MPCA Mercury Risk Estimation Method (MMREM) for the Fish Consumption Pathway:

Impact Assessment of a Nearby Emission Source

Version 1.0

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Interim Final Draft

This document and other materials related to the MMREM process are considered interim final drafts. This means that, while these documents are considered final as of the version date, the MPCA will complete future revisions as necessary to improve the MMREM process or to incorporate new scientific information. All updates will be dated and posted on the MPCA website. The latest version of the MMREM should be used at the beginning of each new project. If submittals for a proposed project are not made using this version within a six month period, the MPCA website should be consulted for updates and incorporated at that time. The latest version of the MMREM for fish consumption can be found online at:
http://www.pca.state.mn.us/air/

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Introduction

The fish in all lakes and rivers of Minnesota are contaminated with mercury to some degree. The mercury is transported by the atmosphere and deposited to surface water and the surrounding watersheds. Even though atmospheric deposition of mercury is relatively uniform across the state, the degree of fish contamination varies a great deal in top predators such as walleye, northern pike, and bass. Fish accumulate mercury as they grow, but even when standardized to a particular length, mercury concentrations vary widely from lake to lake. For instance, mercury in standard-sized walleye varies from about 0.1 to 1.0 ppm among Minnesota lakes. Fish concentrations are variable, even though the atmosphere is generally a uniform source, because different aquatic systems process mercury differently: one system might be more sensitive to mercury deposition because it has contiguous wetlands where inorganic mercury is converted to methylmercury and also has a longer food chain to the top predator fish. Another lake might be more sensitive than average because mercury is methylated efficiently in its anoxic hypolimnion and introduced into surface water each fall during mixing. Each lake has its own way of expressing mercury, as illustrated in Figure 1. Given that it is beyond current science and environmental data collection systems to accurately calculate the differences in mercury methylation and bioaccumulation among lakes, the MPCA has instead adopted a method that relies on empirical fish contamination data, combined with the principle of proportionality between mercury in fish and atmospheric deposition (USEPA 2001).

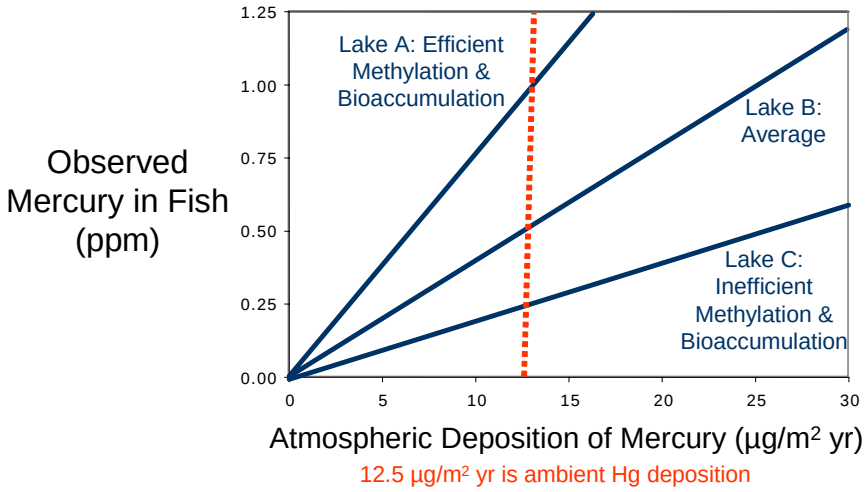

Figure 1. Lakes produce varying levels of fish contamination even when atmospheric deposition is uniform. Minnesota's draft mercury TMDL (MPCA 2006) predicts reductions in mercury concentrations of fish based on the principle of proportionality between atmospheric deposition and mercury in fish (USEPA 2001). As atmospheric deposition declines or increases, each lake will follow its own unique linear relationship after a new steady state is reached (Fig. 2).

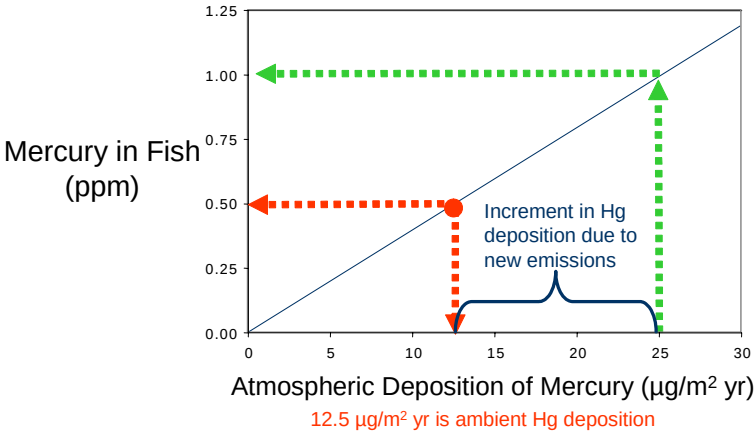

Figure 2. Proportionality can predict the effect of an increment in Hg deposition due to new Hg emissions.

The principle of proportionality between atmospheric deposition and mercury accumulation in fish is most robust when the entire ecosystem—the surface water (lake or river) and its entire terrestrial watershed—is subject to uniform changes in atmospheric mercury. Minnesota's mercury TMDL calculations assume that deposition is uniform between surface water and the terrestrial watersheds because it is assumed that implementation policies will affect the state as a whole, and therefore entire watersheds.

However, this document addresses a question of an entirely different geographic scale: could increases in a single emission source of mercury significantly increase the mercury concentration of fish in a lake adjacent to that source? In such a case, it is no longer defensible to assume that there would be a uniform change in atmospheric mercury over the entire ecosystem. It is theoretically possible that an emission plume is more concentrated over a lake, for instance, than over the rest of the lake's watershed, which is likely to be 5 or more times larger than the lake.

The purpose of this risk estimation method for the local impacts of a particular emission source is to provide a practical way to implement the principle of proportionality between mercury deposition and fish contamination for surface water that is not subject to a uniform change in atmospheric mercury. In the mercury TMDL the scale of cause and effect is entire ecosystems, so the ecosystems can be treated as a unit for purposes of proportionality. But in this effort to assess the impact of a single emission source, the geographic scale will often be smaller than the ecosystem, so utilizing the principle of proportionality is more complicated.

Local assessment is based on proportionality between mercury in fish and total load of mercury to the surface water from direct deposition and terrestrial export. To calculate this load, it is necessary to calculate the amount of mercury that is delivered from the terrestrial watershed to the surface water—a step that is not necessary in the MPCA mercury TMDL, because the delivery coefficient is assumed to be a constant over time, and so it drops out of the equations used for the TMDL (MPCA 2006, p. 25). This is not to say that the mercury deposited to the terrestrial system is regarded as unimportant in the TMDL. On the contrary, mercury from terrestrial runoff often is a larger load than direct deposition, and so is important to address.

Local Impacts Assessment

The MPCA Mercury Risk Estimation Method (MMREM) is not a mechanistic model of mercury methylation and bioaccumulation, but rather combines empirical fish contamination data with the premise that mercury concentrations in fish will achieve a steady state in relation to atmospheric mercury deposition (USEPA 2001). MMREM can be used to estimate the noncancer oral hazard quotients associated with fish tissue consumption based on increases in mercury deposition. MMREM can provide an answer to the question, "If fish in this lake already have a given mercury concentration, how much would that concentration increase if more mercury were added?" Because the ambient methylmercury concentration in fish is used to quantify the sensitivity of the system to mercury, the estimated effect of an increment is likely more accurate than would be predicted by an unconstrained model. The weakest assumptions in this method are the assumed deposition rates for the facility's emitted mercury, which will be a mixture of three forms: gaseous divalent mercury (HgII), elemental mercury (Hg0), and particle-bound divalent mercury (Hgp). The three forms have different removal mechanisms from the atmosphere, and therefore have different deposition velocities, which also may vary with the landscape. If emission rate estimates of these mercury species are not available for the proposed facility, then conservative figures will be used for this risk estimation, as described below.

Key Concepts/Assumptions

The key concepts and assumptions used to estimate any increase in fish tissue concentrations from a project's emissions are as follows:

- For a given water body, an X percent increase in the mass of mercury input to a water body will ultimately result in an X percent increase in the methylmercury fish tissue content.
- Mass mercury input to a water body can be approximated from direct atmospheric deposition to the water body plus export from the terrestrial watershed, which can be estimated as 10 percent of the mass of mercury deposited to the rest of the watershed, when calculated according to the methodology outlined below.
- Atmospheric deposition can be estimated from air-dispersion modeled concentrations of Hgp, HgII and Hg0 over the water body and its watershed.
- Total mercury fish tissue concentration measurements are available for fish species at the top of the food chain from many Minnesota lakes and rivers. Where data on the impacted water bodies are missing, fish concentrations can be estimated based on the data from that region within the state, although the uncertainty of the estimate would be greater than when data are available from the impacted water bodies.
- The statewide Minnesota estimate of ambient annual wet-plus-dry mercury deposition (based on sediment core measurements, Swain et al. 1992) is 12.5 micrograms per square meter (µg Hg/m^2) directly to the water body surface and 33.6 µg Hg/m^2 to terrestrial areas, of which 10% (3.4 µg Hg/m^2) is exported to surface water.[1]

The specific methodology for estimating incremental fish tissue mercury concentrations and hazard quotients associated with the project emissions is outlined below. A spreadsheet developed by MPCA staff as well as relevant Minnesota fish tissue data representing pre-project fish impacts are available to calculate a hazard quotient from eating mercury-contaminated fish. These will be supplied to project proposers.

Methodology

1. Characterize mercury air concentration(s) from proposed project

a. Estimate stack emissions of HgII, Hg0 and Hgp. Estimates can be derived from the existing facility if it is being expanded, or from other existing facilities with similar fuel and pollution control equipment.

b. Perform air dispersion modeling to identify the area of maximum mercury concentration around the facility from the proposed project.

2. Select one or more water bodies for evaluation

Any fishable water body[2] occurring at the area of maximum deposition should be evaluated. If the area of maximum deposition does not fall on a fishable waterbody, consider all water bodies in the specified range around the facility[2] to determine which water body is nearest the area of maximum deposition. This may be the water body to evaluate for worst-case impacts at the screening level. However, it may not be clear whether the water body nearest the site of maximum deposition is the water body that is most highly impacted. There may be a water body with more impact because it has less dilution from its watershed, more fishing, etc., If it is not clear which water bodies should be evaluated, MPCA staff should be contacted.

3. Delineate the watershed

Use a topographic map to delineate watershed boundaries of the selected water bodies. USGS and other pre-defined watershed areas are approximated and often define much larger areas than would actually feed into the water body under evaluation. If the hydrology is complex, e.g., the water body under consideration is other than a simple headwater lake, contact the MPCA. Also contact the MPCA for guidance if there are significant wetland areas that would receive elevated mercury deposition due to the project. Mercury methylation is significantly more efficient in wetlands (St. Louis et al. 1994), so the MPCA would have increased concern if wetlands draining to fishable waters were predicted to receive elevated mercury deposition. Watershed export of methylmercury increases with increasing wetland area as a percentage of total watershed area (Grigal, 2002).

4. Estimate incremental mercury mass loading to water body due to ambient mercury in the atmosphere.

Calculate the annual mass (grams Hg) added to the water body from ambient atmospheric Hg concentrations assuming annual average mercury wet-plus-dry deposition to surface water is 12.5 µg/m^2 and annual average wet-plus-dry deposition to terrestrial surfaces is 33.6 µg Hg/m^2. Assume 10 percent of the mercury deposited on the terrestrial watershed is ultimately transported to the water body.

Total mass Hg deposited annually to water body from ambient Hg air concentrations (µg) = [avg. MN deposition flux to water bodies (12.5 µg Hg / m^2-yr)] * [area of water body (m^2)] +
0.1 * [avg. MN deposition flux to land (33.6 µg Hg / m^2-yr)] * [area of terrestrial watershed (m^2)]

5. Estimate incremental mercury mass deposited to each evaluated water body and its watershed due to proposed project.

For each waterbody, use air dispersion modeling results to estimate annual average concentrations of HgII, Hg0 and Hgp associated with proposed project over the watershed.

a. Estimate the average HgII, Hg0 and Hgp concentrations over the fishable water bodies. This may be done with a screening level model by averaging the concentration modeled at the nearest point on the water body to the source and the furthest point on the water body [(concentration at nearest distance to water body + concentration at furthest distance from water body) / 2]. Alternatively, this may be done with refined modeling by overlaying model plot file results on a map of the water bodies and using geographic information systems (GIS) functions to calculate the average concentration over the water bodies.

b. Estimate the average HgII, Hg0 and Hgp concentrations over the terrestrial part of the watershed (exclude the fishable water bodies). This should be done as described above for the water bodies.

If the watershed extends beyond the modeling domain, it will be assumed that the concentrations over the non-modeled portion of the watershed equal the concentrations at the nearest boundary of non-modeled watershed. The mercury modeling results will be submitted to MPCA for review and approval.

Calculate the annual mass (grams Hg) added to the water bodies from project emissions, assuming that 10 percent of the Hg deposited to the terrestrial watershed is ultimately transported to the water body.

The annual Hg mass deposited is the sum of the deposition of each of the three mercury species. The deposition rate over a unit area (flux in $\mu g/m^2$-yr) = Average Air Concentration ($\mu g\ Hg/m^3$) x Deposition Velocity (m/yr). Multiply the flux over the water body and over the rest of the watershed by their respective areas to get the mass deposited per year. Assume that 10 percent of the Hg deposited on the ground ultimately impacts the water body. Do the following example calculation for all 3 mercury species and sum results.

Total mass of Hg loaded annually to water body from project (μg) =
[avg. Hg air conc over water body ($\mu g/m^3$) * Hg water body dep velocity (m/yr) * area of water body (m^2)] +
0.1 [avg. Hg air conc over terrestrial watershed ($\mu g/m^3$) * Hg terrestrial dep velocity (m/yr) * area of terrestrial watershed (m^2)]

Table 1 provides estimates of average deposition velocities for the 3 mercury species. Alternately, mercury deposition may be directly modeled using an air dispersion and deposition model. If a modeling approach is taken, the details of the proposed assessment would be submitted to MPCA as part of the air dispersion and deposition modeling protocol:

Table 1. Deposition Velocity Estimates for Mercury Species[3]

Deposition to surface of water bodies		
Hg Species	**cm/sec**	**meters/year**
HgII	1.10 cm/sec	347,000 m/yr
Hg0	0.01 cm/sec	3,200 m/yr
Hgp	0.05 cm/sec	15,800 m/yr

Deposition to surface of terrestrial portion of watershed		
Hg Species	**cm/sec**	**meters/year**
HgII	1.10 cm/sec	347,000 m/yr
Hg0	0.05 cm/sec	15,800 m/yr
Hgp	0.10 cm/sec	31,500 m/yr

6. Estimate the percent increase in mercury loading in water bodies from project
Divide the estimated annual water body Hg mass loading from the project by the annual Hg mass loaded to the water body from "ambient conditions".

7. Estimate fish fillet methylmercury concentration from project emissions
The MPCA maintains a database of fish tissue data from fish collected by the DNR that is thought to be representative of fish people catch by angling, especially walleye and northern pike.

If adequate fish tissue data are available for the water bodies under evaluation, total mercury data from the 10 most recent years (exclude data from years before 1980) should be used to calculate the 95% upper confidence limit (UCL) of the mean using data for the top predator species in the water bodies[4]. If the calculated UCL is greater than the maximum detected fish tissue concentration, the maximum value should be used. Relevant data will be sent to project proposers in an Excel file.

If adequate fish tissue data are not available for the water bodies under evaluation, MPCA staff will select an applicable data set from a review of a minimum of 5 water bodies near the water bodies under evaluation for which fish tissue data are available. The extent of the geographic region searched for applicable data will be extended until a data set adequate for a statistical analysis is found. Total mercury data from the 10 most recent years (exclude data from years before 1980) will be used to calculate the 95% UCL of the mean using data for the top predator species[4]. If the calculated UCL is greater than the maximum detected fish tissue concentration, the maximum value should be used.

Multiply the available fish tissue data by the fraction obtained in step 6 to estimate the part of the mercury fish fillet concentrations from the project emissions. Convert the mercury fish tissue concentration associated with the project to methylmercury tissue concentration by multiplying the mercury concentration by 1.075. This is the ratio of the molecular weights of methylmercury to mercury.

8. Estimate the incremental methylmercury exposure for the fisher scenario
The same exposure assumptions as those defined for the other chemicals in the assessment should be used considering the following guidance for the fish consumption rate.

Fish consumption Rate
Fishing is very popular recreationally in Minnesota because of its abundant fishable water bodies and rivers. Locally caught fish also provide a significant food source for some Minnesota populations, including Native Americans, Pacific Asian Americans, and other subsistence consumers. For these reasons, both the recreational and the subsistence fish pathways should be evaluated for risk unless evidence is provided that subsistence fishing does not and could not occur.

The suggested *recreational* fish consumption rate is 30 grams/day based on the consumption rate used to calculate Minnesota human health-based aquatic life standards. This value is based on survey data of the amount of fish eaten by anglers in Wisconsin and Ontario. The amount of freshwater fish consumed by anglers varies from none to more than one meal every day. Thirty grams per day is equivalent to an average of one half-pound meal of freshwater fish per week, or 26 pounds a year.

Minnesota does not have a recommended fish consumption rate for *subsistence* populations, although some tribes may have site-specific information and recommendations. If this information is not available, EPA suggests using 142 grams/day to represent the uncooked weight intake of freshwater/estuarine finfish and shellfish. This would equate to eating about a half-pound of fish 4 to 5 times a week.

9. Estimate the incremental noncancer hazard quotient
Follow EPA risk assessment methodology to estimate the methylmercury hazard quotient for fish consumption. The RfD for methylmercury is 1E-04 mg/kg-day.

MPCA has developed a spreadsheet to perform these calculations. The necessary spreadsheet inputs are as follows:
- Name of proposed facility
- Name of water bodies
- County of water bodies
- Minnesota DNR lake numbers (if available)
- Fish species being evaluated
- Existing ambient mercury concentration in fish (mg/kg wet weight). Submit documentation showing calculations and data used
- Water body surface areas, including areas of contiguous wetlands.
- Terrestrial watershed surface area, including any wetlands not included in the water body.
- Average modeled mercury concentrations above water bodies from the project, for each form of mercury in the air
- Average mercury concentrations above terrestrial watershed areas from the project for each form of mercury in the air

Modeling inputs and assumptions that will not vary among modeling efforts include the following:

- Deposition velocities of Hgp, HgII, and Hg0 directly to the water body surface.
- Deposition velocities of Hgp, HgII, and Hg0 to the terrestrial portion of the watershed.
- A constant proportion of the mercury deposited to the terrestrial watershed, 10%, is exported to the water body.
- All mercury loading to the water body is equally likely to be bioaccumulated by fish.
- Mercury emissions do not change form after exiting the stack.

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[1] Note that earlier draft versions of this protocol assumed that Hg deposition to terrestrial area was equal to deposition to surface water at 12.5 µg Hg/m^2 and that 20%, or 2.5 µg Hg/m^2 was exported to surface water. These alternative assumptions have similar net effects on surface water (3.4 compared to 2.5 µg Hg/m^2) but the new presentation is more compatible with current scientific consensus that total deposition to terrestrial systems is significantly greater than deposition directly to surface water (Grigal 2002). In addition, the use of 3.4 µg Hg/m^2 rather than 2.5 is more similar to the original finding of 3.3 µg Hg/m^2 (Swain 1992).

[2] The AERA definition of a fishable water body is: "A water body may be considered "fishable" if it typically contains water year-round in a year that receives at least 75 percent of the normal annual precipitation for that area. For facilities with stack heights less than 100 meters, a map should be provided showing lakes, rivers and streams within a 3 km radius (approx. 2 miles). For facilities with stack heights greater than 100 meters, show lakes, rivers and streams for the area within a 10 km radius (6 miles). Also show water bodies outside the specified area that may be fed by rivers and streams lying within the radius of interest. The length of the reach of river or stream (or extent of a lake) outside the radius that must be shown will be determined case-by-case based on local data and conditions."

[3] The deposition velocities for the three Hg species in this model are based on the following: Ambient air concentrations are assumed to be about 1% HgII, 1% Hgp, and 98% Hg0, and to result in a direct deposition to lakes rate of 12.5 µg/m^2-yr (Swain et al. 1992), and about 34 µg/m^2-yr to terrestrial systems, within the interquartile range of 32 to 44 µg/m^2-yr found in a review by Grigal (2002). Grigal reports that flux of Hg from watersheds do not range widely, with about 75% of observations in the range of 1 to 3 µg/m^2-yr, with a mean of about 2 µg/m^2-yr. We use a slightly higher flux from watersheds for the ambient Minnesota condition of 3.3 µg/m^2-yr (from Swain et al. 1992), or 10% of ambient deposition. From that finding, we expect that under steady state conditions 10% of any increased Hg deposition to terrestrial systems will be exported to aquatic systems. We assume that the deposition velocity of HgII is similar to that of nitrate, which averages about 1.1 cm/sec in Minnesota (Pratt et al. 1996). We assume that Hgp has the deposition velocity in terrestrial systems that Pratt et al. found for fine particulate matter (0.1 cm/sec), and that the deposition of Hgp to surface water is 50% lower (0.05 cm/sec). It is more difficult to arrive at appropriate deposition velocities for Hg0 to water and terrestrial systems. We would expect the deposition of Hg0 to be appreciably faster to vegetated terrestrial surfaces than to water. The following velocities for Hg0 are assumed in this model, largely chosen to yield total Hg deposition fluxes for ambient conditions of 12.5 µg/m^2-yr to a lake and between 32 and 44 µg/m^2-yr to the terrestrial watershed: 0.01 to a lake and 0.05 cm/sec to the terrestrial watershed.

[4] Due to the uncertainty associated with estimating the true average mercury fish tissue concentration, the 95 percent UCL of the arithmetic mean should be used because it provides reasonable confidence that the true average fish tissue concentration will not be underestimated. For purposes of cancer and chronic noncancer risk assessment, the 95% upper confidence limit of the arithmetic mean (UCL-AM) of fish tissue data should be used. The US Environmental Protection Agency (EPA) has formulated guidance for calculating the UCL-AM: USEPA, OSWER, 2002, *Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites* (http://www.hanford.gov/dqo/training/ucl.pdf). The guidance has been implemented in the EPA ProUCL software (http://www.epa.gov/nerlesd1/tsc/form.htm). This software may be downloaded and run to obtain UCL-AM values from fish tissue data.