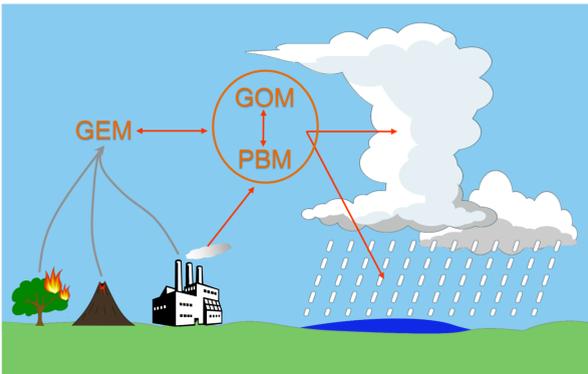


Understanding oxidized Hg transformation and fate using measurements of wet deposition and speciated Hg concentration

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Motivation

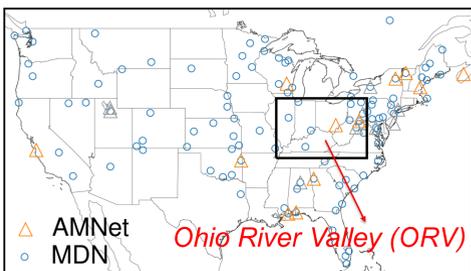
- Although it only represents a small fraction of the atmospheric reservoir, the oxidized Hg is of great importance in determining the input to ecosystem through wet/dry deposition.
- Our understanding of the transformation and fate of oxidized Hg in the atmosphere has been hampered by the bias and/or uncertainty of the current oxidized Hg measurements [1] and by the incomplete knowledge of Hg oxidation/reduction mechanisms and associated kinetics [2].
- Wet deposition measurements have lower uncertainty [3] and may be used to estimate oxidized Hg concentration [4]. However, their relationship is very complex and is affected by many factors (e.g. in-cloud and below-cloud scavenging). In this study, we evaluate several important factors from sensitivity simulations using a chemical transport model.



Wet deposition = f {
[GOM+PBM],
precipitation,
cloud properties,
time,
temperature,
Henry's law constant,
... }

Methodology

Wet deposition and speciated Hg measurements in the USA



- Speciated Hg concentration measurements are from the Atmospheric Mercury Network (AMNet) [5], including 12 rural/remote sites.
- Wet deposition measurements are from the Mercury Deposition Network (MDN) [6], including 104 sites.
- We use AMNet and MDN measurement data in 2010-2012.

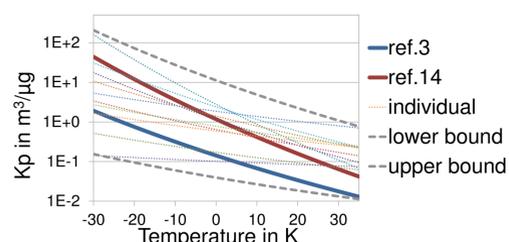
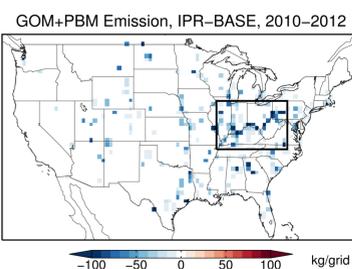
GEOS-Chem nested-grid simulations over North America

- GEOS-Chem (v9-02) is a chemical transport model driven by the NASA GMAO GEOS-5 meteorology [7]. Mercury simulation includes a 3-D atmosphere [8], a 2-D ocean [9], and a 2-D terrestrial reservoir [10].
- We use bromine oxidation chemistry with in-cloud photochemical reduction of oxidized Hg to best match global GEM concentration measurements [11].
- Nest-grid simulations over North America are in a 0.5°x0.667° resolution with initial and boundary conditions from global 2°x2.5° simulations [12].
- Anthropogenic emissions are from the EDGARv4.tox2 inventory [13].

Model setup in different sensitivity simulations

	Difference from BASE
BASE	Standard model
KP1	A different gas-particle partition coefficient K_p [14]
IPR	Different Hg speciation in emission inventory [e.g. 15]
HRY	A different Henry's law constant (H) for GOM

- The gas-particle partition coefficient $K_p = \text{PBM}/(\text{PM}_{2.5} \times \text{GOM})$ has been found linked to local temperature T . The KP1 uses a different K_p [14] from the BASE [3].
- The EDGAR anthropogenic emission inventory used in the BASE assumes a 50:50 GEM:GOM+PBM ratio for the power generation sector, whereas the IPR decreases the share of GOM+PBM. A large difference is observed in the ORV.
- The BASE assumes GOM as HgCl_2 ($H = 1.4 \times 10^6 \text{ M/atm}$) for deposition, but other possible forms have lower H . In the HRY we set H as $1 \times 10^4 \text{ M/atm}$ ($\text{Hg}(\text{OH})_2$).



Results & Discussion

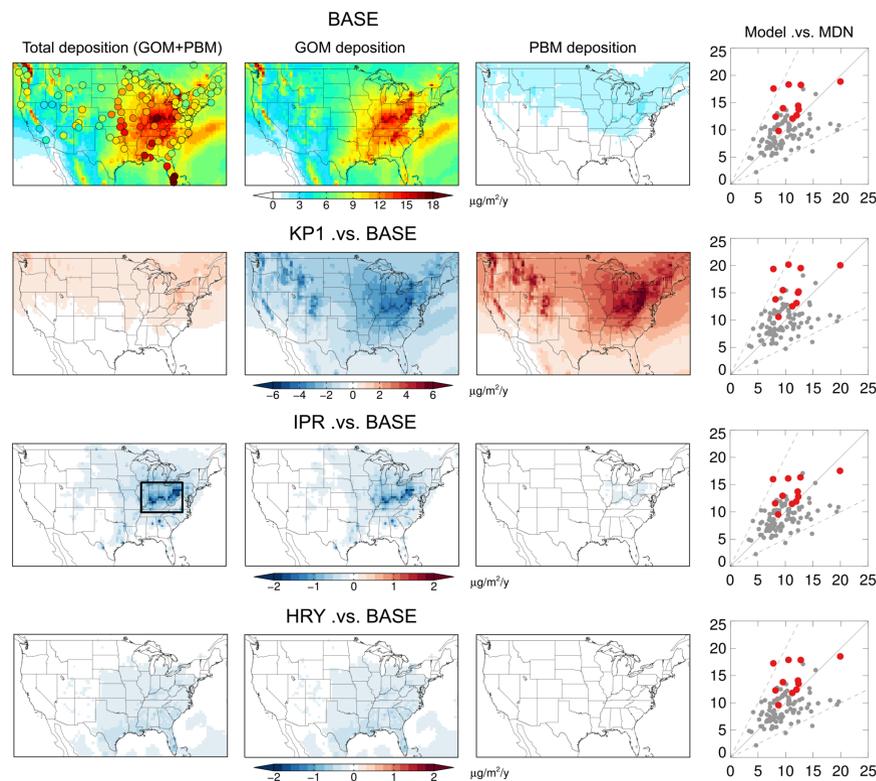


Figure left: the three panels in the left top show the spatial distributions of wet deposition fluxes (total, GOM, and PBM) from the BASE simulation. The wet deposition differences between the sensitivity simulations (KP1, IPR, and HRY) and the BASE are also shown. The rightmost column indicates the comparison between the measured (horizontal axis) and modeled (vertical axis) wet deposition fluxes ($\mu\text{g}/\text{m}^2/\text{y}$). The red circles show sites in the ORV ($N = 11$) whereas the gray circles show all the other sites in the MDN ($N = 93$). The solid straight line show 1:1 ratio, and the two dashed lines show 1:2 and 2:1 ratios.

- In the BASE, most (90%) wet deposition is from GOM. This fraction decreases to 60% in the KP1, as a result of a larger K_p . However, the difference of total deposition between the BASE and KP1 is very small ($< 10\%$).
- The model can reproduce measured wet deposition at most MDN sites within a factor of 2. All the simulations have small biases ($< 5\%$) in the average wet deposition of all MDN sites, but highly overestimate wet deposition in the ORV (20-40%).
- The influences of KP1 and IPR on the wet deposition have different spatial distribution over the USA.
- The HRY suggests that a lower Henry's law constant for GOM has little effect ($\sim 2\%$) on modeled wet deposition.

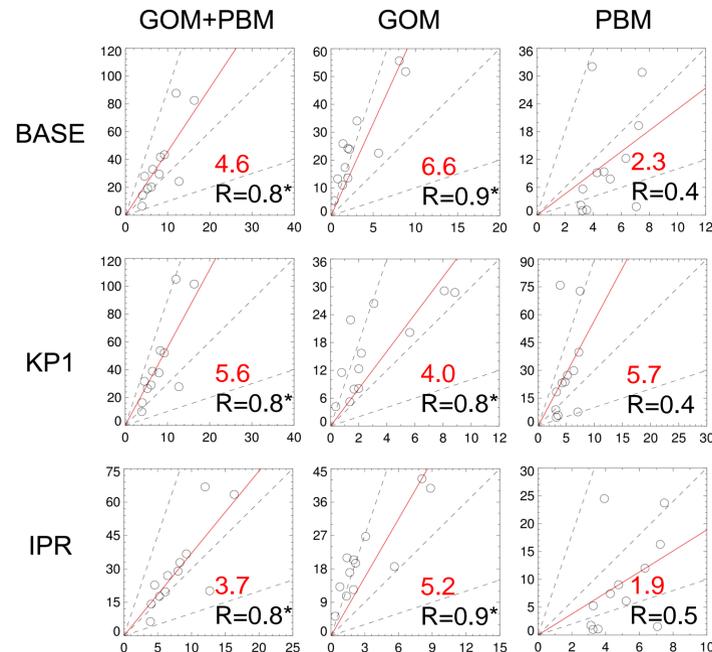


Figure left: horizontal axis shows measured oxidized Hg concentration (pg/m^3) by AMNet, and vertical axis shows modeled concentration (pg/m^3) by different GEOS-Chem simulations. The dashed lines represent 1:1, 1:3, and 1:9 ratios, respectively. The red numbers are ratios of modeled and measured concentrations. Their correlation coefficients (R) are also shown and the * means significant at the 0.05 level. The difference between the BASE and HRY is very small and therefore the HRY is not shown.

- In different simulations, the model overestimates measured GOM+PBM, GOM, and PBM concentrations by factors of 3-6, 4-7, and 2-6, consistent with the lab experiment result [1], depending on the composition of GOM, that the KCl-coated denuder used in current oxidized Hg measurements was too low by a factor of 2-12.
- The model can reproduce site-to-site variability of GOM and GOM+PBM ($R \sim 0.8-0.9^*$) but not PBM ($R \sim 0.4-0.5$).
- The uncertainty of oxidized Hg measurements should be reduced to $< 100\%$ in order to be used as constraints.

Implications & Future Work

- These simulations may suggest significant uncertainties in predicted wet and dry depositions in the global scale.
- Additional sensitivity simulations are required to evaluate the influence of redox chemistry on the modeled wet deposition and oxidized Hg concentration.
- The relationships between wet deposition and oxidized Hg concentration should be examined in more details (e.g. separating the measurement sites by regions and seasons).

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