



# *Gaseous mercury flux from salt marshes is mediated by solar radiation and temperature*

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## 2 **Gaseous mercury flux from salt marshes is mediated by solar radiation and temperature**

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10

### 11 **Abstract**

12 Salt marshes are ecologically sensitive ecosystems where mercury (Hg) methylation and  
13 biomagnification can occur. Understanding the mechanisms controlling gaseous Hg flux from salt  
14 marshes is important to predict the retention of Hg in coastal wetlands and project the impact of  
15 environmental change on the global Hg cycle. We monitored Hg flux from a remote salt marsh over 9  
16 days which included three cloudless days and a 4 mm rainfall event. We observed a cyclical diel  
17 relationship between Hg flux and solar radiation. When measurements at the same irradiance intensity  
18 are considered, Hg flux was greater in the evening when the sediment was warm than in the morning  
19 when the sediment was cool. This is evidence to suggest that both solar radiation and sediment  
20 temperature directly influence the rate of Hg(II) photoreduction in salt marshes. Hg flux could be  
21 predicted from solar radiation and sediment temperature in sub-datasets collected during cloudless  
22 days ( $R^2 = 0.99$ ), and before ( $R^2 = 0.97$ ) and after ( $R^2 = 0.95$ ) the rainfall event, but the combined  
23 dataset could not account for the lower Hg flux observed after the rainfall event that is in contrast to  
24 greater Hg flux from soils after rainfall events.

25 **Keywords** Mercury, Salt marsh, Wetland, Sediment, Dynamic Flux Chamber

26

## 27 **Introduction**

28 Mercury (Hg) is a potent neurotoxin that accumulates at the top of aquatic food webs, often far away  
29 from emission sources due to long-distance atmospheric transport (Morel et al., 1998). The majority  
30 of Hg emitted into the atmosphere is gaseous elemental mercury, Hg(0), which has a residence time of  
31 several months in the atmosphere (Corbitt et al., 2011). Although recent efforts to phase out the use of  
32 Hg in commercial products has reduced atmospheric emissions (Zhang et al., 2016), anthropogenic  
33 sources currently account for only around 30% of emissions (UNEP, 2013). The remainder is  
34 attributed to natural sources (10%) and the re-emission of historically emitted anthropogenic sources  
35 (60%). The mechanisms underlying the emissions of Hg from ecosystems are imperfectly understood  
36 (Agnan et al., 2016). Improving our quantification of these fundamental processes is very important  
37 so that we can predict the impact that climate change will have on the global Hg cycle (Krabbenhoft  
38 and Sunderland, 2013), and the extent to which Hg will be retained in wetland environments where it  
39 can undergo methylation to methylmercury, which is more toxic and biomagnifies through the food  
40 web (Gregory Shriver et al., 2006).

41 Many of the previous attempts to quantify or mechanistically understand gaseous Hg flux from the  
42 terrestrial land surface have focussed on soils and freshwater wetlands (Agnan et al., 2016). Relatively  
43 little attention has been given to coastal wetlands. Although salt marshes do not represent a large  
44 portion of global surface area (they cover a global area of  $3.8 \times 10^7$  Ha (Steudler and Peterson, 1984)  
45 which represents about 0.07% of the total land surface), they are an important Hg sink (Hung and  
46 Chmura, 2006). They provide conditions conducive to Hg methylation (Canário et al., 2007) and they  
47 support Hg-accumulating invertebrates at the base of sensitive food webs (Sizmur et al., 2013). Salt  
48 marshes may become more important sources of Hg flux in the future if more coastal wetlands are  
49 created by managed retreat responses to rising sea levels (Sizmur et al., 2016).

50 The mechanisms controlling Hg flux from coastal sediments is poorly understood since they have  
51 only been monitored during two studies (Sommar et al., 2013). Both studies found a positive  
52 relationship between Hg flux and solar radiation which indicates that emission of Hg(0) is due to  
53 photoreduction of Hg(II) and subsequent volatilisation (Lee et al., 2000; Smith and Reinfelder, 2009).

54 Lee et al (2000) also found a correlation between Hg flux and sediment temperature, but this  
55 relationship is confounded due to the obvious correlation between temperature and solar radiation.  
56 Moore and Carpi (2005) suggested that solar radiation mediates Hg(II) reduction to Hg(0) and that  
57 temperature mediates the volatilisation of Hg(0) from soils. Pannu et al., (2014) identify a fast,  
58 moisture-dependent abiotic process controlling reduction of a small Hg(II) pool, and a concurrent  
59 slower biotic process that generates a larger pool of reducible Hg(II) in forest soils. Lindberg et al.  
60 (2005; 2002) demonstrate that Hg(0) is volatilised during transpiration of wetland plants. The  
61 applicability of these mechanistic insights have not been investigated in coastal wetlands.

62 There are some key differences between salt marshes and soils or terrestrial wetlands, such as the  
63 influence of the tidal cycle, the considerably greater salinity and chloride concentration, and the  
64 adaptations of salt marsh vegetation to the anoxic and saline environment. These differences may  
65 result in different mechanisms that mediate Hg flux in coastal wetlands when compared to soils or  
66 freshwater wetlands. We used a remote, non-point source mercury-contaminated salt marsh on the  
67 Bay of Fundy, Nova Scotia, Canada as a model location to investigate Hg flux from coastal wetlands.

68

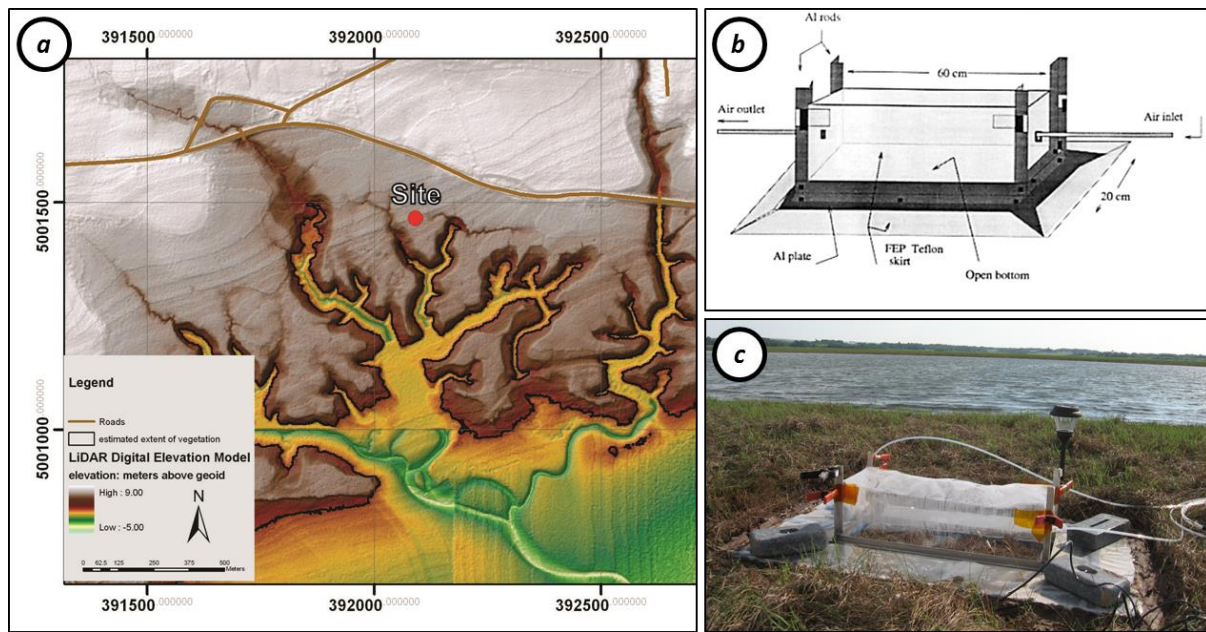
## 69 **Experimental**

### 70 Study site

71 The study took place between 6<sup>th</sup> and 15<sup>th</sup> July 2009. The study site was located at 45°9'13.61" N,  
72 64°21'30.84"W in a salt marsh near the town of Kingsport on the shores of the Minas Basin of the  
73 Bay of Fundy, Nova Scotia, Canada (Figure 1). The Bay of Fundy is well known for its high tidal  
74 amplitude and large intertidal zone. The tide height can range >15 m in its upper reaches (Desplanque  
75 and Mossman, 2001) with a typical period of 12.4 hours. Because of its proximity to the ocean and the  
76 fact it sits close to sea level, the site periodically floods, but was not inundated during the study  
77 period. Salt marsh cordgrass (*Spartina alterniflora*) is the dominant plant, while *Spartina pectinata*,  
78 *Salicornia europaea*, *Cakile edentula* and *Spergularia marina* are also found in the area. The  
79 sediment is a red-brown silty clay loam over strongly mottled brown-gray gleyed silty clay loam

80 derived from red-brown marine sediments. Air temperature during the study had a mean of 16.5°C  
81 and reached as high as 27.1°C during the daytime and fell to a minimum of 7.5°C during the nights.  
82 Wind speeds averaged 2.6 km hr<sup>-1</sup> and gusted up to 20.9 km hr<sup>-1</sup>.

83



84

85 **Figure 1** The location of the study site (a) identified on a digital elevation map of the salt marsh near  
86 Kingsport, Nova Scotia, in the Minas Basin of the Bay of Fundy. Schematic (b) and photograph (c) of  
87 the dynamic Hg flux chamber used to measure Hg flux at the site continuously over a 9-day period.

88

### 89 Sediment sampling and total mercury analysis

90 Two 30 cm sediment cores were sampled at the site using a polypropylene hand corer and transported  
91 to the lab for sectioning. Core sections were separated into mineral and vegetation components in  
92 >18.2 MΩ water and dried for 72 hours in a drying oven at 40°C. Dried samples were homogenized  
93 with a mortar and pestle and all equipment was cleaned between samples using water and trace grade  
94 ethanol. Vegetation samples were flash frozen with liquid nitrogen to aid in the homogenization  
95 process. Wet and dry mass of samples were recorded and total mercury in samples was determined by  
96 thermal degradation of samples and gold amalgamation atomic absorbance analysis using a Nippon  
97 MA-2000.

99 Dynamic Hg Flux Chamber Technique

100 Gaseous Hg flux was measured every 10 minutes over the 9-day study period from 6<sup>th</sup> to 15<sup>th</sup> July  
101 2009 using a dynamic flux chamber technique based on the method described by Carpi and Lindberg  
102 (Carpi and Lindberg, 1997). A Durafilm© chamber (20 cm H x 20 cm W x 60 cm L), covering an  
103 area 0.12 m<sup>2</sup> and made of 5 mil Teflon, was set on the sediment surface (Figure 1). Through an inlet  
104 and outlet at either end of the chamber ambient air was pumped through the chamber at a constant rate  
105 of 1.5 dm<sup>3</sup> min<sup>-1</sup>, following Agnan et al.(2016). Dead air periods in the chamber were avoided by  
106 using a Tekran switching controller and second pump with a mass flow controller.

107 Mercury concentration at the inlet of the chamber reports the ambient concentration, while the  
108 mercury concentration at the outlet reports the chamber concentration. The inlet and outlet Hg  
109 concentrations were measured and compared using a dual channel Tekran Model 2537 mercury  
110 analyzer and used to calculate Hg flux (ng m<sup>-2</sup> h<sup>-1</sup>) from the dynamic chamber using the equation:

$$111 \quad \text{Hg flux} = \frac{[\text{Hg}]_o - [\text{Hg}]_i}{A} \times Q$$

112 Where [Hg]<sub>o</sub> is the Hg concentration (ng m<sup>-3</sup>) of air measured at the outlet, [Hg]<sub>i</sub> is the Hg  
113 concentration (ng m<sup>-3</sup>) at the inlet, A denotes the area (0.12 m<sup>2</sup>) of the bottom of the chamber in  
114 contact with the system measured and Q is the flow rate (1.5 dm<sup>3</sup> min<sup>-1</sup>) of air through the chamber.

115 The dual channel Tekran analyser sampled two successive 5 minute air samples from the chamber  
116 inlet, followed by two successive 5 minute air samples flowing from the chamber outlet, ensuring that  
117 both gold cartridges were used for measuring both inlet and outlet air and any degradation of trap  
118 recoveries could be easily identified. Subsequently the flux was measured every 10 minutes. The time  
119 required to completely recycle the air in the chamber was about 16 minutes.

120 Prior to deploying the chamber at the study site the chamber system was tested for recovery of Hg(0)  
121 using standard injections from a Tekran 2505 mercury vapour external calibration unit and a Hamilton  
122 digital syringe. Recovery rates of Hg(0) injected into the chamber were consistently >90%.

123 Recoveries were also tested via manual injections in the field every 48 hours with similar recoveries  
124 (>90%). As such data were not recovery corrected. Chamber blanks were also measured over a clean  
125 Teflon sheet using mercury free air. The level of mercury measured in the mercury-free gas and  
126 chamber air was below the detection limit of 0.01ng m<sup>-3</sup>. Field measurements less than 0.01 ng m<sup>-3</sup>  
127 were treated as nondetectable (0 readings) in the dataset.

128

### 129 Meteorological Sensors

130 A Davis weather station recorded relative humidity, air temperature, wind speed, solar radiation and  
131 barometric pressure at the study site. In addition, Campbell Scientific 107b thermistors were installed  
132 to measure temperature of (i) the sediment 4 cm underneath the flux chamber, (ii) the air inside the  
133 flux chamber, and (iii) the air outside the chamber every 5 minutes and coupled to a Campbell  
134 Scientific CR1000 datalogger.

135 The intensity and spectral distribution of incoming solar radiation was quantified using an  
136 OceanOptics USB 4000 spectroradiometer with a fibre-optic (10 m length, 200 um diameter) and  
137 spectral diffusion probe (diameter 4.3 mm). The spectroradiometer probe was fastened to the outside  
138 of the frame supporting the mercury flux chamber approximately 20 cm above the ground surface.  
139 Based on controlled measurements in the lab, there is <12% loss of UV radiation (280-400 nm)  
140 through the flux chamber Teflon film. Spectral readings were taken continuously every 5 minutes  
141 during the field campaign for UVA (280-320 nm), UVB (320-400 nm), visible (400-800 nm), and  
142 total UV-visible radiation (280-800 nm) and integrated using spectra suite software.

143 Because meteorological measurements were taken every 5 minutes and Hg flux only calculated every  
144 10 minutes, Hg flux measurements were matched to the average of two sequentially collected  
145 meteorological measurements.

146

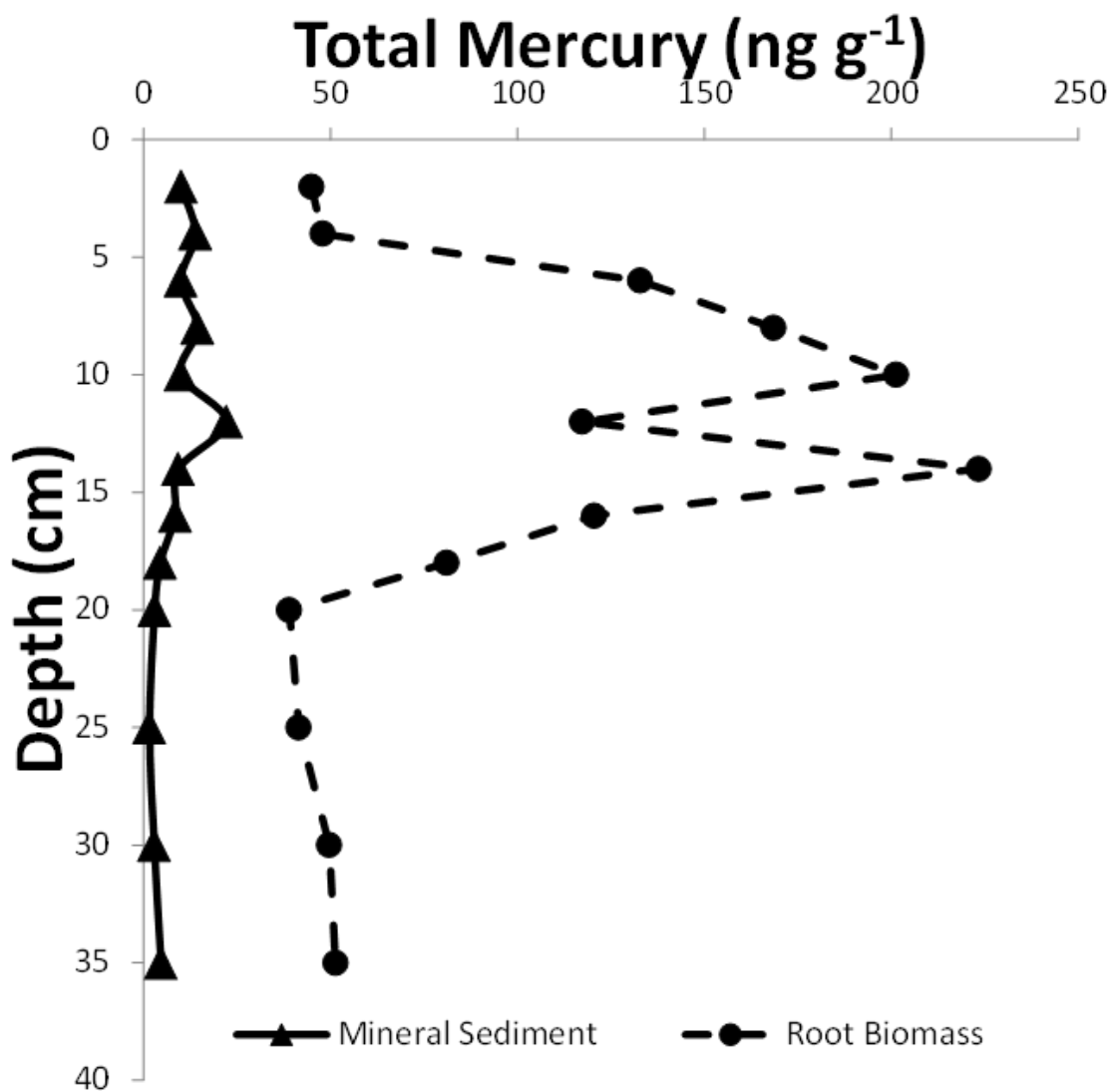
147



148 **Results and discussion**

149 Concentration of total Hg in the sediments

150 The concentration of total Hg in the sediments ranged between 1.6 and 22.1 ng g<sup>-1</sup> in the top 35 cm of  
151 the mineral sediments (Figure 2), peaking at a depth of 12 cm. Concentrations in the root biomass  
152 were considerably higher, ranging between 39.0 and 223.4 ng g<sup>-1</sup> and showing a similar depth profile  
153 to the mineral sediment (Figure 1). Sediment Hg concentrations (Figure 1) were within the range of  
154 previous wetland and mudflat observations in the Minas Basin of the Bay of Fundy (O'Driscoll et al.,  
155 2011; Sizmur et al., 2013) but considerably lower than salt marsh sites affected by local point-source  
156 pollution (Canário et al., 2010; Mitchell and Gilmour, 2008).



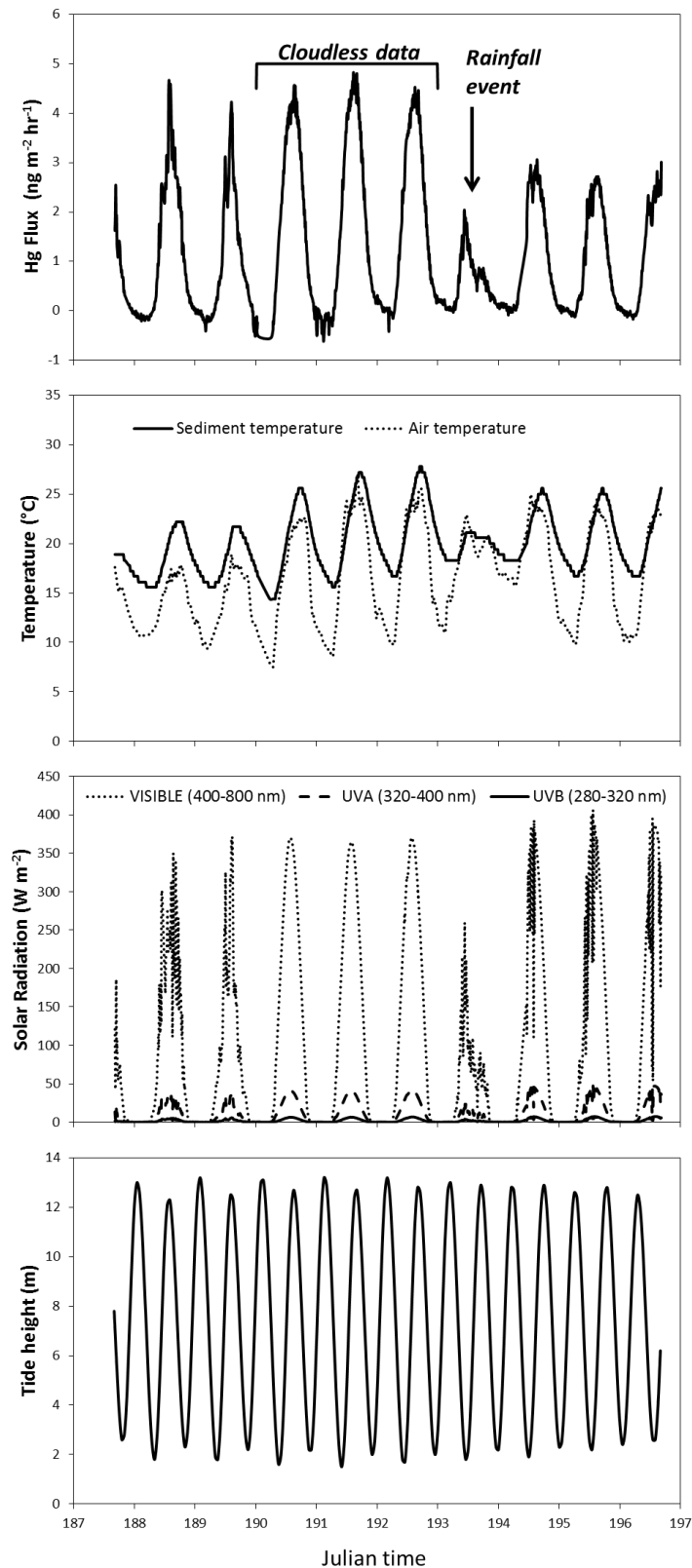
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158 Figure 2 Total mercury concentration with depth in mineral sediments and root biomass at the site.

159 Gaseous Hg flux measurements from salt marshes

160 The Hg flux ranged  $-0.61$  to  $4.83 \text{ ng m}^{-2} \text{ hr}^{-1}$  during the course of the 9-day monitoring period with an  
161 overall mean of  $1.17 \text{ ng m}^{-2} \text{ hr}^{-1}$  (Figure 3). These fluxes are an order of magnitude lower than those  
162 observed from the Great Bay estuary (mean  $17 \text{ ng m}^{-2} \text{ hr}^{-1}$ ), a non-point source mercury-contaminated  
163 ( $450 \text{ ng g}^{-1}$ ) salt marsh in New Jersey (Smith and Reinfelder, 2009). The negative values we observed  
164 (18.4% of total observations) occurred during the night time and are thought to have been due to Hg  
165 deposition. In contrast, Lee et al. (2000) observed negative flux during the daytime and an overall  
166 negative flux (mean  $-3.3 \text{ ng m}^{-2} \text{ hr}^{-1}$ ) at a non-point source mercury-contaminated ( $200\text{-}470 \text{ ng g}^{-1}$ ) salt  
167 marsh in Connecticut during a similar period of the year (Day 180-200 in 1998). Both studies  
168 described above were conducted at sites that, despite being non-point source mercury-contaminated,  
169 had sediment Hg concentrations ( $450 \text{ ng g}^{-1}$  and  $200\text{-}470 \text{ ng g}^{-1}$ ) more than an order of magnitude  
170 greater than our site ( $1.6\text{-}22 \text{ ng g}^{-1}$ ; Figure 2). Both studies also used the micrometeorological method  
171 to measure Hg flux (Sommar et al., 2013).

172 Our study used the dynamic flux chamber method to monitor Hg flux from a salt marsh. The  
173 temperature in the dynamic flux chamber is usually greater than the ambient air temperature and so  
174 often results in the measurement of artificially higher fluxes than the micrometeorological method  
175 (Agnan et al., 2016) but can exhibit lower concentrations due to the absence of turbulence (Zhu et al.,  
176 2015b). Zhu et al (2015b) found that dynamic flux chamber measurements lagged 2 hours behind Hg  
177 flux measured using the micrometeorological methods and exhibited a positive bias in the afternoon  
178 due to the changes in soil temperature lagging behind air temperature (Zhu et al., 2015a). However,  
179 the dynamic flux chamber offers a greater capability to link the environmental conditions in and under  
180 the specific chamber area to the Hg flux observed (especially in heterogeneous environments or in  
181 coastal zones where wind direction changes diurnally).



182

183 Figure 3 Time course data of gaseous Hg flux from the sediment, temperature of the sediment and the  
 184 ambient air, incoming solar radiation (in the visible, UVA and UVB spectrum), and tidal height  
 185 during the course of a continuous 9-day monitoring period from 6<sup>th</sup> to 15<sup>th</sup> July 2009 on a salt marsh  
 186 near Kingsport, Nova Scotia, in the Minas Basin of the Bay of Fundy. Three cloudless days (8<sup>th</sup> to  
 187 11<sup>th</sup>) and a 4 mm rainfall event (at 2pm on the 12<sup>th</sup>) are identified on the Hg flux plot.

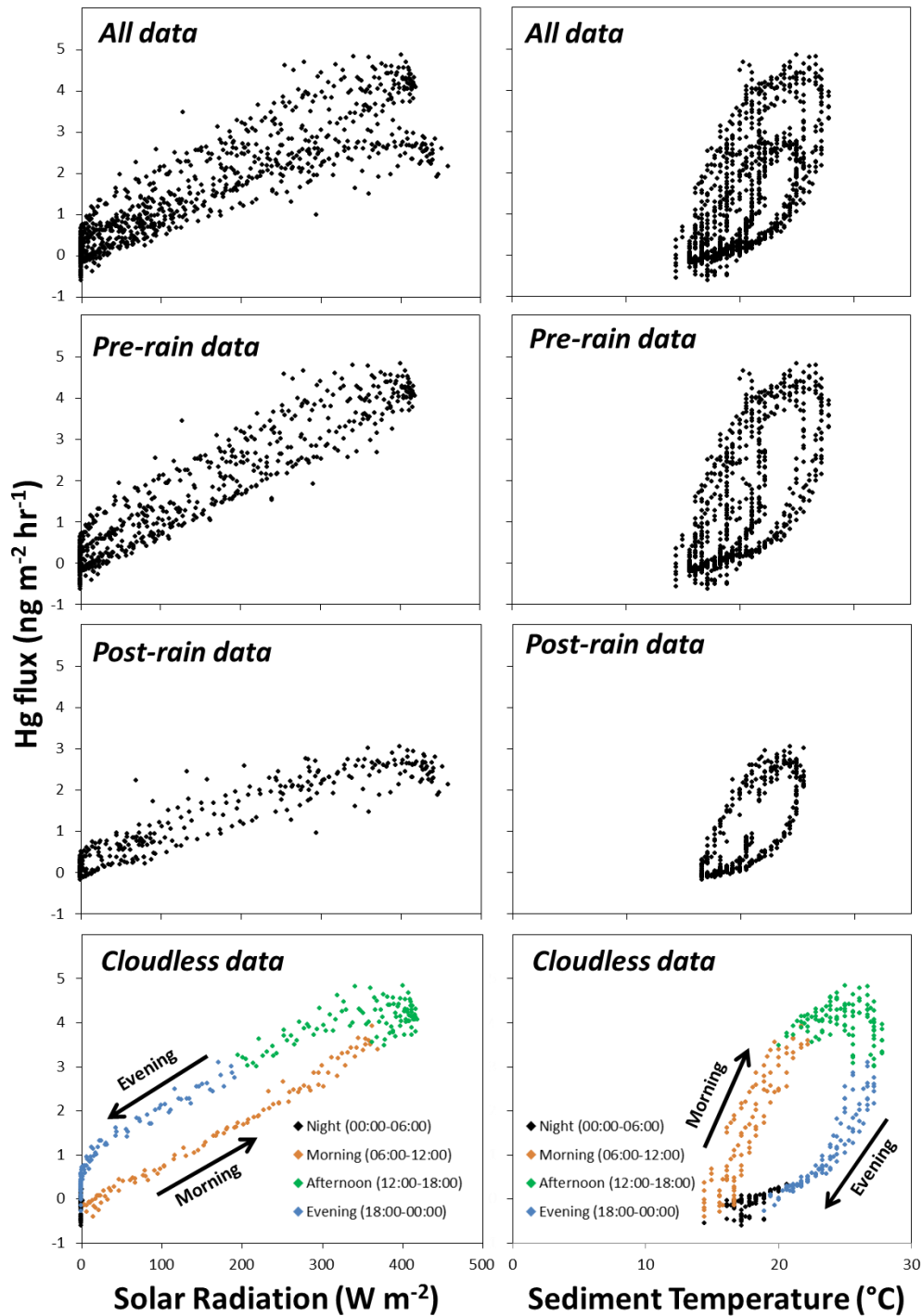
188 During the course of the 9-day continuous monitoring of Hg flux from the salt marsh, there were three  
189 cloudless days, from 8<sup>th</sup> to 11<sup>th</sup> July 2009 (Figure 3), which exposed the chamber to three diurnal  
190 cycles of direct sunlight without interruption. There was also a 4mm rainfall event from 14:00 to  
191 15:30 on 12<sup>th</sup> July (Figure 3) which suppressed the Hg flux thereafter. To aid our interpretation of the  
192 data we analysed our dataset as four sub-datasets:

- 193 • All data (17:17 on 6<sup>th</sup> July to 15:27 on 15<sup>th</sup> July, n = 1212)
- 194 • Pre-rain data (17:17 on 6<sup>th</sup> July to 13:47 on 12<sup>th</sup> July, n = 789)
- 195 • Post rain data (13:57 on 12<sup>th</sup> July to 15:27 on 15<sup>th</sup> July, n = 422)
- 196 • Cloudless data (23:57 on 8<sup>th</sup> July to 23:57 on 11<sup>th</sup> July, n = 393)

197

#### 198 Hysteresis between solar radiation and Hg flux can be explained by sediment temperature

199 There was a clear diurnal fluctuation in Hg flux, which peaked during the middle of the day at the  
200 same time as the peak in solar radiation and air temperature (Figure 3). We found a positive  
201 relationship between solar radiation (280-800 nm) and Hg flux (Figure 4), in agreement with several  
202 other authors finding positive correlations at sites on grassland soils (Obrist et al., 2005), forest soils  
203 (Choi and Holsen, 2009), oceans (Fantozzi et al., 2007), freshwater lakes (O'Driscoll et al., 2003),  
204 snow (Mann et al., 2015), and salt marshes (Lee et al., 2000; Smith and Reinfelder, 2009). These  
205 observations support the hypothesis that Hg flux is driven by photochemical reduction of Hg(II) to  
206 Hg(0) and subsequent volatilisation of Hg(0) from the sediment. Because the intensity of solar  
207 radiation at each waveband (UVA, UVB and visible) co-correlated, we could not elucidate which  
208 wavelength was primarily responsible for stimulating the photochemical reactions.



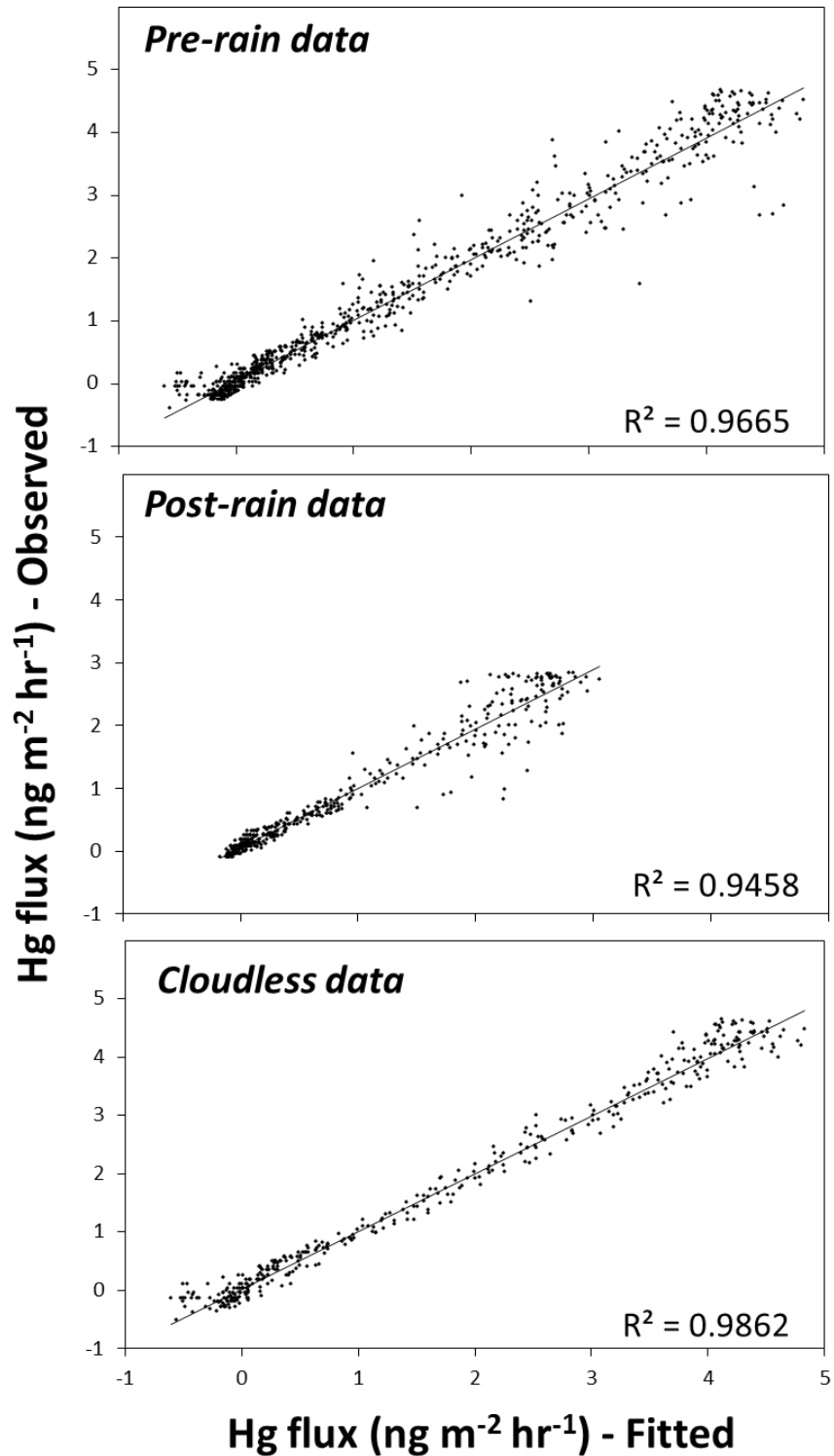
209

210 Figure 4 Gaseous Hg flux data from a salt marsh over a 9-day period plotted against the total  
 211 incoming solar radiation in the range 280-800 nm and the temperature of the underlying sediment at a  
 212 depth of 4 cm. All the data (from 6<sup>th</sup> to 15<sup>th</sup> July 2009) is presented in the top plot above the data  
 213 collected before and after a 4 mm rainfall event (at 2pm on the 12<sup>th</sup>) are presented separately. Data  
 214 collected during three cloudless days (8<sup>th</sup> to 11<sup>th</sup>) before the rainfall event is presented at the bottom  
 215 and divided into measurements made during the night (00:00-06:00), morning (06:00-12:00),  
 216 afternoon (12:00-18:00), and evening (18:00-00:00). There is a clear hysteresis in the data (observed  
 217 most clearly in the cloudless dataset) as Hg flux is greater during the evening when the sediment is  
 218 warm than in the morning when sediment is cool.

219 We found a clear cyclical diel relationship between solar radiation and Hg flux (Figure 4) which can  
220 most easily be identified when plotting the data collected during three cloudless days from 8<sup>th</sup> to 11<sup>th</sup>  
221 July 2009. At the same irradiance intensity, Hg flux is greater in the evening (18:00-00:00) than the  
222 morning (06:00-12:00.) A similar relationship was found in morning and afternoon Hg flux  
223 measurements made from coastal seawater (Lanzillotta and Ferrara, 2001). This cyclical relationship,  
224 also referred to as hysteresis, can result from a time-lag between a controlling variable and its  
225 measured effect, such as the delayed response of soil respiration to increasing temperature (Phillips et  
226 al., 2011). However, it can also be a result of the simultaneous influence of several confounding  
227 variables, such as solar radiation and temperature.

228

229 Several authors have observed positive correlations between Hg flux and air or soil temperature as  
230 well as solar radiation (Lee et al., 2000; Lindberg et al., 1999; Obrist et al., 2005), and some note a  
231 closer relationship between temperature and Hg flux than between solar radiation and Hg flux (Gillis  
232 and Miller, 2000; Ma et al., 2013). However, these measurements confound one another since an  
233 increase in incident radiation causes an increase in temperature. In our study we did not find a  
234 satisfactory correlation between Hg flux and either solar radiation, air temperature or sediment  
235 temperature singularly since all three relationships result in a cyclical relationship (hysteresis) that is  
236 most easily observed in the dataset collected on the cloudless days (Figure SI-1). Multiple linear  
237 regression models fit using only solar radiation and sediment temperature as the explanatory variables  
238 demonstrate that these two variables together can predict Hg flux in our sub-datasets with a high  
239 degree of certainty (Figure 5). The models significantly ( $p < 0.001$ ) predict Hg flux using the pre-rain  
240 dataset ( $R^2 = 0.97$ ), the post-rain dataset ( $R^2 = 0.95$ ) and the cloudless dataset ( $R^2 = 0.99$ ). When  
241 measurements at the same irradiance intensity are considered, Hg flux is greater in the evening  
242 (18:00-00:00) when the salt marsh is warmer than in the morning (06:00-12:00) when the marsh is  
243 cooler (Figure 4). The cyclical relationship between solar radiation and Hg flux can therefore be  
244 explained by differences in the temperature of the sediment in the morning compared to the evening,  
245 supported by Zhu et al (2015b) who observe Hg flux peaking in concert with soil temperature.



246

247 Figure 5 Gaseous Hg flux from a salt marsh before a 4 mm rainfall event (6<sup>th</sup> to 12<sup>th</sup> July 2009), after  
 248 the rainfall event (12<sup>th</sup> to 15<sup>th</sup>), and during three cloudless days (8<sup>th</sup> to 11<sup>th</sup>) before the rainfall event  
 249 plotted against fitted fluxes predicted using multiple linear regression models created with the same  
 250 data. The models use solar radiation (280-800nm) and sediment temperature below the flux chamber  
 251 and as explanatory variables.

252

253 There is uncertainty in the literature concerning whether temperature affects Hg flux by indirectly  
254 increasing the proportion of Hg(II) that is available for photoreduction or whether it directly affects  
255 Hg flux by providing energy for Hg(0) volatilization from soils (Bahlmann et al., 2006; Moore and  
256 Carpi, 2005). Based on our observations, we advance the hypothesis that sediment temperature has an  
257 indirect effect on Hg flux by directly influencing the rate of Hg(II) photoreduction, but not directly  
258 influencing volatilization which may be due to abiotic desorption (Moore and Carpi, 2005), or the  
259 result of transpiration by the salt marsh vegetation (Lindberg et al., 2002). Our hysteresis graphs show  
260 that the direction of the cyclical relationship between sediment temperature and Hg flux occurs in the  
261 opposite direction to the relationship between solar radiation and Hg flux (Figure 4). When  
262 measurements at the same temperature are considered, Hg flux is greater in the morning (06:00-  
263 12:00), when the solar radiation is higher, than the evening (18:00-12:00) when the solar radiation is  
264 lower. If temperature has a direct effect on Hg flux by providing energy for desorption of Hg(0) from  
265 sediment surfaces and subsequent volatilization from the soil then we would expect to see a weak  
266 relationship between solar radiation and Hg flux in the evening because build-up of Hg(0) during the  
267 day would continue to be emitted from the relatively warm sediment during the evening. Instead, it  
268 seems that both solar radiation and sediment temperature are influencing the same rate-limiting  
269 process responsible for Hg flux.

270

#### 271 Rainfall suppresses Hg flux from salt marshes

272 We observed lower Hg flux after a 4 mm 90 minute rainfall event on 12<sup>th</sup> July 2009 but an otherwise  
273 similar cyclical relationship between solar radiation and Hg emissions (Figure 4) that can be  
274 explained by the sediment being cool in the morning and warm in the evening (Figure 5). Our  
275 observations contrast with several papers describing an immediate pulse of Hg released after rainfall  
276 events due to a moisture-dependent displacement of Hg(0)-containing air from pores followed by a  
277 greater rate of Hg flux from bare soil (Song and Van Heyst, 2005), desert soils (Lindberg et al., 1999),  
278 agricultural soils (Briggs and Gustin, 2013), and floodplain soils (Wallschläger et al., 2000).



279 A key difference between the salt marsh where we made our observations and the soils monitored in  
280 the abovementioned studies is that the salt marsh is tidally influenced. We hypothesised that the  
281 incoming tide would cause displacement of Hg(0)-containing air from the sediment and provide a  
282 clear influence of the tidal cycle on Hg flux. However, as observed by Smith and Reinfelder (2009)  
283 and Lee et al (2000), we found no relationship between the tidal cycle and Hg flux. The rainfall event  
284 occurred during an incoming tide and also did not result in a pulse of Hg flux. Therefore,  
285 displacement of Hg(0)-containing air from sediment does not seem to contribute to Hg flux in salt  
286 marshes, probably because the frequent movement of air in the salt marsh sediment (due to the tidal  
287 cycle) does not allow Hg(0)-containing air to build up in the pores.

288 Rinklebe et al., (2010) demonstrate a negative correlation between soil water content and Hg flux in a  
289 seasonally flooded terrestrial wetland, since the soils are generally wetter during the winter when  
290 temperature and solar radiation are lower. However, in laboratory incubations, at constant  
291 temperature, they reveal greater flux from wet or saturated soils compared to dry soils 24 and 48  
292 hours after artificial wetting. These observations are further supported by data from Pannu et al.,  
293 (2014) indicating that Hg flux from soils increases with increasing water-filled pore space (WFPS)  
294 and peaked at 60% WFPS. However, this study also showed that increasing moisture to 80% WFPS  
295 the Hg flux was considerably suppressed. Briggs and Gustin (2013) also note that after the initial  
296 pulse following a rainfall event, the Hg flux can become suppressed if the soil is saturated with water.  
297 This suppression is due to a slower diffusivity of Hg(0) through water-filled pores as opposed to  
298 through air-filled pores. In our experiment it is possible that some of the pores in the sediment became  
299 saturated after the rainfall event and that slower diffusivity of Hg(0) is the reason for the suppressed  
300 Hg flux. If transpiration of Hg(0) by wetland vegetation is a major mechanism controlling Hg flux  
301 from the sediment (Lindberg et al., 2002) then the observed decrease in Hg flux may have been due to  
302 stomatal closure and a subsequent decrease in the rate of transpiration under saturated conditions  
303 (Pezeshki and DeLaune, 2012; Pezeshki, 2001).

304

305 Environmental significance

306 We provide here 9 days of continuous Hg flux measurements made on a salt marsh using the Dynamic  
307 Flux Chamber technique. Because the Hg flux measurements made can be directly related to the  
308 sediment underneath the chamber we elucidate an important diurnal mechanism that has not been  
309 previously identified. Our data supports the hypothesis that photoreduction of Hg(II) to Hg(0) is  
310 mediated by both sediment temperature and solar radiation and that photoreduction (rather than  
311 volatilisation of Hg(0)) is the rate limiting step in these sediments. This mechanistic insight reduces  
312 the uncertainty concerning the role of solar radiation and temperature in Hg flux from terrestrial  
313 surfaces. We also present data to suggest that the impact of rainfall on Hg flux behaves differently at  
314 coastal sites compared to terrestrial wetlands or soils. Here we show that Hg flux is suppressed after a  
315 rainfall event, possibly due to lower transpiration by salt marsh vegetation. The measurements of Hg  
316 flux and insights into the mechanisms controlling Hg flux presented here increase our knowledge of  
317 the global mercury cycle and provide a mechanistic framework for integrating coastal wetlands into  
318 global Hg flux models. However, caution should be exercised when applying this data for modelling  
319 since Hg flux is highly variable both spatially and temporally (During et al., 2009).

320

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