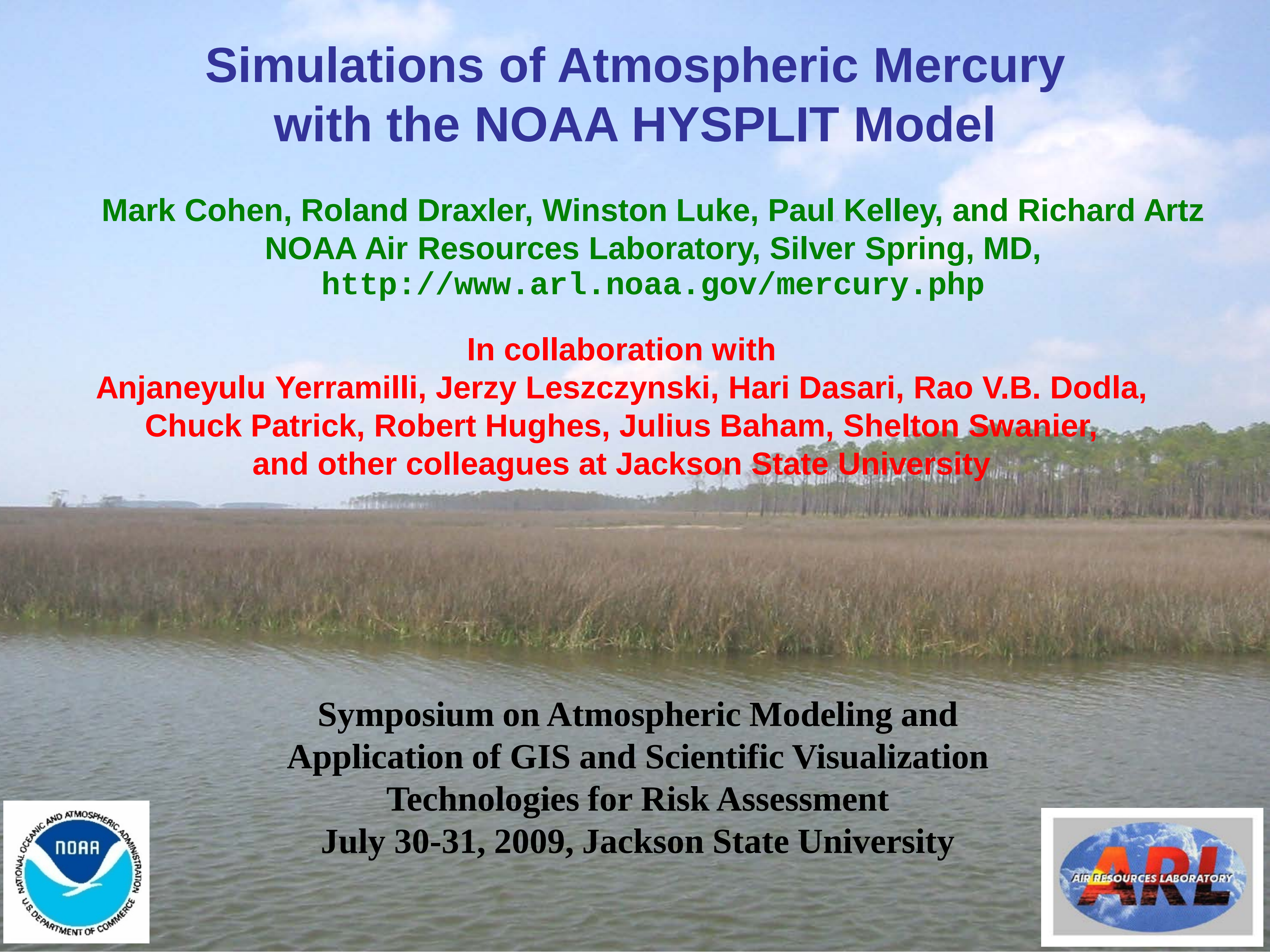


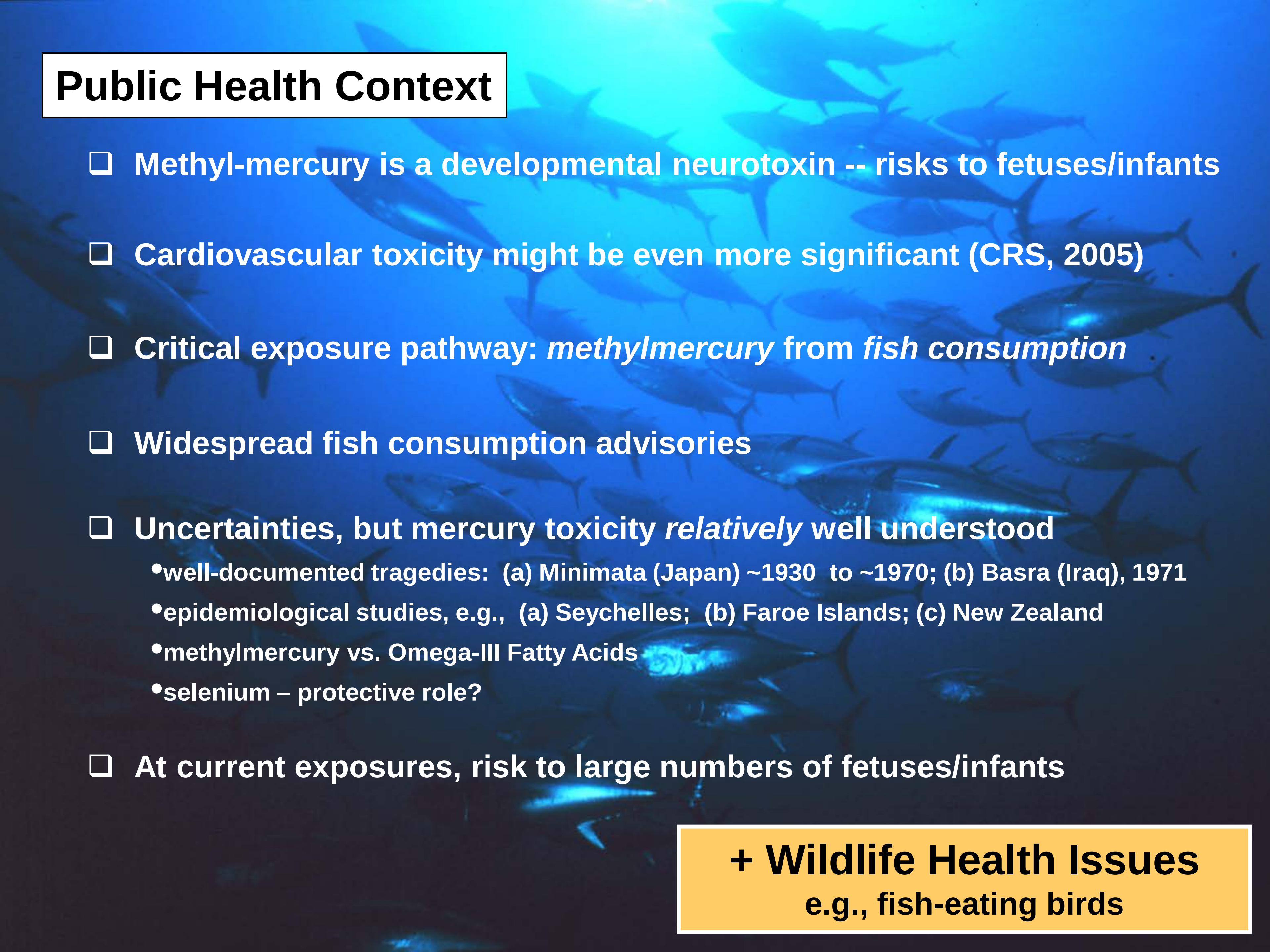
Simulations of Atmospheric Mercury with the NOAA HYSPLIT Model

Mark Cohen, Roland Draxler, Winston Luke, Paul Kelley, and Richard Artz
NOAA Air Resources Laboratory, Silver Spring, MD,
`http://www.arl.noaa.gov/mercury.php`

In collaboration with
Anjaneyulu Yerramilli, Jerzy Leszczynski, Hari Dasari, Rao V.B. Dodla,
Chuck Patrick, Robert Hughes, Julius Baham, Shelton Swanier,
and other colleagues at Jackson State University

Symposium on Atmospheric Modeling and Application of GIS and Scientific Visualization Technologies for Risk Assessment
July 30-31, 2009, Jackson State University

Public Health Context

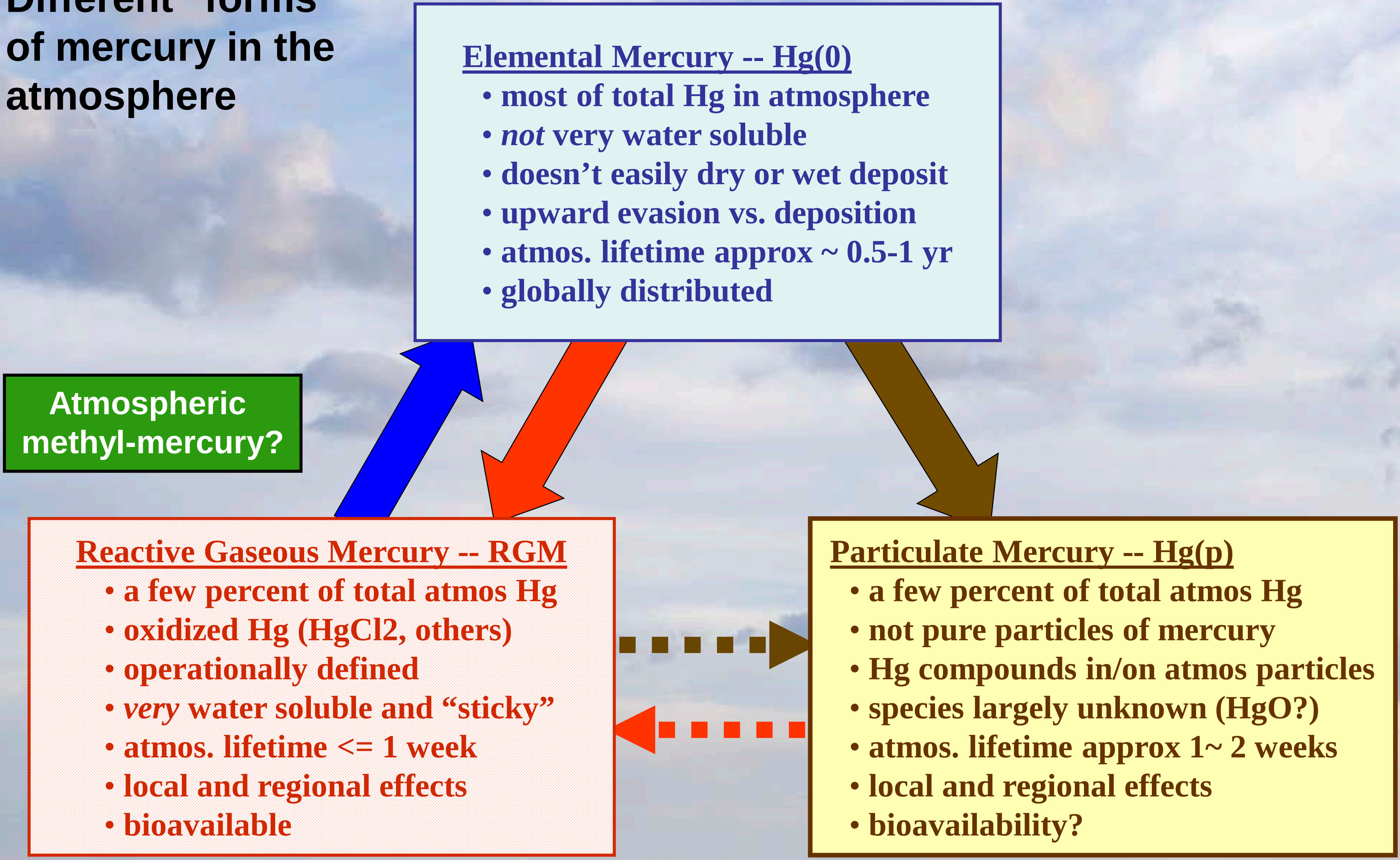


- Methyl-mercury is a developmental neurotoxin -- risks to fetuses/infants
- Cardiovascular toxicity might be even more significant (CRS, 2005)
- Critical exposure pathway: *methylmercury* from *fish consumption*
- Widespread fish consumption advisories
- Uncertainties, but mercury toxicity *relatively* well understood
  - well-documented tragedies: (a) Minimata (Japan) ~1930 to ~1970; (b) Basra (Iraq), 1971
  - epidemiological studies, e.g., (a) Seychelles; (b) Faroe Islands; (c) New Zealand
  - methylmercury vs. Omega-III Fatty Acids
  - selenium – protective role?
- At current exposures, risk to large numbers of fetuses/infants

+ Wildlife Health Issues

e.g., fish-eating birds

Different "forms" of mercury in the atmosphere



Elemental Mercury -- Hg(0)

- most of total Hg in atmosphere
- *not* very water soluble
- doesn't easily dry or wet deposit
- upward evasion vs. deposition
- atmos. lifetime approx ~ 0.5-1 yr
- globally distributed

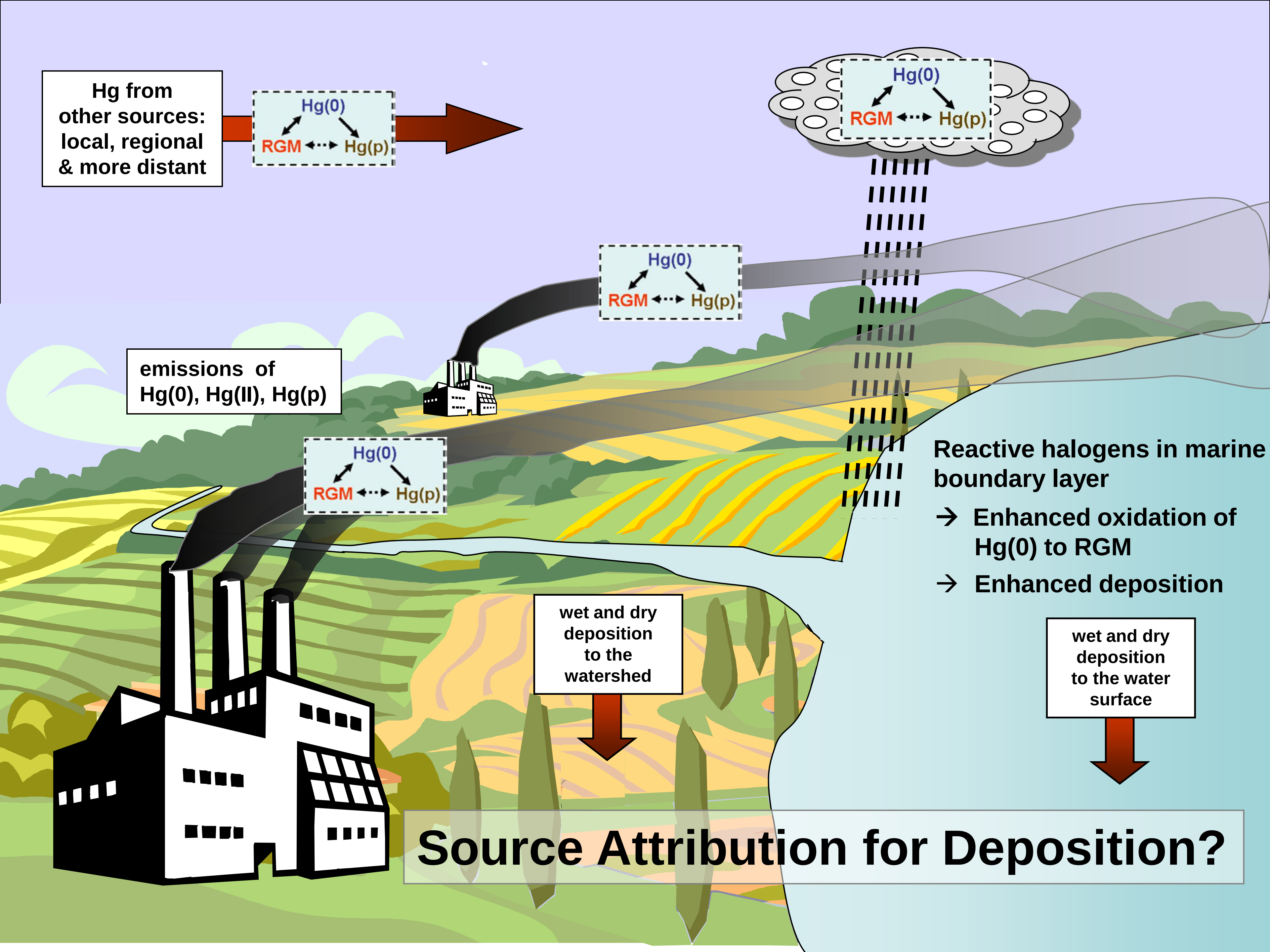
Atmospheric methyl-mercury?

Reactive Gaseous Mercury -- RGM

- a few percent of total atmos Hg
- oxidized Hg (HgCl2, others)
- operationally defined
- *very* water soluble and "sticky"
- atmos. lifetime <= 1 week
- local and regional effects
- bioavailable

Particulate Mercury -- Hg(p)

- a few percent of total atmos Hg
- not pure particles of mercury
- Hg compounds in/on atmos particles
- species largely unknown (HgO?)
- atmos. lifetime approx 1~ 2 weeks
- local and regional effects
- bioavailability?



Hg from
other sources:
local, regional
& more distant

emissions of
Hg(0), Hg(II), Hg(p)

Reactive halogens in marine boundary layer

→ Enhanced oxidation of Hg(0) to RGM

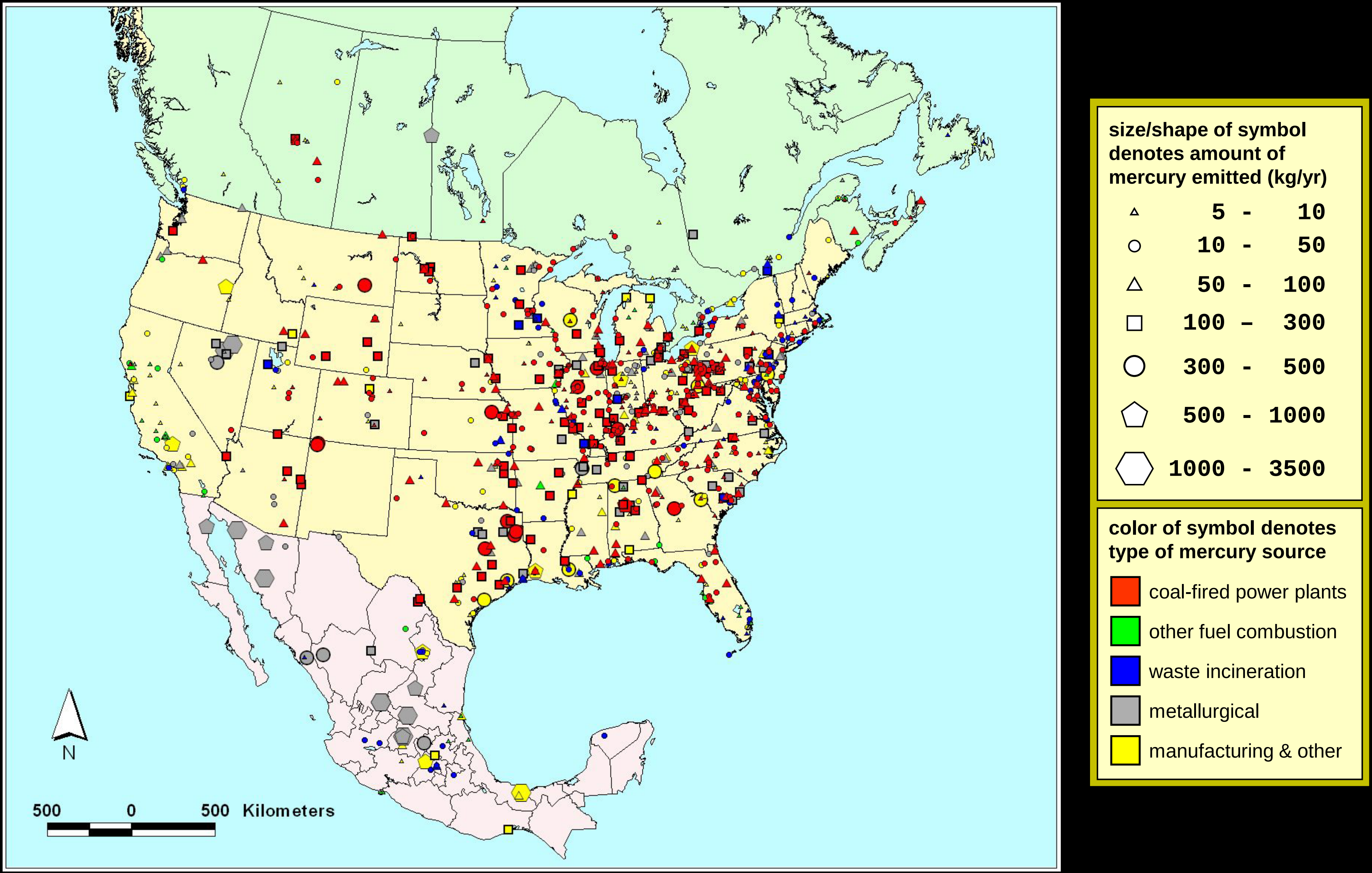
→ Enhanced deposition

wet and dry deposition to the watershed

wet and dry deposition to the water surface

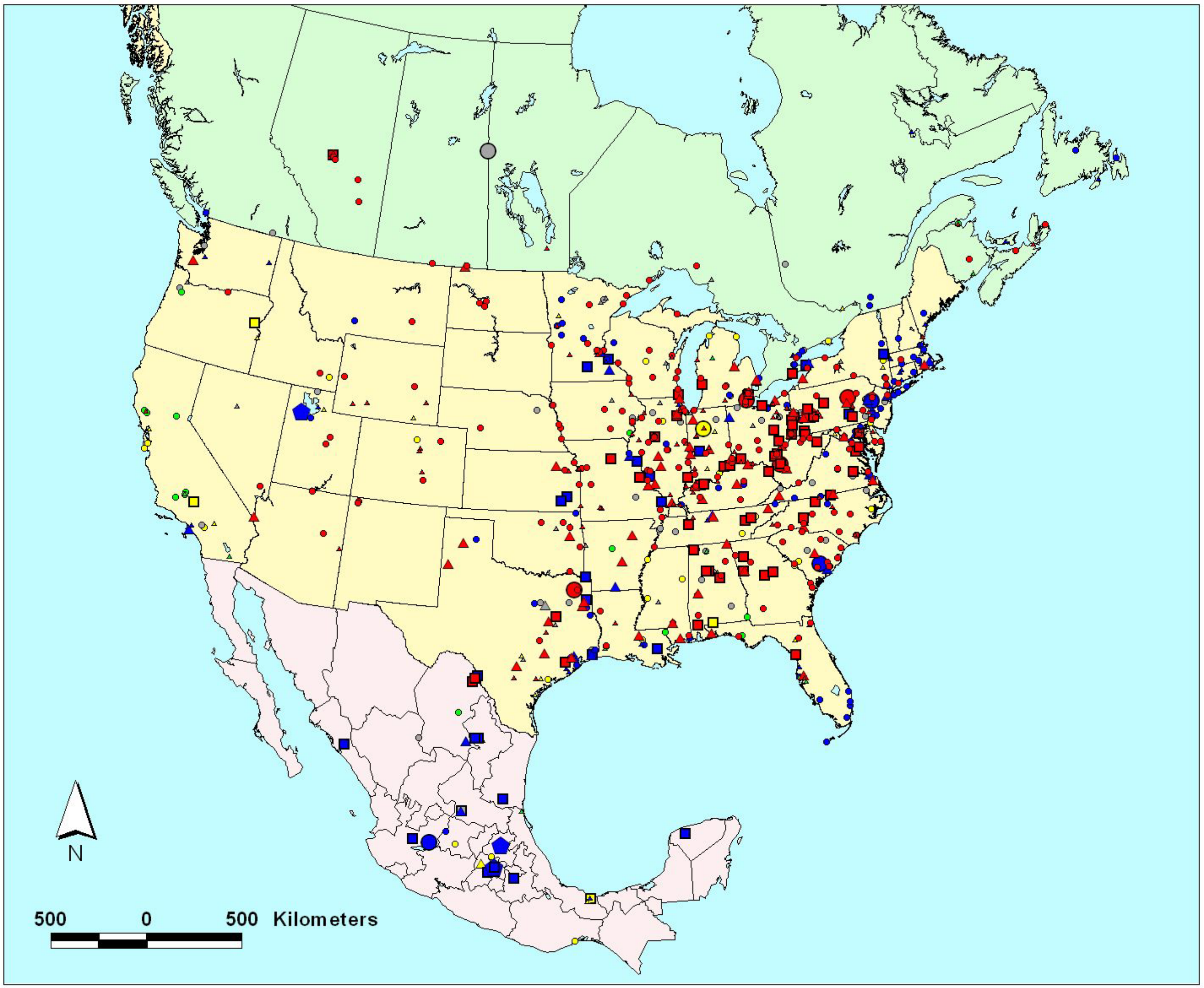
Source Attribution for Deposition?

Elemental Mercury -- Hg(0) -- Emissions to the Air



2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada;
1999 Mexican data from inventory prepared by *Acosta y Asociados* for the Commission for Environmental Cooperation

Reactive Gaseous Mercury – RGM -- Emissions to the Air



size/shape of symbol denotes amount of mercury emitted (kg/yr)

▵	5 - 10
○	10 - 50
△	50 - 100
□	100 – 300
◯	300 - 500
⬠	500 - 1000
⬡	1000 - 3500

color of symbol denotes type of mercury source

🟥	coal-fired power plants
🟩	other fuel combustion
🟦	waste incineration
▨	metallurgical
🟨	manufacturing & other

2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada;
1999 Mexican data from inventory prepared by *Acosta y Asociados* for the Commission for Environmental Cooperation

Particulate Mercury -- Hg(p) -- Emissions to the Air

size/shape of symbol denotes amount of mercury emitted (kg/yr)

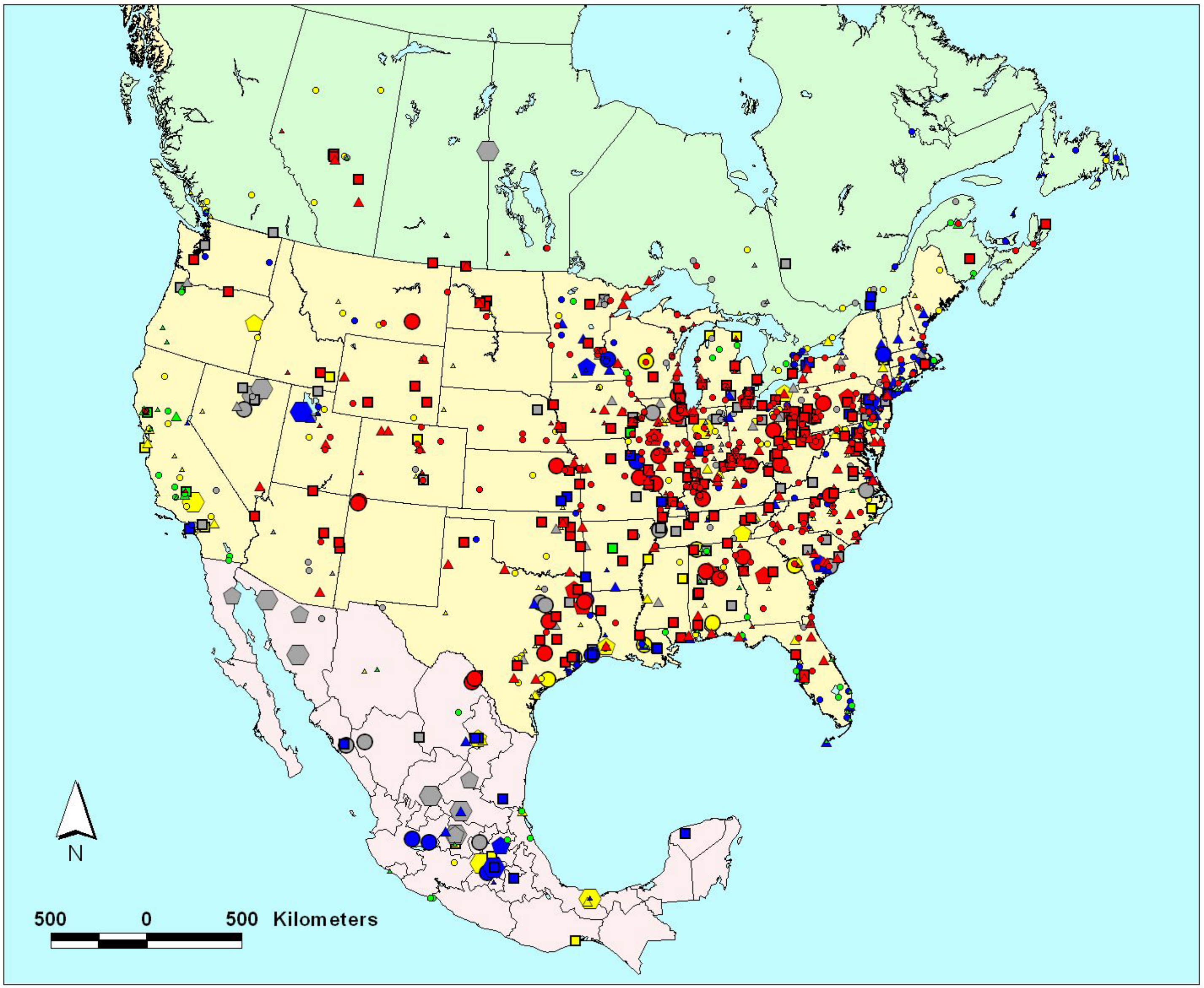
▵	5 - 10
○	10 - 50
△	50 - 100
□	100 – 300
◯	300 - 500
⬠	500 - 1000
⬡	1000 - 3500

color of symbol denotes type of mercury source

🟥	coal-fired power plants
🟩	other fuel combustion
🟦	waste incineration
▨	metallurgical
🟨	manufacturing & other

2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada;
1999 Mexican data from inventory prepared by *Acosta y Asociados* for the Commission for Environmental Cooperation

Total Mercury Emissions to the Air [Hg(0) + RGM + Hg(p)]



size/shape of symbol denotes amount of mercury emitted (kg/yr)

▵	5 - 10
○	10 - 50
△	50 - 100
□	100 – 300
◯	300 - 500
⬠	500 - 1000
⬡	1000 - 3500

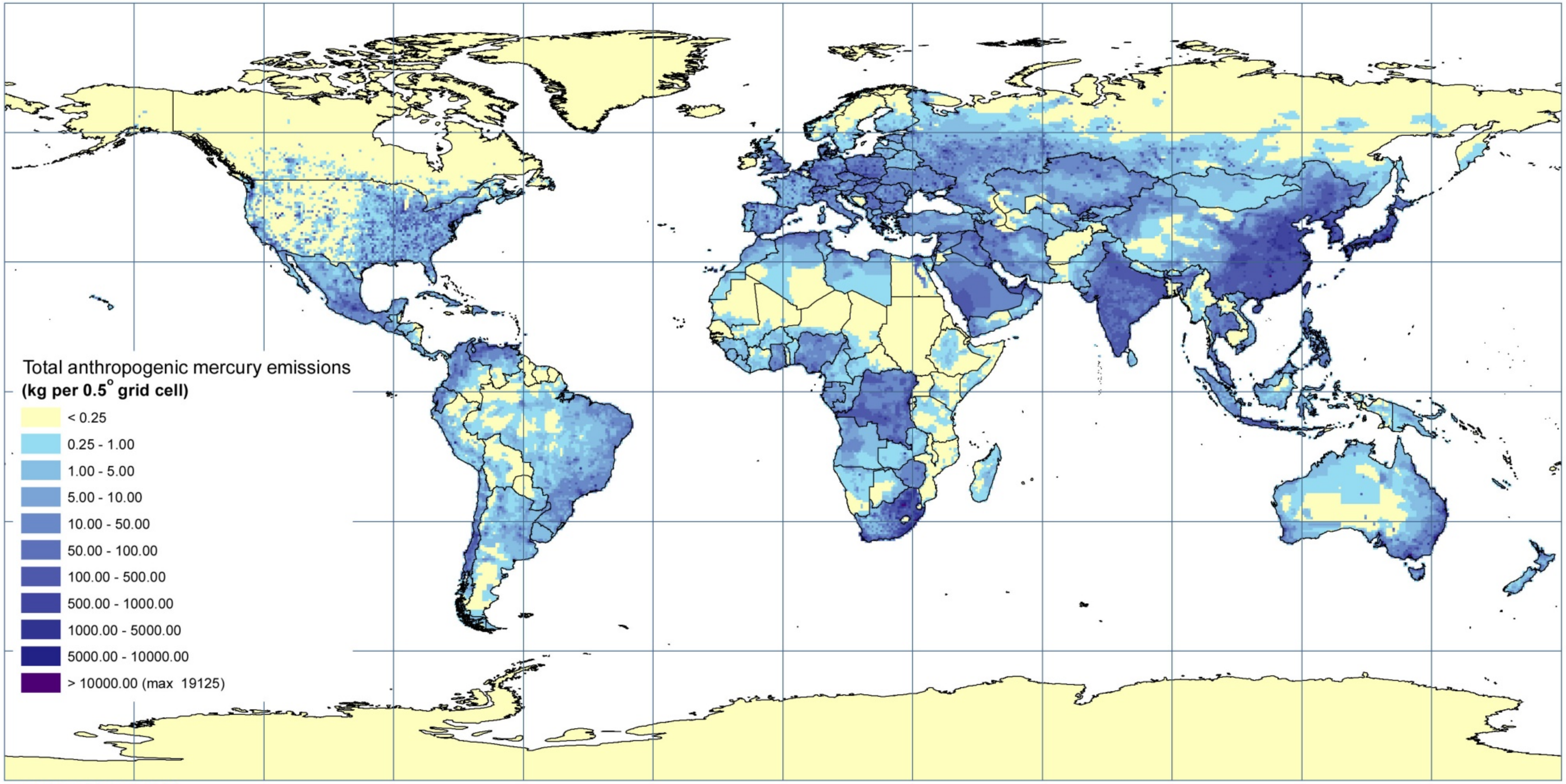
color of symbol denotes type of mercury source

🟥	coal-fired power plants
🟩	other fuel combustion
🟦	waste incineration
⬜	metallurgical
🟨	manufacturing & other

2002 U.S. data from USEPA National Emissions Inventory (NEI); 2002 Canadian data from Environment Canada;
1999 Mexican data from inventory prepared by *Acosta y Asociados* for the Commission for Environmental Cooperation

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

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

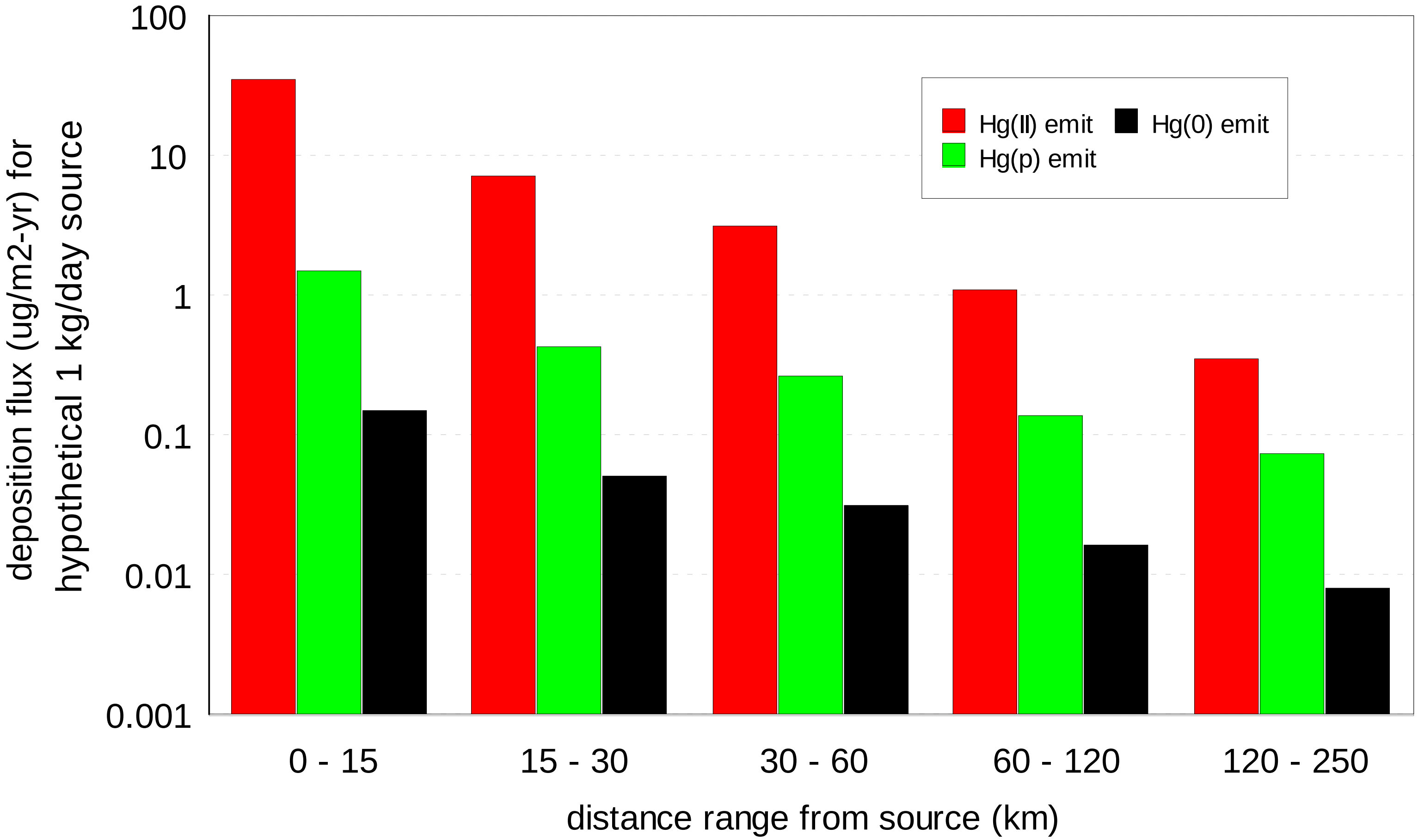


unprojected (geographic)

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)

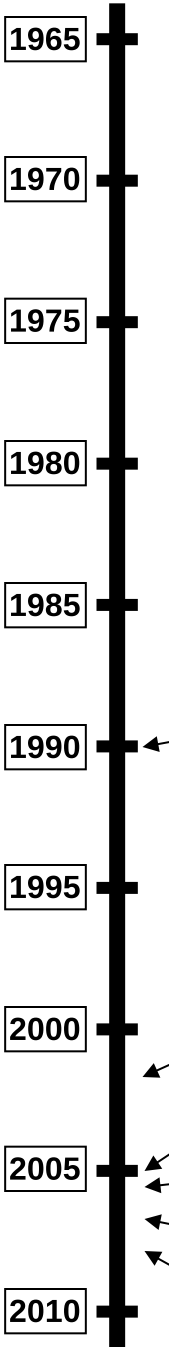
Why is emissions speciation information critical?

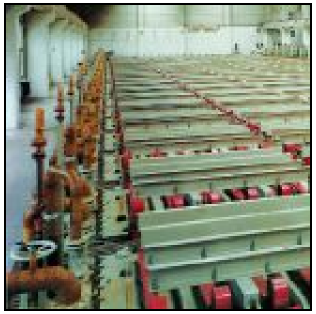


Logarithmic

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

Some events in the U.S. regulation and prevention of mercury emissions





1970's - 1990's:
many mercury-cell chlor-alkali plants converted to alternate processes or closed due to regulatory and other pressures

Clean Air Act Amendments of 1990 – calls for Maximum Achievable Control Technology (MACT) to regulate hazardous air pollutants; *intent is to prohibit emissions trading for these air toxics*

1990's – Hg emissions from municipal and medical waste incinerators fall dramatically due to:

- **closure of *some* municipal waste incinerators and *many* medical waste incinerators**
- **MACT-related pollution control requirements**
- **reduction in mercury content of waste (e.g., battery legislation)**

2002 – Clear Skies Initiative for power plants introduced *(ultimately withdrawn)*

2005 – CAIR (Clean Air Interstate Rule) for power plants (Hg reduced as co-benefit of SO_2 & NO_x controls)

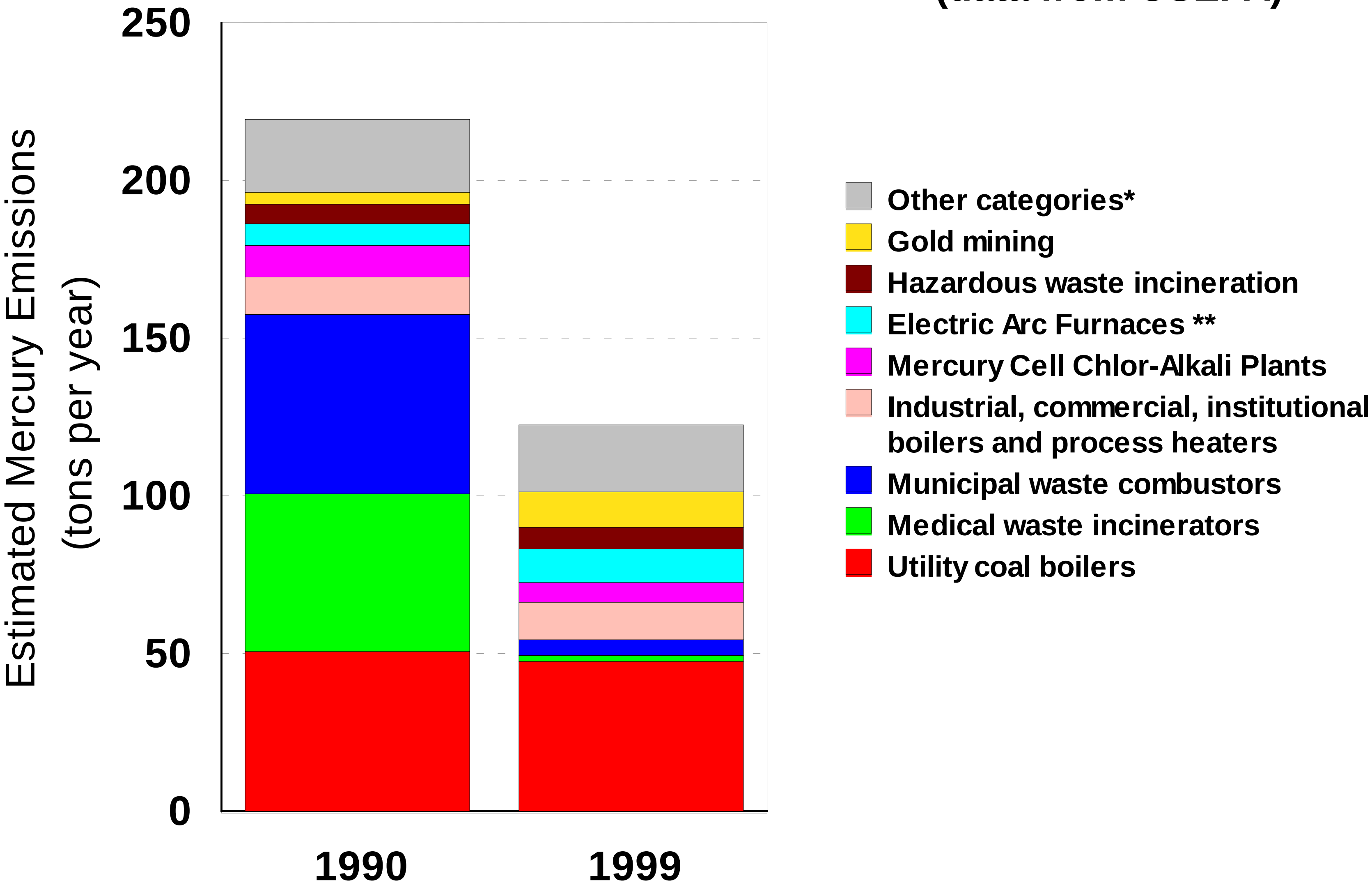
2005 – EPA meets court-ordered deadline and promulgates CAMR (Clean Air Mercury Rule) for power plants – *based on Hg emissions trading*

"Hot Spot" Controversy -- Many States sue EPA & propose / promulgate more strict regulations

2008 – CAMR and CAIR overturned... What is next?

Direct, Anthropogenic Mercury Emissions in the United States

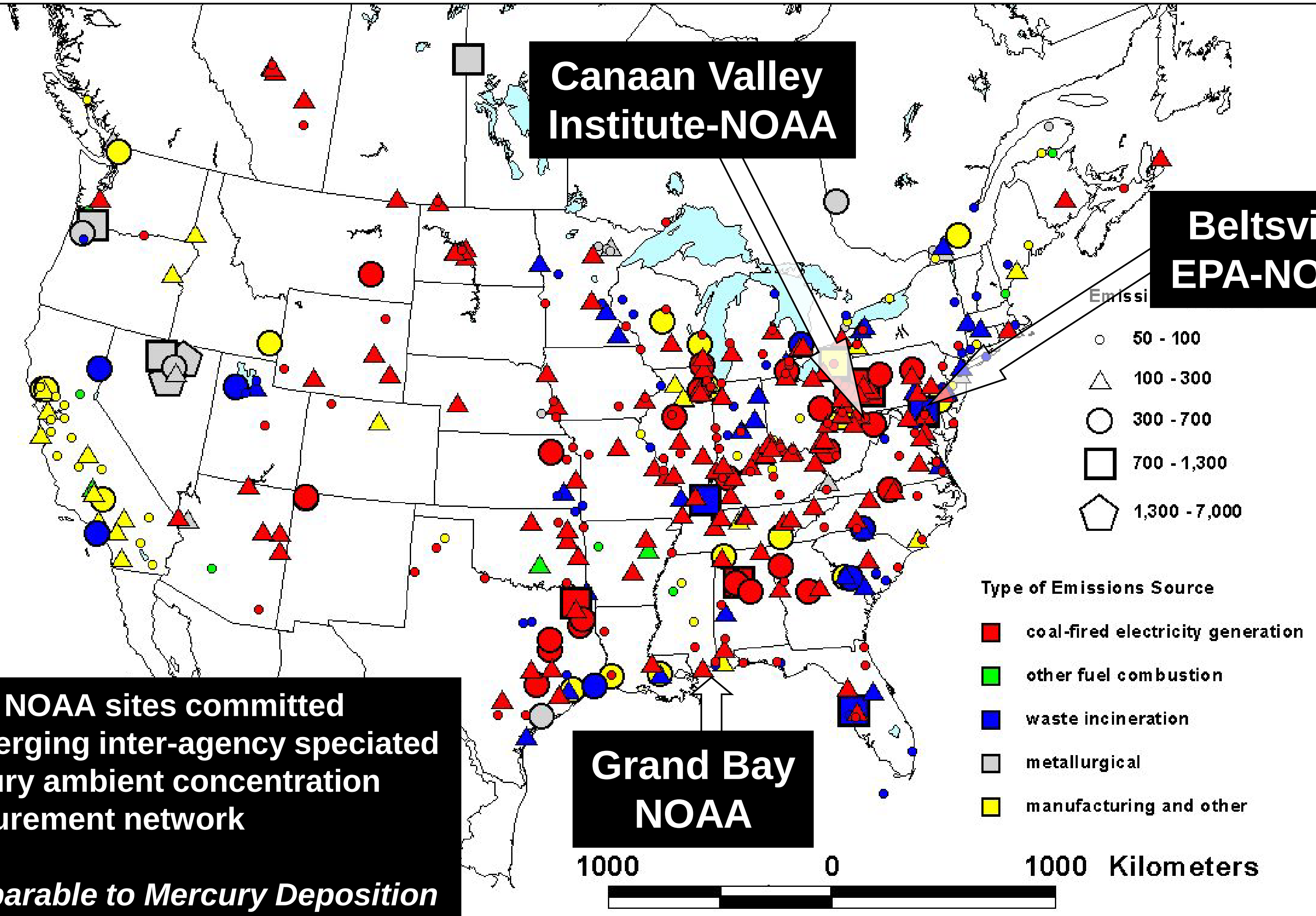
(data from USEPA)



* 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.

Largest sources of total mercury emissions to the air in the U.S. and Canada, based on the U.S. EPA 1999 National Emissions Inventory and 1995-2000 data from Environment Canada



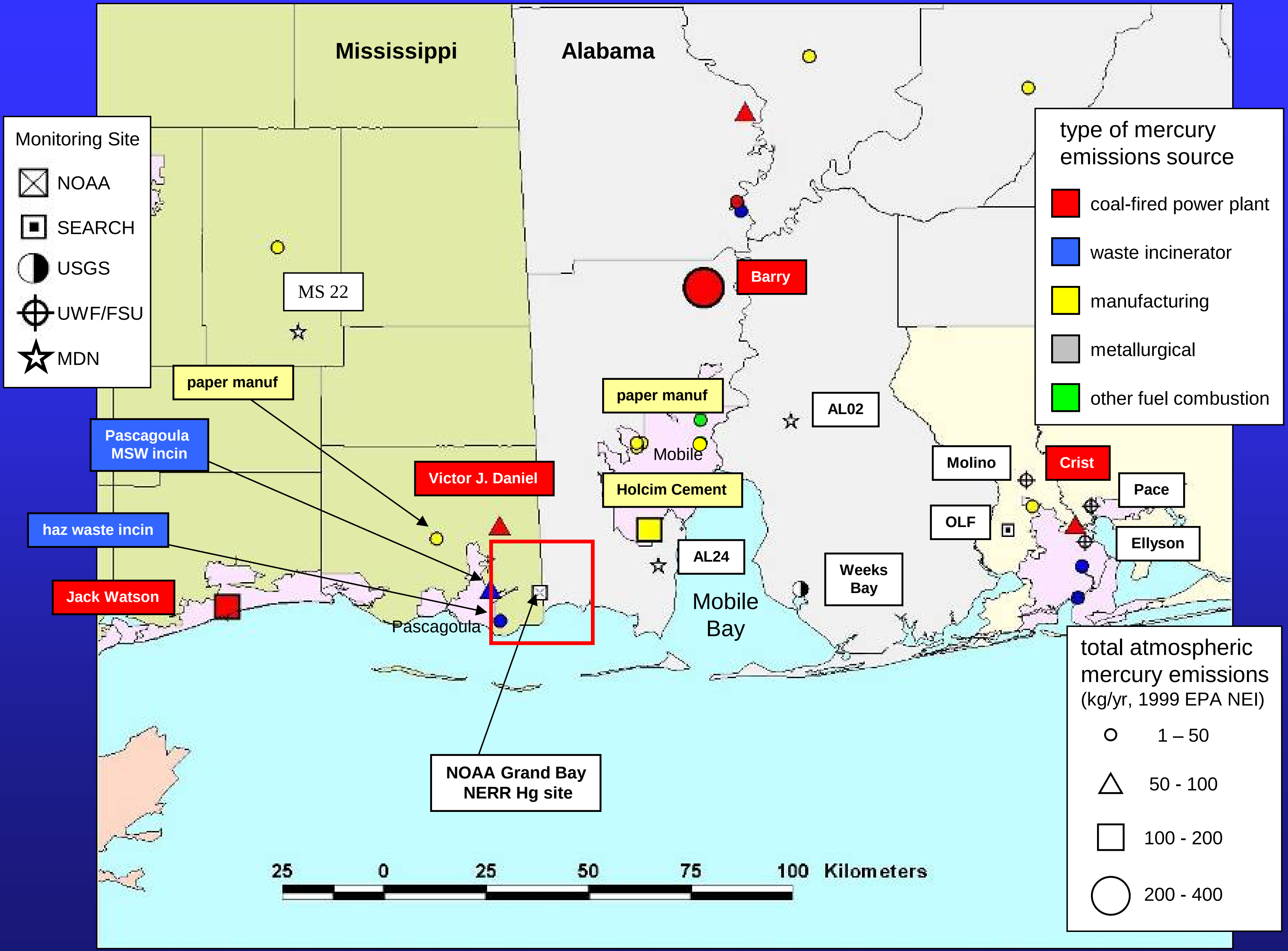
Canaan Valley Institute-NOAA

Beltsville EPA-NOAA

Grand Bay NOAA

Three NOAA sites committed to emerging inter-agency speciated mercury ambient concentration measurement network

(comparable to Mercury Deposition Network (MDN) for wet deposition, but for air concentrations)


Mississippi
Alabama
Monitoring Site
☒ NOAA
▣ SEARCH
◐ USGS
⊕ UWF/FSU
☆ MDN
MS 22
paper manuf
Pascagoula MSW incin
haz waste incin
Jack Watson
Victor J. Daniel
Pascagoula
NOAA Grand Bay NERR Hg site
Barry
paper manuf
Mobile
Holcim Cement
AL02
AL24
Mobile Bay
Weeks Bay
Molino
OLF
Crist
Pace
Ellyson
type of mercury emissions source
🟥 coal-fired power plant
🟦 waste incinerator
🟨 manufacturing
⬜ metallurgical
🟩 other fuel combustion
total atmospheric mercury emissions (kg/yr, 1999 EPA NEI)
○ 1 – 50
△ 50 - 100
□ 100 - 200
○ 200 - 400
25
0
25
50
75
100
Kilometers

Atmospheric Mercury Measurement Site at the Grand Bay NERR, MS

view from top of the tower

mercury and trace gas
monitoring tower
(10 meters)

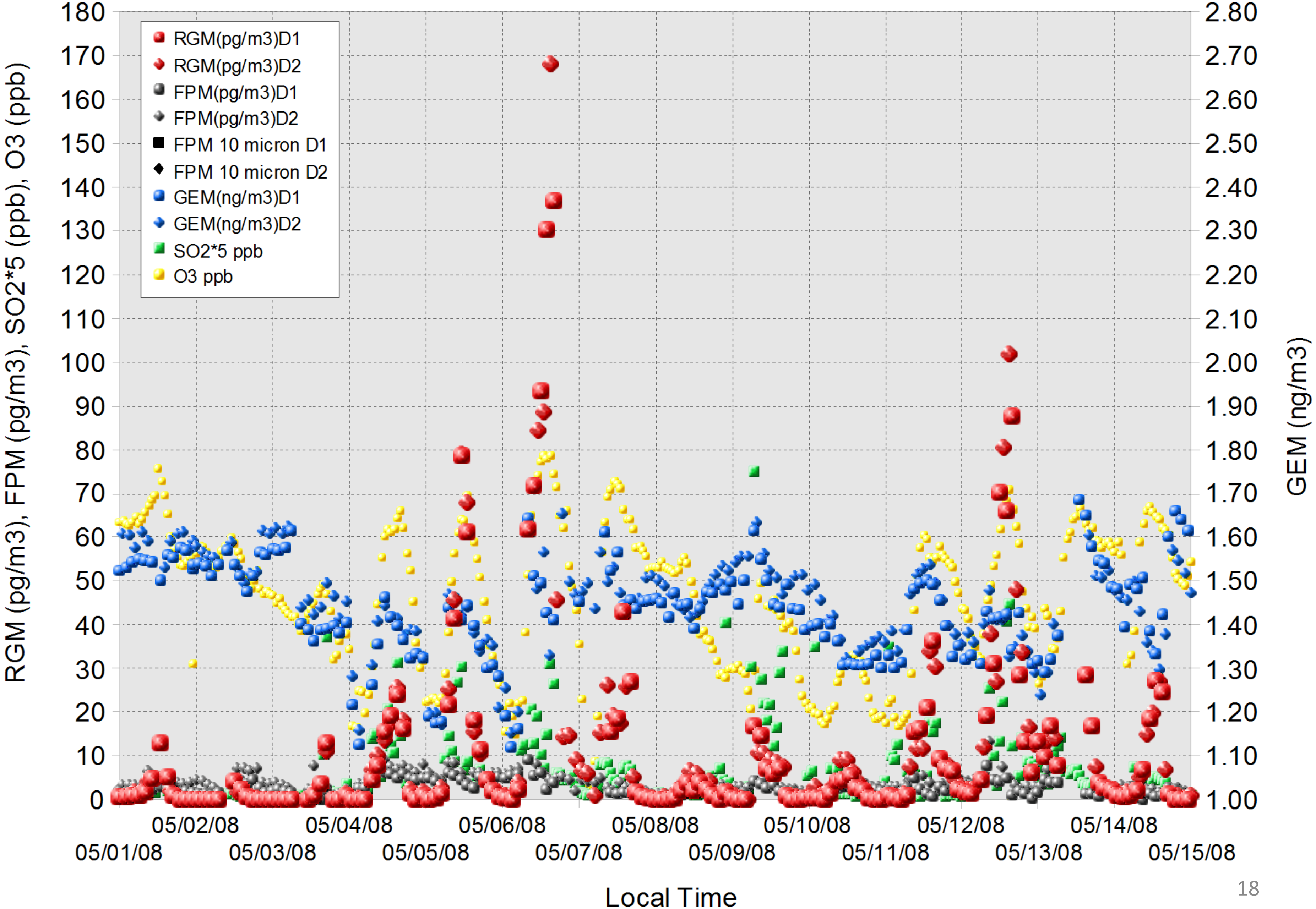
Atmospheric Measurements at the Grand Bay NERR

Elemental mercury * 2	“Speciated” Atmospheric Mercury Concentrations
Fine particulate mercury * 2	
Reactive gaseous mercury * 2	
Sulfur dioxide	Trace gases to help understand and interpret mercury data
Ozone	
Carbon Monoxide	
Nitrogen Oxides (NO, NOy)	
Wind speed, Wind Direction	Meteorological Data
Temperature, Relative Humidity	
Precipitation Amount	
Total Mercury & Methyl Mercury in Precipitation	WET DEPOSITION: Currently being added, in collaboration with MS DEQ and U.S. EPA
Trace Metals in Precipitation	
Major Ions in Precipitation	

Instrumentation inside the trailer at the Grand Bay NERR site

Speciated Atmospheric Mercury and Selected Trace Gas Concentration Measurements at Grand Bay NERR

Courtesy of Winston Luke and Paul Kelley (NOAA ARL) and Jake Walker (Grand Bay NERR) (Preliminary Values)



Can we learn what is needed about atmospheric mercury deposition by making atmospheric measurements alone?

NO…

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:

  - **different source regions (local, regional, national, global)**
  - **different jurisdictions (different states and provinces)**
  - **anthropogenic vs. natural emissions**
  - **different source types (power plants, waste incin., smelters…)**

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:
  - different source regions (local, regional, national, global)
  - different jurisdictions (different states and provinces)
  - anthropogenic vs. natural emissions
  - different source types (power plants, waste incin., smelters…)

- to estimate *deposition over large regions*

  …because deposition fields are highly spatially variable,

  and one can't measure everywhere all the time…

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:
  - different source regions (local, regional, national, global)
  - different jurisdictions (different states and provinces)
  - anthropogenic vs. natural emissions
  - different source types (power plants, waste incin., smelters…)

- 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***

  ... presently, dry deposition can only be estimated via models

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:

  - **different source regions (local, regional, national, global)**
  - **different jurisdictions (different states and provinces)**
  - **anthropogenic vs. natural emissions**
  - **different source types (power plants, waste incin., smelters…)**

- **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***

  ... presently, dry deposition can only be estimated via models

- **to evaluate *potential consequences* of future emissions scenarios**

Models are not perfect

“…Everyone believes monitoring results except for the person making the measurements… and nobody believes modeling results except for the person doing the modeling…”

How not perfect are they?

Results are encouraging, but difficult to evaluate models due to lack of contemporaneous monitoring and emissions inventory data

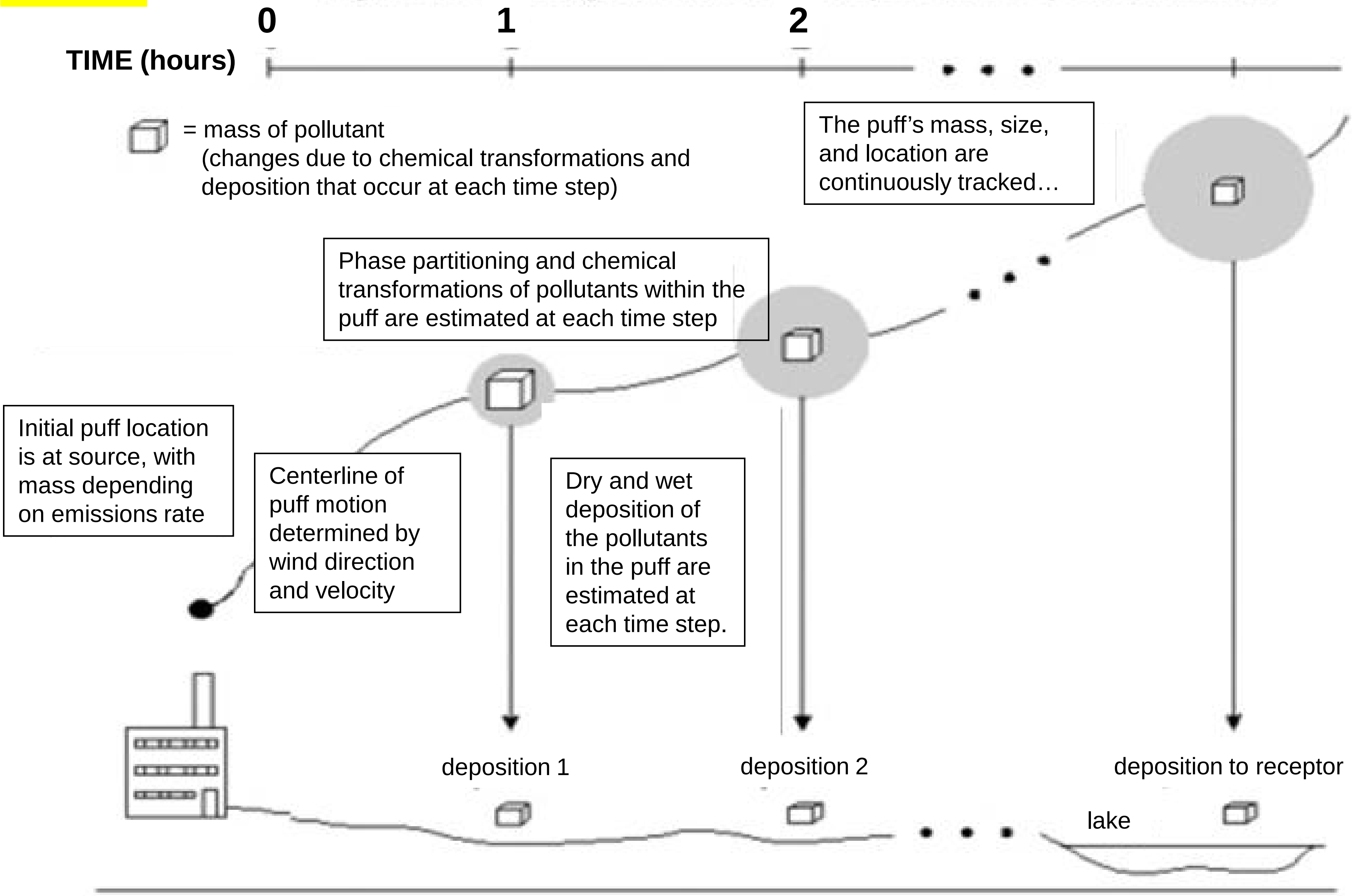
Models are a test of our knowledge…

If they don’t work, fundamental things about our understanding of atmospheric mercury that are wrong or incomplete…

More certain info at a few locations (monitoring) vs. less certain info region-wide (modeling)

NOAA HYSPLIT MODEL

Lagrangian Puff Atmospheric Fate and Transport Model



= mass of pollutant
(changes due to chemical transformations and deposition that occur at each time step)

The puff's mass, size, and location are continuously tracked…

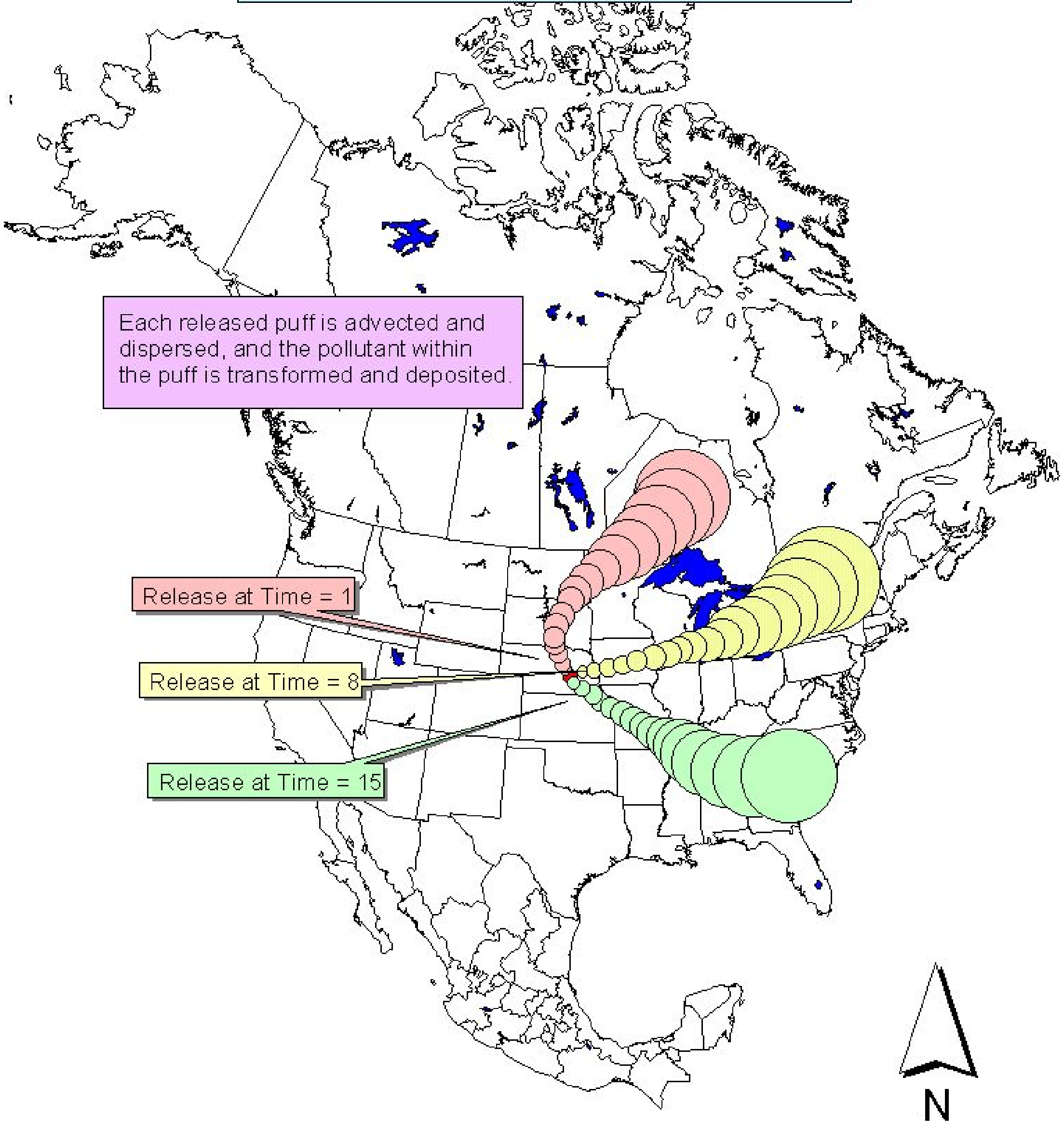
Phase partitioning and chemical transformations of pollutants within the puff are estimated at each time step

Initial puff location is at source, with mass depending on emissions rate

Centerline of puff motion determined by wind direction and velocity

Dry and wet deposition of the pollutants in the puff are estimated at each time step.

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

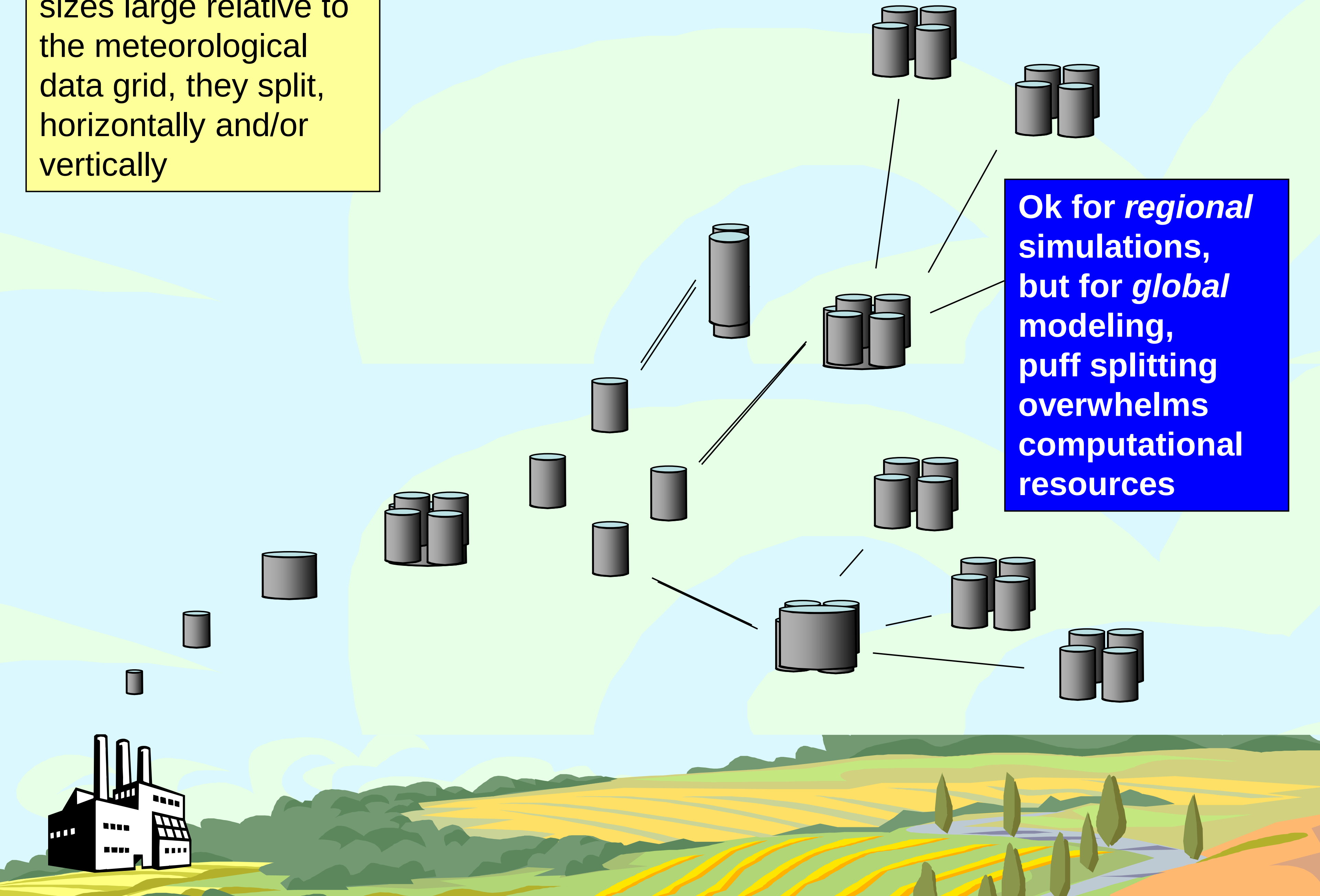
(Evolving) Atmospheric Chemical Reaction Scheme for Mercury

	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)
?	$Hg^0 + OH \rightarrow Hg(p)$	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
new	$Hg^0 + Br \rightarrow HgBr_2$			
	AQUEOUS PHASE REACTIONS			
	$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(\text{molar-sec})^{-1}$	Munthe (1992)
	$Hg^0 + OH \rightarrow Hg^{+2}$	2.0E+9	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1997)
	$HgSO_3 \rightarrow Hg^0$	$T{*}e^{((31.971{*}T)-12595.0)/T)}$ [T = temperature (K)]	sec^{-1}	Van Loon et al. (2002)
?	$Hg(II) + HO_2 \rightarrow Hg^0$	~ 0	$(\text{molar-sec})^{-1}$	Gardfeldt & Jonnson (2003)
	$Hg^0 + HOCl \rightarrow Hg^{+2}$	2.1E+6	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1998)
	$Hg^0 + OCl^{-1} \rightarrow Hg^{+2}$	2.0E+6	$(\text{molar-sec})^{-1}$	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).
	$Hg^{+2} + hv \rightarrow Hg^0$	6.0E-7	$(sec)^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

(Evolving) Atmospheric Chemical Reaction Scheme for Mercury

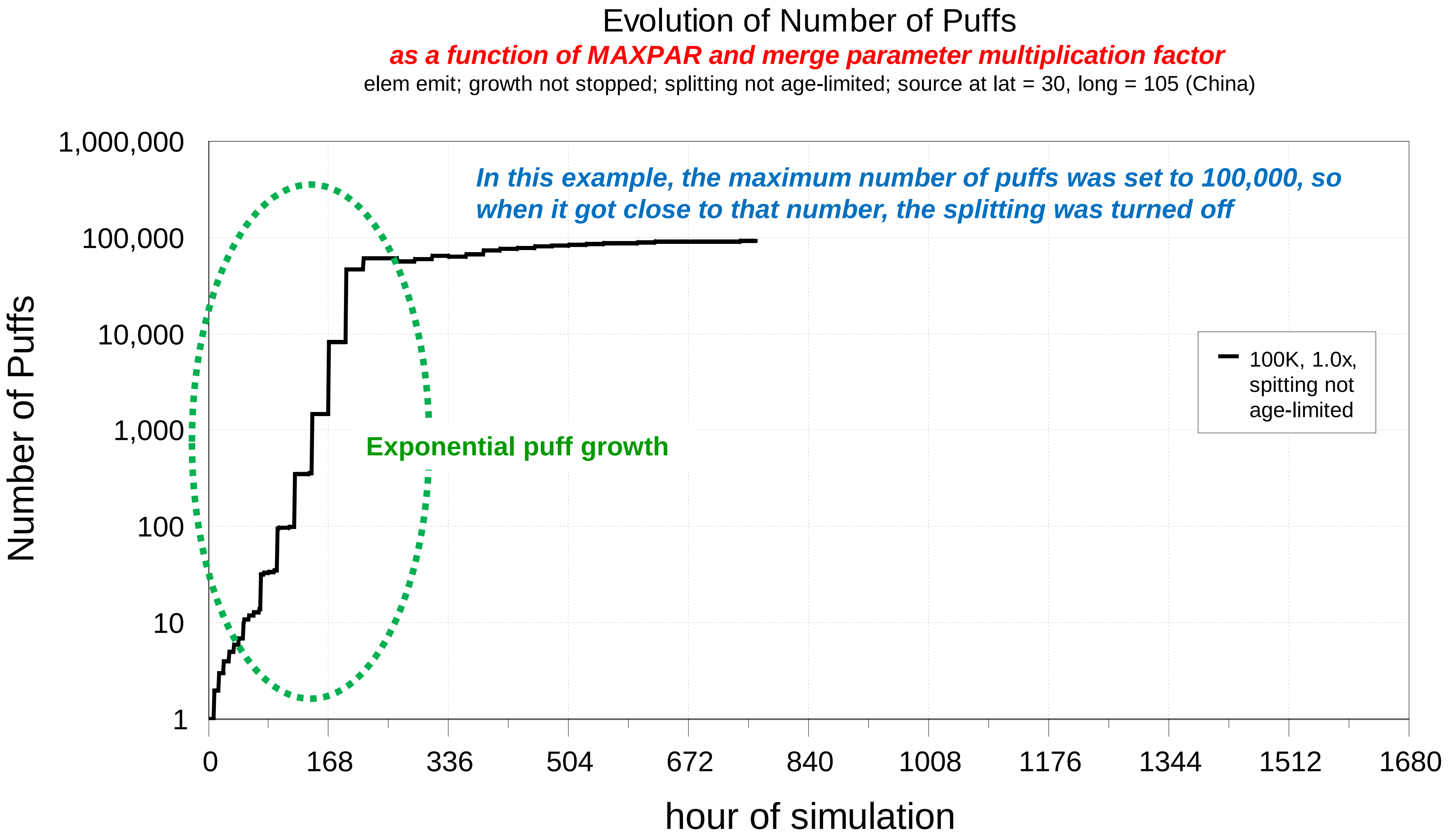
	Reaction	**Rate**	**Units**	**Reference**
	GAS PHASE REACTIONS			
?	$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm^3/molec-sec	Hall (1995)
	$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
	$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
	$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm^3/molec-sec	Calhoun and Prestbo (2001)
?	$Hg^0 + OH \rightarrow Hg(p)$	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
new	$Hg^0 + Br \rightarrow HgBr_2$			
	AQUEOUS PHASE REACTIONS			
	$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(molar\text{-}sec)^{-1}$	Munthe (1992)
	$Hg^0 + OH \rightarrow Hg^{+2}$	2.0E+9	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1997)
	$HgSO_3 \rightarrow Hg^0$	$T*e^{((31.971*T)-12595.0)/T)}$ [T = temperature (K)]	sec^{-1}	Van Loon et al. (2002)
?	$Hg(II) + HO_2 \rightarrow Hg^0$	~ 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).
	$Hg^{+2} + hv \rightarrow Hg^0$	6.0E-7	$(sec)^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

When puffs grow to sizes large relative to the meteorological data grid, they split, horizontally and/or vertically

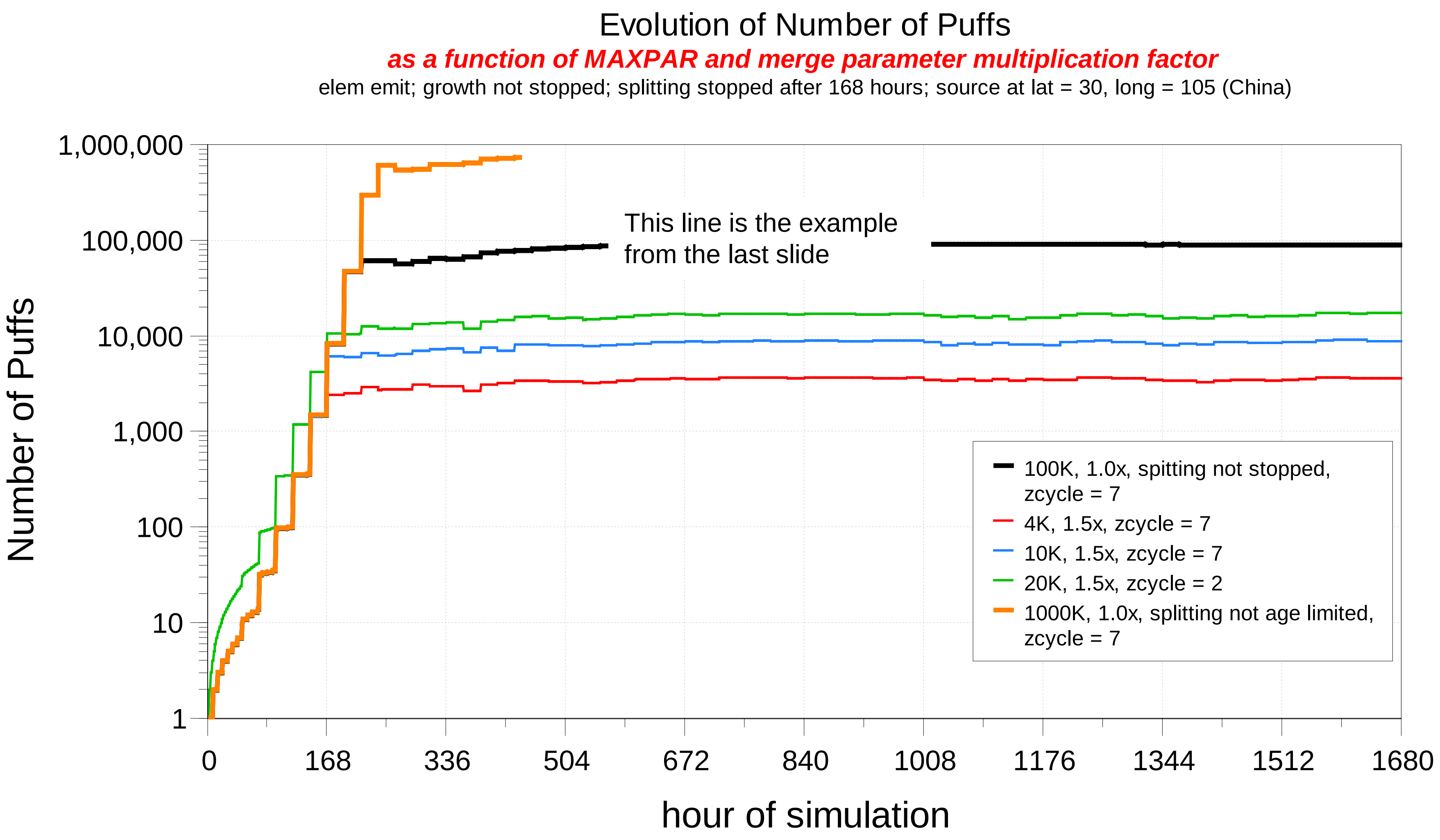


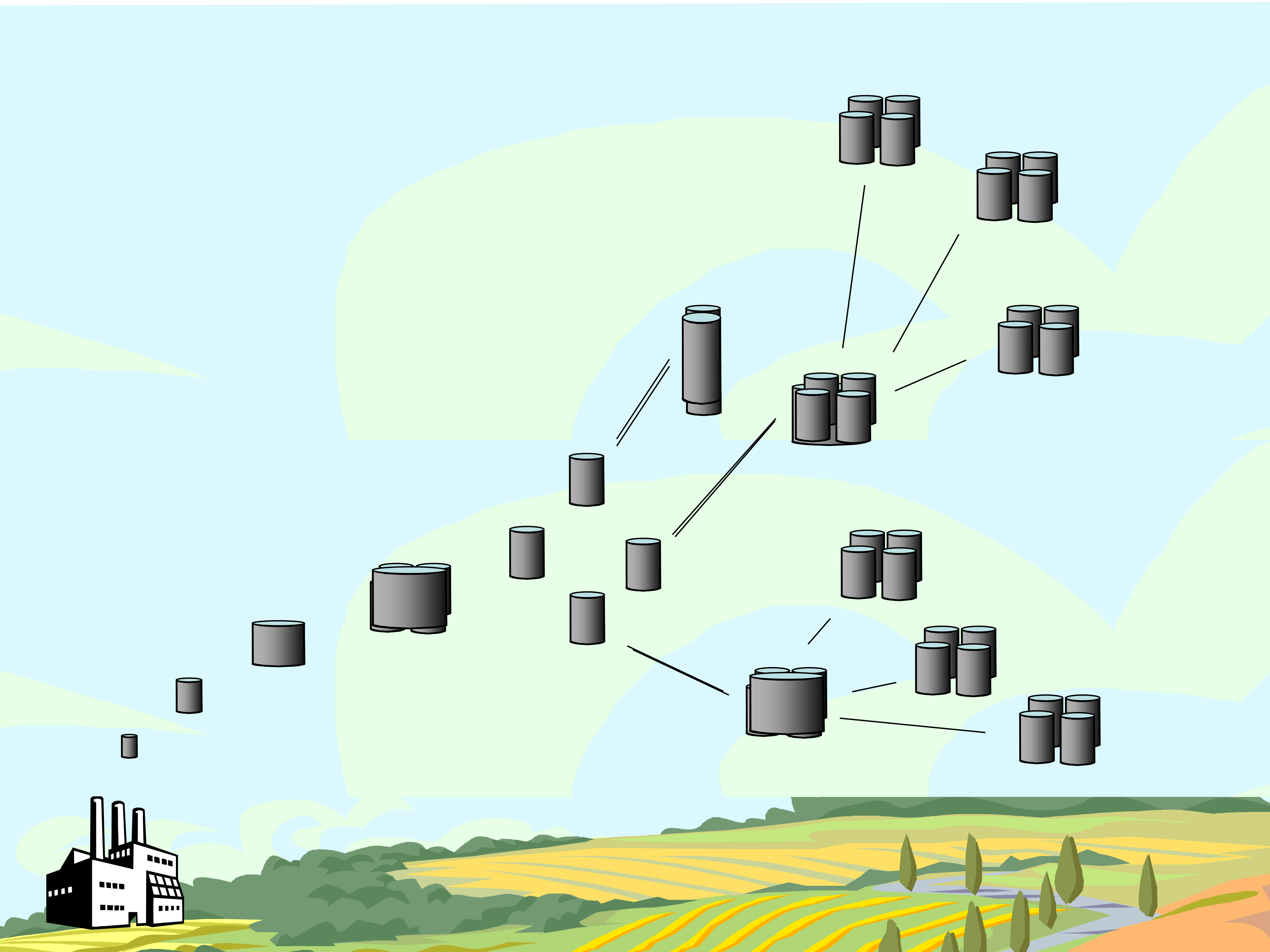
Ok for *regional* simulations, but for *global* modeling, puff splitting overwhelms computational resources

Due to puff splitting, the number of puffs quickly overwhelms numerical resources

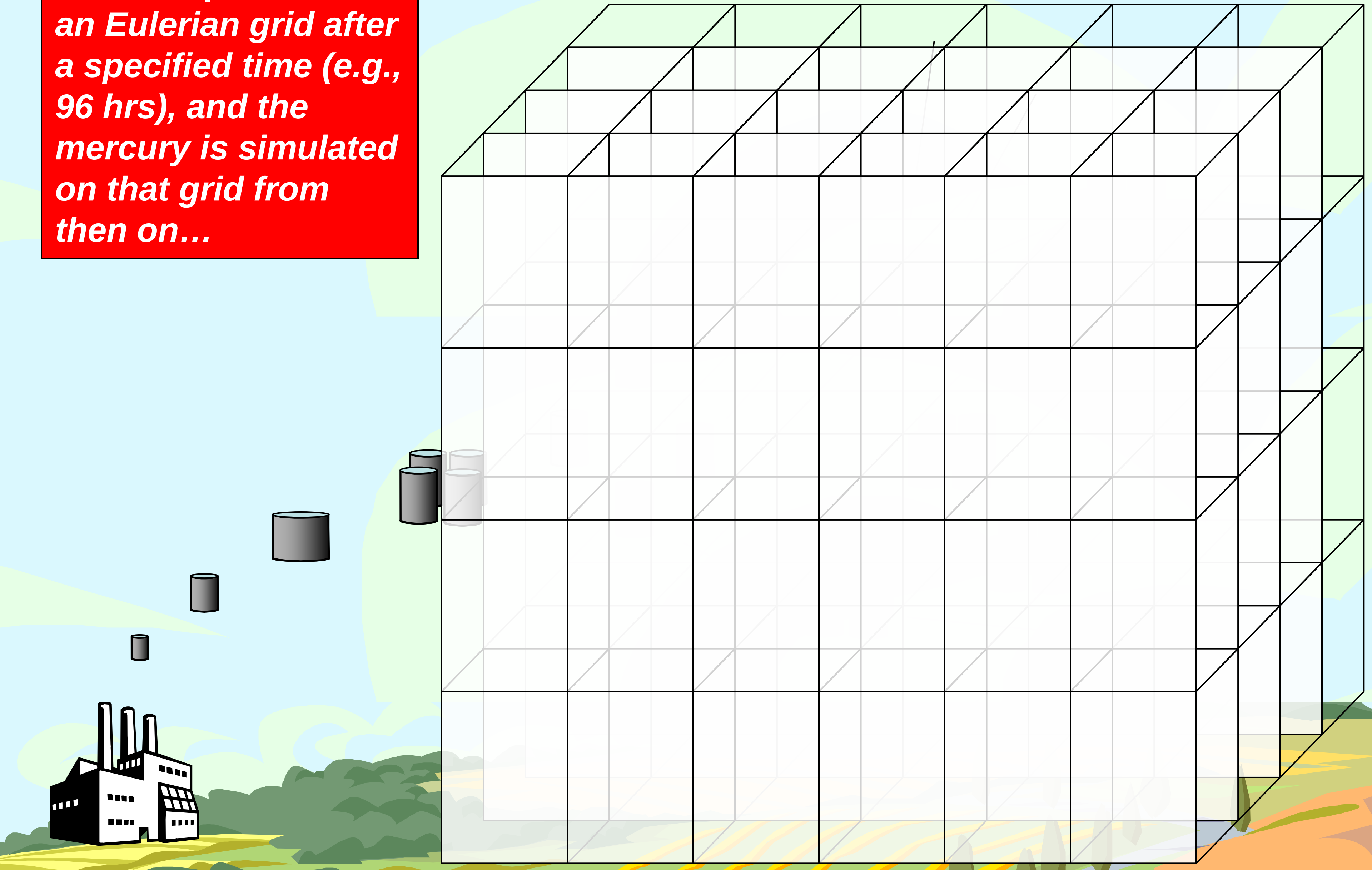


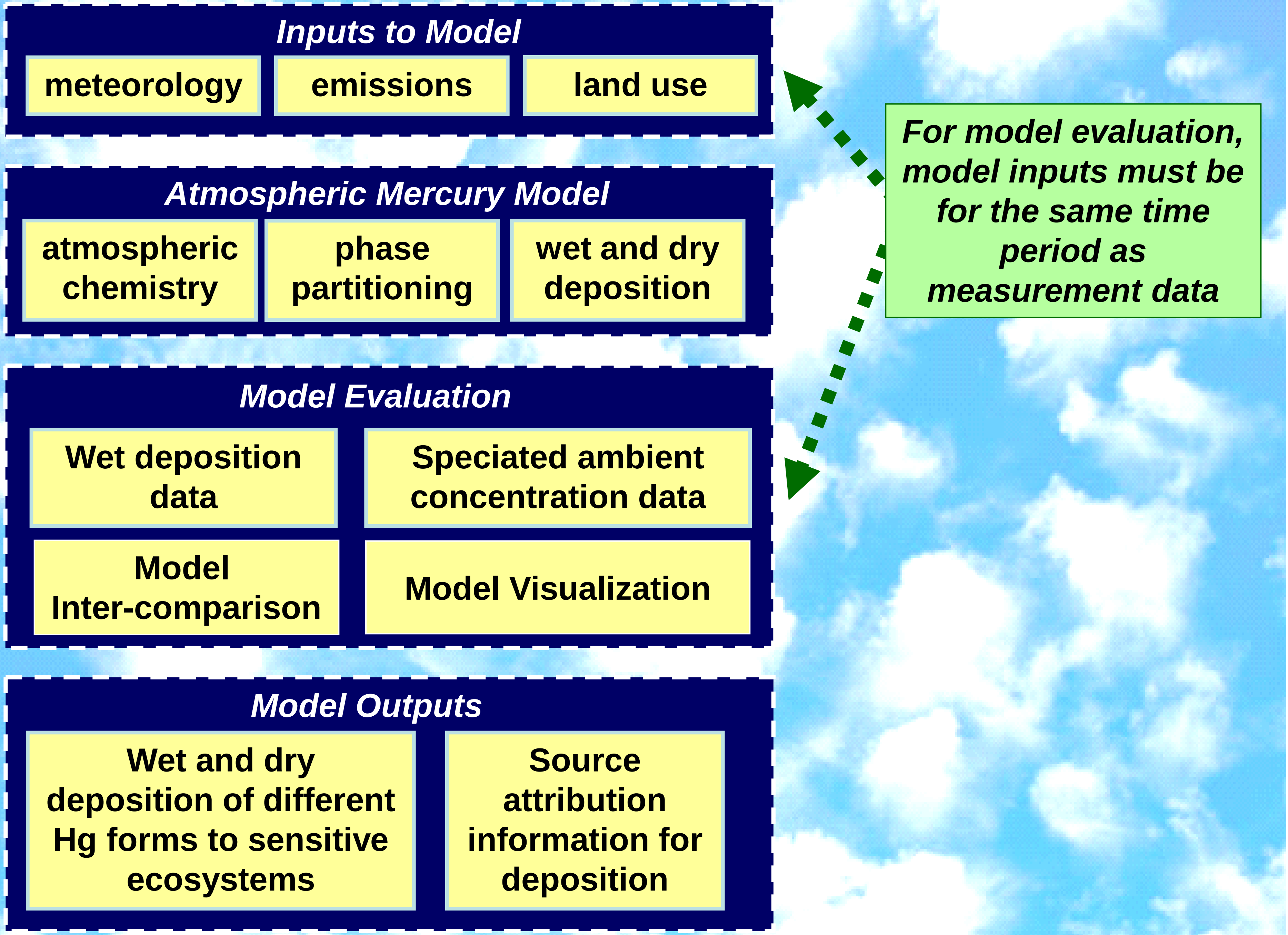
In each test, the number of puffs rises to the maximum allowable within ~ one week





In the new version of HYSPLIT (4.9), puffs are “dumped” into an Eulerian grid after a specified time (e.g., 96 hrs), and the mercury is simulated on that grid from then on…





Inputs to Model

- meteorology
- emissions
- land use

Atmospheric Mercury Model

- atmospheric chemistry
- phase partitioning
- wet and dry deposition

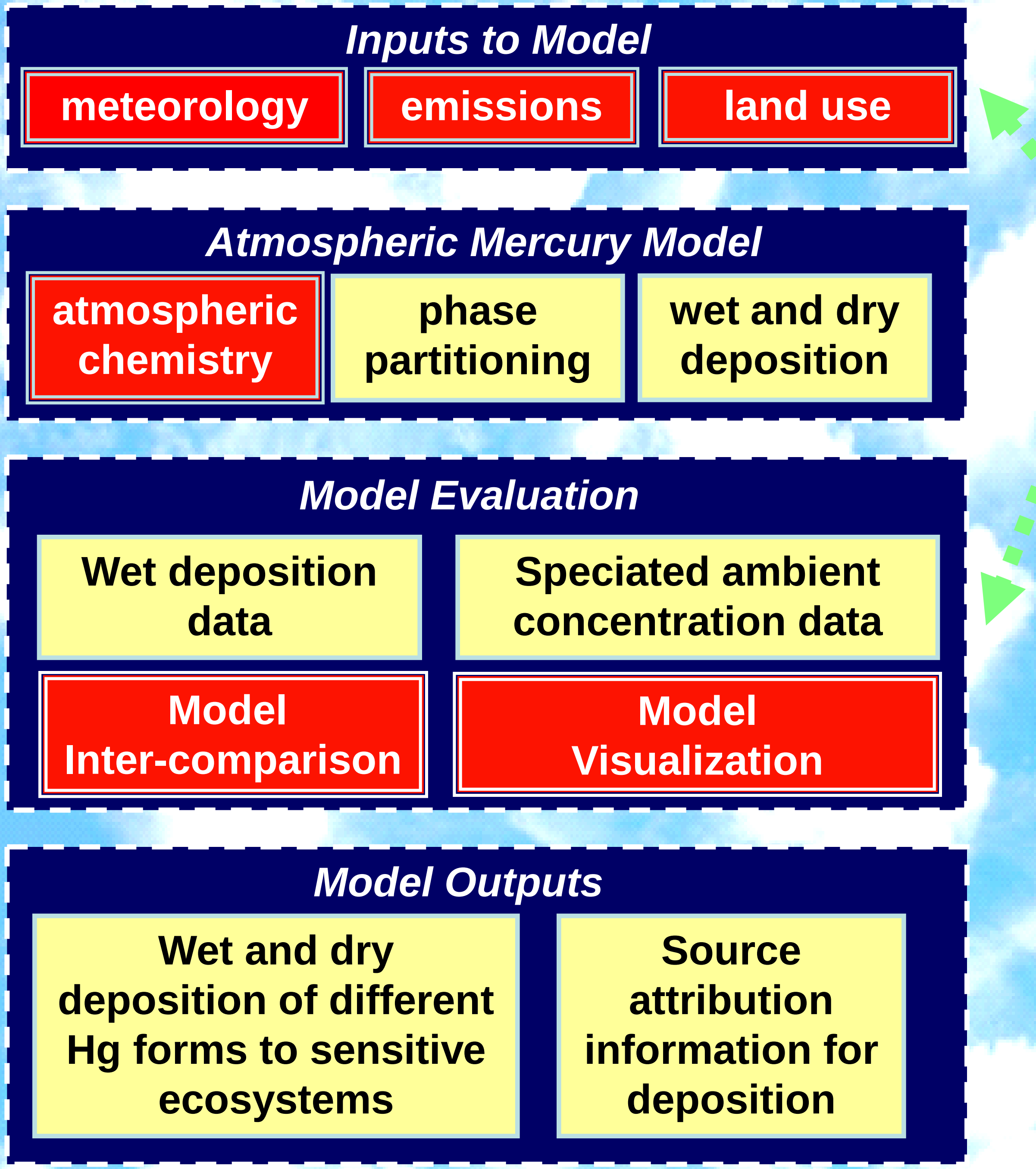
Model Evaluation

- Wet deposition data
- Speciated ambient concentration data
- Model Inter-comparison
- Model Visualization

Model Outputs

- Wet and dry deposition of different Hg forms to sensitive ecosystems
- Source attribution information for deposition

For model evaluation, model inputs must be for the same time period as measurement data



Inputs to Model

meteorology

emissions

land use

Atmospheric Mercury Model

atmospheric chemistry

phase partitioning

wet and dry deposition

Model Evaluation

Wet deposition data

Speciated ambient concentration data

Model Inter-comparison

Model Visualization

Model Outputs

Wet and dry deposition of different Hg forms to sensitive ecosystems

Source attribution information for deposition

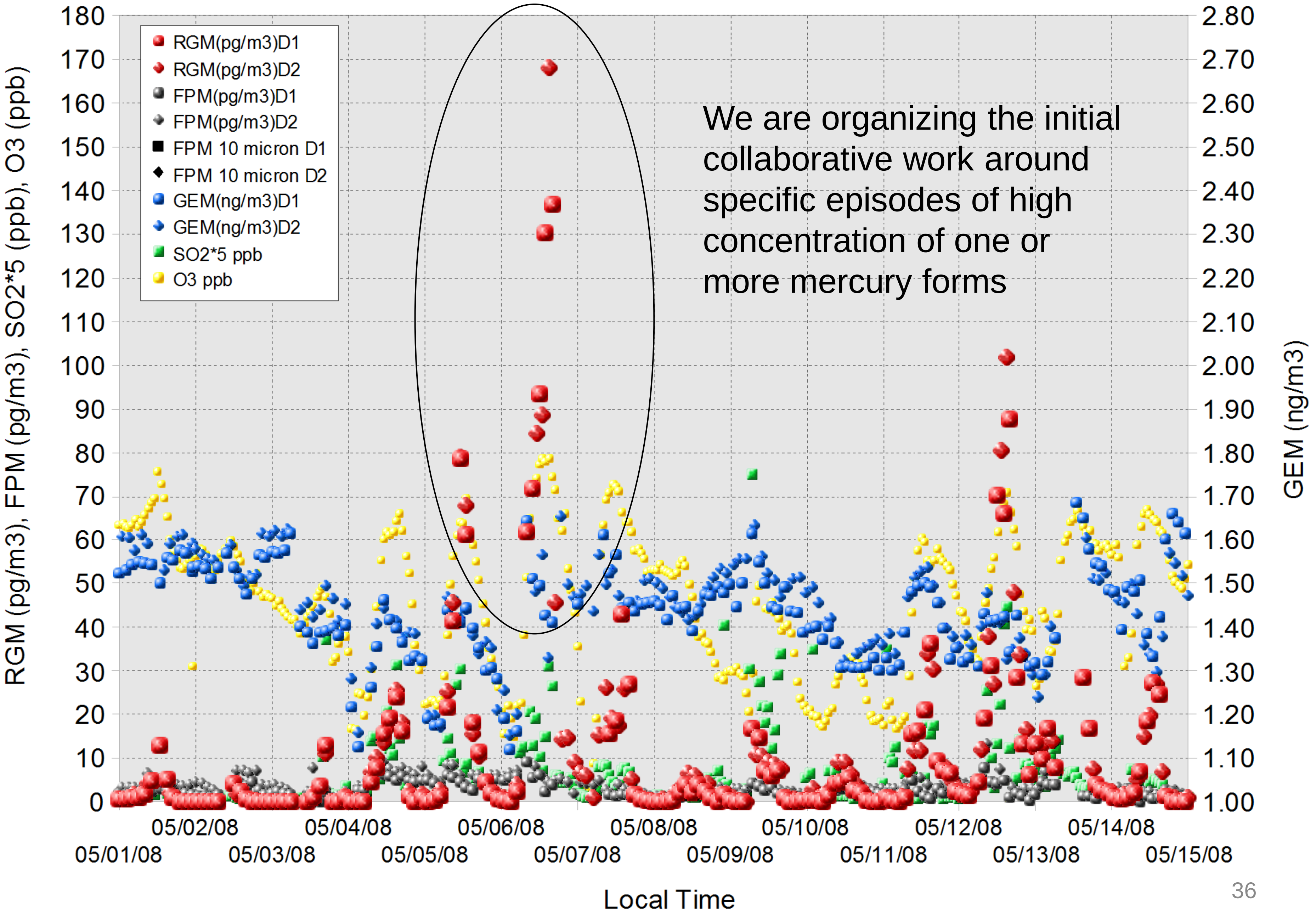
For model evaluation, model inputs must be for the same time period as measurement data

JSU collaboration

Collaboration with JSU is providing a <u>unique and unprecedented</u> opportunity to evaluate and improve atmospheric mercury models

Speciated Atmospheric Mercury and Selected Trace Gas Concentration Measurements at Grand Bay NERR

Courtesy of Winston Luke and Paul Kelley (NOAA ARL) and Jake Walker (Grand Bay NERR)   (Preliminary Values)

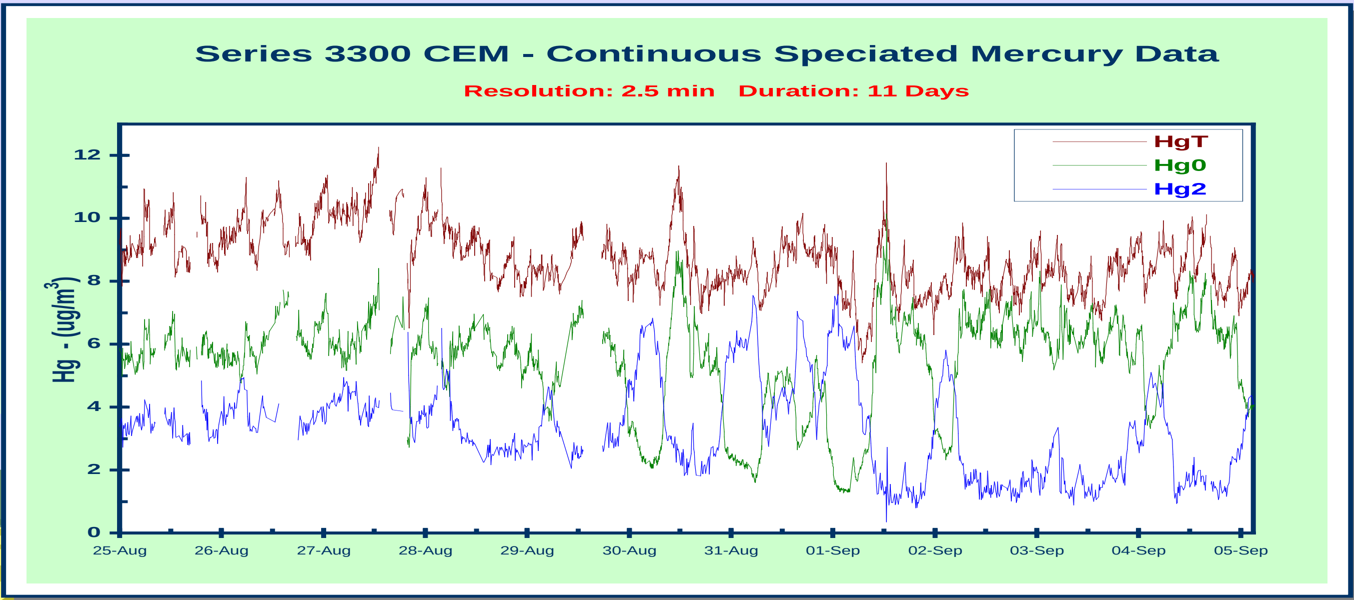


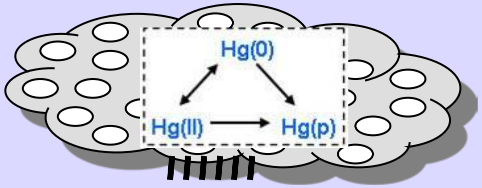
We are organizing the initial collaborative work around specific episodes of high concentration of one or more mercury forms

Thanks!

Extra Slides

Hg from other sources: local, regional & more distant

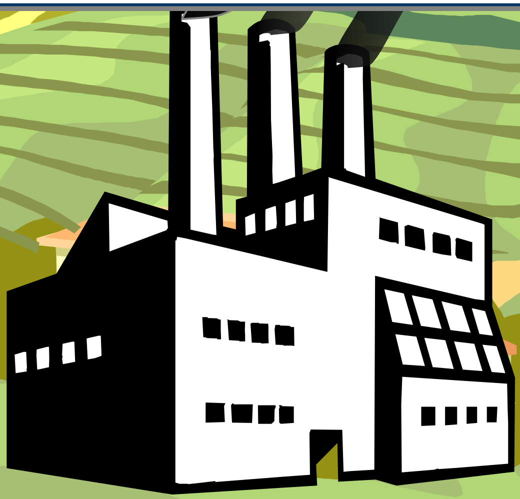




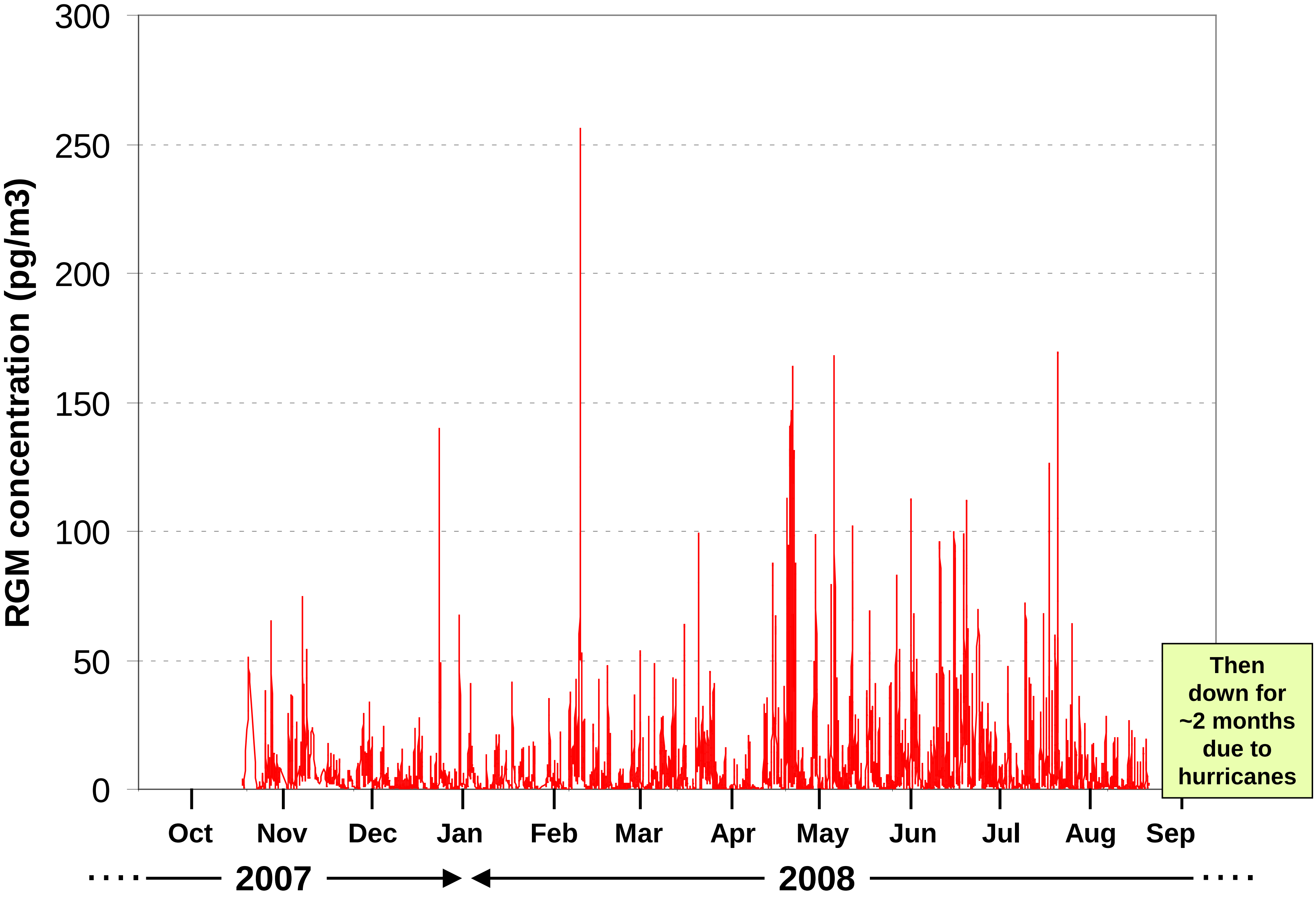
atmospheric deposition to the water surface

Measurement of wet deposition

Measurement of ambient air concentrations

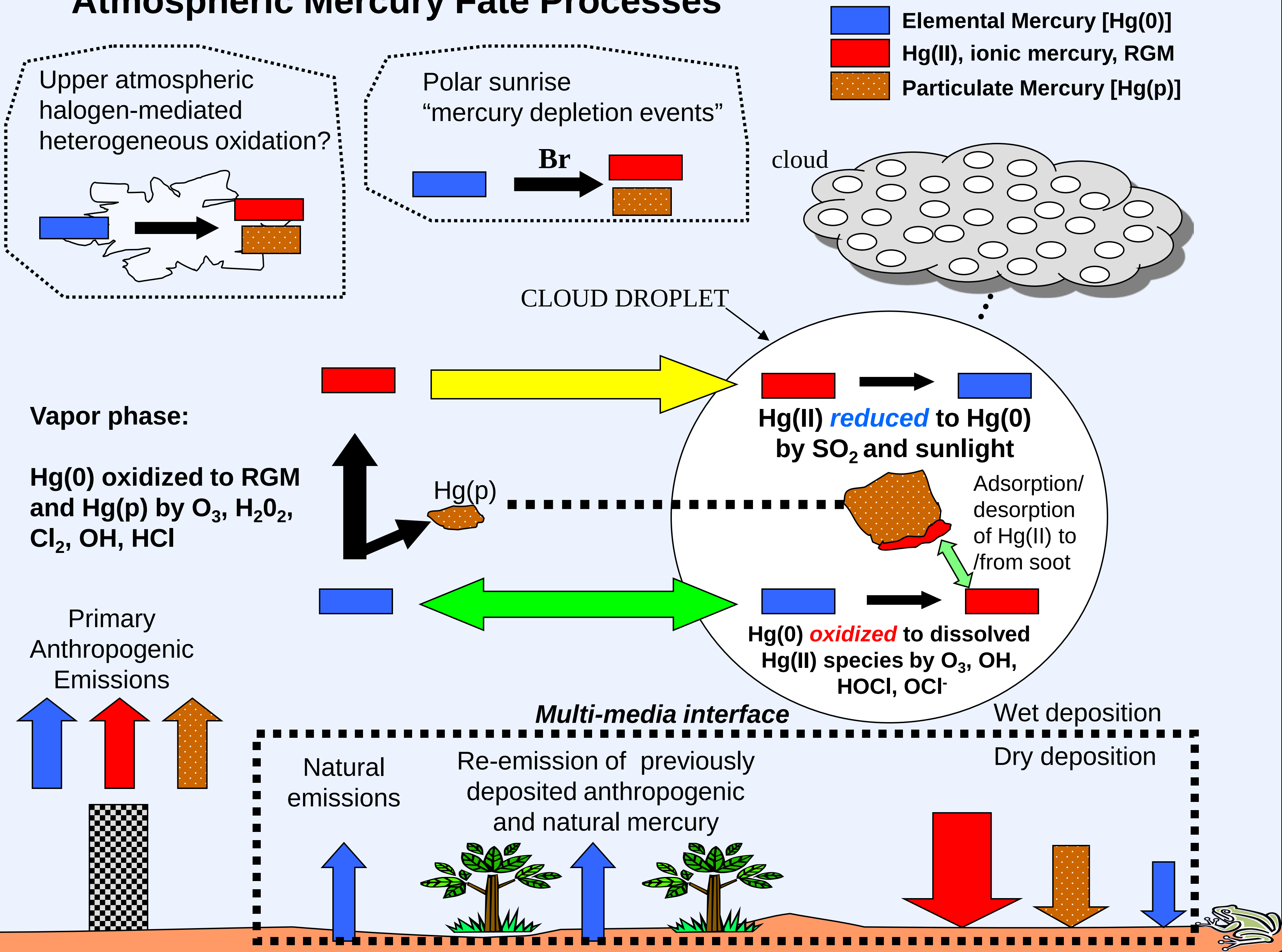


Recent RGM concentrations measured at the Grand Bay NERR



Then down for ~2 months due to hurricanes

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”

Vapor phase:

Hg(0) oxidized to RGM and Hg(p) by O_3, H_20_2, Cl_2, OH, HCl

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

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

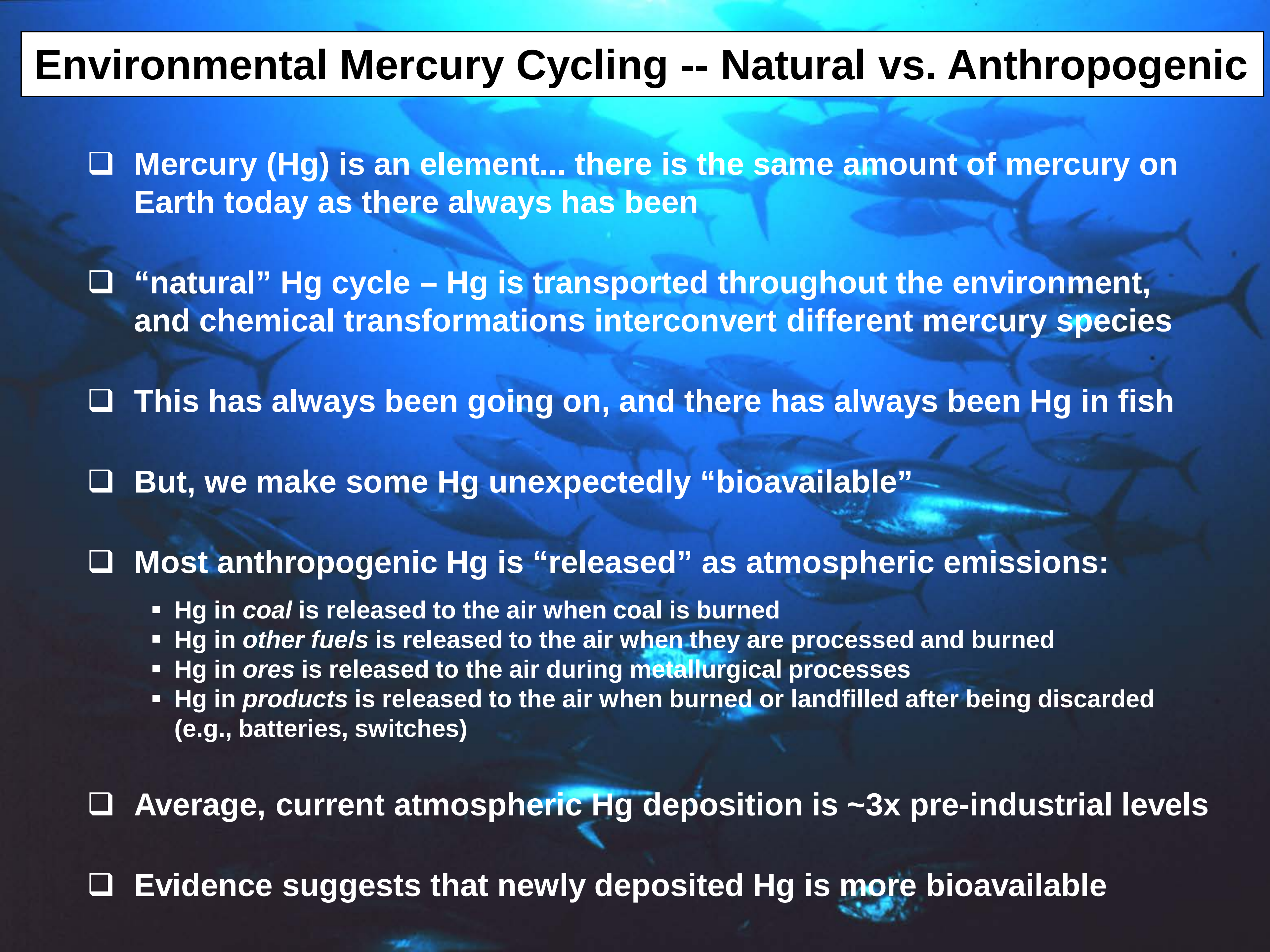
Wet deposition

Dry deposition

Natural emissions

Re-emission of previously deposited anthropogenic and natural mercury

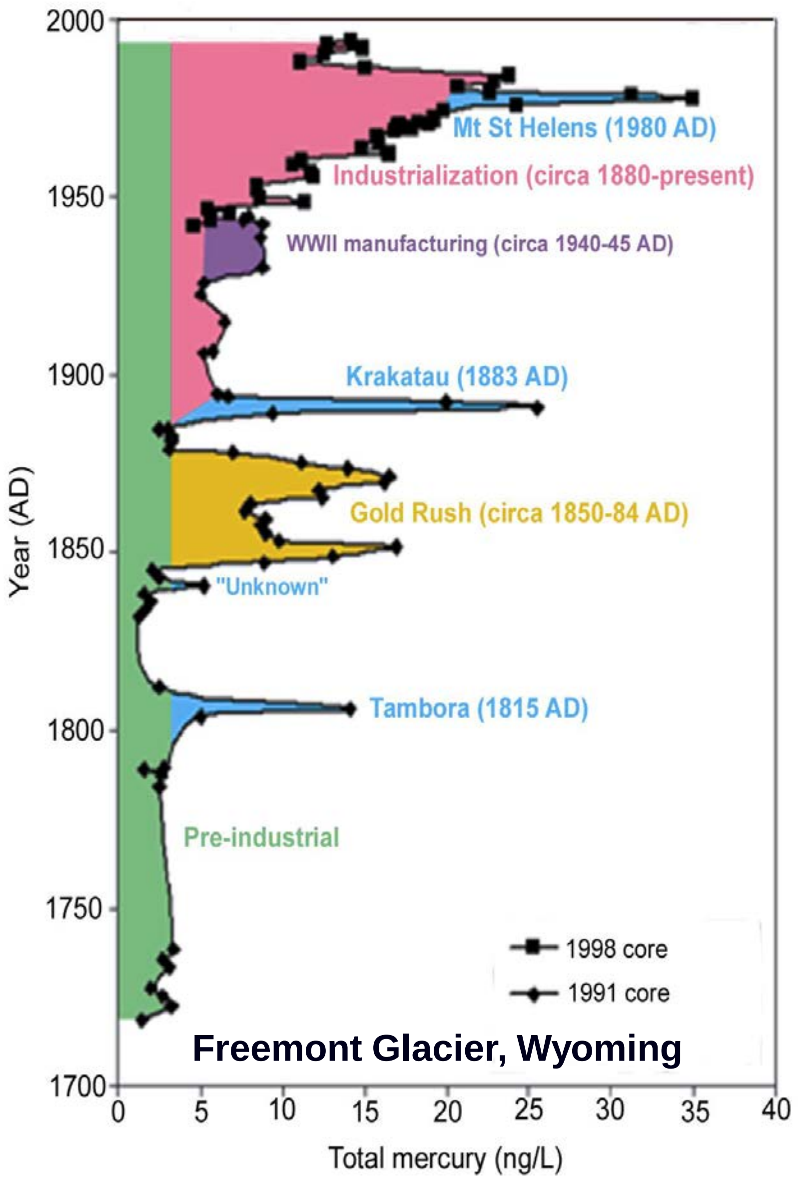
Environmental Mercury Cycling -- Natural vs. Anthropogenic



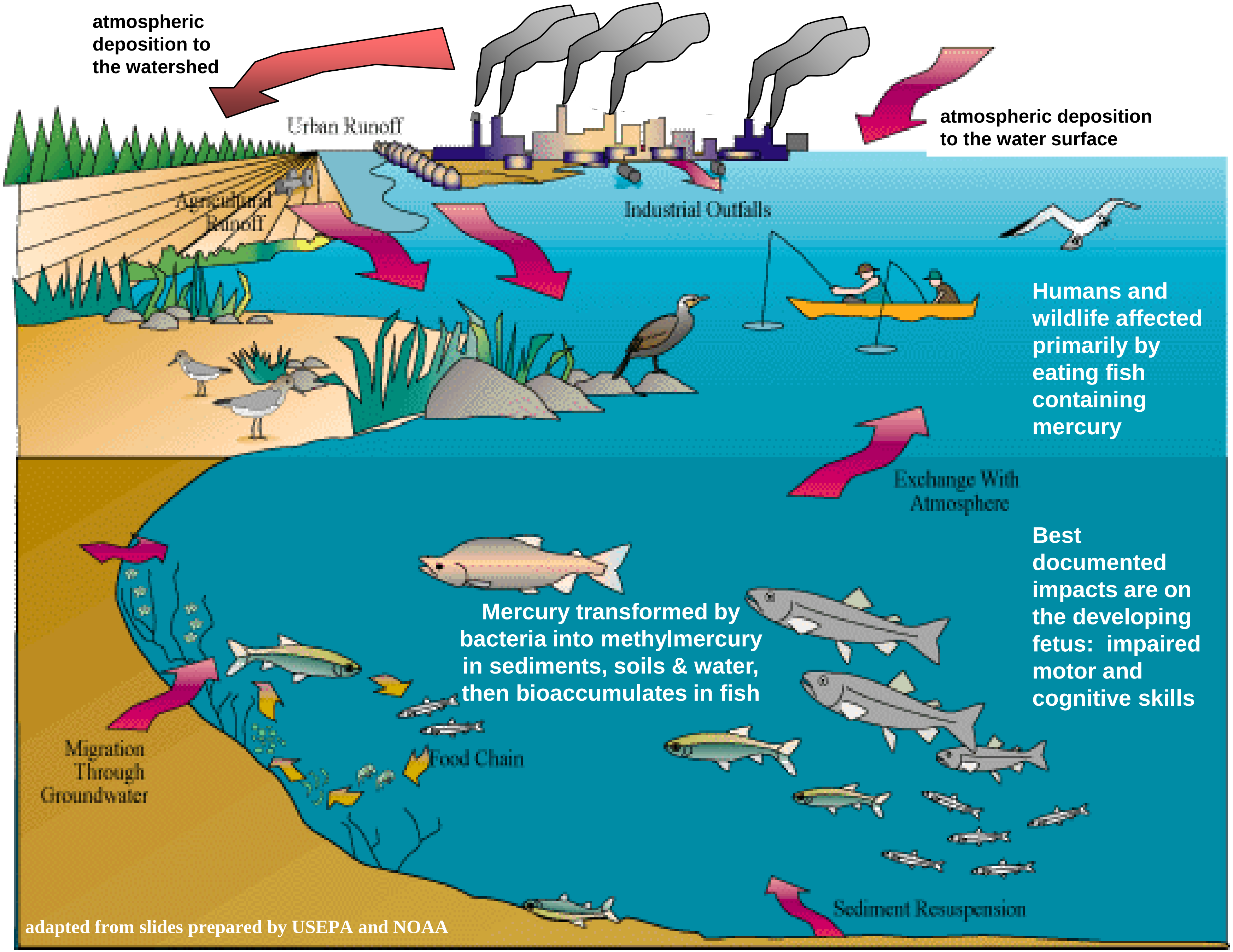
- **Mercury (Hg) is an element... there is the same amount of mercury on Earth today as there always has been**
- **“natural” Hg cycle – Hg is transported throughout the environment, and chemical transformations interconvert different mercury species**
- **This has always been going on, and there has always been Hg in fish**
- **But, we make some Hg unexpectedly “bioavailable”**
- **Most anthropogenic Hg is “released” as atmospheric emissions:**
  - **Hg in *coal* is released to the air when coal is burned**
  - **Hg in *other fuels* is released to the air when they are processed and burned**
  - **Hg in *ores* is released to the air during metallurgical processes**
  - **Hg in *products* is released to the air when burned or landfilled after being discarded (e.g., batteries, switches)**
- **Average, current atmospheric Hg deposition is ~3x pre-industrial levels**
- **Evidence suggests that newly deposited Hg is more bioavailable**

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, Shuster et al., 2002



atmospheric deposition to the watershed

atmospheric deposition to the water surface

Humans and wildlife affected primarily by eating fish containing mercury

Best documented impacts are on the developing fetus: impaired motor and cognitive skills

Mercury transformed by bacteria into methylmercury in sediments, soils & water, then bioaccumulates in fish

adapted from slides prepared by USEPA and NOAA

What Do We Need to Know Regarding Atmospheric Mercury?

Type of Information
Atmospheric deposition*
Source-attribution for deposition
Deposition for historical periods
Deposition for alternative future scenarios

** consistent with the needs of subsequent analyses (e.g., ecosystem modeling) with respect to spatial, temporal, and "species" resolution (e.g., Hg(0) vs. RGM vs. Hg(p))*