Long-Term Monitoring of Atmospheric Mercury

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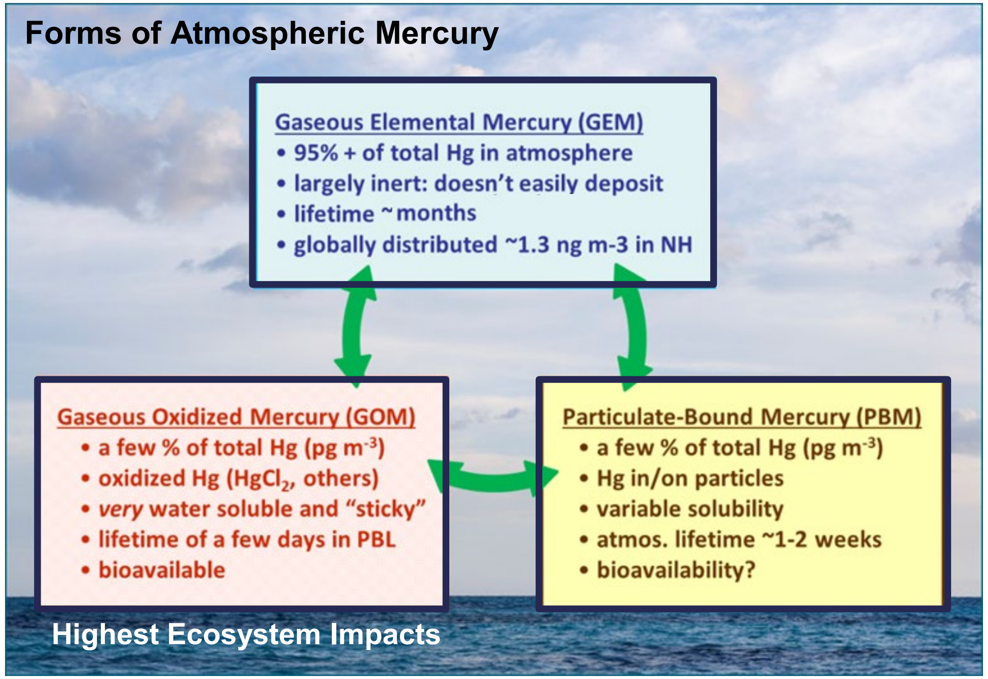
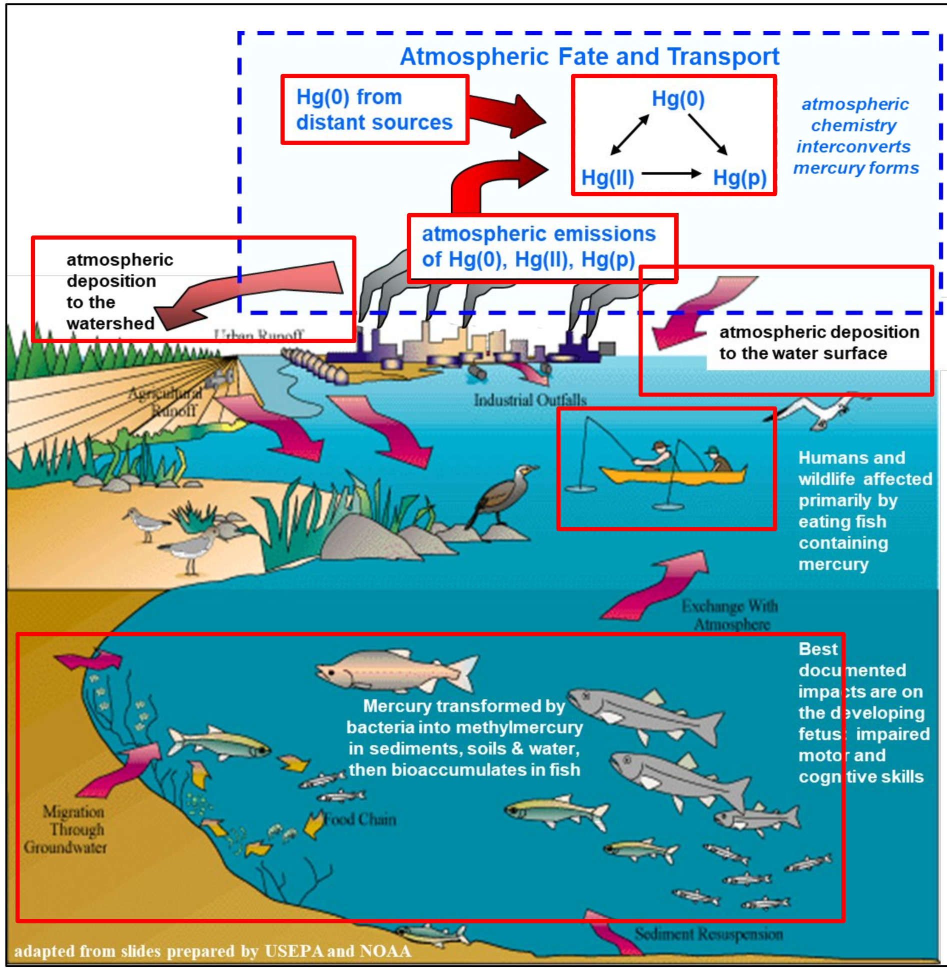
Relevance of NOAA's Mercury Research Program

Mercury is a potent neurotoxin that can impair children's cognitive development & affect behavior/physiology of wildlife

Primary human exposure pathway:
- Emission to the atmosphere (natural/anthropogenic)
- Transport, transformation, deposition
- Bioaccumulation in the food web
- Human consumption of contaminated seafood





Where does the mercury come from that is depositing to any given waterbody or watershed?

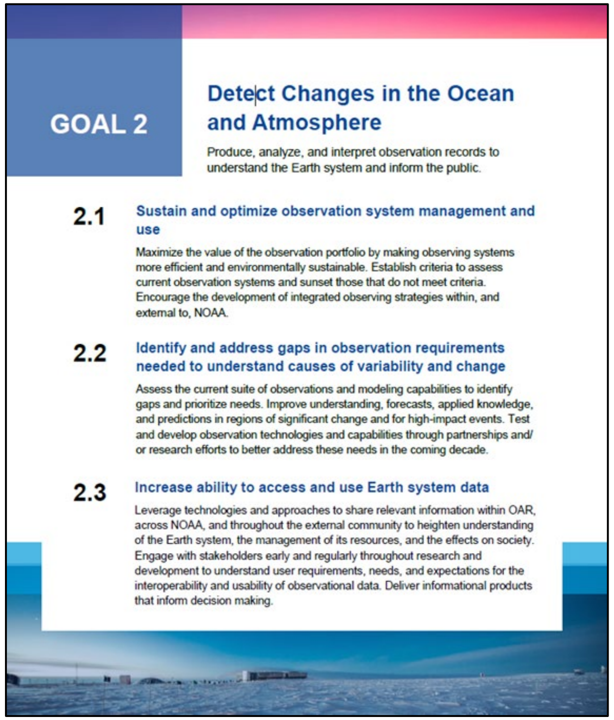
- How much from local/regional sources?
- How much from global sources?
- Monitoring alone cannot give us the answer
- atmospheric models required, "ground-truthed" by atmospheric monitoring

Relevance of NOAA's Mercury Research Program

Mercury adversely impacts human and ecosystem health and is a ubiquitous and multi -media pollutant; ARL's mercury research aligns with multiple elements of NOAA's mission.

NOAA's Next Generation Strategic Plan

Weather-Ready Nation • Healthy people & communities • More productive & efficient economy
Healthy Oceans • Improved understanding of ecosystems • Sustainable fisheries & safe seafood



GOAL 2

Detect Changes in the Ocean and Atmosphere

Produce, analyze, and interpret observation records to understand the Earth system and inform the public.

2.1 Sustain and optimize observation system management and use

Maximize the value of the observation portfolio by making observing systems more efficient and environmentally sustainable. Establish criteria to assess current observation systems and sunset those that do not meet criteria. Encourage the development of integrated observing strategies within, and external to, NOAA.

2.2 Identify and address gaps in observation requirements needed to understand causes of variability and change

Assess the current suite of observations and modeling capabilities to identify gaps and prioritize needs. Improve understanding, forecasts, applied knowledge, and predictions in regions of significant change and for high-impact events. Test and develop observation technologies and capabilities through partnerships and/or research efforts to better address these needs in the coming decade.

2.3 Increase ability to access and use Earth system data

Leverage technologies and approaches to share relevant information within OAR, across NOAA, and throughout the external community to heighten understanding of the Earth system, the management of its resources, and the effects on society. Engage with stakeholders early and regularly throughout research and development to understand user requirements, needs, and expectations for the interoperability and usability of observational data. Deliver informational products that inform decision making.

OAR Strategic Plan

Goal 1.2 Determine how climate change impacts marine ecosystems, coastal communities, and the global ocean system

Goal 2. Detect Changes in the Ocean and Atmosphere
- 2.1 Sustain/optimize observation system management and use
- 2.2 Identify/address gaps in observation requirements needed to understand causes of variability and change
- 2.3 Increase ability to access and use Earth system data

Long-Term Monitoring of Atmospheric Mercury

ARL operates 3 sites for long-term monitoring of Hg species in the atmosphere at hourly resolution; Barrow, AK and Mauna Loa, HI in collaboration with NOAA's Global Monitoring Laboratory (GML)

Sites operate within the National Atmospheric Deposition Program's (NADP's) Atmospheric Mercury Network (AMNet)

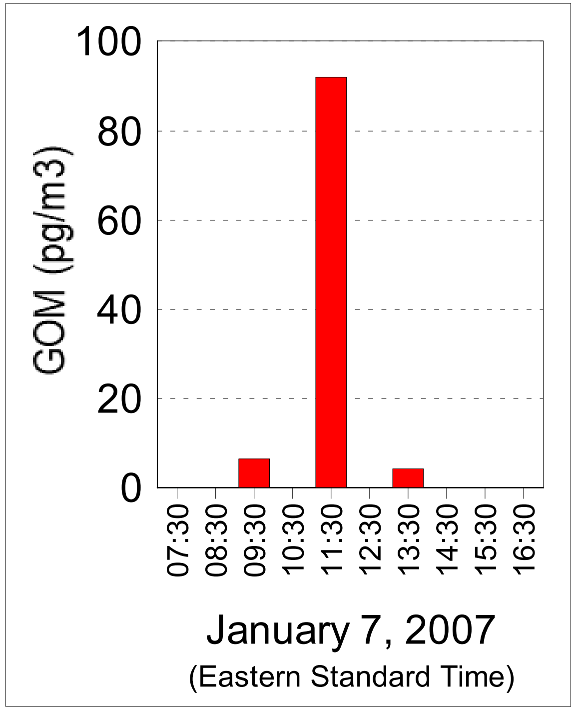
- Harmonized operating and data reduction protocols across the network (13 sites)
- NADP calculates bi-directional air-surface exchange of GEM, deposition of GOM and PBM
- Publicly available data and products

Long-term Hg monitoring is essential for:

- Local/regional/global source attribution and characterization
- Model evaluation
- Understanding atmospheric physical/chemical transformations
- Trend detection in response to regulatory emissions reductions and/or emissions increases (e.g., ASGM)
- Test bed for process/QA studies, method evaluation and development

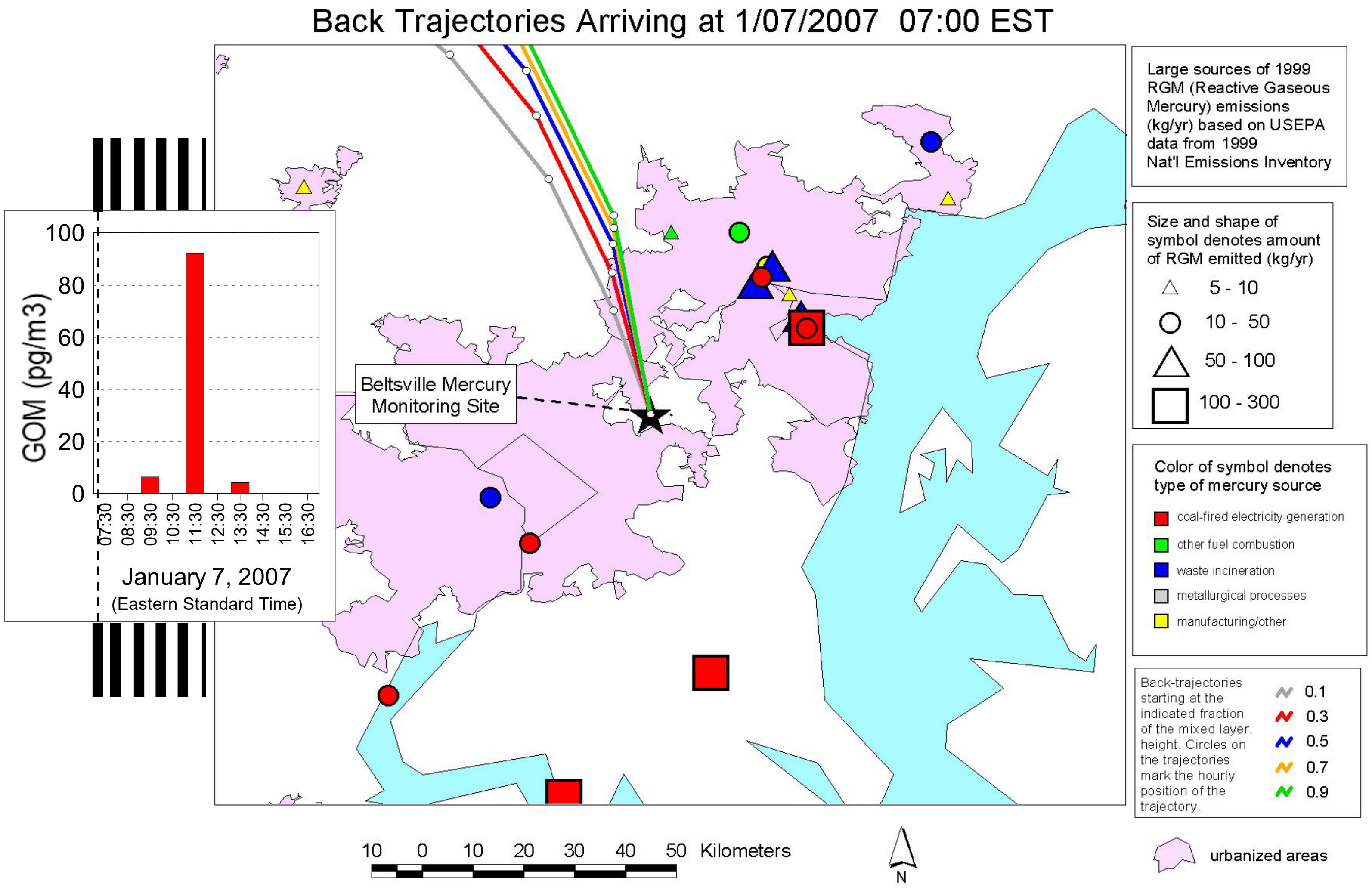
Source Attribution and Characterization

Using ARL's HYSPLIT model to interpret ambient measurements and identify local/regional Hg sources in plume events

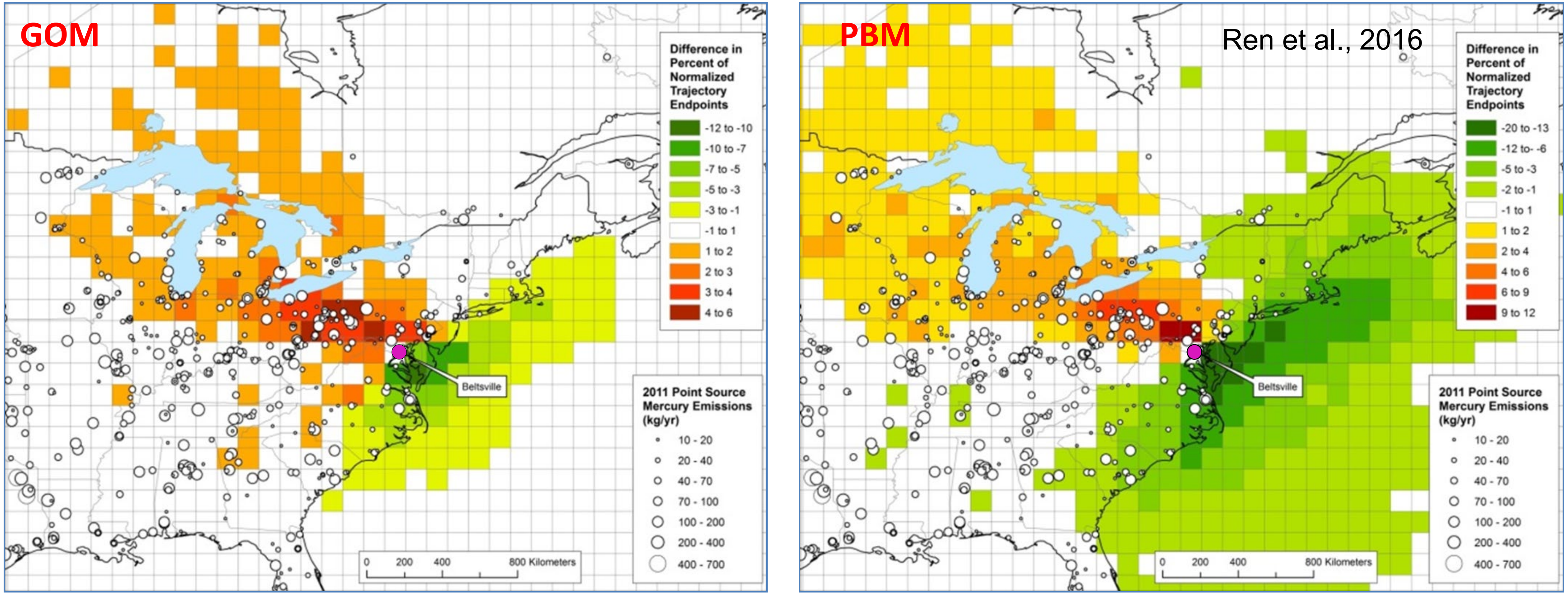


Beltsville, MD Plume Event January 7, 2007

Source Attribution and Characterization

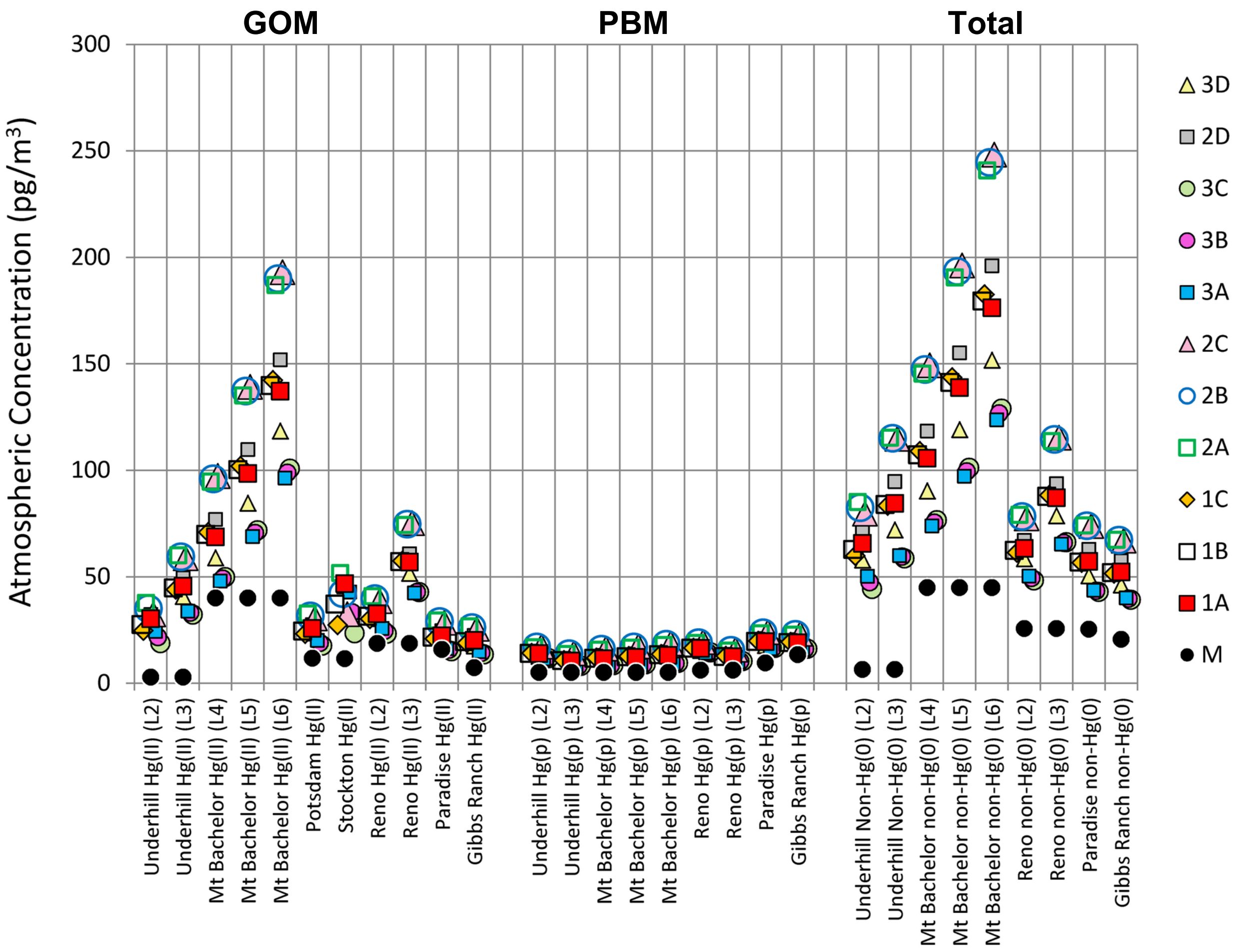


Source Attribution and Characterization



Combining HYSPLIT back trajectory frequency calculations <u>with multi -year mercury dataset</u> at Beltsville identifies the emission source regions impacting the site over time. Red/orange indicate those regions more likely to have been encountered during high [GOM] & [PBM] events.

Model Evaluation



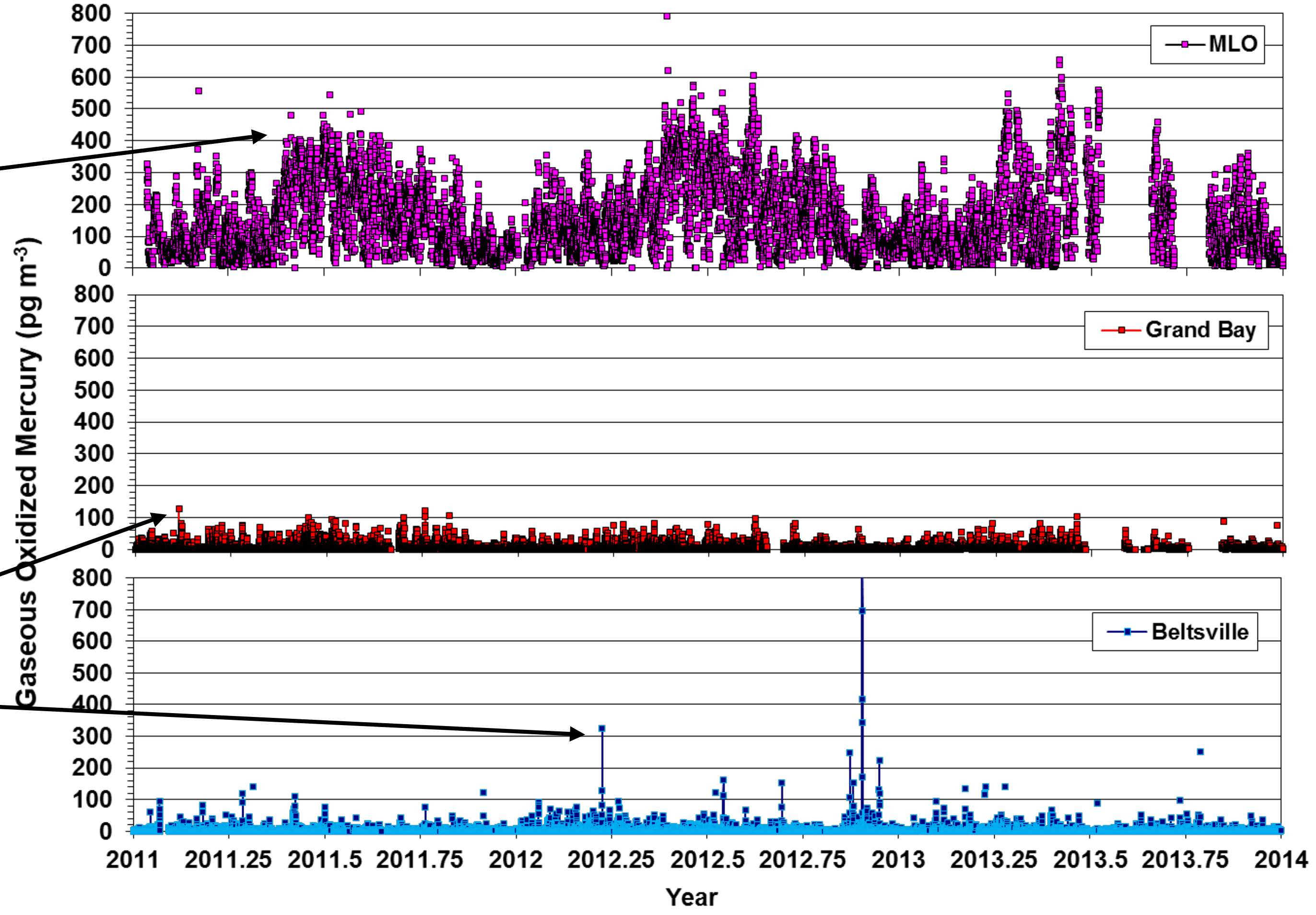
Average 2005 measured GOM, PBM, and total non-Hg(0) concentrations compared with simulation results. From Cohen et al., 2016

- Comparing model results to measurements provides essential information to assess model uncertainties and develop model improvements.
- This example shows that the model provided relatively reasonable results at some sites but that in general, the model predictions were higher than measured concentrations, especially for GOM, all 11 different model configurations considered.
- These results suggest that model physics and chemistry may need to be adjusted, and they raise the possibility that measurements are potentially biased low.

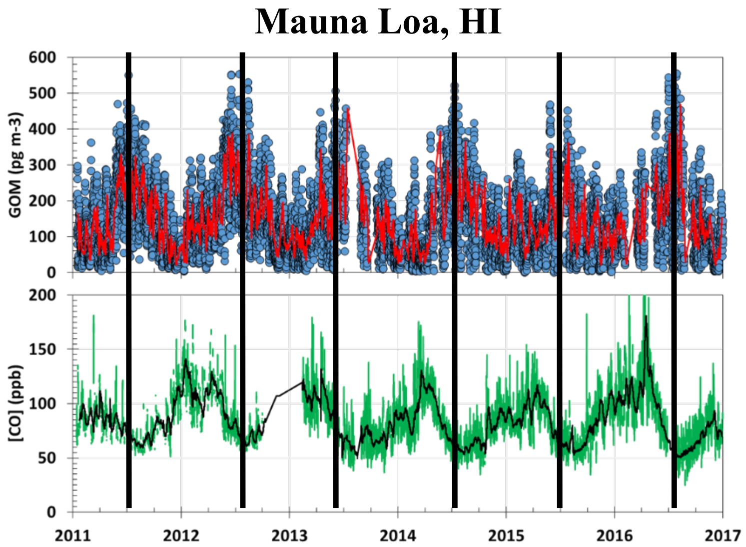
Atmospheric Transformations

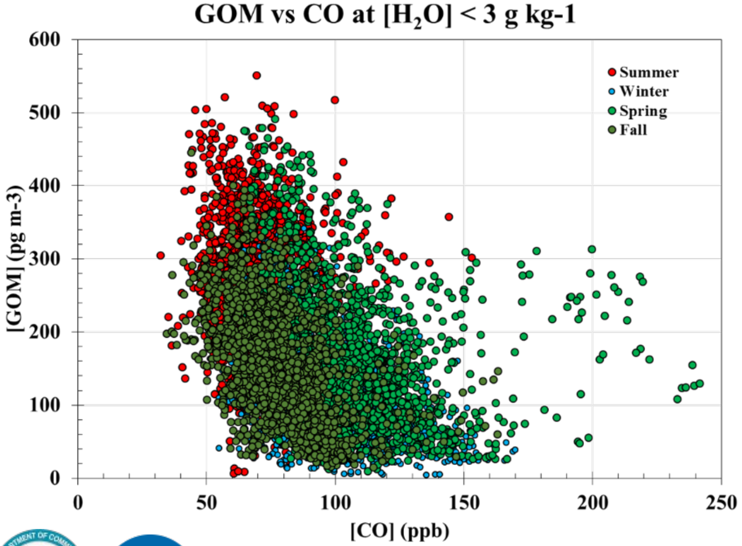
In the background free troposphere (Mauna Loa), GOM displays a *pronounced seasonal* dependence and concentrations up to several hundred pg m^{-3}.

Sea level sites display a slight seasonal dependence of GOM (↑spring, summer) and concentrations ~ 10 - 100 pg m^{-3} (*higher in short-duration local and regional emission plumes*).

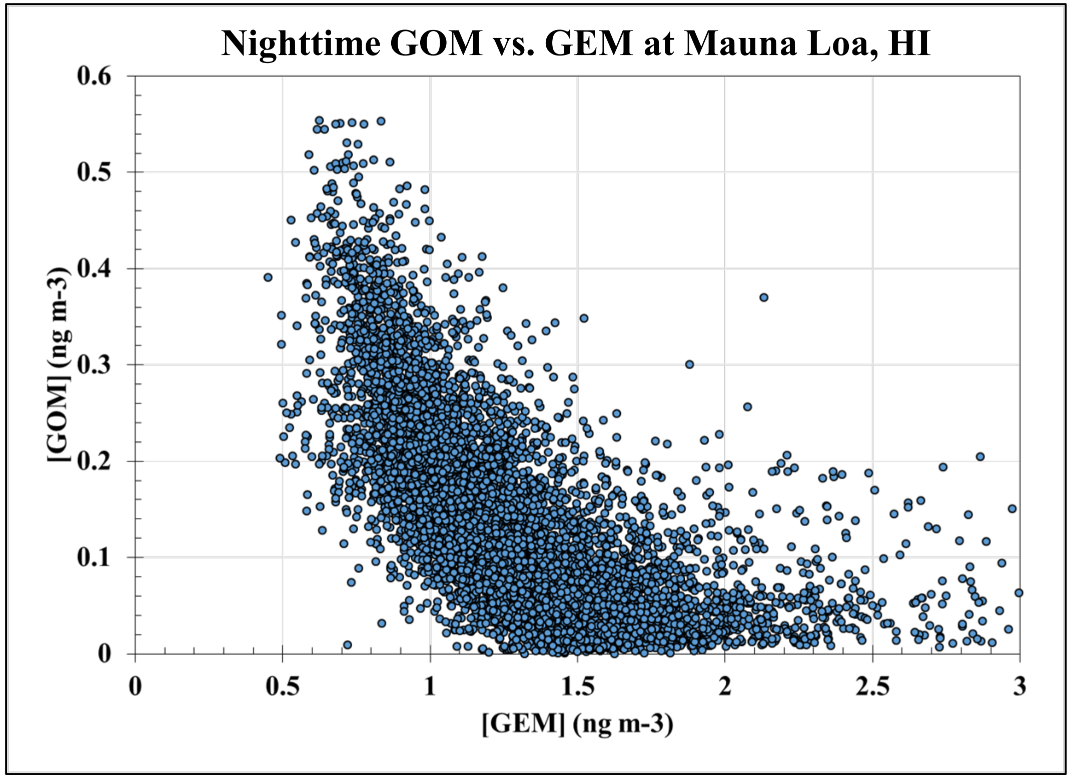


Atmospheric Transformations



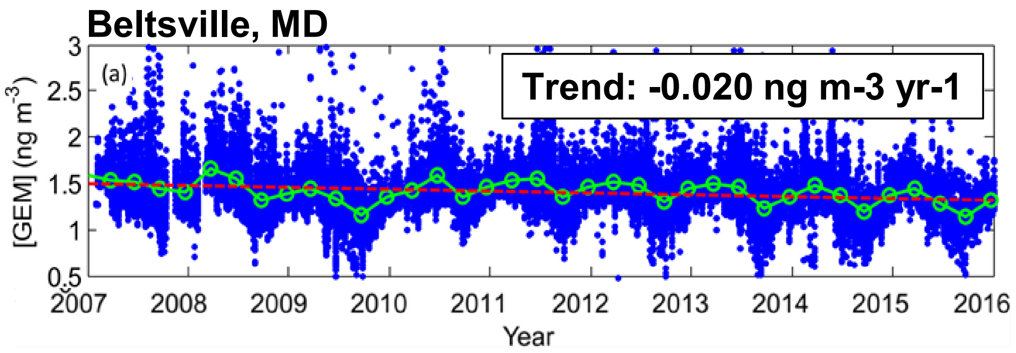


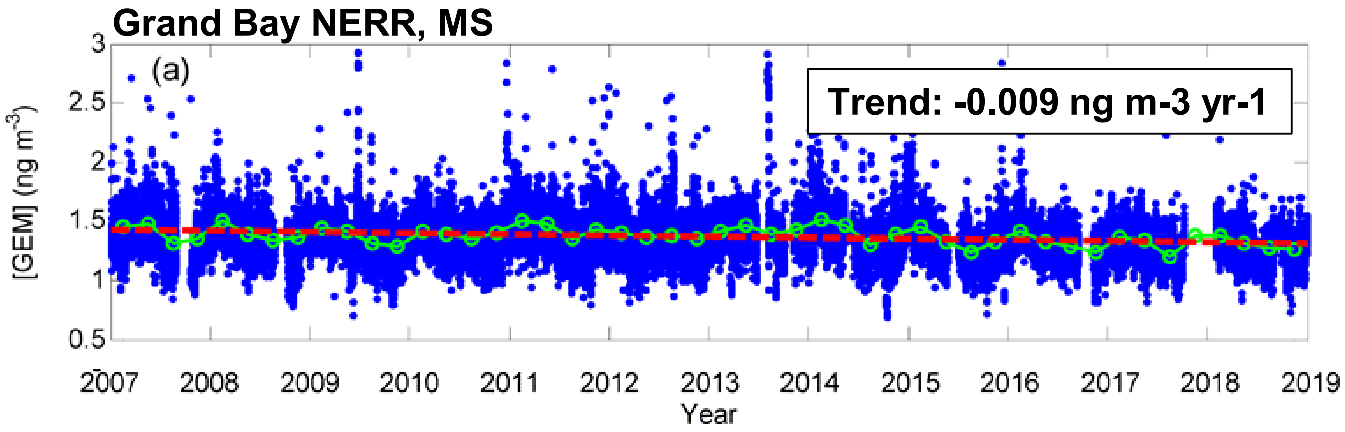
Summer maxima of GOM at MLO correspond to minima in CO (CO’s seasonality determined by seasonal variations in ·OH as a sink), suggesting a *photochemical* origin of GOM in the remote free troposphere.

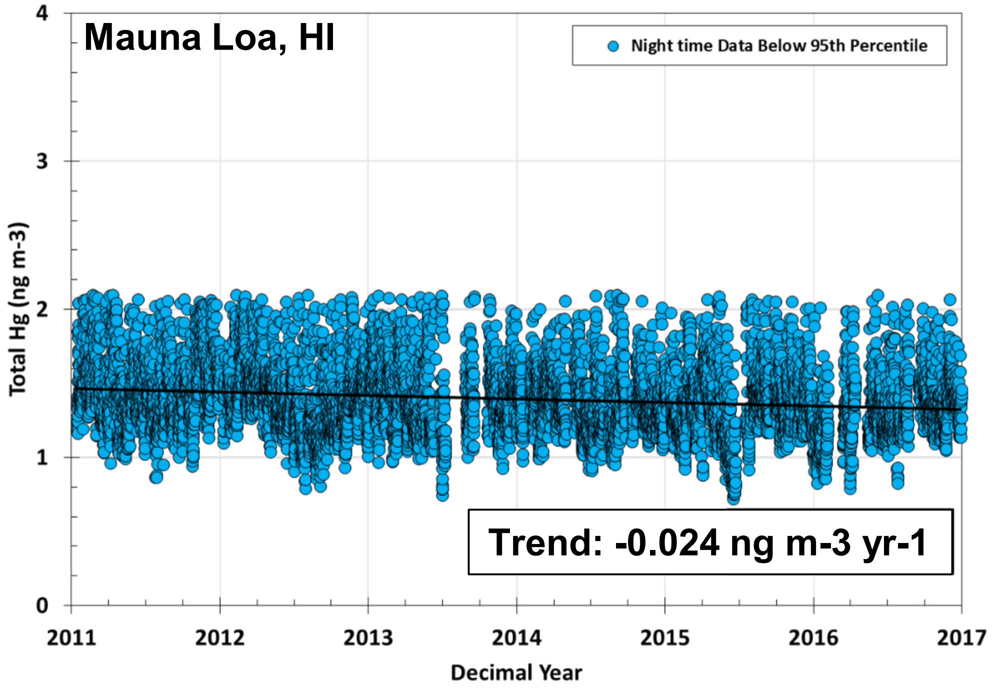


Anticorrelation of GEM and GOM indicative of direct oxidation of elemental mercury to GOM

Trend Detection

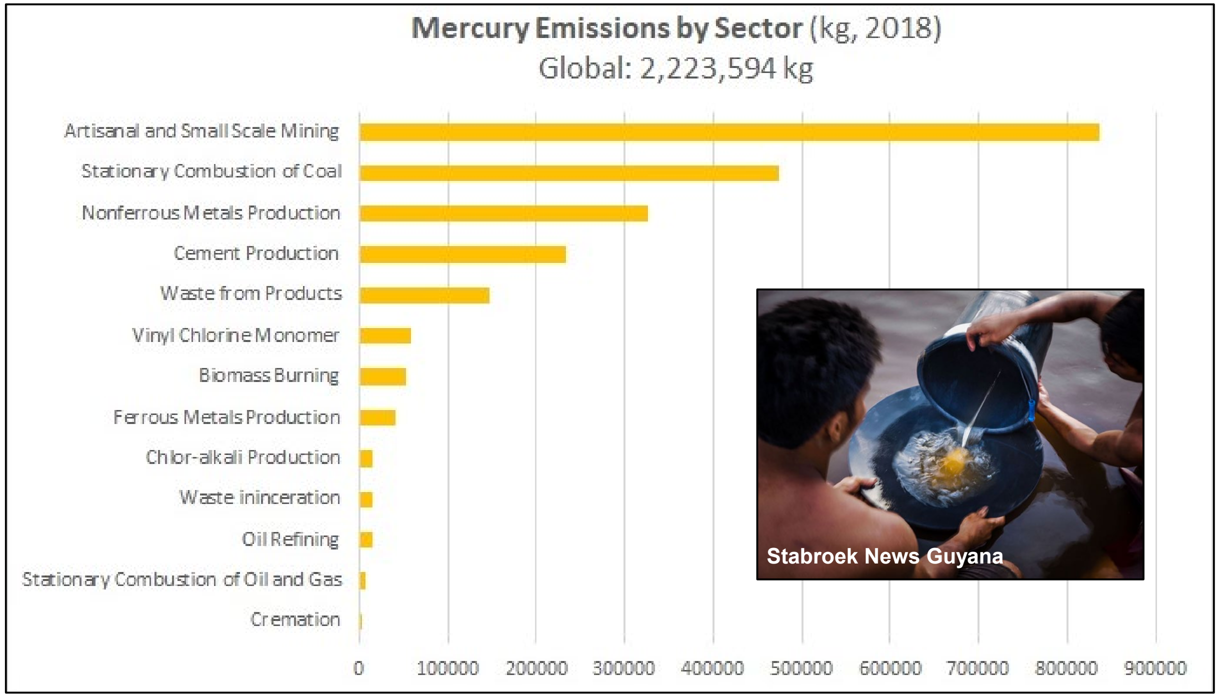




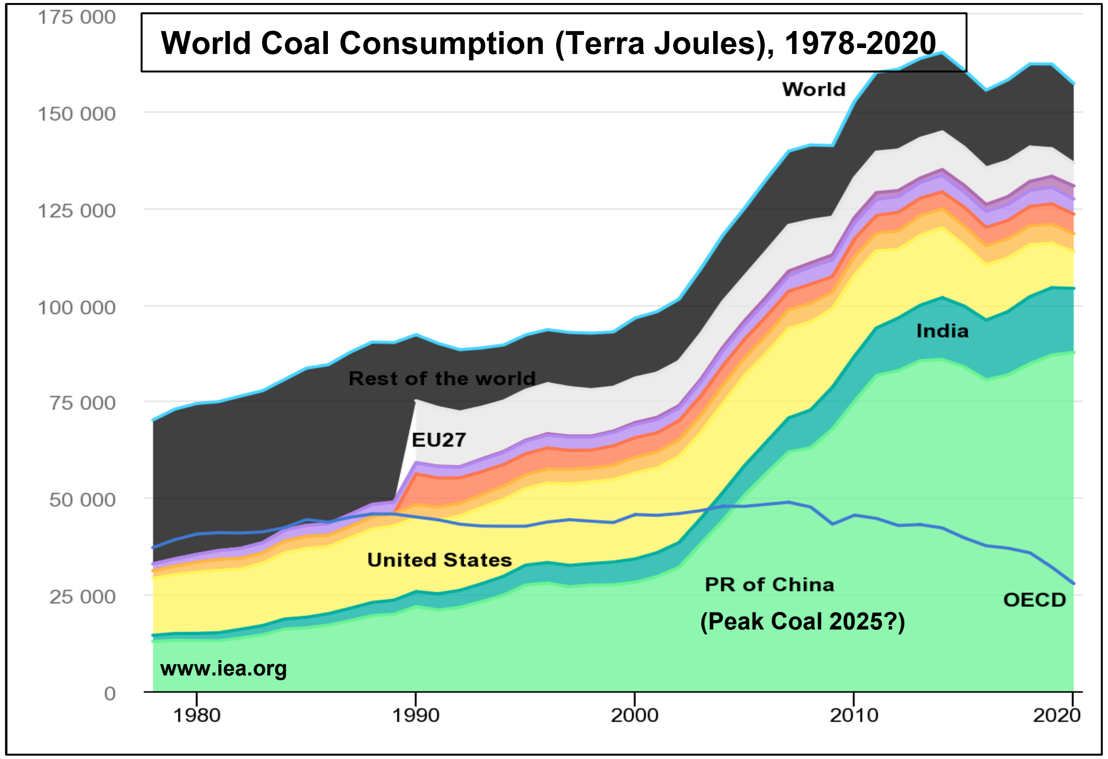


Atmospheric mercury levels have decreased throughout the U.S. in recent years in response to regulatory reductions of mercury emissions from a variety of anthropogenic sources.

Trend Detection

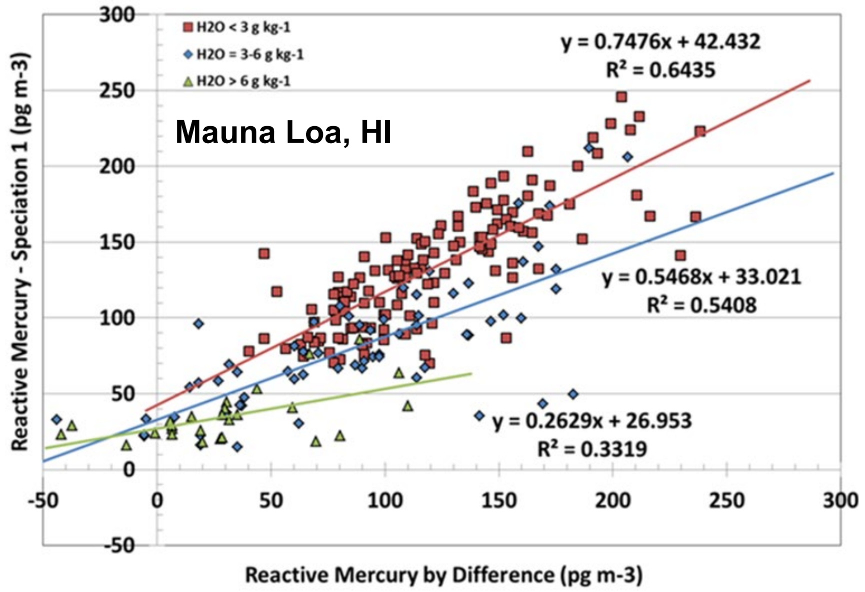


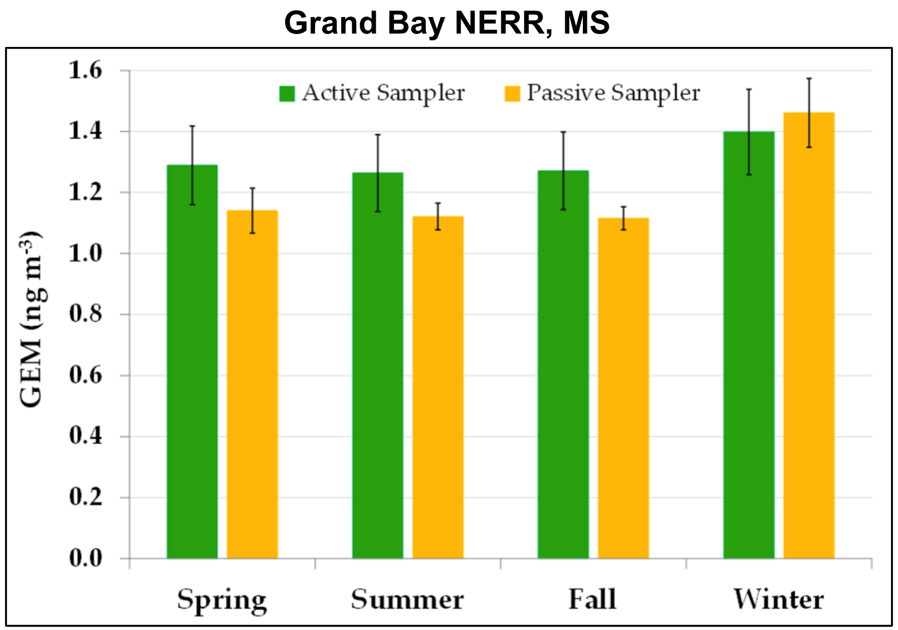
https://www.epa.gov/international-cooperation/mercury-emissions-global-context



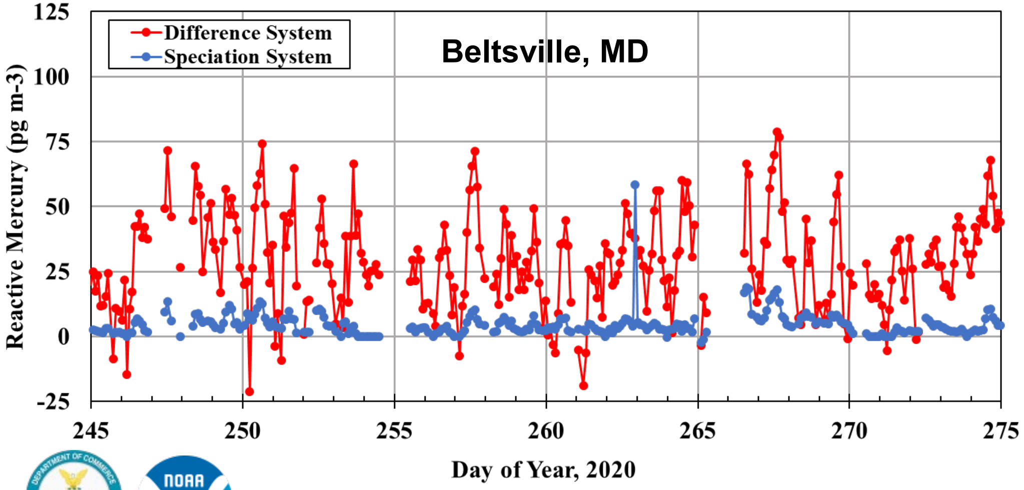
However, continued/increasing coal combustion (China, developing nations), the rise of Artisanal and Small -scale Gold Mining (ASGM), and the effects of climate change may stall or reverse this trend. Long -term monitoring is critical to quantify atmospheric trends and is required by Article 22 of the Minimata Convention on Mercury, a global treaty to protect human health and the environment.

Method Development and Intercomparison





Jeon et al., 2020



Fixed, long-term monitoring sites provide crucial infrastructure for new method development and deployment; method intercomparisons; and addition of ancillary supporting measurements .

Quality and Performance

Awards

- Department of Commerce Bronze medal award, 2019. "For sustained excellence in measurements and modeling leading to improved understanding of the emissions, transport, and fate of atmospheric mercury."

Publications

B. Jeon, J.V. Cizdziel, J.S. Brewer, W.T. Luke, M.D. Cohen, X. Ren, and P. Kelley, Gaseous Elemental Mercury Concentrations along the Northern Gulf of Mexico Using Passive Air Sampling, with a Comparison to Active Sampling. *Atmosphere* 2020, 11(10), 1034; https://doi.org/10.3390/atmos11101034

A. Luippold, M.S. Gustin, S.M. Dunham-Cheatham, M. Castro, W. Luke, S. Lyman, and L. Zhang, Use of Multiple Lines of Evidence to Understand Reactive Mercury Concentrations and Chemistry in Hawai'i, Nevada, Maryland, and Utah, USA. *Environ. Sci. Technol.* 2020, 54, 13, 7922–7931. https://doi.org/10.1021/acs.est.0c02283

X. Ren, W.T. Luke, P. Kelley, M.D. Cohen, M.L.Olson, J. Walker, R. Cole, M. Archer, R.Artz, and A.F. Stein, Long-Term Observations of Atmospheric Speciated Mercury at a Coastal Site in the Northern Gulf of Mexico during 2007–2018. *Atmosphere* 2020, 11(3), 268; https://doi.org/10.3390/atmos11030268

D.S. McLagan, C.P.J. Mitchell, A. Steffen, H. Hung, C. Shin, G.W. Stupple, M.L. Olson, W.T. Luke, P. Kelley, D. Howard, G.C. Edwards, P.F. Nelson, H. Xiao, G.-R. Sheu, A. Dreyer, H. Huang, B.A. Hussain, Y.D. Ling, I.Tavshunsky, and F. Wania, Global Evaluation and Calibration of a Passive Air Sampler for Gaseous Mercury. *Atmos. Chem. Phys*, 18, 5905–5919, 2018. https://doi.org/10.5194/acp-18-5905-2018

Quality and Performance (Continued)

Publications (Continued)

J. Bieser, F. Slemr, J. Ambrose, C. Brenninkmeijer , S. Brooks, A. Dastoor, F. DeSimone, R.Ebinghaus, C. Gencarelli, B. Geyer, L.E. Gratz, I.M. Hedgecock, D. Jaffe, P. Kelley, C.-J. Lin, V. Matthias, A. Ryjkov, O. Travnikov, A. Weigelt, W. Luke,, X. Ren, A. Zahn, X. Yang, Y. Zhu, N. Pirrone, N.E. Selin, and S. Song, Multi-model Study of Mercury Dispersion in the Atmosphere: Vertical and Interhemispheric Distribution of Mercury Species. *Atmos. Chem. Phys.,*6925–6955, 2017. https://doi.org/10.5194/acp -17-6925-2017

C. Zhou C, M.D Cohen, B.A. Crimmin, H. Zhou, T.A. Johnson, P.K. Hopke, and T.M. Holsen, Mercury Temporal Trends in Top Predator Fish of the Laurentian Great Lakes from 2004 to 2015: Are Concentrations Still Decreasing? *Environmental Science & Technology*51: 7386-7394. 2016 DOI: 10.1021/acs.est.7b00982.

H. Zhou, C. Zhou, M.M Lynam, J.T Dvonch, J.A Barres, P.K. Hopke, M.D Cohen, and T.M. Holsen, Atmospheric Mercury Temporal Trends in the Northeastern United States from 1992 to 2014: Are Measured Concentrations Responding to Decreasing Regional Emissions? *Environmental Science & Technology Letters*4: 91-97. 2017 DOI: 10.1021/acs.estlett.6b00452. (Featured on Cover of March 2017 Issue)

M. Cohen, R. Artz, R. Draxler, P. Miller, L Poissant, D. Niemi, D. Ratte, M. Deslauriers, R. Duval, R.Laurin, J. Slotnock, T. Nettesheim, and J. McDonald, Modeling the Global Atmospheric Transport and Deposition of Mercury to the Great Lakes. *Elementa: Science of the Anthropocene* 4: 000118. 2016 DOI: 10.12952/journal.elementa.000118

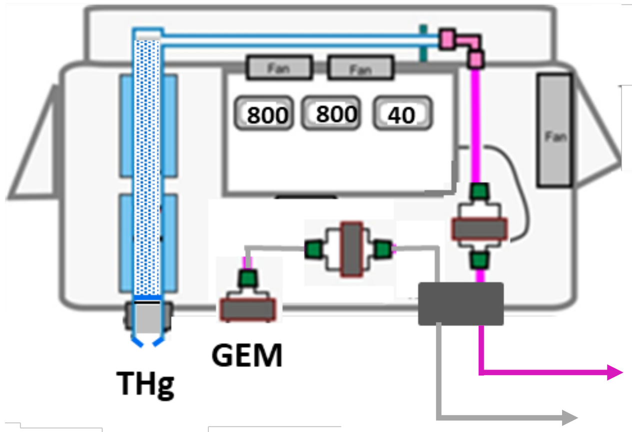
X. Ren, W.T. Luke, P. Kelley, M.D. Cohen, R.Artz, M.L. Olson, D. Schmeltz, M. Puchalski, D.L. Goldberg, A. Ring, G.M.Mazzuca, K.A. Cummings, L. Wojdan, S. Preaux, and J.W. Stehr,. Atmospheric mercury measurements at a suburban site in the Mid -Atlantic United States: Inter-annual, seasonal and diurnal variations and source -receptor relationships, *Atmos. Env.*, 146, 141-152, 2016. https ://doi.org/10.1016/j.atmosenv.2016.08.028

Quality and Performance (Continued)

- NOAA/ARL is a founding member of AMNet and operates 3 flagship sites generating high-quality data in the 13-site network (11 in the U.S).
- Provides technical guidance for development/implementation of the Asia-Pacific Mercury Monitoring Network (APMMN), a USEPA initiative to enhance monitoring efforts in Southeast Asia
- Members of the US Government Mercury Interagency Group (MIG) to inform US policy on the Minimata Convention on Mercury
- Collaborates with numerous NOAA (OAR/GML, NOS/NCCOS), national (e.g., EPA, USGS, USDA) and international partners (e.g., National Central University, Taiwan, APMMN, etc.)
- Actively engaged in method development for: improved accuracy; operational robustness; reduction of sample bias & artifacts
- Co-chaired a workshop at the 2017 International Conference on Mercury as a Global Pollutant to address measurement uncertainties in monitoring data, best practices for measurements
- Serves in a leadership role of the National Atmospheric Deposition Program (NADP)

Future plans

ARL has developed a simple, robust technique for the measurement of the sum of GOM and PBM to address measurement biases in conventional measurement methods, and will continue to test and refine the method.



- Modified Tekran® 1135 Particulate Module
- Total Mercury (THg) determined by pyrolysis (800 °C)
- GEM determined using Cation Exchange Membrane (CEM) to capture GOM and PBM
- Reactive Mercury by difference = THg-GEM = GOM + PBM

Thank you!

We will deploy the method at our Beltsville AMNet site, which will serve as an NADP test bed to compare multiple measurement techniques to new, low-cost methods which will be key to monitor mercury globally to evaluate the effectiveness of the Minimata Convention on Mercury.

With recent staff changes at NADP, ARL will assume a leadership role in training site operators and independent auditors in AMNet .

Continue with data analysis and publication