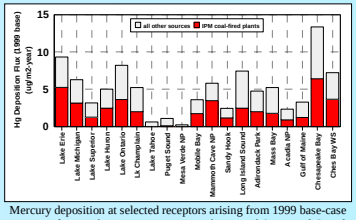
Atmospheric Mercury in the Chesapeake Bay Region: A Measurement and Modeling Study

Margaret Kerchner[1], Richard Artz[1], Steve Brooks[1], Bob Brunette[2], Mark Cohen[1], Paul Kelley[1], Winston Luke[1], Mike Newell[3], Eric Prestbo[2], Joseph Scudlark[4], Gerard van der Jagt[2], Robert Wood[5]

1. NOAA Air Resources Laboratory; 2. Frontier GeoSciences; 3. University of Maryland Wye Research and Education Center; 4. University of Delaware; 5. NOAA Cooperative Oxford Laboratory

Motivation

- Mercury is being increasingly recognized as a significant public health threat.
- Fish consumption appears to be the most important route of exposure for humans and wildlife.
- Modeling studies have suggested that the Chesapeake Bay region is subject to relatively high mercury deposition, owing to the prevalence of large mercury sources in the region.
- While there is known concern for mercury contamination of fish in freshwater impoundments in the Bay's Watershed, less is known about the mercury-to-methylmercury conversion processes in the estuary and its potential significance.
- It is believed that estuaries (as well as coastal wetlands and salt marshes) can be significant producers of methylmercury as conditions in these locations favor anaerobic bacteria that facilitate methylation.
- Atmospheric deposition is thought to be a significant loading pathway of mercury to the Chesapeake Bay.
- There are few atmospheric measurement data in the Chesapeake Region which can be used for model evaluation and improvement.
- The overall goal of this study is to further our understanding of the amount, spatial and temporal variations, and sources of atmospheric deposition of mercury to the Bay.



Mercury deposition at selected receptors arising from 1999 base-case emissions from anthropogenic sources in the United States and Canada (IPM coal fired plants are large coal-fired plants in the U.S. only).

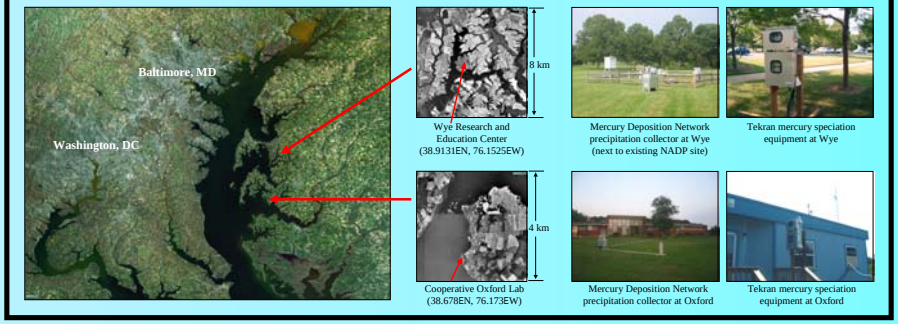
Experimental Details

Parameter	Oxford	Wye
Event-based precipitation samples analyzed for Hg	T	T
Speciated Hg concentrations in ambient air (RGM, Hg(p), Hg^0)	T	T
Continuous Ambient Concentrations of Ozone	T	T
Ambient Concentrations of Sulfur Dioxide	T (Continuous)	T (Weekly via AIRMoN)
Continuous Ambient Concentrations of Carbon Monoxide	T	
Meteorology	T	T (via NADP/NTN site)
Major ions in precipitation		T (via NADP/NTN site)

Continuous measurements of the atmospheric concentrations of Reactive Gaseous Mercury (RGM), Fine Particulate Mercury (FPM) and Gaseous Elemental Mercury (GEM) were made using Tekran automated mercury speciation units from June 7-August 12, 2004 at two coastal sites on the Eastern Shore of the Chesapeake Bay (Cooperative Oxford Laboratory and Wye Research and Education Center). Event-based precipitation samples were collected using standard Mercury Deposition Network (MDN) samplers, and analyzed for total mercury by the Hg Analytical Laboratory at Frontier GeoSciences (Seattle, WA).

At the Cooperative Oxford Laboratory, continuous measurements were made of SO_2, O_3, and CO, using modified commercial instrumentation (Thermo Environmental Instruments, Inc.). The SO_2 and CO instruments were carefully calibrated with certified gas-phase standards at 17h intervals, and frequently zeroed chemically to monitor baseline drift (for maximum accuracy at low pollutant concentrations). The ozone detector was calibrated with a secondary transfer standard before and after the measurement period. Continuous meteorological data were also collected.

The Wye site is an NADP/NTN and AIRMoN-dry site with associated measurements of SO_2,O_3, major ions in precipitation, and meteorology.



Wye Research and Education Center (38.9131EN, 76.1525EW)

Mercury Deposition Network precipitation collector at Wye (next to existing NADP site)

Tekran mercury speciation equipment at Wye

Cooperative Oxford Lab (38.678EN, 76.173EW)

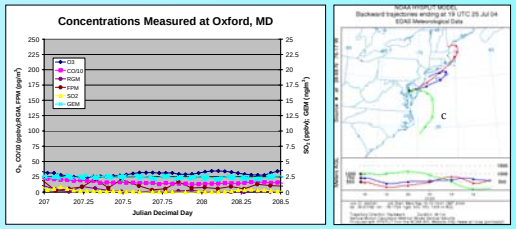
Mercury Deposition Network precipitation collector at Oxford

Tekran mercury speciation equipment at Oxford

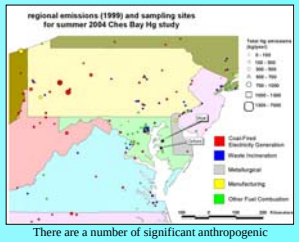
Initial Summary and Next Steps

- Previous modeling studies have suggested that there are elevated atmospheric mercury concentrations and deposition in the Chesapeake Bay region. Coal-fired power plants and incinerators appear to the most significant contributors.
- Data analysis is still underway, but measurements at two sites on the Eastern Shore (Oxford and Wye) conducted during summer 2004 appear to confirm these earlier studies, showing relatively high levels of RGM in the region. Of all the forms of atmospheric mercury, RGM is of the greatest concern as it (a) deposits much more readily than other mercury forms and (b) may be more bioavailable once deposited.
- Initial examination of the data suggests that both transport from sources and photochemistry may play important roles in influencing observed concentrations of different atmospheric mercury forms.
- Next steps include: (a) assembly of the full data set from the summer 2004 measurements, including meteorology, trace gases (SO_2, CO, O_3), and event-based wet deposition of mercury; (b) examination of the data to discern patterns and to generate hypotheses; (c) modeling the atmospheric fate and transport of mercury during the measurement period using the NOAA HYSPLIT-Hg model; (d) evaluating the model by comparison against the measurement data; (e) detailed consideration of the measurement and modeling results to further our understanding of the atmospheric dynamics of mercury in the Chesapeake Bay region.

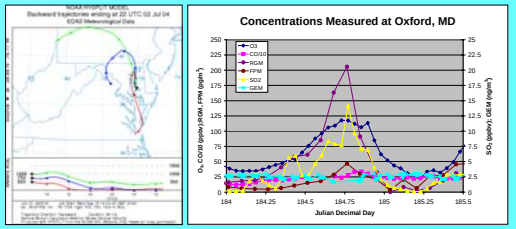
Preliminary Results



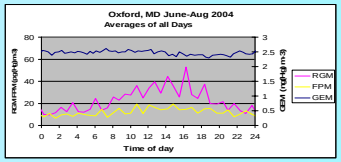
Time series of gas and aerosol phase trace constituents measured at Oxford, MD on July 25-26, 2004. Measured concentrations of all species were relatively low and invariant, implying a lack of influence from local sources during this particular period. Back trajectories calculated with the NOAA/ARL HYSPLIT model (*http://www.arl.noaa.gov/ready/hysplit4.html*), driven by 40 km EDAS meteorological data, indicate that the air masses arriving at the Oxford site during this period did not traverse nearby anthropogenic sources.

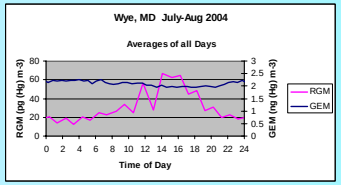


There are a number of significant anthropogenic sources in the Chesapeake Bay region. The above map shows these regional sources, based on the EPA's 1999 National Emissions Inventory (NEI).



Time series of gas and aerosol phase trace constituents measured at Oxford, MD on July 2-3, 2004. Elevated concentrations of primary and secondary pollutants at ~6 PM local time on July 2 suggest that the site was impacted by local/regional sources. Modeled back trajectories for this event suggest that local sources in the Baltimore metropolitan area may have been responsible for the observed elevated concentrations. As can be seen in the illustration below, there are a number of large mercury sources along the estimated air mass trajectory.

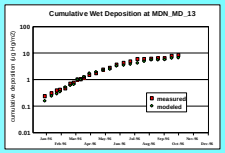


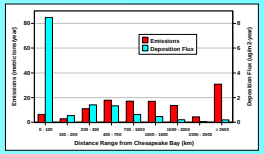


- The diurnal profiles of different mercury forms measured at Oxford and Wye are shown to the left, averaged over the entire measurement period.
- At Oxford and Wye, the maximum concentrations of RGM appear to occur in the mid-late afternoon.
- At Oxford, daytime concentrations of FPM appear to be somewhat higher than concentrations at night*.
- There is no discernable average diurnal trend for GEM at Oxford, but at Wye, there may be slightly lower average concentrations during the mid-late afternoon.
- The above observations suggest that photochemistry may be affecting the transformations among different mercury forms in the atmosphere.
- Ancillary trace gas data (CO, SO_2, O_3) and modeling will be utilized to better understand the roles that transport and dispersion (from sources), atmospheric deposition, and atmospheric chemistry play in influencing ambient concentrations of different mercury forms.

*There were difficulties with the FPM-measuring equipment at Wye. It has not yet been determined if the FPM data at Wye are of acceptable quality, and so they are not presented here.

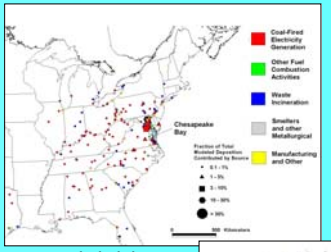
Initial Modeling Results





Emissions and direct deposition contributions from different distance ranges away from the Chesapeake Bay, using 1996 meteorology and the 1999 U.S. EPA National Emissions Inventory as inputs to the HYSPLIT-Hg model. More than half of the deposition appears to arise from sources within 100 km.

A preliminary model evaluation exercise has shown that the HYSPLIT-Hg model provided results consistent with the previous wet deposition measurements made at Wye.



Largest regional individual sources contributing to mercury deposition directly to the Chesapeake Bay using 1996 meteorology and the 1999 U.S. EPA National Emissions Inventory as inputs to the HYSPLIT-Hg model. Coal-fired power plants and incinerators appear to the most significant contributors