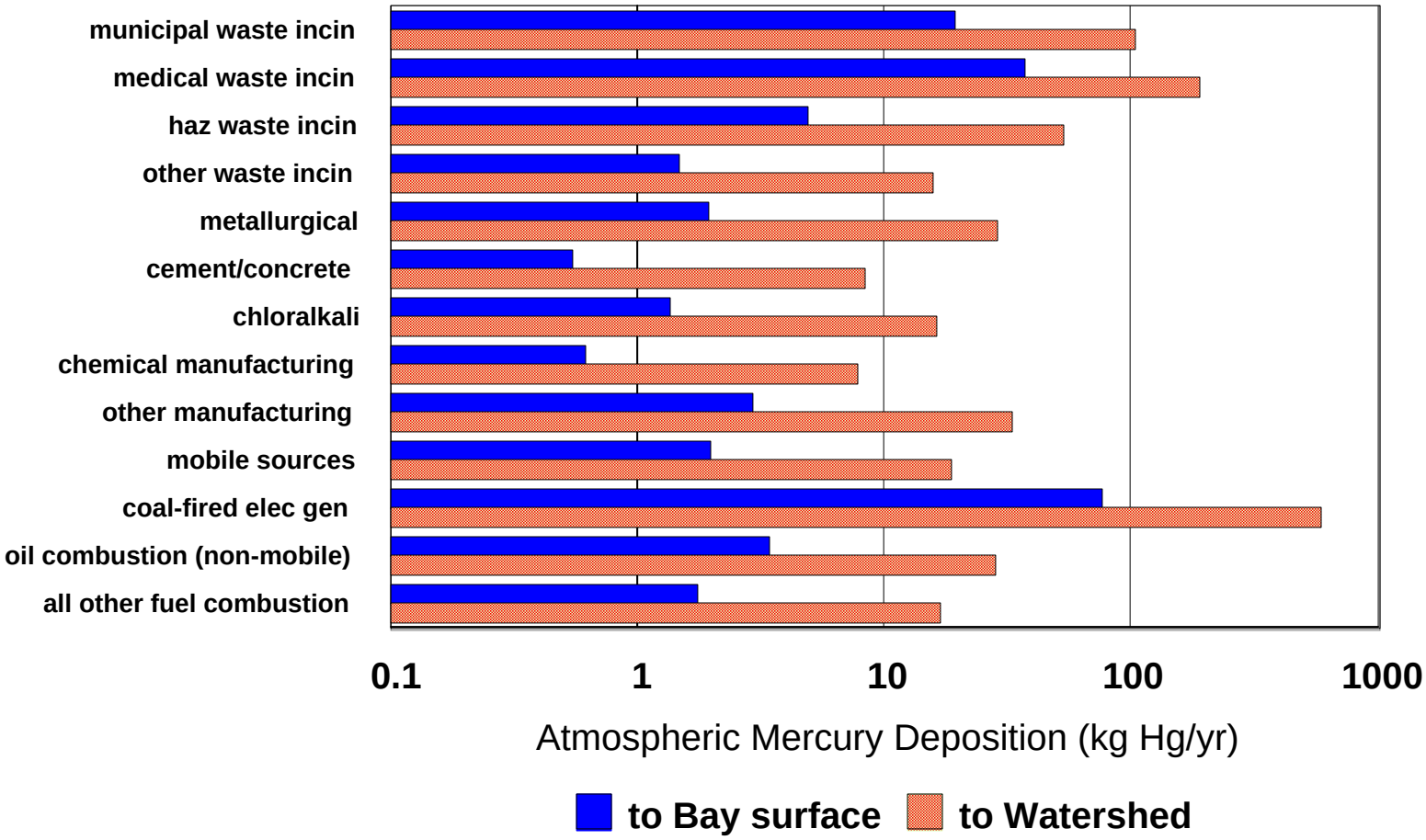
Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay



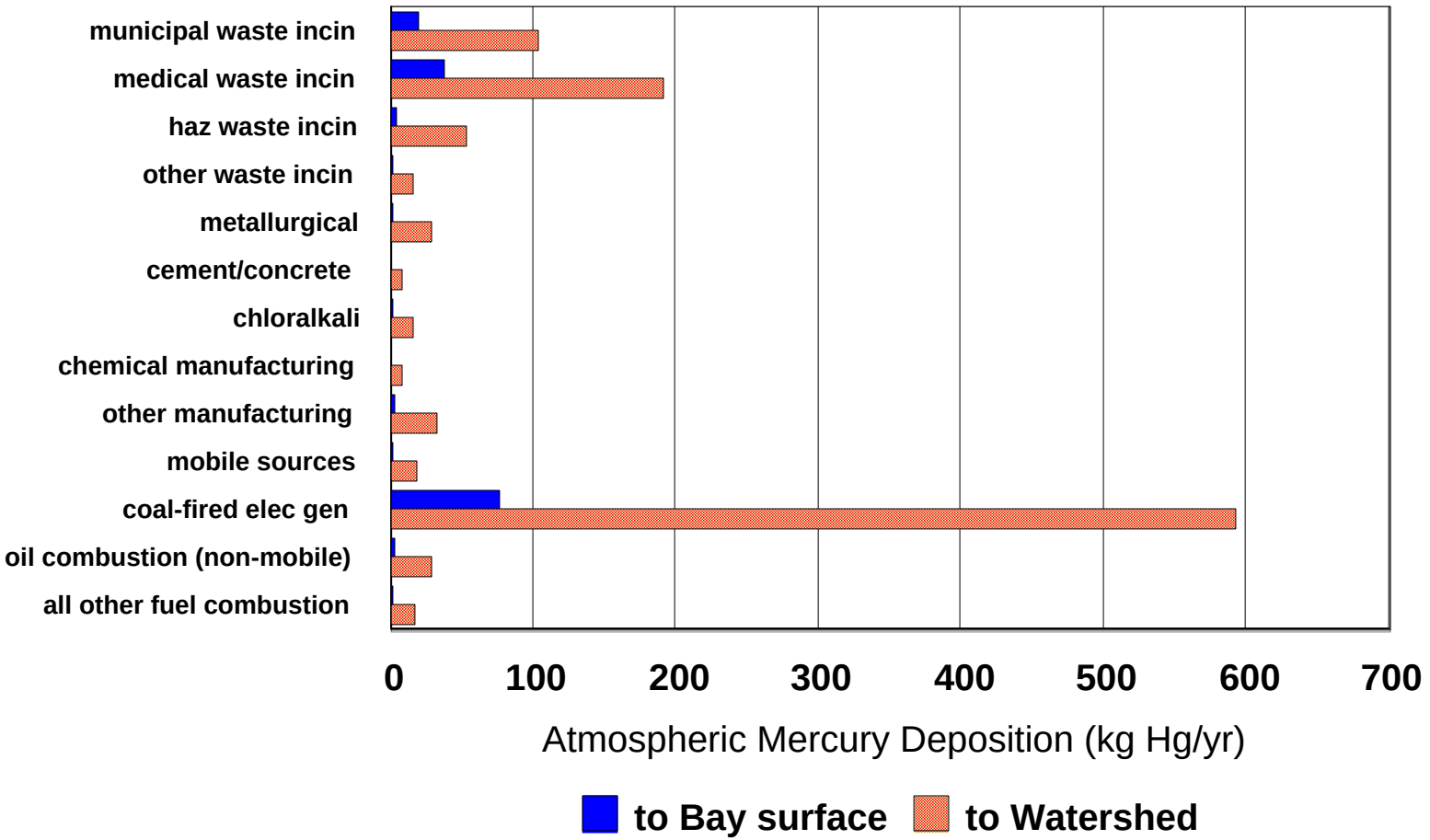
Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay



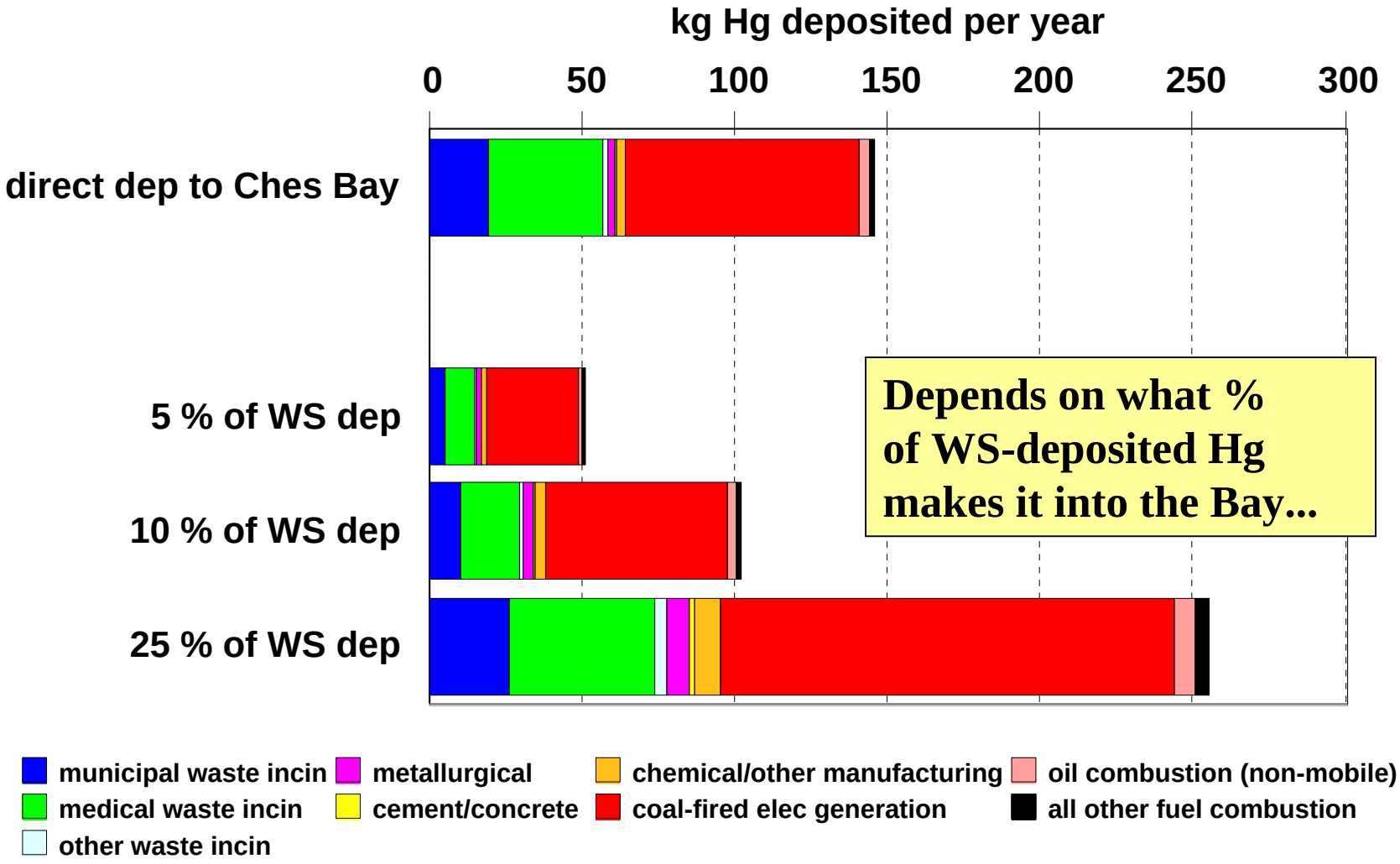
Deposition to the Chesapeake Bay and to its Watershed (~1999) (logarithmic graph)



Deposition to the Chesapeake Bay and to its Watershed (~1999) (linear graph)

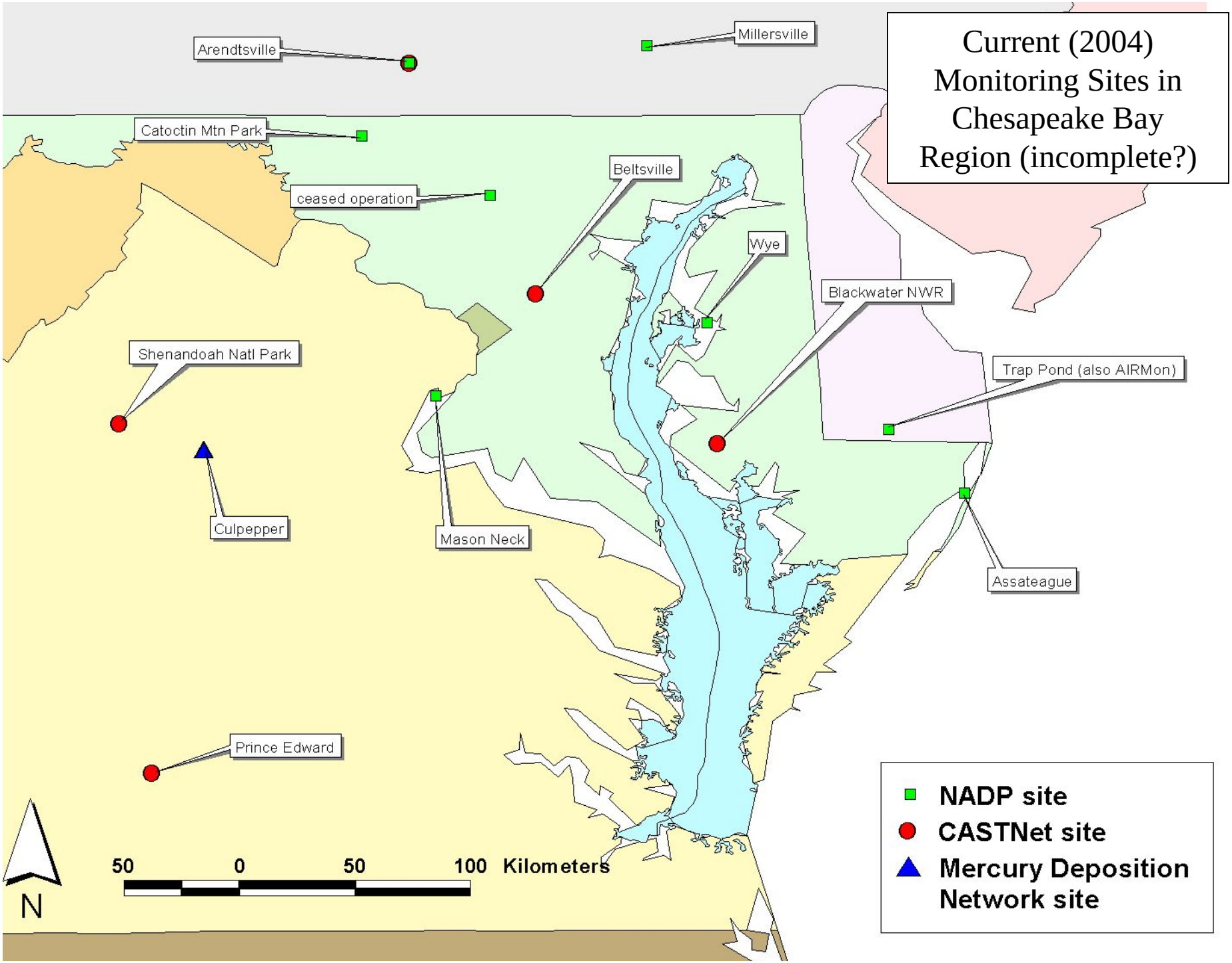


What is Relative Importance of Hg Deposited Directly to Chesapeake Bay Surface vs. Deposition to Watershed (?)



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 (e.g., not just wet deposition).
- Sensitivity analyses and examination of atmospheric Hg chemistry in the marine boundary layer and at upper elevations...


Current (2004) Monitoring Sites in Chesapeake Bay Region (incomplete?)
Arendtsville
Millersville
Catoctin Mtn Park
ceased operation
Beltsville
Wye
Blackwater NWR
Shenandoah Natl Park
Trap Pond (also AIRMon)
Culpepper
Mason Neck
Assateague
Prince Edward
N
50 0 50 100 Kilometers
NADP site
CASTNet site
Mercury Deposition Network site