

Use of Stable Isotope Signatures to Determine Mercury Sources in the Great Lakes

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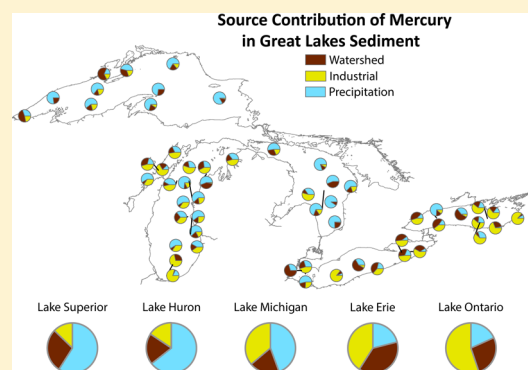
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Supporting Information

ABSTRACT: Sources of mercury (Hg) in Great Lakes sediments were assessed with stable Hg isotope ratios using multicollector inductively coupled plasma mass spectrometry. An isotopic mixing model based on mass-dependent (MDF) and mass-independent fractionation (MIF) ($\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$) identified three primary Hg sources for sediments: atmospheric, industrial, and watershed-derived. Results indicate atmospheric sources dominate in Lakes Huron, Superior, and Michigan sediments while watershed-derived and industrial sources dominate in Lakes Erie and Ontario sediments. Anomalous $\Delta^{200}\text{Hg}$ signatures, also apparent in sediments, provided independent validation of the model. Comparison of $\Delta^{200}\text{Hg}$ signatures in predatory fish from three lakes reveals that bioaccumulated Hg is more isotopically similar to atmospherically derived Hg than a lake's sediment. Previous research suggests $\Delta^{200}\text{Hg}$ is conserved during biogeochemical processing and odd mass-independent fractionation (MIF) is conserved during metabolic processing, so it is suspected even is similarly conserved. Given these assumptions, our data suggest that in some cases, atmospherically derived Hg may be a more important source of MeHg to higher trophic levels than legacy sediments in the Great Lakes.



INTRODUCTION

Mercury (Hg), a persistent global pollutant, is transported atmospherically and enters freshwater systems through direct atmospheric deposition (wet and dry), through watershed inputs, or directly through point source discharge.^{1–3} In aquatic ecosystems, microbially mediated pathways can transform Hg to methylmercury (MeHg), a more toxic form that is biomagnified in aquatic food webs.⁴ Bioaccumulated MeHg is a potential threat to aquatic ecosystems and to human health through fish consumption. Anthropogenic activity has largely altered sources of Hg, and our understanding of the impacts on the aquatic environment continues to improve.⁴ The use of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) to accurately resolve and measure isotopic ratios of the seven natural stable isotopes of Hg (^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , and ^{204}Hg) has enhanced our understanding of both sources and biogeochemical processes.^{5,6} Specifically, determination of mass-dependent (MDF) and mass-independent (MIF) fractionation patterns provides

critical information useful for management of Hg contamination of valued aquatic resources.

Mass-dependent fractionation, identified by delta notation, is calculated by utilizing a standard bracketing solution (eq 1):

$$\delta^{xxx}\text{Hg}(\text{‰}) = \left[\frac{(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{NIST-3133}}} - 1 \right] \times 1000 \quad (1)$$

where ^{xxx}Hg is the isotope of interest. A National Institute of Standards and Technology standard (NIST-3133) is the chosen normalization solution, and ^{198}Hg is the denominator.⁷ MDF can occur either during kinetic processes or via equilibrium exchange of Hg. Processes affecting MDF include microbially mediated reactions (e.g., reduction, methylation, and demethylation).

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lation), abiotic chemical reactions (e.g., photoreduction and chemical reduction), and physical processes (e.g., volatilization, evaporation, adsorption, and dissolution).^{5,6}

An advantage of Hg isotope geochemistry in terms of understanding sources and transformation processes is the use of mass-independent fractionation (MIF)^{8,9} data signified by an uppercase delta (Δ) that can be calculated by (eq 2):

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

MIF describes the difference between β -scaled $\delta^{202}\text{Hg}$ values and measured $\delta^{\text{xxx}}\text{Hg}$ values. The scaling factor, β , is an independent isotope-specific constant determined by the theoretical laws of MDF.⁷ Specific processes resulting in odd MIF, a result of nuclear volume and magnetic isotope effects,^{10,11} include photoreduction of aqueous Hg (II), photodegradation of MeHg, elemental Hg evaporation, and equilibrium Hg–thiol complexation.⁵ More recently, MIF anomalies of even isotopes (e.g., ^{200}Hg) have been reported in elemental gaseous Hg(0) and atmospheric precipitation [as divalent Hg(II)]. This has led to the hypothesis that atmospheric photochemical oxidation of Hg alone causes MIF for even number Hg isotopes.^{5,9} To date, large variations ($\sim 10\%$) of $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, and $\Delta^{200}\text{Hg}$ ($\sim 1\%$) have been reported.^{9,12–15} We propose that these three isotopic markers of MDF and MIF are effective tracers of biotic and abiotic fractionating processes that operate to differing degrees in various environmental compartments (e.g., atmosphere, watershed, and within lake), thus resulting in an ability to discriminate among mercury sources to receiving points as well as to infer important Hg geochemical transformation processes.⁵

The Laurentian Great Lakes are presently the focus of a large scale ecosystem restoration effort by the United States and Canada (e.g., Great Lakes Restoration Initiative¹⁶). The lakes currently range from oligotrophic conditions in the western Great Lakes (Superior, Michigan, and Huron) to oligomesotrophic (Ontario) to mesotrophic (Erie) in the Eastern Great Lakes. However, specific embayments (i.e., Green Bay, Lake Michigan; Saginaw Bay, Lake Huron) and western Lake Erie exhibit eutrophic conditions.¹⁶ Previous Hg research has focused on loading (atmospheric and tributary inputs) and transformation of Hg within the lakes, including biological uptake at river mouths, particle partitioning and sedimentation, methylation in both benthic waters and sediments, and bioaccumulation of MeHg in pelagic food webs.^{1,2,17–19} For the two lakes (Superior and Michigan) from which enough data have been collected to support a mass balance, those calculations support the notion that atmospheric deposition is the largest Hg source.^{1,19,20}

The frequency of application of Hg studies to the Great Lakes has increased dramatically in the past few years, particularly for providing a better understanding of atmospheric deposition signatures, cycling within the watershed, and observations of isotopic distribution in fish.^{8,9,14,21,22} Here, we extend these recent studies and propose the use of Hg isotope signatures to infer relative contributions of mercury from key end-member sources to the Great Lakes. Specifically, we hypothesize that the use of $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ measurements on sediment samples from across the Great Lakes can be used to derive a triple mixing model that provides estimates of the relative amounts of mercury derived from atmospheric deposition, watershed runoff, and point source (near field) Hg sources. The results from our Hg source model compared

to an independent $\Delta^{200}\text{Hg}$ binary mixing model to confirm the utility of $\Delta^{200}\text{Hg}$. Finally these measurements are extended to predatory fish to ascertain the relative importance of our end-member sources to the food web.

MATERIALS AND METHODS

Sample Collection. Surface sediment samples were collected using a ponar dredge sampler from the U.S. Environmental Protection Agency's *R/V Lake Guardian* in 2012–2014. Sediment was subsampled (0–2 cm; $n = 58$), promptly stored, and frozen in either clean Teflon vials or acrylic centrifuge tubes. Surface sediments collected from each lake integrate different time periods ranging from 3 years (Western Lake Erie) to 220 years (offshore Lake Huron) as sedimentation rates range from 0.0043 to 0.88 g cm⁻² year⁻¹.²³ These temporal differences in sediment accumulation time periods for the top 2 cm constitute a limitation of our model. Once they had been returned to the lab, samples were lyophilized, homogenized by a ball mill, and stored in borosilicate vials. Lake trout samples from Lakes Superior and Ontario were collected by Clarkson University during U.S. Environmental Protection Agency (EPA) monitoring cruises in 2006. Each sample represents a homogenized composite of five equally portioned samples of fish axial tissue. Upon receipt in the laboratory, samples were lyophilized, homogenized by a ball mill, and stored in borosilicate vials.

Total Hg Analysis. HgT in sediments was analyzed by a direct combustion system with an atomic absorbance detection system²⁴ at the United States Geological Survey (USGS) Mercury Research Lab. Standard reference material (SRM) recoveries (IAEA SL 1) were within 90–110%; the detection limit was 1.38 ng/g of dry weight, and coefficients of variation of triplicate analyses were <10%. HgT analyses of fish tissues were performed by Clarkson University using methods based on U.S. EPA 7473 and atomic absorbance detection.²⁵ Lake Superior Fish Tissue (dried, NIST 1946) SRM was used to validate accuracy with recoveries of 90–110%; relative differences between replicates were <10%.

Hg Isotope Analysis. Sediment samples were digested in 5 mL of aqua regia [3:1 (v:v) HCl:HNO₃ ratio] in a water bath (95 °C, 120 min). Solutions were diluted with Milli-Q water to a Hg concentration of 0.5–2.0 ng mL⁻¹ and to <20% acid. Two SRMs, NIST 2711, and MESS-1 were used in the isotopic analyses both to conform to previous research and to establish a SRM with a concentration similar to those of the samples measured here [recoveries were 90–100% ([Supporting Information](#))].^{26,27} Fish samples were digested in 5 mL of concentrated nitric acid in a water bath (95 °C, 180 min) and subsequently diluted to 20% acid with 5% bromine monochloride. For fish analyses, two SRMs, DORM-2 and IAEA-407, were used in the isotopic analyses to conform to previous research, again choosing SRMs with concentrations similar to those of the samples measured in our study [recoveries were 90–100% ([Supporting Information](#))]. Differences between Hg concentrations in the bracketing solutions (NIST SRM 3133) and samples were <10%. Hg isotope ratios were determined using a Neptune Plus MC-ICP-MS instrument coupled with an Apex-Q nebulizer and cold gas phase introduction system ([Table S1](#)) housed at the Wisconsin State Lab of Hygiene.⁷

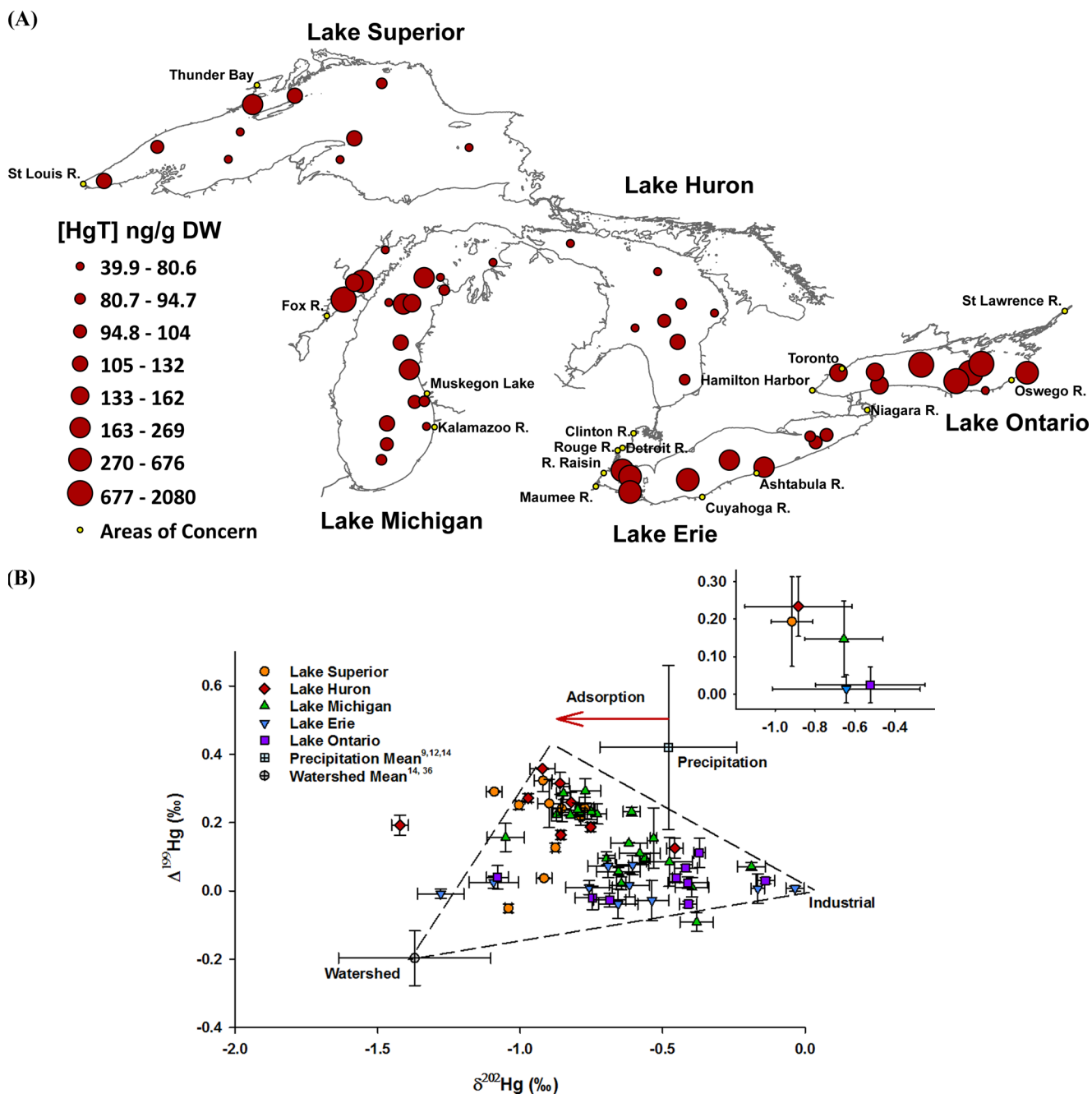


Figure 1. (A) Total mercury (HgT) concentrations of surface sediments in the five Great Lakes. (B) ^{202}Hg MDF and ^{199}Hg MIF in Great Lakes sediments and end-members used for the triple-mixing model. Literature-derived mean isotopic data with one standard deviation error for watershed-derived^{14,36} and precipitation-derived Hg^{9,13,15,21} as well as the associated shift in $\delta^{202}\text{Hg}$ for adsorption⁴⁰ for precipitation are shown. Error bars on samples in the main panel indicate one standard deviation of the analytical uncertainty. The inset of panel B shows the mean sediment isotopic composition for each lake. Error bars represent the standard deviation for each lake data set.

RESULTS AND DISCUSSION

Development of a Source Apportionment Model for Great Lakes Sediments. Our analyses of total Hg (HgT) in sediments reveal a wide concentration range across Great Lakes sediment, which is consistent with previous studies.²⁹ The lowest HgT concentrations were observed offshore in Lakes Huron and Superior and higher concentrations in Western Lake Erie and in Lake Ontario (Figure 1A and Table S2). Regional increases in Hg concentration relative to those offshore were apparent in Lake Michigan (Green Bay) and

Lake Superior sediment (Thunder Bay and near the St. Louis River).

The use of Hg isotopes in sediments for Hg source apportionment studies is typically based on binary and ternary mixing models with well-defined end-members.^{13,14,26,28} Prior mercury research on the Great Lakes that did not employ Hg isotopes has pointed to three possible Hg sources in sediments: local industrial sources, atmospheric deposition, and watershed loading.^{2,12,14,22} Here, we demonstrate a mixing model based on literature-supported end-member Hg isotope composition

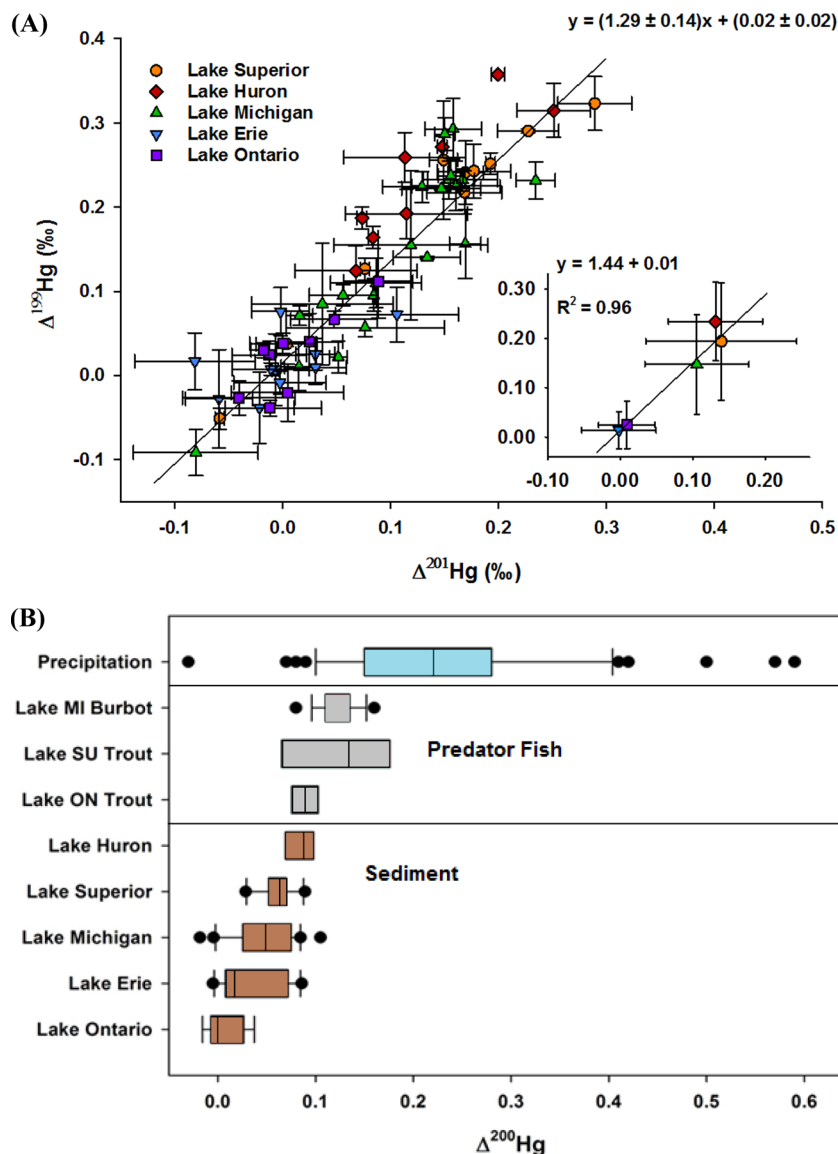


Figure 2. (A) Odd isotope MIF and slope for the photoreduction of Hg in Great Lakes sediment. Error bars indicate one standard deviation analytical uncertainty. The inset shows the mean sediment isotopic composition for each lake. Values in the Western Great Lakes are significantly higher than those in the Eastern Great Lakes by *t* test ($\Delta^{199}\text{Hg}$, two-tail $P = 0.0001$, $t = 6.0352$, $df = 55$, 95% confidence). Error bars represent the standard deviation for each lake data set. (B) Box and whisker plot of the mean even isotope $\Delta^{200}\text{Hg}$ MIF of the five Great Lakes sediments compared to previously published burbot⁸ and our lake trout composites from sampling in 2006, together with published atmospheric precipitation data, used in end-member calculation for our proposed binary mixing model.^{9,14,21,22}

to support source apportionment estimates across the Great Lakes.

Industrial Sources. Polluted industrial sources have been shown to exhibit higher $\delta^{202}\text{Hg}$ values (-1 to 0‰) and insignificant MIF ($\Delta^{199}\text{Hg} \sim 0$).^{26,27} Within the Great Lakes, Hg derived from industrial sources will be strongly partitioned to particles or dissolved organic carbon (DOC) prior to entering the lakes. While Hg associated with DOC may undergo many complex reactions that dramatically alter Hg signatures, Hg associated with particles most likely deposits near their source.³⁰ For this reason, limited water column processing of particle-associated Hg might occur, thereby conserving the odd MIF of the source Hg.^{31,32} We chose NIST 3133 as our end-member because currently in the literature no reliable published industrial signature has been identified for the Great Lakes system. A location in Lake Ontario, elevated in

HgT concentration (327 ng g^{-1}), is quite similar in isotopic composition to NIST 3133 ($\delta^{202}\text{Hg}$ of $-0.14 \pm 0.03\text{‰}$; $\Delta^{199}\text{Hg}$ of $0.03 \pm 0.01\text{‰}$). Our chosen end-member is similar to an industrially sourced end-member in another isotopic study.²⁶

Watershed Soils. Hg in terrestrial soils is primarily a result of atmospheric Hg deposition and subsequent evasion equilibrium, resulting in negative Hg-MIF ($\Delta^{199}\text{Hg} < 0$).¹⁴ Studies have shown that Hg from watershed sources (tributaries and rivers) is a result of erosion,^{2,19,20,33} and it is expected that recalcitrant Hg from these watershed particles³⁴ will settle with minimal water column processing (conserving sourced odd isotope MIF). Furthermore, organic soils, because of their low density, are most susceptible to erosion and, thus, can represent our watershed-derived Hg end-member. Previous studies in the Great Lakes and other regions have investigated the Hg

isotopic composition in varied soil types, and we utilize the means of these studies for our watershed end-member ($\delta^{202}\text{Hg}$ of $-1.83 \pm 0.51\text{‰}$; $\Delta^{199}\text{Hg}$ of $0.30 \pm 0.12\text{‰}$; $n = 27$).^{14,35,36}

Precipitation. Isotopic signatures of Hg in precipitation show highly variable results for $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ with mean values for the Great Lakes region of $-0.48 \pm 0.24\text{‰}$ ($n = 92$) for $\delta^{202}\text{Hg}$ and $0.42 \pm 0.24\text{‰}$ ($n = 92$) for $\Delta^{199}\text{Hg}$.^{9,12,14} HgT particle concentrations in Great Lakes waters typically constitute $\sim 23 \pm 14\%$ of the total Hg species ($n = 202$; excluding Western Lake Erie $\sim 84 \pm 10\%$ $n = 25$; Table S3). In addition, particles in atmospheric precipitation have been shown to account for $\sim 25\%$ of the total Hg.³⁷ During deposition or once Hg is deposited in the aquatic system, particle adsorption is expected.^{38,39} Laboratory-based studies show an MDF shift (-0.4‰) as Hg adsorbs to goethite.⁴⁰ For this reason, and because of the low percentage of Hg associated with the particle phase, we suspect that kinetics favor light isotope absorption of Hg from atmospheric precipitation to water column particles prior to sedimentation. Therefore, the Hg isotopic signature in precipitation is not directly comparable to sedimentary signatures unless one accounts for an adsorptive shift. We applied an adsorption shift similar to published data⁴⁰ to account for particle adsorption for our atmospheric precipitation end-member ($-0.88 \pm 0.24\text{‰}$ for $\delta^{202}\text{Hg}$ and $0.42 \pm 0.24\text{‰}$ for $\Delta^{199}\text{Hg}$).

End-Member Evaluation. Our end-members adequately encompass our data set (Figure 1B). We acknowledge the uncertainty of this model as exact end-members have not been directly measured. We compare our end-members to those from related studies. For example, in studies of lake sediment geochronology, where recent industrial contamination is apparent, profiles exhibit a $\delta^{202}\text{Hg}$ shift of $\sim 0.9\text{‰}$ in China and $0.7\text{--}0.8\text{‰}$ near a smelter in Flin Flon, Manitoba.⁴¹ Our MDF values (Figure 1B) span a similar range. This combination of the MDF and MIF signatures in Great Lakes sediments provides justification for a ternary mixing model rather than binary models utilized in similar pollution studies.⁴² Equations suggested in previous work were amended for this study (eqs 1–3 of the Supporting Information);²⁶ however, to the best of our knowledge, this is the first study to attempt to use atmospheric precipitation as an end-member to a ternary mixing model with both odd isotope MIF and MDF.

Sources of Hg in Great Lakes Sediments. The Western Great Lakes generally show Hg signatures most reflective of atmospheric deposition and watershed-derived loading, while the Eastern Great Lakes exhibit signatures suggestive of enhanced watershed and anthropogenic influence (Figure 1B, Table S4, and graphic in the abstract). Lakes Superior and Michigan exhibit the largest source variation because of local anthropogenic inputs that do not appear to impact offshore signatures. Gradients in source apportionment and local sources are most apparent in regions of Lake Huron and Superior where the largest fraction of sediment Hg in offshore regions is attributed to atmospheric deposition. However, specific sites near river mouths in Lake Superior (e.g., St. Louis River and Thunder Bay) reveal significant increases in watershed-sourced Hg. Likewise, in Lake Michigan, river mouths near Green Bay and the Grand River reflect contributions from industrial and watershed-derived sources. In Lake Erie, watershed-derived Hg loading predominates in the western basin. Sediments of central and eastern Lake Erie have a greater fraction of industrially derived Hg. Among all the

Great Lakes, Lake Ontario is most heavily influenced by industrial activity.^{3,43}

Our sediment work confirms previous mass balance studies that suggest inputs to Lakes Michigan and Superior are dominated by atmospheric deposition.^{19,20,38} Cumulative effects of photochemical processes [photodemethylation of MeHg and photoreduction of Hg(II)] on Hg species can be assessed by $\Delta^{199}\text{Hg}:\Delta^{201}\text{Hg}$ (Figure 2A) ratios.^{6,8,44} Prior to deposition, we suspect suspended particles may absorb fractionated Hg, conserve MIF from water column processes, and accumulate in sediments. Here, the magnitudes of the $\Delta^{199}\text{Hg}:\Delta^{201}\text{Hg}$ ratio are significantly greater ($\Delta^{199}\text{Hg}$, two-tail $P = 0.0001$, $t = 6.0352$, $df = 55$, 95% confidence) in the Western Basin Lakes (Figure 2A, inset), suggesting that residual Hg(II) in sediments of the Western Great Lakes reflects aqueous Hg that has undergone more extensive photochemical mass-independent fractionation, consistent with elevated water clarity.⁴⁵ In addition to decreased water clarity, Eastern Great Lakes sediment deposition zones are closer to agricultural, urban, and industrial contaminant sources,³ and therefore, odd isotope MIF may be suppressed by enriched particle-bound Hg that does not undergo aqueous photochemical processing. Isotopic Hg patterns further confirm previous work suggesting elevated Hg concentrations in Lakes Erie and Ontario sediments are linked to industry and urbanization.³ Further, our conclusions are consistent with those of Jackson et al.,⁴¹ who suggested that elevated Hg and isotopic patterns in a core from Lake Ontario near the mouth of the Niagara River reflect recent industrial (chloroalkali) contamination.

$\Delta^{200}\text{Hg}$ in Precipitation, Sediments, and Fish from Lake Michigan. We further validate our $\delta^{202}\text{Hg}:\Delta^{199}\text{Hg}$ source model by separately utilizing $\Delta^{200}\text{Hg}$ as a tracer.¹⁵ The primary process for the development of positive $\Delta^{200}\text{Hg}$ signatures appears to be reaction in the atmosphere, a phenomenon currently explained by nuclear self-shielding.⁴⁶ Unlike odd isotope MIF, $\Delta^{200}\text{Hg}$ has been shown to be fairly conservative in other environmental settings (water column and soils), susceptible to dilution by only sources of Hg not exhibiting positive $\Delta^{200}\text{Hg}$.⁹ We propose that $\Delta^{200}\text{Hg}$ within the sediments may also be used as a confirmatory signature for atmospheric source apportionment. We observed a range of $\Delta^{200}\text{Hg}$ from -0.02‰ (Lake Ontario) to 0.12‰ (Lake Huron) (Figure S1). In sediment, previous studies have either not reported $\Delta^{200}\text{Hg}$, reported insignificant $\Delta^{200}\text{Hg}$ values, or reported $\Delta^{200}\text{Hg}$ values (-0.05 to 0.16‰) but failed to interpret their presence.^{13,27,47}

On the basis of a general agreement between ternary and binary mixing models (Figure S2), and the presumed lack of $\Delta^{200}\text{Hg}$ fractionation during water column processing, we propose that $\Delta^{200}\text{Hg}$ can also be used for source identification at higher trophic levels (Figure 2B). Previous work linked inorganic Hg and MeHg in sediments and fish, utilizing the photodemethylation slope ($m = 2.4$) for the $\Delta^{199}\text{Hg}:\delta^{202}\text{Hg}$ ratio.⁴⁸ Complex processes (such as methylation and photodemethylation) affect odd MIF and MDF Hg signatures. In addition, fish are integrators of Hg both temporally and spatially, which may further complicate biotic source determination. Direct confirmation of sources in biota may be aided by separation of MeHg from inorganic Hg at each trophic level. The technology, however, is currently emerging, and very few measurements have even been attempted,⁴⁹ so few that we cannot generalize the results and apply them here. Since $\Delta^{200}\text{Hg}$ has been suggested to be a conservative Hg tracer

for precipitation-derived Hg that is deposited from the atmosphere to terrestrial and aquatic systems,^{9,15,21} we extend that argument to infer it is also conservative through bioaccumulation (similar to odd MIF)⁵ and therefore a conservative tracer in biota.

Though published $\Delta^{200}\text{Hg}$ data are sparse, recent data on Great Lakes fish, coupled with our data (Table S5), offer insights into potential sources of bioaccumulative Hg at higher trophic levels. Small but significant $\Delta^{200}\text{Hg}$ anomalies were measured in burbot (*Lota lota*) collected in 2006 from Lake Michigan [$\Delta^{200}\text{Hg} = 0.08\text{--}0.16\text{‰}$ (Table S4)]⁸ and lake trout (*Salvelinus namaycush*) collected in 2006 as part of the EPA Great Lakes Fish Monitoring and Surveillance Program from geographical end-members from Lakes Superior and Ontario (Table S2). We compared the $\Delta^{200}\text{Hg}$ levels from the sediment to those from the fish and precipitation from the Great Lakes region (Figure 2B).^{8,9,14,21,22} By inferring a simple binary mixing model from these data, qualitative assessment shows that $\Delta^{200}\text{Hg}$ values reported for burbot and lake trout (assumed to be 100% MeHg) are more reflective of atmospheric precipitation signatures than each lake's sedimentary signature. In Lakes Superior and Ontario, which represent different Hg sedimentary sources, lake trout $\Delta^{200}\text{Hg}$ signatures are similar. This suggests that atmospheric sources, rather than contaminated historical sediments, may be an important source of bioaccumulative Hg in Great Lakes fish. Additional investigation of the lower food web (phytoplankton, zooplankton, and small fish), specifically focused on the isotopic composition of the MeHg fraction⁴⁸ from sediments, through the aquatic food web will strengthen the utility of $\Delta^{200}\text{Hg}$ as a tracer of bioaccumulative sources. However, if the only process of $\Delta^{200}\text{Hg}$ fractionation occurs in the atmosphere, and $\Delta^{200}\text{Hg}$ enhancement appears in predatory fish, then regardless of the site of methylation, preferential methylation of atmospherically-derived Hg must have occurred.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.5b00277](https://doi.org/10.1021/acs.estlett.5b00277).

Quality assurance and control of isotopic analyses; development of mass-independent fractionation of the Hg^{200} model; supporting equations; odd isotope versus even isotope MIF (precipitation indicator) for Great Lakes sediment (Figure S1); comparison of triple-mixing and binary-mixing model outputs for precipitation (Figure S2); MDF of the Great Lakes sediments (Figure S3); operating parameters of the Neptune Plus MC-ICP-MS instrument (Table S1); Hg isotopic distribution in Great Lakes surface sediments (Table S2); particle and dissolved HgT concentration averages from the Great Lakes water column (Table S3); model results for the percent distribution of Hg sources in Great lakes surface sediments (Table S4); isotopic Hg data on lake trout and burbot collected from the Great Lakes in 2006 (Table S5) (PDF)

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Notes

The authors declare no competing financial interest.

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