P3.2

BIDIRECTIONAL MERCURY EXCHANGE OVER SURFACE WATERS SIMULATED BY A REGIONAL AIR POLLUTION MODEL

Jesse O. Bash*, Ellen J. Cooter
NOAA/ARL/ASMD
(In collaboration with the U.S. Environmental Protection Agency, National Exposure Research Laboratory)
Research Triangle Park, North Carolina

1. INTRODUCTION

Natural emissions of gaseous elemental mercury (GEM), including the evasion of previously deposited mercury and mercury present in the surface media, are estimated to be as large as or larger than the total anthropogenic mercury emissions to the atmosphere with a substantial fraction of natural emissions originating from surface waters, Lindberg *et al.* (2007). Measurements of dissolved gaseous elemental mercury concentrations in surface waters are higher than predicted by Henry's constant and the atmospheric concentrations due to the photo-reduction of aqueous reactive mercury, Hg^{2+}_{aq} , (Lalonde *et al.* 2001; Whalin and Mason, 2006). Air quality models currently parameterize the atmosphere-surface water exchange of mercury by eliminating the atmospheric deposition and parameterizing the evasion as a function of meteorological parameters (Lin *et al. 2004*), using a resistance model with predefined surface water dissolved gaseous elemental mercury concentration, Hg^{0}_{aq} , to estimate evasion (Xu *et al.* 1999, Bash *et al.* 2004; Gbor *et al.* 2006), or as a fraction of the deposition from a previous model run (Seigneur *et al.* 2004). Recent flux chamber measurements indicate a seasonal pattern in the atmospheric – surface water exchange of mercury correlating with incoming solar radiation during the summer and with wind speed during the winter (Feng *et al.* 2004).

A parameterization of the atmosphere-surface water flux using a transfer velocity and a dynamic concentration gradient across the atmosphere-surface water interface would be more physically sound than current uncoupled treatments of emissions and deposition (Wesely and Hicks, 2000). A mass conservative physically descriptive multimedia bi-directional mercury exchange model, following the conceptual framework of Bash et al. (2007), was added to the U.S. Environmental Protection Agency's Community Multiscale Air Quality (CMAQ) modeling system (Byun and Schere, 2006). The wind driven atmosphere – surface water mercury fluxes are being parameterized using a two – film turbulent diffusion model and a surface water photo-reduction scheme to better capture the enrichment of surface water Hg^{0}_{aq} concentrations. Both of these processes require mercury concentrations in the surface waters and a dynamic surface media layer to simulate surface accumulation and depletion of mercury from deposition and evasion respectively.

2. METHODS

The atmosphere-surface water flux of mercury is parameterized using a two-film resistance model coupling atmospheric and surface water concentrations. Hg^{2+}_{aq} and Hg^{0}_{aq} concentrations in the surface waters are coupled via a photo-reduction and –oxidation scheme such that:

$$\frac{d\vec{C}}{dt}=\left[\frac{F_{AW}}{z_l}\right]+\left[\frac{F_{WD}}{z_l}\right]+\left[k_{rx}\right]\vec{C} \tag{1}$$

Where $\vec{C}$ is a vector containing the ambient and surface water concentrations, F_{AW} is the gaseous flux across the air-water interface, F_{WD} is the wet deposition flux, [k_{rx}] is a matrix of photo-reduction and oxidation rates, z_l is the depth of surface water layer.

The air water flux of GEM is driven by the disequilibrium between the gaseous and aqueous phases Hg^{0} concentrations. The enrichment of Hg^{0}_{aq} in surface waters is parameterized as arising from the photo-reduction of Hg^{2+}_{aq} .

2.1 *Air-Surface Water Transfer Velocity*

The gaseous flux across the air-water interface is parameterized following Schwarzenbach *et al.* (1993).

$$F_{AW}=K_{OL}\left(C_g-H\,C_{aq}\right) \tag{2}$$

Here, K_{OL} is the overall air-water transfer coefficient, C_{aq} and C_g are the concentrations in water and air respectively, and H is the dimensionless Henry's coefficient.

The overall air-water transfer velocity is parameterized following Schwarzenbach *et al.* (1993).

$$\frac{1}{K_{OL}}=\frac{1}{k_l}+\frac{1}{H\,k_{atm}} \tag{3}$$

---

* *Corresponding author address:* U.S. Environmental Protection Agency, National Exposure Research Laboratory, Atmospheric Modeling Division, 109 T.W. Alexander Drive MD-E243-04, RTP NC, 27711. bash.jesse@epa.gov and jesse.bash@noaa.gov

Here, k_l is the liquid mass transfer coefficient and k_{atm} is the atmospheric mass trasfer coefficient. k_{atm} is calculated following Byun and Dennis (1995) and k_l is calculated following Wanninkhof (1992).

2.2 *Surface Water Redox Reactions*

Measured Hg^{0}_{aq} concentrations in surface water are typically higher than would be predicted by Henry's constant and the ambient atmospheric GEM concentrations (Mason *et al.* 1998). The recently deposited mercury is parameterized using a photo-reduction of Hg^{2+}_{aq} and photo-oxidation of Hg^{0}_{aq} (Whalin *et al.* 2007; Whalin and Mason, 2006; Lalonde *et al.* 2001) as in, Equation 4.

$$\begin{aligned} Hg_{aq}^{2+} + hv &\xrightarrow{k_r} Hg_{aq}^{0} \\ Hg_{aq}^{0} + hv &\xrightarrow{k_o} Hg_{aq}^{2+} \end{aligned} \tag{4}$$

Here, k_r is the photo-reduction rate, and k_o is the photo-oxidation rate. Surface water redox rates have been taken from the literature and adjusted for incoming solar radiation following O'Driscoll *et al.* (2006) as in, Equation 5.

$$k(\lambda) = k_{ref} \frac{I(\lambda)}{I(\lambda)_{ref}} \tag{5}$$

Here, $k(\lambda)$ is the photo-reduction or oxidation rate as a function of incoming solar radiation, $I(\lambda)$, at the wavelength λ, k_{ref} is the reference rate reported in the literature and $I(\lambda)_{ref}$ is the radiation intensity of the measurement of k_{ref}.

2.3 *Model Parameters*

Four simulations were performed to explore CMAQ sensitivity to the inclusion of the photo-oxidation process in surface waters and to facilitate comparison of model results to literature estimates of surface water concentrations. The first simulation was a base case which used the NEIV3 Toxics inventory surface water emissions and assumed no photo-oxidation or reduction scheme. Following the general technique of Seigneur *et al.* (2004), surface water emissions of mercury in NEI V3 Toxics are estimated by increasing deposition fields from a previous model simulation that assumes no natural emissions by 50%. Each of the remaining three simulations considered here assumed a different photo-oxidation or reduction rate from the literature and NEI V3 Toxics water body emissions were removed to avoid double counting.

CMAQ Hg was run from July 22nd through August 1st, 2001 using a 36 km grid cell domain covering the continental U.S., and portions of Canada and Mexico. The water surface was treated as a one meter deep slab with no horizontal transport. CMAQ Hg was driven using MM5, the Penn State/NCAR Mesoscale Model (Grell *et al.* 1995) Version 5 with the Pleim-Xiu land surface scheme (Pleim and Xiu, 1995). Boundary and initial conditions were provided from GEOS-CHEM Hg (Strode *et al.* 2007).

Table 1, redox parameters of CMAQ Hg air-surface water exchange model

Source	$k_{o,ref}$	$k_{r,ref}$	k_r/ k_o	$I(\lambda)_{ref}$
NEI V3 Toxics	-	-	-	-
Lalonde *et al.* 2001	$2.4\text{x}10^{-4}\ s^{-1}$	$1.6\text{x}10^{-4}\ s^{-1}$	1.5	0.4 w m^{-2} UVB
Whaling and Mason 2006	$7.0\text{x}10^{-4}\ s^{-1}$	$12.0\text{x}10^{-4}\ s^{-1}$	0.6	240 w m^{-2} Visible
Whalin *et al.* 2007	$7.2\text{x}10^{-4}\ s^{-1}$	$6.5\text{x}10^{-4}\ s^{-1}$	0.9	240 w m^{-2} Visible

3 RESULTS

3.1 *Domain – wide* Hg^{0} *emissions from surface waters*

All three CMAQ photo-oxidation and -reduction simulations predicted evasion of mercury from surface waters to be lower than the estimates in NEI V3 toxics. However, recent measurements of the ratio of isotopic GEM evasion to RGM deposition indicate that approximately 45% of RGM deposited to surface waters is later evaded, (Southworth *et al.* 2007). The CMAQ air-surface water exchange model agrees remarkably well with these measurements, (Table 2).

Table 2, model emissions and deposition to water bodies

Case	Hg^{0} emissions	Total Hg^{2+} deposition	Emissions /deposition
NEI V3 Toxics	276 kg/day	266 kg/day	103.8%
$k_r/ k_o= 1.5$	136 kg/day	265 kg/day	51.3%
$k_r/ k_o= 0.6$	100 kg/day	265 kg/day	37.7%
$k_r/ k_o= 0.9$	116 kg/day	265 kg/day	44.9%

All three photo-oxidation and -reduction simulations predicted enrichment of Hg^{0}_{aq} above what would be predicted using Henry's constant and ambient GEM concentrations reported by Mason *et al.* (1998), (Table 3). The redox parameterization recommended by Wahlin *et al.* (2007), $k_r/ k_o= 0.9$, matched the mean surface water concentrations observed by Mason *et al.* (1998) most closely, (Table 3), and so the remainder of the analysis will focus on these simulation results.

Table 3, Model surface water concentrations for the three redox cases and observations from Mason *et al. 1998*

Case	$Hg^{0}_{aq}+Hg^{2+}_{aq}$	$\frac{Hg^{0}_{aq}}{Hg^{0}_{aq}+Hg^{2+}_{aq}}$	Hg^{0}_{aq} enrichment
$k_r/ k_o= 1.5$	1.74 pM	58%	4.29
$k_r/ k_o= 0.6$	2.16 pM	36%	3.35
$k_r/ k_o= 0.9$	1.96 pM	46%	3.85
Observations	1.45±0.5 pM	45%	16.25-18.57

3.2 *Temporal patters of* Hg^{0} *emission and concentration fields*

NEI V3 toxics temporally allocates GEM emissions from surface waters by incoming solar radiation to capture the diel patterns in elemental mercury emissions, (Figure 1). CMAQ with bidirectional surface water exchange of mercury parameterizes the emissions of mercury as a function of previously deposited GEM and RGM stored in the surface water layer, wind speed, incoming solar radiation and the ambient GEM concentrations. In areas where there is ample RGM input via dry and wet deposition associated with contaminated air parcels, the emissions are dominated by the factors controlling the photo-reduction of Hg^{2+}_{aq}, incoming solar radiation, and transport of Hg^{0} across the air – water interface, ambient GEM concentrations and wind speed. In most areas of the modeling domain the evasion of Hg^{0} was limited by the wet and dry deposition inputs of mercury.

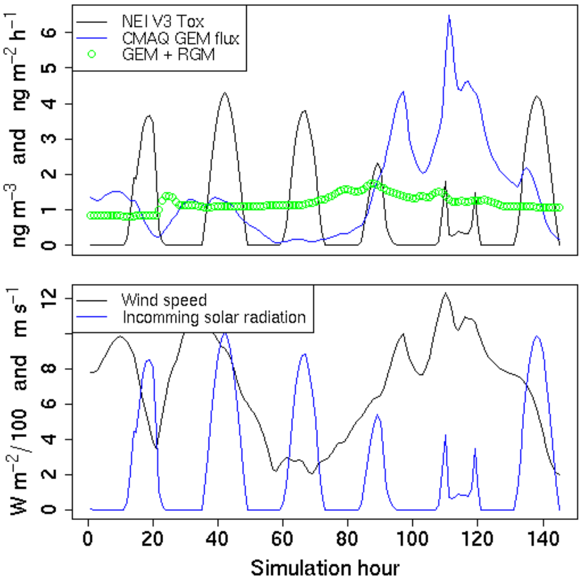

Figure 1: Example model GEM emissions, concentrations, wind speed and incoming solar radiation from July 26th through August 1st 2001 off the coast of New Jersey, USA

The incorporation of a surface water redox scheme coupled to mass transfer across the air-water interface results in a much more dynamic representation of the air – surface water flux of mercury. The current estimation method which allocates elemental mercury evasion from surface waters as a function of previous deposition simulations and incoming solar radiation results in high emissions on the western side of the model domain, (Figure 3).

3.3 *Spatial patterns in* Hg^{0} *emission and Hg concentration fields*

The median emission rate of GEM from surface waters was greatest in the Caribbean and off the Mid-Atlantic coast, Figure 2. The elevated emission rates in these areas are a response to previously deposited mercury from contaminated air parcels advected off the Eastern coast of North America. In contrast the largest surface water elemental mercury emissions in NEI V3 toxics were along the coast of the Pacific Northwest and California, Figure 3. While elevated concentrations are still noted off the Pacific Northwest coast, GEM concentrations are reduced by a median value of 25%, Figure 4. This reduction most likely reflects the influences of boundary conditions on estimate GEM evasion in NEI V3 Toxics.

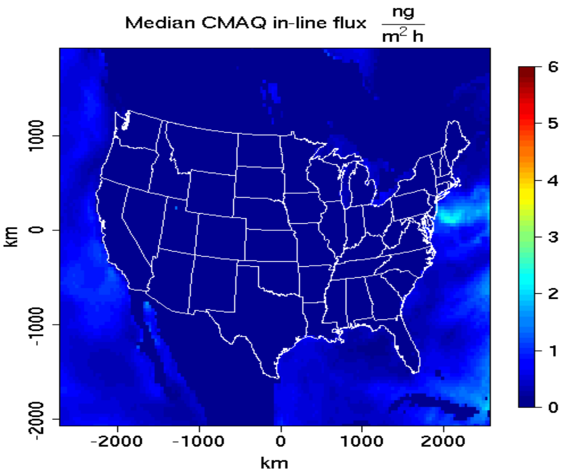

Figure 2: The median emissions rate of elemental mercury evasion from surface waters from July 29th through August 1st, 2001.

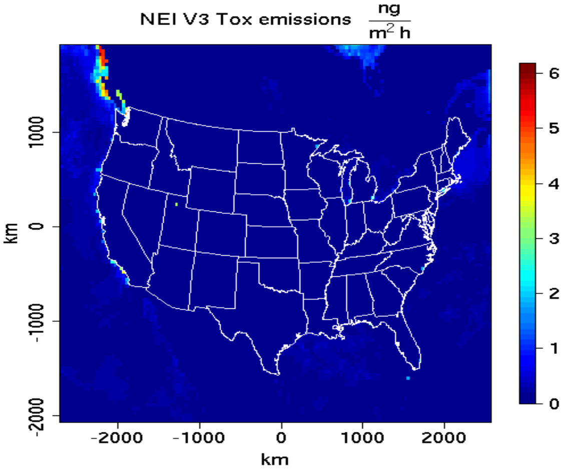

Figure 3: The median emissions rate of elemental mercury from surface waters from July 29th through August 1st, 2001 in NEI V3 toxics.

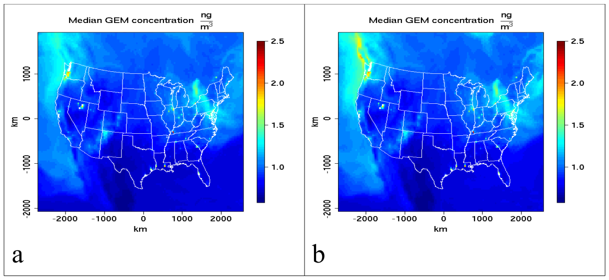

Figure 4: a) Median model concentrations using the photo-redox scheme of Whalin *et al.* (2007) and b) using the NEI V3 toxics estimates of surface water emissions.

4. PRELIMINARY CONCLUSIONS

A surface water mercury photo – redox scheme coupled to a two film air – surface water exchange model has been successfully incorporated in the CMAQ model. Preliminary results of a summertime simulation predicted air surface – water fluxes and ambient and surface water concentrations of elemental and reactive mercury species within the range of observations. This treatment of the air – surface water flux is more mass conservative and physically descriptive than previous techniques that rely on the allocation of previous deposition simulations as emissions or parameterizing the surface concentrations of elemental mercury as a constant currently in use in regional air quality models.

5. DISCLAIMER

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

6. REFERENCES

Bash, J.O., Bresnahan, P.A., Miller, D.R., 2007: Dynamic surface interface exchanges of mercury: a review and compartmentalized modeling framework. *J. Appl. Meteor. Clim.* 46(10) 1606-1618

Bash, J.O., Miller, D.R., Meyer, T.H., Bresnahan, P.A., 2004. Northeast United States and Southeast Canada natural mercury emissions estimated with a surface emissions model. *Atmos. Environ.* 38, 5683-5692

Byun, D., Schere, K.L., 2006: Review of the governing equations, computational algorithms, and other components of the models-3 community multiscale air quality (CMAQ) modeling system, *Applied Mechanics Reviews* 59, 51-77

Byun, D.W., Dennis, R., 1995: Design artifacts in Eulerian air quality models: evaluation of the effects of layer thickness and vertical profile corrections on surface ozone concentrations. *Atmos. Environ.* 29(1), 105-126

Feng, X., Yan, H., Wang, S., Qui, G., Tang, S., Shang, L., Dai, Q., Hou, Y., 2004: Seasonal variation of gaseous mercury exchange rate between air and water surface over Baihua resevoir, Guizhou, China, *Atmos. Environ.* 38 4721-4732

Gbor, P.K., Wen, D., Meng, F., Yang, F., Zhang, B., Sloan, J.J., Improved model for mercury emissions, transport and deposition. *Atmos. Environ.* 40, 973-983

Grell, G.A., Dudhia, J., Stauffer, D.R., 1995. A description of the fifth – generation Penn State/NCAR mesoscale model (MM5), NCAR Technical note, NCAR/ TN-398+STR, Boulder CO., 138 pp

Lalonde, J.D., Amyot, M., Kraepiel, A.M.L., Morel, F.M.M., 2001: Photooxidation of Hg(0) in artificial and natural waters. *Environ. Sci. Technol.*, 35(7). 1367-1372.

Lin, C-J., Lindberg, S.E., Ho, T.C., Jang, C., 2005: Develpment of a processor in BEIS3 for estimating vegetative mercury emissions in the continental United States, *Atmos. Environ.* 39, 7529-7540

Lindberg, S.E., Bullock, R., Ebingaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, C., 2007: Synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* 36(1). 19-32

Mason, R.P., Rolfhus, K.R., Fitzgerald, W.F., 1998: Mercury in the North Atlantic, *Mar. Chem.* 61, 37-53

O'Driscoll, N.J., Siciliano, S.D., Lean, D.R.S., Amyot, M., 2006: Gross photoreduction kinetics of mercury in temperate freshwater lakes and rivers: application to a general model of DGM dynamics. *Environ. Sci. Technol.,* 40. 837-843.

Pleim, J.E., Xiu, A., 1995: development and testing of a surface flux and planetary boundary layer model for application in mesoscale models. *J. Appl. Meteor.* 34, 16-32

Schwarzenbach, R.P., Imboden, D.M., 1993: Environmental organic chemistry. Wiley, New York, NY. 1088 pp.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C., 2004: Global source attribution for mercury deposition in the United States, *Environ. Sci. Technol.* 38, 555-569

Southworth, G., Lindberg, S., Hintelmann, H., Amyot, M., Poulain, A., Bogle, M., Peterson, M., Rudd, J., Harris, R., Sandilands, K., Krabbenhoft, D., Olsen, M., 2007: Evasion of added isotopic mercury from a northern temperate lake, *Environ. Tox. And Chem.* 26(1), 52-60

Strode, S.A., Jaegle, L., Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Mason, R.P., Slemr, F., 2007: Air-sea exchange in the global mercury cycle, *Glob. Biogeochem. Cycles* 21, GB1017

Wanninkhof, R., 1992: Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.,*97(C5). 7373-7382.

Whalin, L.M., Kim, E-H., Mason, R., 2007: Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. *Mar. Chem.* 107(3). 278-284.

Whalin, L.M., Mason, R., A new method for the investigation of mercury in natural waters utilizing deflatable Teflon® bags and additions of isotopically labeled mercury. *Analytica Chimica Acta.* 558, 211-221.

Xu, X., Yang, X., Miller, D.R., Helble, D., Carley, R.J., 1999. Formulation of bi-directional atmospheric-surface exchange of elemental mercury. *Atmos. Environ.* 33, 4345-4355