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# Aquatic Ecosystem Exposure Associated with Atmospheric Mercury Deposition: Importance of Watershed and Water Body Hot Spots and Hot Moments Christopher D. Knightes (Knightes.Chris@epa.gov) and Heather E. Golden (Golden.Heather@epa.gov)

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## ABSTRACT

Atmospheric deposition of divalent mercury (Hg(II)) is often the primary driving force for mercury contamination in fish tissue, resulting in mercury exposure to wildlife and humans. Transport and transformation of the deposited mercury into the environmentally relevant form, methylmercury (MeHg), proceeds at different rates largely regulated by physical characteristics such as watershed land use types and water body hydraulic residence times and water body chemistry, such as pH and trophic status. To fully represent mercury exposure in aquatic ecosystems, we must couple watershed models with water body models and explore where, why, and when hot spots and hot moments of transformation and transport occur. Here we use a spatially resolved, dynamic multi-media modeling framework to simulate mercury species cycling over time for the different river reaches and watersheds within the Cape Fear River Basin, NC, USA. Through these simulations we investigate the importance of specific watershed and surface water system characteristics in simulating MeHg exposure concentrations. Because the models are dynamic and spatially-distributed, we are able to resolve and investigate the importance of different spatial and temporal factors in transporting and transforming deposited mercury.

## **III. MERCURY MODELING FRAMEWORK**

Multi-media model framework incorporates a linkable structure of models developed for specific media. Models are listed below (Here we focus on CMAQ, GBMM, and WASP7).



Figure III. USEPA Multi-media modeling framework with connections for nulation mercury exposure concentrations

#### Atmosphere

The Community Multiscale Air Quality (CMAQ) model combines current knowledge in atmospheric science and air quality modeling with multi-processor computing techniques in an open-source framework to deliver fast, technically sound estimates of ozone. particulates, toxics, and acid deposition.

#### Watershed

The Grid Based Mercury Model (GBMM) is a dynamic, differential mass balance watershed loading model that calculates runoff, erosion, and mass loadings of mercury species to associated water bodies

#### Water Body

The Water Quality Analysis Simulation Program version 7 (WASP7) is a dynamic, mass balance framework for modeling contaminant transport and fate in surface water systems. Kinematic wave routing is used to simulate stream hydrology. The mercury module specifically simulates solids and mercury species.





## IV. COMPARISON of WATERSHED LAND USES to MERCURY LOADINGS



Figure IV-2a. 1998 HaT Loading [g/yr]



1998 Normalized HoT Loading [g/m2/yr]



Developed, Medium Intensity Developed, High Intensity Woody Wetlands Pasture, Hay Cultivated Crops Grassland, Herbaceous Emergent Herbaceous Wetlands Shrub, Scrub Deciduous Fores Everareen Forest Barren Rock, Sand, Clay Mixed Forest Developed, Open Space Open Water Figure IV-2b. 1998 MeHg Loading [mg/yr

Figure IV-2d

Loading [mg/km2/yr]

Yearly average mercury dry deposition rates and mercury concentrations in rainfall were implemented using CMAQ provided simulations. Daily rainfall came from rainfall observations stations over the region with Thiessan polygon extrapolation. GBMM was run for test-case Cape Fear watersheds for 105 vrs via 7 vr intervals starting in 1858. GBMM simulates soil mercury concentrations and surface hydrology to provide a daily output of runoff, soils erosion, and total and methyl mercury loadings. Runs were performed at a 90m x 90m grid cell resolution for GBMM and then aggregated or the watershed of interest, effectively integrating mercury loads across the landscape. The soil concentration the landscape are preserved over time, allowing for accumulation of mercury in the soils and future losses via erosion runoff, and infiltration/leaching.

An example watershed from our simulations is provided to the left. Figure IV-1 shows the breakdown of the land-use types showing and the predominance of deciduous forest and agricultural land (pasture/hay). Figure IV-2a shows the HgT load associated with different land-uses. Despite deciduous forest being a dominant land-type, it represents a small fraction of the total Hg loading to the associated water bodies (rivers/streams). Pasture is a large fraction of the watershed and has a large loading, but not as large as the fraction it makes. Cultivated crops and Developed, Low Intensity are a small fraction of the watershed, but result in a larger fraction of the HgT load. Figure IV-2b shows the shifts in loading due to the different transformation and transport processes due to MeHg.

Normalizing for land area, Figures IV-2c and IV-2d show how different land-uses result in different loading fluxes for the Cape Fear

The modeling results illustrate the potential for how different regions of the landscape can result in "hot spots" of mercury loading, either HgT or MeHg depending on the landscape itself. Interestingly, some regions may have larger HgT while others may receive larger MeHg fractions.

	Area [km2]	HgT Loading [g/yr]	Normalized HgT Loading [g/m2/yr]	MeHg Loading [mg/yr]	Normalized MeHg Loading [mg/km2/yr]
Developed, Low Intensity	3.2	1.8	0.55	26	8
Developed, Medium Intensity	0.76	1.3	1.7	20	26
Developed, High Intensity	0.23	0.4	1.7	6	26
Woody Wetlands	1.5	0.2	0.12	42	29
Pasture, Hay	60	4.2	0.07	255	4
Cultivated Crops	1.6	2.3	1.5	140	90
Grassland, Herbaceous	6	0.3	0.05	17	3
Emergent Herbaceous Wetlands	0.01	0.0	0.02	0	5
Shrub, Scrub	5.7	0.0	0.0	2	0
Deciduous Forest	79	0.3	0.0	16	0
Evergreen Forest	8	2.0	0.25	118	15
Barren Rock, Sand, Clay	0.21	0.2	0.81	3	12
Mixed Forest	4.5	0.1	0.02	6	1
Developed, Open Space	9.7	0.5	0.06	8	1
Open Water	1.3	5.7	4.5	340	267

Total Mercury Loading = 19.22 g/yr Total Methyl Mercury Loading = 997 mg/yr



simple WASP model was developed to simulate mercury concentrations (HgII, Hg0, and MeHg) along the Cape Fear River by dividing the basin into 6 surface water segments and 6 underlying sediment segments related to the 6 8-digit HUCs. Simulation was lesigned to investigate overall mass balance, transport, and transformation of Hg within the riverine system eliminary results demonstrate the importance of location within the Cape ear Watershed for Hg concentrations. For example, the upper Cape Fear has higher Hg concentrations (HgT and MeHg) than the lower despite identical atmospheric deposition at each reference site (Figures V-1 and V-2). This suggests that total mercury mass is being lost via settling and evasion along the river, while dilution is occurring via ncreasing discharge to the lower Cape Fear, Additionally, more solids enter the system in the upper reaches of the watershed, which increases sorption and settling and suggests that hot spots of Hg will be more prevalent in the headwaters of the Cape Fear resulting in a more sensitive region of the reach

## **VI. CONCLUSIONS**

 This preliminary modeling work helps us understand mercury cycling dynamics in a large watershed system including a range of different land use types and their implications on temporal and spatial mercury cycling dynar

· Process modeling affords us the opportunity to evaluate long term trends and dynamics and to e feasible hot spots and moments of mercury within a multimedia fram

• The watershed modeling effort demonstrates how different land uses result in different spatial loadings to associated water bodies and the overall construct of the watershed (having higher or lower fractions of high loading land-use types) can result in regions of higher or lower mercury

• The physical setting and location within the Cape Fear Basin influences mercury concentrations even when simulations are run under the same mercury deposition forcing function

## VII. FUTURE DIRECTIONS

Collaborate with partners to gather field data to evaluate mercury cycling algorithms within each land type and evaluate success of modeling mercury loadings to water body

· Continue to improve mercury algorithms in GBMM and WASP with improved understanding of mercury science

· Further refine mercury modeling to investigate importance of timing in modeling. For example, timing of runoff and erosion events and the importance of different time functions, like the growing season for agriculture and litter fall for deciduous trees versus coniferous trees

· Improve wetlands functionality in watershed model, possibly permitting wetland functionality in WASP as well as GBMM

· Improve linkages of air, land, and water models

Presentation Thursday Morning. 11:05 – 11:20 Room 2022. H. Golden, C Knightes B42A-04: Modeling Watershed Mercury Response to Atmospheric Loadings: Resp nse Times and Simulation Challend

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