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Mercury Temporal Trends in Top Predator Fish of the Laurentian Great Lakes from 2004 to 2015: Are Concentrations Still Decreasing?

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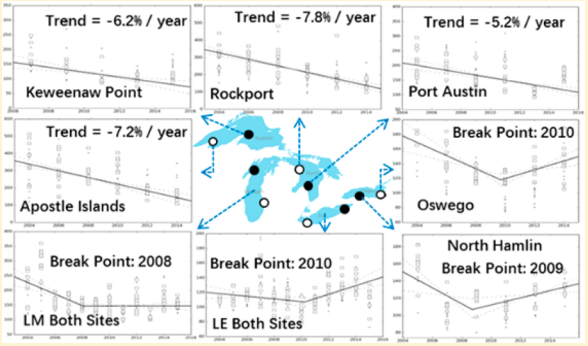
Supporting Information

ABSTRACT: Mercury (Hg) concentration trends in top predator fish (lake trout and walleye) of the Great Lakes (GL) from 2004 to 2015 were determined by Kendall−Theil robust regression with a cluster-based age normalization method to control for the effect of changes in lake trophic status. When data from the GLs (except Lake Erie) are combined, a significant decreasing trend in the lake trout Hg concentrations was found between 2004 and 2015 with an annual decrease of 4.1% per year, consistent with the decline in regional atmospheric Hg emissions and water Hg concentrations. However, a breakpoint was detected with a significant decreasing slope (−8.1% per year) before the breakpoint (2010), and no trend after the breakpoint. When the lakes are examined individually, Lakes Superior and Huron, which are dominated by atmospheric Hg inputs and are more likely than the lower lakes to respond to declining emissions from areas surrounding the GL, have significant decreasing trends with rates between 5.2 and 7.8% per year from 2004 to 2015. These declining trends appear to be driven by decreasing regional atmospheric Hg emissions although they may be partly counterbalanced by other factors, including increasing local emissions, food web changes, eutrophication, and responses to global climate change. Lakes Michigan, Erie and Ontario may have been more impacted by these other factors and their trends changed from decreasing to non-decreasing or increasing in recent years.



INTRODUCTION

The Great Lakes watershed is a major water resource and fishery for North America.[1] For this ecosystem, mercury (Hg) pollution is recognized as a serious environmental and health concern.[2−4] Hg can be transformed among elemental, ionic, and organic species when it cycles within and among air, water, land, and the biosphere.[5] Once transformed into methylmercury (MeHg) in aquatic ecosystems, it becomes more toxic, highly bioaccumulative,[6,7] and a potential threat to aquatic ecosystems and to human health through fish consumption.[8,9] Currently, there are more than 3900 fish consumption advisories for Hg in the United States (US), including in the Great Lakes (GL),[10,11] and Hg is one of the major contaminants causing restriction on consuming fish.[12] EPA and FDA issued updated draft advice on fish consumption in June 2014, which suggests that pregnant women and young children should eat fish with lower mercury concentration to gain important developmental and health benefits.[13] Hg is one of the analytes of Great Lakes Fish Monitoring and Surveillance Program (GLFMSP), which monitors spatiotemporal trends of bioaccumulative chemicals in the GL using top predator fish as biomonitors.[2]

Atmospheric Hg emissions and subsequent deposition can be strongly correlated with Hg levels in aquatic biota and fish[14−16] and are likely the main contemporary source of Hg to the GL[17−24] as the direct discharges of Hg containing effluents (e.g., chlor-alkali plants) were largely eliminated in the early 1990s.[25,26] Atmospheric Hg emissions in the GL region declined by approximately 50% between 1990 and 2005, largely due to controls of Hg emissions through state, regional, binational, and voluntary actions.[14,27,28] These and subsequent reductions contributed to observed decreases in atmospheric Hg concentrations from 2002 to 2010.[29] However, the benefits of these reductions could be offset by increasing global Hg emissions which have been largely due to increases from Asian countries.[30]

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The trophic status of a lake, fish species, size, and age are important determinants of fish Hg concentrations.[31−33] For example, positive correlations have been reported between Hg concentration and fish size or age of a given species;[6,34] however, consumption of prey with a higher caloric content could cause a lower Hg concentration in predator fish due to growth dilution.[35] These variables need to be analyzed and then controlled to better determine concentration trends and allow meaningful lake-to-lake comparisons.[32,36,37] Fish growth rate has varied significantly in some GL ecosystems because of changing lake-specific food webs caused primarily by invasive species and eutrophication.[38−40] Invasive species can also affect the methylation rate in a lake. For example, increased MeHg concentrations were found in nearshore regions of Lake Michigan (LM) with prominent invasive mussel infestations and associated filamentous benthic green algae.[41]

Other factors related to eutrophication and climate change can also affect fish Hg levels. Because the methylation process occurs primarily in organic-rich particles (in the water column) or surface sediment,[42,43] eutrophication can accelerate the production of MeHg by increasing organic carbon loading and the extent of anoxic conditions favorable for methylating bacteria. Hg methylation rates also increase with sediment and water column temperature, leading to increasing bioaccumulation,[44,45] and so a warming climate can impact MeHg concentrations in fish. Climate change may also alter the Hg wet deposition and tributary runoff inputs to the lakes due to changes in precipitation depth.[18] A warmer climate can also increase lake sediment resuspension events due to increased and more intense storms and decreased ice cover, causing the release of Hg accumulated in sediment.[8,42,46]

In this study, Hg concentrations and fish age in top predator fish (lake trout for all of the lakes except for Lake Erie (LE), where walleye are the top predator fish) were measured as part of the GLFMSP from 2004 to 2015. Hg concentration trends within and among lakes were determined using nonparametric Kendall's tau test and Kendall−Theil robust regression after age normalization using a cluster-based method to evaluate the potential impacts of changes in atmospheric Hg inputs, regional Hg emissions, eutrophication, and climate change.

METHODS

Sample Collection and Total Hg Analysis. Lake trout (*Salvelinus namaycush*) samples (600−700 mm) were collected in Lakes Huron (LH), Michigan (LM), Ontario (LO), and Superior (LS). Walleye (*Sander vitreus*) samples (400−500 mm) were collected in LE. Fifty fish samples were collected annually and grouped into ten composites (based on size similarity before 2012 and based on age similarity after 2012 as a new aging technique became available) from two sampling sites for each lake, one site for even years (shallow site), and the other one for odd years (deep site). Note that all the sites are in offshore water ecosystems (both industrial area and non-industrial areas in each lake).[47,48] Composites were kept frozen before being analyzed with a DMA-80 Direct Mercury Analyzer (Milestone Srl, Bergamo, Italy) based on US EPA Method 7473. Other sample collection, preparation, and analysis details are described in the Supporting Information and by Zananski et al.[2]

Fish Age Analysis. Fish ages were determined by otoliths, fin clips, coded wire tags (CWT), and scales prior to 2012. A maxillae estimation method, developed at the Michigan Department of Natural Resources (MDNR), was added to the aging techniques and scales were dropped as a method in 2012. A collaboration between the MDNR and the GLFMSP to refine the maxillae estimation between laboratories has increased the accuracy and speed for GLFMSP sample aging and allowed samples to be composited according to a known age instead of an assumed age based on length.[49] Ages used in this research were an average number of these methods. Significant increasing annualized age trends (%/yr) were found in LH (7.2% even years; 7.4% odd years), LM (4.8% even years), and LS sites (8.3% even years; 6.9% odd years). Additional details regarding the fish age analysis are presented in the Supporting Information.

Age Normalization Method. The correlations between age and Hg concentration were found to be nonlinear and year-dependent (Figures 1b and S4). These results are unlike previous reported results that could be described using linear or logarithmic equations.[6,34] Therefore, traditional age normalization approaches such as the general linear model or analysis of covariance (ANCOVA)[6,14,33,50−53] were not appropriate. To normalize fish Hg concentration to a consistent age so that all the fish concentrations used for trends analysis likely resulted from the same Hg exposure time, sampling years with similar bioaccumulation patterns were grouped together (clustered) before normalization as follows: (1) An equation was used to describe the annual bioaccumulation patterns; in this case, a

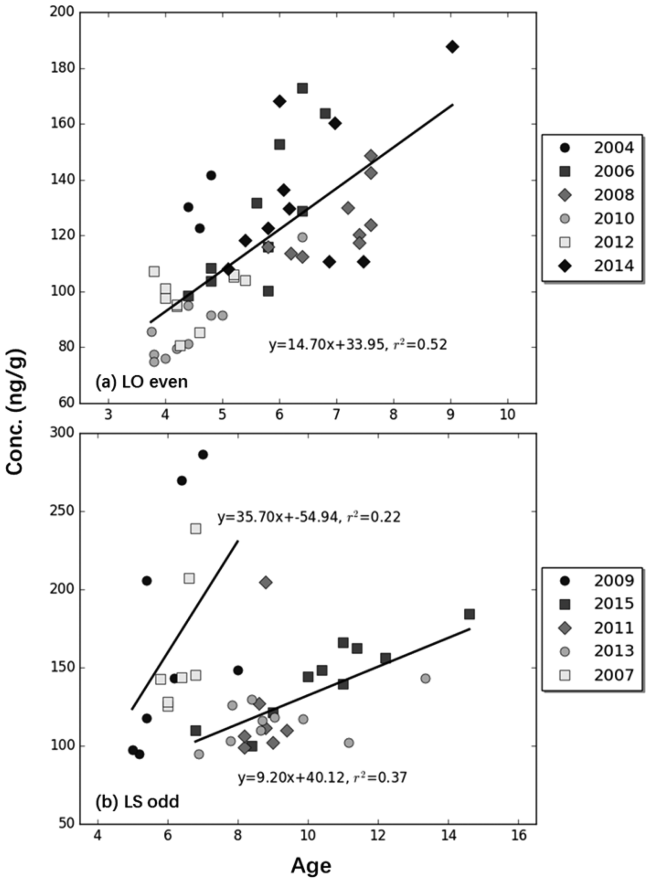

Figure 1. Bioaccumulation patterns of (a) Lake Ontario even years with one cluster and (b) Lake Superior odd years with multiple clusters (2007 and 2009 are in the same cluster, and other years are in the other cluster). The equations shown were obtained from corresponding clusters and used for age normalization. Clustering results for other sites are presented in the Supporting Information.

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linear model was used because it yielded the best fits to the data with an average r^2 in each year of 0.35 ranging from 0−0.85. (2) The distance between each year's bioaccumulation pattern was calculated based on the equations obtained in step 1; the distance was determined by the average distance of each data point in one group to the other regression line (this approach considers both the distance of data points between the groups and the similarity of the regression lines). (3) Hierarchical clustering was performed to define the clusters based on the distances obtained in step 2; as hierarchical clustering will generate new group combinations, the distances among new groups is recalculated in each step of hierarchical clustering. (4) Linear regression equations were calculated for each cluster obtained in step 3. (5) Hg concentrations were normalized to an average age (7.0 years) based on the equations obtained in step 4. A more detailed discussion and the algorithms used are presented in the Supporting Information.

Trend Analysis. The nonparametric Kendall's tau test and Kendall−Theil robust line (Sen's slope) were used for trends and breakpoint analysis using SPSS 22 (2014 IBM Corporation) and KTRLine software developed by the US Geological Survey (USGS).[54−62] Age data were only available for fish from 2004 to present; therefore, earlier fish Hg data (1999−2003) were not included in this analysis. An overall trend analysis for all the lake trout data following age normalization (2004−2015) was performed. In this analysis, all lake trout data among sites and lakes (except Erie) were combined to develop a regional temporal trend. LE was not included in this regional trend analysis because a different fish species was collected during this period. The changes in fish Hg concentrations are generally smooth; however, a breakpoint analysis can be used when times between sampling periods are long. Trends were also analyzed lake-by-lake with the shallow and deep sites analyzed separately if the age normalized concentrations had significant differences between the sites based on a rank sum test. A more detailed discussion of the trend analysis methodology is presented in the Supporting Information.

Hg Emission Inventory. US Hg point-source air emissions data were obtained from the National Emissions Inventory (NEI) (1999−2014)[63] and the Toxic Release Inventory (TRI) (2000−2015).[64] For Canada, point-source Hg air emissions data from the National Pollutant Release Inventory (NPRI) were used (2000−2015).[65] Additional information regarding these emissions data sets is provided in the Supporting Information.

RESULTS AND DISCUSSION

Age Normalization. Age normalization was used to control for biases in concentration trends caused by the differences in ages among the sampled fish. As shown in Figures 1 and S4, the clustering results for each site fell into one or multiple clusters. One cluster was found for the LO and LM even years and LE and LO odd years, indicating that there was no significant change in the Hg bioaccumulation rates at those sites over time. Multiple clusters were found for other sites, suggesting that changes in Hg bioaccumulation rates between 2004 and 2015 were significant. Detailed age normalization clustering results, including r^2 values for each lake, are presented in Figure S4 and Table S1. The LM odd years and all of the sites in LH and LS have multiple clusters with clear patterns: (1) the clusters are separated by breakpoint year, which means that Hg bioaccumulation rate in lake trout changed between the early years and recent years, and (2) the slope and intercept of regression lines have decreased in recent years. These results indicate that the recently sampled fish in the upper lakes (LH and LS) have both lower Hg concentrations (smaller intercepts) and less Hg bioaccumulated over time (shallower slopes), indicating that the recent fish have lower Hg concentrations at the same age when compared to those of the earlier samples. Note that LE even years do not have a breakpoint year, but do have multiple clusters. The change in the Hg bioaccumulation pattern can be caused by changes in Hg inputs[15] and/or changes in the food web structure and other ecosystem characteristics.[35,41]

Overall Trend. A significant decreasing trend in lake trout Hg concentrations was found between 2004 and 2015 (Kendall's tau = −0.32, $p < 0.01$) in the GL (excluding LE) with a Kendall−Theil regression annual decrease of 4.1% per year (Figure 2a). If age normalization is not applied, the slope is approximately halved (−2.0% per year) (Table S2). Similar decreasing trends have also been reported over longer time intervals (1976−2009) in LS, LH, and LO.[2,61] If breakpoint analysis is used, a breakpoint was detected with a steeper decreasing slope (8.1% per year) before the breakpoint (2004−

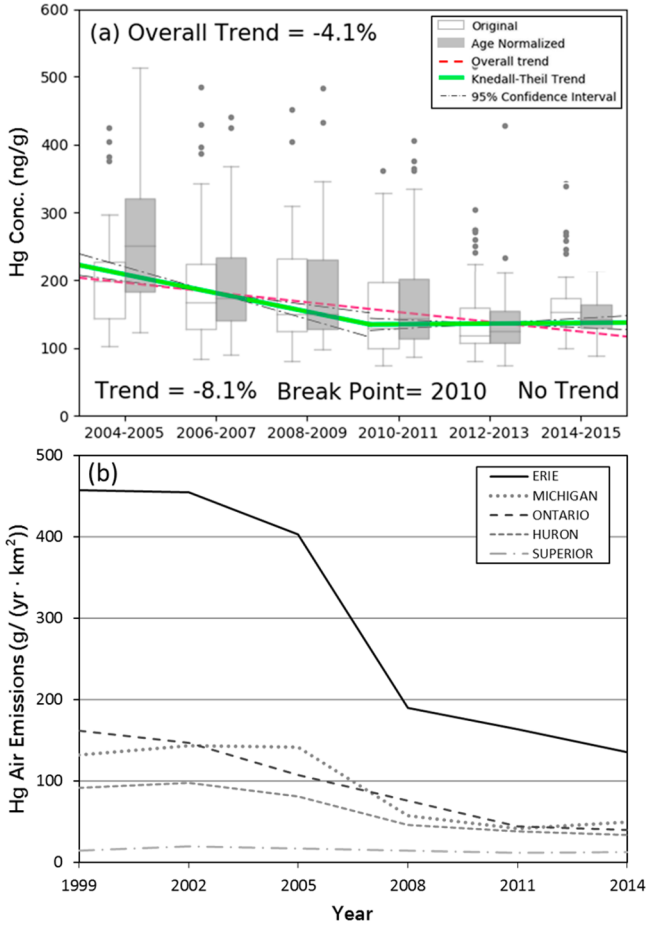

Figure 2. Overall Kendall−Theil trend and trends with breakpoint of fish Hg after age normalization in GL excluding Lake Erie from 2004 to 2015 (a) and anthropogenic point-source Hg air emissions within 200 km of each lake from 2000 to 2014 (b). The upper and lower 95% confidence intervals of the first segment for two segment trends are −5.2 and −11.4% per year, while no trend was determined for the second segment. The upper and lower 95% confidence intervals of the overall trend are −3.2 and −5.1% per year (which are not plotted in the figure).

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Table 1. Lake Trends with Age Normalization from 2004 to 2015[a]

lake	Kendall's tau Coefficient[b]	Kendall–Theil trend (percentage/year)[c]	break point[d]	trend before and after break point (percentage/year)[c]
Erie both sites	**+0.16, p = 0.01**	**+1.2 (+0.3, +2.4)**	V, 2010	−1.6 (−3.7, +0.3); **+5.0 (+2.8, +7.7)**
Ontario shallow site	−0.10, p = 0.28	−0.67 (−2.3, +0.8)	V, 2010	**-6.7 (−9.6, −3.6)**; **+4.6 (+1.6, +7.3)**
Ontario deep site	+0.01, p = 0.93	+0.1 (−1.7, +1.5)	V, 2009	**−7.5 (−11.8, −1.7)**; **+3.3 (+0.8, +5.2)**
Michigan both sites	**−0.29, p < 0.01**	**−3.9 (−5.7, −2.2)**	_, 2008	**−11.7 (−15.9, −7.4)**; +0.0 (−1.9, +1.9)
Huron shallow site	**−0.63, p < 0.01**	**−7.8 (−9.4, −6.3)**	NB	
Huron deep site	**−0.42, p < 0.01**	**−5.2 (−7.1, −3.5)**	NB	
Superior shallow site	**−0.53, p < 0.01**	**−7.2 (−9.3, −5.4)**	NB	
Superior deep site	**−0.38, p < 0.01**	**−6.2 (−9.7, −3.4)**	NB	
overall	**−0.32, p < 0.01**	**−4.1 (−3.2, −5.1)**	_, 2010	**−8.1 (−5.2, −11.4)**; +0.2 (−2.0, +2.3)

[a]Results in bold and with an underline indicate **strong** (p < 0.05) and **very strong** (p < 0.01) statistical power, respectively [b]Kendall's tau coefficient (from −1 to 1) indicating the slope of the trend. [c]The two numbers in parentheses indicate lower 95 and upper 95% slopes. [d]V, decreasing then increasing; _, increasing then no trend; NB, no break point.

2010) and no trend (Kendall's tau = 0.01, p = 0.87) after the breakpoint (2010–2015). Similar absences of trends were also reported in the GLs (for example in LO) in recent years.[4,14]

Individual Lake Trends. For LE and LM, sites within each lake were combined before the trends analysis as they were not significantly different (t test result shown in Table S3). For the other lakes, sites were treated individually. Fish Hg concentrations from 2004 to 2015 have statistically significant decreasing trends (p < 0.01) with large slopes from −3.9 to −7.8% per year in LH, LM, and LS, a significant increasing trend of 1.2% per year (Kendall's tau = +0.16, p = 0.01) in LE, and no statistically significant trend in LO (Table 1, Figures S5 and S6). Using breakpoint analysis, a two-segment pattern, decreasing then increasing, with a breakpoint between 2009 and 2010 was detected for LE and LO. A breakpoint (2008) was also detected in LM. However, no significant trend was detected after the break (Kendall's tau = 0.03, p = 0.75). The individual lake rank-sum test and trends results without age normalization are presented in the Supporting Information.

Regional Hg Emissions. Temporal trends in anthropogenic Hg air emissions within 200 km of each lake from 2000 to 2014 were determined by aggregating NEI and NPRI emissions data and normalizing by lake areas (Figure 2b). These GL regional Hg emission trends have a pattern similar to that of the overall fish Hg trend, and the decreased emissions over this period were also consistent with a decreasing regional atmospheric Hg concentration trend observed from 2002 to 2010.[29,66] However, the emissions reductions appear to have slowed in recent years.

The annual change in spatially averaged Hg emissions in the GL region for 2000–2008 and 2008–2014 were compared by aggregating the NEI and NPRI emissions data onto a 1 × 1° grid (Figure 3). In some locations, particularly in the lower GL region, the emissions have leveled off and even increased. Emission increases in the vicinity of a given lake can have a disproportionate effect as plumes are more concentrated in the near-field than further downwind. SO_2 emissions from power plants, likely associated with Hg emissions,[21] have shown similar spatiotemporal patterns (Figures S14 and S15) with significantly slower emissions reductions in the GL region in recent years. It is plausible the time trends observed in the Hg and SO_2 emissions data (i.e., larger decreases up through ~2009 with smaller decreases and even some increases in later years) is at least due in part to decreased industrial and other activities in the region during the 2008–2009 economic recession followed by increasing activity in the following

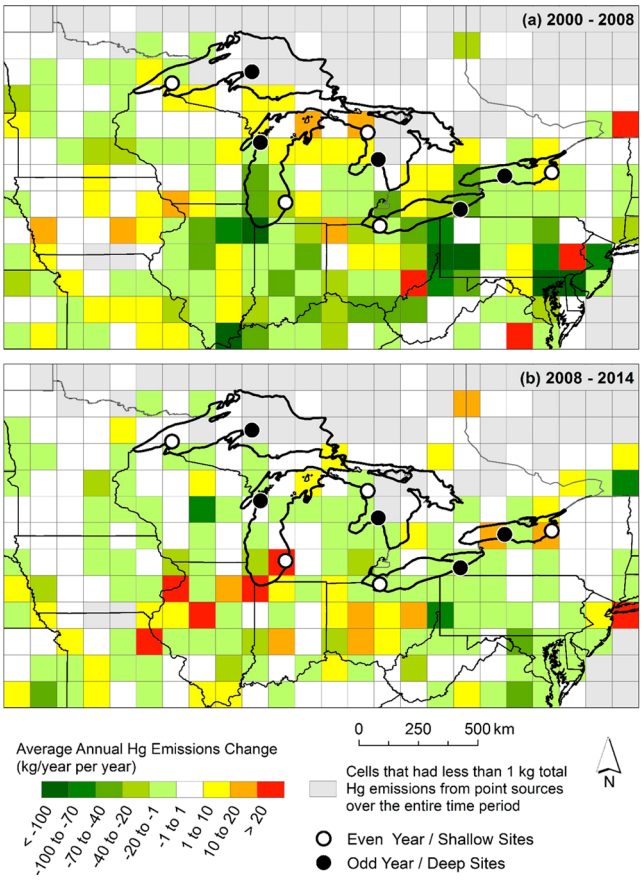

Figure 3. Gridded average annual mercury emissions change (kg/yr per year) in 1 × 1° grid cells from earlier period, 2000–2008 (a), and recent period, 2008–2014 (b), based on NEI and NPRI point source emissions data.

years as the economy recovered. Other related Hg and SO_2 air emission results are presented in the Supporting Information.

Atmospheric Inputs. Atmospheric inputs to the GL are important for many contaminants.[14–16,22–24,67,68] For example, significant concentrations of toxaphene, which was only used sparingly in the GL basin, are observed in LS fish, the most remote of the GL, demonstrating it has a significant connection to the atmosphere.[69] Fish Hg (MeHg), which is estimated to have a relatively short half-life in at least some fish (about 3 months),[70] has also been closely linked (and rapidly responsive to) atmospheric inputs,[71] although it is well-known that it has a

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Environ. Sci. Technol. 2017, 51, 7386–7394

complex set of loading and transformation pathways. For example: (1) in Massachusetts, there was a strong correlation between declines in fish Hg concentration and regional air Hg emission reductions (1990s−2008).[15] (2) There is experimental evidence of a linear relationship between atmospheric Hg loading and MeHg accumulated in aquatic biota.[16] (3) Aqueous Hg, which mostly derives from atmospheric deposition, was found to be an important Hg source for fish using ^{202}Hg spiked into a temperate lake.[72] (4) Hg in GL fish has been found to be more isotopically similar to Hg in atmospheric deposition than to Hg in GL sediments or other sources.[8]

An overall decreasing trend in fish Hg concentrations is consistent with the long-term regional Hg emission reductions that began in 1990. The significant decreasing trends in fish Hg concentrations in the early years of this study with recently nondecreasing trends is consistent with the decreased aqueous Hg concentrations in the GLs (before 2009),[73] and the sharp regional Hg emissions decline before ∼2010 and relatively constant Hg emissions after 2010, as shown in Figure 2b. Although there are significant uncertainties in estimates of the total Hg deposition flux to the GL for any given year and little information about time trends of this deposition, there are a limited number of wet deposition measurements made in the GL basin as part of the Mercury Deposition Network (MDN) with sampling periods consistent with the time period of this study (13 sites). Overall, those data suggest there has been an increase in Hg wet deposition flux in the GL region in recent years driven primarily by an increasing amount of rainfall which counterbalances a general decrease in Hg concentration in rain (details are presented in Supporting Information). The decreasing trend reversal may also be influenced by the transport of increasing Hg emissions from Asia,[18,25,74] in particular from China, which was found to be second largest anthropogenic Hg contributor to the GL in recent global transport modeling.[75]

Hg emissions in the region have been reduced significantly, and future reductions may be more modest. Thus, the relationship between regional Hg emissions and fish Hg concentrations may weaken. The slowed decrease in Hg concentrations suggests that reductions in regional atmospheric Hg emissions are becoming less important in controlling Hg concentrations in fish. Other factors such as local Hg emission changes, eutrophication, invasive species, and climate change are likely becoming more important. Although the influence from increasing global Hg emissions is largely unknown, the current increases in fish Hg concentration in the lower GLs are likely not the result of these global Hg emission increases, as the upper lakes − which are more sensitive to global inputs because they have lower loading rates with a smaller fraction from regional emissions,[75] less legacy mercury, and fewer nonatmospheric sources − have clear decreasing trends.

Local Impacts. The different trends found for individual lakes are likely due to changes in Hg inputs or in-lake processes because the impact of trophic status change is at least partially controlled by age normalization. The consistent bioaccumulation rate in the lower lakes suggests that overall MeHg inputs to fish are relatively constant and that increasing local Hg input or increased methylation efficiency may be offsetting the impact of regional Hg emission declines. Although the five lakes are in relatively close spatial proximity, the Hg inputs into individual lakes are different. The atmospheric deposition impacts from industrial areas in the upper Midwest and Northeast have been estimated to be relatively high for the lower lakes (LE, LM, and LO).[25,75−80] These lakes also have aggregated airshed Hg emissions (Figures S8−9) higher than those of the upper lakes, and several Hg emission sources near these lakes have increased in recent years (Figures 3, S10−13). In addition, LE and LO may be more sensitive to changing Hg inputs due to their smaller surface areas, shallower depth, and shorter water residence times.[81,82] Although most GLs (except LH as no available MDN sites in the LH basin) have increasing wet deposition flux from 2004 to 2015 (Figure S16), the driving force for the increasing fluxes are different. The increasing Hg flux in LS and LM was mainly caused by an increasing amount of precipitation as the concentrations in precipitation are decreasing. In contrast, Hg concentrations in precipitation near LE and LO are increasing. Note that areas near LE have the most significant increasing Hg wet deposition flux as the amount of and concentration in precipitation are increasing.

LS and LH, with significant decreasing trends in fish Hg (also with lower bioaccumulation rates in recent years as shown in Figures 1 and S4), have few local emission sources. However, their main Hg input is still likely atmospheric deposition. They have relatively large surface areas and long water residence times,[2,65,83] and mass balances have suggested 75% of the Hg input to LS and LM came from atmospheric deposition.[67,84] This result is consistent with recent findings using isotopic signatures[8] that the largest Hg contribution to sediments is from atmospheric deposition (LS (59%) and LH (64%)). The decreasing trends seen in these lakes suggest that decreased atmospheric emissions from US and Canadian sources since the early 1990s have been more influential in affecting the fish Hg concentration trends in upper lakes region than the increasing anthropogenic Hg emissions elsewhere in the world.

Other Factors. Climate change, eutrophication, and the effects of invasive species can also be important for the changes in the trends seen in the recent years for the lower lakes as these processes can provide additional Hg inputs or impact methylation rates.[85] The large amount of Hg accumulated in GLs sediment (also with relatively high Hg concentrations in Lake St. Clair[86]), in part from local chlor-alkali production, could be more available due to increased resuspension of sediments caused by increasing storms and less ice cover driven by the warmer climate and become a more important Hg source to these lakes.[23,46] Although the Great Lakes ice cover data set is relatively short (1973 to present), there appears to be a downward trend.[87] Climate change can also increase Hg wet deposition inputs by increasing precipitation depth (as mentioned above) even when atmospheric concentrations are decreasing.

Methylation occurs in organic-rich sediments, mediated by microorganisms such as anaerobic sulfate-reducing bacteria (SRB), iron reducers (FeRP), and methanogens (MPA), as well as in the water column, associated with periphyton and lactate-utilizing bacteria on settling organic-rich particles.[42,88−90] The rate and extent of this transformation is an important driver of Hg bioaccumulation in food webs. Methylation is a biological process that occurs only under anoxic conditions. It can be accelerated by higher temperatures and eutrophic conditions[44,91] and by effects related to invasive species.[41] Higher temperatures can increase the Hg uptake rate of aquatic organisms from the water column.[45,85,92] Average surface water temperatures have increased slightly since 1995 for each of the Great Lakes driven by warming during the spring and summer months. These trends could relate in part to an earlier melting of winter ice.[93] Increasing temperatures can be important to

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methylation rates directly and can also decrease the dissolved oxygen concentrations (important for anaerobic microbe growth).[42,89] The increased MeHg production and concentration in aquatic systems can also be related to eutrophication, which can be important in the lower lakes.[40] Eutrophication can increase methylation rates by either changing sediment microbial metabolism or increasing the organic carbon loading in sediment, and expanding anoxic zones[94−96] though the impact of eutrophication to methylation rate can vary depending on characteristics of the lake.[97,98] The shift in fish prey source from offshore to nearshore (which contains more Hg) caused by eutrophication and invasive species can also be important for fish Hg concentrations.[41,99] The impact of eutrophication and invasive species has been relatively significant in the lower lakes (LM, LE, and LO) in recent years, and as a result and in combination with other factors mentioned above, the lakes could have increased net methylation rates. The increased influence of these factors, coupled with the significant slow-down in the rate of local and regional emissions reductions over recent years (and in some cases, an apparent increase in emissions), may at least partially explain the change in fish−Hg trends in these lakes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00982.

Additional details on sampling site locations, trends analysis procedures, total fish Hg concentrations, Hg and SO_2 emissions, and Hg wet deposition (PDF)

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Notes

The authors declare no competing financial interest.

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