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Factors Affecting Mercury Stable Isotopic Distribution in Piscivorous Fish of the Laurentian Great Lakes

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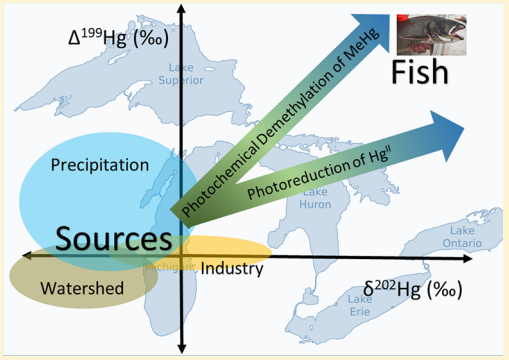
Supporting Information

ABSTRACT: Identifying the sources of methylmercury (MeHg) and tracing the transformations of mercury (Hg) in the aquatic food web are important components of effective strategies for managing current and legacy Hg sources. In our previous work, we measured stable isotopes of Hg (δ^{202}Hg, Δ^{199}Hg, and Δ^{200}Hg) in the Laurentian Great Lakes and estimated source contributions of Hg to bottom sediment. Here, we identify isotopically distinct Hg signatures for Great Lakes trout (*Salvelinus namaycush*) and walleye (*Sander vitreus*), driven by both food-web and water-quality characteristics. Fish contain high values for odd-isotope mass independent fractionation (MIF) with averages ranging from 2.50 (western Lake Erie) to 6.18‰ (Lake Superior) in Δ^{199}Hg. The large range in odd-MIF reflects variability in the depth of the euphotic zone, where Hg is most likely incorporated into the food web. Even-isotope MIF (Δ^{200}Hg), a potential tracer for Hg from precipitation, appears both disconnected from lake sedimentary sources and comparable in fish among the five lakes. We suggest that similar to the open ocean, water-column methylation also occurs in the Great Lakes, possibly transforming recently deposited atmospheric Hg deposition. We conclude that the degree of photochemical processing of Hg is controlled by phytoplankton uptake rather than by dissolved organic carbon quantity among lakes.



INTRODUCTION

Despite reduction in contaminant point-source inputs since the 1970s, fish consumption advisories remain in the Laurentian Great Lakes. In an ongoing effort to address beneficial use impairments in the Great Lakes Areas of Concern (AOC), water resource managers continue to develop tools that address water quality, the range of trophic status, the disparate sources of contaminants, and the magnitude of watershed inputs versus those from direct atmospheric deposition.[1−3] Variations in land use may lead to differing rates of contaminant loading, which, in turn, can influence contaminant cycling in lakes. In addition, estuaries and many AOCs are typically zones of elevated primary production, thus creating an entry point for watershed-derived and locally discharged contaminants to the aquatic food web. The Great Lakes span a wide range in trophic status, from hypereutrophic in western Lake Erie to oligotrophic in offshore regions of Lakes Superior, Michigan, and Huron.[1] The drivers for trophic status are similar to drivers for contaminant levels in lakes. These include land use, nutrient loading, and agricultural and urban influences.

Sources of mercury (Hg) in the Great Lakes include local industrial discharge, watershed runoff, and direct atmospheric deposition,[4] but the reactivity of the mercury derived from these sources susceptible to bioaccumulation is dependent on microbially mediated conversion of inorganic Hg to methylmercury (MeHg).[5] In the Great Lakes, microbial Hg methylation is typically assumed to occur in anoxic sediment, wetlands, and in nearshore regions such as the growth and depositional zones of *Cladophora*.[5−8] The identification of sources of MeHg to biota is crucial to understanding why pelagic fish in the Great Lakes are elevated in MeHg. The offshore regions of the Great Lakes exhibit some of the lowest aqueous MeHg concentrations reported, often rivaling the open oceans.[6,9−11]

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The ability to quantify the reactivity of Hg from specific sources susceptible to methylation is a key to contaminant management. Analyses of natural isotopic variations of Hg stable isotopes have been useful for this purpose.[12] Measuring subtle changes in natural isotopic Hg ratios using high-resolution multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) allows researchers to discriminate among Hg sources and better understand the physical, chemical, biological, and photochemical processes affecting Hg cycling.[12]

Processes driven by kinetics, or as the result of equilibrium exchange, are delineated through an analysis of isotope-specific mass-dependent fractionation (MDF).[13−18] Typically, δ^{202}Hg is used to denote MDF, and MDF is a useful indicator for differentiating Hg sources.[19−21] In addition, unlike many other heavy-metal stable isotopes in natural ecosystems, Hg is susceptible to mass-independent fractionation (MIF), often the result of photochemical processing.[22] When exposed to sunlight, odd isotopes of Hg undergo magnetic isotope effects (MIE)[23] and, to a lesser extent, nuclear volume effects (NVE).[24] These effects lead to an enrichment of odd Hg isotopes in the reactant pool (i.e., natural waters) and a depletion of odd-numbered Hg isotopes in the product pool (i.e., evasive gaseous Hg°). Odd-MIF is denoted here as Δ^{199}Hg. It should be noted that the MIF-forming processes also impact MDF signatures, often in a semiquantitative manner. Although not fully delineated, even-MIF has been observed in environmental matrices and linked to atmospherically sourced Hg in the gaseous phase,[25] precipitation,[26,27] sediment,[4,28] surface waters,[28,29] and fish.[30] While the mechanistic understanding of this process is still developing, research suggests that even-MIF formation is the result of reactions in the tropopause involving UV-induced halogen radicals (with •Br being of greatest impact).[26,31,32] Upon deposition to terrestrial or aquatic ecosystems, even-MIF is presumed conservative; however, it is susceptible to dilution. Together, these three isotopic fingerprinting techniques (MDF, odd-MIF, and even-MIF) can serve as a three-dimensional roadmap to better understand Hg sources and processing of Hg in the natural environment.[4,19,21]

In this study, we investigate Hg stable isotopic signatures in piscivorous fish from the Laurentian Great Lakes to better understand the sources and processing pathways for Hg in the ecosystem. To date, Hg isotope research has focused primarily on sedimentary inorganic Hg, which is then susceptible to methylation, as the primary source of MeHg to fish.[12] Studies have also suggested the magnitude of odd-MIF is correlative with aqueous dissolved organic carbon (DOC) concentration and quality due to both DOC−Hg associations promoting photoreactions and DOC as a factor inhibiting light attenuation.[33−36] Our study compares isotopic signatures of MeHg, measured as HgT, in higher-trophic-level fish in the Great Lakes, to signatures from bottom sediments. We also investigate the role of water quality on the isotopic Hg composition of these key fish species used for monitoring ecosystem health. Based on preliminary results from our previous work,[4] we hypothesized that sources of MeHg to the food web would be decoupled from sediment. Here, we compare MDF and MIF in piscivorous fish and compare water-quality characteristics among the lakes in an effort to understand both the sources and the processes that influence isotopic signatures for these bioindicators.

MATERIALS AND METHODS

Fish Collection and HgT Analysis. Fish were obtained from each of the Great Lakes (Michigan, Huron, Superior, Ontario, and Erie) from 2004 to 2013 following protocols in the Great Lakes Fish Monitoring and Surveillance Program (GLFMSP).[37] A pair of annually alternating locations per lake included an even-year shallow (nearshore) and an odd-year deep (offshore) location. Composited samples representing five equally proportioned (600−700 mm) lake trout (*Salvelinus namaycush*) were collected from all lakes except Erie, where walleye (*Sander vitreus*, 400−500 mm) represented the indicator fish species due to insufficient lake trout harvests. Detailed site locations (Figure S1) are described elsewhere (GLFMSP 2012).[37] Upon collection, fish were frozen (−20 °C) until laboratory analysis, during which they were thawed and homogenized whole as composites prior to Hg analysis. Preparation of wet fish tissues for total mercury (HgT) analysis was performed at Clarkson University using methods based on the United States Environmental Protection Agency (U.S. EPA) Method 7473 followed by atomic absorbance detection.[38] Lake Superior fish tissue SRM (NIST 1946; 430 ng g^{-1} wet weight Hg) was used to validate HgT accuracy (90−110%). In addition, relative differences among replicates were less than 10%.[38]

Hg Isotope Analysis. Fish tissue (~0.3 g) was digested in 5 mL of concentrated nitric acid in a 95 °C water bath for 180 min. Prior to analysis, solutions were diluted with 5% bromine monochloride in Milli-Q water to allow for complete oxidation of Hg.[4] Final acid concentrations for the dilutions were less than 20% (v/v). IAEA-407 was used as the isotopic Hg standard reference material (SRM), and quality assurance results are found in the Supporting Information. Sample and SRM digestion recoveries were 100 ± 5%. Stable Hg isotope ratios were quantified at the Wisconsin State Laboratory of Hygiene using a Neptune Plus MC-ICPMS coupled with an Apex-Q nebulizer, which was set to free-flow mode to introduce Tl into the custom-designed liquid- and gas-phase separator.[39] A continuous flow of sample solution (0.90 to 1.1 ng mL^{-1} Hg) and $SnCl_2$ (3% w/v in 10% HCl) were also introduced to the phase separator, resulting in the reduction of Hg(II) to dissolved gaseous elemental mercury (Hg^0). Hg^0 was subsequently stripped from the solution with argon, and mixed with the nebulized internal standard Tl, and introduced as a mixture directly into the instrument to produce a steady-state signal. Percent difference between Hg concentrations in the bracketing solutions (NIST SRM 3133) and samples was less than 10%.[40]

Mass-dependent fractionation, identified by δ notation and designated as a per mil (‰) measurement, is calculated by utilizing the following standard bracketing solution equation, with x representing the Hg isotope number (eq1):[40]

$$\delta^{x}\mathrm{Hg}(‰) = \{(^{x}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{sample}})/(^{x}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{NIST-3133}}) - 1\} \times 100 \quad (1)$$

In eq 1, NIST-3133 is used as the normalizing standard, allowing for a benchmark for interlaboratory comparison of mercury isotope results.[40]

An advantage of Hg-isotope geochemistry is that it allows for better discrimination of both sources and transformation processes for Hg is MIF, signified by Δ and calculated as:

$$\Delta^{x}\mathrm{Hg} \approx \delta^{x}\mathrm{Hg} - (\delta^{202}\mathrm{Hg} \times \beta) \quad (2)$$

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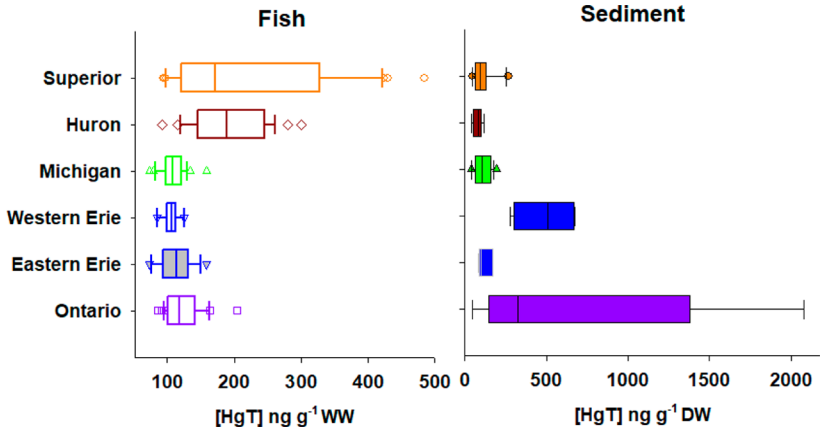

Figure 1. Comparison of total mercury (HgT) in fish tissue (left) and sediment (right) from the Great Lakes. In fish,[36] HgT concentrations represent wet weight (ng g^{-1}) where the box ends, whiskers are quartiles, and the center line the median, and outliers are shown. The right-side bar graphs are mean dry weight HgT concentrations (ng g^{-1}) in sediment, previously published in Lepak et al.[4]

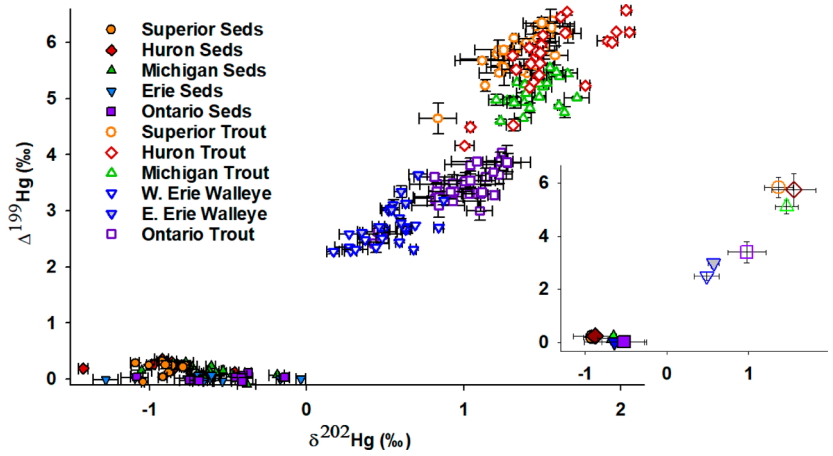

Figure 2. Odd-mass-independent fractionation (Δ^{199}Hg) vs mass-dependent fractionation(δ^{202}Hg) for lake sediment[2] (black outline colored interior) and Great Lakes piscivorous fish (colored outline and white or gray interior). Every fish data point represents a single measurement (~30 per lake) on a whole body composite of 5 similarly sized fish. Error bars represent 1 standard deviation of the analytical certainty. Inset: averaged measurements for each lake, where error bars represent 1 standard deviation of the overall data set.

where β is the mass-specific scaling term, predictable by the laws of mass-dependent kinetic and equilibrium fractionation and equal to 0.2520 for ^{199}Hg, 0.5024 for ^{200}Hg, 0.7520 for ^{201}Hg, and 1.493 for ^{204}Hg.[40] In this study, we describe MDF as δ^{202}Hg, odd-MIF as Δ^{199}Hg, and even-MIF as Δ^{200}Hg.

Ancillary Water-Quality Data. Data used for calculation of the euphotic depth and assessment of pertinent water quality parameters and water column profiles were obtained from the Great Lakes Monitoring Program (GLMP).[41] Using photosynthetically active radiation (PAR; 400 to 700 nm wavelength range),[42] the light-attenuation characteristics of each basin were determined, and the basin-specific euphotic depth was calculated for each site (Figure S1) from 2000 to 2013. At 0.5 m, PAR values greater than 100 μmol (photons) m^{-2} s^{-1} were confirmed to represent daytime hours, and the euphotic depth was defined as the depth where PAR was 1% of the incident radiation at 0.5 m.[43] Sites nearest to the GLFMSP sampling locations were selected (typically three to five sites) as well as data sets that covered multiseasonal sampling.

Profiles of UV intensity were unavailable from PAR measurements and absent in both the literature and online databases. To better understand the impact of contrasting UV wavelengths responsible for the photochemical Hg reactions, lake-specific UV profiles were collected. In the summer of 2011, the United States Geological Survey (USGS) obtained one offshore profile in each lake using a submersible UV radiometer (Biospherical Instruments, PUV-2500; see the Supporting Information and Figures S2A–S6A). Wavelength-specific intensity was compared with simultaneous PAR measurements to determine the relationship between wavelength attenuation and PAR attenuation over varied depths and lakes (Figures S2–S6). This relationship was applied to the more broadly measured PAR data set provided by GLMP.[41]

RESULTS AND DISCUSSION

Sediment vs Fish Hg Concentrations. The total mercury (HgT) concentrations of fish collected in the five lakes (Figure 1) spanned a more modest range (approximately a factor of 3)[38] than the sediment from these basins (a factor larger than 10).[4] Sedimentary Hg, ranging from a few parts per billion (dry weight) to 2 ppm,[44,45] is primarily inorganic Hg typically sourced from atmospheric, watershed, and industrial sources.[4] Hg in fish, ranging from 80 to 500 ppb (wet weight) is primarily methylmercury (MeHg). Lake Superior and Lake Huron exhibit the lowest sediment Hg concentrations (averages of 108 and 81 ng g^{-1}, respectively) while having

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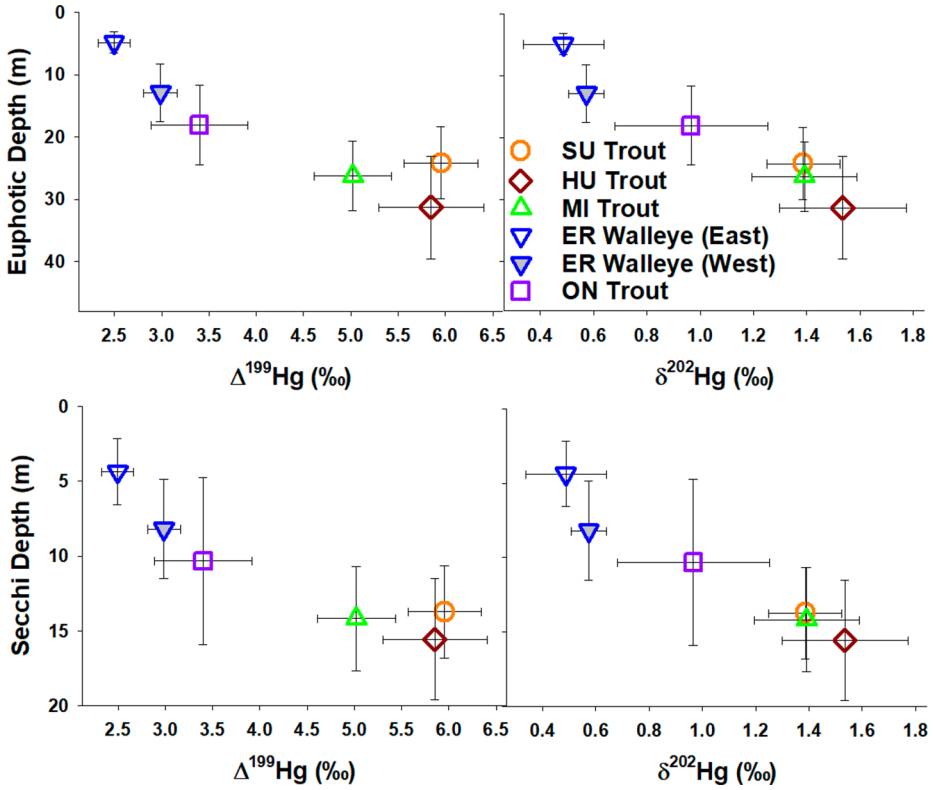

Figure 3. Site-specific Hg isotope means vs the euphotic depth (top) from 2003 to 2013. Isotope error bars represent 1 standard deviation of the individual data points, and the symbol is placed at the mean. Euphotic depth error bars represent 1 standard deviation and are the result of calculated 1% photosynthetically active radiation over at least 3 sites nearest the Great Lakes Fish Monitoring and Surveillance Program fish sampling sites from 2003−2013 (provided by the EPA Great Lakes Monitoring Web site). The bottom graphs compare Secchi depth from 2003 to 2013 (provided by the EPA Great Lakes Monitoring Web site) to Hg isotope signatures.

the highest HgT concentrations in trout (averages of 223 and 195 ng g^{-1}, respectively). Regions of greater sedimentary contamination, such as Lake Erie and Lake Ontario, exhibit lower fish HgT concentrations. Sources of MeHg are often found near zones of microbial methylation[6,10] and a lack of correlation between Hg concentrations in fish and sediment suggests that sedimentary sources may not be the dominant source of Hg to fish in the Great Lakes, especially if methylation rates were proportional to HgT concentration.

Fish Hg Isotopic Signatures. Hg isotopic composition in fish from the lakes spanned a large range in δ^{202}Hg and Δ^{199}Hg, 0.17 to 2.06‰ and 2.27 to 7.16‰, respectively (Figure 2 and Table S1). The Δ^{199}Hg range found across the Great Lakes is comparable to open ocean fish found in the upper 150m (2.66 to 5.50‰)[49] and lake trout from Lakes Huron and Superior are among the highest Δ^{199}Hg reported in the literature. Lake mean δ^{202}Hg and Δ^{199}Hg separate the upper Great Lakes trout (Superior, Huron, and Michigan) from the lower Great Lakes (Erie and Ontario) fish (Figure 2 inset). Sediment isotope signatures suggest that in the upper Great Lakes, a proportionally larger fraction of Hg is derived from atmospheric sources rather than from the watershed or direct pollution sources.[4] Additionally, these lakes exhibit clearer waters and are described collectively as oligotrophic to ultraoligotrophic, presumably resulting in a greater amount of photochemical fractionation.[1] This in part results in the separation of the upper and lower Lakes as Lake Erie and Lake Ontario are defined as eutrophic−mesotrophic and mesotrophic, respectively.[1]

Lake Erie was the only Great Lake to have distinct differences in fish Hg isotope composition between sampling sites (Figure 3), with the eastern basin walleye significantly higher in Δ^{199}Hg (0.5‰) than those in the western basin ($p < 0.001$), suggesting that the populations do not intermix. HgT concentrations in Lake Erie walleye are similar in each basin; however, the source of bioaccumulative Hg to eastern walleye is photochemically fractionated to a greater extent prior to incorporation. Further evidence includes water-column dissolved MeHg concentrations that are lower in the eastern basin than the western basin[4] and MeHg in the sediment of eastern Lake Erie that is lower than the western basin.

Additionally, ratios of Δ^{199}Hg to Δ^{201}Hg have been used to assess processing pathways of Hg sources to biota.[33,34,36] In these laboratory-based studies, photochemical demethylation resulted in a Δ^{199}Hg/Δ^{201}Hg slope of 1.36 ± 0.02, (2 SE) and a photoreduction slope for inorganic Hg of 1.00 ± 0.02, 2 SE. For Great Lakes fish, the overall slope was 1.26 ± 0.01 (York regression; 2SE) with individual lakes ranging 1.24 to 1.33. For this reason, we assume most of the odd-MIF in fish is the result of MeHg photochemical fractionation in situ rather than from sources of inorganic Hg containing odd-MIF prior to methylation.

Relationship of Photochemical Fractionation and Euphotic Depth. While near-shore littoral predation on forage fish is occasionally observed in lake trout (primarily when the food supply is scarce in open waters), lake trout typically derive their energy from offshore pelagic reservoirs.[46,47,50] We assume that, similar to the results of recent research in the oceans, the entry point for MeHg into the pelagic food web can be through uptake from offshore primary and secondary production.[51,52] To determine sources of MeHg

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to an aquatic food web, attention is usually focused on trophic level one (in this case, phytoplankton), where biomagnification is the greatest. In large deep-water lakes, a majority of primary producers exist within the photic zone, and the relative attenuation of light is often a useful marker for regions of phytoplanktonic productivity. Primary producers are extremely effective at sequestering energy at very low light intensities and at long wavelengths.[53] In most of the Great Lakes, phytoplankton densities are often greatest at depths near the thermocline within a region of measurable PAR.[41]

For offshore regions of individual Great Lakes, euphotic depth averaged from 4 to over 31 m (Figure 3). No obvious differences among intralake basins were observed with the exception of Lake Erie. In Lake Erie, the eastern basin exhibits a considerably deeper euphotic zone ($z \approx 13$ m) than the western basin ($z \approx 5$ m), suggesting lower MeHg in the water column is correlated with water clarity in Lake Erie. When the mean euphotic depth was compared for all of the lakes to δ^{202}Hg and Δ^{199}Hg in the fish (Figure 3), positive correlations were found with δ^{202}Hg (slope = $-20.3 \pm 5.2x$, 1 sd, $R^2 = 0.92$; York regression) and Δ^{199}Hg (slope = $7.0 \pm 1.47x$, 1 sd, $R^2 = 0.78$; York regression). Sedimentary δ^{202}Hg differs substantially among lakes, while δ^{202}Hg in fish correlated with euphotic depth.[4] If sedimentary Hg was the main source of MeHg to fish, δ^{202}Hg in fish should correlate to δ^{202}Hg in sediment and not with euphotic depth. Because Δ^{199}Hg and δ^{202}Hg are related to euphotic depth, the source of methylated Hg for fish is more likely to be from the upper water column where photofractionation occurs.

The penetration depth of the wavelengths responsible for Hg fractionation (UV) and the penetration depth of PAR are linearly related (Figures S2−S6). Unfortunately, there are only a few UV depth profiles available for the Great Lakes, and, therefore, we used the linear relationship shared between PAR and UV extinction rates to estimate the depth-specific UV wavelengths that penetrate the water column from the more commonly measured PAR (see the discussion and Figures S2−S6 in the Suppporting Information). This provides UV penetration depths over a broader range of sites and dates. We focus on UV penetration depth because UV light is primarily responsible for Hg photofractionation.[54] UVA (315−400 nm) is less reactive on Hg than UVB (280−315 nm);[54] however, in the open water column, the penetration of UVA is 1.2 to 5 times deeper than UVB (which ranges 0 to 4 m from Erie to Superior; Figures S2−S6). The midsummer chlorophyll maxima in the Great Lakes is typically at depths lower than the penetration depth of UVB wavelengths.[41] With the exception of western Lake Erie, average UVA values were considerably less than incident intensities (0−10% of maxima) at the deep chlorophyll maxima. In the upper epilimnion, where UV intensities are greatest, the potential for photodemethylation is greatest. Odd-MIF is produced in the epilimnetic MeHg pool here, and once MeHg is bioaccumulated, further odd-MIF fractionation is unlikely.[12] Therefore, the displacement between the UV zone and the euphotic depth also influences how quickly photofractionated MeHg is bioaccumulated, and the resulting odd-MIF is then reflected in fish. With increasing depth between the region where photochemical demethylation occurs and the chlorophyll maxima exists, the MeHg pool can further photodemethylate, therefore decreasing the proportion of the initial MeHg pool that is bioaccumulated. Because a greater proportion of the MeHg pool is removed by photochemical fractionation, the residual pool of unreacted MeHg becomes more enriched in both heavy Hg isotopes and in odd-MIF.[22] Using extrapolations first performed by Point et al,[55] the Laurentian Great Lakes range from some of the least efficient for photochemical demethylation [Lake Erie; $z = 31 \pm 4\%$ (1SD) and range = 26 to 42%] to the most efficient Lake Superior [$z = 68 \pm 5\%$ (1SD) and range = 51 to 80%]. During spring and fall mixing, euphotic depth does not change appreciably; however, the distribution of the planktonic community becomes less defined as phytoplankton densities become more uniform. Decreases in fractionation during spring and fall are expected as solar intensity is decreased and phytoplankton growth is dispersed throughout the water column, placing biota in the region of photofractionation.

DOC and the Extent of Photochemical Fractionation. Previous studies have assessed light-penetration depths comparing Secchi depths and dissolved organic carbon concentrations to Δ^{199}Hg.[35] Compared to our study, the range in depths in Florida lakes (3 m) was small and corresponded to a smaller range of Δ^{199}Hg (4.5‰). Furthermore, the variance observed in the Secchi depth was attributable to DOC content (1.5 to 40 mg L^{-1}); therefore, light attenuation by DOC was likely the largest driver of Δ^{199}Hg changes.[35] Using Secchi depths provided by GLMP,[41] similar trends are found with Hg isotopic composition as Secchi depth and euphotic depths are linearly related ($R^2 = 0.98$). The use of PAR is preferable to Secchi depth, however, because it reflects a direct measurement of photointensity, which is relatable to UV penetration and is less prone to human error (visual bias) encountered when determining Secchi depths.

The partitioning of MeHg to suspended particles (plankton and detritus) in freshwater systems is highly dependent particle type, particle density, and organic matter composition.[56,57] Factors affecting photochemical demethylation and biological uptake of MeHg include DOC concentration and quality, the abundance of microbial methylators and demethylators, and overall level of phytoplanktonic productivity.[13,35,56] In the Great Lakes, dissolved MeHg concentrations are among the lowest in the literature,[6,11] and DOC is highly photochemically processed, with spectral characteristics, (humification index, biological index and specific UV absorbance), rivaling temperate oceans.[58,59] The source of DOC in the offshore regions of the Great Lakes is largely a result of in situ biotic production and is low in aromaticity and low in humic content.[59] With the exception of Western Lake Erie, the Great Lakes exhibit low DOC concentrations (0.7 to 1.8 mg L^{-1}),[59] and particle concentrations are also typically low (less than 1 mg/L).[6,9,52,60,61] Therefore, while distribution coefficients for Hg are high for particles and DOC, only a small fraction of MeHg sorbs to particles due to low densities. This likely results in a pool of dissolved MeHg and inorganic Hg with a greater susceptibility to photochemically induced fractionation (less shading) with minimal light attenuation by DOC.[6]

Previous laboratory-based studies have also been conducted with high DOC concentration ranges and specific ligands to explain observations of environmental Hg isotopic fractionation.[33,34,36,61] Often, these experiments are performed at high Hg-to-DOC ratios (34−100 000 ng Hg mg^{-1} C^{1-}) or high Hg concentrations (2000−100 000 ng L^{-1}) that are not comparable with typical ambient lake conditions.[33,34,36,61] Because DOC in the Great Lakes ranges from 0.7 to 1.8 mg L^{-1}[59] and HgT from 0.09 to 1.31 ng L^{-1}[12] (0.13 to 1.0 ng Hg mg^{-1} C^{1-}), it is plausible to assume laboratory experiments may not accurately describe Great Lakes ambient conditions, especially

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when Hg concentrations in water are low. The Δ^{199}Hg values in fish from open waters range 4.89‰ with an inverse relationship to DOC concentration (R^2 = 0.89); however, this is expected because the UV that produces odd-MIF also oxidizes the DOC.[54,57] For this reason, the variance observed in Δ^{199}Hg may not be solely dependent on the DOC content but also on overall water clarity and euphotic depth. Therefore, the mechanism that induces photochemical demethylation is reliant on the presence of DOC,[36,54,55] but the extent of photofractionation appears more closely connected to the depth of elevated phytoplankton activity.

Sources of Hg(II) for Methylation. Understanding sources of MeHg to fish is critical to develop strategies to reduce fish consumption advisories within the Great Lakes. Fish MeHg content is closely linked to the food web and bioaccumulation of MeHg from phytoplankton to forage fish. Sources of MeHg to piscivorous fish may include MeHg formed in sediment and transferred from the benthic food web,[5] MeHg from direct precipitation,[62] production within the water column due to settling and recycling of organic carbon at depth,[63] forage fish from near-shore zones, or a combination of these.[6,64] Our previous work on isotopic fingerprinting identified Great Lakes sediment with the highest concentrations of Hg as those most influenced by industrial inputs (Lake Ontario).[4] Sedimentary MeHg content, however, is frequently <1% of HgT in contaminated sediment and, given the predominance of the nonmethyl fraction, it is difficult to detect the direct influence of the source of MeHg, which contributes to bioaccumulation. Techniques are emerging to separate and assess the isotopic composition of the MeHg fraction[13,65] but researchers often use mathematical approaches.[66] For instance, in the absence of direct isotopic quantification, a positive ~0.45‰ shift in δ^{202}Hg has been shown to occur during methylation, without any shift in odd-MIF.[12−14] Additionally, the process of photodemethylation has been shown to produce a slope of Δ^{199}Hg/δ^{202}Hg = 2.4. Benchtop experiments, however, use high concentrations and Hg-to-DOC ratios and likely underestimate the complexities of in-lake methylation and demethylation processes.[13,14] Within contaminated bays and rivers, these extrapolations may be more reasonable.[67,68]

Sediment Hg isotope signatures (Δ^{199}Hg and δ^{202}Hg), in comparison with resident fish (Figure 2 inset), result in slopes ranging from 2.47 to 2.25 from Superior and Ontario with an average of 2.36. While in good agreement with experimental results (slope = 2.4),[36] this comparison may be slightly misleading. Although few in number, bioenergetic studies of the consumption pathways of lake trout and walleye from the Great Lakes suggest that lake trout are open-water, pelagic predators, and, therefore, the source of MeHg should be inherently linked to the dietary source in which biomagnification is initiated at trophic level 1.[46−48] Recent evidence suggests littoral energy pathways are increasing in Lake Michigan, Lake Huron, and Lake Erie as a result of nearshore capture and recycling of carbon and nutrients by *Dreissenid* mussels ("near-shore shunt") and the co-invasion of the round goby (*Neogobius melanostomus*); however, the extent of this transition has not been fully characterized.[50,60]

Under thermal stratification, if MeHg is formed in the sediment of the offshore zone, it must diffuse to the upper epilimnion to become photofractionated and gain a large positive odd-MIF prior to bioaccumulation. It is unlikely, however, that benthic MeHg would pass through deep chlorophyll maxima and most of the euphotic zone without being partitioned or bioaccumulated. The aqueous flux of MeHg containing enriched odd-MIF would then need to be preferentially incorporated into the primary producers and the signature preserved.[69] This would appear an unlikely pathway for the major source of MeHg to fish. Further evidence against the sediments as the main source of MeHg is the lack of hypolimnetic enrichment of MeHg in the upper Great Lakes during stratification.[9,51]

Studies in the Canadian experimental lakes area suggest that the direct atmospheric Hg source was most readily bioavailable for methylation.[70] Previous Hg mass balances constructed for both Lake Michigan[9] and Lake Superior[51] identified that Hg loading from direct atmospheric precipitation represents the largest source of externally derived Hg to the lakes (though nearshore bays and river mouths represented zones of enhanced MeHg bioaccumulation).[71] Atmospheric precipitation can contain on average 6% of the HgT as MeHg, so direct wet deposition must also be considered as a source of MeHg to the Great Lakes.[62] Precipitation is highly variable in total Hg isotope composition, both temporally and spatially, due to sources of varying isotopic composition and variation in the extent the atmospheric Hg pool is processed.[26,27] Until more-frequent isotopic precipitation measurements are performed in the Great Lakes region, we cannot assess the true extent of atmospheric Hg as a source of Hg to fish using δ^{202}Hg and Δ^{199}Hg. In addition, only a limited mass of MeHg is delivered to the Great Lakes via atmospheric deposition, and to produce sufficiently large odd-MIF values that were observed in trout, a considerable fraction of the MeHg pool must be photoreacted, leaving the resident pool too small to account for the MeHg observed in the water column and biota. The dependency of odd-MIF signatures on euphotic depth suggests that direct atmospheric deposition of MeHg alone cannot account for the odd-MIF observed in fish.

The slope of Δ^{199}Hg/Δ^{201}Hg provides evidence of Hg transformation mechanisms via photochemical reduction or photochemical demethylation.[22] Photochemical demethylation is the dominant mechanism resulting in the odd-MIF observed. In our study, Great Lakes fish reflect an isotopic Hg composition for a MeHg source that has been extensively photodemethylated.[26,27] Distinct bands of low oxygen waters are present in the open oceans and have recently been shown to produce considerable MeHg, and upwelling and diffusion delivers it to surface waters, where it is partitioned to phytoplankton.[63] Similarly, we hypothesize that the formation of MeHg can occur during stratification in the water column as a result of remineralization of autochthonous organic matter in the epilimnion or at the thermocline. If formed in the water column, the MeHg pool would be quite susceptible to photochemical fractionation. Obsersved odd-MIF distributions cannot occur primarily from Hg that was methylated in the hypolimnion or bottom sediment because photochemically derived demethylation is not present in these regions.

Δ^{200}Hg as a Source Indicator for Fish. The tracer, Δ^{200}Hg, is directly linked to atmospheric-precipitation-derived Hg.[4,26,72] To determine whether the source of MeHg to fish more closely resembles precipitation or sediment, we compare Δ^{200}Hg between the two end members (Figure 4). Stork et al.[29] suggested that Δ^{200}Hg signatures are strongest in epilimnetic waters due to direct contact with precipitation and, with increasing depth, Δ^{200}Hg diminishes due to either evasion, dilution, absorption, or biotic uptake. Precipitation-sourced

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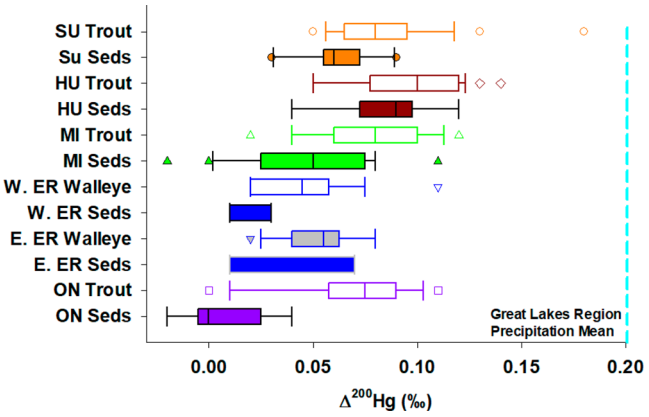

Figure 4. Mass-independent fractionation of Hg^{200} ($\Delta^{200}Hg$) was assessed in piscivorous fish and sediment to show the disconnect between sediment and fish in lakes, where the proportion of precipitation sourced Hg in sediments is low. Bar colors are consistent with Figures 1−3 and data points represent outliers. Box centerline represents median, box edges represent the lower quartile, and the whiskers represent the upper quartile. The dotted line represents the mean of Great Lake precipitation obtained from the literature.[25−27]

inorganic divalent Hg susceptible to MeHg formation likely provides $\Delta^{200}Hg$ to fish. Likewise, the inorganic fraction of Hg in precipitation, associated with $\Delta^{200}Hg$ would be labile and susceptible to methylation.[70] In regions where precipitation is an important component to the sedimentary load of Hg (upper Great Lakes),[4] sedimentary and fish $\Delta^{200}Hg$ are similar; however, a clear disconnect between fish $\Delta^{200}Hg$ and sedimentary $\Delta^{200}Hg$ exists in regions where precipitation is a smaller proportion of the Hg budget in sediment. In Lake Ontario and western Lake Erie, where sedimentary sources are overwhelmingly industrial and watershed-derived, lake trout and walleye exhibit $\Delta^{200}Hg$ values elevated relative to local sediment, and, in these fish, $\Delta^{200}Hg$ levels are similar to those in Lake Superior trout. These results highlight the complexities of source determination for MeHg to fish and further support the disconnect between sedimentary sources and fish in these lakes. They suggest that, similar to open oceans,[63] atmospheric deposition to the upper water column of Great Lakes can be a source of bioaccumulative MeHg in fish, a possible result of direct water column methylation.

Based on multiple Hg isotopic results presented here, MeHg in the Great Lakes must be photochemically reacted in the upper epilimnion prior to bioaccumulation, which results in enriched $\Delta^{199}Hg$ values in the residual MeHg of fish. For this process to occur, and for MeHg in biota to exhibit large odd-MIF, MeHg sources, such as precipitation, must have large $\Delta^{199}Hg$, in situ MeHg production must occur largely in or near the photic zones of the lakes, or both conditions are true. MeHg from sediment, however, is formed from the inorganic pool absent of considerable odd-MIF. To ascribe MeHg solely to sedimentary sources, diffusion and advection to the photic zone would be necessary, followed by photochemical reactions to produce large $\Delta^{199}Hg$ values, an unlikely scenario. Thus, we ascribe substantial nonsedimentary sources of MeHg, including a fraction formed within the water column.

To more fully understand source portfolios using Hg isotopic distribution in in fish, research must be additionally focused on mechanisms that affect fractionation during initial uptake of MeHg by phytoplankton and subsequent trophic transfer. Difficulties in quantification are often encountered due to the need to preconcentrate large-volume samples of water and suspended particulate matter for accurate Hg isotopic measurements. Recent advances in the direct isotopic analysis of the MeHg fraction[65] will also aid in determining sources to the small fraction of MeHg in phytoplankton (usually <10% of HgT)[6,71] and the preservation or transformation of that initial isotopic MeHg source signal during bioaccumulation. Together with measurements similar to ours in biomonitoring species, these additional advances will further aid resource managers in better understanding the reactivity of current and legacy sources of this persistent, bioaccumulative toxin.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site at DOI: 10.1021/acs.est.7b06120.

Additional details on quality control and quality assurance of isotopic analyses. Figures showing sampling locations and UV and PAR profiles. Tables showing HgT and isotopic Hg data for fish and York regressions of Hg isotopes and euphotic depth. (PDF)

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