Sources, Transport, and Fate of Mercury in the Atmosphere

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Overview of this presentation:

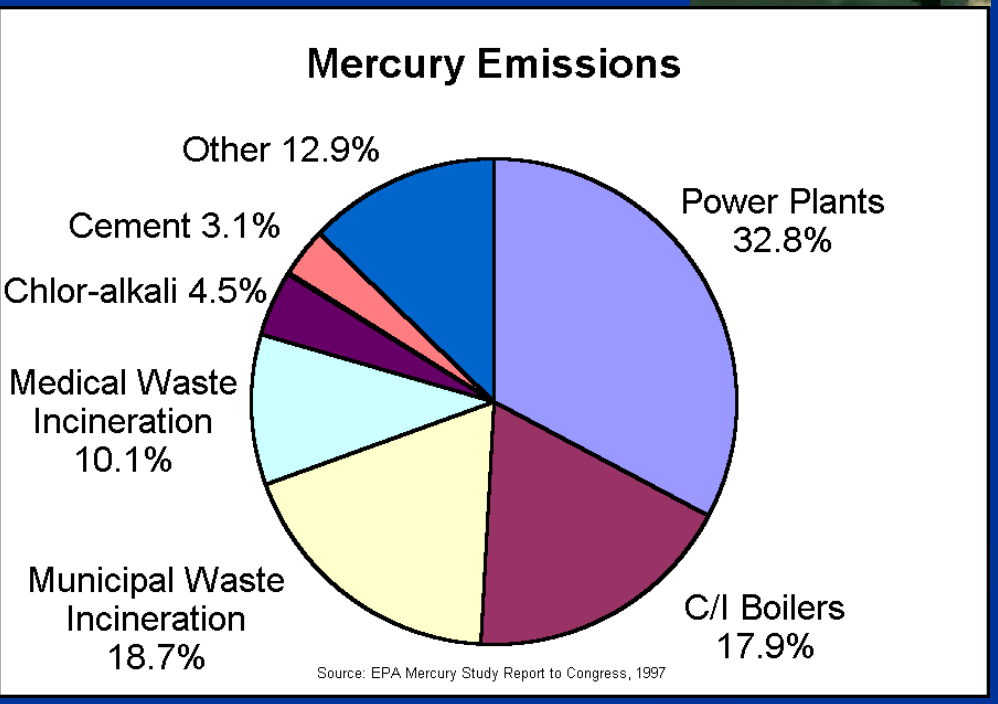
- Sources of mercury in the atmosphere and it’s chemical forms.
- How mercury is removed from the atmosphere.
- Measurements of mercury deposition from the atmosphere.
- Modeling of mercury in the atmosphere and predicting deposition.

Typical Sources of Atmospheric Mercury

Anthropogenic

~2-3x natural emissions (maybe more)

(US c.1997 from EPA)



Natural

- Degassing of Hg rich soils
- Geothermal emissions
- Forest fires

In what form is mercury emitted and transported in the atmosphere?

		Typical Abundance	Typical transport dist. before deposition
As a gas in two forms:	elemental (Hg^0)	90 – 99%	global
	ionic (Hg^{2+})	0 – 10%	0 – 150 mi
As an aerosol particle:	particulate (Hg_p)	0 – 5%	0 – 250 mi

Typical Fractionation of emissions by point sources

Industrial facilities emit mercury in different proportions based on raw materials, facility design, control technologies, etc.

Point source groups	Hg^0 %	Hg^{2+} %	Hg_P %
Chemical production	80	10	10
Chlor-alkali factories	70	30	0
Electric utilities	50	30	20
Iron and steel production	80	10	10
Non-ferrous metal smelting	80	10	10
Portland cement manufacturing	80	10	10
Waste combustion	20	60	20

(Bullock, 2000)

How is Mercury Removed From the Atmosphere?

<u>Wet deposition</u> (i.e., in precipitation)

Mainly removes
Hg^{2+}
Hg_p

rain

snow

fog

rime ice

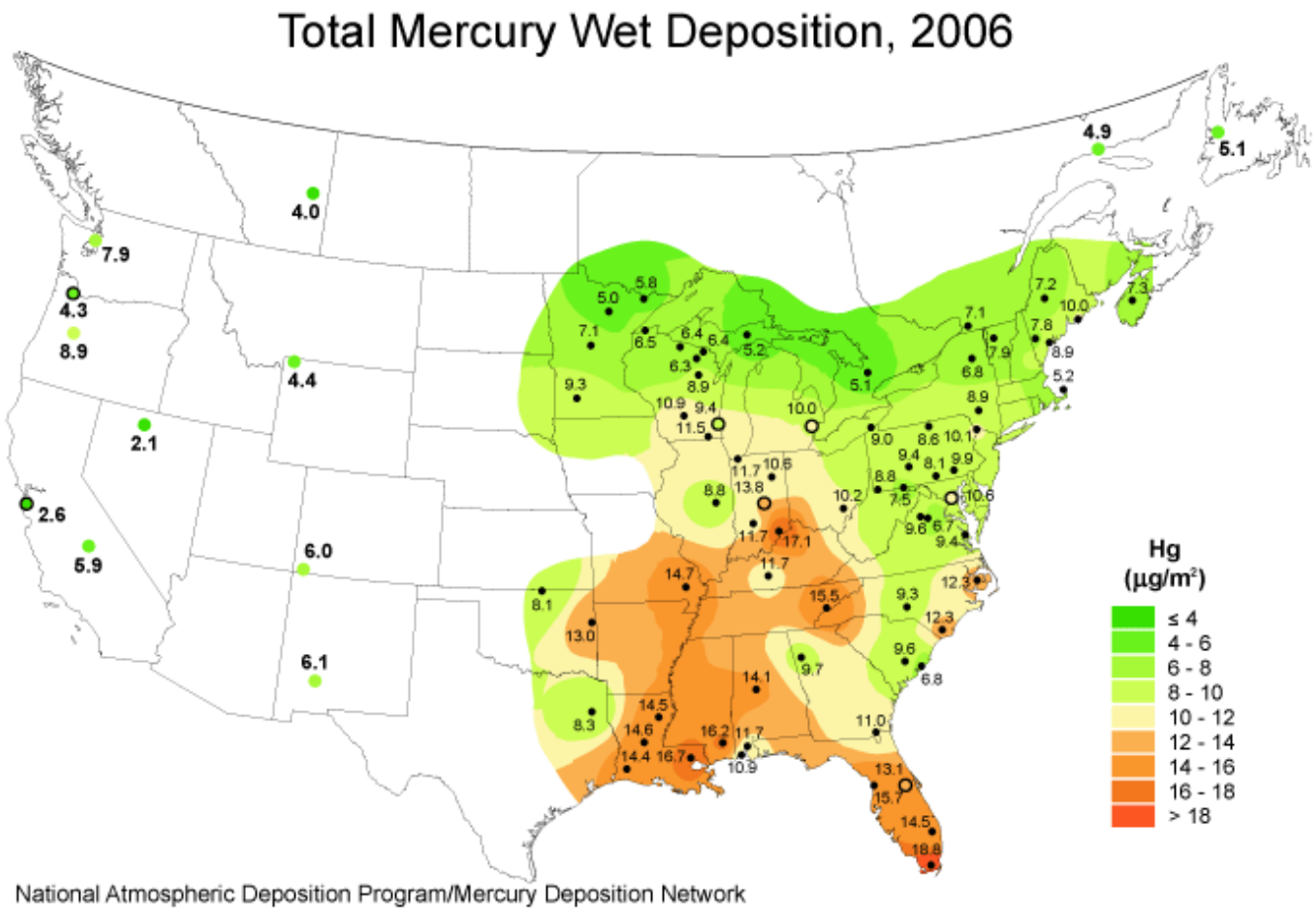
<u>Dry deposition</u> – adhesion of gasses and particulates to foliage, surface waters, and land (acts on all 3 forms of atmospheric Hg)

<u>Mercury deposition is enhanced by:</u>

- high ground level ozone (enhances oxidation of Hg^0 to Hg^{2+})
- proximity of sources (sources with significant Hg^{2+} and Hg_p emissions)
- forest cover (enhanced dry deposition)
- sea salt (enhances oxidation of Hg^0 to Hg^{2+})

How is Mercury Deposition Quantified?

<u>Wet deposition</u> (generally 50-90% of total deposition) is routinely measured by a national monitoring network (MDN). However, the network is more focused on the Eastern US.

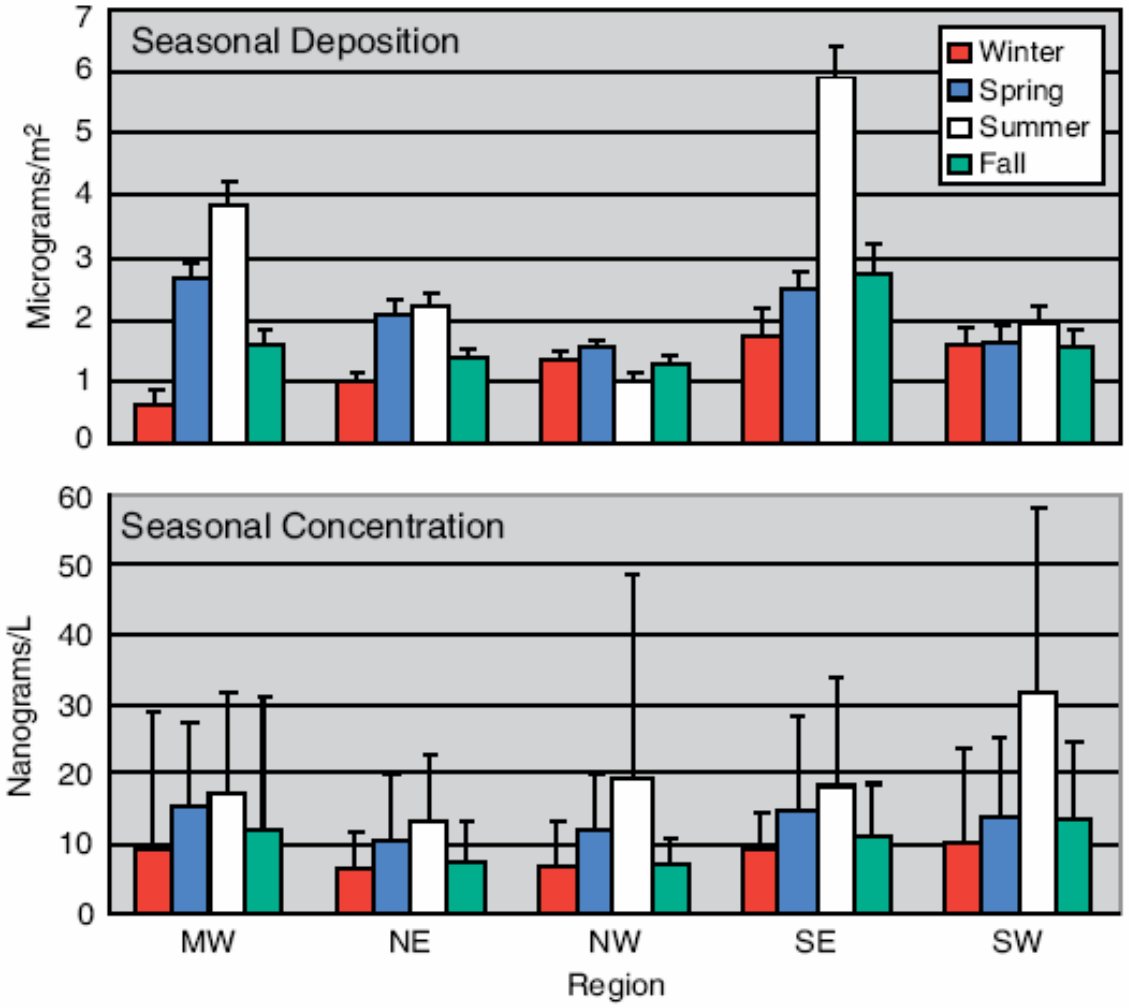


Wet Deposition by US Region and Season

Things to note:

Typical pattern is for higher deposition in summer, probably due to higher levels of oxidants (e.g., ozone) converting Hg^0 to Hg^{2+}.

However, NW has lower deposition in summer, even though the mercury concentrations in summer precipitation is higher. This is likely because we tend to get most of our precipitation in fall, winter & spring and have relatively dry summers.



Mercury wet deposition and concentration by region and season with standard deviations as measured, 1997-2003.

How is Mercury Dry Deposition Quantified?

The short answer is not often.

- **Dry deposition is not well understood, little data exists, and is site specific.**
- **Dry deposition rates depend on meteorological conditions, surface characteristics, and the atmospheric mercury composition.**
- **Measurement of mercury dry deposition is a research level effort.**

A more simple technique (and therefore more widely used) involves measuring atmospheric concentrations of mercury and then assuming a dry deposition rate, taken from literature estimates. Having said that, measuring atmospheric concentrations of mercury not trivial and therefore expensive.

Another approach, rather than monitoring, is to estimate mercury transport and deposition using atmospheric models.

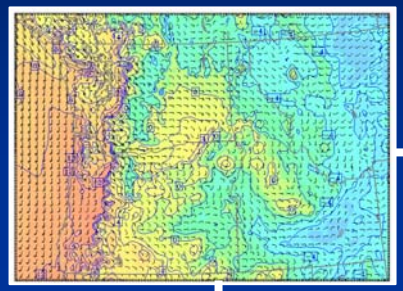
Advantages to modeling – relatively inexpensive and provides deposition estimates over a wide geographic area.

Atmospheric Modeling of Mercury Emissions, Transport, and Fate

- **Modeling process flow diagram**

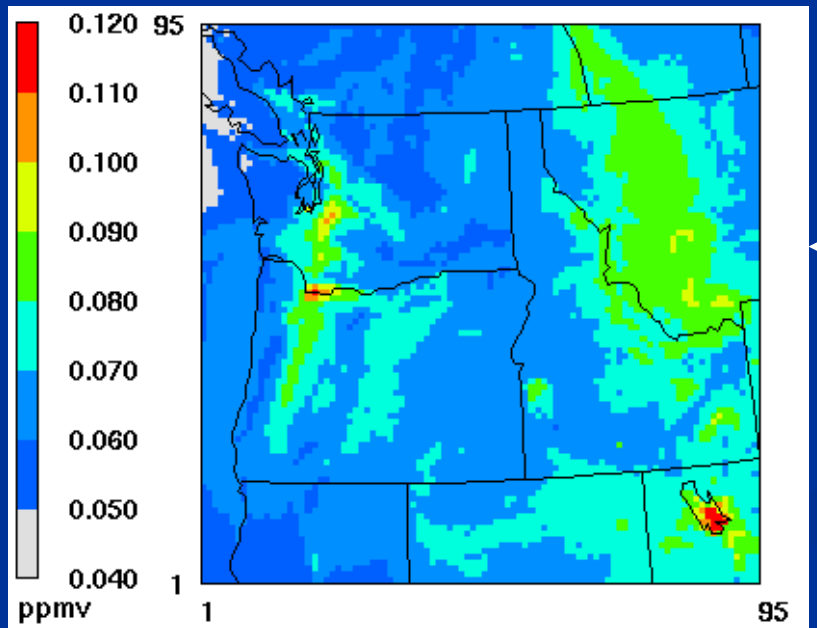
Met model data
Hourly winds, temperature, precip., etc.

Emissions Model
Hourly emissions
Hg^0, Hg^{2+}, Hg_p
Other anthrop. and natural emissions



Photochemical Grid Model
- Chemical mechanism
- Chemical processes - Gas phase, aqueous (cloud), surface (aerosols), & photolysis reactions.
- Physical processes – dilution, deposition, advection, etc.
- Gives hourly concentration and deposition predictions

Model prediction (example below is O_3)



Currently, model predictions of Hg deposition are highly uncertain.

Sources of uncertainty are numerous, a short list is:

- **Estimates of the main kinetic rate constant for gas phase O_3 oxidation of Hg^0 to Hg^{2+} vary by a factor of 25.**

- **Oxidation reaction products are not well understood (reaction products influence deposition rates)**

- **Hg concentrations entering the western boundary of models is not well understood. There are many varying estimates and few measurements.**

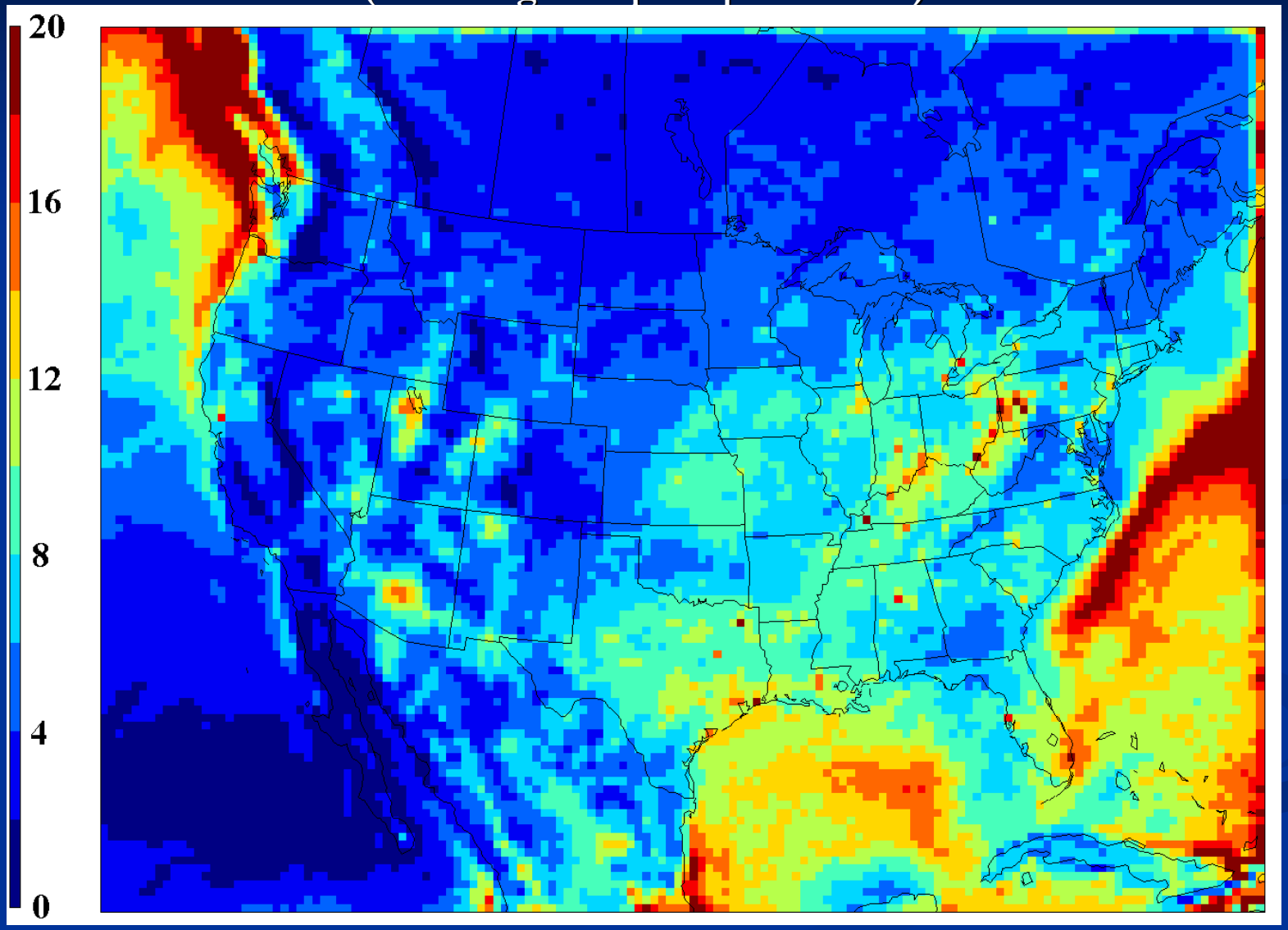
- **Speciation of Hg anthropogenic emissions is often uncertain or not reported.**

- **The presence of other pollutants can strongly effect redox cycling of Hg, leading to diverse interactions and non-linear chemistry.**

… this does not stop scientists from trying

CMAQ-Simulated Hg Wet Deposition for the 2001

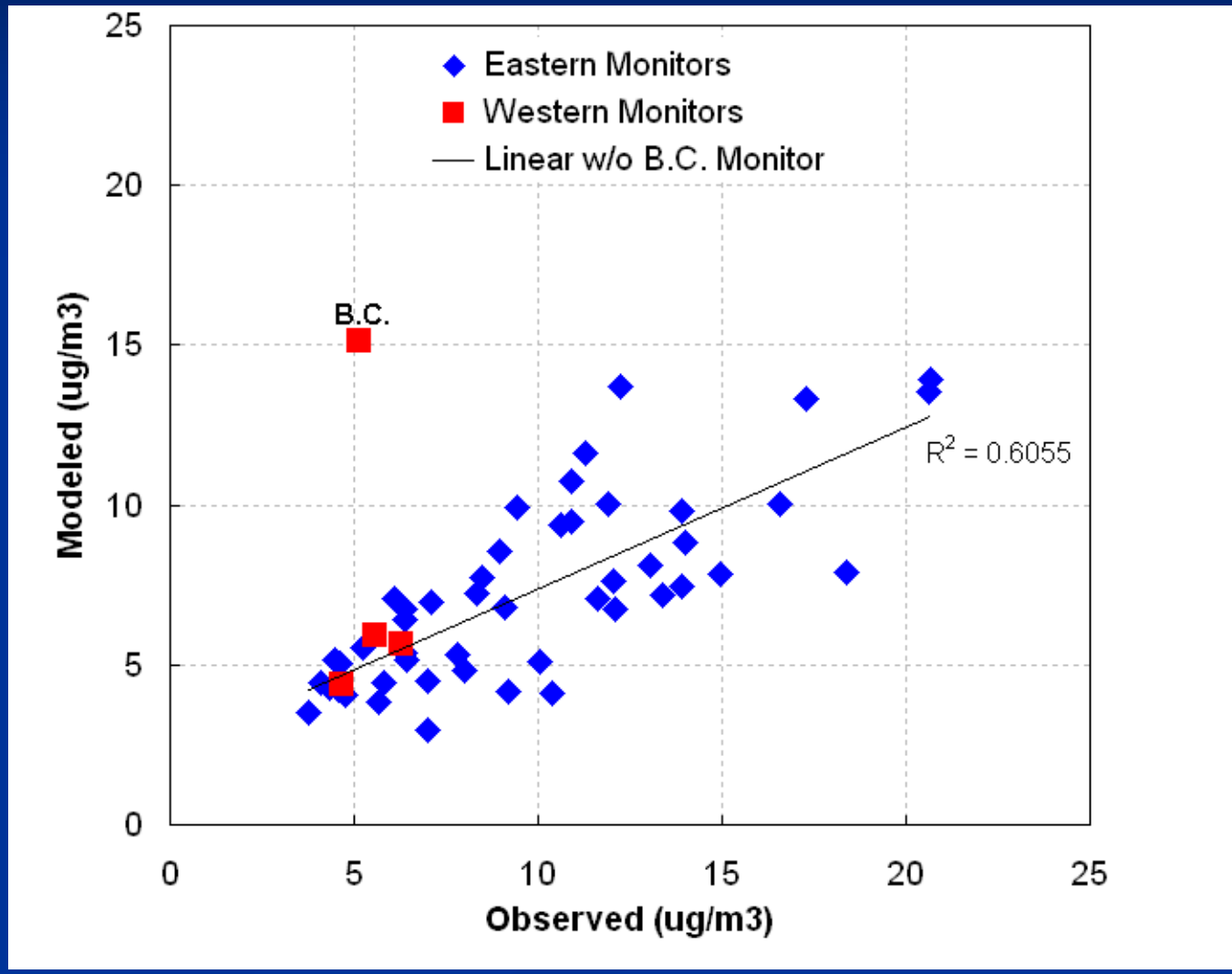
(in micrograms per square meter)



Slide & Model results from Russ Bullock, NOAA ASMD/US EPA

Comparison of CMAQ Model Predictions to MDN Hg Wet Deposition Measurements (annual totals)

While many modeling results look decent given large uncertainties, it is quite possible that compensating uncertainties lead to performance that looks good for the wrong reasons.



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Final thoughts:

Our scientific understanding of atmospheric mercury fate and transport is rapidly evolving due to energetic research efforts.

Expect significant improvements in both measurements methods and model predictions in the coming years.