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

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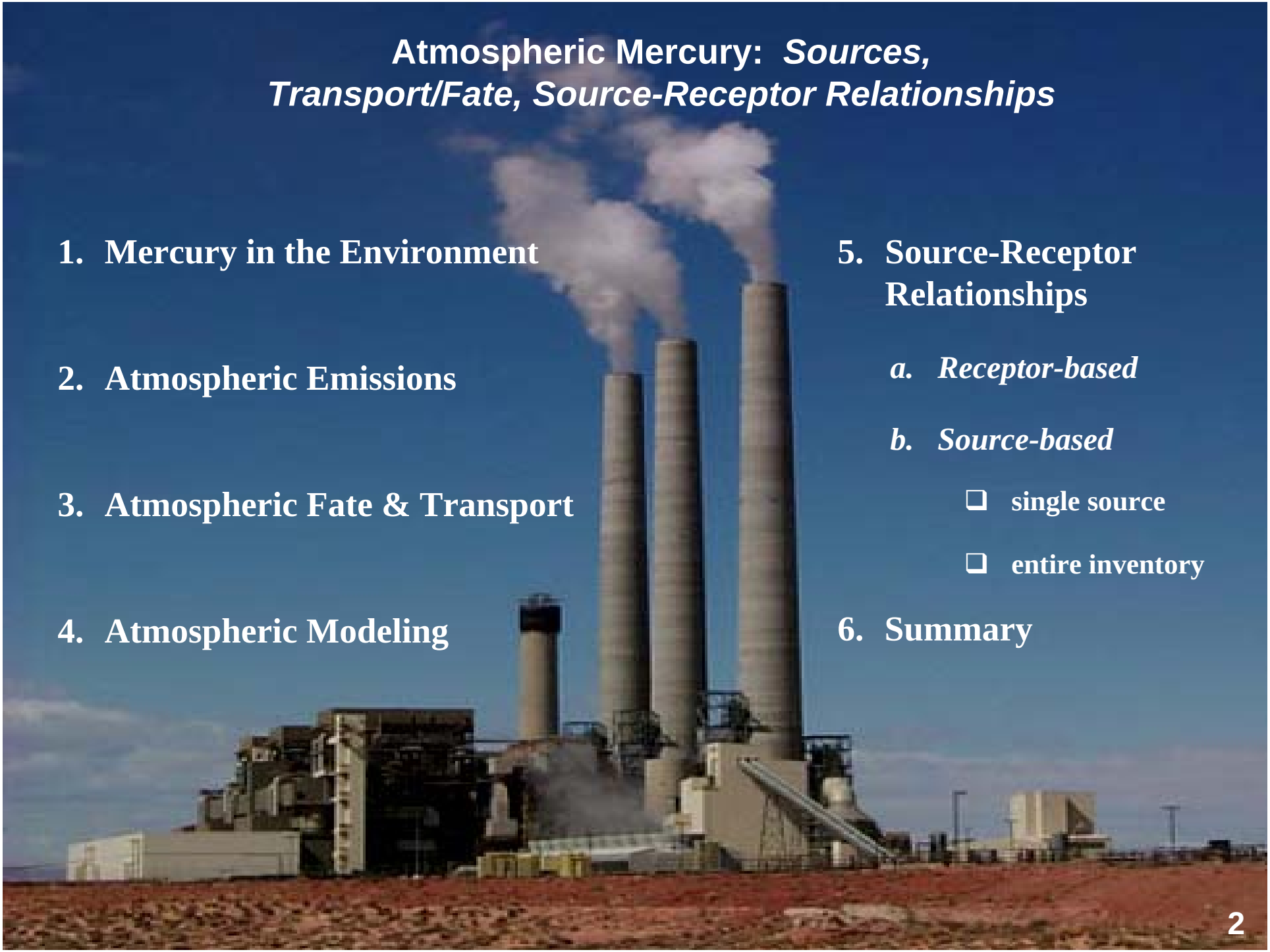
Presentation at the Appalachian Laboratory,
University of Maryland Center for Environmental Science
Frostburg State University, April 27, 2006

Atmospheric Mercury: *Sources, Transport/Fate, Source-Receptor Relationships*



1. **Mercury in the Environment**
2. **Atmospheric Emissions**
3. **Atmospheric Fate & Transport**
4. **Atmospheric Modeling**
5. **Source-Receptor Relationships**
   - *a. Receptor-based*
   - *b. Source-based*
     - ❑ single source
     - ❑ entire inventory
6. **Summary**

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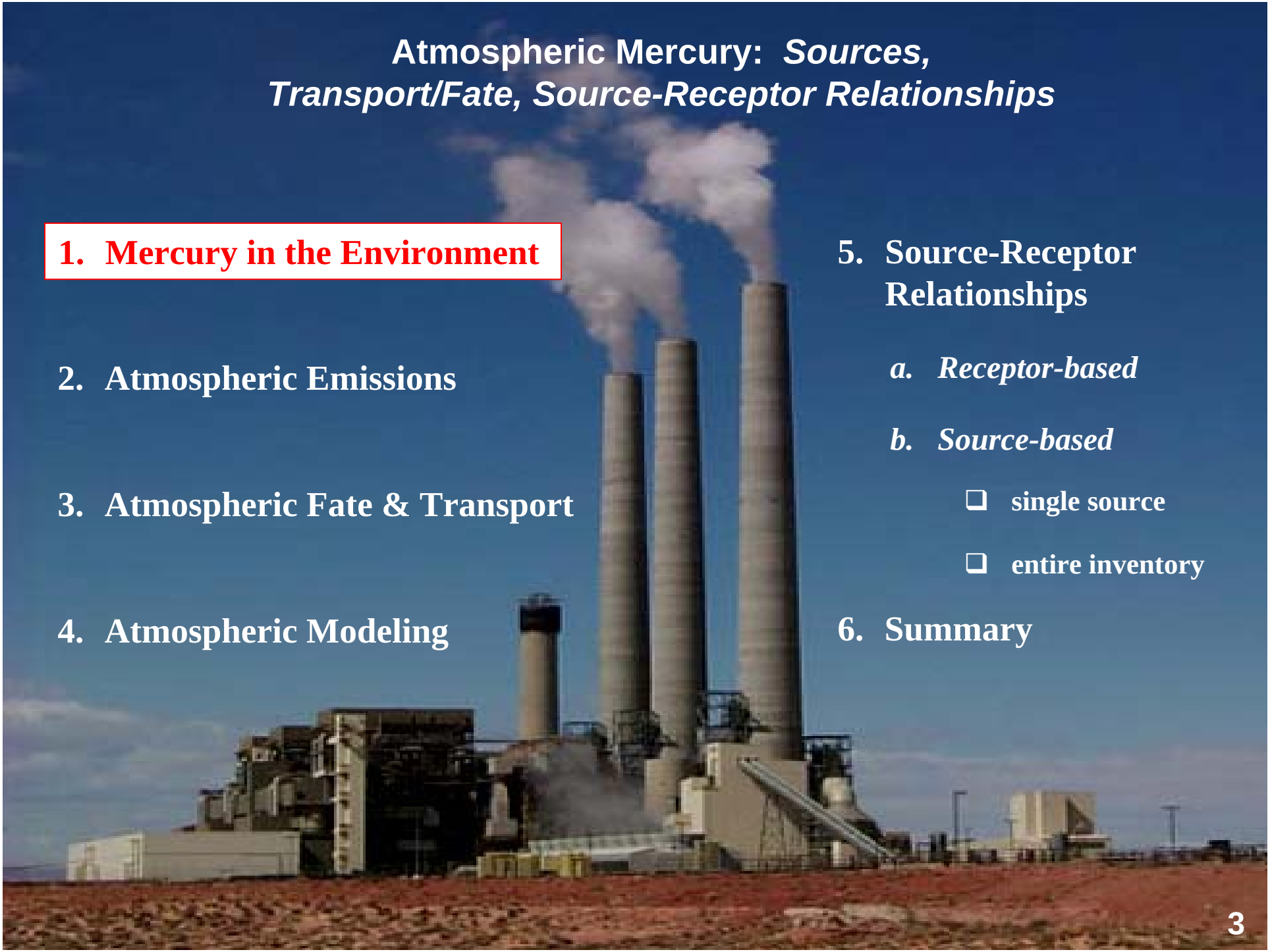

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Many waterbodies throughout the U.S. have fish consumption advisories due to high mercury levels

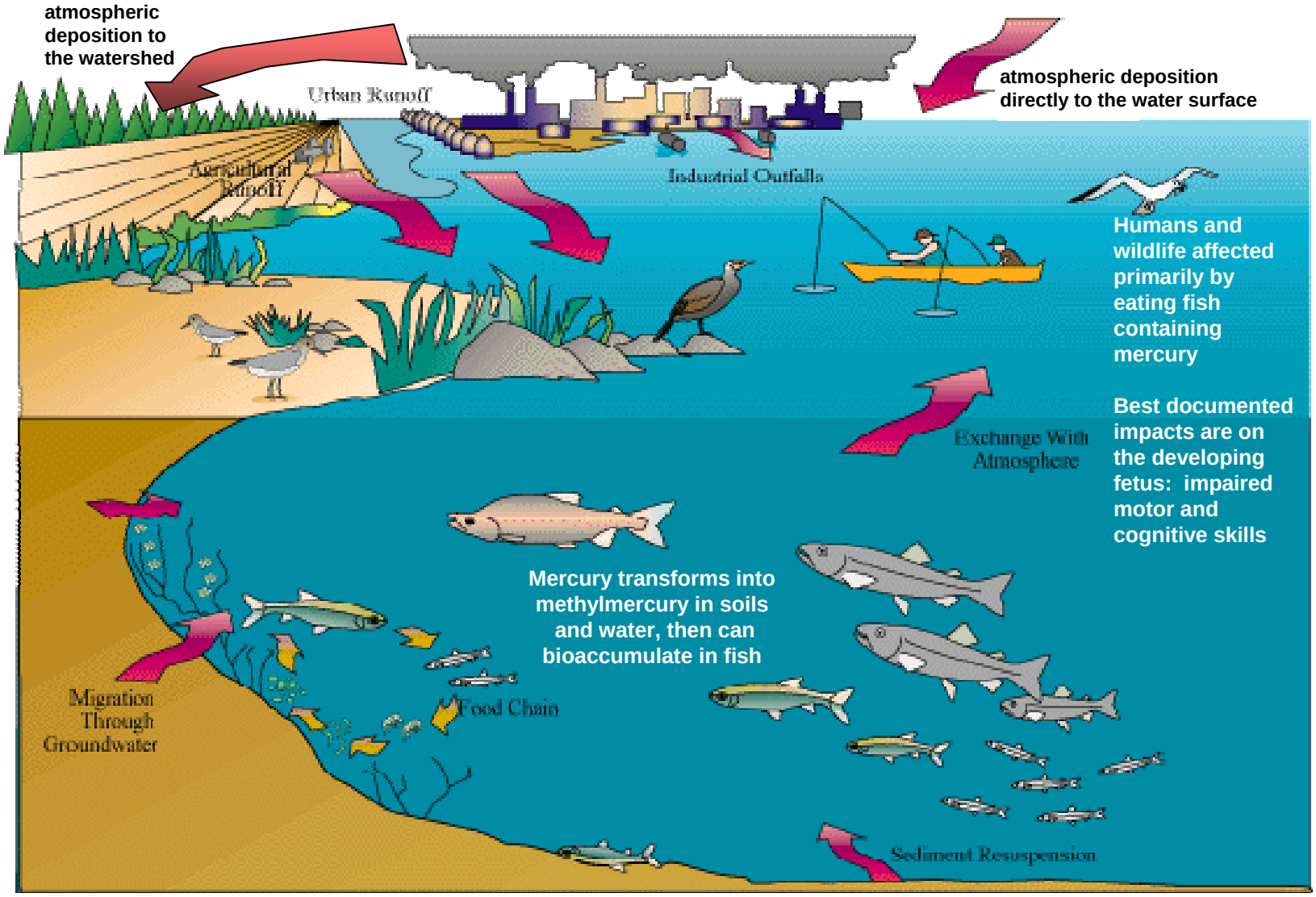
Significant numbers of people are currently being exposed to levels of mercury that may cause adverse effects –

- ***in the general population, 1 out of every 6 children born in the U.S. has already been exposed in-utero to levels of mercury that may cause neuro-developmental effects;***
- ***in some sub-populations, fish consumption & mercury exposure may be higher***

Fish consumption is the most important mercury exposure pathway for most humans and wildlife

For many aquatic ecosystems, much of the mercury loading comes directly or indirectly through the atmospheric pathway...

There are many ways in which mercury is introduced into a given aquatic ecosystem... atmospheric deposition can be a very significant pathway

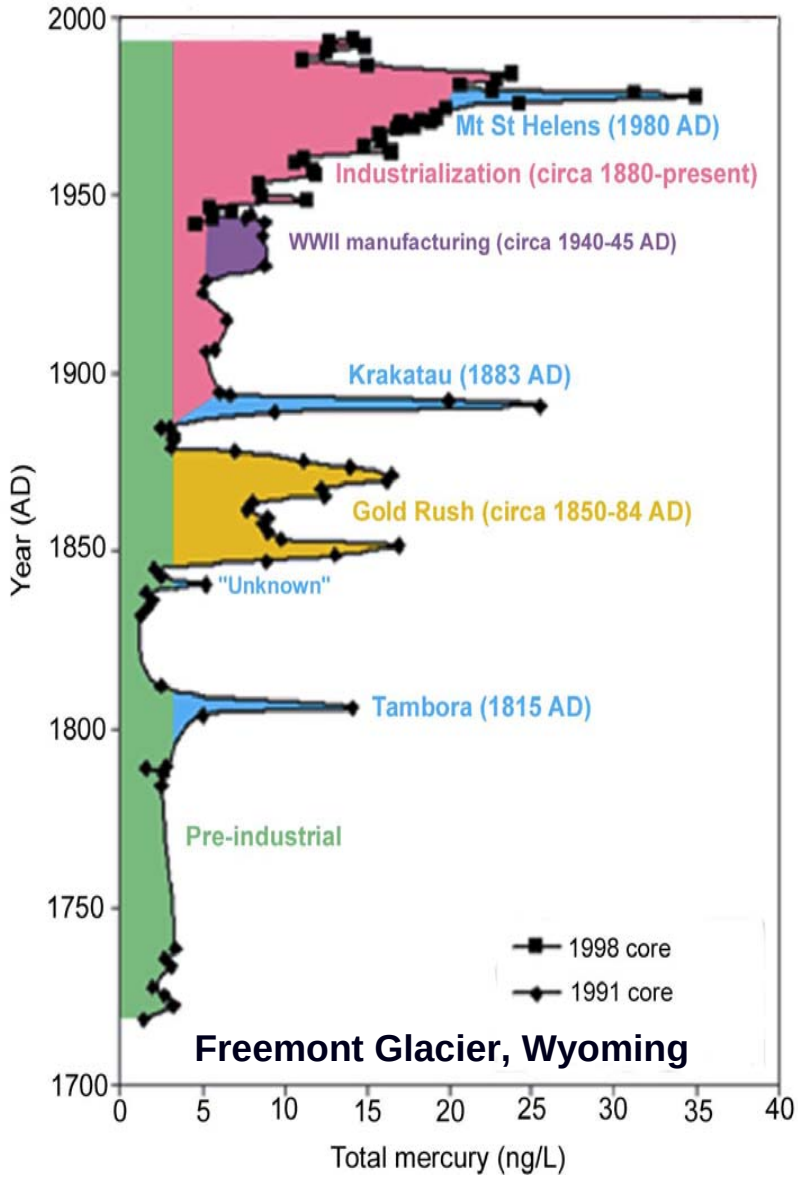


many policy-relevant questions regarding mercury

- **Relative importance of different loading pathways?**
  (e.g. atmospheric deposition, industrial discharge, etc?)
- **Relative importance of natural vs. anthropogenic contamination?**
- **Relative importance of different source regions?**
  (e.g., how much from local, regional, national, global…)
- **Relative importance of current vs. past loadings?**
- **Have these answers changed over time? How will they change in the future?**
- **How are these answers different for different ecosystems?**
- **Which sources should be regulated, and to what extent?**
- **Is "emissions trading" workable and ethical?**
- **Is the recently promulgated Clean Air Mercury Rule a reasonable approach?**

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, Schuster et al., 2002

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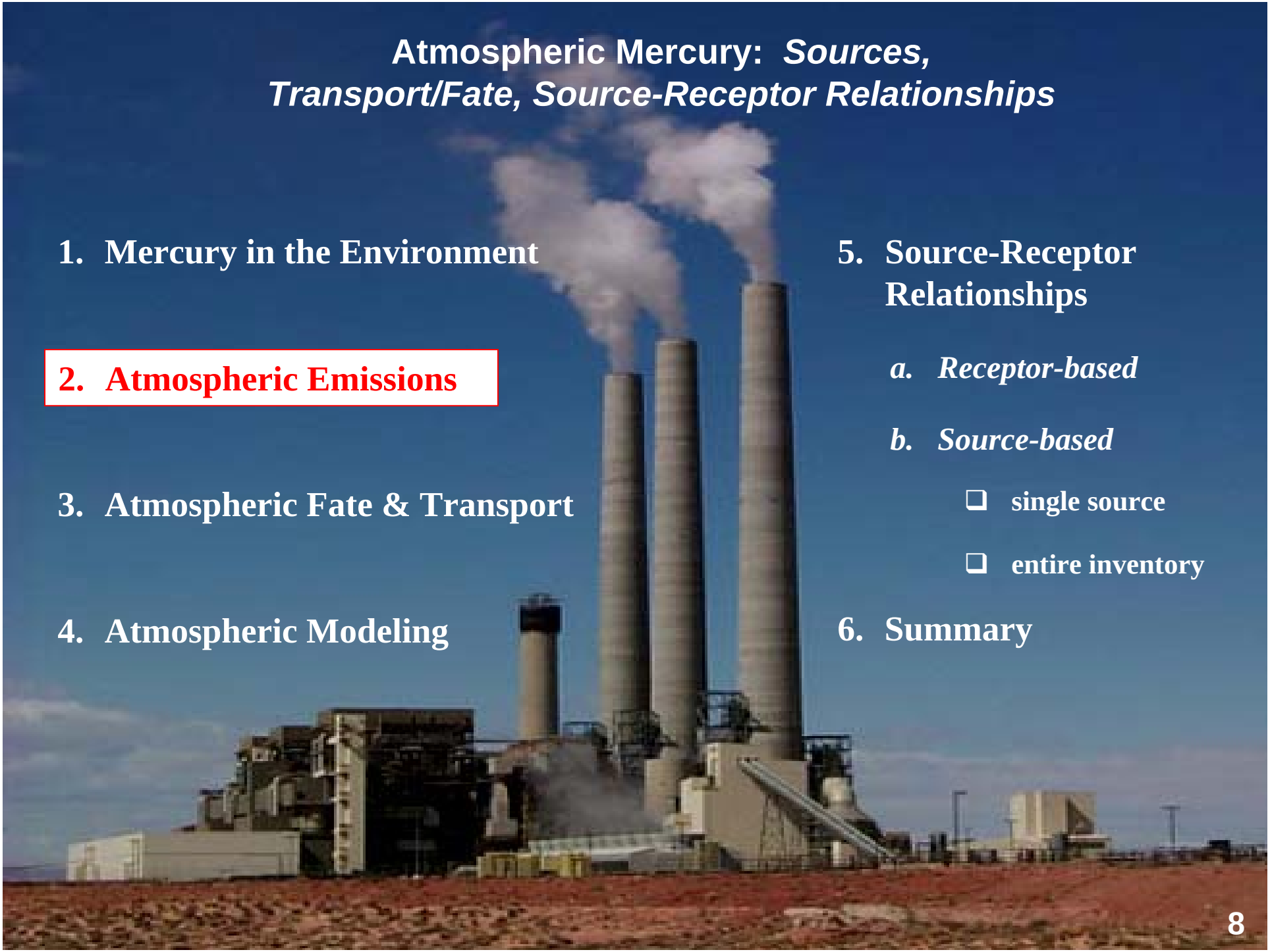

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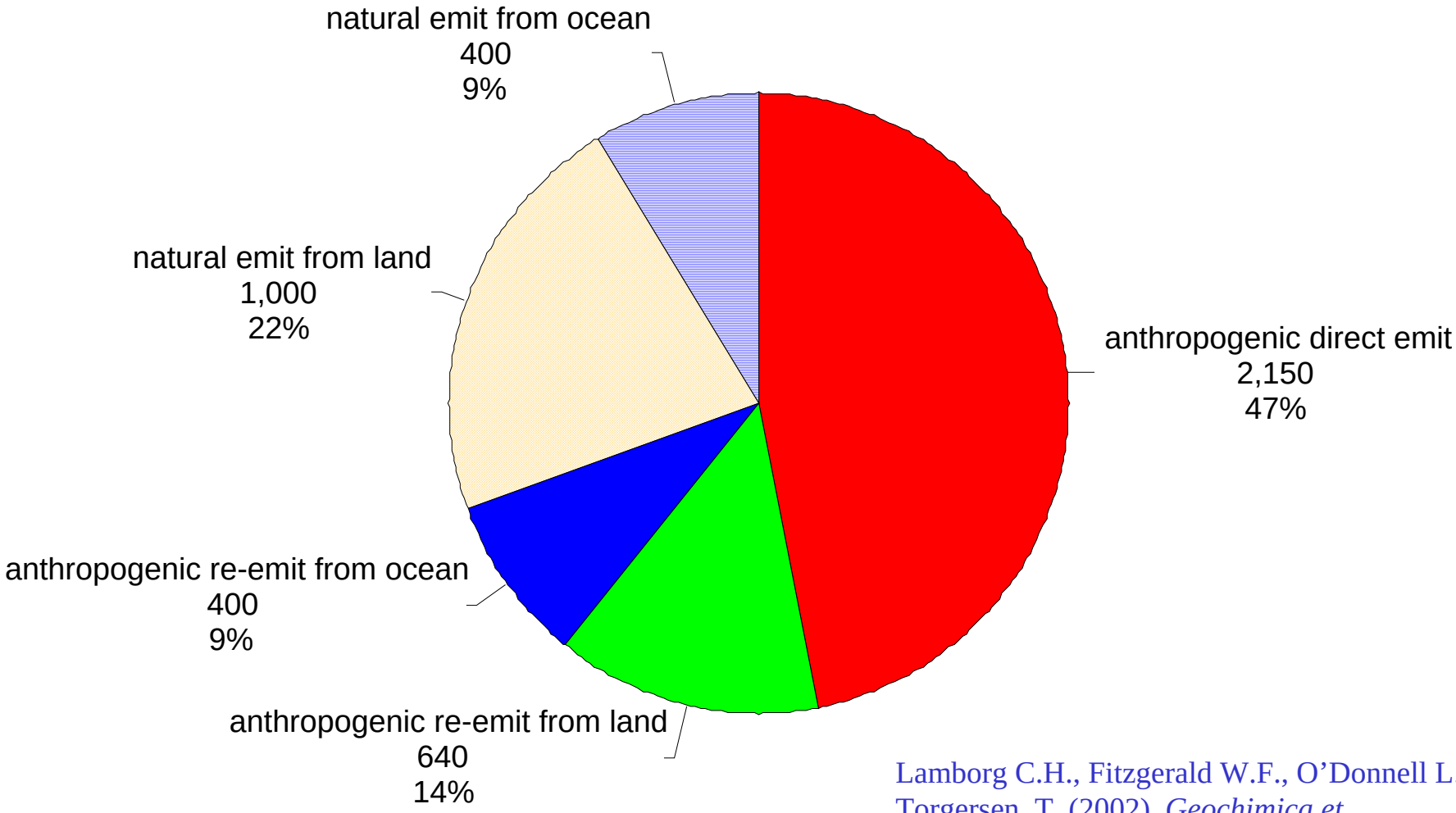
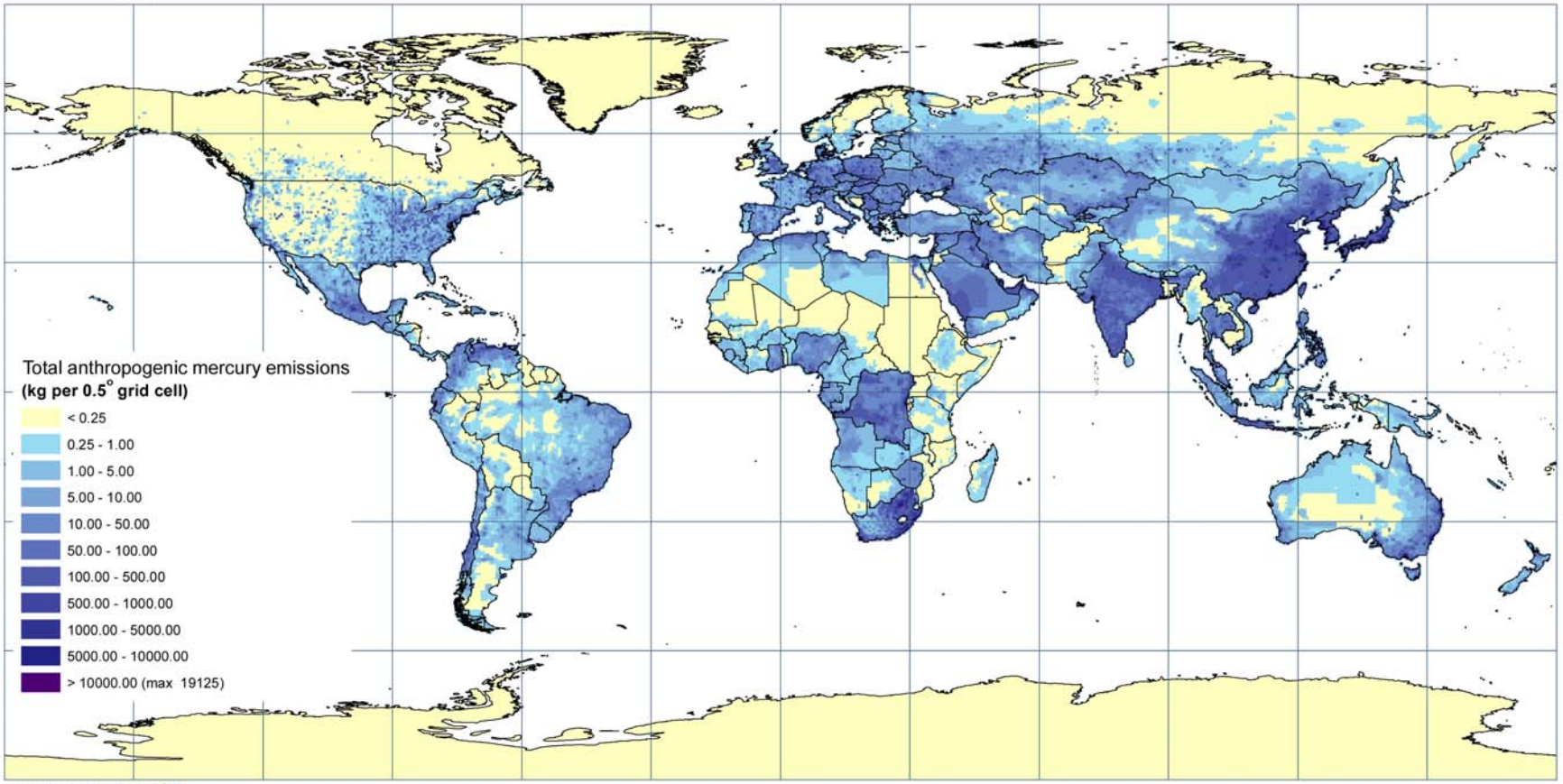
Global natural and anthropogenic emissions of mercury. Estimates taken/ inferred from Lamborg et al. (2002). All values are in metric tons per year, and are for ~1990.



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

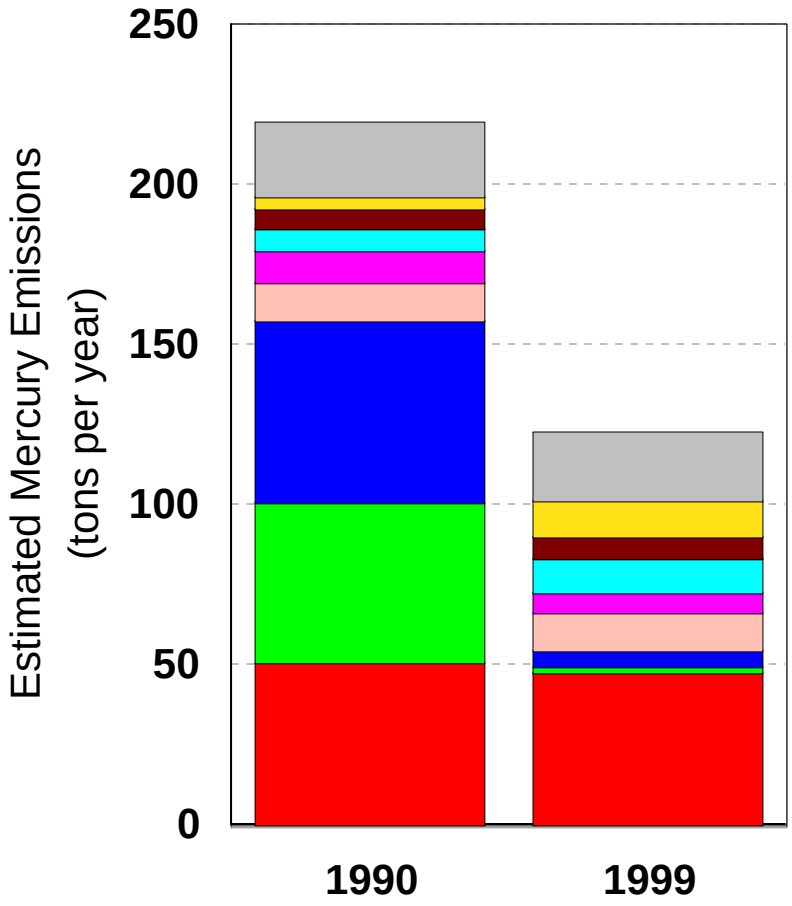


unprojected (geographic)

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)

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

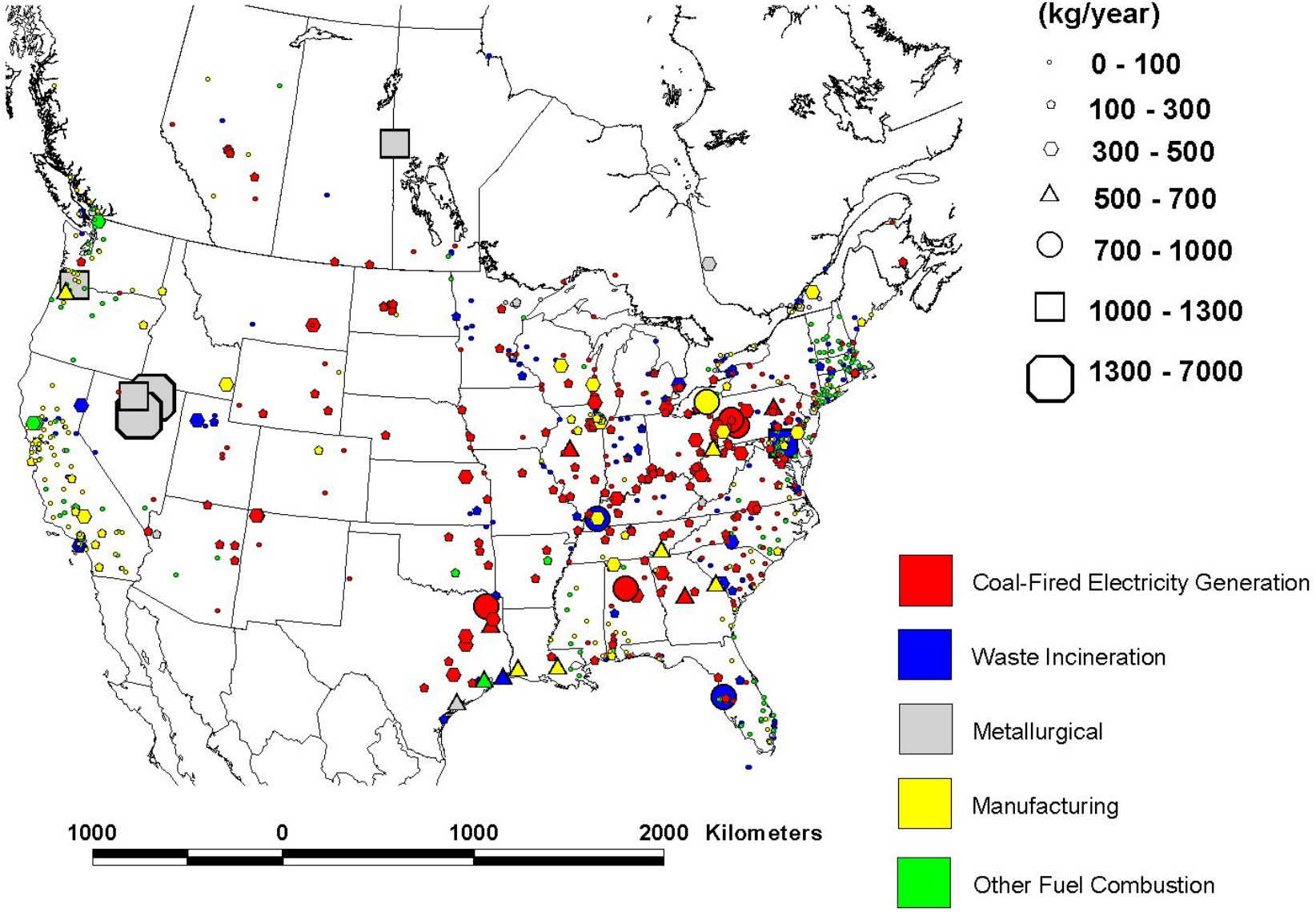


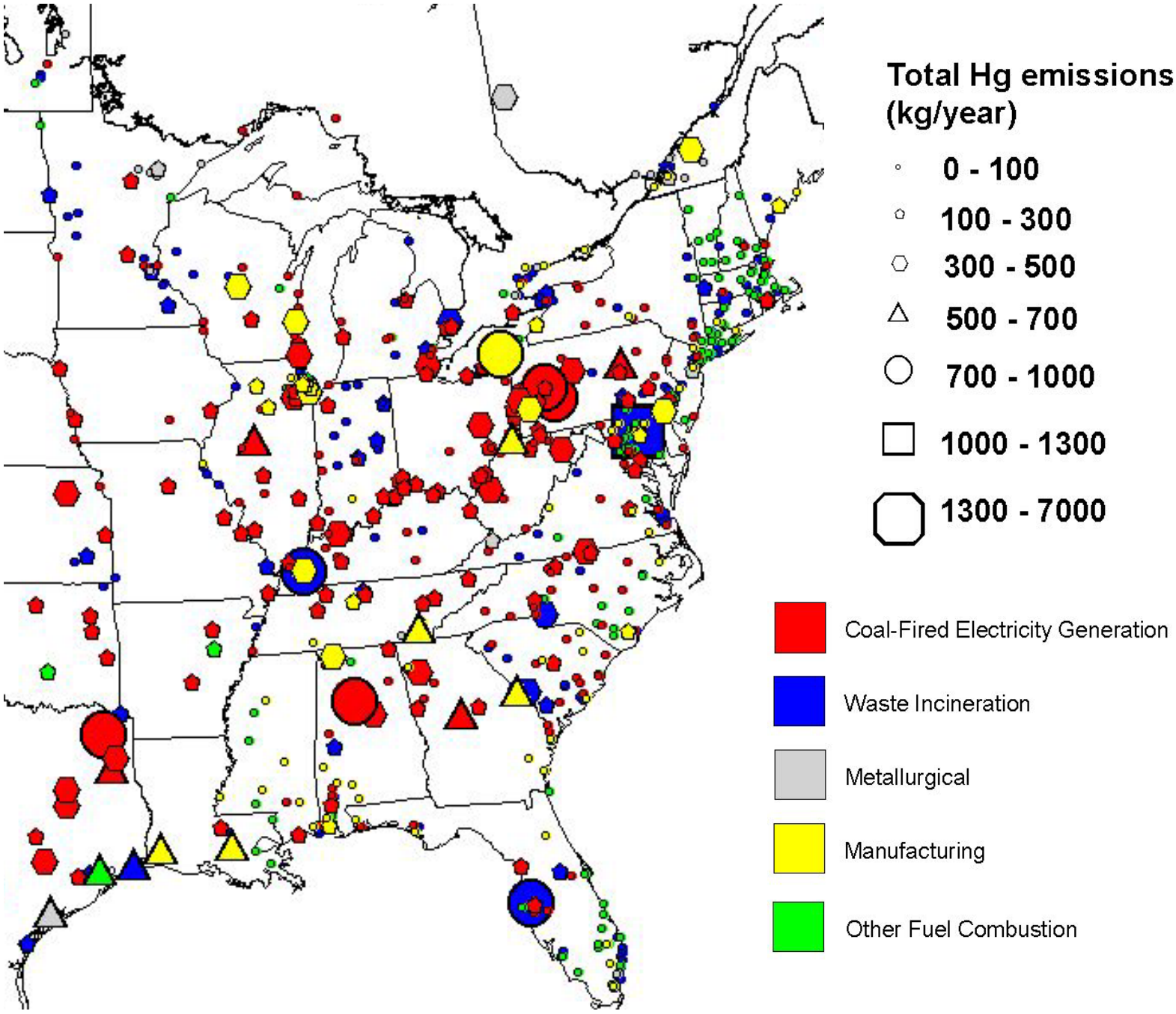
There were big reported changes in emissions between 1990 and 1999, but when did these occur? And when did they occur for individual facilities?

- 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.

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



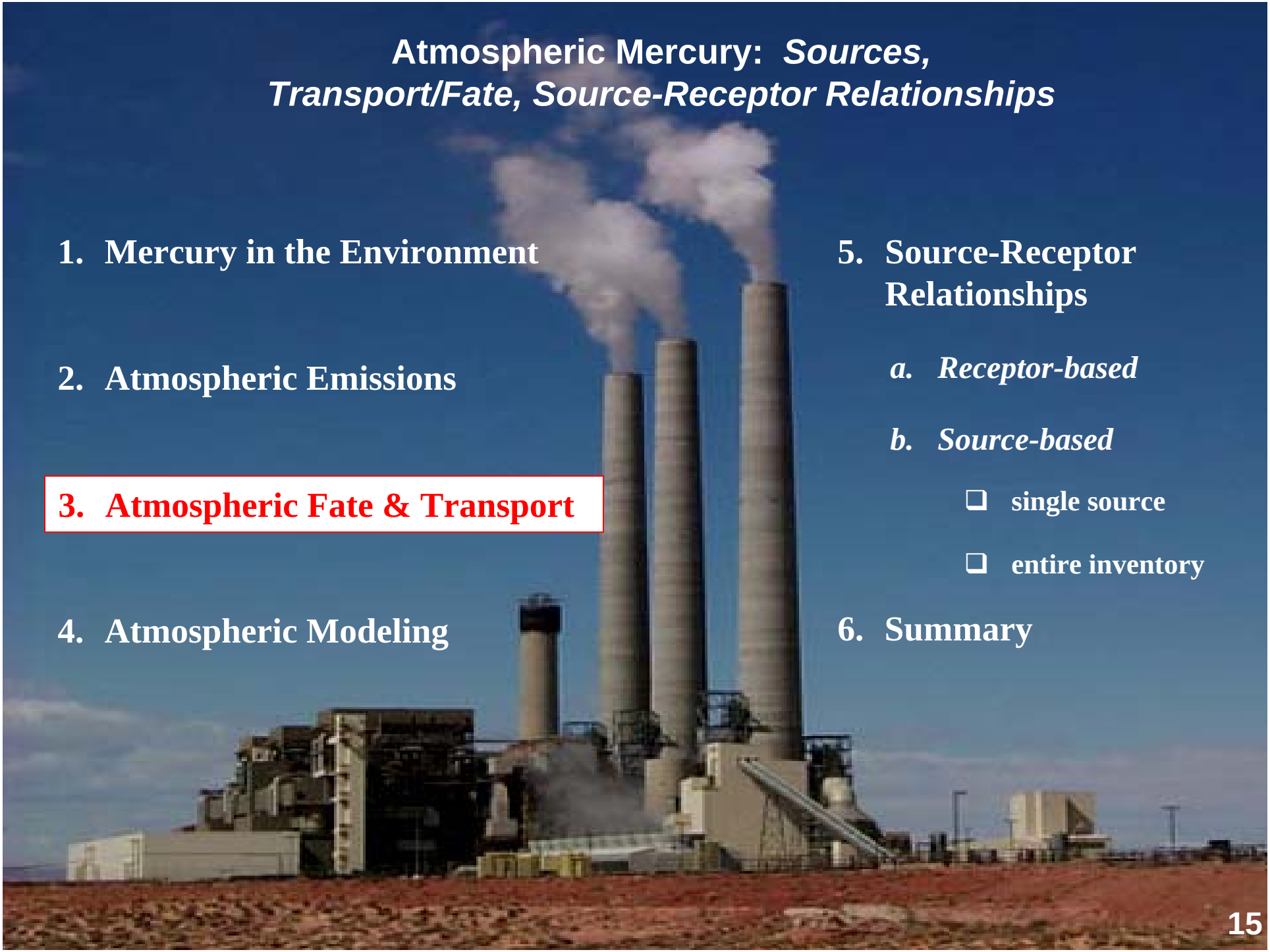

Total Hg emissions
(kg/year)
0 - 100
100 - 300
300 - 500
500 - 700
700 - 1000
1000 - 1300
1300 - 7000
Coal-Fired Electricity Generation
Waste Incineration
Metallurgical
Manufacturing
Other Fuel Combustion

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

Atmospheric Mercury: *Sources, Transport/Fate, Source-Receptor Relationships*



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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**

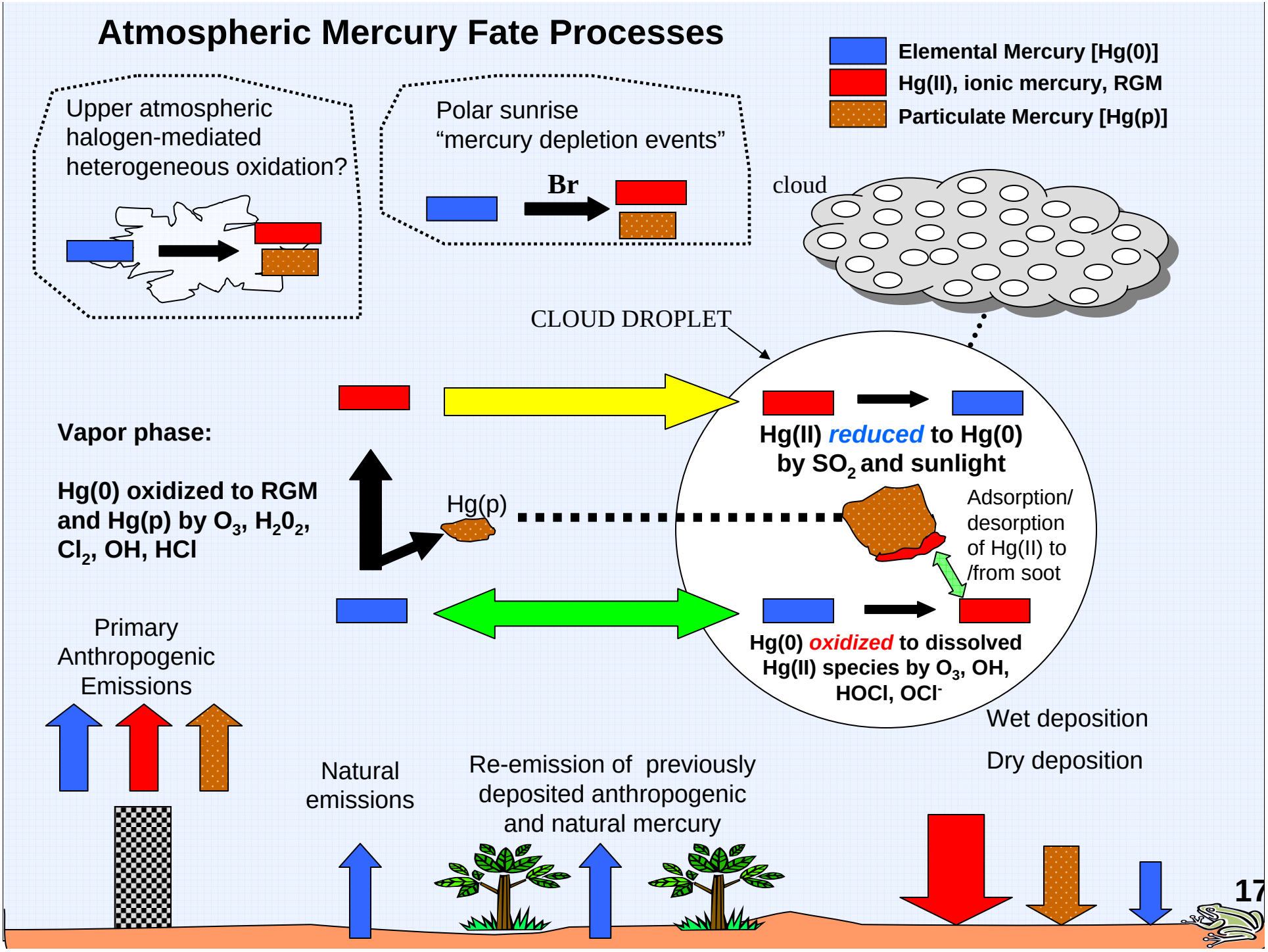
Reactive Gaseous Mercury (“RGM”)

- **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 Mercury Fate Processes



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)

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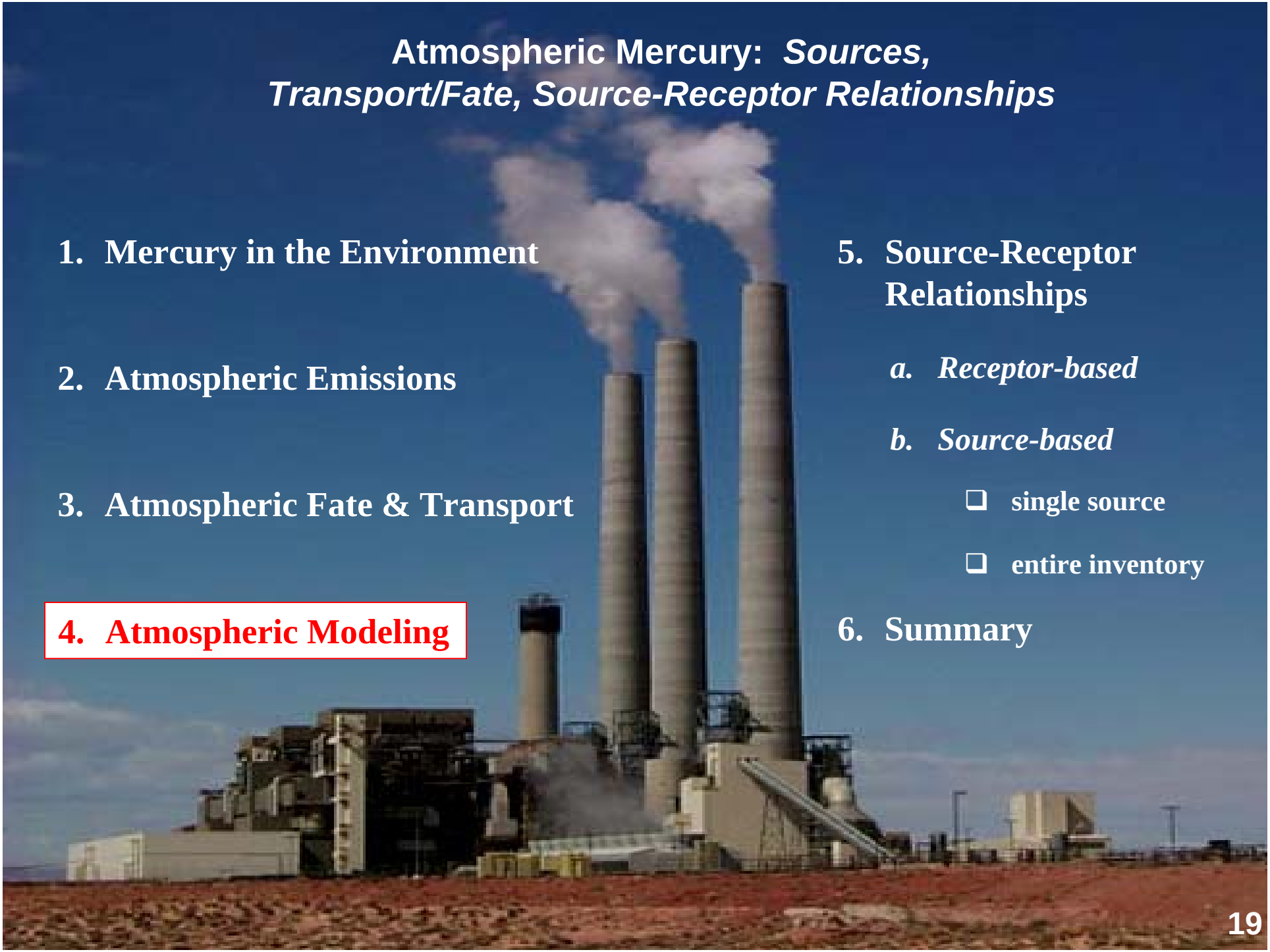

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The Role and Potential Value of Models

1. **Models are mathematical and/or conceptual descriptions of real-world phenomena**

   - **They are necessarily a simplification – the real world is *very* complicated**
   - ***Hopefully* the most important aspects are treated sufficiently well…**

The Role and Potential Value of Models

2. Models and measurements are inextricably linked

- Most models are created only after extensive measurement data are collected and studied
- Models are based on the data in one form or another
- In almost all cases, models must be continually "ground-truth'ed" against actual measurements – *(definitely the case with current atmospheric mercury models)*

The Role and Potential Value of Models

3. Models are potentially valuable for:

- **Examining large-scale scenarios that cannot easily be tested in the real world**
- **Interpreting measurements**
  (e.g., filling in spatial and temporal gaps between measurements)
- **Providing Source-Receptor Information**
  (maybe the only way to really get this…)

The Role and Potential Value of Models

4. Models are a test of our collective knowledge

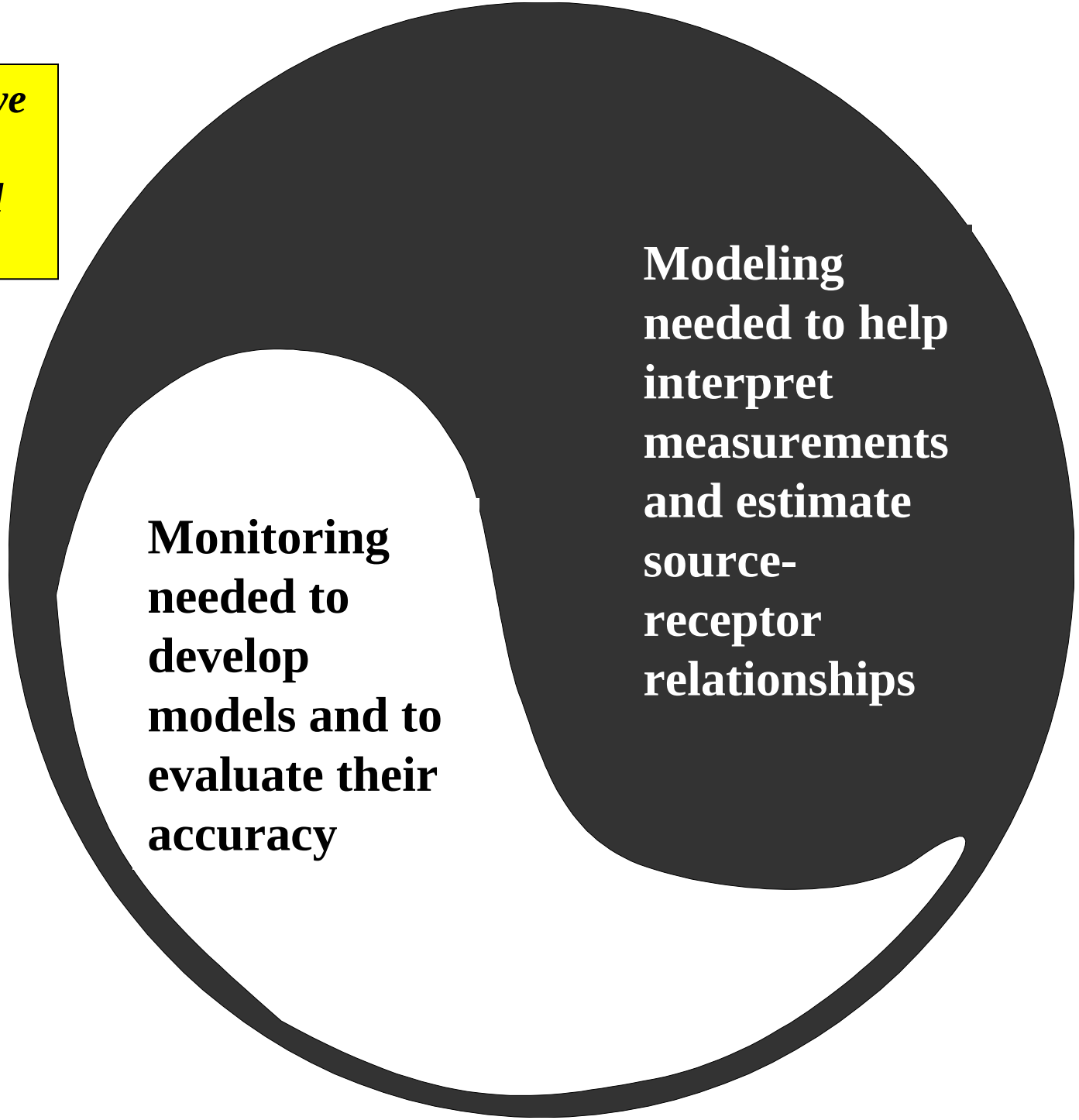
- They attempt to synthesize everything important that we know about a given system
- If a model fails, it means that we may not know everything we need to know…

The Role and Potential Value of Models

5. **Whether we like it or not, models are used in developing answers to most information necessary for environmental policy decisions…**

   - **EFFECTS (e.g., on human and wildlife health)**
   - **CAUSES (e.g., environmental fate and transport of emitted substances)**
   - **COSTS (e.g. for remediation)**

To get the answers we need, we need to use both monitoring and modeling -- <u>together</u>



What is an atmospheric model?

- **a computer simulation of the fate and transport of emitted pollutants**

- **two different types of models**
  - **Eulerian**
  - **Lagrangian**

What do atmospheric mercury models need?

Emissions Inventories

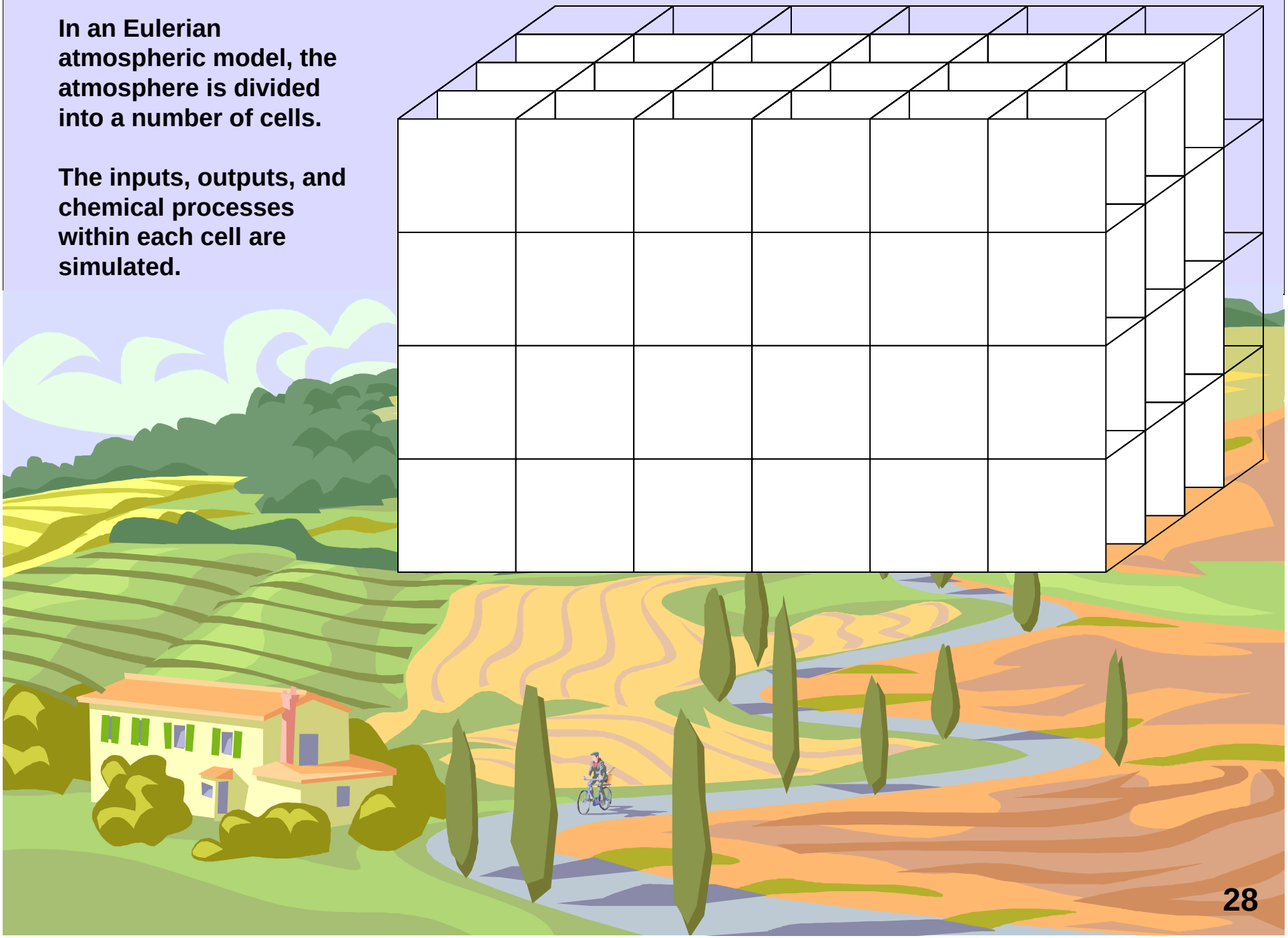
Meteorological Data

Scientific understanding of phase partitioning, atmospheric chemistry, and deposition processes

Ambient data for comprehensive model evaluation and improvement

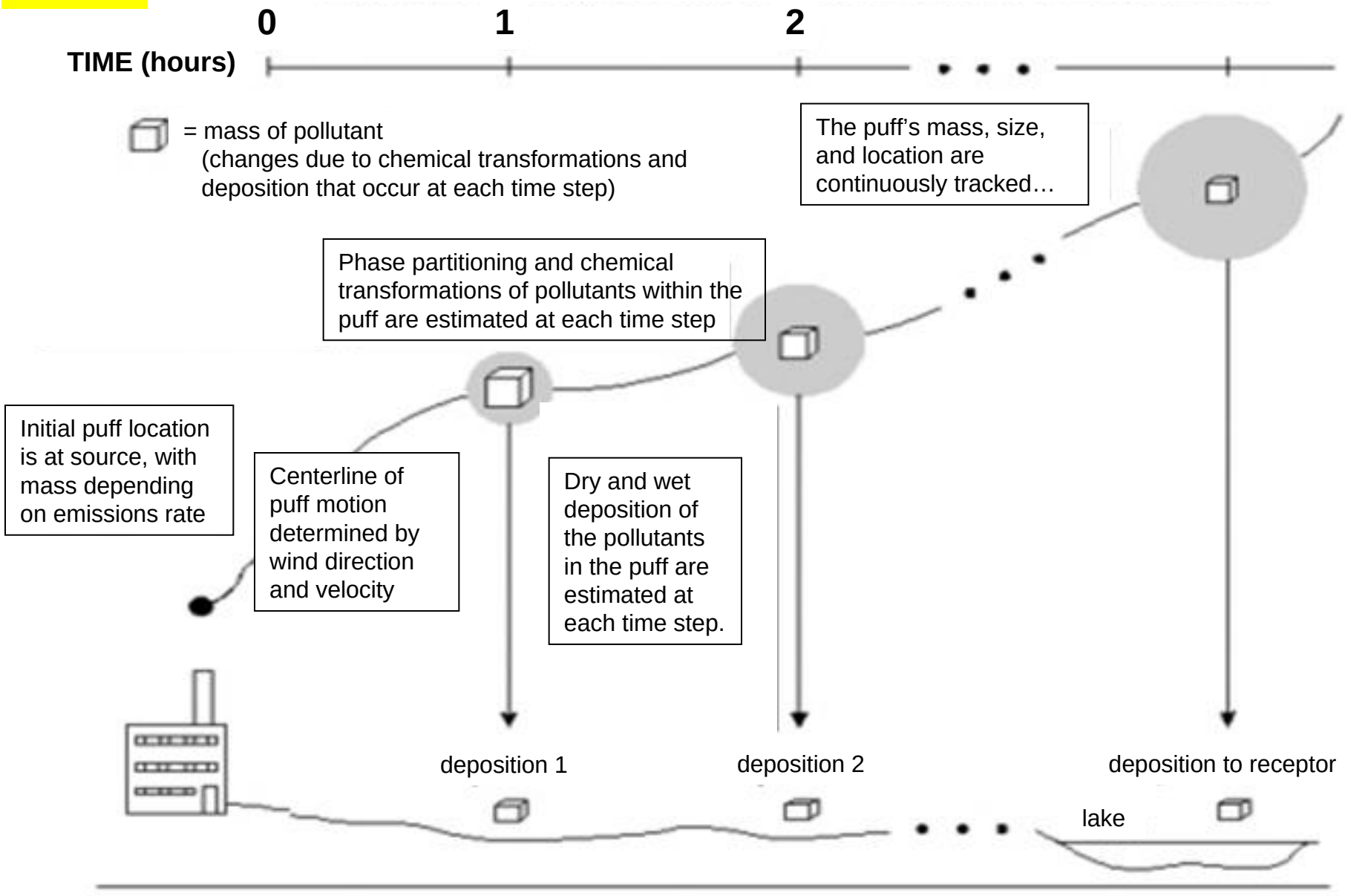
In an Eulerian atmospheric model, the atmosphere is divided into a number of cells.

The inputs, outputs, and chemical processes within each cell are simulated.

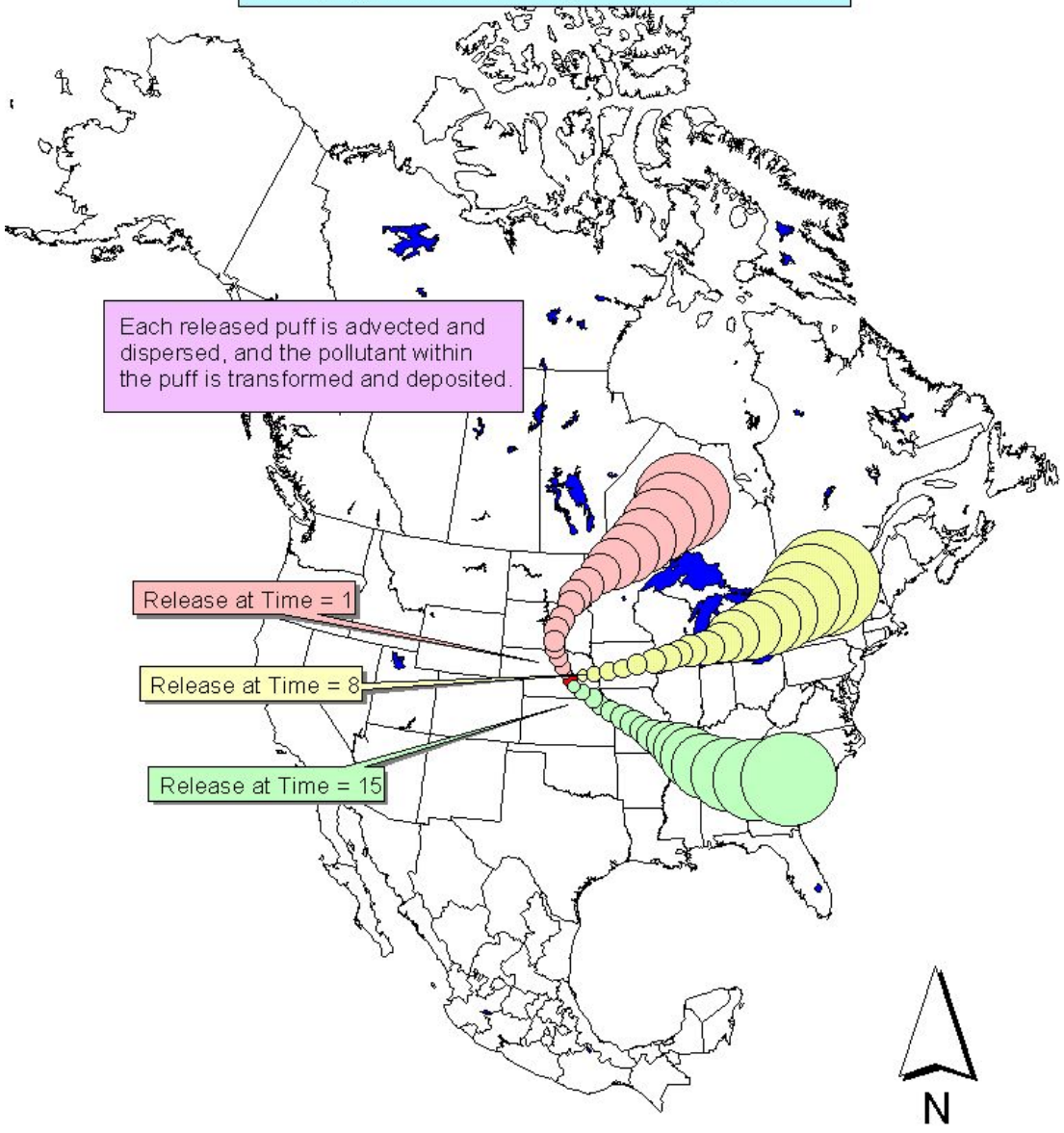


NOAA HYSPLIT MODEL

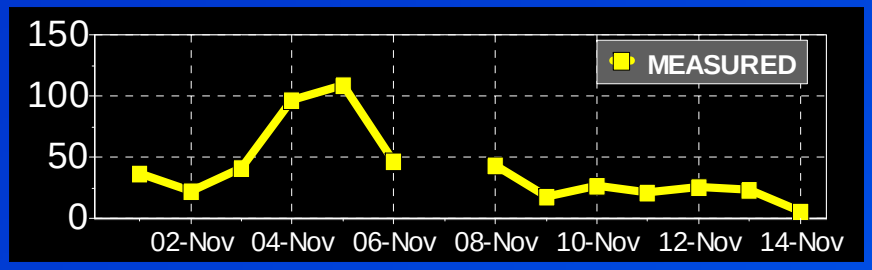
Lagrangian Puff Atmospheric Fate and Transport Model

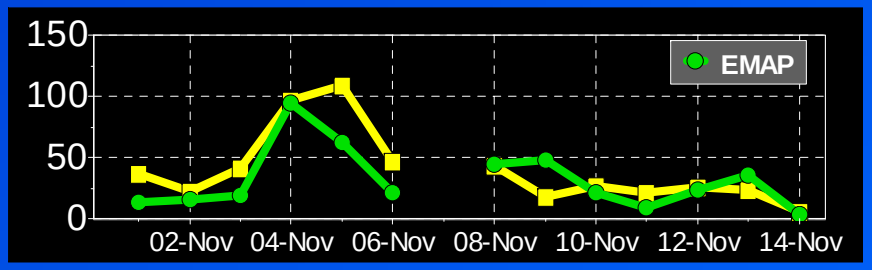


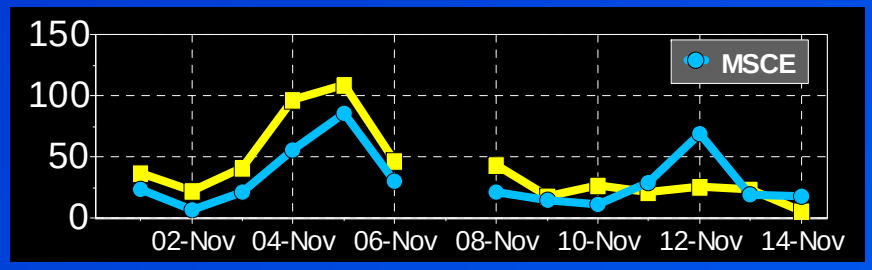
Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).

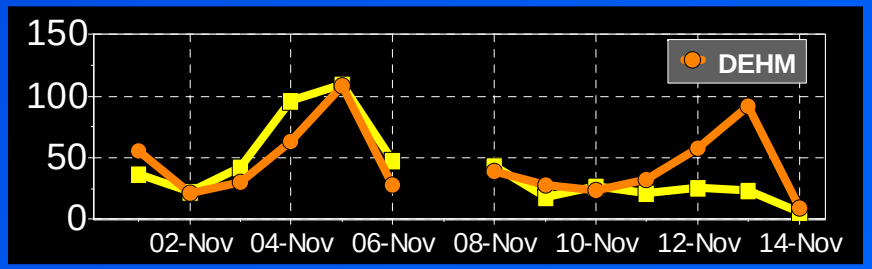


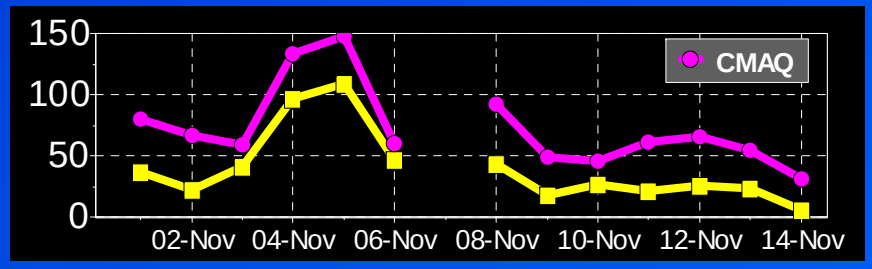
Total *Particulate* Mercury (pg/m^3) at Neuglobsow, Nov 1-14, 1999

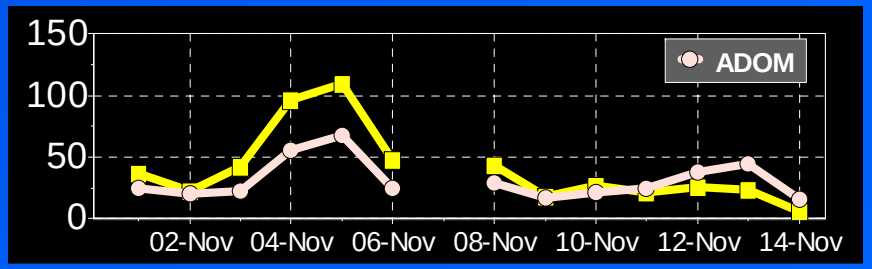


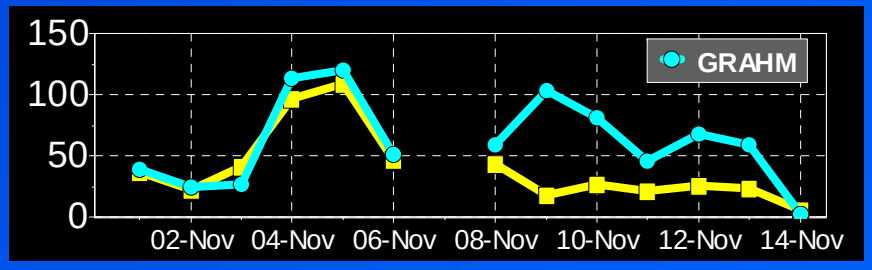


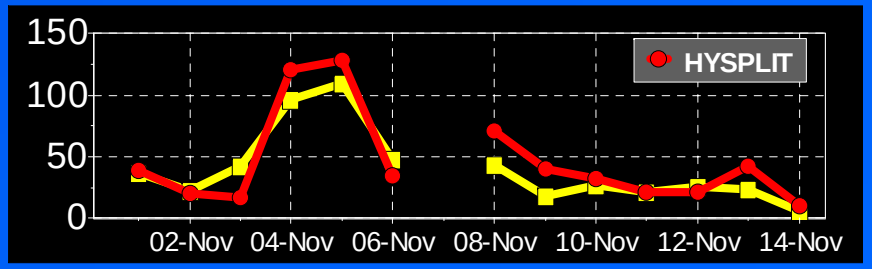




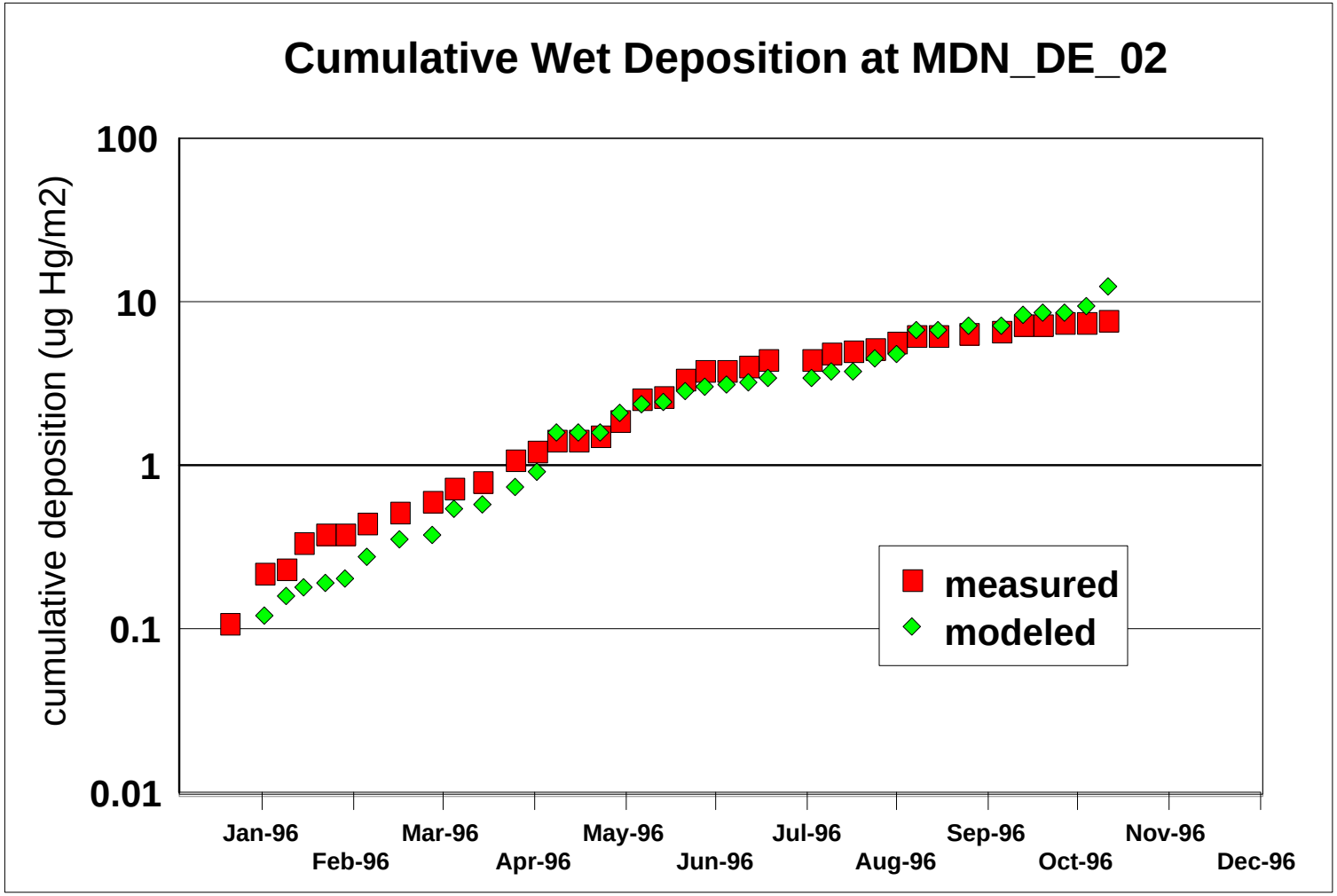








Modeled vs. Measured Wet Deposition at Mercury Deposition Network Site DE_02 during 1996



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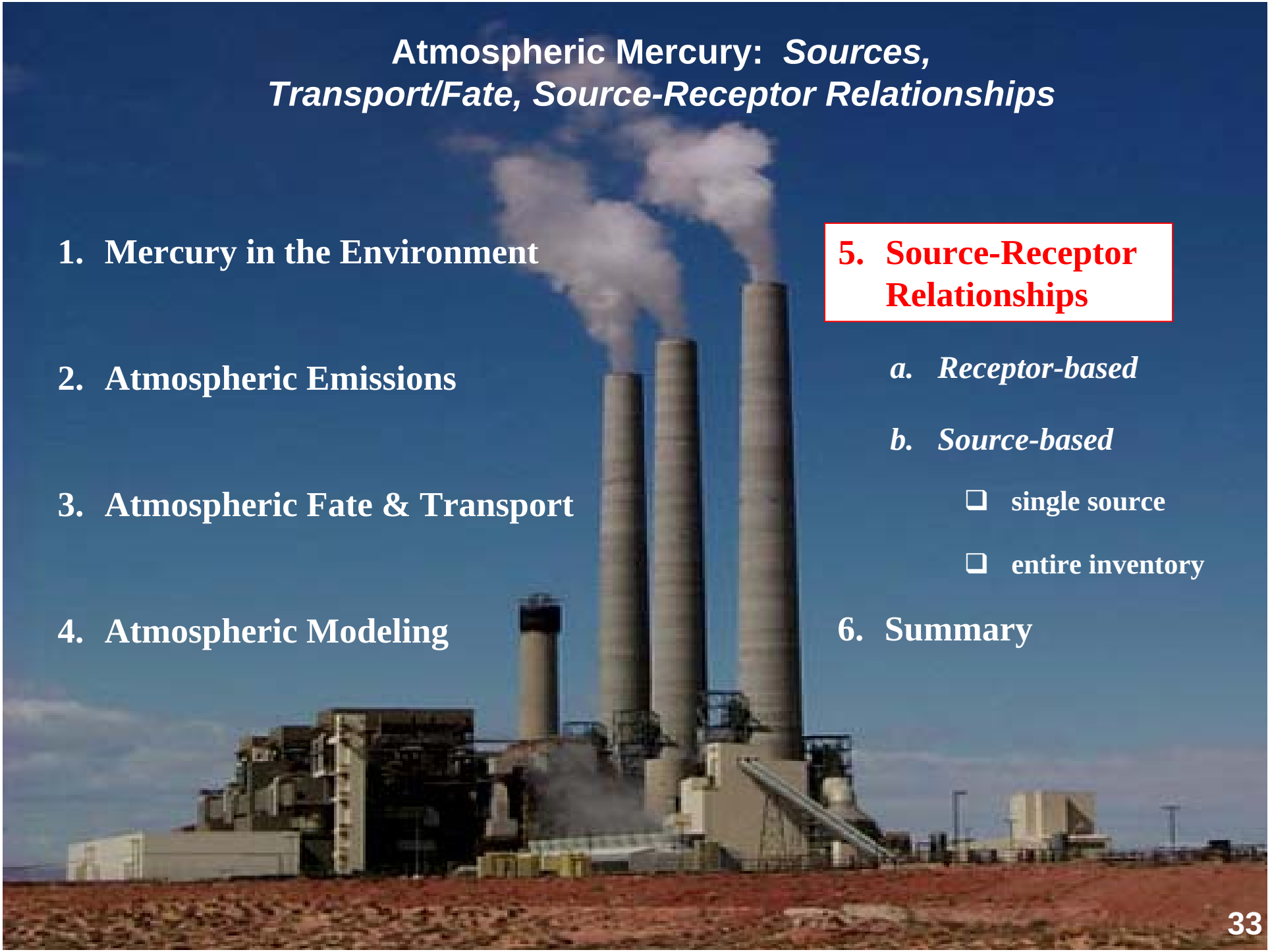

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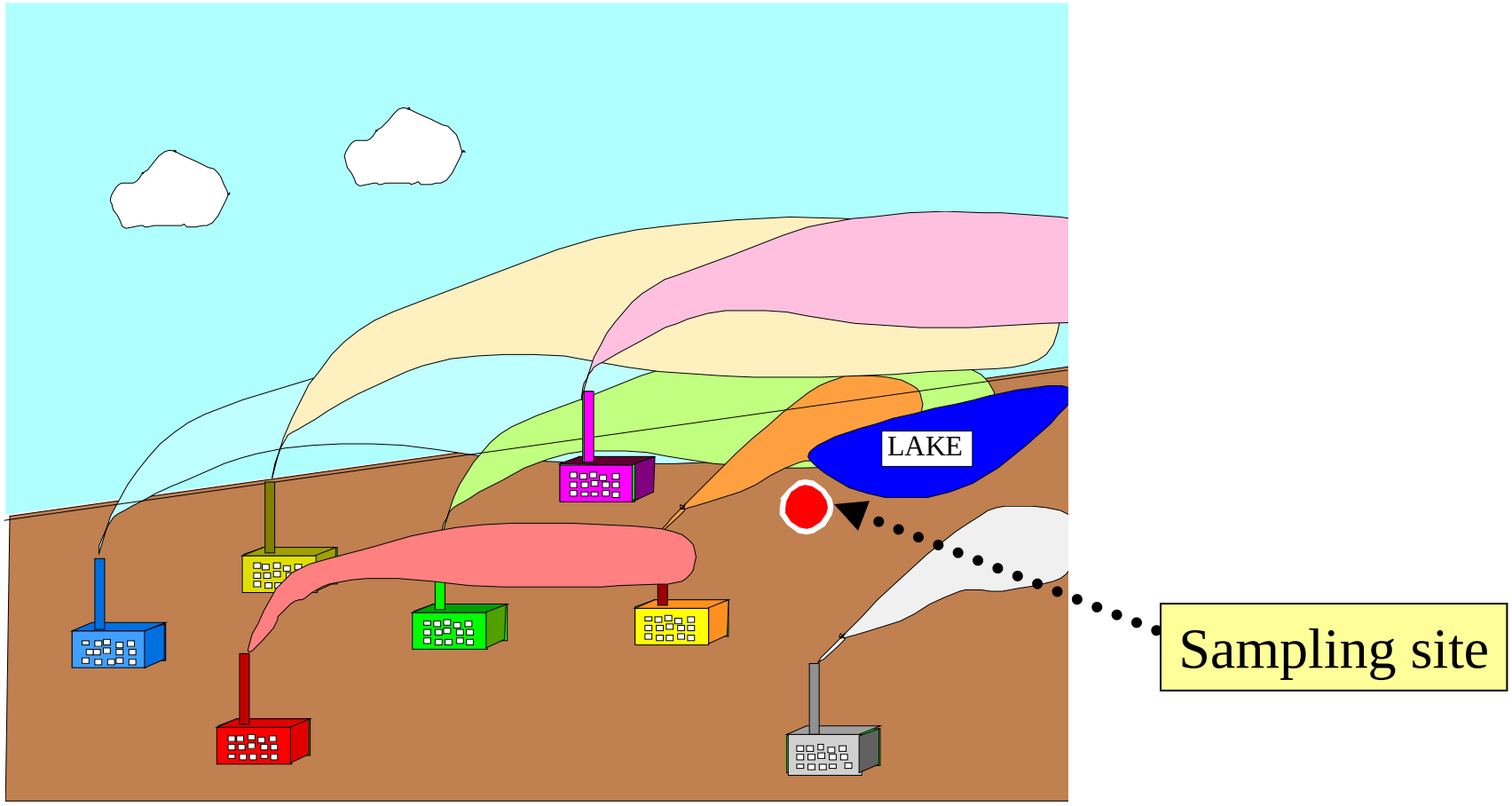
Source-receptor information can be estimated using either *receptor-based* or *source-based* techniques



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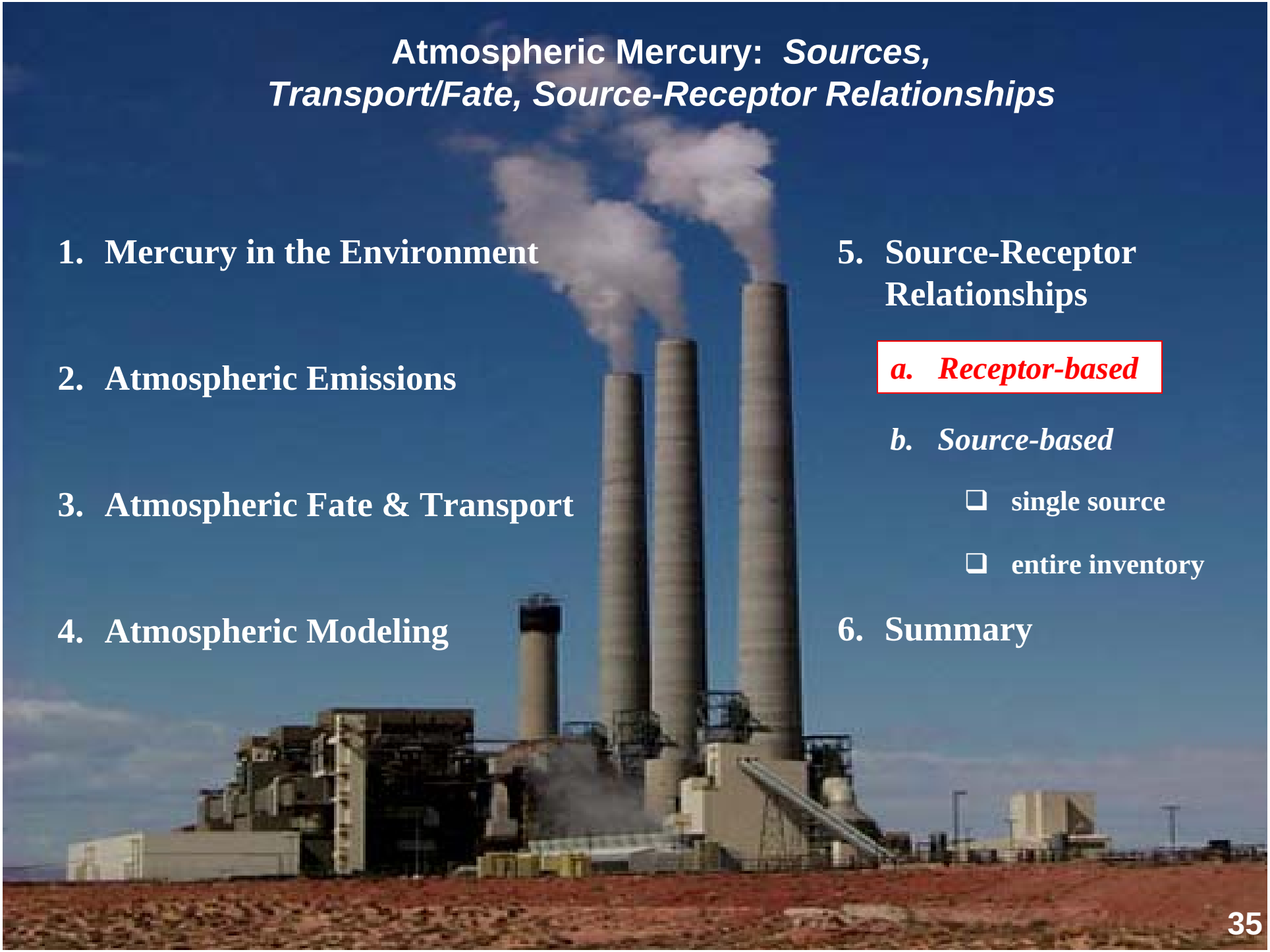

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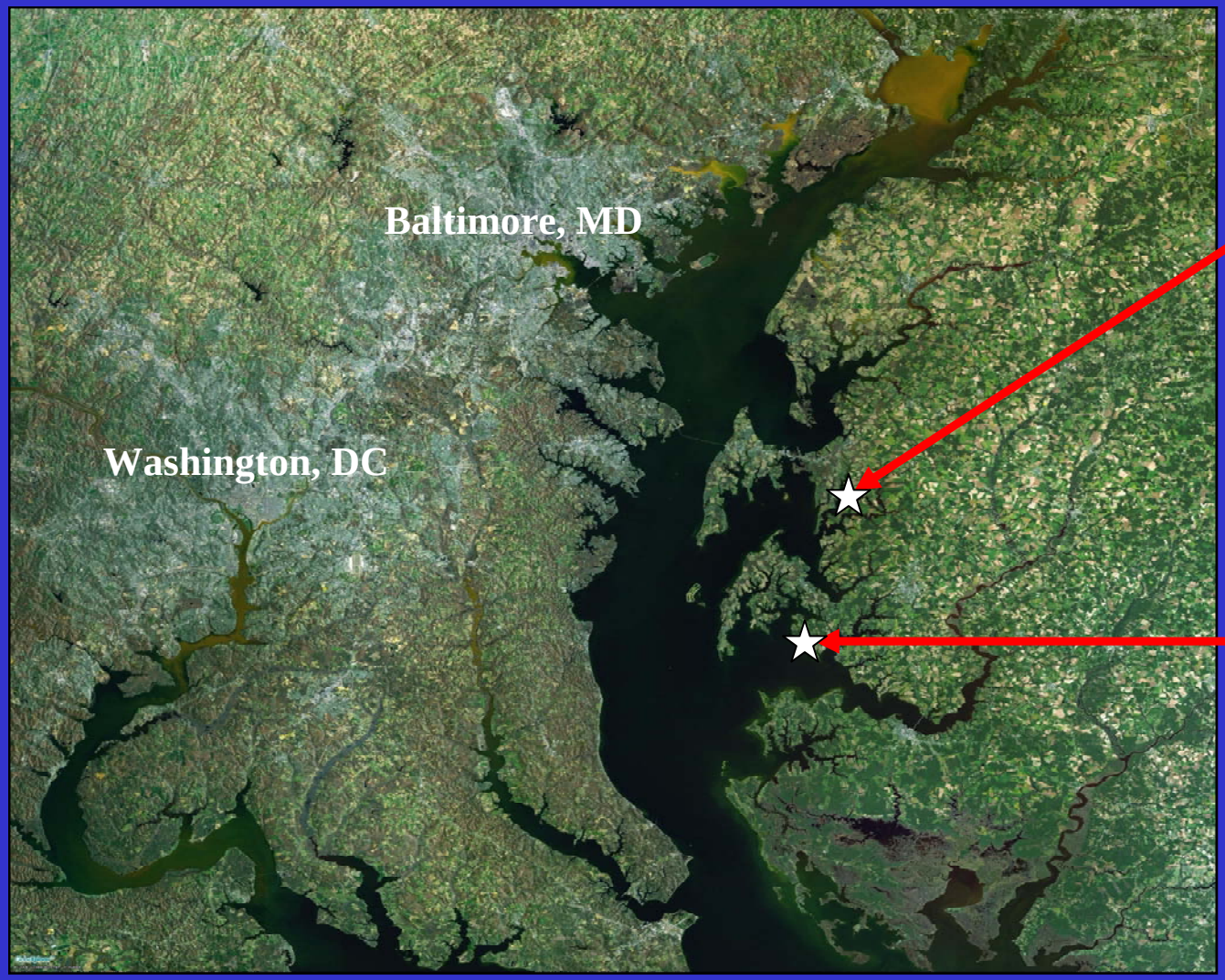
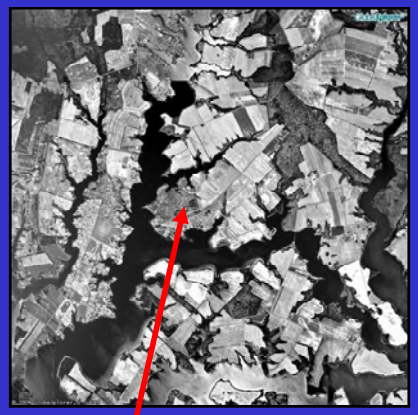
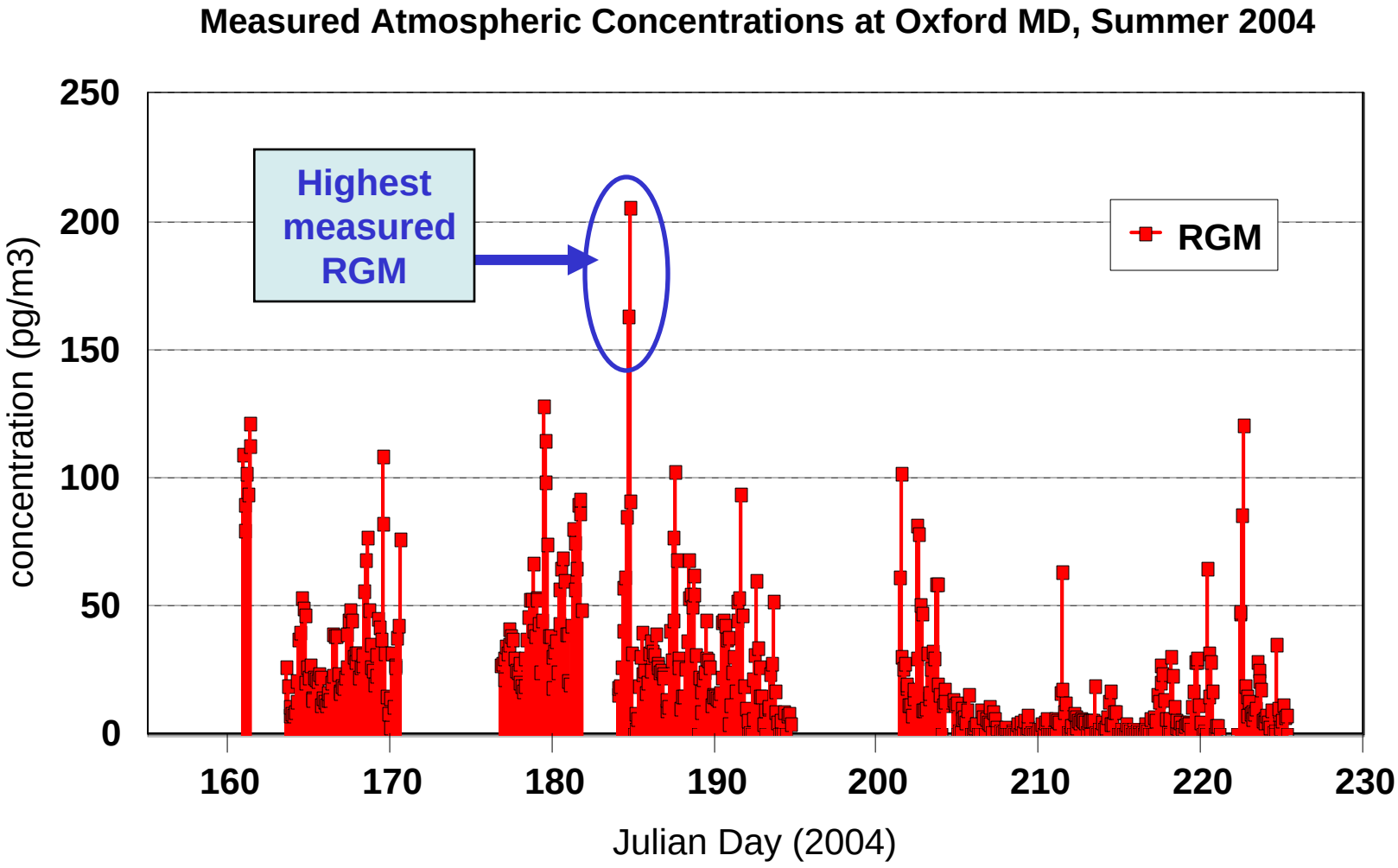
Summer 2004 NOAA ARL Hg Measurement Sites



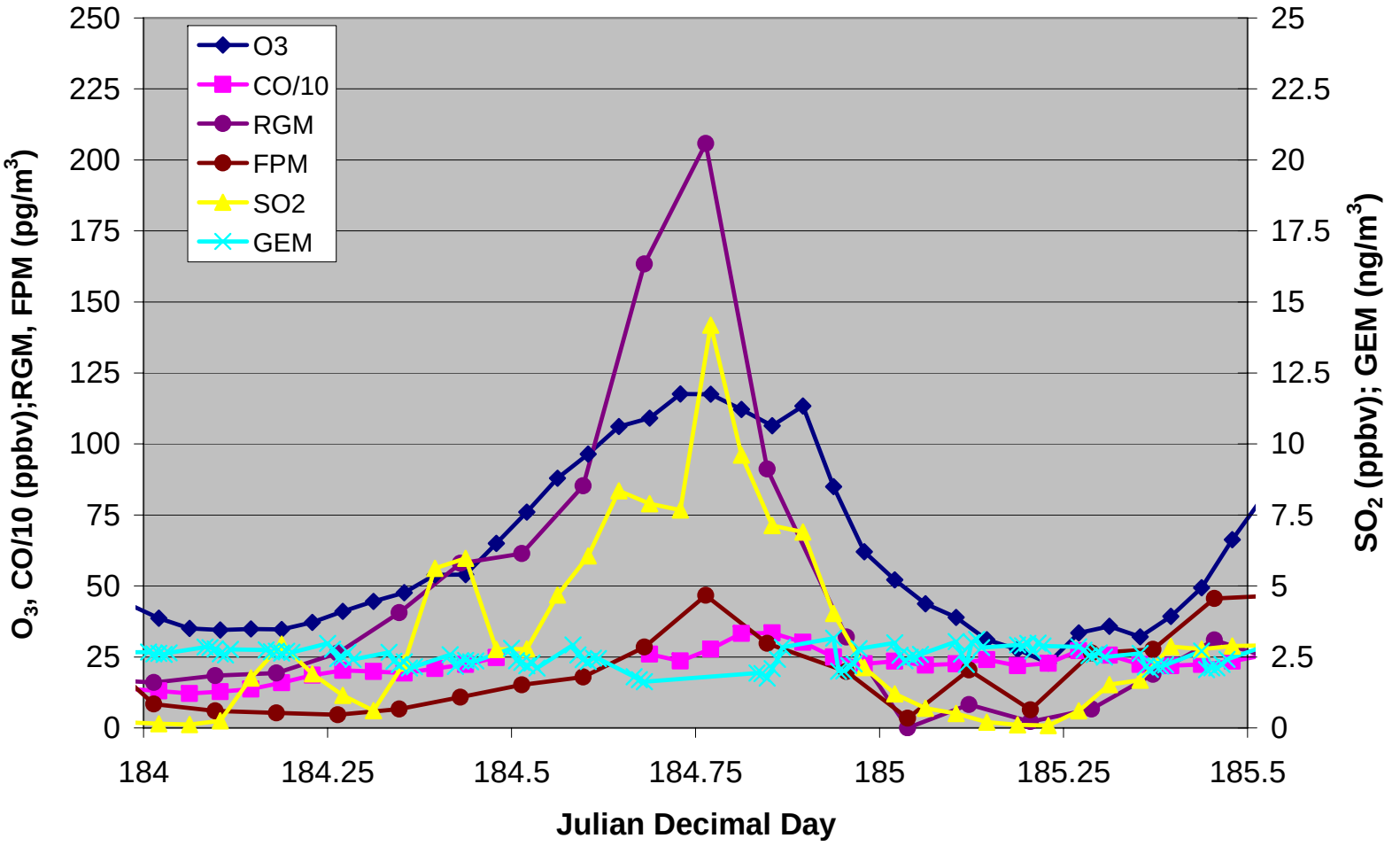


Wye Research and
Education Center
(38.9131EN, 76.1525EW)

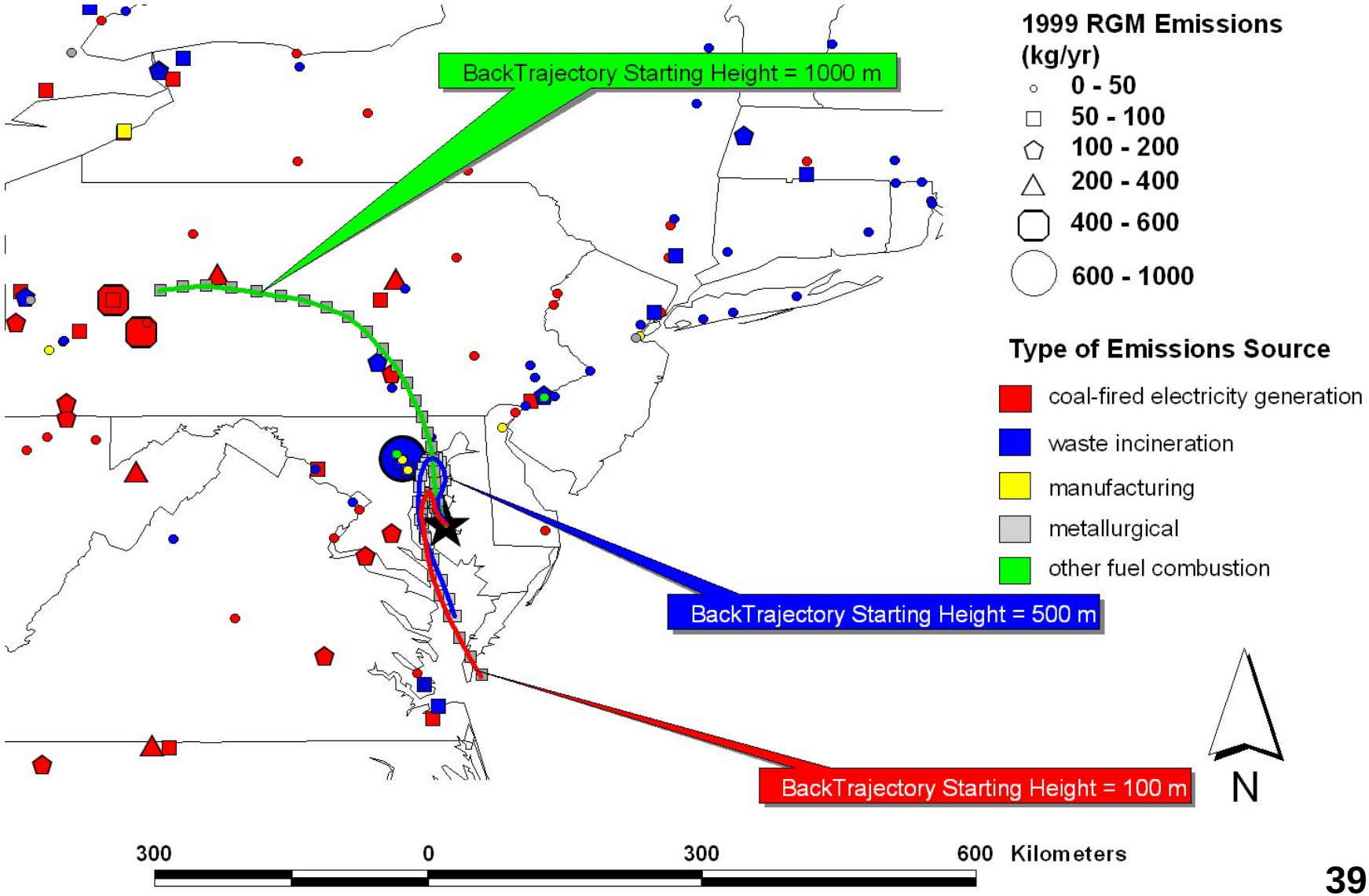
Cooperative Oxford Lab
(38.678EN, 76.173EW)


Measured Atmospheric Concentrations at Oxford MD, Summer 2004
Highest measured RGM
RGM
concentration (pg/m3)
250
200
150
100
50
0
160
170
180
190
200
210
220
230
Julian Day (2004)

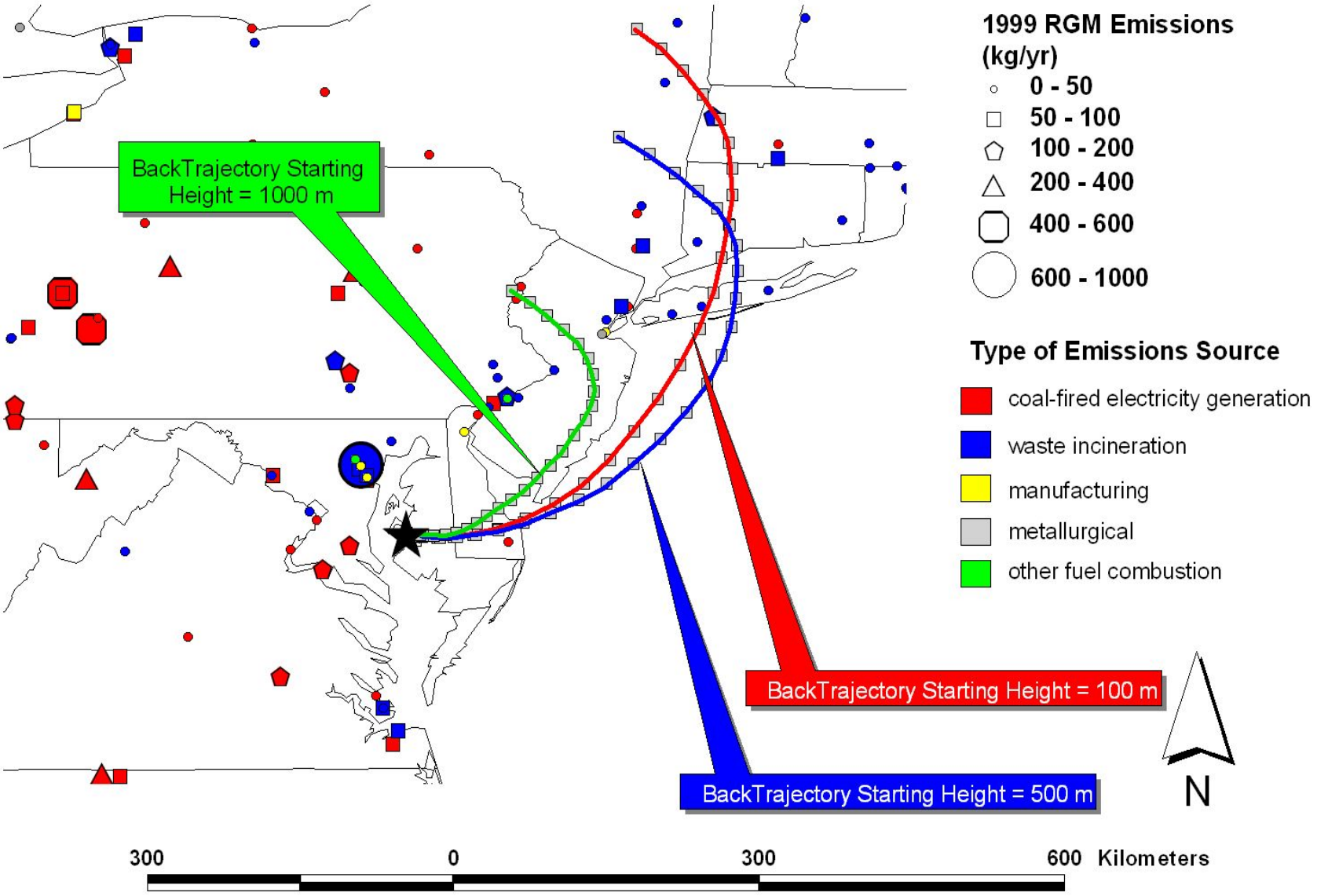
Concentrations Measured at Oxford, MD



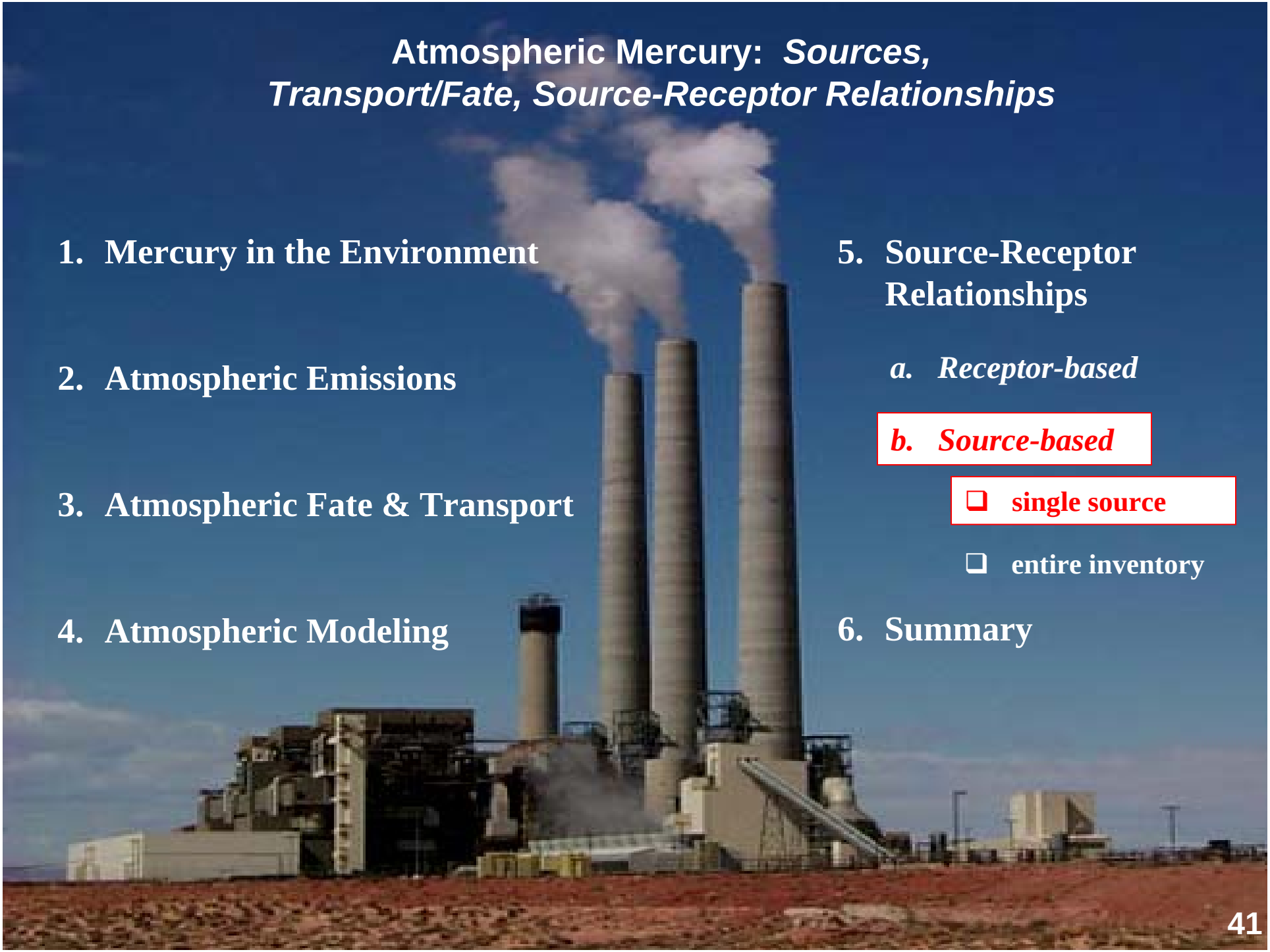
Oxford July 2, 2004 Peak Concentration in RGM



Oxford July 3, 2004 -- one day after Peak Concentration in RGM



Atmospheric Mercury: *Sources, Transport/Fate, Source-Receptor Relationships*



1. Mercury in the Environment
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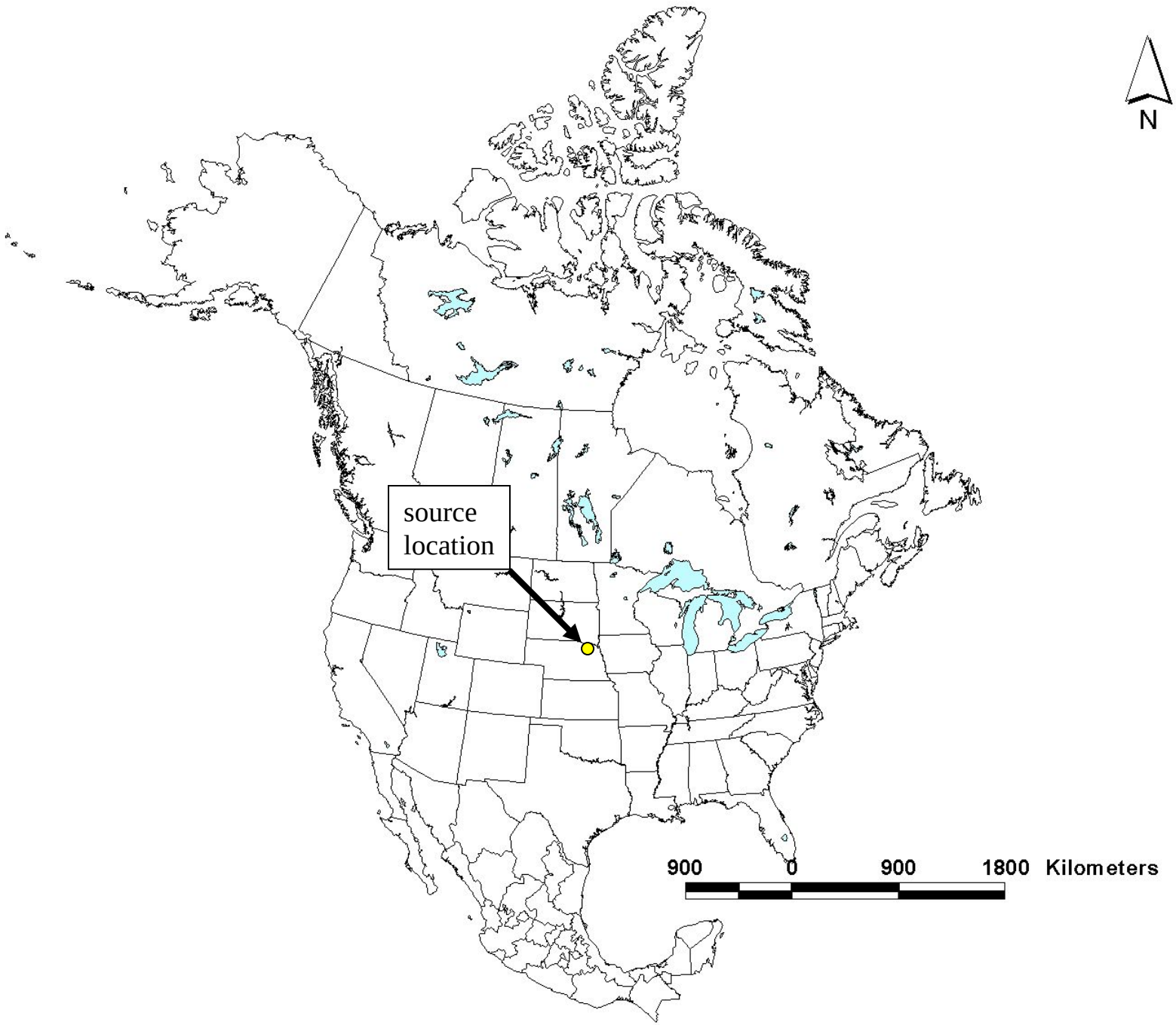
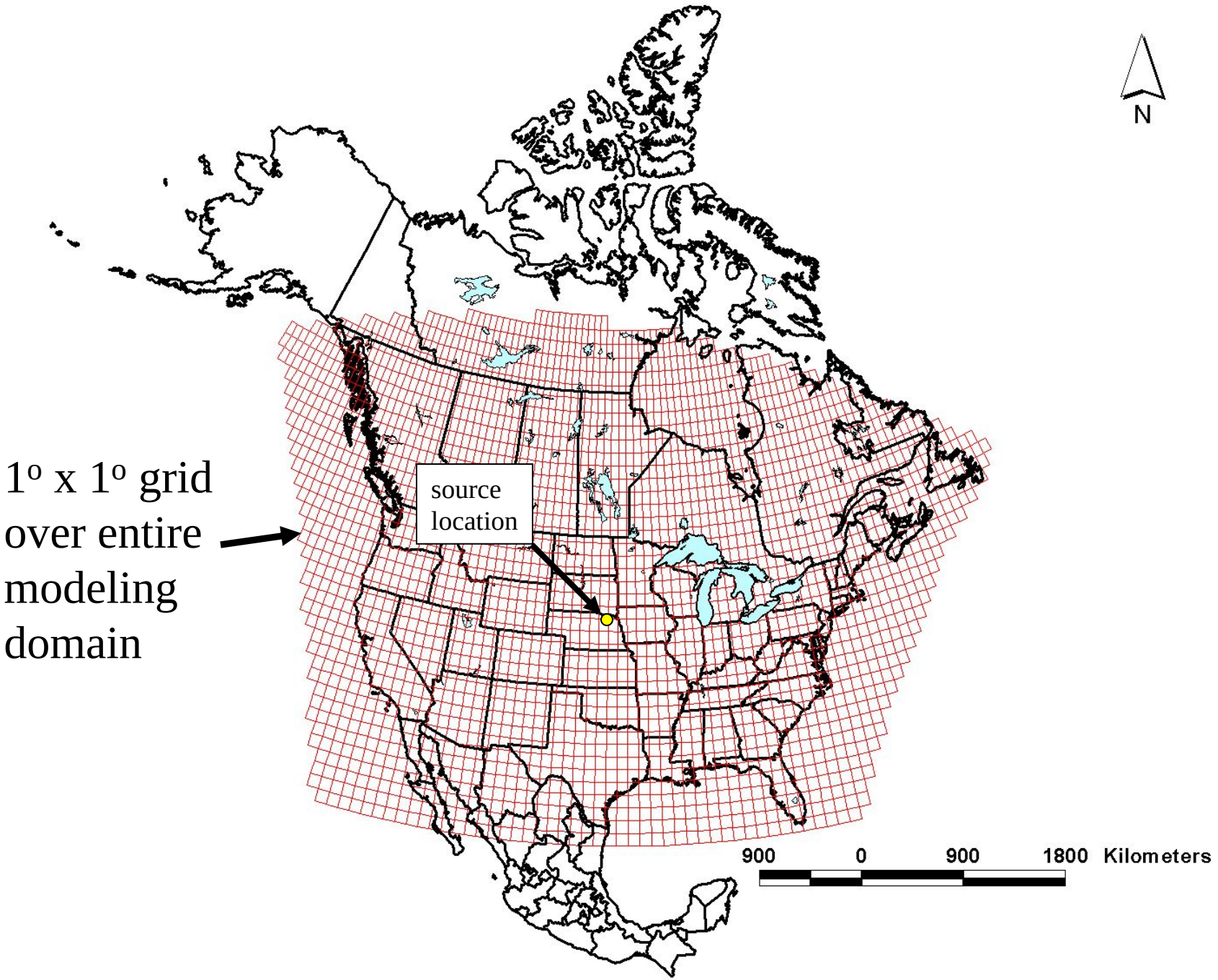
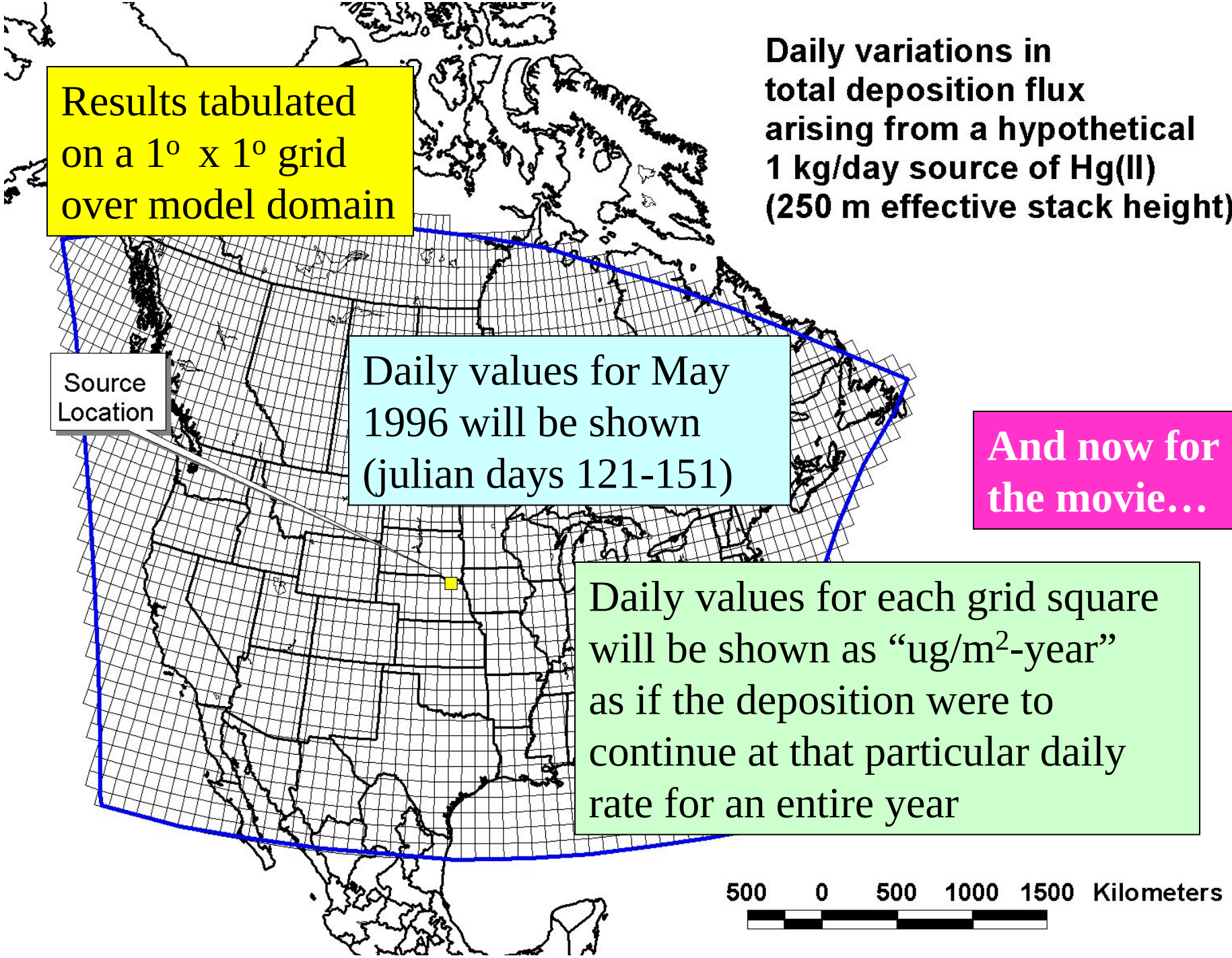
   - *a. Receptor-based*
   - *b. Source-based*
     - ❑ single source
     - ❑ entire inventory
6. Summary

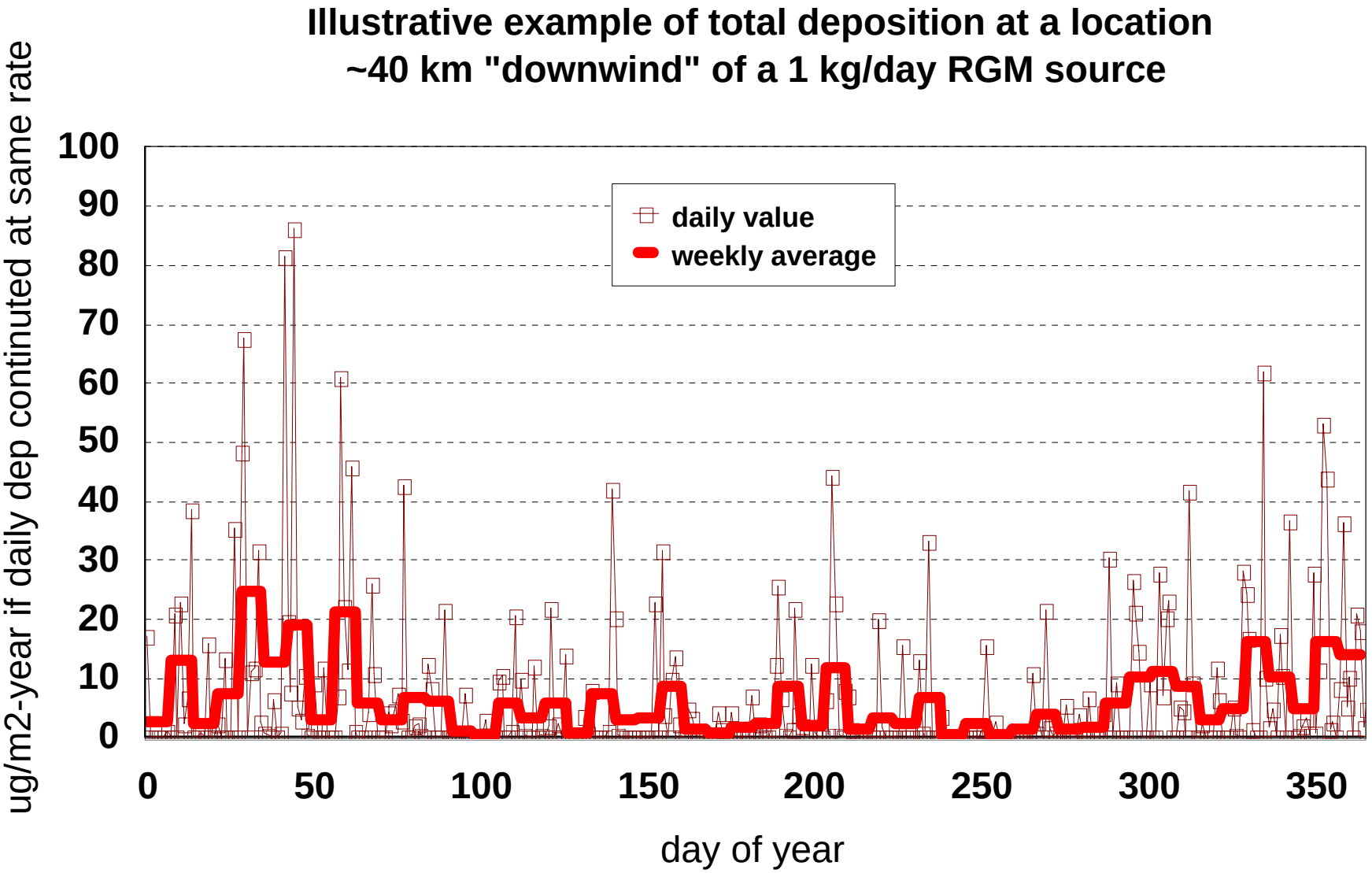
Example simulation of the atmospheric fate and transport of mercury emissions:

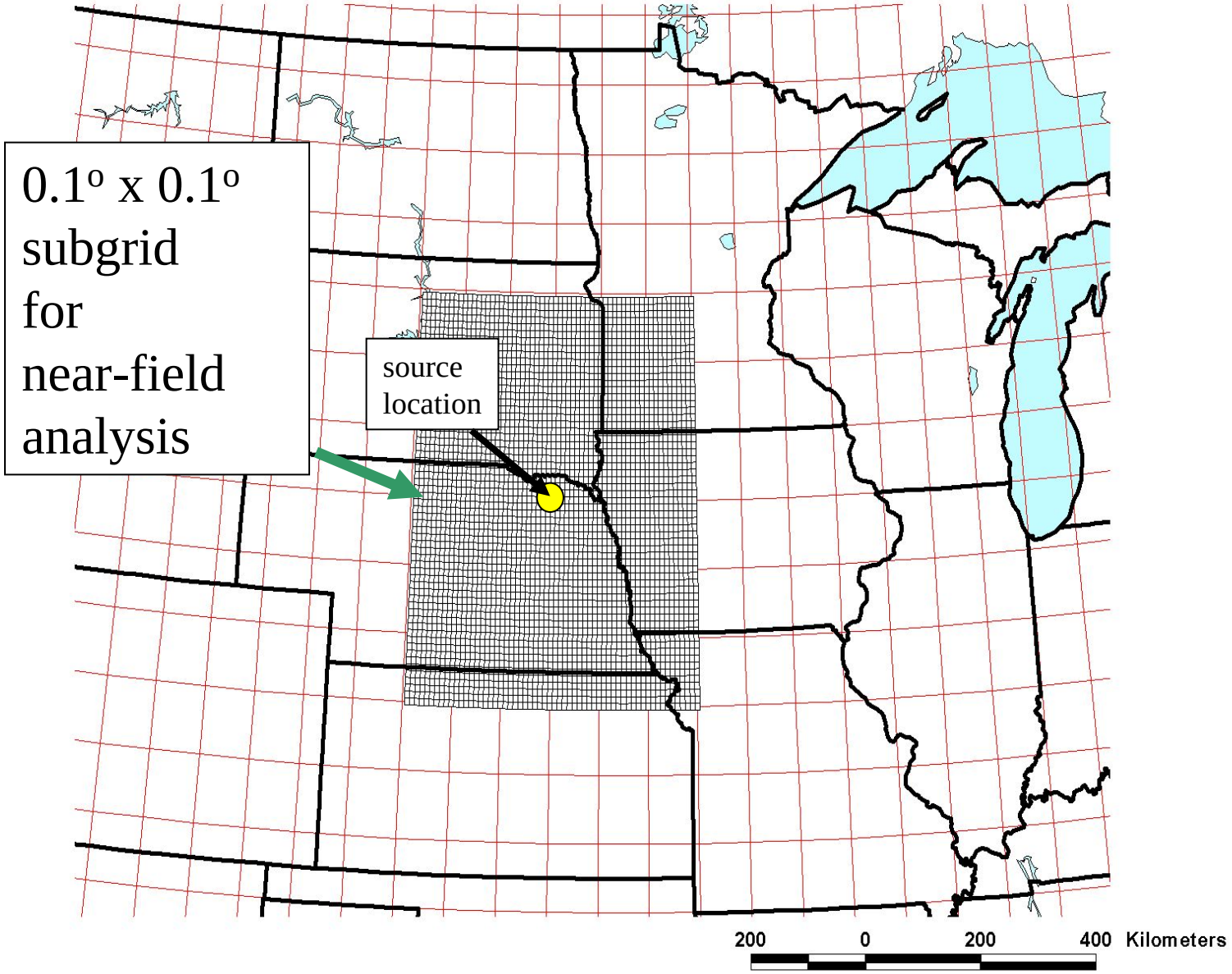
- **hypothetical 1 kg/day source of RGM, Hg(p) or Hg(0)**
- **source height 250 meters**
- **results tabulated on a 1^{o} x 1^{o} receptor grid**
- **annual results (1996)**


N
source
location
900 0 900 1800 Kilometers

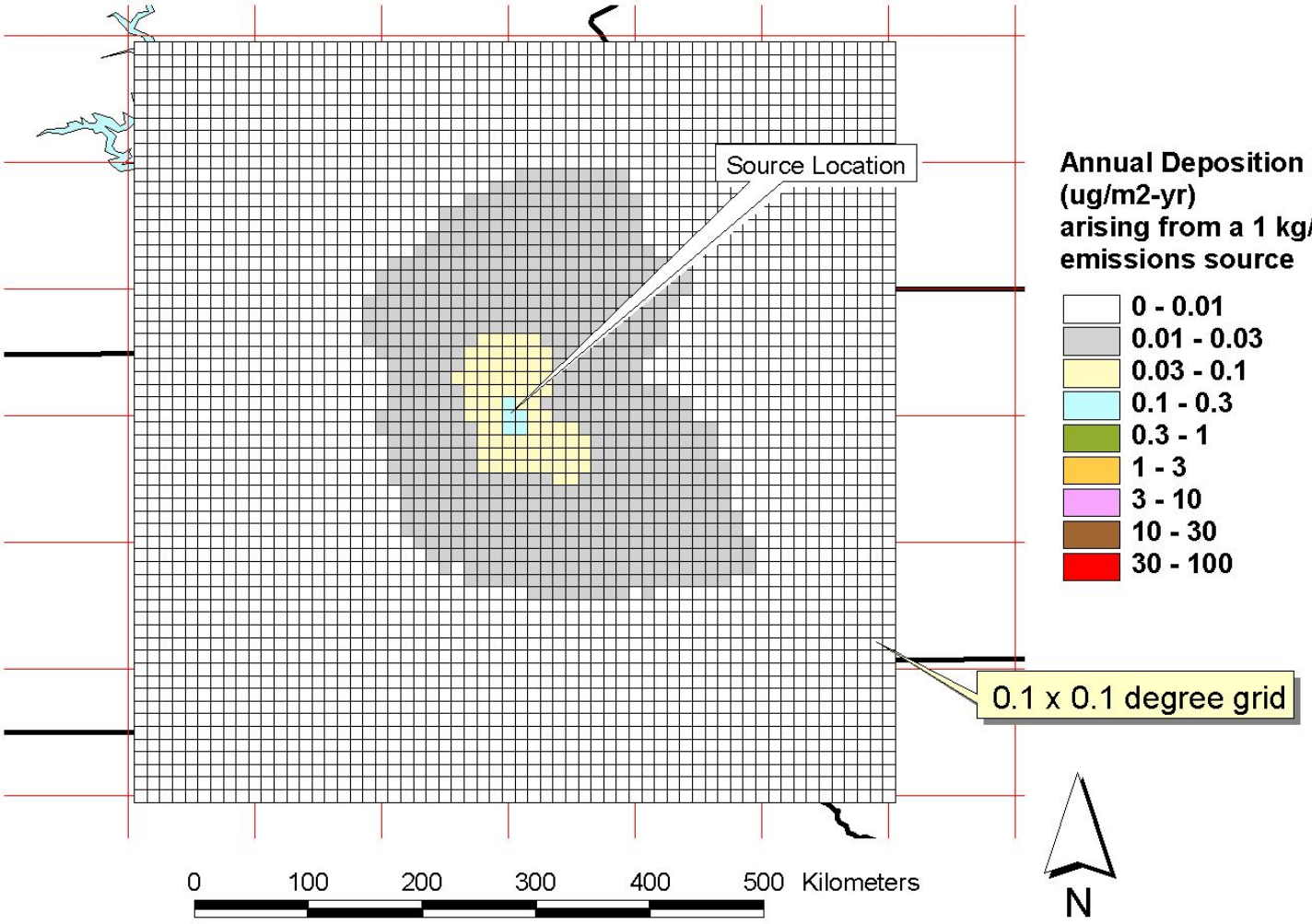

1º x 1º grid over entire modeling domain
source location
N
900 0 900 1800 Kilometers


Results tabulated on a 1° x 1° grid over model domain
Source Location
Daily values for May 1996 will be shown (julian days 121-151)
Daily variations in total deposition flux arising from a hypothetical 1 kg/day source of Hg(II) (250 m effective stack height)
And now for the movie…
Daily values for each grid square will be shown as "ug/m2-year" as if the deposition were to continue at that particular daily rate for an entire year
500 0 500 1000 1500 Kilometers


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

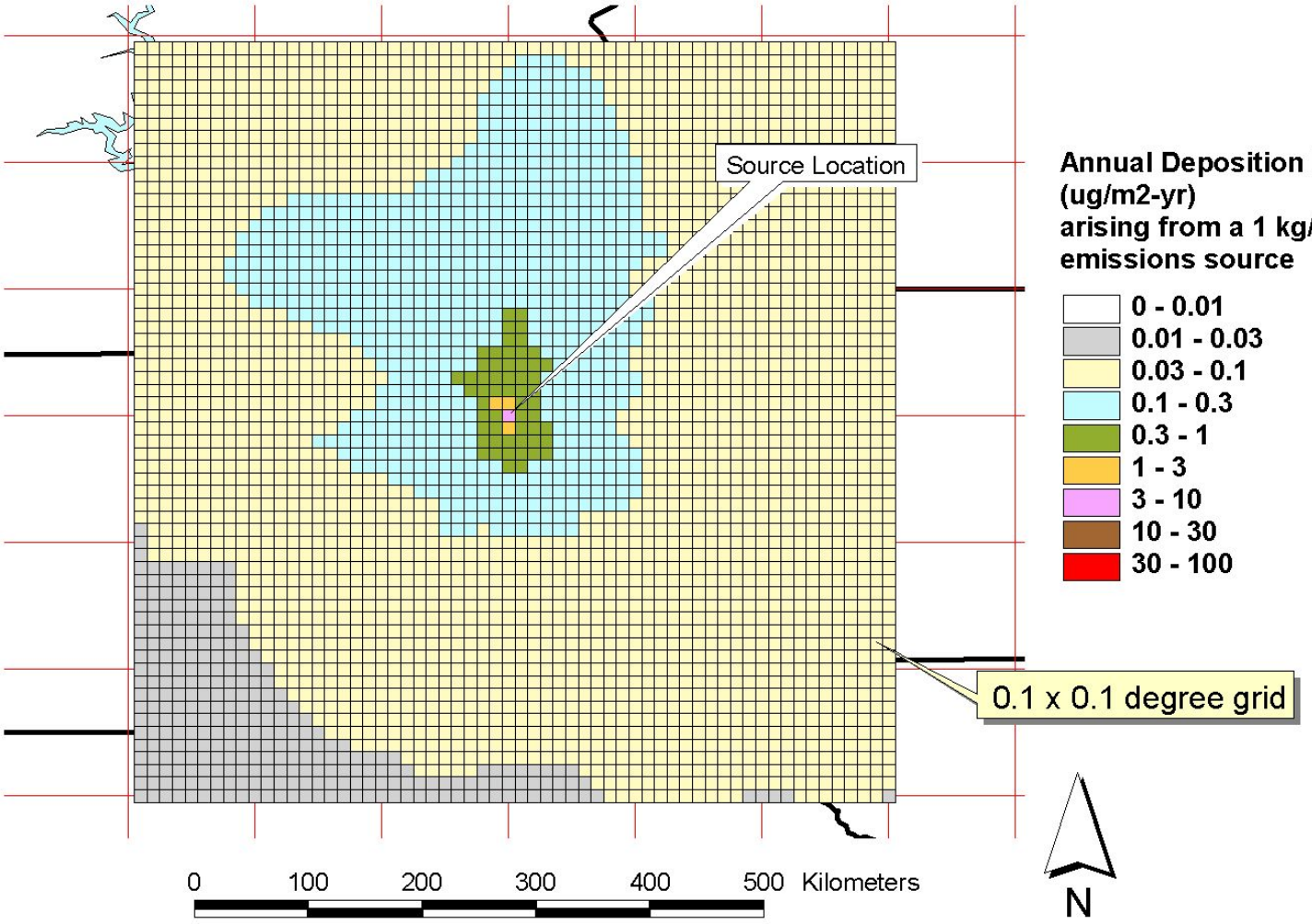

0.1° x 0.1° subgrid for near-field analysis
source location
200 0 200 400 Kilometers

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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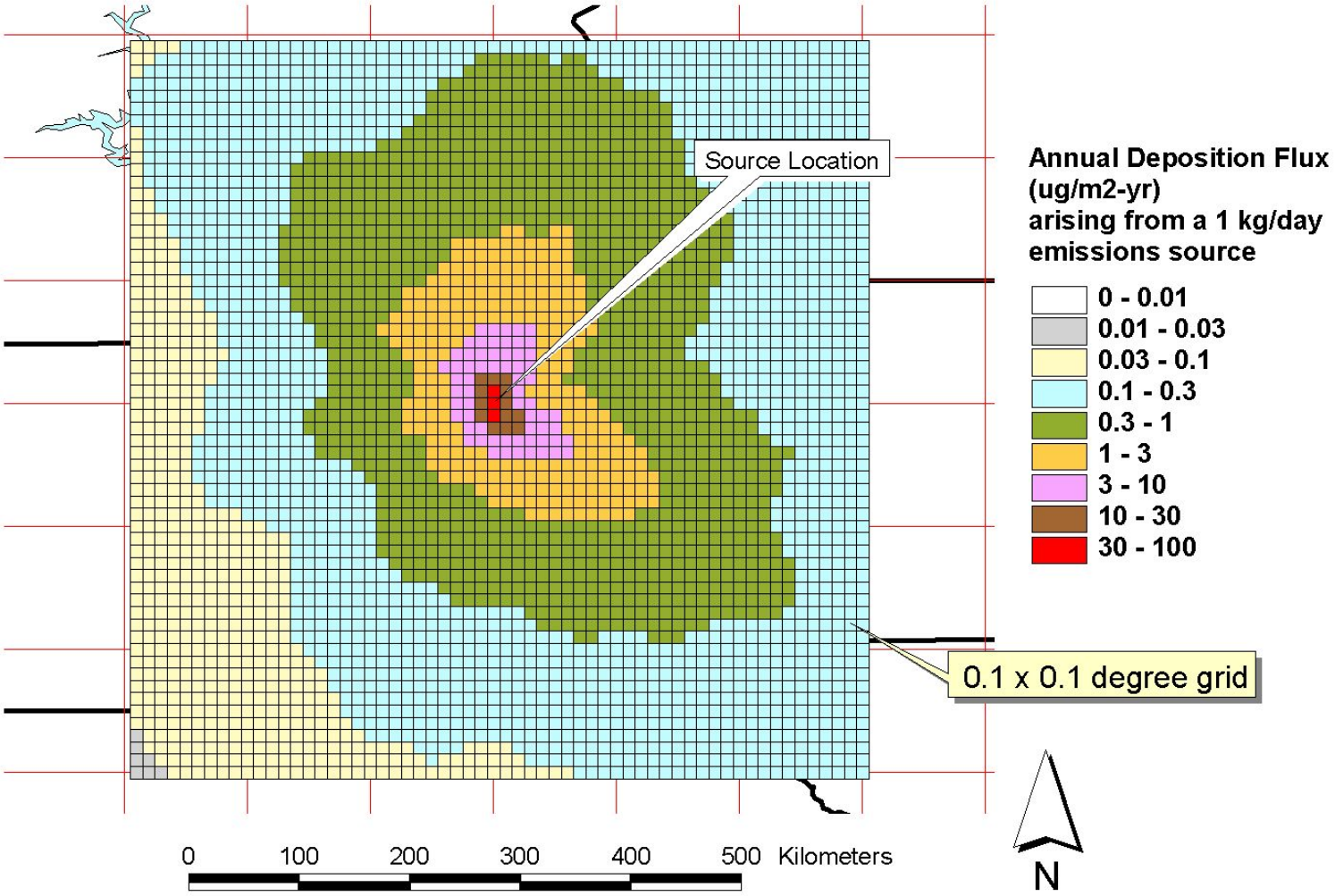

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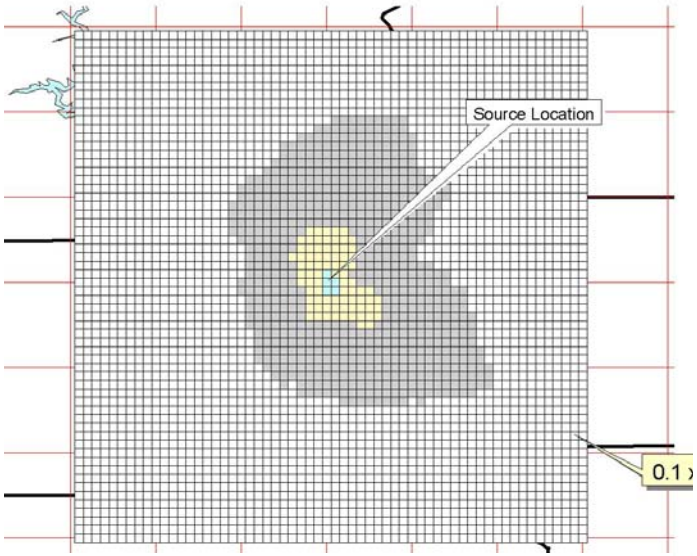
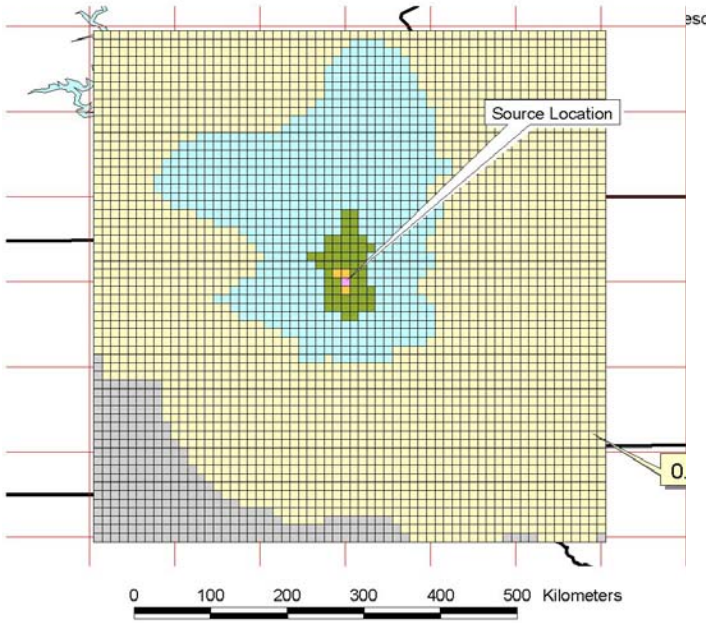


Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source

- 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



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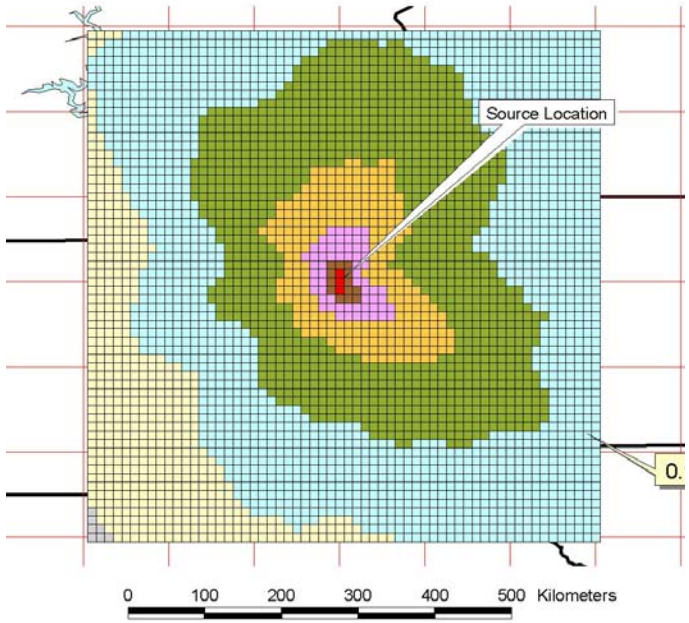
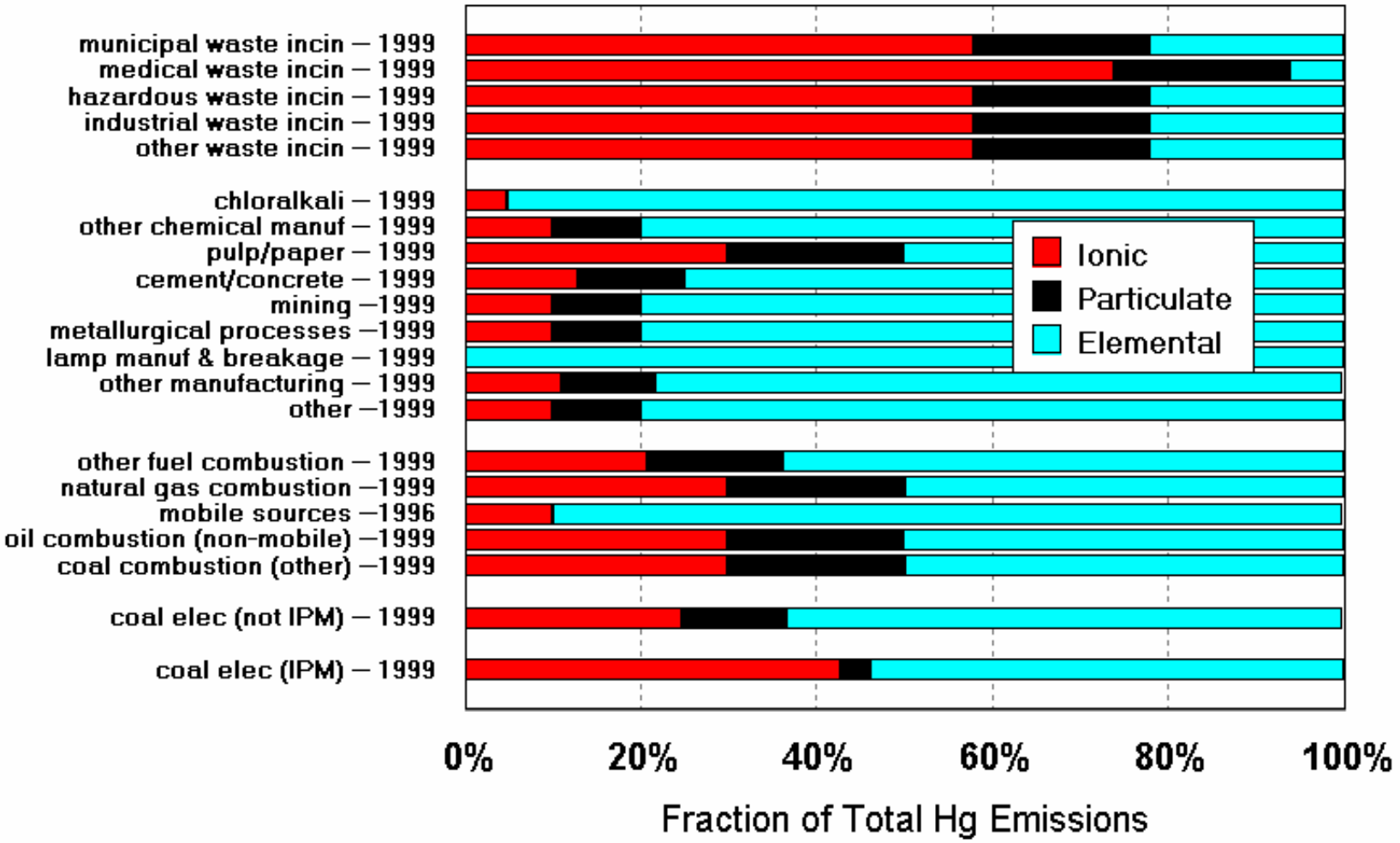
Annual deposition summary for emissions of ionic Hg from a 250 meter high source



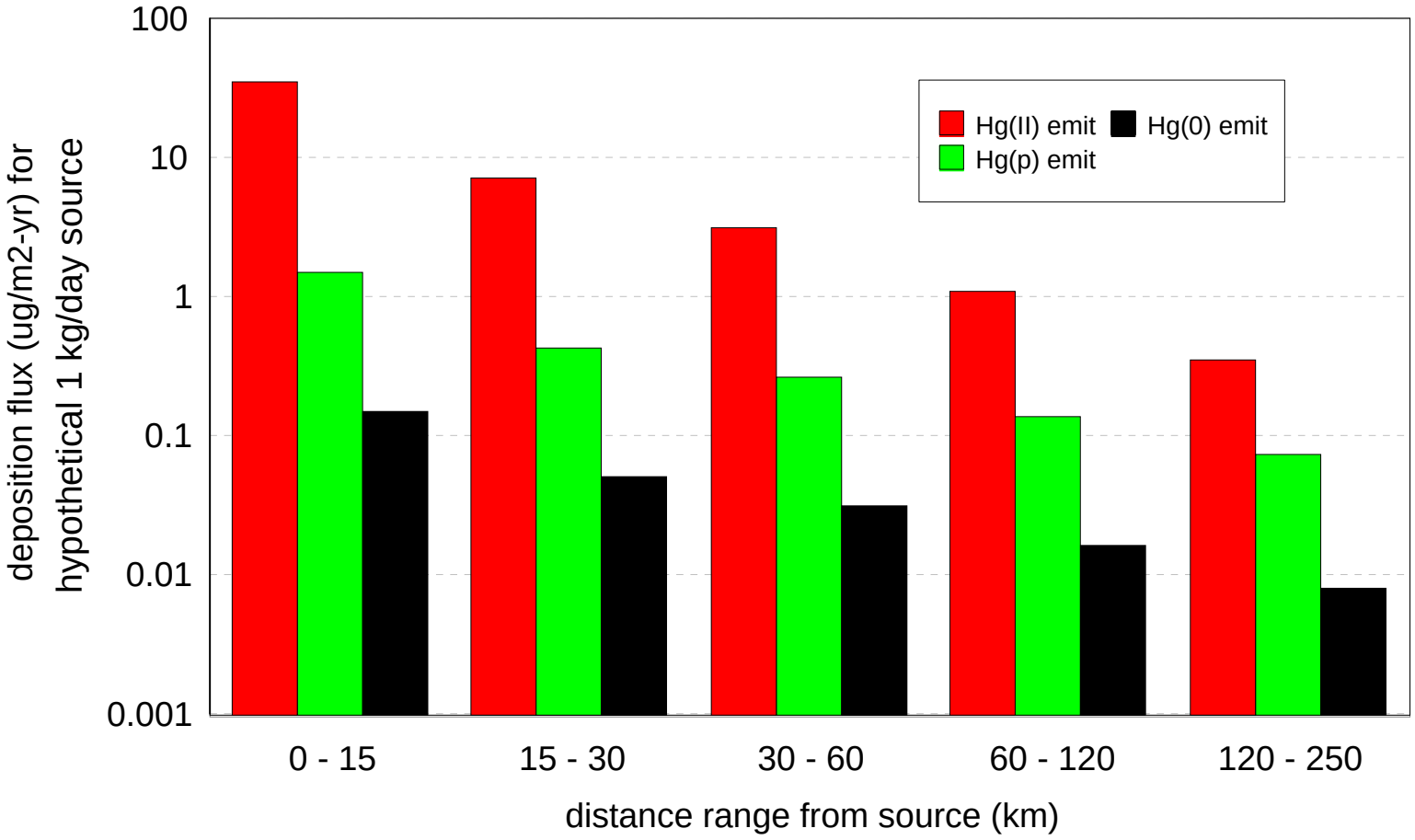
Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km

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

Very uncertain for most sources



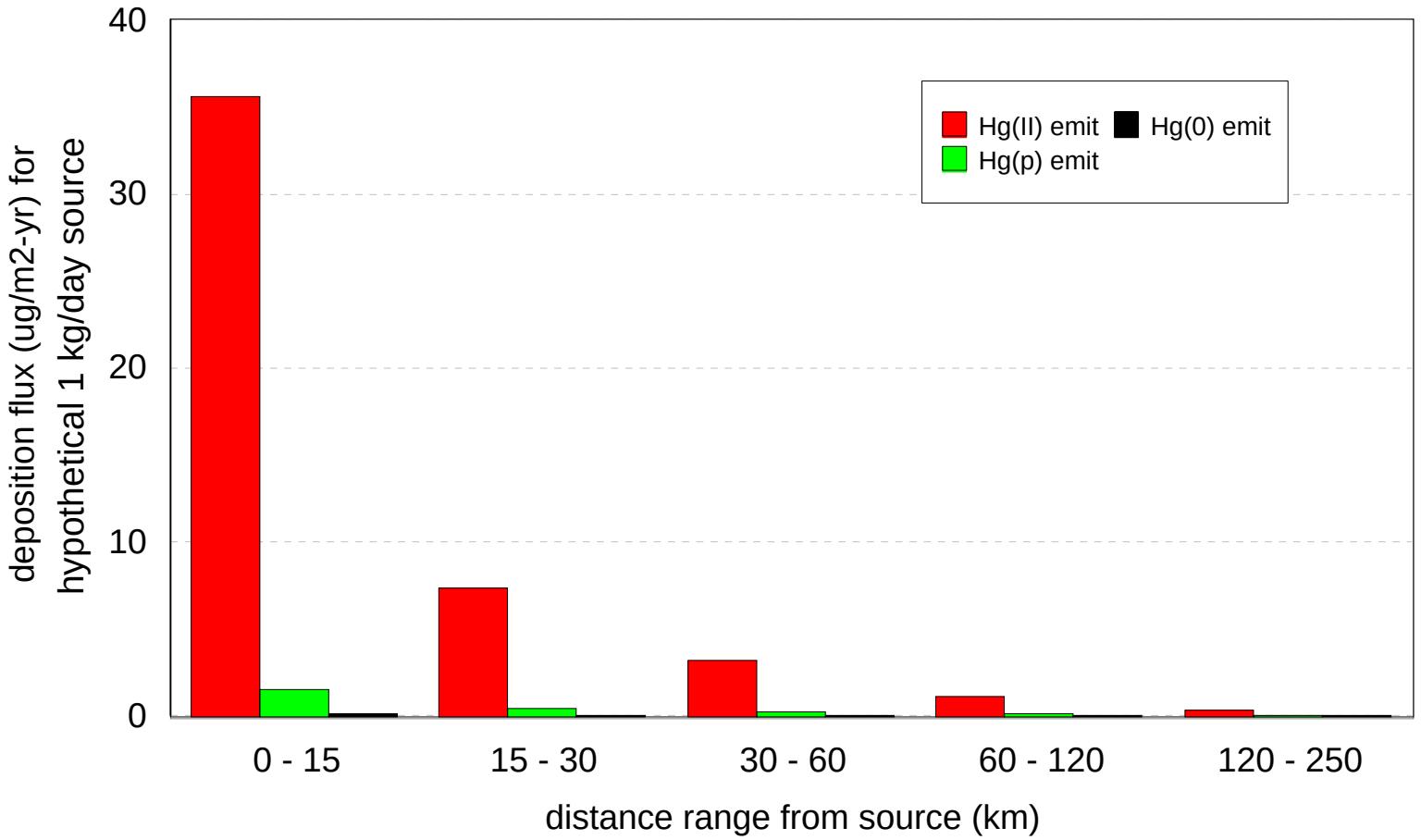
Why is emissions speciation information critical?



Logarithmic

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

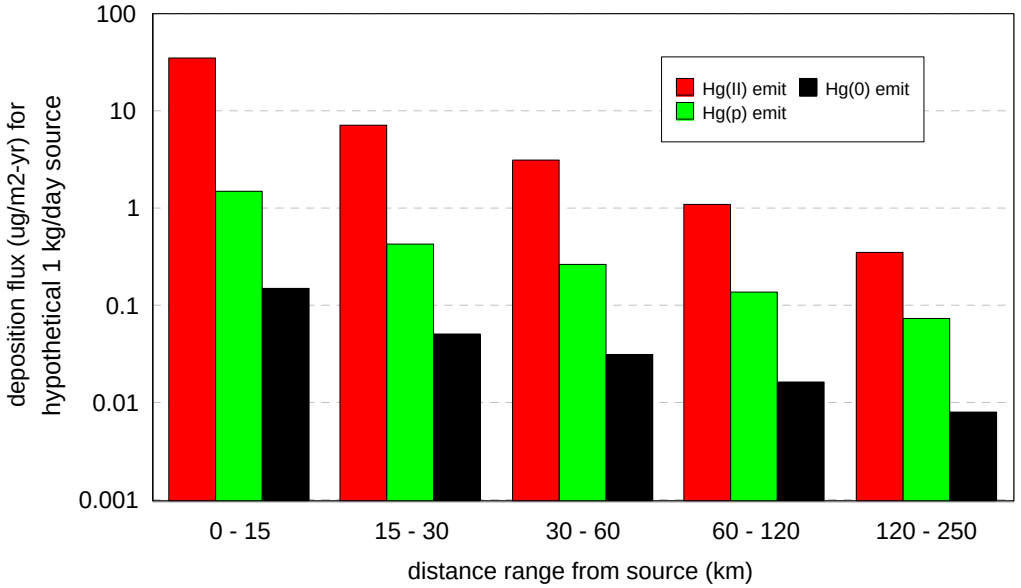
Why is emissions speciation information critical?



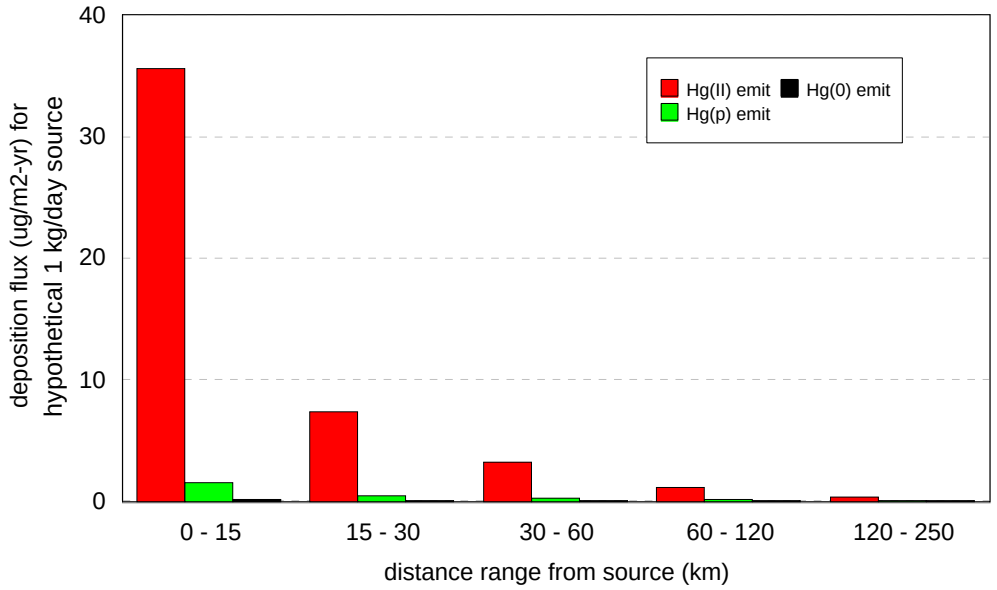
Linear

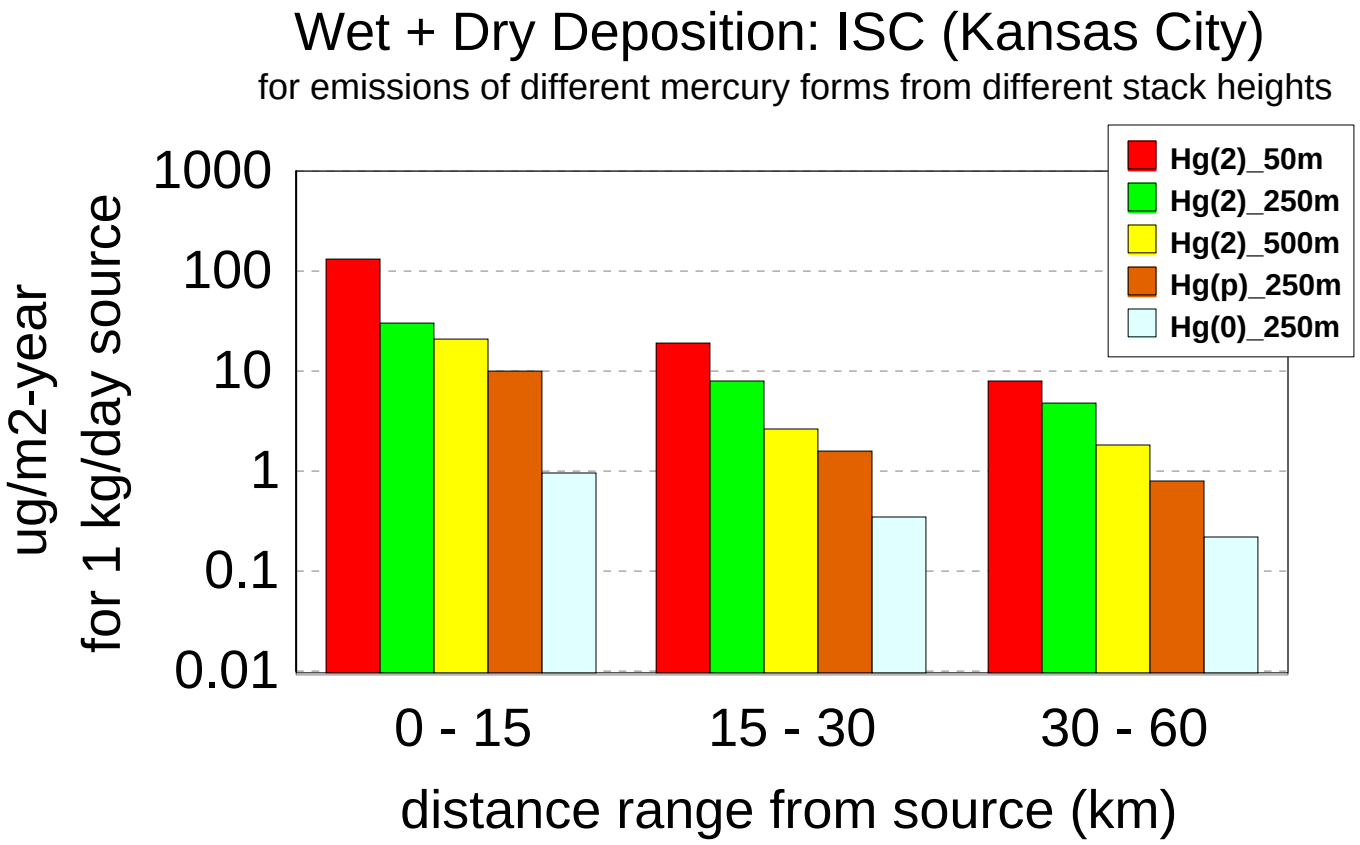
Why is emissions speciation information critical?

Logarithmic



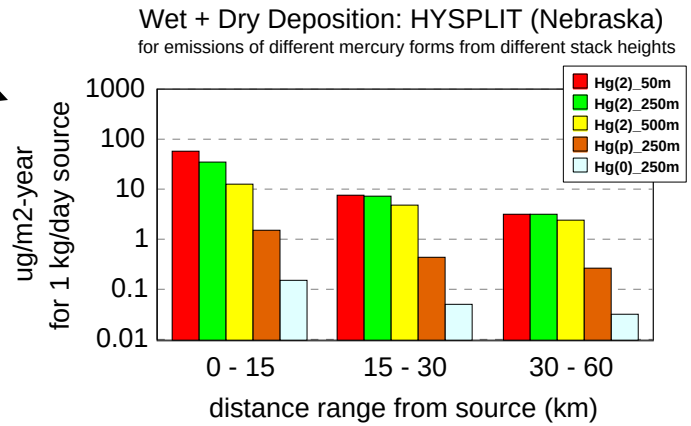
Linear





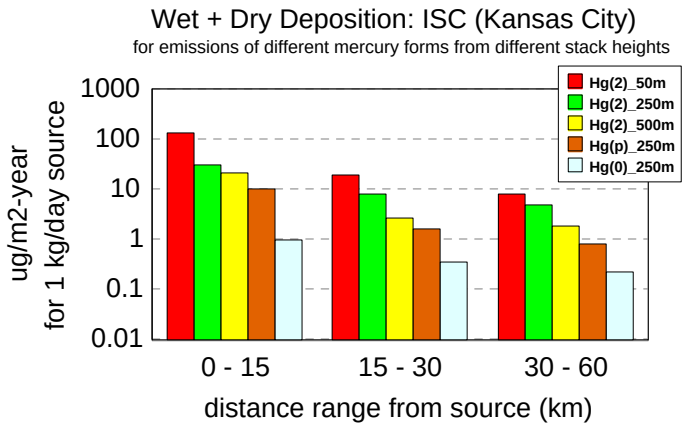
Calculated from data used to produce Appendix A of USEPA (2005): Clean Air Mercury Rule (CAMR) Technical Support Document: Methodology Used to Generate Deposition, Fish Tissue Methylmercury Concentrations, and Exposure for Determining Effectiveness of Utility Emissions Controls: Analysis of Mercury from Electricity Generating Units

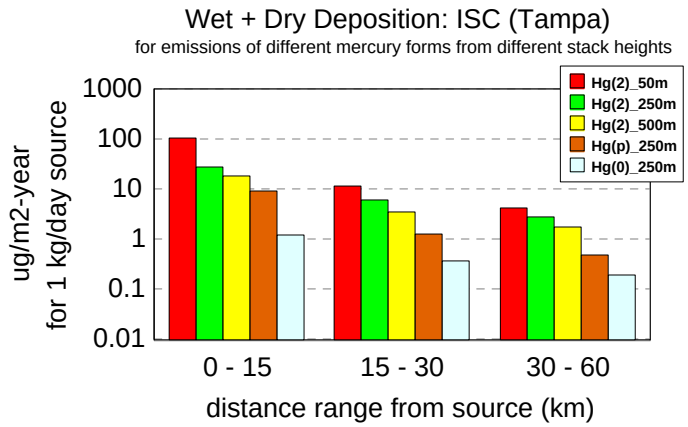
HYSPLIT 1996

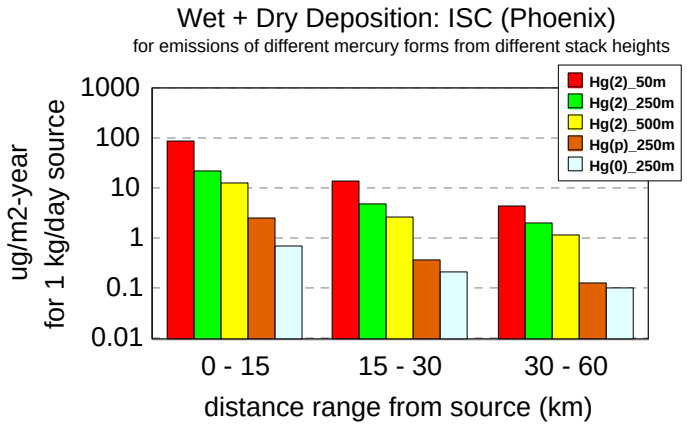


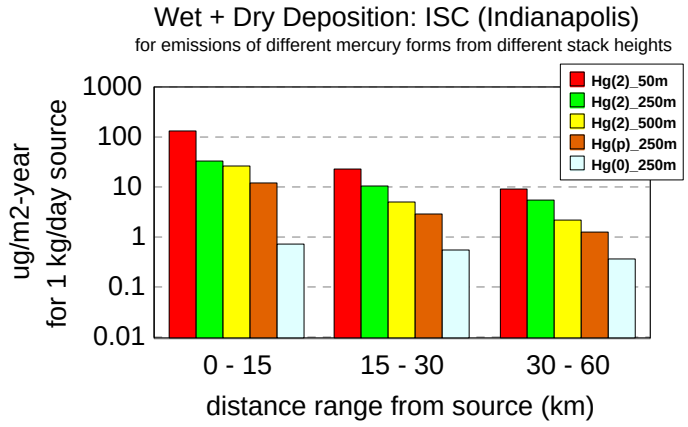
Different Time Periods and Locations, but Similar Results

ISC: 1990-1994



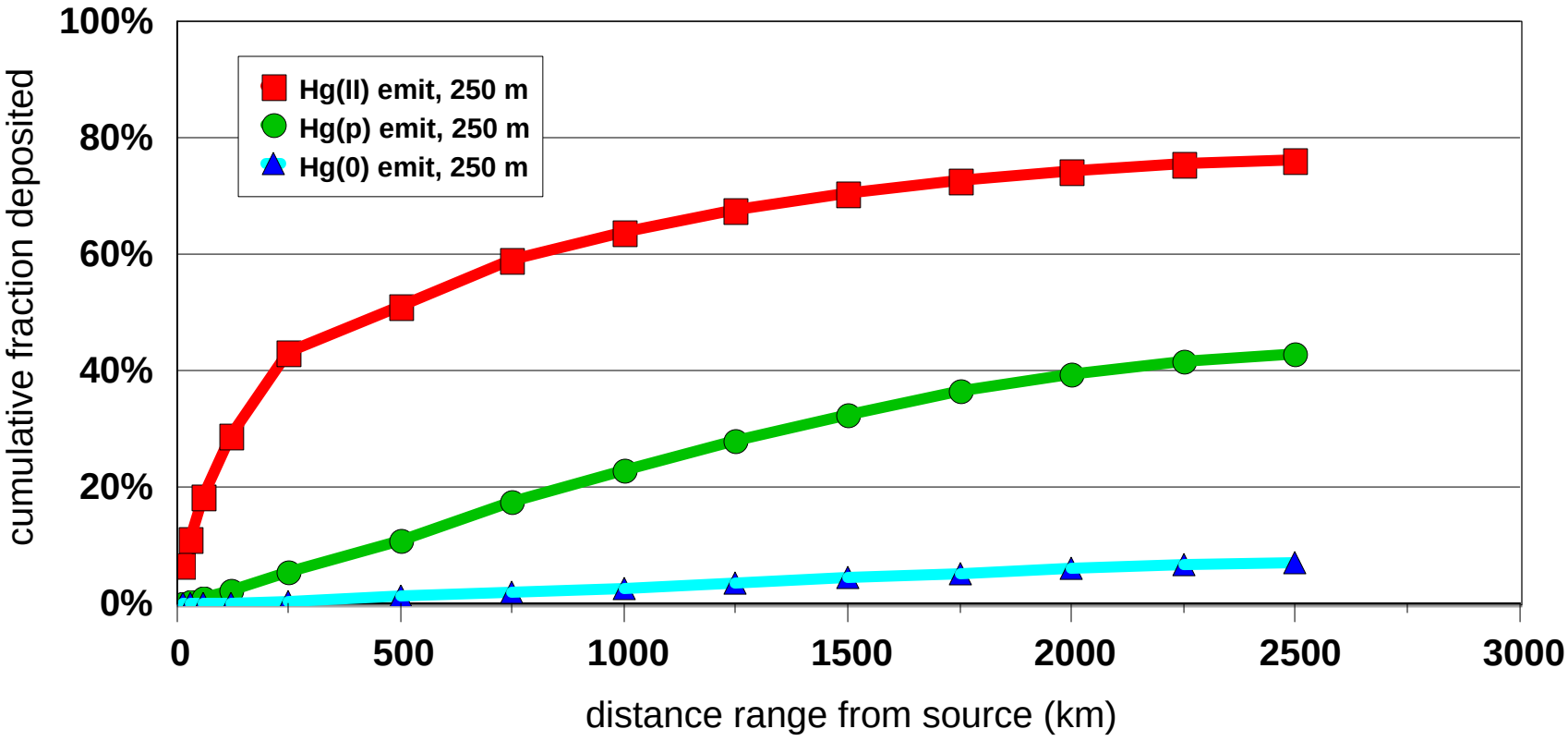






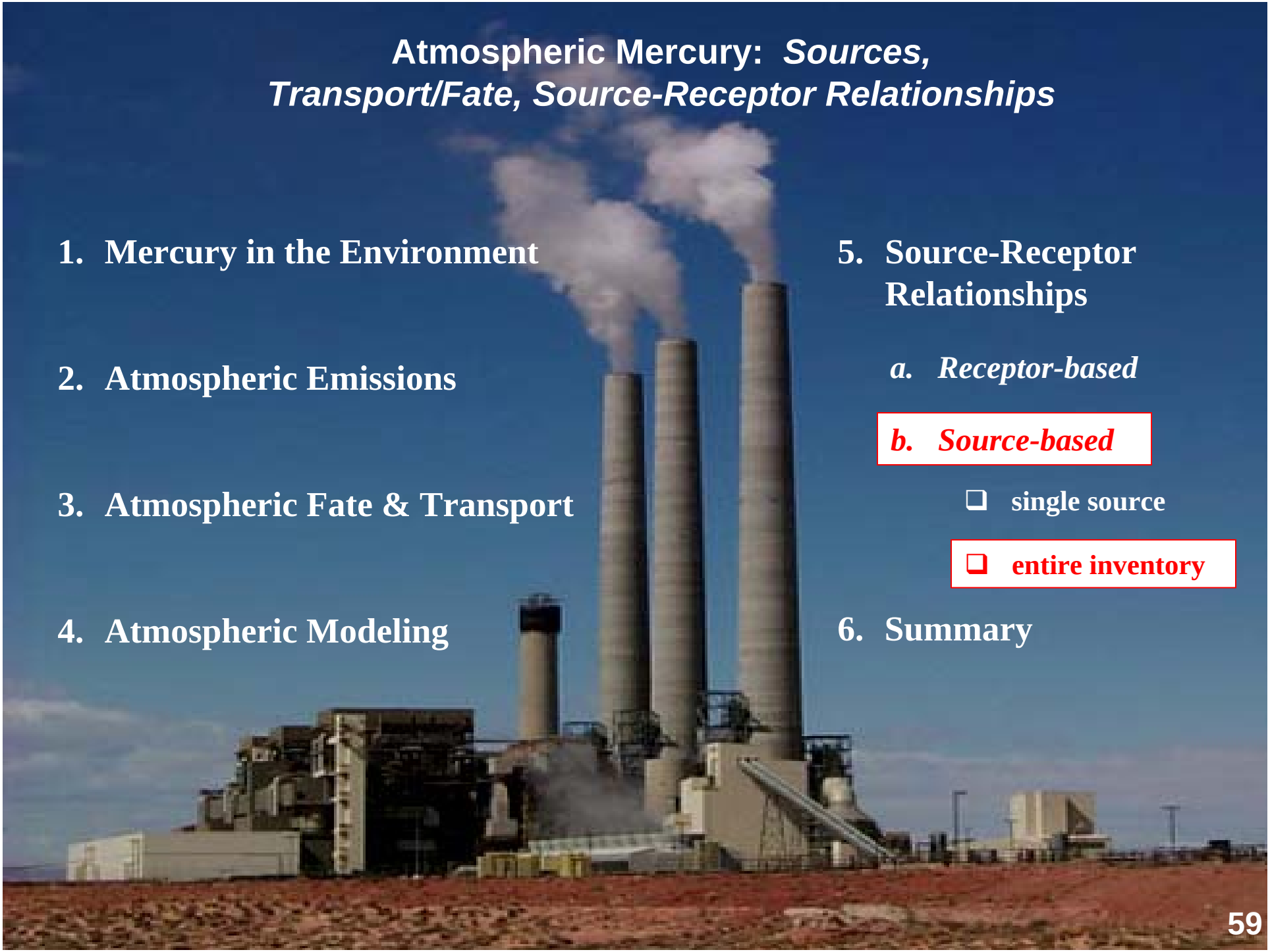
The <u>fraction deposited</u> and the <u>deposition flux</u> are both important, but they have very different meanings…
The fraction deposited nearby can be relatively "small",
But the area is also small, and the relative deposition flux can be very large…

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

Atmospheric Mercury: *Sources, Transport/Fate, Source-Receptor Relationships*



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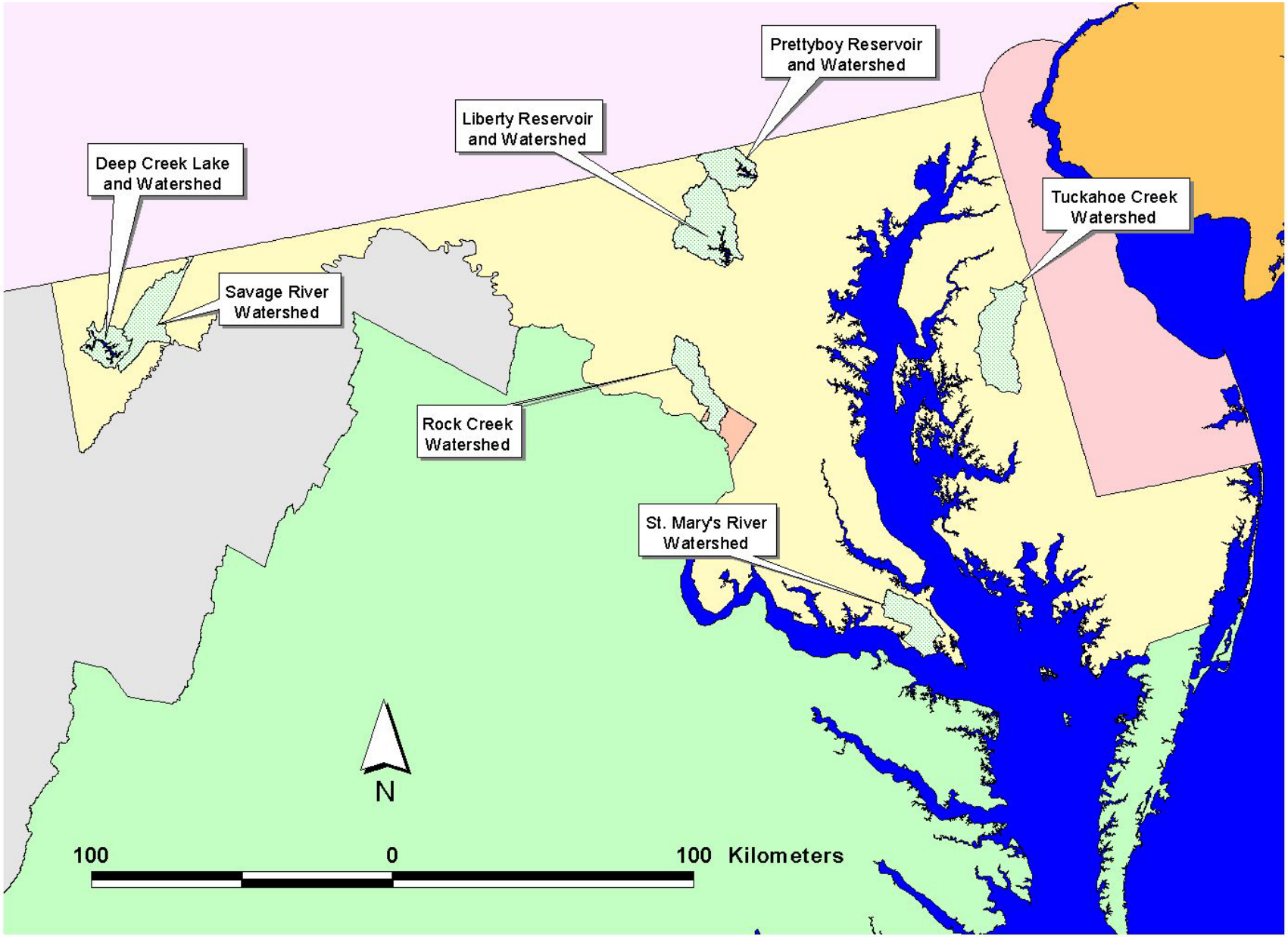
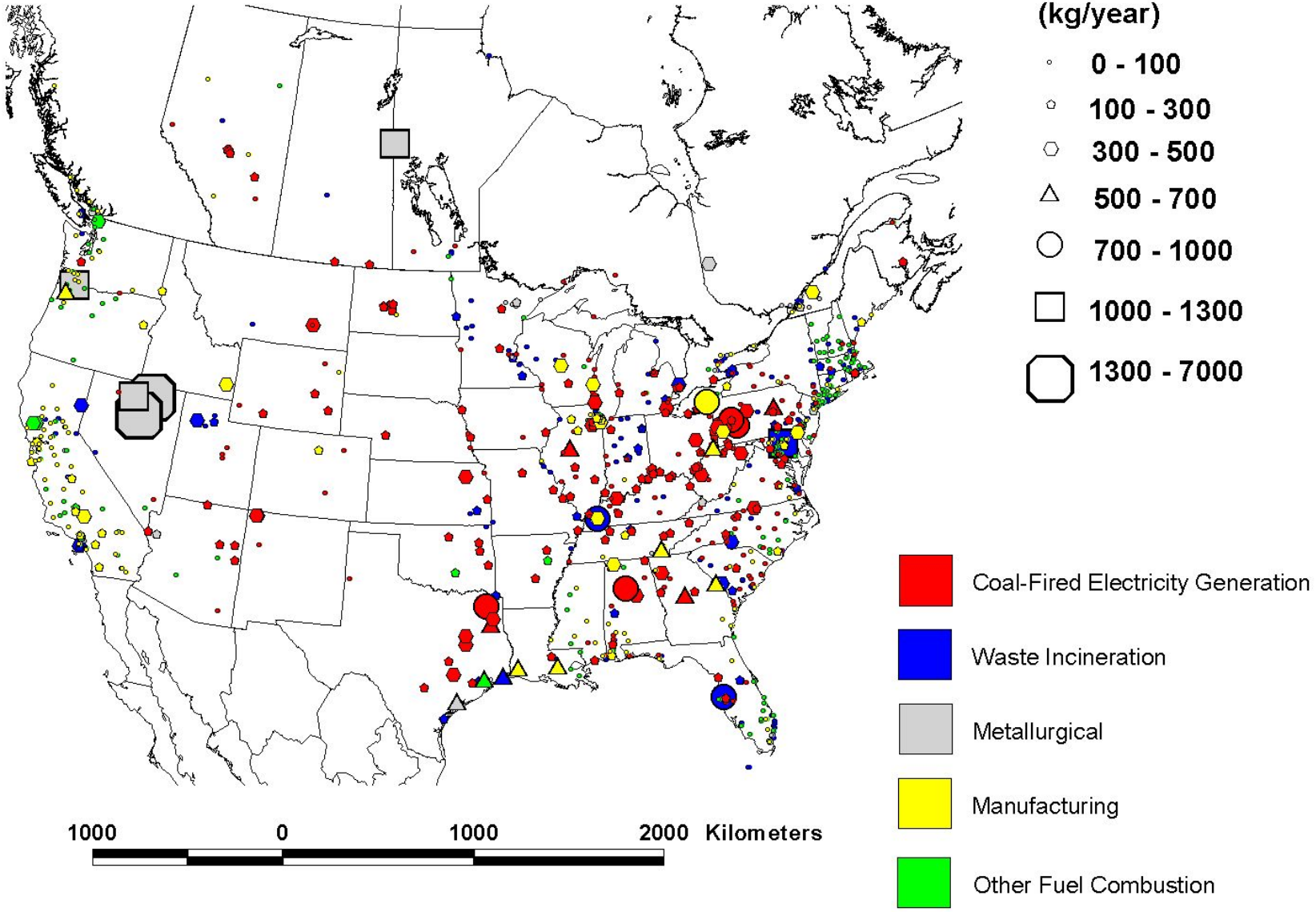
     - ❑ entire inventory
6. Summary

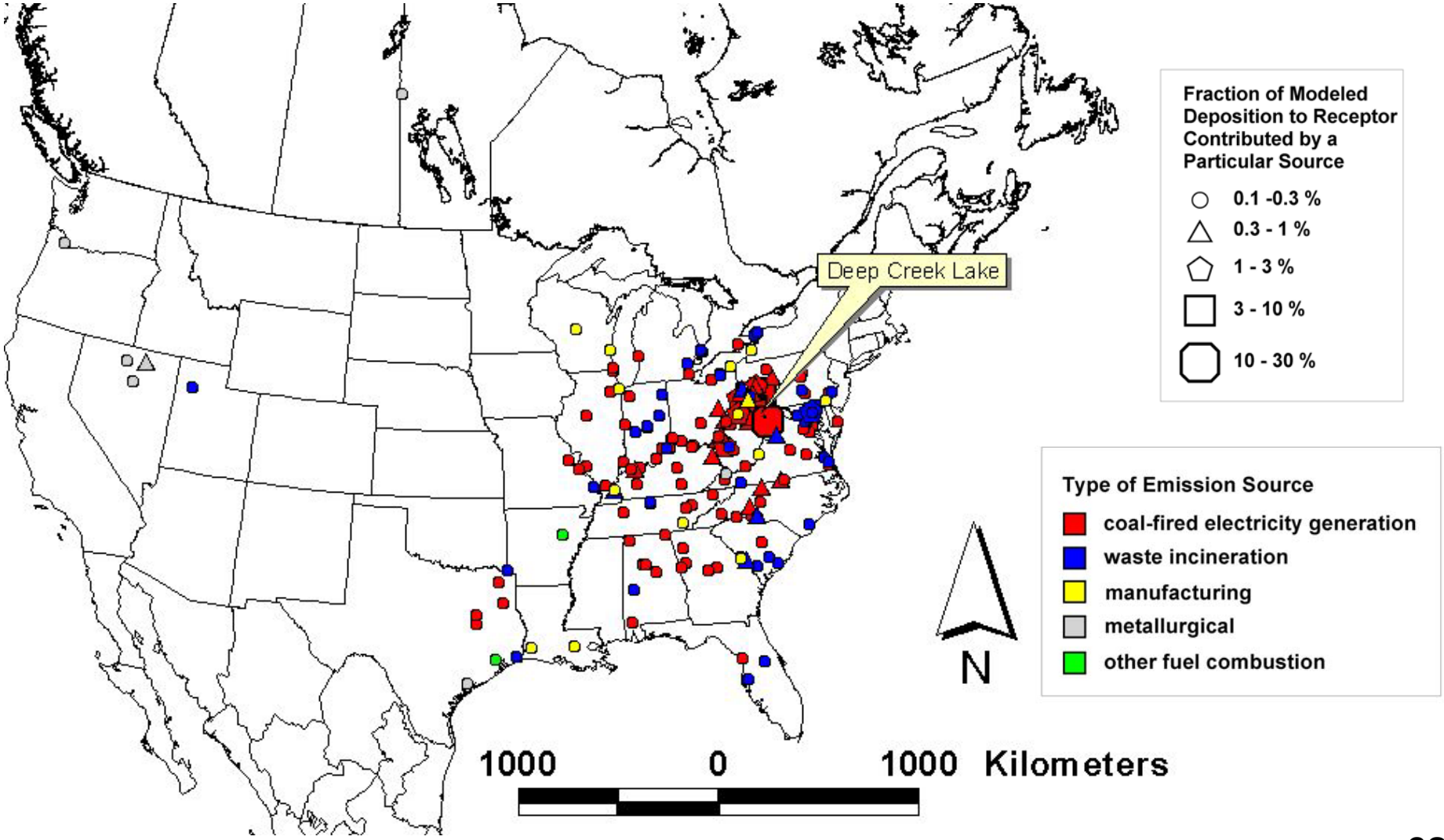
Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling *(but modeling was not optimized for these receptors!)*



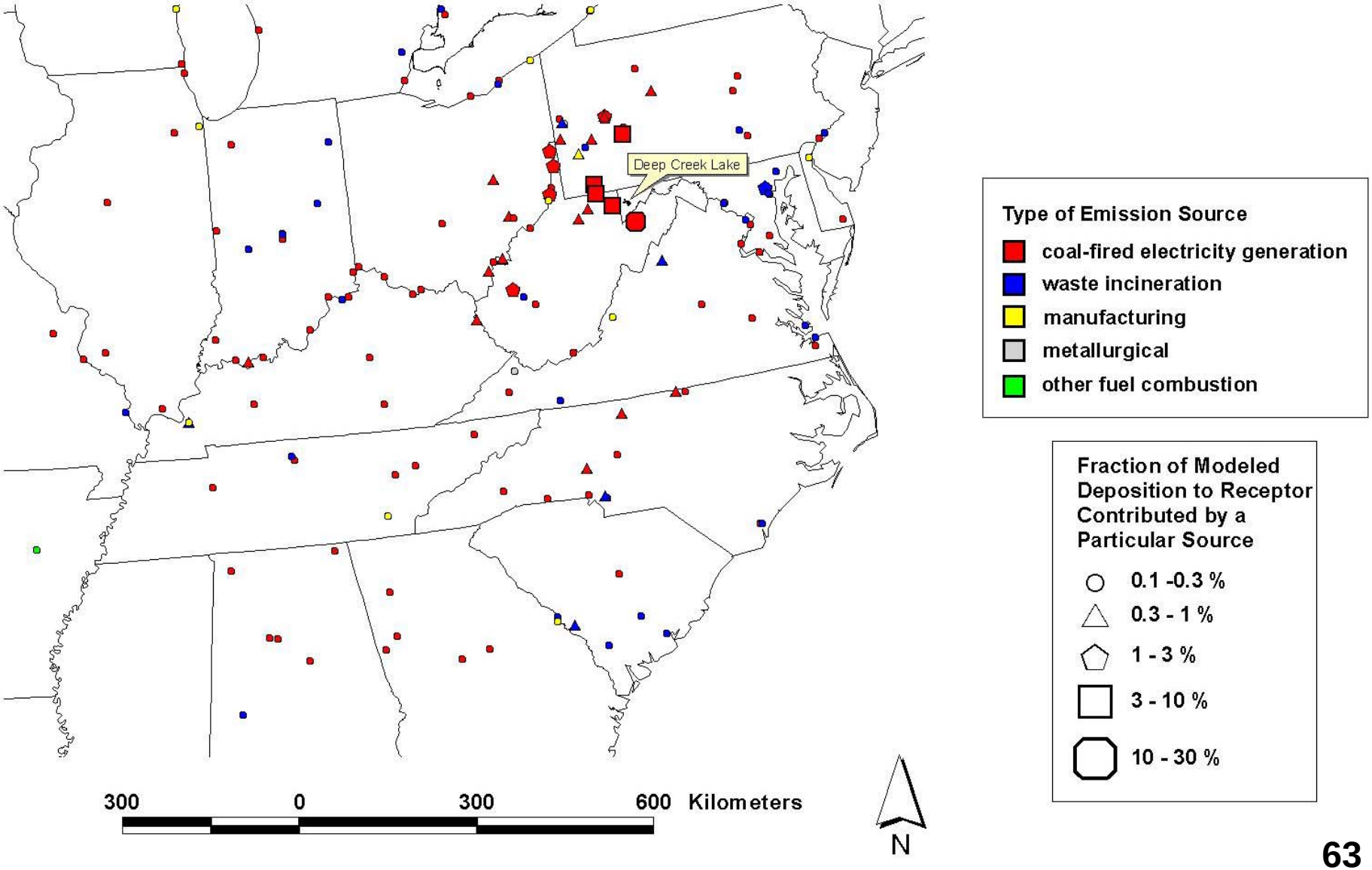
Geographic Distribution of Largest Anthropogenic Mercury Emissions Sources in the U.S. (1999) and Canada (2000)



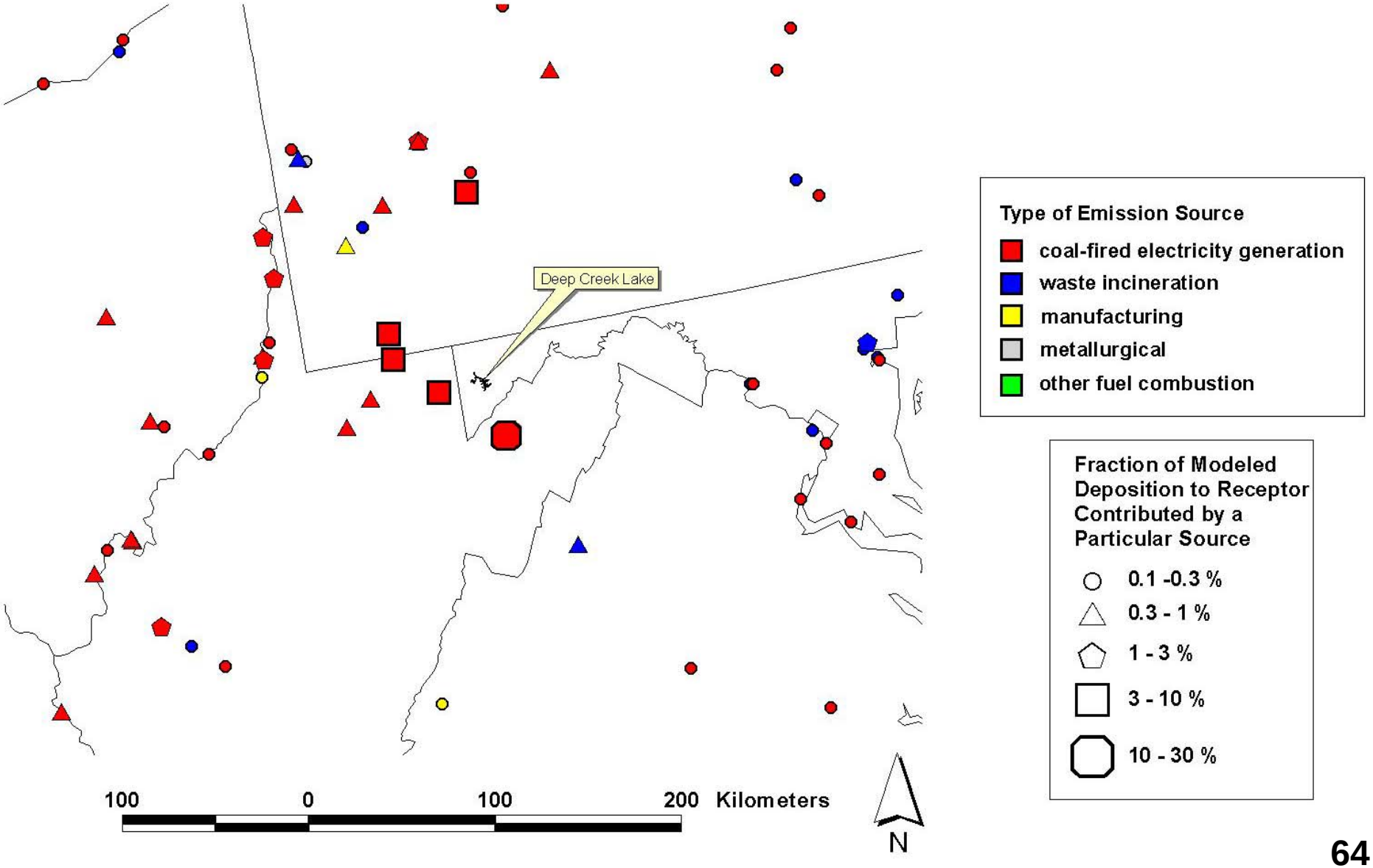
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (national view)



Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (regional view)



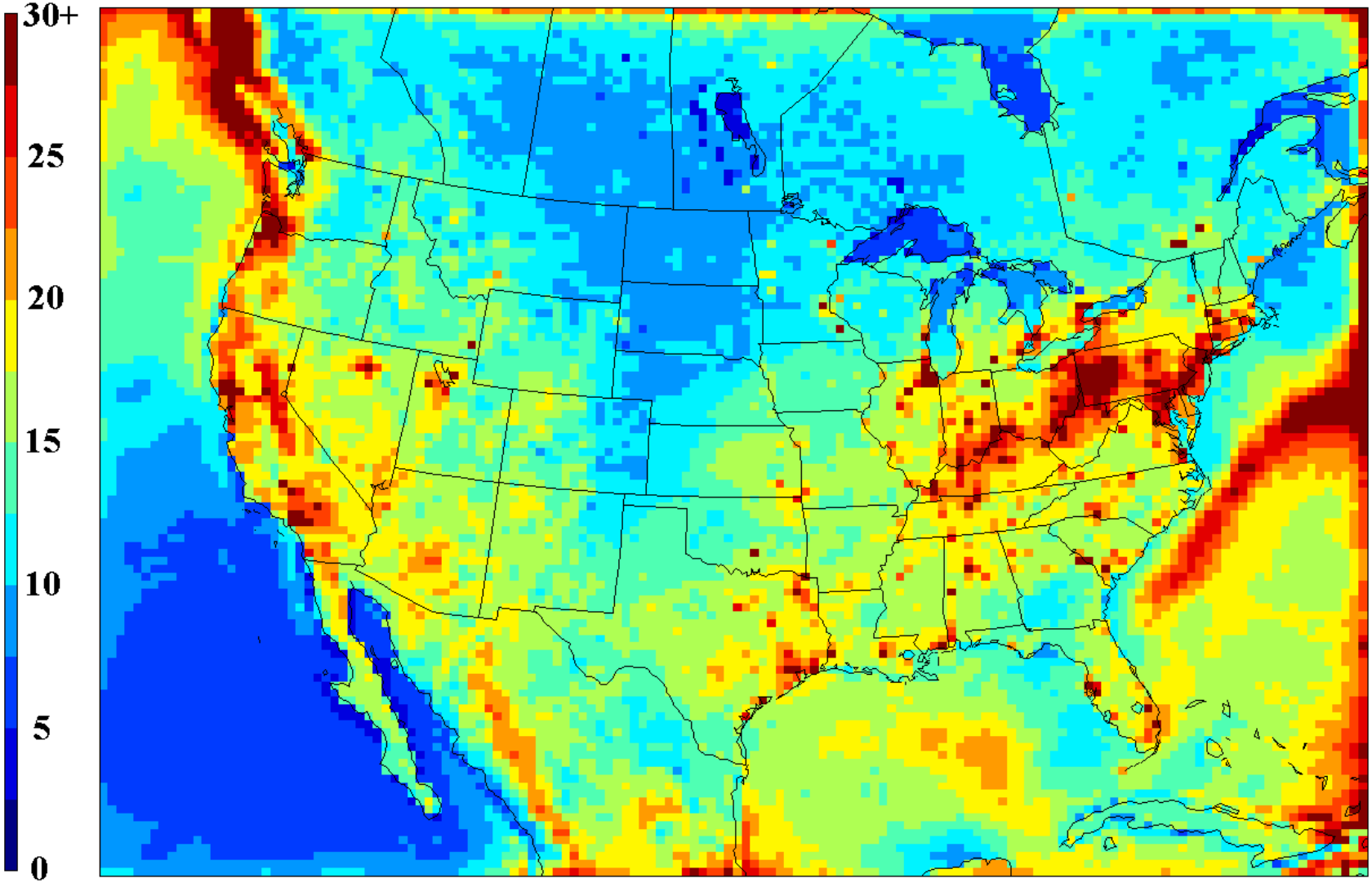
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (close-up view)



Some CMAQ results,
used in the development
of the CAMR rule,
courtesy of
Russ Bullock, EPA

CMAQ-simulated total mercury deposition for 2001

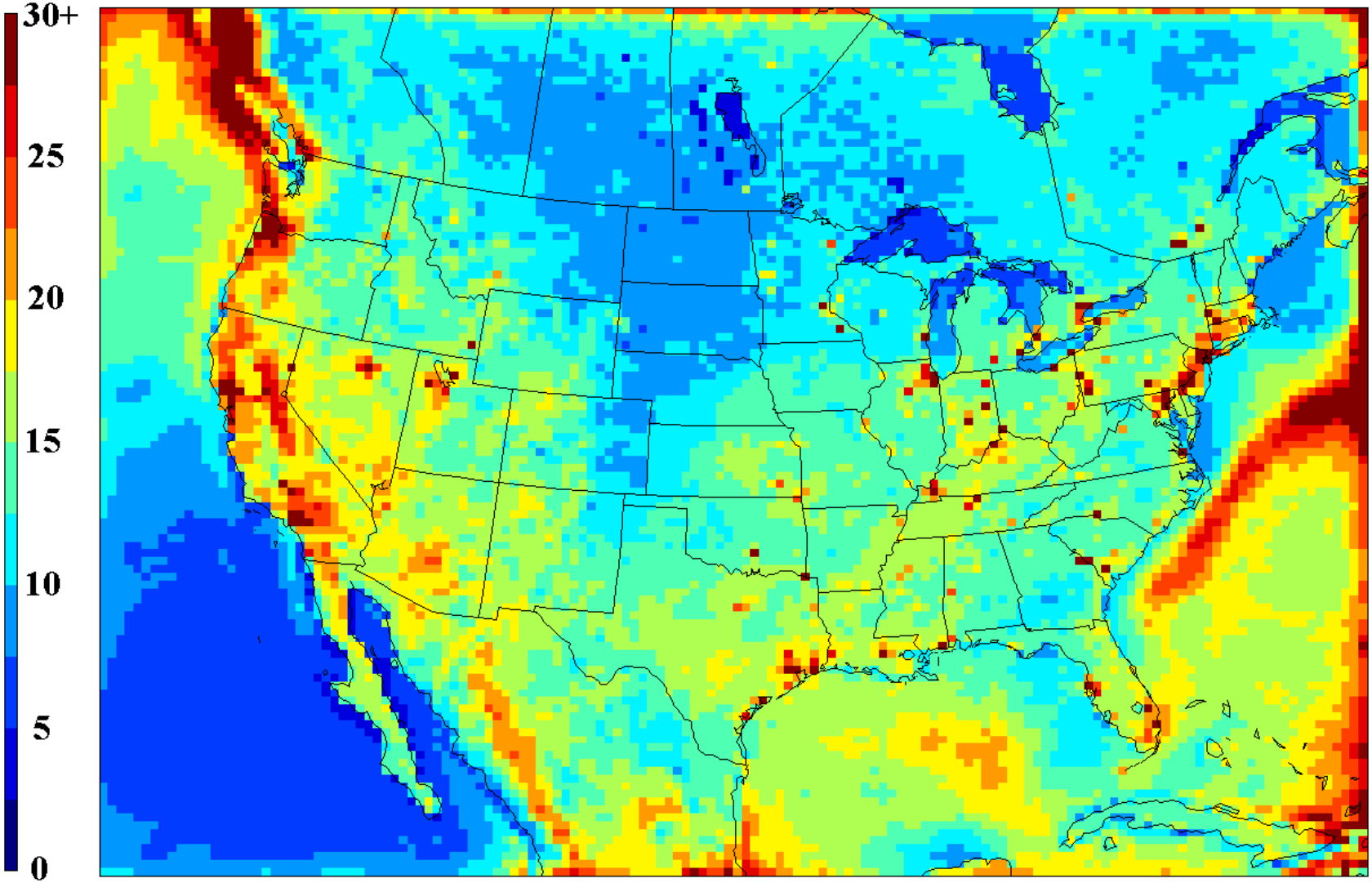
(micrograms per square meter)



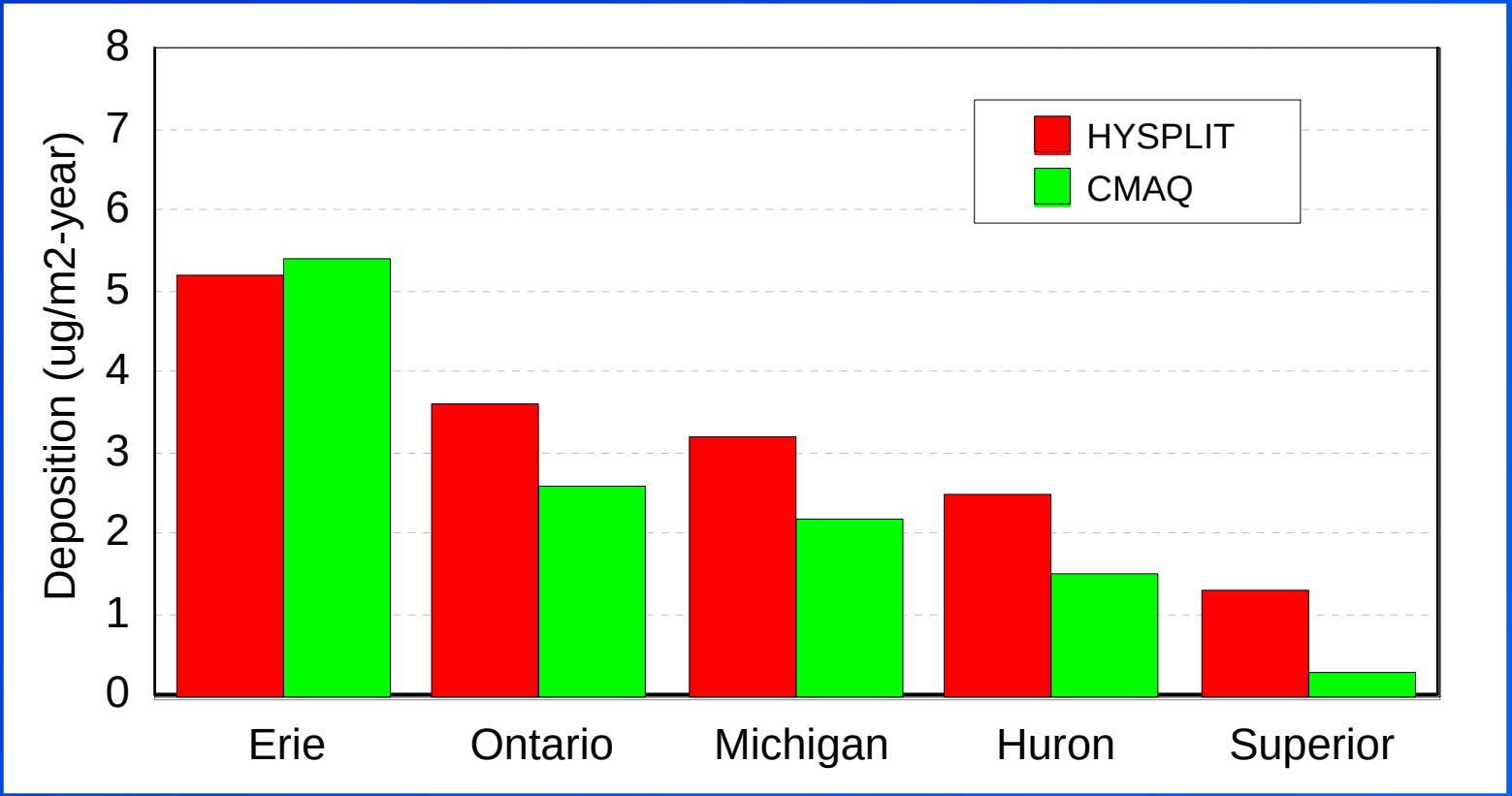
Base case

CMAQ-simulated total mercury deposition for 2001

(micrograms per square meter)



Utility Zero Out



Model-estimated U.S. utility atmospheric mercury deposition contribution to the Great Lakes: HYSPLIT-Hg (1996 meteorology, 1999 emissions) vs. CMAQ-HG (2001 meteorology, 2001 emissions).

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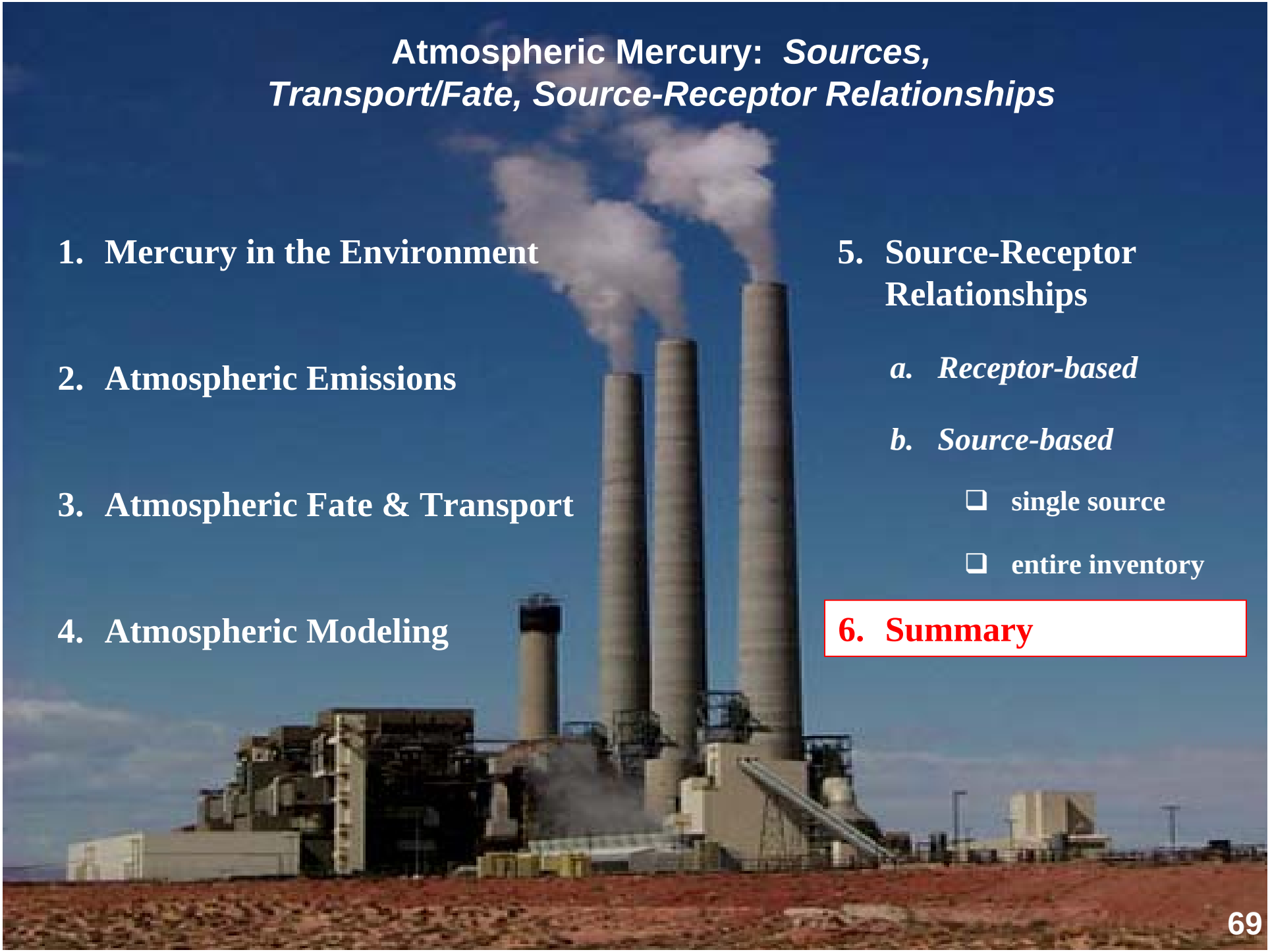

Summary

- Models needed for source-receptor and other info
- At present, many model uncertainties & data limitations
- Measurements needed to develop, evaluate & improve models
- Some useful model results appear to be emerging
- Future is much brighter because of increased coordination between measurer's and modelers! Thanks Mark Castro!

Thanks!

For more information on this research:
http://www.arl.noaa.gov/ss/transport/cohen.html