Atmospheric Mercury: Emissions, Transport/Fate, Source-Receptor Relationships

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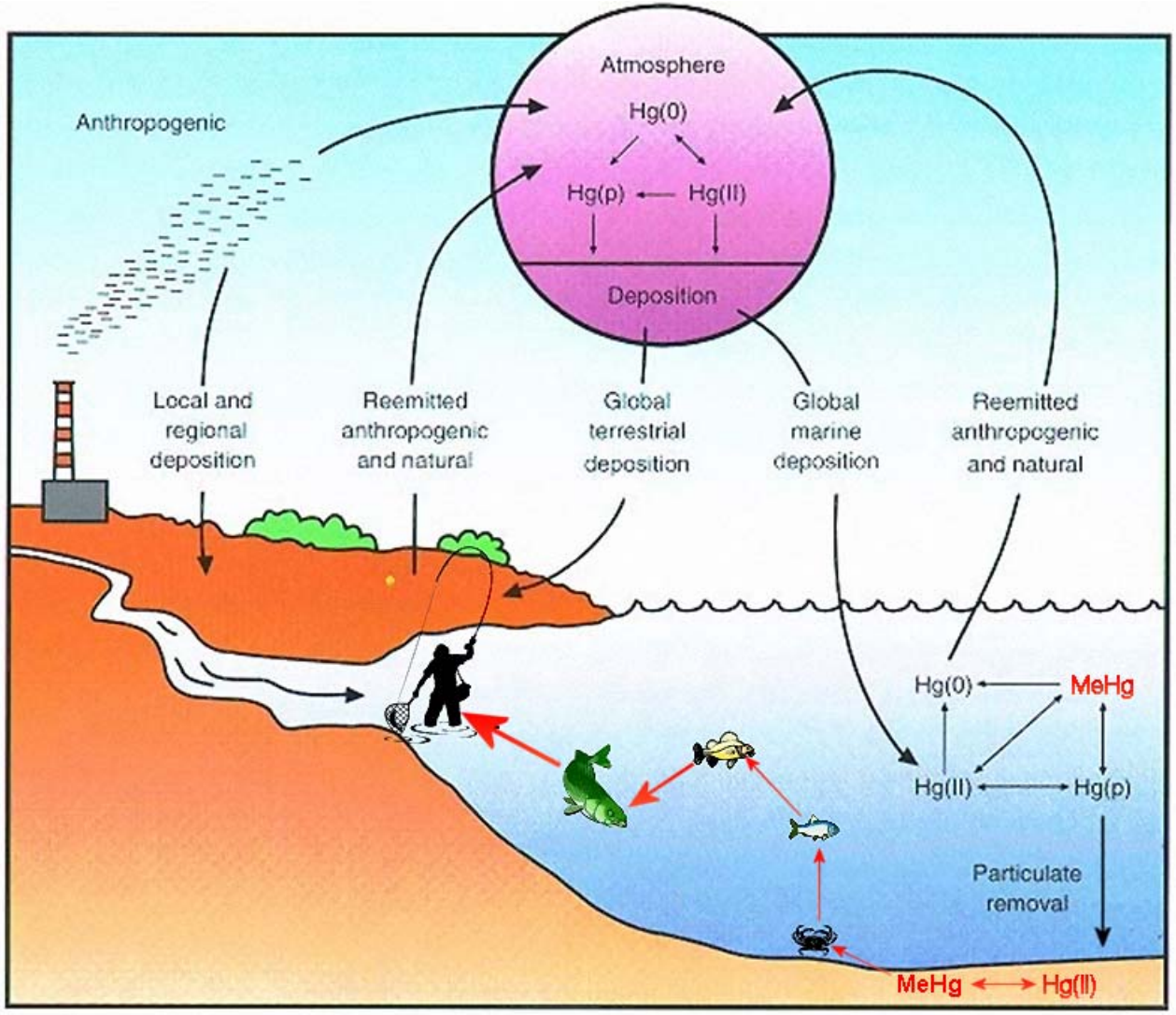
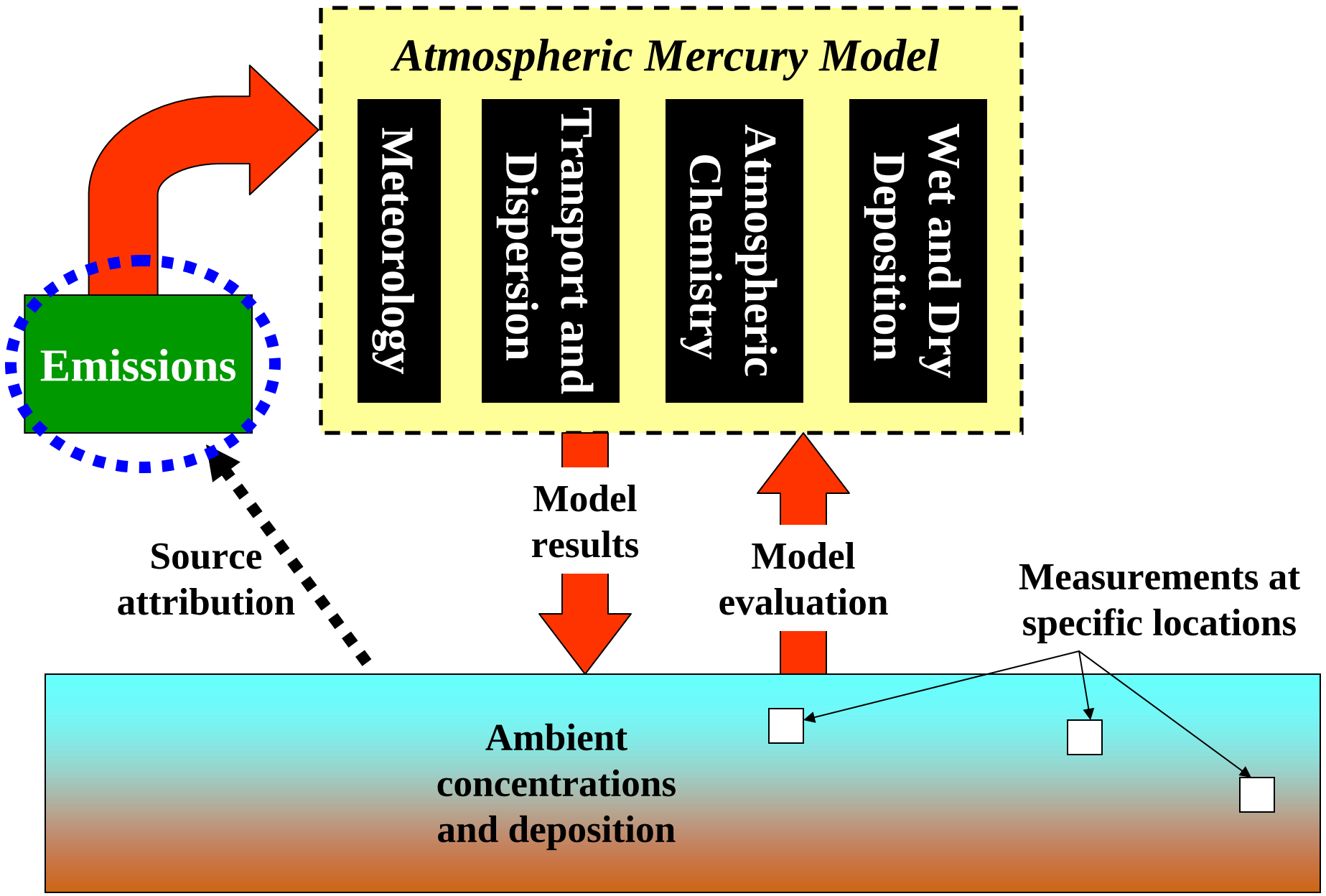
Presentation at
Collaborative Meeting on Modeling Mercury in Freshwater Environments
Niagara Falls, NY, January 19-20, 2006

Mercury in the Environment

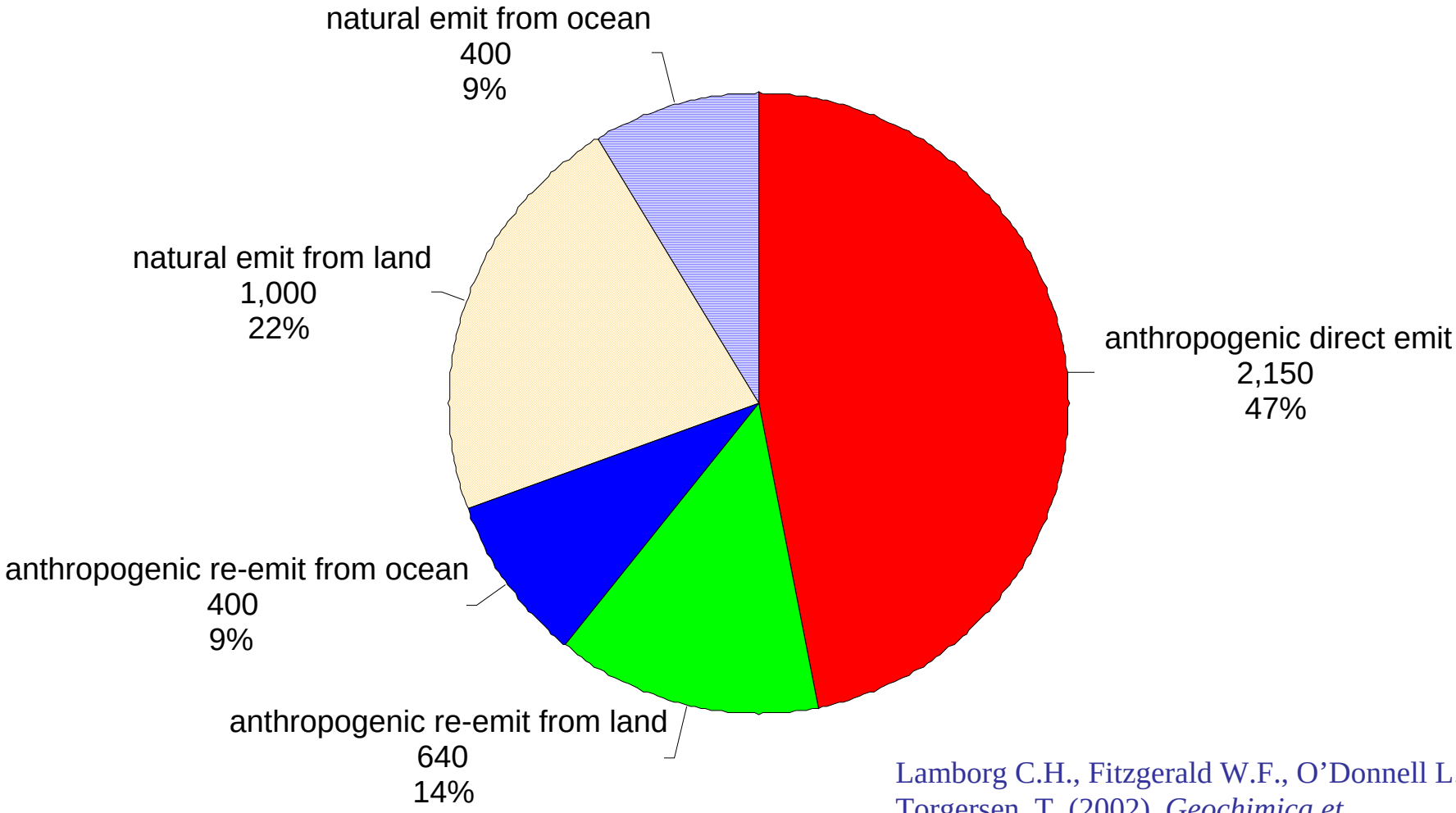


- 3 emission source types:
  - anthropogenic;
  - natural;
  - re-emitted
- 3 forms of emissions:
  - reactive: Hg(II);
  - particulate: Hg(p);
  - elemental: Hg(0).
- Hg(0) has a long atmospheric lifetime; can be transported globally; >90% in air is Hg(0)
- Hg(II) and Hg(p) have shorter atmospheric lifetimes and deposit more locally and regionally.
- Deposition within the US and Canada comes from domestic sources and the global pool

Source: adapted from slides prepared by USEPA and NOAA


Atmospheric Mercury Model
Meteorology
Transport and Dispersion
Atmospheric Chemistry
Wet and Dry Deposition
Emissions
Source attribution
Model results
Model evaluation
Measurements at specific locations
Ambient concentrations and deposition

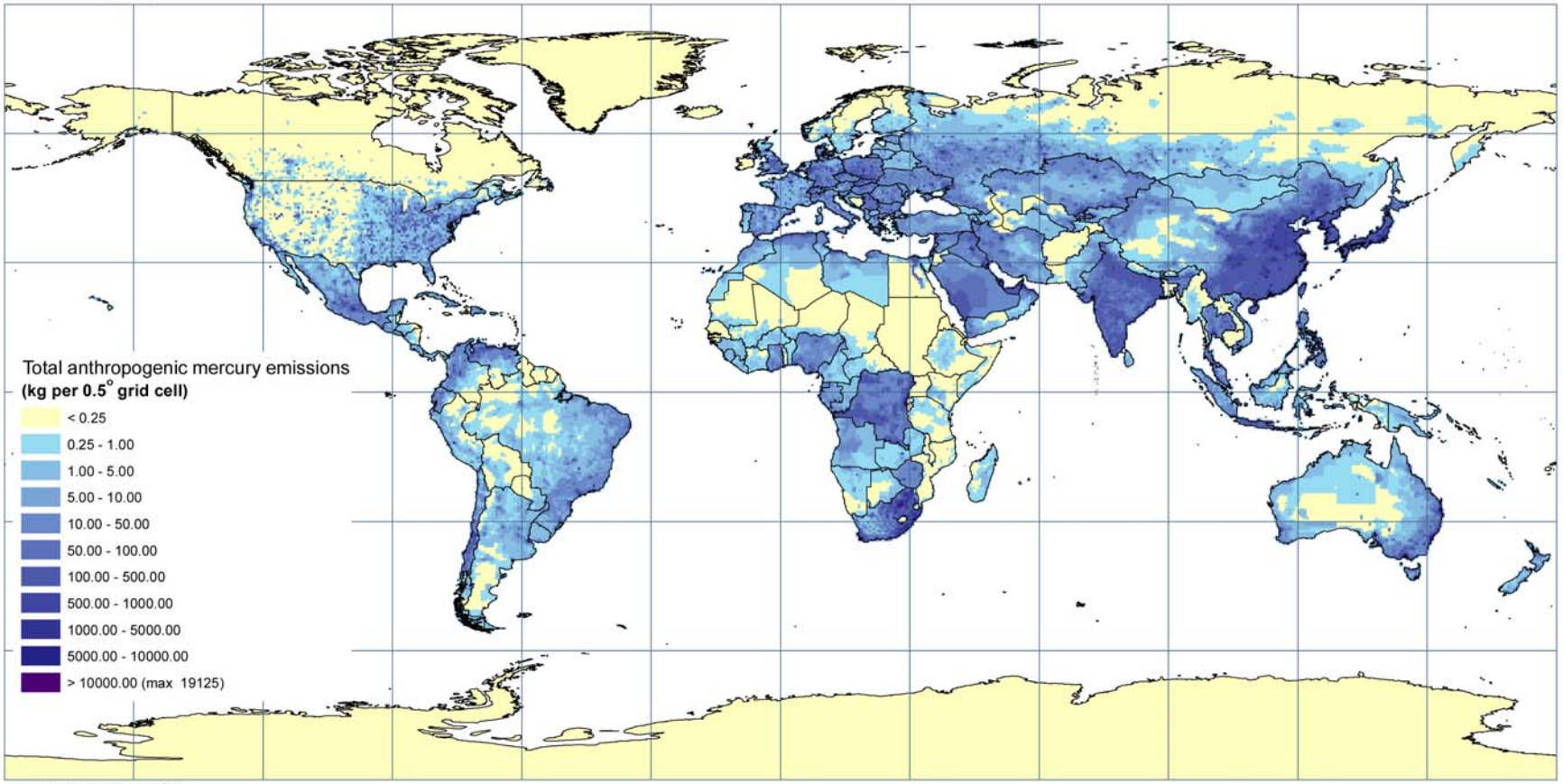
Global natural and anthropogenic emissions of mercury. Estimates taken/ inferred from Lamborg et al. (2002). All values are in metric tons per year, and are for ~1990.



Lamborg C.H., Fitzgerald W.F., O'Donnell L., Torgersen, T. (2002). *Geochimica et Cosmochimica Acta* **66**(7): 1105-1118.

Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere, 2000

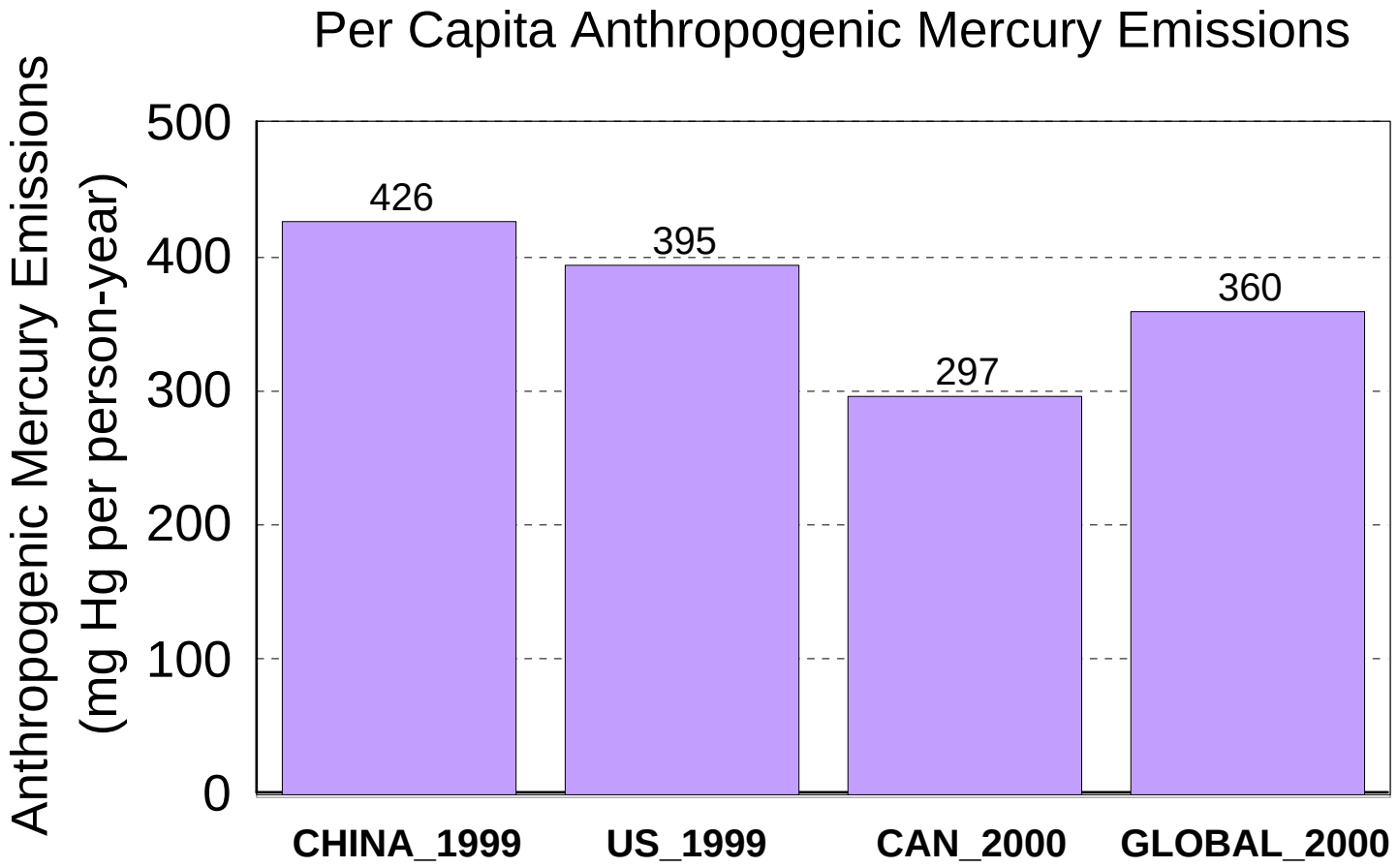
Total Hg, point sources + distributed sources, 0.5° grid



unprojected (geographic)

citation:
Pacyna, J., S. Wilson and F. Steenhuisen. 2005.
Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere.
(www.amap.no/Resources/HgEmissions/HgInventoryMain.html)

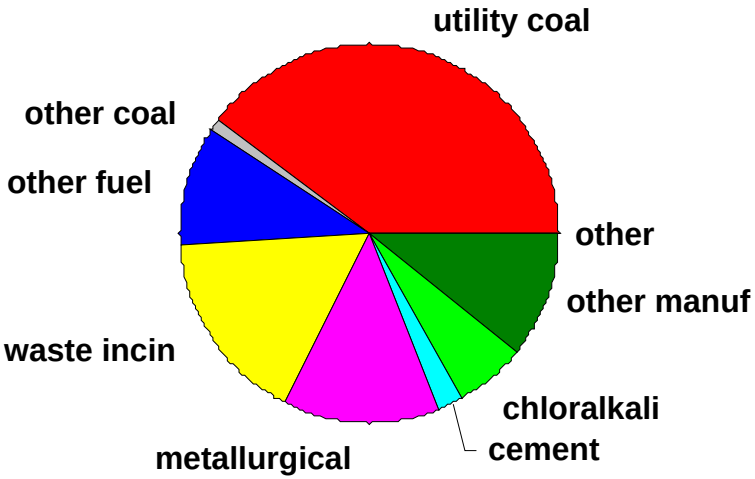
S. Wilson (AMAP), F. Steenhuisen (Arctic Centre, RuG), J. Pacyna (NILU)



Source of global data: Global Anthropogenic Mercury Emission Inventories for 2000 and 1995: Pacyna, J. and E. Pacyna. Journal of Air and Waste Management Association (in prep. 2005); *http://www.amap.no/Resources/HgEmissions/HgInventoryDocs.html*

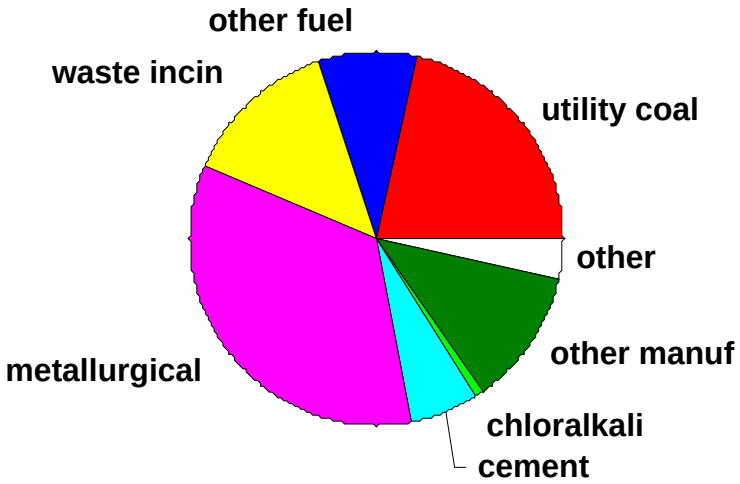
Different patterns of anthropogenic mercury emissions

U.S. Anthopogenic Mercury Emissions, 1999



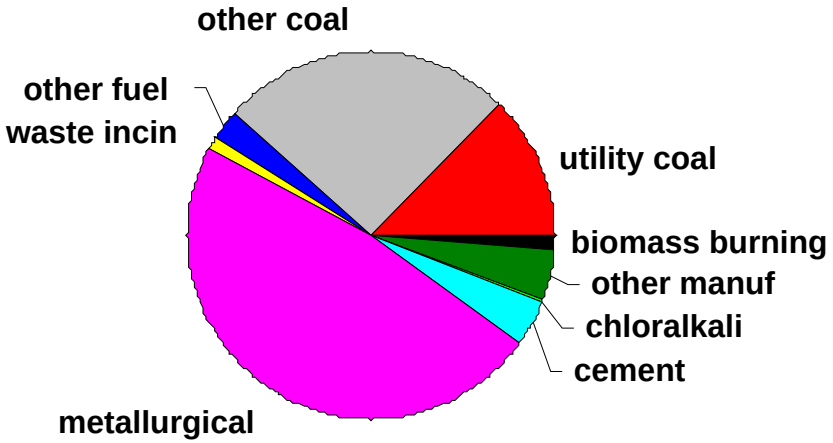
Source: U.S. EPA

Canada Anthopogenic Mercury Emissions, 2000



Source: Environment Canada

China Anthopogenic Mercury Emissions, 1999



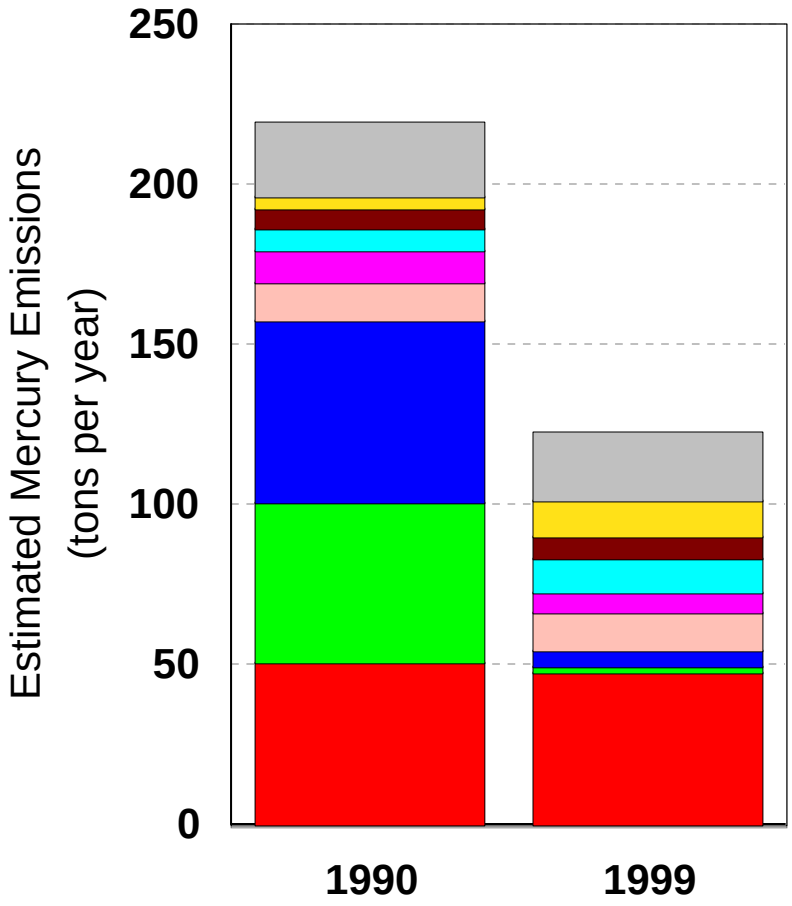
Source: Streets et al., 2005, "Anthropogenic mercury emissions in China", Atmospheric Environment 39, 7789-7806

Some Current Emissions Inventory Challenges

- Re-emissions of previously deposited anthropogenic Hg
- Emissions speciation [at least among Hg(0), Hg(II), Hg(p); more specific species if possible]
- Reporting and harmonization of source categories
- Mobile source emissions?
- Enough temporal resolution to know when emissions for individual point sources change significantly

  Note: Hg continuous emissions monitors now commercially available

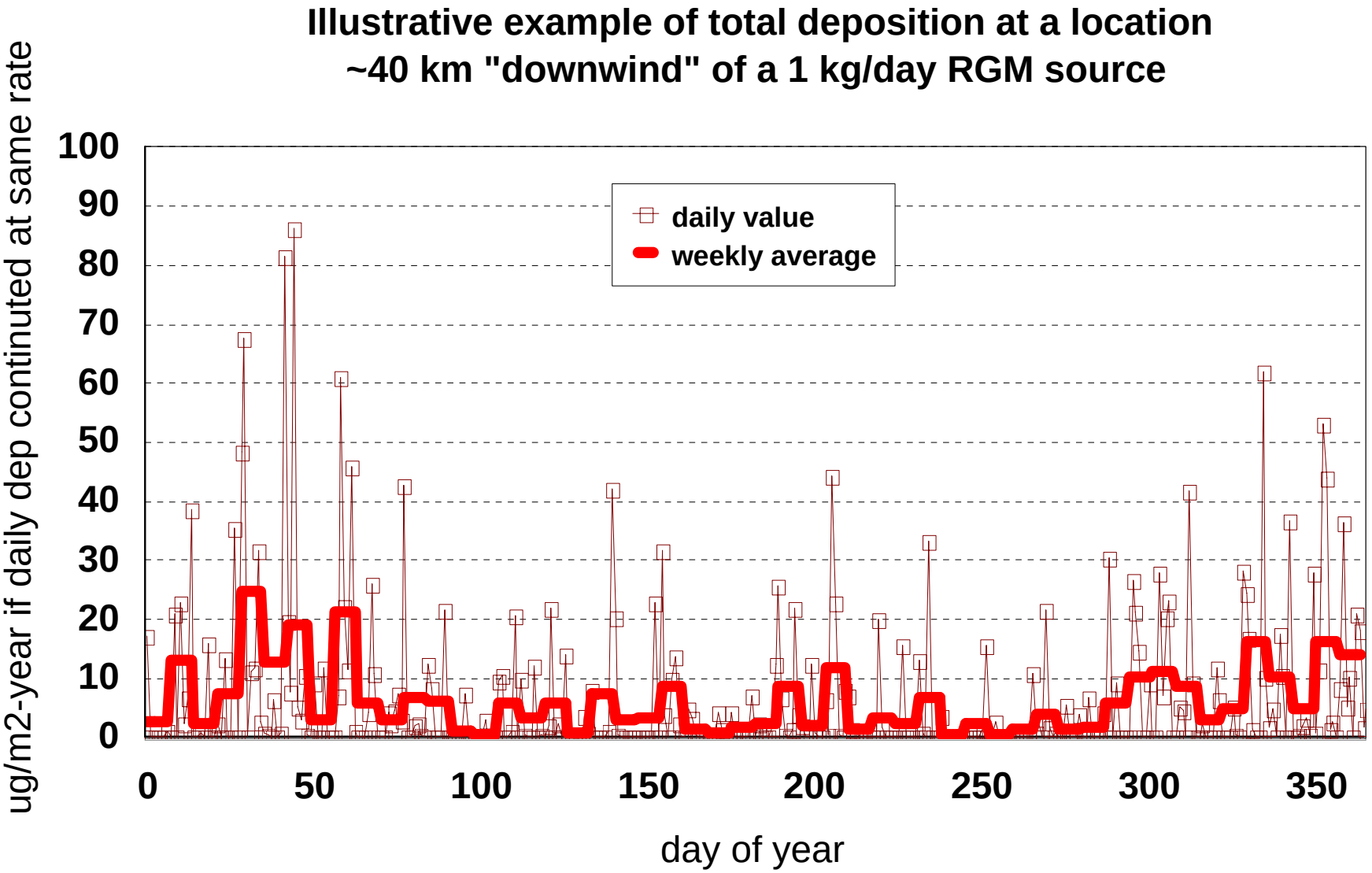
U.S. Anthropogenic Emissions for 1990 and 1999 (USEPA)

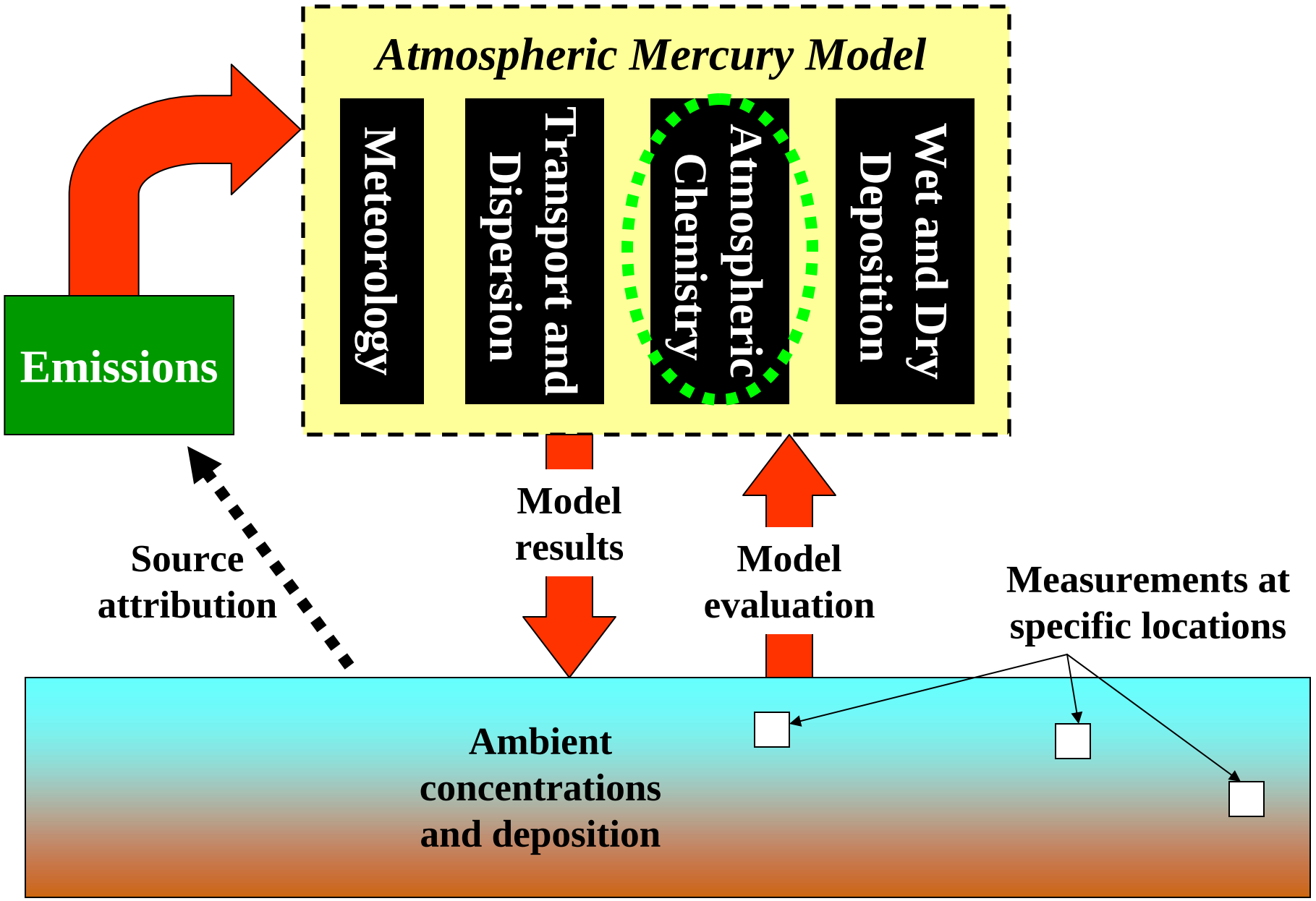


There were big reported changes in emissions between 1990 and 1999, but when did these occur? And when did they occur for individual facilities?

- Other categories*
- Gold mining
- Hazardous waste incineration
- Electric Arc Furnaces **
- Mercury Cell Chlor-Alkali Plants
- Industrial, commercial, institutional boilers and process heaters
- Municipal waste combustors
- Medical waste incinerators
- Utility coal boilers

* Data for Lime Manufacturing are not available for 1990.
** Data for Electric Arc Furnaces are not available for 1999. The 2002 estimate (10.5 tons) is shown here.


Illustrative example of total deposition at a location
~40 km "downwind" of a 1 kg/day RGM source
ug/m2-year if daily dep continuted at same rate
100
90
80
70
60
50
40
30
20
10
0
daily value
weekly average
0
50
100
150
200
250
300
350
day of year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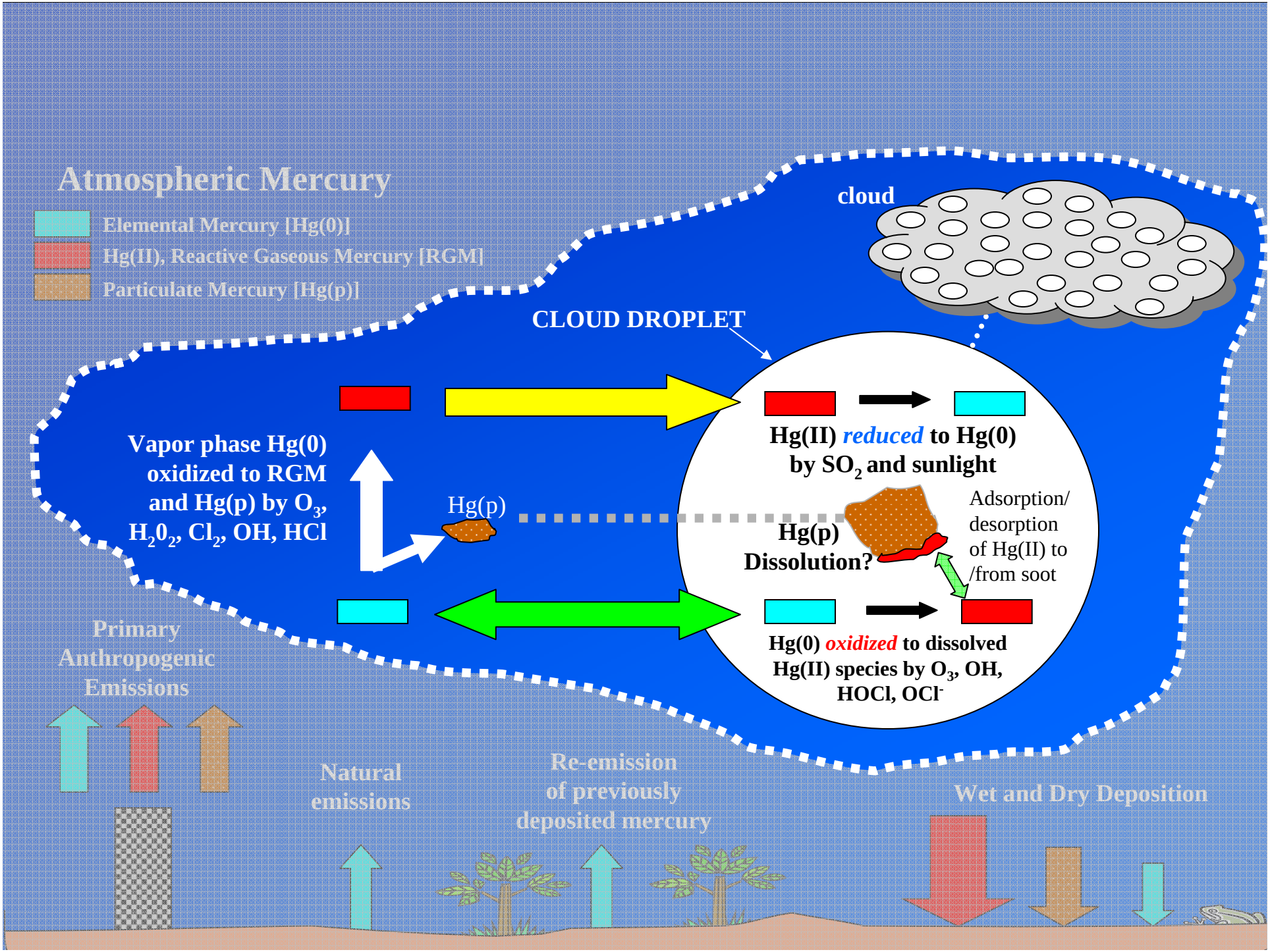
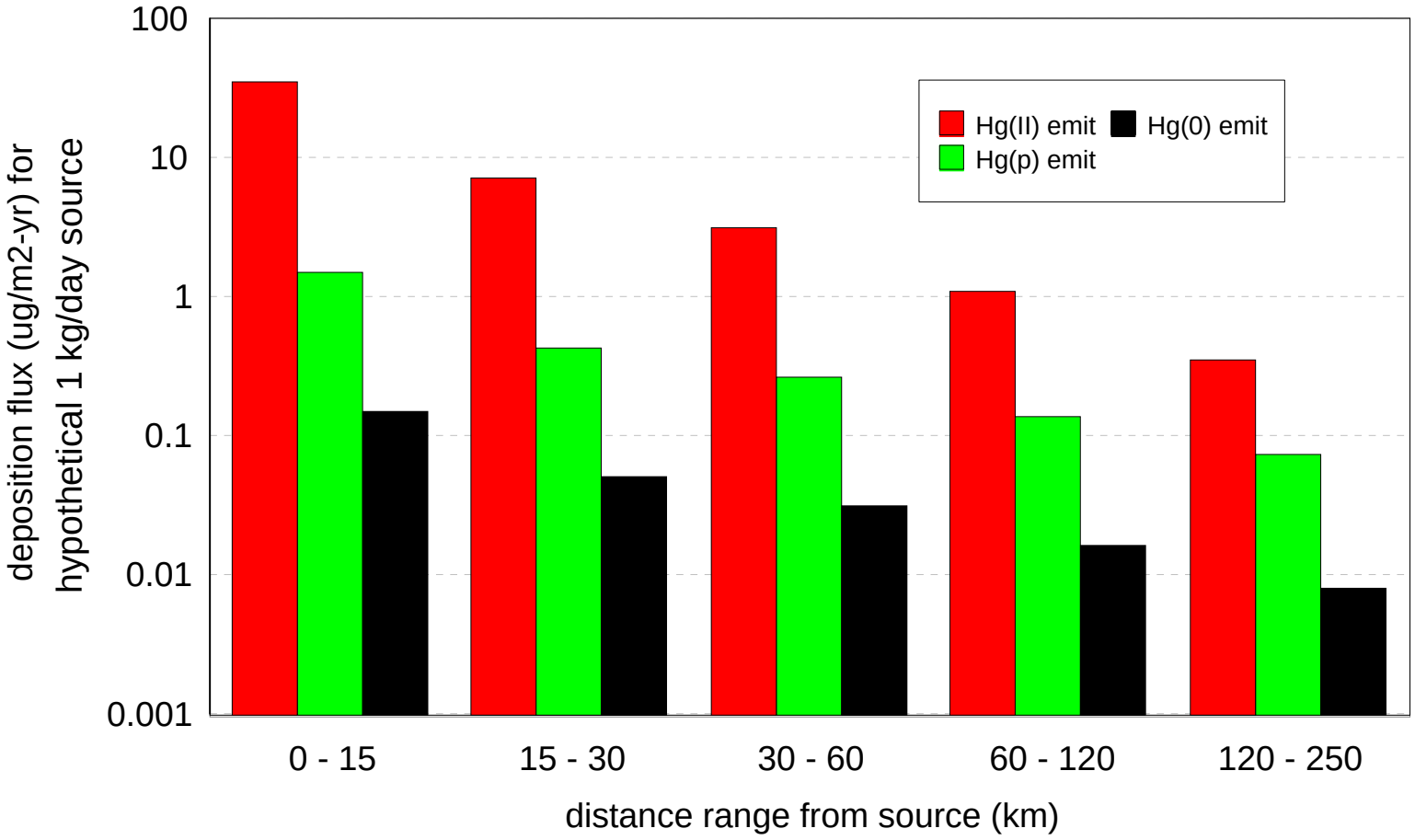

Atmospheric Mercury
Elemental Mercury [Hg(0)]
Hg(II), Reactive Gaseous Mercury [RGM]
Particulate Mercury [Hg(p)]
cloud
CLOUD DROPLET
Vapor phase Hg(0) oxidized to RGM and Hg(p) by O3, H2O2, Cl2, OH, HCl
Hg(p)
Hg(II) reduced to Hg(0) by SO2 and sunlight
Hg(p) Dissolution?
Adsorption/ desorption of Hg(II) to /from soot
Hg(0) oxidized to dissolved Hg(II) species by O3, OH, HOCl, OCl-
Primary Anthropogenic Emissions
Natural emissions
Re-emission of previously deposited mercury
Wet and Dry Deposition

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)

Why are emissions speciation data - and potential plume transformations -- critical?



Logarithmic

NOTE: distance results averaged over all directions – Some directions will have higher fluxes, some will have lower

Some Current Atmospheric Chemistry Challenges

- ***Plume chemistry***, e.g., rapid reduction of RGM to elemental mercury?

  - ***If* significant reduction of RGM to Hg(0) is occurring in power-plant plumes, then much less local/regional deposition**

RGM reduction in power-plant plumes?

- *If* significant reduction of RGM to Hg(0) is occurring in power-plant plumes, then much less local/regional deposition

- No known chemical reaction is capable of causing significant reduction of RGM in plumes – e.g. measured rates of SO_2 reduction can't explain some of the claimed reduction rates

- Very hard to measure
  - Aircraft
  - Static Plume Dilution Chambers (SPDC)
  - Ground-based measurements

Interconversion of Emitted Atmospheric Mercury Species in Coal-Fired Power Plant Plumes

E. Prestbo and P. Swartzendruber (Frontier Geosciences)
L. Levin (EPRI)
D. Laudal, R. Schulz and G. Dunham (EERC),
W. Aljoe (U.S. Department of Energy)
J. Jansen and L. Monroe (Southern Company)
R. Valente (TVA)
D. Michaud (WE Energies)

Air Quality V Conference
September 2005

SPDC - Hg Species Interconversion Results for all Study Sites 1995-2003

Power Plant	Year	Coal	PCD	Hg(II) to Hg^0 conversion as a percent of total mercury	Mass Balance	n
Presque Ilse, MI*	1995	W-SB	ESP	**33% ± 6.8%**	96% ± 14%	10
Dickerson, MD*	1998	E-SB	1 Unit Scrubber 2 Units ESP	**41% ± 7.9%**	128% ± 22%	8
Dickerson, MD	1998	MW	Scrubber and-Carbon Inj.	**-23% ± 12%**	84% ± 15%	7
EERC Pilot Plant	2000	E-B	ESP	**23% ± 6.0%**	86% ± 19%	8
EERC Pilot Plant	2000	E-B	Baghouse	**11% ± 8.0%**	75% ± 9.2%	6
Bowen, GA	2002	E-B	ESP	**9.4% ± 2.9%**	109% ± 6.6%	6
Pleasant Prairie, WI	2003	PRB	ESP/SCR	**3.2% ± 3.7%**	90% ± 22%	3

*value may be biased high due to bias in fluegas speciation measurments

Eric Prestbo Ph.D. (ericp@frontiergeosciences.com)

Frontier GeoSciences Inc.

Comparison of SPDC and Airplane Plume Hg Species Interconversion at Bowen and P4

Power Plant	Method	Hg(II) to Hg^0 conversion as a percent of total mercury	Mass Balance	n
Bowen, GA	2002	9.4% ± 2.9%	109% ± 6.6%	6
"	Aircraft	13%		4
Pleasant Prairie, WI	SPDC	3.1% ± 3.7%	90% ± 22%	3
"	Aircraft - 0km	15% ± 6.5%	123% ± 24%	5
"	Aircraft - 8km	23% ± 2.6%	198% ± 120%	4
"	Aircraft - 16km	24% ± 5.3%	152% ± 62%	3

- Note: Airplane results were as of July, 2004

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Frontier GeoSciences Inc.

RGM reduction in power-plant plumes?

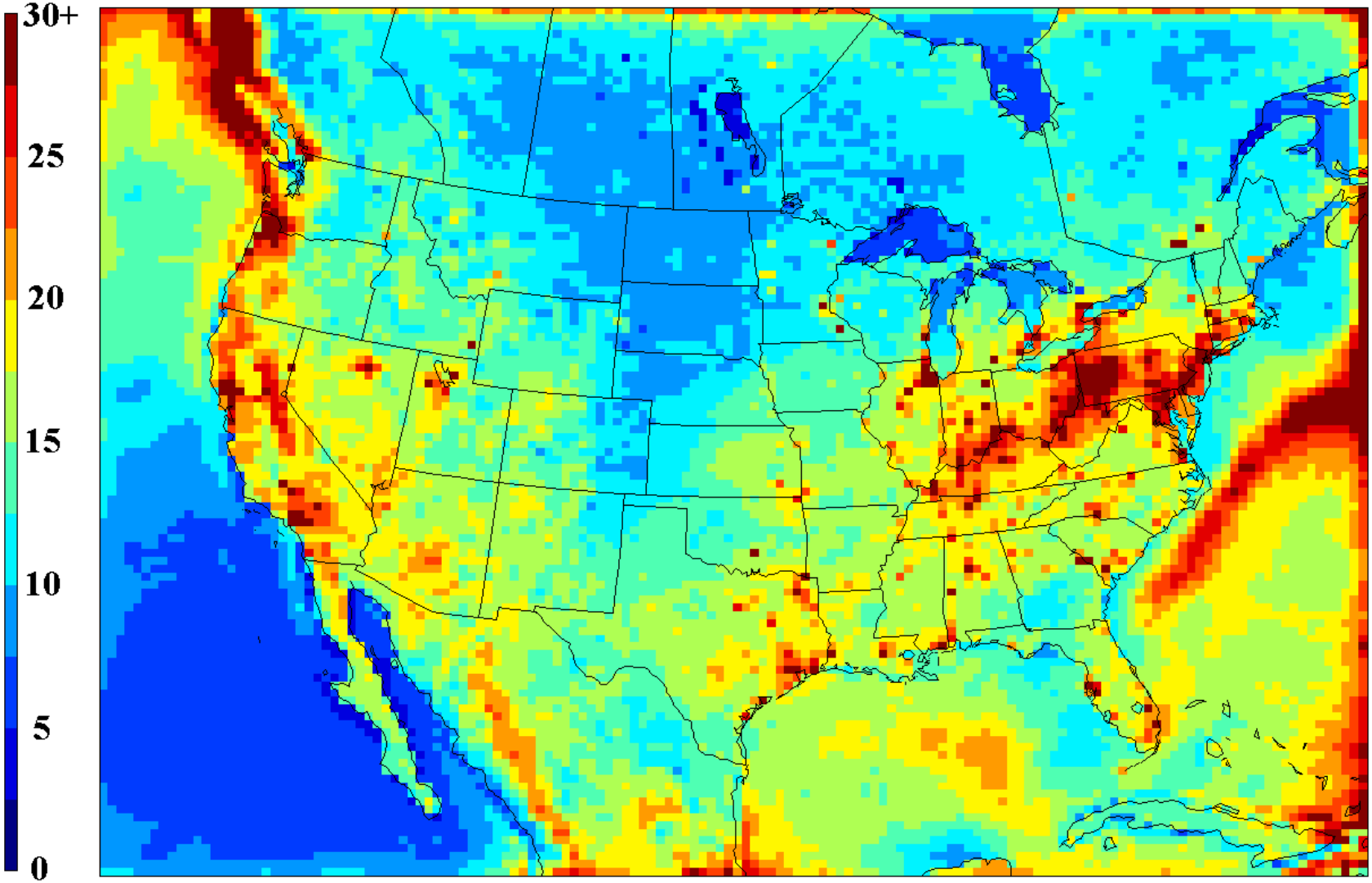
- **Most current state-of-the-science models do not include processes that lead to significant reduction in plumes**
- **Recent measurement results show less reduction**
- **Significant uncertainties – e.g., mass balance errors comparable to measured effects…**
- **Current status – inconclusive… but weight of evidence suggest that while some reduction may be occurring, it may be only a relatively small amount**
- **Recent measurements at Steubenville, OH appear to show strong local mercury deposition from coal-fired power plant emissions.**

Some Current Atmospheric Chemistry Challenges

- ***Plume chemistry***, e.g., rapid reduction of RGM to elemental mercury?
- ***Boundary conditions*** for regional models?

CMAQ-simulated total mercury deposition for 2001

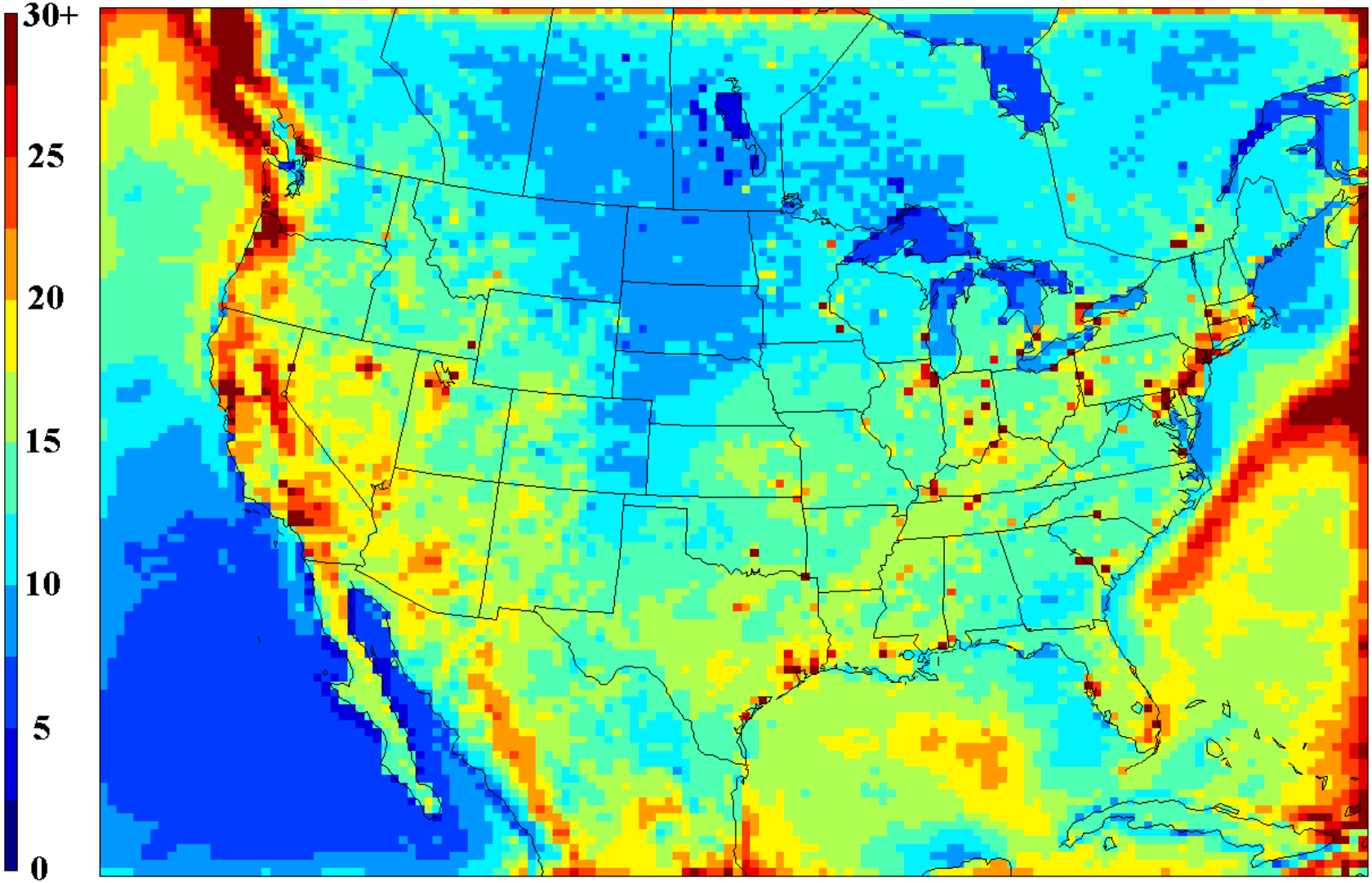
(micrograms per square meter)



Base case

CMAQ-simulated total mercury deposition for 2001

(micrograms per square meter)



Utility Zero Out

Some Current Atmospheric Chemistry Challenges

- ***Plume chemistry***, e.g., rapid reduction of RGM to elemental mercury?
- ***Boundary conditions*** for regional models?
- ***Oxidation of elemental mercury by O_3 and $OH^\bullet$ may be over-represented***, leading to overestimation of the contribution of global sources to regional deposition

  Calvert, J., and S. Lindberg (2005). Mechanisms of mercury removal by O3 and OH in the atmosphere. Atmospheric Environment 39: 3355-3367.

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- ***Atmospheric methyl-mercury:*** significance? sources? transport? chemistry? deposition?

  e.g., Hall et al. (2005). Methyl and total mercury in precipitation in the Great Lakes region. Atmospheric Environment 39: 7557-7569.

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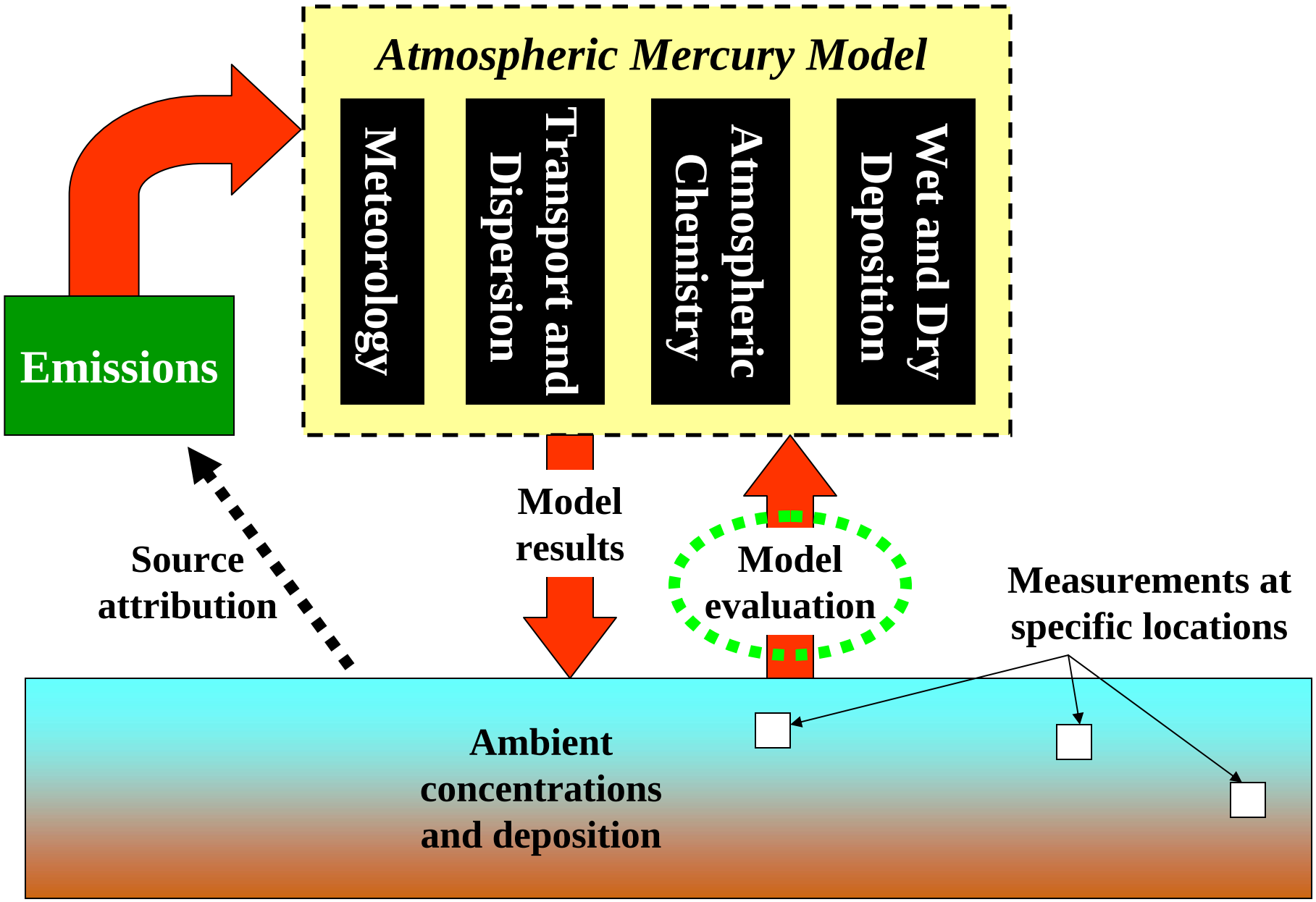
- ***Source-Receptor answers influenced by above factors***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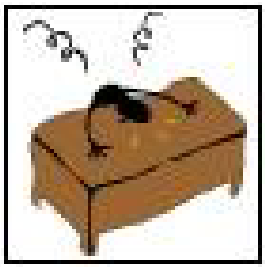
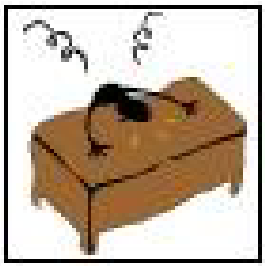
Some Model Evaluation Issues

- **Data availability**
- **Simple vs. Complex Measurements**

Data availability



A major impediment to evaluating and improving atmospheric Hg models has been the lack of speciated Hg air concentration data



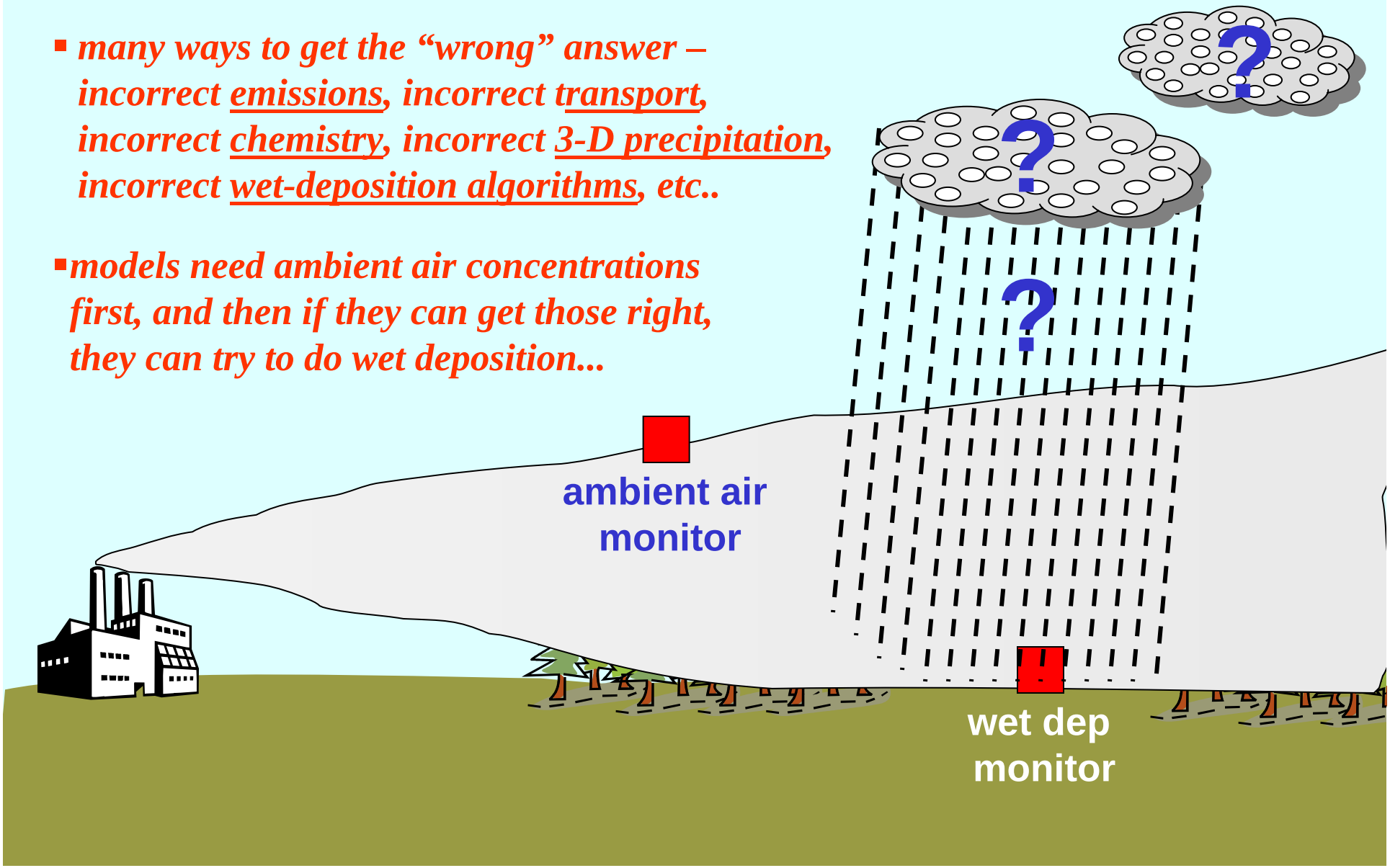
There have been very few measurements to date, and these data are rarely made available in a practical way (timely, complete, etc.)

Situation may be getting better, largely because of meetings like this!

Simple vs. Complex Measurements:
1. Wet deposition is a very complicated phenomena...

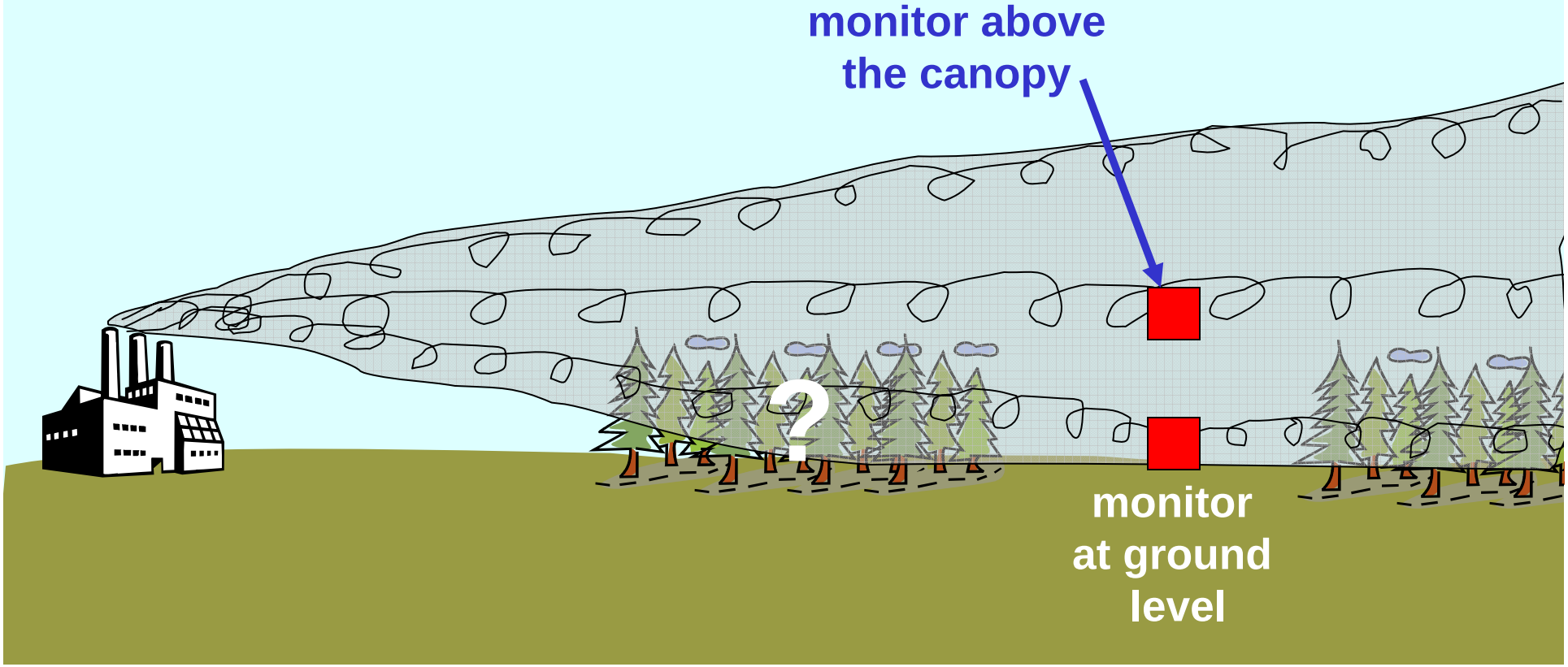
- ***many ways to get the "wrong" answer – incorrect emissions, incorrect transport, incorrect chemistry, incorrect 3-D precipitation, incorrect wet-deposition algorithms, etc..***

- ***models need ambient air concentrations first, and then if they can get those right, they can try to do wet deposition...***



Simple vs. Complex Measurements:
2. Potential complication with ground-level monitors...
("fumigation", "filtration", etc.)...

- ***atmospheric phenomena are complex and not well understood;***
- ***models need "simple" measurements for diagnostic evaluations;***
- ***ground-level data for rapidly depositing substances (e.g., RGM) hard to interpret***
- ***elevated platforms might be more useful (at present level of understanding)***



Simple vs. Complex measurements - 3. Urban areas:

a. **Emissions inventory poorly known**

b. **Meteorology very complex (flow around buildings)**

c. **So, measurements in urban areas not particularly useful for current large-scale model evaluations**

Simple vs. Complex Measurements – 4: extreme near-field measurements

- Sampling near intense sources?
- Must get the fine-scale met "perfect"

Ok, if one wants to develop hypotheses regarding *whether or not this is actually a source* of the pollutant *(and you can't do a stack test for some reason!).*

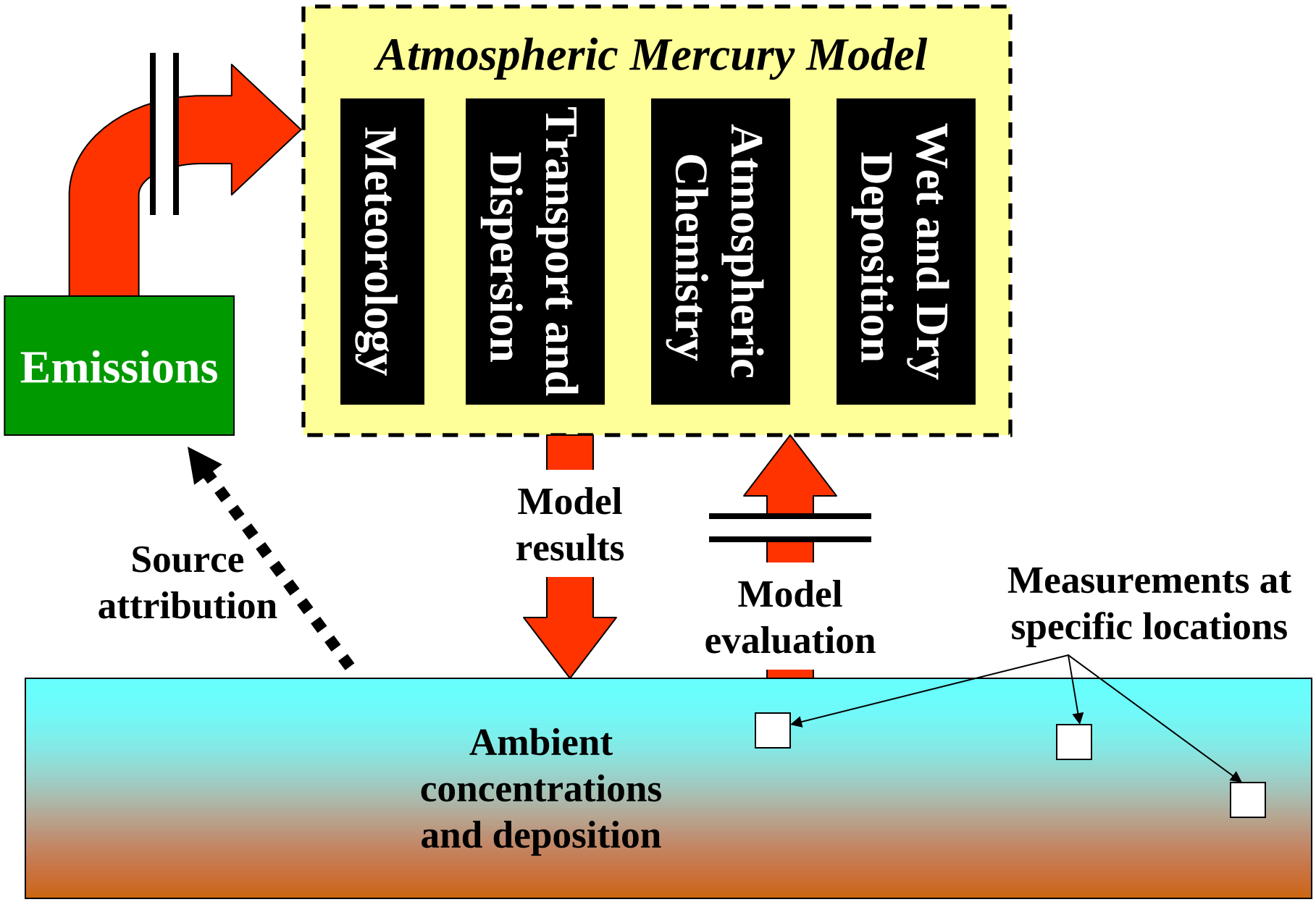
Complex vs. Simple Measurements – 5: Need some source impacted measurements

- **Major questions regarding plume chemistry and near-field impacts (are there "hot spots"?)**
- **Most monitoring sites are designed to be "regional background" sites (e.g., most Mercury Deposition Network sites).**
- **We need some source-impacted sites as well to help resolve near-field questions**
- ***But not too close – maybe 20-30 km is ideal (?)***

Some Current Model Evaluation Challenges

- ***Lack of speciated atmospheric concentration measurements, at ground level and aloft***
- ***Emissions inventory uncertainties, including speciation and temporal resolution – i.e., is the model wrong or is the inventory wrong?***
- ***It has not really been possible to adequately evaluate current atmospheric mercury models***

SUMMARY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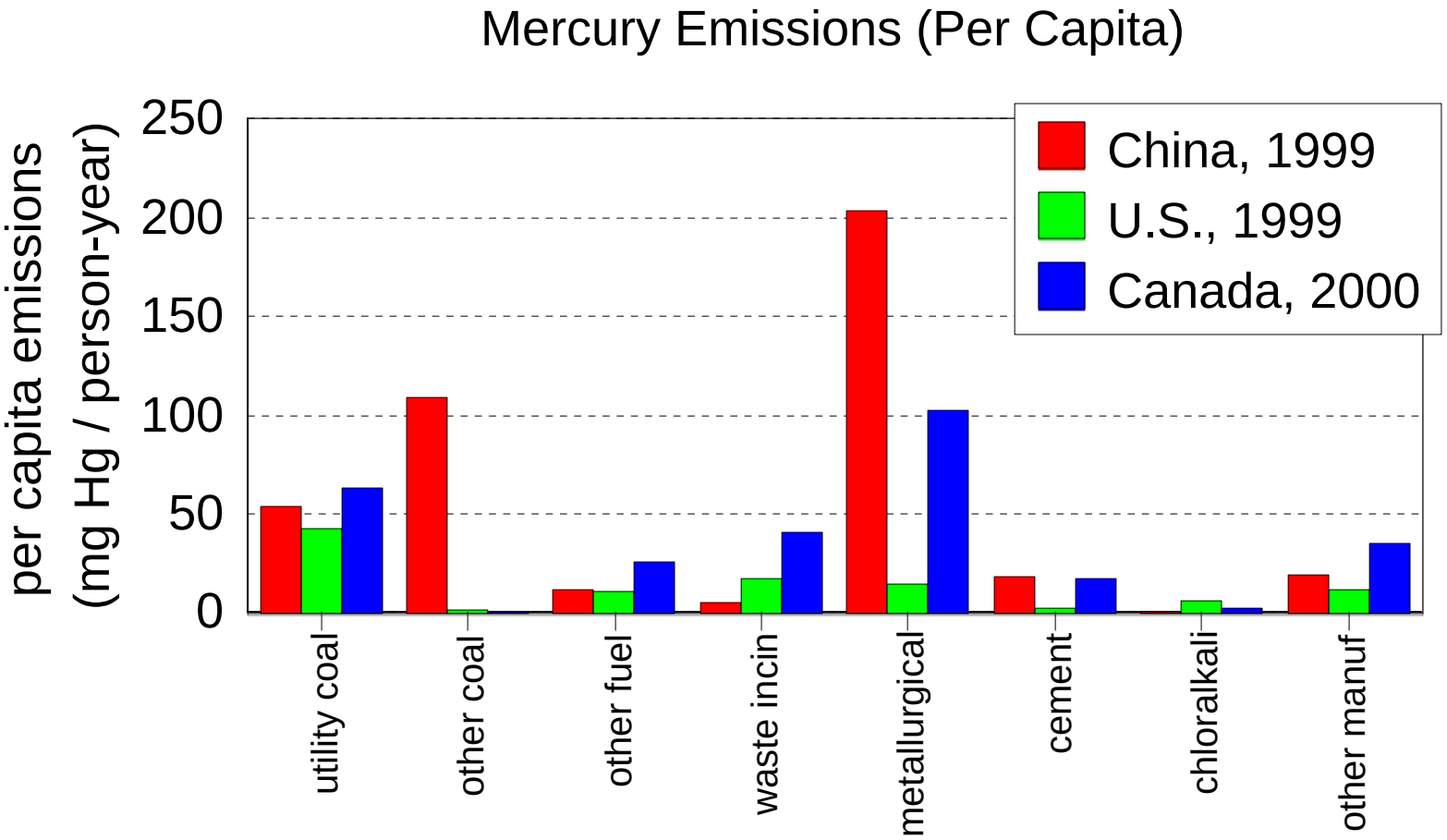
Thanks!

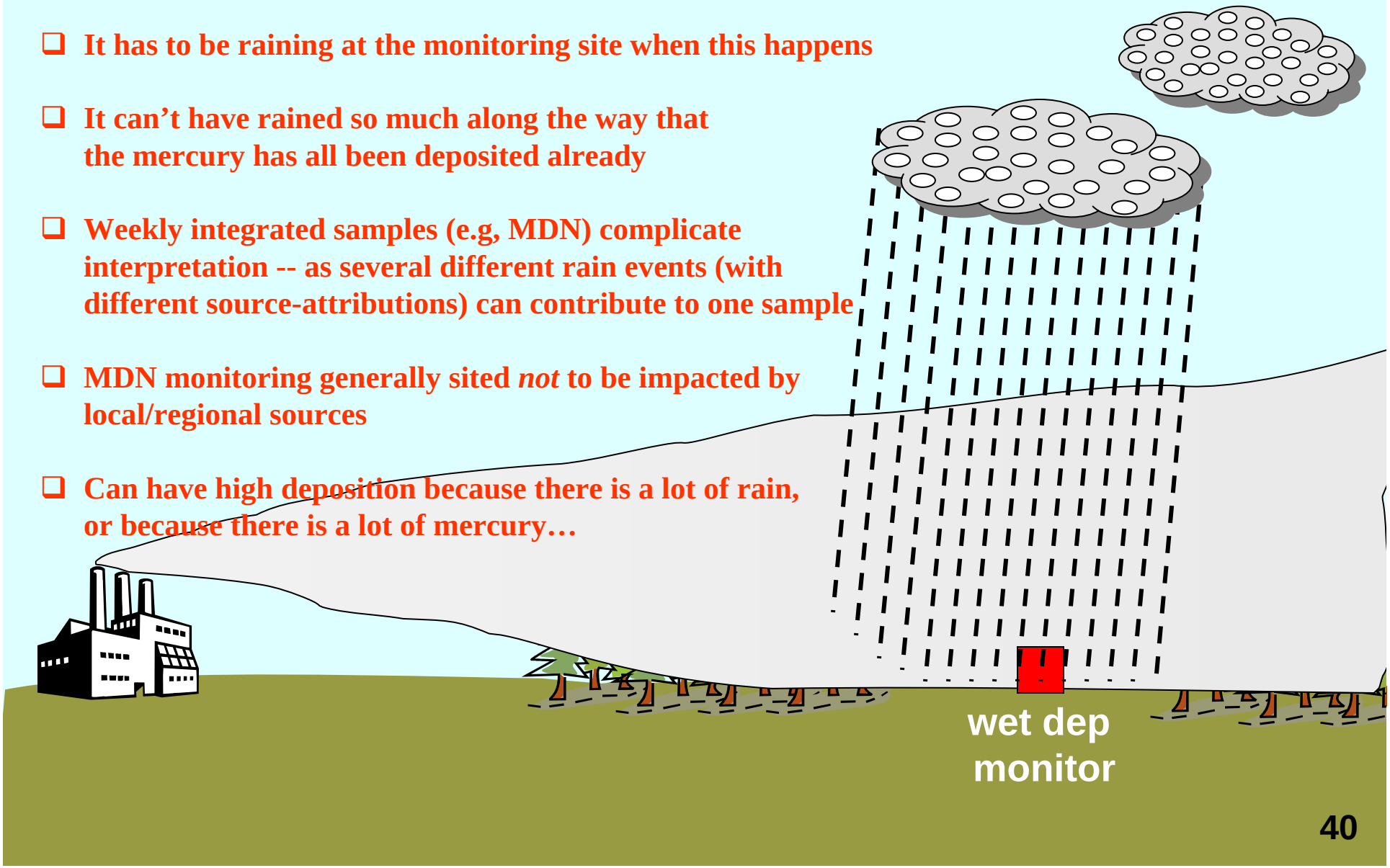
EXTRA SLIDES



Sources of Data: **U.S.** [USEPA], **Canada** [Environment Canada], **China** [Streets et al., 2005, "Anthropogenic mercury emissions in China", Atmospheric Environment 39, 7789-7806]

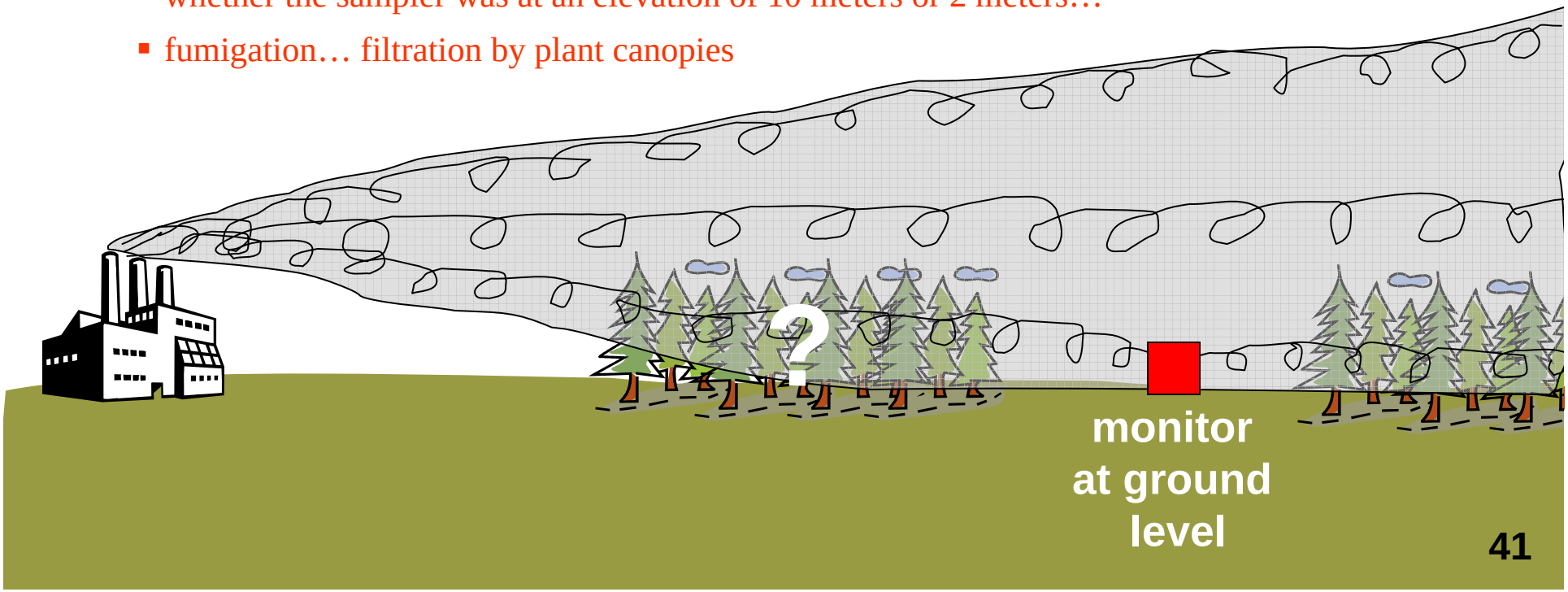
Challenges of using wet deposition data to assess local and regional deposition impacts…

- Wind has to blow from source to monitoring site
- It has to be raining at the monitoring site when this happens
- It can't have rained so much along the way that the mercury has all been deposited already
- Weekly integrated samples (e.g, MDN) complicate interpretation -- as several different rain events (with different source-attributions) can contribute to one sample
- MDN monitoring generally sited *not* to be impacted by local/regional sources
- Can have high deposition because there is a lot of rain, or because there is a lot of mercury…



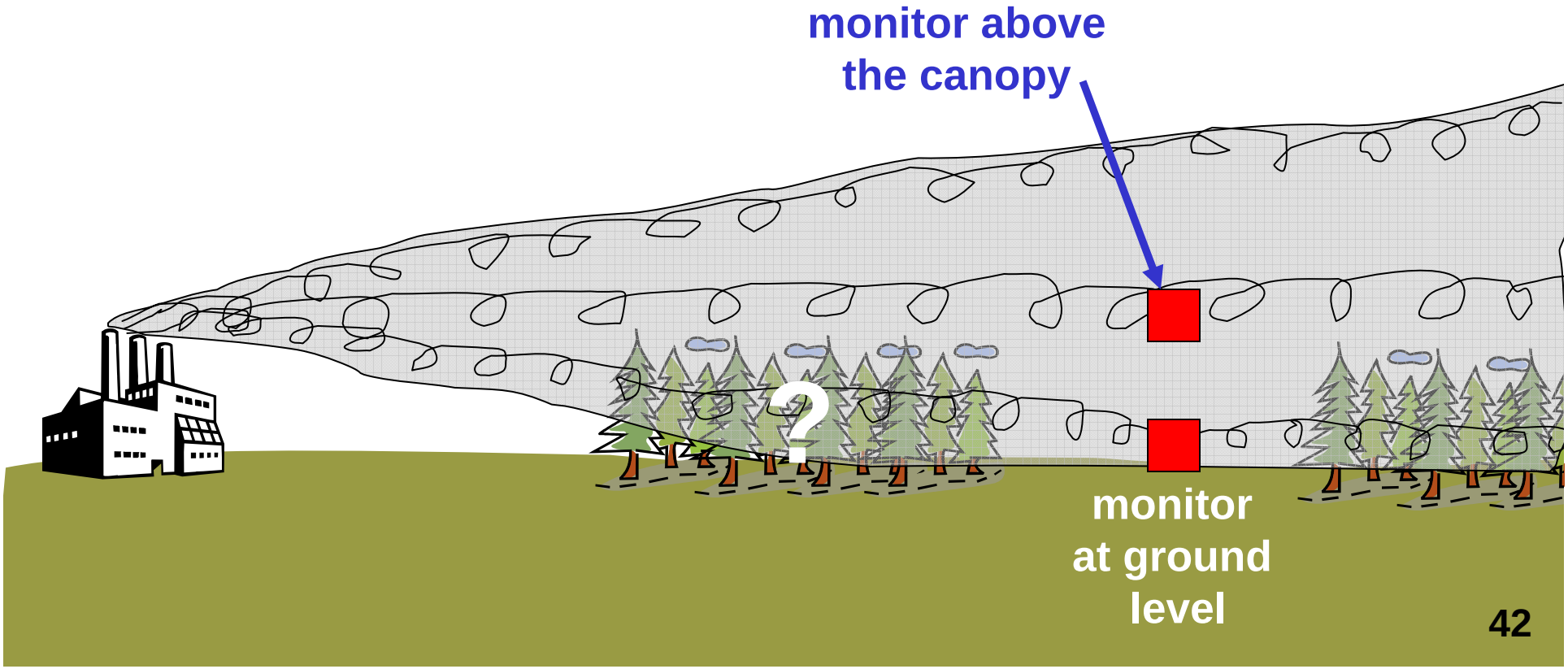
Challenges of using air concentration data to assess local and regional deposition impacts…

- **Need speciated data (Hg0, Hg(p), RGM)**
- **Relatively expensive and time-consuming**
- **Still have problem of having the plume hit the site, but can measure continuously… and the plume hit and rain doesn't have to occur at the same time (as with wet dep monitors) …**
- **Results from ground-level monitors can be hard to interpret –**
  - rapid dry deposition … large vertical gradients … measuring right where things are changing very rapidly … don't want the whole analysis to depend on whether the sampler was at an elevation of 10 meters or 2 meters…
  - fumigation… filtration by plant canopies



Observations of “depleted” RGM at ground-based stations downwind of power plants – sometimes thought to be evidence of RGM reduction to Hg0 -- might be strongly influenced by RGM dry deposition…

would be better to have a monitor far above the canopy…



Preliminary Results from Steubenville Hg Deposition Source Apportionment Study

Briefing for Tim Oppelt
April 27, 2005

Presented by Tim Watkins, NERL
Research conducted by Matt Landis, Gary Norris, and David Olson
in collaboration with the University of Michigan

Results

- Approximately 70% of Hg wet deposition at Steubenville site is attributable to local/regional fossil fuel (coal and oil) combustion sources
  - Not entirely attributable to electric utilities
- Preliminary results
  - Additional analysis to finalize results will be completed within a month

Questions about 1990 Baseline Inventory

- There were few stack tests for waste incineration (and other sources), and thus, 1990 inventory must have been based primarily on emissions factors.
- How confident can we be about 1990 emissions estimates?
- Example: Phoenix Services medical waste incinerator in Baltimore MD:
  - Estimated to be the largest source of RGM in the U.S., in 1999 EPA emissions inventory.
  - This inventory estimate was apparently made using standard emissions factors for medical waste incineration.
  - However, stack tests appear to indicate that the inventory estimates were on the order of a factor of 10 too high!

Questions about 1996 Inventory

From the U.S. EPA website (re-checked Dec 12, 2005):

"October 1, 2003:

• The 1996 National Toxics Inventory and the 1996 Emission Inventory for criteria pollutants data and documentation are no longer available.

• The EPA has released the 1999 National Emissions Inventory for Criteria and Hazardous Air Pollutants. It is the most recent inventory available.

• We recommend the use of the 1999 NEI because better quality data were submitted to EPA and new methodologies have been used."

http://www.epa.gov/ttn/chief/net/1996inventory.html

Questions about 1999 Inventory

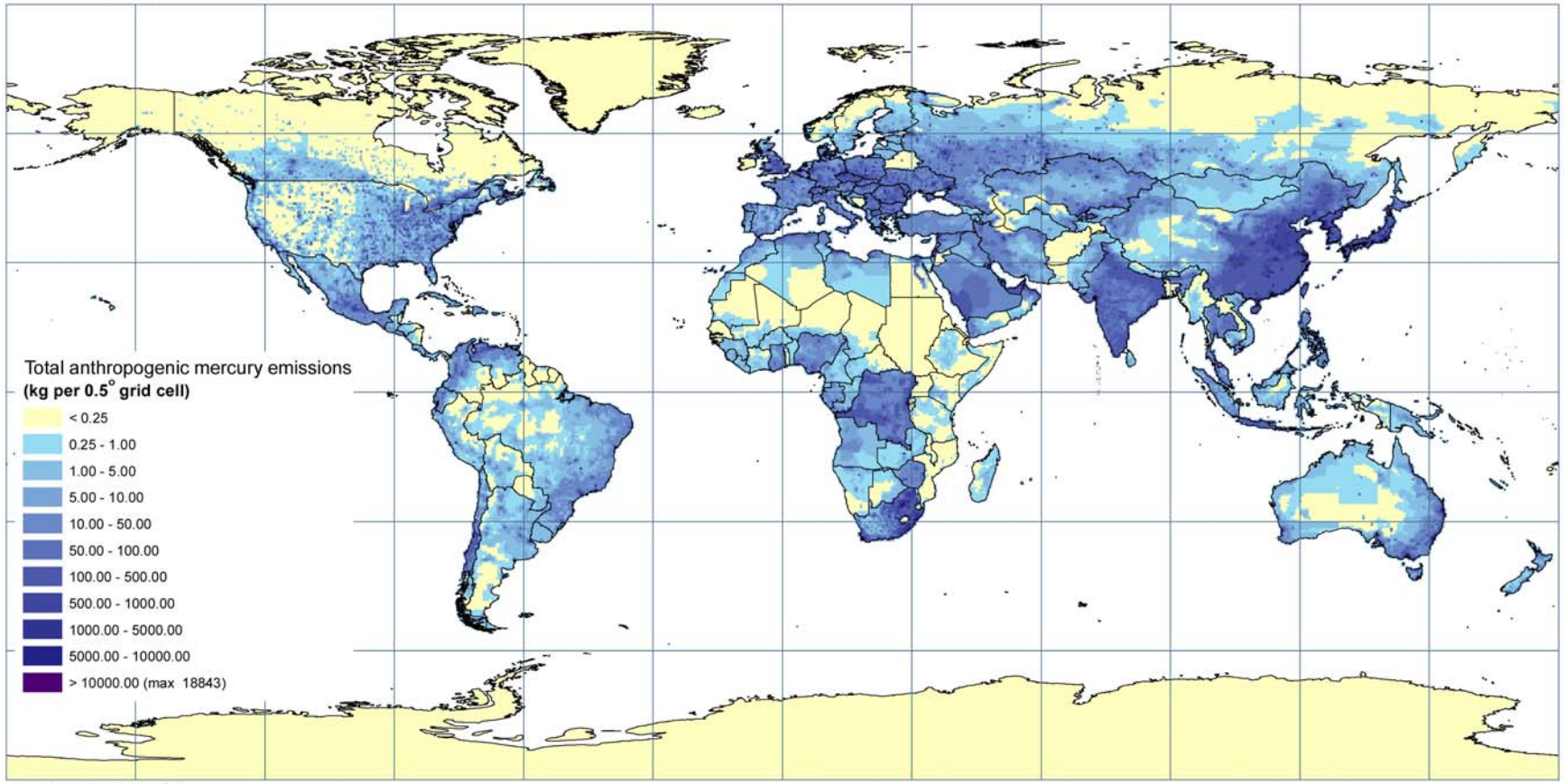
- The 1999 emissions inventory for municipal waste incinerators is believed to have assumed a level of compliance with regulations that did not actually exist in 1999 for all facilities.

  USEPA (2005). Emissions Inventory And Emissions Processing For The Clean Air Mercury Rule (CAMR). Office Of Air Quality Planning And Standards, Research Triangle Park, NC
  http://www.epa.gov/ttn/atw/utility/emiss_inv_oar-2002-0056-6129.pdf

- The assumed 1999 emissions may not have actually been realized at some facilities until sometime in 2000 or 2001

Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere, 1995

Total Hg, point sources + distributed sources, 0.5° grid



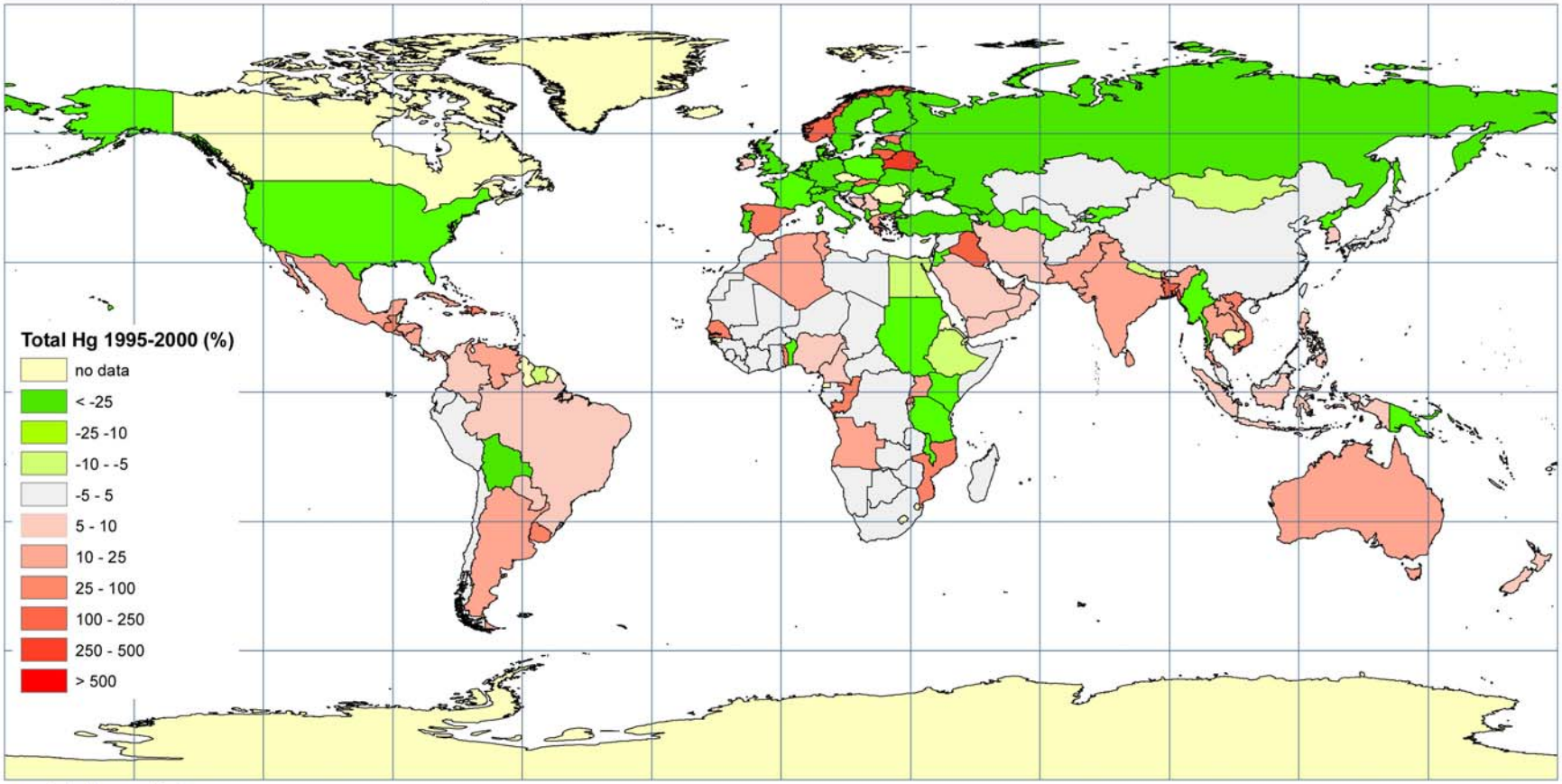
unprojected (geographic)

citation:
Pacyna, J., S. Wilson and F. Steenhuisen. 2005.
Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere.
(www.amap.no/Resources/HgEmissions/HgInventoryMain.html)

S. Wilson (AMAP), F. Steenhuisen (Arctic Centre, RuG), J. Pacyna (NILU)

Spatially Distributed Inventories of Global Anthropogenic Emissions of Mercury to the Atmosphere

Total Hg, 1995-2000 difference (%)



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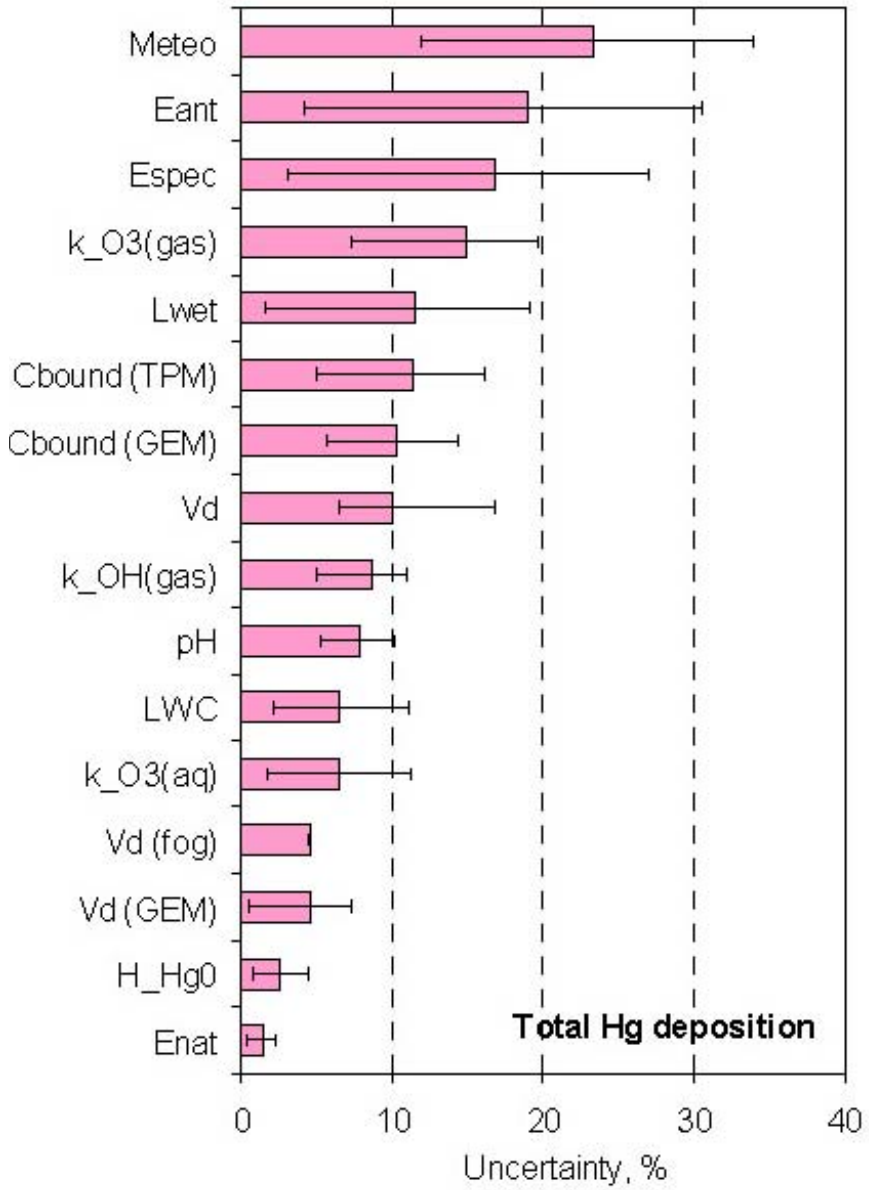
Sensitivity Analysis of Modeled Mercury Deposition



O. Travnikov, I. Ilyin (2005). Regional Model MSCE-HM of Heavy Metal Transboundary Air Pollution in Europe. EMEP/MSC-E Technical Report 6/2005. Meteorological Synthesizing Centre – East, Moscow, Russia.

http://www.msceast.org/events/review/hm_description.html