Mercury in the Atmosphere

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Outline

- Sources of Atmospheric Hg
  - Anthropogenic vs natural
  - Anthropogenic sources
- Forms of Hg in the atmosphere
- Hg concentrations in NYS
- Hg deposition processes

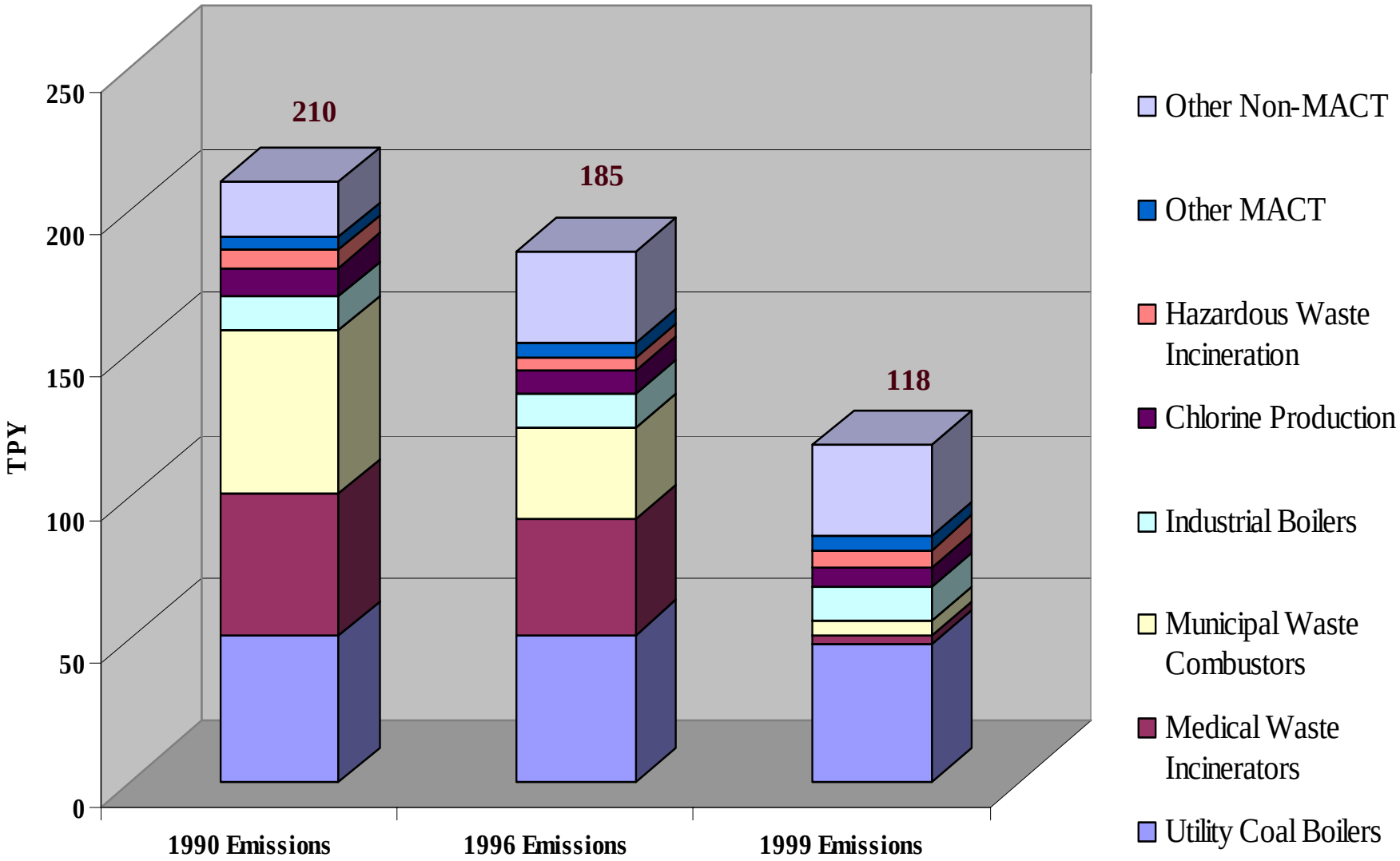
Acknowledgements – C Driscoll, M Cohen, NY DEC, YJ Han, S Lai, J Pagano, M Milligan

Global Sources of Mercury to the Atmosphere (in metric tons per year)

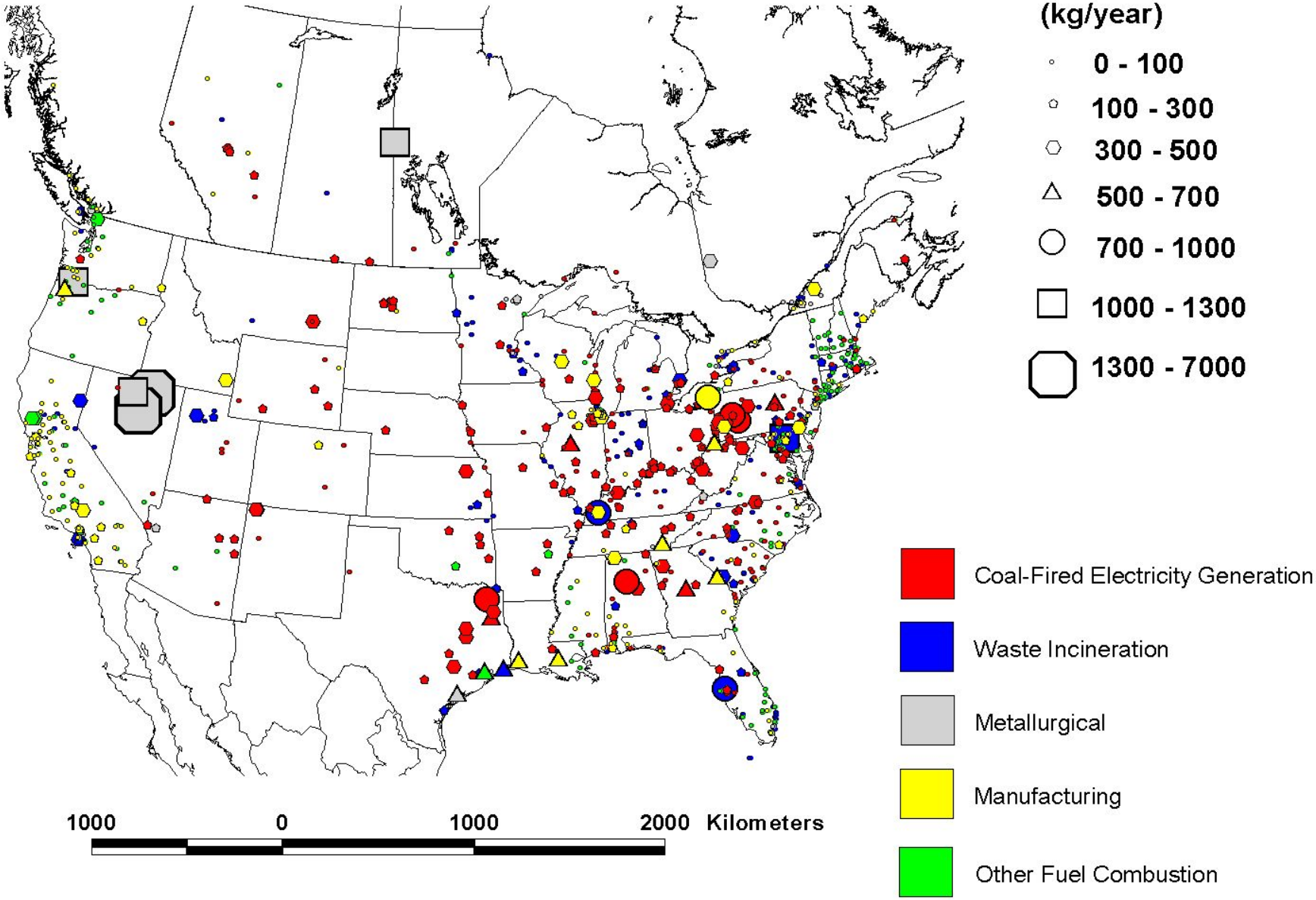
Source	Seigneur et al. 2004	Bergan et al. 1999	Mason & Sheu 2002
Direct Anthropogenic	2143	2160	2400
Recycled Anthropogenic	2134	2000	2090
Total Anthropogenic	4277	4160	4490
Natural	2134	1900	2110
Total (% of Anthropogenic Origin)	6411 (67%)	6060 (69%)	6600 (68%)

from C. Driscoll

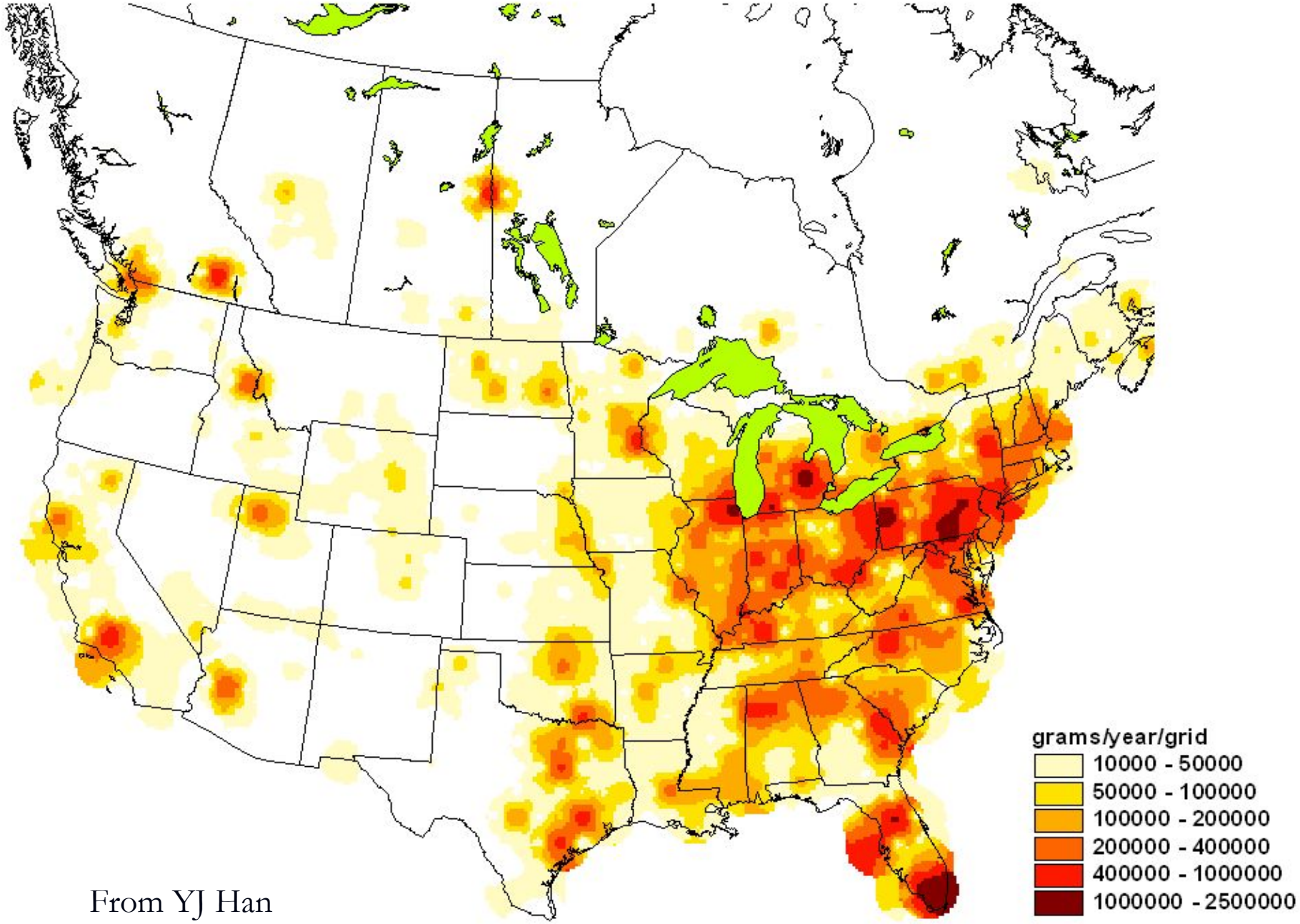
U.S. Anthropogenic Emissions of Mercury



Source: EPA 1990, 1996 NTI and EPA 1999 NEI. Short tons per year.


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

From M. Cohen


grams/year/grid
10000 - 50000
50000 - 100000
100000 - 200000
200000 - 400000
400000 - 1000000
1000000 - 2500000

From YJ Han

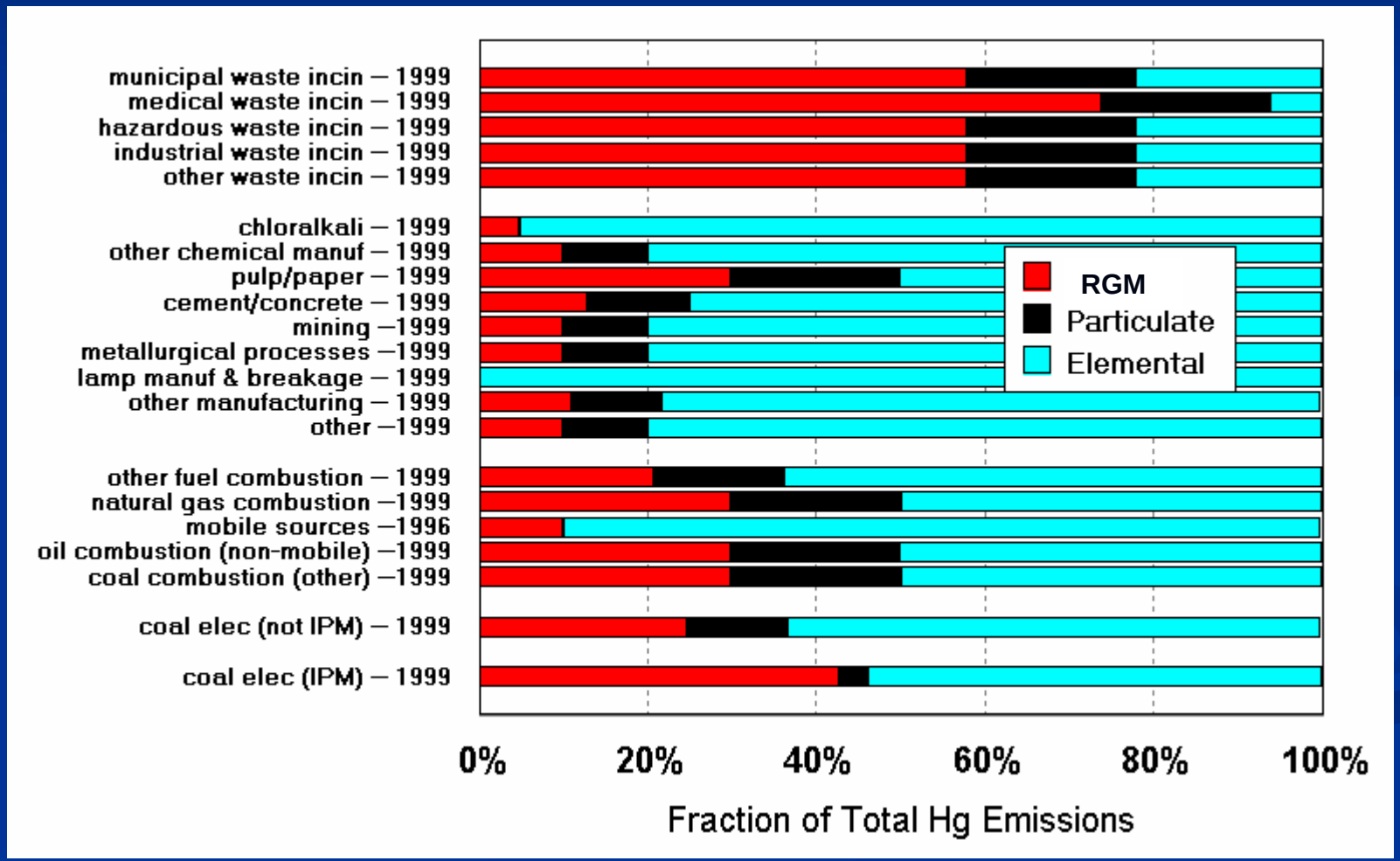
Atmospheric Mercury Species

- Elemental Mercury (Hg^0)
  Predominant species, Long range transport
  Globally distributed, 0.5 to 2 years residence time

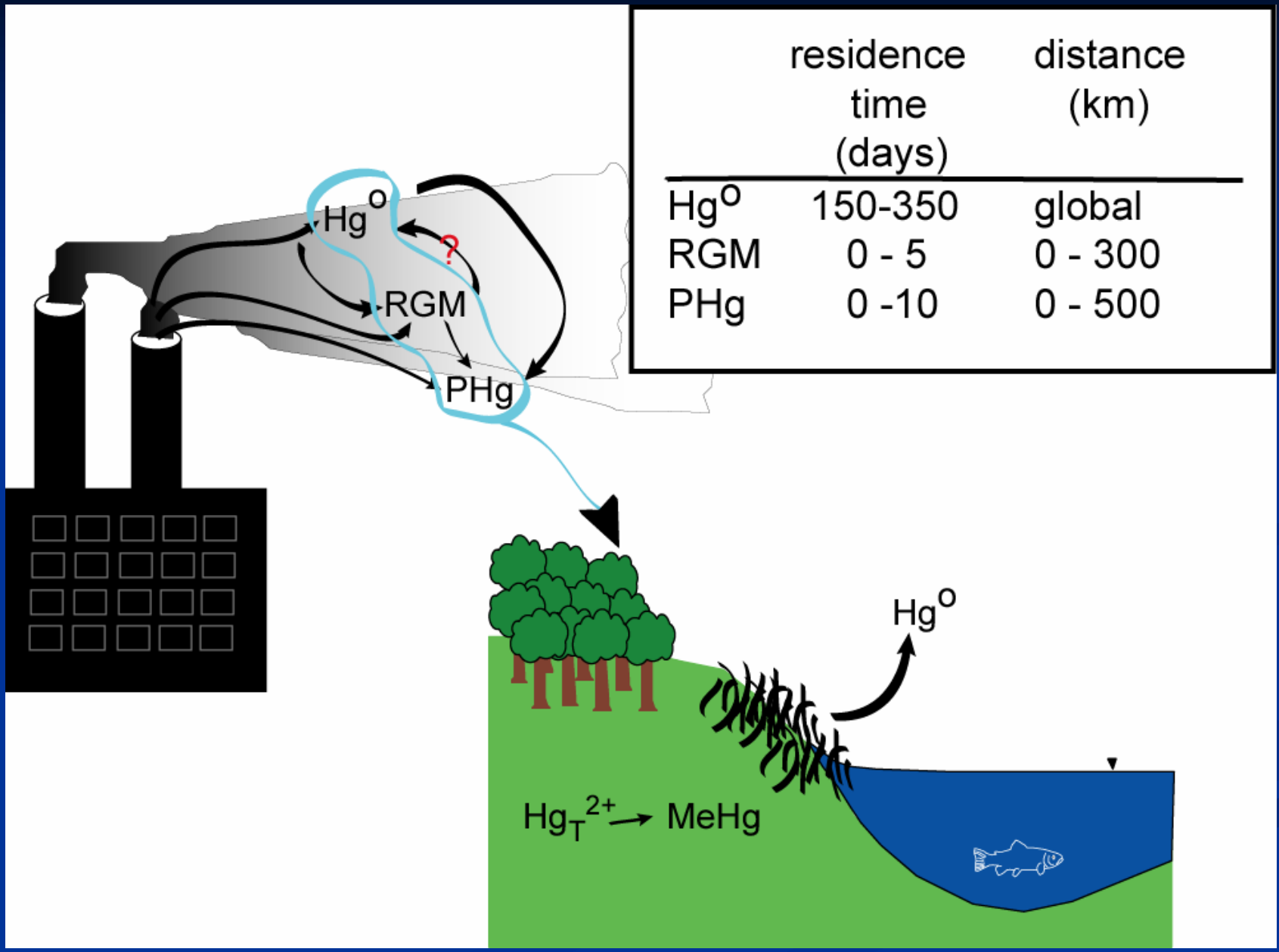
- Gaseous divalent mercury (RGM, $Hg^{2+,}$)
  Oxidized mercury: Hg(II) : $HgCl_2$, other species?
  Highly water soluble -> short atmospheric life time (0.5-2 days)
  Local and Regional effects

- Particulate Mercury (Hg_p)
  Species largely unknown – probably Hg(II)
  Local and Regional Effects (0.5-2 days)

Estimated Speciation Profile for U.S. Atmospheric Mercury Emissions (1999)



Simplified Mercury Cycle from C. Driscoll



	residence time (days)	distance (km)
Hg^0	150-350	global
RGM	0 - 5	0 - 300
PHg	0 -10	0 - 500

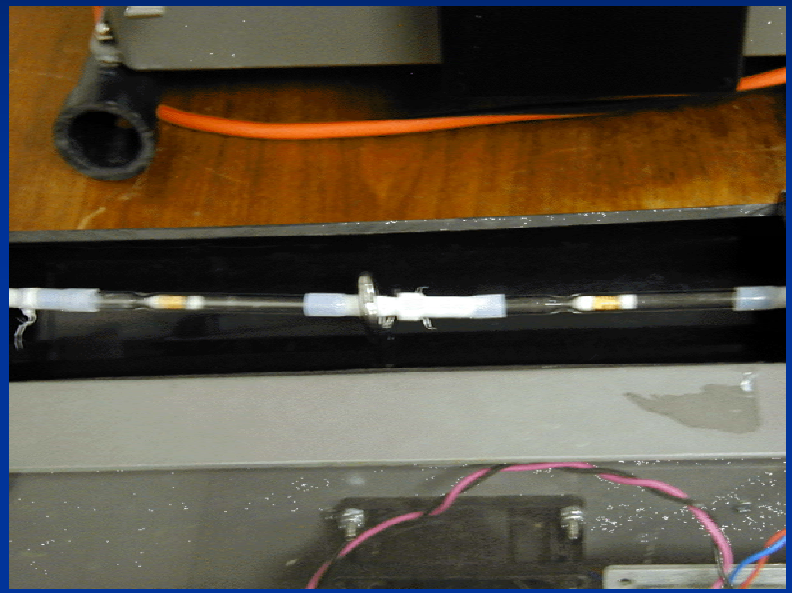
Hg sampling sites in NYS

Potsdam and Stockton funded by NYSERDA, Sterling by US EPA

Sterling, NY

Between Oswego and Rochester on a bluff overlooking the lake

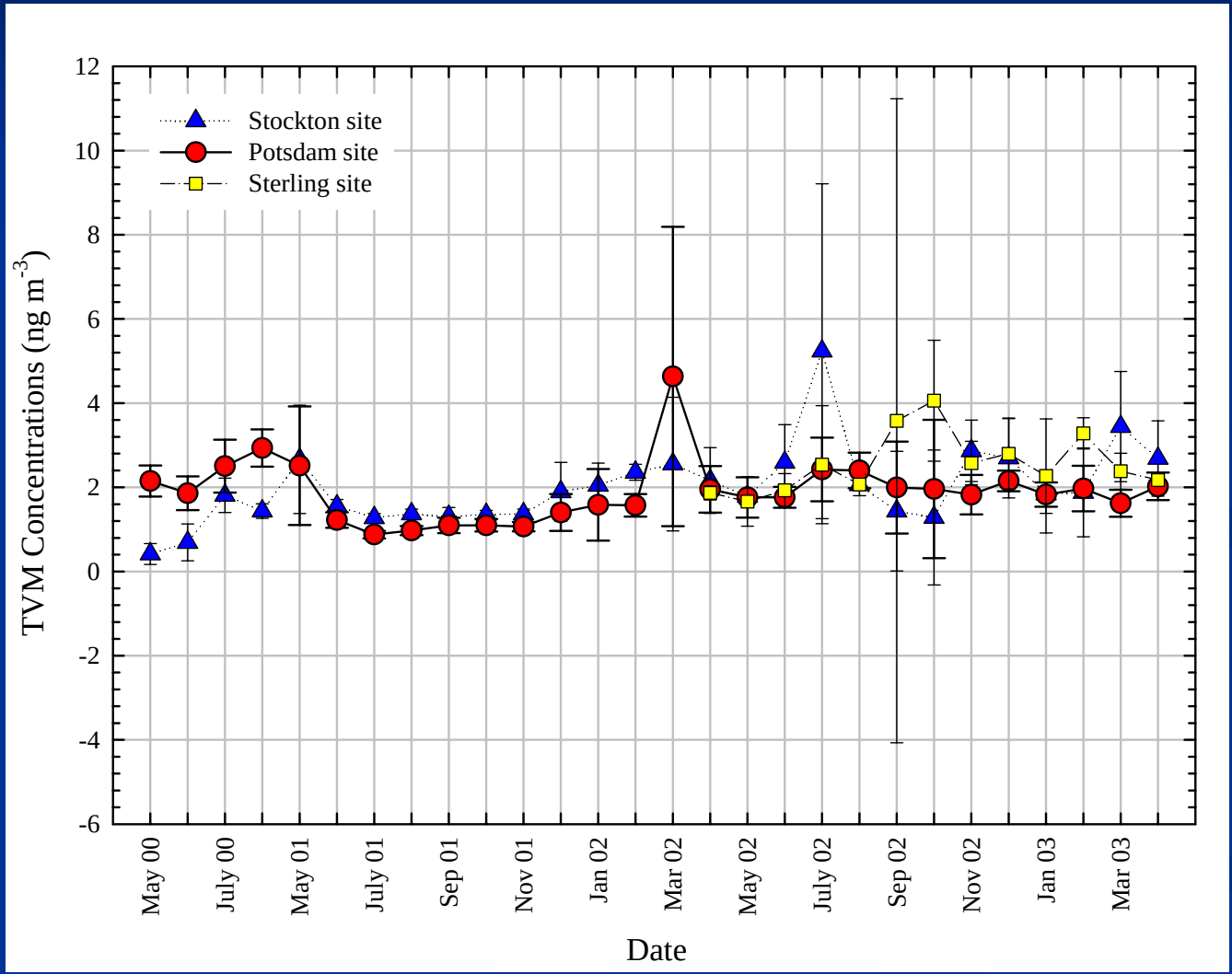
Manual Air Sampling



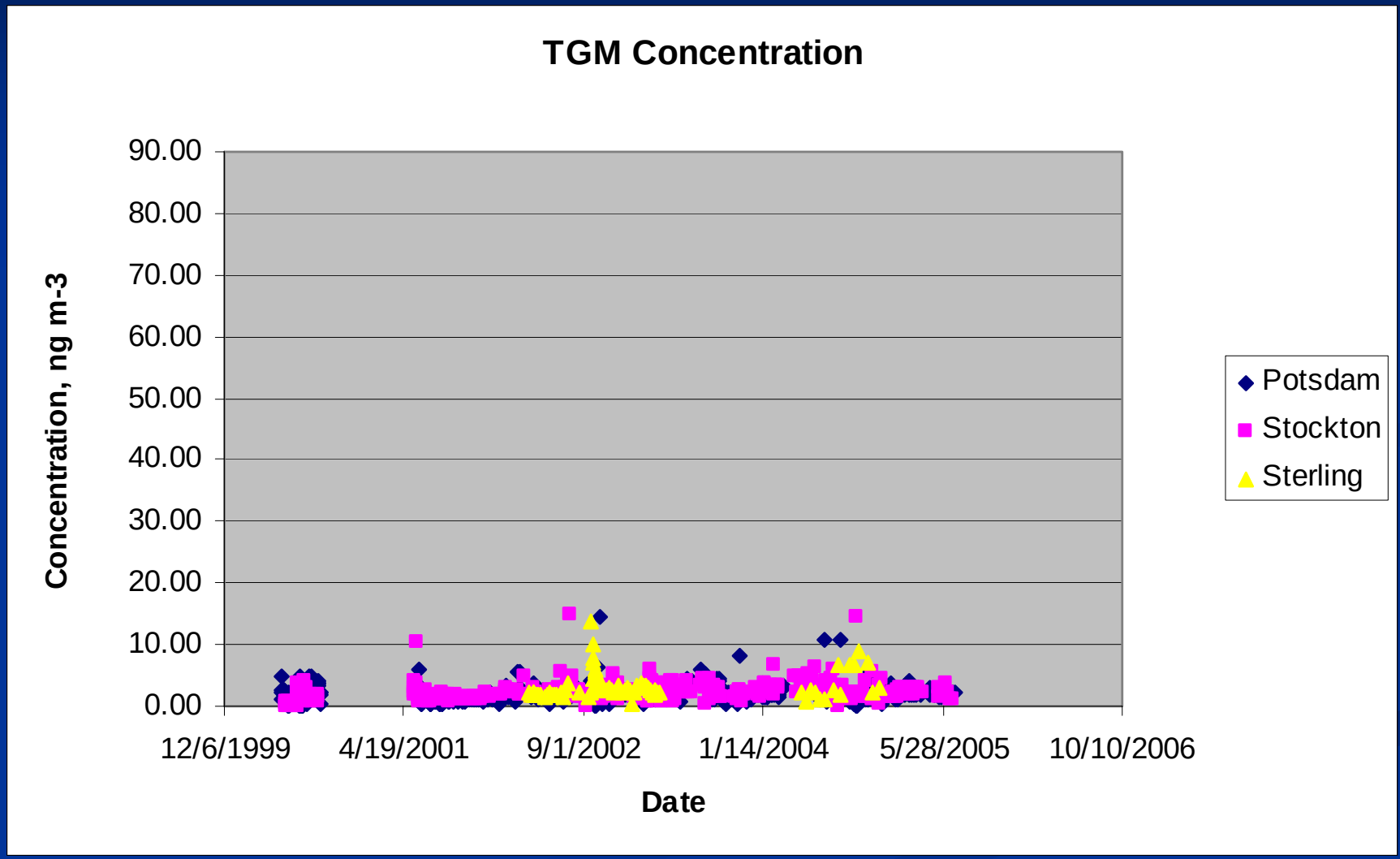
TGM: Adsorption into Gold traps

RGM: Annular Denuder coated by KCl

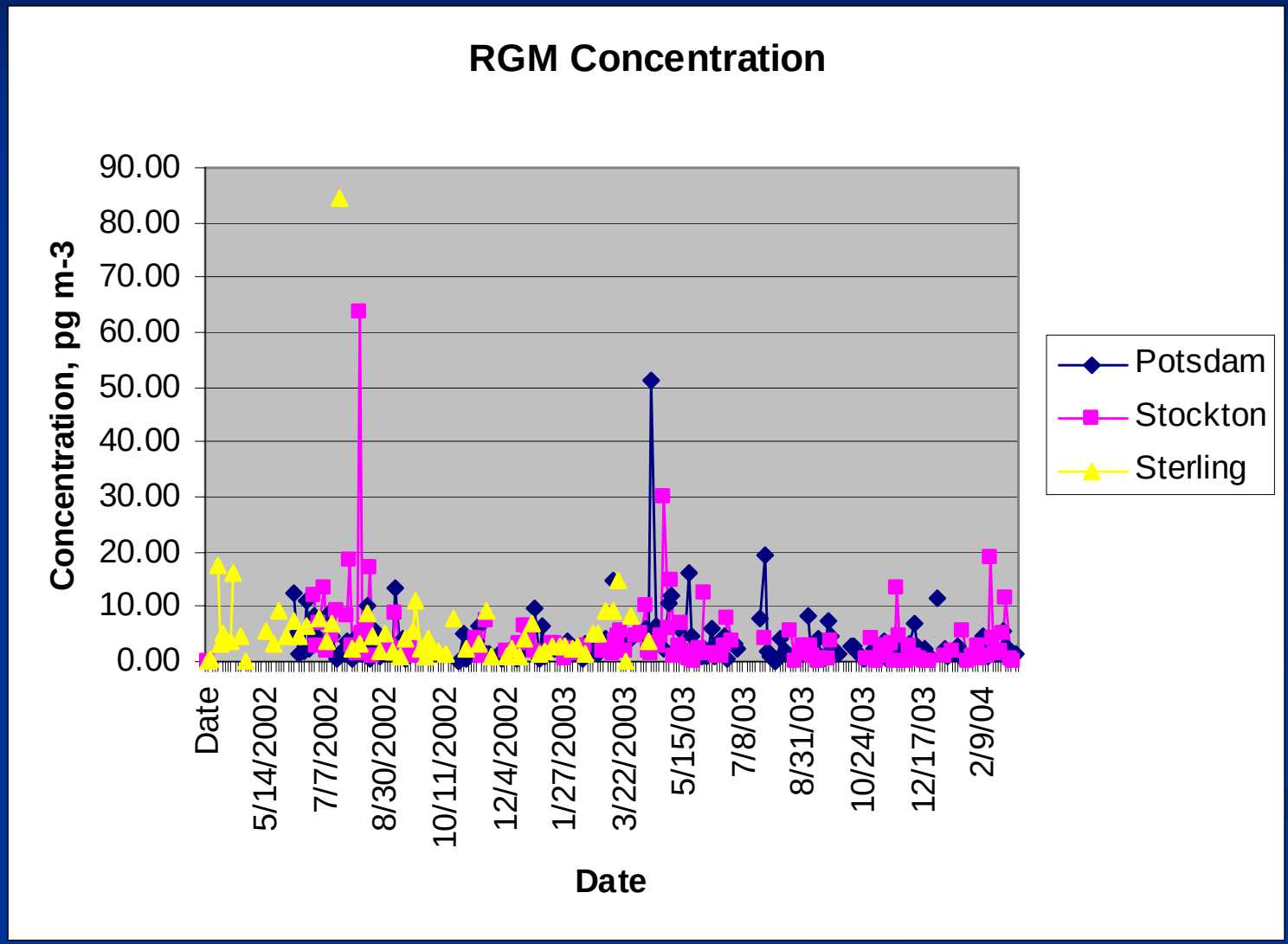
Monthly Average TGM Concentrations, ng/m^3



Daily TGM Concentrations, ng/m^3

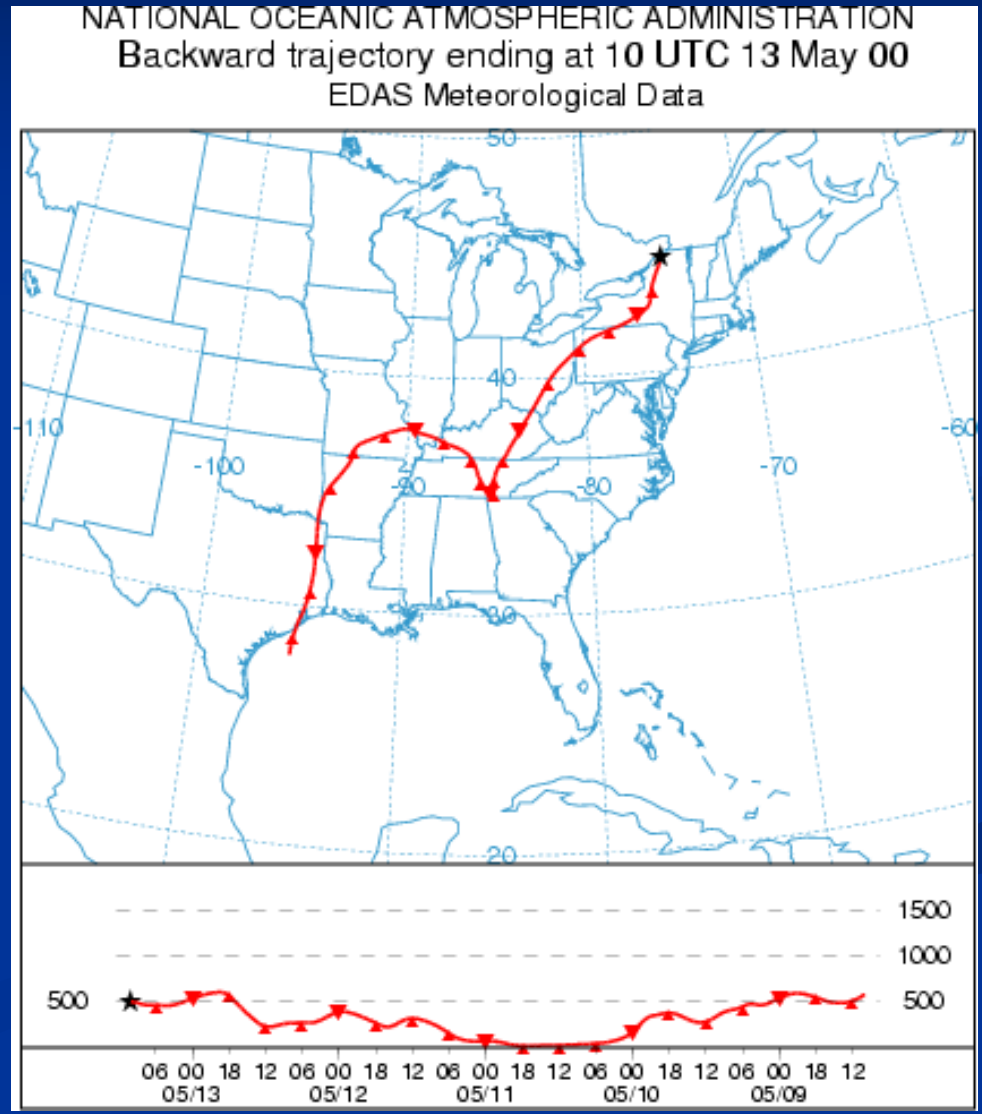


Daily RGM Concentrations, pg/m^3

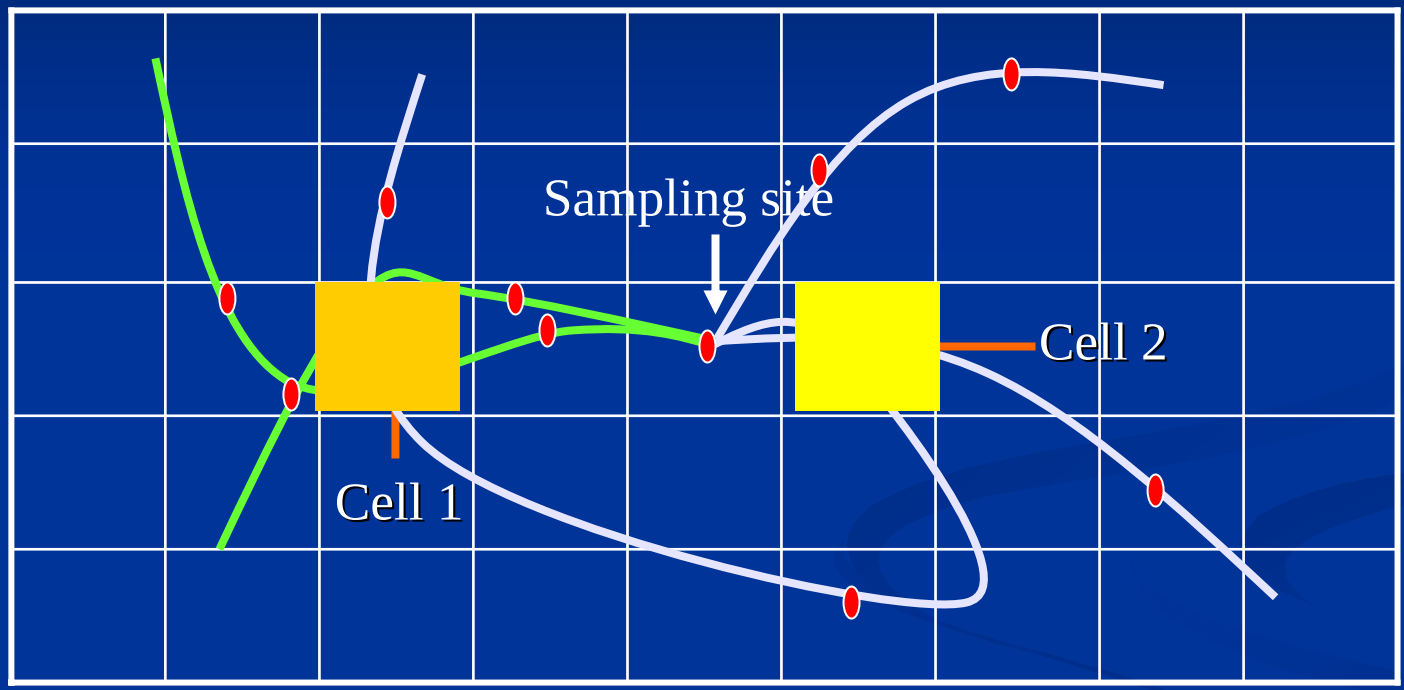


Computation of Trajectories - HYSPLIT4

- NOAA Model
- Predicts history of air movement



Potential Source Contribution Function (PSCF)



Back-trajectory representing high concentration

Back-trajectory representing low concentration

PSCF value
Cell 1 = 2/3
Cell 2 = 0/2

JP-PSCF result for TGM measurements taken in Potsdam, Stockton, and Sterling in NY

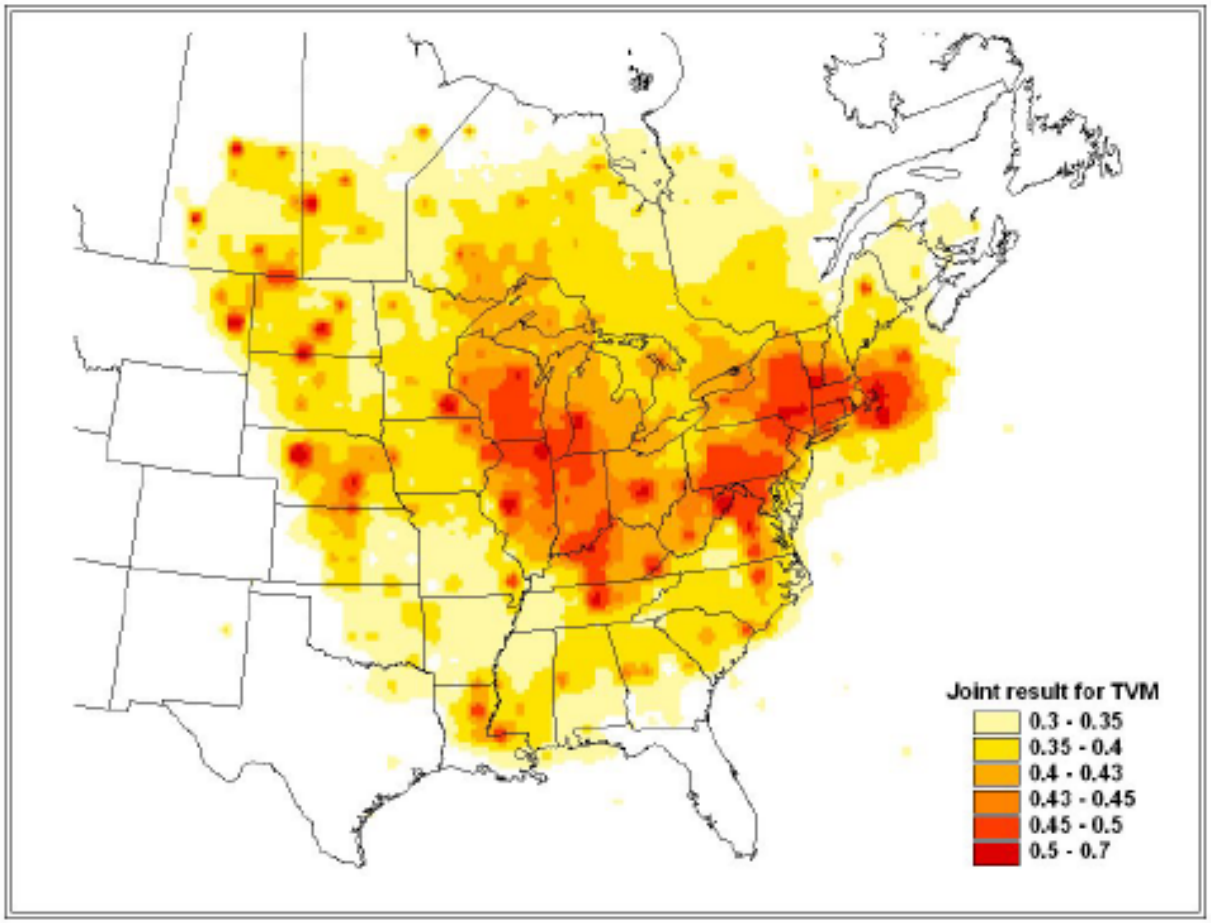
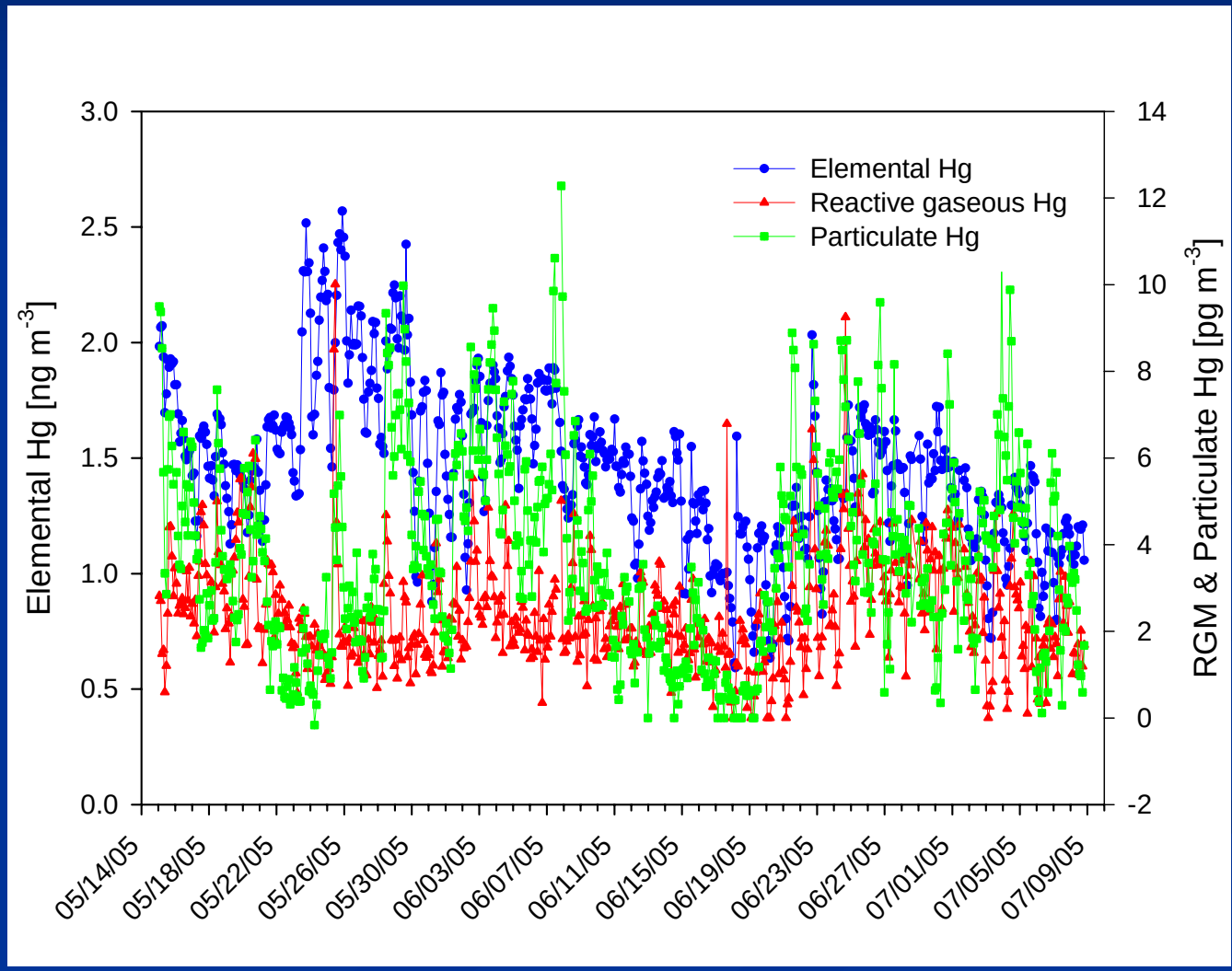


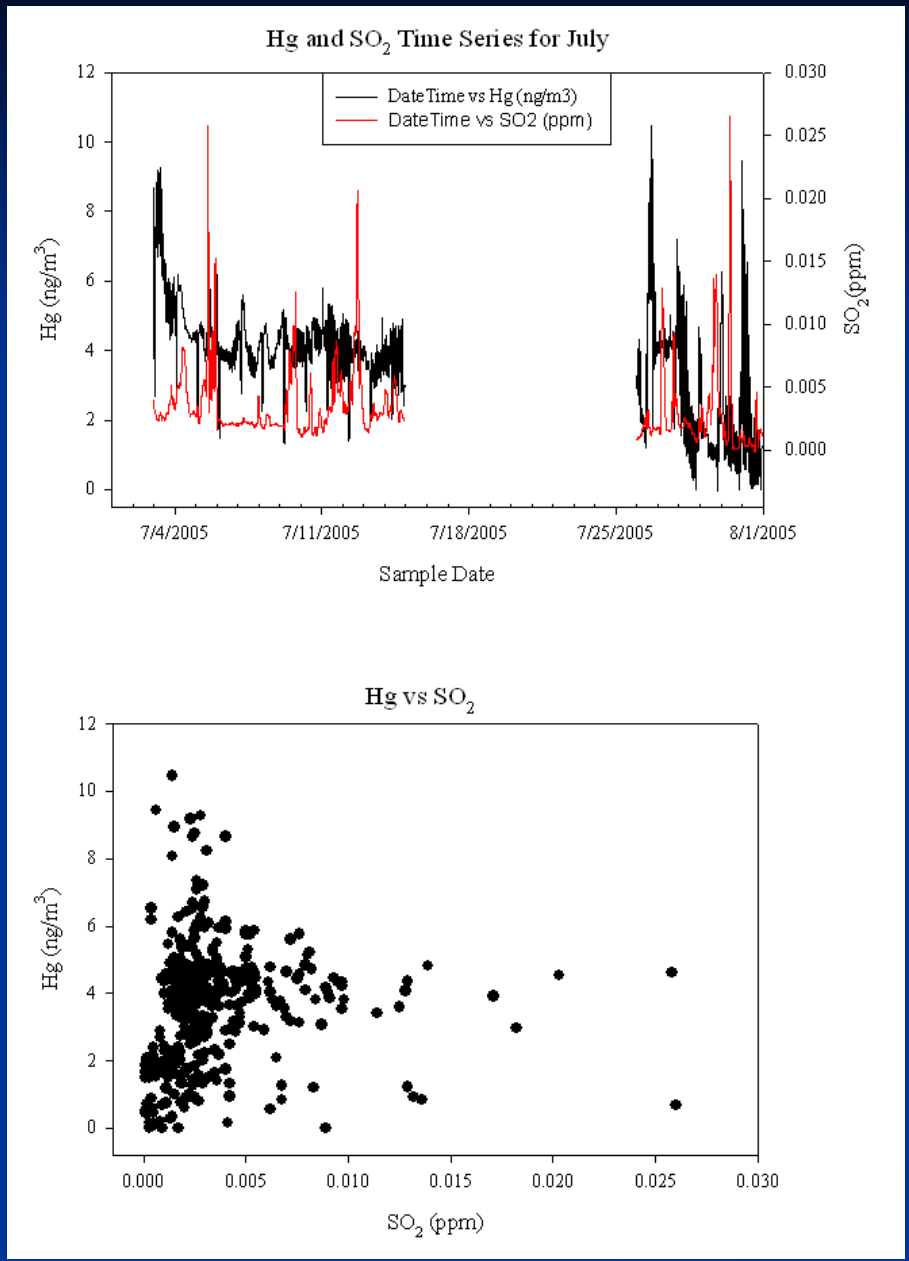
Figure 6. Source areas identified by three modeling results including MS-PSCF, multi-site RTWC, and multi-site SQTBA.

Tekran Automated Speciation System –

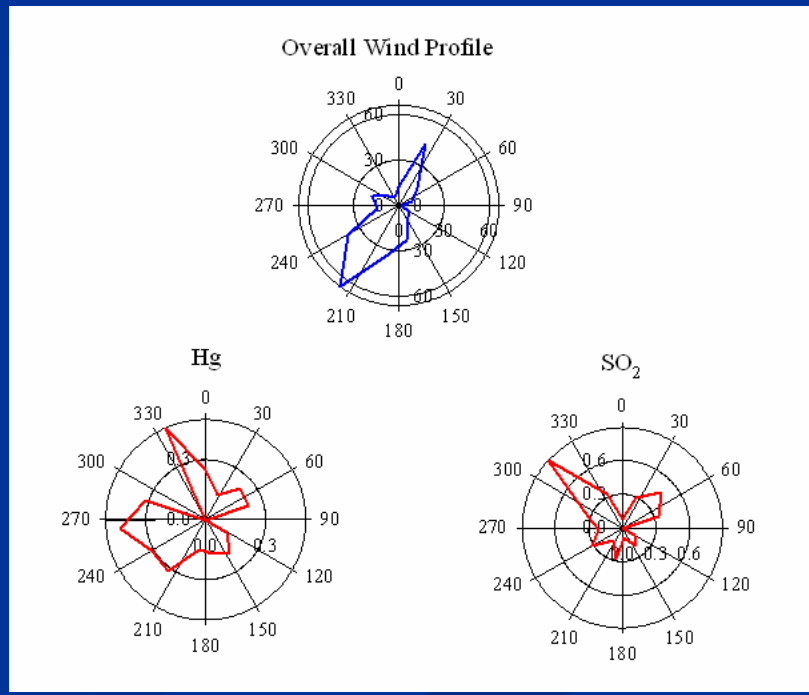
highly time resolved concentrations

Hg concentrations obtained with a Tekran Speciation System





Relationship between Hg and SO_2 concentrations in Rochester, NY

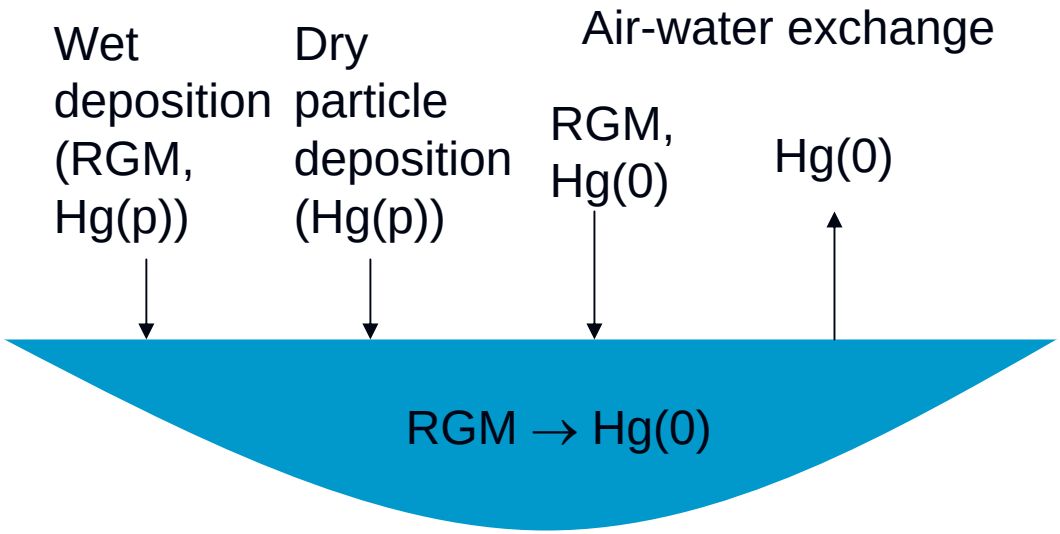


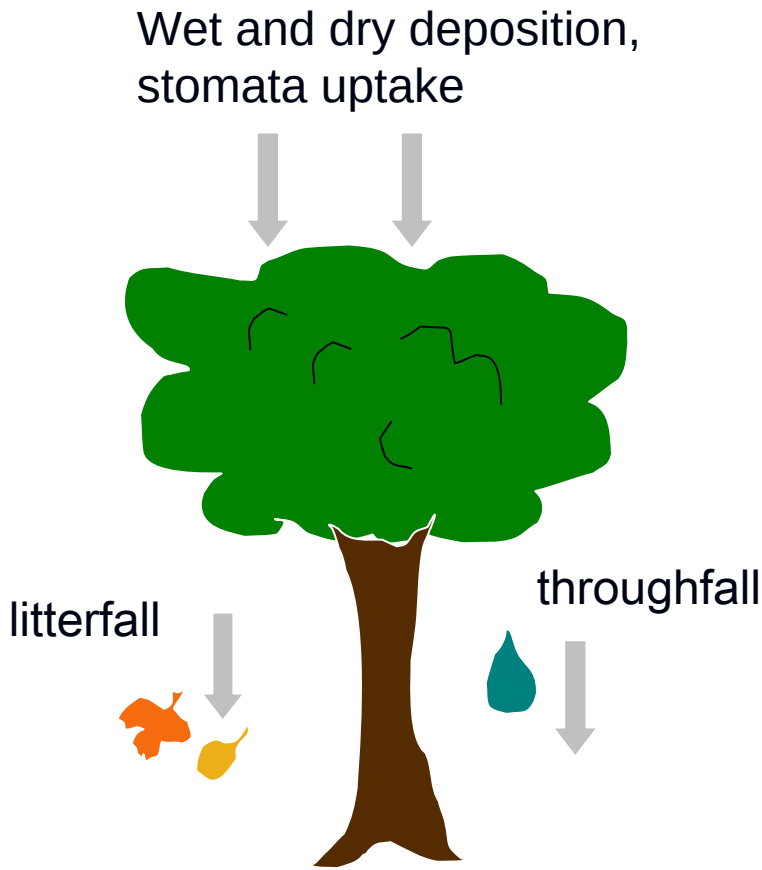
Data from NY DEC

Hg Deposition Processes

- Wet deposition – Hg associated with rain, dew, snow, fog (mostly RGM)
- Particle dry deposition – Hg associated with atmospheric particles (mostly RGM)
- Air-surface exchange (water and vegetation)
  - RGM deposition only
  - Hg(0) deposition and emission

Deposition Processes



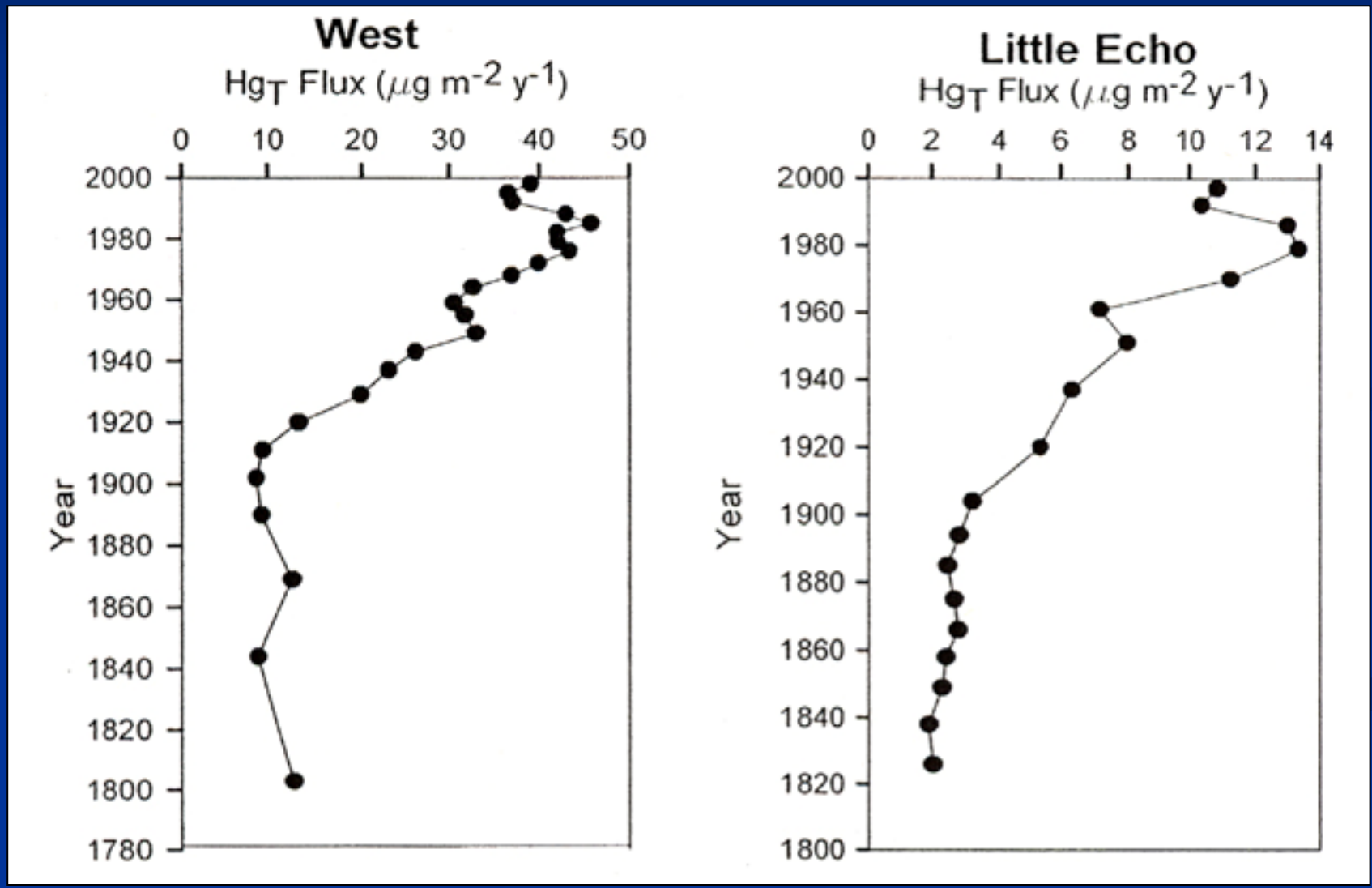


Mercury Deposition

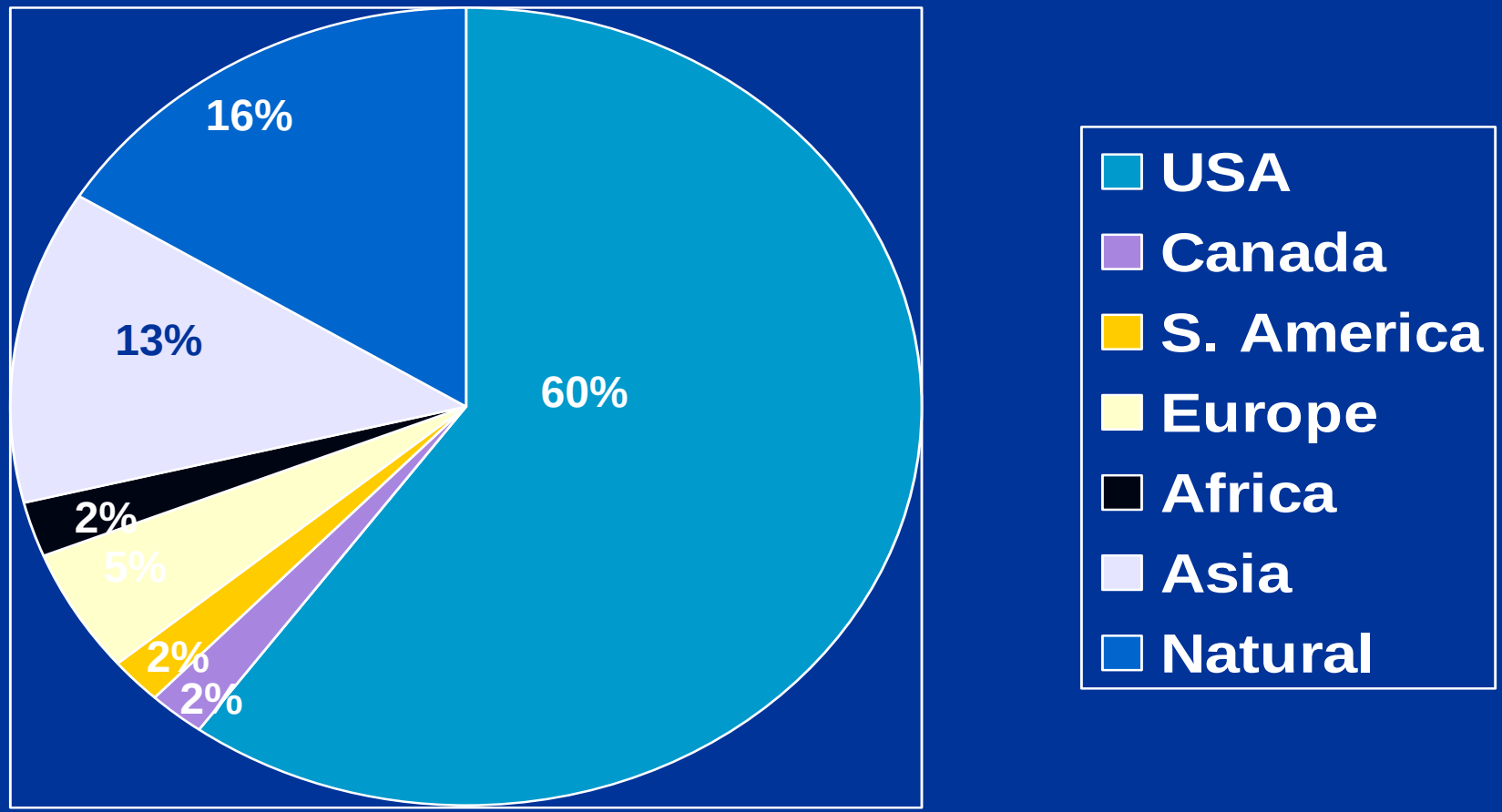
- **Predominant source of mercury in most watersheds is atmospheric deposition (Lindqvisit et al. 1991; Mason 1994).**
- **Deposition of mercury has increased two to three-fold over the past two centuries, with some locations exhibiting greater than a twenty fold increase (Meili 2003; Nriaguand Becker 2003).**

From C. Driscoll

Historical deposition of mercury to sediments in West Pond and Little Echo Pond in the Adirondack region (Lorey and Driscoll, 1999)

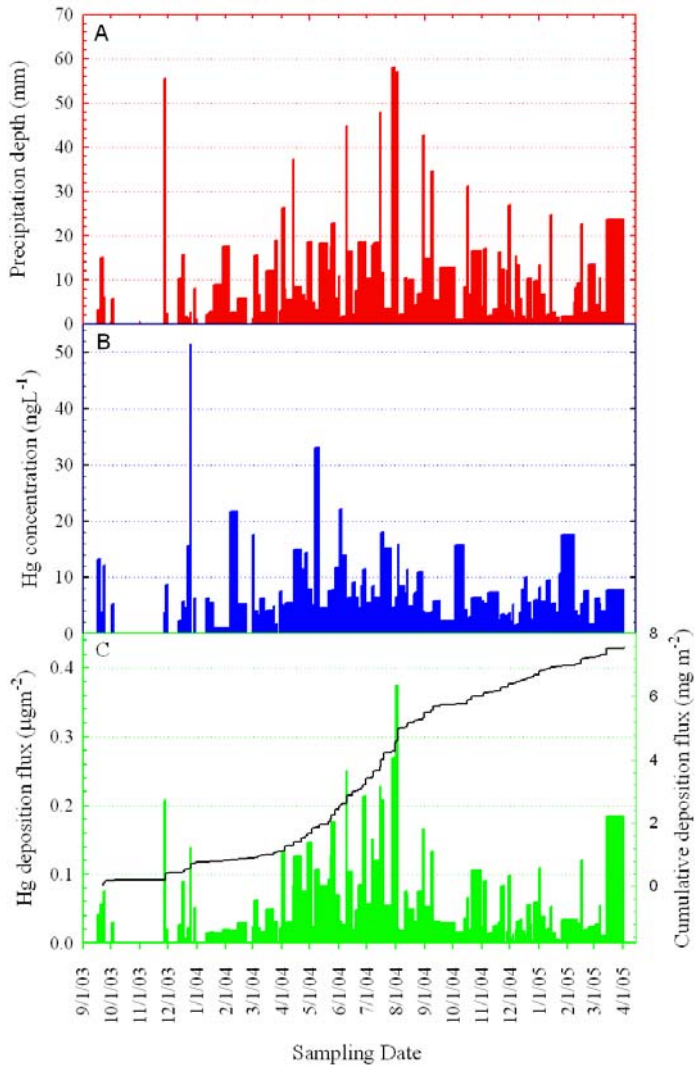


Regional and Global Contributions to Total Hg Deposition to the Catskill, NY Receptor Site



Seigneur et al. 2002 for NYSERDA

Event-based wet deposition Potsdam, NY, Sept. 2003 – Apr. 2004)



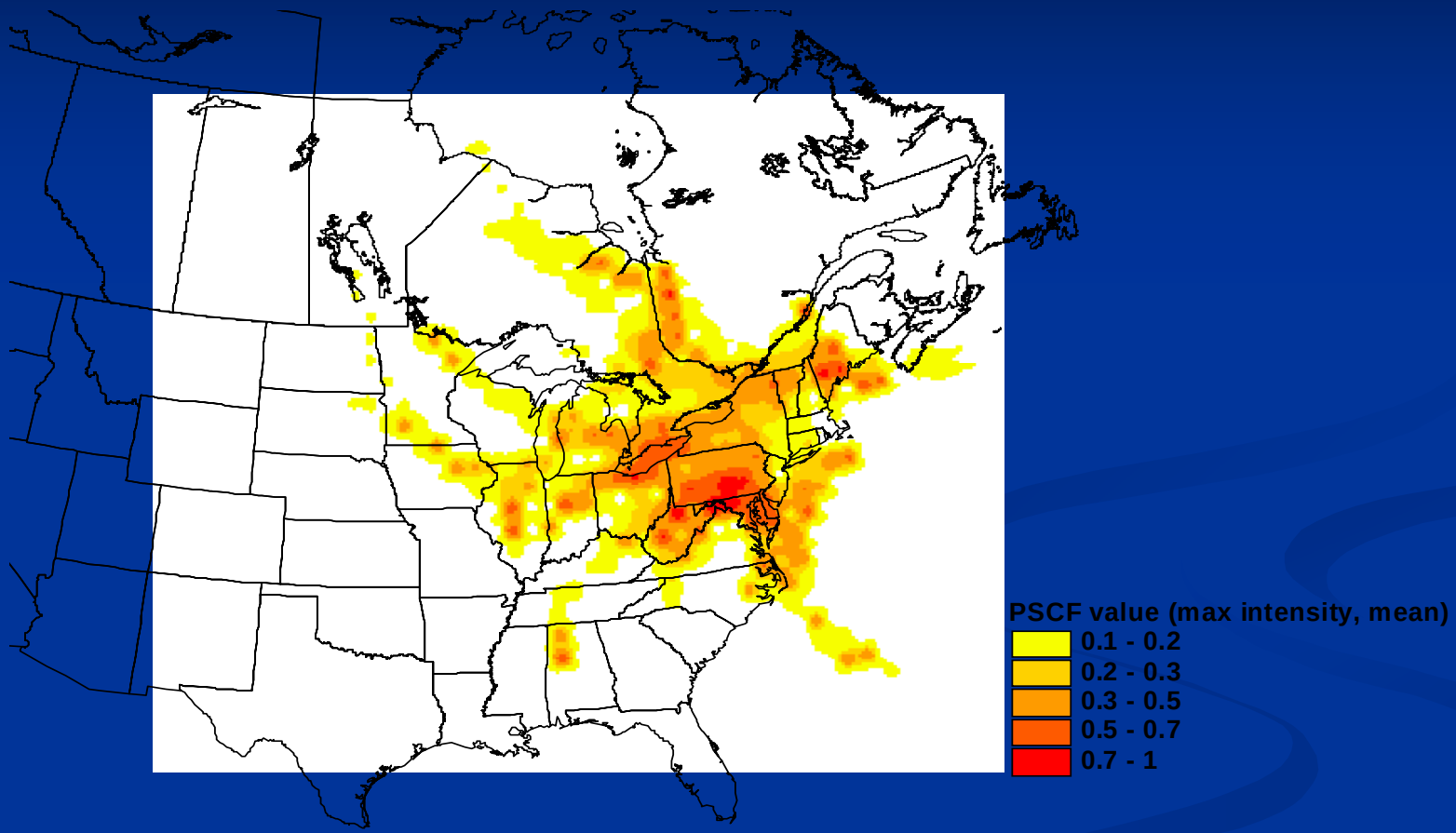
(A) Precipitation Depth (mm)

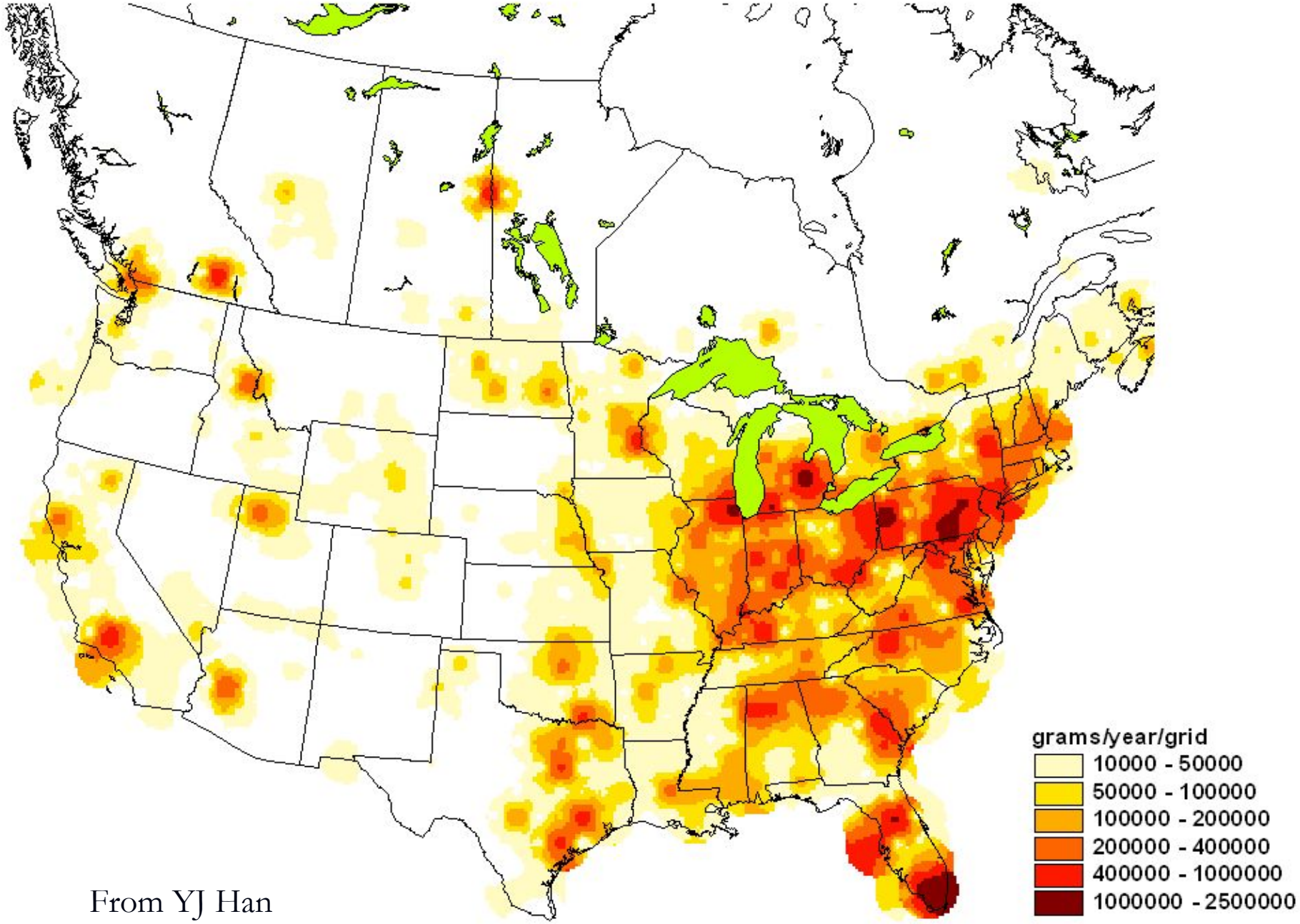
(B) Hg concentration in precipitation (ng L^{-1})

(C) Hg wet deposition flux (µg m^{-2})

Sponsored by NYSERDA and US EPA

PSCF result for wet deposition




grams/year/grid
10000 - 50000
50000 - 100000
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1000000 - 2500000

From YJ Han

Dry Deposition

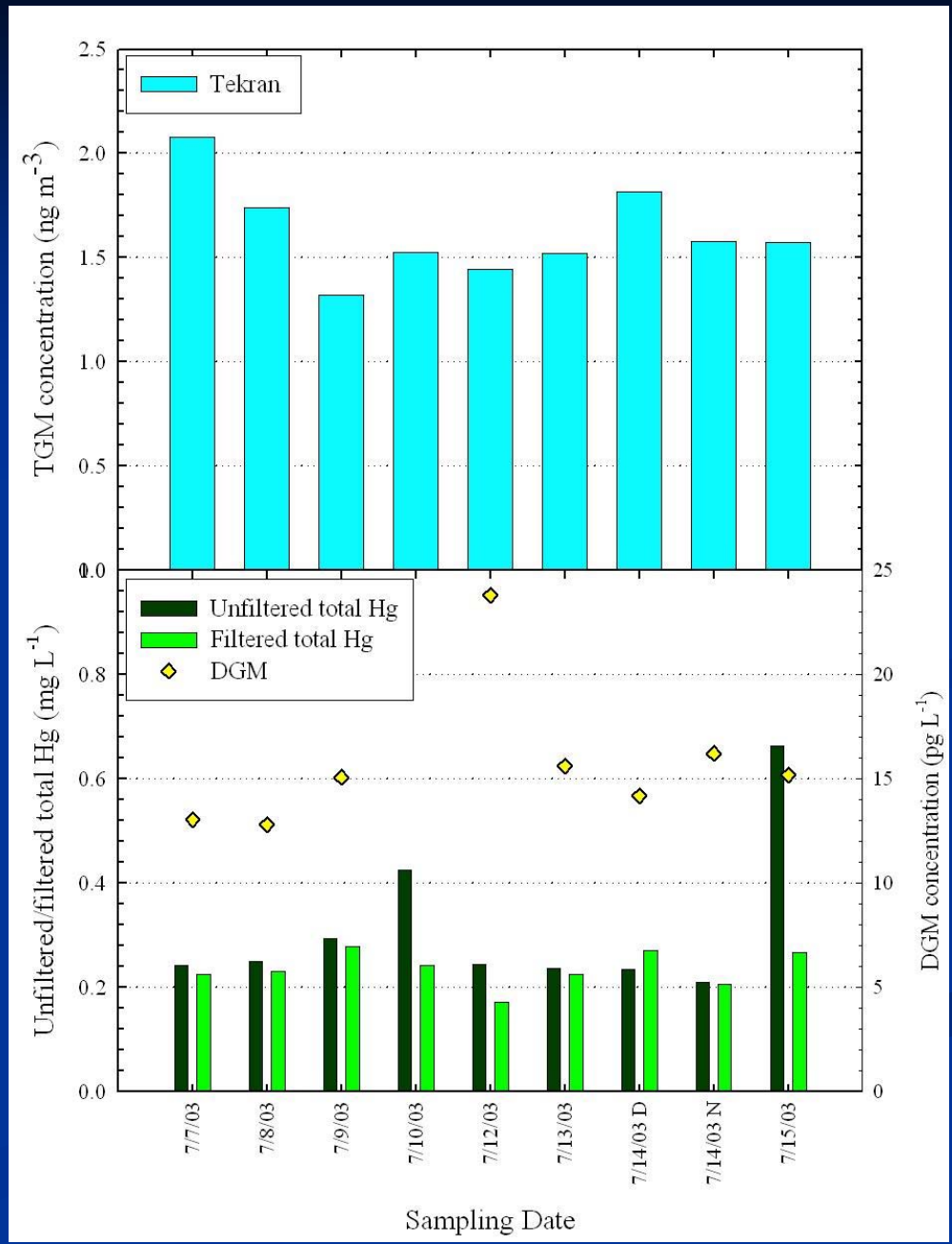
- Difficult to measure
- Function of surface type, Hg species, particle size, meteorological conditions
- Modeled as product of particle concentration and deposition velocity, Flux = $V_d \times Hg(p)$
- Generally thought to be equal to or greater than wet deposition
- Area that needs additional research

Air-Water Exchange of Hg^0

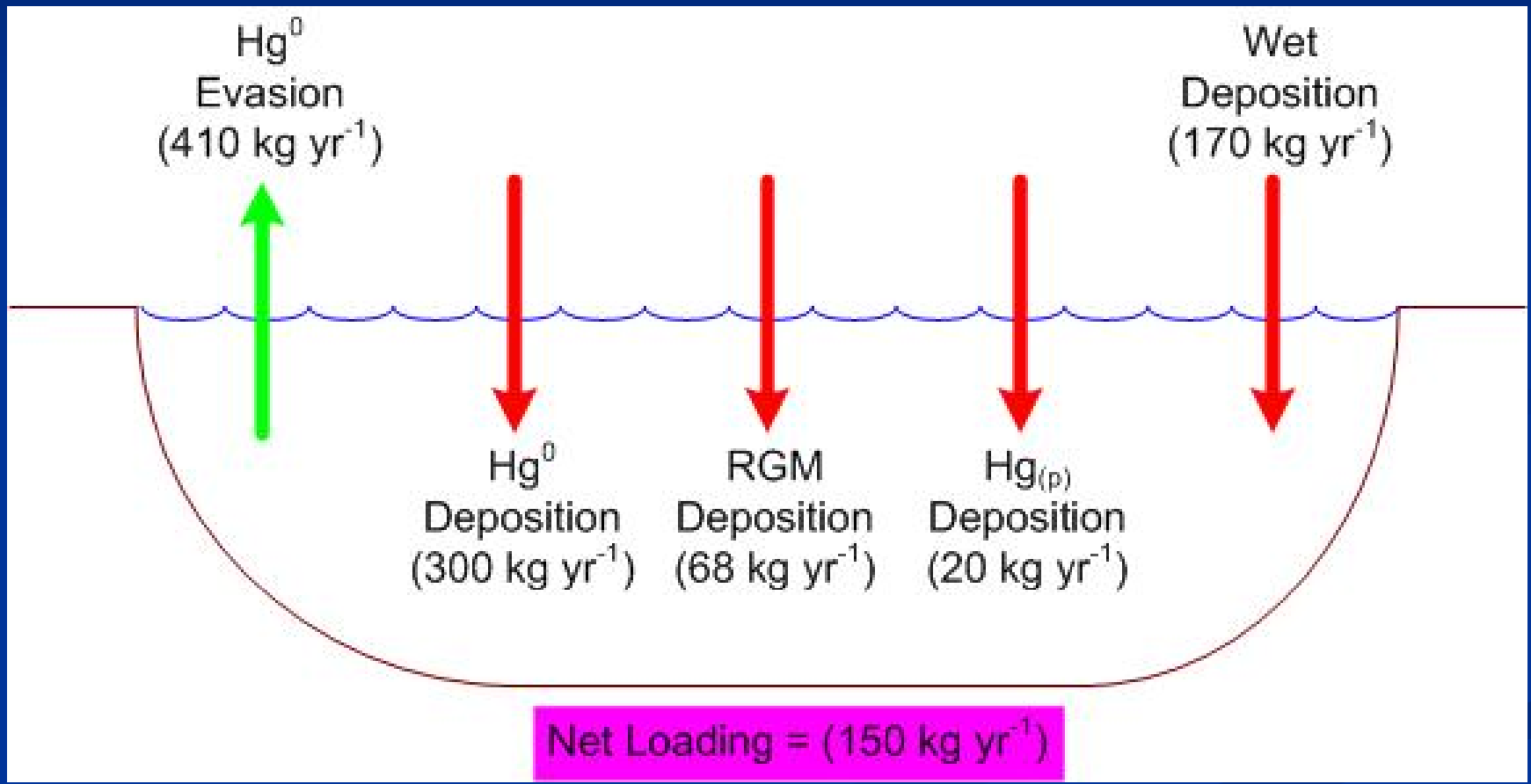
$= K_{OL} (C_d - C_a/H)$

K_{OL}: mass transfer coeff.
C_d – dissolved concentration
Ca – air concentration
H – Henry's Law constant

→ RGM - deposition only
→ Hg(0) - deposition and evasion



Hg Mass Balance for Lake Ontario



Conclusions

- There are significant anthropogenic emissions of Hg – biggest source in US is utility coal combustion
- The form of Hg in the atmosphere controls its fate and transport
- There is evidence that North America sources contribute significantly to ambient Hg concentrations and deposition in NYS