The River Runs Through It: the Athabasca River Delivers Mercury to Aquatic Birds Breeding Far Downstream

Short Title: Athabasca River Delivers Mercury Far Downstream

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Abstract

26   This study examined factors contributing to temporal variability (2009-2017) in total mercury

27   (THg) concentrations in aquatic bird eggs collected in the Peace-Athabasca Delta and Lake

28   Athabasca in northern Alberta. Factors examined included annual changes in oil sands

29   production, bird diets, forest fires, and flow of the Athabasca River. Surface mining activities

30   associated with Alberta's Athabasca oil sands are centered north of Fort McMurray, Alberta,

31   adjacent to the northward-flowing Athabasca River. Previous studies have found that oil sands

32   industrial operations release mercury into the local (within ~50 km) environment. However,

33   temporal trends in egg THg levels did not track trends in synthetic oil production from the oil

34   sands. Intraspecific fluctuations in bird diet also could not explain annual variability in egg THg

35   levels. Annual extent of forest fires in Alberta was only related to egg THg concentrations in

36   California Gulls from Lake Athabasca; annual levels in other species showed no relationship

37   with fire extent. The inclusion of more terrestrial foods in gull diets may have contributed to this

38   difference. For the majority of species, annual fluctuations in maximal flow of the Athabasca

39   River were important in influencing annual egg THg levels. Eggs collected following years of

40   high flow had higher THg concentrations with distinct stable Hg isotope compositions. Riverine

41   processes associated with suspended sediment were likely critical in regulating Hg availability to

42   nesting birds. This study highlights the importance of the Athabasca River as a conduit for Hg

43   transport to ecologically-sensitive downstream ecosystems such as the Peace-Athabasca Delta

44   and Wood Buffalo National Park (a UNESCO World Heritage Site). Human activities that

45   increase atmospheric Hg deposition to the Athabasca River watershed, or that enhance Hg

46   releases to the river through erosion of Hg-bearing soils, will likely increase the availability of

47   Hg to organisms inhabiting downstream areas.

Introduction

48

49   The Athabasca River is a major river flowing northeast 1200 km from the Rocky

50   Mountains to Lake Athabasca. Along the way, it passes through Alberta's oil sands, a region of

51   large-scale, open-pit mines used to extract bitumen for synthetic oil production. The river

52   discharges into the Peace-Athabasca Delta (PAD) and western Lake Athabasca approximately

53   200 km downstream of Fort McMurray (see [1]). Since 1967, when oil sands operations

54   commenced, industrial exploitation of the bitumen-rich oil sands has expanded greatly [2] (Fig.

55   S1). Previous research has indicated that industrial development associated with the oil sands is a

56   source of mercury (Hg) to the environment [3, 4]. For example, Kirk et al. [4] found that

57   deposition of both total mercury (THg) and methyl mercury (MeHg) in snow resembled a

58   bullseye pattern with higher Hg levels in snow collected closer to oil sands developments.

59   However, snow Hg levels declined rapidly with distance from such developments with most Hg

60   being deposited within approximately 50 km. These studies [3, 4] highlighted the possibility that

61   spring snowmelt could result in the release of chemicals, such as Hg, into the aquatic

62   environment. Similarities in relative concentrations of metals in snow and river water provided

63   evidence of metals emitted to the air finding their way into the Athabasca River and tributaries

64   [3]. Kelly et al. [3] also found that Hg concentrations in water were greatest downstream of

65   areas disturbed by oil sands development. Passage of water through the surface-mineable oil

66   sands region, in itself, was not responsible for elevated water Hg levels. Degree of land

67   disturbance caused by oil sands operations was important in enhancing water Hg concentrations.

68   The significance of these findings in terms of effects on Hg concentrations in biota inhabiting

69   areas farther downstream, e.g. the PAD, has not been documented and deserves further study.

3

70   The PAD is a wetland of international significance [5] and it is a defining feature of

71   Wood Buffalo National Park (WBNP), a UNESCO World Heritage Site. It provides habitat for

72   millions of birds and WBNP is the only breeding area for the endangered Whooping Crane (*Grus*

73   *americana*) [6]. The surrounding region also provides important wildlife habitat. For example,

74   Egg Island in western Lake Athabasca is a provincial ecological reserve harboring a variety of

75   colonially-nesting aquatic birds including the largest breeding colony of Caspian Terns

76   (*Hydroprogne caspia*) in Alberta [7]. The PAD and Lake Athabasca are also important to

77   Indigenous land users who rely on traditional wild foods [8]. Hence, environmental changes

78   brought about by human activities have the potential to significantly affect wildlife and human

79   inhabitants of this region.

80   Colonial aquatic birds, e.g. gulls and terns, are commonly used to monitor the state of the

81   environment [9]. These birds are top predators resulting in their accumulation of high levels of

82   biomagnifying contaminants. Eggs are a useful sampling matrix for contaminant studies as their

83   collection has little impact on bird populations and eggs of these species are formed from

84   exogenous, locally-obtained resources [10]. Since 2009, gull and tern eggs have been collected

85   annually from sites in WBNP (Mamawi Lake) and western Lake Athabasca (Egg Island). The

86   goal of this study was to examine temporal trends (2009-2017) in egg THg levels and determine

87   whether they were influenced by a variety of factors including: oil sands production, bird diet,

88   forest fires, and flow of the Athabasca River. We briefly discuss each of these factors below.

89   From 2009-2016, oil production from surface mineable sources in the Athabasca oil

90   sands increased by 47% (761,000 bpd (barrels per day) to 1,117,000 bpd) and accounted for

91   approximately 46% of total oil sands production in 2016 (in-situ production accounted for the

92   remainder) [2]. As oil sands operations are a known source of Hg [3, 4], it is plausible that

4

93   increases in oil/bitumen production might be accompanied by increases in Hg releases to the

94   environment that could result in increased Hg levels in wildlife receptors such as bird eggs.

95   Because MeHg biomagnifies, it is possible that annual changes in bird diets, particularly with

96   respect to bird trophic position, could be important in regulating annual egg THg concentrations.

97   Inter-specific differences in food sources could also be important in regulating Hg exposure.

98   Forest fires are known to release Hg into the environment [11, 12] and Alberta experienced very

99   large forest fires in some years during the study period [13]. It is possible that such fires could

100   increase Hg levels in the food webs used by birds with resultant increases in egg THg

101   concentrations. Previous research on aquatic birds has highlighted the possibility that the

102   Athabasca River may be a source of Hg to wildlife inhabiting downstream environments [14]. In

103   a large-scale spatial assessment of Hg levels in western Canadian gull eggs, Dolgova et al. [15]

104   found that levels were greatest in eggs collected from breeding sites in receiving waters of the

105   Athabasca River. Hence, factors associated with the regulation of Hg transport via the Athabasca

106   River may be important in regulating Hg levels in downstream wildlife. One such critical factor

107   is annual maximal river flow. Long and Pavelsky [16] documented the influence of river flow on

108   sediment transport down the Athabasca River into the PAD and Lake Athabasca. In the river,

109   there was a linear relationship between flow and suspended sediment concentrations (SSC) with

110   SSC notably increasing around flows of 1500 m^3/s. In addition, a non-linear relationship between

111   river flow and downstream SSC in western Lake Athabasca was observed after maximal flow

112   exceeded a threshold of 1700 m^3/s. Riverine transport of sediment-bound Hg is an important

113   mechanism for the transfer of that element to downstream environments [17]. SSC may also

114   influence Hg dynamics in the environment through effects on the photochemical reduction of

115   MeHg. These effects, and possible Hg sources, can be evaluated using Hg stable isotopes.

5

116   Mass-dependent (MDF) and mass-independent (MIF) fractionation of stable Hg isotopes

117   (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg) can provide insights into processes regulating

118   Hg dynamics in the environment. MDF, e.g. δ^{202}Hg, is influenced by a variety of factors

119   including physical processes as well as by biological reactions [18] and can be useful in

120   identifying the flow of mercury from terrestrial and aquatic systems to consumers [19]. MIF, on

121   the other hand, has largely been documented for the odd mass Hg isotopes (^{199}Hg, ^{201}Hg) and is

122   thought to primarily be the result of a magnetic isotope effect, i.e. dissimilarities in magnetic spin

123   of even and odd mass isotopes result in their reacting at different rates. Existing evidence

124   suggests that MIF is not influenced by food web/trophic interactions [20] but occurs during

125   photochemical MeHg degradation and photoreduction of Hg^{2+} [21]. Therefore, factors that affect

126   Hg exposure to light, e.g. light penetration through the water column, are expected to influence

127   MIF of Hg isotopes [22]. Photodegradation of MeHg to Hg^0 may be an important MeHg

128   removal mechanism, particularly in systems characterized by clear water with a high degree of

129   light penetration, and this can be assessed using Hg isotopes [23]. However, only a portion of the

130   MeHg in such systems will undergo photochemical demethylation. The remaining MeHg will

131   exhibit MIF of ^{199}Hg and ^{201}Hg and that MeHg may be incorporated into food webs with Hg

132   isotope values in consumers (e.g. birds) reflecting MIF of Hg isotopes [23].

133   The slope of the MIF of ^{201}Hg versus ^{199}Hg is useful in differentiating the Hg species

134   (MeHg or Hg^{2+}) undergoing photoreduction (MeHg slope ~ 1.3, Hg^{2+} slope ~1.0) [21, 23, 24]. A

135   slope near 1.3 indicates that photoreduction of MeHg is the main mechanism underlying MIF

136   values. If photochemical reduction of MeHg is the main process underlying MIF of Hg isotopes

137   then Δ^{199}Hg and/or Δ^{201}Hg values in consumer tissues can be used to estimate the amount of

138   MeHg that has been photodegraded [21, 25].

6

139   In this study, annual THg levels in eggs of aquatic birds nesting downstream of the

140   Athabasca River are assessed. As described above, various factors, i.e. oil sands production, bird

141   diet, forest fires, and riverine processes, are investigated to determine the degree to which they

142   explain patterns in annual egg THg concentrations. As part of this analysis, the degree to which

143   maximal annual flow of the Athabasca River and concomitant changes in SSC are important in

144   regulating Hg availability to birds is investigated. Mercury isotopes are used to gain insights into

145   the processes regulating Hg dynamics and availability in this ecosystem.

146

147   **Methods**

148   Field Methods

149   Aquatic bird, i.e. gull and tern, egg collections were made in June, 2009-2017 (no

150   collections were made in 2010) at two sites located in receiving waters of the Athabasca River.

151   Mamawi Lake (58.60N, -111.47W) is located in the Peace-Athabasca Delta within the

152   boundaries of Wood Buffalo National Park. Egg Island (59.98N, -110.44W) is located in the

153   western end of Lake Athabasca approximately 40 km northeast of the mouth of the Athabasca

154   River (see Dolgova et al. [15] for map showing collection locations). In most years, 10 eggs were

155   collected per species per site. At Mamawi Lake, Ring-billed Gull (*Larus delawarensis*) and

156   Common Tern (*Sterna hirundeo*) eggs were collected. Low water levels in 2011 prevented

157   access to that location so no eggs were collected that year. Also, in 2014 it was impossible to

158   collect Common Tern eggs at that site. At Egg Island, 10 eggs were collected annually from

159   three species: California Gull (*Larus californicus*), Caspian Tern, and Common Tern. The first

160   recorded nesting of Common Terns on Egg Island was in 2011 so eggs of that species were not

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161   collected from that site in 2009. Eggs were transported to the National Wildlife Research

162   Centre, Ottawa, ON, Canada in padded cases.

163   In 2013, prey fish, i.e. cyprinids, were collected from Mamawi Lake and two sites in

164   western Lake Athabasca to provide isotope data for bird prey. Whole-body fish were analyzed of

165   two surface-schooling species: Spottail Shiner (*Notropis hudsonius*) and Emerald Shiner (*N.*

166   *atherinoides*). These species are accessible to surface-feeding birds. Details regarding prey fish

167   collections are available in Dolgova et al. [15].

168   Epiphytic lichen was collected from the branches of coniferous tree species in 2013 (May

169   or July) from 14 locations north, south, east and west of Fort McMurray. All sites were within

170   100 km of that city. Samples (n=26, two samples per site except at two sites where only one

171   sample was analyzed) were cleaned by removing foreign debris, freeze dried, and pulverized into

172   a fine powder before analysis. The utility of tree lichens as passive collectors of atmospheric

173   pollutants, including mercury, has been demonstrated [26, 27]. Mercury isotope measurements in

174   lichens were used to establish baseline Hg isotopic "signatures" associated with atmospherically

175   deposited mercury in the Fort McMurray region. This would include mercury from all sources to

176   that region including the oil sands.

177

178   Laboratory Methods

179   Egg contents (i.e. yolk, albumen, embryonic tissue) and whole-body prey fish were

180   homogenized/pulverized using liquid nitrogen and a cryogenic ball-mill. Homogenates were

181   aliquoted into acid-washed glass and polypropylene containers and stored at -40° C prior to

182   analysis.

8

183   Details regarding egg THg analysis are identical to those reported in Hebert and Popp

184 [28]. In eggs, approximately 97% of THg is in the organic MeHg form [29] so measuring THg is

185 a cost-effective way to assess MeHg levels in eggs. THg concentrations measured in all samples

186 were within concentration ranges of certified reference materials (OT1566b, TORT-3, DOLT-4,

187 IAEA-407, BCR-463). Limit of detection for THg was 0.006 µg/g (dry weight).

188   Stable isotopes of nitrogen (^{15}N and ^{14}N expressed as δ^{15}N) and carbon (^{13}C and ^{12}C

189 expressed as δ^{13}C) were measured in prey fish (collected in 2013) and in the contents of

190 individual eggs (all years) to assess bird diets across years. Details regarding stable isotope

191 analysis are identical to those reported in Hebert and Popp [28]. Dietary change affecting the

192 trophic position of laying females is reflected in egg δ^{15}N values (‰) as nitrogen isotopes

193 undergo MDF. MDF leads to enrichment of ^{15}N in higher trophic level organisms with

194 increasing δ^{15}N values with increasing trophic position. Because Hg biomagnifies, temporal

195 changes in trophic position would be expected to affect female exposure to, and uptake of, MeHg

196 with concomitant effects on egg THg levels. Carbon isotopes are useful in evaluating carbon

197 sources utilized by consumers [30]. Because lipid content of samples can affect δ^{13}C values, a

198 mathematical approach was used to adjust δ^{13}C values in eggs and prey fish based upon C:N

199 ratios in individual samples (C:N ratios for all samples were > 4.0). For eggs, the equation used

200 was from Elliott et al. [31], $\delta^{13}C_{lipid-corrected} = \delta^{13}C_{non-corrected} - 4.46 + 7.32 * \text{Log (C:N ratio)}$. For

201 fish, $\delta^{13}C_{lipid-corrected} = \delta^{13}C_{non-corrected} - 3:32 + 0:99 * \text{C:N}$ [32].

202   Mercury isotope analysis was conducted at Trent University's Water Quality Centre.

203 Details regarding mercury isotope analysis have been reported previously [33]. Mass-

204 independent fractionation (MIF) of Hg isotopes is unrelated to isotope mass and is reported in

205 capital delta (Δ) notation. MIF describes the difference between measured δ^{xxx}Hg values and

9

206   scaled δ^{202}Hg values (Δ^{xxx}Hg = δ^{xxx}Hg − (δ^{202}Hg × β)). β, the scaling factor, is determined by

207   theoretical laws of mass dependent fractionation (MDF) and is an isotope-specific constant.

208   Here, the focus is on the interpretation of MDF (δ^{202}Hg) and MIF results (Δ^{199}Hg and Δ^{201}Hg).

209   MDF data can provide insights into pathways of mercury exposure, e.g. terrestrial versus aquatic

210   [19], while MIF can be useful in assessing the processes influencing mercury isotope values in

211   eggs. Hg isotope analyses were conducted on eggs from all four study species from both study

212   sites allowing an assessment of whether MIF of Hg isotopes was influenced by bird trophic

213   position (as inferred from egg δ^{15}N values; see below). Samples were analyzed from a variety of

214   years (2009-2017) for the different species.

215

216   Analytical and Statistical Methods

217   Annual estimates of synthetic oil/bitumen production from surface-mined oil sands

218   deposits were obtained from CAPP [2].

219   Annual estimates of total forest fire extent (ha) for the province of Alberta were obtained

220   from the National Forestry Database [13]. During the period of study, 99% of total annual area

221   burned occurred during May-August with June-August usually being the focal months. Hence,

222   these fires would have occurred after the egg-laying period in that same calendar year. Caldwell

223   et al. [34] reported sediment MeHg levels peaked within three months after a wildfire, further

224   delays would be expected in terms of wildfire-generated Hg being incorporated into food webs.

225   Therefore, fire extent in the year preceding egg collection was used to assess the impact of fire

226   on egg THg levels. The one-year time lag between forest fire extent and egg THg levels allowed

227   time for Hg released from fires to be incorporated into, and passed through, the food webs

228   utilized by birds.

10

229   Annual monthly estimates of Athabasca River flow were obtained from a hydrometric

230   station located five km north of Fort McMurray (station 07DA001)

231   (https://wateroffice.ec.gc.ca/mainmenu/historical_data_index_e.html). During the period of

232   study, maximal monthly river flows were most often observed in June (seven of 10 years from

233   2008-2016), therefore, June flow was used to estimate maximal annual river flow. Based upon

234   Long and Pavelsky [16], years were categorized as being low (June mean monthly flow <1600

235   m^3/s) or high (June mean monthly flow $\geq$1600 m^3/s) flow years. River flow in the year preceding

236   egg collections was used to categorize egg collections as being influenced by low or high flow

237   years. For example, mean river flow in June 2011 was >1600 m^3/s, hence egg collections made

238   in June 2012 were categorized as being influenced by a high flow year. The one-year time lag

239   between river flow and egg THg levels allowed for the influence of river processes on Hg

240   availability/dynamics to be incorporated into downstream food webs. This period of time is

241   consistent with work examining the rapidity with which Hg is incorporated into foodwebs. For

242   example, mercury levels in small fish responded within 1-2 years to changes in levels of Hg in

243   the environment [35]. Such small fish species are an important component of the diet of gulls

244   and terns and because eggs of these species are formed from locally-obtained exogenous

245   resources, e.g. prey fish, we would expect egg Hg levels to respond within a similar time-frame

246   to prey fish. For statistical comparisons, years were combined into either low or high flow

247   categories and these categories were compared.

248   True color Landsat images [36] of the PAD and western Lake Athabasca were obtained

249   from years of low (2002, 2010, 2015) and high (2011, 2014, 2017) Athabasca River flow. These

250   images were used to qualitatively visualize annual differences in the extent of sediment plumes

251   entering western Lake Athabasca.

11

252   Data regarding suspended sediment concentrations (SSC) and secchi depth (a measure of

253   water clarity) were obtained from Long and Pavelski [37]. Data were available from sampling

254   sites situated along a southeast-northwest transect crossing the western basin of the lake (see

255   [16]). Distance of each sampling site from the mouth of the Athabasca River was estimated

256   based upon georeferenced data. Data from low (2010) and high (2011) flow years were used to

257   assess inter-year differences in the influence of the river on SSC in western Lake Athabasca and

258   resultant impacts on water transparency.

259   Inter-year differences in variables were assessed using ANOVA or Kruskal-Wallis tests

260   followed by selected post-hoc tests (Tukey's HSD or Dunn's test). Relationships between

261   variables were evaluated using Pearson correlation coefficients (*r*). Student's two-tailed t-tests

262   were used to compare egg THg levels and Hg isotope values between years of low and high

263   Athabasca River flow. All statistical analyses were conducted using Statistica Ver 12 [38] with α

264   = 0.05. Assumptions underlying the use of parametric statistics were tested using Q-Q plots, the

265   Shapiro-Wilk W test (normality), and Levene's test (homogeneity of variances).

266

Results

268   Temporal trends in egg THg concentrations (2009-2017)

269   Egg THg concentrations showed inter-year differences for most species/site combinations

270   (Egg Island: Caspian Terns ANOVA $F_{(7,72)}$ = 8.83, $p < 0.001$; Common Terns ANOVA

271    $F_{(6,63)}$ = 8.96, $p < 0.001$; Mamawi Lake: Ring-billed Gulls Welch's ANOVA $F_{(6,30)}$ = 3.61, p

272   = 0.01; Common Terns Welch's ANOVA $F_{(5,20)}$ = 3.92, $p = 0.01$) except for Egg Island

273   California Gulls (Welch's ANOVA $F_{(7,31)}$ = 0.89, $p = 0.53$). However, egg THg concentrations

274   were not correlated with year of collection for Egg Island Caspian Terns (n = 80, $r = -0.01$, $p =$

12

275   0.97), Egg Island Common Terns (n = 70, r = 0.08, p = 0.53), or Mamawi Lake Ring-billed Gulls

276   (n = 83, r = -0.13, p = 0.24) (Figure 1A, B). THg levels in eggs of Egg Island California Gulls

277   increased through time (n = 81, r = 0.24, p = 0.03) while THg levels in Common Tern eggs from

278   Mamawi Lake decreased (n = 55, r = -0.40, p = 0.002) (Fig.1*A, B*). In both these cases, temporal

279   trends were influenced by data from one year. For the Egg Island California Gull eggs, high THg

280   levels in 2017 were responsible for the temporal increase. When 2017 data were removed from

281   the analysis, there was no significant relationship with time (n = 71, r = 0.08, p = 0.52).

282   Similarly, the declining temporal trend in THg in Common Tern eggs from Mamawi Lake was

283   driven by the 2009 data. When data from that year were omitted from the analysis, no temporal

284   trends were evident (n = 45, r = -0.06, p = 0.71).

285

286   **Fig 1.** Annual mean (± SE) THg levels (ug/g, dry weight) in gull and tern eggs from sites in

287   receiving waters of the Athabasca River. (a) Egg Island, western Lake Athabasca: Caspian

288   Terns, Common Terns, California Gulls (b) Mamawi Lake: Common Terns, Ring-billed Gulls.

289

290   Influence of oil sands production, forest fires, and bird diet on egg THg

291   Temporal trends in egg THg concentrations were not related to annual production of

292   synthetic oil/bitumen from surface-mined oil sands deposits for any of the species/site

293   combinations (2009-2016 annual data. Egg Island CAGU n = 8, r = .56, p = .15; CATE n = 8, r

294   = -.03, p = .94; COTE n = 7, r = .07, p = .89; Mamawi Lake RBGU n = 7, r = -.13, p = .78;

295   COTE n = 6, r = -.67, p = .14). The production of synthetic oil/bitumen from surface mining

296   showed a significant increase during the period of study (r = 0.996, p < 0.001) (Fig. S1) which

297   was not reflected in the annual fluctuations observed in egg THg levels (Fig.1*A, B*).

13

298   Annual extent of forest fires preceding the year of egg collection showed no relationship

299   with THg levels in Mamawi Lake eggs (Ring-billed Gulls, $r = 0.23$, $p = 0.59$; Common Terns $r =$

300   -0.46, $p = 0.36$) nor in eggs of Caspian Terns ($r = -0.18$, $p = 0.64$) or Common Terns ($r = -0.54$, p

301     $= 0.16$) at Egg Island. However, mean annual egg THg levels were correlated with forest fire

302   extent in eggs of California Gulls ($r = 0.73$, $p = 0.03$) at that location (Fig. 2).

303

304   **Fig 2.** Annual extent (ha) of forest fires in Alberta versus annual mean (± SE) THg levels (ug/g,

305   dry weight) in California Gull eggs from Egg Island, Lake Athabasca. Annual egg THg levels

306   were compared to forest fire extent in the year preceding egg collections.

307

308   Egg stable nitrogen isotope values (δ^{15}N) were different among all species comparisons

309   (Kruskal-Wallis $H(3,369) = 171.85$, $p < 0.001$, Dunn's test, Caspian Tern > Common Tern >

310   California Gull > Ring-billed Gull). δ^{15}N values within most species and sites showed no

311   differences across years (Egg Island: California Gulls ANOVA $F(7,73) = 2.12$, $p = 0.051$;

312   Caspian Terns ANOVA $F(7,72) = 1.09$, $p = 0.38$; Common Terns Kruskal-Wallis $H(6,70) =$

313   9.37, $p = 0.15$; Mamawi Lake: Ring-billed Gulls Kruskal-Wallis $H(6,83) = 12.86$, $p = 0.05$,

314   Dunn's post-hoc test no differences). Only Mamawi Lake Common Terns showed significant

315   inter-year differences in egg δ^{15}N values (Kruskal-Wallis $H(5,55) = 20.76$, $p = 0.01$, Dunn's test)

316   (Table S1). For three of the five species/site combinations, inter-year differences in δ^{13}C values

317   were observed but these were minimal with most years having similar values (Table S2).

318   Interspecific comparisons of stable Hg and carbon isotope values revealed significant

319   differences among species (Fig.3). Egg δ^{202}Hg values reflecting MDF of Hg isotopes were

320   greater in California Gulls than the other bird species (ANOVA $F(3,185) = 100.0$, $p < 0.001$,

14

321   followed by Tukey's HSD test). Egg δ^{13}C values were less negative in California Gulls (mean =

322   -23.7‰) than the other three species (mean values; Common Tern = -26.3‰, Caspian Tern = -

323   25.8‰, Ring-billed Gull = -25.7‰). δ^{13}C values in Ring-billed Gulls were also less negative

324   than Common Terns (Welch's ANOVA $F(3,185) = 91.1$, $p < 0.001$, followed by Tukey's HSD

325   test). δ^{13}C values in California Gulls showed the greatest deviation from those in prey fish (mean

326   ± 1 SD values, Emerald Shiner = -28.33 ± 2.10 (n=46), Spottail Shiner = -28.00 ± 3.41 (n=22)).

327

328   **Fig 3.** Three-dimensional plot showing mass-dependent fractionation (MDF, as δ^{202}Hg) and

329   mass independent fractionation (MIF, as Δ199) of Hg in gull and tern eggs from Egg Island and

330   Mamawi Lake. Also shown are lipid-corrected δ^{13}C values in eggs. Samples shown here were

331   collected in 2009, 2011, 2012, or 2014. Symbols: circles are Caspian Terns, squares are

332   Common Terns, closed triangles are California Gulls, open triangles are Ring-billed Gulls.

333

334   Influence of riverine processes on egg THg, SSC, water clarity and Hg isotopes

335   Annual maximal June flow for the Athabasca River indicated large inter-year differences

336   with flow varying approximately three-fold during the period of study (Fig. S2). The Athabasca

337   River is unregulated by dams and annual flow is related to the volume of snowpack and glacier

338   melt [39-41]. Mean annual THg concentrations in eggs were linearly correlated with river flow

339   from the previous year in two of the five species/site comparisons (Egg Island: Caspian Terns n

340   = 8, $r = 0.90$, $p = 0.003$; Common Terns n = 7, $r = 0.89$ $p = 0.007$) (Fig.4).

341

342   **Fig 4.** Annual mean June flow (m³/s) of the Athabasca River versus annual mean (± SE) THg

343   levels (ug/g dry weight) in gull and tern eggs collected the following year. (a) Egg Island,

15

344   western Lake Athabasca: Caspian Terns, Common Terns, California Gulls (b) Mamawi Lake:

345   Common Terns, Ring-billed Gulls. Annual egg THg levels were compared to river flow in the

346   year preceding egg collections.

347

348   However, visual examination of the data indicated that the relationship between egg THg

349   concentrations and river flow might not be best described by a linear relationship. Instead, a

350   threshold effect seemed more appropriate with greater egg THg levels being observed in years

351   when river flow surpassed a mean June threshold of 1600 m^3/s. To investigate this further, years

352   were categorized as being low (<1600 m^3/s) or high (≥1600 m^3/s) flow based on June mean

353   monthly flow. Years classified as low flow years were: 2008, 2010, 2012, 2015, 2016; high flow

354   years were 2011, 2013, 2014. THg levels in eggs were elevated following high river flow years

355   in the majority of species/sites examined (Fig.5). THg concentrations in eggs collected following

356   high flow years were greater in Caspian Terns (Egg Island) (mean$_{low}$ = 1.51 µg·g^{-1} dry wt,

357   mean$_{high}$ = 2.49 µg·g^{-1} dry wt; t = 6.85, 78 $d.f.$, p < 0.0001), Common Terns (Egg Island)

358   (mean$_{low}$ = 1.02 µg·g^{-1} dry wt, mean$_{high}$ = 1.58 µg·g^{-1} dry wt; t = 5.45, 68 $d.f.$, p < 0.0001), and

359   Ring-billed Gulls (Mamawi Lake) (mean$_{low}$ = 0.38 µg·g^{-1} dry wt, mean$_{high}$ = 0.86 µg·g^{-1} dry wt; t

360   = 5.60, 81 $d.f.$, p < 0.0001). THg concentrations in eggs from these species/sites were on average

361   82% greater in high flow versus low flow years. Eggs from Egg Island California Gulls (t = 0.24,

362   79 $d.f.$, p = 0.81) and Mamawi Lake Common Terns (t = 0.19, 53 $d.f.$, p = 0.85) did not show a

363   significant difference in THg levels between low and high flow years. However, exclusion of the

364   anomalously high 2009 egg THg data for Mamawi Lake Common Terns (highest mean δ^{15}N

365   value observed that year may have indicated possible influence of dietary differences) resulted in

16

366   detection of elevated THg levels in high flow years (mean$_{low}$ = 0.98 μg·g^{-1} dry wt, mean$_{high}$ =

367   1.20 μg·g^{-1} dry wt; t = 2.74, 43 $d.f.$, p = 0.01).

368

369   **Fig 5.** Annual mean (± SE) THg levels (ug/g dry weight) in eggs collected following years of

370   low and high flow in the Athabasca River. Low flow years were categorized as those having a

371   maximal annual flow of less than 1600 m^3/s.   (a) Egg Island Caspian Terns (b) Egg Island

372   Common Terns (c) Mamawi Lake Ring-billed Gulls (d) Mamawi Lake Common Terns (e) Egg

373   Island California Gulls.

374

375   Athabasca River flow affected the extent of sediment plumes entering Lake Athabasca

376   (Fig.6). Furthermore, lake SSC concentrations were greater in a high flow year (2011) versus a

377   low flow year (2010) (Fig.S3). Differences in SSC were likely responsible for inter-year

378   differences in secchi depth in western Lake Athabasca as water clarity was lower at sites with

379   higher SSC, particularly at sites closer to the mouth of the Athabasca River (Fig.S3). Decreased

380   water clarity was evident in the high flow year.

381

382   **Fig 6.** True color Landsat images of the PAD and western Lake Athabasca during years of low

383   (<1600 m^3/s June flow) and high (≥1600 m^3/s June flow) Athabasca River flow. In high flow

384   years, there is a notable increase in the extent of the brown sediment plume entering the lake.

385   2015 image is obscured to some extent by white cloud cover but sediment is clearly visible. Red

386   and white circles indicate the locations of Mamawi Lake and Egg Island, respectively. Brown

387   oval indicates the Athabasca River mouth. Dates of image acquisition are shown.

388

17

389   For each species, differences in egg Δ^{199}Hg values were observed following years of low

390   and high Athabasca River flow (Table 1). Statistical comparison of mean Δ^{199}Hg values in eggs

391   collected following low flow years versus high flow years indicated higher Δ^{199}Hg values

392   following low flow years in California Gulls (t (67) = 3.50, p < 0.001), Caspian Terns (t (38) =

393   2.16, p = 0.04), Common Terns (t (19) = 2.10, p = 0.049), Ring-billed Gulls (t (55) = 3.18, p =

394   0.002). Similarly, egg Δ^{201}Hg values were greater following low flow years than high flow years;

395   California Gulls (t (67) = 2.62, p = 0.01), Caspian Terns (t (38) = 2.16, p = 0.04), Common Terns

396   (t (19) = 2.68, p = 0.02), Ring-billed Gulls (t (55) = 5.04, p < 0.001) (data not shown). Δ^{199}Hg

397   and Δ^{201}Hg values in eggs of all species were correlated (Δ^{199}Hg = 0.22 + 1.07 * Δ^{201}Hg, n =

398   187, r = 0.89, p < 0.001). Based upon inter-specific differences between gulls and terns in egg

399   δ^{13}C values (both California and Ring-billed Gulls differed from one or both tern species) and

400   δ^{202}Hg (California Gulls differed) separate regression analyses were completed for terns and

401   gulls. For gulls, Δ^{199}Hg = 0.36 + 0.89 * Δ^{201}Hg, n = 126, r = 0.81, p < 0.001, and for terns,

402   Δ^{199}Hg = 0.09 + 1.25 * Δ^{201}Hg, n = 61, r = 0.99, p < 0.001. δ^{202}Hg values in eggs only differed

403   between low and high flow categories for Common Terns (t (19) = 3.12, p < 0.01), other species

404   showed no differences between low and high flow (t-tests, p > 0.3) (Table 1).

405

406   **Table 1.** Annual mean (‰) mass dependent fractionation (MDF, δ^{202}Hg) and mass-independent

407   fractionation (MIF, Δ^{199}Hg) of Hg isotopes in aquatic bird eggs. California Gulls (CAGU),

408   Caspian Terns (CATE), Common Terns (COTE), and Ring-billed Gulls (RBGU) collected from

409   Egg Island and Mamawi Lake. Athabasca River flow in the year preceding egg collections was

410   categorized as low or high ($\geq$ 1600 m³/s in June) for each year. MDF and MIF values were

411   compared between flow categories for each species. * indicates statistically significant

18

412 differences (t-test, $p < 0.05$) between flow categories. n is the number of egg samples included in

413 each category.

		Egg Island, Lake Athabasca						Mamawi Lake, Peace-Athabasca Delta	
Collection Year		CAGU		CATE		COTE		RBGU	
	Flow	$\delta^{202}Hg$	$\Delta^{199}Hg$	$\delta^{202}Hg$	$\Delta^{199}Hg$	$\delta^{202}Hg$	$\Delta^{199}Hg$	$\delta^{202}Hg$	$\Delta^{199}Hg$
2009	Low	0.78	1.60	-0.49	1.38			-0.43	0.92
2011	Low	0.60	1.47	-0.21	1.36	0.10	2.11		
2012	High	0.58	1.50	-0.32	1.12			0.01	0.90
2014	High	0.91	1.27	-0.51	1.03	-0.48	1.74	-0.24	0.74
2015	High	0.89	1.25					-0.15	0.91
2016	Low	1.16	1.70					-0.13	1.16
2017	Low	1.11	1.51					-0.05	0.95
Mean	Low	0.90	1.56*	-0.35	1.37*	0.10*	2.11*	-0.20	1.01*
	n	42		20		11		30	
Mean	High	0.79	1.34	-0.42	1.08	-0.48	1.74	-0.13	0.85
	n	27		20		10		29	

414

415 Analysis of epiphytic lichen samples from the Fort McMurray region indicated relatively

416 little spatial variation in $\Delta^{199}Hg$ (mean = -0.46 ± 0.15‰, range -0.20 to -0.77‰) or $\Delta^{201}Hg$

417 (mean = -0.54 ± 0.17‰, range -0.18 to -0.86) values. Lichen $\Delta^{199}Hg$ values were used to

418 estimate baseline MIF of Hg isotopes in atmospherically deposited Hg, an important source of

419 Hg entering the Athabasca River. Lichen $\Delta^{199}Hg$ values measured here were similar to those in

420 abiotic environmental compartments in the oil sands region, i.e. surface soil (overburden) and

421 road material, bitumen and mined oil sand, processed oil sand, and Athabasca River oil sand

422 [27]. Using egg MIF data for terns from Egg Island and Mamawi Lake, the proportion of MeHg

423 photodegraded was estimated using a modified equation from Bergquist and Blum [21].

424 $$\ln(f) = \{10^3 * \ln[10^{-3}(\Delta^{199}Hg_{egg} - \Delta^{199}Hg_{lichen}) + 1]\}/S$$

425   where f = fraction of MeHg photodegraded, $\Delta^{199}Hg_{egg}$ = $\Delta^{199}Hg$ in individual eggs, $\Delta^{199}Hg_{lichen}$ =

426   average $\Delta^{199}Hg$ in lichen samples (-0.46), S = -7.82 (from the 10 mg/L dissolved organic carbon

427   (DOC) photochemical demethylation experiment in Bergquist and Blum [21]; June 2015 DOC

428   values in Lake Athabasca ranged from 4-7 mg/L). The amount of MeHg photodegraded was

429   estimated to be $21.6 \pm 5.5\%$ (mean ± SD).

430

431   **Discussion**

432   In this study, annual differences in oil sands production, bird diets, and extent of forest

433   fires had little impact on THg levels in eggs of aquatic birds. Conversely, THg concentrations in

434   eggs were consistently influenced by processes associated with the Athabasca River. For the

435   majority of species/site analyses, higher egg THg concentrations were observed in eggs laid

436   following years of high river flow. The threshold effect of river flow on egg THg levels was

437   consistent with Long and Pavelsky's [16] results demonstrating the influence of river flow on

438   SSC in Lake Athabasca. Enhanced movement of sediment-associated Hg into downstream

439   ecosystems following high river flow may be a critical factor regulating Hg availability in

440   downstream biota. Studies in freshwater rivers have demonstrated the importance of seasonal

441   events on the fate of Hg. In some cases, the annual export of Hg from a watershed can be

442   determined by a single high flow event [42]. Hence, flow was likely of critical importance in

443   moving contaminated sediments to downstream areas with resultant impacts on the

444   bioavailability of Hg to wildlife such as birds.

445   Two processes may have contributed to higher egg THg levels following years of high

446   river flow. The first stems from the possibility that in high flow years, light attenuation

447   associated with high water SSC may have reduced the amount of photochemical degradation of

20

448   MeHg. This could have resulted in an increase in the amount of MeHg available for uptake into

449   foodwebs elevating MeHg exposure of laying females with resultant increases in egg THg

450   concentrations. This mechanism cannot likely account for the inter-year differences in egg THg

451   concentrations associated with river flow because only 22% of the MeHg in the tern species was

452   estimated to have been photodegraded. The Athabasca River downstream of Fort McMurray is

453   characterized by high SSC which reduces water transparency and possibly limits the scope for

454   photochemical degradation of MeHg to occur. Despite the fact that photochemical degradation of

455   MeHg was not likely responsible for inter-year fluctuations in egg THg concentrations, inter-

456   year variability in MIF of Hg isotopes was useful in linking river sources of Hg to Hg

457   accumulated in bird eggs. Inter-year differences in egg Δ^{199}Hg and Δ^{201}Hg values between years

458   of low and high flow provided evidence that riverine processes not only regulated the amount of

459   Hg to which birds were exposed but also the isotopic composition of that Hg.

460   The slope (1.25) of the Δ^{201}Hg/Δ^{199}Hg regression for terns was similar to the value

461   associated with photoreduction of MeHg (1.3) indicating that MeHg photoreduction was likely

462   responsible for Δ^{199}Hg and Δ^{201}Hg values observed in eggs of those species. However, for gulls,

463   a lower slope (0.89) was observed which was more similar to that associated with the

464   photochemical reduction of Hg^{2+} (slope = 1.0, [21]). Tsui et al. [19] reported similar Hg isotope

465   patterns in biota associated with aquatic (slope = 1.20 in benthic invertebrates, slope = 1.24 in

466   trout) versus terrestrial food webs (slope = 1.05). They hypothesized that the mechanisms

467   underlying MIF of Hg differed between aquatic and terrestrial ecosystems. In terrestrial systems,

468   Hg^{2+} may be extensively photoreduced before the non-photoreduced Hg^{2+} undergoes

469   methylation. Hence, differences in Hg sources, pathways of exposure, and environmental Hg

470   processing, could explain the differences in egg Hg trends detected in California Gulls (i.e.

21

471 detection of a fire signal) versus the other species. Increased use of terrestrial resources by gulls

472 was supported by both the egg Hg MDF (δ^{202}Hg) and δ^{13}C data. Tsui et al. [19] reported higher

473 δ^{202}Hg values in organisms associated with terrestrial systems; similar to what was observed for

474 California Gulls in this study. Carbon isotope results corroborated this interpretation as egg δ^{13}C

475 values in terns were more negative than those measured in gulls. This was consistent with what

476 would be expected based upon differences in δ^{13}C values of food originating from freshwater

477 and terrestrial ecosystems [43] and suggested that gulls were incorporating terrestrial foods into

478 their diets in addition to aquatic prey. These results reflected the well-characterized, more

479 omnivorous diet of gulls (see [44] for an example). However, all of the bird species, including

480 gulls, exhibited MIF of Hg that reflected the importance of aquatic processes in regulating egg

481 Hg isotope values. Consistent differences in Δ^{199}Hg values between low and high flow year

482 categories for all bird species indicated that all of them were linked to aquatic ecosystem

483 processes. It is just possible that gulls may also show connections with terrestrial processes as

484 well.

485   Here, we do not provide direct evidence linking Hg levels in eggs to oil sands sources.

486 However, previous studies have demonstrated that oil sands developments are a source of Hg to

487 the local environment [3, 4]. For example, Hg in snow was 5.6 times greater within 50 km of oil

488 sands processing facilities than outside that area [3]. Hg levels in water sampled in summer were

489 three times greater downstream of areas disturbed by oil sands development than at upstream

490 locations situated in the mineable oil sands region [3]. Water Hg concentrations further

491 downstream in the Athabasca River and PAD were two times greater than these upstream

492 concentrations [3]. Elevated levels of Hg in abiotic environmental matrices are also reflected in

493 biota. For example, THg concentrations in prey fish sampled from the Athabasca River in the

22

494   surface mineable oil sands region were five times greater than fish collected from the Athabasca

495   River upstream of the oil sands [15]. THg levels in prey fish collected in the PAD and Lake

496   Athabasca were two to four times greater than fish from the upstream Athabasca River site [15].

497   THg levels in eggs of California Gulls and Herring Gulls (*Larus argentatus*) were two and three

498   times greater, respectively, at Egg Island (Lake Athabasca) than at Namur Lake, an inland lake

499   isolated from the Athabasca River but in close proximity (~60 km west) to open-pit oil sands

500   mines [15]. Taken together, these results indicate that the oil sands are a source of Hg to the

501   environment and that biota inhabiting waters in or downstream of the oil sands have higher Hg

502   levels. To understand this further, an integrated research program involving Hg measurements in

503   air, water, land, and biota is required to assess the relative importance of oil sands sources as a

504   contributor to the overall Hg budget of the Athabasca River and downstream ecosystems. With

505   respect to bird eggs, we can begin to predict expected Hg levels based upon river flow. For

506   example, in 2017, mean June river flow was high (~1590 m^3/s), hence egg THg levels in 2018

507   are also predicted to be high. Eggs are currently being analyzed to test this hypothesis.

508   Until now, uncertainty surrounded the degree to which Hg may be transported by the

509   Athabasca River to ecosystems far downstream. Following spring melt of the snowpack in the

510   Athabasca River watershed, it is likely that some of the snow-associated mercury finds its way

511   into the river. This is particularly true in the spring when frozen soils may limit infiltration of

512   runoff into soil leading to efficient Hg export to the Athabasca River from overland sources [45,

513   46]. Furthermore, during high flow years, Athabasca River sediments are mobilized and

514   transported to downstream environments such as the PAD and western Lake Athabasca [16].

515   River systems can convey 90% of their total heavy metal load via sediment transport [17, 42,

516   46]. Hence, it is highly likely that Athabasca River sediments are transporting Hg to areas far

23

517   downstream. This hypothesis was supported by Long and Pavelsky's [37] data and by satellite

518   images showing inter-year differences in sediment plumes into Lake Athabasca. Aquatic bird

519   egg THg concentrations and Hg isotope data indicate that this Hg is being incorporated into

520   downstream food webs.

521   The importance of the current study lies in its highlighting the degree to which local

522   inputs of Hg to the river via atmospheric releases, mobilization associated with land disturbance,

523   or dust/leakage from tailings ponds (but see [47]) will not remain confined to the local receiving

524   environment. Hg from these sources will be transported long distances via the river to sensitive

525   downstream ecosystems, e.g. PAD, WBNP, that are recognized for their unique, world-class

526   ecological characteristics. New surface-mine oil sands projects are being proposed that will bring

527   development much closer (~30 km) to the southern boundary of the PAD/WBNP. This will

528   likely increase Hg inputs into the local environment through Hg mobilization stemming from

529   further land development and atmospheric Hg releases. The zone of atmospheric deposition may

530   encompass southern parts of the PAD/WBNP based upon the size of depositional zones

531   previously characterized for oil sands operations [3, 4]. Hence, further oil sands development

532   may result in increased delivery of Hg to downstream/downwind areas. The impacts of multiple

533   stressors (including oil sands) on WBNP have resulted in it being investigated as an UNESCO

534   World Heritage Site in Danger. Cumulative impact assessment of existing and proposed oil sands

535   mining projects needs to consider potential Hg impacts on wildlife and humans inhabiting this

536   globally-recognized area of ecological importance.

537

538   **SUPPORTING INFORMATION**

24

539   **Figure S1** shows temporal trends in surface-mineable oil sands production. **Figure S2** shows

540   annual trends in Athabasca River June flow. **Figure S3** contrasts suspended sediment

541   concentrations and water transparency in Lake Athabasca in years of low versus high river flow.

542   **Table S1** and **Table S2** tabulate stable carbon and nitrogen isotope data by species, site and year,

543   respectively.

544

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562

References

563 **References**

564 1. Hebert CE, Campbell D, Kindopp R, MacMillan S, Martin P, Neugebauer E, Patterson L,

565 Shatford J (2013). Mercury trends in colonial waterbird eggs downstream of the oil sands region

566 of Alberta, Canada. Environ Sci Technol 47: 11785-11792.

567

568 2. CAPP (Canadian Association of Petroleum Producers) (2018) Statistical Handbook.

569 https://www.capp.ca/publications-and-statistics/statistics. Accessed Oct 3, 2018.

570

571 3. Kelly EN, Schindler DW, Hodson PV, Short JW, Radmanovich R, Nielsen CC (2010) Oil

572 sands development contributes elements toxic at low concentrations to the Athabasca River and

573 its tributaries. Proc Natl Acad Sci USA 107: 16178−16183.

574

575 4. Kirk JL, Muir DCG, Gleason A, Wang XW, Lawson G, Frank RA, Lehnherr I, Wrona F

576 (2014) Atmospheric deposition of mercury and methylmercury to landscapes and waterbodies of

577 the Athabasca Oil Sands region. Environ Sci Technol 48: 7374-7383.

578

579 5. Ramsar (2016) The Ramsar Convention Manual: a Guide to the Convention on Wetlands, 4th

580 ed. Ramsar Convention Secretariat, Gland, Switzerland.

581

582 6. Kuyt E (1993) Whooping crane, *Grus americana*, home range and breeding range expansion

583 in Wood Buffalo National Park, 1970−1991. Can Field Nat 107: 1−12.

584

585   7. Hebert CE, Nordstrom W, Shutt JL (2010) Colonial waterbirds nesting on Egg Island, Lake

586   Athabasca. Can Field Nat 124: 49−53.

587

588   8. Chan L, Receveur O, Batal M, David W, Schwartz H, Ing A, Fediuk K, Tikhonov C (2016)

589   First Nations Food, Nutrition and Environment Study (FNFNES): Results from Alberta 2013.

590   University of Ottawa, Ottawa, ON, pp. 155.

591

592   9. Hebert CE, Norstrom RJ, Weseloh DV (1999a) A quarter century of environmental

593   surveillance: the Canadian Wildlife Service's Great Lakes Herring Gull Monitoring Program.

594   Environ Rev 7: 147-166.

595

596   10. Hobson KA, Hughes KD, Ewins PJ (1997) Using stable isotope analysis to identify

597   endogenous and exogenous sources of nutrients in eggs of migratory birds: Applications to Great

598   Lakes contaminants research. Auk 114: 467–478.

599

600   11. Biswas A, Blum JD, Klaue B, Keeler GJ (2007) Release of mercury from Rocky Mountain

601   forest fires. Global Biogeochem Cycles. doi: 10.1029/2006GB002696

602

603   12. Wiedinmyer C, Friedli H (2007) Mercury emission estimates from fires: an initial inventory

604   for the United States. Environ Sci Technol 41: 8092–8098.

605

606   13. National Forestry Database (2018). Annual forest area burned for Alberta. National

607   Resources Canada, Ottawa, ON, Canada. http://nfdp.ccfm.org/en/data/fires.php. Accessed Oct 3,

608   2018.

609

610   14. Hebert CE, Weseloh DVC, MacMillan S, Campbell D, Nordstrom W (2011) Metals and

611   PAHs in colonial waterbird eggs from Lake Athabasca and the Peace-Athabasca Delta, Canada.

612   Environ Toxicol Chem 30: 1178-1183.

613

614   15. Dolgova S, Popp BN, Courtoreille K, Espie RHM, Maclean B, McMaster M, Straka JR,

615   Tetreault GR, Wilkie S, Hebert CE (2018) Spatial trends in a biomagnifying contaminant:

616   application of amino acid compound specific stable nitrogen isotope analysis to the interpretation

617   of bird mercury levels. Environ Toxicol Chem 37: 1466−1475.

618

619   16. Long CM, Pavelsky TM (2013) Remote sensing of suspended sediment concentration and

620   hydrologic connectivity in a complex wetland environment. Remote Sens Environ 129: 197–209.

621

622   17. Carroll RWH, Warwick JJ, Heim KJ, Bonzongo JC, Miller JR, Lyons WB (2000) Simulation

623   of mercury transport and fate in the Carson River, Nevada. Ecol Model 125: 255-278.

624

625   18. Blum JD, Sherman SL, Johnson ML (2014) Mercury isotopes in earth and environmental

626   sciences. Annu Rev Earth Planet Sci 42: 249–69.

627

628   19. Tsui MTK, Blum JD, Finlay JC, Balogh SJ, Nollet YH, Palen WJ, Power ME (2014)

629   Variation in terrestrial and aquatic sources of methylmercury in stream predators as revealed by

630   stable mercury isotopes. Environ Sci Technol 48: 10128-10135.

631

632   20. Kwon SY, Blum JD, Carvan MJ, Basu N, Head JA, Madenjian CP, David SR (2012)

633   Absence of fractionation of mercury isotopes during trophic transfer of methylmercury to

634   freshwater fish in captivity. Environ Sci Technol 46: 7527-7534.

635

636   21. Bergquist BA, Blum JD (2007) Mass-dependent and −independent fractionation of Hg

637   isotopes by photoreduction in aquatic systems. Science 318: 417−420.

638

639   22. Tsui MTK, Blum JD, Finlay JC, Balogh SJ, Kwon SY, Nollet YH (2013) Photodegradation

640   of methylmercury in stream ecosystems. Limnol Oceanogr 58: 13–22.

641

642   23. Point D, Sonke JE, Day RD, Roseneau DG, Hobson KA, Vander Pol SS, Moors AJ, Pugh

643   RS, Donard OFX, Becker PR (2011) Methylmercury photodegradation influenced by sea-ice

644   cover in Arctic marine ecosystems. Nature Geoscience 4: 188-194.

645

646   24. Day RD, Roseneau DG, Berail S, Hobson KA, Donard OFX, Vander Pol SS, Pugh RS,

647   Moors AJ, Long SE, Becker PR (2012) Mercury stable isotopes in seabird eggs reflect a gradient

648   from terrestrial geogenic to oceanic mercury reservoirs. Environ Sci Technol 46: 5327−5335.

649

650   25. Sherman LS, Blum JD (2013) Mercury stable isotopes in sediments and largemouth bass

651   from Florida lakes, USA. Sci Total Environ 448: 163–175.

652

653   26. Bargagli R, Barghigiani C (1991) Lichen biomonitoring of mercury emission and deposition

654   in mining, geothermal and volcanic areas of Italy. Environ Monit Assess 16: 265−275.

655

656   27. Blum J, Johnson M, Gleason J, Demers J, Landis M, Krupa S (2012) Mercury concentration

657   and isotopic composition of epiphytic tree lichens in the Alberta oil sands region. In: Percy KE,

658   ed. Alberta Oil Sands: Energy, Industry, and The Environment. Elsevier Ltd, Oxford, UK. pp

659   373-390.

660

661   28. Hebert CE, Popp BN (2018) Temporal trends in a biomagnifying contaminant:

662   Application of amino acid compound specific stable nitrogen isotope analysis to the

663   interpretation of bird mercury levels. Environ Toxicol Chem 37: 1458-1465.

664

665   29. Ackerman JT, Herzog MP, Schwarzbach SE (2013) Methylmercury is the dominant form of

666   mercury in bird eggs: A synthesis. Environ Sci Technol 47: 2052−2060.

667

668   30. Kelly JF (2000) Stable isotopes of carbon and nitrogen in the study of avian and mammalian

669   trophic ecology. Can J Zool 78: 1–27.

670

671   31. Elliott KH, Davis M, Elliott JE (2014) Equations for lipid normalization of carbon stable

672   isotope ratios in aquatic bird eggs. PLOS ONE 9: e83597.

673

30

674   32. Post DM, Layman CA, Arrington DA, Takimoto G, Quattrochi J, Montaña CG (2007)

675   Getting to the fat of the matter: models, methods and assumptions for dealing with lipids in

676   stable isotope analyses. Oecologia 152: 179–189.

677

678   33. Georg RB, Newman K (2015) The effect of hydride formation on instrumental mass

679   discrimination in MC-ICP-MS: a case study of mercury (Hg) and thallium (Tl) isotopes. J Anal

680   At Spectrom 30: 1935-1944.

681

682   34. Caldwell CA, Canavaan CM, Bloom NS (2000) Potential effects of a forest fire and storm

683   flow on total mercury and methylmercury in sediments of an arid-lands reservoir. Sci Total

684   Environ 260: 125–133.

685

686   35. Harris RC, Rudd JWM, Amyot M, Babiarz CL, Beaty KG, et al. (2007) Whole-ecosystem

687   study shows rapid fish-mercury response to changes in mercury deposition. Proc Natl Acad Sci

688   USA 104: 16586–16591.

689

690   36. USGS (United States Geological Survey) (2018) Landsat Missions. https://landsat.usgs.gov/.

691   Accessed Oct 3, 2018.

692

693   37. Long CM, Pavelsky TM (2012) Water Quality and Spectral Reflectance, Peace-Athabasca

694   Delta, Canada, 2010 - 2011. Data set. 2012. Available online [http://daac.ornl.gov] from Oak

695   Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

696   http://dx.doi.org/10.3334/ORNLDAAC/1133. Accessed Oct 3, 2018.

697

698   38. StatSoft (2013). Statistica (Data Analysis Software System), Ver 12. Tulsa, OK, USA.

699

700   39. Schindler DW (2001) The cumulative effects of climate warming and other human

701   stresses on Canadian freshwaters in the new millennium. Can J Fish Aquat Sci 58: 18–29.

702

703   40. Schindler DW, Donahue WF (2006). An impending water crisis in Canada's western

704   prairie provinces. Proc Natl Acad Sci USA 103: 7210–7216.

705

706   41. DibikeaY, Eumb H, Prowse T (2018) Modelling the Athabasca watershed snow response to a

707   changing climate. J Hydrol: Regional Studies 15: 134−148.

708

709   42. Babiarz CL, Hurley JP, Benoit JM, Shafer MM, Andren AW, Webb DA (1998) Seasonal

710   influences on partitioning and transport of total and methyl–mercury in rivers from contrasting

711   watersheds. Biogeochem 41: 237–257.

712

713   43. Hebert CE, Shutt JL, Hobson KA, Weseloh DV (1999b) Spatial and temporal differences in

714   the diet of Great Lakes herring gulls (*Larus argentatus*): Evidence from stable isotope analysis.

715   Can J Fish Aquatic Sci 56: 323-338.

716

717   44. Nisbet IC, Weseloh DV, Hebert CE, Mallory ML, Poole AF, Ellis JC, Pyle P, Patten MA

718   (2017) Herring Gull (*Larus argentatus*). In: Rodewald PG, ed. The Birds of North America.

719   Cornell Lab of Ornithology, Ithaca, NY Retrieved from the Birds of North America:

720   https://birdsna.org/Species-Account/bna/species/hergul. Accessed Oct 3, 2018.

721

722   45. Hurley JP, Shafer MM, Cowell SE, Overdier JT, Hughes PE, Armstrong DE (1996) Trace

723   metal assessment of Lake Michigan tributaries using low-level techniques. Environ Sci Technol

724   30: 2093–2098.

725

726   46. Balogh SJ, Meyer ML, Johnson DK (1997) Mercury and suspended sediment loadings in the

727   lower Minnesota River. Environ Sci Technol 31: 198–202.

728

729   47. Willis CE, St Louis VL, Kirk JL, St Pierre KA, Dodge C (2018) Tailings ponds of the

730   Athabasca Oil Sands Region, Alberta, Canada, are likely not significant sources of total mercury

731   and methylmercury to nearby ground and surface waters. Sci Total Environ 647: 1604–1610.

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742   **Supplementary Information**

743   Captions

744   S1_Table. Annual mean (± 1 SD) $\delta^{15}N$ values (‰) in eggs of California Gulls (CAGU), Caspian

745   Terns (CATE), Common Terns (COTE), and Ring-billed Gulls (RBGU) collected from Egg

746   Island and Mamawi Lake. At each site, inter-year differences in species-specific $\delta^{15}N$ values

747   were evaluated using ANOVA or Kruskal-Wallis/Dunn's tests. Superscript letters indicate

748   statistically significant differences ($p < 0.05$) between years. Means with the same letter are not

749   different. n is the number of samples analyzed for each species at each site.

750

751   S2_Table. Annual mean (± 1 SD) $\delta^{13}C$ values (‰) in eggs of California Gulls (CAGU), Caspian

752   Terns (CATE), Common Terns (COTE), and Ring-billed Gulls (RBGU) collected from Egg

753   Island and Mamawi Lake. $\delta^{13}C$ values were adjusted for lipid content. At each site, inter-year

754   differences in species-specific $\delta^{13}C$ values were evaluated using ANOVA/Tukey's HSD or

755   Kruskal-Wallis/Dunn's tests. Superscript letters indicate statistically significant differences ($p <$

756   0.05) between years. Means with the same letter are not different. n is the number of samples

757   analyzed for each species at each site.

758

759   S1_Fig. Surface-mineable oil sands production (synthetic oil and bitumen) in millions of barrels

760   per day, 1967-2016. Data are from CAPP [2]. The dashed line indicates the beginning of the

761   period during which egg samples were collected to assess temporal trends in mercury levels.

762

763   S2_Fig. Mean June flow (m^3/s) of the Athabasca River north of Fort McMurray (station

764   07DA001) from 1958-2016. The dashed line indicates the beginning of the period during which

34

765   the influence of river flow on egg THg levels was investigated. Data are from Canadian

766   Hydrographic Service (https://wateroffice.ec.gc.ca/mainmenu/historical_data_index_e.html).

767

768   S3_Fig. Suspended sediment concentrations (SSC) (mg/L) and secchi disc depth (cm) along a

769   transect from a point (58.6724 N, -110.8477 W) at the mouth of the Athabasca River. Data for a

770   low flow (2010) and a high flow year (2011) are shown. Data are from Long and Pavelsky [37].
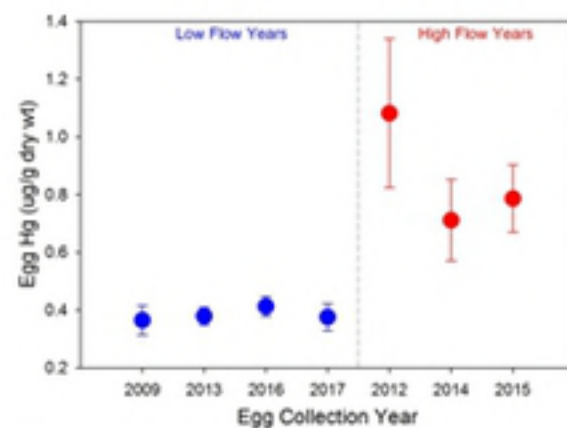
(A)

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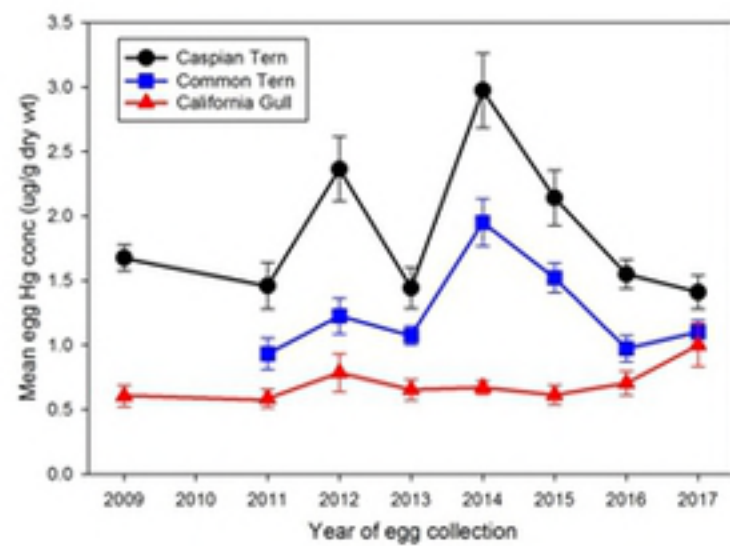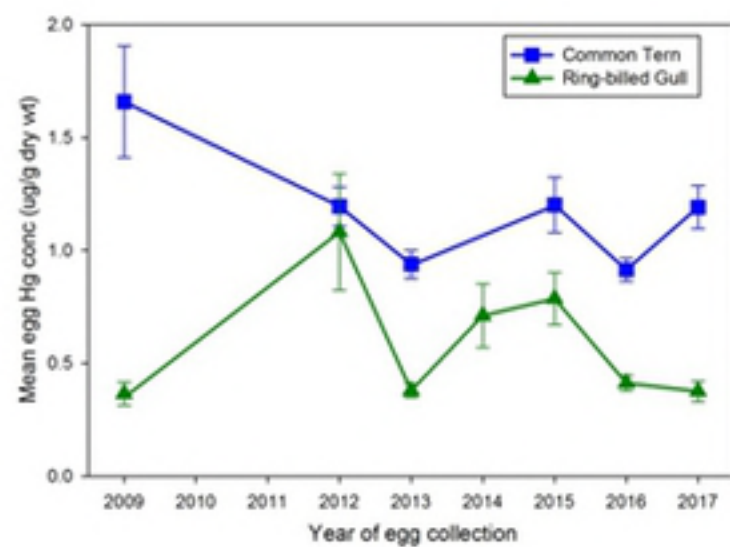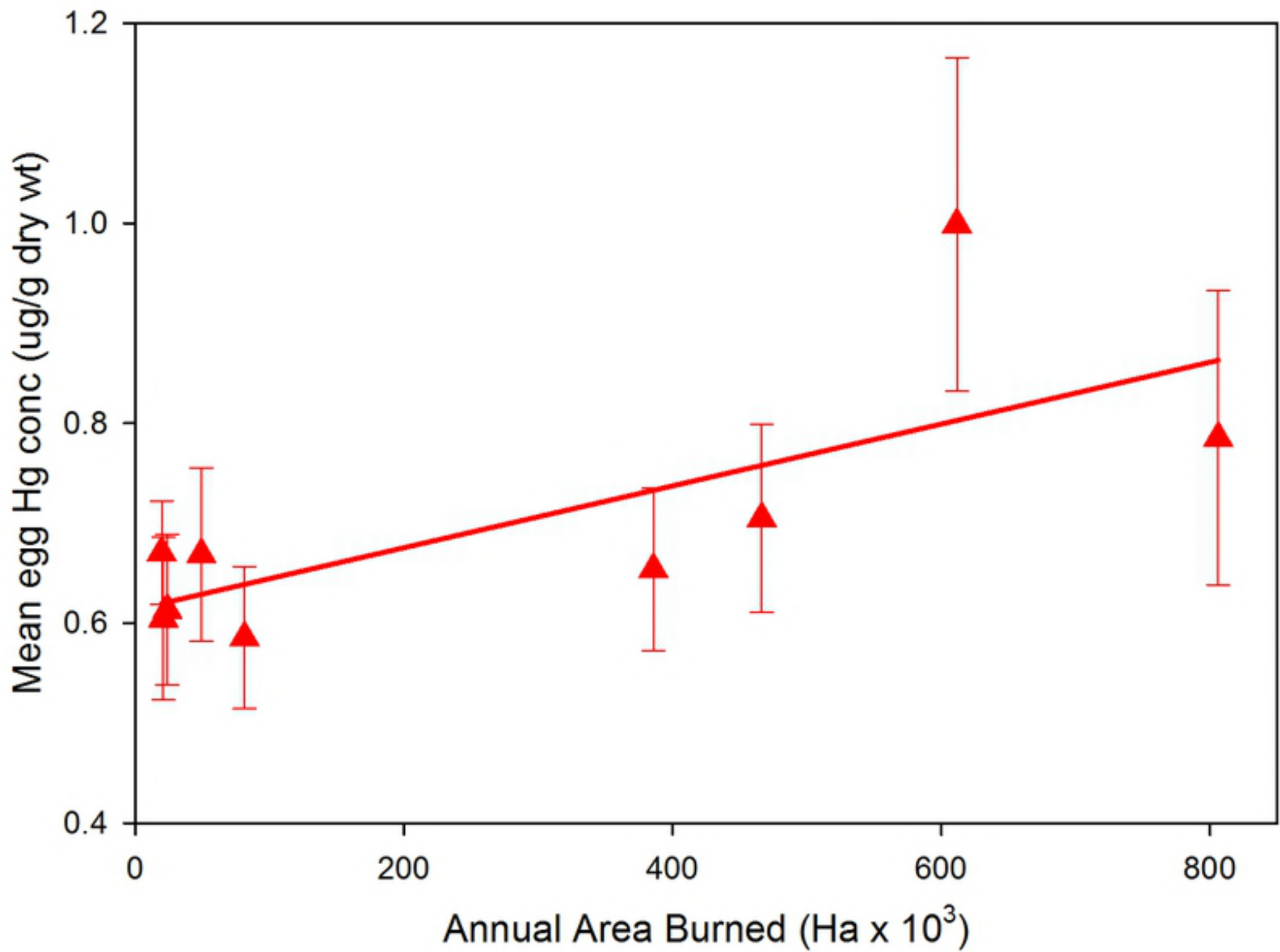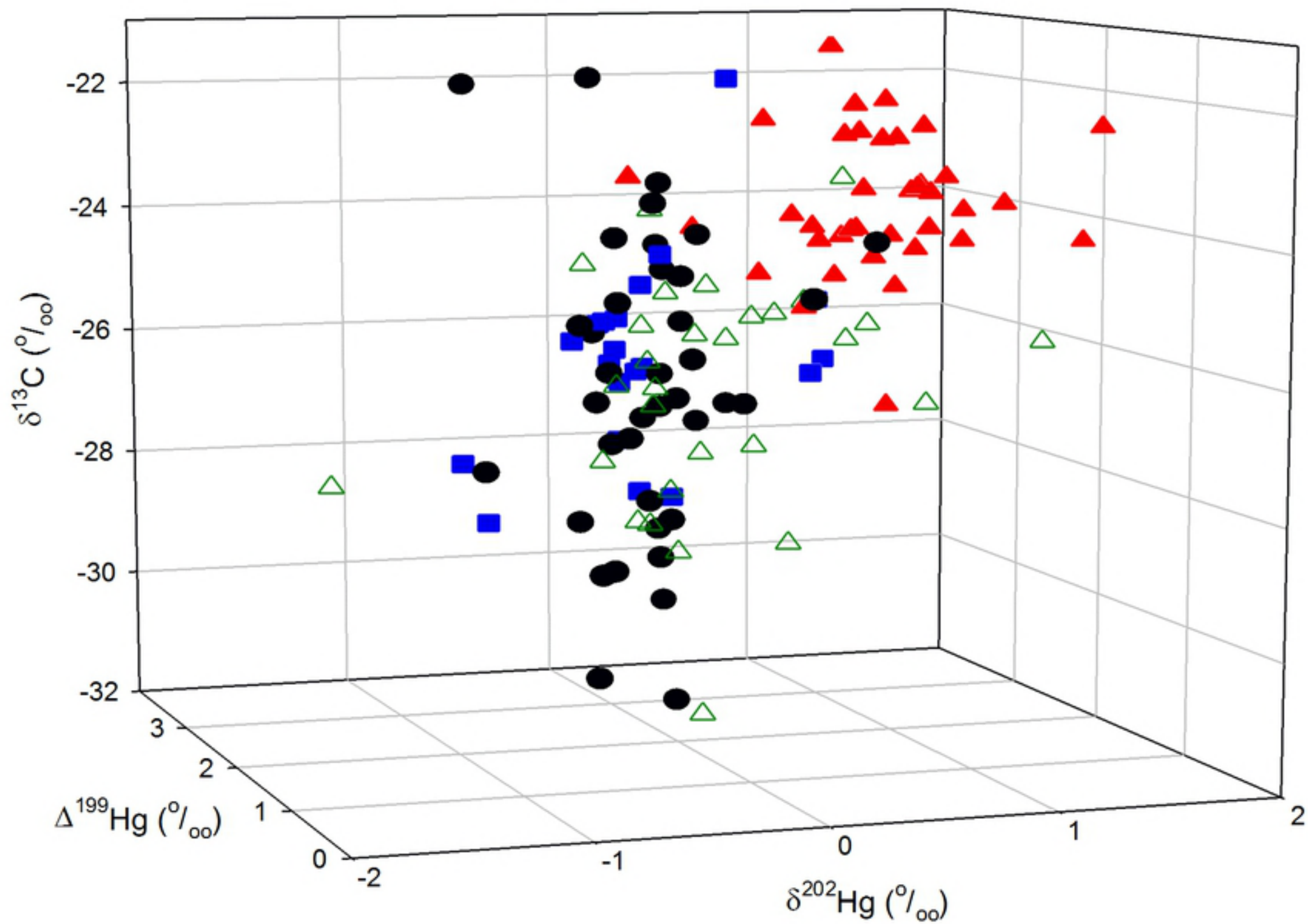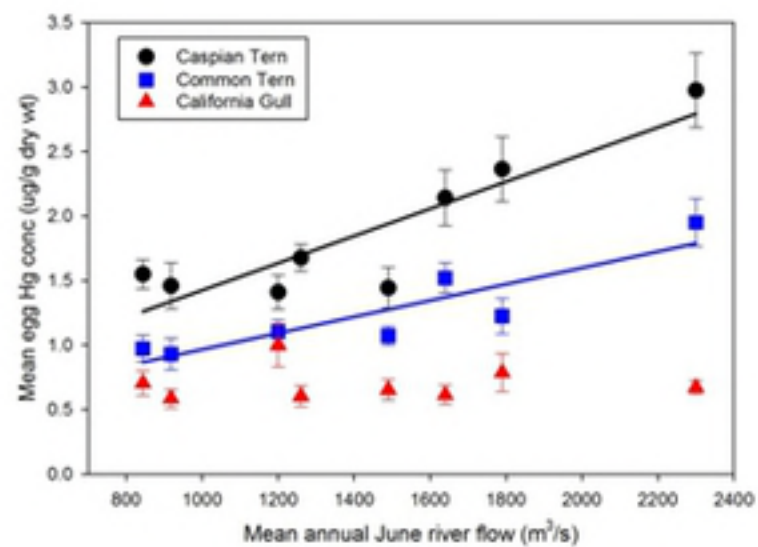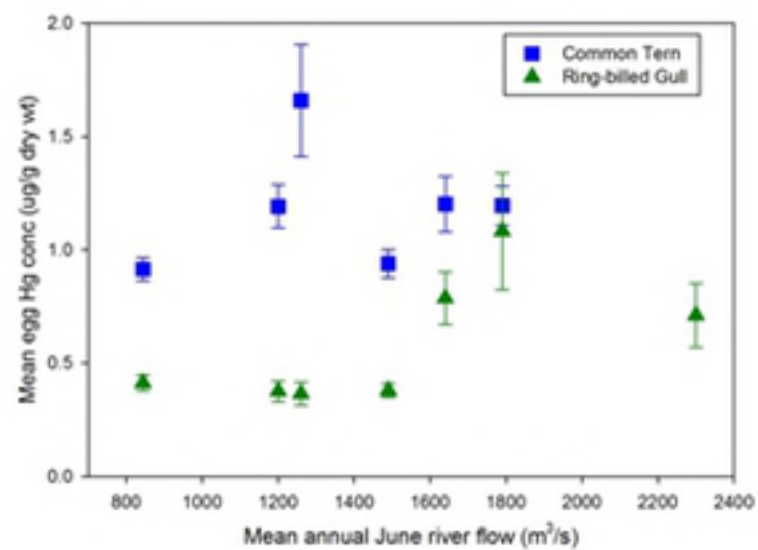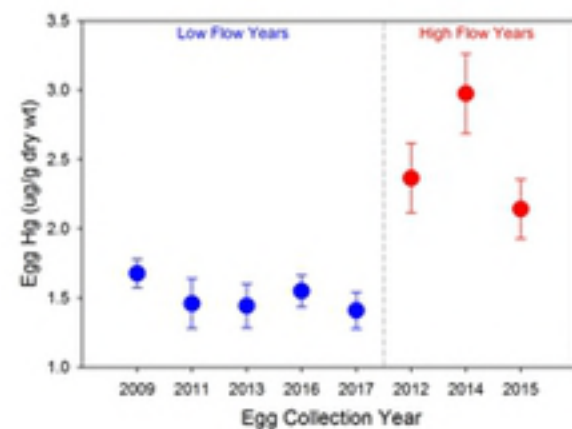
(A) Caspian Tern – Egg Island
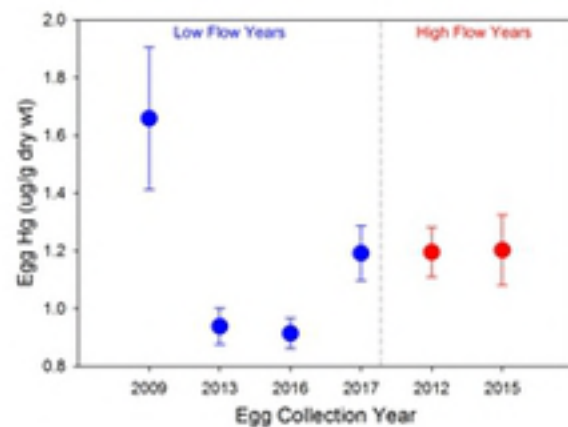(B) Common Tern – Egg Island
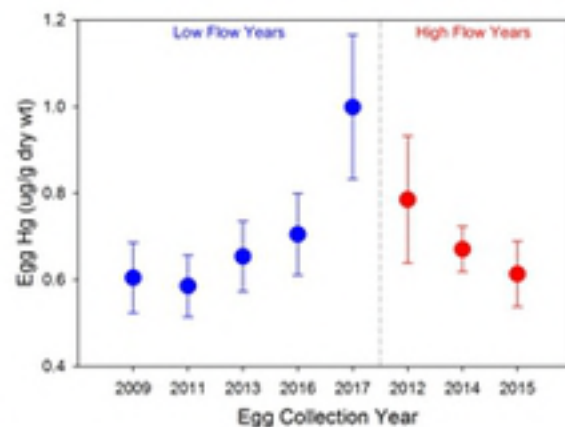(C) Ring-billed Gull – Mamawi Lake
(D) Common Tern – Mamawi Lake
(E) California Gull – Egg Island
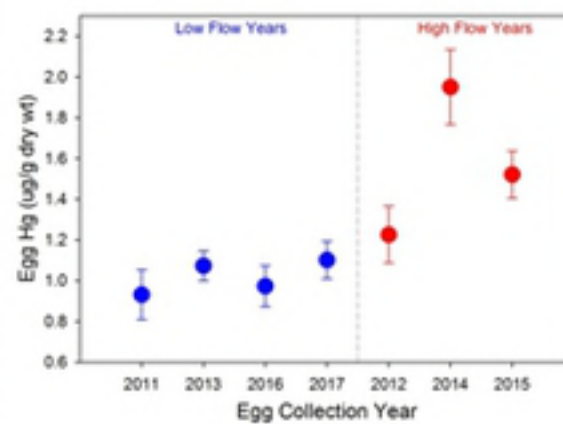
(A)

2002   22/06

2010   28/05

2015   02/06

(B)

2011   31/05

2014   08/06

2017   16/06