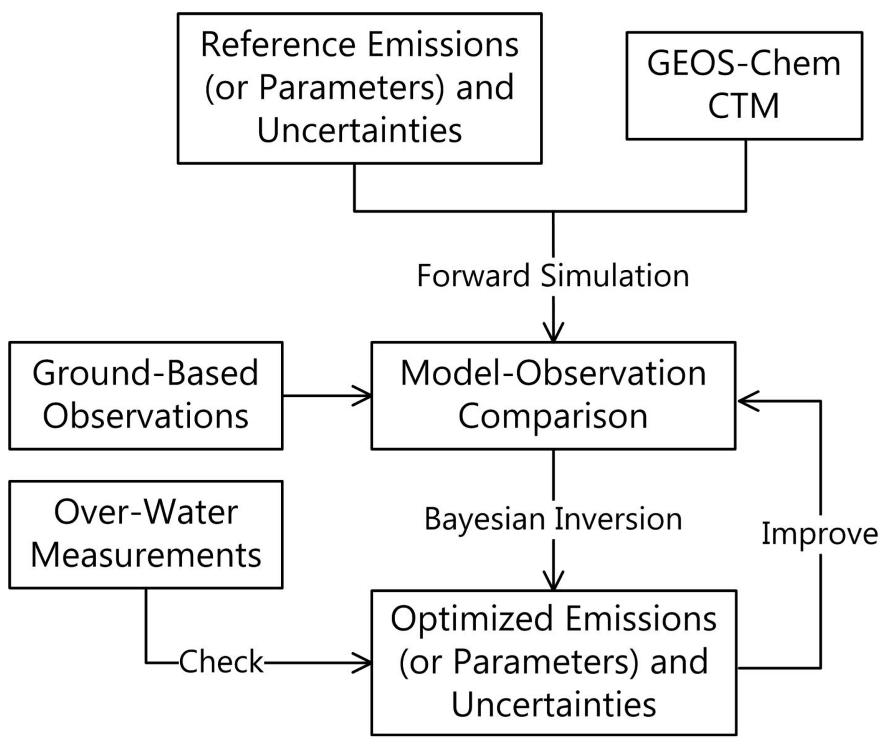
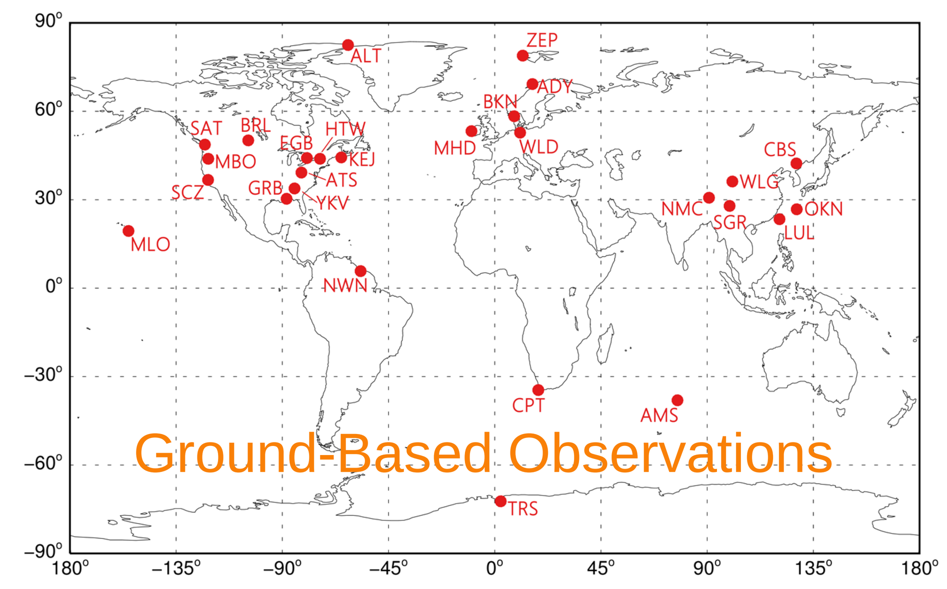
Top-down constraints on Hg emissions at global and regional scales: combining atmospheric observations and modeling

Shaojie Song[1], Noelle E. Selin[1,2], Anne L. Soerensen[3], Viral Shah[4], Amanda Giang[2], Lynne Gratz[5], Jesse L. Ambrose[5], Daniel A. Jaffe[4,5], Lyatt Jaeglé[4], Lisa Kaser[6], Bin Yuan[7], Eric Apel[6], Rebecca Hornbrook[6], Alan Hills[6], Daniel Riemer[6], Nicola Blake[6], Hélène Angot[8], Richard Artz[9], Steve Brooks[10], E.-G. Brunke[11], Gary Conley[12], Aurélien Dommergue[8], Ralf Ebinghaus[13], Thomas M. Holsen[14], Shichang Kang[15], Paul Kelley[9], Winston T. Luke[9], Olivier Magand[8], Kohji Marumoto[16], Katrine A. Pfaffhuber[17], Xinrong Ren[9], Guey-Rong Sheu[18], Franz Slemr[19], Thorsten Warneke[20], Andreas Weigelt[13], Peter Weiss-Penzias[21], Dennis C. Wip[22], Qianggong Zhang[23]

An inverse modeling study at global scale

- This study quantitatively estimates present-day mercury emission sources combining ground-based observations and a global chemical transport model (the GEOS-Chem CTM). Several key parameters in GEOS-Chem (including two ocean parameters) are also investigated to explain the emission changes.





Bayesian Inversion Approach

observational vector: monthly Hg^0 observations at all 27 sites

state vector: changes of emissions

$$y^{obs} = y^{ref} + Hx + \varepsilon$$

modeled Hg^0 observations w/ reference emissions

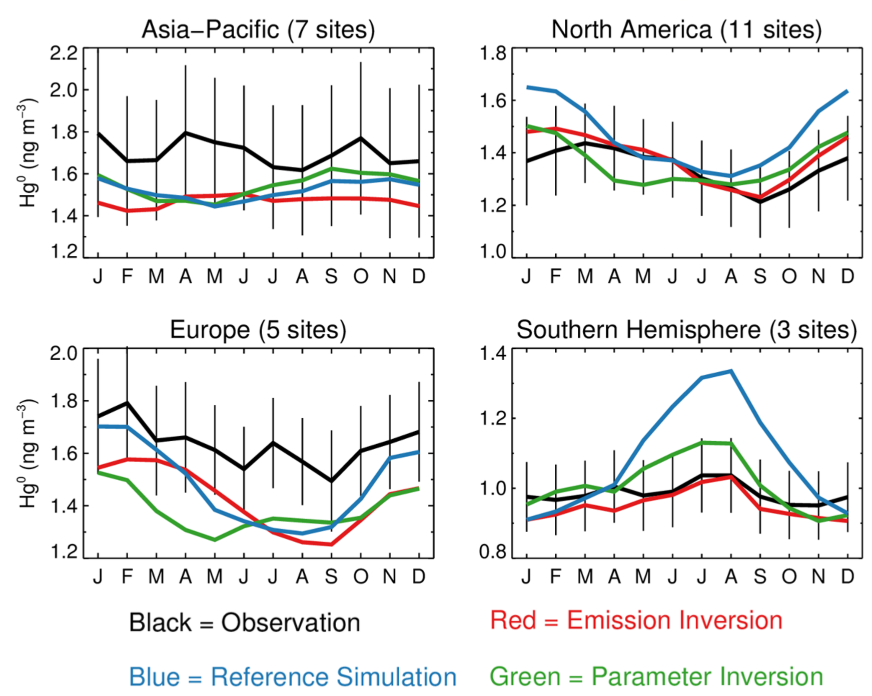
sensitivity matrix

$h_{ij} = (y_i - y_i^{ref})/(x_j - x_j^{ref}) \approx \partial y_i/\partial x_j$

observation / model errors

- The optimized emissions depend on the *a priori* uncertainties associated with the reference emissions and Hg^0 observations.
- The 1-σ uncertainties of reference emissions are set as 50%.
- The total observation/model errors contain mismatch, instrumental precision, sampling frequency, and **intercomparison errors (the most important)**.

Model-Observation Comparison



- The emission inversion better reproduces ground-based Hg^0 observations (particularly for sites in the Southern Hemisphere and North America, note seasonal variability) than the reference simulation, and matches measured Hg^0 over the North Atlantic Ocean and wet deposition fluxes in North America.

Optimized and Reference Emissions / Uncertainties (Mg/y)

Source	Included in inversion?[b]	Reference emission	Optimized emission	Bottom-up estimate[1]
Anthropogenic[c]		1960 (420–3510)	2250 (1150–3360)	
Asia	Y	770 ± 390	1060 ± 110	
Other regions	N	760	760	
Contaminated sites	N	80 (70–100)	80 (70–100)	
Oxidized Hg	N	350	350	
Net ocean		2990 (470–5510)	3160 (1160–5160)	**2800 (800-5300)**
Net NH ocean	Y	1230 ± 630	1670 ± 530	
Net SH ocean	Y	1760 ± 880	1490 ± 680	
Net terrestrial[d]		1070 (−510–3130)	340 (−590–1750)	**1600 (800-3000)**
Soil	Y	1680 ± 840	860 ± 440	
Prompt reemission	N	520	500	
Hg^0 dry deposition	N	−1430	−1320	
Geogenic	N	90 (60–600)	90 (60–600)	
Biomass burning	N	210	210	
TOTAL[e]		6020 (380–12 150)	5750 (1720–10 270)	

- The global ocean accounts for 55% of the total mercury emissions. The terrestrial ecosystem is neither a net source nor a net sink of atmospheric Hg^0, in contrast to its bottom-up estimate as a large source [1].
- The optimized Asian anthropogenic emissions suggest that bottom-up inventories (ranging from 550–800 Mg/y) may have underestimated their values.

Identified knowledge gaps in mercury measurements and modeling

- Effective inversions are hampered by the large intercomparison errors in measured GEM. Research aimed at quantifying/reducing the intercomparison errors should be given high priority by the community.
- More sites in some regions (e.g. the Southern Hemisphere) are necessary to further constrain emissions.
- Improving our understanding of atmospheric Hg chemistry is of great importance for emissions since it affects our inversion results (e.g. ocean emissions/parameters).

This study has been published in open access ACPD (scan the QR code right):

Song, S., Selin, N. E., Soerensen, A. L., Angot, H., Artz, R., Brooks, S., Brunke, E. G., Conley, G., Dommergue, A., Ebinghaus, R., Holsen, T. M., Jaffe, D. A., Kang, S., Kelley, P., Luke, W. T., Magand, O., Marumoto, K., Pfaffhuber, K. A., Ren, X., Sheu, G. R., Slemr, F., Warneke, T., Weigelt, A., Weiss-Penzias, P., Wip, D. C., and Zhang, Q.: Top-down constraints on atmospheric mercury emissions and implications for global biogeochemical cycling, Atmos. Chem. Phys. Discuss., 15, 5269-5325, doi:10.5194/acpd-15-5269-2015, 2015.

MIT ATMOSPHERIC CHEMISTRY

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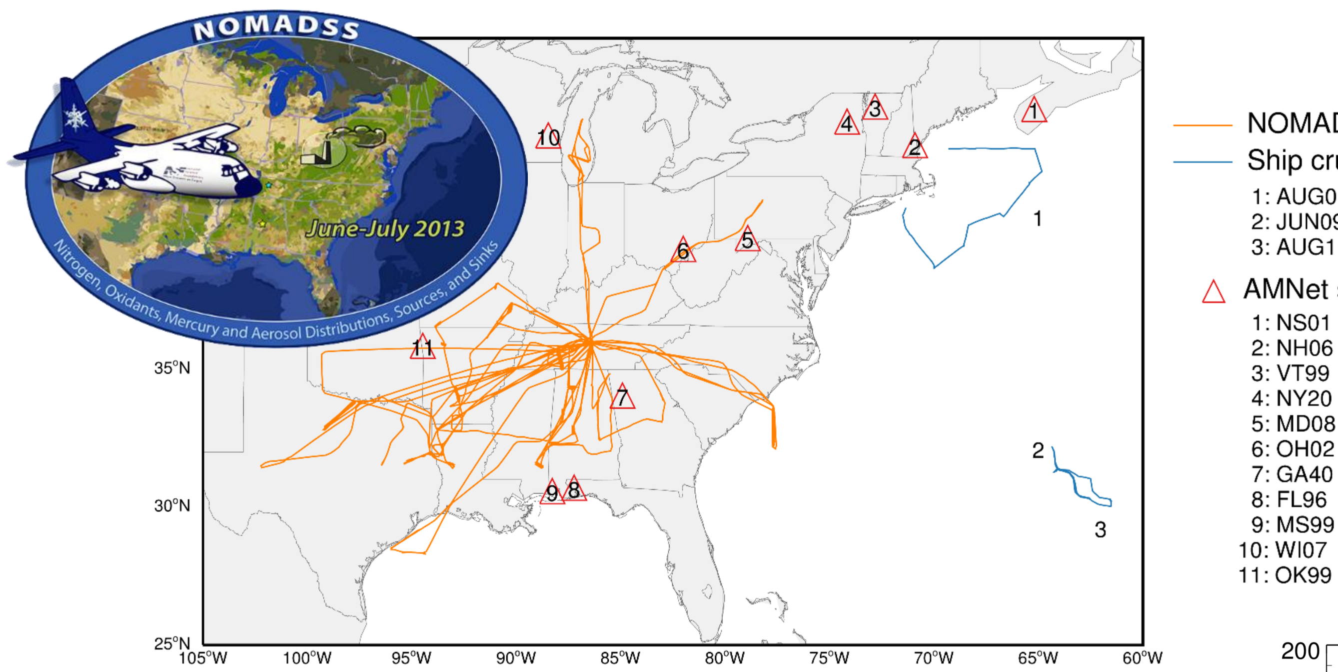
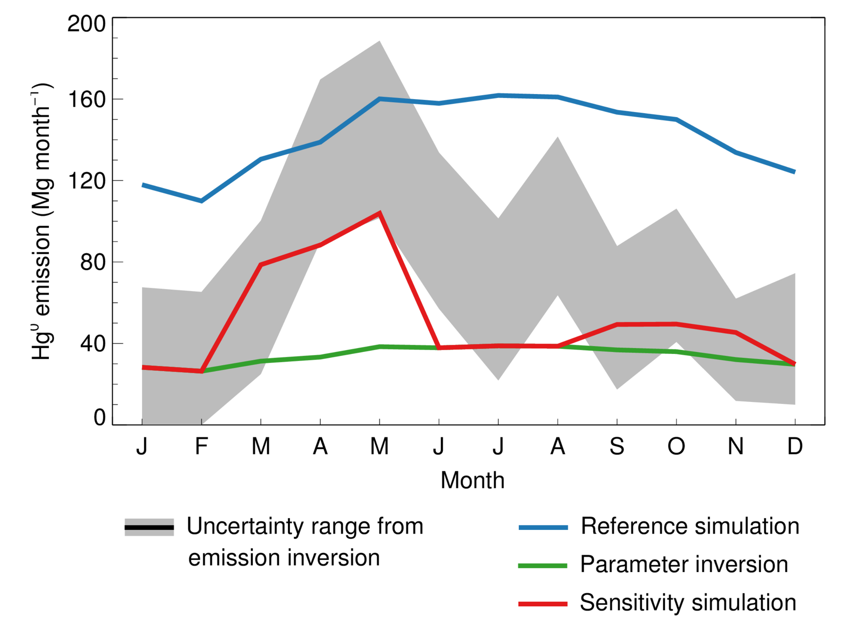
Atmosphere-surface exchange of Hg^0 over the Eastern USA and Northwest Atlantic

- This study combines three types of mercury measurements (ground-based stations, aircraft campaign, and ship cruises) and the GEOS-Chem CTM nested grid simulations.



- We conduct three GEOS-Chem simulations: reference simulation, parameter inversion, and a sensitivity simulation. The sensitivity simulation is based on the parameter inversion with elevated springtime soil emission in the mid-latitude region (*by a factor of 4*) and elevated summertime bromine columns in the tropics and subtropics (*by a factor of 3*).

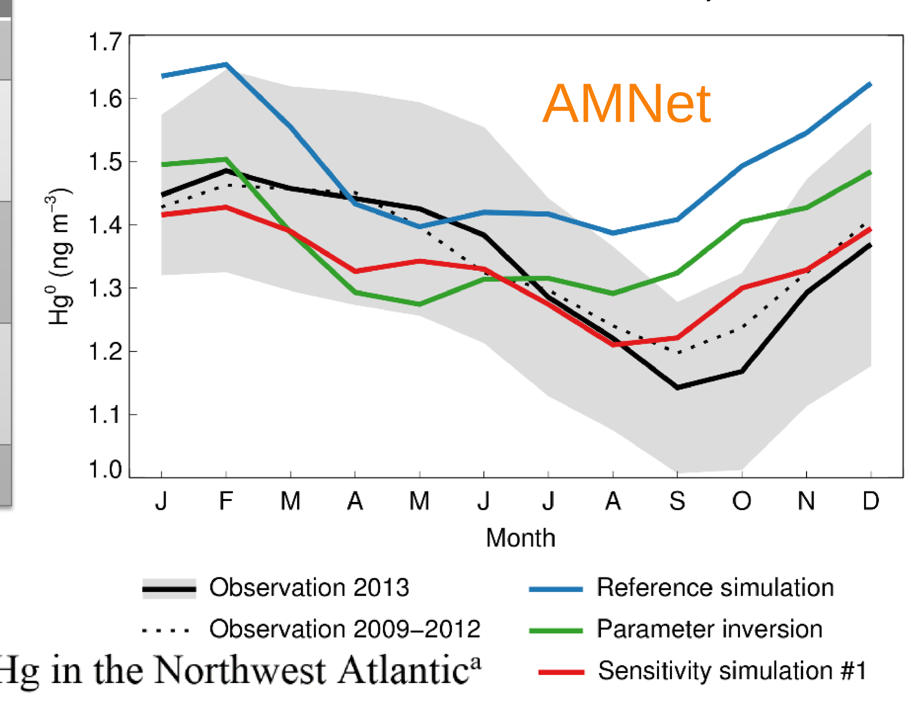


- An increase of springtime soil emission is consistent with the emission inversion. Agricultural activities and a larger land surface Hg pool due to deposition in the snow may contribute to such seasonal pattern.

Comparison between model results and different types of observations

NOMADSS within boundary layer

	Over-land	Over-ocean	M–W U test
Measurement	1.44 ± 0.09	1.56 ± 0.11	$p < 0.001$
Reference simulation	1.40 ± 0.04	1.32 ± 0.03	$p < 0.001$
Parameter inversion	1.30 ± 0.03	1.28 ± 0.02	$p < 0.001$
Sensitivity simulation	1.29 ± 0.06	1.26 ± 0.05	$p < 0.001$
N of samples	356	69	



Ship cruises

Table. Measured and modeled concentrations of air and aqueous Hg in the Northwest Atlantic[a]

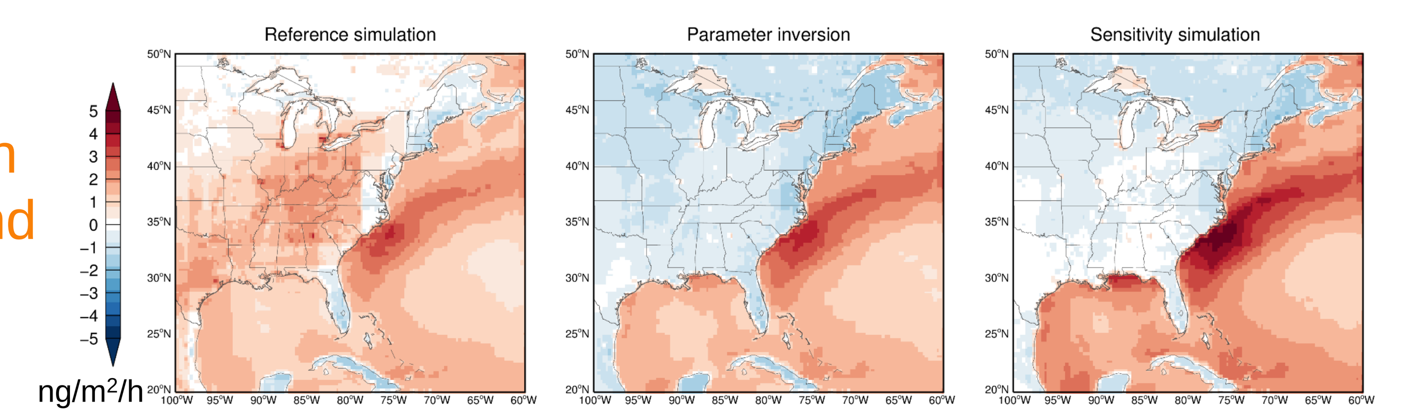
Ship cruise	AUG08			JUN09			AUG10		
Hg species[b]	air Hg^0	Hg_{aq}^0	Hg_{aq}^T	air Hg^0	Hg_{aq}^0	Hg_{aq}^T	air Hg^0	Hg_{aq}^0	Hg_{aq}^T
Measurement	1.4 ± 0.2	133 ± 14	1.3-2.9	1.4 ± 0.1	120 ± 7	NA[c]	NA	196 ± 34	1.2-1.6
Reference simulation	1.40	110	1.3	1.33	78	0.9	1.31	91	1.1
Parameter inversion	1.37	117	1.6	1.31	94	1.2	1.30	96	1.3
Sensitivity simulation #1	1.32	143	1.9	1.32	98	1.3	1.17	123	1.6

[a] Ship cruise measurement data are from Soerensen et al. (2013). For the cruise of August 2008, we exclude aqueous Hg data measured in the coastal region because they are affected by anomalously high freshwater inputs.

[b] The units of air Hg^0, Hg_{aq}^0, and Hg_{aq}^T (filtered total aqueous mercury) are ng m^{-3}, fM (10^{-12} mol m^{-3}), and pM (10^{-9} mol m^{-3}), respectively.

- The sensitivity simulation best captures the seasonal pattern of the AMNet Hg^0 concentration.
- In 2013 June/July, the sensitivity simulation has a small bias (-0.03 ng/m^3) when compared to the AMNet.
- The sensitivity simulation gives the closest Hg_{aq}^0, but still 8-40% less than ship cruises measurements.
- The median Hg^0 in NOMADSS is 1.46 ng/m^3, ~ 10% higher than the sensitivity simulation (1.29 ng/m^3).

Modeled Hg^0 emission fluxes from the land and ocean in JJA



Take-home message: GEOS-Chem simulations and observations suggest that the Eastern US terrestrial ecosystem is a net sink of Hg^0 while the Northwestern Atlantic Ocean is a source.

Author affiliations & References & Acknowledgments

[1]EAPS, Massachusetts Institute of Technology, Cambridge, MA, USA; [2]ESD, Massachusetts Institute of Technology, Cambridge, MA, USA; [3]Stockholm University, Stockholm, Sweden; [4]University of Washington, Seattle, WA, USA; [5]University of Washington-Bothell, Bothell, WA, USA; [6]National Center for Atmospheric Research, Boulder, CO, USA; [7]National Oceanic and Atmospheric Administration, Boulder, CO, USA; [8]Univ. Grenoble Alpes, CNRS, LGGE, Grenoble, France; [9]National Oceanic and Atmospheric Administration, College Park, MD, USA; [10]University of Tennessee Space Institute, Tullahoma, TN, USA; [11]South African Weather Service c/o CSIR, Stellenbosch, South Africa; [12]Ohio University, Athens, OH, USA; [13]Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; [14]Clarkson University, Potsdam, NY, USA; [15]Chinese Academy of Sciences (CAS), Lanzhou, China; [16]National Institute for Minamata Disease, Kumamoto, Japan; [17]Norwegian Institute for Air Research (NILU), Norway; [18]National Central University, Jhongli, Taiwan; [19]Max Planck Institute for Chemistry, Mainz, Germany; [20]University of Bremen, Germany; [21]University of California, Santa Cruz, CA, USA; [22]Anton de Kom Universiteit van Suriname, Paramaribo, Suriname; [23]Chinese Academy of Sciences, Beijing, China

[1] Pirrone et al., doi:10.5194/acp-10-5951-2010

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