Modeling the Atmospheric Transport and Deposition of Mercury

Dr. Mark Cohen
NOAA Air Resources Laboratory
Silver Spring, Maryland
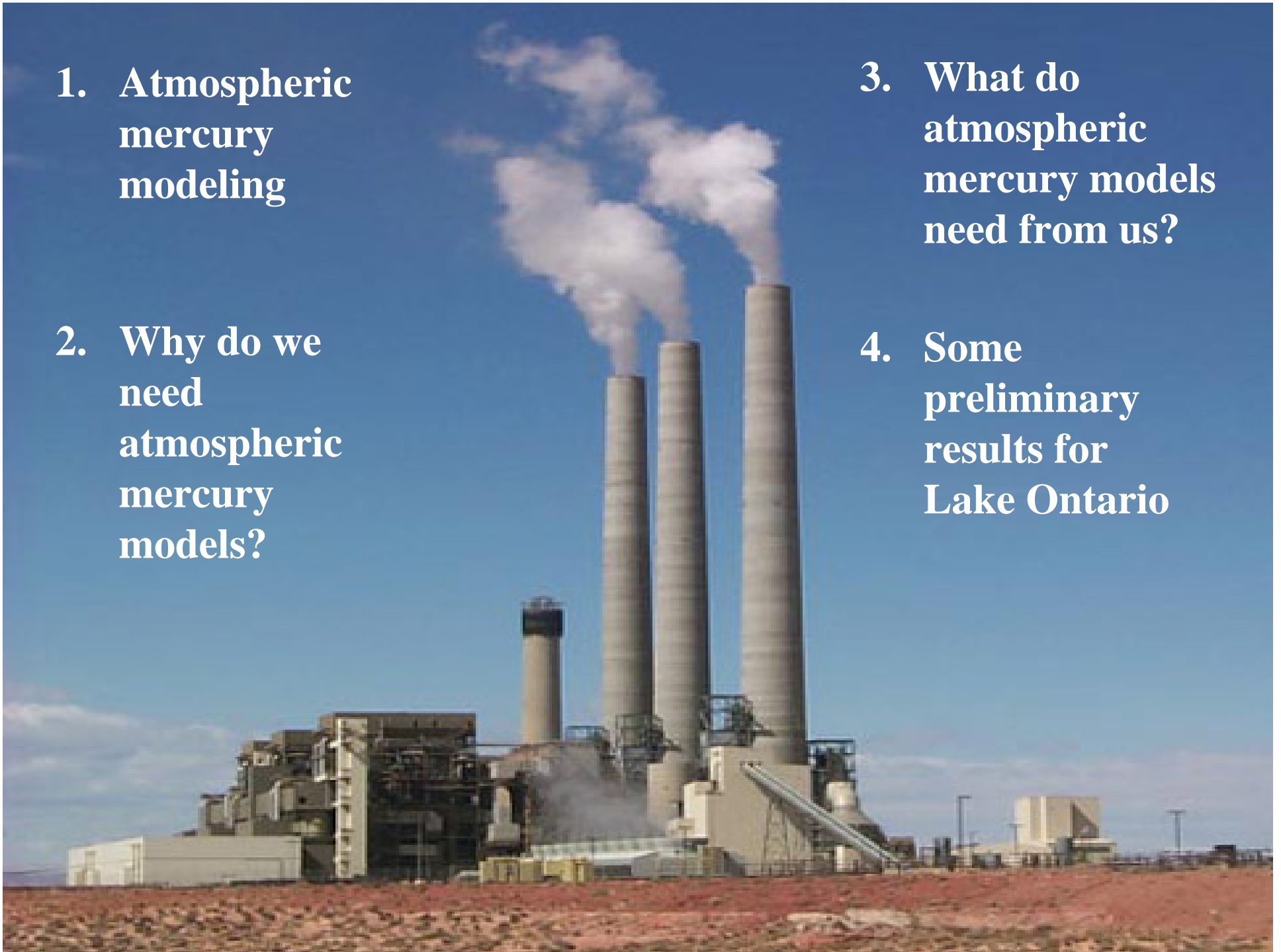
Mercury Workshop, Great Lakes Biennial Meeting,
Kingston, Ontario, Canada June 9, 2005

1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results for Lake Ontario

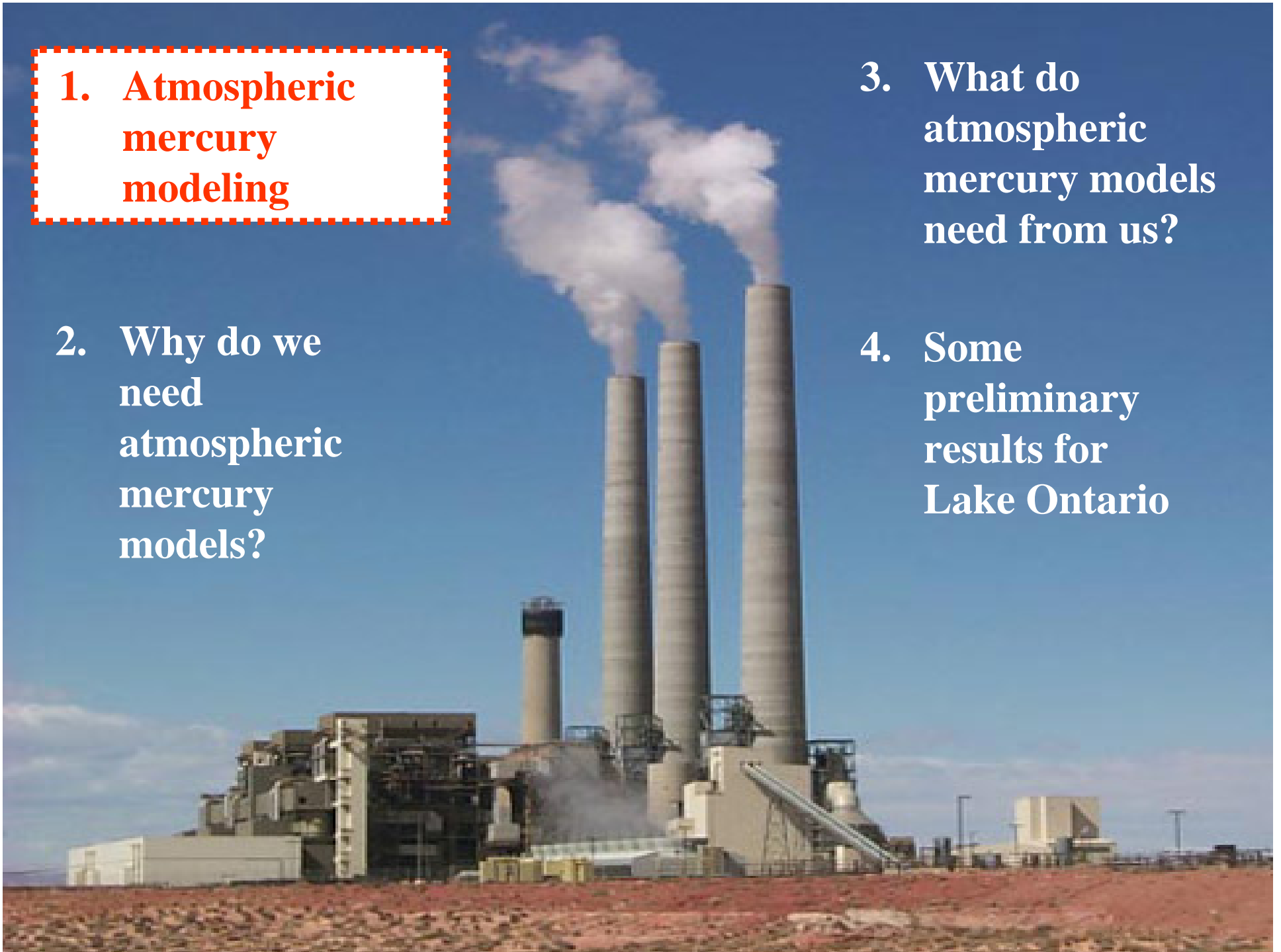1. **Atmospheric mercury modeling**

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results for Lake Ontario

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);
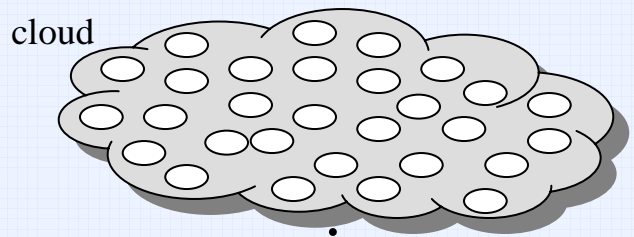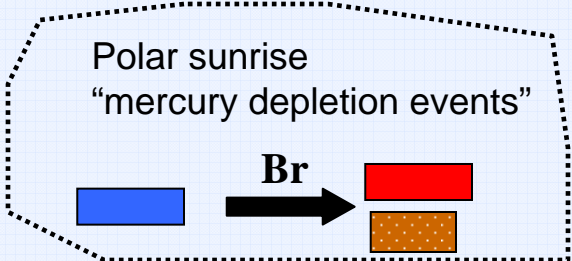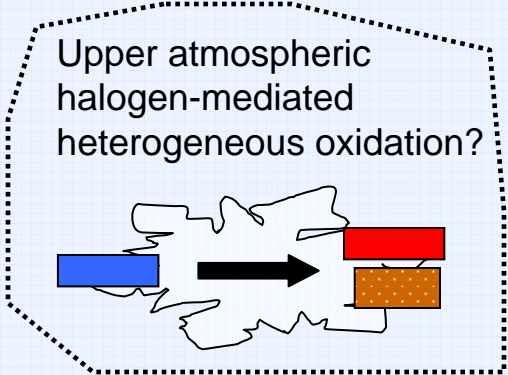- more local and regional effects

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?
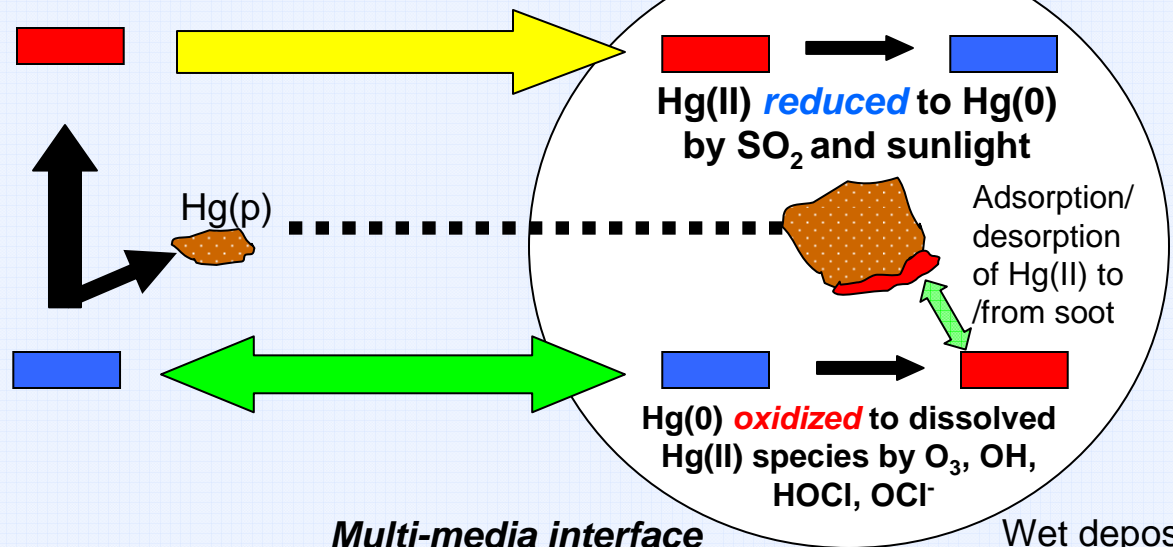
4

Atmospheric Mercury Fate Processes

■ Elemental Mercury [Hg(0)]
■ Hg(II), ionic mercury, RGM
■ Particulate Mercury [Hg(p)]

Upper atmospheric halogen-mediated heterogeneous oxidation?

Polar sunrise "mercury depletion events"

Br

cloud

CLOUD DROPLET

Hg(II) *reduced* to Hg(0) by SO_2 and sunlight

Vapor phase:

Hg(0) oxidized to RGM and Hg(p) by O_3, H_2O_2, Cl_2, OH, HCl

Hg(p)

Adsorption/ desorption of Hg(II) to /from soot

Hg(0) *oxidized* to dissolved Hg(II) species by O_3, OH, HOCl, OCl^-

Primary Anthropogenic Emissions

Multi-media interface

Wet deposition

Dry deposition

Natural emissions

Re-emission of previously deposited anthropogenic and natural mercury
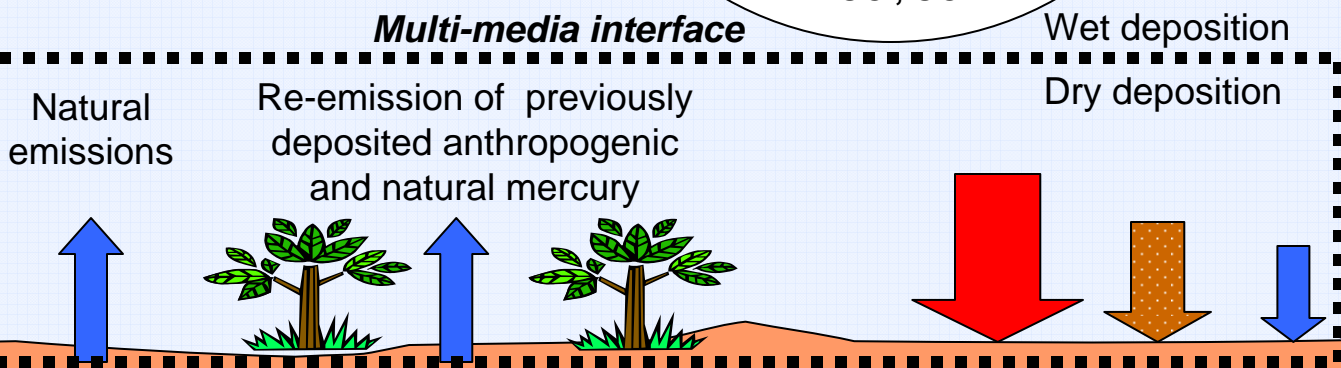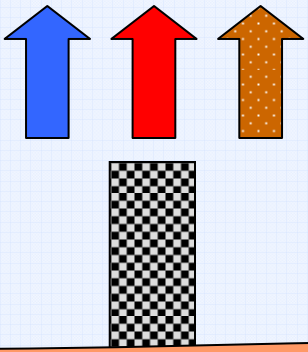
Figure 1. Lagrangian Puff Air Transport and Deposition Model

TIME (hours)   0   1   2   · · ·

☐ = mass of pollutant
(decreases as destruction and
deposition occur each time step)

Puff's mass, size, and
location continually
tracked. . .

Centerline of puff motion
determined by wind
direction and velocity

Photolytic and chemical
transformation of pollutant also
estimated at each time step

Initial puff
location is at
source, with
initial mass
& size

Total deposition
from a puff during
a given time step is
calculated from the
sum of the estimat-
ed dry and wet
deposition of gas
and particle-phase
material, based on
pollutant conc. in
the puff, the local
weather, and the
nature of the
surface.

deposition 1   deposition 2   deposition to lake

Lake

6

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

7
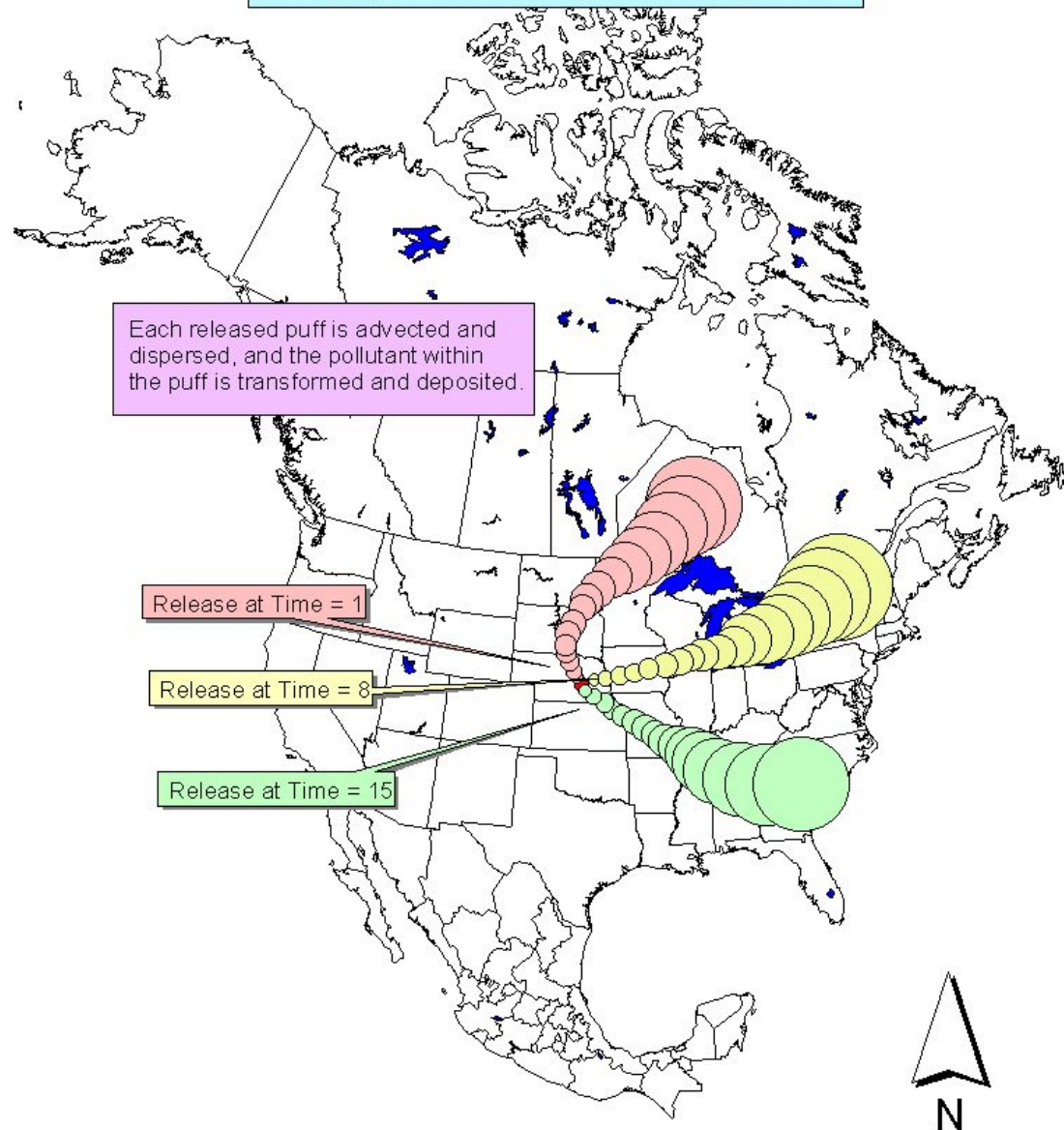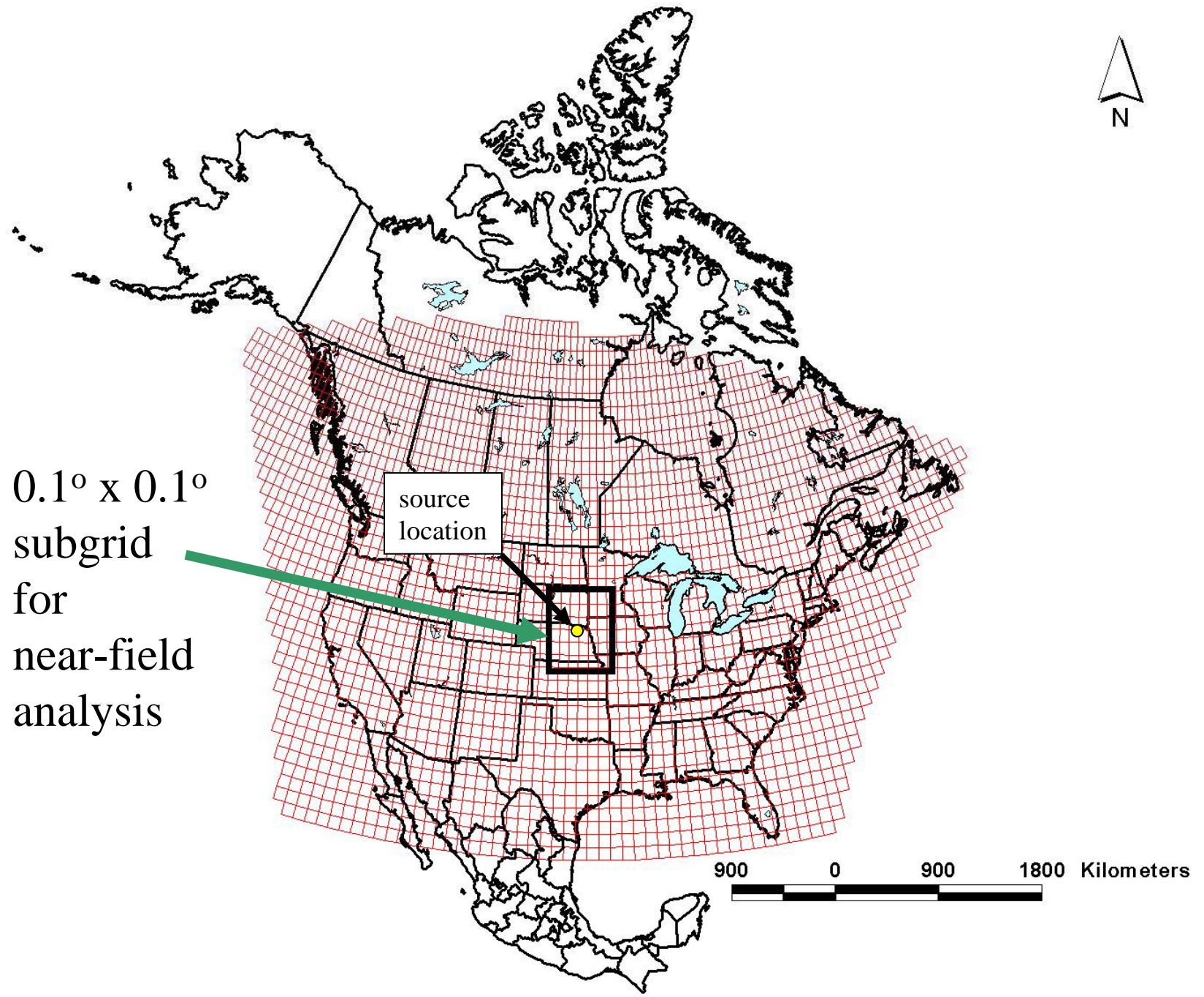
0.1º x 0.1º subgrid for near-field analysis

source location

N

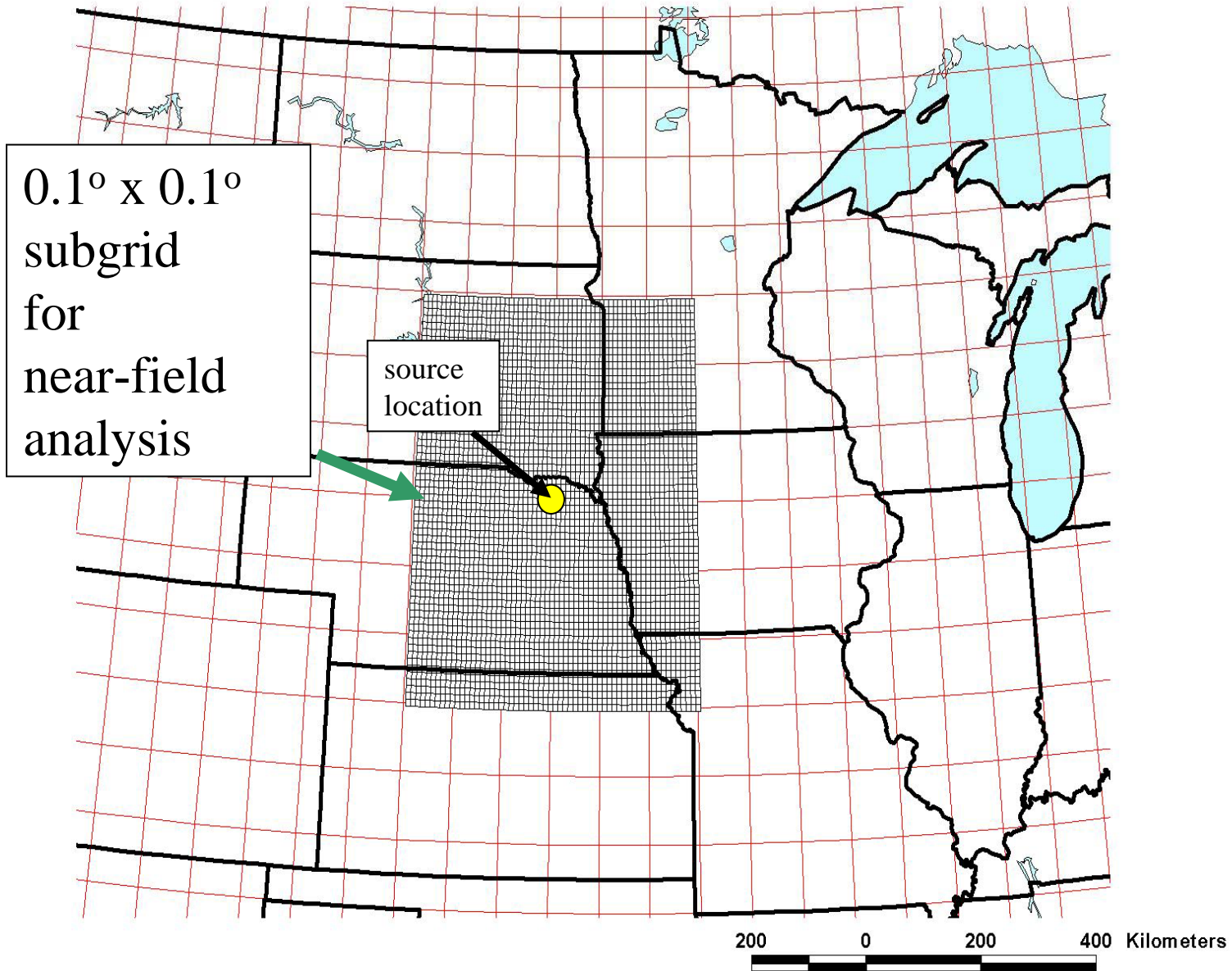900   0   900   1800   Kilometers
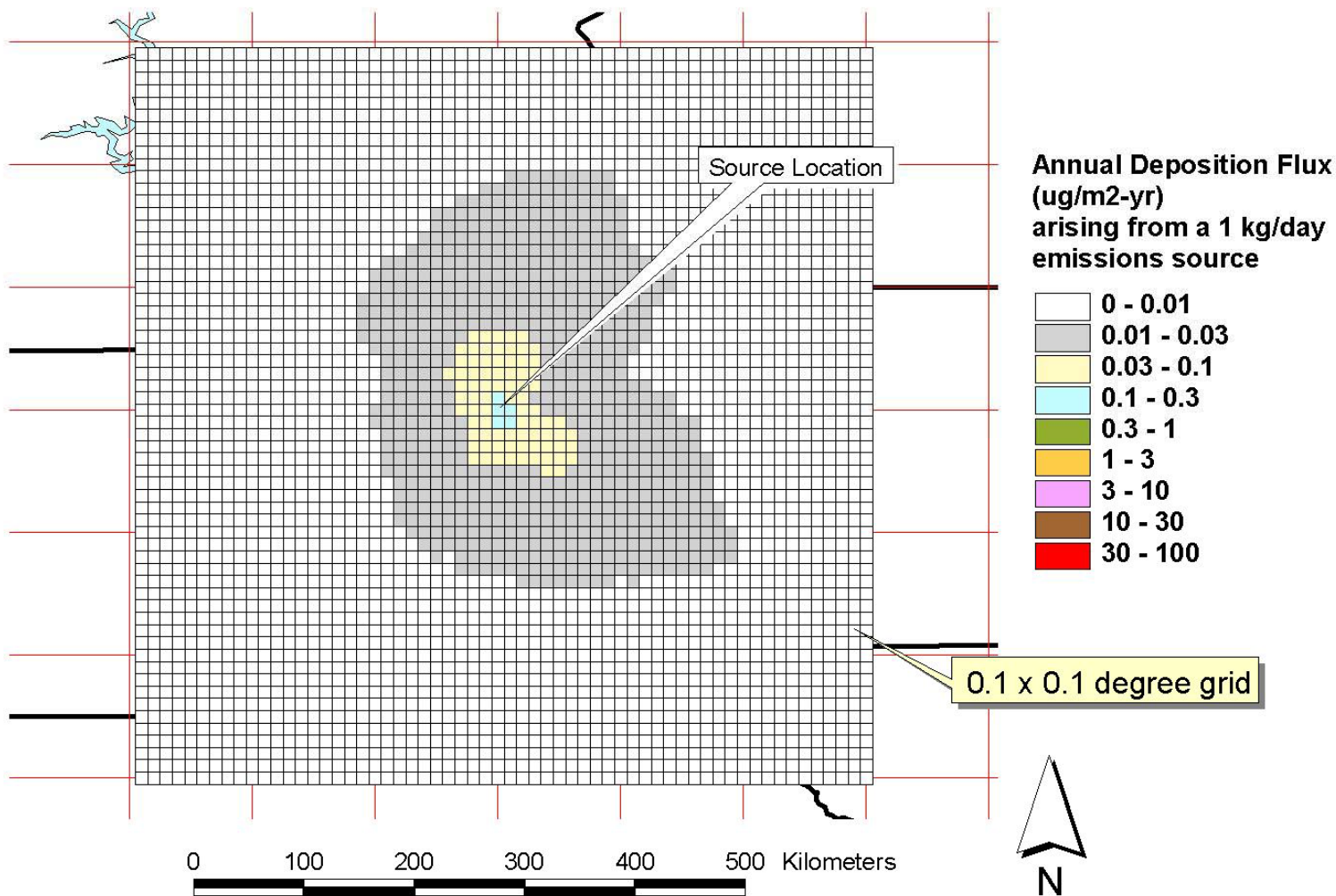
0.1º x 0.1º subgrid for near-field analysis

source location

200   0   200   400 Kilometers

9

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

Source Location

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

0.1 x 0.1 degree grid

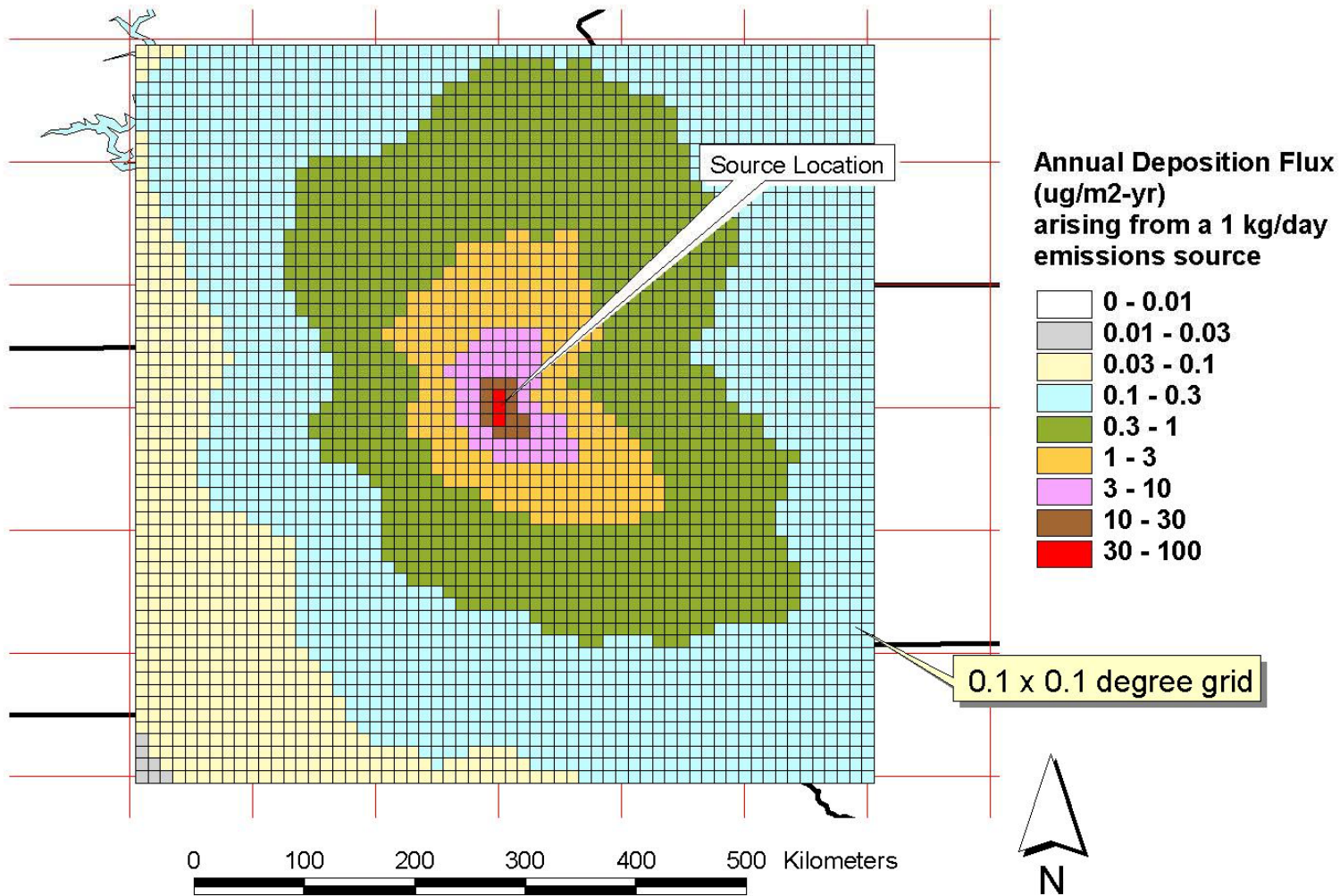0   100   200   300   400   500   Kilometers

N

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

10

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

Source Location

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

0.1 x 0.1 degree grid

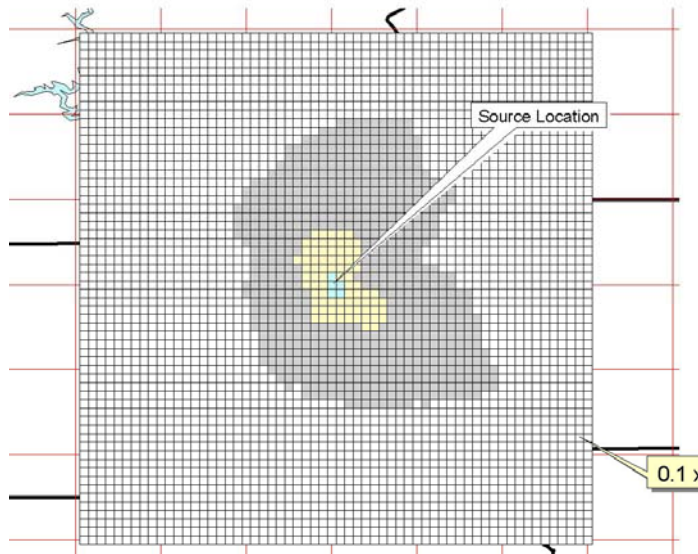0   100   200   300   400   500   Kilometers

N

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

11

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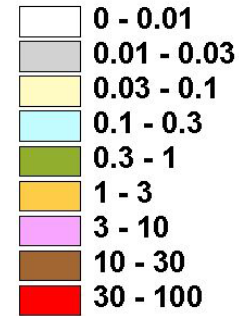

Source Location

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

0.1 x 0.1 degree grid

0   100   200   300   400   500   Kilometers

N

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

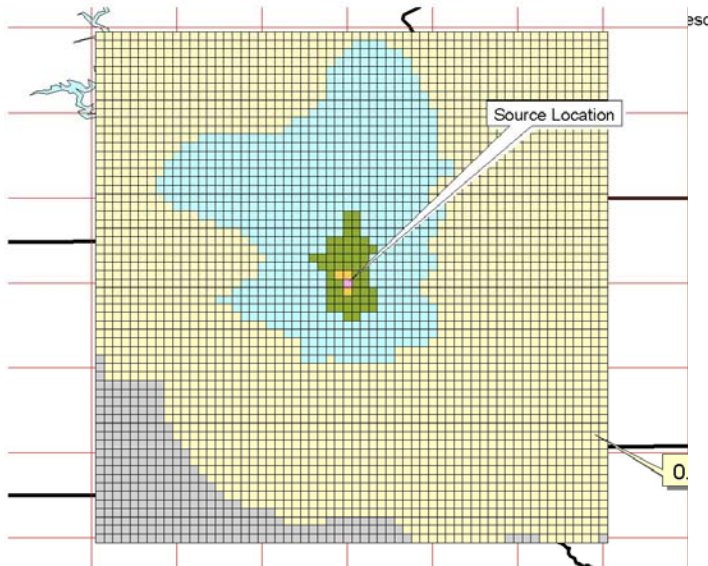**Annual deposition summary for emissions of elemental Hg from a 250 meter high source**

Source Location

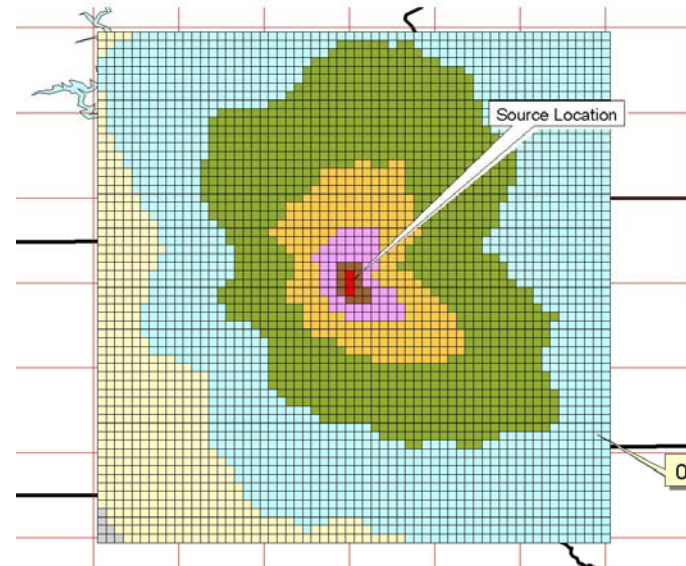**Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source**

	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

0.1

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

Source Location

0.

0   100   200   300   400   500   Kilometers

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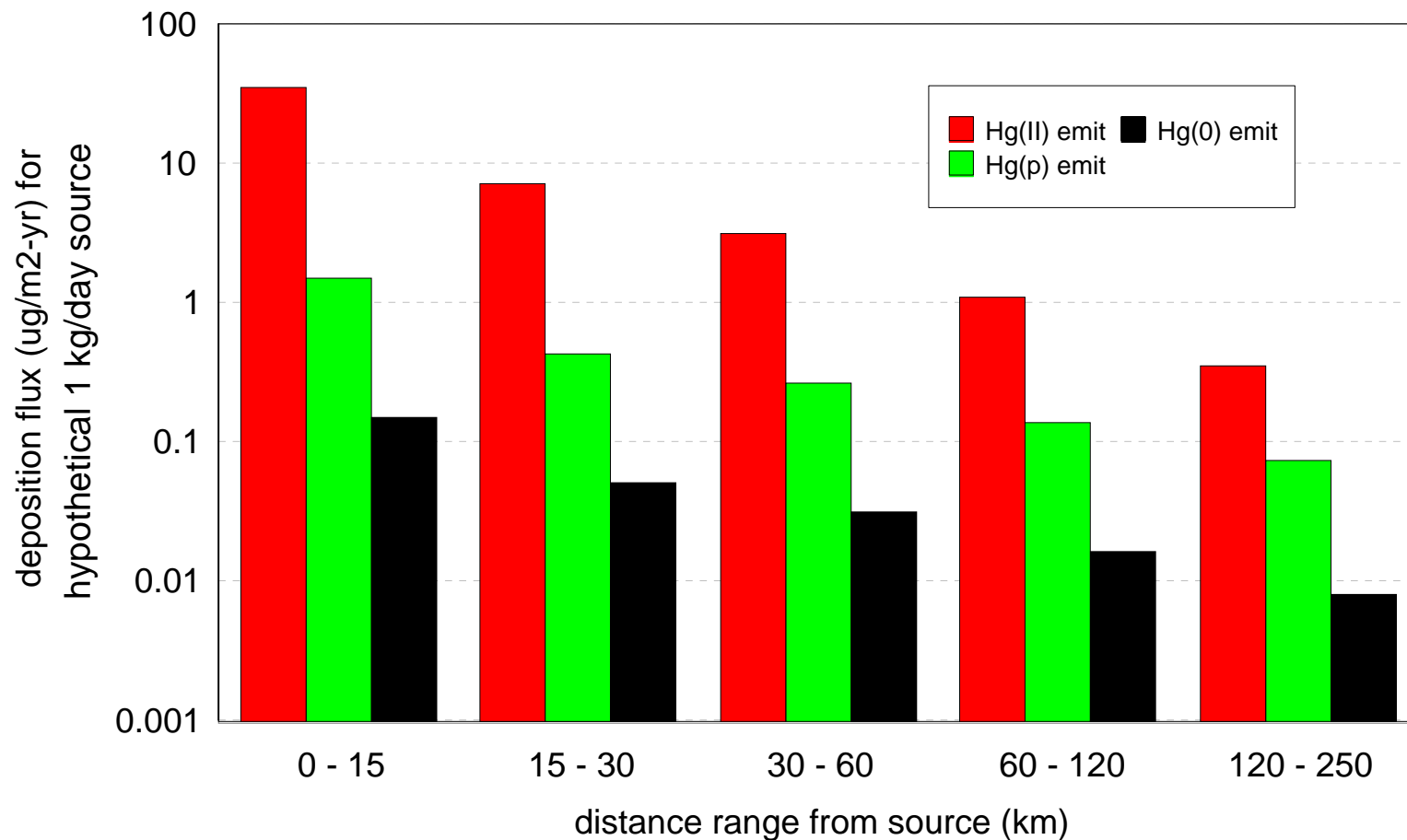simulation for entire year 1996 using archived NGM meteorology (180 km

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

Source Location

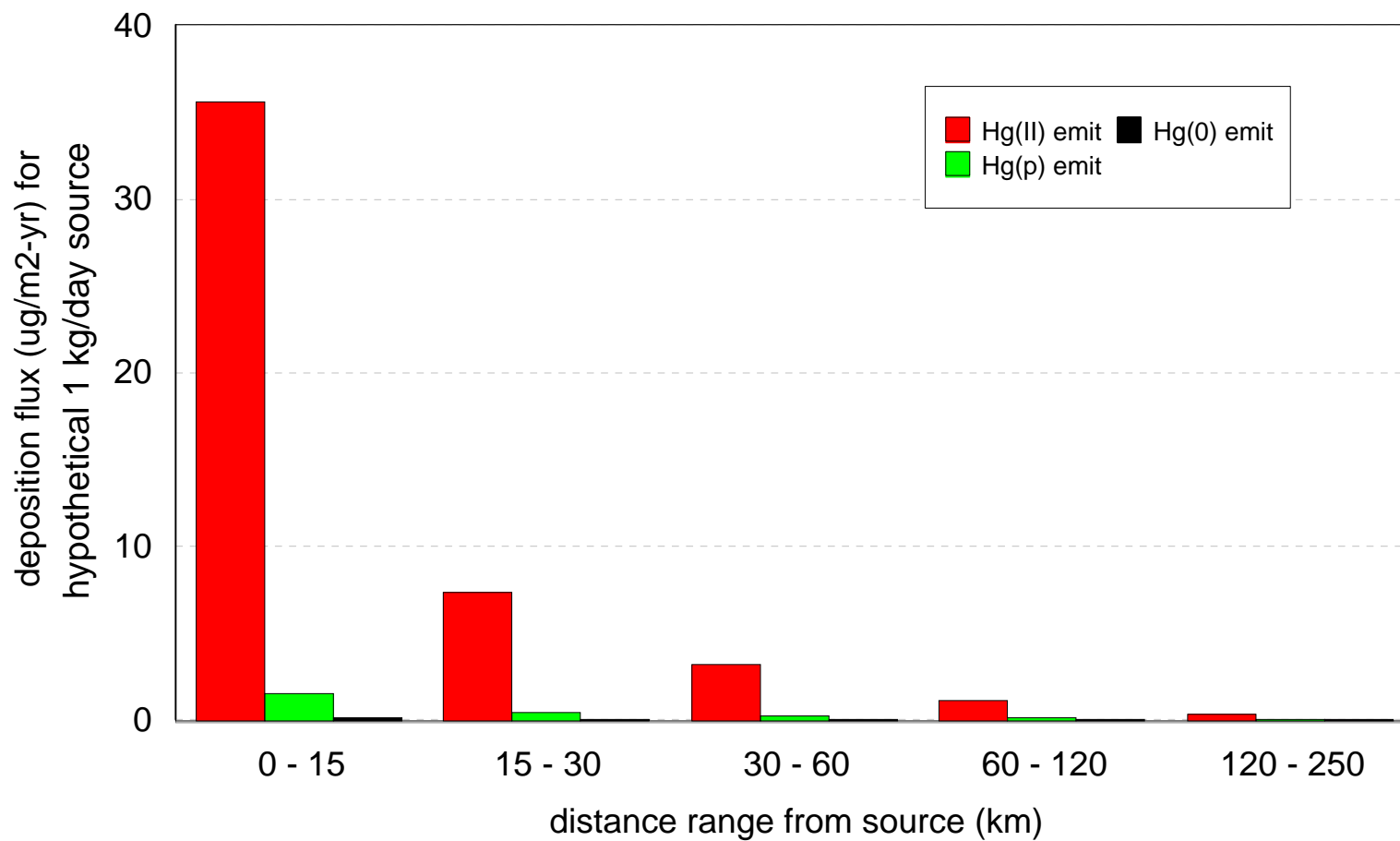0.

0   100   200   300   400   500   Kilometers

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

13

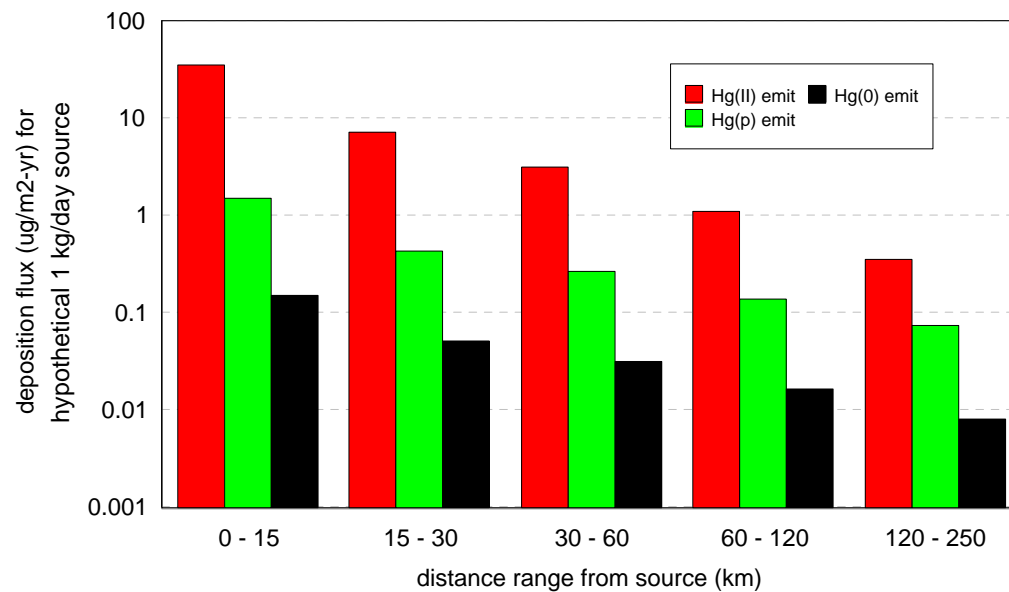# Why is emissions speciation information critical?

Logarithmic

Why is emissions speciation information critical?
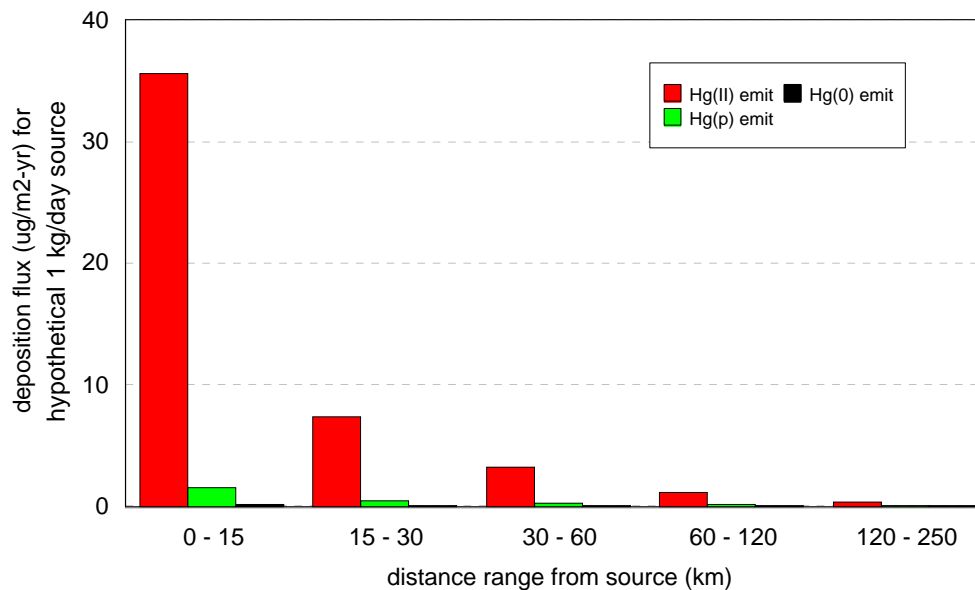

Linear

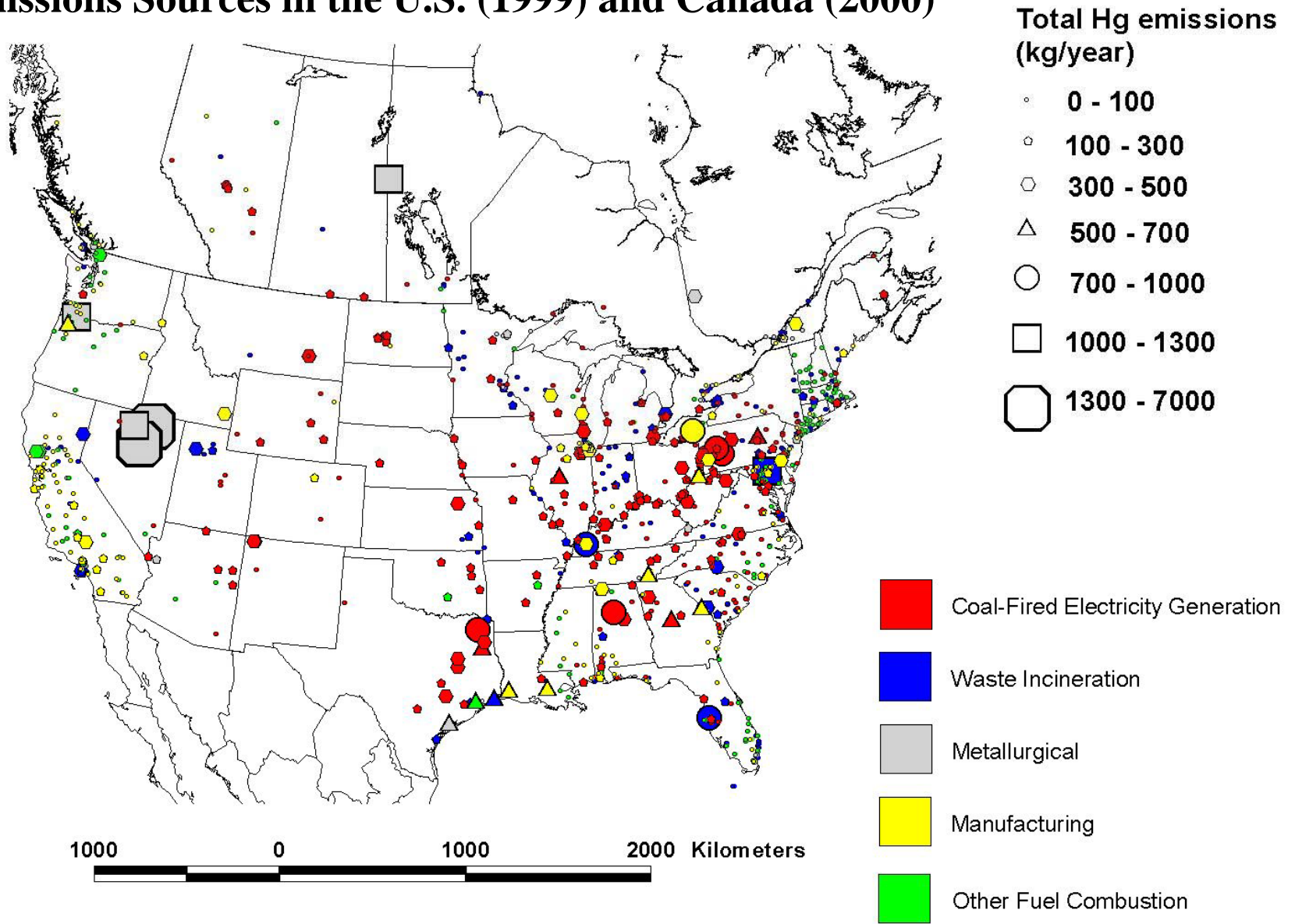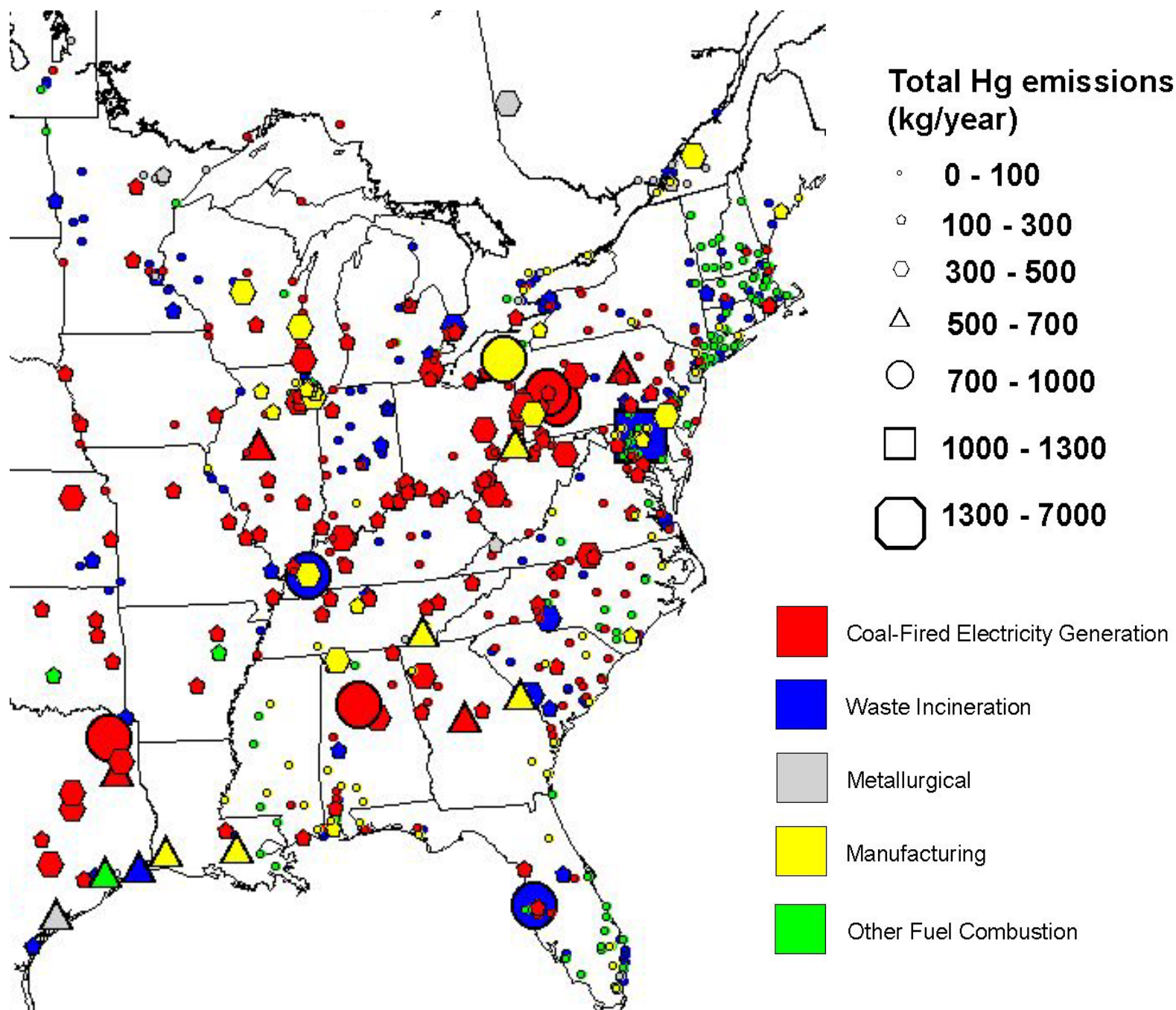# Why is emissions speciation information critical?

Logarithmic

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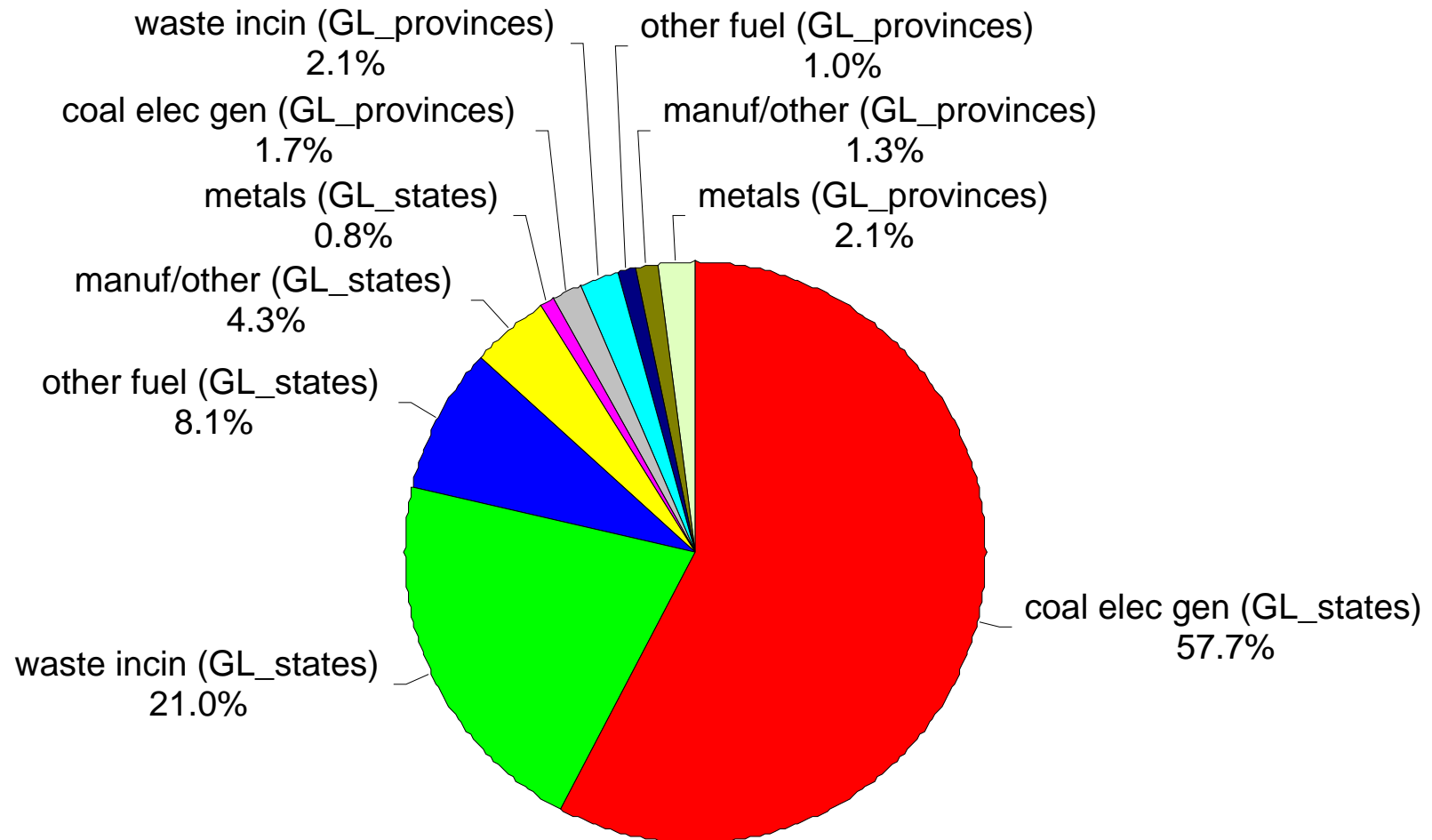
Geographic Distribution of Largest Anthropogenic Mercury Emissions Sources in the U.S. (1999) and Canada (2000)

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

1000   0   1000   2000   Kilometers

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

18

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]

waste incin (GL_provinces)
2.1%

coal elec gen (GL_provinces)
1.7%

metals (GL_states)
0.8%

manuf/other (GL_states)
4.3%

other fuel (GL_states)
8.1%

waste incin (GL_states)
21.0%

other fuel (GL_provinces)
1.0%

manuf/other (GL_provinces)
1.3%

metals (GL_provinces)
2.1%

coal elec gen (GL_states)
57.7%

1. Atmospheric mercury modeling

2. **Why do we need atmospheric mercury models?**

3. What do atmospheric mercury models need from us?

4. Some preliminary results for Lake Ontario
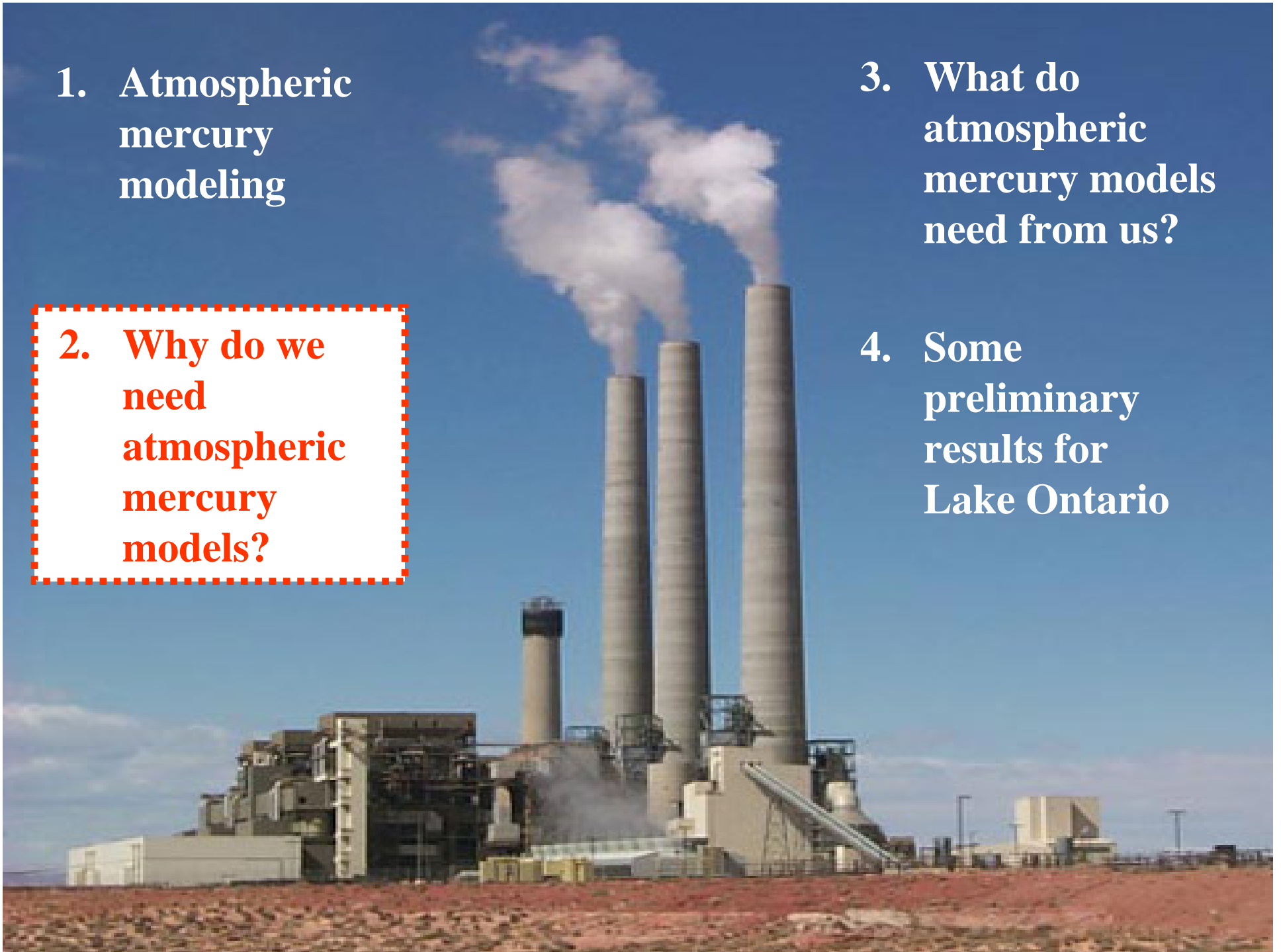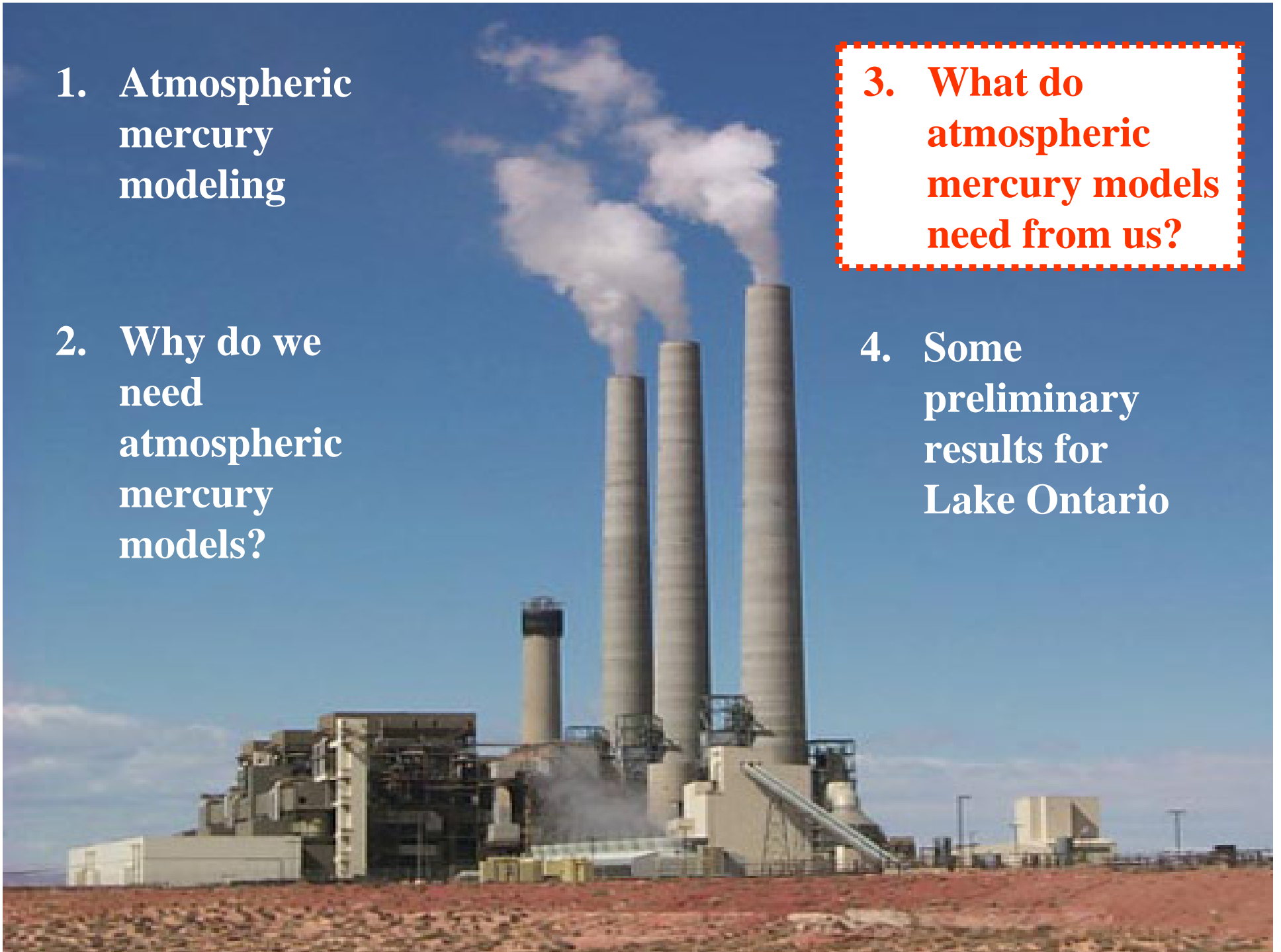
Why do we need atmospheric mercury models?

➢ to get *comprehensive source attribution* information ---
we don't just want to know how much is depositing at any given location, we also want to know where it came from…

➢ to estimate *deposition over large regions,*
…because deposition fields are highly spatially variable, and one can't measure everywhere all the time…

➢ to estimate *dry deposition*

➢ to evaluate *potential consequences* of alternative future emissions scenarios

1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need from us?

4. Some preliminary results for Lake Ontario

What do atmospheric mercury models need?
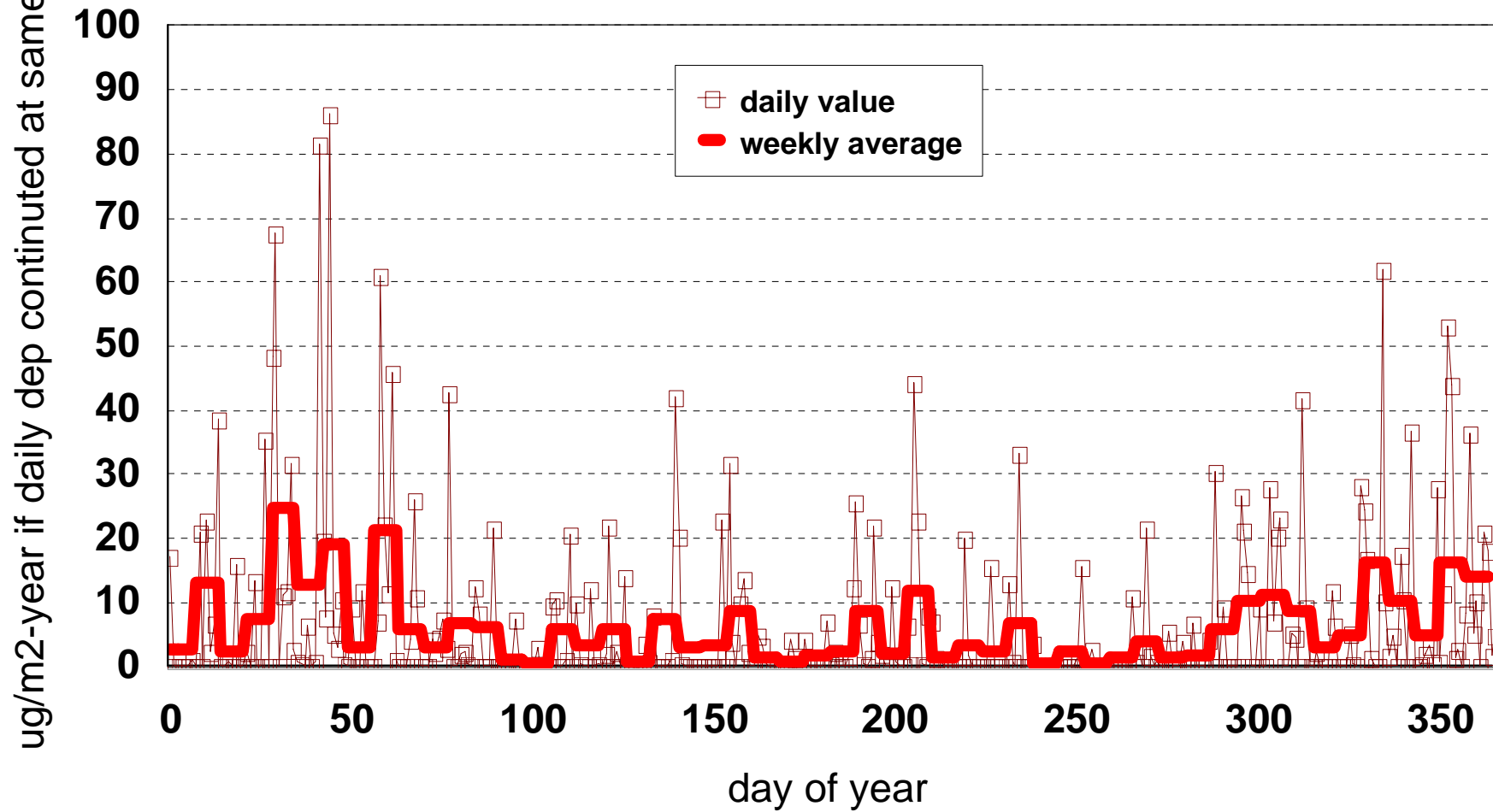
Emissions Inventories

Meteorological Data

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

Ambient data for comprehensive model evaluation and improvement

	some challenges facing mercury modeling
emissions inventories	• need *all* sources • accurately divided into *different Hg forms* • **U.S. 1996, 1999, 2003** / **CAN 1995, 2000, 2005** • *temporal* variations (e.g. shut downs)
meteorological data	• precipitation not well characterized
scientific understanding	• what is RGM? what is Hg(p)? • accurate info for known reactions? • do we know all significant reactions? • natural emissions, re-emissions?
ambient data for model evaluation	• Mercury Deposition Network (MDN) is great, but: • also need RGM, Hg(p), and Hg(0) concentrations • also need data above the surface (e.g., from aircraft) • also need source-impacted sites (not just background)

Illustrative example of total deposition at a location ~40 km "downwind" of a 1 kg/day RGM source

	some challenges facing mercury modeling
emissions inventories	• need *all* sources • accurately divided into *different Hg forms* • **U.S. 1996, 1999, 2003 / CAN 1995, 2000, 2005** • *temporal* variations (e.g. shut downs)
meteorological data	• precipitation not well characterized
scientific understanding	• what is RGM? what is Hg(p)? • accurate info for known reactions? • do we know all significant reactions? • natural emissions, re-emissions?
ambient data for model evaluation	• Mercury Deposition Network (MDN) is great, but: • also need RGM, Hg(p), and Hg(0) concentrations • also need data above the surface (e.g., from aircraft) • also need source-impacted sites (not just background)

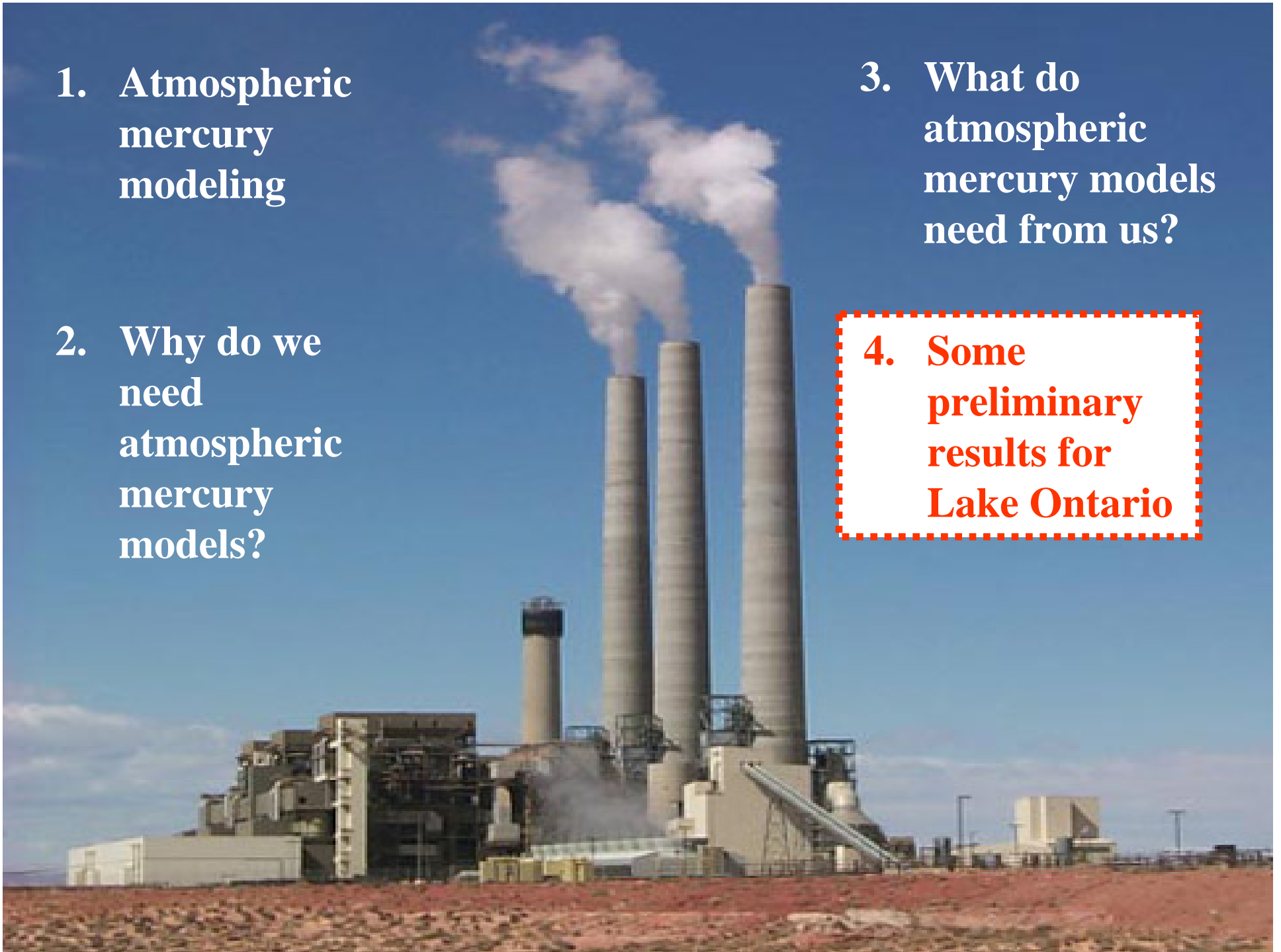|	some challenges facing mercury modeling
emissions inventories	• need *all* sources • accurately divided into *different Hg forms* • **U.S. 1996, 1999, 2003 / CAN 1995, 2000, 2005** • *temporal* variations (e.g. shut downs)
meteorological data	• precipitation not well characterized
scientific understanding	• what is RGM? what is Hg(p)? • accurate info for known reactions? • do we know all significant reactions? • natural emissions, re-emissions?
ambient data for model evaluation	• Mercury Deposition Network (MDN) is great, but: • also need RGM, Hg(p), and Hg(0) concentrations • also need data above the surface (e.g., from aircraft) • also need source-impacted sites (not just background)

|	**some challenges facing mercury modeling**
emissions inventories	• need *all* sources • accurately divided into *different Hg forms* • **U.S. 1996, 1999, 2003 / CAN 1995, 2000, 2005** • *temporal* variations (e.g. shut downs)
meteorological data	• precipitation not well characterized
scientific understanding	• what is RGM? what is Hg(p)? • accurate info for known reactions? • do we know all significant reactions? • natural emissions, re-emissions?
ambient data for model evaluation	• Mercury Deposition Network (MDN) is great, but: • also need RGM, Hg(p), and Hg(0) concentrations • also need data above the surface (e.g., from aircraft) • also need source-impacted sites (not just background)

1. **Atmospheric mercury modeling**

2. **Why do we need atmospheric mercury models?**

3. **What do atmospheric mercury models need from us?**

4. **Some preliminary results for Lake Ontario**

Sites with 1996 mercury wet deposition data in the Great Lakes region

Comparison of Modeled vs. Measured Cumulative Wet Deposition at Underhill Center, VT during 1996
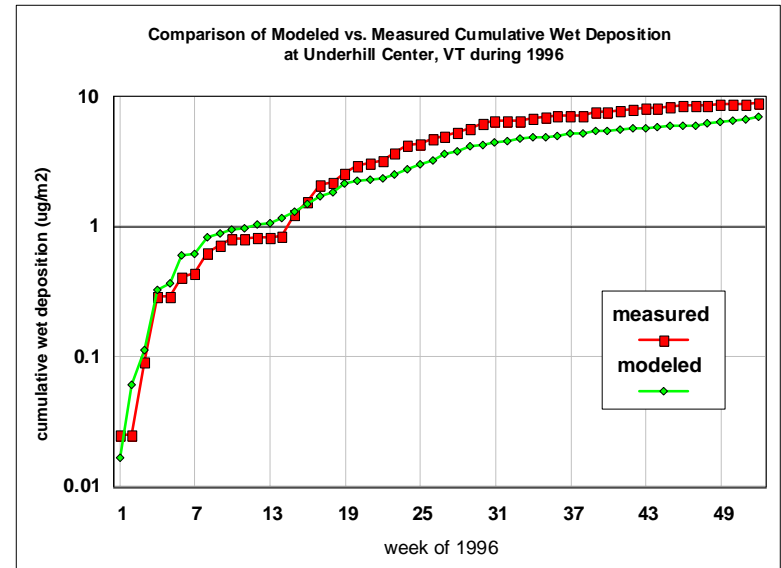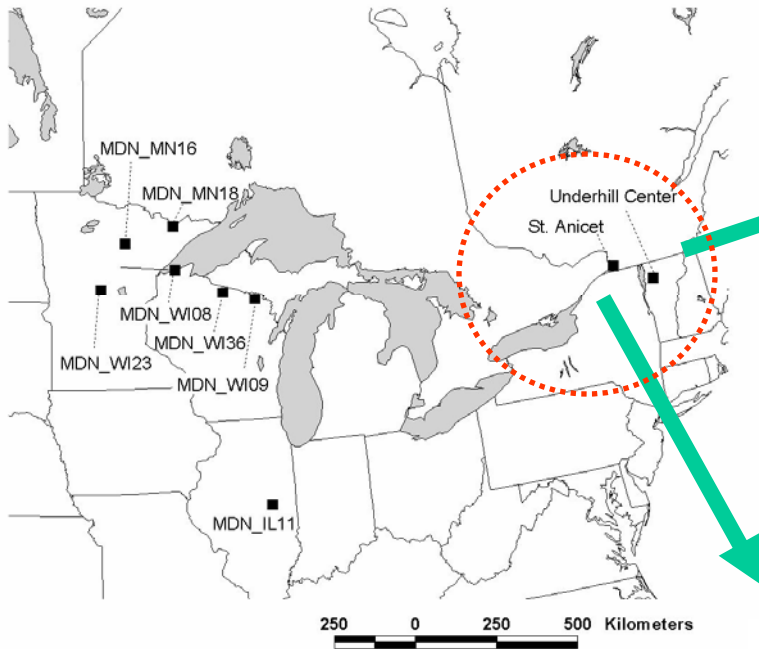
Seem to be getting reasonable results near Lake Ontario, but need to do much more evaluation…

Maybe we just got lucky!
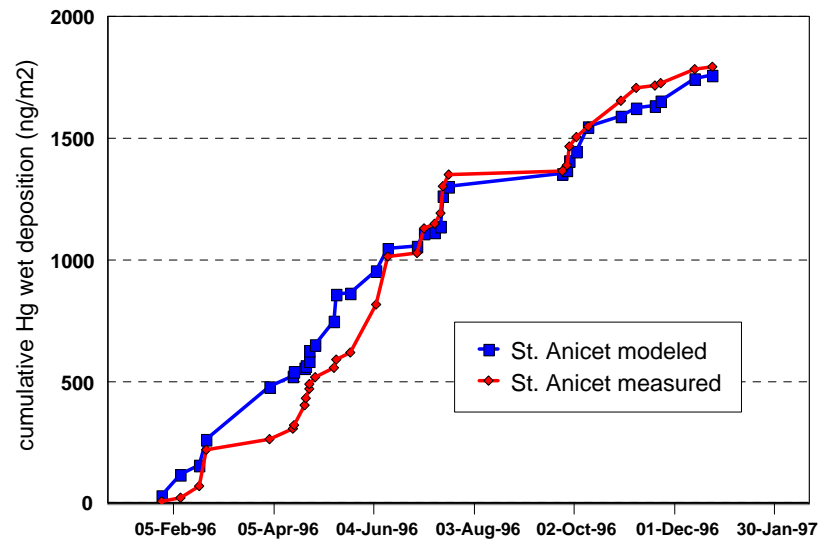
Where does the mercury come from that's deposited directly onto Lake Ontario?

Deposition Contribution of Source Area to Receptor (ug deposited / year per km² of receptor area) per (km² of source area)

Color	Range
	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

31
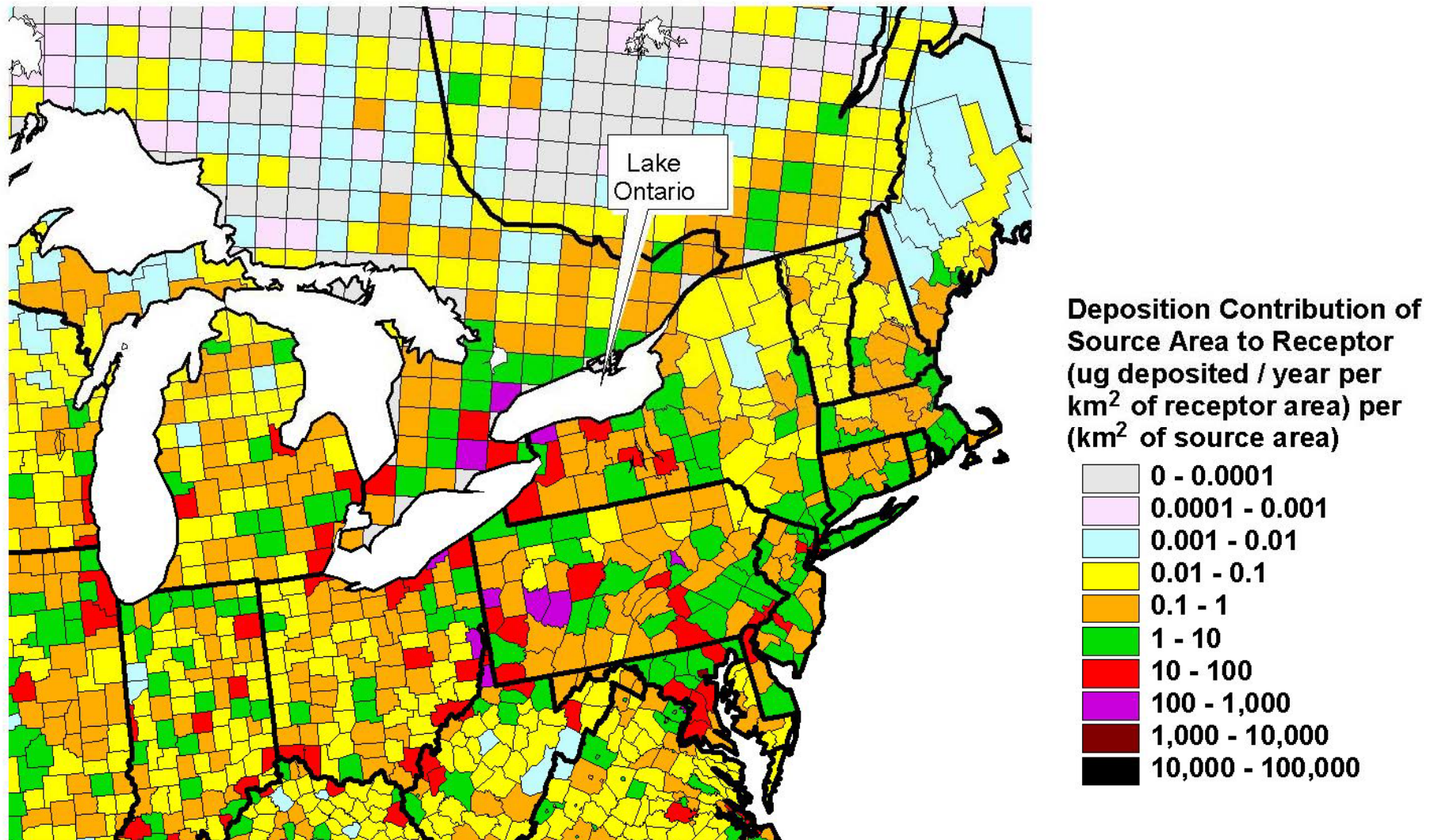
Largest atmospheric deposition contributors to Lake Ontario based on 1999-2000 emissions

Fraction of total modeled deposition contributed by a particular source

- ○ 0.1 - 0.3 %
- △ 0.3 - 1 %
- ⬠ 1 - 3 %
- ▢ 3 - 10 %
- ⬡ 10 - 30 %

Type of Emission Source

- 🟥 coal-fired electricity generation
- 🟦 waste incineration
- 🟨 manufacturing
- ⬜ metallurgical
- 🟩 other fuel combustion

1000   0   1000   2000   Kilometers

N

Fraction of total Modeled deposition Contributed by a Particular source

⬡	**0.1 - 0.3 %**
△	**0.3 - 1 %**
⬠	**1 - 3 %**
⬜	**3 - 10 %**
⬣	**10 - 30 %**

Type of Emission Source

- 🟥 coal-fired electricity generation
- 🟦 waste incineration
- 🟨 manufacturing
- ⬜ metallurgical
- 🟩 other fuel combustion

33

Total Atmos. Dep Flux to Lake Ontario (g Hg/km2-year)

Top 25 Contributors to Hg Deposition Directly to Lake Ontario based on 1999-2000 U.S./Canadian emissions

Rank (y-axis) vs. **Cumulative Fraction of Hg Deposition** (x-axis)

- OH ● Lubrizol Corp. (25)
- CAN ▼ DOFASCO (Hamilton) (24)
- NV ▼ JERRITT CANYON (23)
- WV ■ John E Amos (22)
- OH ■ W. H. Sammis (21)
- NY ● Univ. of Rochester (20)
- OH ■ Cardinal (19)
- OH ■ Conesville (18)
- PA ● Medusa Cement (17)
- PA ■ Bruce Mansfield (16)
- CAN ● Toronto Sewage Sludge Incin. (15)
- WV ■ Mt. Storm (14)
- OH ■ Eastlake (13)
- NY ■ Dunkirk (12)
- PA ■ Montour (11)
- PA ■ Shawville (10)
- NY ■ C. R. Huntley (9)
- NY ▢ Niagara Mohawk (8)
- CAN ● KMS Peel Incin. (7)
- MD ● Phoenix Services (6)
- CAN ■ NANTICOKE TGS (5)
- NY ● Niagara Falls Incin. (4)
- PA ■ Keystone (3)
- PA ■ Homer City (2)
- NY ● American Ref-Fuel (Niagara) (1)

Legend:
- ■ coal-fired elec gen
- ▲ other fuel combustion
- ● waste incineration
- ▼ metallurgical
- ▢ manufacturing/other

Some Next Steps

■ **Use more highly resolved meteorological data grid**

■ **Expand model domain to include global sources**

■ **Simulate natural emissions and re-emissions of previously deposited Hg**

■ **Additional model evaluation exercises ... more sites, more time periods, more variables *[Measurements in Chesapeake Bay region]***

■ **Sensitivity analyses and examination of atmospheric Hg chemistry (e.g. marine boundary layer, upper atmosphere)**

■ **Dynamic linkage with ecosystem cycling models**

Conclusions

■ **Source-attribution information is important**

■ **Impacts are episodic & depend on form of mercury emitted**

■ **Modeling needed to get source-attribution information**

■ **Not enough monitoring data to evaluate and improve models**

■ **Many uncertainties but useful model results are emerging**

■ **Models don't have to be perfect to give useful information**