

Prepared in cooperation with the Natural Resources Department,
Bad River Band of Lake Superior Chippewa

Compilation of Mercury Data and Associated Risk to Human and Ecosystem Health, Bad River Band of Lake Superior Chippewa, Wisconsin

Open-File Report 2020–1095
Version 1.1, December 2020

U.S. Department of the Interior
U.S. Geological Survey

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By Douglas A. Burns

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**U.S. Department of the Interior
U.S. Geological Survey**

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Conversion Factors

International System of Units to U.S. customary units

| Multiply | By | To obtain |
|-------------------------------------|-----------|--------------------------------|
| Length | | |
| centimeter (cm) | 0.3937 | inch (in.) |
| Area | | |
| square meter (m ²) | 10.76 | square foot (ft ²) |
| square kilometer (km ²) | 247.1 | acre |
| Volume | | |
| liter (L) | 33.81402 | ounce, fluid (fl. oz) |
| liter (L) | 0.2642 | gallon (gal) |
| Mass | | |
| gram (g) | 0.03527 | ounce, avoirdupois (oz) |

U.S. customary units to International System of Units

| Multiply | By | To obtain |
|-----------------|-----------|------------------|
| Length | | |
| inch (in.) | 2.54 | centimeter (cm) |

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Supplemental Information

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L) for mercury species and milligrams per liter (mg/L) for dissolved organic carbon.

Concentrations of chemical constituents in sediment or biota are given in nanograms per gram (ng/g) for mercury species or percent for organic carbon.

Mercury to dissolved organic carbon ratios are given in nanograms per milligram (ng/mg).

Fish lengths are given in inches (in.) or millimeters (mm).

Deposition is given in nanograms per square meter per year ([ng/m²]/yr).

Sieve size is given in millimeters (mm).

Abbreviations

| | |
|-------|------------------------------|
| DOC | dissolved organic carbon |
| n | number of samples |
| p | probability value |
| R^2 | coefficient of determination |
| USGS | U.S. Geological Survey |

Compilation of Mercury Data and Associated Risk to Human and Ecosystem Health, Bad River Band of Lake Superior Chippewa, Wisconsin

By Douglas A. Burns

Abstract

Mercury is an environmentally ubiquitous neurotoxin, and its methylated form presents health risks to humans and other biota, primarily through dietary intake. Because methylmercury bioaccumulates and biomagnifies in living tissue, concentrations progressively increase at higher trophic positions in ecosystem food webs. Therefore, the greatest health risks are for organisms at the highest trophic positions and for humans who consume organisms such as fish from these high trophic positions. Data on environmental mercury concentrations in various media and biota provide a basis for comparison among sites and regions and for evaluating ecosystem health risks. The U.S. Geological Survey, in cooperation with the Natural Resources Department, Bad River Band of Lake Superior Chippewa, have compiled a dataset from analyses of mercury concentrations in surface water, bed sediment, fish tissue, *Rana clamitans* (green frog) tissue, *Haliaeetus leucocephalus* (bald eagle) feathers, *Lontra canadensis* (North American river otter) hair, *Zizania palustris* (northern wild rice), and litterfall from samples collected in the Bad River watershed, Wisconsin during 2004–18. These data originated from either the Natural Resources Department or another agency based on samples collected within or near to Bad River Tribal lands before transfer to the U.S. Geological Survey for compilation and analysis at the onset of the project. This report describes the compiled mercury dataset, provides comparisons to similar measurements in the region and elsewhere, and evaluates health risks to humans and to the sampled biota. Except for litterfall, data were not collected on a consistent, regular basis over a sufficient period to evaluate temporal patterns. The reported mercury concentrations are generally similar to those reported elsewhere in the upper Great Lakes region. Reported values are consistent with atmospheric deposition as the principal source and reflect a favorable environment for mercury methylation. Fish mercury concentrations increased at higher food web positions and generally increased with length in most species measured. *Sander vitreus* (walleye) present the greatest risk to humans among fishes considered here because of their high trophic position and associated elevated mercury concentrations in combination with relatively high walleye

consumption rates by the Native American community. Methylmercury concentrations in wild rice are generally low and likely pose little health risk. Despite reports of declining atmospheric mercury deposition across eastern North America during the past decade, a downward trend in litterfall mercury deposition was not evident in samples collected during 2012–18. Limitations in this data compilation and analysis were noted due to missing information such as collection dates and site locations for some samples. Regular monitoring of mercury in litterfall and surface waters along with periodic collection of fish would enable evaluation of temporal change in the mercury cycle that might affect future risk to humans and aquatic ecosystem inhabitants.

Introduction

Mercury contamination of aquatic and terrestrial ecosystems remains a widespread concern across the United States and globally, posing health risks to humans and wildlife (Beckers and Rinklebe, 2017). In its methylated form, mercury is a potent neurotoxin that biomagnifies and bioaccumulates in food webs, presenting the greatest risks to those organisms at the highest trophic levels (Mergler and others, 2007). The origin of mercury to most ecosystems is atmospheric deposition of wet and dry forms that originate from local, regional, and global emissions (Driscoll and others, 2013). Fossil fuel combustion (particularly coal burning), artisanal mining, cement manufacturing, and medical waste incineration are the dominant sources of global mercury emissions (Pacyna and others, 2010). Additionally, natural geologic sources can be important in some settings, particularly those with an extensive mining history (Pacyna and others, 2010).

Because of the ubiquitous nature of mercury contamination, fish consumption advisories are widespread across the United States and globally (Oken and others, 2012), and Native Americans may be at particularly high risk because of a prevalence of subsistence fisheries and the cultural importance of fishing rituals (Roe, 2003). The Wisconsin Department of Natural Resources has issued mercury advisories for human consumption of several fish species, especially focused on

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women of childbearing years and children under 15 years of age (Wisconsin Department of Natural Resources, 2020a). Also, neurological effects of mercury contamination to fish, birds, and other species have been extensively reported across the United States and globally (Evers and others, 2011).

To better understand the temporal and spatial dynamics of the mercury cycle and to evaluate risks in a given region, sampling and analysis of mercury (total mercury and methylmercury) in a variety of environmental media along with related chemical constituents and landscape metrics is warranted (Riva-Murray and others, 2011; Burns and others, 2012; Burns and others, 2013; Janssen and others, 2019). These data can be helpful in determining temporal trends that may indicate increasing or decreasing risk with time, where risks are greatest within a landscape, and which media are of greatest concern.

The study described in this report was initiated by the Natural Resources Department, Bad River Band of Lake Superior Chippewa, and is a cooperative project with the U.S. Geological Survey (USGS). The objective of the study was to compile and evaluate currently available data collected or accessed by the Natural Resources Department to improve understanding of risk and to guide future sampling efforts. The specific objectives of this study were to (1) compile mercury data collected by or accessed by the Natural Resources Department, Bad River Band of Lake Superior Chippewa, (2) present these data in an organized tabular form to facilitate access, (3) summarize the data in a report and provide broad comparisons to other similar data in the region or nationally, (4) describe health risks to humans and to ecosystem inhabitants relative to known effects or other guidance levels, and (5) describe data gaps that might guide future sample collection efforts.

Methods

This report describes mercury data as provided in several files that were shared with the USGS for compilation in this project. The data compiled and reported here, as well as in the accompanying data release (Burns, 2020), are total mercury and methylmercury concentrations in various environmental media including streams and rivers, streambed sediment, fish tissue, *Rana clamitans* (green frog) tissue, *Haliaeetus leucocephalus* (bald eagle) feathers, *Lontra canadensis* (North American river otter) hair, *Zizania palustris* (northern wild rice), and litterfall. These concentrations represent different reservoirs and pathways in the mercury cycle during transport from the atmosphere to surface waters where uptake by biota may occur that reflects bioaccumulation and biomagnification

of mercury in ecosystem food webs (Driscoll and others, 2013). Many of the data files provided to the USGS included ancillary data such as concentrations of other chemical constituents. Data directly relevant to the reported parameters such as sample collection depth for surface waters, length or weight for fish, and reach length for bed sediment were included in the data compilation. Additionally, any chemical measures of organic matter such as dissolved organic carbon (DOC) concentrations in surface waters were also included in the data compilation because of the fundamental role that organic matter serves in environmental mercury transport and bioaccumulation. Other constituents such as trace metals and ancillary chemical measures were not included in the compilation but may be available in the original files in possession of the Natural Resources Department. The USGS did not collect the samples of environmental media and for the majority of the data reported here, was not involved in sample handling or chemical analyses. Therefore, sampling and analytical methods are not described here, but may be included as metadata associated with each dataset reported in the accompanying data release (Burns, 2020). Available information such as sampling methods, collection dates, sampling locations, analytical methods, and quality-assurance and quality-control procedures were not always available in the original files that are the basis for the data release.

Pertinent mercury data files were transferred to the USGS in May 2018. Available metadata (such as date, time, location, and accompanying measurements) were also transferred to the USGS at this time. These data files were examined, organized, compiled into eight Comma Separated Value (CSV) files each with an accompanying Extensible Markup Language (XML) metadata file, and archived in the USGS ScienceBase digital repository (Burns, 2020). In the summer of 2018, the principal investigator visited the Natural Resources Department and was led on a field trip to observe the landscape and to see many of the sites where samples were collected. [Figure 1](#) shows the Bad River Band of Lake Superior Chippewa (hereafter referred to as just Bad River) Tribal lands and the adjoining landscape. Many of the surface waters referred to in this report are listed in the figure along with some frequently sampled sites.

Examination and analysis of data included basic statistical summaries, graphics, and comparisons to other regional data. Risk assessment included comparisons to known guidelines for human health and ecosystem inhabitants. An evaluation of data gaps was also undertaken relative to organisms and landscape elements previously sampled, sampling frequency, and sampling duration. Preliminary results were shared with Natural Resources Department staff via a webinar during May 2019. Publication of this report marks the final project requirement.



Figure 1. Bad River Tribal lands and adjoining landscape where samples were collected for mercury analysis, including 9 of 18 surface-water sampling locations on the Bad River, its tributaries, and adjacent rivers and the principal mercury litterfall collection site (WI195).

Data Summary and Analysis of Risk

Data are summarized below and shown as boxplots that provide a comprehensive, visual data representation. Data shown are not distinguished by individual site locations but reflect groupings of all data for a particular constituent (for example, total mercury concentration) and category (for example, fish tissue).

Surface Water

These data represent filtered total mercury, filtered methylmercury, particulate total mercury, particulate methylmercury, and DOC concentrations in 63 surface-water samples (mainly streams and rivers) collected at 18 sites during 2006–16 (fig. 2). Nine of these sites were established by the USGS; the locations of these are shown in figure 1, and name descriptions and drainage areas are provided in table 1. Values reported as total mercury (number of samples [n]=21) and total organic carbon (n =4) are not included in figure 2 because of incompatibility with the other species that were distinguished as filtered or particulate forms. Additionally, these total mercury (11 of 21 values) and total organic carbon (2 of 4 values) data included some censored values reflecting concentrations below the method detection limit. The concentrations of these unfiltered species reported as less than a detection limit are included in the data release. Additional details such as method detection limits and ancillary data are also provided in the companion data release (Burns, 2020).

The filtered mercury species were dominant over particulate species in the surface waters sampled in Bad River Tribal lands (fig. 2), which is surprising considering that the Bad River has among the highest suspended-sediment yields (load per unit watershed area) of any tributary in the Lake Superior Basin (Robertson, 1997). The median filtered total mercury concentration of 3.1 nanograms per liter (ng/L) was more than tenfold greater than the median particulate total mercury concentration of 0.3 ng/L, and similarly the median filtered methylmercury concentration of 0.16 ng/L was more than sevenfold greater than the median particulate methylmercury concentration 0.021 ng/L. The sum of the median concentrations of filtered and particulate total mercury are equivalent to total mercury, and the median value of 3.4 ng/L observed in the surface waters on Bad River Tribal lands is more than twofold greater than both the wildlife criterion of 1.3 ng/L and human threshold of 1.5 ng/L for total recoverable mercury in a water supply prescribed by the State of Wisconsin (Wisconsin Department of Natural Resources, 2020b). Of the 28 filtered total mercury concentrations represented in figure 2A, 89 percent exceed the 1.3 ng/L wildlife criterion, and 71 percent exceed the 1.5 ng/L human threshold for water supply. These results indicate that humans and wildlife are generally not protected from adverse effects when ingesting water or aquatic organisms from the Bad River and the tributaries that are included in figure 2A.

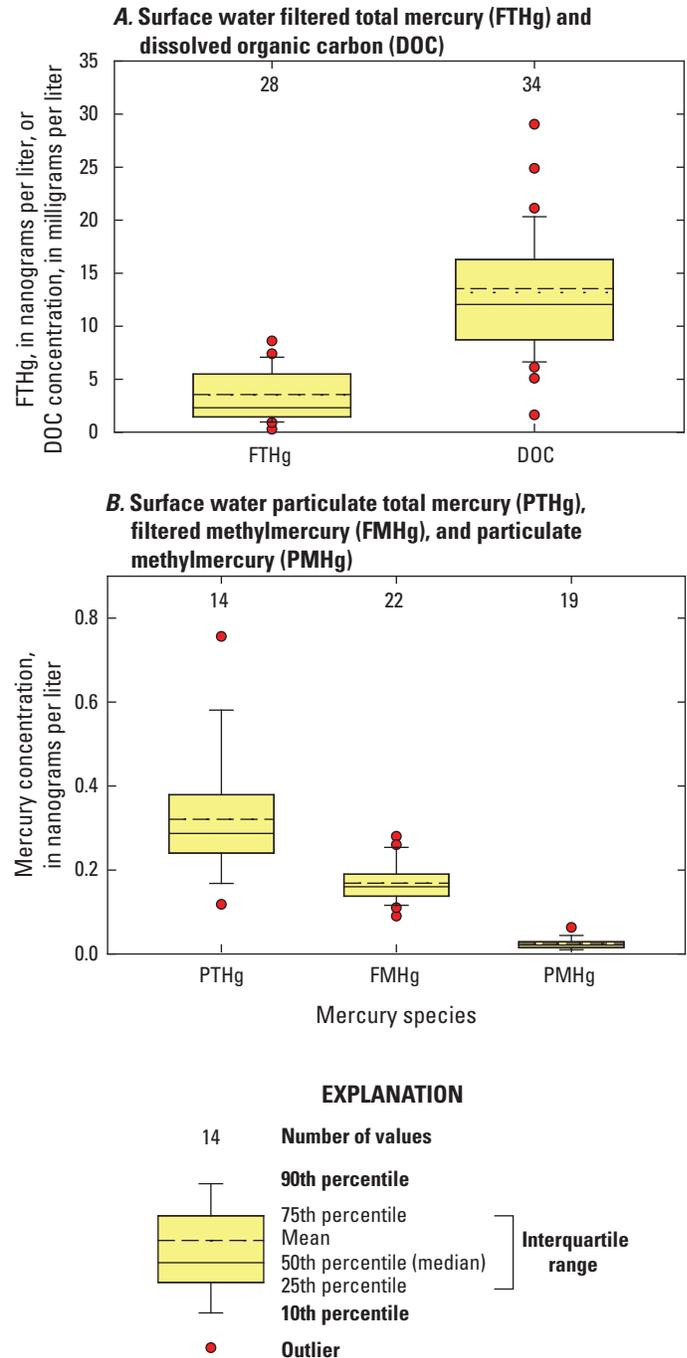


Figure 2. Mercury species and dissolved organic carbon concentrations in surface water from samples collected at 18 sites on Bad River Tribal lands during 2006–16. *A*, filtered total mercury and dissolved organic carbon concentrations; and *B*, particulate total mercury, filtered methylmercury, and particulate methylmercury concentrations.

Table 1. U.S. Geological Survey (USGS) identifiers, names, and drainage areas for the nine USGS river and stream sites where surface water samples were collected for mercury analysis within or near Bad River Tribal lands.

[Data are from the U.S. Geological Survey (USGS) National Water Information System (NWIS) database (USGS, 2019). Lk, lake; Rd, road; nr, near; WI, Wisconsin; NA; drainage area not available; US, United States; St Hwy, State Highway]

| USGS NWIS identifier (fig. 1) | USGS NWIS name | Drainage area (km ²) |
|-------------------------------|--|----------------------------------|
| 04026530 | Tyler Forks River at Caroline Lk Rd nr Mellen, WI | 56.9 |
| 040265373 | Bull Gus Creek near Upson, WI | NA |
| 04026450 | Bad River near Mellen, WI | 212 |
| 04026511 | Bad River at US Highway 169 near Mellen, WI | 273 |
| 04026559 | Tyler Forks River upstream St Hwy 169 nr Mellen WI | 166 |
| 04026561 | Tyler Forks River at Stricker Road near Mellen, WI | 183 |
| 04027000 | Bad River near Odanah, WI | 1,550 |
| 04027580 | Bad River at Government Road near Odanah, WI | NA |
| 04027595 | Bad River at Odanah, WI | 2,510 |

Dissolved organic carbon concentrations are typically strongly related to filtered total mercury and filtered methylmercury in waters of undeveloped settings because of the important role of organic matter in hydrologic transport of mercury and the role of DOC as an indicator of mercury source areas, and favorable biogeochemical source and transport conditions. In the data compiled here, a strong and significant (probability value [*p*] less than [$<$] 0.05) least squares linear regression relation was identified between filtered total mercury (FTHg) and DOC concentrations ($FTHg = -0.707 + [0.295 \times DOC]$, coefficient of determination [R^2] = 0.61, $p < 0.001$). The regression slope is broadly consistent with many past studies that show filtered total mercury to DOC ratios ranging from about 0.1 to greater than 1.0 nanogram per milligram (Grigal, 2002; Shanley and others, 2008; Brigham and others, 2009; Stoken and others, 2016). A least squares linear regression relation that is weaker than that between filtered total mercury and DOC concentrations and of marginal statistical significance was evident between filtered methylmercury (FMHg) and DOC concentrations ($FMHg = 0.0813 + [0.00860 \times DOC]$, $R^2 = 0.18$, $p = 0.07$). Generally, relations of concentrations of filtered methylmercury and DOC tend to be weaker and more wide ranging in surface waters than those of filtered total mercury and DOC (Brigham and others, 2009; Burns and others, 2012) as observed in this dataset. Finally, the filtered methylmercury to

filtered total mercury ratio was calculated because it provides a good indicator of the methylation efficiency of a watershed or water body and can be a predictor of high rates of mercury bioaccumulation in food webs (Fleck and others, 2016). The median ratio in these samples was 10.9 percent, and the interquartile range was 2.6 to 12.7 percent. These values are relatively high compared with those reported in other parts of North America (Fleck and others, 2016) but correspond to reports of high ratios greater than 10 percent in other surface waters of northern Wisconsin (Babiarz and others, 1998; Shanley and others, 2008).

Bed Sediment

Bed sediment samples were collected on 51 occasions (including one duplicate sample, 52 samples total) at 44 stream and river sites across Bad River Tribal lands between 2006 and 2015 over a reach length that was not indicated for all samples collected. Both sieved (2 millimeters) and unsieved samples are part of this dataset, and whether samples were sieved was not always indicated. The data source files do not state whether concentrations are reported on a wet weight or dry weight basis, but it is highly likely that values are reported on a dry weight basis because this is standard practice when reporting sediment chemistry results (Wait and others, 2015). Figure 3 is a boxplot of total mercury concentrations in these bed sediment samples. In four of the samples, mercury concentrations were below an analytical method detection limit of 20 ng/L, and these values are not included in the figure. Concentrations ranged from 10 to 110 nanograms per gram (ng/g), with a median value of 20 ng/g and mean value of 26 ng/g. These concentrations are consistent with those reported in three Wisconsin streams by Marvin-DiPasquale and others (2009) in which upstream runoff from non-channel sources rather than bed sediment was the likely dominant source of mercury in stream water. Percent organic carbon was significantly and strongly related to mercury concentrations in bed sediment samples according to the following least squares linear regression: mercury concentration (in nanograms per gram) = $14.565 + (3.490 \times \text{organic carbon percent})$, $R^2 = 0.74$, $p < 0.001$. This relation is consistent with an observed strong association of mercury with organic matter in stream sediment as well as in soil, a major sediment source, across a wide range of landscapes (DeLaune and others, 2009; Obrist and others, 2016).

Fish Tissue

Total mercury concentrations were available for 104 fish tissue samples collected at 7 sites during 2004–13 at locations on the Bad River and its tributaries, at the mouths of nearby rivers, and in Lake Superior. These fish tissue samples span nine species and include a mix of skin-off fillets and muscle (tissue type was not indicated for some samples or was designated as just “tissue”). Analyses were performed on single fish

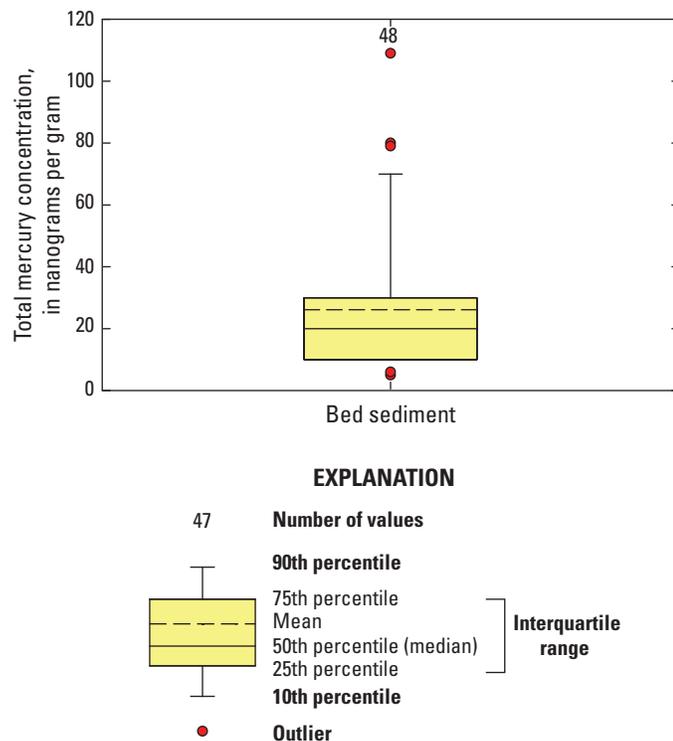


Figure 3. Total mercury concentrations in 48 bed sediment samples collected at 44 stream and river sites on Bad River Tribal lands during 2006–15.

or on composite samples (9 of 104 samples) of 2 or more fish (most were 3 sample composites). *Catostomus* *Catostomus* (longnose sucker, $n=1$), *Moxostoma* spp. (redhorse, $n=3$), and *C. commersonii* (white sucker, $n=20$) were combined into one family group, Catostomidae. Mercury concentration data available in files from the Natural Resources Department were expressed as dry weight or wet weight, and both values were available for some fish samples. Figure 4 presents wet weight mercury concentrations, and when only dry weight was available, wet weight concentrations were estimated using a median moisture content of 77.6 percent, the mean value of all fish samples that included both values. All concentration data are expressed as total mercury. However, methylmercury is the dominant form in fish and methylmercury to total mercury ratios in tissue generally range from 66 to greater than 90 percent (Bloom, 1992; Houserová and others, 2007). Median wet weight total mercury concentrations decreased in this order: *Esox lucius* (northern pike, 219 ng/g), *Sander vitreus* (walleye, 168 ng/g), *Perca flavescens* (yellow perch, 128 ng/g), *Micropterus dolomieu* (smallmouth bass, 65.0 ng/g), *Acipenser fulvescens* (lake sturgeon, 60.0 ng/g), suckers (58.2 ng/g), and *Salvelinus fontinalis* (brook trout, 22.4 ng/g).

Figure 4 shows boxplots for 7 fish groups (6 species and 1 family) relative to consumption guideline thresholds not to exceed 1 meal per week for children less than 15 years of age

and women of child-bearing age of 50 ng/g (wet weight), and a second guideline threshold for the general adult population of 160 ng/g (wet weight). These guidelines originate from the 2007 addendum to the “Protocol for a Uniform Great Lakes Sport Fish Consumption Advisory” and have been implemented by the Wisconsin State Department of Health (Great Lakes Fish Advisory Workgroup, 2007). Assumptions about reference dose, body weight, and meal size that were applied to arrive at the two guideline values are described in Great Lakes Fish Advisory Workgroup (2007). Values in figure 4 show generally increasing mercury concentrations as fish diets shift from invertivorous (those that consume mainly invertebrates and small fish) such as those of brook trout and lake sturgeon, to piscivorous (those that consume mainly fish) such as walleye and northern pike. Most fish samples of every species other than brook trout exceed the 50 ng/g guideline. All walleye, yellow perch, and northern pike samples exceed the 50 ng/g guideline concentration, and more than 50 percent of the walleye and northern pike samples exceed the 160 ng/g guideline concentration. In contrast, the 160 ng/g guideline concentration is not exceeded by any brook trout, lake sturgeon, or smallmouth bass samples, and by only a few sucker and yellow perch samples.

Surface waters of the Great Lakes region generally have high fish mercury concentrations (Evers and others, 2011). The pattern of mercury concentrations across species and their relation to human-health guideline levels reported here are generally consistent with previously reported results in this region (Rasmussen and others, 2007; Wiener and others, 2012). Results reported here indicate the highest risk to humans is from consumption of northern pike and walleye. Walleye is of particular concern because a previous investigation determined that the highest levels of blood mercury among native Chippewa individuals was correlated with recent consumption of walleye (Peterson and others, 1994). It is worth noting that some fish species that are commonly consumed by humans such as *Micropterus salmoides* (largemouth bass) and *Esox masquinongy* (muskellunge) are known to have mercury concentrations that often exceed human consumption guidelines (Rypel, 2010; Monson and others, 2011), but these species are not included in the current dataset.

The limited size of the fish mercury dataset described in this report combined with a narrow time range of 9 years did not allow a temporal trend analysis. Studies in the Great Lakes region show varied temporal patterns in fish mercury concentrations with increasing, decreasing, and mixed trends reported (Evers and others, 2011; Monson and others, 2011; Zananski and others, 2011; Zhou and others, 2017). Regardless of the temporal trends, fish mercury concentrations remain elevated above historic values (Zananski and others, 2011)

When interpreting the fish mercury levels reported in this dataset, an important consideration is that most of the fish (68 of 104) were collected near river mouths as they empty into Lake Superior or in the lake itself, though only brief site location titles and not geographic coordinates were available. Past studies have noted that fish mercury concentrations are

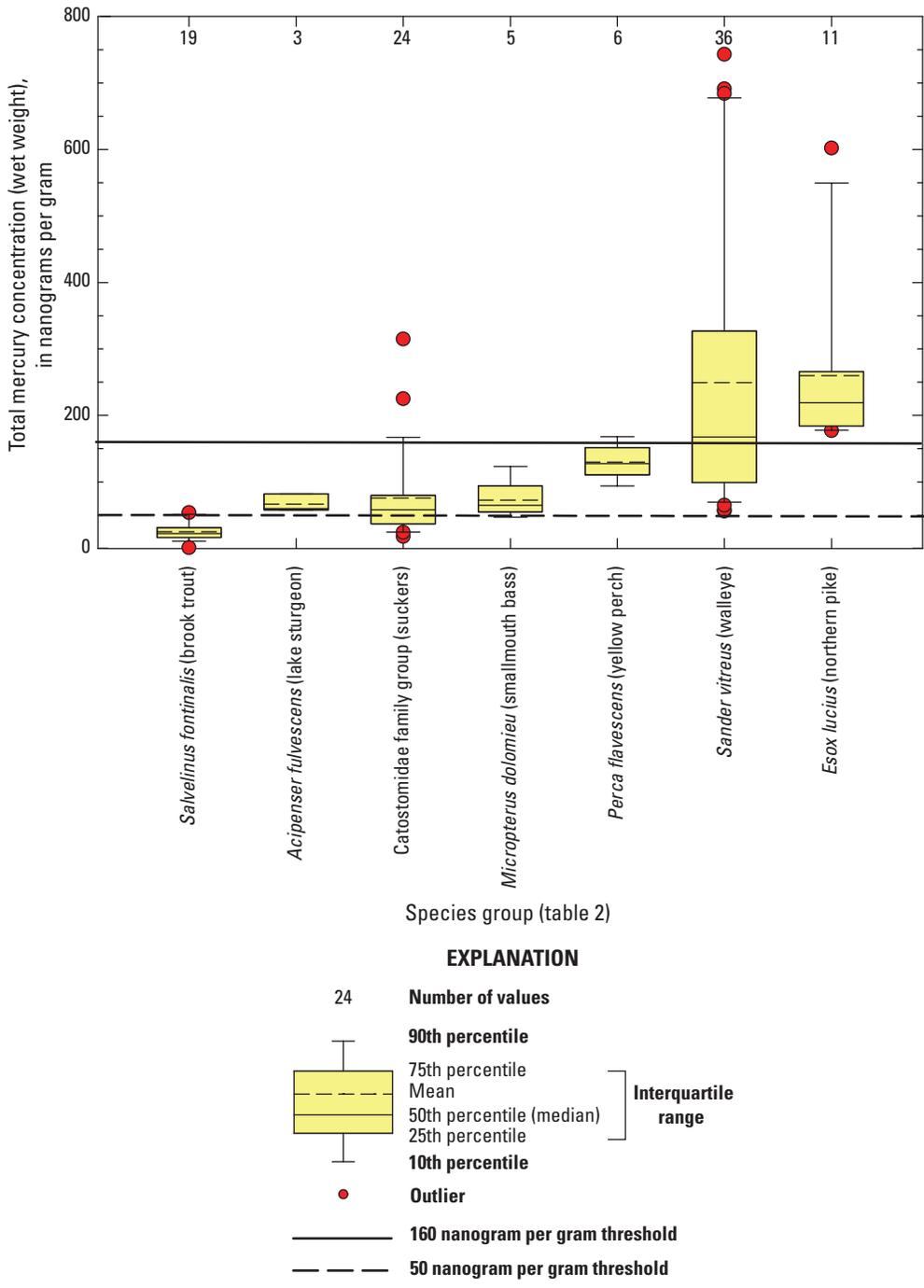


Figure 4. Fish mercury concentrations for 104 samples from 7 groups at 7 sites that include streams and rivers on Bad River Tribal lands and Lake Superior sampled during 2004–13.

generally lower in the Great Lakes than in adjacent inland waters (Monson and others, 2011; Wiener and others, 2012). All or nearly all lake sturgeon, northern pike, walleye, and yellow perch sampled may have resided for at least part of their lives in Lake Superior, though this is not known with certainty. This suggests the possibility that mercury concentrations measured in these species may be less than if fish were collected

in inland waters that lack a direct fish migration connection to Lake Superior. In contrast, all brook trout and most suckers and smallmouth bass were collected in Tyler Forks River, located upstream in the Bad River drainage, indicating lower likelihood that these fish were directly influenced by residence in Lake Superior.

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Beyond fish species trophic position and diet, other important factors that govern progressive fish mercury bioaccumulation include age, weight, and length (Boening, 2000). Length is a commonly measured fish metric, and models and studies of mercury in fish as well as risk assessments to humans often use a length-normalization approach (Peterson and others, 2007; Bhavsar and others, 2011). Although relations of length to mercury concentration can often show complex nonlinear patterns (Simoneau and others, 2005), linear regression was applied here to provide a preliminary assessment of length-related patterns in fish mercury, which may inform human consumption risk. Table 2 provides these linear regression relations including the statistical significance ($p \leq 0.05$) of the y-intercepts and coefficients (slopes). The y-intercept for walleye was the only one among fish species groups that was significantly different than zero. The threshold lengths above which each species group is predicted to have total mercury concentrations greater than the two fish consumption guidelines according to the linear regression are also shown in table 2. Note that threshold lengths were not provided for lake sturgeon and yellow perch in table 2 because the coefficients for these species are not statistically significant. A lack of statistical significance should not be assumed to indicate that a length to total mercury concentration relation is not expected, but rather that the limited number of analyses available for these two species were not great enough to establish clear statistical significance.

The linear regression relation for walleye is the strongest among fish species groups in this dataset and is of particular interest because walleye is commonly consumed by native Chippewa individuals in Wisconsin. This regression relation predicts that the not to exceed one meal per month guideline of 160 ng/g for the general adult population will be reached on average at a length of 23.7 inches (in.; 601 millimeters). This

is generally consistent with the high end of the range recommended by the Wisconsin Department of Natural Resources for the general adult population not to eat more than one walleye meal per month across several inland surface waters (mostly lakes) in northern Wisconsin if length exceeds 15 to 24 in. (length varies with water body, Wisconsin Department of Natural Resources, 2016). For Lake Superior, the guideline is not to exceed one meal per month for walleye of any length (Wisconsin Department of Natural Resources, 2016).

Green Frog Tissue

Eighteen *Rana clamitans* (green frog) specimens were collected from the Bad River during 2012–13 and analyzed for total mercury (dry weight). Figure 5A is a boxplot of these data. Median mercury concentration was 24.0 ng/g, and the interquartile range (difference between 75th and 25th percentile concentrations) was 18.5 to 28.0 ng/g among these samples. Few available studies have measured mercury concentrations in frogs (Loftin and others, 2012; Burger and others, 2014), and even fewer for green frogs (Bank and others, 2007). Among nine ponds in Acadia National Park, Maine, the mean mercury concentration in green frog tadpoles was 25.1 ng/g, and the standard error was 1.5 ng/g (Bank and others, 2007), similar to the mean value of 23.7 ng/g for green frog tissue in the Bad River. Less than half of reported total mercury in green frogs and other frog species is in the form of methylmercury (Bank and others, 2007; Loftin and others, 2012), substantially less than the proportion believed to be present in most fish species (Scudder and others, 2009). The mercury concentrations in green frog tissue were substantially less than those of the fish tissue and other biota described in this report. In particular, total mercury concentrations in green frog tissue were about four to fivefold less than those of brook

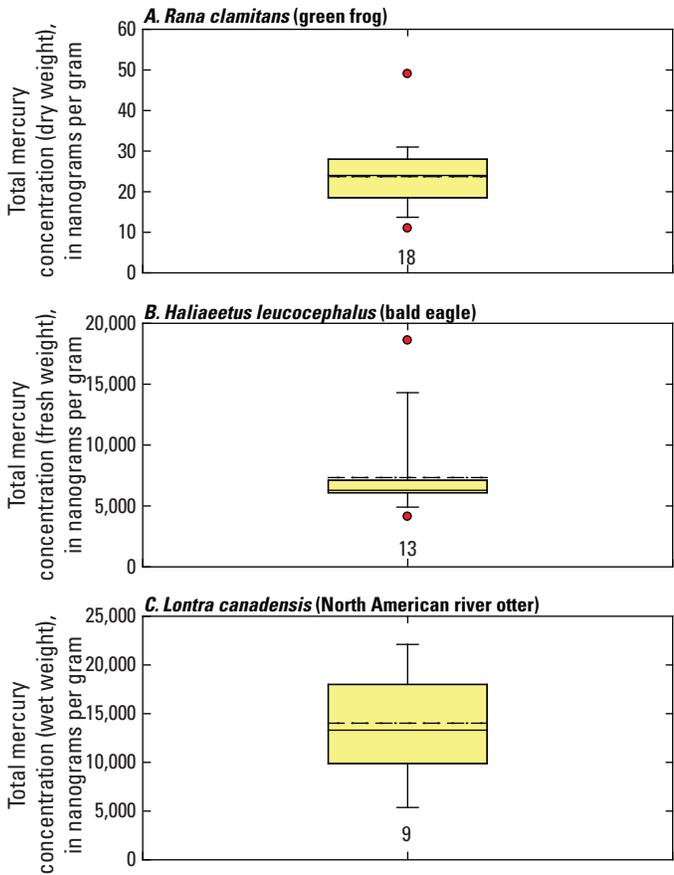
Table 2. Least squares linear regression relations for prediction of fish mercury concentrations as a function of length.

[Equation: length (in millimeters [mm])= $m \times \text{Hg} + b$, where m is a coefficient, Hg is the mercury concentration, in nanograms per gram (ng/g), and b is the y-intercept. n , number of samples; R^2 , coefficient of determination; p , probability value; –, no data <, less than]

| Species group ¹ | n | R^2 | y-intercept (b) | | Coefficient (m) | | Length at 50 ng/g (mm) ² | Length at 160 ng/g (mm) ² |
|---|-----|-------|---------------------|--------|---------------------|--------|-------------------------------------|--------------------------------------|
| | | | Value | p | Value | p | | |
| <i>Salvelinus fontinalis</i> (brook trout) | 15 | 0.36 | -17.78 | 0.20 | 0.204 | 0.01 | 245 | 784 |
| <i>Acipenser fulvescens</i> (lake sturgeon) | 3 | 0.52 | 0.61 | 0.99 | 0.051 | 0.33 | – | – |
| <i>Catostomus Catostomus</i> , <i>Moxostoma</i> spp., and <i>C. commersonii</i> (suckers) | 15 | 0.33 | -17.40 | 0.68 | 0.315 | 0.02 | 159 | 508 |
| <i>Perca flavescens</i> (yellow perch) | 6 | 0.21 | 50.21 | 0.40 | 0.449 | 0.20 | – | – |
| <i>Sander vitreus</i> (walleye) | 30 | 0.86 | -516.77 | <0.001 | 1.127 | <0.001 | 503 | 601 |
| <i>Esox lucius</i> (northern pike) | 11 | 0.29 | -136.37 | 0.46 | 0.614 | 0.05 | 81 | 261 |

¹Length data are not available for *Micropterus dolomieu* (smallmouth bass).

²Guideline lengths at 50 and 160 ng/g were calculated only when $p < 0.05$ for the coefficient (slope).



EXPLANATION

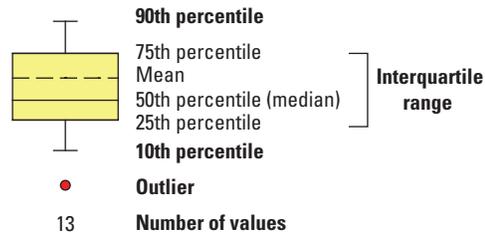


Figure 5. Total mercury concentrations collected in or near Bad River Tribal lands. *A*, tissue from 18 *Rana clamitans* (green frogs) collected in the Bad River during 2012–13; *B*, breast feathers (fresh weight) from 13 *Haliaeetus leucocephalus* (bald eagles) collected at 11 locations on or near Bad River Tribal lands during 2014–16; and *C*, hair from 9 *Lontra canadensis* (North American river otters) collected on or near Bad River Tribal lands on unknown dates.

trout, a species whose diet is primarily insects but can also include small fish. The low total mercury concentrations found in green frog tissue reflects their diet, which consists almost exclusively of insects and other invertebrates (Werner and others, 1995).

Bald Eagle Feathers

Thirteen samples of *Haliaeetus leucocephalus* (bald eagle) breast feathers were collected for analysis of total mercury (fresh weight) concentrations during 2014–16 along several rivers and sloughs at 11 locations on or near to Bad River Tribal lands. These mercury concentrations generally varied over a narrow range from 6,060 to 7,870 ng/g with two exceptions, a sample from the Potato River watershed with a concentration of 18,600 ng/g, and a sample from the center of Long Island with a concentration of 4,120 ng/g. Median mercury concentration is 6,300 ng/g, and the interquartile range is 6,100–7,100 ng/g (fig. 5B). Consideration of typical relations between mercury in feathers and expected concentrations in blood, liver, and brain tissue (Dykstra and others, 2010; Rutkiewicz and others, 2011) suggests that the total mercury concentrations reported here for bald eagles are high relative to those reported for other biota such as fish and green frog in this dataset. However, this observation is consistent with the role of bald eagles as piscivores, compared with those of invertivores and herbivores such as frog and small fish that feed at lower trophic levels.

To describe risk to bald eagles based on these data, the age and size of the eagles and the particular tissue sampled are necessary for quantitative evaluation. Bald eagle age was estimated for only two breast feather samples collected in 2014 and ranged from 7 to 9 weeks. A reasonable assumption based on the stated sampling goal of collecting nestling feathers is that all the breast feathers collected were from young nestlings, but this could not be confirmed based on the pertinent files shared with the USGS. Because tissue total mercury concentrations can increase by an order of magnitude as bald eagles age from nestlings to adults (Rutkiewicz and others, 2011), establishment of age is critical information in risk evaluation. Furthermore, a wide range of effect thresholds have been reported in the literature from about 5,000 ng/g to values as high as 40,000 ng/g in body feathers (Cristol and others, 2012). A variety of health effects are possible, including neurological impairment that affects survival and reproductive success. Ameliorative factors such as blood selenium concentrations and demethylation in the brain are likely to affect neurological outcomes at a given total mercury concentration (Scheuhammer and others, 2008). Considering these broad effects ranges and uncertainty about the ages of the eagles sampled here, the bald eagles sampled were exposed to total mercury levels that may be capable of sublethal neurological effects, but uncertainty about effects thresholds does not allow a definitive statement of health risk for these eagles. Finally, the concentrations measured in breast feathers are broadly similar to those reported previously in other studies in the Great Lakes region (Dykstra and others, 2010; Rutkiewicz and others, 2011).

North American River Otter Hair

Hair samples were collected from nine *Lontra canadensis* (North American river otters) at nine sites on or near Bad River Tribal lands on unknown dates. The median total mercury concentration (wet weight) is 13,300 ng/g, and the interquartile range is 9,880–18,000 ng/g (fig. 5C). These values represent the highest total mercury levels among any of the media or biota tissue reported in this dataset. Mercury concentrations in river otter hair are typically higher but correlated with values measured in muscle, organs, and brains (Strom, 2008). These values are within the range reported for otter hair of 6,500–48,000 ng/g among studies in North America (Crowley and others, 2018) and a range of 3,100–19,000 ng/g reported for otter hair in northern Wisconsin (Strom, 2008). Neurotoxicological effects are not well known for river otter, but a general lowest threshold value of 30,000 ng/g for adverse effects in terrestrial mammals has sometimes been used as a reference (Crowley and others, 2018), which is greater than those measured among all nine samples from the Bad River Tribal lands. Nevertheless, mercury concentrations in the brains of river otter were inversely related to neurochemical enzymes in a study from Canada suggesting that environmentally relevant mercury concentrations may have neurological effects in these mammals (Basu and others, 2007).

Northern Wild Rice

Eleven *Zizania palustris* (northern wild rice) samples were harvested in 2006 from surface waters in 10 locations on or near to Bad River Tribal lands and analyzed for methylmercury. Concentrations ranged from 1.0 to 3.1 ng/g (dry weight), and the median concentration was 1.6 ng/g (fig. 6). These values are much lower than those for total mercury in fish tissue, green frog tissue, bald eagle feathers, and river otter hair reported in this dataset. There are few published mercury values available for northern wild rice to compare to those reported here. Bennett and others (2000) reported a mean of 35 ng/g for total mercury in northern wild rice seed at four locations in northern Wisconsin. A Master of Science thesis reported methylmercury values that ranged from 0.3 to 1.4 ng/g in unfinished (raw) northern wild rice seed from six lakes in northern Minnesota (Mahr, 2015). Methylmercury to total mercury ratios in the Minnesota northern wild rice ranged from 15 to 37 percent, which is higher than ratios typically observed in surface waters but lower than ratios typically observed in fish. Little is known about mercury bioaccumulation in humans from northern wild rice consumption, but given the low levels reported here, little human-health risk from northern wild rice consumption is likely. Additionally, Bennett and others (2000) and Mahr (2015) describe little to no human health risk based on typical consumption levels of northern wild rice in the Great Lakes region.

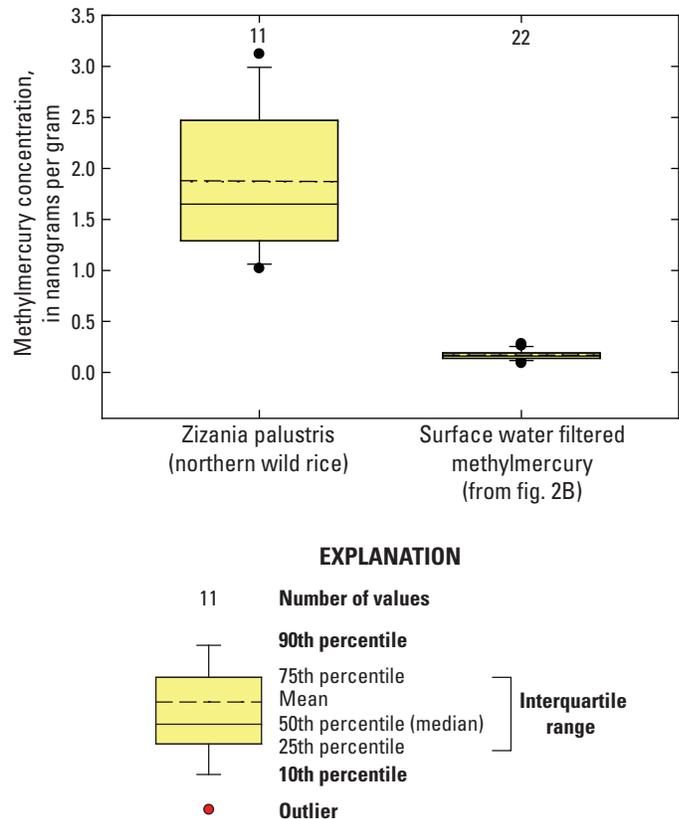


Figure 6. Methylmercury concentrations in 11 *Zizania palustris* (northern wild rice) samples collected in 2006 on or near to Bad River Tribal lands. The filtered methylmercury concentrations measured in surface water and depicted in figure 2B are shown for comparison.

Litterfall

Litterfall samples were collected annually during 2012–18 at a site (WI95, fig. 1) and during 2012 only at a second site (WI01) on Bad River Tribal lands. Forest cover at both sites was deciduous hardwoods with aspen, maple, and ash dominant (Risch and others, 2017). Litterfall was sampled to capture all falling leaves for the season in each of eight collectors, from which the annual dry weight deposition mass was determined on an areal basis as described by Risch and others (2017). Analyses for total mercury concentrations were performed on samples from four of these collectors each year. A mass-weighted sample based on aliquots from the four total mercury samples was analyzed for methylmercury concentration. These measurements are important because litterfall represents the principal mechanism by which atmospherically deposited mercury enters ecosystems and food webs in forested environments (Wang and others, 2016). Annual mean concentrations of total mercury and methylmercury (dry weight) ranged from 24 to 36 ng/g and 0.1 to 0.18 ng/g, respectively, during 2012–18 (figs. 7A and 7B). Annual mean deposition of total mercury and methylmercury ranged from

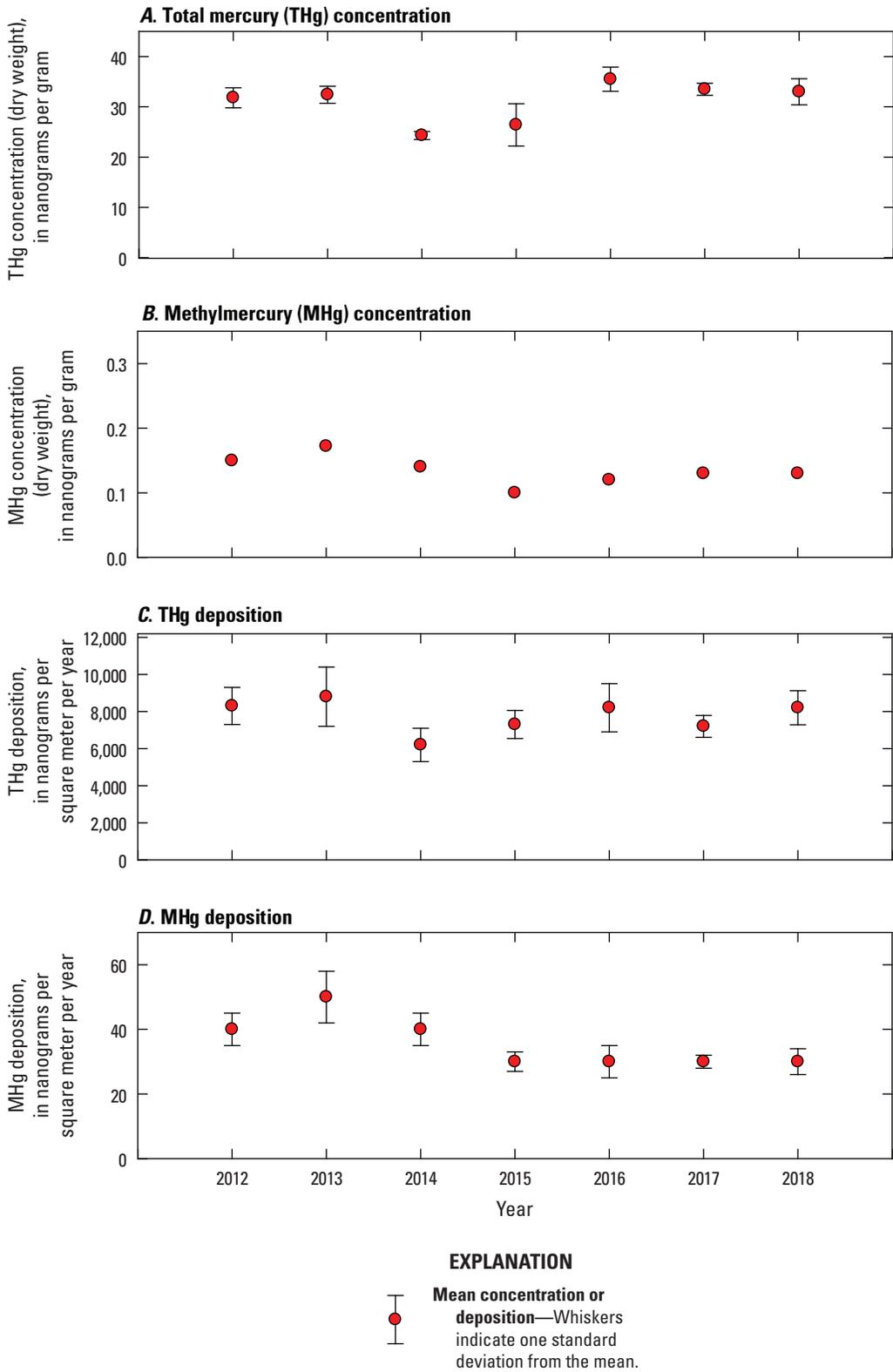


Figure 7. Litterfall mercury concentrations and deposition during 2012–18 at the WI95 site on Bad River Tribal lands. Deposition is calculated as concentration multiplied by mean annual mass per unit area of litterfall. *A*, total mercury concentrations (mean of four collectors); *B*, methylmercury concentrations (one analysis based on weighted mean of sample from four collectors); *C*, total mercury deposition; and *D*, methylmercury deposition.

6,200 to 8,800 nanograms per square meter per year ($[\text{ng}/\text{m}^2]/\text{yr}$) and 30 to 50 $[\text{ng}/\text{m}^2]/\text{yr}$, respectively, over this same period (figs. 7C and 7D). Methylmercury ranged from 0.3 to 1.3 percent of total mercury during 2012–18 and did not show a clear temporal trend pattern.

Although quantitative temporal trend analysis was not performed on these data, qualitative examination of figure 7 suggests no clear temporal pattern in total mercury concentrations or deposition in litterfall at this site. However, the highest methylmercury concentrations and deposition occurred during 2012–14, the first 3 years of data collection, suggesting a broad downward pattern over time. Despite the lack of clearly evident decline in total mercury concentrations and deposition at this Bad River site, Risch and others (2017) in an analysis that included WI95, reported that total mercury deposition has declined in the eastern United States during 2007–14 (temporal patterns in methylmercury deposition were not described). Declines in total mercury deposition are likely driven by decreased mercury emissions in the United States during 2007–14, and a recent analysis indicates that mercury emissions have declined across the United States during 2010–15 despite increased emissions globally (Streets and others, 2019). Furthermore, gaseous elemental mercury concentrations, the form captured by litterfall, are broadly declining across the globe (Lyman and others, 2020). If mercury emissions within the United States and globally decline in the future, a goal of implementing the Minamata Convention on Mercury (United Nations, 2019), lower levels of mercury deposition and similarly lower mercury concentrations in biota are expected in the future (Evers and others, 2016).

Data Gaps and Future Considerations

The collection dates for the data presented in this report and in the accompanying data release (Burns, 2020) are highly varied in frequency and magnitude. Therefore, considering a more systematic and synchronized data collection effort would improve future evaluations. Appropriate frequency should be based on patterns of change in sources, principally atmospheric mercury deposition to Bad River Tribal lands, as well as known response times of different media. Seasonal conditions are also a consideration because variation in air temperature and stream or river discharge may greatly affect concentrations in surface waters. An interval of about 2–3 years is likely to be adequate for evaluating long-term changes in mercury in biota such as fish, river otter, and bald eagles, depending on the life stage of interest (shorter sampling intervals for juveniles). Atmospheric deposition via litterfall and surface-water concentrations are more dynamic and therefore worthy of annual evaluation. Consistent seasonal and flow conditions

are optimal for analysis of mercury species concentrations in surface waters and are an important consideration in the timing of water sample collection. Generally, late summer is an optimal sampling time because flow conditions tend to be low, methylation rates are high, and, therefore, methylmercury concentrations in surface waters are generally high. Late summer sampling provides insight to a “worst-case scenario” for mercury concentrations, which has been shown to be an important driver of bioaccumulation (Riva-Murray and others, 2013).

Data on mercury concentrations in biota such as green frogs, bald eagles, and river otter are helpful to evaluate risk to individual species and to provide a perspective on food web dynamics and trophic transfer. However, from a human-health perspective, prioritizing sampling and measurement of mercury concentrations in fish is suggested, particularly walleye because it is a commonly consumed species with generally high concentrations and is therefore the greatest human-health risk. Another consideration is that species and size classes positioned lower in the food web are likely to reflect changes in mercury sources more rapidly than species at higher trophic levels. This suggests that sampling young-of-year fish such as brook trout or yellow perch or minnows (*Cyprinidae spp.*) may be advantageous for providing early information on the response of aquatic biota to changes in atmospheric mercury deposition.

Collection of annual litterfall for mercury analysis provides information on the major source of atmospheric mercury deposition to ecosystems on Bad River Tribal lands. Annual evaluation of litterfall mercury deposition when combined with data on mercury in precipitation from two nearby sites (WI08 and WI36) that are part of the National Atmospheric Deposition Program’s Mercury Deposition Network (National Atmospheric Deposition Program, 2020) can be used to evaluate how mercury sources are responding to patterns of emissions reflecting air quality policy implementation within the United States and globally.

Measurement of methylmercury concentrations in surface waters is suggested as a priority for annual sampling in addition to litterfall. This suggestion is based on recognition that methylmercury is an important immediate mercury source to aquatic biota that bioaccumulates in food webs and is likely to drive patterns in fish and piscivores. The low concentrations of particulate methylmercury relative to those of filtered methylmercury suggests that analysis of unfiltered samples would be adequate for environmental interpretation. Temporal patterns in methylmercury concentrations in surface waters do not always directly parallel those of atmospheric mercury deposition due to climatic and other factors that affect the rates of methylation (production of methylmercury by bacteria) and demethylation (loss of methylmercury by bacterial and other processes).

Summary

A dataset that includes measurements of mercury species concentrations in surface waters, bed sediment, fish tissue, *Rana clamitans* (green frog) tissue, *Haliaeetus leucocephalus* (bald eagle) feathers, *Lontra canadensis* (North American river otter) hair, *Zizania palustris* (northern wild rice), and litterfall was compiled and published by the U.S. Geological Survey based on samples collected within or near to Bad River Tribal lands in northern Wisconsin. This report describes the datasets, makes comparisons to similar data from the upper Great Lakes region and elsewhere, and describes health risks relative to known guidelines for humans and animals. Highlights of these data are as follows:

- Filtered total mercury and methylmercury are the dominant forms in surface waters, greatly exceeding the concentrations of particulate forms. These filtered forms are strongly related to dissolved organic carbon concentrations, particularly filtered total mercury. Median filtered methylmercury was 10.9 percent of filtered total mercury among samples in this dataset reflecting relatively high methylation potential that is not unusual among other reported values in the northern Wisconsin and upper Great Lakes regions.
- Median total mercury concentration in bed sediment was 20 nanograms per gram (ng/g), which is similar to other values reported for streams in northern Wisconsin.
- Most fish tissue total mercury concentrations exceeded 50 ng/g (exceptions were *Salvelinus fontinalis* [brook trout] and *Catostomidae* spp. [suckers]), which is a Wisconsin State guideline for consumption of no more than one fish meal per week by children less than 15 years of age and women of child-bearing age. *Sander vitreus* (walleye) and *Esox lucius* (northern pike) were the only fish species for which most samples exceeded a 160 ng/g general adult guideline for consumption of no more than one fish meal per week.
- Walleye consumption poses the greatest human health risk because of high mercury concentrations (median=168 ng/g) and previously demonstrated high rates of consumption among Lake Superior native Chippewa individuals.
- Green frog tissue had a median mercury concentration of 24.0 ng/g, and values were low relative to those of other animals in this dataset, reflecting a diet dominated by insects and other invertebrates.
- Median mercury concentration (fresh weight) in bald eagle feathers was 6,300 ng/g, a value that may be capable of causing sublethal health effects, but this conclusion is tentative reflecting high uncertainty in health effects thresholds.
- North American river otter hair had a median mercury concentration (dry weight) of 13,300 ng/g, the highest among the tissues of any animal reported in this dataset, reflecting a piscivorous diet. These levels are less than those believed to be correlated with neurological effects in river otter, but health effects thresholds are highly uncertain.
- Median methylmercury concentration in wild rice was 1.6 ng/g, and measured values are believed to pose little risk to humans based on typical human consumption patterns.
- Litterfall is the principal atmospheric source of mercury to forested ecosystems such as Bad River Tribal lands. Annual collections from 2012 to 2018 do not reveal a downward trend in total mercury deposition despite the identification of broad downward trends in litterfall and other mercury indicators across eastern North America.

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Glossary

bioaccumulation The accumulation of a substance in an organism over time.

biomagnification The process by which the concentration of a substance increases in the tissues of organisms as it travels up the food chain.

demethylation The process by which methylmercury is converted by bacteria to inorganic mercury through removal of a methyl group (CH_3).

herbivore An animal that feeds primarily or exclusively on plants.

invertivore An animal that feeds primarily or exclusively on organisms that lack a backbone such as insects, worms, and snails.

litterfall Plant material such as leaves and needles that falls to the ground. Annual litterfall is the total mass of plant material that falls to the ground in a year.

methylation The process by which mercury is converted by bacteria from its inorganic form to its organic form and is associated with methyl groups (CH_3).

methylmercury Any of several neurotoxic organometallic compounds, formed from metallic mercury by the action of microorganisms and capable of entering and bioaccumulating in food webs.

piscivore An animal that feeds primarily or exclusively on fish.

trophic level or position The level or position of an organism within a food web. An organism that eats plants is a primary consumer and an animal that eats a primary consumer is a secondary consumer, and so on.

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