Organization of Course

INTRODUCTION

1. Course overview
2. **Air Toxics overview**
3. HYSPLIT overview

HYSPLIT Theory and Practice

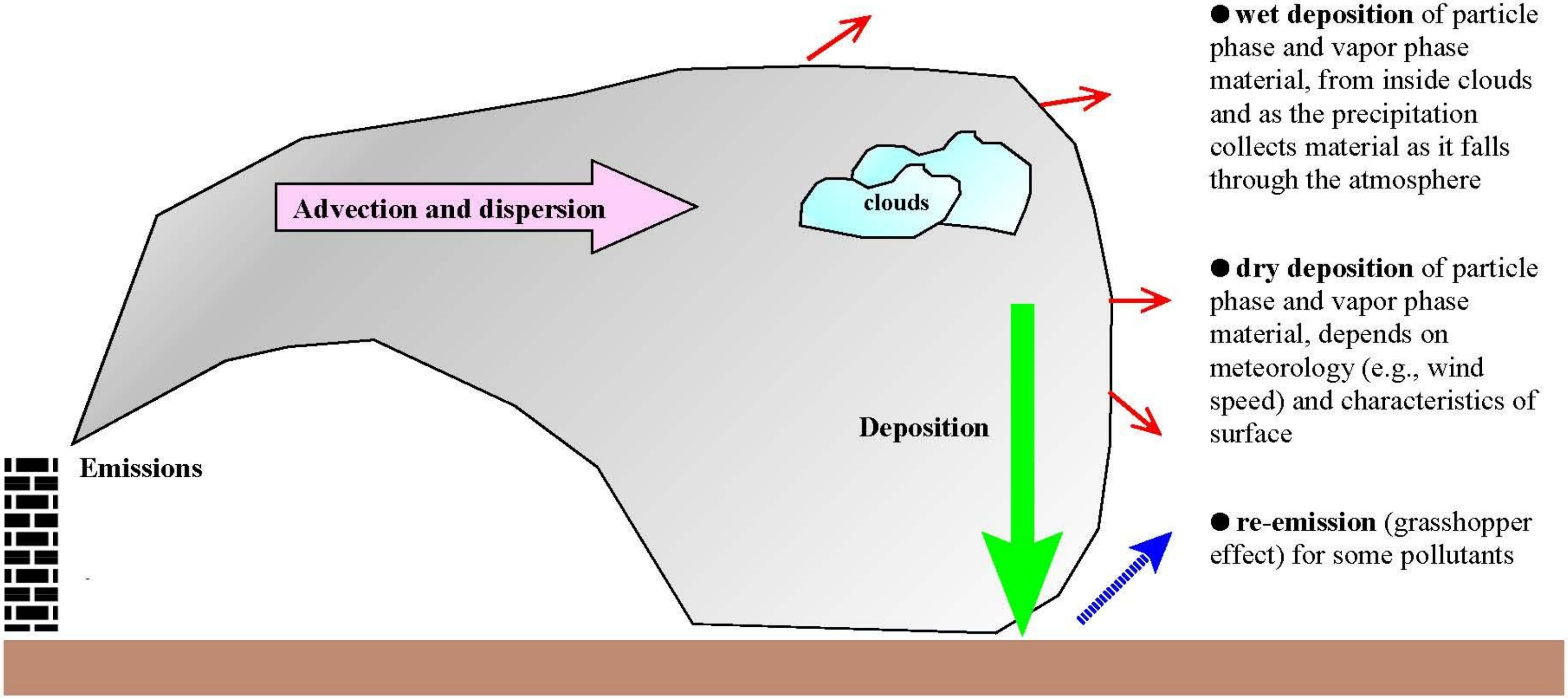
4. Meteorology
5. Back Trajectories
6. Concentrations / Deposition
7. HYSPLIT-SV for semivolatiles (e.g, PCDD/F)
8. HYSPLIT-HG for mercury

Overall Project Issues & Examples

9. Emissions Inventories
10. Source-Receptor Post-Processing
11. Source-Attribution for Deposition
12. Model Evaluation
13. Model Intercomparison
14. Collaboration Possibilities

TRANSPORT and FATE of ATMOSPHERIC POLLUTANTS

- **vapor-particle partitioning** at low relative humidity
- **vapor-droplet partitioning** in clouds (and/or at high relative humidity)
- **chemical transformations** producing new compounds (may be more or less toxic) due to reactions and photolysis in the *vapor phase, on the surface of particles*, and/or *within droplets* (note: this may involve interaction with compounds from other emissions sources)

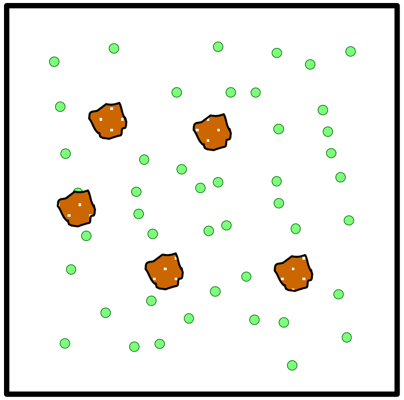


- **wet deposition** of particle phase and vapor phase material, from inside clouds and as the precipitation collects material as it falls through the atmosphere
- **dry deposition** of particle phase and vapor phase material, depends on meteorology (e.g., wind speed) and characteristics of surface
- **re-emission** (grasshopper effect) for some pollutants

For the atmospheric fate of air toxics, everything depends on vapor-particle partitioning

☐ **Atmospheric Chemistry**

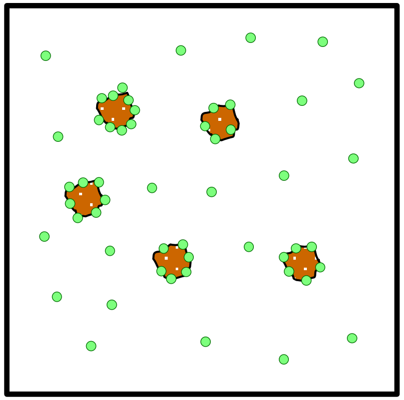
☐ **Wet and Dry Deposition**



vapor-phase pollutant

example:

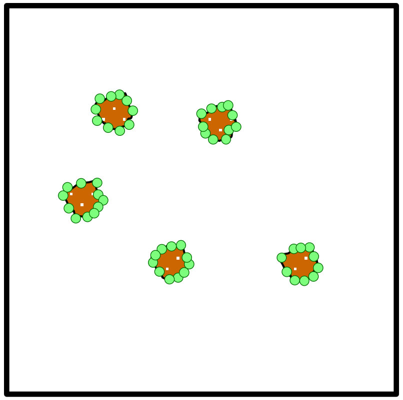
Hexachloro-benzene (HCB)



semi-volatile pollutant

example:

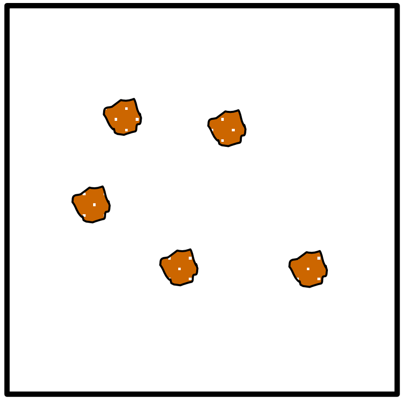
2,3,7,8-TCDD



low volatility pollutant

example:

OCDD



particle-phase pollutant

example:

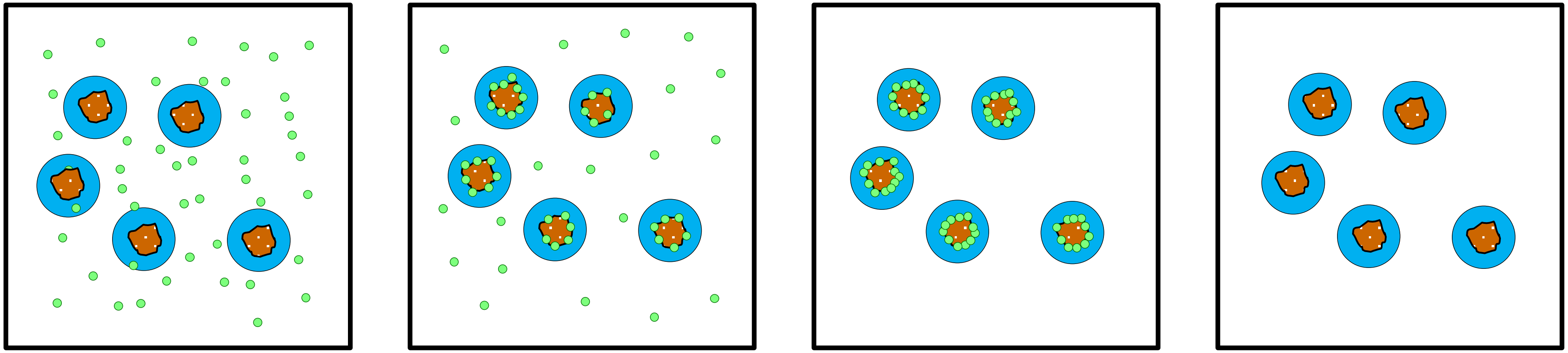
Cadmium

For the atmospheric fate of air toxics, everything depends on vapor-particle partitioning

❑ **Atmospheric Chemistry**

❑ **Wet and Dry Deposition**

If the local atmospheric relative humidity is above 70-80%, particles become droplets and this affects partitioning, chemistry, and deposition



vapor-phase pollutant

example:

Hexachloro-benzene (HCB)

semi-volatile pollutant

example:

2,3,7,8-TCDD

low volatility pollutant

example:

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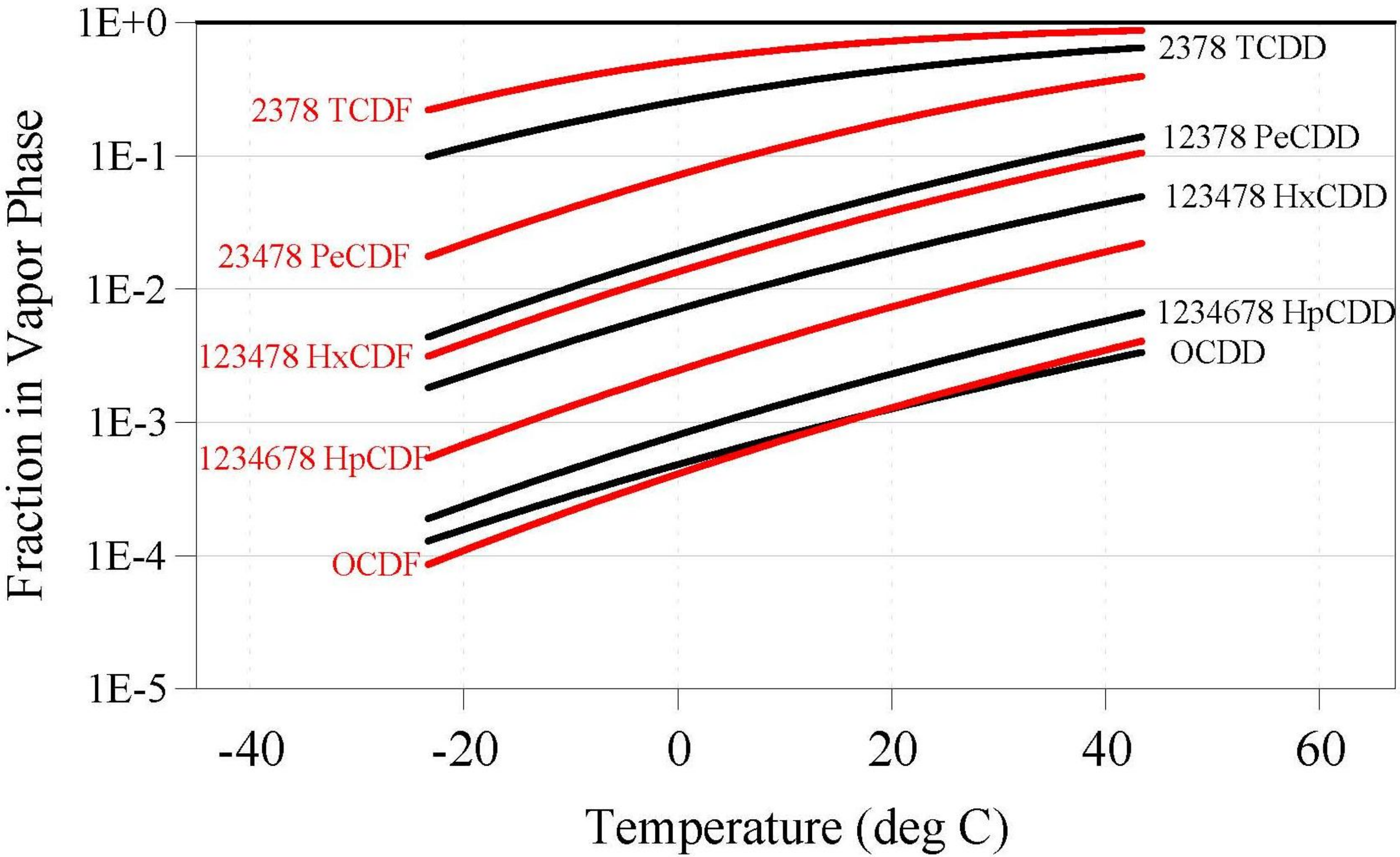
particle-phase pollutant

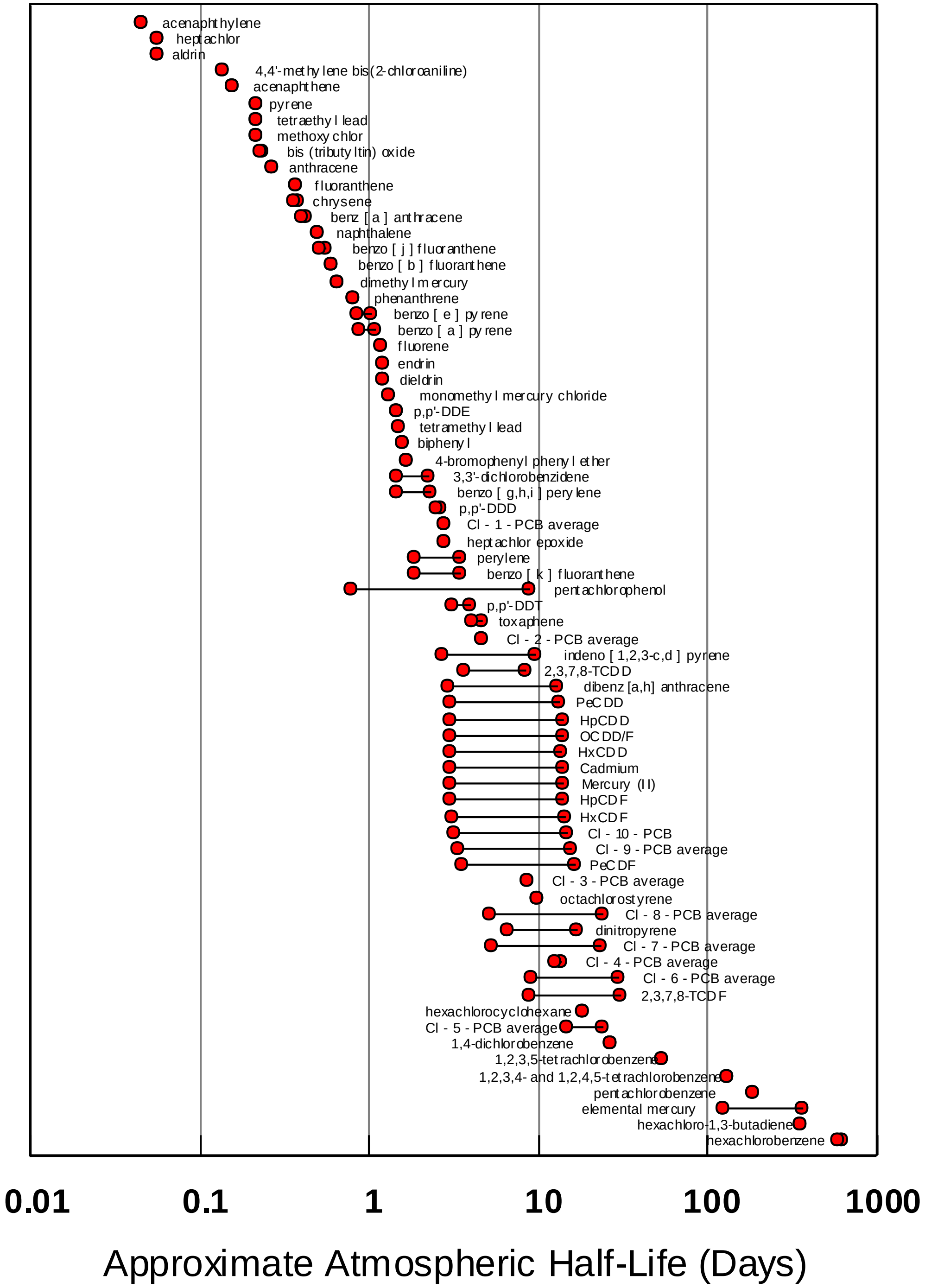
example:

Cadmium

Figure 1. Estimated vapor/particle partitioning characteristics of selected PCDD/F congeners



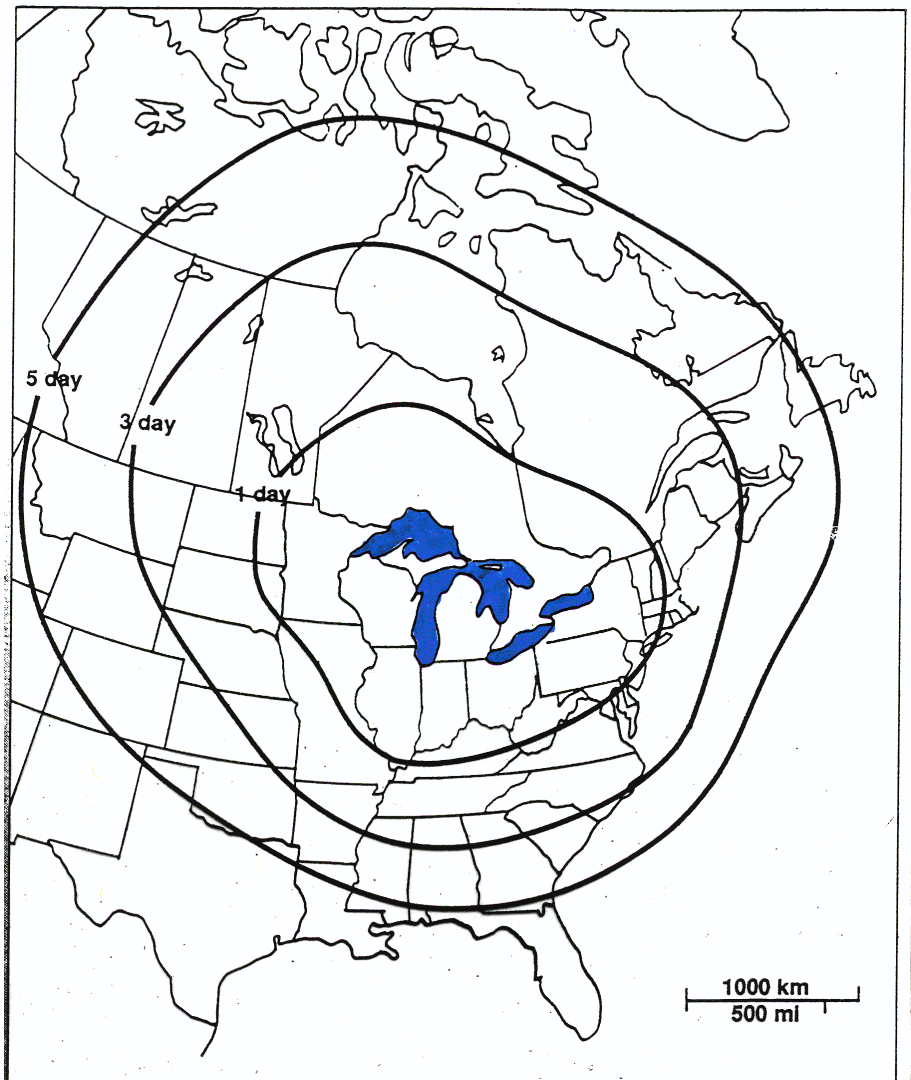
The aerosol surface area used in these calculations is 3.5e-06 cm2/cm3, equivalent to "Background + Local Sources".



Approximate Atmospheric Half-Life (Days), based on:

- ☐ vapor/particle partitioning
- ☐ vapor-phase rxn with hydroxyl radical (OH)
- ☐ dry and wet deposition of particle-phase and vapor phase fractions

Typical atmospheric “travel distance” is ~400 km/day, but this can vary a lot depending on the meteorological conditions



Lines indicate the median location of airborne contaminants originating 1,3 and 5 days before their arrival in the Great Lakes hydrological basin.

Source: International Air Quality Advisory Board, 1988.

Estimated Long-Range Air Transport Potential of BVES Compounds

LONG RANGE TRANSPORT RATING			
1	**2**	**3**	**4**
APPROXIMATE ATMOSPHERIC HALF LIFE			
1 year or more	1 week-few mos.	few hrs-few days	seconds-minutes
GEOGRAPHIC DISTRIBUTION (approx. average transport distance associated with half-life)			
global	1,000-10,000 km (possibly global)	100-1,000 km	local
elemental mercury hexachloro-1,3-butadiene tetrachlorobenzenes pentachlorobenzene hexachlorobenzene	particulate mercury mercury dichloride alkylated lead cadmium DDT/DDD/DDE mirex toxaphene HCH's (á, â, ä, ã) pentachlorophenol octachlorostyrene 3,3'-dichloro-benzidene 1,4-dichlorobenzene PCDD/F's PCBs dinitropyrenes benzo[a]pyrene benz[a]anthracene perylene benzo[g,h,i]perylene PAHs (as a group)	aldrin(?) heptachlor(?) 4,4'-methylene bis (2-chloroaniline) (?) tributyltin (?) heptachlor epoxide methoxychlor dieldrin endrin 4-bromophenyl phenyl ether phenanthrene anthracene	aldrin (?) heptachlor (?) 4,4'-methylene bis (2-chloroaniline) (?)

Consideration of the Exposure Pathway is Very Important

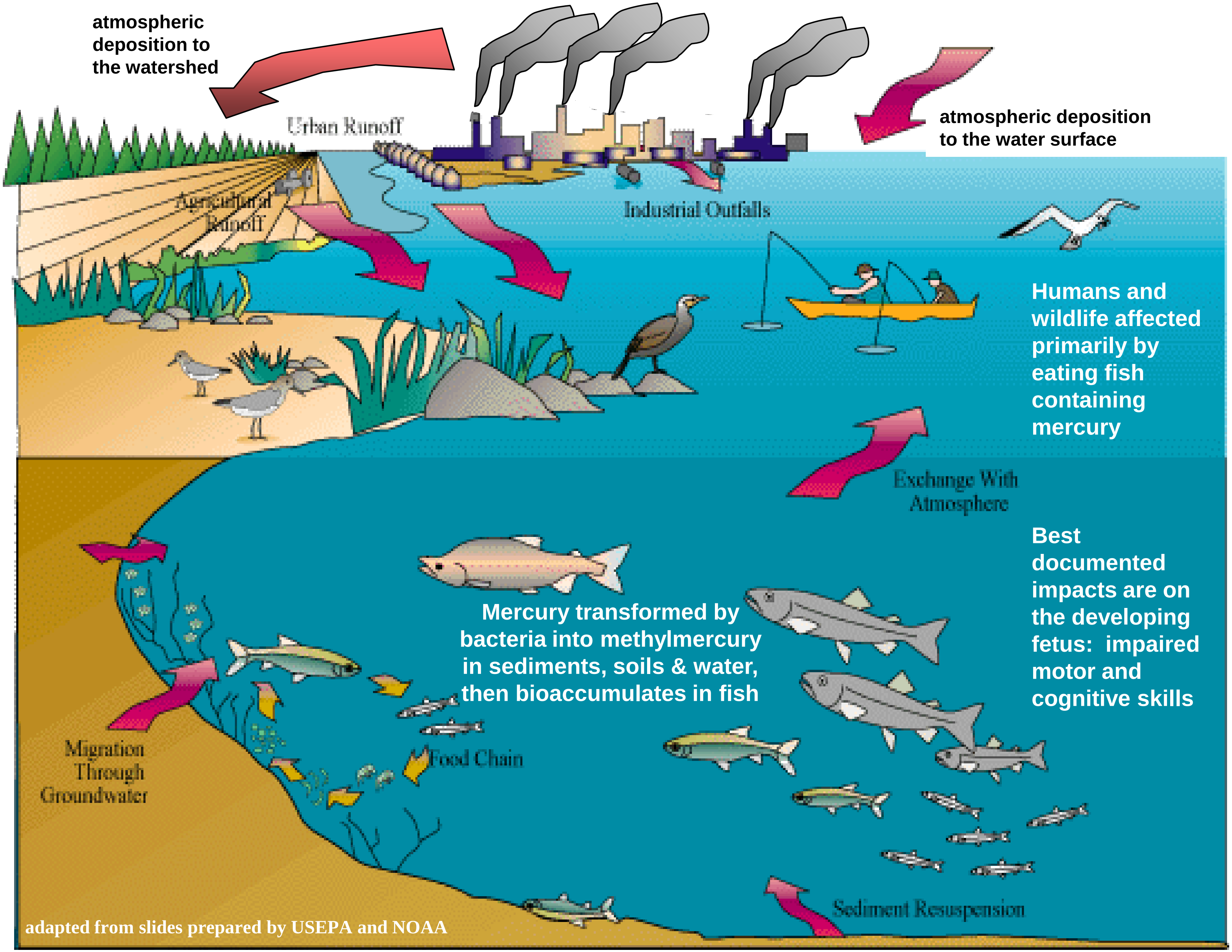
☐ **Inhalation?**

☐ **Dermal (skin)?**

☐ **Water?**

☐ **Food? (and if so, which foods?**

This governs what you want to try to find out, (by modeling, by measurements, or by both)



atmospheric
deposition to
the watershed

atmospheric deposition
to the water surface

Humans and wildlife affected primarily by eating fish containing mercury

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

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

adapted from slides prepared by USEPA and NOAA

Atmospheric Models and Atmospheric Measurements

Why do we need atmospheric 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…)

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  …because deposition fields are highly spatially variable,

  and one can't measure everywhere all the time…

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- **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?

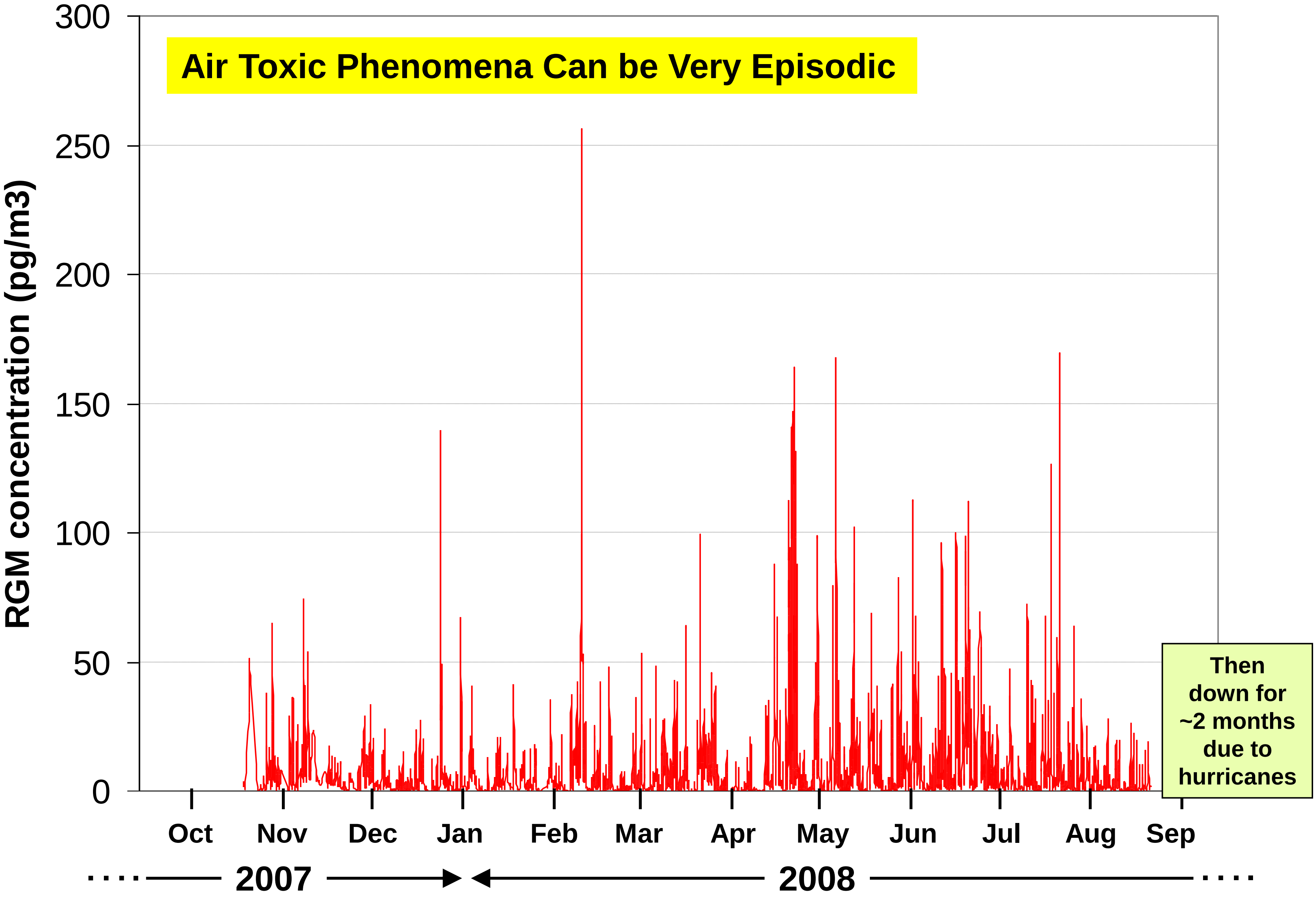
Results are encouraging, but difficult to evaluate models due to lack of contemporaneous monitoring and emissions inventory data

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)

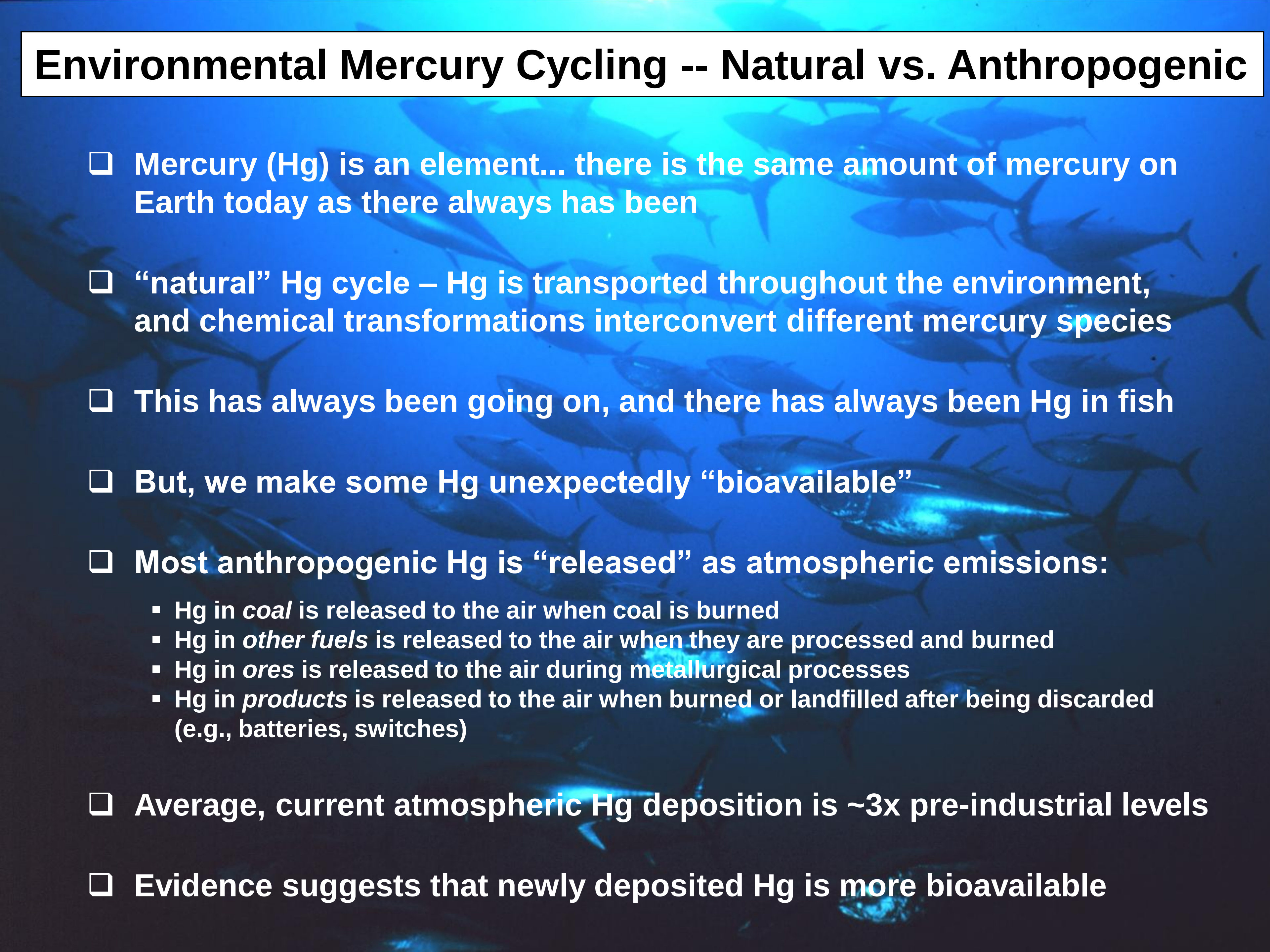
Recent Reactive Gaseous Mercury concentrations at the Grand Bay NERR, MS



Air Toxic Phenomena Can be Very Episodic

Then down for ~2 months due to hurricanes

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”

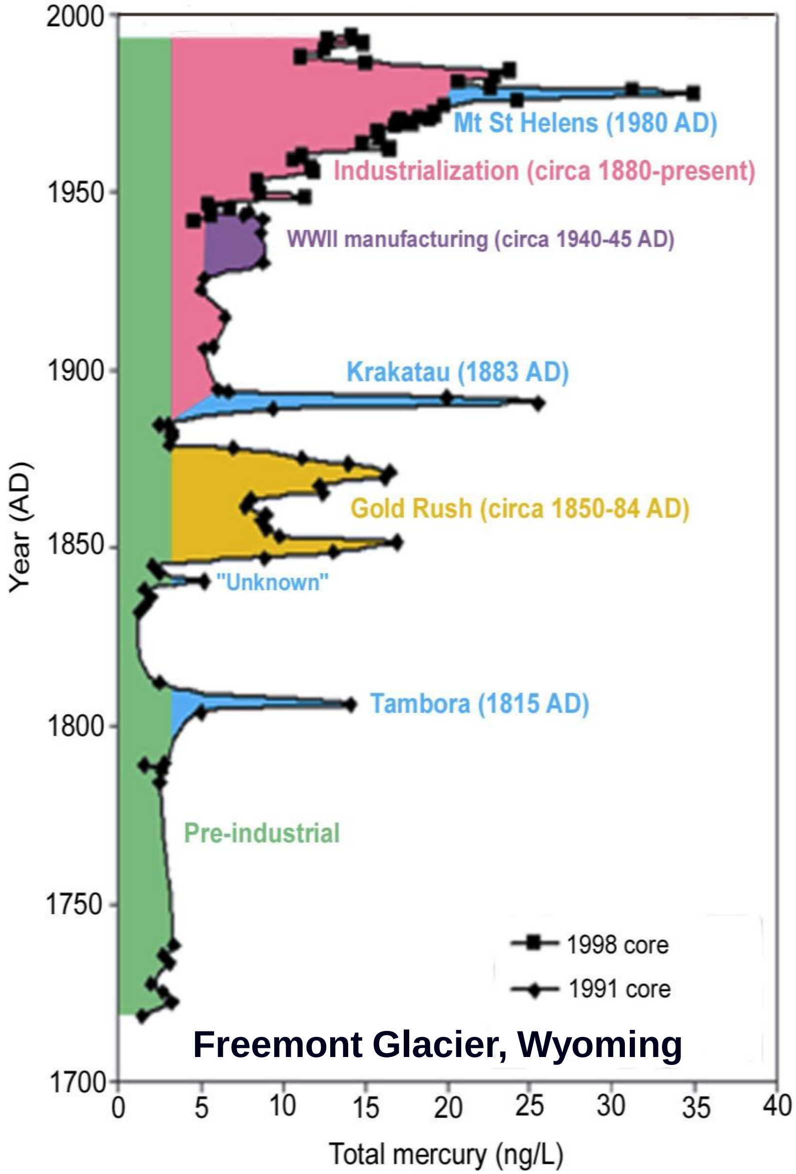
- Most anthropogenic Hg is “released” as atmospheric emissions:
  - Hg in *coal* is released to the air when coal is burned
  - Hg in *other fuels* is released to the air when they are processed and burned
  - Hg in *ores* is released to the air during metallurgical processes
  - Hg in *products* is 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