

Linkages Between Environmental Monitoring and Modeling

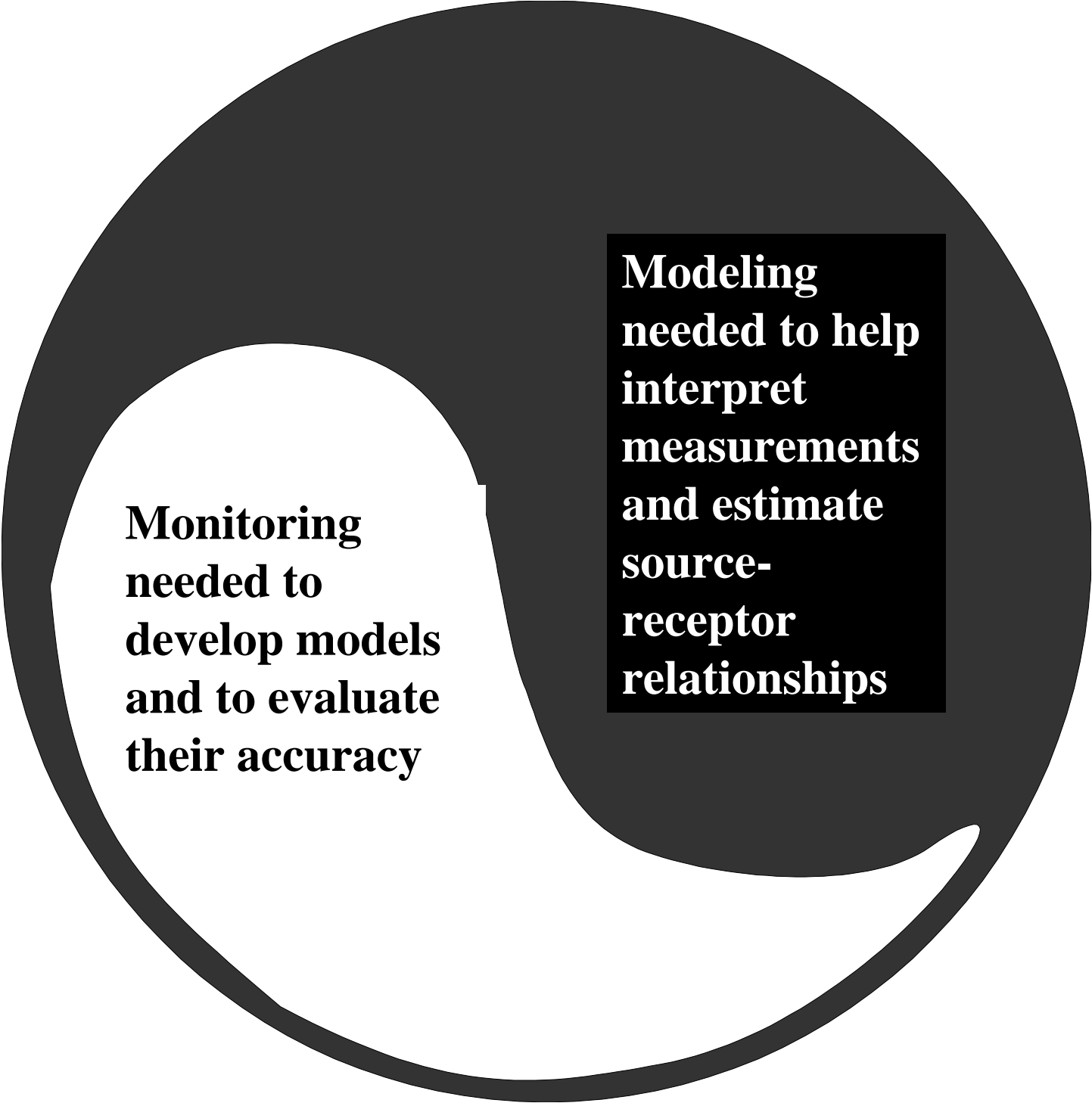
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Long Term Monitoring:
Supporting Science and Informing Policy
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Inextricable Linkage Between Modeling and Monitoring



**Monitoring
needed to
develop models
and to evaluate
their accuracy**

**Modeling
needed to help
interpret
measurements
and estimate
source-
receptor
relationships**

- **Two Main Approaches in Linking Modeling and Monitoring**
- **Challenges in Exploiting Synergisms Between Modeling and Monitoring**

Two Main Approaches in Linking Modeling & Monitoring

- 1. Receptor-Oriented Methods
(e.g., Back Trajectory Analysis)**
- 2. Comprehensive Fate and
Transport Models based on
Emissions Inventories**

Receptor-Oriented Methods

Back Trajectory Analysis

- Start with measurements at a given location
- Use meteorology to estimate back trajectories of air parcels constituting each measurement
- Can develop estimates of relative importance of different source regions in influencing concentrations at the site
- Enhancements include Cluster Analysis; and Potential Source Contribution Function (PSCF) Analysis

Receptor-Oriented Methods

Advantages of Back-Trajectory Analyses

- **Emissions inventory not needed**
- **Relatively simple calculations – little computational resources required**
- **Don't need information about fate processes**

Receptor-Oriented Methods

Difficulties with Back-Trajectory Analyses

- Need a *lot* of measurements
- Measurements must be *short duration* (e.g., a few hours or at most a day)
- Can't start back trajectory at the *ground* (where the measurement was made) must "guess" where to start the back-trajectory (500, 1000 meters?)
...answers will be influenced by this decision
- Not sure *where* on the back trajectories the important sources really are
- Very difficult to account for fate processes (deposition, chemical transformation)

Receptor-Oriented Methods

Chemical Mass Balance Methods

- **Start with emissions profiles of different source categories**
- **Determine what proportion of contributions from each source category would be required to match the existing measurements**
- **Yields estimates of the impact of these different source categories at the measurement site**

Receptor-Oriented Methods

Difficulties with Chemical Mass Balance Methods

- Emissions profiles for different source categories not always known
- Need measurements of many different pollutants to carry out analysis
- Don't get information about the spatial extent of the significant sources
- Fate processes not accounted for (e.g., chemical transformation)

Receptor-Oriented Methods

Summary

- **Receptor-oriented measurements can provide limited source-receptor information**
- **With no emissions inventory, its all you can do...**

Two Main Approaches in Linking Modeling & Monitoring

**1. Receptor-Oriented Methods
(e.g., Back Trajectory Analysis)**

**2. Comprehensive Fate and
Transport Models based on
Emissions Inventories**

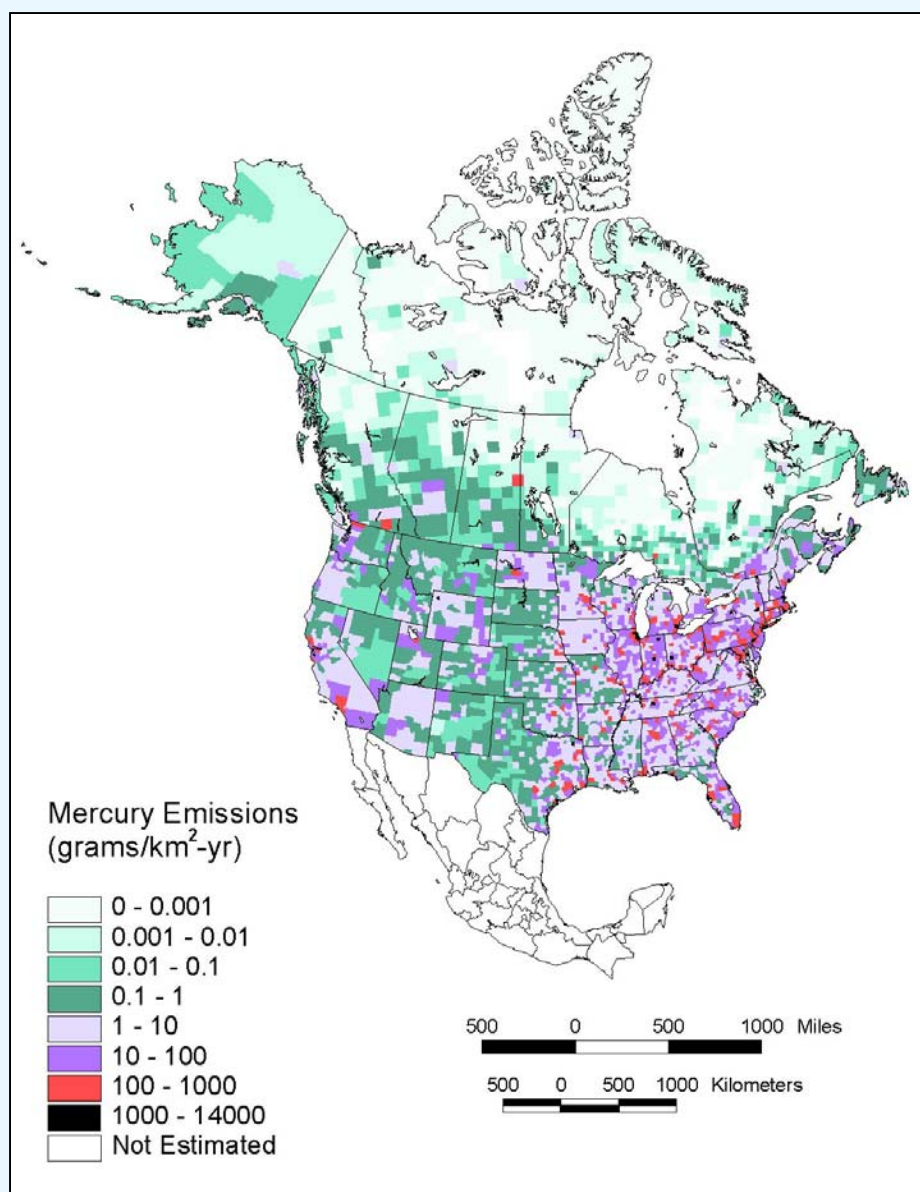
Comprehensive Fate and Transport Models Based on Emissions Inventories

Methodology

- Start with emissions inventory

Geographic distribution of total mercury emissions to the atmosphere from U.S. and Canadian anthropogenic sources (1995/1996).

(Speciation?)



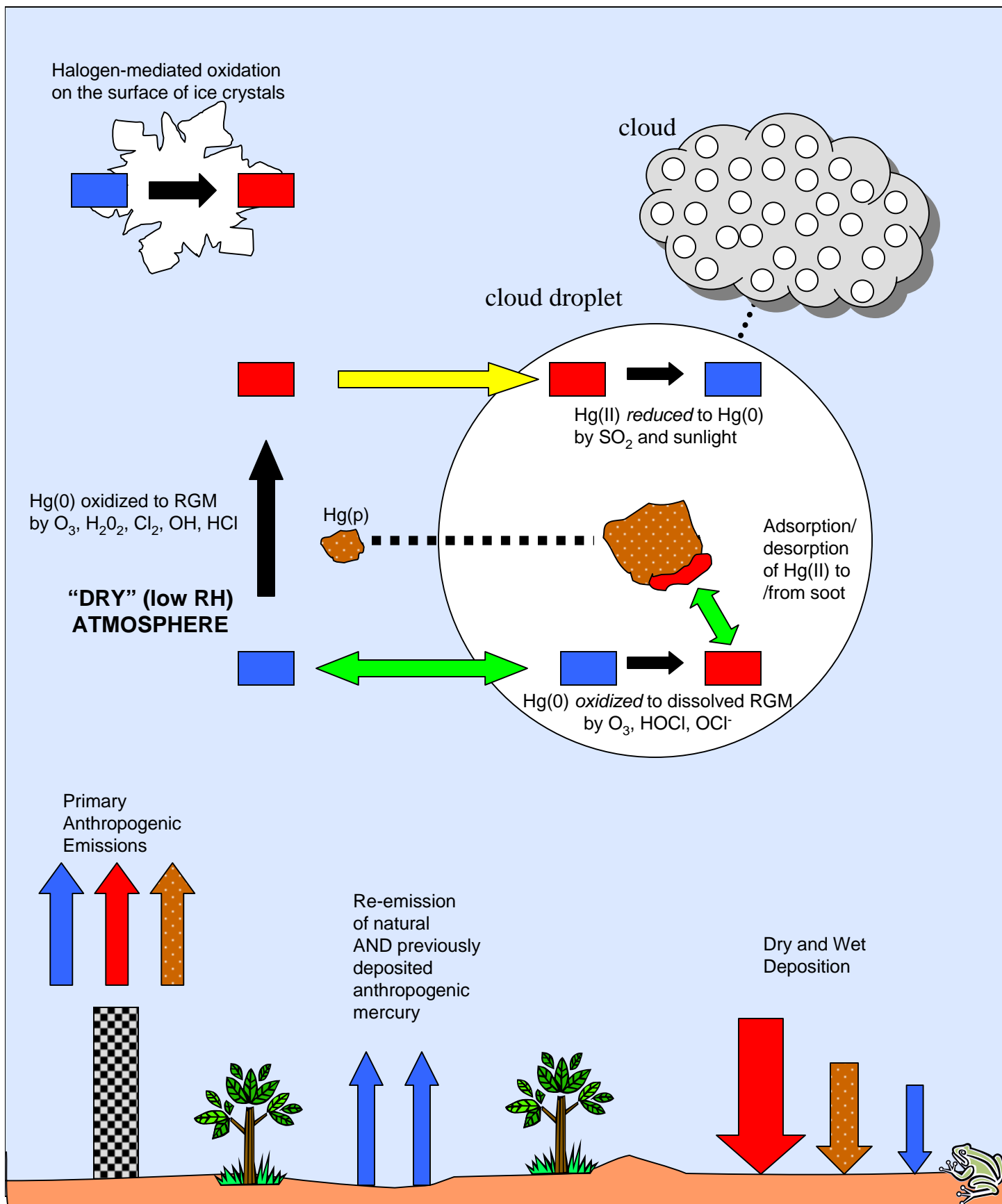
Comprehensive Fate and Transport Models Based on Emissions Inventories

Methodology

- Start with emissions inventory
- **Incorporate atmospheric behavior of pollutant(s) into 3-D fate & transport model:**
 - Phase-partitioning
 - Chemical transformation
 - Wet and dry deposition

Atmospheric Fate Processes for Hg

- Elemental Mercury: Hg(0)
- Reactive Gaseous Mercury: RGM
- Particulate Mercury: Hg(p)



Atmospheric Chemical Reaction Scheme for Mercury

Reaction	Rate	Units	Reference
<i>GAS PHASE REACTIONS</i>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg(p)}$	3.0E-20	cm ³ /molec-sec	Hall (1995)
$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1.0E-19	cm ³ /molec-sec	Hall and Bloom (1993)
$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg(p)}$	8.5E-19	cm ³ /molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	4.0E-18	cm ³ /molec-sec	Calhoun and Prestbo (2001)
$\text{Hg}^0 + \text{OHC} \rightarrow \text{Hg(p)}$	8.7E-14	cm ³ /molec-sec	Sommar et al. (2001)
<i>AQUEOUS PHASE REACTIONS</i>			
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2}$	4.7E+7	(molar-sec) ⁻¹	Munthe (1992)
$\text{Hg}^0 + \text{OHC} \rightarrow \text{Hg}^{+2}$	2.0E+9	(molar-sec) ⁻¹	Lin and Pehkonen(1997)
$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T^*e^{((31.971*T)-12595.0)/T}$ sec ⁻¹ [T = temperature (K)]		Van Loon et al. (2002)
$\text{Hg(II)} + \text{HO}_2\text{C} \rightarrow \text{Hg}^0$	~ 0	(molar-sec) ⁻¹	Gardfeldt & Jonnson (2003)
$\text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2}$	2.1E+6	(molar-sec) ⁻¹	Lin and Pehkonen(1998)
$\text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2}$	2.0E+6	(molar-sec) ⁻¹	Lin and Pehkonen(1998)
$\text{Hg(II)} \leftrightarrow \text{Hg(II)}_{(\text{soot})}$	9.0E+2	liters/gram; t = 1/hour	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
$\text{Hg}^{+2} + \text{h} \leftarrow \rightarrow \text{Hg}^0$	6.0E-7	(sec) ⁻¹ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

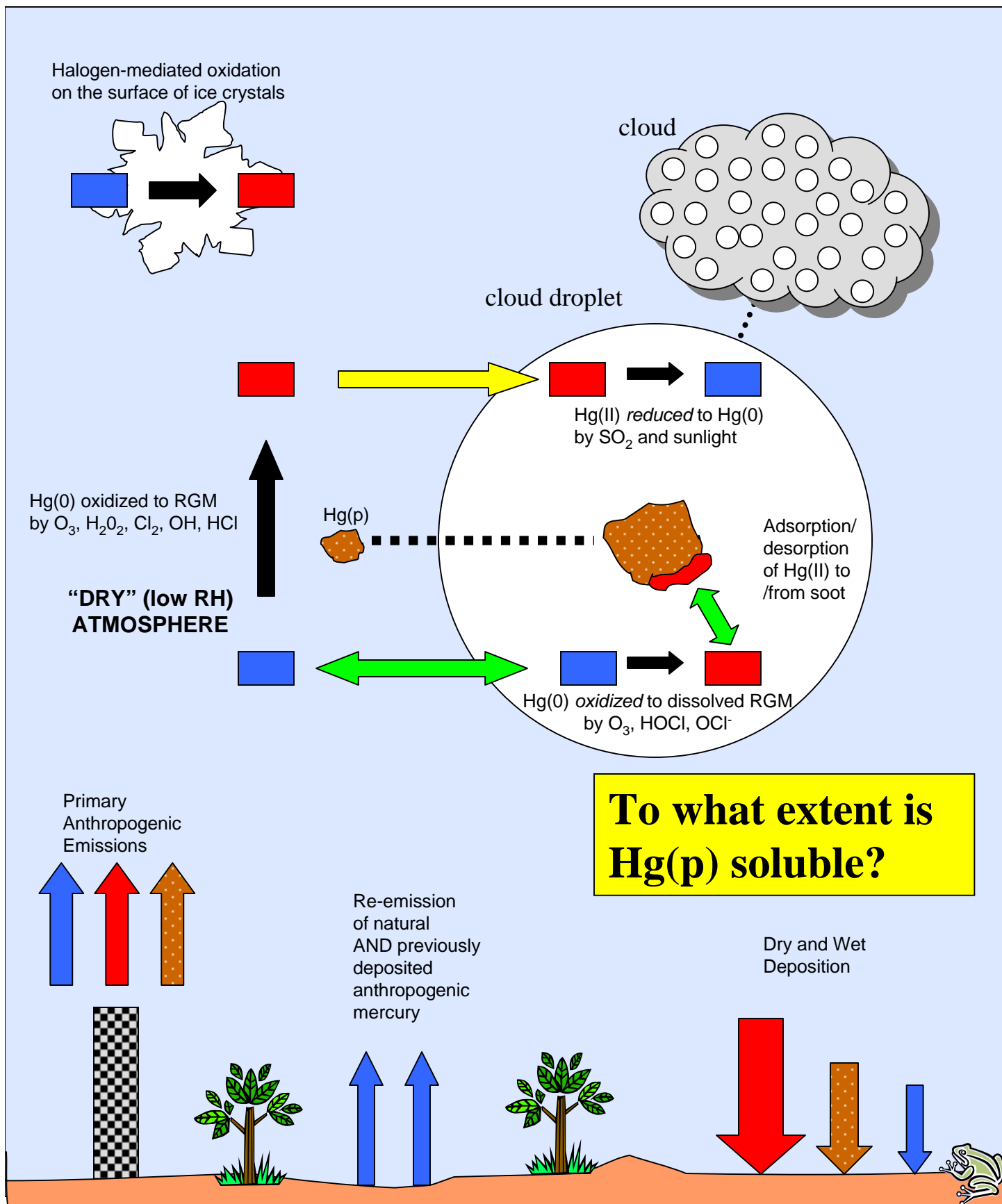
Comprehensive Fate and Transport Models Based on Emissions Inventories

Methodology

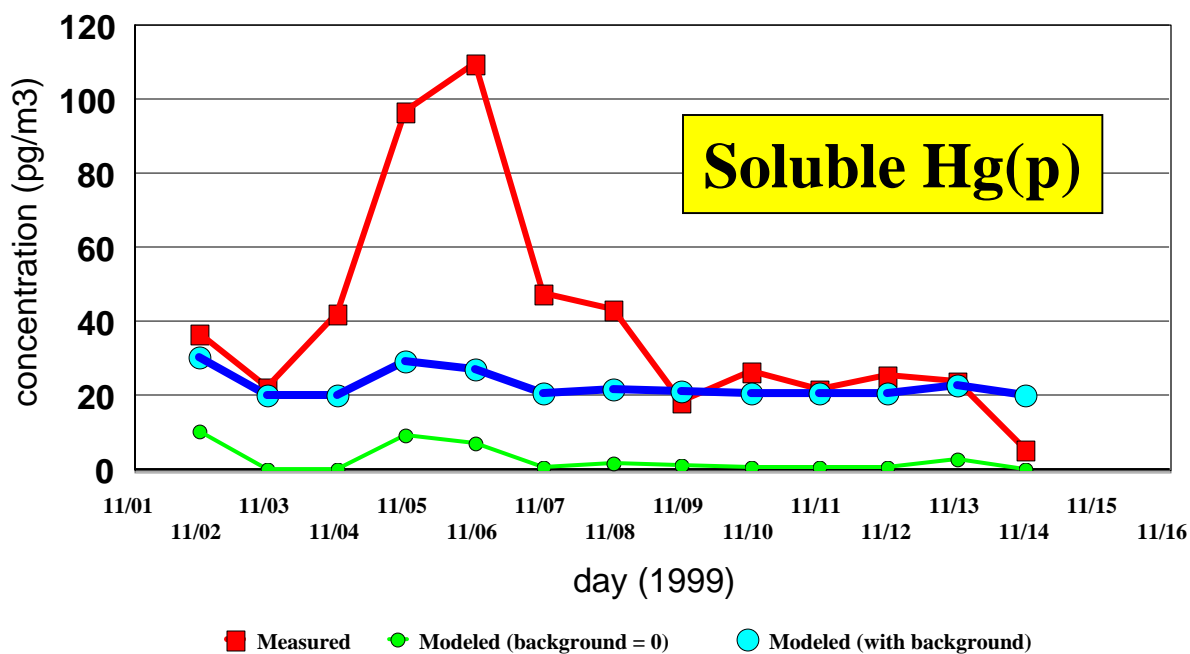
- Start with emissions inventory
- Incorporate atmospheric behavior of pollutant(s) into 3-D fate & transport model:
 - Phase-partitioning
 - Chemical transformation
 - Wet and dry deposition
- **Provide model with meteorology**
- **Simulate the fate and transport of emissions, keeping track of the impact of different sources on receptors of interest**
- **Evaluate model by comparison against monitoring data... (improve model if necessary and possible)**

Atmospheric Fate Processes for Hg

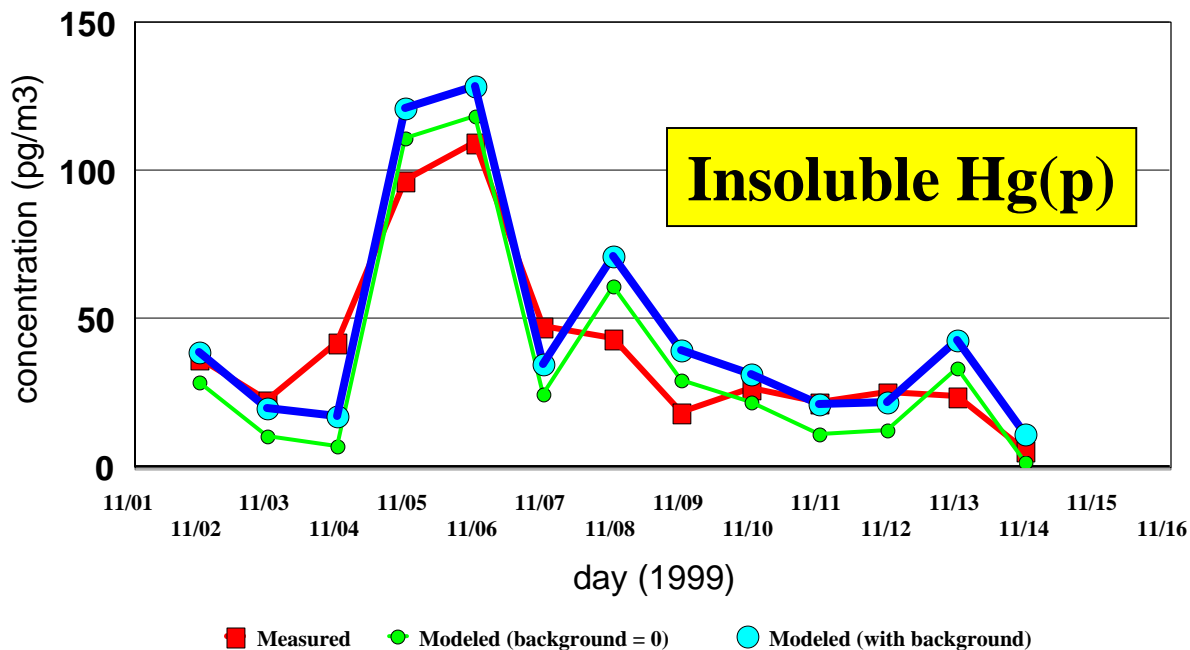
- Elemental Mercury: Hg(0)
- Reactive Gaseous Mercury: RGM
- Particulate Mercury: Hg(p)



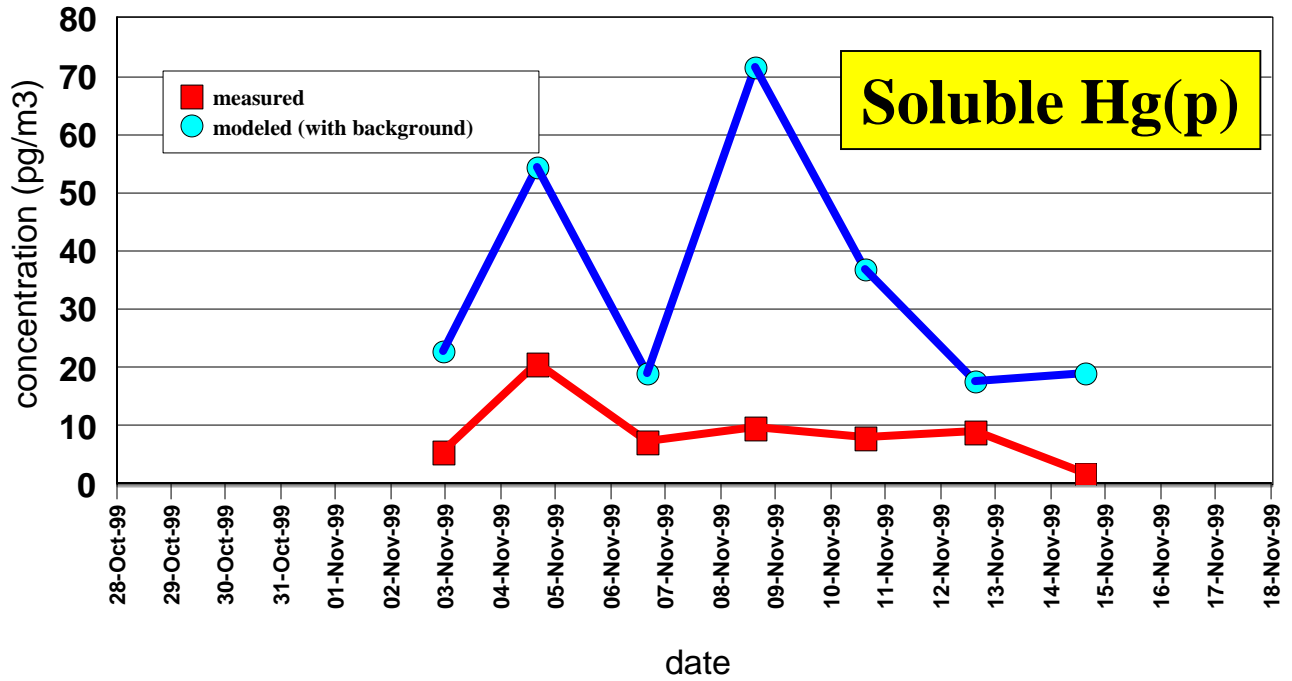
Comparison of measured vs. modeled TPM
Neuglobsow



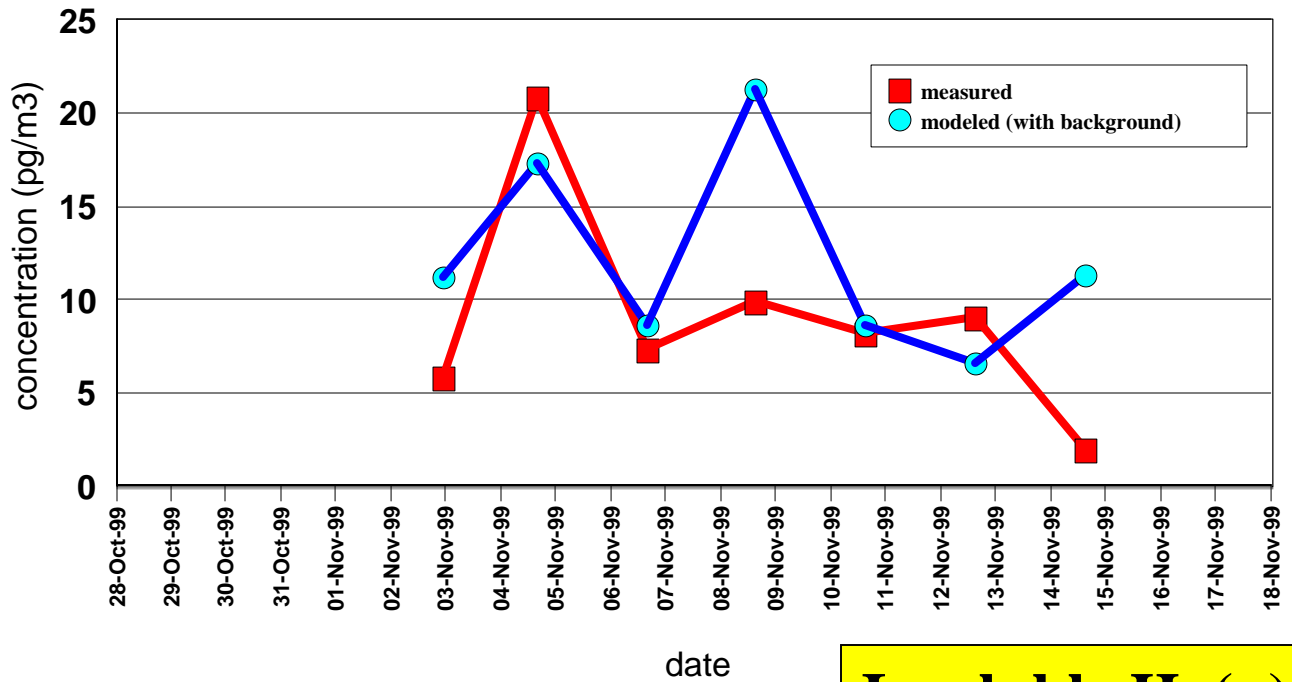
Comparison of measured vs. modeled TPM
Neuglobsow



Comparison of Measured vs. Modeled RGM
Neuglobsow, 1999 (Measurement Periods Only)



Comparison of Measured vs. Modeled RGM
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Comprehensive Fate and Transport Models Based on Emissions Inventories

Methodology

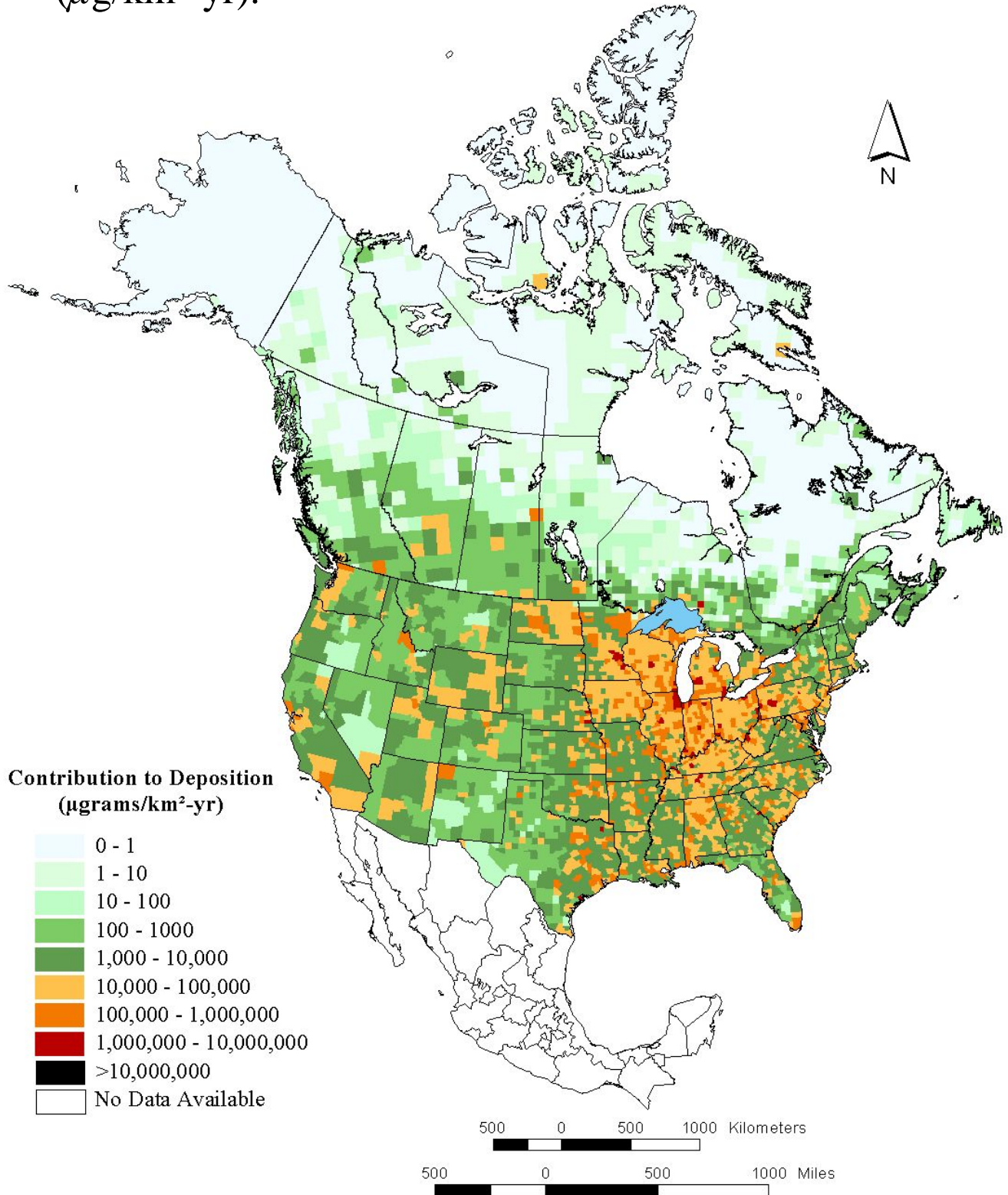
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- Provide model with meteorology
- Simulate the fate and transport of emissions, keeping track of the impact of different sources on receptors of interest
- Evaluate model by comparison against monitoring data; improve model if necessary and possible
- **If evaluation shows results are reasonable, report source-receptor information**

Comprehensive Fate and Transport Models Based on Emissions Inventories

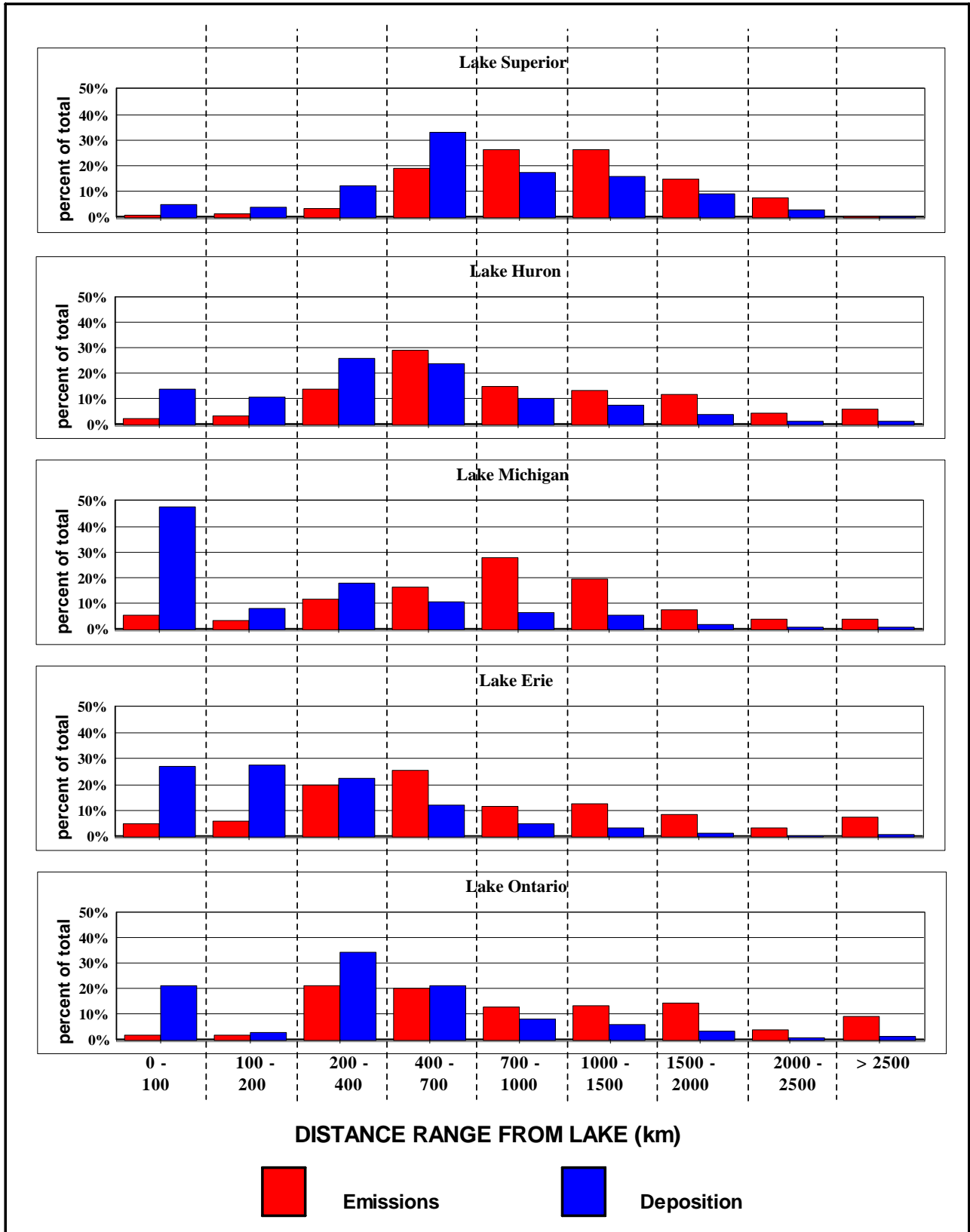
Advantages

- **Can potentially develop detailed source-receptor information**

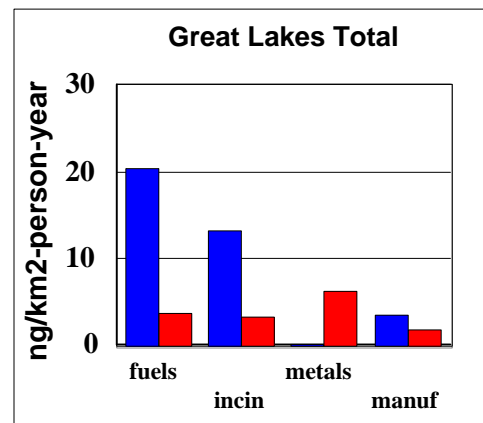
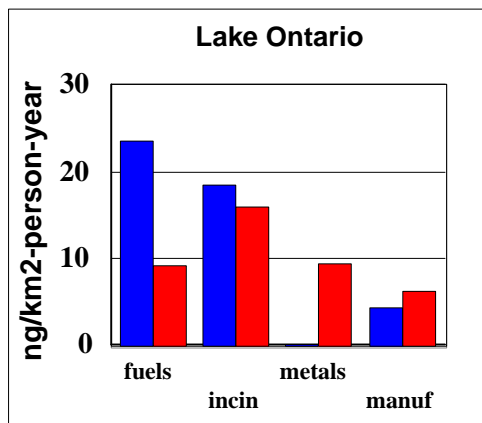
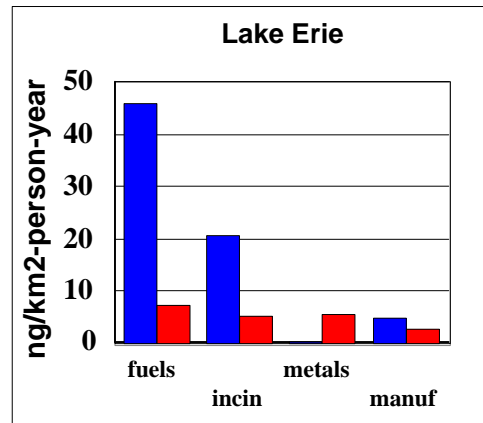
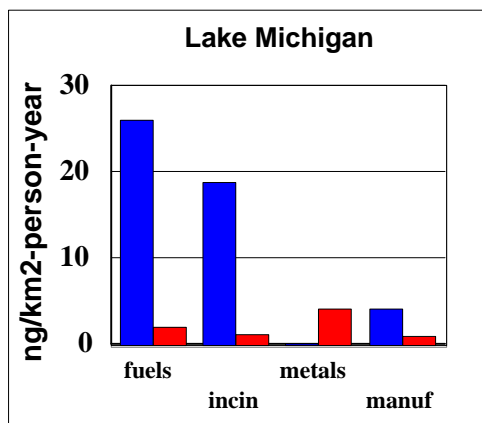
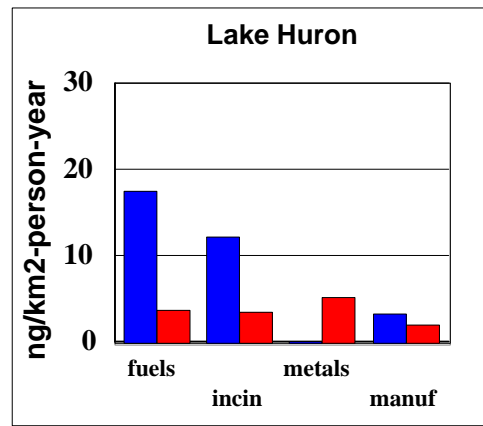
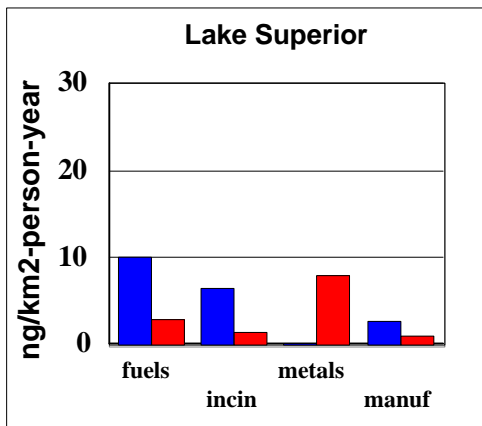
Figure A. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Superior ($\mu\text{g}/\text{km}^2\text{-yr}$).



Percent of total estimated emissions and model-estimated deposition of mercury to the Great Lakes contributed from different distance ranges away from each lake.



Per-capita mercury contributions to the Great Lakes from U.S. and Canadian sources (ng Hg deposited per km² of lake surface per person per year); “fuels” = fuel combustion; “incin” = waste incineration; “metals” = metallurgical processes; “manuf” includes “other” source types (e.g., lamp breakage) in addition to manufacturing processes (e.g., chloralkali production).



 United States

 Canada

Comprehensive Fate and Transport Models Based on Emissions Inventories

Advantages

- Can potentially develop detailed source-receptor information
- **Can analyze different emissions or climate scenarios**
- **Can fill in the spatial and temporal gaps between measurements**
- **Can estimate quantities not easily measured (e.g., dry deposition)**
- **A test of our knowledge – if models fail, it means we still don't know enough emissions and/or atmospheric fate phenomena...**

Comprehensive Fate and Transport Models Based on Emissions Inventories

Difficulties

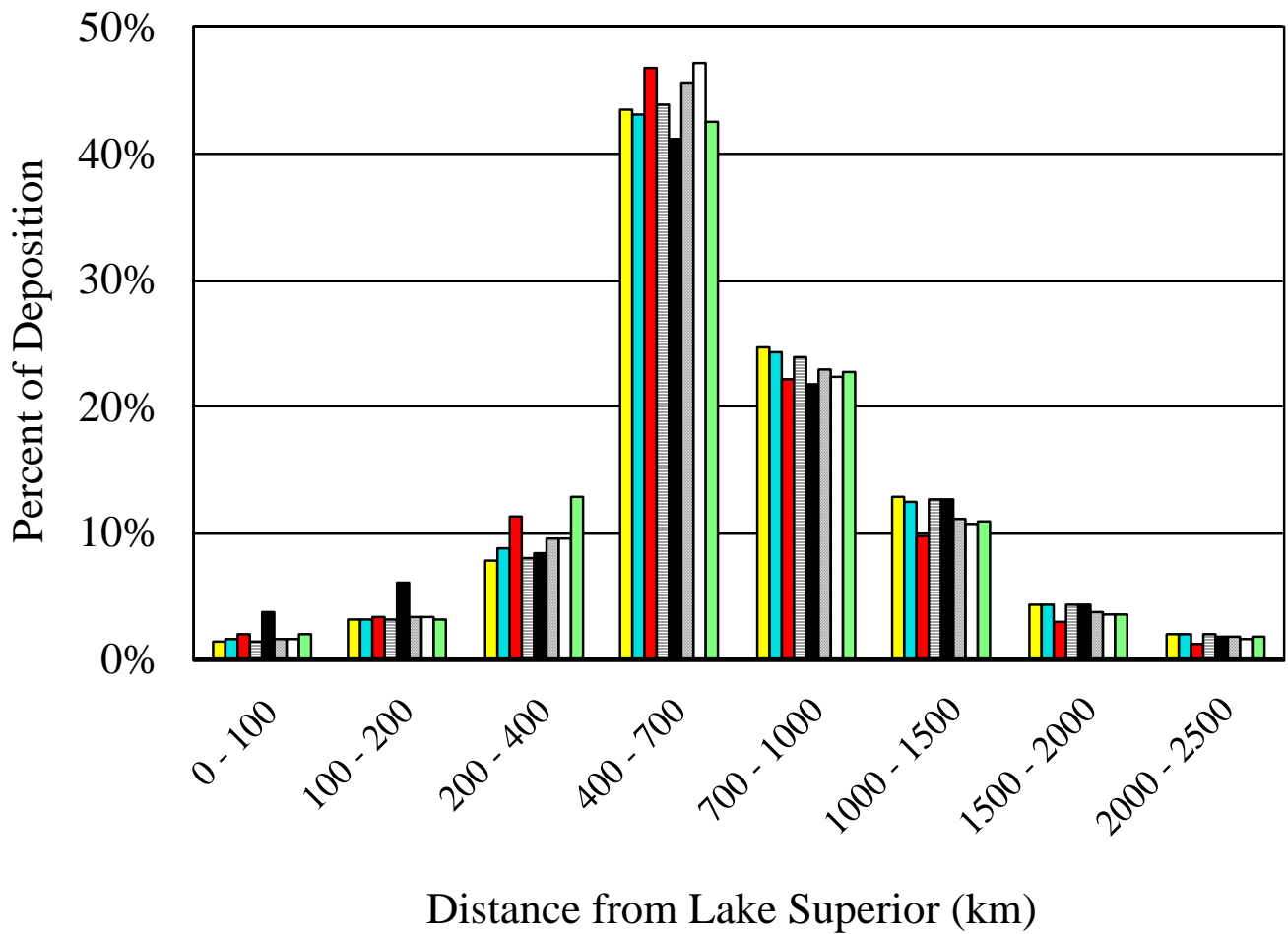
- **Emissions inventories uncertain & incomplete**
- **Even if average emissions are well known, temporal variations of emissions from any given source are largely unknown**
- **Atmospheric behavior often not well known ... so, difficult to model**
- **High resolution meteorological data expensive (one year of met data for the U.S. at ~24 km resolution costs ~\$100-200K; ~500 GB of data)**

Comprehensive Fate and Transport Models Based on Emissions Inventories

Difficulties (continued)

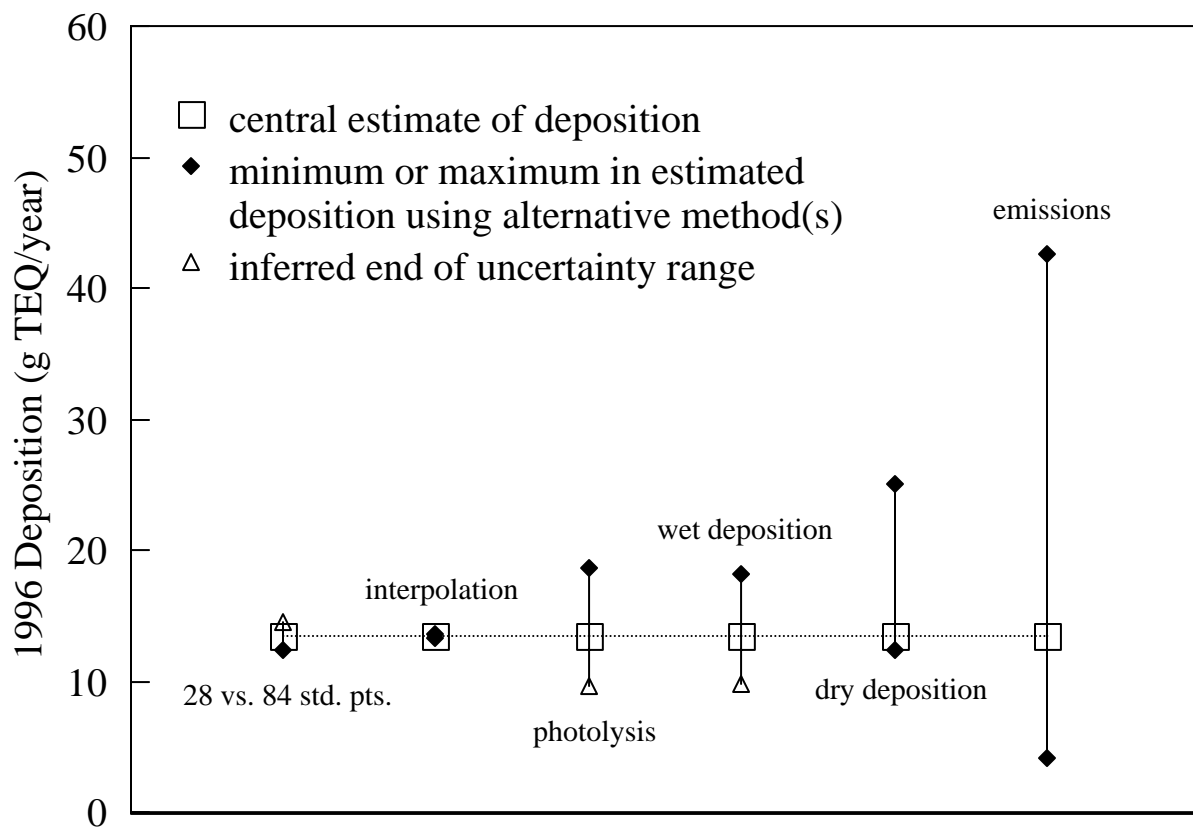
- **Need emissions and meteorology for same time period as monitoring**
- **Difficult to determine causes of poor model performance**
- **Effect of sources outside the model domain**
- **Multimedia phenomena difficult to model**
- **How to deal with uncertainties?**

Effect of fate simulation variations on the geographical pattern of PCDD/F deposition contributions to Lake Superior.



- Dry Dep D
 Dry Dep A (base case)
 particle washout x 4
- Dry Dep B
 Dry Dep A (84 std points)
 Dry Dep E
- Dry Dep C
 vapor-phase photolysis = 0

Uncertainties in model estimates of total 1996 dioxin deposition to Lake Superior.



**Challenges in
Exploiting
Synergisms
Between
Modeling
and
Monitoring**

Challenges in Exploiting Synergisms Between Modeling and Monitoring

Data availability

- **Measurement data often not available (NADP/MDN are wonderful exceptions!)**
- **Not all parameters measured to comprehensively evaluate the model:**
 - **Ambient concentrations (vs. wet deposition)**
 - **Speciation (e.g., different forms of mercury)**
 - **Vapor-particle partitioning**
 - **Size distribution of particulate pollutant**
 - **Data above ground level**
 - **Measurements in clouds**

Challenges in Exploiting Synergisms Between Modeling and Monitoring

Spatial Scale of Data

- **Measurement data may not be appropriate for model use (e.g., urban measurements not useful to evaluate large-scale comprehensive models)**



1. **Emissions inventory not precisely known**
2. **Meteorology very complex (flow around buildings)**

Challenges in Exploiting Synergisms Between Modeling and Monitoring

Spatial Scale of Data

- Measurement data may not be appropriate for model use (e.g., urban measurements not useful to evaluate large-scale comprehensive models)
- **Corollary: If monitoring location near intense source, then unrealistically accurate characterization of that source and detailed micro-meteorology of near-field region needed**



- Sampling near intense sources?
- Must get the fine-scale met “perfect”
- Not really a relevant test

Ok, if one wants to develop hypotheses regarding *whether or not this is actually a source* of the pollutant (and you can't do a stack test for some reason!).

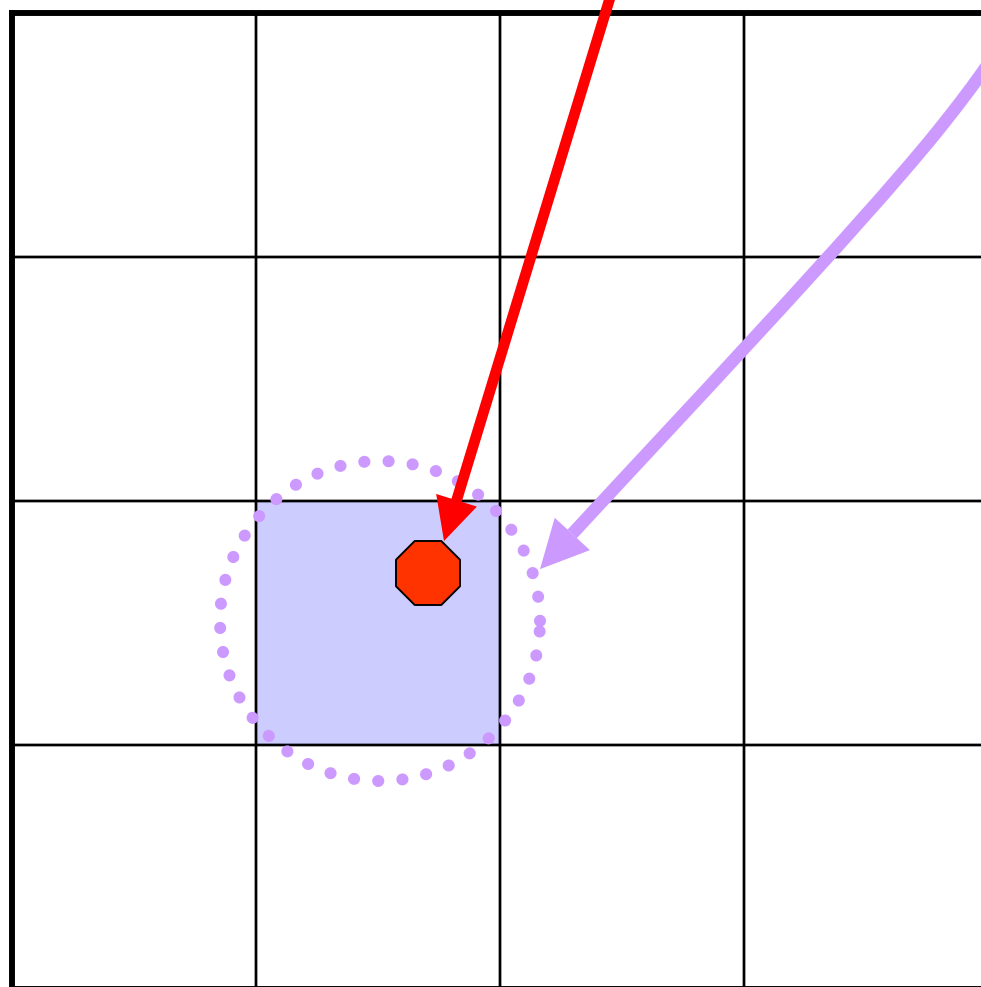
Challenges in Exploiting Synergisms Between Modeling and Monitoring

Spatial Scale of Data

- Measurement data may not be appropriate for model use (e.g., urban measurements not useful to evaluate large-scale comprehensive models)
- Corollary: If monitoring location near intense source, then unrealistically accurate characterization of that source and detailed micro-meteorology of near-field region needed
- **Grid-average model results difficult to compare with point measurements**

**Eulerian grid models give
grid-averaged values –**

**...difficult to compare against
measurement at a single location**

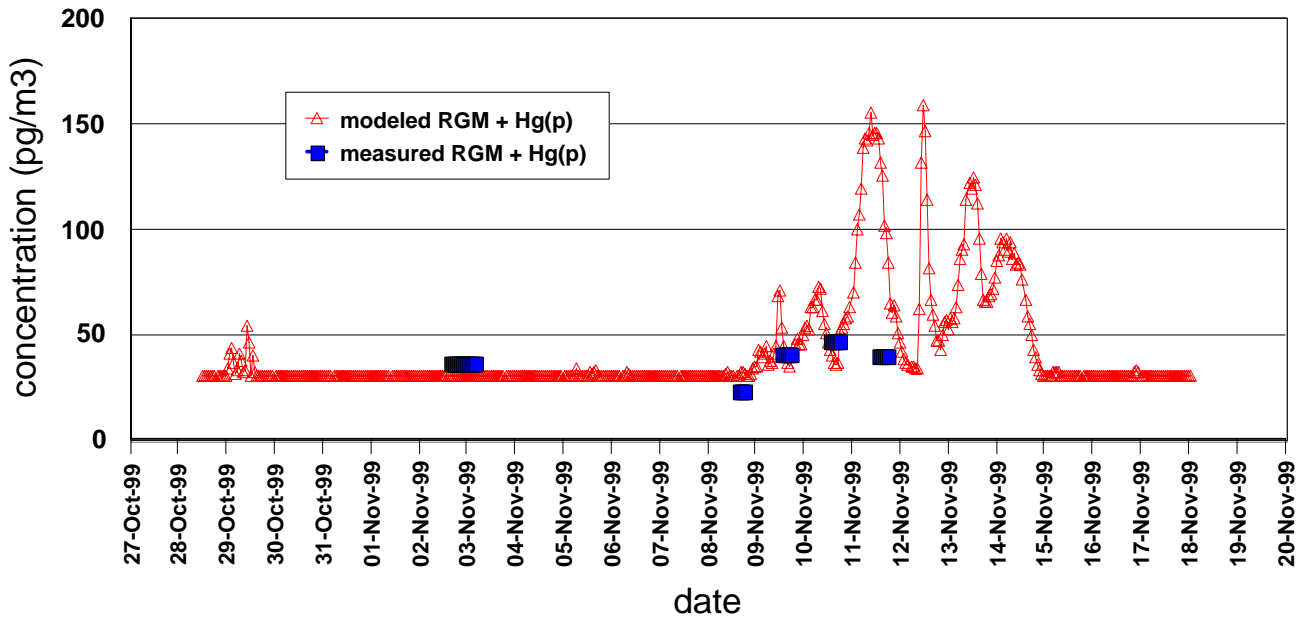


Challenges in Exploiting Synergisms Between Modeling and Monitoring

Temporal Scale of Data

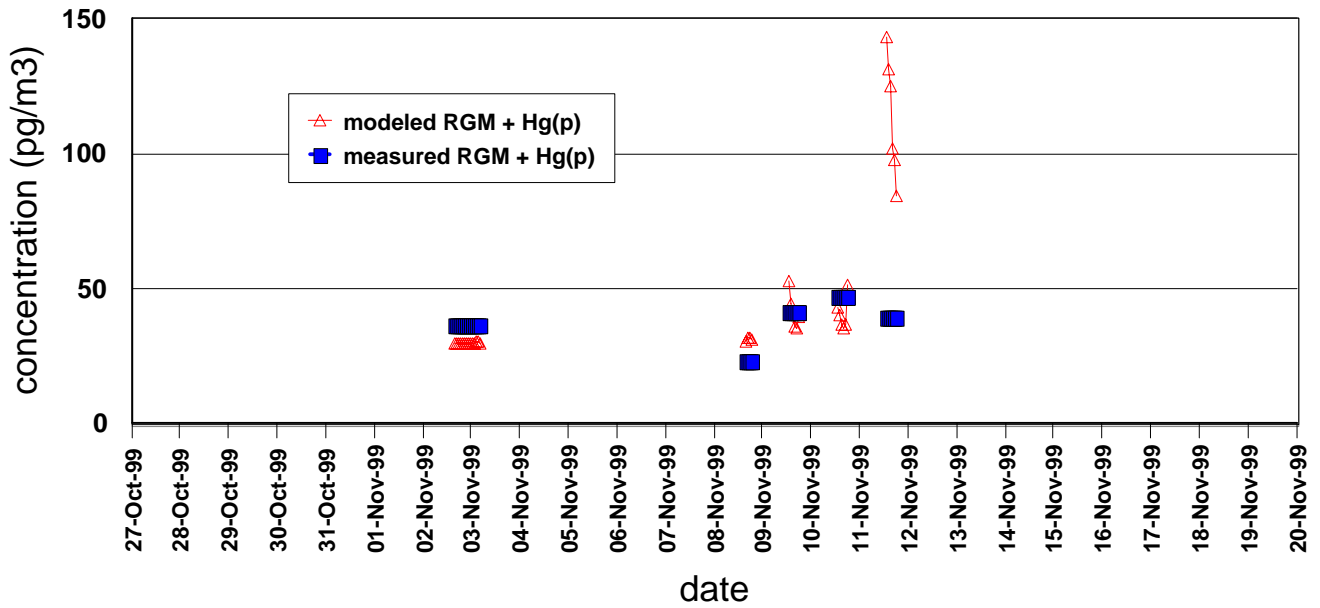
- **Short term measurements needed for receptor-oriented approaches**
- **But, short-term measurements can confound comprehensive emissions-based modeling systems**

Comparison of measured vs. modeled RGM + TPM at Mace Head



NOTE: measurement data are plotted only at times when there were measurements of BOTH RGM and TPM

Comparison of measured vs. modeled RGM + TPM at Mace Head



NOTE: measurement data are plotted only at times when there were measurements of BOTH RGM and TPM
modeled data are plotted only at times when there are measurement data

Challenges in Exploiting Synergisms Between Modeling and Monitoring

Collaboration Issues

- **Timing issue: measurements made “now”; emissions inventories to support comprehensive modeling not available for many years**
- **Competition between measurements and modeling for scarce resources**
- **This competition affects data availability...**

Summary

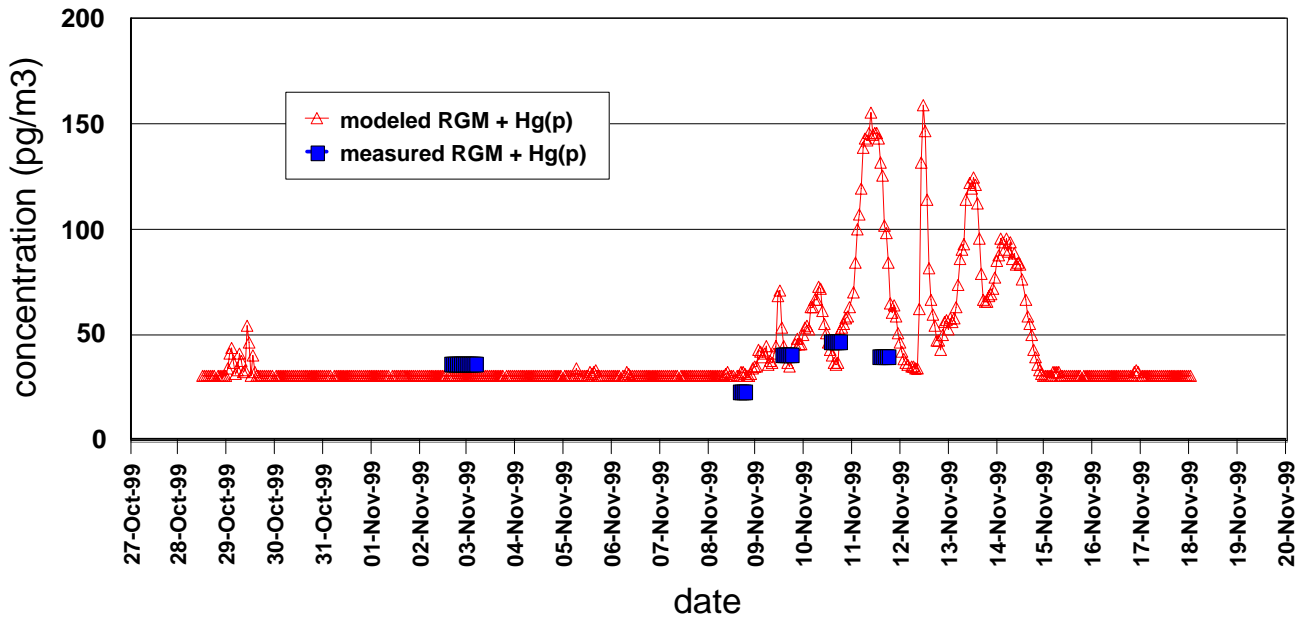
- **Monitoring is absolutely essential, but it cannot provide all the answers we need**
- **Models can be used to obtain additional information from monitoring data**
- **Measurements are used directly in receptor-oriented modeling approaches**
- **Measurements are essential for ground-truthing comprehensive modeling approaches**
- **Measurements can be used to improve models although a wider range of measurements would be even more helpful**
- **There are challenges in linking models and monitoring, *but if all monitoring programs were like the NADP and MDN, the linkages would be greatly facilitated...***



Extra Slides

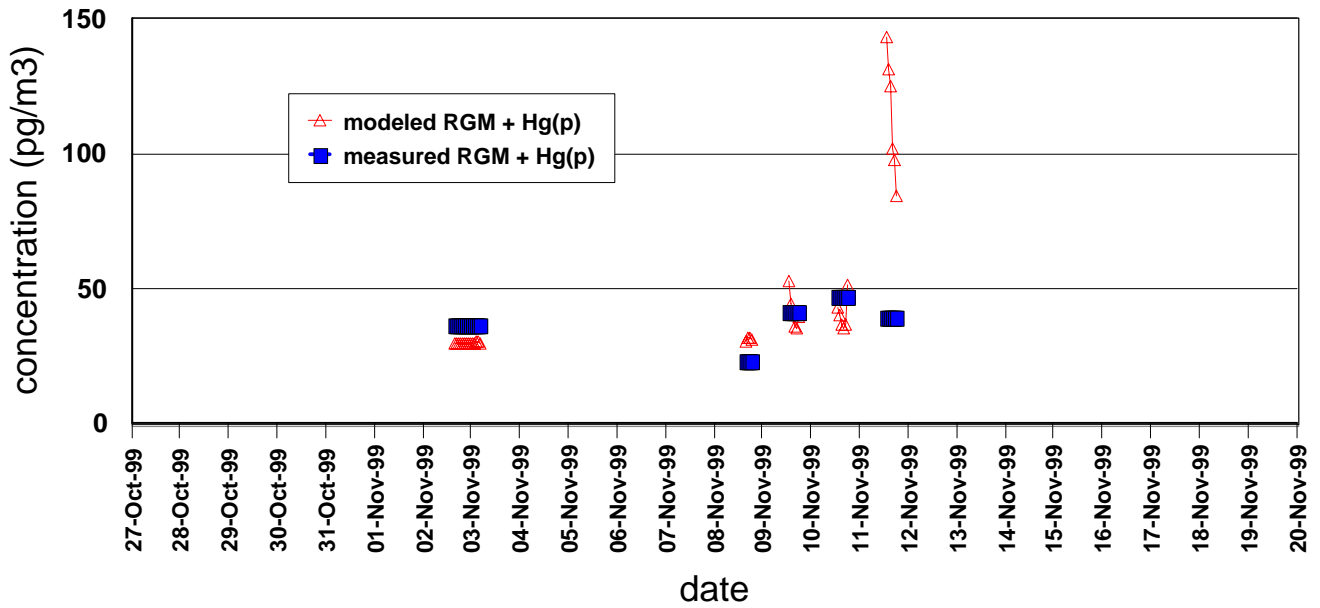
- In the *first* version of the HYSPLIT-Hg model used in this intercomparison, Hg(p) was assumed to be completely converted to dissolved Hg(II) whenever a particle becomes a droplet (e.g., above approximately 80% relative humidity); and dissolved Hg(II) assumed to become Hg(p) whenever the droplet dries out
- Hg(p) and Hg(II) were thus somewhat “equivalent” in the model
- With this assumption, the model tended to *underpredict* Hg(p) and *overpredict* Hg(II), suggesting that the assumption of *complete* conversion was not valid.
- However, it was encouraging to note that the model was getting approximately the right answer for the sum of the two forms of mercury (Hg(p) + Hg(II)), representing the total pool of oxidized Hg in the atmosphere [*see the following graphs*]

Comparison of measured vs. modeled RGM + TPM at Mace Head



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Comparison of measured vs. modeled RGM + TPM at Mace Head



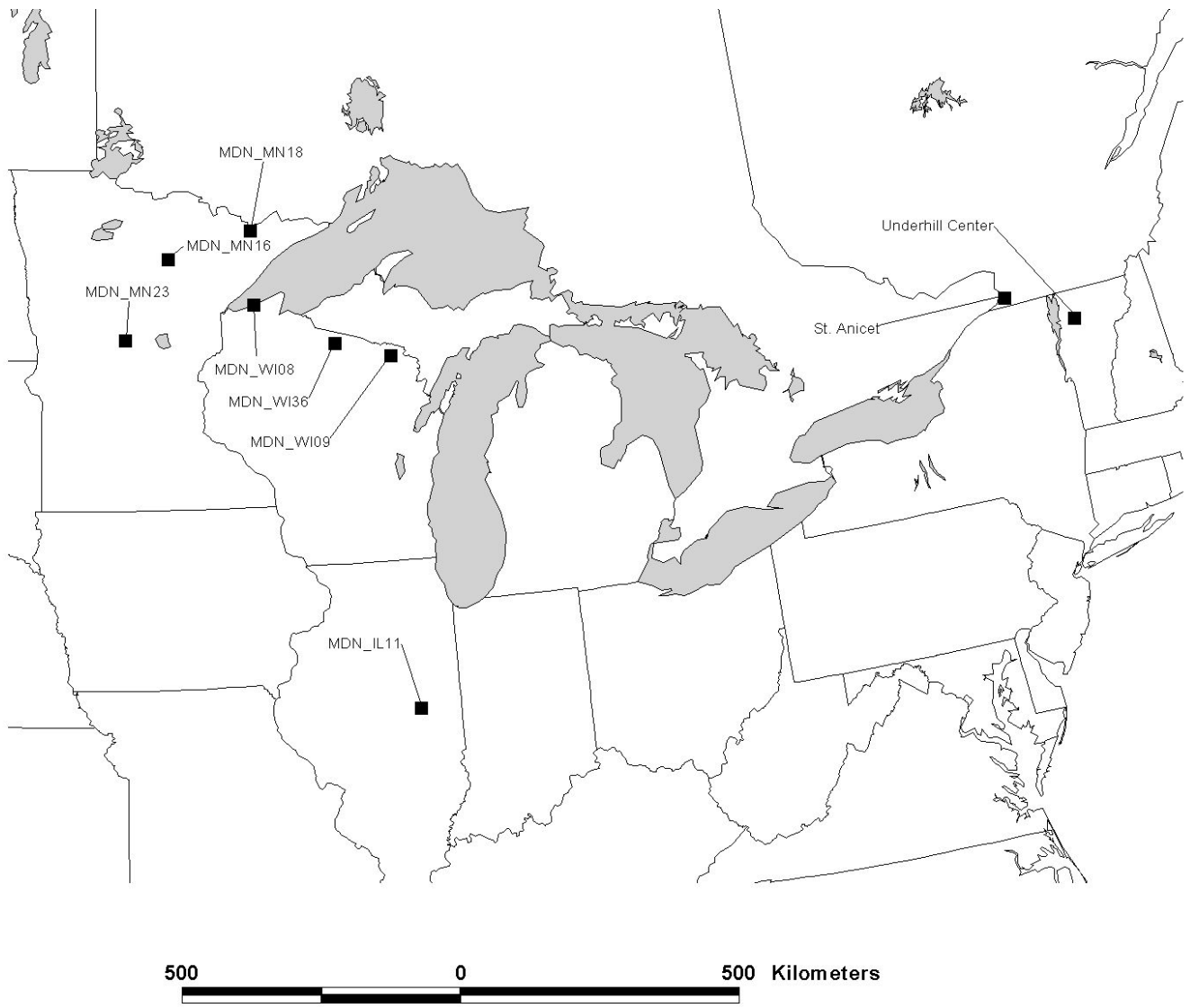
NOTE: measurement data are plotted only at times when there were measurements of BOTH RGM and TPM
modeled data are plotted only at times when there are measurement data

As a result of this observation, the model was re-run with the assumption that Hg(p) was *not* soluble.

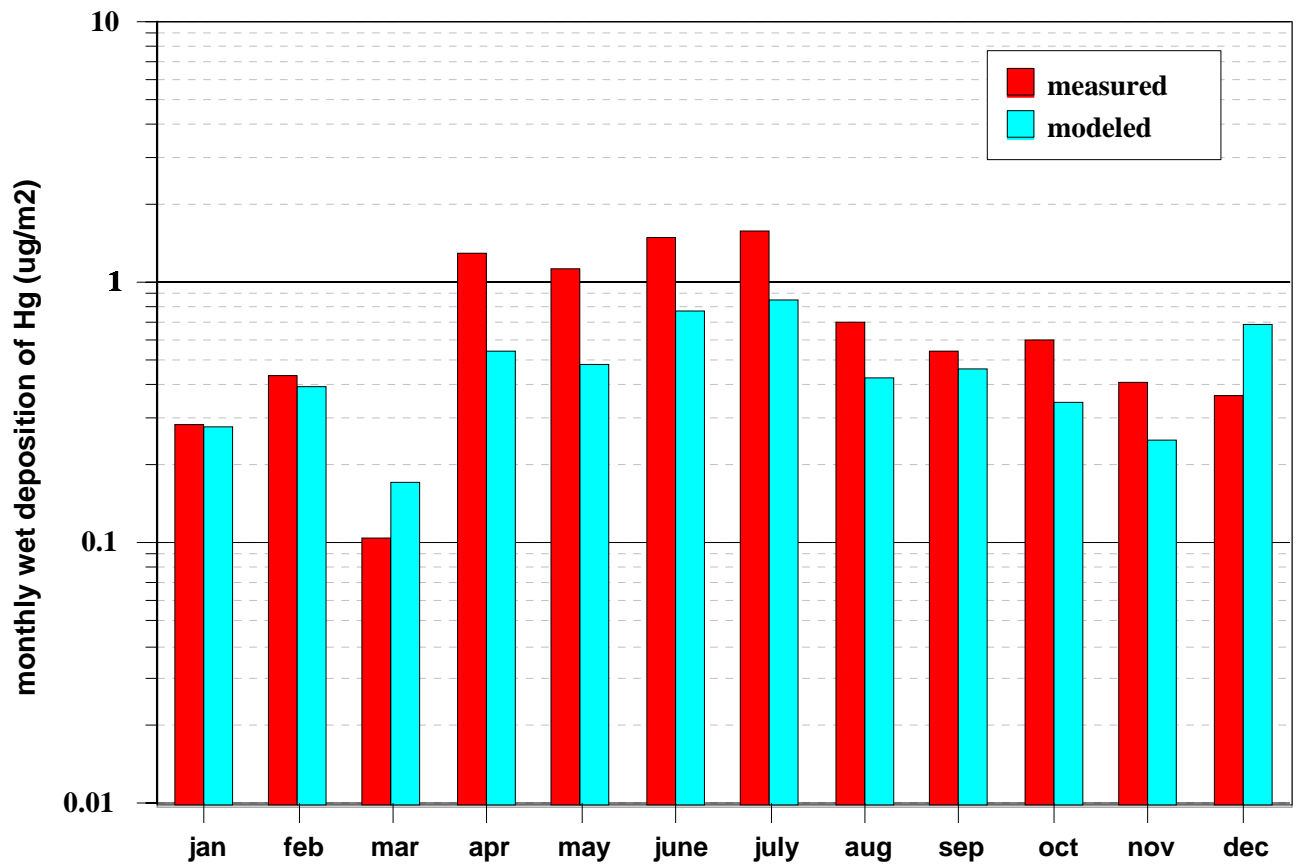
With this assumption, the results for Hg(p) and RGM were dramatically better. [These new results are what have been shown in this presentation, except for the immediately preceding RGM+Hg(p) graphs]

The affect of changing this assumption had a negligible impact on Hg(0), as might be expected, given the generally very low concentrations of Hg(II) and Hg(p) relative to Hg(0).

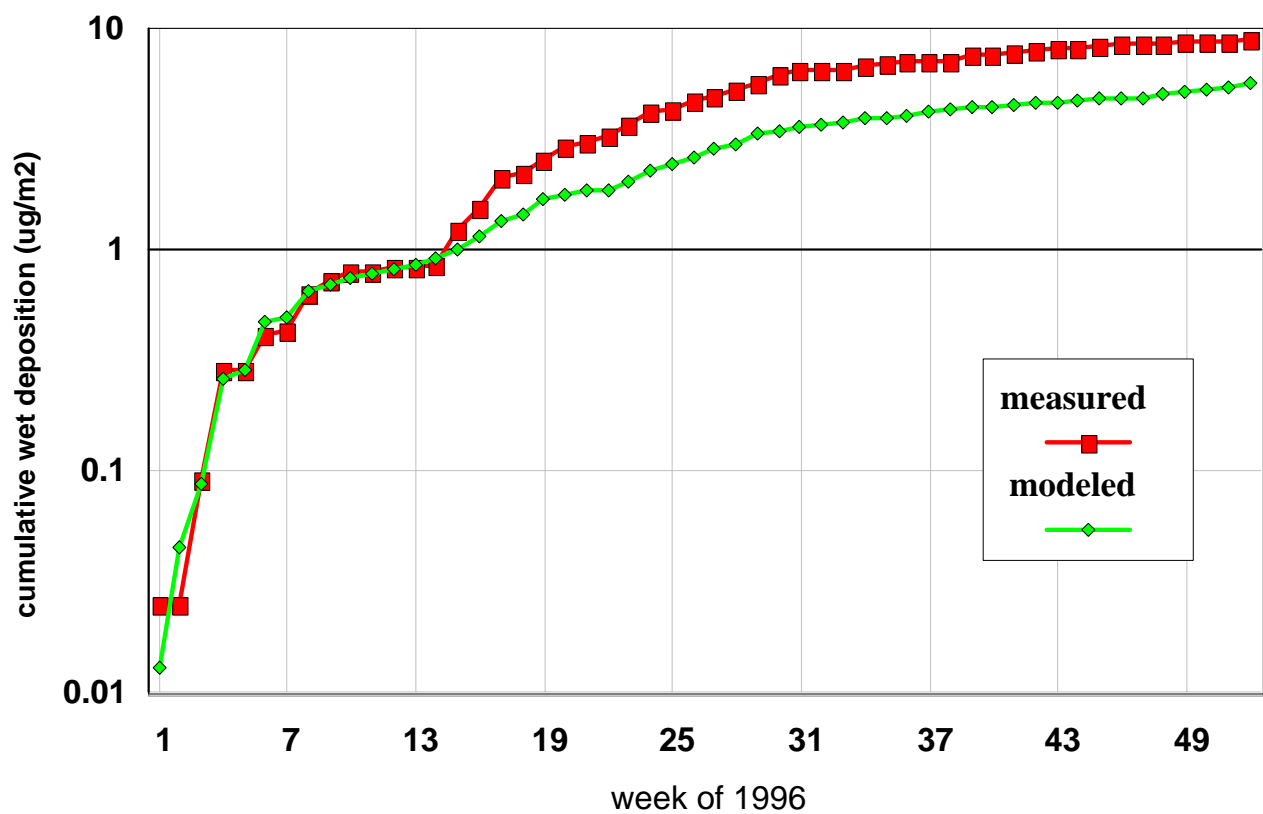
Figure 7. Model evaluation sites for wet deposition fluxes within 250 km of any Great Lake with available data for 1996.



Comparison of Modeled vs. Measured Wet Deposition at Underhill Center, VT during 1996



Comparison of Modeled vs. Measured Cumulative Wet Deposition
at Underhill Center, VT during 1996



Cumulative Deposition Flux at St. Anicet (1996)

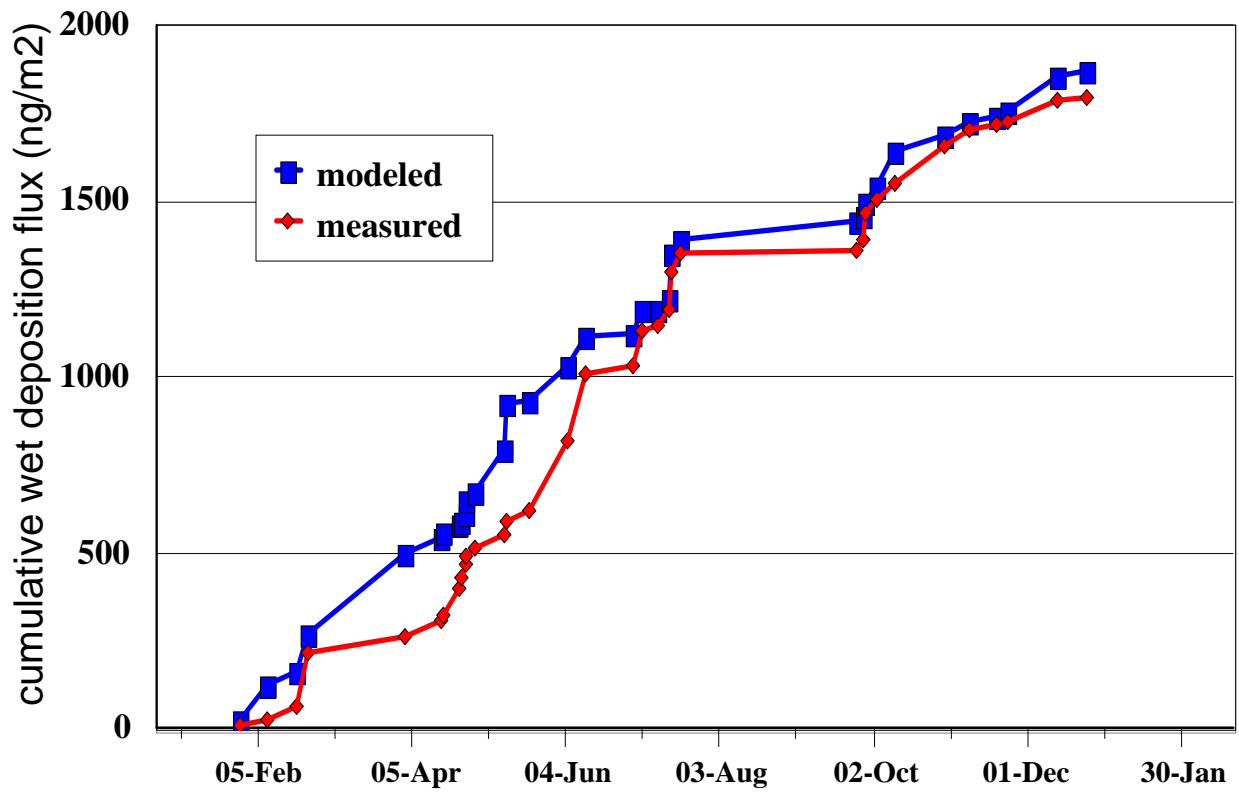


Figure 8. Comparison of model-estimated wet deposition fluxes with measured values at sites in the vicinity of the Great Lakes during 1996.

