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Spatial and Temporal Patterns of Mercury Accumulation in Lacustrine Sediments across the Laurentian Great Lakes Region

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Abstract

Data from 104 sediment cores from the Great Lakes and "inland lakes" in the region were compiled to assess historical and recent changes in mercury (Hg) deposition. The lower Great Lakes showed sharp increases in Hg loading c. 1850-1950 from point-source water dischargers, with marked decreases during the past half century associated with effluent controls and decreases in the industrial use of Hg. In contrast, Lake Superior and inland lakes exhibited a pattern of Hg loading consistent with an atmospheric source - gradual increases followed by recent (post-1980) decreases. Variation in sedimentary Hg flux among inland lakes was primarily attributed to the ratio of watershed area:lake area, and secondarily to a lake's proximity to emission sources. A consistent region-wide decrease (~20%) of sediment Hg flux suggests that controls on local and regional atmospheric Hg emissions have been effective in decreasing the supply of Hg to Lake Superior and inland lakes.

Keywords: mercury, sediment cores, sediment mercury deposition, Great Lakes, paleolimnology

Capsule: An analysis of data from 104 sediment cores from the Laurentian Great Lakes and nearby inland lakes indicates sedimentary Hg flux is declining region-wide.

1. Introduction

Human releases of mercury (Hg) to the atmosphere, and to a lesser extent surface waters, have contaminated ecosystems on a global scale (Fitzgerald et al. 1998). In aquatic ecosystems, bacteria (principally sulfate reducers) transform divalent inorganic Hg into methylmercury (MeHg), which strongly bioaccumulates within food webs, resulting in exposure to humans and wildlife (National Research Council 2000). All of the states and provinces of the Great Lakes Region, including the Great Lakes and their connecting waters, have fish consumption advisories due to MeHg contamination (Environment Canada 2011; U.S. Environmental Protection Agency 2011).

Lake sediments have been widely used to document the historical and spatial dimensions of Hg pollution (Biester et al. 2007). Sediment cores can be used, for example, to evaluate the magnitude of change in Hg deposition over long time-scales (Lamborg et al. 2002) and to explore recent depositional trends owing to changes and decreases in emissions (Engstrom and Swain 1997). Over the last two decades, numerous dated sediment records of Hg flux have been compiled for the Great Lakes region (e.g., Bookman et al. 2008; Drevnick et al. 2007; Engstrom and Swain 1997; Engstrom et al. 2007; Johnson et al. submitted; Kamman and Engstrom 2002; Lorey and Driscoll 1999; Mills et al. 2009; Muir et al. 2009; Parsons et al. 2007; Pirrone et al. 1998; Rossmann 1999; Rossmann 2010; Swain et al. 1992). These records have been interpreted largely within a local (state or provincial) context, but have not been systematically compiled or evaluated across the entire Great Lakes region.

In this study, we synthesized data from 104 dated sediment cores collected in the region to address the following key questions: (1) temporal trends: *How much has atmospheric Hg*

deposition in the Great Lakes region changed during the industrial period (i.e., 1850-present)? What are the recent trends in sediment Hg deposition (increase, decrease, stable)? (2) spatial patterns: *Do historical and recent trends in Hg deposition vary systematically across the region? Are there spatial differences related to distance/proximity to local/regional Hg emission sources?* (3) Great Lakes versus inland lakes: *Do the time trends and fluxes of sediment Hg in the Great Lakes differ from those of inland lakes within the region? And what does that tell us about the relative importance of atmospheric deposition vs. direct water discharges to the different Great Lakes?* With other factors being equal, the extent of MeHg contamination of fish is thought to be roughly proportional to long-term atmospheric Hg deposition (Harris et al. 2007; Munthe et al. 2007). Therefore, answering these questions may inform recent and sometimes conflicting (e.g., Bhavsar et al. 2010; Monson 2009) reports of temporal trends in MeHg contamination of fish in the Great Lakes region.

2. Methods

The study area for this synthesis is the Great Lakes airshed (Figure 1). The Canada-United States Air Quality Agreement (2005) defined an airshed as "a geographic area within which air pollution is freely and routinely transported and that is influenced by shared sources of pollutants, weather, and terrain." Based on these criteria, we consider the airshed of the Great Lakes to include: (1) all of the U.S. states bordering the Great Lakes plus Vermont and New Hampshire and (2) the Canadian provinces of Ontario and Quebec, excluding far northern portions.

Data used in the synthesis were obtained from dated sediment cores collected from the Great Lakes and inland lakes within the Great Lakes airshed and, with few exceptions, have been

published in the peer-reviewed literature. Data were solicited from potential contributors with the following criteria: (1) reliable and detailed dating by ^{210}Pb; (2) sediment core records extending back to preindustrial times (pre-1850); and (3) for inland lakes, relatively undisturbed watersheds, which otherwise greatly increase Hg loading through erosion, and an absence of direct inputs of Hg from wastewater or industrial waste. We defined an inland lake as any natural lake, excluding the Great Lakes themselves, within the study area. Potential contributors were asked to provide the following information for each core: lake name, locality, date of collection, latitude and longitude of core site, sediment Hg fluxes (pre-1850, 1970, recent, peak), ^{210}Pb-based focus factor, lake surface area, watershed surface area (excluding lake), and dominant land use within watershed (qualitatively or by GIS). Contributors (all co-authors) provided data from dated sediment cores from Lake Superior (n = 9, Muir et al. 2009; Johnson et al. submitted), Lake Michigan (n = 1, Rossmann 2010), Lake Ontario (n = 3, Pirrone et al. 1998; D.G.C. Muir, Environment Canada, Burlington, Ontario, unpublished data), and from inland lakes in Minnesota (n = 31, Engstrom et al. 2007 and unpublished), Michigan (n = 26, Drevnick et al. 2007; Parsons et al. 2007), Ontario (n = 9, Muir et al. 2009), New York (n = 14, Bookman et al. 2008; Lorey and Driscoll 1999; Muir et al. 2009), Quebec (n = 2, Muir et al. 2009), and Vermont/New Hampshire (n = 11, Kamman and Engstrom 2002; Muir et al. 2009). All sediment cores were collected during 1994-2006, except the cores from Lake Ontario, which were collected in 1981 (2 cores) and 2008 (1 core).

To represent external Hg loading to the lakes, we used ^{210}Pb-based focus factors to derive focus-corrected Hg flux to each lake's sediments. Focusing, defined as the redistribution of sediments within a lake from shallower to deeper areas (where cores are usually collected), generally increases with lake size and fetch. Focusing is responsible for the observation that Hg

flux to the coring site is generally greater than the average flux to the lake as a whole. The focus factor is the ratio of the core specific ^{210}Pb flux to the atmospheric ^{210}Pb flux (*c.* 0.5 pCi/cm^2/yr for the Great Lakes region). Because ^{210}Pb has a short half-life (22 years) relative to its residence time in soils, no more than 1-2% of annual ^{210}Pb fallout to the watershed is removed to the lake (Appleby, 2001). Direct atmospheric deposition to the lake surface is thus the dominant ^{210}Pb load except in cases where watersheds are very large or highly disturbed. The important point here is that focusing corrections based on ^{210}Pb do not account for watershed Hg inputs, which must instead be determined following other methods (see below).

The Great Lakes, because they are large and have significant wind-driven currents, are subject to considerable sediment focusing (e.g., Rossmann 2010), and it appears from a positive relationship between lake surface area and the ^{210}Pb-based focus factor (lake surface area natural log transformed; n = 91, r = 0.298, p = 0.004) that sediment focusing is also significant in inland lakes. Focus-corrected sediment Hg flux is calculated by dividing a lake's Hg flux by its ^{210}Pb-based focus factor.

For each lake, we also calculated Hg flux ratios by dividing the sediment Hg fluxes for 1970, recent, and peak by the pre-1850 Hg flux. Flux ratios normalize the data across lakes by providing an estimate of relative change in sediment Hg fluxes.

Data from inland lakes (n = 91; Figure 1) were grouped into three geographic sub-regions. Sediment cores were collected from fairly discrete sub-regions that facilitated the geographic divisions: west (west of 87˚ W; n = 44; includes cores from Minnesota, northwestern Ontario, Isle Royale, and the western Upper Peninsula of Michigan); central (81-87˚ W, n = 15, includes cores from northeastern Ontario from the rest of Michigan); and east (east of 81˚ W, n = 32, includes cores from southern Ontario, New York, Quebec, Vermont, and New Hampshire).

144 Data from inland lakes, as the entire dataset and by sub-region, were examined for
145 patterns of sediment Hg fluxes and Hg flux ratios, including relative watershed influence, Hg wet
146 deposition, and the distance/proximity to local/regional sources of atmospheric Hg emissions.
147 Analyses were performed with JMP software (SAS Institute, Inc., Cary, NC, USA) and,
148 depending on the nature of the data, included Student's t-tests, one-way analysis of variance
149 (ANOVA), simple linear regression, and stepwise multiple regression. Data were transformed, if
150 necessary, to meet the assumptions of the analyses.

151 The influence of a lake's watershed on sedimentary Hg flux was examined with two
152 metrics: the watershed area:lake area ratio (A_W:A_L) and dominant land use type. Lakes derive a
153 variable portion of their total Hg load from watershed export of atmospheric deposition, which
154 we estimate from A_W:A_L by assuming that a similar proportion (24%) of Hg deposition to the
155 terrestrial watershed is exported to all lakes. This approach allows us estimate the atmospheric
156 Hg flux for each lake (and sub-region) by adjusting the focus-corrected Hg fluxes for watershed
157 contributions. It is a direct modification of the method of Swain et al. (1992) and is described
158 more fully in the discussion section below.

159 Of the 91 sediment cores from inland lakes, 80 were collected from lakes with forested
160 catchments, and 11 were collected from lakes dominated by "other" land use: agriculture,
161 agriculture/forest, or agriculture/urban. We observed no difference in sediment Hg fluxes or Hg
162 flux ratios between lakes with forested watersheds and lakes with "other" dominant land use
163 (Student t-test). This result was predictable, considering that we selected lakes *a priori* with
164 relatively undisturbed (largely forested) catchments. Thus, while land use can significantly
165 influence Hg flux to a lake (Engstrom et al. 2007), it is not a factor in our dataset and is not
166 considered further.

Estimates of Hg wet deposition were obtained from the Mercury Deposition Network (MDN; National Atmospheric Deposition Program 2011). The MDN operates more than 25 sites (varies by year) within the Great Lakes region. For each site, total Hg is measured in precipitation weekly, and annual Hg wet deposition is calculated. Where there is sufficient spatial coverage, isopleth maps are produced that interpolate annual wet deposition between sites. Beginning in 2004, isopleth maps have been produced for the entire Great Lakes region. For this study, estimates of annual Hg wet deposition for inland lakes were obtained by overlaying the GPS coordinates of sediment cores onto maps displaying MDN isopleths for the years 2004-2006 (the latter being the final year of core collection for this study). The average of the 3 years represents recent Hg wet deposition for each site. In addition, Hg wet deposition as a percentage of recent focus-corrected Hg flux was calculated for each site.

To examine Hg wet deposition and sedimentary Hg flux in the context of distance/proximity to local/regional sources of atmospheric Hg emissions, we made crude estimates of distance to the nearest major urban area and the number of major urban areas within 500 km. We define a major urban area as having a human population greater than 1,000,000 (city plus suburbs). Distances were calculated, according to latitude and longitude, from core sites to the approximate centers of the major urban areas.

3. Results and Discussion

3.1. Great Lakes

A review of studies from the Great Lakes (Table 1) indicates that relatively little work has been done to understand sedimentary Hg fluxes in these important ecosystems. Most previous studies have compared Hg concentrations in surficial sediments collected from selected

stations at different time periods (e.g., 1970 versus 2000) (Marvin et al. 2004). This approach has shown that there are differences in Hg concentrations in surficial sediments within and among the Great Lakes, and that there have been marked decreases in Hg concentrations since the late 1960s/early 1970s. However, if more work is to be done on Hg contamination of Great Lakes sediments, efforts should focus on dated sediment cores, as this approach is more useful for lake management. Dated sediment cores yield temporal data that are highly detailed, as well as flux estimates that can be used for source characterization and mass-balance calculations. While surficial sediments can be useful in identifying pollution from direct wastewater discharges, estimates from dated sediment cores indicate that more than 90% of modern sedimentary Hg fluxes are due to atmospheric deposition directly to the lake surface, at least for Lake Superior (Rolfhus et al. 2003) and Lake Michigan (Rossmann 2010).

The sedimentary records from Lake Ontario and Lake Michigan indicate that Hg loading from direct wastewater discharge had been elevated in the past, with Lake Ontario more strongly affected than Lake Michigan. Pre-1850 sediment Hg fluxes for both lakes were relatively low and stable, but by approximately 1950 had reached peak fluxes of 760 $\mu g/m^2$-yr in Lake Ontario and 53 $\mu g/m^2$-yr in Lake Michigan, resulting in peak to pre-industrial flux ratios of 76 and 17, respectively. These ratios greatly exceed the typical values of 2-5 observed worldwide for lakes unaffected by point-source water pollution (Biester et al. 2007). For Lake Ontario and Lake Michigan, respectively, Hg fluxes decreased from peak values by one-half and one-third by 1970 and another one-half and one-third by recent estimates. The human populations along the shorelines of these two Great Lakes are large, with many well-documented point-source wastewater discharges (e.g., Marvin et al. 2004), including chlor-alkali and pulp and paper facilities that used Hg in industrial processes, as well as municipal wastewater treatment plants.

Both the timing and magnitude of change in these sediment records suggest that direct (end-of-pipe) water discharges, not atmospheric deposition, were responsible for the mid-20th century Hg peaks and large subsequent declines.

In contrast, the sedimentary records from Lake Superior indicate primarily an atmospheric signal. The human population along the shoreline of Lake Superior is the smallest of the Great Lakes, but there are, and have been, significant direct wastewater discharges to the lake (Kerfoot et al. 1999). The areal extent of pollution from wastewater discharges may be localized near the outfalls to this largest Great Lake, however. From cores collected in 1983, Rossmann (1999) reported Hg fluxes to surficial sediments as high as 100 μg/m^2-yr for nearshore areas affected by point sources, but lower Hg fluxes for offshore areas (recalculated in Rossmann 2010; means in μg/m^2-yr of 7.2 for pre-1850 sediments and 27.7 for surficial sediments; flux ratio of 4). These earlier values reported by Rossman (1999) were crude estimates, however, because core chronologies and sedimentation rates were not measured, but taken from previously published reports. The data contributed for the present synthesis were from cores collected from offshore areas (Johnson et al. submitted; Muir et al. 2009). Loading of Hg to offshore waters of Lake Superior is dominated by atmospheric deposition (Rolfhus et al. 2003). Sediment Hg fluxes, compared to values from Lake Ontario and Lake Michigan, are low for all periods (in μg/m^2-yr; pre-1850 2.7, peak 12.8, recent 10.8), but agree well with estimates of atmospheric fluxes derived from inland lakes in adjacent northeastern Minnesota (Engstrom and Swain 1997; Swain et al. 1992; see below inland lakes). The sediment cores from Lake Superior and those of Engstrom and Swain (1997) also had similar Hg flux ratios (3-4 vs. 4-5) and peak years of Hg flux (1977 vs. mid-1970s). Sediments from offshore areas of Lake Superior appear to be a near-ideal recorder of net atmospheric Hg deposition.

236

237 3.2. Inland Lakes

238 Sediment Hg fluxes (Figure 2), peak year of flux (Figure 3), and flux ratios (Figure 4)
239 from sediment records from inland lakes indicate that atmospheric Hg deposition was generally
240 uniform across the Great Lakes region. Inland lakes from each geographic region exhibited
241 similar patterns of relative change in Hg fluxes. Median pre-1850 sediment fluxes for the west
242 (W), central (C), and east (E) were 7.5, 4.6, and 15.2 μg/m^2-yr, respectively. Fluxes had
243 increased approximately three-fold by 1970 (W 21.1, C 16.1 , E 51.4 μg/m^2-yr) and by four- to
244 five-fold at peak during the late 1980s (W 29.9, C 24.8, E 68.7 μg/m^2-yr). Recent fluxes (W
245 24.0, C 20.5, E 55.8 μg/m^2-yr) have declined about 20%, to near 1970 levels. Peak and recent
246 fluxes, especially those for the central and east sub-regions, showed the greatest variation (Figure
247 2).

248 For each period, the median Hg flux to the sediment in the east lakes was two to three
249 times greater than that in the west and central sub-regions. Atmospheric Hg deposition may be
250 elevated in the east due to generally higher precipitation, but probably not because of human
251 influence, as Hg flux ratios in this sub-region were similar to those in the west and central sub-
252 regions. Most likely the high Hg flux in the eastern lakes was primarily due to greater Hg inputs
253 from their relatively larger watersheds (Lorey and Driscoll 1999), as A_W:A_L tended to be greatest
254 in this sub-region (one-way ANOVA; $F_{2,88} = 3.01$, $p = 0.054$). The central sub-region had higher
255 flux ratios for peak:pre-1850 (one-way ANOVA; $F_{2,88} = 5.11$, $p = 0.008$) and recent:pre-1850
256 (one-way ANOVA; $F_{2,88} = 3.28$, $p = 0.042$) than the west and east. We cannot rule out, however,
257 that the high flux ratios in this sub-region may have been an artifact of the small number of lakes
258 with a large range in flux ratios.

Based on previous reports, we did not expect a clear region-wide pattern of recent declines in Hg flux. Engstrom and Swain (1997) reported from a suite of Minnesota lakes that Hg flux peaked in the 1970s and was declining region wide (upper Midwest). A more comprehensive dataset from Minnesota, however, suggested that the declines (of 20-30% since peak) were limited to lakes near (<60 km from) sources of atmospheric Hg emissions (Engstrom et al. 2007). Parsons et al. (2007) stressed the importance of watershed-scale sources to Michigan lakes, reporting that only 11 of 26 (42%) lakes studied had recent declines in Hg flux. Similarly, Muir et al. (2009) observed only 5 of 14 (36%) lakes within the Great Lakes airshed showing recent declines in sediment Hg flux. In contrast, the literature suggests that recent declines are more pronounced in lakes in the eastern reaches of the Great Lakes region (Bookman et al. 2008; Kamman and Engstrom 2002). The present synthesis incorporated all of the above-mentioned studies, as well as others, but as mentioned previously, included only lakes with relatively undisturbed watersheds, to more clearly examine trends in atmospheric Hg deposition without the confounding influence of land use. Of the lakes in our synthesis, 76 of 91 (84%) showed a recent decline in sedimentary Hg flux. If the 15 lakes that showed no decline are removed from the data analysis, median values for all lakes, as well as for each of the three sub-regions, for peak year (91 lakes, 1989; 76 lakes, 1985) and the flux ratio of recent:peak (91 lakes, 0.85; 76 lakes, 0.81) were little affected.

Watershed factors

The relationship between A_W:A_L and sedimentary Hg flux for a given set of lakes has been used to derive atmospheric Hg flux for a given area (Swain et al. 1992). This approach involves simple linear regression of sedimentary Hg flux (dependent variable) against A_W:A_L (independent variable). The intercept of the regression line at A_W:A_L = 0 approximates Hg

loading to a lake with no watershed, i.e. atmospheric Hg deposition. The slope divided by the intercept approximates the proportion of atmospheric Hg deposition delivered to the lake from the watershed. We performed simple linear regressions of A_W:A_L and Hg fluxes (pre-1850, peak, recent) from inland lakes for the Great Lakes airshed as a whole and for the west, central, and east sub-regions separately (Table 2). Relationships with the entire Great Lakes airshed and with the east sub-region were statistically significant, whereas those with the central and west sub-regions were not. And while the regressions with the entire dataset provided reasonable estimates (when back transformed) for atmospheric Hg deposition (pre-1850 = 5.5, recent = 20 $\mu g/m^2$-yr) the same estimates for the eastern sub-region were substantially higher (pre-1850 = 11, recent = 30 $\mu g/m^2$-yr). Present-day values for wet Hg deposition from MDN monitoring (5-10 $\mu g/m^2$-yr) are much lower than either of these estimates and show little regional differentiation (Figure 1). The values for the ratio of slope to intercept (when both are back transformed) are also questionable, because they indicate very low delivery of atmospheric Hg deposition from watershed to lake (5% or less). Empirical measurements generally indicate that watersheds deliver much higher (~20%) proportions of atmospheric Hg deposition to lakes (e.g., Aastrup et al. 1991).

In an attempt to provide more realistic estimates, we performed the analyses for the Great Lakes airshed as a whole and for the west, central, and east sub-regions separately, but with lakes with A_W:A_L <10 and again with A_W:A_L <5. Most of the relationships are not significant, however, and the values for slope and intercept do not improve estimates for atmospheric Hg deposition and watershed influence. Perhaps, as noted by Muir et al. (2009), this regression approach is not ideal for a diverse group of lakes, but is more suitable for lakes in close proximity (e.g., Lorey and Driscoll 1999, Kamman and Engstrom 2002).

There was also no apparent relationship between A_W:A_L and flux ratios or peak year of flux. For the Great Lakes airshed as a whole and for the west, central, and east sub-regions separately, we performed simple linear regressions between A_W:A_L and flux ratios for peak:pre-1850, recent:pre-1850, recent:peak, and peak year. As above, we performed the analyses with data from all lakes, lakes with A_W:A_L <10, and lakes with A_W:A_L <5. None of the 48 relationships tested were statistically significant (statistics not shown).

We believe that much of the difficulty in using the regression approach to estimate atmospheric Hg deposition may arise from unaccounted-for variation in Hg export, in-lake cycling, and sedimentation among our large and diverse group of lakes and watersheds. Hence we developed an alternative method that independently estimates atmospheric Hg deposition for each lake and thus removes the influence of outliers that otherwise may distort the regression analyses. In this approach we corrected the sediment Hg flux in each lake for the relative size of the lake's watershed by rearranging terms in the relationship of Swain et al. (1992), so that:

$$\text{Atmospheric Hg flux} = \text{focus-corrected sediment Hg flux} / (1 + (0.24\ A_W{:}A_L)) \quad (1)$$

We assume here that 24% of Hg deposition to the terrestrial watershed is exported to each lake, a coefficient chosen as the mid-point between the value of 26% found for modern deposition in the western Great Lakes sub-region by Swain et al. (1992) and 22% reported by Lorey and Driscoll (1999) in the east. By estimating atmospheric deposition in this manner, we make the gross assumption that all terrestrial watersheds behave similarly, not only in the present, but also in the past.

The median atmospheric Hg deposition calculated in this manner is broadly uniform across the Great Lakes region and shows a similar magnitude of change to that of the sediment Hg fluxes. In preindustrial times (pre-1850) median Hg deposition rates for the west, central, and east were 2.6, 2.1, and 3.7 μg/m^2-yr, respectively (Figure 5). These rates increased to 9.1, 9.1, and 13.1 μg/m^2-yr by 1970, peaked at 13.1. 15.0 and 16.9 μg/m^2-yr in the 1980s, and declined to 10.3, 13.1, and 10.8 μg/m^2-yr in recent times (west, central, and east, respectively). These values are very similar to those reported by Swain et al. (1992) from a different group of Minnesota lakes (pre-1850 = 3.7 μg/m^2-yr, and recent (c. 1990) = 12.5 μg/m^2-yr), and are only slightly higher (for the modern rate) than MDN measurements of wet deposition for the Great Lakes airshed (generally 5-10 μg/m^2-yr).

Relationship with emissions and wet Hg deposition

For all lakes across the Great Lakes airshed, estimates of Hg wet deposition from MDN are not correlated with recent sedimentary Hg flux (recent sedimentary Hg flux natural log transformed; n = 91, r = 0.039, p = 0.715). Perhaps this result is not surprising as there is little spatial variation in estimates of Hg wet deposition across the airshed (Prestbo and Gay 2009; Risch et al. this issue), but there is a significant gradient in sedimentary Hg flux (east higher than west and central; for all time periods examined). Moreover, dry Hg deposition generally exceeds wet Hg deposition (Miller et al. 2005; Driscoll et al. 2007a). For each lake, we calculated Hg wet deposition as a percent of recent focus-corrected Hg flux, finding values ranging from 2% to 112%, with a median of 21%. For the three sub-regions (Figure 6), the percentage of recent sediment Hg deposition as wet deposition was significantly lower in the east (16%) than the west (29%) and central (42%) (natural log of Hg wet deposition divided by recent Hg flux; one-way ANOVA; $F_{2,88} = 14.8$, $p < 0.001$).

An examination of the relationship between Hg wet deposition as a percentage of recent sedimentary Hg flux and A_W:A_L (Figure 7) teases out the influence of watershed size on Hg flux in inland lakes. The two variables were significantly and negatively related (both variables natural log transformed; $n = 91$, $r = -0.435$, $p < 0.001$). It would appear that the lower inferred percent Hg wet deposition (relative to recent sedimentary Hg flux) in the eastern lakes is a proximal result of higher sediment-Hg fluxes in this sub-region. At a mechanistic level, it could indicate that lakes with relatively large watersheds receive a greater portion of their Hg inputs from runoff (as opposed to direct atmospheric deposition), or that lakes with small surface areas receive more Hg from litterfall (dry deposition) than do large lakes, which have a smaller "edge effect". If the latter is true, it might also explain the relatively high Hg fluxes in the east.

There are distinct effects of local sources of atmospheric Hg emissions on wet and dry Hg deposition and on sedimentary Hg flux in the Great Lakes airshed. We performed simple linear regressions of (1) distance to the nearest major urban area; and (2) the number of major urban areas within 500 km with (i) Hg wet deposition, (ii) Hg wet deposition as a percentage of recent sedimentary Hg flux, (iii) sedimentary Hg fluxes (pre-1850, peak, recent), and (iv) Hg flux ratios (peak:pre-1850, recent:pre-1850, recent:peak) (Table 3). Relationships were significant with Hg wet deposition and Hg wet deposition as a percentage of recent sedimentary Hg flux, indicating that atmospheric Hg deposition (wet and dry) is elevated in the proximity/vicinity of atmospheric Hg sources. For the sediment records, relationships were significant with peak and recent flux rates and inconsistent with flux ratios. These relationships were predictable because gaseous Hg(II) emitted by combustion sources has a relatively short atmospheric residence time (Lindberg et al. 2007). Engstrom and Swain (1997) estimated that 40% of atmospheric Hg deposition in Minnesota lakes originated from sources within the region,

373 however, as short-stack, high pHg/Hg(II) emissions have decreased, sources within the region
374 now contribute generally less than 30% to atmospheric Hg in the region (Selin et al. 2007).
375 Denkenberger et al. (this issue) estimated that 40% of the total Hg emissions in 2005 in the Great
376 Lakes watershed were from oxidized Hg.

377 A step-wise multiple regression analysis indicates that much of the variation ($R^2 = 0.553$)
378 in recent sedimentary Hg flux in inland lakes can be explained by the pre-1850 flux, A_W:A_L, and
379 the number of major urban areas within 500 km. Other variables considered by the model, but
380 not entered in the regression equation (probability to enter = 0.25), included Hg wet deposition
381 and distance to the nearest major urban area. The regression equation is:
382
383 $$\ln(\text{recent flux}) = 1.91 + 0.480 \times \ln(\text{pre-1850 flux}) + 0.159 \times MUA^{1/2} + 0.121 \times \ln(A_W{:}A_L) \quad (2)$$
384
385 Pre-1850 flux accounts for underlying differences among the lakes and geological sources of Hg,
386 the number of major urban areas (MUA) within 500 km accounts for wet and dry atmospheric
387 Hg deposition, and A_W:A_L accounts for watershed delivery of atmospheric Hg to the lake (Mills
388 et al. 2009).
389
390 3.3 Great Lakes versus Inland Lakes

391 Similarities in sedimentary Hg flux between the Great Lakes and inland lakes were
392 observed in temporal trends and spatial patterns. Both types of systems responded to post-1850
393 increases in Hg loading, reached a peak during the mid to late 20th century (although nearly 40
394 years apart), and now show declines in Hg flux. For spatial patterns, both the Great Lakes and
395 inland lakes show elevated Hg fluxes toward the eastern sub-region of the Great Lakes airshed.

396 The spatial patterns arise from different reasons, however. The lower Great Lakes (e.g., Lake
397 Ontario) exhibit greater Hg contamination than the upper Great Lakes (e.g., Lake Michigan,
398 Lake Superior) because of greater wastewater and industrial waste discharges, whereas relatively
399 high Hg fluxes for inland lakes are found in the east (for all time periods examined), likely due to
400 watersheds that are large relative to the areas of the lakes.

401 Differences in sedimentary Hg flux between the Great Lakes and inland lakes are
402 observed in the magnitude of change during the industrial period. Lake Ontario and Lake
403 Michigan, both affected by point-source wastewater discharges, have peak:pre-1850 flux ratios
404 of 76 and 17, respectively. Sediment Hg deposition has declined more than 50% since peak
405 values in these systems. In contrast, inland lakes have peak:pre-1850 flux ratios of
406 approximately 5, with declines generally less than 20% since peak values.

407 Hg fluxes, the peak year of flux, and flux ratios for Lake Superior are more similar to
408 inland lakes than to the other lower Great Lakes. This finding likely relates to sediments from
409 offshore areas of Lake Superior yielding what appears to be a record of net atmospheric Hg flux.
410 The sedimentary Hg fluxes (pre-1850, peak, recent) from Lake Superior are lower than our
411 focus-corrected sediment Hg flux derived from inland lakes (Table 2), but are similar to our
412 median estimates of atmospheric Hg flux in the west (in $\mu g/m^2$-yr; Lake Superior and west are,
413 respectively: pre-1850 2.7 and 2.6, 1970 11.1 and 9.1, peak 12.8 and 13.1, recent 10.8 and 10.3).
414

415 **4. Conclusions**

416 The most important finding from our synthesis may be that sedimentary Hg flux is
417 declining in both the Great Lakes and inland lakes of the Great Lakes region. Local, regional,
418 and (inter)national management of Hg discharges to water and air are making significant

progress in decreasing Hg loads to lakes, big and small, across the region. Another important and perhaps unexpected finding is that atmospheric Hg deposition appears uniform across the Great Lakes airshed. This consistent observation has important management implications. First, it suggests that local and regional sources of atmospheric Hg emissions are important sources of Hg deposition compared to global sources. Atmospheric Hg emissions within the Great Lakes region have decreased in recent decades (Pirrone et al. 1998; Driscoll et al. 2007b; Evers et al. 2007), whereas global sources have increased (AMAP/UNEP 2008). Second, it suggests that regional and local controls on atmospheric emissions have been effective in decreasing the delivery of Hg to lakes, across the region regardless of watershed size. This important observation was unexpected, because a region-wide trend of declining atmospheric Hg deposition is not evident from MDN data (for the period 1996-2005; Prestbo and Gay 2009) or from previous sediment core data (see second paragraph of section 3.2).

We also anticipated significant relationships between A_W:A_L and (1) recent:peak and (2) peak year, although none were discerned in our analysis. It has been hypothesized (Fitzgerald and Lamborg 2004; Grigal 2002), and shown in a few studies (e.g., Lorey and Driscoll 1999, Kamman and Engstrom 2002, Harris et al. 2007), that continued flux of "legacy" Hg (i.e., historical Hg deposition) from a watershed will cause a lag in recovery of Hg loading to lakes, and that this effect is magnified in lakes with large watersheds. The combined observations that sediment-Hg declines were recorded in lakes regardless of watershed size and the absence of clear trends in recent MDN monitoring suggest that sediment records may be responding to decreases in Hg deposition that occurred decades earlier.

We have a concern that this pattern of recent declines in Hg deposition relies on interpretation of data from the most recent strata of lake sediments, which are characterized by

some uncertainty concerning disturbance and diagenesis in deposition processes. An important test of the veracity of these declines will come with future core work on the same or another suite of regional lakes. However, given that recent declines in sediment Hg deposition have been observed in a large number of lakes sampled by a broad suite of investigators, we believe that these observations suggest a "cause and effect" relationship between controls on local and regional emissions of Hg to the atmosphere and partial ecosystem recovery from Hg contamination. Note that at least one regional study has reported recent decreases in fish Hg concentrations (Dittman and Driscoll 2009). Deviations from our findings for sedimentary Hg flux, either temporal (e.g., the recent increase in Hg concentrations in walleye in Minnesota; Monson 2009) or spatial (e.g., exceptionally high Hg concentrations in fish in an area of low Hg flux, Voyageurs National Park; Wiener et al. 2006), are likely related to ecosystem factors, such as Hg methylation or lake productivity, and not atmospheric Hg flux.

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Figure captions

Figure 1. Map of the Great Lakes study area, with an overlay of wet Hg deposition obtained from the Mercury Deposition Network (National Atmospheric Deposition Program 2011). Shown are the location of sediment cores used in this synthesis, the boundary of the Great Lakes watershed, provincial and state boundaries, and the west, central and east sub-regions used in data analysis.

Figure 2. Box plots of accumulation rates (or flux) of mercury (Hg) in dated sediment cores from inland lakes of the Great Lakes airshed. Plots are presented for four time periods (pre-1850, 1970, peak, recent) for the entire region (all) and for three subregions: west (west of 87˚ W), central (81-87˚ W), and east (east of 81˚ W). Boxes represent interquartile ranges, whiskers delineate upper and lower 10%, and the center line is the median.

Figure 3. Box plot of peak year of accumulation rates (or flux) of mercury (Hg) in dated sediment cores from inland lakes in three subregions (west, central, east; further described in Figure 2 and text) of the Great Lakes airshed. Box plot as described in Figure 2.

Figure 4. Box plots of the ratio of mercury (Hg) accumulation (flux ratios) for peak:pre-1850, recent:pre-1850, and recent:peak from dated sediment cores from inland lakes in three subregions (west, central, east; further described in Figure 2 and text) of the Great Lakes airshed. Dashed line denotes a flux ratio of 1 (no change). Box plots as described in Figure 2. The upper

656 whiskers for the central subregion extend to 68 and 30 for peak:pre-1850 and recent:pre-1850,
657 respectively.
658
659 Figure 5. Box plots of atmospheric mercury (Hg) deposition calculated by correcting sediment
660 Hg fluxes for sediment focusing and watershed Hg inputs (see text). Results shown for inland
661 lakes in three subregions (west, central, east; further described in Figure 2 and text) of the Great
662 Lakes airshed and for the entire region. Box plots as described in Figure 2.
663
664 Figure 6. Box plot of mercury (Hg) wet deposition as a percent of recent Hg accumulation rates
665 (flux) for sediment coring sites at inland lakes in three subregions (west, central, east; further
666 described in Figure 2 and text) of the Great Lakes airshed. Data for Hg wet deposition are from
667 the Mercury Deposition Network for the years 2004-2006. Box plot as described in Figure 2.
668
669 Figure 7. Scatter plot of watershed area : lake area ratio (A_W:A_L) and mercury (Hg) wet
670 deposition as a percent of recent Hg accumulation rates (flux) for inland lakes in three
671 subregions (west, central, east; further described in Figure 2 and text) of the Great Lakes airshed.
672 Data for Hg wet deposition are from the Mercury Deposition Network for the years 2004-2006.
673