Using CMAQ in Managing Mercury Deposition to Sensitive Ecosystems

Russell Bullock and Jesse Bash

Environmental Issue

Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment. Although its potential for toxicity in highly contaminated areas is well documented, research has shown that mercury can be a threat to the health of people and wildlife in many environments that are not obviously polluted. The primary human health effects of mercury exposure involve neurological impairment, but cardiovascular effects have also been documented. The risk is determined by the degree of exposure, the chemical form of mercury present, and the geochemical and ecological factors that influence how mercury moves and changes form in the environment.

Inhalation of mercury at the concentrations normally found in outdoor air (ppqv) is not a concern. Human exposure to mercury is primarily from consumption of contaminated fish. Mercury cycles naturally through atmospheric, terrestrial and aquatic systems. Research has shown the global mercury flux through the air pathway is now approximately three times the pre-industrial level due to anthropogenic releases to the environment. With the widespread cessation of the disposal of mercury to water since the 1960's, atmospheric deposition is now the primary source of mercury in most cases of serious risk. Many aquatic ecosystems can take mercury deposited from the atmosphere and convert it to chemical forms that accumulate to hazardous concentrations in fish (ppmw).

Research Objectives

Atmospheric mercury is known to exist in various physical and chemical forms which have widely differing behaviors. Deployable ambient air sampling technology does not yet provide speciation in terms of individual mercury compounds for gases or aerosols. We also rely on industrial emission inventories for mercury that do not provide this type of speciation. As more precise information on ambient concentrations and sources of mercury become available, along with better information about chemical kinetics in air and in cloud water, we strive to keep CMAQ up to date and perform model evaluations similar to those done for other pollutants. Our specific objectives include the following:

• Develop atmospheric mercury simulation capabilities in CMAQ that can be used to attribute the sources of mercury depositing to sensitive ecosystems

• Continue to address mercury using an expandable multi-pollutant modeling approach with feedback effects on gas/aerosol chemistry

• Develop multi-media modeling capabilities to address the uptake and release of mercury by water and vegetation

• Characterize episodic events such as forest fires and mechanical disturbances that cause rapid releases of mercury from soils

• Continue to guide field and laboratory research by highlighting the scientific uncertainties most responsible for variations in model simulations

Modeling Approach

Current CMAQ Mercury Chemistry Reactions

The table below shows the reactions and kinetic rate constants currently used to simulate mercury in CMAQ. For some of these reactions, a variety of rate constants have been published in the scientific literature. It has also been suggested that some additional substances may react with atmospheric mercury (e.g., bromine). Further research and development will likely bring changes to this reaction table.

Reaction	k or K	Reference
Gaseous-phase reaction of Hg		
$Hg^0_{(g)} + O_{3(g)} - 50\%$ RGM, 50% PHg	$2.11 \times 10^{-18} e^{-1256.5/T}$ cm³ molec⁻¹ s⁻¹	Hall (1995)
$Hg^0_{(g)} + Cl_{2(g)} - RGM$	2.6×10^{-18} cm³ molec⁻¹ s⁻¹	Ariya et al. (2002)
$Hg^0_{(g)} + H_2O_{2(g)} - RGM$	8.5×10^{-19} cm³ molec⁻¹ s⁻¹	Tokos et al. (1998)
$Hg^0_{(g)} + OH_{(g)} - 50\%$ RGM, 50% PHg	7.7×10^{-14} cm³ molec⁻¹ s⁻¹	Pal and Ariya (2004)
Aqueous-phase reactions of Hg		
$Hg^0_{(aq)} + O_{3(aq)} - Hg^{2+}_{(aq)} + products$	$4.7 \times 10^7 M^{-1} s^{-1}$	Munthe (1992)
$HgSO_{3(aq)} - Hg^0_{(aq)} + products$	$T \cdot e^{((31.971 \times T) - 12595)/T} s^{-1}$	Van Loon et al. (2000)
$Hg(OH)_{2(aq)} + h\nu - Hg^0_{(aq)} + products$	$6.0 \times 10^{-7} s^{-1}$ (max) †	Xiao et al. (1994)
$Hg^0_{(aq)} + OH_{(aq)} - Hg^{2+}_{(aq)} + products$	$2.0 \times 10^9 M^{-1} s^{-1}$	Lin and Pehkonen (1997)
$Hg^{2+}_{(aq)} + HO_{2(aq)} - Hg^0_{(aq)} + products$	$1.1 \times 10^4 M^{-1} s^{-1}$	Pehkonen and Lin (1998)
$Hg^{2+}_{(aq)} + HOCl_{(aq)} - Hg^{2+}_{(aq)} + products$	$2.09 \times 10^6 M^{-1} s^{-1}$	Lin and Pehkonen (1998)
$Hg^{2+}_{(aq)} + OCl^-_{(aq)} - Hg^{2+}_{(aq)} + products$	$1.99 \times 10^6 M^{-1} s^{-1}$	Lin and Pehkonen (1998)

† Rate constant is scaled to the cosine of solar zenith angle

Bi-Directional Mercury Exchange

• Mercury emissions from natural sources are parameterized as reduction of existing and recently deposited Hg^{2+} and subsequent evasion of Hg^0.

• Air surface flux is dependent on the atmospheric and near surface concentration gradient.

• Air-surface water fluxes are modeled using a two film resistance model and a surface water photo-redox scheme.

• Air-terrestrial fluxes modeled using air-vegetation partitioning parameters and air-soil partitioning and reduction processes

| Air-terrestrial exchange	Variables	
$F_{Hg^0} = \frac{1}{r_a + r_b}\left([Hg^0]_{eq} - [Hg^0]_{atm}\right)$	F_{Hg^0}	Hg⁰ air surface exchange
	r_a	Atmospheric resistance
	r_b	Boundary layer resistance
	K_{OA}	Overall air-sea exchange coefficient
Air-water exchange	H	Henry's constant
$F_{Hg^0} = K_{OA}\left([Hg^0]_{eq}H - [Hg^0]_{atm}\right)$	$[Hg^0]_{eq}$	Near surface Hg⁰ concentration
	$[Hg^0]_{eq}$	Surface water Hg⁰ concentration
	$[Hg^0]_{atm}$	Atmospheric Hg⁰ concentration

Linking Global to Regional

• Mercury is known as a "global pollutant", but emissions of oxidized forms have been shown to have regional effects.

• Hg^0 gas has an atmospheric lifetime of months, while Hg^{+2} gas has an atmospheric lifetime of hours or days, thus regional modeling is necessary.

• Separate Global/Hemispheric models are currently used to define boundary conditions, but recent research (NAMMIS) has shown downscaling problems.

• Future development of hemispheric CMAQ will allow consistent representation of Hg on all spatial scales.

Results and Discussion

CMAQ Mercury Model Testing

European Monitoring and Evaluation Program (EMEP) model intercomparison (2000-2005)
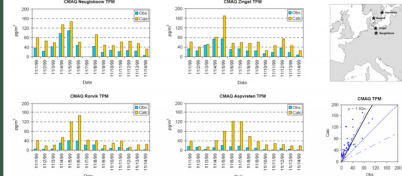

Comparison of CMAQ air concentrations to observations showed relatively strong correlations as compared to other models, but a high bias for total particulate mercury (TPM) was found. As a result, the assumed product of reaction with ozone, hydrogen peroxide and hydroxyl radical was changed from 100% TPM to 50% reactive gaseous mercury (RGM) and 50% TPM.

North American Mercury Model Intercomparison Study (NAMMIS) (2004-2008)
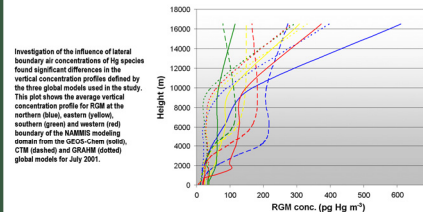
Investigation of the influence of lateral boundary air concentrations of Hg species found significant differences in the vertical concentration profiles defined by the three global models used in the study. This plot shows the average vertical concentration profile for RGM at the northern (blue), eastern (yellow), southern (green) and western (red) boundary of the NAMMIS modeling domain from the GEOS-Chem (solid), CTM (dashed) and GRAHM (dotted) global models for July 2001.
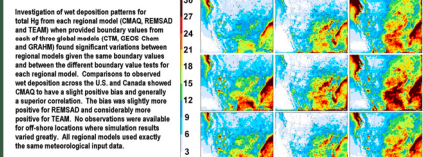
Investigation of wet deposition patterns for total Hg from each regional model (CMAQ, REMSAD and TEAM) when provided boundary values from each of three global models (CTM, GEOS-Chem and GRAHM) found significant variations between regional models given the same boundary values and between the different boundary value tests for each regional model. Comparisons to observed wet deposition across the U.S. and Canada showed CMAQ to have a slight positive bias and generally a superior correlation. This was slightly more positive for REMSAD and considerably more positive for TEAM. No observations were available for off-shore locations where simulation results varied greatly. All regional models used exactly the same meteorological input data.

Clean Air Mercury Rule Analysis

CAMR Zero Hg Emission - Percent Reduction in Hg Deposition
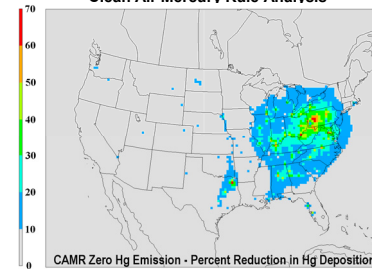
Conclusions

• Industrial emissions of atmospheric mercury can influence deposition on local and regional scales due to the rapid deposition of their oxidized component.

• Long range transport of oxidized mercury can occur on an episodic basis.

• The fraction of mercury deposited to the U.S. from domestic industrial sources varies greatly (<1 – 70%) depending on proximity to oxidized Hg emission sources.

• The majority of the U.S. gets most of its mercury deposition from the atmospheric oxidation of Hg^0 from non-U.S. sources.

• Much of the Hg^0 that is oxidizing and depositing is emitted from terrestrial and aquatic sources.

• Because of the cycling nature of mercury in the biosphere, most of the Hg^0 emitted through terrestrial and aquatic processes is anthropogenic in origin.

Future Directions

• Further development of bi-directional mercury exchange

• Hemispheric scale CMAQ with grid nesting

• Keep mercury reactions up to date with evolving science

• Support EPA Office of Water modeling assessments

Impact

• Inform federal policymakers of the importance of domestic emissions of mercury on deposition to sensitive ecosystems (e.g., CAMR analysis)

• Inform federal/state/local policymakers of the industrial sources responsible for deposition to specific ecosystems

• Provide to the research community indications of critical knowledge gaps (e.g., emissions, chemistry)

Contributors/Collaborators