The Atmospheric Deposition of Mercury to the Great Lakes

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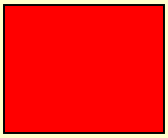
- **Atmospheric Processes for Mercury**
- **Key questions regarding atmospheric deposition**
- **Methodological approaches to answer these questions**
- **Preliminary results of an atmospheric modeling analysis**

Three “forms” of atmospheric mercury

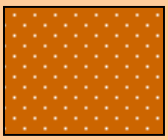
Elemental Mercury: Hg(0)

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



Reactive Gaseous Mercury (“RGM”)

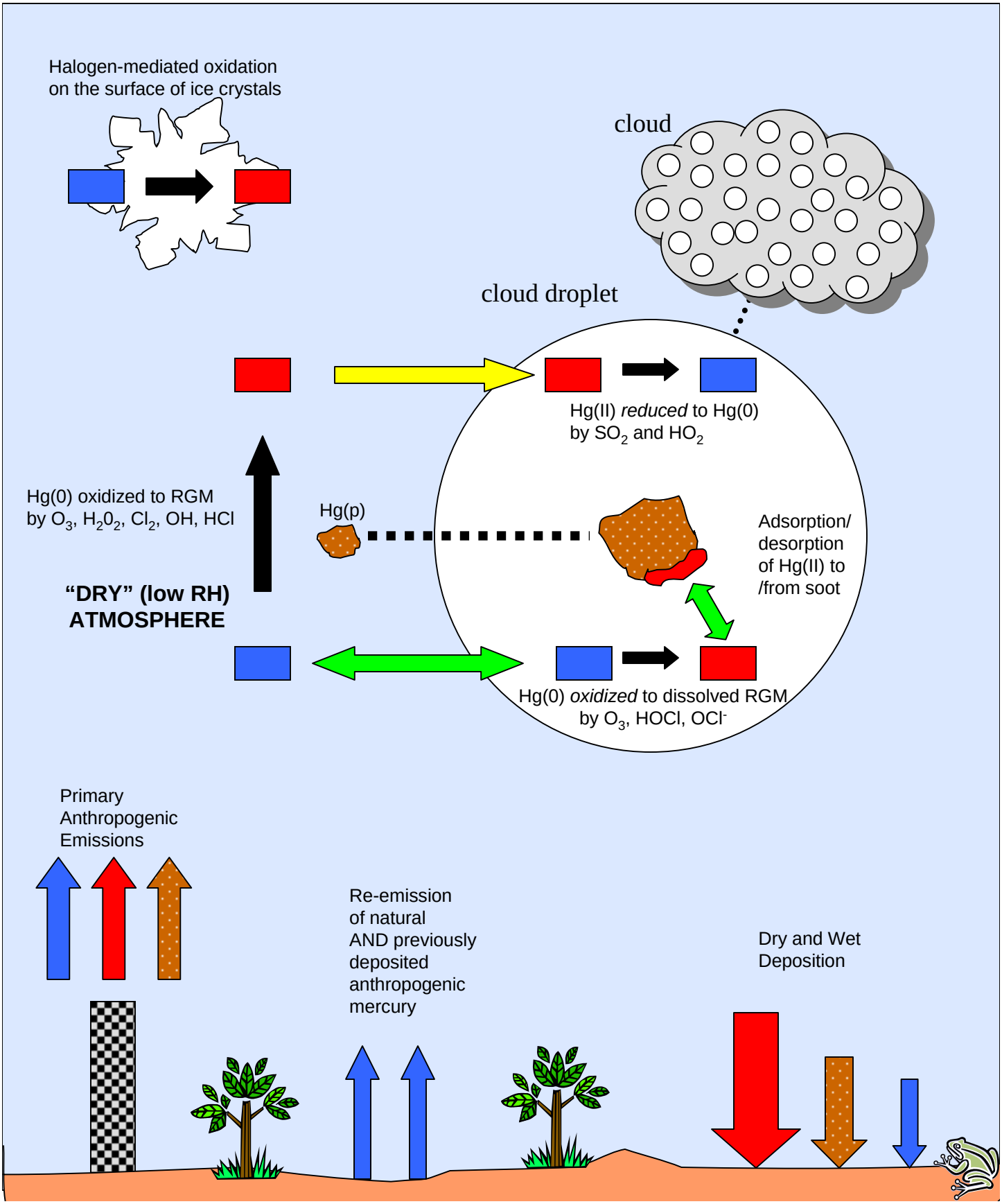
- a few percent of total Hg in atmosphere
- oxidized mercury: Hg(II)
- HgCl2, others species?
- somewhat operationally defined by measurement method
- *very* water soluble
- short atmospheric lifetime (~ 1 week or less)
- more local and regional effects



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



Key questions regarding atmospheric deposition:

1. How much is being deposited in each Lake?

2. How important is direct deposition to a given lake relative to indirect loading via deposition to the lake's watershed?

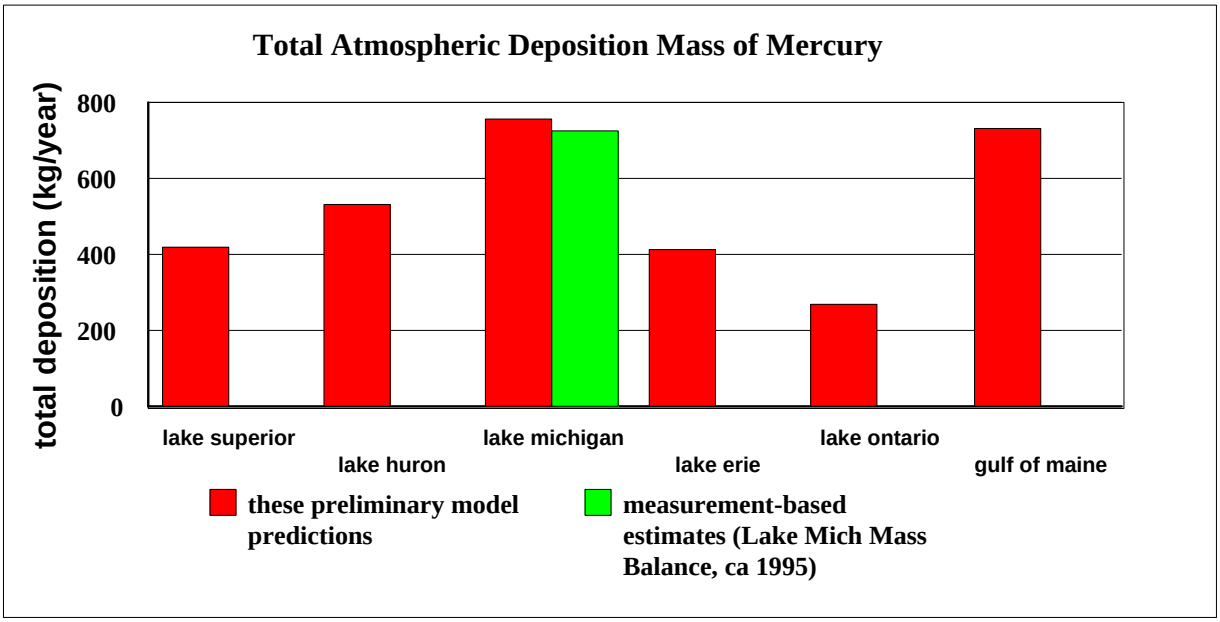
3. How important is atmospheric deposition relative to other loading pathways (e.g., direct discharge to the Lake or its tributaries)

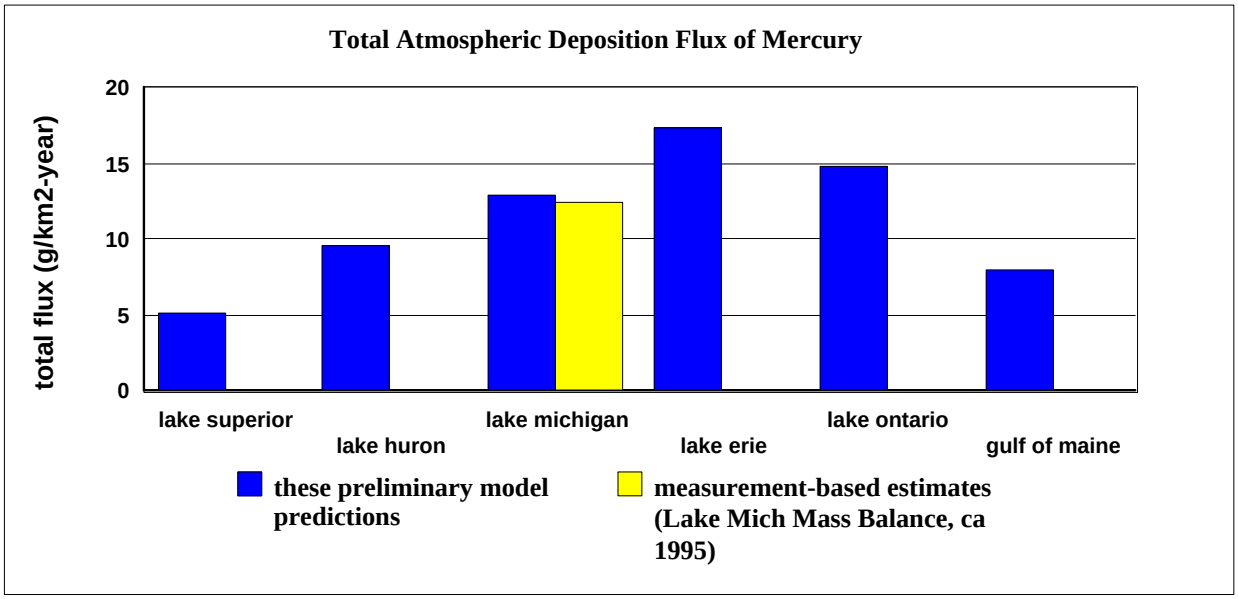
4. What is the relative importance of the contributions from local, regional, national, continental, and global sources?

5. What is the relative importance of contributions from different types of sources, e.g, coal fired utilities, incinerators, natural emissions, etc.?

We need to know all these things to efficiently direct action to reduce the contamination levels in a given lake.

Estimated atmospheric deposition of mercury to the Great Lakes and the Gulf of Maine





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

- **Many uncertainties in the existing estimates, e.g., significance of watershed processing**

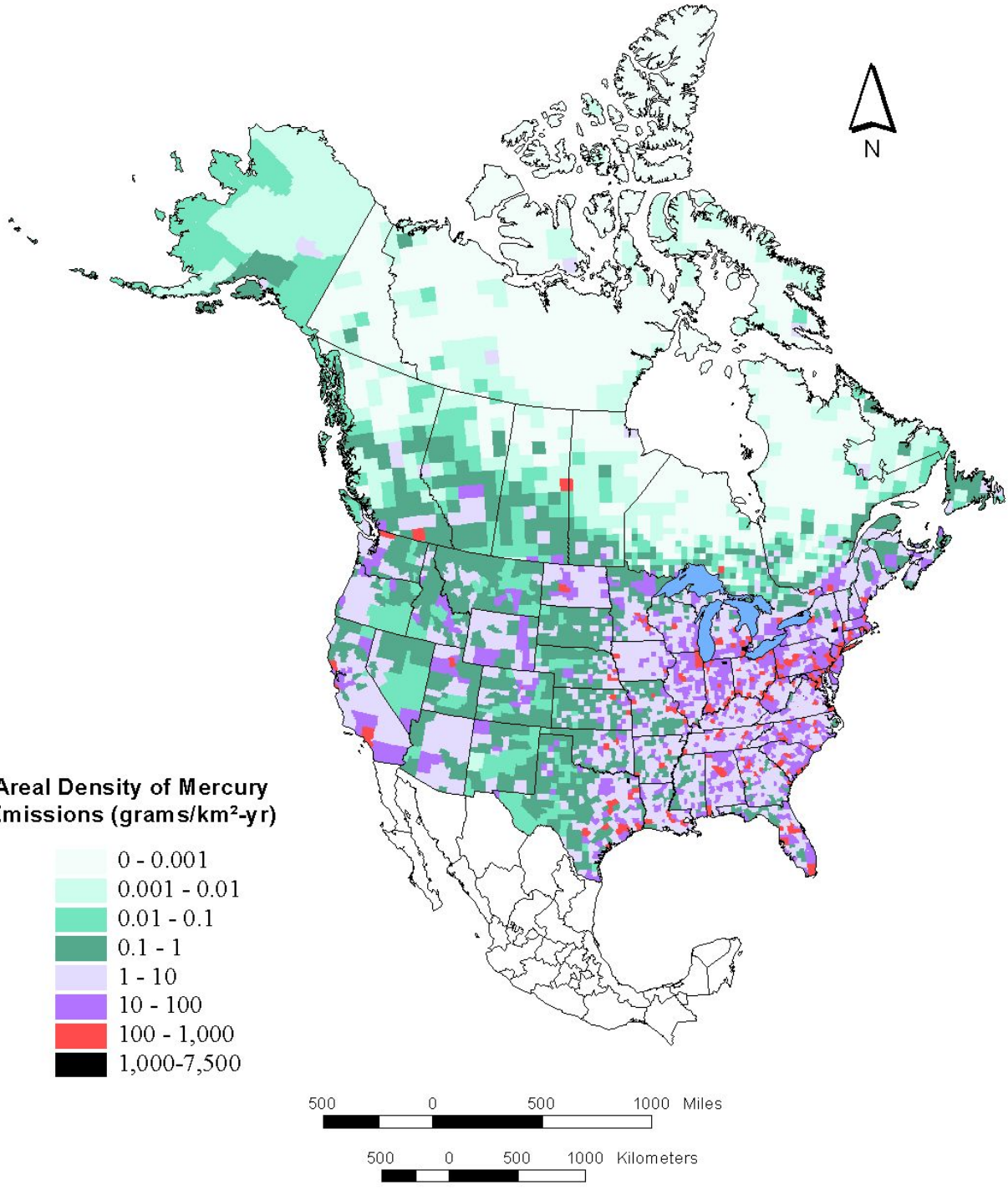
- **We don't have data for all the lakes**

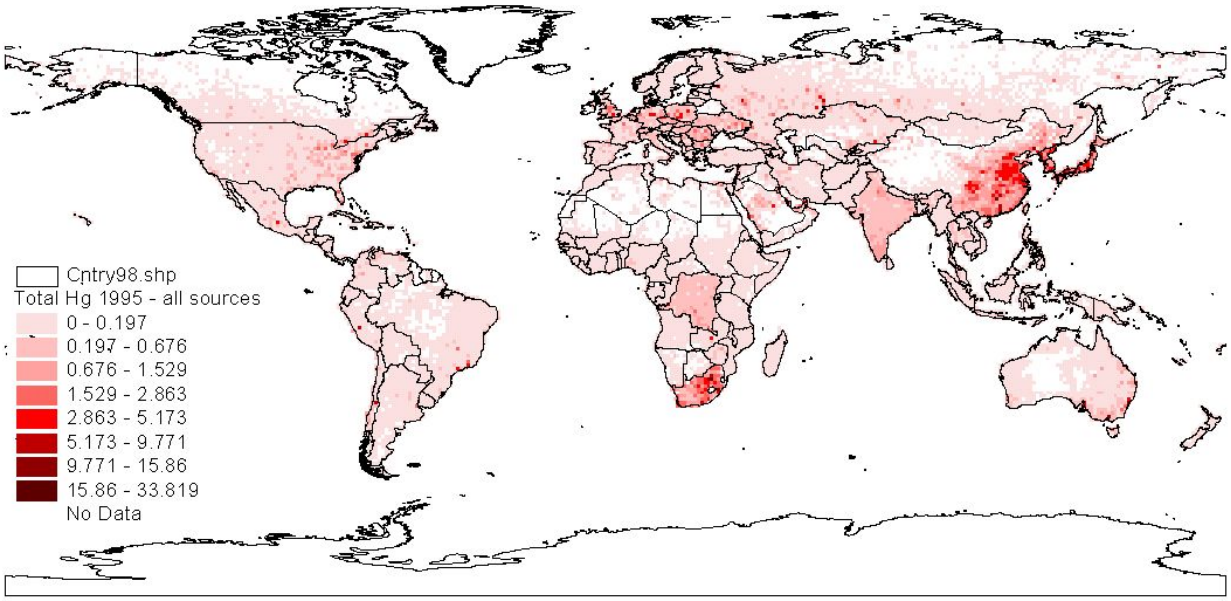
- **In general, insufficient measurements and modeling analysis to obtain accurate, timely estimates of this simple mass balance information for the Great Lakes**

Atmospheric deposition *almost certainly* plays a very significant role in the mercury contamination of the Great Lakes

Atmospheric Mercury Emissions

(Canada: 1995; U.S. 1996, 1999)



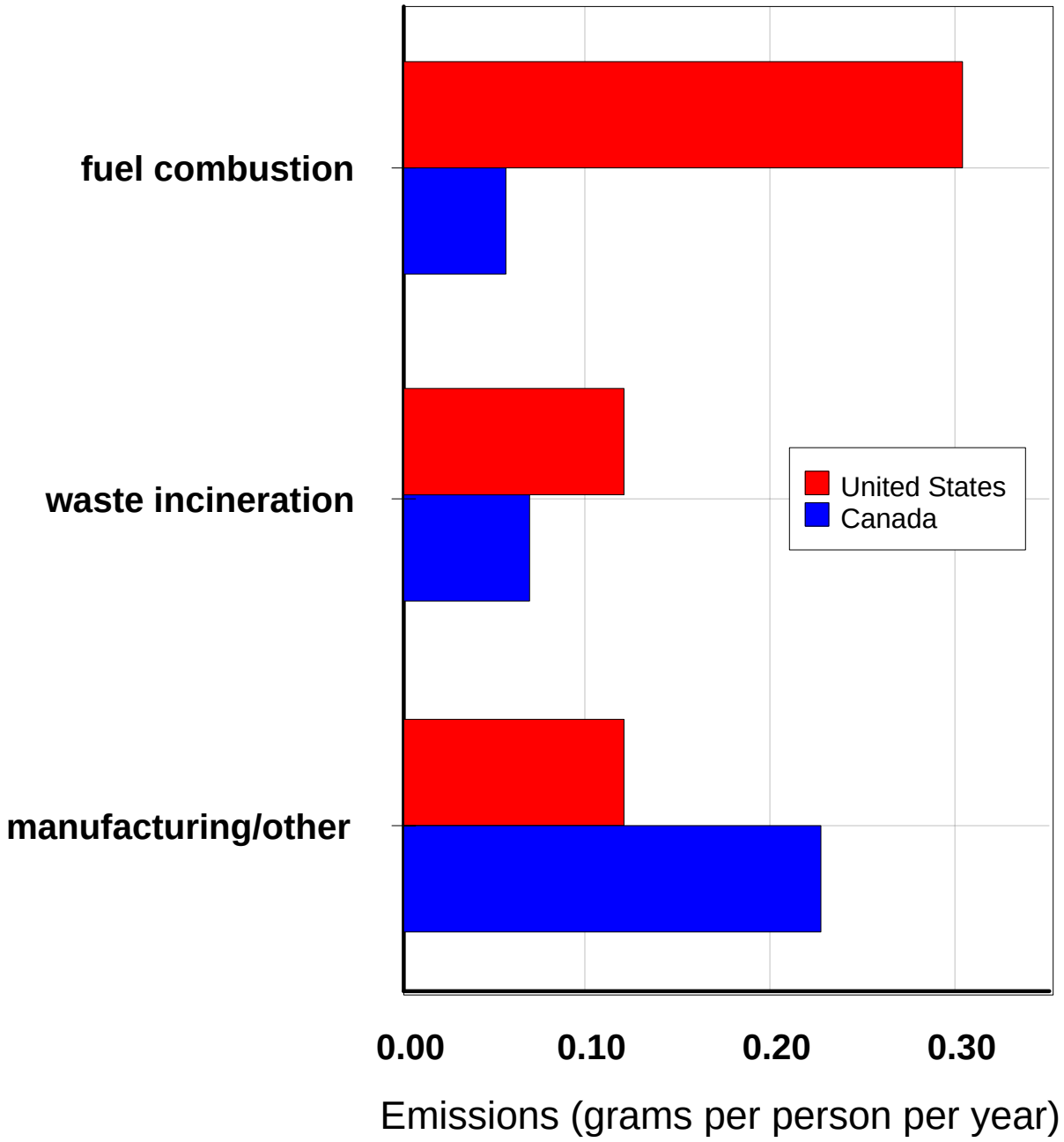


1995 Global Hg Emissions Inventory,

courtesy of Josef Pacyna, NILU, Norway (2001)

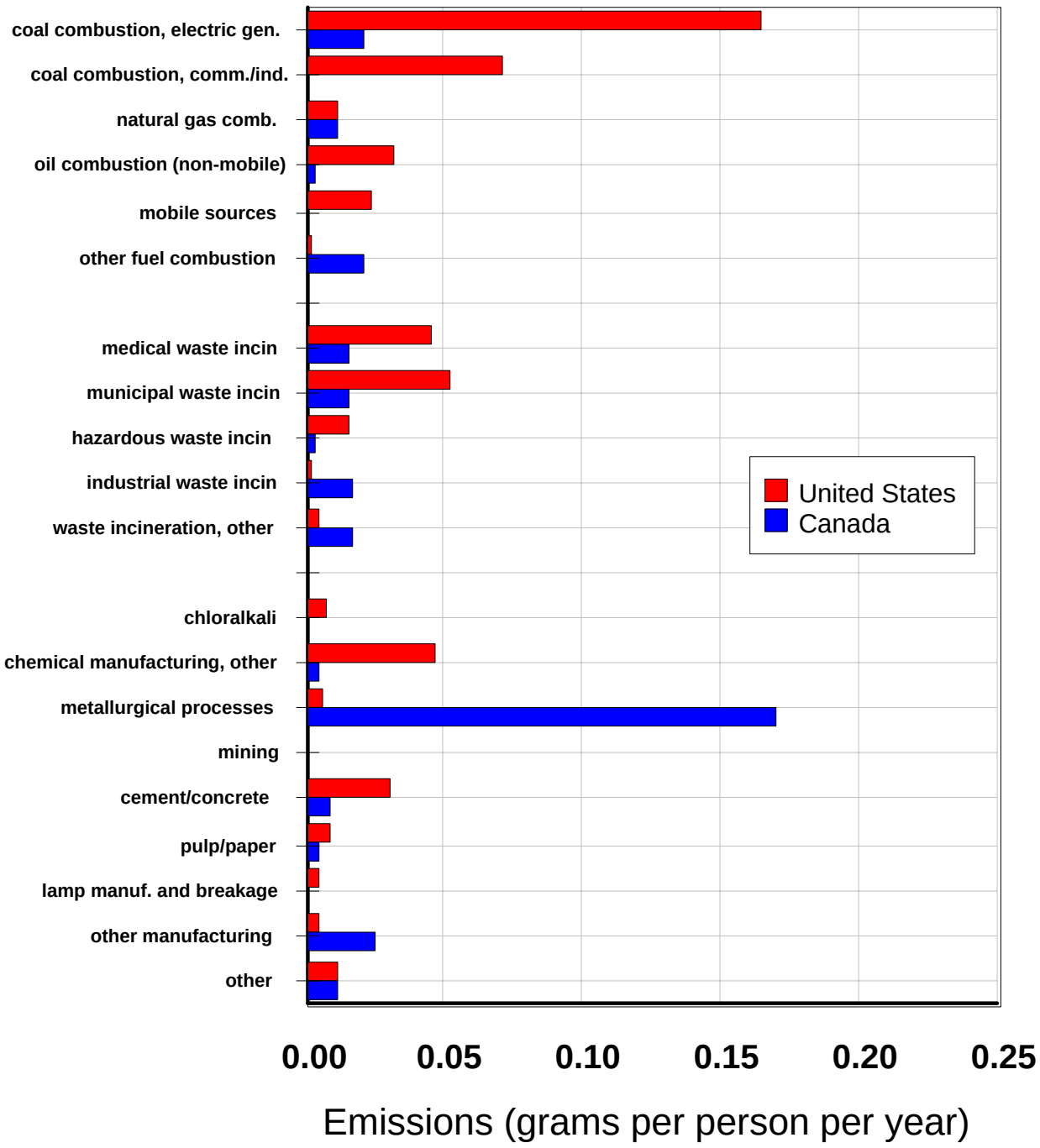
Per Capita Emissions of Mercury

(aggregated source categories)



U.S. emissions from a hybrid EPA inventory, representing 1996 for some sources, 1999 for others
The Canadian emissions estimates are from an Environment Canada inventory for 1995

Per Capita Emissions of Mercury



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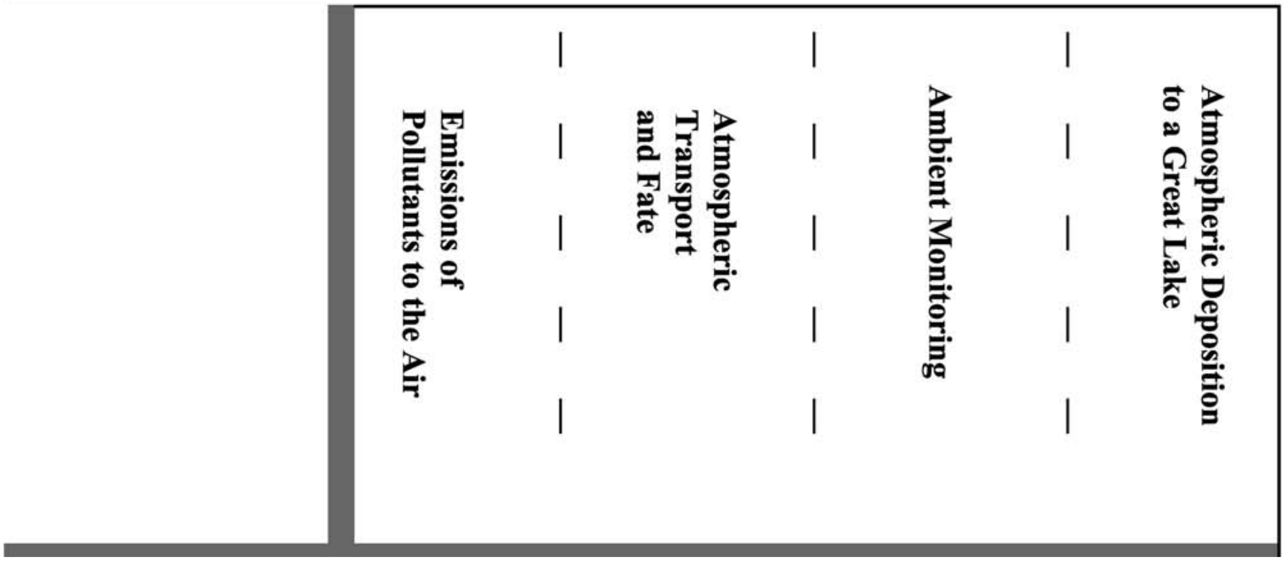
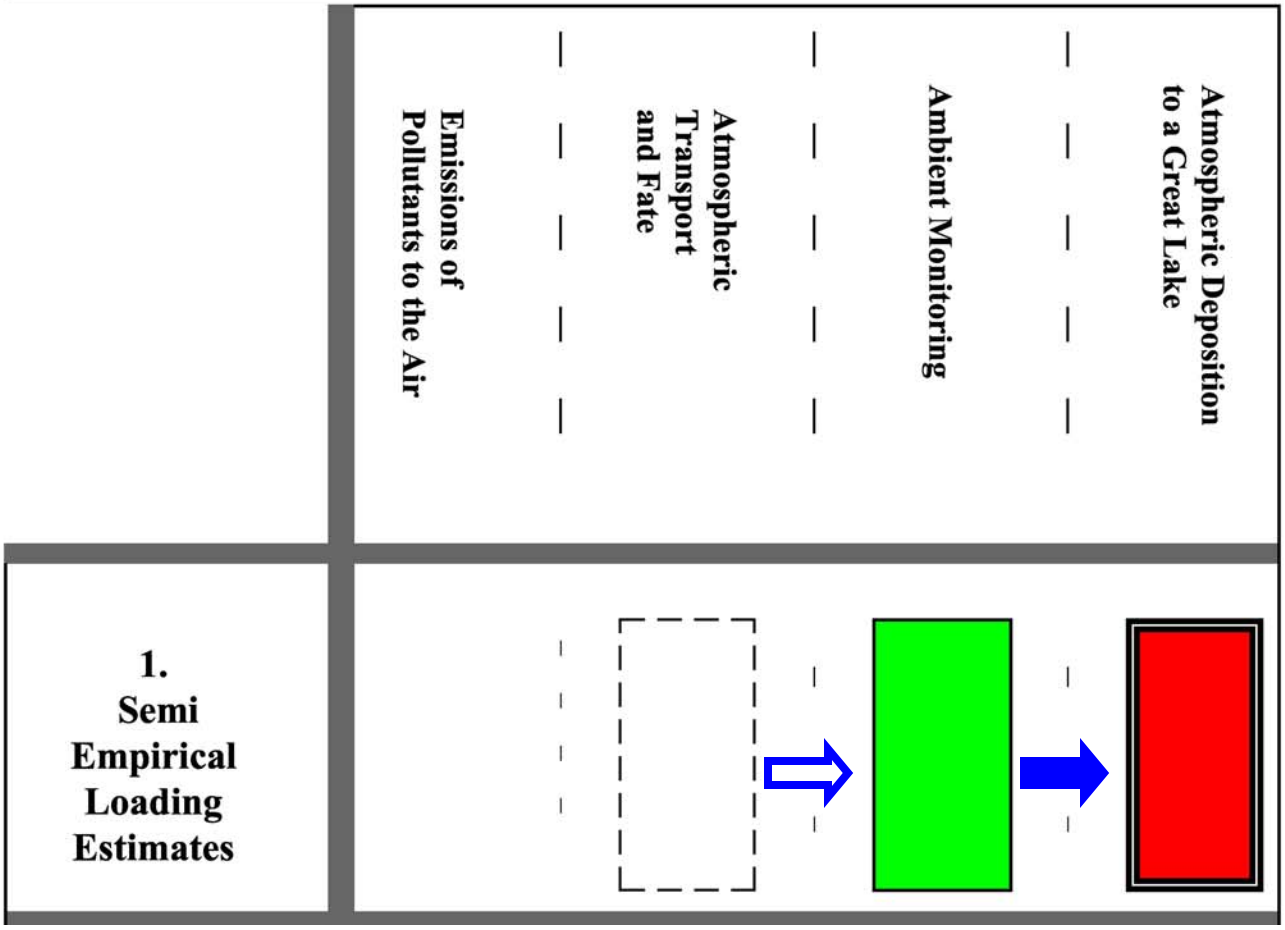
Methodological Approaches for Analysis of the Atmospheric Deposition Pathway



Methodological Approaches for Analysis of the Atmospheric Deposition Pathway



Mercury Monitoring in Ambient Air

- **Mercury is not included in the Integrated Atmospheric Deposition Network (IADN)…** ***(but may be soon)***

- **Mercury Deposition Network: weekly *wet* deposition measurements; many sites in the U.S. and Canada; data are easily available through the web**

- **CAMNET – Hg(0) ambient air concentrations at a number of locations (Canada)**

- **While several research programs measure RGM and Hg(p), there is no systematic network collecting publicly accessible data for these compounds, analogous to the MDN.**

- **Unfortunate, because:**
- **(1) they are important for dry deposition;**
- **(2) they are needed for model evaluation**

- **We are generally *not* actually interested in the concentration or deposition at a single monitoring site…**

- **We are interested in the deposition to an *entire* water body, or to a particular ecosystem**

- ***We are just using the few monitoring sites that we might have to give us a clue as to what the total impact might be…***

There are large spatial variations in wet deposition

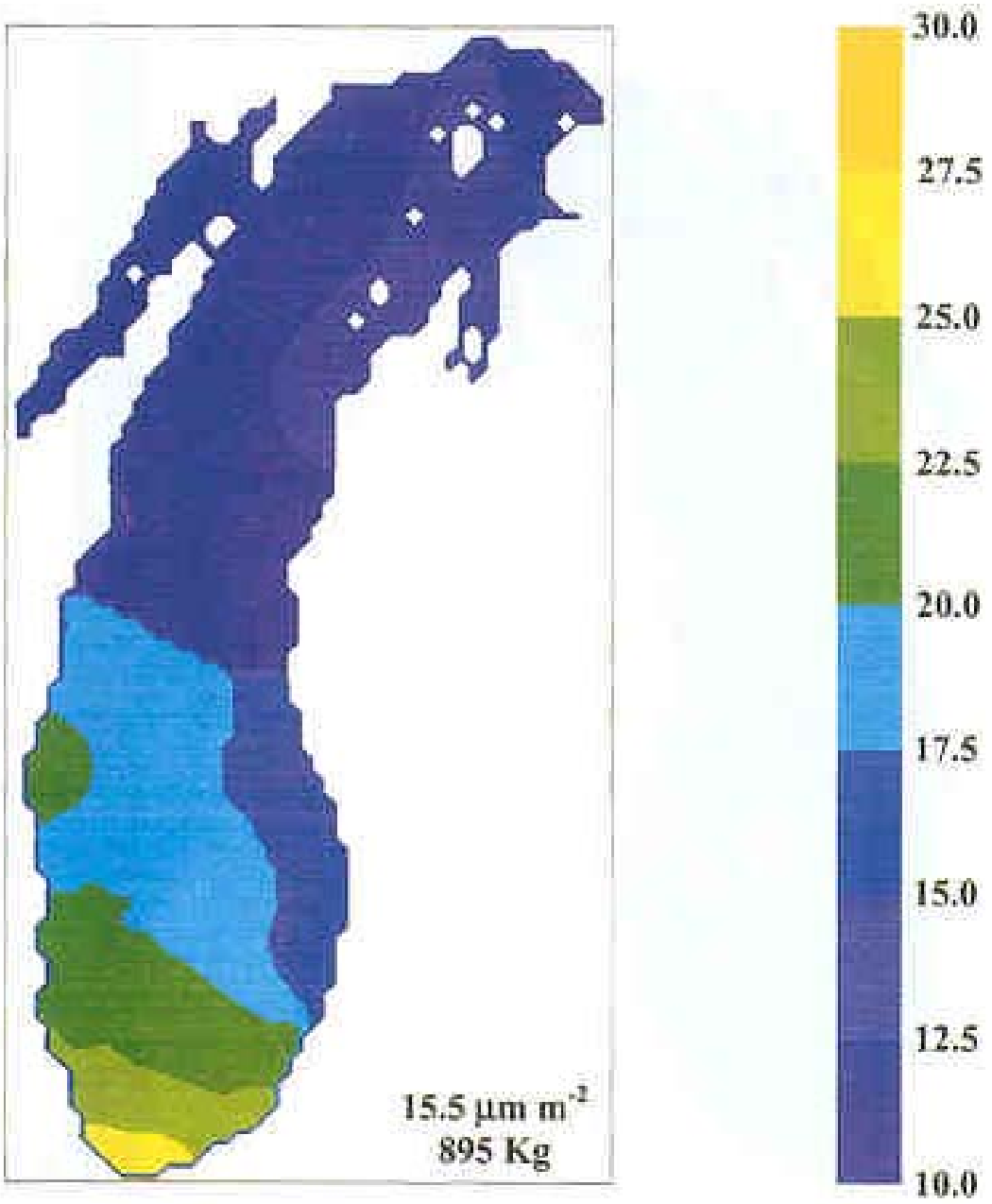


FIGURE 5. Estimated over-water wet deposition flux (July 1, October 31, 1995).

Source: M. Landis and G. Keeler, Atmospheric Mercury Deposition to Lake Michigan during the Lake Michigan Mass Balance Study. Environmental Science and Technology 36:4518-4524, 2002

There are large spatial variations in dry deposition and re-emission

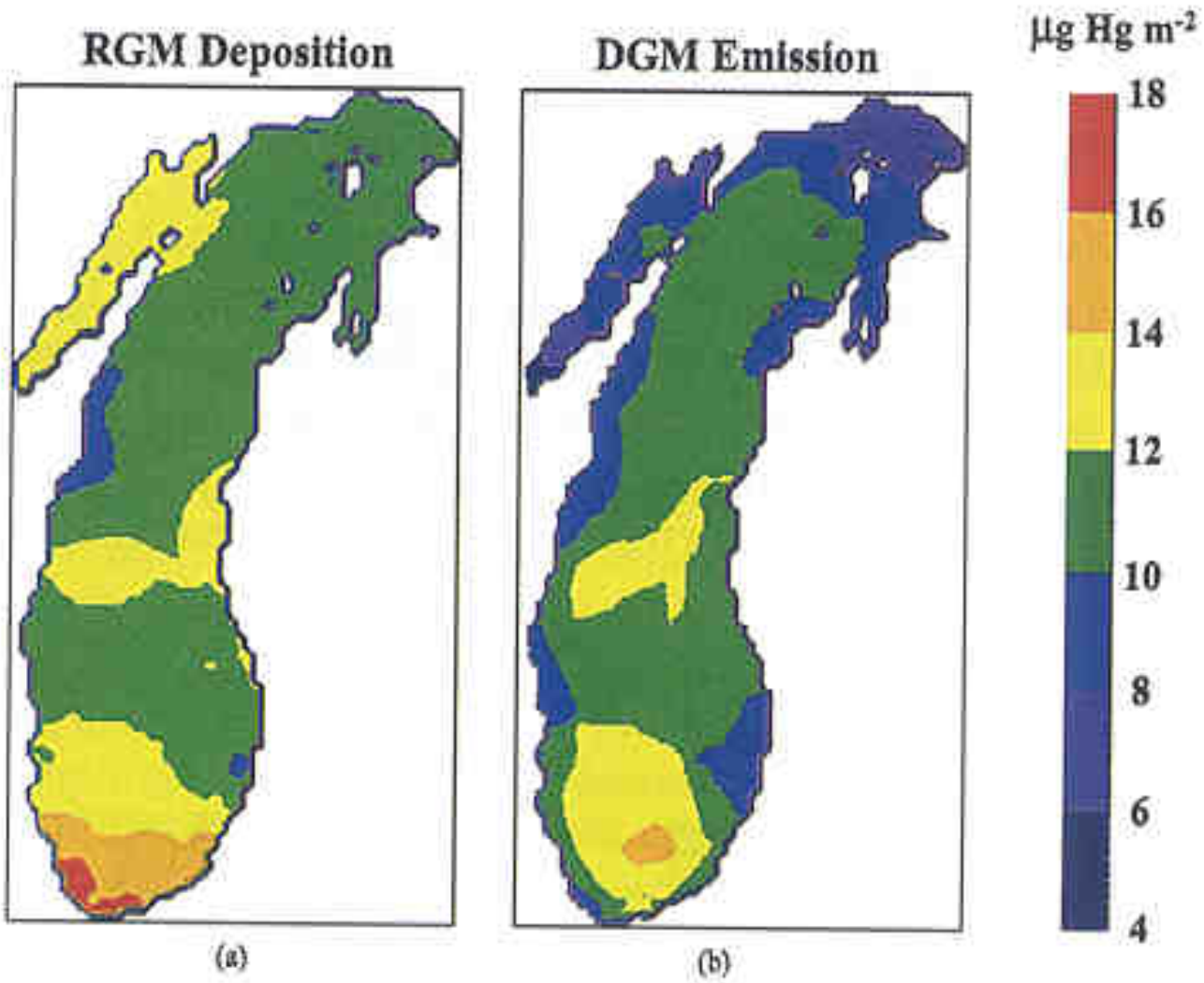
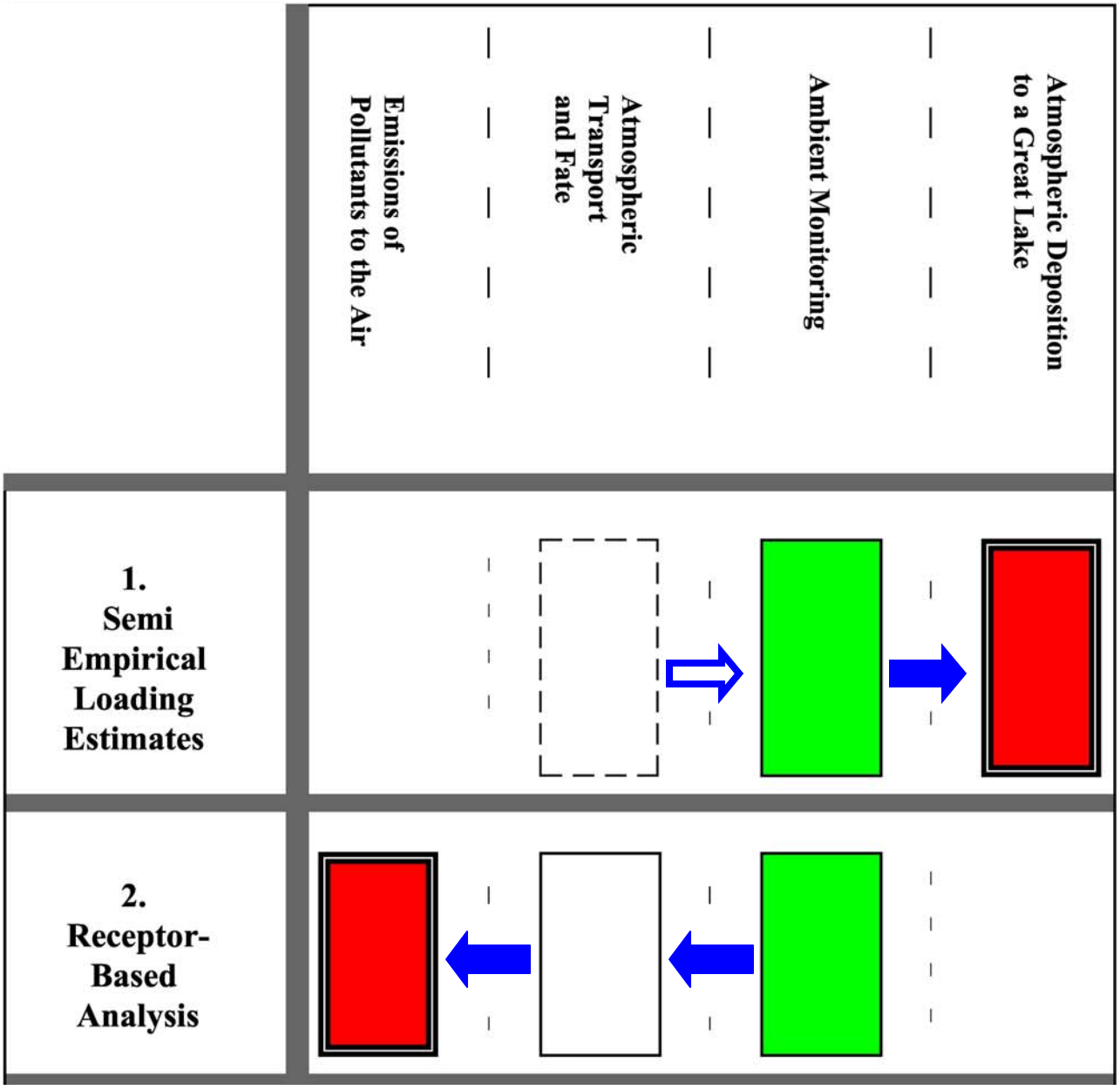


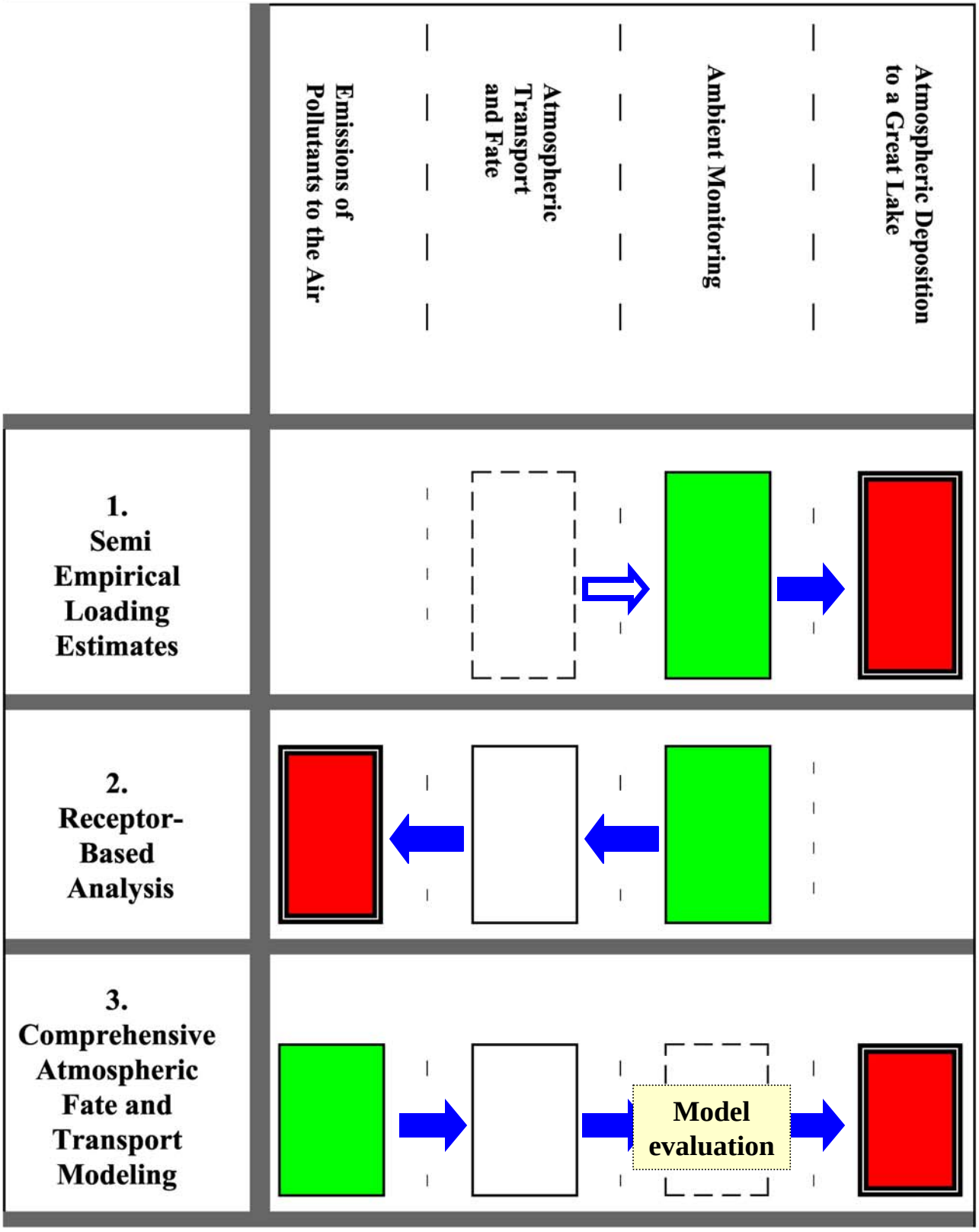
FIGURE 7. Spatial variation in the modeled (a) reactive gaseous Hg (RGM) deposition and (b) dissolved gaseous Hg (DGM) emission fluxes during the Lake Michigan Mass Balance study (July, 1994 to October, 1995).

Source: A. Vette, M. Landis and G. Keeler, Deposition and Emissions of Gaseous Mercury to and from Lake Michigan during the Lake Michigan Mass Balance Study (July, 1994-October 1995).
Environmental Science and Technology 36:4525-4532, 2002

Methodological Approaches for Analysis of the Atmospheric Deposition Pathway



Methodological Approaches for Analysis of the Atmospheric Deposition Pathway



Can’t reliably estimate the *amount* of deposition or *source-receptor relationships* using monitoring alone…

Modeling can potentially give you these answers, but cannot be done credibly without using monitoring to ground-truth the results

Overall Project Goal

Develop atmospheric mercury source-receptor information for the Great Lakes, the Gulf of Maine, and other selected receptors,
to estimate the *amount of deposition* and the relative contributions of different

source *regions*
(local, regional, national, continental, global)

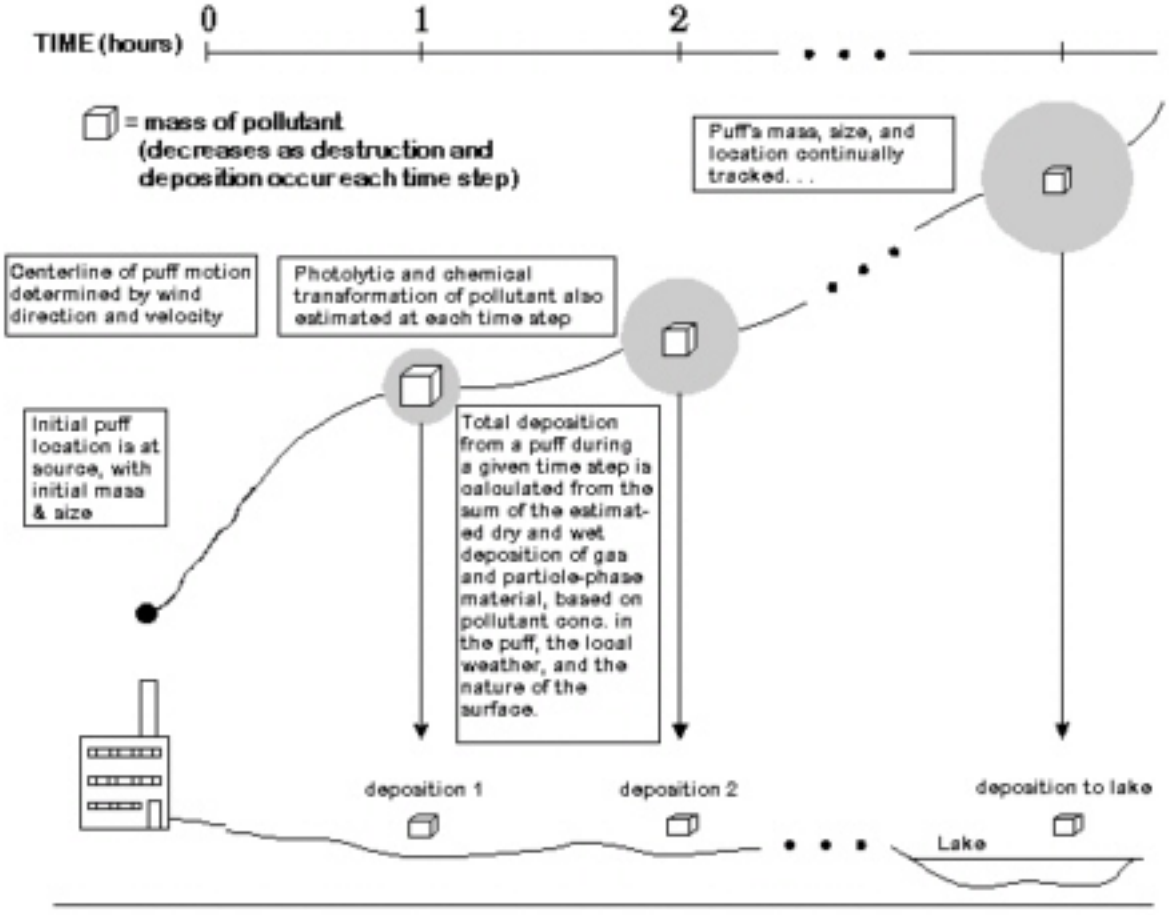
source *categories*
(e.g., coal combustion, waste incineration, etc.)

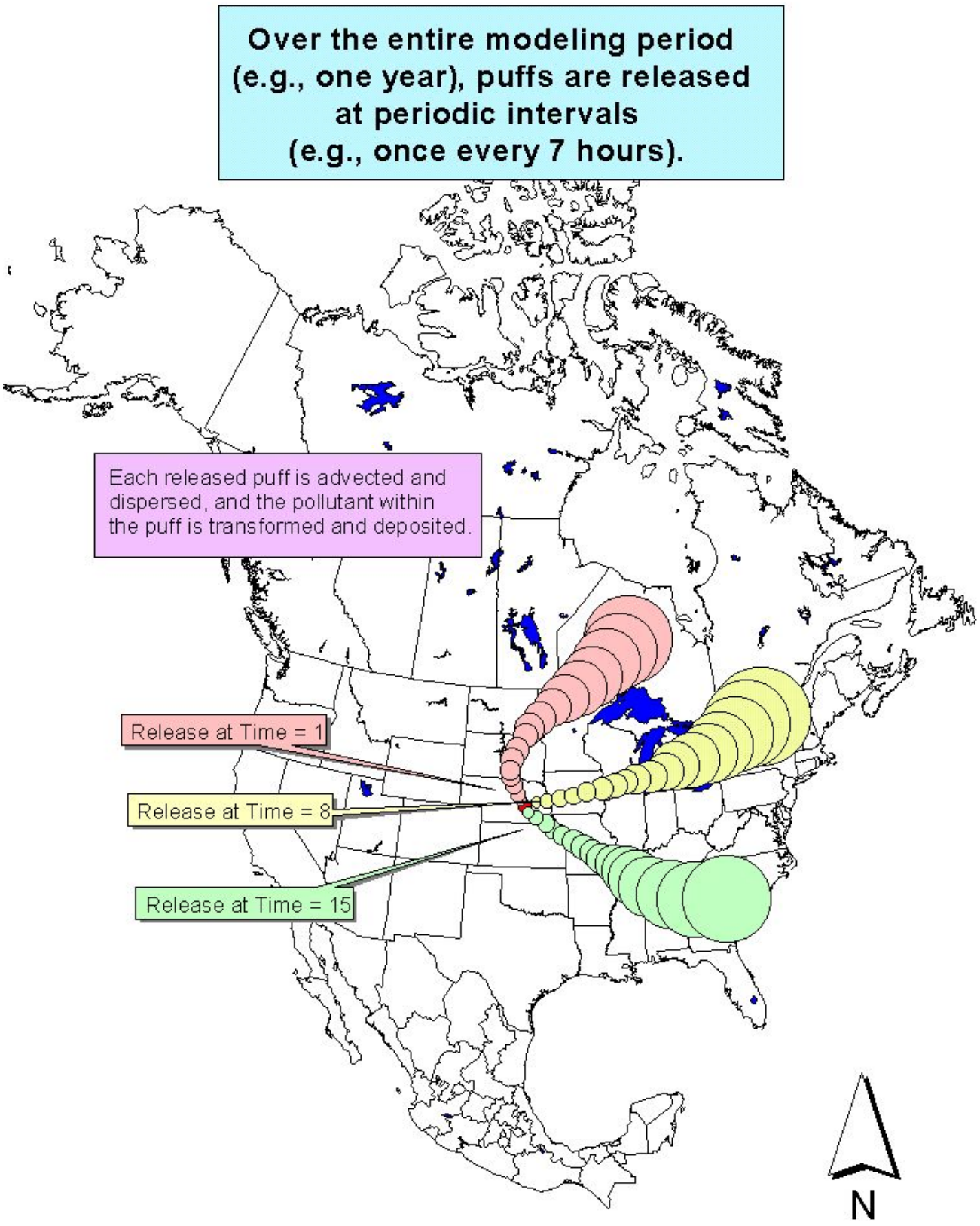
…to the atmospheric deposition to any given receptor

Overall Methodology

- **Start with atmospheric mercury *emissions inventory***
- **Perform *atmospheric fate and transport modeling* of these emissions (using a modified version of NOAA's HSYPLIT model)**
- **Keep track of *source-receptor information* during the modeling**
- **Evaluate the modeling by *comparison* of the predictions *against ambient monitoring data***
- ***If model is performing satisfactorily*, report source-receptor results from the simulations**
- **(Similar to earlier work with dioxin and atrazine)**

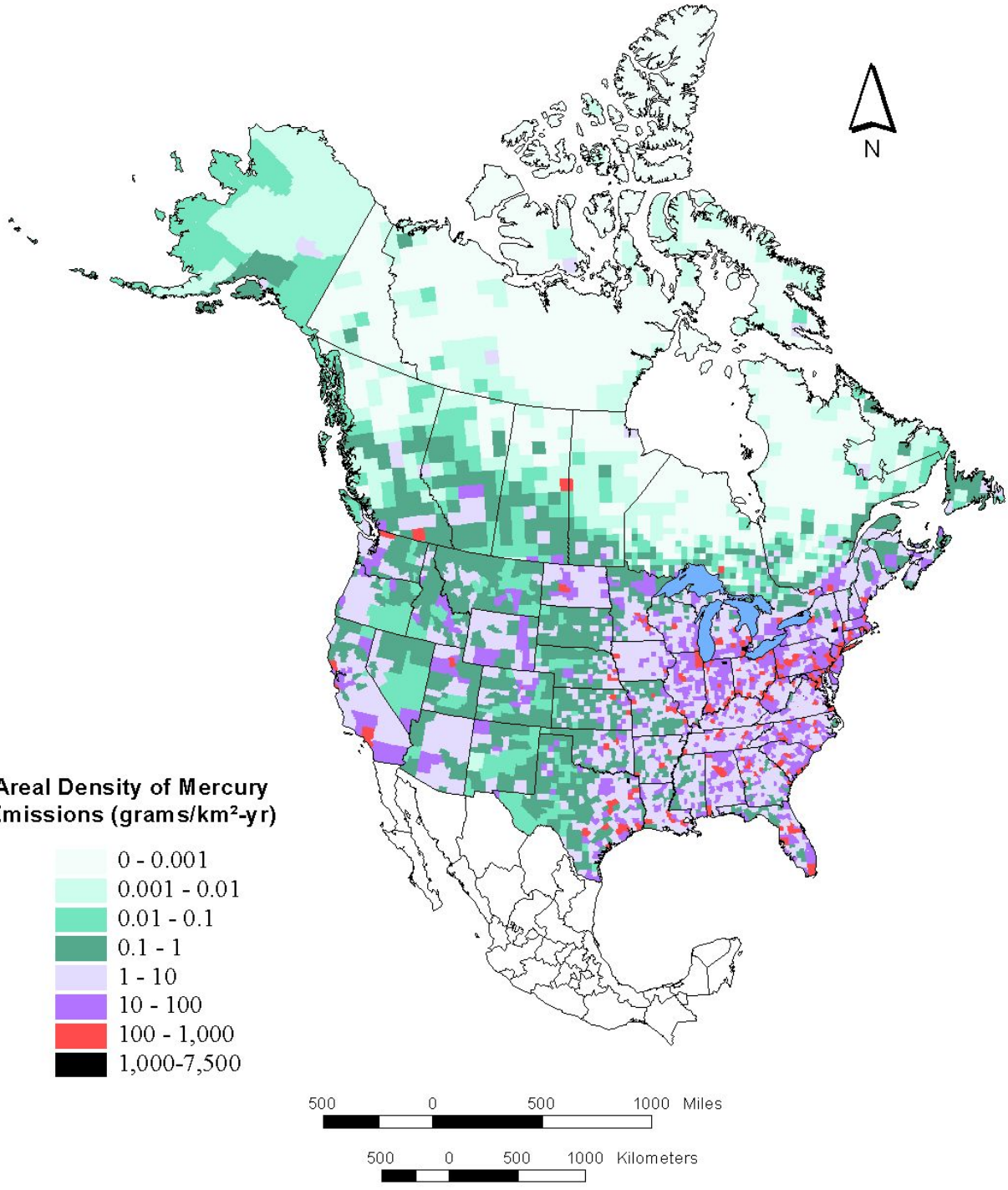
Figure 1. Lagrangian Puff Air Transport and Deposition Model

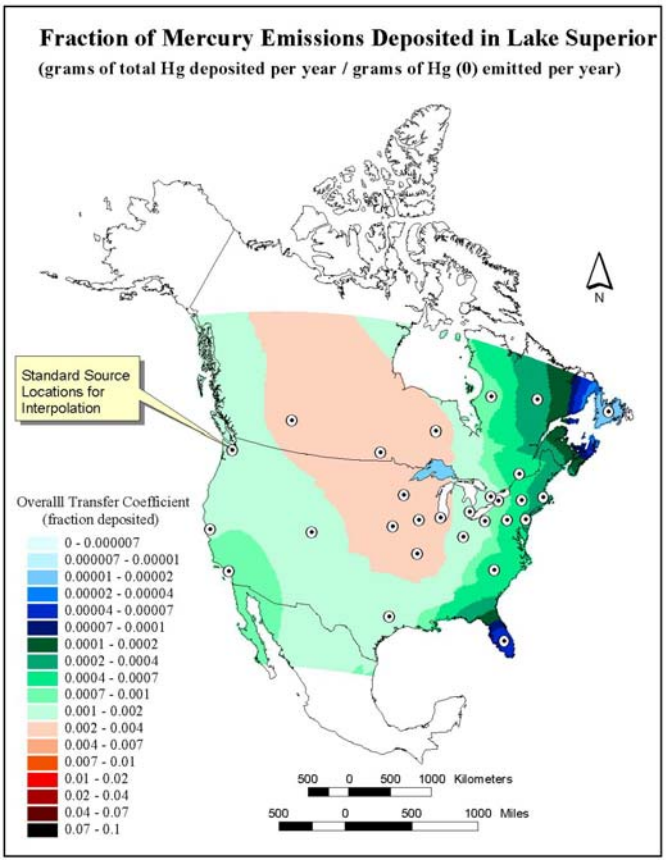


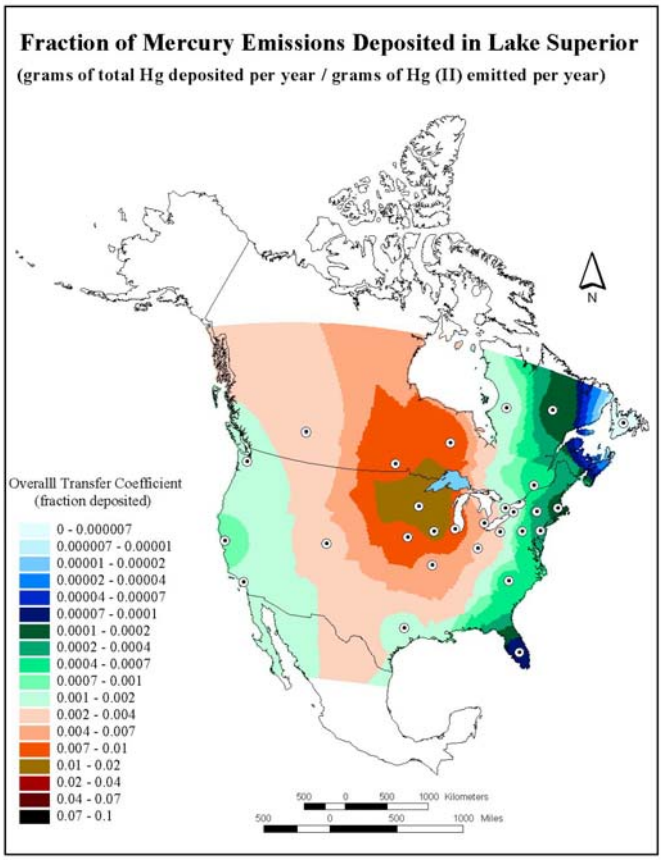

Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).
Each released puff is advected and dispersed, and the pollutant within the puff is transformed and deposited.
Release at Time = 1
Release at Time = 8
Release at Time = 15
N

Atmospheric Mercury Emissions

(Canada: 1995; U.S. 1996, 1999)

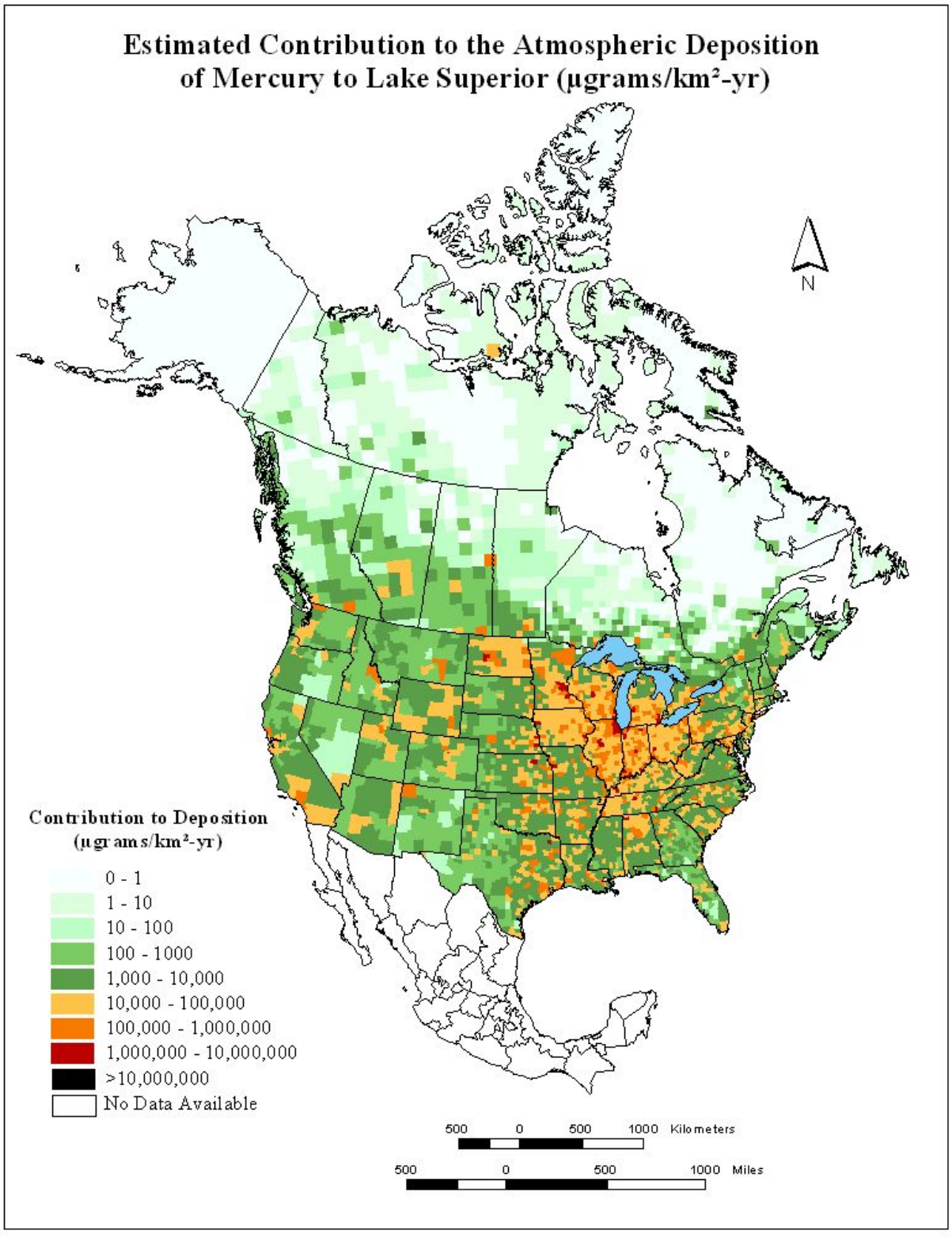




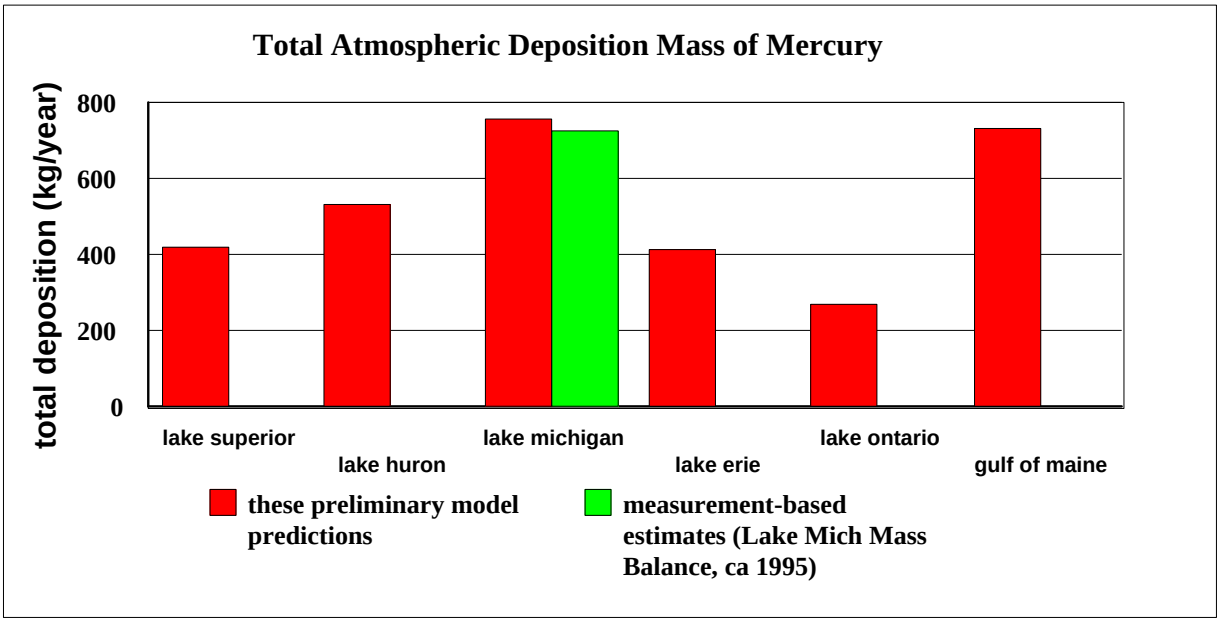


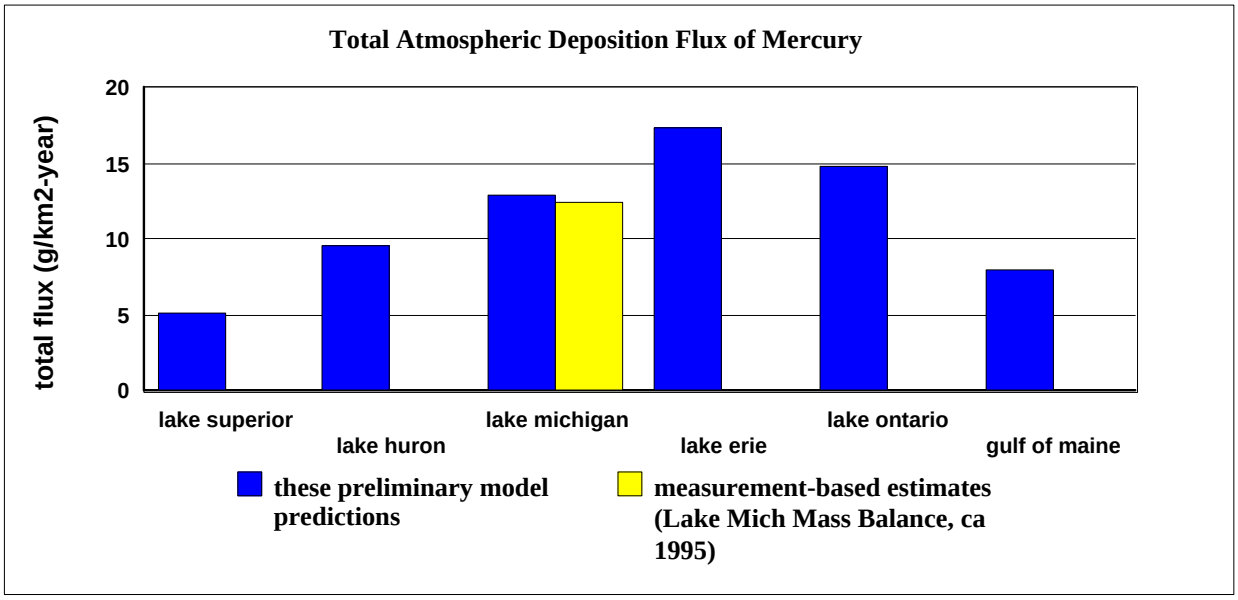
Transfer Coefficients for Hg are strongly influenced by the “type” of Hg emitted

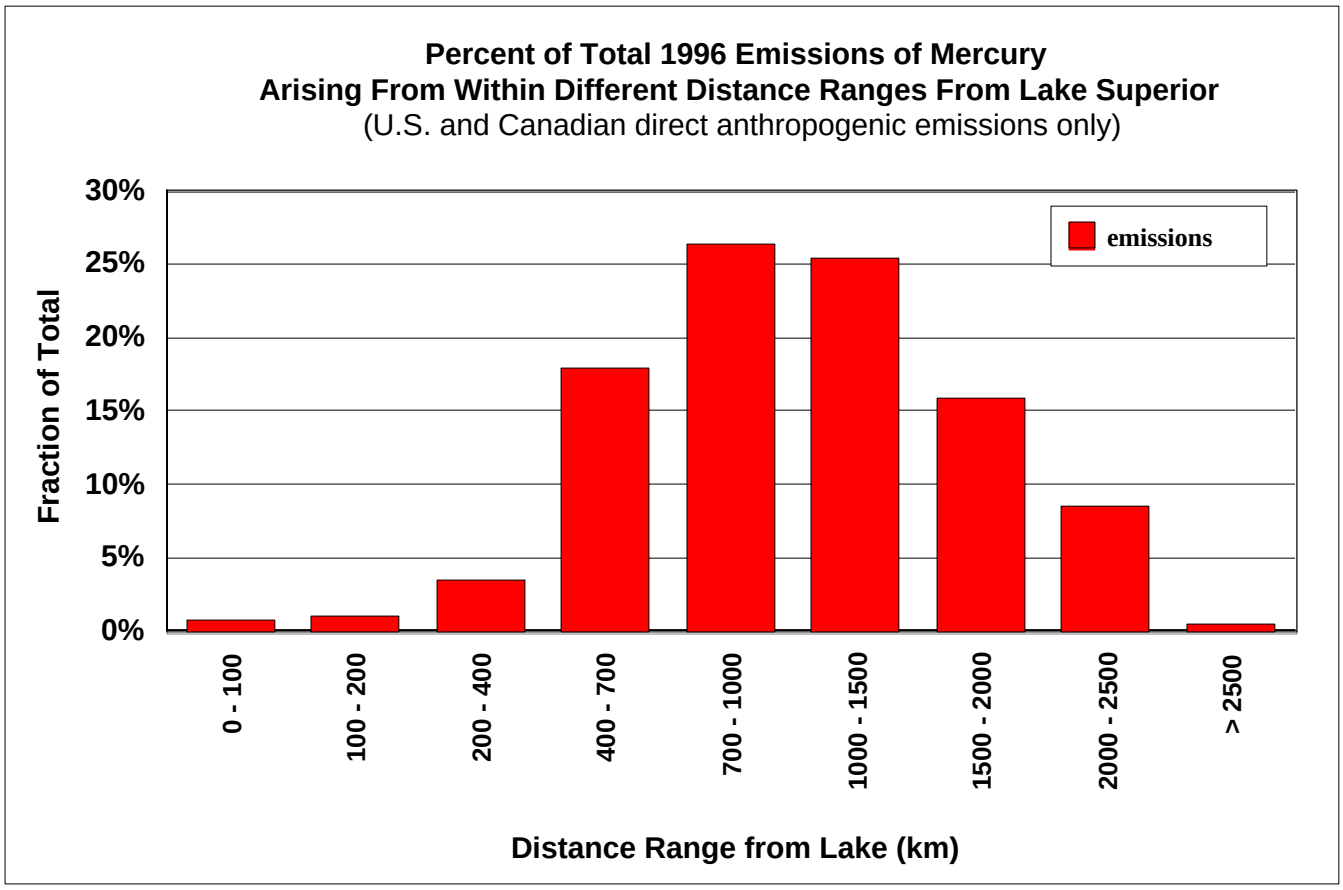
[Hg(II) has much greater local impacts than Hg(0)]

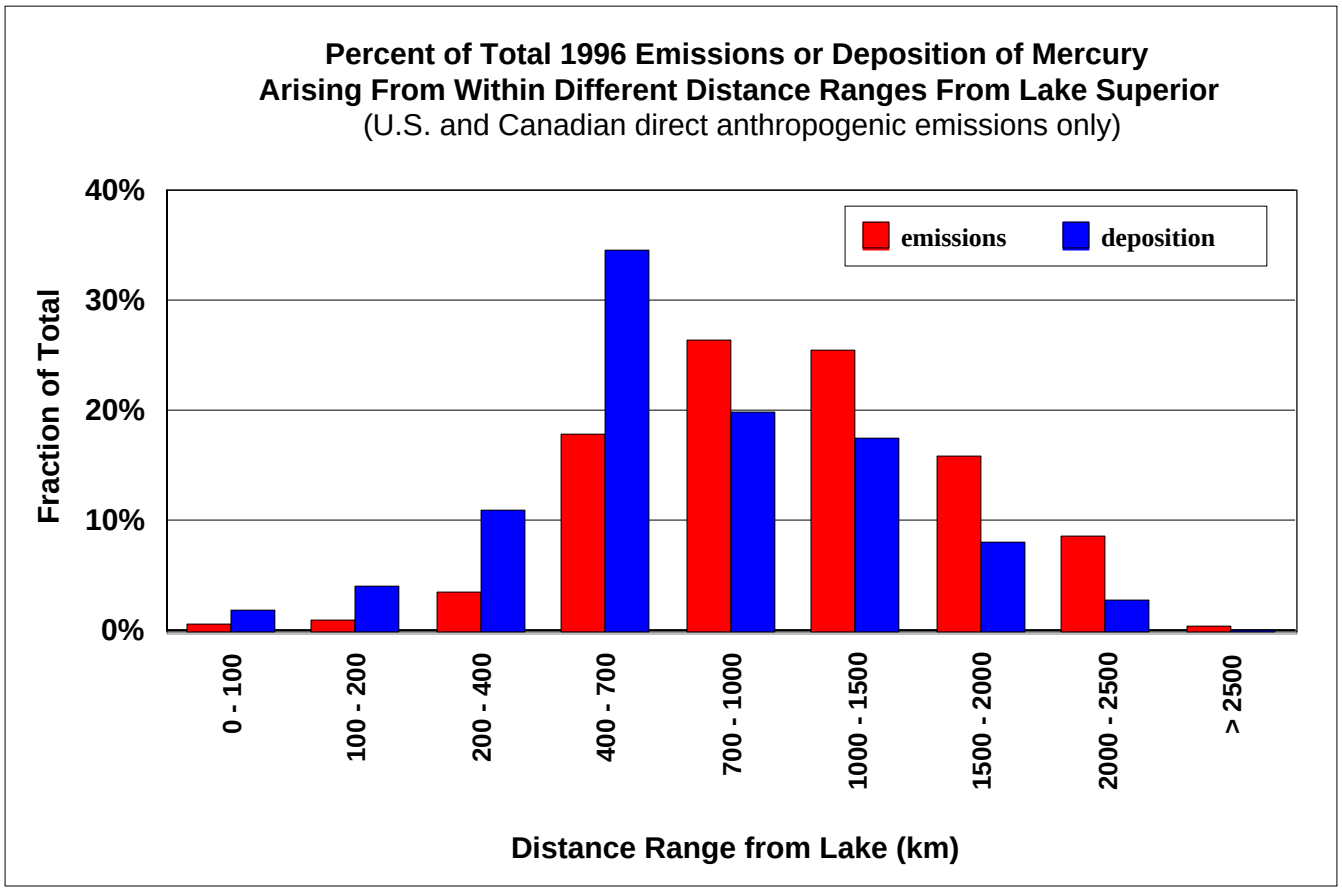

Estimated Contribution to the Atmospheric Deposition of Mercury to Lake Superior (µgrams/km²-yr)
N
Contribution to Deposition (µgrams/km²-yr)
0 - 1
1 - 10
10 - 100
100 - 1000
1,000 - 10,000
10,000 - 100,000
100,000 - 1,000,000
1,000,000 - 10,000,000
>10,000,000
No Data Available
500 0 500 1000 Kilometers
500 0 500 1000 Miles

Estimated atmospheric deposition of mercury to the Great Lakes



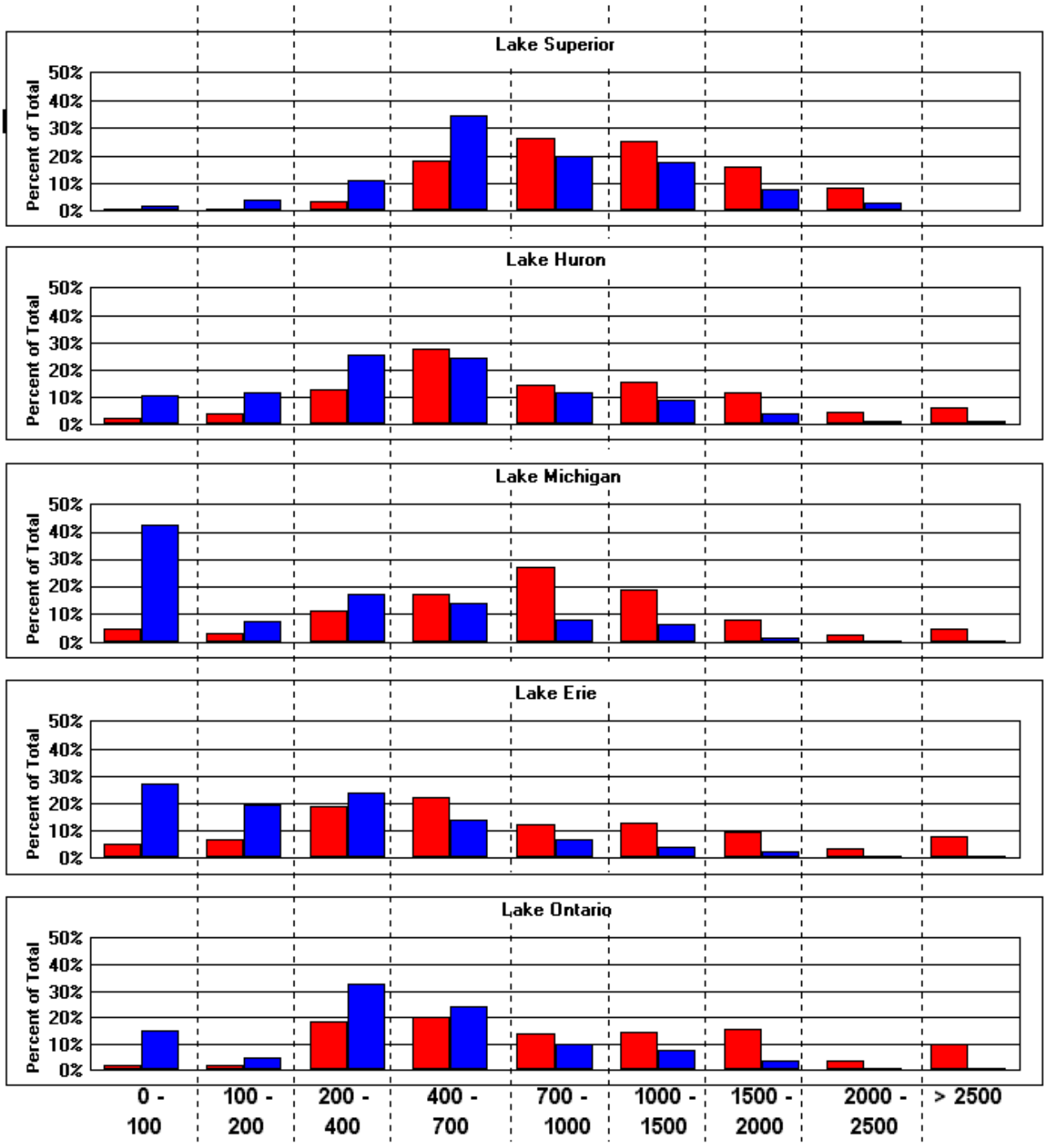



Percent of Total 1996 Emissions of Mercury
Arising From Within Different Distance Ranges From Lake Superior
(U.S. and Canadian direct anthropogenic emissions only)
Fraction of Total
30%
25%
20%
15%
10%
5%
0%
emissions
0 - 100
100 - 200
200 - 400
400 - 700
700 - 1000
1000 - 1500
1500 - 2000
2000 - 2500
> 2500
Distance Range from Lake (km)


Percent of Total 1996 Emissions or Deposition of Mercury
Arising From Within Different Distance Ranges From Lake Superior
(U.S. and Canadian direct anthropogenic emissions only)
Fraction of Total
40%
30%
20%
10%
0%
emissions
deposition
0 - 100
100 - 200
200 - 400
400 - 700
700 - 1000
1000 - 1500
1500 - 2000
2000 - 2500
> 2500
Distance Range from Lake (km)

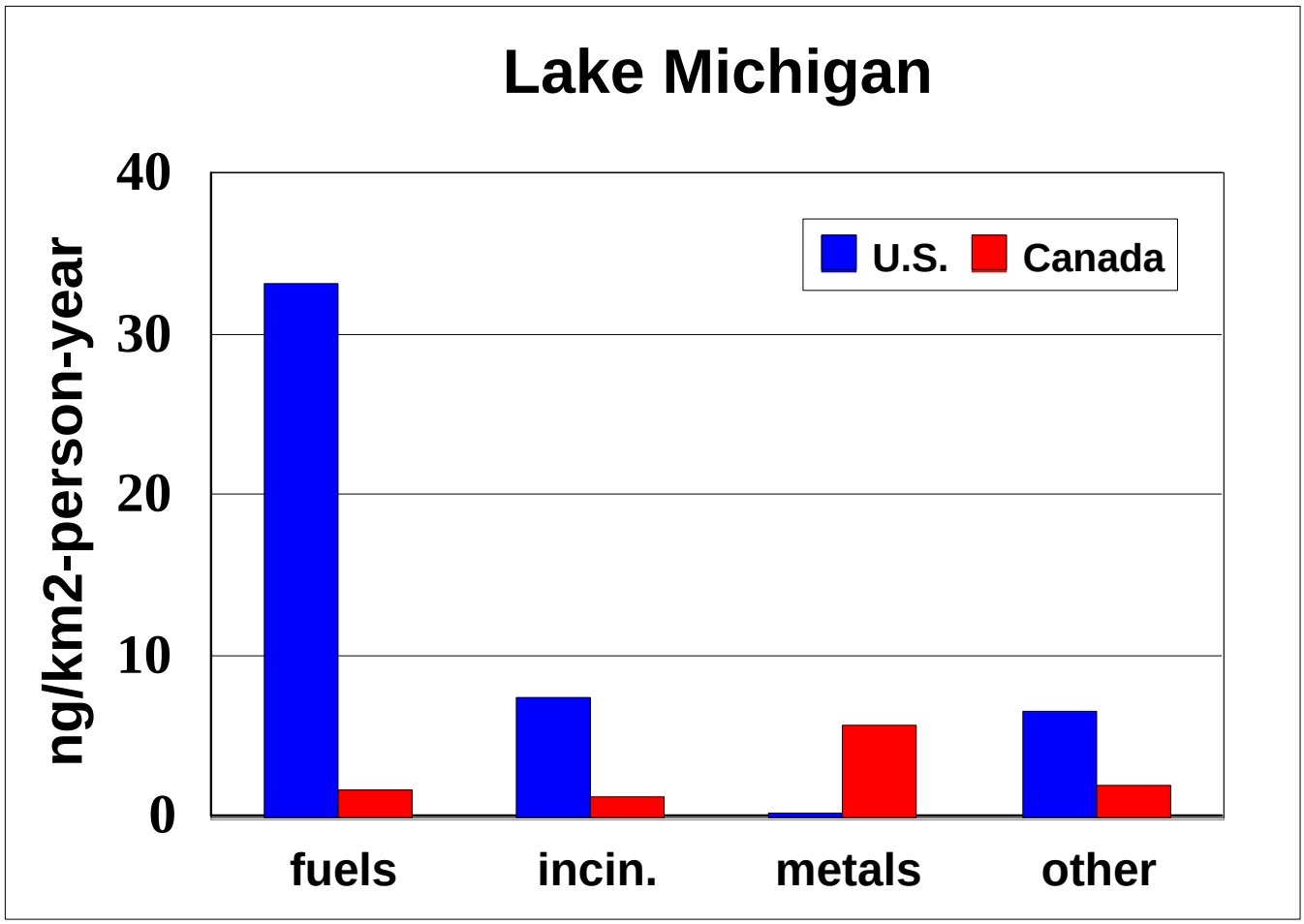
Percent of Total Emissions or Deposition of Mercury Arising From Within Different Distance Ranges From Each of the Great Lakes

[for sources in the United States (1996,1999) and sources in Canada (1995); preliminary analysis - Sept 2001]



Contributions of different overall source sectors to the atmospheric deposition of mercury in 1996

***per capita flux*, i.e., nanograms of mercury deposited per km2 of lake per person per year**



“fuels" = fuel combustion;
"incin." = waste incineration;
"metals" = metallurgcial processes

Contributions of different overall source sectors to atmospheric deposition of mercury to the Great Lakes and the Gulf of Maine

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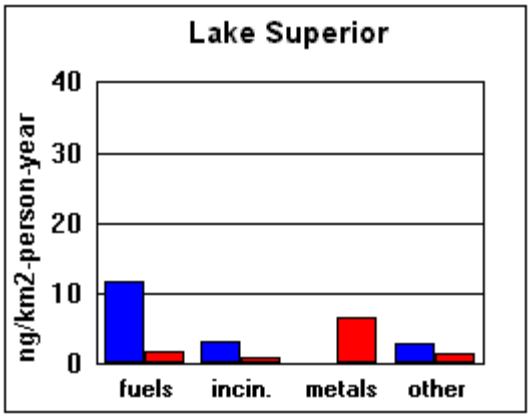

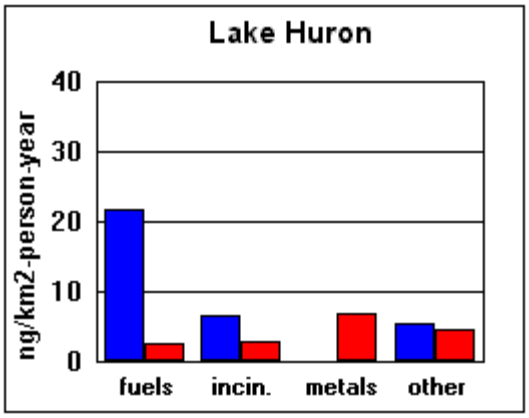

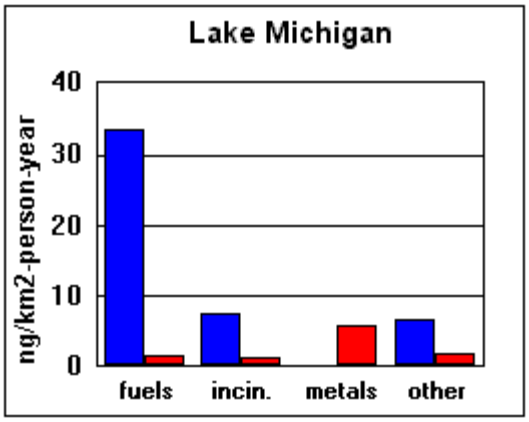

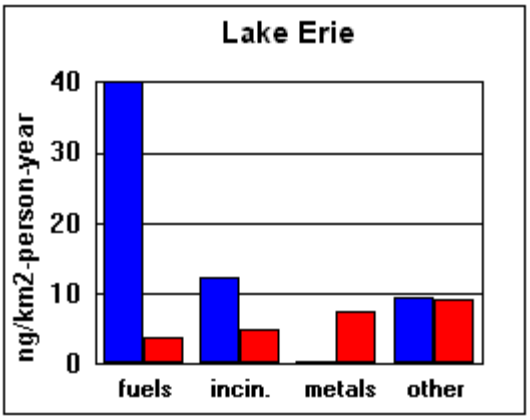

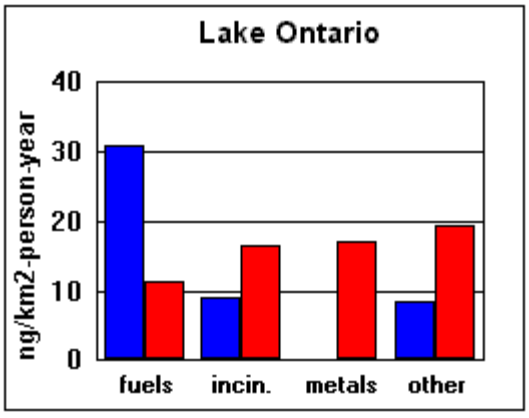

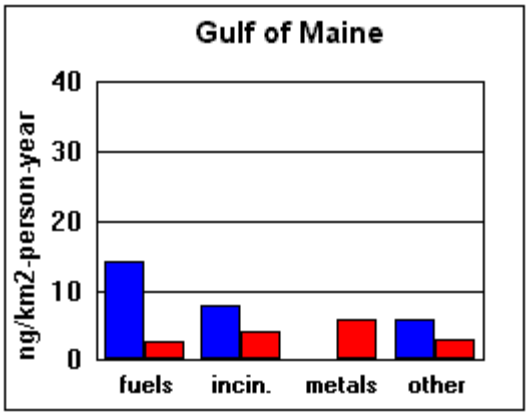

United States

Canada

Some concluding observations

***Both monitoring and modeling must be used together* to answer the key questions we need answered about atmospheric deposition of mercury to the Great Lakes**

- ***magnitude***
- ***relative importance***
- ***source-receptor relationships***

For the Great Lakes, atmospheric deposition of mercury is almost certainly a very significant loading pathway.

***Preliminary* results for source receptor relationships suggest the importance of coal-fired power plants, over at least a regional and national scales**

processes are complex, and there is still much work to do to iron out the details…