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

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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 pCi/cm$^2$/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 (81-87˚ 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 $\mu g/m^2$-yr in Lake Ontario

205      and 53 $\mu g/m^2$-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 $\mu g/m^2$-yr for

222  nearshore areas affected by point sources, but lower Hg fluxes for offshore areas (recalculated in

223  Rossmann 2010; means in $\mu g/m^2$-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 $\mu g/m^2$-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 $\mu g/m^2$-yr, respectively. Fluxes had

243     increased approximately three-fold by 1970 (W 21.1, C 16.1 , E 51.4 $\mu g/m^2$-yr) and by four- to

244     five-fold at peak during the late 1980s (W 29.9,  C 24.8, E 68.7 $\mu g/m^2$-yr).  Recent fluxes (W

245     24.0, C 20.5, E 55.8 $\mu g/m^2$-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.

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    $\mu g/m^2$-yr) the same estimates for the eastern sub-region were substantially higher (pre-1850 =

291    11,  recent = 30 $\mu g/m^2$-yr). Present-day values for wet Hg deposition from MDN monitoring (5-

292    10 $\mu g/m^2$-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        Atmospheric Hg flux = focus-corrected sediment Hg flux / (1 + (0.24 $A_W:A_L$))    (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 $\mu g/m^2$-yr, respectively (Figure 5). These rates increased to 9.1, 9.1,

331 and 13.1 $\mu g/m^2$-yr by 1970, peaked at 13.1. 15.0 and 16.9 $\mu g/m^2$-yr in the 1980s, and declined to

332 10.3, 13.1, and 10.8 $\mu g/m^2$-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 $\mu g/m^2$-yr, and recent (c. 1990) = 12.5 $\mu g/m^2$-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 $\mu g/m^2$-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

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

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

455   **Acknowledgement**

458

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633

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