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

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36 **Abstract**

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

48

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

50

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

53 1. Introduction

54 Human releases of mercury (Hg) to the atmosphere, and to a lesser extent surface waters,
55 have contaminated ecosystems on a global scale (Fitzgerald et al. 1998). In aquatic ecosystems,
56 bacteria (principally sulfate reducers) transform divalent inorganic Hg into methylmercury
57 (MeHg), which strongly bioaccumulates within food webs, resulting in exposure to humans and
58 wildlife (National Research Council 2000). All of the states and provinces of the Great Lakes
59 Region, including the Great Lakes and their connecting waters, have fish consumption advisories
60 due to MeHg contamination (Environment Canada 2011; U.S. Environmental Protection Agency
61 2011).

62 Lake sediments have been widely used to document the historical and spatial dimensions
63 of Hg pollution (Biester et al. 2007). Sediment cores can be used, for example, to evaluate the
64 magnitude of change in Hg deposition over long time-scales (Lamborg et al. 2002) and to
65 explore recent depositional trends owing to changes and decreases in emissions (Engstrom and
66 Swain 1997). Over the last two decades, numerous dated sediment records of Hg flux have been
67 compiled for the Great Lakes region (e.g., Bookman et al. 2008; Drevnick et al. 2007; Engstrom
68 and Swain 1997; Engstrom et al. 2007; Johnson et al. submitted; Kamman and Engstrom 2002;
69 Lorey and Driscoll 1999; Mills et al. 2009; Muir et al. 2009; Parsons et al. 2007; Pirrone et al.
70 1998; Rossmann 1999; Rossmann 2010; Swain et al. 1992). These records have been interpreted
71 largely within a local (state or provincial) context, but have not been systematically compiled or
72 evaluated across the entire Great Lakes region.

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

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

87

88 **2. Methods**

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

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

98 published in the peer-reviewed literature. Data were solicited from potential contributors with
99 the following criteria: (1) reliable and detailed dating by ^{210}Pb ; (2) sediment core records
100 extending back to preindustrial times (pre-1850); and (3) for inland lakes, relatively undisturbed
101 watersheds, which otherwise greatly increase Hg loading through erosion, and an absence of
102 direct inputs of Hg from wastewater or industrial waste. We defined an inland lake as any
103 natural lake, excluding the Great Lakes themselves, within the study area. Potential contributors
104 were asked to provide the following information for each core: lake name, locality, date of
105 collection, latitude and longitude of core site, sediment Hg fluxes (pre-1850, 1970, recent, peak),
106 ^{210}Pb -based focus factor, lake surface area, watershed surface area (excluding lake), and
107 dominant land use within watershed (qualitatively or by GIS). Contributors (all co-authors)
108 provided data from dated sediment cores from Lake Superior (n = 9, Muir et al. 2009; Johnson et
109 al. submitted), Lake Michigan (n = 1, Rossmann 2010), Lake Ontario (n = 3, Pirrone et al. 1998;
110 D.G.C. Muir, Environment Canada, Burlington, Ontario, unpublished data), and from inland
111 lakes in Minnesota (n = 31, Engstrom et al. 2007 and unpublished), Michigan (n = 26, Drevnick
112 et al. 2007; Parsons et al. 2007), Ontario (n = 9, Muir et al. 2009), New York (n = 14, Bookman
113 et al. 2008; Lorey and Driscoll 1999; Muir et al. 2009), Quebec (n = 2, Muir et al. 2009), and
114 Vermont/New Hampshire (n = 11, Kamman and Engstrom 2002; Muir et al. 2009). All sediment
115 cores were collected during 1994-2006, except the cores from Lake Ontario, which were
116 collected in 1981 (2 cores) and 2008 (1 core).

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

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

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

135 For each lake, we also calculated Hg flux ratios by dividing the sediment Hg fluxes for
136 1970, recent, and peak by the pre-1850 Hg flux. Flux ratios normalize the data across lakes by
137 providing an estimate of relative change in sediment Hg fluxes.

138 Data from inland lakes ($n = 91$; Figure 1) were grouped into three geographic sub-
139 regions. Sediment cores were collected from fairly discrete sub-regions that facilitated the
140 geographic divisions: west (west of 87° W ; $n = 44$; includes cores from Minnesota, northwestern
141 Ontario, Isle Royale, and the western Upper Peninsula of Michigan); central ($81\text{-}87^\circ \text{ W}$, $n = 15$,
142 includes cores from northeastern Ontario from the rest of Michigan); and east (east of 81° W , $n =$
143 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.

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

178 To examine Hg wet deposition and sedimentary Hg flux in the context of
179 distance/proximity to local/regional sources of atmospheric Hg emissions, we made crude
180 estimates of distance to the nearest major urban area and the number of major urban areas within
181 500 km. We define a major urban area as having a human population greater than 1,000,000
182 (city plus suburbs). Distances were calculated, according to latitude and longitude, from core
183 sites to the approximate centers of the major urban areas.

184

185 **3. Results and Discussion**

186 3.1. Great Lakes

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

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

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

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

216 In contrast, the sedimentary records from Lake Superior indicate primarily an
217 atmospheric signal. The human population along the shoreline of Lake Superior is the smallest
218 of the Great Lakes, but there are, and have been, significant direct wastewater discharges to the
219 lake (Kerfoot et al. 1999). The areal extent of pollution from wastewater discharges may be
220 localized near the outfalls to this largest Great Lake, however. From cores collected in 1983,
221 Rossmann (1999) reported Hg fluxes to surficial sediments as high as 100 $\mu\text{g}/\text{m}^2\text{-yr}$ for
222 nearshore areas affected by point sources, but lower Hg fluxes for offshore areas (recalculated in
223 Rossmann 2010; means in $\mu\text{g}/\text{m}^2\text{-yr}$ of 7.2 for pre-1850 sediments and 27.7 for surficial
224 sediments; flux ratio of 4). These earlier values reported by Rossman (1999) were crude
225 estimates, however, because core chronologies and sedimentation rates were not measured, but
226 taken from previously published reports. The data contributed for the present synthesis were
227 from cores collected from offshore areas (Johnson et al. submitted; Muir et al. 2009). Loading of
228 Hg to offshore waters of Lake Superior is dominated by atmospheric deposition (Rolfhus et al.
229 2003). Sediment Hg fluxes, compared to values from Lake Ontario and Lake Michigan, are low
230 for all periods (in $\mu\text{g}/\text{m}^2\text{-yr}$; pre-1850 2.7, peak 12.8, recent 10.8), but agree well with estimates
231 of atmospheric fluxes derived from inland lakes in adjacent northeastern Minnesota (Engstrom
232 and Swain 1997; Swain et al. 1992; see below inland lakes). The sediment cores from Lake
233 Superior and those of Engstrom and Swain (1997) also had similar Hg flux ratios (3-4 vs. 4-5)
234 and peak years of Hg flux (1977 vs. mid-1970s). Sediments from offshore areas of Lake
235 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 $\mu\text{g}/\text{m}^2\text{-yr}$, respectively. Fluxes had
243 increased approximately three-fold by 1970 (W 21.1, C 16.1, E 51.4 $\mu\text{g}/\text{m}^2\text{-yr}$) and by four- to
244 five-fold at peak during the late 1980s (W 29.9, C 24.8, E 68.7 $\mu\text{g}/\text{m}^2\text{-yr}$). Recent fluxes (W
245 24.0, C 20.5, E 55.8 $\mu\text{g}/\text{m}^2\text{-yr}$) 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.

259 Based on previous reports, we did not expect a clear region-wide pattern of recent
260 declines in Hg flux. Engstrom and Swain (1997) reported from a suite of Minnesota lakes that
261 Hg flux peaked in the 1970s and was declining region wide (upper Midwest). A more
262 comprehensive dataset from Minnesota, however, suggested that the declines (of 20-30% since
263 peak) were limited to lakes near (<60 km from) sources of atmospheric Hg emissions (Engstrom
264 et al. 2007). Parsons et al. (2007) stressed the importance of watershed-scale sources to
265 Michigan lakes, reporting that only 11 of 26 (42%) lakes studied had recent declines in Hg flux.
266 Similarly, Muir et al. (2009) observed only 5 of 14 (36%) lakes within the Great Lakes airshed
267 showing recent declines in sediment Hg flux. In contrast, the literature suggests that recent
268 declines are more pronounced in lakes in the eastern reaches of the Great Lakes region
269 (Bookman et al. 2008; Kamman and Engstrom 2002). The present synthesis incorporated all of
270 the above-mentioned studies, as well as others, but as mentioned previously, included only lakes
271 with relatively undisturbed watersheds, to more clearly examine trends in atmospheric Hg
272 deposition without the confounding influence of land use. Of the lakes in our synthesis, 76 of 91
273 (84%) showed a recent decline in sedimentary Hg flux. If the 15 lakes that showed no decline
274 are removed from the data analysis, median values for all lakes, as well as for each of the three
275 sub-regions, for peak year (91 lakes, 1989; 76 lakes, 1985) and the flux ratio of recent:peak (91
276 lakes, 0.85; 76 lakes, 0.81) were little affected.

277 ***Watershed factors***

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

282 loading to a lake with no watershed, i.e. atmospheric Hg deposition. The slope divided by the
283 intercept approximates the proportion of atmospheric Hg deposition delivered to the lake from
284 the watershed. We performed simple linear regressions of $A_W:A_L$ and Hg fluxes (pre-1850,
285 peak, recent) from inland lakes for the Great Lakes airshed as a whole and for the west, central,
286 and east sub-regions separately (Table 2). Relationships with the entire Great Lakes airshed and
287 with the east sub-region were statistically significant, whereas those with the central and west
288 sub-regions were not. And while the regressions with the entire dataset provided reasonable
289 estimates (when back transformed) for atmospheric Hg deposition (pre-1850 = 5.5, recent = 20
290 $\mu\text{g}/\text{m}^2\text{-yr}$) the same estimates for the eastern sub-region were substantially higher (pre-1850 =
291 11, recent = 30 $\mu\text{g}/\text{m}^2\text{-yr}$). Present-day values for wet Hg deposition from MDN monitoring (5-
292 10 $\mu\text{g}/\text{m}^2\text{-yr}$) are much lower than either of these estimates and show little regional
293 differentiation (Figure 1). The values for the ratio of slope to intercept (when both are back
294 transformed) are also questionable, because they indicate very low delivery of atmospheric Hg
295 deposition from watershed to lake (5% or less). Empirical measurements generally indicate that
296 watersheds deliver much higher (~20%) proportions of atmospheric Hg deposition to lakes (e.g.,
297 Aastrup et al. 1991).

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

305 There was also no apparent relationship between $A_W:A_L$ and flux ratios or peak year of
306 flux. For the Great Lakes airshed as a whole and for the west, central, and east sub-regions
307 separately, we performed simple linear regressions between $A_W:A_L$ and flux ratios for peak:pre-
308 1850, recent:pre-1850, recent:peak, and peak year. As above, we performed the analyses with
309 data from all lakes, lakes with $A_W:A_L < 10$, and lakes with $A_W:A_L < 5$. None of the 48
310 relationships tested were statistically significant (statistics not shown).

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

318

$$319 \quad \text{Atmospheric Hg flux} = \text{focus-corrected sediment Hg flux} / (1 + (0.24 A_W:A_L)) \quad (1)$$

320

321 We assume here that 24% of Hg deposition to the terrestrial watershed is exported to each lake, a
322 coefficient chosen as the mid-point between the value of 26% found for modern deposition in the
323 western Great Lakes sub-region by Swain et al. (1992) and 22% reported by Lorey and Driscoll
324 (1999) in the east. By estimating atmospheric deposition in this manner, we make the gross
325 assumption that all terrestrial watersheds behave similarly, not only in the present, but also in the
326 past.

327 The median atmospheric Hg deposition calculated in this manner is broadly uniform
328 across the Great Lakes region and shows a similar magnitude of change to that of the sediment
329 Hg fluxes. In preindustrial times (pre-1850) median Hg deposition rates for the west, central, and
330 east were 2.6, 2.1, and 3.7 $\mu\text{g}/\text{m}^2\text{-yr}$, respectively (Figure 5). These rates increased to 9.1, 9.1,
331 and 13.1 $\mu\text{g}/\text{m}^2\text{-yr}$ by 1970, peaked at 13.1, 15.0 and 16.9 $\mu\text{g}/\text{m}^2\text{-yr}$ in the 1980s, and declined to
332 10.3, 13.1, and 10.8 $\mu\text{g}/\text{m}^2\text{-yr}$ in recent times (west, central, and east, respectively). These values
333 are very similar to those reported by Swain et al. (1992) from a different group of Minnesota
334 lakes (pre-1850 = 3.7 $\mu\text{g}/\text{m}^2\text{-yr}$, and recent (c. 1990) = 12.5 $\mu\text{g}/\text{m}^2\text{-yr}$), and are only slightly
335 higher (for the modern rate) than MDN measurements of wet deposition for the Great Lakes
336 airshed (generally 5-10 $\mu\text{g}/\text{m}^2\text{-yr}$).

337 ***Relationship with emissions and wet Hg deposition***

338 For all lakes across the Great Lakes airshed, estimates of Hg wet deposition from MDN
339 are not correlated with recent sedimentary Hg flux (recent sedimentary Hg flux natural log
340 transformed; $n = 91$, $r = 0.039$, $p = 0.715$). Perhaps this result is not surprising as there is little
341 spatial variation in estimates of Hg wet deposition across the airshed (Prestbo and Gay 2009;
342 Risch et al. this issue), but there is a significant gradient in sedimentary Hg flux (east higher than
343 west and central; for all time periods examined). Moreover, dry Hg deposition generally exceeds
344 wet Hg deposition (Miller et al. 2005; Driscoll et al. 2007a). For each lake, we calculated Hg
345 wet deposition as a percent of recent focus-corrected Hg flux, finding values ranging from 2% to
346 112%, with a median of 21%. For the three sub-regions (Figure 6), the percentage of recent
347 sediment Hg deposition as wet deposition was significantly lower in the east (16%) than the west
348 (29%) and central (42%) (natural log of Hg wet deposition divided by recent Hg flux; one-way
349 ANOVA; $F_{2,88} = 14.8$, $p < 0.001$).

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

360 There are distinct effects of local sources of atmospheric Hg emissions on wet and dry
361 Hg deposition and on sedimentary Hg flux in the Great Lakes airshed. We performed simple
362 linear regressions of (1) distance to the nearest major urban area; and (2) the number of major
363 urban areas within 500 km with (i) Hg wet deposition, (ii) Hg wet deposition as a percentage of
364 recent sedimentary Hg flux, (iii) sedimentary Hg fluxes (pre-1850, peak, recent), and (iv) Hg
365 flux ratios (peak:pre-1850, recent:pre-1850, recent:peak) (Table 3). Relationships were
366 significant with Hg wet deposition and Hg wet deposition as a percentage of recent sedimentary
367 Hg flux, indicating that atmospheric Hg deposition (wet and dry) is elevated in the
368 proximity/vicinity of atmospheric Hg sources. For the sediment records, relationships were
369 significant with peak and recent flux rates and inconsistent with flux ratios. These relationships
370 were predictable because gaseous Hg(II) emitted by combustion sources has a relatively short
371 atmospheric residence time (Lindberg et al. 2007). Engstrom and Swain (1997) estimated that
372 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:

$$382 \ln(\text{recent flux}) = 1.91 + 0.480 \times \ln(\text{pre-1850 flux}) + 0.159 \times \text{MUA}^{1/2} + 0.121 \times \ln(A_W:A_L) \quad (2)$$

383
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 $\mu\text{g}/\text{m}^2\text{-yr}$; 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

419 progress in decreasing Hg loads to lakes, big and small, across the region. Another important
420 and perhaps unexpected finding is that atmospheric Hg deposition appears uniform across the
421 Great Lakes airshed. This consistent observation has important management implications. First,
422 it suggests that local and regional sources of atmospheric Hg emissions are important sources of
423 Hg deposition compared to global sources. Atmospheric Hg emissions within the Great Lakes
424 region have decreased in recent decades (Pirrone et al. 1998; Driscoll et al. 2007b; Evers et al.
425 2007), whereas global sources have increased (AMAP/UNEP 2008). Second, it suggests that
426 regional and local controls on atmospheric emissions have been effective in decreasing the
427 delivery of Hg to lakes, across the region regardless of watershed size. This important
428 observation was unexpected, because a region-wide trend of declining atmospheric Hg
429 deposition is not evident from MDN data (for the period 1996-2005; Prestbo and Gay 2009) or
430 from previous sediment core data (see second paragraph of section 3.2).

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

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

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

454

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458

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634 Figure captions

635

636 Figure 1. Map of the Great Lakes study area, with an overlay of wet Hg deposition obtained
637 from the Mercury Deposition Network (National Atmospheric Deposition Program 2011).

638 Shown are the location of sediment cores used in this synthesis, the boundary of the Great Lakes
639 watershed, provincial and state boundaries, and the west, central and east sub-regions used in
640 data analysis.

641

642 Figure 2. Box plots of accumulation rates (or flux) of mercury (Hg) in dated sediment cores
643 from inland lakes of the Great Lakes airshed. Plots are presented for four time periods (pre-
644 1850, 1970, peak, recent) for the entire region (all) and for three subregions: west (west of 87°
645 W), central (81-87° W), and east (east of 81° W). Boxes represent interquartile ranges, whiskers
646 delineate upper and lower 10%, and the center line is the median.

647

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

651

652 Figure 4. Box plots of the ratio of mercury (Hg) accumulation (flux ratios) for peak:pre-1850,
653 recent:pre-1850, and recent:peak from dated sediment cores from inland lakes in three
654 subregions (west, central, east; further described in Figure 2 and text) of the Great Lakes airshed.
655 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