Toxic Pollutants in the Atmosphere: Understanding Fate, Transport, and Policy

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Transport and Fate of Pollutants: Science and Policy at Multiple Scales

Anthropogenic sources are both intentional and unintentional (byproducts)

Atmospheric transport and deposition leads to effects in wildlife, humans (uncertainties about atmospheric chemistry, processes)

Ongoing efforts to regulate emissions

Particular concern in the Arctic environment due to contamination of traditional foods

UNEP
United Nations Environment Programme
Chemicals
Mercury Programme

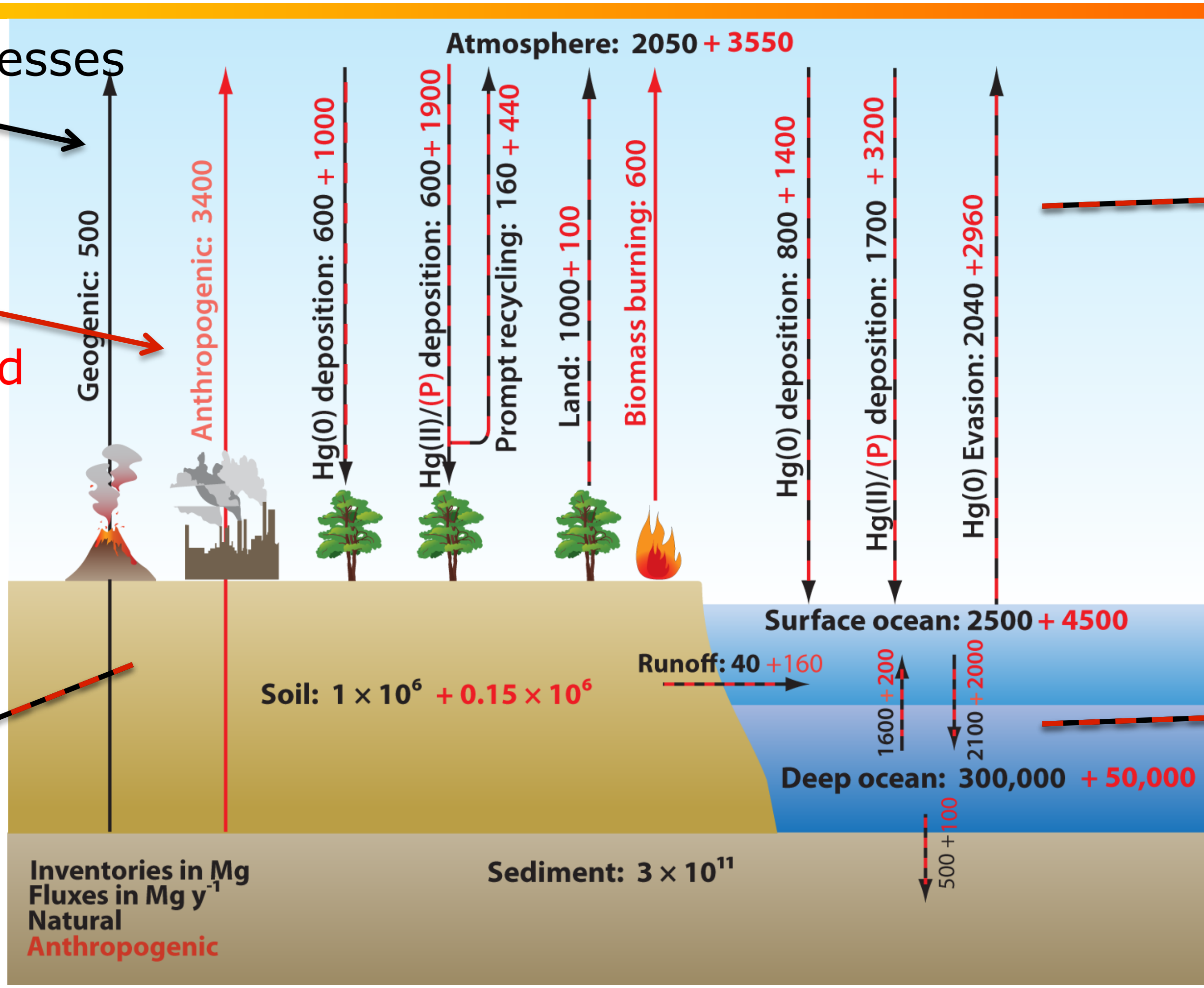
Global treaty negotiations on mercury began June 2010; Stockholm Convention on POPs signed in 2001

Understanding the Present and Future Global Biogeochemical Cycle of Mercury

Natural Processes

Human activities and policy interactions

Soil lifetime: Role of Historic Mercury

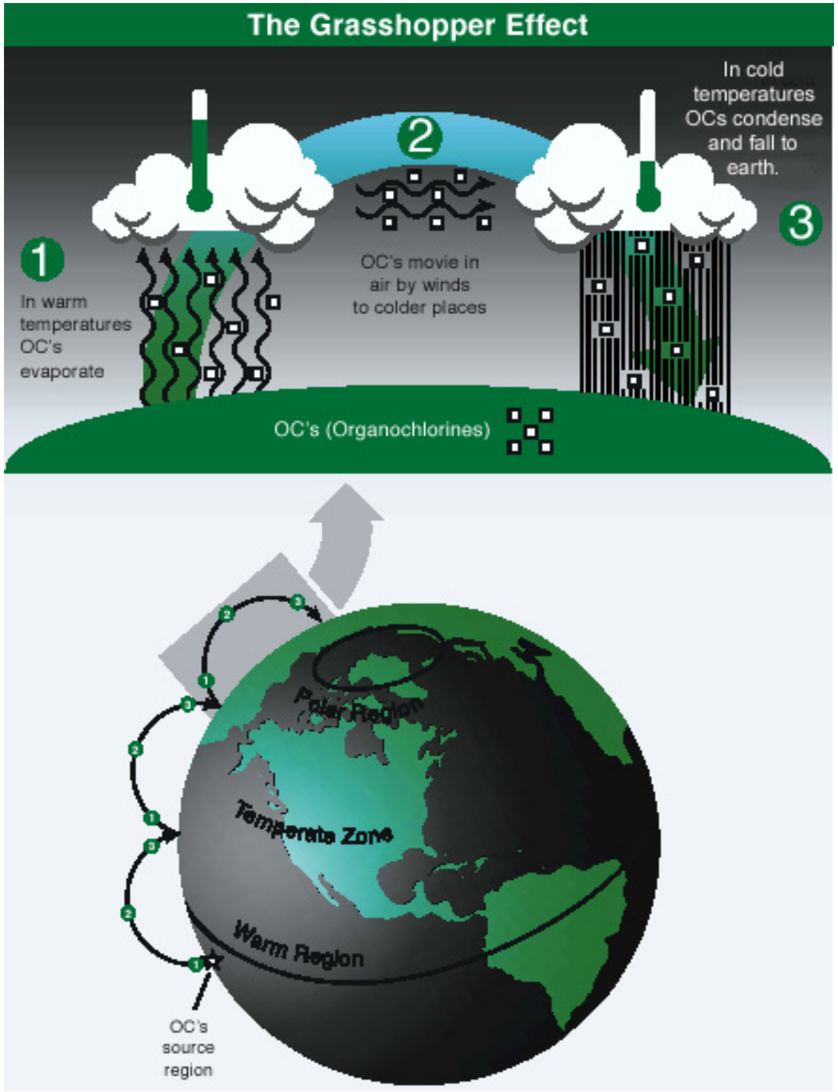


Technical, policy and ecosystem uncertainty

Human and environment impacts

[Selin, Ann. Rev. Env. Res., 2009]

POPs transport pathways to the Arctic

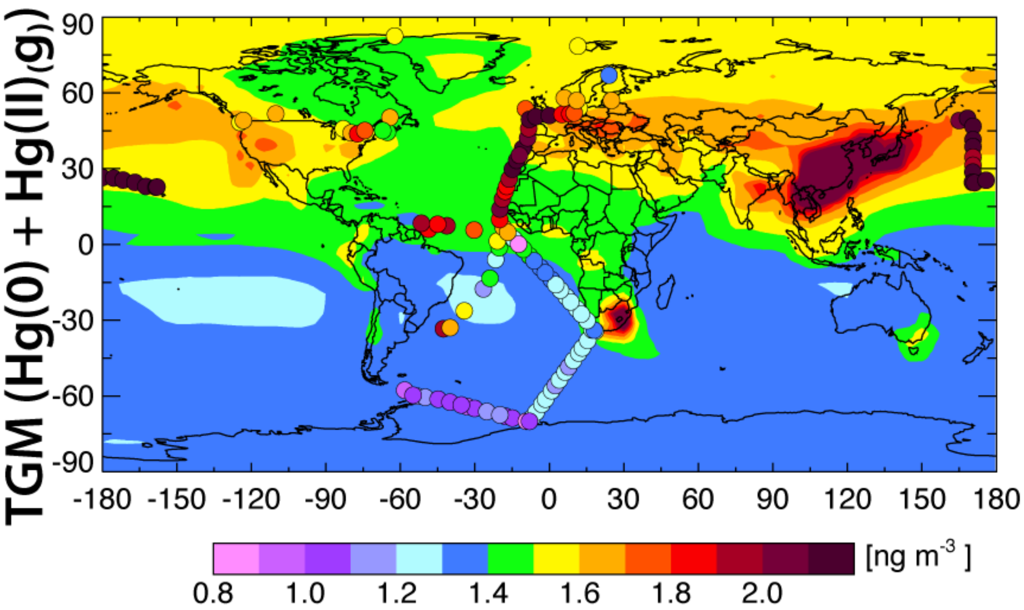


Source: Environment Canada

Research Questions: Outline

- What atmospheric reactions affect the ability of Hg to travel long distances?
  - What are the redox reactions controlling Hg speciation?
  - What is the source of Hg deposition?
- How do various Hg sources affect human exposure, and on what timescales?
- What sources influence episodic transport of POPs to the Arctic?

GEOS-Chem: Modeling Transport and Fate of Persistent Pollutants



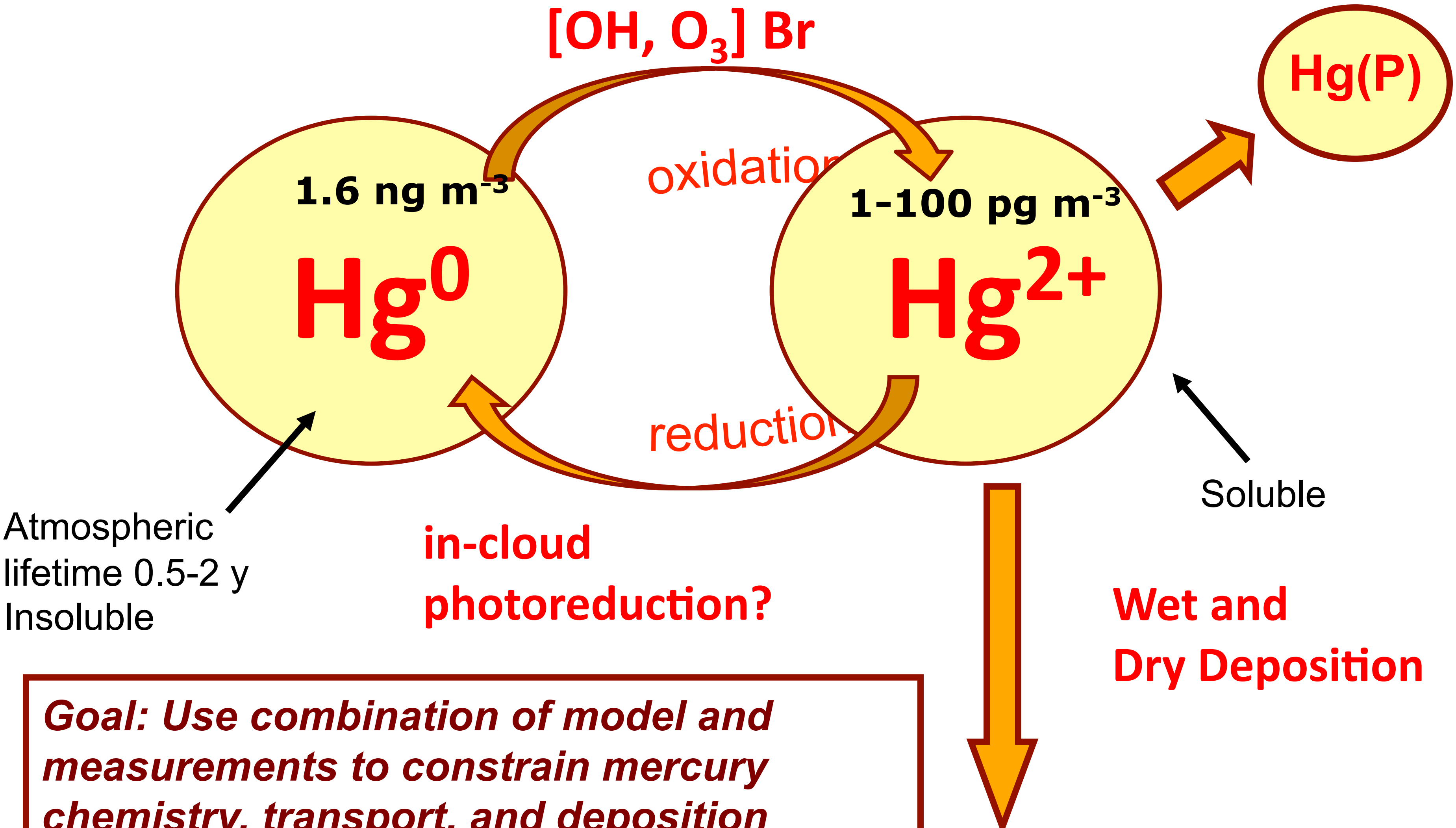
Global, 3D tropospheric chemistry model, 4x5 degree resolution, assimilated meteorology

[*Bey et al*., 2001]

Mercury simulation includes land-atmosphere-ocean coupling *(Selin et al., 2007, 2008; Strode et al., 2007; Holmes et al., 2010; Soerensen et al., 2010)*

POPs simulation includes atmospheric processes *(so far…for PAHs, Friedman and Selin, in prep)*

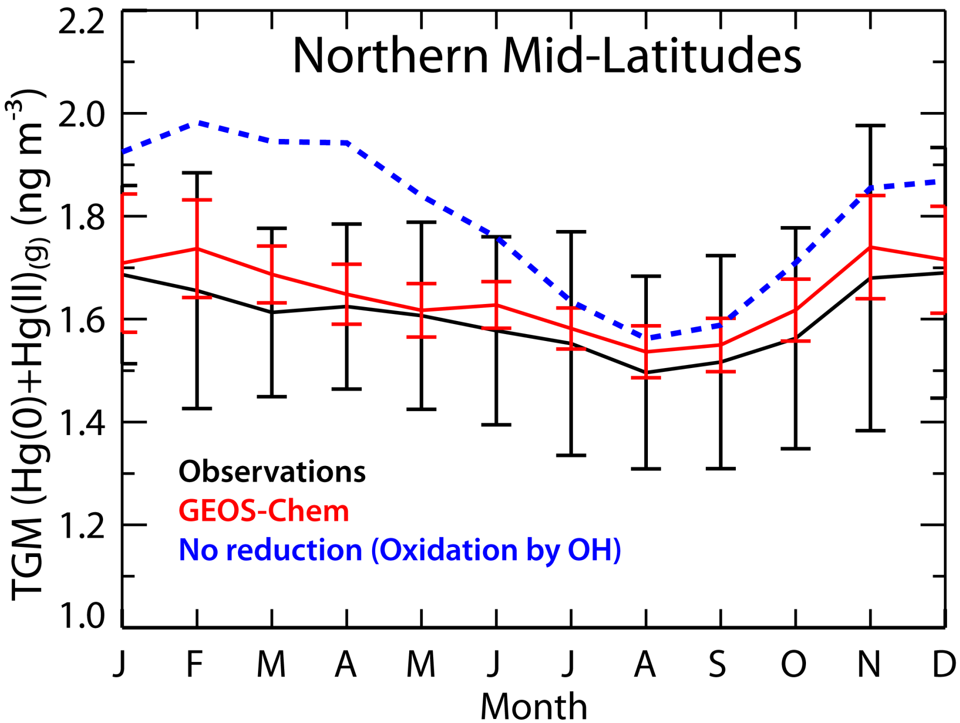
Atmospheric Reactions of Mercury



Goal: Use combination of model and measurements to constrain mercury chemistry, transport, and deposition

Measurements: TGM=Total Gaseous Mercury, RGM=Reactive Gaseous Mercury

Oxidation and Reduction Processes



Seasonal variation of TGM is consistent with photochemical oxidation of Hg(0) partially balanced by reduction of Hg(II)

- *Consensus was that OH is the dominant Hg(0) oxidant. (Included in GEOS-Chem)*
- *But the OH reaction may not occur in the atmosphere [Calvert & Lindberg 2005]*

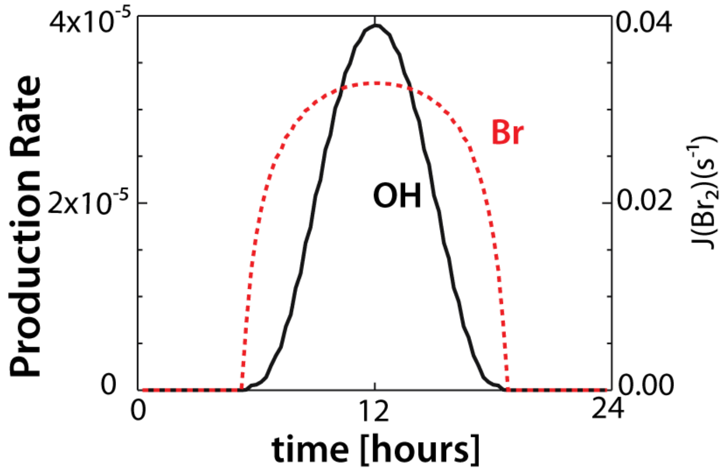
$$Hg + OH \rightarrow HgOH$$

~~$HgOH + O_2 \rightarrow HgO + HO_2$~~

- *Could the dominant oxidant be Br? [Holmes et al. 2006]*

[*Selin et al. JGR 2007*]

Diurnal Pattern: Br Oxidation, Sea-Salt Uptake

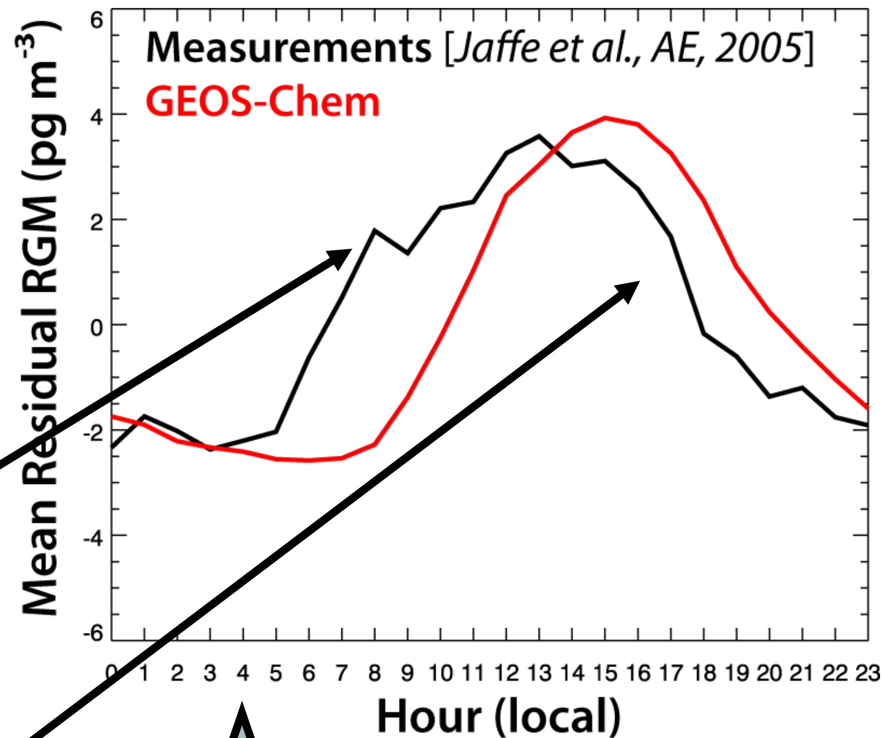


[*von Glasow et al. JGR 2002*]

Measured RGM begins to increase earlier in the day than the model

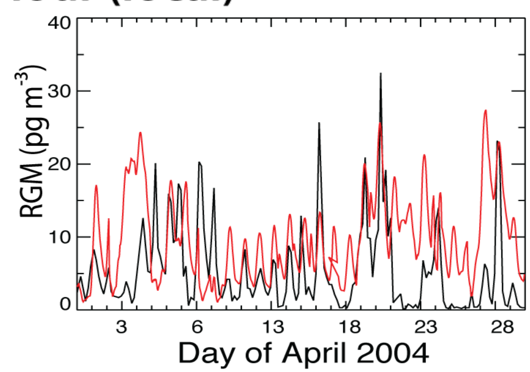
Production of Br begins earlier than OH

Evidence for Br oxidation



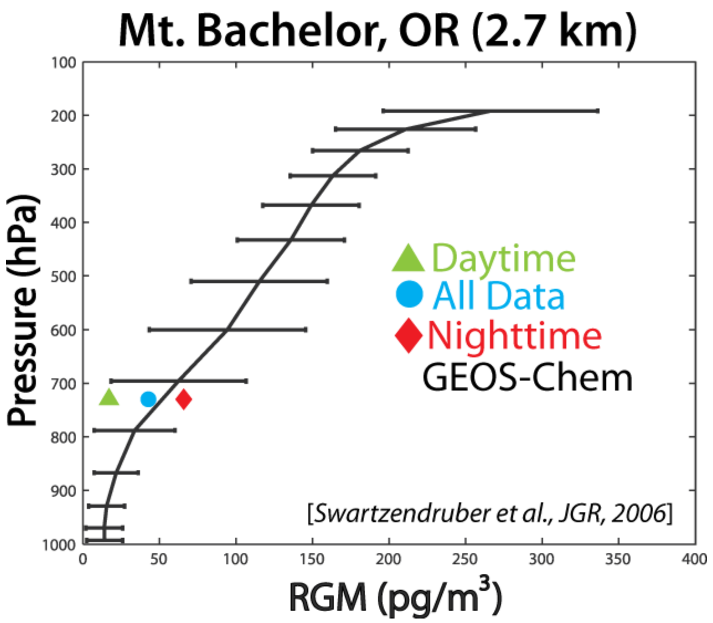
Rapid afternoon decline can't be explained by dry deposition alone.

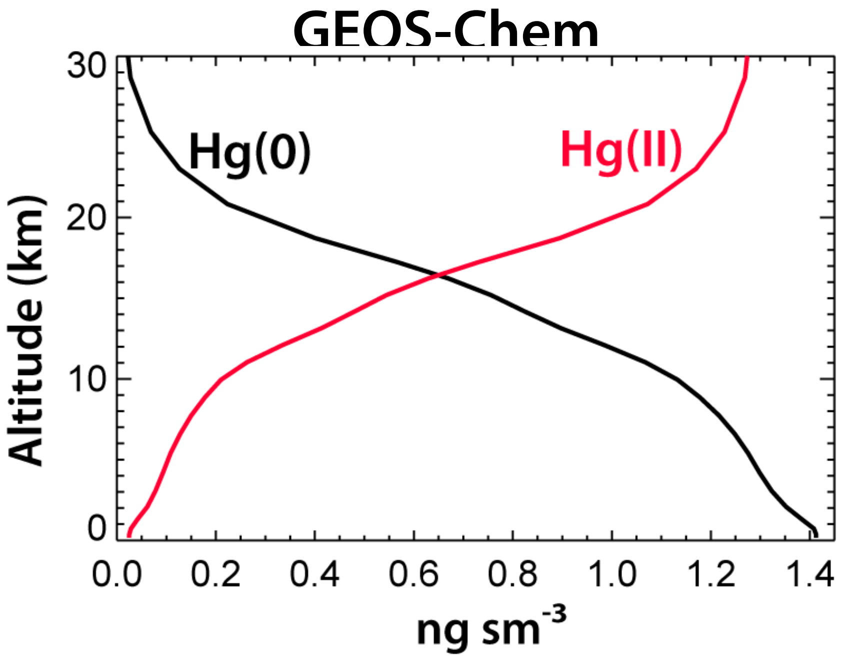
Hypothesis: uptake onto sea-salt aerosol



[*Selin et al. JGR 2007*]

High Levels of Hg(II) at Altitude



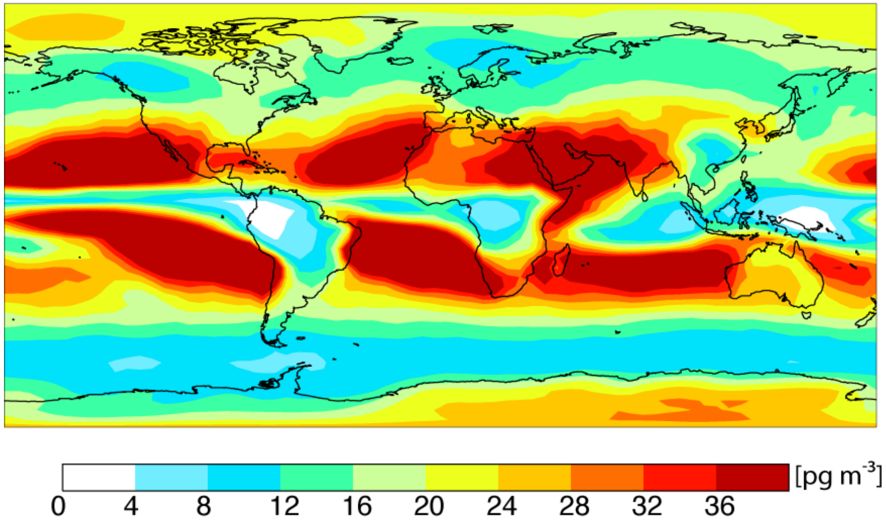


- Measurements from Mt. Bachelor show elevated RGM over surface levels (higher levels in subsidence at night)
- Murphy et al. [2006] show Hg associated with particles in the upper troposphere
- GEOS-Chem shows increasing Hg(II) with altitude:
  - Source = oxidation from Hg(0) with OH, O3
  - Sinks = Aqueous reduction (dry at altitude), wet and dry deposition (near-surface)
- Supported by aircraft measurements (more to come?)

[*Selin et al. JGR 2007*]

Subsidence brings Hg(II) downwards

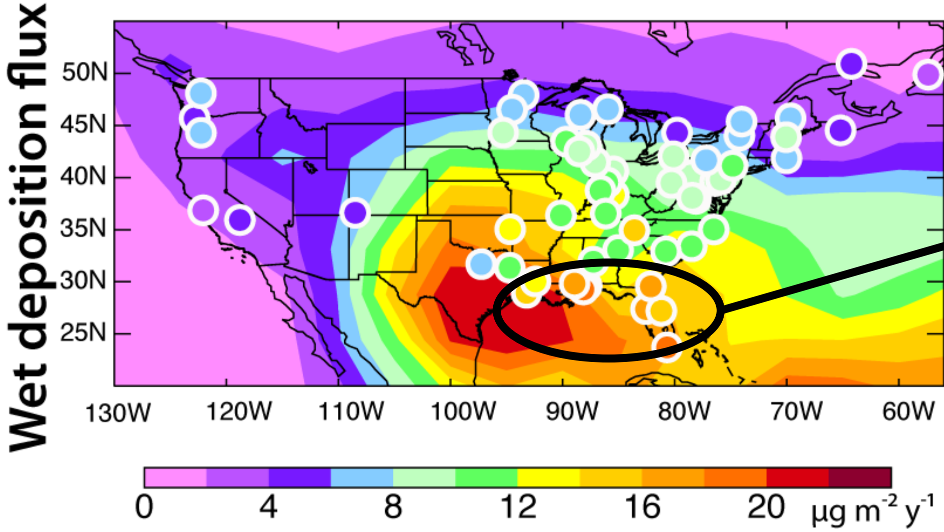
Hg(II) at 800 hPa



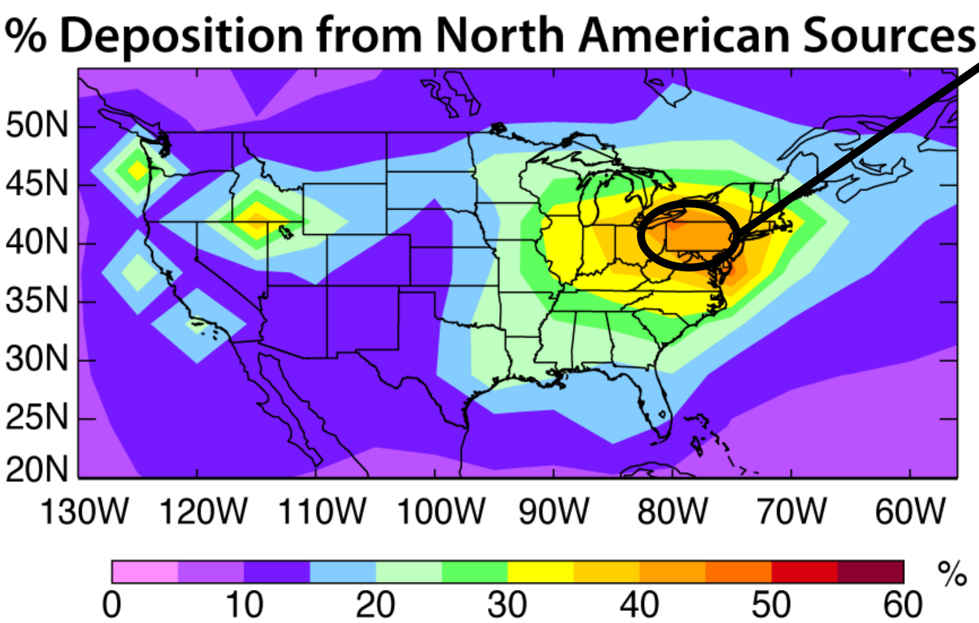
- Hg(II) at higher altitudes will descend where there is subsidence
- High levels of Hg(II) in the model associated with subsidence in the Hadley Cell (subtropical desert regions)
- Potential to affect the surface, but few measurements in these areas!

[*Selin et al. GBC 2008*]

North American Contribution to Mercury Deposition



Southeast has highest wet deposition in the U.S., but mostly from non-US sources: this is due to rainout of mercury from higher altitudes in summertime

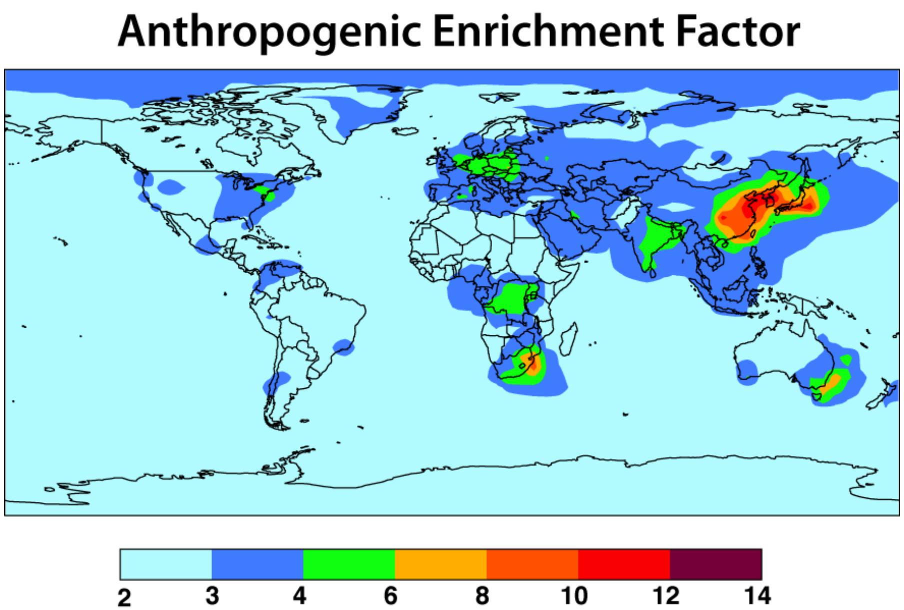


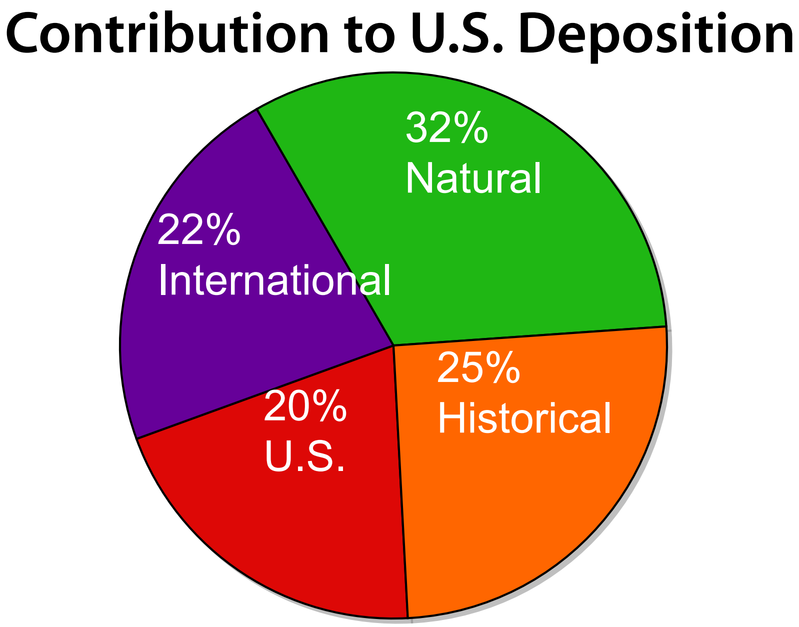
Up to 60% of deposition in Midwest/Northeast U.S. is from domestic sources

Policy implications:
Reducing deposition in both Midwest and Southeast will require policy actions on multiple political scales (national and global)

[*Selin & Jacob, Atmos. Env. 2008*]

Present vs. Historical Sources of Mercury

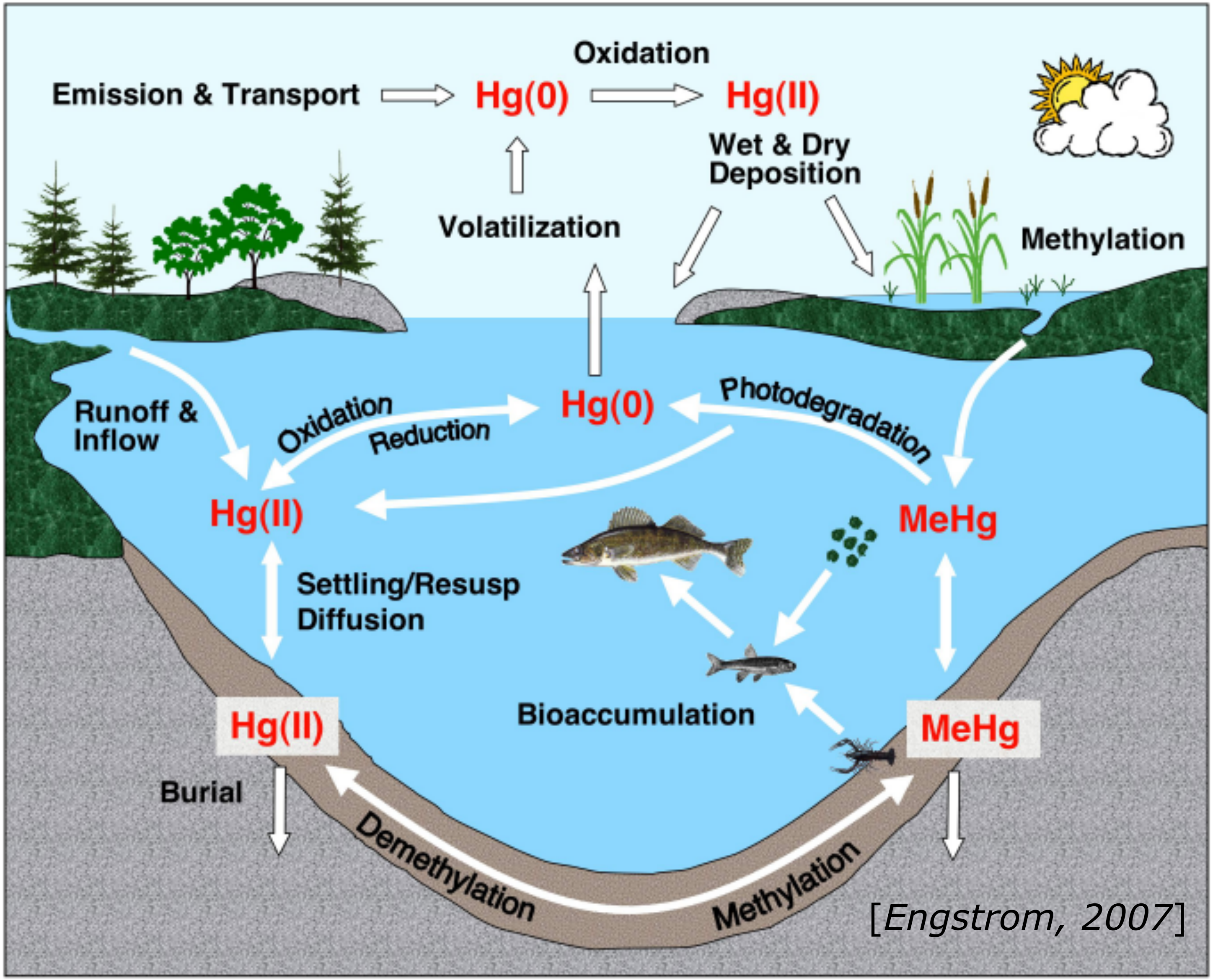




- Factor of 3 enrichment on average since pre-industrial times (constrained by sediment core records), but spatial variation
- Historical legacy continues to affect ecosystems through deposition

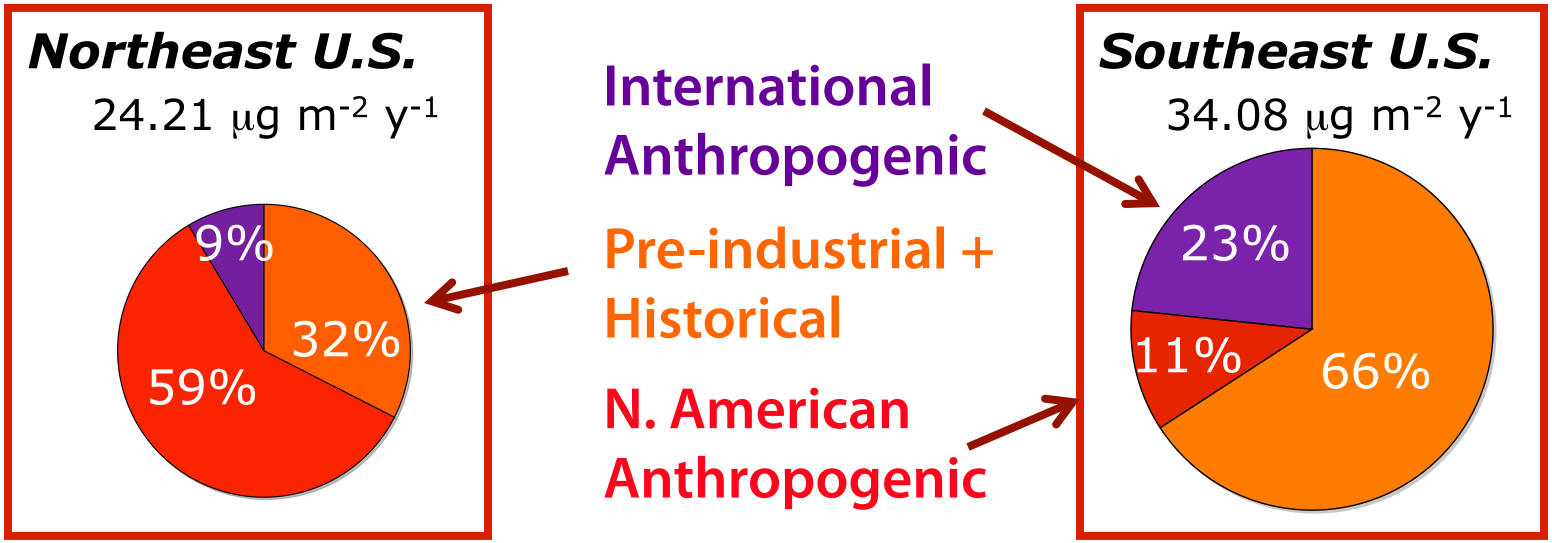
[*Selin et al., GBC 2008*]

From Deposition to Fish Methylmercury



Freshwater Deposition and Source Attribution

How do sources affect fish methylmercury, and on what timescales?



Lake, River, Watershed, and Aquatic food web models
[Knightes et al., 2009]

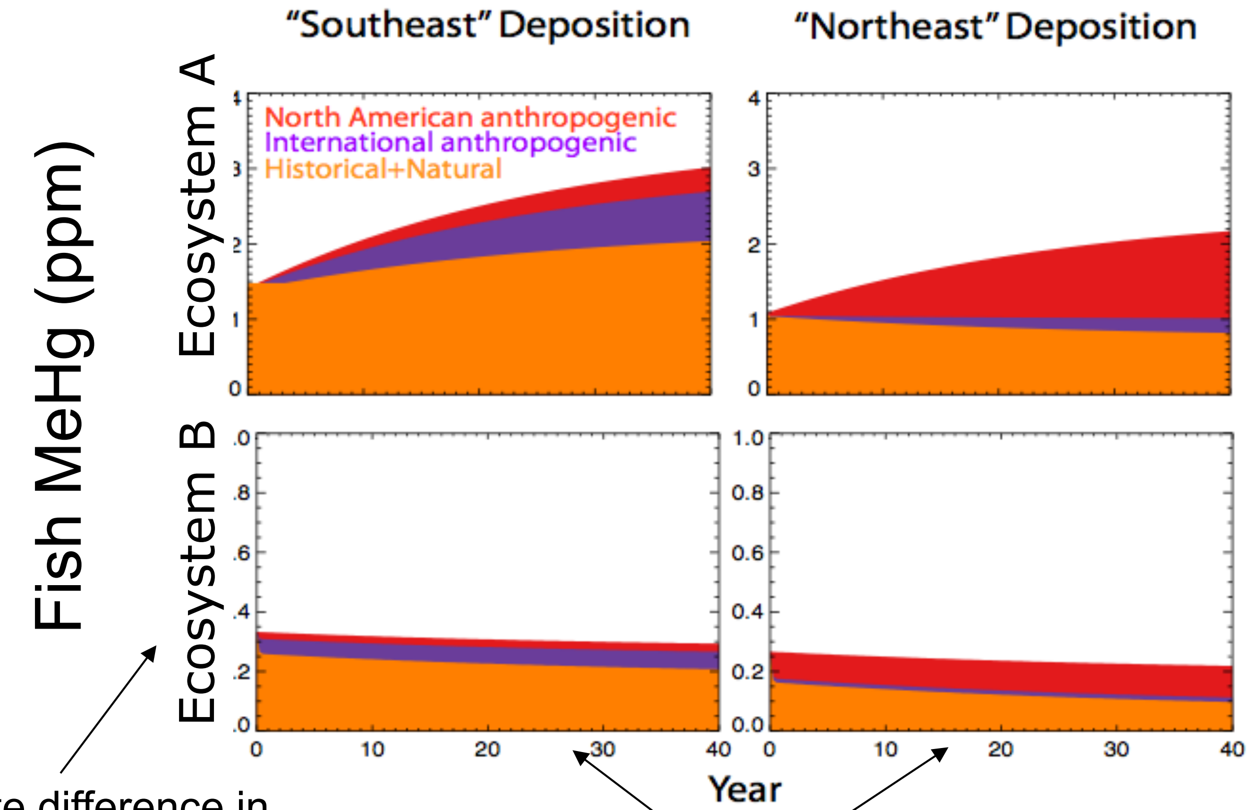
Policy and Timescale Analysis

[Selin et al., Environ. Health Persp., 2010]

Freshwater Ecosystem Timescale Analysis

Each ecosystem driven by present-day deposition for 40 years

Policy experiment: All Hg is "historical" at t=0. How is anthropogenic signal reflected in fish, and on what timescale?



Same deposition,but different ecosystem dynamics lead to very different source attributions (and concentrations) over time (watershed role)

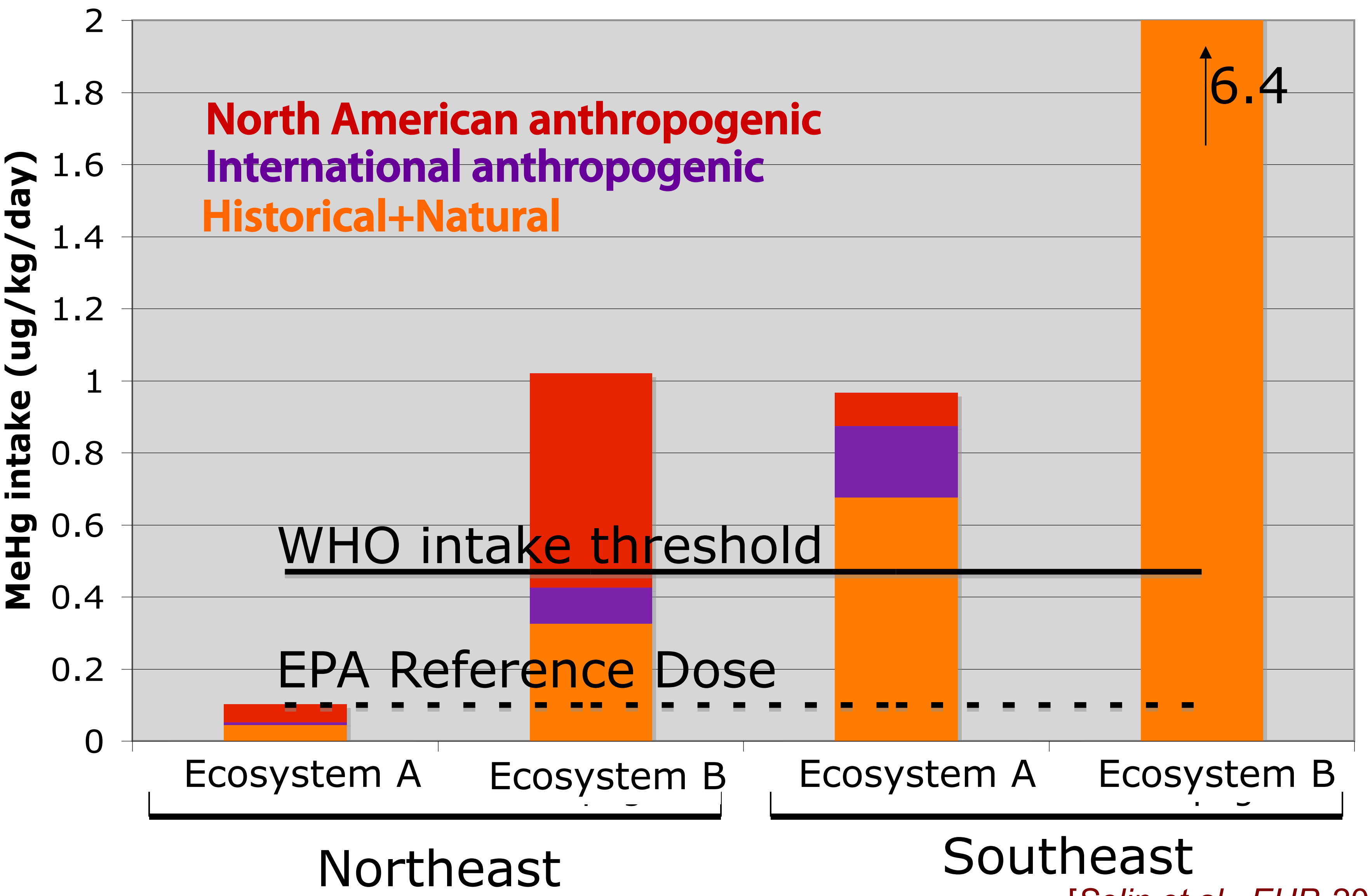
Note difference in scale!

Regional differences in deposition sources lead to different attributions in similar ecosystems

[*Selin et al., EHP,* 2010]

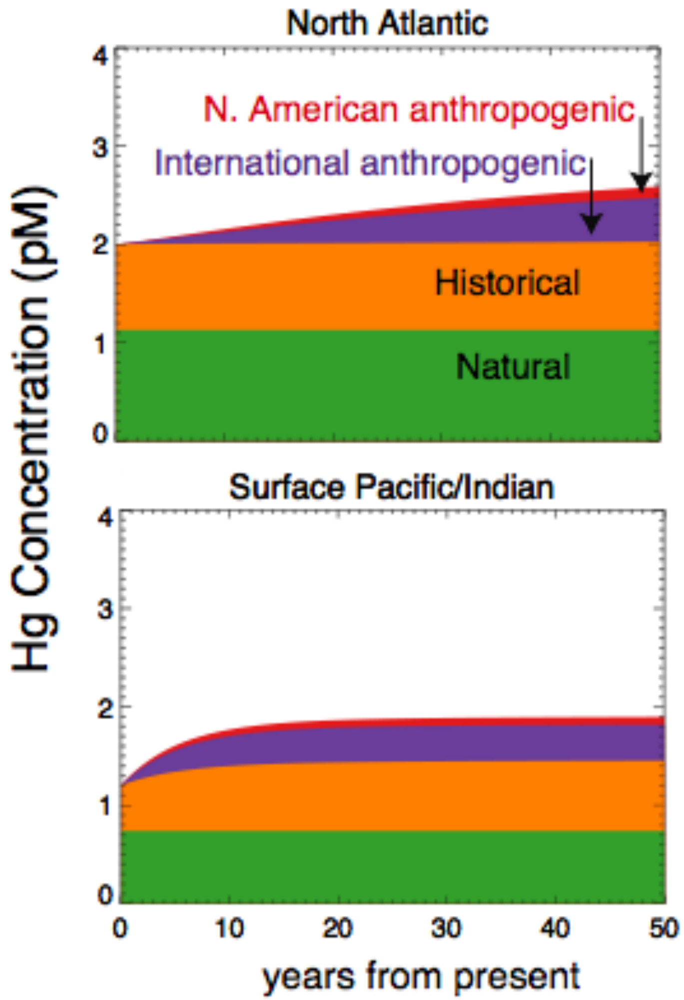
Local Exposure from Freshwater Fish

2 x 100 g fish meals/week (60 kg person) @ t=40 y



[*Selin et al.*, *EHP*, 2010]

Population-Wide Hg Exposure from Marine Fish



"current emissions" scenario

14-box ocean model: Sunderland and Mason, 2007

No mechanistic link (yet) from oceanic Hg concentration to fish methylmercury

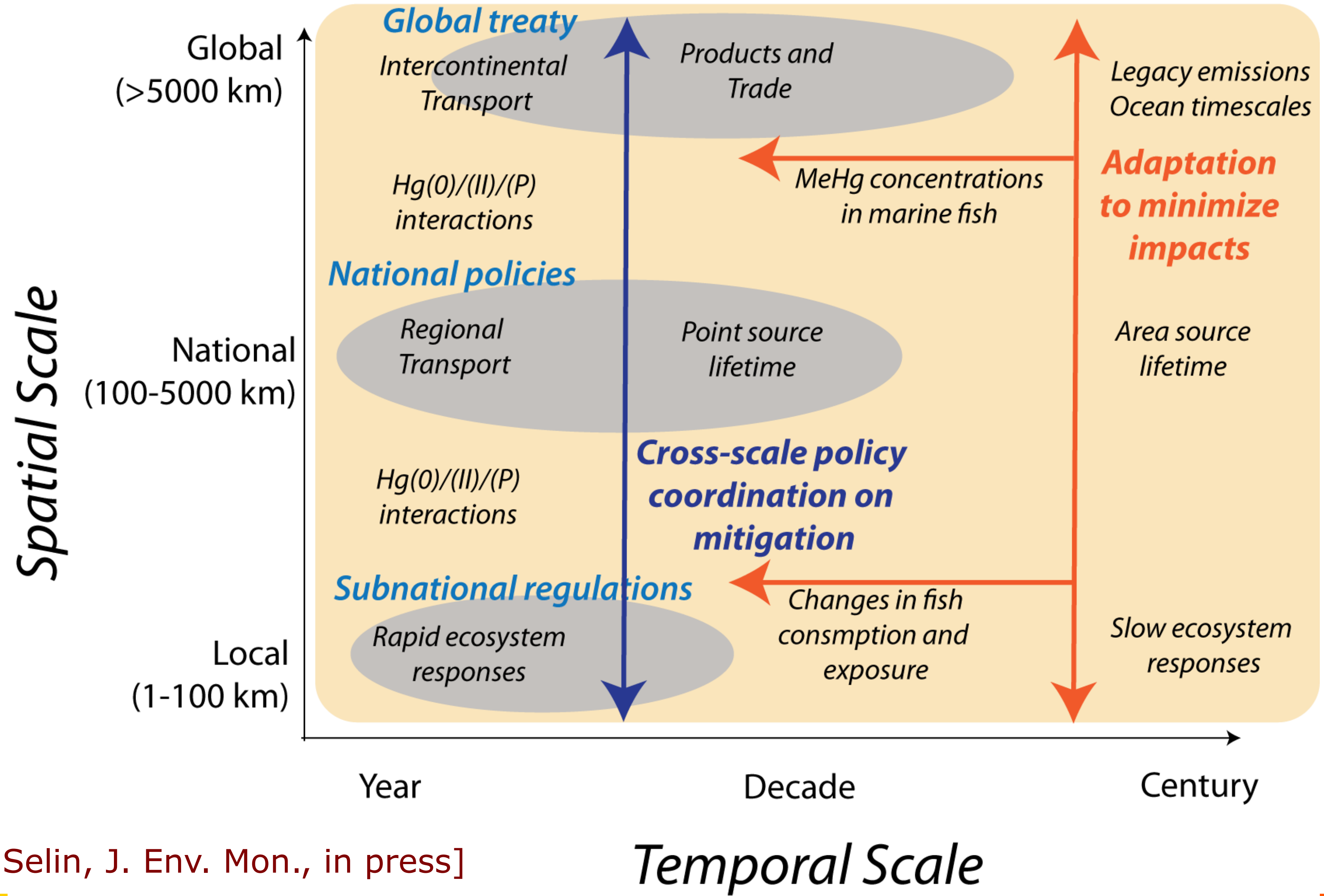
Historical exposure could continue to increase, complicating policy decision-making

Different challenges on different scales (local to global)

Adaptation and mitigation necessary? (Learning lessons from other issue areas)

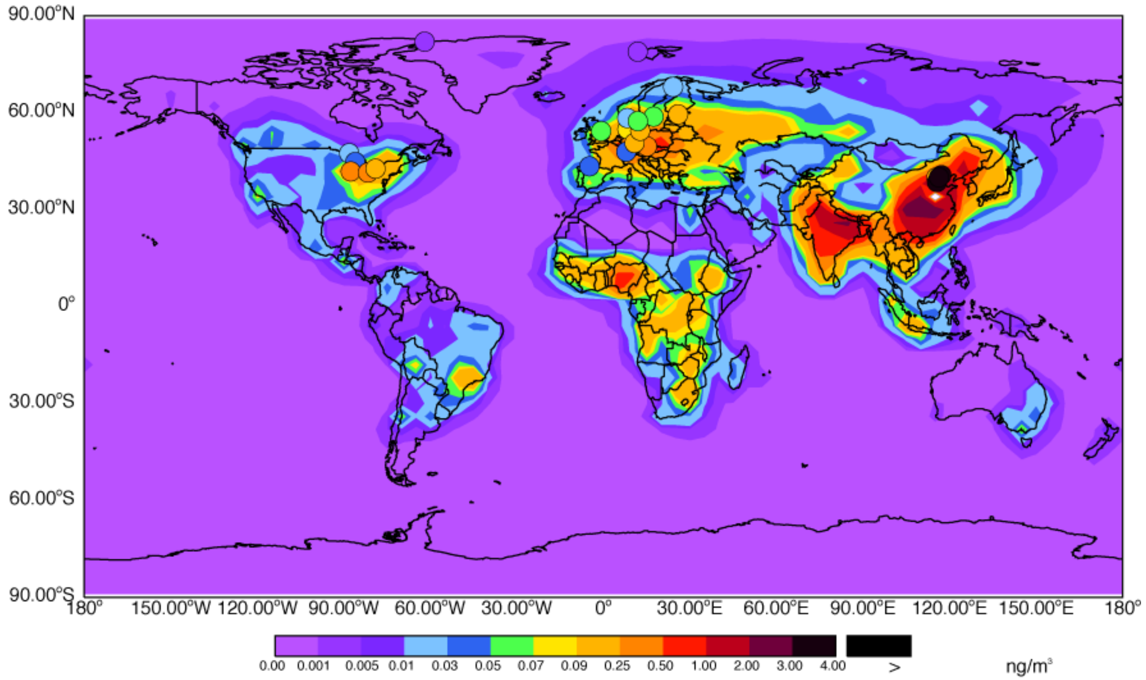
[*Selin et al., EHP,* 2010]

Mercury as a cross-scale science-policy problem



[Selin, J. Env. Mon., in press]

Polycyclic Aromatic Hydrocarbons in the atmosphere

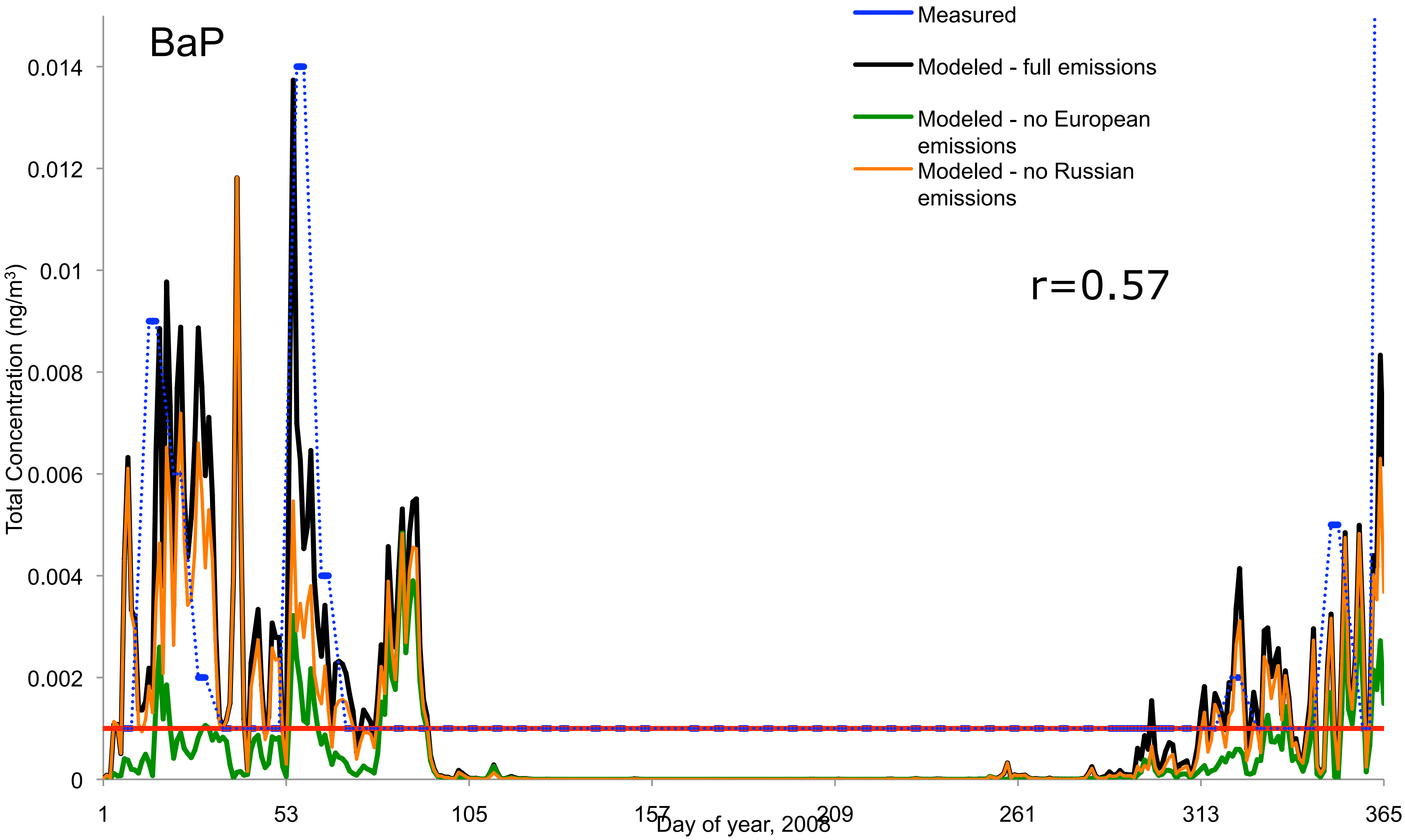


Simulated Benzo(a)pyrene (left) Phenanthrene Pyrene

- Model simulates global mean, seasonal variation for all 3 PAHs (and relative differences)…but relatively few measurements
- On-particle oxidation is important for benzo(a)pyrene
- Major developments in gas-particle partitioning, deposition parameterizations for semivolatile species

[Friedman and Selin, in prep.]

Simulating sources of episodic transport of B(a)P to the Arctic: Spitzbergen, NO



[Friedman and Selin, in prep.]

Interested in linking science to policy? Introducing the "Mercury Game"!

Simulate using science in developing global policy:

- ❑ Play the role of a country, a non-governmental organization, or a scientific organization
- ❑ Use scientific data to argue your positions!

Play the "Mercury Game":

- ❑ Collaboration with MIT graduate student Leah Stokes and Prof. Lawrence Susskind (Department of Urban Studies and Planning)
- ❑ Designed to teach scientists and engineers about the process and how to participate
- ❑ Freely available on the web at http://mit.edu/mercurygame

Funding for game development: NSF Atmospheric Chemistry Program

Play the Mercury game in Halifax at Mercury 2011: Short course on Sunday, July 24th

The Selin Group 2011: http://mit.edu/selingroup

- **Postdocs:**
  - Carey Friedman (PhD, URI): Transport and fate of persistent organic pollutants
  - Tammy Thompson (PhD, U. Texas): Regional-to-global atmospheric chemistry modeling
- **Doctoral Students:**
  - Rebecca Saari, Engineering Systems: Future climate policy and air pollution health impacts
  - Leah Stokes, Department of Urban Studies and Planning: Mercury science-policy
- **Undergraduates:**
  - Anastasia Maheras (EAPS Senior): Mercury data analysis

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