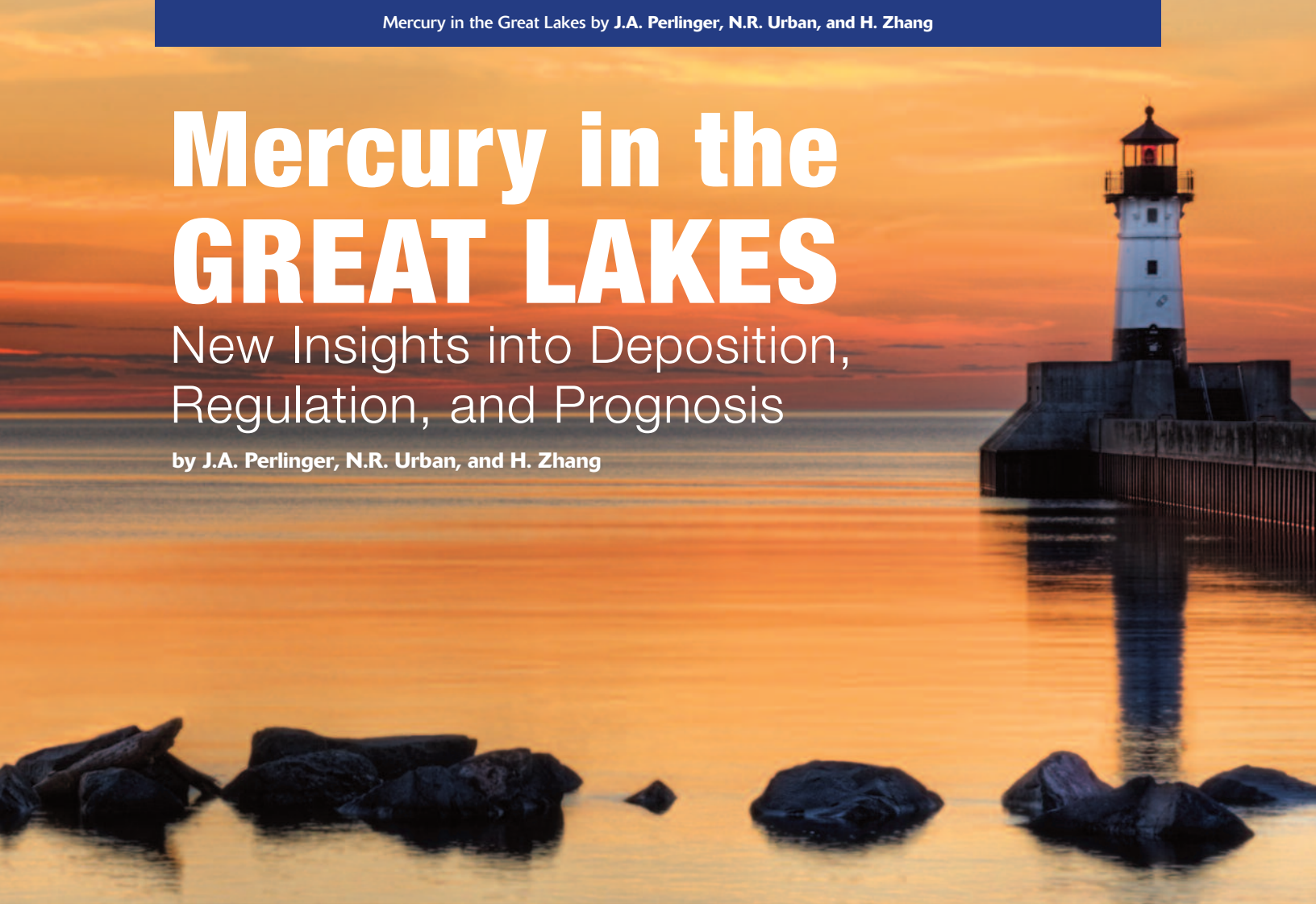

Mercury in the GREAT LAKES

New Insights into Deposition, Regulation, and Prognosis

by J.A. Perlinger, N.R. Urban, and H. Zhang

Mercury (Hg) pollution of the Laurentian Great Lakes region of the United States has led to fish consumption advisories not only for the Great Lakes themselves, but also for inland lakes in the Great Lakes region. These policies are of considerable concern to First Nation and American Indian communities and others who remain heavily reliant on fish consumption. Advice to restrict fish consumption results from human emissions of Hg into the atmosphere, Hg transport through the atmosphere, and eventual deposition some distance downwind. In this article, we first relate how atmospheric Hg, or rather its toxic form methylmercury (MeHg), ends up in fish we consume, then discuss how Hg environmental cycling is influenced by differing landscapes and examine how Hg regulations affect Hg deposition differently within the upper and lower Great Lakes and their inland water bodies.

Mercury enters the environment through natural sources, such as volcanoes and volatilization from rocks and soils with elevated Hg content (see Figure 1). An increasing amount of Hg also enters the environment through human activities, including fossil fuel combustion, metal refining, and artisanal small-scale gold mining. Once in the environment, the volatile form of mercury, Hg(0), can be transported through the atmosphere to far distant locales, because of the long atmospheric residence time (3–12 months) due to the combination of its moderately high air–water exchange coefficient and its relatively low octanol-water partition coefficient.[1,2] Some oxidized Hg, Hg(2), also is emitted, but this form is rapidly scavenged from the air and deposited relatively close to its source in dry and wet deposition. Hg(0) can also be re-emitted from land and water, forming so-called "secondary emissions". The form of Hg of most concern is methyl mercury (MeHg), which is formed in low-oxygen environments. Although it may be present at low concentrations in surface waters, MeHg bioaccumulates millions of times in aquatic food webs such that it reaches toxic concentrations in top predator fish in lakes.

The Role of the Landscape in Hg Cycling

The landscape itself influences Hg deposition from the atmosphere. Both particulate and gaseous Hg(2) are scavenged more effectively by vegetation than by water surfaces; in models, this phenomenon is expressed as higher deposition velocities to vegetation than to lakes or oceans. Additionally, Hg(0) passively enters the stomata of plants, becomes fixed within the leaves and contributes Hg to the watershed when the leaves fall and decompose.[3] Consequently, Hg dry deposition is greater (~10-fold) to watersheds than to lakes, especially to large lakes (see Figure 2). Dry deposition is notoriously difficult to measure; careful examination of field measurements is required to determine appropriate mathematical parameterizations[4] that may subsequently be incorporated into models to improve model accuracy in predicting deposition.

It has long been known that some fraction of atmospherically deposited Hg is revolatilized to the atmosphere, but the magnitude of these secondary emissions has been poorly quantified. A recent compilation of measurements of Hg emission fluxes[5] yielded a rate of 5 μg m^{-2} yr^{-1} or 28% of deposition for the Great Lakes region. However, this value underestimates the total secondary emissions from the Great Lakes area because of the functioning of lakes within the landscape. Some fraction (1–30%) of atmospherically deposited Hg runs off of catchments into lakes. Some of this Hg runoff is buried in lake sediments, but a significant fraction is reduced and revolatilized back to the atmosphere as Hg(0). Estimates for watersheds ranging in size from those of small lakes (a few km^2) to that of Lake Superior (128,000 km^2) suggest that lakes increase secondary emissions of Hg(0) by 5–30% over that from the terrestrial landscape.

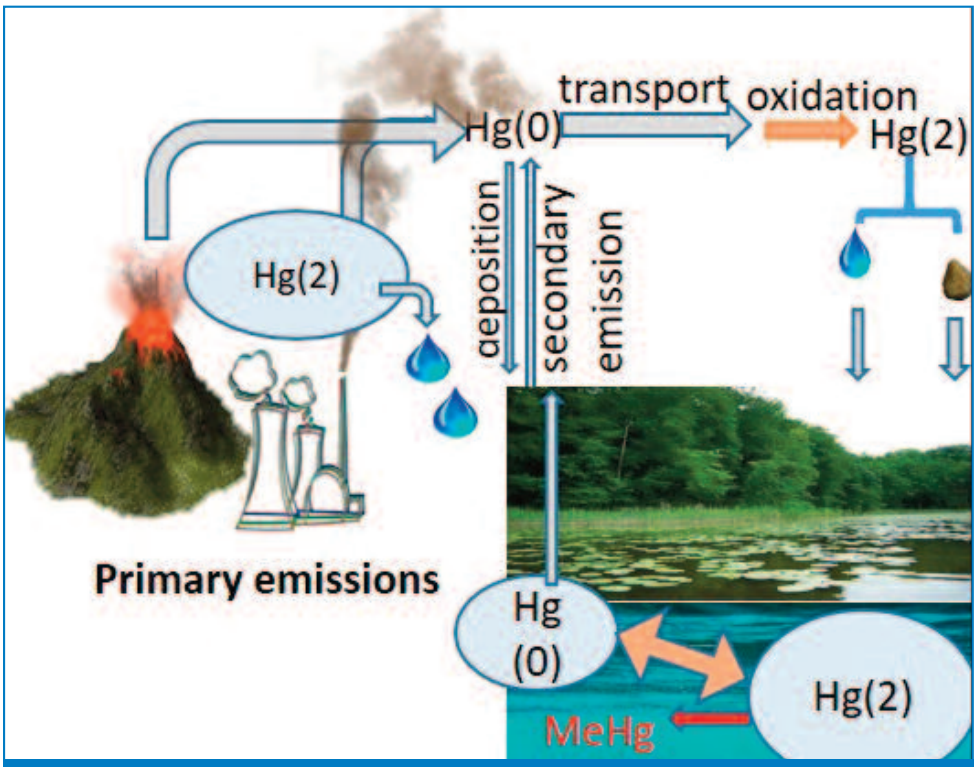

Figure 1. Schematic of atmospheric Hg emission, transformation, transport, and deposition to the Great Lakes region. Blue arrows correspond to transport features while orange and red arrows represent chemical reactions.

Another important influence of the landscape on Hg cycling is regulation of the efficiency with which atmospherically deposited Hg is methylated. Methylation, conducted by a variety of microbial types, occurs in low oxygen environments such as in the deep waters of productive lakes, as well as in waterlogged soils such as in wetlands and lake sediments. The more abundant are wetlands and low oxygen lakes in the landscape, the more efficiently is Hg deposition converted to the toxic and bioaccumulative MeHg. The distribution of these sensitive

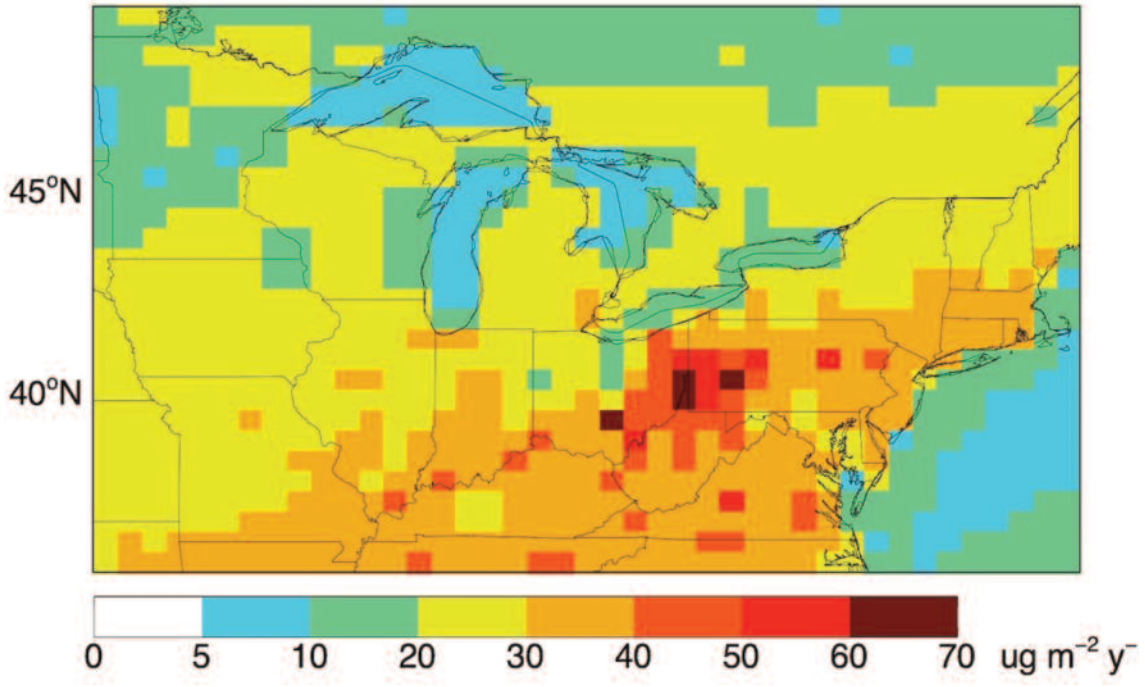

Figure 2. GEOS-Chem modeled estimates for total Hg deposition (= wet + dry) in the Great Lakes region. Adapted from Ref.[11] with permission from The Royal Society of Chemistry.

landscapes is reflected in the distribution of statewide fish consumption advisories due to Hg. States bordering Canada from Washington to Maine (including all Great Lakes states), have statewide fish consumption advisories. In Michigan's Upper Peninsula, nearly 80% of lakes have fish Hg above the U.S. Environmental Protection Agency's (EPA) water quality limit of 0.3 μg g^{-1} because of the particularly high capability of this landscape to methylate Hg.[6]

Greater Upwind U.S. Emissions in Lower Great Lakes Region, Greater Impact of Regulation on Deposition

The propensity of landscapes for runoff and MeHg formation, and their proximity to upwind primary emitters, as well as policies regulating those emissions determine the spatial distribution of Hg contamination in lakes. Mercury emissions in the United States and Canada were estimated to contribute ~22% and ~12%, respectively, to the total deposition to the Great Lakes.[7] The emissions sources leading to Hg deposition in the entire Great Lakes region are estimated through modeling simulations to be dominated by oceanic secondary emissions (a component of global emissions) and emissions within the Great Lakes region (see Figure 3; in References 6 and 8, the Great Lakes region was defined as bounded by 40° and 50° N latitude and by 73° to 95° W longitude, which includes a part of Canada).[8] Local and regional Hg emissions, primarily U.S. coal-fired power plants in the Great Lakes area, are greater in the vicinity of the lower Great Lakes (Lakes Erie and Ontario), but are smaller in the airsheds of the upper Great Lakes (Lakes Superior, Michigan, and Huron).[8] Therefore, it is mainly global emissions through long-range atmospheric transport and deposition that impact the upper Great Lakes region, and the amount of Hg deposition is predicted and observed to be less to the upper Great Lakes as compared to the lower Great Lakes. For example, the present-day deposition to Michigan's Upper Peninsula (located on the southern shore of Lake Superior) is estimated to be 24%

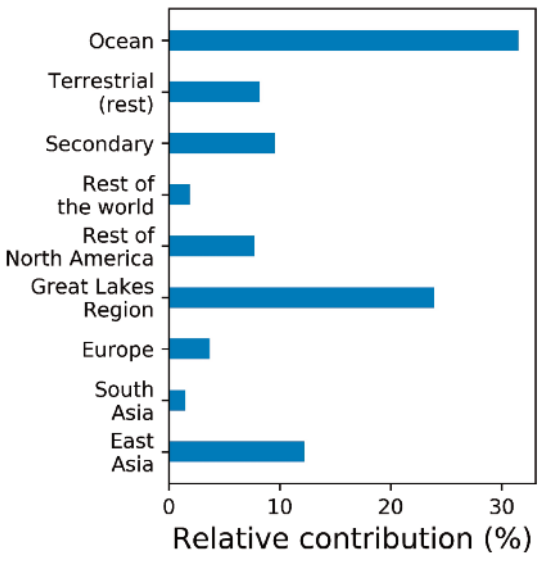

Figure 3. Relative contribution from different sources of Hg emissions to deposition in the Great Lakes region.[8]

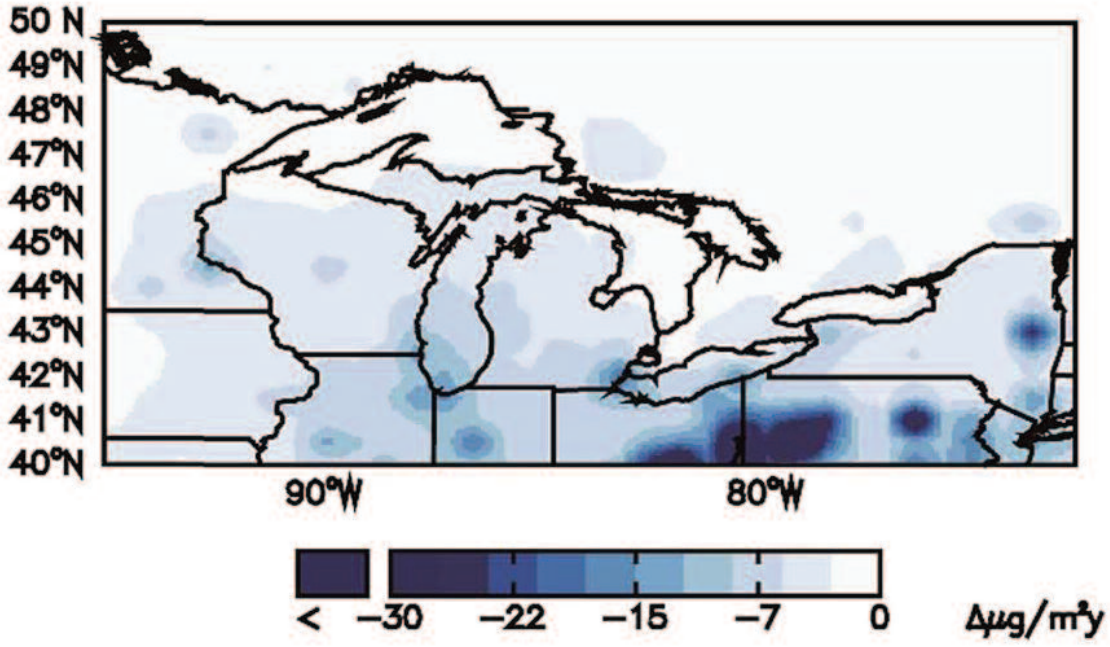

Figure 4. Combined policy-in-action scenario (ZDDP + MATS + ROW) total Hg deposition benefits from the present day to 2050, in Δ μg m^{-2} yr^{-1}. Reproduced from Ref.[6] with permission from The Royal Society of Chemistry.

less than the deposition to the Adirondack region in upper New York (located to the east of Lake Ontario).

Existing policies affecting Hg deposition to the Great Lakes include Canada-wide standards (CWS) on emissions from coal-fired power plants, Ontario regulations on emissions from coal-fired power plants,[9] the Binational Program's Zero Discharge Demonstration Program (ZDDP; Lake Superior only), the U.S. Mercury and Air Toxics Standards (MATS), and the Minamata Convention (MC). When only the last three of these policies were considered,[6] deposition was predicted to decrease by 20% from the present to 2050, and of that 20%, the contribution of the MATS was 85% whereas the MC and ZDDP accounted for 14% and 1%, respectively. Also, the U.S. MATS were predicted to cause the Adirondacks to receive 21% less deposition than Michigan's Upper Peninsula in 2050 (see Figure 4).[6] Therefore, although the entire Great Lakes region was predicted to be most affected by MATS (relative to the MC and ZDDP policies) in 2050, local landscape sensitivity and lesser impact of the MATS in Michigan's Upper Peninsula suggest that Hg deposition will be both greater and have a greater impact in Michigan's Upper Peninsula than in the Adirondacks.

No Short-Term Fixes in Remote Areas of Great Lakes

The wheels of policy creation and implementation turn slowly. Fully 22 years elapsed between authorization by U.S. Congressional amendments to the U.S. Clean Air Act (1990) and EPA's release of the MATS (2012); this timeline will be extended further if the current U.S. administration revokes the MATS. In contrast, Ontario banned power generation from coal and its associated Hg emissions in 2015. Awareness of Hg as an international problem led to the first International Conference on Mercury as a Global Pollutant in 1990. Efforts within the UN Environment Program date back to at least 2001 when a global assessment of Hg was initiated. These efforts culminated in 2013 with the signing of the Minamata Conven-tion that entered into force in 2017 after being ratified by 50 countries. Because of the voluntary nature of the Convention, implementation of all articles will require additional decades.

The timescale for recovery of ecosystems following reduction of inputs is highly variable. Because of the lag between regulation and impacts, it is important to implement regulations quickly.[10] One of the biggest unknowns regarding recovery times is how long the inventories in soils and wetlands of historically deposited Hg will continue to bleed into streams and lakes. Among the Great Lakes, Lake Superior has the highest concentrations of Hg in lake trout although it receives the lowest input from atmospheric deposition; this "anomaly" may reflect the high potential for MeHg formation in the catchment. Model simulations suggest that because Lake Superior receives a greater proportion of Hg inputs from global rather than regional sources, it will respond most slowly to current regulations.[6]

The combination of high geologic potential for MeHg formation combined with low inputs from local sources suggest that Lake Superior will not experience a rapid decline in fish Hg in the coming decades. For fish-reliant communities, the heavy burden of health risk is likely to persist for at least another generation. **em**

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