Source-attribution for atmospheric mercury deposition: Where does the *mercury* in *mercury deposition* come from?

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

Presentation given via speakerphone to a meeting of the Mercury Working Group, Office of Air Quality, Indiana Department of Environmental Management (IDEM)
April 21, 2005

For mercury, how important is atmospheric deposition relative to other loading pathways?

Estimates of the Percent of Great Lakes Loadings Attributable to the Atmospheric Deposition Pathway

Pollutant	Lake Superior	Lake Michigan	Lake Huron	Lake Erie	Lake Ontario
DDT	97[a]	98[a]	97[a]	22[a]	31[a]
Lead	97[a]; 64[b]; 69[d]	99[a]	98[a]	46[a]	73[a]
Mercury	73[d]	> 80[j]	k	k	k
PCB's	90[a]; ~ 95[b,c]; 82[d]	58[a]	78[a]	13[a]	7[a]
PCDD/F	~100[e] ~80[f]	50-100[e] (PCDD) 5-35[e] (PCDF) 88[f]	86[f]	~40[f]	5-35 (PCDD)[e] < 5 (PCDF)[e]
Benzo(a)pyrene	96[a]	86[a]	80[a]	79[a]	72[a]
Hexachloro-benzene	99[f]	95[f]	96[f]	> 17[f]	40[f]
Atrazine	97[h]	~30[g]; 23[h]	~20[h]	~10-20[h]	~5[h]
Mirex	k	k	k	k	~5[a]

References and Notes

(a) Strachan and Eisenreich (1988), percentages of total inputs; (b) Hoff *et al.* (1996); (c) Net loss of PCB's to the atmosphere of 1600 kg/year; total non-atmospheric inputs of approximately 70 kg/year; (d) Dolan *et al.* (1993); (e) Pearson *et al.* (1998); (f) Cohen *et al.* (1995); (g) Rygwelski et al. (1999); (h) Schottler and Eisenreich (1997); (j) Mason and Sullivan (1997); (k) no estimates could be found

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?**

modeling the fate and transport of atmospheric mercury

Atmospheric Fate Processes for Hg

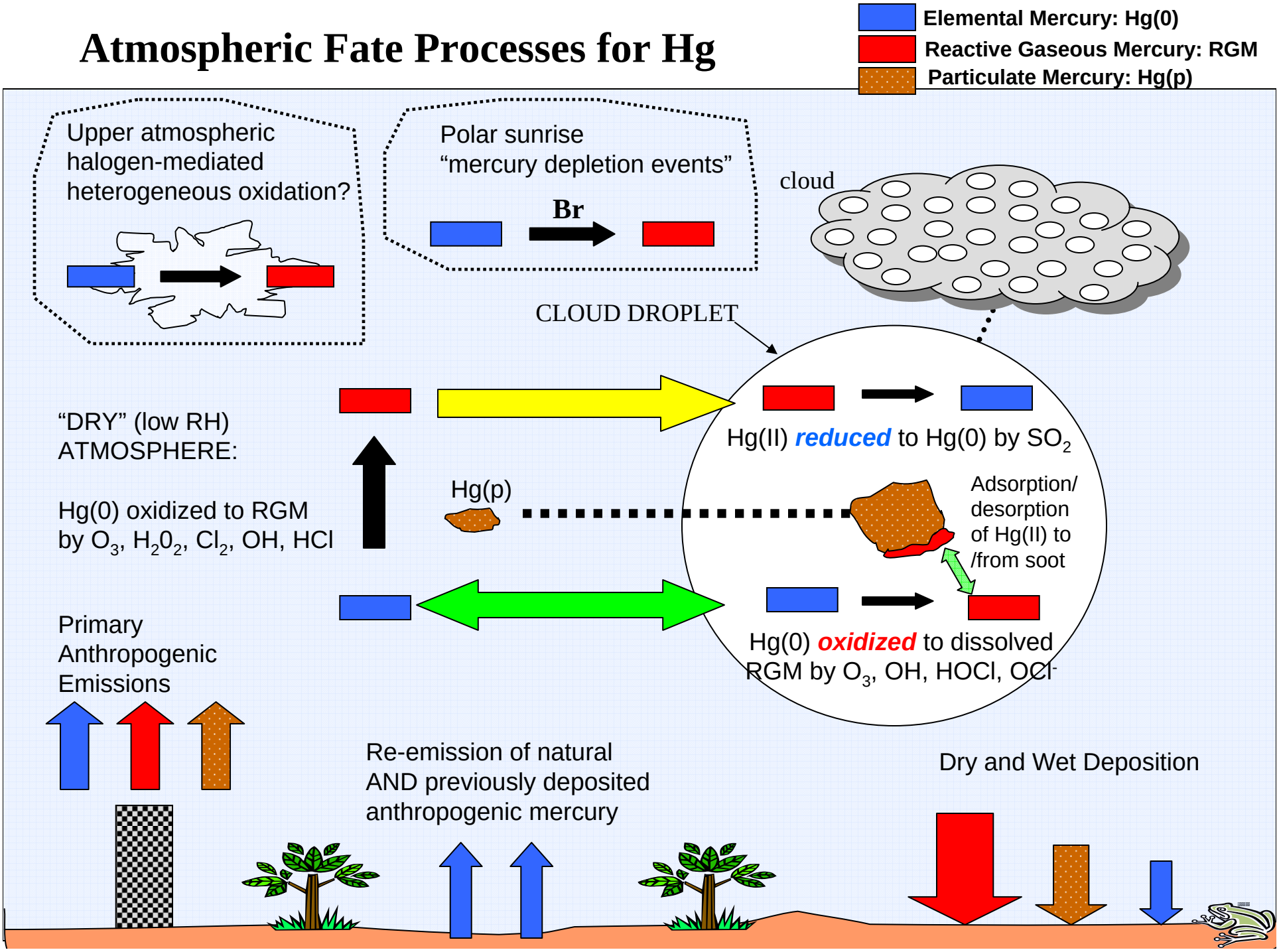
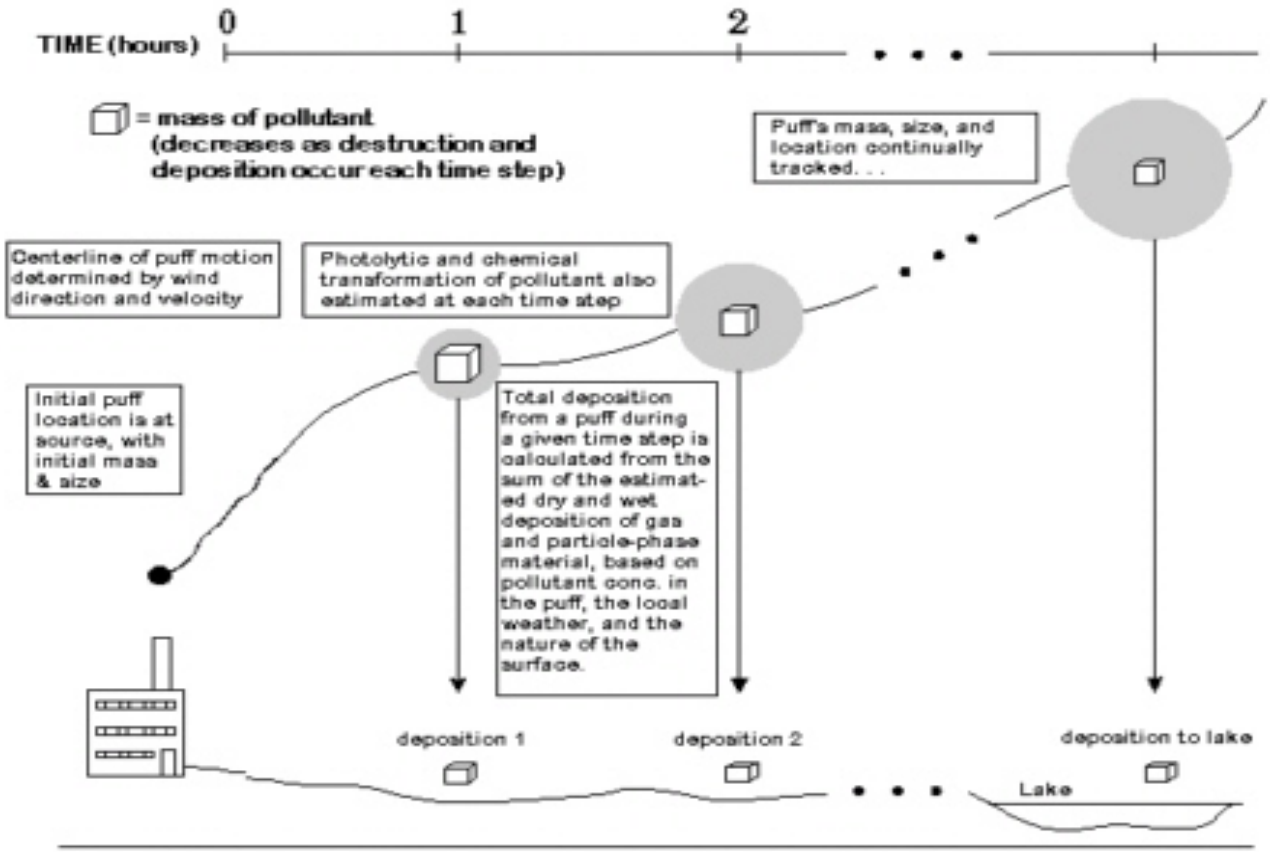
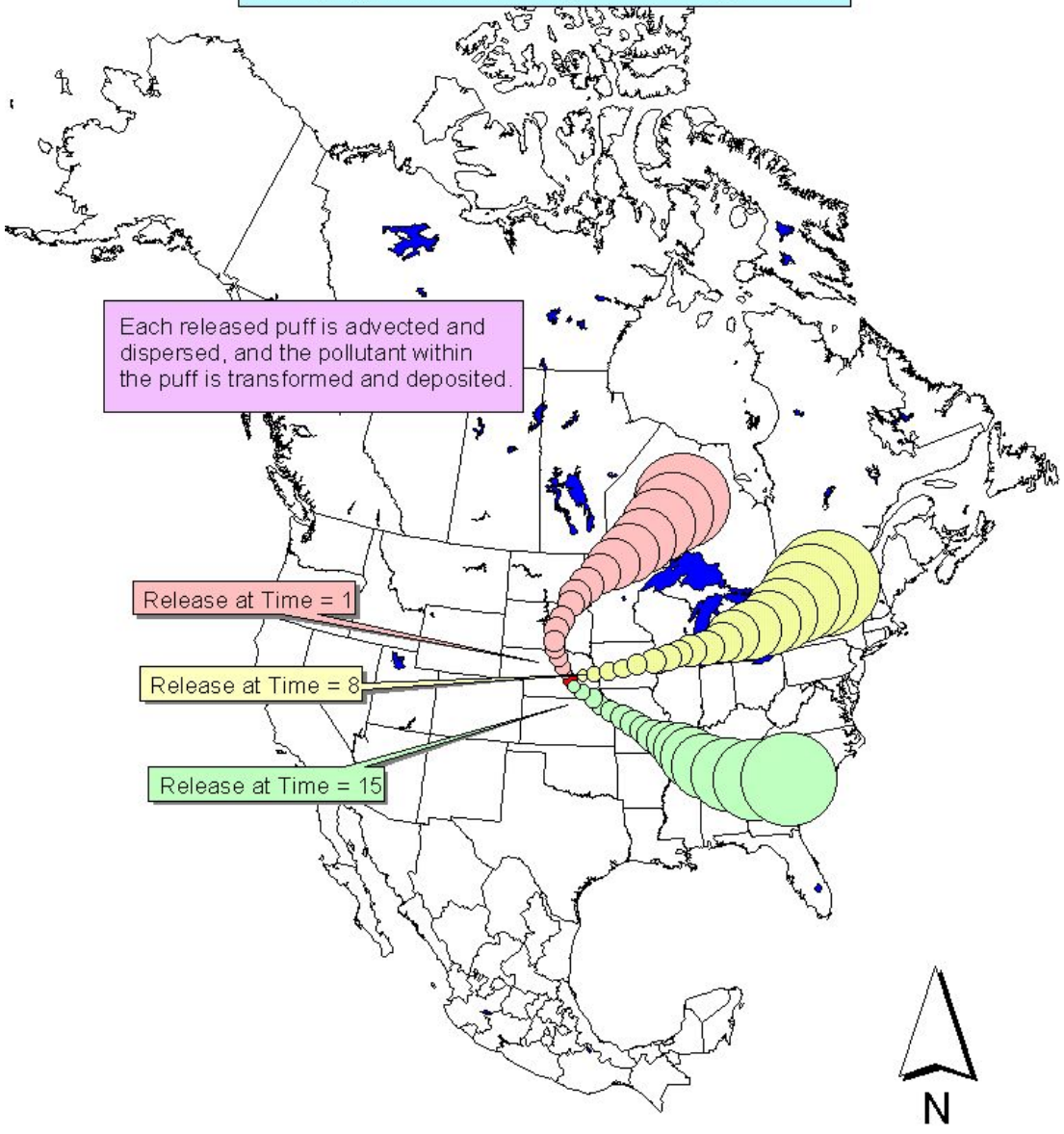


Figure 1. Lagrangian Puff Air Transport and Deposition Model

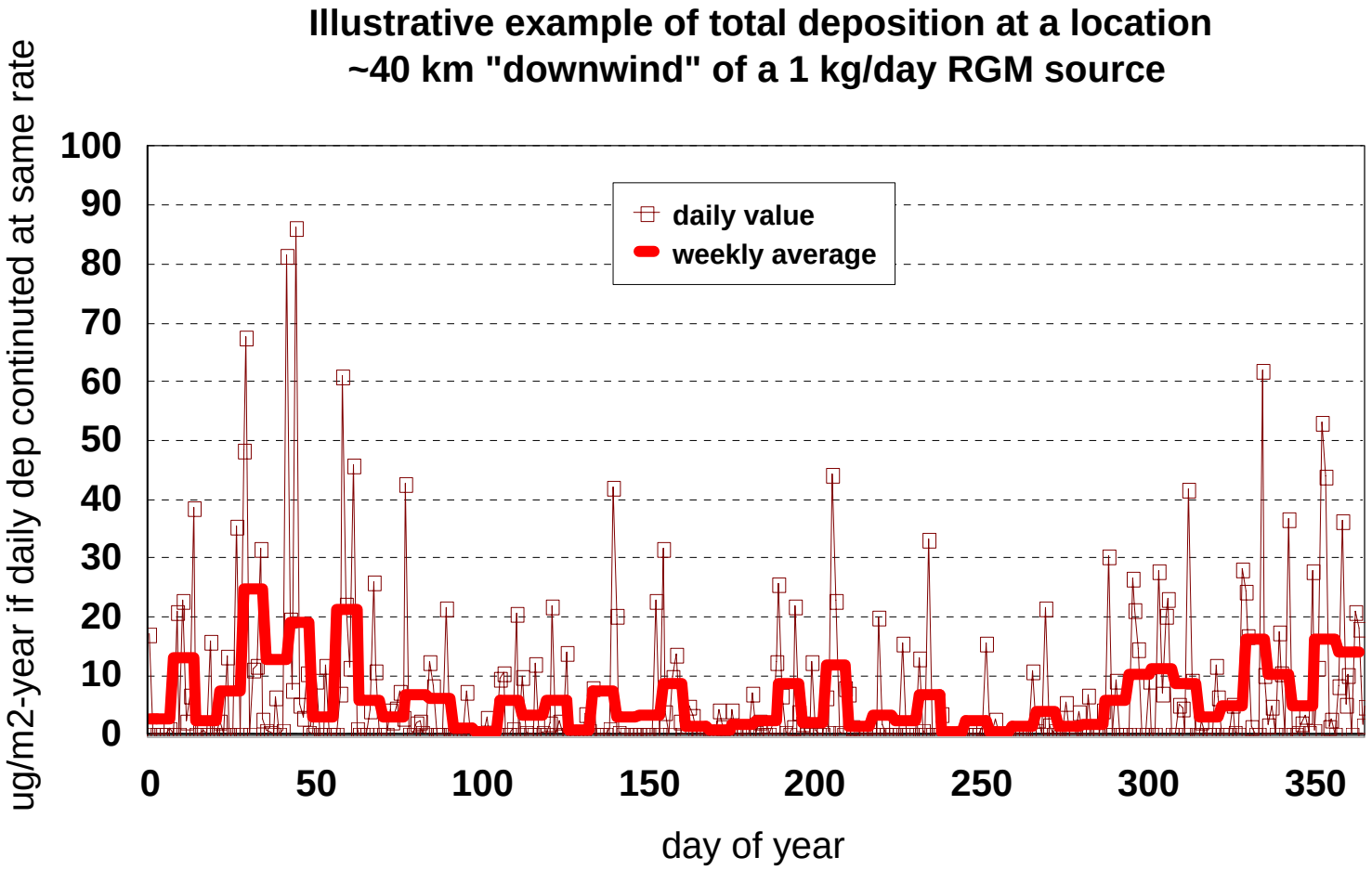


Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).



some illustrative modeling results

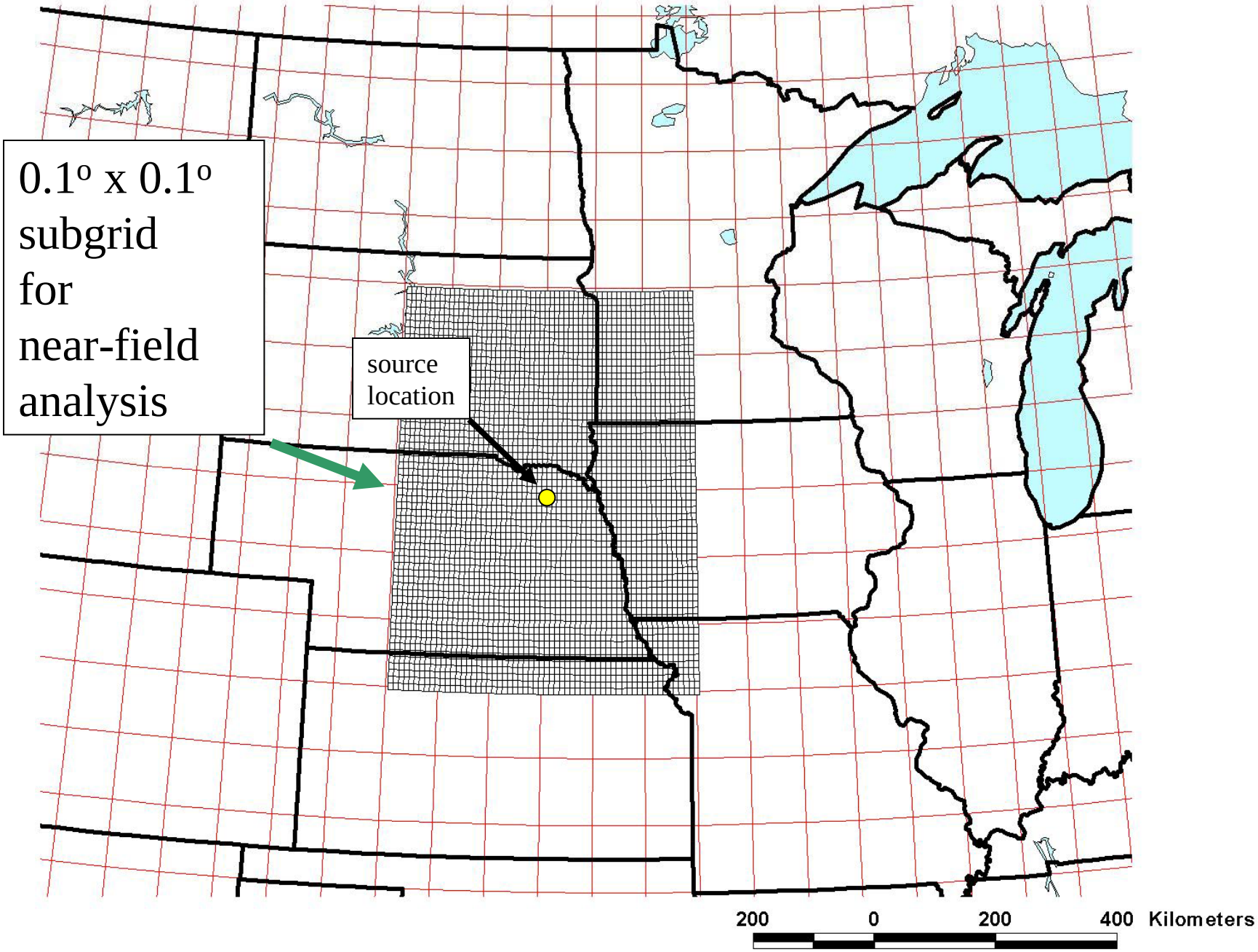
The impact of any given mercury emissions source on any receptor is highly variable, both in space and in time



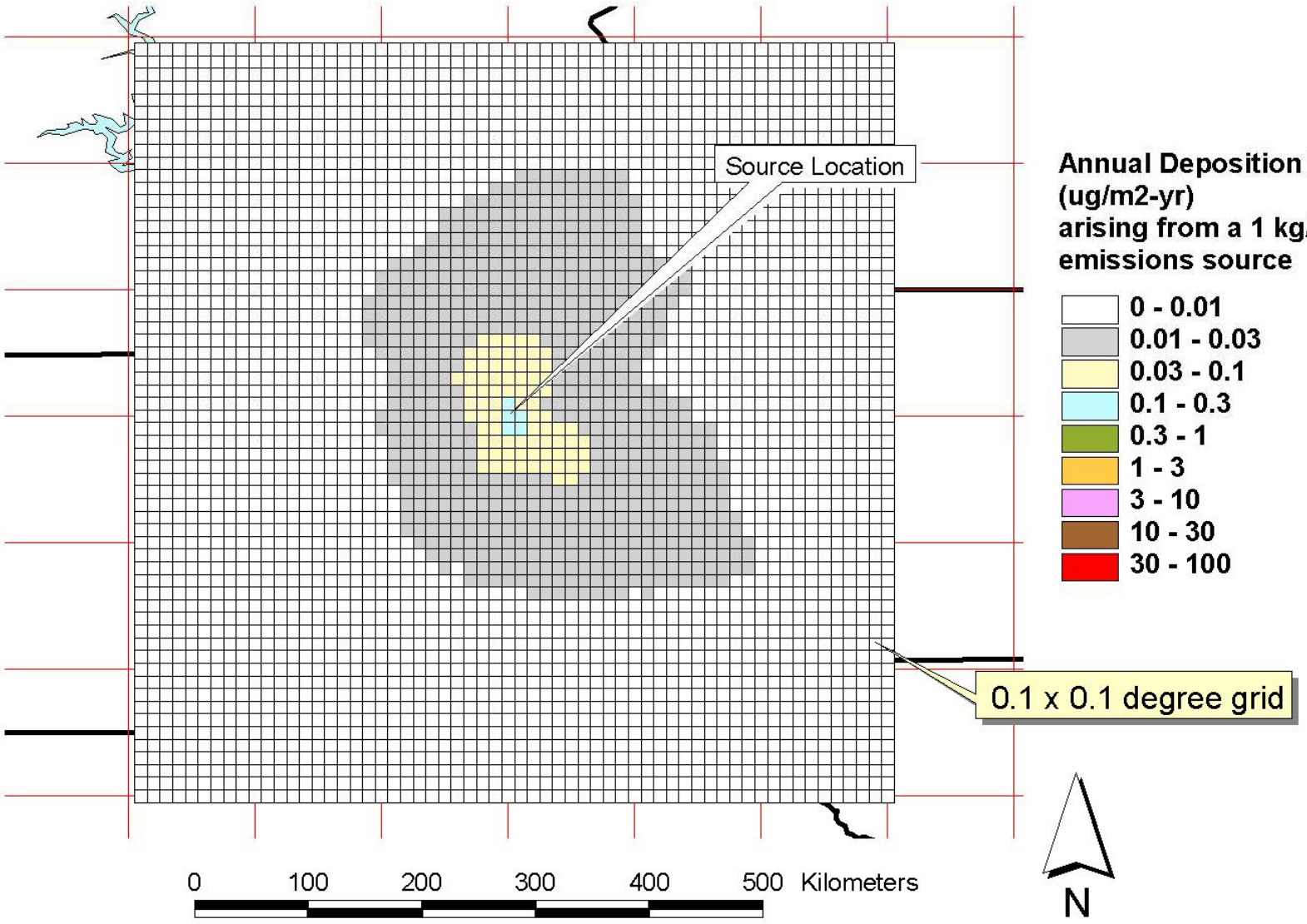
Think about the weather and then add in all the chemistry and physics of mercury's interactions with the weather

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 very easily dry and wet deposited**
  - ***Conversion of RGM to Hg^0 in plumes*?**

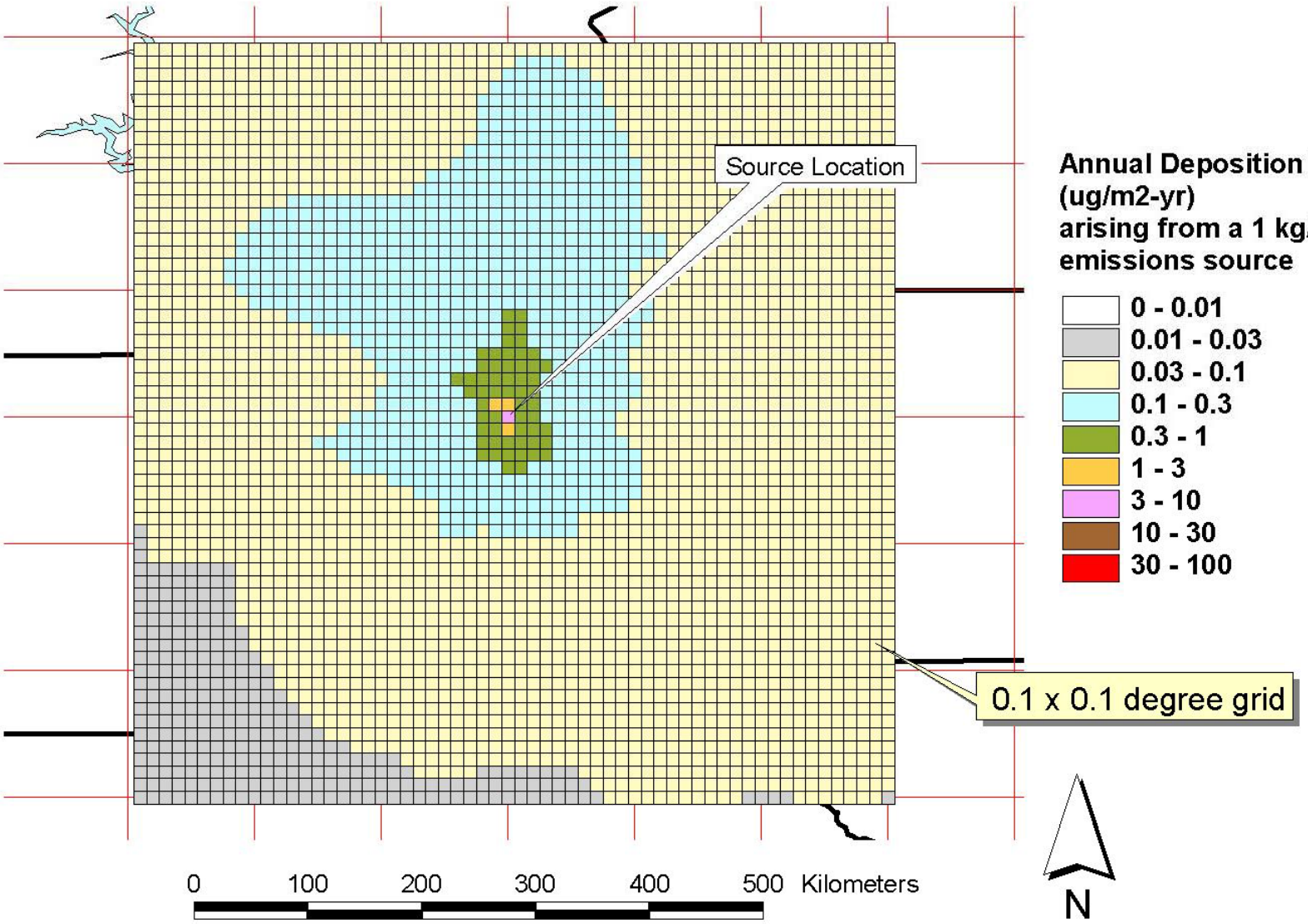

0.1° x 0.1° subgrid for near-field analysis
source location
200
0
200
400
Kilometers

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



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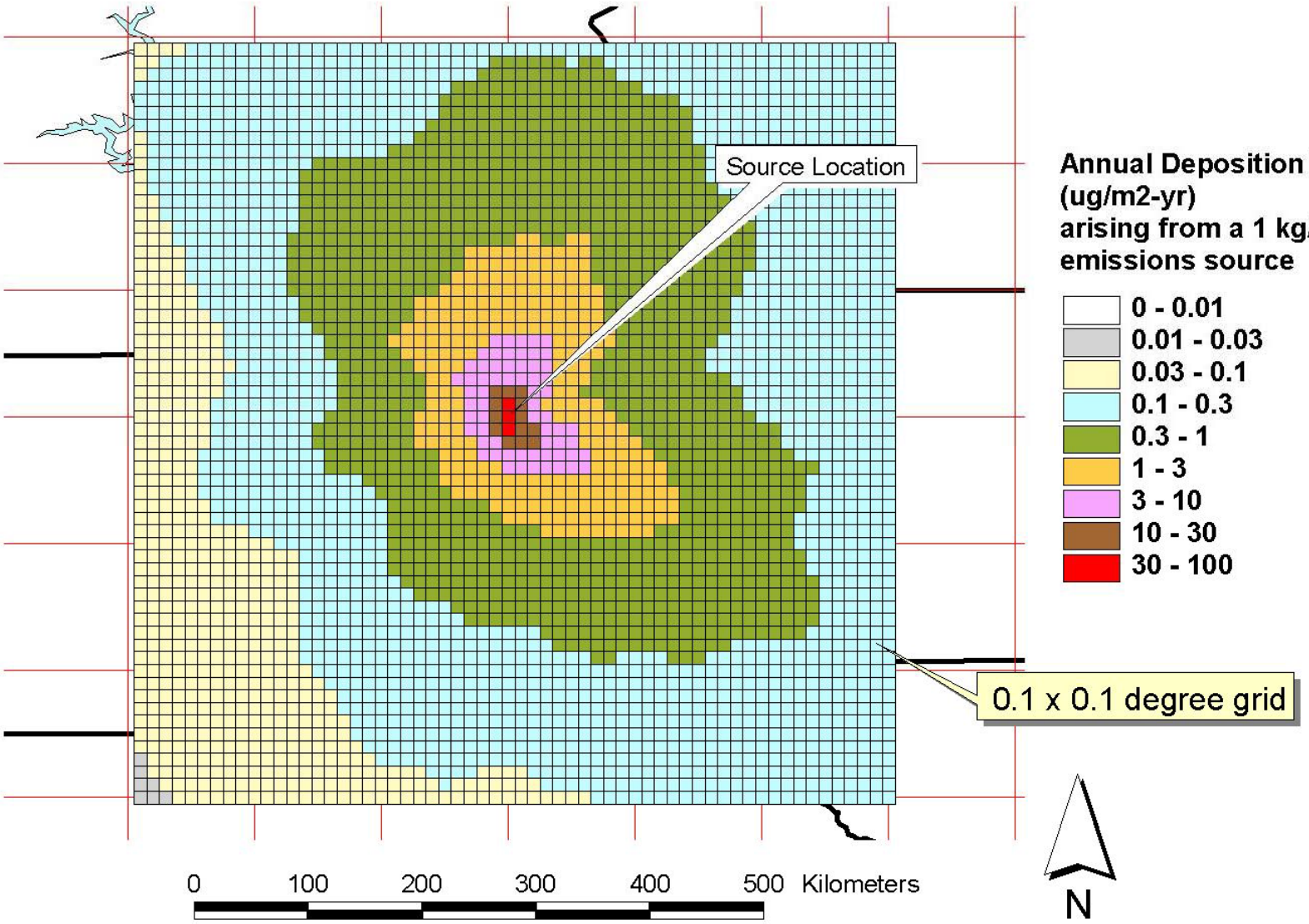
Annual deposition summary for emissions of ionic Hg from a 250 meter high source



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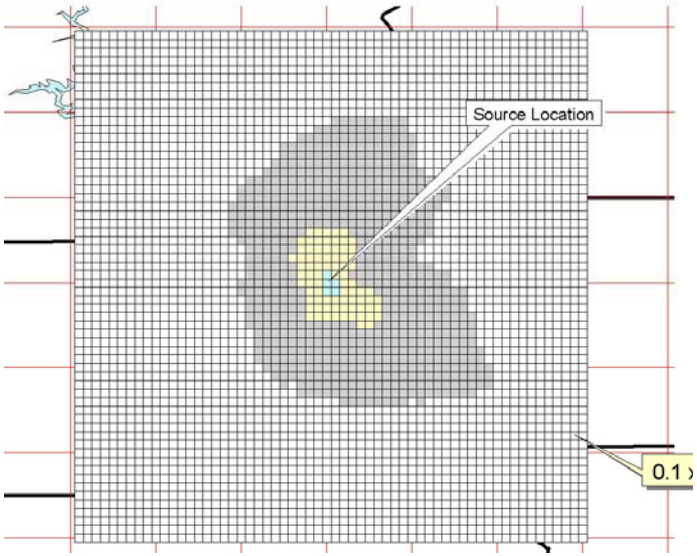
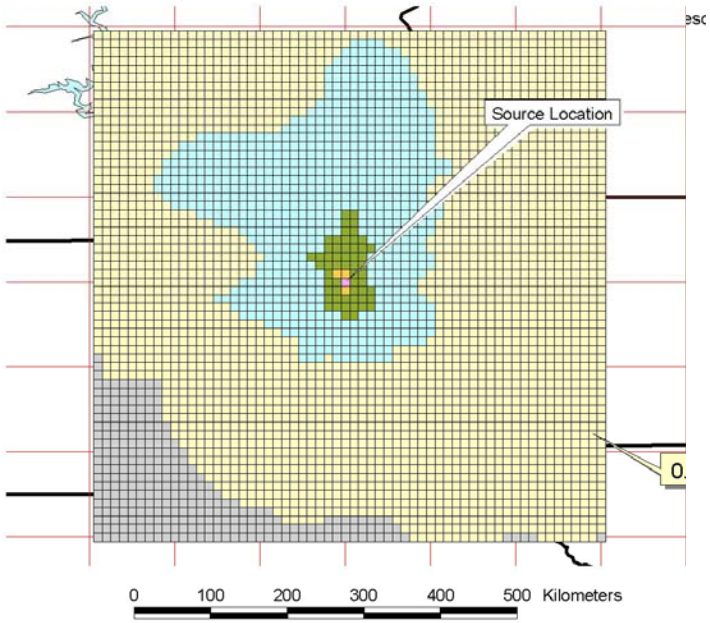


Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source

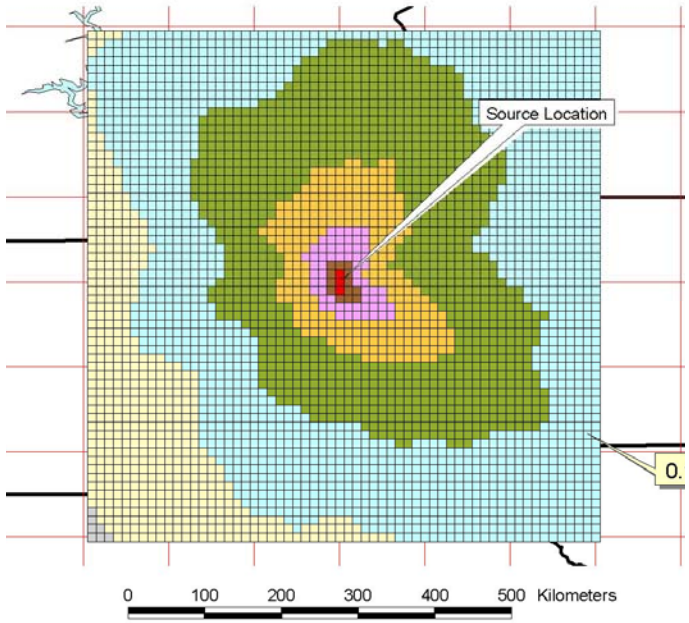
- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

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

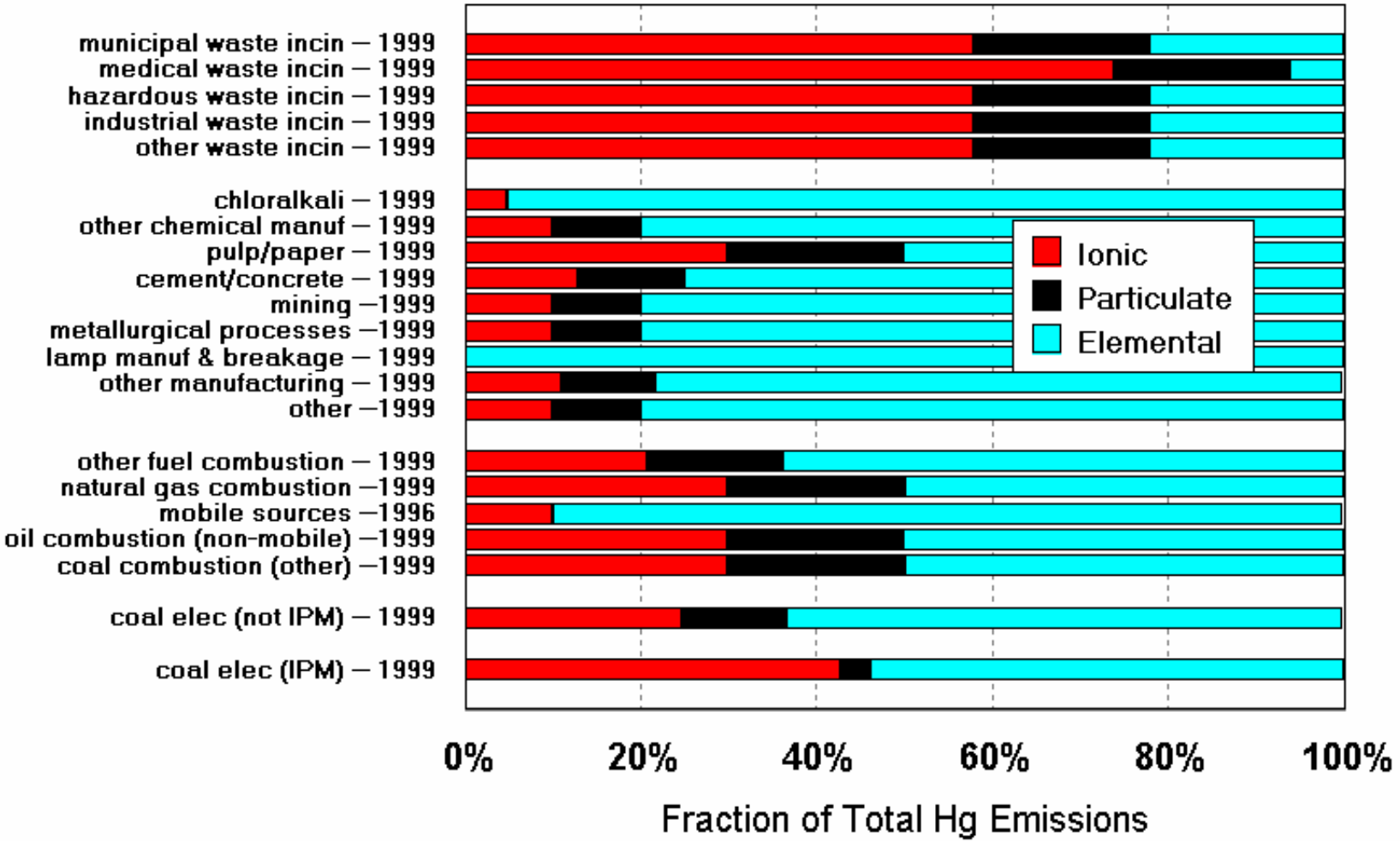
Annual deposition summary for emissions of ionic Hg from a 250 meter high source



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

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

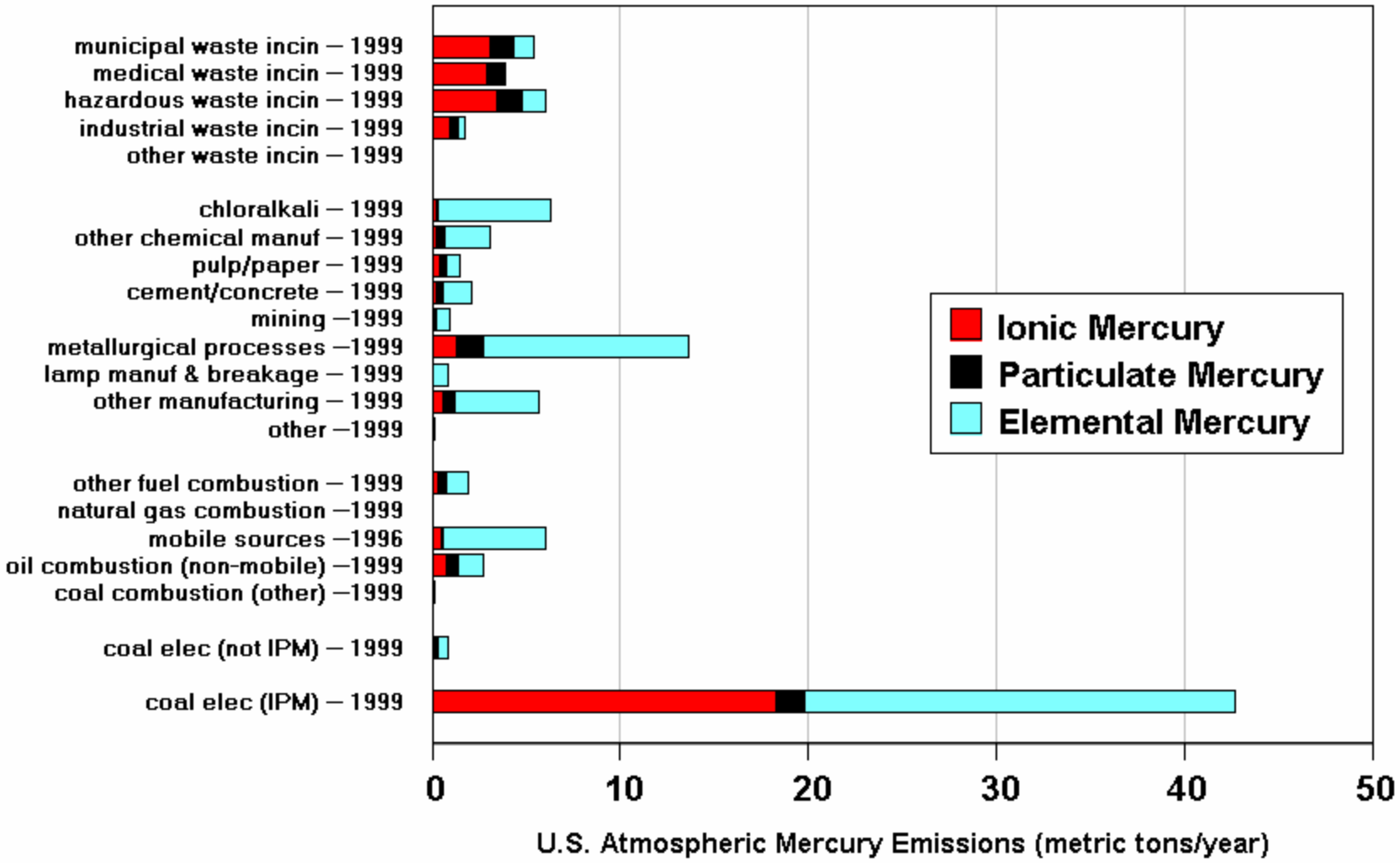
Very uncertain for most sources



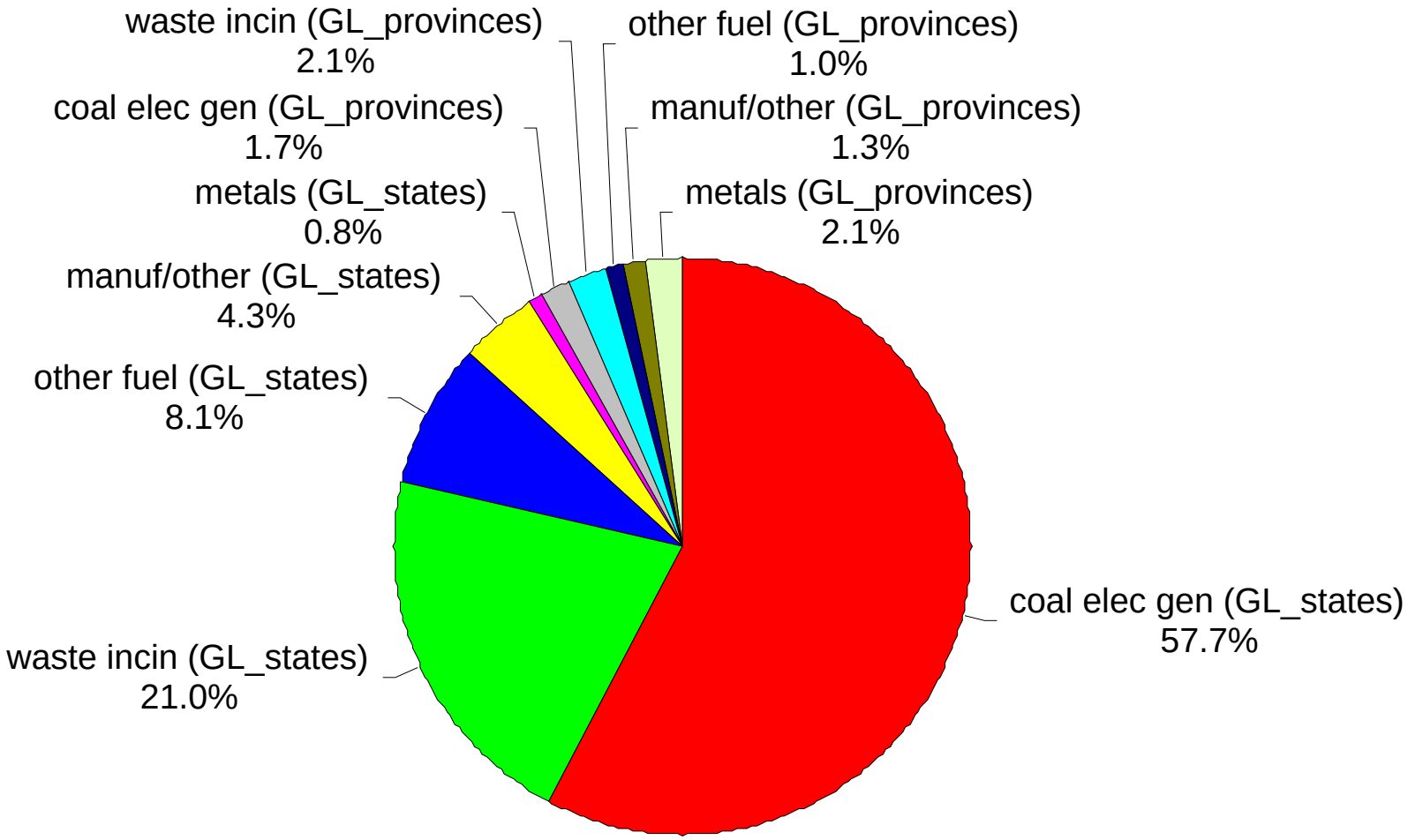
- **Each type of source has a very different emissions speciation profile**

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

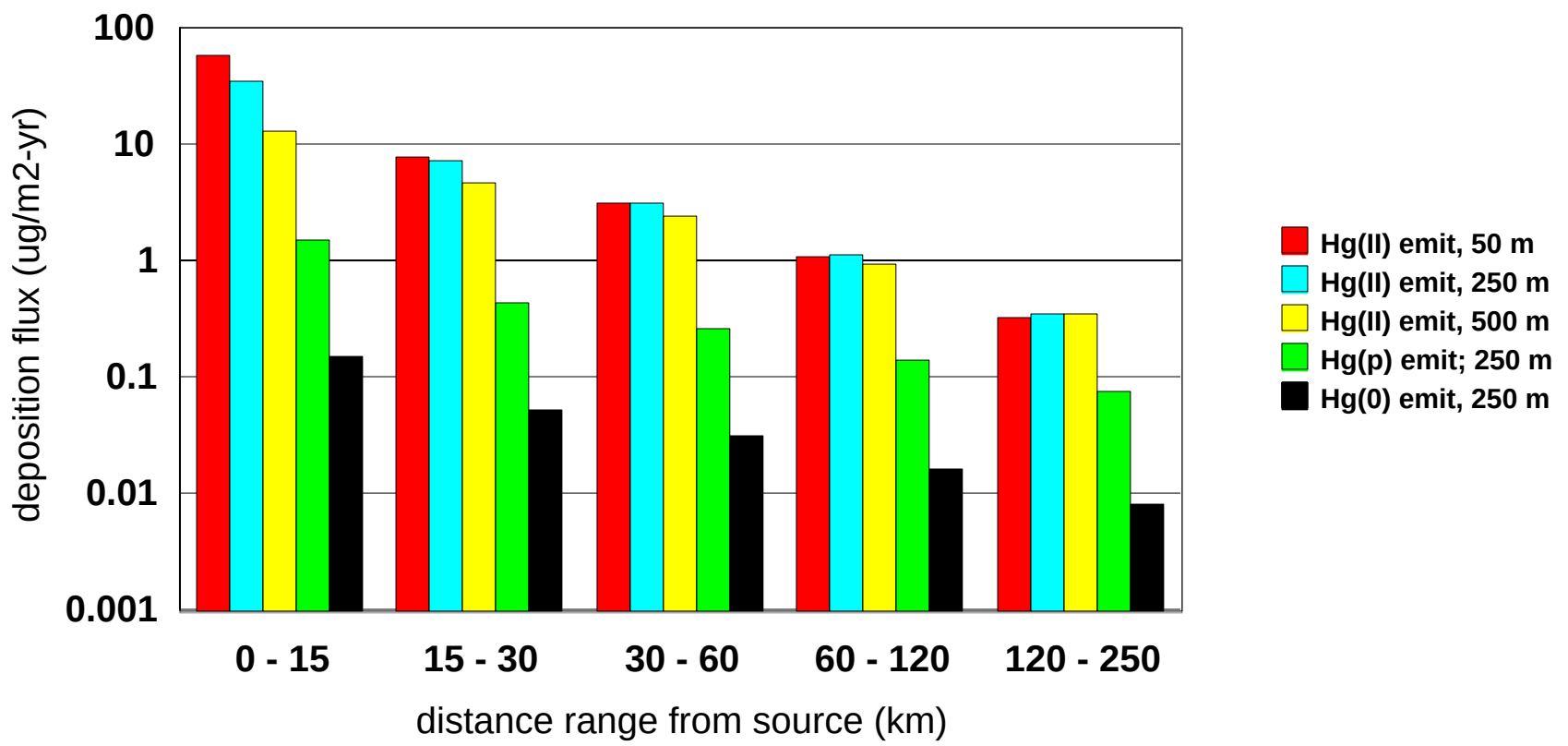
Estimated 1999 U.S. Atmospheric Anthropogenic Mercury Emissions



Emissions of Ionic Mercury (RGM) from Different Anthropogenic Source Sectors in Great Lakes States and Provinces (~1999-2000)
[Total RGM emissions = 13.4 metric tons/year]



There can be large local and regional impacts

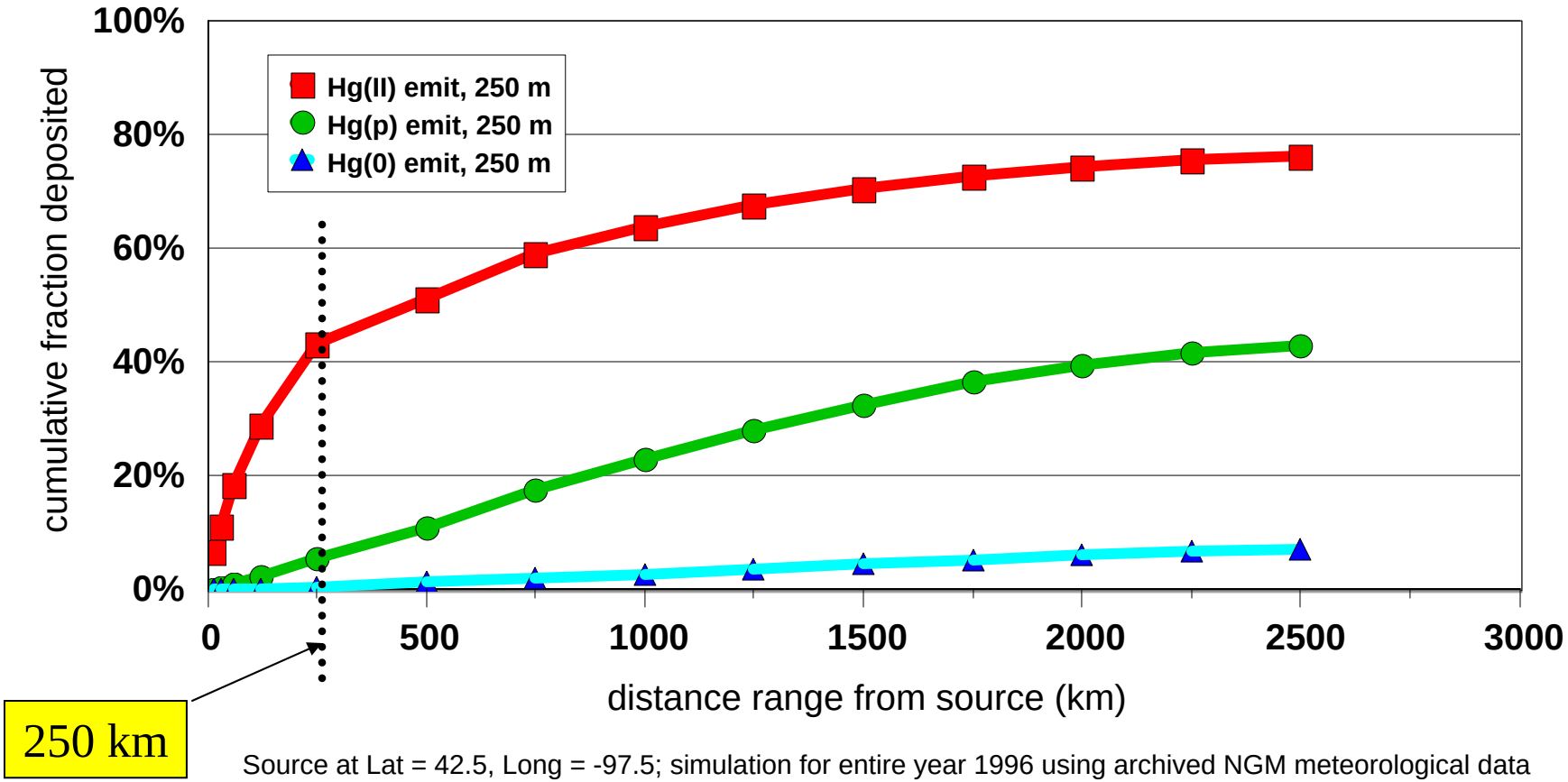


Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

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

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

Cumulative fraction deposited out to different distance ranges from a hypothetical source

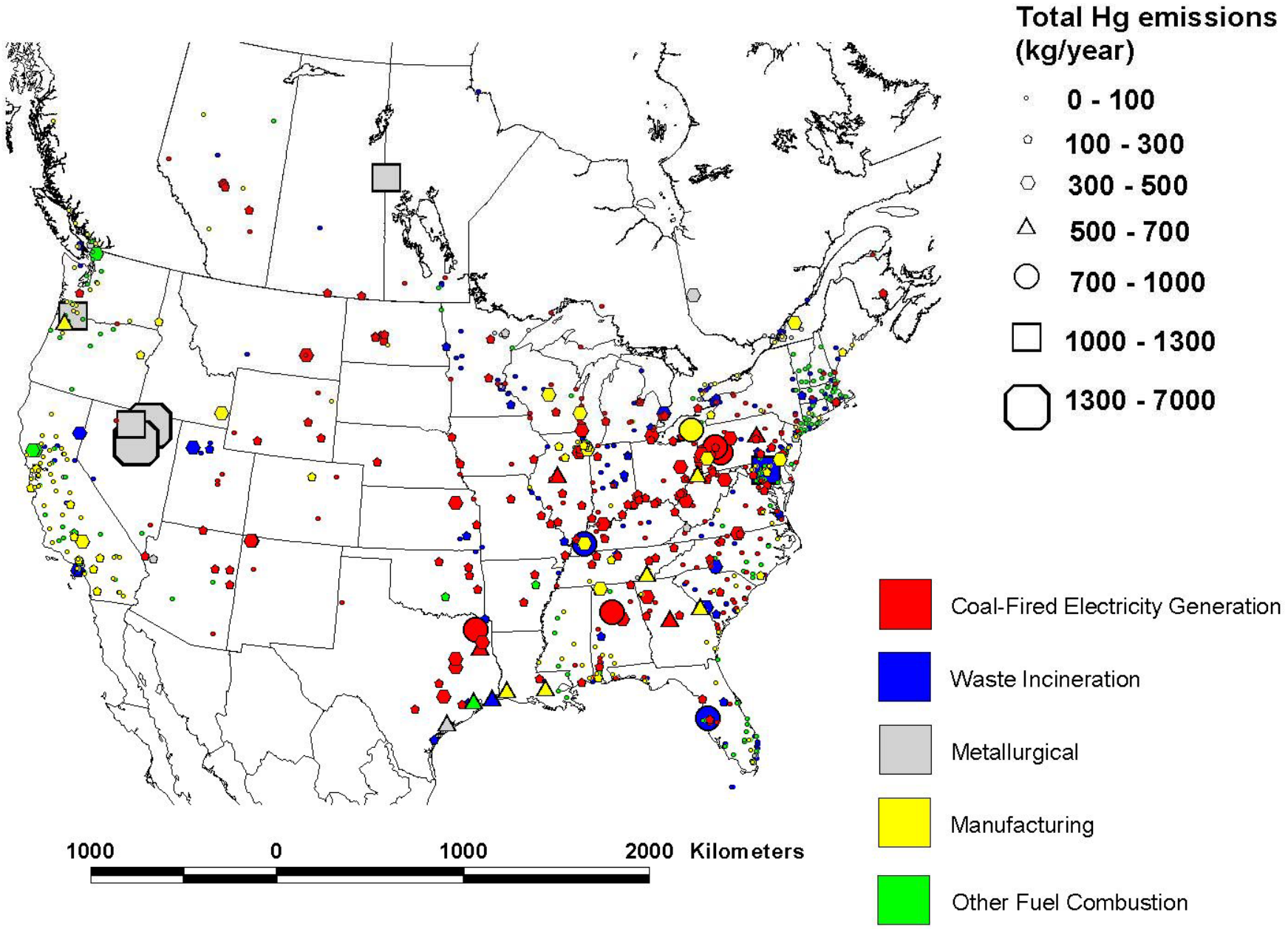


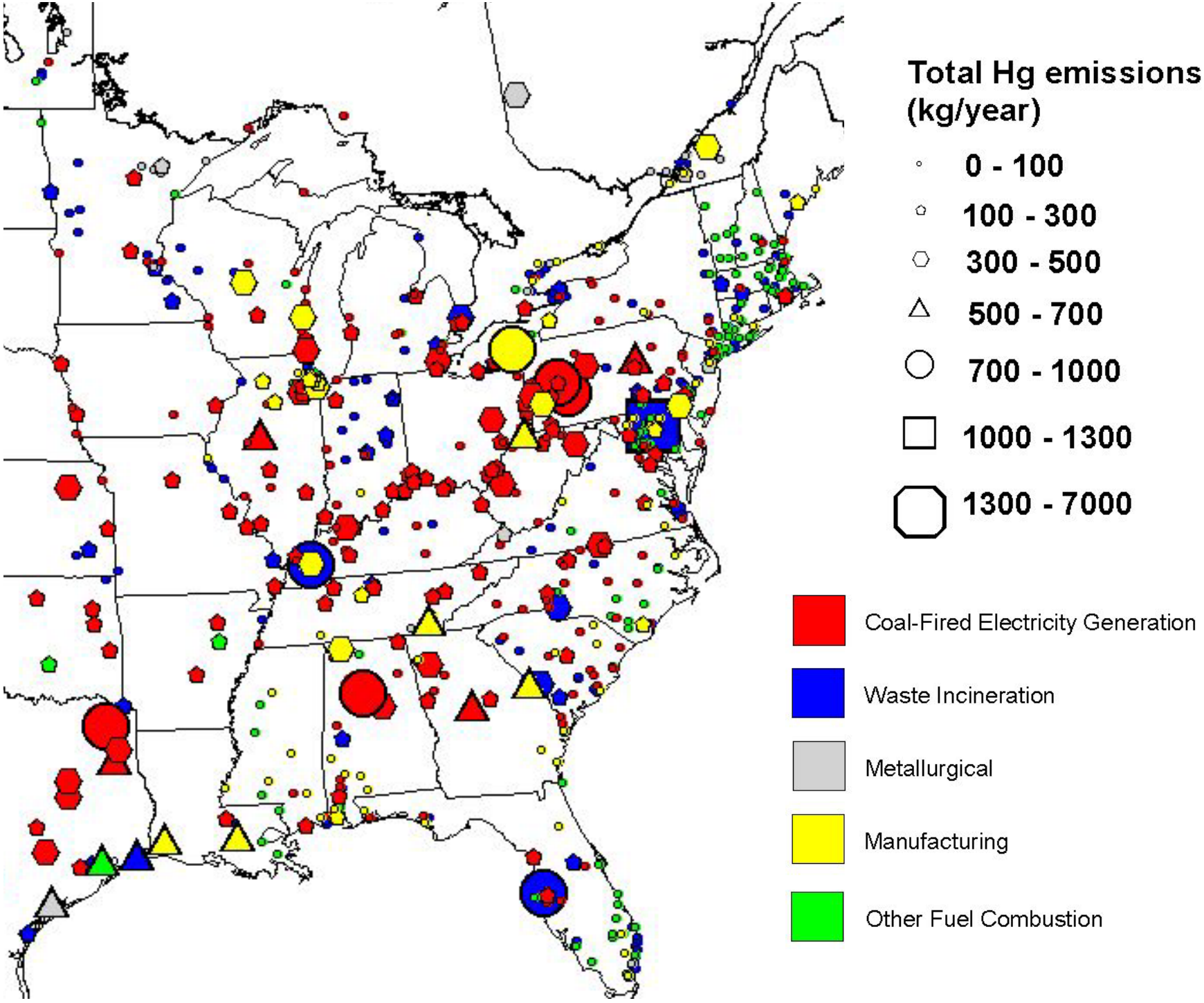
Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

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

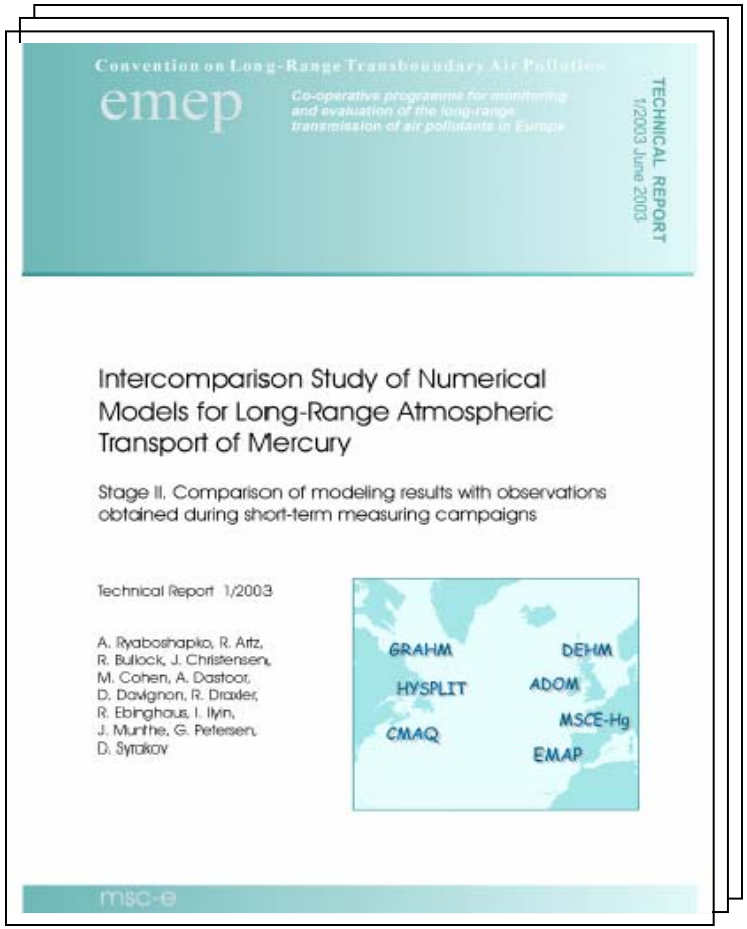


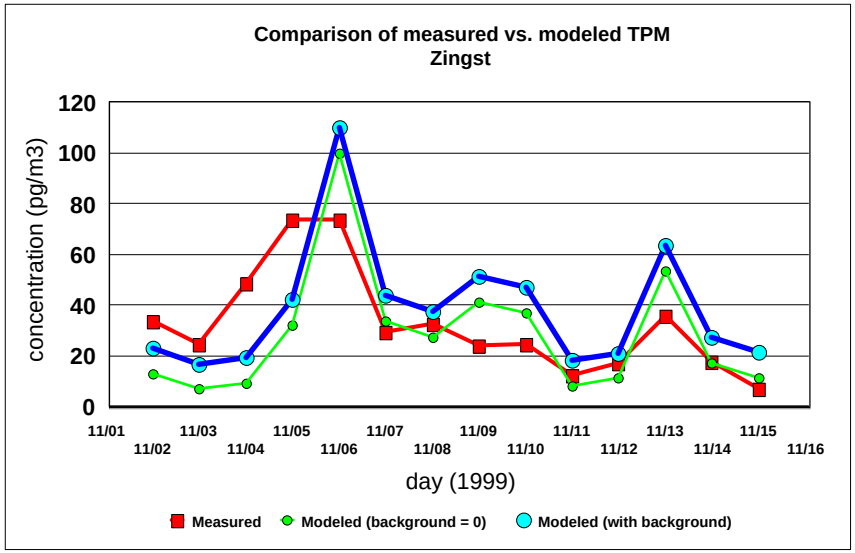

Total Hg emissions
(kg/year)
0 - 100
100 - 300
300 - 500
500 - 700
700 - 1000
1000 - 1300
1300 - 7000
Coal-Fired Electricity Generation
Waste Incineration
Metallurgical
Manufacturing
Other Fuel Combustion

Getting the source-apportionment information we all want 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**

There are a lot of uncertainties in current comprehensive fate and transport models... Nevertheless, many models seem to be performing reasonably well, i.e., are able to explain a lot of what we see





some source-receptor results for the Great Lakes

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

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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 evalua
the Great Lakes region ar
from the Great Lakes co
significant contributions
contributor to atmospher
Published by Elsevier Inc

Keywords: Mercury; Atmos

Mercury contaminat
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human exposure to m
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are believed to be cons
levels of mercury (e.
2000). Historical disc
production using the m
to have caused large

☆Supplementary data ass
the online version, at doi=1
*Corresponding author. F
E-mail address: mark.coh
[1]Current address: DPRA
Research, Concord, Ontario

0013-9351/$ - see front matter Published by Elsevier Inc.
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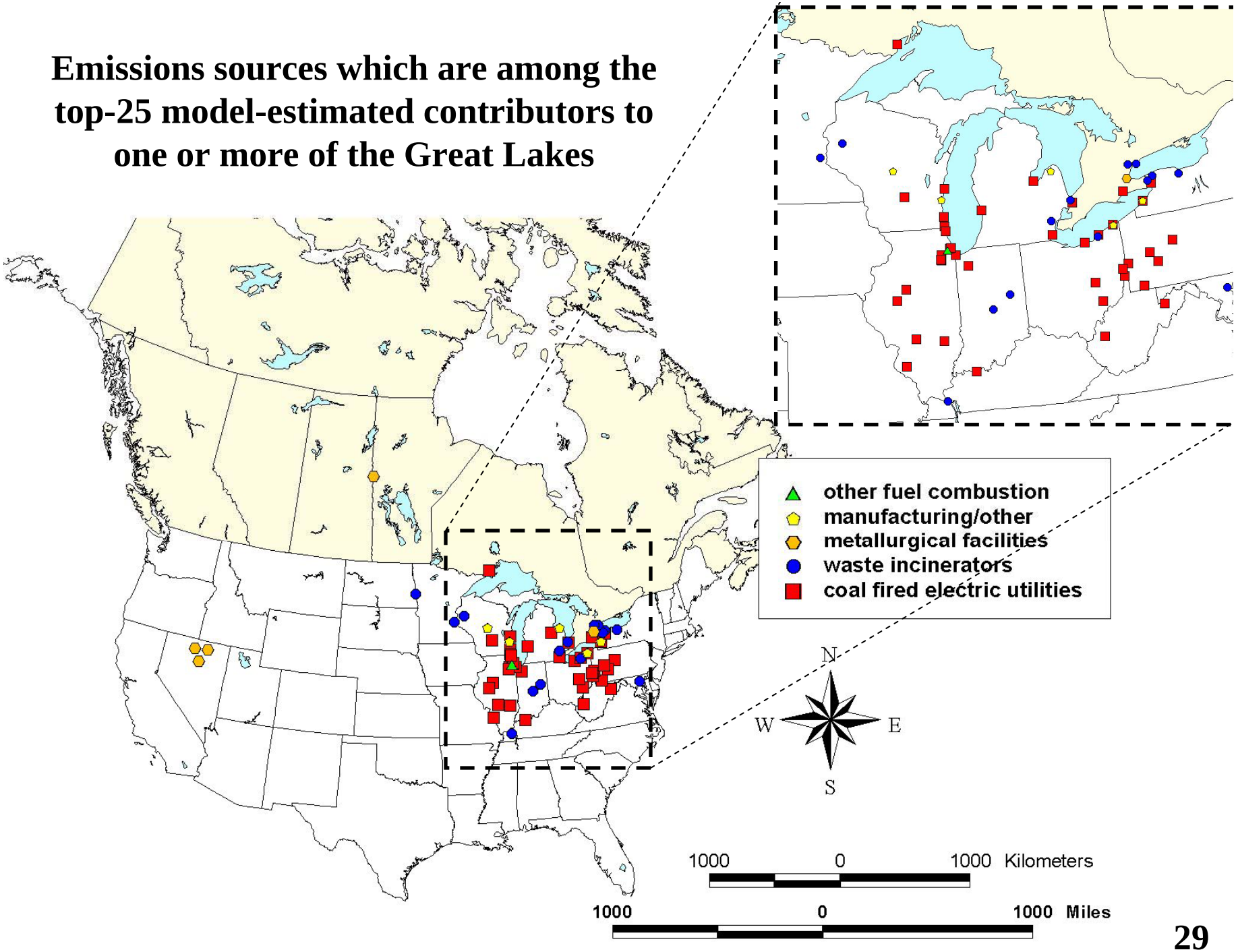
Note: results in this paper are for 1996;

Results shown in the following slides have been updated to 1999 →

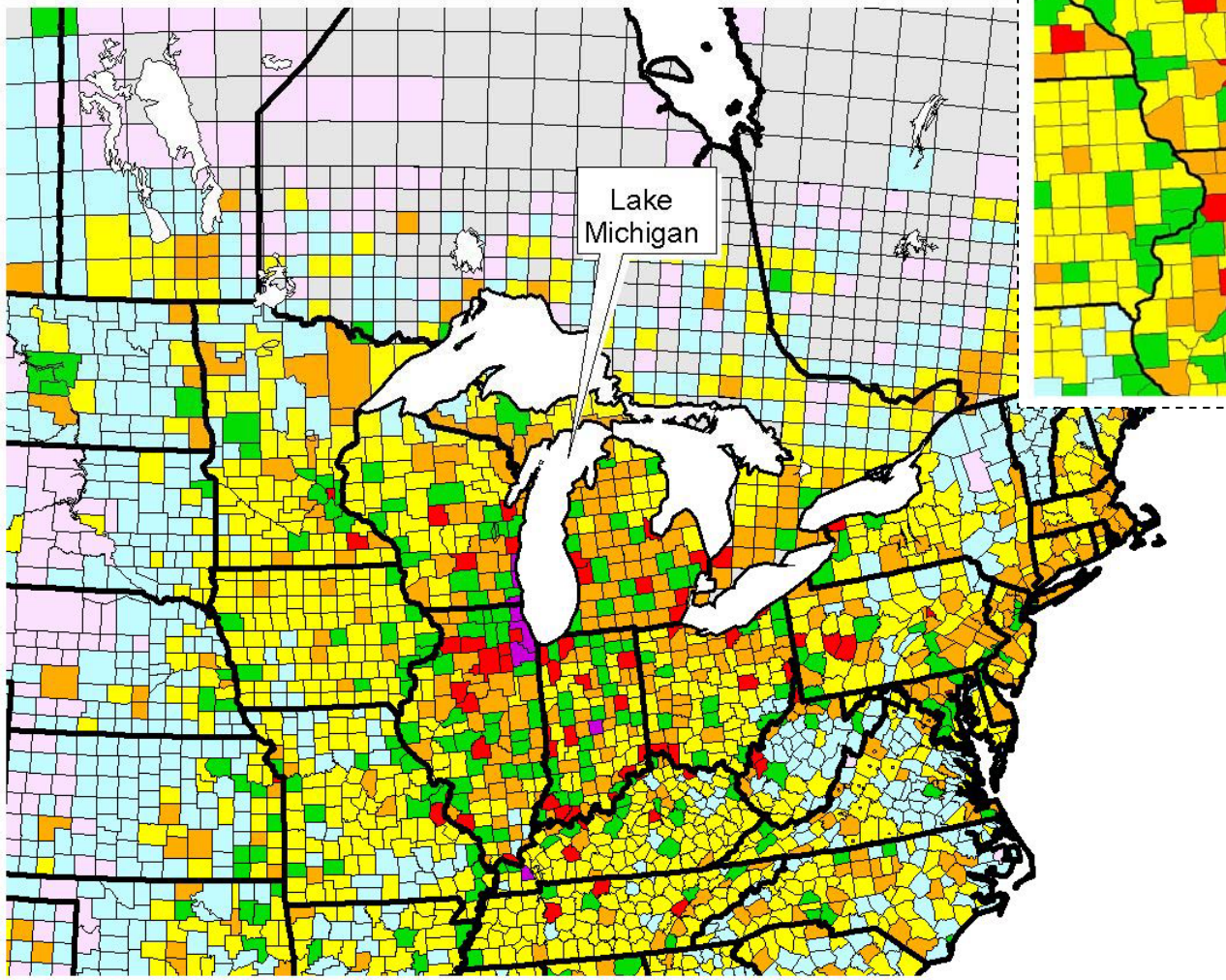
Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratte, D., Deslauriers, M., Duval, R., Laurin, R., Slotnick, J., Nettesheim, T., McDonald, J. "Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes." ***Environmental Research*** **95(3), 247-265, 2004.**

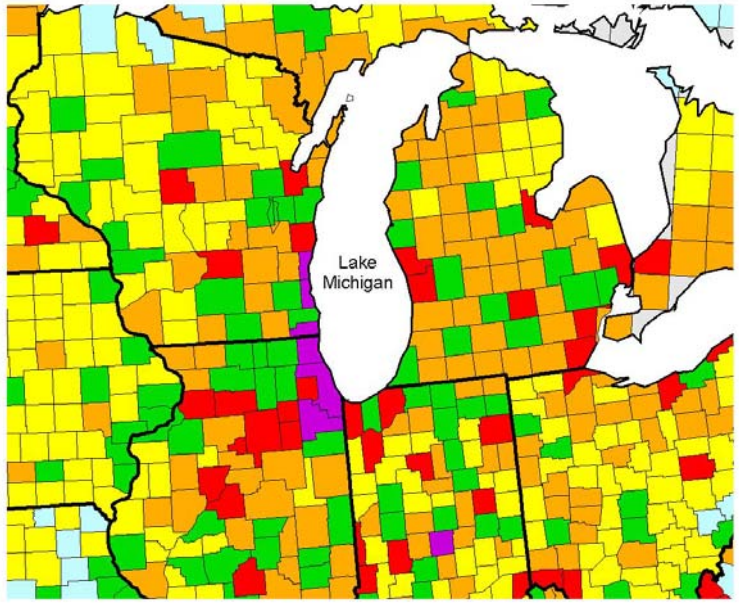
Note: Volume 95(3) is a Special Issue: "An Ecosystem Approach to Health Effects of Mercury in the St. Lawrence Great Lakes", edited by David O. Carpenter.

Emissions sources which are among the top-25 model-estimated contributors to one or more of the Great Lakes



Geographical Distribution of 1999 Direct Deposition Contributions to Lake Michigan



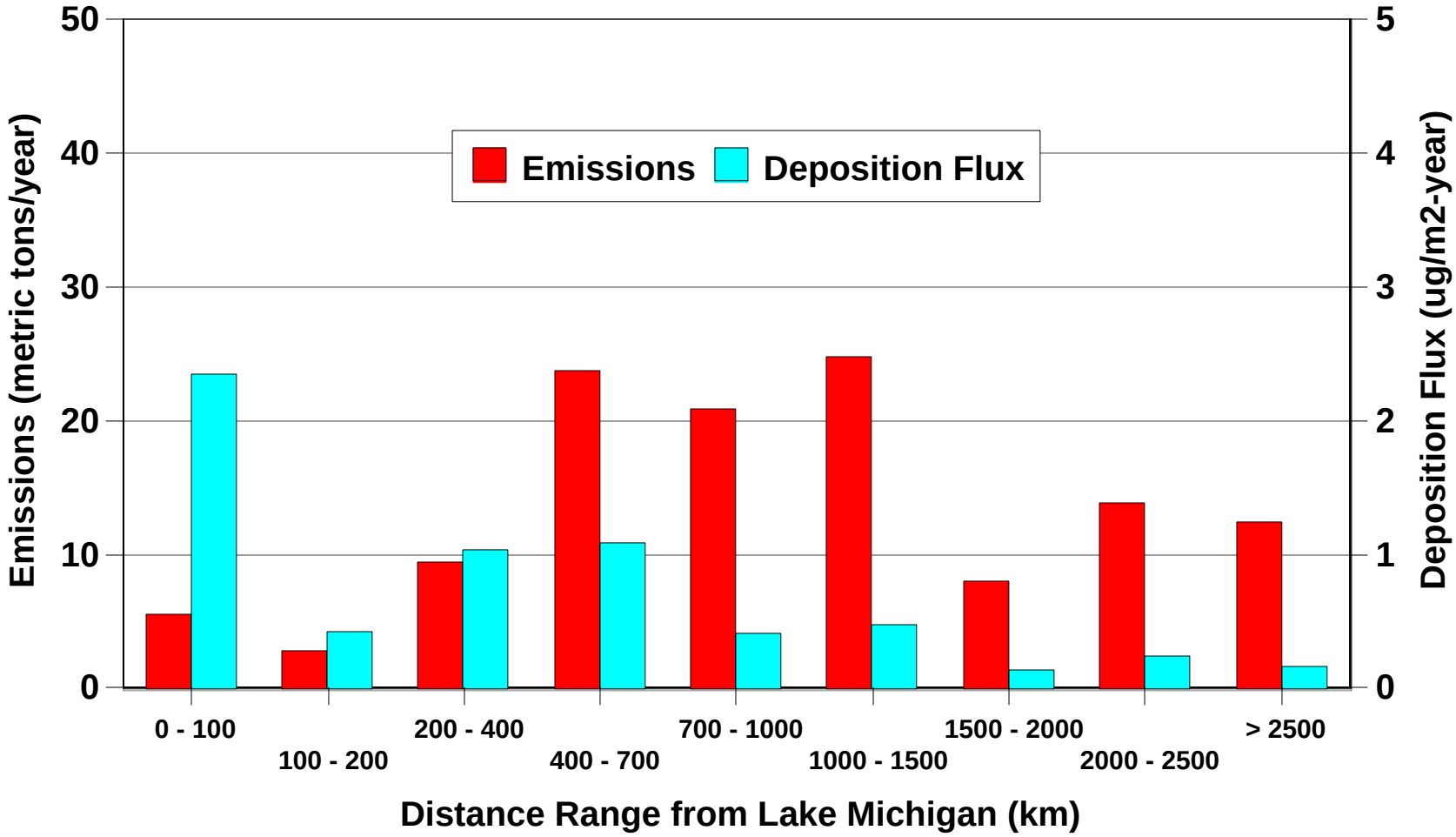


Deposition Contribution of Source Area to Receptor (ug deposited / year per km^2 of receptor area) per (km^2 of source area)

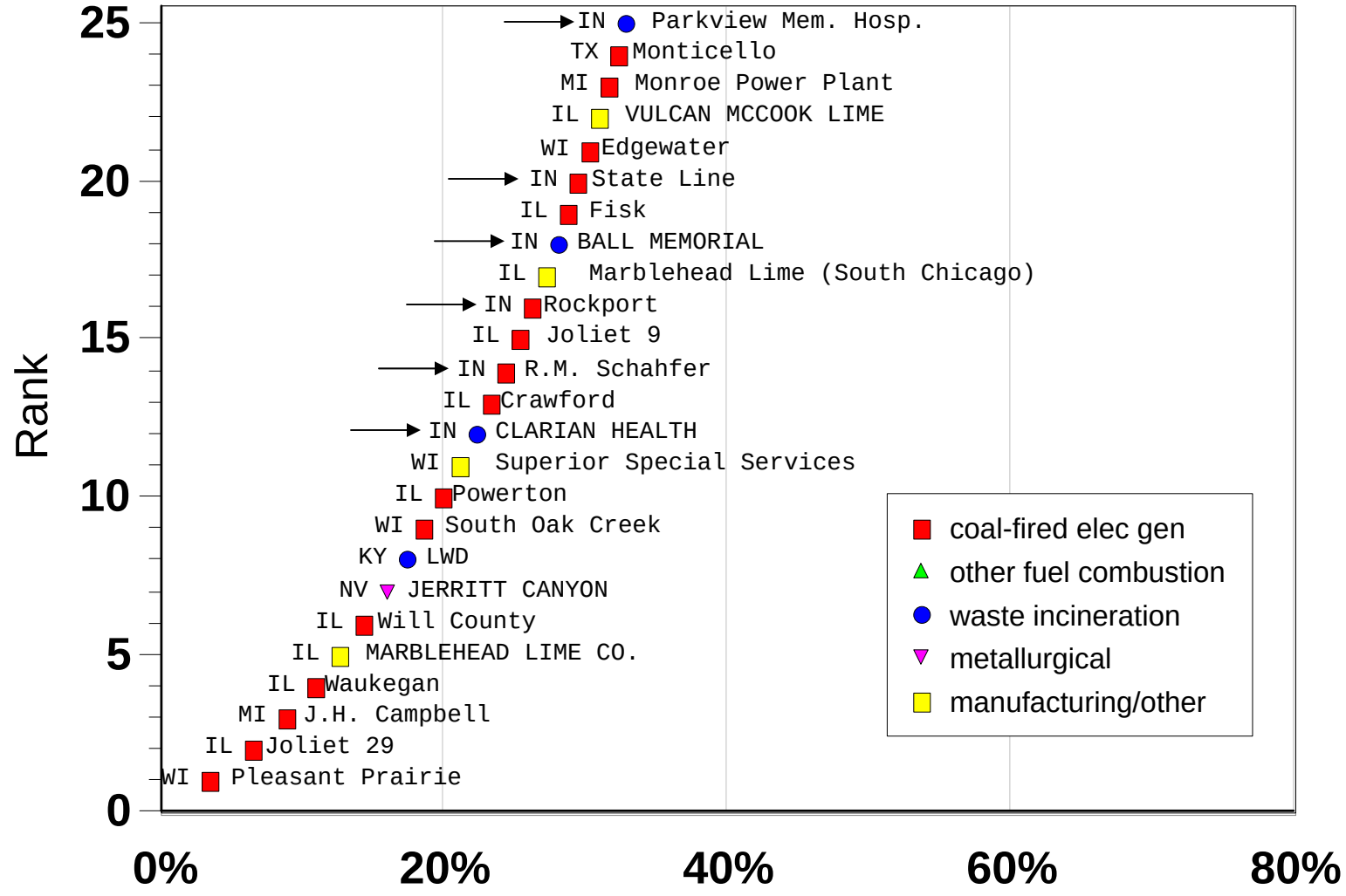
- 0 - 0.0001
- 0.0001 - 0.001
- 0.001 - 0.01
- 0.01 - 0.1
- 0.1 - 1
- 1 - 10
- 10 - 100
- 100 - 1,000
- 1,000 - 10,000
- 10,000 - 100,000

1000 0 1000 Kilometers

Emissions and Deposition Contributions from Different Distance Ranges Away From Lake Michigan



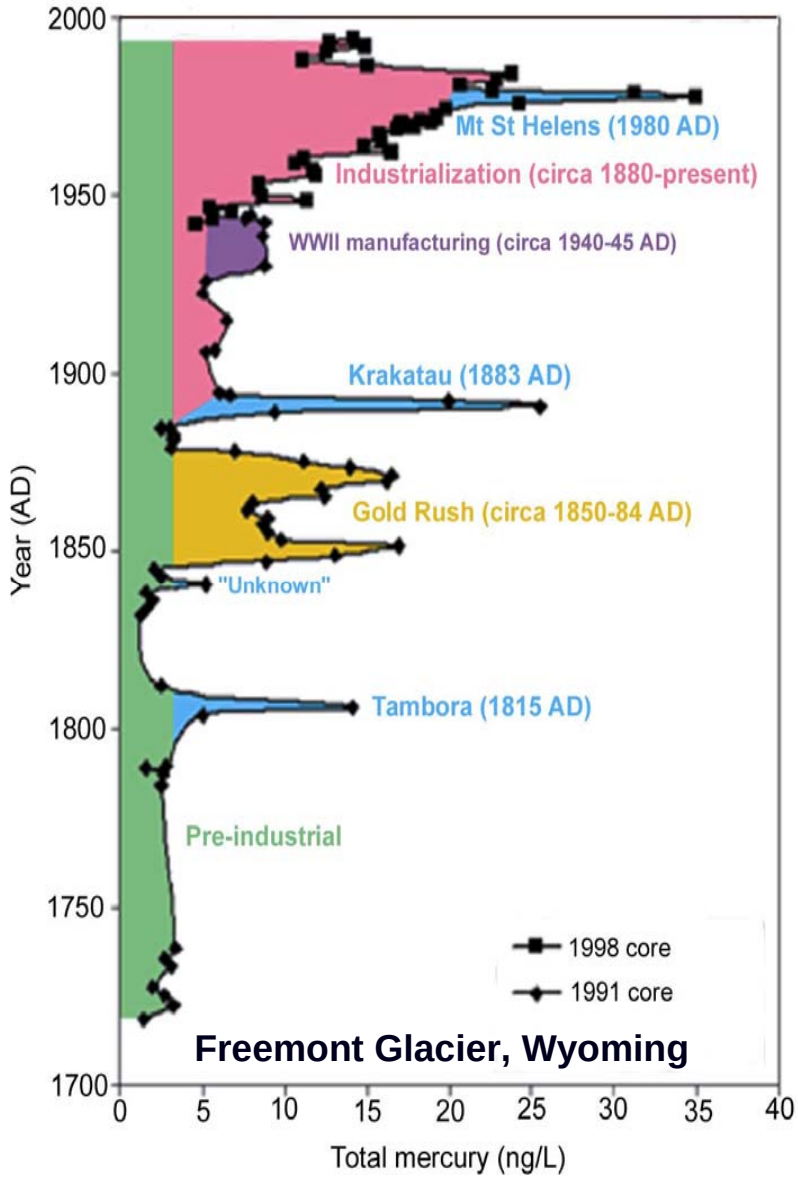
Top 25 Contributors to 1999 Hg Deposition Directly to Lake Michigan



source-attribution – the “big picture”

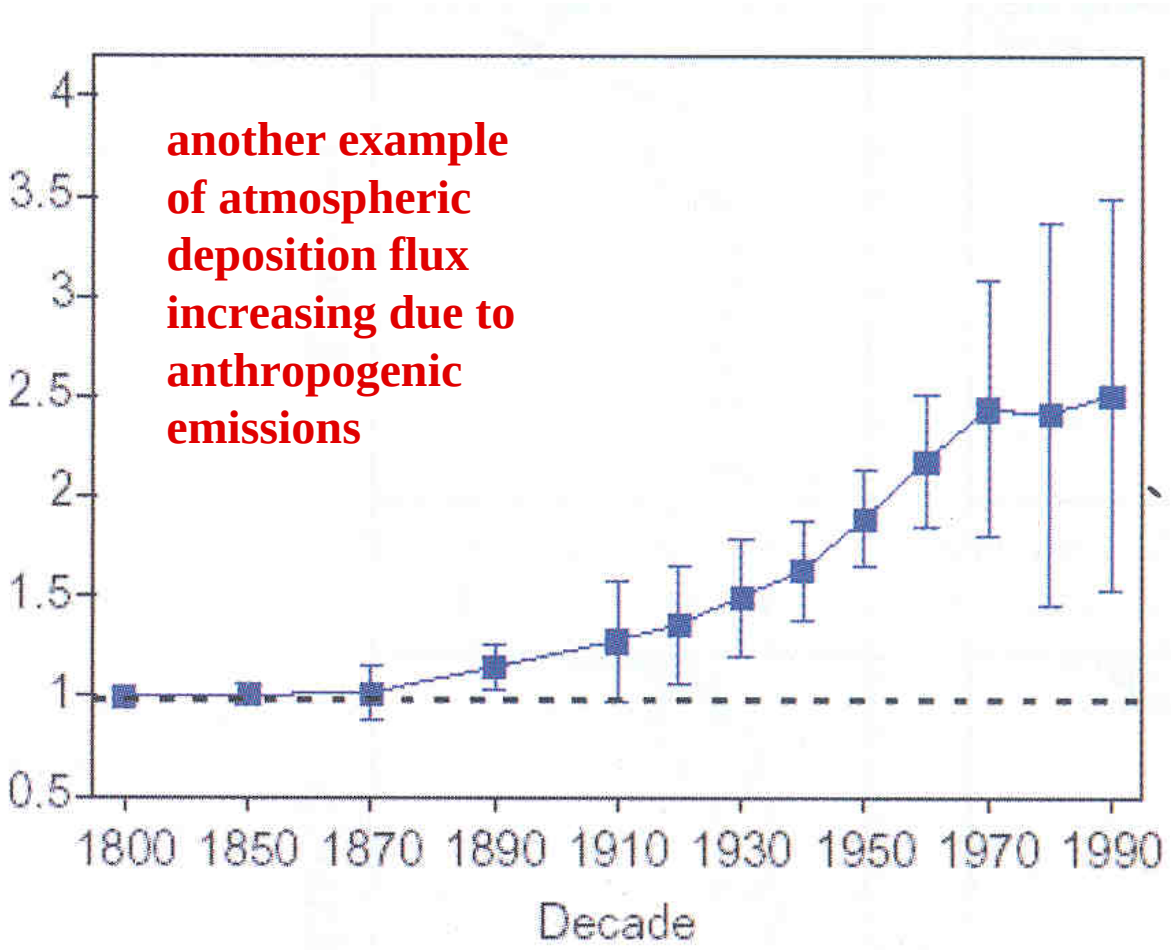
Natural vs. anthropogenic mercury?

Studies show that anthropogenic activities have typically increased bioavailable Hg concentrations in ecosystems by a factor of 2 – 10



source: USGS, Shuster et al., 2002

Hg flux / pre-industrial Hg flux



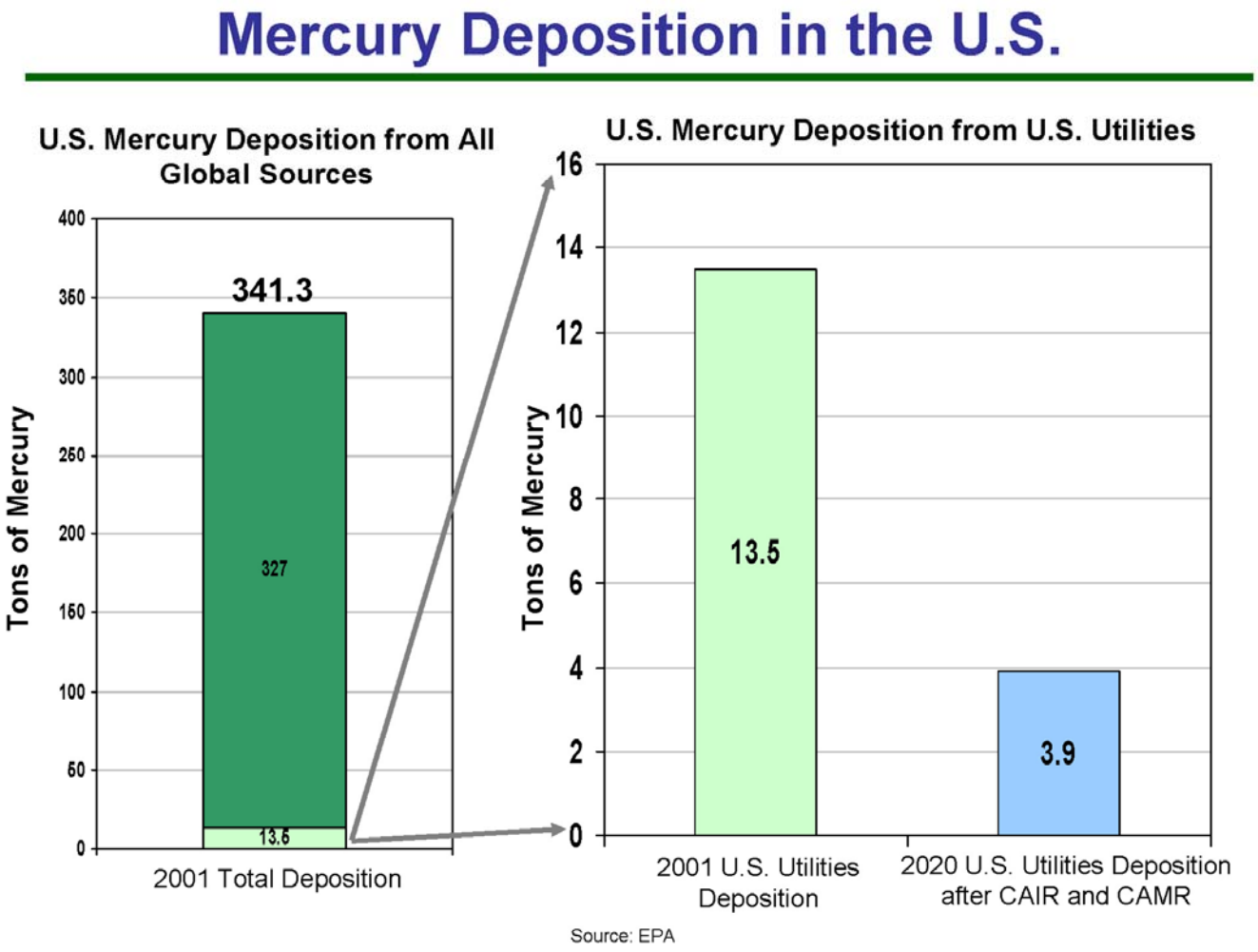
Average mercury accumulation rate relative to pre-industrial (1800-1850) accumulation rate in five lakes in Northern Alaska (based on sediment cores)

from Fitzgerald et al. (2005), "Modern and Historic Atmospheric Mercury Fluxes in Northern Alaska: Global Sources and Arctic Depletion" *Environ Sci Tech* **39**, 557-568

What is the relative importance of global, national, regional, and local sources?

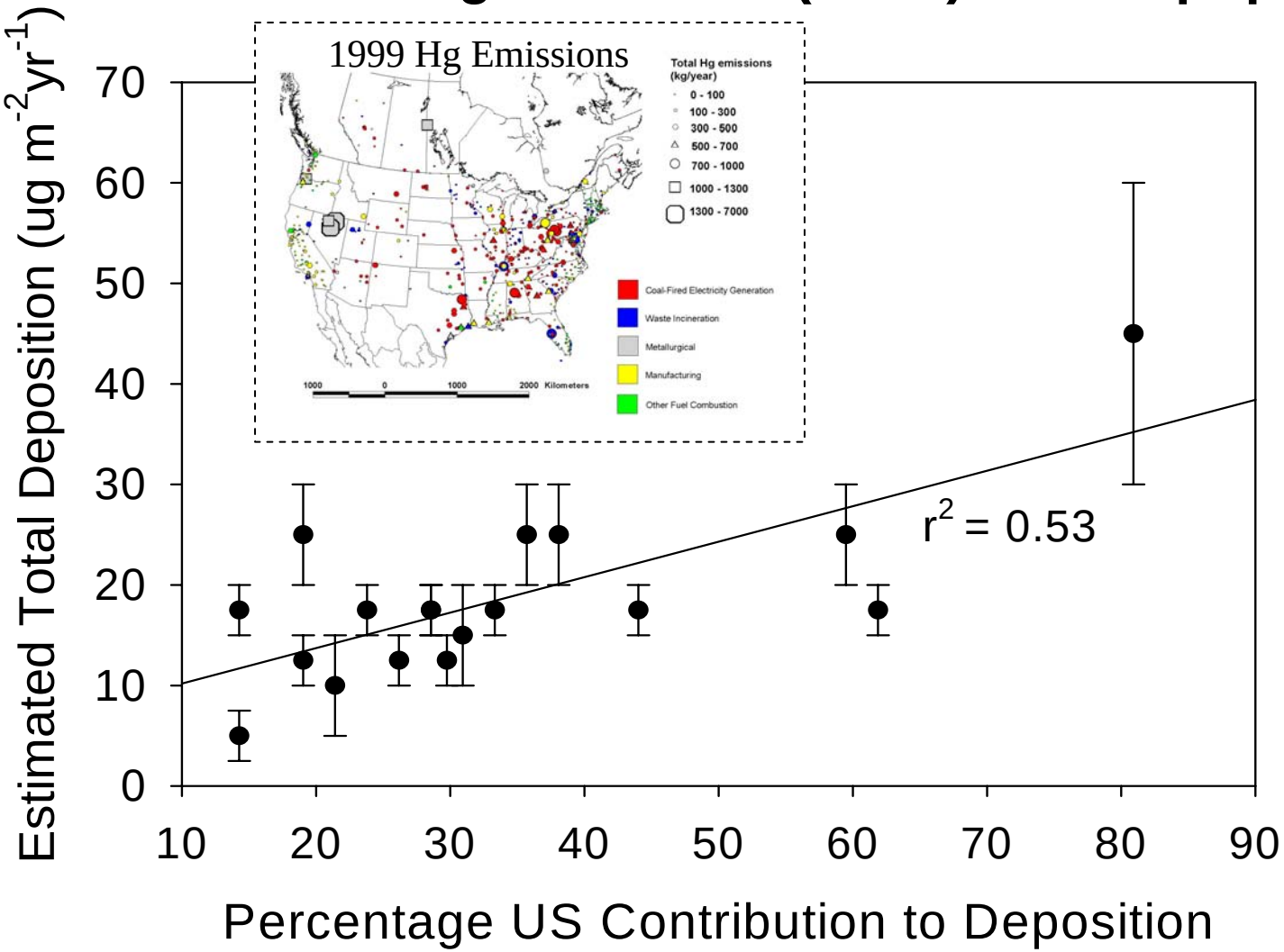
Data used by EPA to support recent Clean Air Mercury Rule

?



(slide courtesy of Rob Mason, Univ. of CT)

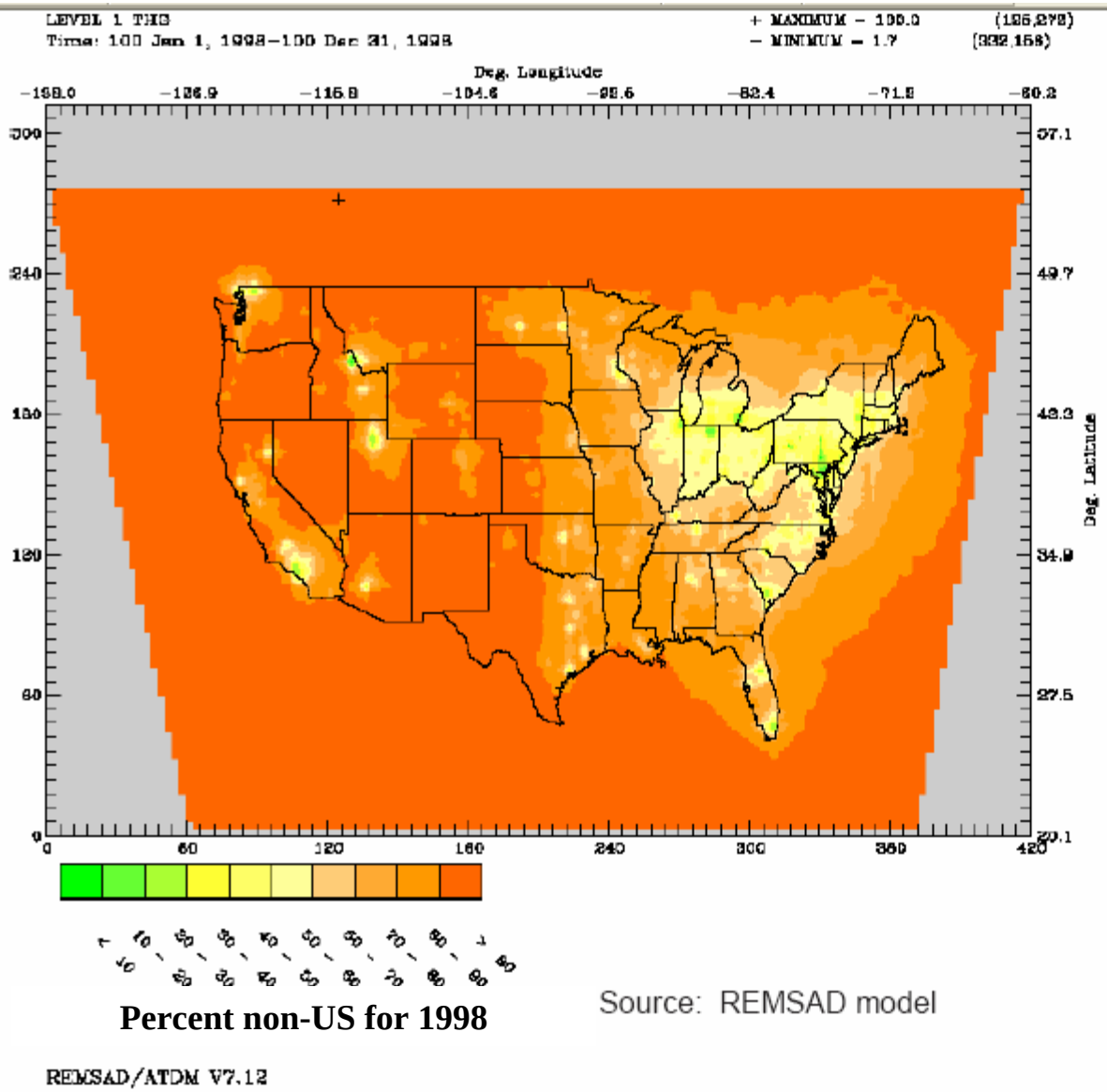
Data from Seigneur et al. (2004) model paper



the Seigneur et al. (2004) paper shows that, for regions where deposition is high, the impact of local/regional sources is the main cause for these elevated concentrations.

[Seigneur et al., (2004), "Global Source Attribution for Mercury Deposition in the United States", *ES&T* **38**, 555-569.]

Results from the EPA REMSAD Mercury model



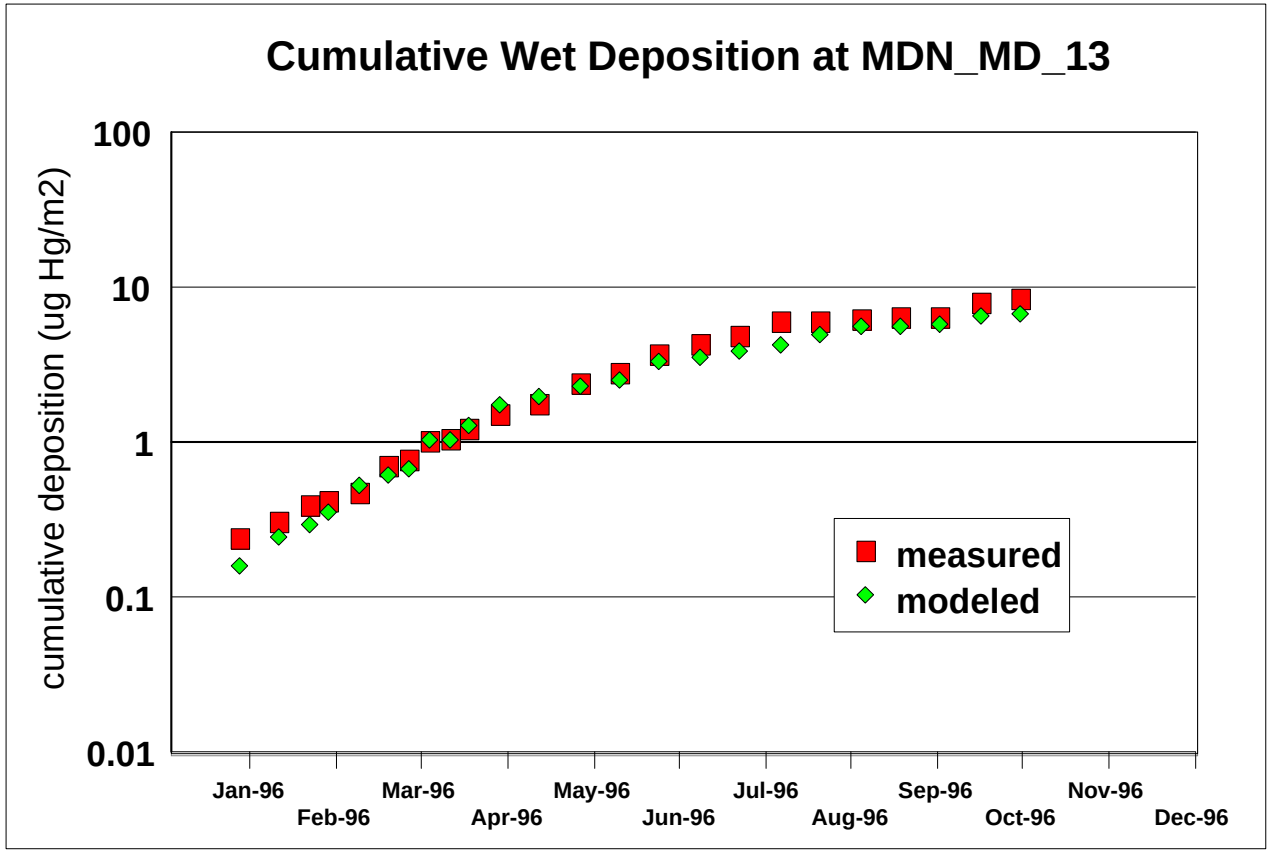
Percent non-US for 1998

Source: REMSAD model

- Based on this modeling approximately half of U.S. mercury deposition is from domestic anthropogenic sources and half is from other sources
- Domestic sources dominate deposition for large part of Eastern U.S.
- Global sources are dominant in the Western U.S.

Source: slide developed by Anne Pope for the Hg Roundtable conference call April 21, 2005

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



HYSPLIT modeling has shown that in areas of significant local and regional anthropogenic sources, ambient measurements can be explained reasonably well by considering only these local and regional anthropogenic sources.

Source-apportionment answers depend a lot on where you are

- **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...**

What is the relative importance of global, national, regional, and local sources?

Possible answers are emerging as our understanding improves, but there is no scientific consensus yet...

Conclusions

- **Source-attribution information is important**
- **Impacts are episodic & depend on form of mercury emitted**
- **Modeling needed to get source-attribution information**
- **(more!) Monitoring needed for model evaluation & refinement**
- **Many uncertainties but useful model results are emerging –**
  these HYSPLIT model results are being extended to include global & natural emissions, and re-emissions
- **The question of the relative importance of global vs. national vs. regional vs. local sources is complex –**
  the answer depends on *location* and on *what model* one is using...