Sources, chemistry, and deposition of atmospheric mercury in the Arctic

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**10th International Conference on Mercury as a Global Pollutant**  
28 July 2011
Sources, chemistry, and deposition of atmospheric mercury in the Arctic or...

Can we explain Arctic observations with our current understanding of mercury cycling?

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Motivation

Mercury accumulation in the Arctic Ocean is an ecological and human health concern

High mercury concentrations have been observed in the tissues of many Arctic species, including those that make up the diet of indigenous communities.

The Arctic is subject to a unique set of physical, chemical, and environmental conditions (e.g., seasonal sea ice, polar day/night, atmospheric mercury depletion events) that can strongly influence mercury cycling.

Atmospheric transport and deposition brings mercury to the Arctic cryosphere, but the ultimate fate of atmospheric mercury and impacts on ocean cycling are uncertain.
Goal: Understand the fate and impacts of atmospheric mercury in the Arctic

Approach: Apply GEOS-Chem integrated ocean-atmosphere mercury model to the Arctic

GEOS-Chem 3D chemical transport model - represents our best current understanding of processes driving Arctic mercury cycling

Driven by MERRA meteorological data at 4°x5° horizontal resolution

Atmosphere based on Holmes et al. (2010)
- Natural and anthropogenic emissions
- Dry and wet deposition
- Br as the global oxidant

Surface ocean based on Soerensen et al. (2010)
- Chemistry includes biotic and photo-reduction, dark and photo-oxidation
- Dynamically coupled to atmosphere and intermediate waters
- Air-sea exchange based on Nightingale et al. (2000)
Special considerations in the Arctic

**Atmospheric Mercury Depletion Events (AMDEs)**
AMDEs driven by high Br emissions from sea ice in polar spring.

Modeled BrO/Br emission requires sea ice coverage, incident solar radiation, and cold temperatures. [BrO] is temperature-dependent, ranges from 5-20 pptv.

**Snowpack reduction and emission**
Oxidized mercury deposited to snowpacks can be photo-reduced and re-emitted to atmosphere. Huge uncertainty in reducible fraction of mercury (<40-90%) and rate of net reduction in snow (7×10^{-6}-0.1 h^{-1}).

Modeled photo-reduction requires solar radiation and assumes 60% of deposited mercury is reducible. The net reduction rate is scaled to solar radiation such that $k \approx 1\times10^{-3}$ h^{-1} when $R = 100$ W m^{-2}.

**Arctic Ocean physical parameters**
Temperature, sea ice fractions from MERRA assimilated data

All other variables (mixed layer depths, productivity, etc.) best estimates from literature
Testing our current understanding: comparison to atmospheric observations

Observations: multi-year mean over Alert, Zeppelin, Amderma

Summer rebound: snow/ice emission?

Spring AMDEs
Testing our current understanding: comparison to atmospheric observations

The simulation successfully reproduces fall-winter-spring seasonality and spring AMDEs. The observed peak in summer peak in boundary layer Hg0 is significantly underestimated.

Can we explain this peak using our standard understanding of Arctic mercury cycling combined with known uncertainties?

Observations: multi-year mean over Alert, Zeppelin, Amderma

Model: GEOS-Chem at these sites in 2008
Hypothesis 1: re-emission from Arctic snow/ice

Standard hypothesis:
Summer peak can be attributed to re-emission of mercury deposited to the snowpack in spring

Changing model assumptions about snowpack reduction and re-emission does not improve ability to simulate timing or magnitude of summer peak:
• 25-30% of deposition occurs over ocean, where it is not available for re-emission
• Some meltwater formation and delivery to ocean occurs before all mercury deposited to snowpack can be re-emitted
• Large amount of re-emission happens in spring, leaving limited mercury in snowpack to be re-emitted during summer rebound

Snowpack emission cannot explain the summer peak in boundary layer Hg0
Hypothesis 2: atmospheric transport from mid-latitudes

Second hypothesis:
Summer peak can be explained by enhanced poleward atmospheric transport from large sources at mid-latitudes

Observations show more mercury in the Arctic than at mid-latitudes; hence the Arctic troposphere is more likely a net exporter than importer of mercury in the summer

Neither the snowpack nor the atmosphere can explain the summer peak - therefore the ocean must be responsible
Observational data suggest a large source from the Arctic Ocean in summer.

Cruise data show elevated mercury in the boundary layer above areas of the Arctic Ocean with partial sea ice, suggesting evasion of mercury stored under the ice in the ocean.

Additional cruise data show elevated and supersaturated mercury in the surface Arctic Ocean, both under ice and in river outflow regions.

Statistical analysis of Hg0 data from Zeppelin station show the highest observed concentrations are associated with transport from the ocean.

**Mechanistically, what drives the large mercury concentrations in the Arctic Ocean that are necessary to explain the summer Hg0 peak in the atmosphere?**
Hypothesis 3: chemical kinetics in the Arctic surface ocean

Third hypothesis:
Summer peak can be explained by an increase in the ratio of reduction to oxidation in the surface ocean, leading to higher concentrations of oceanic Hg0 that can be evaporated to the Arctic atmosphere.

Model sensitivity tests show that even with the rates of biotic and photo-reduction increased to their maximum observed values and photo-oxidation decreased to a minimum, the summer peak cannot be captured.

Chemical processes cannot create enough oceanic Hg0 to explain elevated boundary layer concentrations - therefore there must be an additional source to the Arctic Ocean with a strong seasonal cycle peaking in spring/summer.
Hypothesis 4: a large, seasonal source to the Arctic ocean

Requires a source to the Arctic Ocean of $\approx300$ Mg a$^{-1}$
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Requires a source to the Arctic Ocean of \( \approx 300 \text{ Mg a}^{-1} \)

We propose that this source comes from rivers
(major source of freshwater and DOC, large catchment basins, peak inputs in spring-summer).

This source is \( \sim 25x \) larger than the 13 Mg a\(^{-1}\) estimated by Outridge et al. (2008), but Russian river Hg concentrations are very poorly constrained.
Proposed budget of mercury in the Arctic surface ocean

Atmosphere
- Snowpack emission: 32 Mg a⁻¹
- Deposition to snow/ice: 62 Mg a⁻¹

Snow / Ice
- Runoff to land
- Deposition: 220 Mg a⁻¹
- Evasion: 86 Mg a⁻¹
- Meltwater: 17 Mg a⁻¹

Surface Ocean
- [Hg⁰] = 0.18 pM
- [Hg²⁺] = 2.5
- [Hg₅⁺] = 0.64
- Hg⁰: 8 Mg
- Hg²⁺: 112 Mg
- Hg₅⁺: 25 Mg

Intermediate Waters

Rivers?
- Hg²⁺: Hg₅⁺
- River delivery: 320 Mg a⁻¹

All fluxes in Mg a⁻¹
Conclusions and future directions

The **summer peak in atmospheric mercury observed at Arctic sites cannot be explained** in terms of conventional ideas (snowpack re-emission, atmospheric transport, ocean chemistry).

An additional **major source to the ocean in spring-summer of \( \approx 300 \text{ Mg a}^{-1} \)**, followed by evasion to the Arctic boundary layer, is **necessary** to explain atmospheric observations. We propose **rivers**, but many uncertainties remain.

With this large oceanic source, the **Arctic Ocean may be a net source of mercury** to the atmosphere. Implications for climate change are uncertain.

*Feedback, ideas, and suggestions welcome!*