Modeling the Atmospheric Transport and Deposition of Mercury

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Materials assembled for
“Mercury in Maryland” Meeting, Appalachian Lab,
Univ. of Maryland Center for Environmental Science
301 Braddock Road, Frostburg MD, Nov 2-3, 2005
1. Atmospheric mercury modeling

2. Why do we need atmospheric mercury models?

3. What do atmospheric mercury models need?

4. Some preliminary results:
   - Model evaluation
   - Source Receptor Information
1. Atmospheric mercury modeling

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Atmospheric Mercury Fate Processes

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_2O_2, Cl_2, OH, HCl

Primary Anthropogenic Emissions

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, HOCI, OCl-

Multi-media interface

Natural emissions

Re-emission of previously deposited anthropogenic and natural mercury

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

Cloud

Dry deposition

Wet deposition
Lagrangian Puff Air Transport and Deposition Model

- **TIME (hours)**
  - 0
  - 1
  - 2
  - ...

- **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 estimated 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

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

- Deposition to lake

- Lake
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.
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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
But models must have measurements

Monitoring required to develop models and to evaluate their accuracy

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

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<th>Scientific Understanding</th>
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Why is emissions speciation information critical?

Hypothesized rapid reduction of Hg(II) in plumes? If true, then dramatic impact on modeling results…
### Some Challenges Facing Mercury Modeling

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## Atmospheric Chemical Reaction Scheme for Mercury

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<th>Rate</th>
<th>Units</th>
<th>Reference</th>
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<td><strong>GAS PHASE REACTIONS</strong></td>
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<tr>
<td>( \text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg(p)} )</td>
<td>3.0E-20</td>
<td>cm³/molec-sec</td>
<td>Hall (1995)</td>
</tr>
<tr>
<td>( \text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2 )</td>
<td>1.0E-19</td>
<td>cm³/molec-sec</td>
<td>Hall and Bloom (1993)</td>
</tr>
<tr>
<td>( \text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg(p)} )</td>
<td>8.5E-19</td>
<td>cm³/molec-sec</td>
<td>Tokos et al. (1998) (upper limit based on experiments)</td>
</tr>
<tr>
<td>( \text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2 )</td>
<td>4.0E-18</td>
<td>cm³/molec-sec</td>
<td>Calhoun and Prestbo (2001)</td>
</tr>
<tr>
<td>( \text{Hg}^0 + \text{OHC} \rightarrow \text{Hg(p)} )</td>
<td>8.7E-14</td>
<td>cm³/molec-sec</td>
<td>Sommar et al. (2001)</td>
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<tr>
<td><strong>AQUEOUS PHASE REACTIONS</strong></td>
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<tr>
<td>( \text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2} )</td>
<td>4.7E+7</td>
<td>(molar-sec)⁻¹</td>
<td>Munthe (1992)</td>
</tr>
<tr>
<td>( \text{Hg}^0 + \text{OHC} \rightarrow \text{Hg}^{+2} )</td>
<td>2.0E+9</td>
<td>(molar-sec)⁻¹</td>
<td>Lin and Pehkonen (1997)</td>
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<tr>
<td>( \text{HgSO}_3 \rightarrow \text{Hg}^0 )</td>
<td>( T<em>e^{(31.971</em>T)-12595.0}/T) ) sec⁻¹</td>
<td>( T = \text{temperature (K)} )</td>
<td>Van Loon et al. (2002)</td>
</tr>
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<td>( \text{Hg(II)} + \text{HO}_2\text{C} \rightarrow \text{Hg}^0 )</td>
<td>~ 0</td>
<td>(molar-sec)⁻¹</td>
<td>Gardfeldt &amp; Jonnson (2003)</td>
</tr>
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<td>( \text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2} )</td>
<td>2.1E+6</td>
<td>(molar-sec)⁻¹</td>
<td>Lin and Pehkonen (1998)</td>
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<td>( \text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2} )</td>
<td>2.0E+6</td>
<td>(molar-sec)⁻¹</td>
<td>Lin and Pehkonen (1998)</td>
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<tr>
<td>( \text{Hg(II)} \leftrightarrow \text{Hg(II)} )</td>
<td>9.0E+2</td>
<td>liters/gram; ( t = 1/\text{hour} )</td>
<td>eqlbrm: Seigneur et al. (1998)</td>
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<tr>
<td>( \text{Hg}^{+2} + \text{h} \leftrightarrow \text{Hg}^0 )</td>
<td>6.0E-7</td>
<td>(sec)⁻¹ (maximum)</td>
<td>Xiao et al. (1994); Bullock and Brehme (2002)</td>
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Some Additional Measurement Issues (from a modeler’s perspective)

- Data availability
- Simple vs. Complex Measurements
Some Additional Measurement Issues (from a modeler’s perspective)

- Data availability
- Simple vs. Complex Measurements
Data availability

A major impediment to evaluating and improving atmospheric Hg models has been the lack of speciated Hg air concentration data.

There have been very few measurements to date, and these data are rarely made available in a practical way (timely, complete, etc.).

The data being collected at Piney Reservoir could be extremely helpful!
Some Additional Measurement Issues (from a modeler’s perspective)

• Data availability
• Simple vs. Complex Measurements
Simple vs. Complex Measurements:
1. Wet deposition is a very complicated phenomena...

- many ways to get the “wrong” answer –
  incorrect emissions, incorrect transport,
  incorrect chemistry, incorrect 3-D precipitation,
  incorrect wet-deposition algorithms, etc..

- models need ambient air concentrations
  first, and then if they can get those right,
  they can try to do wet deposition...
Simple vs. Complex Measurements:

2. Potential complication with ground-level monitors... (“fumigation”, “filtration”, etc.)...

- atmospheric phenomena are complex and not well understood;
- models need “simple” measurements for diagnostic evaluations;
- ground-level data for rapidly depositing substances (e.g., RGM) hard to interpret
- elevated platforms might be more useful (at present level of understanding)
Simple vs. Complex measurements - 3. Urban areas:

a. Emissions inventory poorly known

b. Meteorology very complex (flow around buildings)

c. So, measurements in urban areas not particularly useful for current large-scale model evaluations
Sampling near intense sources?

Must get the fine-scale met “perfect”

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!).
Complex vs. Simple Measurements – 5: Need some source impacted measurements

- Major questions regarding plume chemistry and near-field impacts (are there “hot spots”?)
- Most monitoring sites are designed to be “regional background” sites (e.g., most Mercury Deposition Network sites).
- We need some source-impacted sites as well to help resolve near-field questions
- But not too close – maybe 20-30 km is ideal (?)
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EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

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Participants

D. Syrakov .............................................. Bulgaria.....NIMH
A. Dastoor, D. Davignon ..................... Canada.....MSC-Can
J. Christensen ................................. Denmark....NERI
G. Petersen, R. Ebinghaus ................. Germany.....GKSS
J. Pacyna ................................. Norway.....NILU
J. Munthe, I. Wängberg ....................... Sweden.....IVL
R. Bullock ........................................... USA........EPA
M. Cohen, R. Artz, R. Draxler .............. USA........NOAA
C. Seigneur, K. Lohman ...................... USA........AER/EPRI
A. Ryaboshapko, I. Ilyin, O.Trvnikov...EMEP......MSC-E
## Intercomparison Conducted in 3 Stages

**I.** Comparison of chemical schemes for a cloud environment

**II.** Air Concentrations in Short Term Episodes

**III.** Long-Term Deposition and Source-Receptor Budgets
### Participating Models

<table>
<thead>
<tr>
<th>Model Acronym</th>
<th>Model Name and Institution</th>
<th>Stage</th>
</tr>
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<td>CAM</td>
<td>Chemistry of Atmos. Mercury model, Environmental Institute, Sweden</td>
<td><img src="image" alt="Green" /> <img src="image" alt="Green" /></td>
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<td>MCM</td>
<td>Mercury Chemistry Model, Atmos. &amp; Environmental Research, USA</td>
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<td>Community Multi-Scale Air Quality model, US EPA</td>
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<td>ADOM</td>
<td>Acid Deposition and Oxidants Model, GKSS Research Center, Germany</td>
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<td>MSCE-HM</td>
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Anthropogenic Mercury Emissions Inventory and Monitoring Sites for Phase II
(note: only showing largest emitting grid cells)

- Mace Head, Ireland grassland shore
- Rorvik, Sweden forested shore
- Aspvreten, Sweden forested shore
- Zingst, Germany sandy shore
- Neuglobsow, Germany forested area
Total Gaseous Mercury (ng/m³) at Neuglobsow: June 26 – July 6, 1995
**EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury**

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**Total Particulate Mercury (pg/m³) at Neuglobsow, Nov 1-14, 1999**

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**MEASURED**

- **02-Nov**
- **04-Nov**
- **06-Nov**
- **08-Nov**
- **10-Nov**
- **12-Nov**
- **14-Nov**

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Reactive Gaseous Mercury at Neuglobsow, Nov 1-14, 1999

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August 1999 Mercury Wet Deposition
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2. Why do we need atmospheric mercury models?

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4. Some preliminary results:
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Example of Detailed Results: 1999 Results for Chesapeake Bay
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (entire domain)
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (regional close-up)
Geographical Distribution of 1999 Direct Deposition Contributions to the Chesapeake Bay (local close-up)
Largest Regional Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

Fraction of Total Modeled Deposition Contributed by Source

- 0.1 - 1%
- 1 - 3%
- 3 - 10%
- 10 - 30%
- > 30%

- Coal-Fired Electricity Generation
- Other Fuel Combustion Activities
- Waste Incineration
- Smelters and other Metallurgical
- Manufacturing and Other
Largest Local Individual Sources Contributing to 1999 Mercury Deposition Directly to the Chesapeake Bay

- Phoenix Services
- Baltimore RESCO
- Chalk Point
- Morgantown
- Yorktown
- Chesterfield
- Stericycle, Inc.
- Indian River
- NASA Incinerator
- Brandon Shores
- H.A. Wagner
- Norfolk Navy Yard
- Chesapeake Energy Center

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- 1 - 3%
- 3 - 10%
- 10 - 30%
- > 30%
Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay

![Graph showing emissions and deposition flux across different distance ranges from the Chesapeake Bay.](image-url)
Top 25 Contributors to 1999 Hg Deposition Directly to the Chesapeake Bay

- Phoenix Services
- Brandon Shores
- Stericycle Inc.
- Morgantown
- Chalk Point
- NASA Incinerator
- Norfolk Navy Yard
- Hampton/NASA Incin.
- Chesapeake Energy Ctr.
- Chesterfield
- Yorktown
- INDIAN RIVER
- Roxboro
- BALTIMORE RESCO
- Belews Creek
- Harrisburg Incin.
- Harford Co. Incin.
- Montour
- Possum Point
- Keystone
- Homer City
- Mt. Storm
- Chesapeake Energy Ctr.
- Hampton/NASA Incin.
- Navy Yard
- H.A. Wagner
- NASA Incinerator
- Chalk Point
- Morgantown
- Stericycle Inc.
- Brandon Shores
- Phoenix Services

Cumulative Fraction of Hg Deposition

Coal-fired elec gen
Other fuel combustion
Waste incineration
Metallurgical
Manufacturing/other
Preliminary Results for other Maryland Receptors
Maryland Receptors Included in Recent Preliminary HYSPLIT-Hg modeling (but modeling was not optimized for these receptors!)
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (national view)
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (regional view)
Largest Modeled Atmospheric Deposition Contributors Directly to Deep Creek Lake based on 1999 USEPA Emissions Inventory (close-up view)
Some Next Steps

- Use more highly resolved meteorological data grids
- 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
- Sensitivity analyses and examination of atmospheric Hg chemistry (e.g. marine boundary layer, upper atmosphere)
- Dynamic linkage with ecosystem cycling models
Conclusions

- Models needed for source-receptor and other info
- At present, many model uncertainties & data limitations
- Monitoring data required to evaluate and improve models
- For this, simple may be better than complex measurements
- Some useful model results appear to be emerging
- Future is much brighter because of this coordination!
Thanks
Why might the atmospheric fate of mercury emissions be essentially linearly independent?

• Hg is present at extremely trace levels in the atmosphere

• Hg won’t affect meteorology (can simulate meteorology independently, and provide results to drive model)

• Most species that complex or react with Hg are generally present at much higher concentrations than Hg

• Other species (e.g. OH) generally react with many other compounds than Hg, so while present in trace quantities, their concentrations cannot be strongly influenced by Hg

• Wet and dry deposition processes are generally 1st order with respect to Hg

• The current “consensus” chemical mechanism (equilibrium + reactions) does not contain any equations that are not 1st order in Hg
Spatial interpolation

Impact of source 4 estimated from weighted average of impacts of nearby explicitly modeled sources

Impacts from Sources 1-3 are Explicitly Modeled
• Perform separate simulations at each location for emissions of pure Hg(0), Hg(II) and Hg(p)

[after emission, simulate transformations between Hg forms]

• Impact of emissions mixture taken as a linear combination of impacts of pure component runs on any given receptor
“Chemical Interpolation”

Impact of Source Emitting Pure Hg(0) = 0.3 x Impact of Source Emitting Pure Hg(II) + 0.5 x Impact of Source Emitting Pure Hg(p)

Impact of Source Emitting 30% Hg(0), 50% Hg(II), 20% Hg(p)
Standard Source Locations in Maryland region during recent simulation
Illustrative example of total deposition at a location ~40 km "downwind" of a 1 kg/day RGM source
Eulerian grid models give grid-averaged estimates – difficult to compare against measurement at a single location.
• In principle, we need to do this for each source in the inventory.

• But, since there are more than 100,000 sources in the U.S. and Canadian inventory, we need shortcuts…

• Shortcuts described in Cohen et al. *Environmental Research* 95(3), 247-265, 2004

Note: Volume 95(3) is a Special Issue: "An Ecosystem Approach to Health Effects of Mercury in the St. Lawrence Great Lakes", edited by David O. Carpenter.
• For each run, simulate fate and transport everywhere, but only keep track of impacts on each selected receptor (e.g., Great Lakes, Chesapeake Bay, etc.)

• Only run model for a limited number (~100) of hypothetical, individual unit-emissions sources throughout the domain

• Use spatial interpolation to estimate impacts from sources at locations not explicitly modeled
0.1° x 0.1°
subgrid for
near-field analysis
0.1° x 0.1° subgrid for near-field analysis
Annual deposition summary for emissions of elemental Hg from a 250 meter high source

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 particulate Hg from a 250 meter high source

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

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 ionic Hg from a 250 meter high source

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

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- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

Source Location

0.1 x 0.1 degree grid

Hypothetical emissions source at lat = 42.5, long = -97.5; simulation for entire year 1996 using archived NGM meteorology (180 km resolution)
Deposition flux within different distance ranges from a hypothetical 1 kg/day source

Hypothesized rapid reduction of Hg(II) in plumes?
If true, then dramatic impact on modeling results…
Why is emissions speciation information critical?

- Hg(II) emit
- Hg(0) emit
- Hg(p) emit

**Linear**
Why is emissions speciation information critical?

**Logarithmic**

**Linear**
Emissions and Chemistry

- *The form of mercury emissions* (elemental, ionic, particulate) is often very poorly known, but *is a dominant factor in estimating deposition* (and associated source-receptor relationships).

- Questions regarding atmospheric chemistry of mercury may also be very significant.

- *The above may contribute more to the overall uncertainties in atmospheric mercury models* than uncertainties in dry and wet deposition algorithms.
**EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury**

<table>
<thead>
<tr>
<th>Stage I</th>
<th>Stage II</th>
<th>Stage III</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intro-duction</td>
<td>Hg$^0$</td>
<td>Hg(p)</td>
<td>RGM</td>
</tr>
<tr>
<td>Chemistry</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Solutions

#### Stage III

- **Mace Head**: Neuglobsow
- **Rorvik**: Zingst
- **Aspvreten**: Neuglobsow

---

**mercury emissions (g/km2-year)**

- ▲ 100 - 200
- ● 200 - 500
- ■ 500 - 1000
- ▣ 1000 - 2100

---

500 0 500 1000 Kilometers
EMEP Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

<table>
<thead>
<tr>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
<tr>
<td>Stage III</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hg(p)</th>
<th>RGM</th>
<th>Wet Dep</th>
<th>Dry Dep</th>
<th>Budgets</th>
</tr>
</thead>
</table>

Total Gaseous Mercury at Neuglobsow: June 26 – July 6, 1995

Total Gaseous Mercury (ng/m³)

0.0 0.5 1.0 1.5 2.0 2.5 3.0

0 26-Jun 28-Jun 30-Jun 02-Jul 04-Jul 06-Jul

Kilometers

Neuglobsow

- MEASURED

- NW

- S

- SE

- NW
The emissions inventory is a critical input to the models…

Using default emissions inventory

Using alternative emissions inventory
Some Additional Measurement Issues (from a modeler’s perspective)

- Data availability
- Simple vs. Complex Measurements
- Process Information
Process Information:
1. Dry Deposition - Resistance Formulation

\[ \frac{1}{V_d} = \frac{1}{R_a + R_b + R_c + R_a R_b V_g} + V_g \]

in which

- \( R_a \) = aerodynamic resistance to mass transfer;
- \( R_b \) = resistance of the quasi-laminar sublayer;
- \( R_c \) = overall resistance of the canopy/surface (zero for particles);
- \( V_g \) = the gravitational settling velocity (zero for gases).
Dry Deposition

- depends intimately on vapor/particle partitioning and particle size distribution information

- resistance formulation \([R_a, R_b, R_c...]\)

- for gases, key uncertainty often \(R_c\) (e.g., “reactivity factor” \(f_0\))

- for particles, key uncertainty often \(R_b\)

- How to evaluate algorithms when phenomena hard to measure?
**Particle dry deposition phenomena**

- **Atmosphere above the quasi-laminar sublayer**
  - **Quasi-laminar Sublayer (~ 1 mm thick)**
    - **Ra**: Very large particles can just fall through the layer.
    - **Rb**: In-between particles can’t diffuse or fall easily so they have a harder time getting across the layer.
    - **Rc**: Very small particles can diffuse through the layer like a gas.

- **Wind speed = 0 (?)**
Typical Deposition Velocities Over Water with Different Rb Formulations

- **Diffusion high; Settling velocity low; Vd governed by Ra**
- **Diffusion low; Settling velocity low; Vd governed by Rb**

Deposition Velocity (m/sec)

particle diameter (microns)

- Rb assumed small ( = 10 sec/m)
- Slinn and Slinn
Process information needed:

1. For particle dry deposition, must have particle size distributions!
PROCESS INFORMATION:

2. The gas-exchange flux at a water surface depends on the concentration of pollutant in the gas-phase and the truly-dissolved phase (but these are rarely measured...).