

1 **Mercury concentration and isotopic composition of epiphytic tree lichens in the**
2 **Alberta Oil Sands Region**

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10
11 **ABSTRACT**

12
13 Mercury (Hg) is a toxic heavy metal that is found associated with fossil fuel deposits and that
14 can be released to the atmosphere during fossil fuel combustion and/or processing. Hg
15 emitted to the atmosphere can be deposited to aquatic and terrestrial ecosystems where it can
16 be methylated by bacteria. Methylmercury is strongly biomagnified in food webs and this
17 leads to toxic levels in high trophic level fish, the consumption of which is a major human
18 exposure pathway. Epiphytic tree lichens have been widely used to investigate the
19 relationship between atmospheric point sources of Hg and regional Hg deposition patterns.
20 An intensive study of Hg concentration and stable isotopic composition of the epiphytic tree
21 lichen *Hypogymnia physodes* was carried out in the area within 150 km of the Alberta oil
22 sands region (AOSR) industrial developments. Concentrations of Hg were comparable to
23 background values measured in previous studies from remote areas and were far below
24 values observed near significant atmospheric industrial sources of Hg. Spatial patterns
25 provide no evidence for a significant atmospheric point source of Hg from the oil sands
26 developments and Hg accumulation actually decreases in lichens within 25 km of the
27 AOSR development, presumably due to physiological responses of *Hypogymnia physodes*
28 to enhanced SO₂ deposition. Stable mercury isotope ratios show an increase in • ¹⁹⁹Hg
29 and • ²⁰¹Hg within 25 km of the AOSR and we speculate that this is due to a change in
30 the proportion of the various ligands to which Hg is bonded in the lichens, and a resulting
31 change in the isotope fractionation during partial photochemical reduction and loss of Hg
32 from lichen surfaces.

33
34
35 **INTRODUCTION**

36
37 Mercury (Hg) is a highly toxic and globally distributed atmospheric trace
38 pollutant. It is released to the atmosphere from a range of industrial activities primarily as
39 gaseous elemental mercury (Hg(0)) and reactive gaseous mercury (Hg(II)). Hg(0) has a
40 long atmospheric residence time (~1 year) and can travel long distances before being
41 oxidized to Hg(II) and deposited (Schroeder and Munthe 1998). Hg(II) has a much
42 shorter residence time than Hg(0) and is rapidly deposited locally in precipitation and dry
43 deposition downwind of atmospheric point sources (Keeler et al 2006; Sherman et al
44 2012). Once Hg(II) is deposited to aquatic and terrestrial ecosystems it can be methylated
45 by sulfate and iron reducing bacteria producing highly toxic and bioaccumulative
46 methylmercury. Biomagnification of atmospherically deposited mercury can result in the
47 acquisition of high levels of methylmercury in high trophic position fish in remote lakes.

48 Consumption of fish is a major human exposure pathway for methyl mercury, especially
49 for indigenous peoples (Chan and Receveur 2000).

50
51 Mercury bonds strongly to marine and terrestrial organic matter and is often
52 associated with organic-rich geological deposits. The most important anthropogenic
53 source of Hg to the atmosphere is through the burning of coal (Pirrone et al 2010).
54 However, natural gas processing (Spiri• and Mashyanov 2000) and oil refining (Wilhelm
55 2001) can also produce significant emissions of mercury. Although detailed studies have
56 not been conducted previously, several studies have inferred that AOSR processing may
57 result in enhanced atmospheric Hg emissions (Wilhelm 2000; Kelly et al 2010; Timony
58 and Lee 2009) and that Hg is methylated and bioaccumulated resulting in elevated levels
59 in fish in the region (Timony and Lee 2009). A study by Kelly et al. (2010) also reported
60 that mercury, along with other trace metals, was elevated in snow near the AOSR
61 developments.

62
63 There is a great need for monitoring of Hg deposition spatially near potential
64 atmospheric point sources. Monitoring is particularly difficult in remote areas such as the
65 Alberta oil sands region (AOSR) where atmospheric concentrations and deposition rates
66 are difficult to measure due to lack of road access and electrical power needed to run
67 atmospheric monitoring sites. The industrial development of the AOSR north of Fort
68 McMurray, Alberta, Canada, has resulted in increases in some industrial atmospheric
69 emissions in the region (Percy et al, this volume). The present study was designed to use
70 a single species of naturally occurring tree lichens to evaluate if Hg deposition in the
71 region close to the AOSR was enhanced relative to background values further from the
72 AOSR developments.

73
74 Many different species of epiphytic tree lichen have been used previously as
75 passive collectors of a variety of atmospheric pollutants (e.g, Purvis and Halls 1996),
76 including mercury (e.g., Bargagli and Barghigiani 1991). Physiological differences
77 between lichen species result in differing metal accumulation properties, and so we
78 focused our study on a single species of epiphytic lichen, *Hypogymnia physodes*, that is
79 widely distributed in the AOSR and that has been used extensively in previous studies of
80 Hg deposition in other geographic regions (e.g., Makhholm and Bennett 1998, Horvat et al
81 2000). Mercury was measured in the same lichen samples used for major and trace
82 elements analyses (Edgerton et al, this volume) and Pb isotope studies (Graney et al, this
83 volume). A gridded circular sampling pattern was used to allow the use of Hg and other
84 major and trace elements in receptor modeling and impact assessment (Landis et al, this
85 volume).

86
87 Some previous studies have analyzed variations in the Hg content of naturally
88 growing *Hypogymnia physodes* near atmospheric pollution sources (Makhholm and
89 Bennett 1998 and references therein, Horvatt et al 2000, Sensen and Richardson 2002)
90 and others have transplanted *Hypogymnia physodes* with low natural Hg concentrations
91 to locations near atmospheric point sources and monitored changes in Hg concentration
92 with time (Makhholm and Bennett 1998 and references therein, Horvatt et al 2000,
93 Bialonska and Dayan 2005, Williamson et al 2008). Additionally, studies have been

94 carried out on the organic compounds produced by *Hypogymnia physodes* and their effect
95 on metal binding in this species of lichen (Bialonska and Dayan 2005, Hauck and Huneck
96 2007, Hauck 2008). Collectively, these studies have shown that Hg concentrations in
97 lichen increase near atmospheric point sources for Hg, and that *Hypogymnia physodes*, as
98 well as other epiphytic lichens, can provide a useful semi-quantitative proxy for
99 atmospheric Hg deposition.

100
101 In addition to the many studies that have measured Hg concentrations in epiphytic
102 lichens, two previous studies explored variations in the stable isotopic composition of Hg
103 in epiphytic lichens; but in species other than *Hypogymnia physodes*. Carignan et al
104 (2009) and Estrade et al (2010) measured Hg concentrations and isotopic compositions of
105 four tree lichen species (*Usnea*, *Ramalinia*, *Evernia* and *Bryoria*) from remote areas in
106 Canada and Switzerland and rural and urban areas in France. They did not find a
107 correlation between Hg concentration and that of other heavy metals (Cd and Pb) but they
108 did document mass independent isotope anomalies in the odd mass Hg isotopes for all
109 lichens sampled. Furthermore, these studies observed decreased mass independent Hg
110 isotope anomalies near industrial atmospheric sources of Hg, and suggested that this was
111 the result of additions of local anthropogenic Hg.

112
113 In this study, we measured total Hg concentrations (n=121) and stable isotopic
114 composition (n=38) in *Hypogymnia physodes* collected in 2008 from trees at proximal
115 and remote sites in a nested circular grid pattern distributed over 0.5 to 150 km from the
116 AOSR industrial complex north of Fort McMurray, Alberta, Canada (see Edgerton et al.,
117 this volume). Spatial trends in Hg concentration and isotopic composition are used to
118 evaluate the extent to which the AOSR developments have affected atmospheric Hg
119 deposition. Hg concentrations and isotopic compositions are compared to values from the
120 literature for measurements made in remote areas and near known point sources of Hg.
121 Hg isotopic compositions are also compared to values measured from a variety of
122 geological materials from the AOSR developments and nearby areas.

123 124 125 METHODS

126 127 *Sample Collection and Preparation*

128
129 A detailed field-sampling program was implemented during August-September 2008.
130 Most sites were accessed by helicopter and others were visited by ground. At each site,
131 composite samples of the lichen *Hypogymnia physodes* were collected from the branches
132 of 6 trees within Jack Pine (*Pinus banksiana*) tree stands. Samples were stored in
133 polyester sample bags and air dried in a laboratory at the University of Minnesota. Using
134 Teflon coated tweezers, tissue samples were cleaned by removing all foreign materials
135 (bark and other debris) and were then stored frozen until analysis. GPS location data for
136 all sample collection sites were used to determine the distance from a midpoint located at
137 the center of the AORS industrial operations (Edgerton et al., this volume). In 2009 bulk
138 geological samples of oil sands, bitumen, processed tailing sand, overburden, and mine
139 road material were acquired from active mining and energy processing operations in the

140 AOSR. Bulk samples of other undeveloped oil sand deposits exposed in outcrop in the
141 Athabasca River valley north of the AOSR industrial developments were also obtained.
142 All samples were shipped to the University of Michigan where they were freeze-dried,
143 and ground to a powder. Lichen samples were ground in a ball mill (Spex 8000M) using
144 a zirconium grinding vial and balls that were thoroughly cleaned between each sample.
145 Geological materials were ground by hand in an agate mortar and pestle that was
146 thoroughly cleaned between each sample. An ~50 mg aliquot of each powdered sample
147 was used for Hg concentration analysis and a 500 mg to 4 g aliquot of a sub-set of the
148 samples was used for Hg stable isotope analysis.

149

150 *Hg Concentration Analysis*

151

152 Mercury concentrations were measured using quality control methods that
153 included analysis of analytical standards, procedural blanks and replicate samples.
154 Lichens and geologic samples were analyzed for total Hg concentration by combustion at
155 850°C and quantification by cold-vapor atomic absorption spectrometry (CVAAS; MA-
156 2000, Nippon Instruments). Replicate analyses agreed within $\pm 7\%$ and the reporting limit
157 was 0.5 ng Hg. The IRMM powdered lichen reference material BCR482 was run with
158 each batch of eight samples and we obtained an average Hg concentration of 454 ± 8 ng/g
159 (1sd, n=19), which is within 5% of the certified value of 480 ± 20 ng/g.

160

161 *Sample Preparation for Isotope Analysis*

162

163 Hg was separated for isotopic analysis from lichens and geologic samples by
164 combustion at 750°C, thermal decomposition at 1000°C, and inline trapping in a 1%
165 KMnO_4 solution. To further purify Hg in the KMnO_4 solutions, the solutions were
166 reduced with SnCl_2 , purged with Hg-free air, and re-trapped in another 1% KMnO_4
167 solution. The Hg concentration of each of the KMnO_4 solutions was measured to
168 determine recoveries, and to allow matching of standard and sample concentrations for
169 isotope analysis. Details of the method are given in Biswas et al (2008) and Demers et al.
170 (2012). Mean recovery following combustion for IRMM lichen reference material
171 BCR482 was 94% ($\pm 4\%$, 1SD, n = 5), and mean recovery following both combustion
172 and secondary purge and trap of BCR482 was 93% ($\pm 3\%$, 1SD, n = 5).

173

174 *Mass Spectrometry*

175

176 Mercury in KMnO_4 solutions separated from lichens and bulk geologic samples
177 was analyzed for isotopic composition with a multiple collector inductively coupled
178 plasma mass spectrometer (MC-ICP-MS; Nu Instruments) using continuous flow cold
179 vapor generation with SnCl_2 reduction (Lauretta et al 2001, Blum and Bergquist 2007).
180 Instrumental mass bias was corrected using an internal Tl standard (NIST SRM 997,
181 $^{205}\text{Tl}/^{203}\text{Tl}=2.38714$) and sample-standard bracketing with the NIST SRM 3133 Hg
182 standard. Analyses and standards were run at 5 ppb Hg. On-peak zero corrections were
183 applied to all masses and isobaric interference from ^{204}Pb was monitored using mass 206,
184 but was always negligible.

185

186 We report isotopic compositions as permil (‰) deviations from the average of
187 NIST SRM 3133 bracketing standards using delta notation following equation 1:

$$\delta^{xxx}\text{Hg} (\text{‰}) = [(\text{xxxHg}/^{198}\text{Hg})_{\text{unknown}} / (\text{xxxHg}/^{198}\text{Hg})_{\text{NIST SRM 3133}} - 1] * 1000 \quad (1)$$

191 where xxx is the mass of each mercury isotope between ^{199}Hg and ^{204}Hg . We use $\delta^{202}\text{Hg}$
192 to describe isotopic differences due to mass dependent fractionation (MDF). Mass
193 independent fractionation (MIF) is defined as the deviation of the isotope ratios involving
194 odd mass isotopes from the theoretically expected values determined by the kinetic mass-
195 dependent fractionation law based on the measured $\delta^{202}\text{Hg}$ (Blum and Bergquist 2007).
196 MIF is reported in “capital delta” notation ($\Delta^{xxx}\text{Hg}$) in units of permil (‰), and is well
197 approximated for small ranges in delta values ($\Delta \approx 10 \text{‰}$) by equation 2:

$$\Delta^{xxx}\text{Hg} (\text{‰}) = \delta^{xxx}\text{Hg} - (\delta^{202}\text{Hg} \times \alpha) \quad (2)$$

201 where xxx is the mass of each Hg isotope 199 and 201 and α is a constant (0.252 and
202 0.752, respectively; Blum and Bergquist 2007).

203 *Analytical Uncertainty*

206 The uncertainty of Hg isotope measurements was characterized using a secondary
207 standard solution that is widely distributed (UM-Almaden) and an international lichen
208 reference material (BCR482). The UM-Almaden standard solution is useful for inter-
209 laboratory comparison and we obtained the following values for 10 replicate analyses
210 carried out during the analyses of samples for this study: $\delta^{202}\text{Hg} = -0.59 \pm 0.03\text{‰}$ (2sd),
211 $\delta^{199}\text{Hg} = -0.01 \pm 0.04\text{‰}$ (2sd), $\delta^{201}\text{Hg} = -0.04 \pm 0.03\text{‰}$ (2sd). The lichen IRMM BCR482 is
212 useful for assessment of the uncertainty of complete Hg separation and analyses and we
213 obtained the following values for 6 replicate analyses carried out during the analyses of
214 samples for this study: $\delta^{202}\text{Hg} = -1.67 \pm 0.04\text{‰}$ (2sd), $\delta^{199}\text{Hg} = -0.67 \pm 0.04\text{‰}$ (2sd) and
215 $\delta^{201}\text{Hg} = -0.68 \pm 0.03\text{‰}$ (2sd).

218 RESULTS AND DISCUSSION

220 *Hg concentrations of Hypogymnia physodes*

222 Total Hg concentrations for the 121 *Hypogymnia physodes* samples analyzed
223 ranged from 71 to 268 ng/g with a mean value of 144 ± 33 ng/g (1sd) (Figure 1). These
224 values are in the range typical for remote areas unaffected by point source Hg emissions.
225 Makhholm and Bennett (1998) reported background Hg concentrations for *Hypogymnia*
226 *physodes* in northern Wisconsin of 110 to 155 ng/g and Bennett and Wetmore (1997)
227 reported background values of 103 to 143 ng/g for northern Minnesota. Makhholm and
228 Bennett (1998, and references within) compiled background Hg concentration values for
229 European studies as of 1998 and reported that most values (9 separate studies) ranged
230 from 200 to 400 ng/g, whereas two studies in Scandinavia reported background values of
231 100 ng/g and 160 ng/g respectively. Since 1998 two additional studies measured

232 background Hg values in *Hypogymnia physodes*. Horvat (2000) measured a mean
233 background value of 110 ± 10 ng/g at a remote location in Slovenia and Sensen and
234 Richardson (2002) measured a mean background Hg value of 148 ± 46 ng/g at a remote
235 location in New Brunswick, Canada. Altogether, comparison of the values reported here
236 for Hg in *Hypogymnia physodes* in the AOSR are consistent with background values
237 measured in a large number of studies of Hg in *Hypogymnia physodes* in both North
238 America and Europe. This suggests that any Hg deposition associated with the AOSR
239 development has not significantly elevated the Hg concentrations in lichens.

240
241 Previous studies have shown that Hg concentrations in natural *Hypogymnia*
242 *physodes* collected near atmospheric Hg point sources, and Hg in *Hypogymnia physodes*
243 transplanted to the vicinity of Hg point sources, have lichen tissue concentrations much
244 higher than those that we measured in the AOSR. Makhholm and Bennett (1998)
245 transplanted *Hypogymnia physodes* downwind of a chlor-alkali plant and after a year of
246 exposure concentrations ranged up to 4418 ng/g at a distance of 250 m from the plant and
247 up to 403 ng/g at a distance of 1250 m. Makhholm and Bennett (1998, and references
248 therein) also compiled the results of earlier studies of Hg in *Hypogymnia physodes* near
249 point sources and found that in each of seven studies Hg concentrations were highly
250 elevated near the source with values ranging from 770 to 36000 ng/g. In a more recent
251 study, Horvat et al (2000) transplanted *Hypogymnia physodes* to locations around a
252 natural gas treatment plant in Molve, Croatia and locations around a Hg mining area in
253 Idrija, Slovenia, where measurements of the concentration of ambient total gaseous
254 mercury (TGM) in air were also made. They found a strong correlation between the
255 logarithm of the total Hg concentration in *Hypogymnia physodes* and the logarithm of the
256 TGM concentration in air. Hg concentrations in *Hypogymnia physodes* were 110 ng/g at
257 the time of transplant and ranged from 540 to 4430 ng/g after 6 months in the mining
258 area. In another recent study Sensen and Richardson (2002) analyzed Hg in naturally
259 growing *Hypogymnia physodes* on spruce trees along transects near a Hg cell chlor-alkali
260 plant in New Brunswick, Canada. They documented systematic increases in Hg
261 concentration from a background value of 148 ng/g at a distance of 8 km from the plant
262 to maximum value of 790 and 980 ng/g at a distance of 125 m along two different
263 transects. In sum, these studies show that within about 1 to 8 km of atmospheric Hg point
264 sources the Hg concentrations of *Hypogymnia physodes* are generally elevated far above
265 background values. This reinforces our conclusion that the AOSR development is not a
266 significant atmospheric Hg source that is detectable using lichen analysis and certainly
267 does not generate atmospheric Hg levels near the magnitude of chlor-alkali plants,
268 smelters, gas processing plants, or Hg mining areas that have been studied previously.

269 270 *Hg concentrations of other species of epiphytic lichen*

271
272 The literature is rich with investigations that have used epiphytic lichens other
273 than *Hypogymnia physodes* to study Hg levels in the atmosphere. Because of
274 physiological differences between species it is not advisable to directly compare metal
275 concentrations between species. Nevertheless, these studies do confirm that for most
276 species a concentration range of 100-200 ng/g total Hg is a common background
277 concentration that is often observed in remote areas. Large increases in Hg

278 concentrations are often observed within about 8 km of large atmospheric Hg point
279 sources, and lichen Hg concentrations generally correlate with TGM concentrations in air
280 (Bargagli and Barghigiani 1991; Guevara et al 2004; Grangeon et al 2012; Tretiach et al
281 2011). Using four different lichen species (but not including *Hypogymnia physodes*)
282 Landers et al (1995) observed increased Hg concentrations in Alaska with closer
283 proximity to the marine coastline. Carignan and Sonke (2010) measured Hg in three
284 lichen species (but again not in *Hypogymnia physodes*) in Canada (mostly in Quebec) and
285 found that Hg concentrations were well correlated with Br concentrations, and that both
286 elements increased in concentration with decreasing distance to Hudson Bay. These
287 authors attributed the spatial trends to a marine source of Br to the atmosphere, which is
288 known to oxidize background Hg(0) in the atmosphere, which then led to increased
289 deposition of Hg(II). The Carignan and Sonke (2010) study documents lichen Hg
290 concentrations as high as 2060 ng/g in the lichen species *Bryoria*, 20 km from Hudson
291 Bay but far from anthropogenic point sources. Hg concentrations dropped below 250
292 ng/g at distances greater than 800 km from Hudson Bay. The AOSR is about 800 km
293 from both the Pacific Ocean and Hudson Bay and appears to be unaffected by this Hg
294 deposition mechanism.

295

296 Spatial Variation in Hg concentrations of *Hypogymnia physodes*

297

298 In order to explore whether the observed variability in the Hg concentration of
299 *Hypogymnia physodes* in the vicinity of the AOSR is affected by the mining and energy
300 production activities, we plotted the Hg concentrations of lichens as a function of the
301 distance from the center of the production area (Figure 1). Regression of the data reveals
302 a small (slope=0.33 ng/g per km) but significant ($p=0.0002$) decrease in the Hg
303 concentration of lichens as the active mining and upgrading facilities are approached. The
304 regression line drops from a Hg concentration of 171 ng/g at 155 km to 122 ng/g at 5 km.
305 This behavior is the opposite of what has been documented in the literature near
306 atmospheric point sources of Hg and is (as far as we are aware) the first documentation of
307 decreasing Hg concentration in lichen as an industrial development is approached. We do
308 note, however, that previous studies documenting increases in the Hg concentration of
309 *Hypogymnia physodes* in the vicinity of atmospheric Hg sources, found elevated Hg in
310 lichens only at distances of 8 km or less from the sources. The sampling distances in our
311 study were generally much farther from the potential source than previous studies, and
312 only 8 of the 121 *Hypogymnia physodes* samples were from 8 km or less distance from
313 the center of the AOSR mining and energy production areas. However, even these
314 samples within close proximity of the AOSR industrial development did not have
315 elevated Hg concentrations.

316

317 Although a decrease in Hg in epiphytic lichens near industrial facilities has not
318 been previously reported, a study comparing naturally growing and transplanted
319 *Hypogymnia physodes* within a km of a chlor-alkali plant in Norway may provide some
320 insight into this phenomenon. Steinnes and Krog (1977) found that Hg concentrations in
321 naturally occurring *Hypogymnia physodes* reached a maximum of 950 ng/g in close
322 proximity to a chlor-alkali plant. However, when they transplanted *Hypogymnia physodes*
323 from a remote site to the industrial site they observed an increase in Hg content with time

324 and found Hg concentrations in *Hypogymnia physodes* as high as 6000 to 8000 ng/g after
325 16 weeks of exposure. The authors suggested that the lower uptake of Hg by the naturally
326 occurring lichens compared to the transplants may have been related to SO₂ exposure and
327 resulting loss of vigor in the *Hypogymnia physodes* (Steinnes and Krog 1977). In the
328 vicinity of the AOSR the sulfur content of *Hypogymnia physodes* is higher due to SO₂
329 deposition (Edgerton et al, Landis et al, this volume) and we suggest that this may have
330 resulted in decreased Hg accumulation as suggested in the study of Steinnes and Krog
331 (1977). Graney et al (this volume) observed a subtle decrease in Zn and Mn
332 concentrations toward the center of the AOSR region in the same lichen samples we
333 analyzed. They suggested that this trend may be related to canopy interactions or
334 physiological processes in the lichens.

335
336

337 *Hg Isotopic composition of Hypogymnia physodes*

338

339 A subset of 38 *Hypogymnia physodes* samples that were analyzed for Hg
340 concentration were also analyzed for their stable mercury isotopic composition.
341 Variations in the isotopic composition related to mass dependent fractionation of Hg are
342 reported as $\delta^{202}\text{Hg}$ and samples ranged in values from -2.66 to -1.41‰ with an average
343 value of $-1.87 \pm 0.22\text{‰}$ (1sd) (Figure 2). Mass independent fractionation (MIF) is
344 reported here as $\bullet^{199}\text{Hg}$ (but note that $\bullet^{201}\text{Hg}$ shows the same behavior) and samples
345 ranged in values from -0.55 to +0.33‰ with an average value of $-0.24 \pm 0.17\text{‰}$ (1sd)
346 (Figure 3). The ratio of $\bullet^{199}\text{Hg}/\bullet^{201}\text{Hg}$ is 0.997 (Figure 4), suggesting that the MIF
347 results from photochemical reduction of Hg(II) to Hg(0) involving short-lived radical pair
348 reactions and is caused by the magnetic isotope effect (Bergquist and Blum 2007; Blum
349 2011).

350

351 Two other investigations of Hg isotopic compositions of lichens have been
352 published previously, but there have been no previous Hg isotopic studies of the lichen
353 species *Hypogymnia physodes*. Carignan et al. (2009) and Estrade et al. (2010) measured
354 Hg isotope values in remote areas in Canada and Switzerland and both urban and
355 industrial areas in France in many different lichen species. These lichens ranged widely
356 in $\delta^{202}\text{Hg}$ values from 1.5 down to -2.2‰. The lichens analyzed in these previous studies
357 also displayed negative values for $\bullet^{199}\text{Hg}$ (and $\bullet^{201}\text{Hg}$), with values ranging from -0.2 to
358 -0.9‰. Lichens from remote areas showed the lowest $\bullet^{199}\text{Hg}$ values (Carignan et al
359 2009) and values tended to become less negative in urban and industrial areas (Estrade et
360 al 2010). At that time these authors interpreted the negative $\bullet^{199}\text{Hg}$ values to be
361 indicative of regional atmospheric Hg isotopic values and the increase in $\bullet^{199}\text{Hg}$ near
362 industrial areas as the impact of adding industrial point sources of Hg that had near-zero
363 $\bullet^{199}\text{Hg}$ values.

364

365 More recently, several studies of atmospheric Hg isotopes have shown that Hg(II)
366 deposited from the atmosphere in precipitation has positive $\bullet^{199}\text{Hg}$ (and $\bullet^{201}\text{Hg}$) values,
367 and that gaseous Hg(0) in the atmosphere has negative $\bullet^{199}\text{Hg}$ (and $\bullet^{201}\text{Hg}$) values.
368 Furthermore, these studies have demonstrated that there are fractionation mechanisms
369 that can cause Hg with more positive $\bullet^{199}\text{Hg}$ to be released from surfaces following

370 photochemical reduction of Hg(II) to Hg(0) (Gratz et al 2010; Sherman et al 2010, 2012;
371 Demers et al 2012). In a recent investigation of Hg isotope systematics in a forested
372 ecosystem in northern Wisconsin (USA), Demers et al (2012) found that gaseous
373 elemental Hg(0) with $\delta^{199}\text{Hg}$ of -0.2‰ is oxidized and deposited to tree leaf surfaces, and
374 that subsequent photochemical reduction and loss of a portion of this Hg results in
375 increasingly negative values for $\delta^{199}\text{Hg}$ in leaves, averaging about -0.3‰ . This same Hg
376 isotope fractionation process may occur on lichen surfaces as well as on leaves. We
377 suggest that Hg(0) is deposited to lichen surfaces, becoming oxidized to Hg(II) as it binds
378 with ligands in organic acids. Photochemical reactions then cause partial reduction and
379 loss of some Hg(II) as Hg(0) with more positive $\delta^{199}\text{Hg}$, and the Hg(II) that remains in
380 the lichen acquires more negative $\delta^{199}\text{Hg}$ values.

381

382 *Spatial Variation in Hg Isotopic composition of Hypogymnia physodes*

383

384 The $\delta^{202}\text{Hg}$ values of the lichens from this study are plotted versus distance from
385 the active mining and energy production activities on Figure 2. $\delta^{202}\text{Hg}$ values do not vary
386 significantly with distance ($p = 0.350$) from the active energy production areas and are
387 similar to values for foliage from trees in northern Wisconsin (USA) measured by
388 Demers et al (2012). Values are unaffected by proximity to the AOSR developments, as
389 would be expected, because Hg concentrations show no evidence for addition of Hg from
390 this source.

391

392 In contrast, $\delta^{199}\text{Hg}$ (and $\delta^{201}\text{Hg}$) values shift dramatically with distance from the
393 AOSR development (Figure 3). At distances of >25 km the average $\delta^{199}\text{Hg}$ value is
394 $-0.38 \pm 0.07\text{‰}$ whereas at <25 km the average $\delta^{199}\text{Hg}$ value is $-0.13 \pm 0.15\text{‰}$ and reaches a
395 maximum value of $+0.33\text{‰}$. The dramatic increase in $\delta^{199}\text{Hg}$ values combined with the
396 decrease in Hg concentrations of *Hypogymnia physodes* near the AOSR development is
397 somewhat puzzling. It appears that either i) the AOSR development is emitting Hg with
398 very high $\delta^{199}\text{Hg}$ values, but accumulation of Hg in the lichens near the AOSR is
399 suppressed to the point that Hg concentrations actually appear to decrease near the active
400 energy production areas or ii) there are physiological effects in the lichens near the active
401 energy production areas due to deposition of other pollutants (in particular SO_2) that both
402 suppresses Hg accumulation and alters the mass independent fractionation of Hg on
403 lichen surfaces resulting in an increase in $\delta^{199}\text{Hg}$ values. Each of these alternate
404 explanations is discussed in more detail below.

405

406 *Hg isotopic composition of Oil Sands Materials*

407

408 To explore the possibility that the AOSR development is emitting Hg with highly
409 elevated $\delta^{199}\text{Hg}$ values, and that this is responsible for the high $\delta^{199}\text{Hg}$ values in lichens
410 in close proximity to the AOSR, we analyzed bulk samples of geological materials from
411 the AOSR (see Landis et al, this volume). Oil sand, bitumen, processed tailings sand,
412 overburden and road materials from mines between Ft McMurray and Ft McKay were
413 analyzed. Weathered oil sand that naturally outcrops along the Athabasca River north of
414 Fort McKay (and has not been mined) was also analyzed. The concentration of Hg in the
415 oil sands ranged from 4.1 to 38.8 ng/g, processed sands from tailings ranged from 1.9 to

416 10.6 ng/g, and the bitumen, overburden and road material were 14.3, 13.1 and 32.8 ng/g,
417 respectively. In comparison, Hg concentrations are 3.5 ng/g in mean volume weighted
418 US crude oil and 100 ng/g in mean volume weighted US coal (Wilhelm et al 2007;
419 Toole-O'Neil et al 1999). The mean background Hg concentration for lake sediments in
420 Alberta was recently reported as 36 ng/g (Nasr et al 2011), and indicates that the oil sands
421 and associated materials do not have Hg concentrations that are far above background
422 sediment concentrations.

423

424 • ^{199}Hg and $\delta^{202}\text{Hg}$ values of the geologic materials analyzed are plotted along
425 with values for the lichens on Figure 5. Oil sand, bitumen, processed sand and
426 overburden from mines between Fort McMurray and Fort McKay fall in a narrow range
427 of Hg isotope values that overlap with values for *Hypogymnia physodes* collected >25 km
428 from the mines, but have lower • ^{199}Hg and higher $\delta^{202}\text{Hg}$ than *Hypogymnia physodes*
429 collected <25 km from the mines. A single sample of road material from the mines has
430 • ^{199}Hg ~0.3‰ higher than the other mine samples and could possibly represent addition
431 of Hg from oil, brake pads or diesel fuel. The three samples of oil sand from the
432 Athabasca River north of Fort McKay also have • ^{199}Hg values about ~0.3‰ higher than
433 the mine samples. These samples have • ^{199}Hg closer to the values of the *Hypogymnia*
434 *physodes* <25 km from the mines, and $\delta^{202}\text{Hg}$ values about ~0.5‰ higher, but these
435 deposits are not currently mined or processed.

436

437 Potential Hg sources from the mining operations are similar to the background
438 isotopic values in lichens >25 km from the mining areas. Therefore, addition of this
439 potential source of Hg would not shift the lichen Hg isotopic values appreciably. Even if
440 all of the Hg in the lichens near the AOSR had the maximum observed • ^{199}Hg from the
441 undeveloped Athabasca River oil sand, this could only explain the lichens with
442 intermediate values and could not explain the highest lichen • ^{199}Hg values. Therefore, we
443 can rule out addition of oil sand-derived Hg as the sole cause for the increase in • ^{199}Hg
444 values of *Hypogymnia physodes* within 25 km of the AOSR area.

445

446

447 *Proposed mechanism to explain Hg isotopic variability*

448

449 We have argued above that the addition of Hg from the active mining and energy
450 production activities does not adequately explain the changes in Hg isotopic composition
451 observed in lichens within 25 km of the AOSR. Furthermore, the observed lower Hg
452 concentrations in lichens near the AOSR are not consistent with addition of Hg from a
453 point source to the regional background. We suggest that the increase in • ^{199}Hg values of
454 *Hypogymnia physodes* within 25 km of the AOSR is caused by a change in the processes
455 by which *Hypogymnia physodes* binds Hg (II) species onto ligands present in the lichens.
456 Following deposition of Hg to the lichens, there appears to be a change in the reaction
457 pathway and degree of photochemical reduction of Hg (II) from the lichen surfaces. This
458 reduction in the loss of Hg(0) from the lichen surfaces appears to result in a change in the
459 lichen • ^{199}Hg values.

460

461 Experimental studies of Hg isotope fractionation have shown that large magnitude
462 mass independent fractionation (>0.2‰) is generally the result of photochemical
463 reactions involving short-lived radical pairs (Blum 2011). The ratio of \bullet ^{199}Hg to \bullet ^{201}Hg
464 and the observation of either the preferential loss or gain of odd isotopes of Hg in
465 volatilized Hg(0) during reduction, has been shown to be related to the ligands to which
466 Hg is bonded (Zheng and Hintelmann 2010). Regression of \bullet ^{199}Hg versus \bullet ^{201}Hg for
467 lichens from this study yield a slope of 0.997 ($r^2 = 0.947$; Figure 4) and values are
468 negative (meaning odd isotopes were preferentially lost). Hg (II) is known to be
469 photochemically reduced to Hg(0) and emitted from leaf surfaces (Mowat et al 2011).
470 Zheng and Hintelmann (2010) showed that when Hg (II) is bonded to a sulfur-containing
471 ligand photochemical reduction and loss of Hg(0) from aqueous solutions results in
472 residual Hg(II) with negative \bullet ^{199}Hg and \bullet ^{201}Hg . When the binding ligand is sulfurless,
473 residual Hg(II) is observed to have positive \bullet ^{199}Hg and \bullet ^{201}Hg .

474
475 Lichens are known to produce a wide range of organic ligands, both containing
476 and not containing sulfur, that play an important role in metal binding. Both intracellular
477 binding of metals to sulfur-containing peptides (metallothioneins) and extracellular
478 binding to sulfur-less organic acids is known to occur in lichens (Sarret et al, 1998).
479 Although experiments exploring Hg isotope fractionation in the presence of these ligands
480 have not yet been performed, we would expect that both positive and negative MIF could
481 be produced by photochemical reduction of Hg(II) complexed with these various
482 compounds. It seems likely that the net isotopic composition of lichen is the result of
483 simultaneous negative and positive mass independent fractionation of Hg associated with
484 different bonding environments in the lichen. Given this assumption, we suggest that
485 *Hypogymnia physodes* collected >25 km from the active mining and energy production
486 facilities have negative \bullet ^{199}Hg and \bullet ^{201}Hg that resulted from the dominance of
487 photochemical reduction of Hg(II) from sulfur-bearing ligands compared to sulfur-less
488 ligands. The increase in \bullet ^{199}Hg and \bullet ^{201}Hg that is observed closer to the active mining
489 and energy production facilities could then be interpreted as a shift in the balance toward
490 reduction of Hg(II) from sulfur-less ligands.

491
492 A study by Bialonska and Dayan (2005) measured changes in the production of
493 organic acids by samples of *Hypogymnia physodes* when they were transplanted to four
494 different sites where they were exposed to industrial emissions of metals and SO₂. Site-
495 specific changes in production of various organic acids was observed, with some
496 increasing and others decreasing with exposure. For example, an increase in the content
497 of physodic acid was observed in all transplanted lichens and the authors suggested a
498 possible role for this compound in defense against stress caused by exposure to pollutants
499 (Bialonska and Dayan 2005). Although highly speculative, we suggest that exposure of
500 *Hypogymnia physodes* in the AOSR near active mining and energy production facilities
501 to SO₂ and other metals could have changed the balance of the various organic acids
502 produced in the lichens. Increased complexation of Hg(II) to these sulfur-less
503 compounds, with resulting enhanced photochemical reduction of Hg and loss back to the
504 atmosphere, is a possible explanation for both the increase in \bullet ^{199}Hg and \bullet ^{201}Hg and
505 decrease in total Hg concentration observed in the lichens <25 km from the mining and
506 energy production facilities.

507

508

509 CONCLUSIONS

510

511 A single species of epiphytic tree lichen (*Hypogymnia physodes*) was sampled in
512 2008 at remote sites in a nested, circular grid pattern 0.5 to 150 km from the center of
513 industrial development in the Alberta Oil Sands Region north of Fort McMurray, Alberta,
514 Canada. Total Hg concentrations in epiphytic lichens have been used in previous studies
515 as a measure of spatial variations in atmospheric Hg deposition and to delineate the near
516 field influence of atmospheric point sources of Hg. The stable Hg isotopic composition
517 has also recently been used as a monitor of additions of local anthropogenic Hg to
518 regional background deposition. Hg concentrations in *Hypogymnia physodes* in the
519 AOSR ranged from 71 to 268 ng/g, which is similar to that measured by others for
520 remote sites in other regions. Based on concentration alone there is no evidence for
521 anomalously high atmospheric Hg deposition near the AOSR mining and energy
522 production facilities. In fact, small variations with distance show that Hg concentrations
523 decrease with proximity to the facilities. This conclusion is in contrast with the finding of
524 Kelly et al (2010) who observed increased Hg concentrations in snow near the AOSR
525 energy development facilities.

526

527 The stable Hg isotope composition of the lichens does, however, change
528 systematically with distance from the potential industrial sources. Most notably the
529 lichens display varying levels of mass independent fractionation with both $\bullet^{199}\text{Hg}$ and
530 $\bullet^{201}\text{Hg}$ ranging from near 0.0‰ close to the oil sands developments and systematically
531 falling to -0.4‰ about 25 km away. The $\bullet^{199}\text{Hg}/\bullet^{201}\text{Hg}$ slope is close to one, suggesting
532 that the mass independent fractionation results from photochemical reduction of Hg(II) to
533 Hg(0). Mass dependent fractionation does not change systematically with distance from
534 the oil sands developments, and $\delta^{202}\text{Hg}$ averages -1.9‰. The spatial trends show that the
535 energy production activities influence the $\bullet^{199}\text{Hg}$ and $\bullet^{201}\text{Hg}$ values without significantly
536 affecting the $\delta^{202}\text{Hg}$ values and have the effect of lowering the Hg concentrations of the
537 lichens. Measurements of the Hg isotopic composition of the oils sands themselves show
538 that they cannot explain the variation in Hg isotopic composition of *Hypogymnia*
539 *physodes* near the energy production facilities. It is possible that other atmospheric
540 pollutants, such as SO₂ (which is known to affect the vitality of lichens), are influencing
541 Hg retention in the lichens. *Hypogymnia physodes* is also known to respond to SO₂ by
542 changing its production of organic acids. This may affect the proportions of different
543 ligands to which Hg is bonded, thus influencing the photochemical reduction of Hg on
544 lichen surfaces, which we suggest is the cause of the observed mass independent
545 fractionation.

546

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548

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554

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668

669 FIGURE CAPTIONS

670
671 Figure 1. The concentration of Hg in lichens (in ng/g) versus the distance of the sample
672 collection point from the center of the energy production activities (in km).

673
674 Figure 2. The $\delta^{202}\text{Hg}$ value of Hg in lichens (in permil) versus the distance of the sample
675 collection point from the center of the energy production activities (in km).

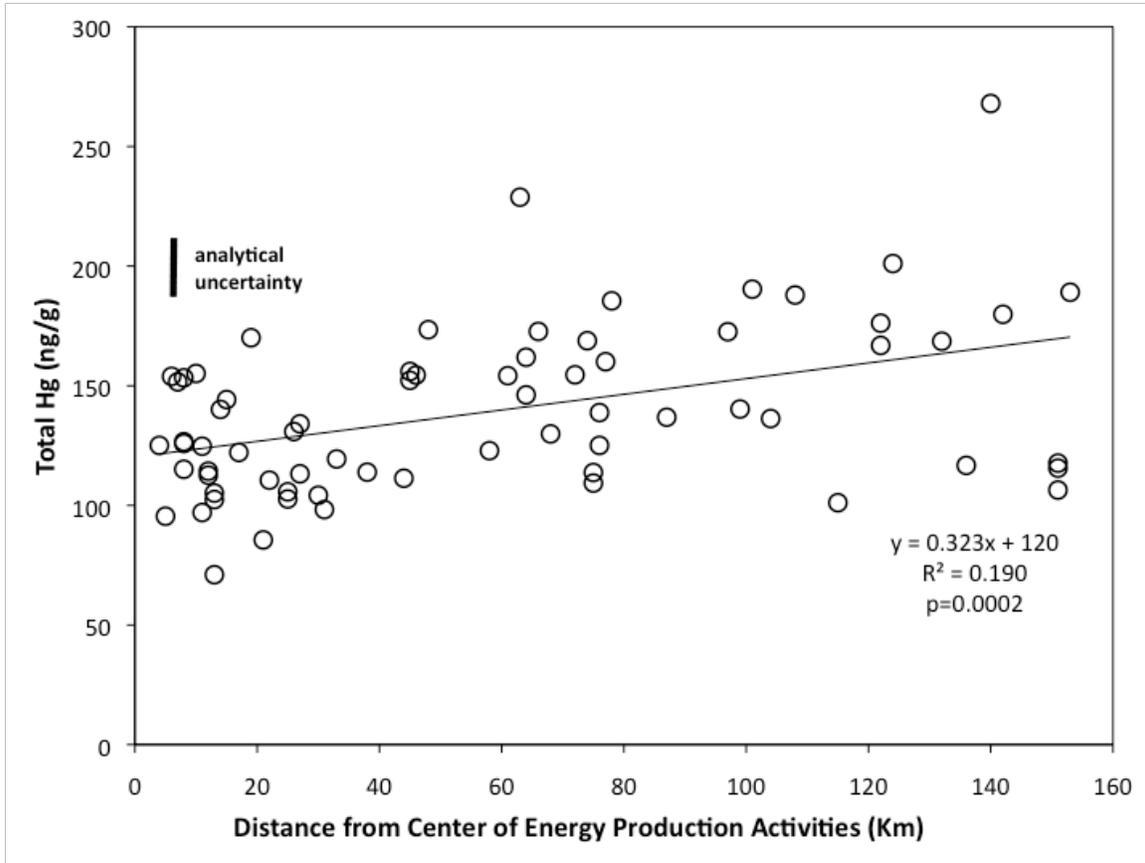
676
677 Figure 3. The $\Delta^{199}\text{Hg}$ value of Hg in lichens (in permil) versus the distance of the sample
678 collection point from the center of the energy production activities (in km).

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680 Figure 4. The $\Delta^{199}\text{Hg}$ value of Hg in lichens (in permil) versus the $\Delta^{201}\text{Hg}$ value of Hg in
681 lichens (in permil).

682
683 Figure 5. The $\Delta^{199}\text{Hg}$ value of Hg (in permil) versus the $\delta^{202}\text{Hg}$ value of Hg (in permil) in
684 lichens as well as in a variety of geological materials from the AOSR region.
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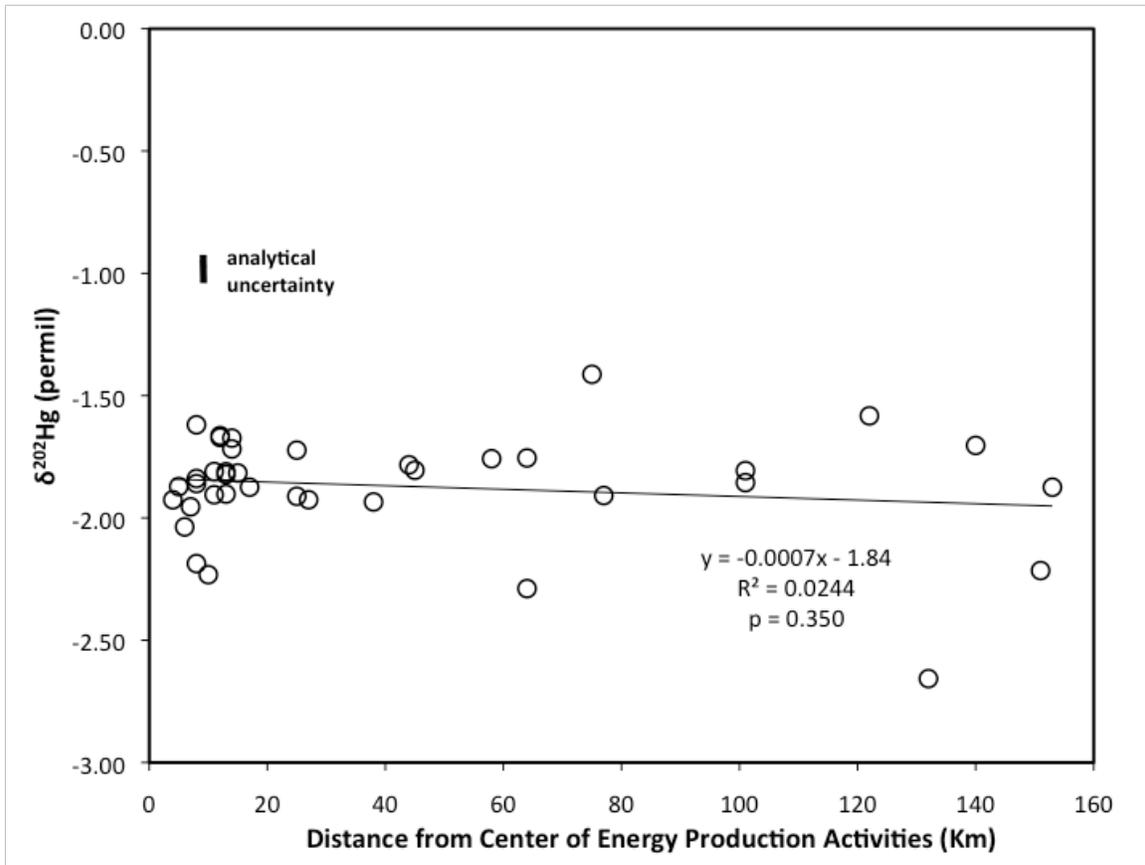
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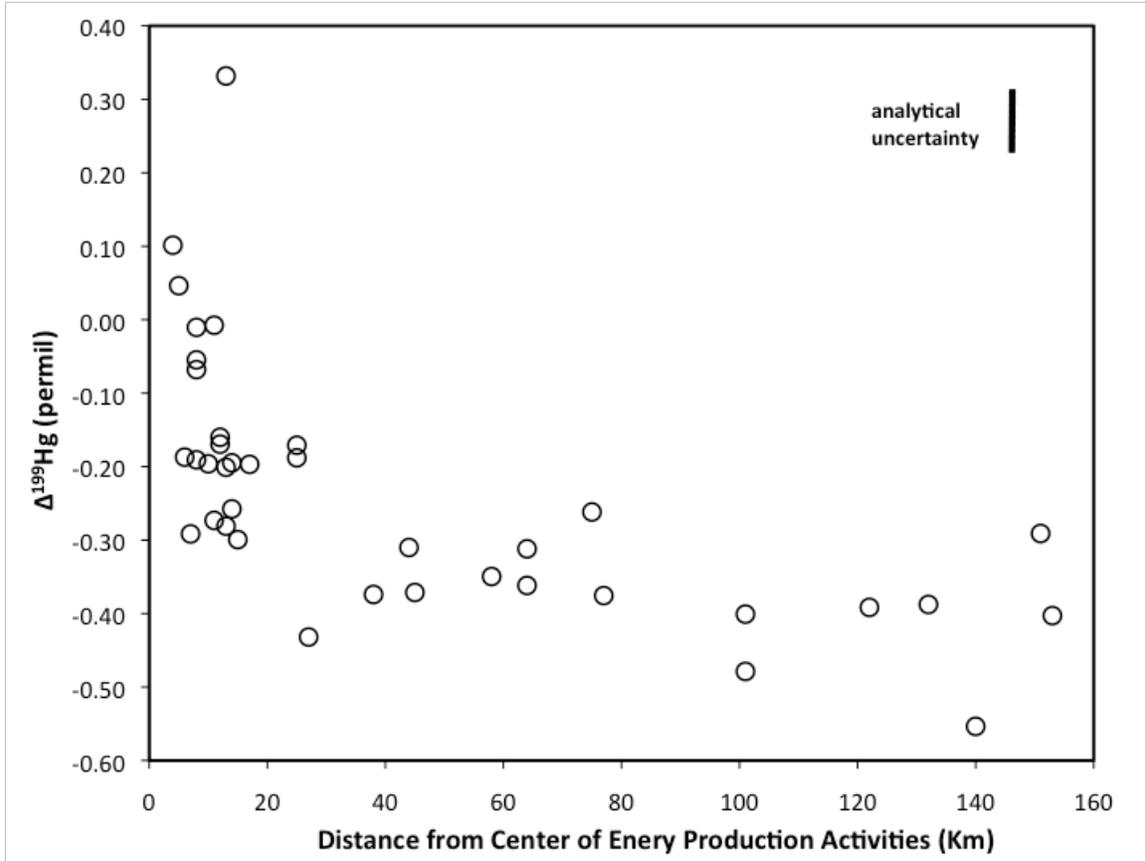
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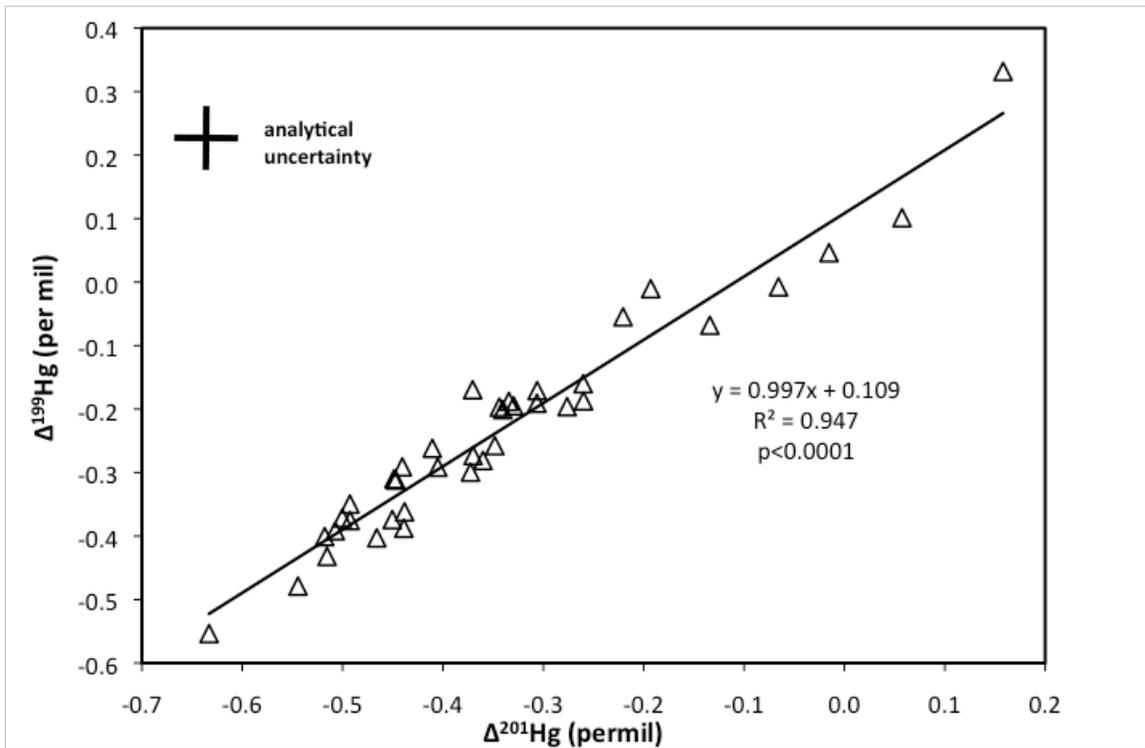
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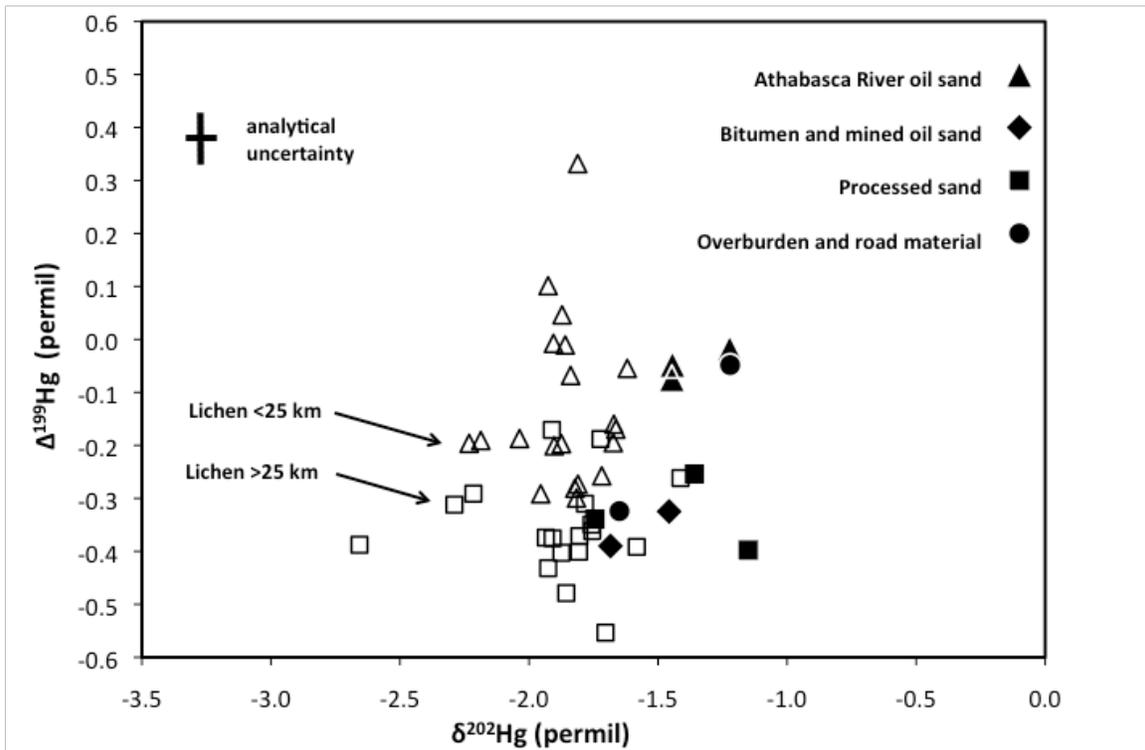
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Figure 5.



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