



1 **Reactive mercury flux measurements using cation exchange membranes**

2 Matthieu B. Miller^{1*}, Mae S. Gustin², Grant C. Edwards^{1,3}

3 ¹Faculty of Science and Engineering, Department of Environmental Science, Macquarie University, Sydney, NSW,
4 2113, Australia

5 ²Department of Natural Resources and Environmental Science, University of Nevada, Reno NV, 89557, United
6 States

7 ³Deceased 10 September 2018.

8 *Correspondence to:* Mae Sexauer Gustin mgustin@cabnr.unr.edu

9 **ABSTRACT**

10 A method was developed to measure gaseous oxidized mercury (GOM) air-surface exchange
11 using 2 replicated dynamic flux chambers (DFCs) in conjunction with cation exchange
12 membrane (CEM) filters. The experimental design and method was developed and tested in a
13 laboratory setting, using materials collected from industrial scale open pit gold mines in central
14 Nevada, USA. Materials used included waste rock, heap leach ore, and tailings, with substrate
15 concentrations ranging from 0.1 to 40 $\mu\text{g g}^{-1}$ total mercury (THg). CEM filters were used to
16 capture GOM from the DFC sample lines while a Tekran[®] 2537A analyzer measured GEM
17 concurrently. Previous and ongoing work demonstrated that CEM do not collect GEM and
18 efficiently collects multiple compounds of GOM. Positive GOM emission rates up to 4000 pg m^{-2}
19 h^{-1} were measured from tailings materials with high Hg substrate concentrations, and this has
20 significant implication with respect to air-Hg surface exchange. GOM flux was variable for
21 lower Hg concentration substrates, with both emission and deposition observed, and this
22 was affected by ambient air GOM concentrations. For substrates that experienced GOM
23 deposition, deposition velocities were in the range 0.01 – 0.07 cm s^{-1} .

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25

26 **1 Introduction**

27 On 16 August 2017, the United Nations Environment Program (UNEP) Minamata Convention
28 came into force with a mission to protect human health and the environment from exposure to
29 the toxic effects of mercury (Hg) and its various compounds (UNEP, 2013). The Convention
30 proposes to fulfill this mission through a strategy of globally coordinated scientific research, and
31 ongoing monitoring of Hg in the environment where possible. The mission poses a significant
32 challenge as there are over 3000 known Hg contaminated sites worldwide due to mining and
33 industrial activity, not including legacy and small scale operations involving Hg (Kocman et al.,
34 2013; Krabbenhoft and Sunderland, 2013). Past emissions were dominantly from natural sources,
35 but are now largely from anthropogenic activities and have led to large reservoirs of Hg in all
36 environmental compartments (Pacyna et al., 2016; Pirrone et al., 2010; Streets et al., 2017). Even
37 in the absence of new anthropogenic emissions, cycling of Hg between different spheres will
38 continue at large scales and in possibly unexpected directions, driven by processes and
39 mechanisms that are not fully understood, and susceptible to increasing human and climate
40 perturbations (Obrist et al., 2018).

41 The atmosphere, a global common, is the dominant conduit for transport, transformation,
42 emission, deposition, and re-emission of Hg and Hg compounds amongst Earth's ecosystems.
43 Mercury in the atmosphere is classified on the basis of three physiochemical forms: gaseous
44 elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury
45 (PBM), with PBM and GOM defined together as reactive mercury ($RM = GOM + PBM$) (Gustin
46 et al., 2015). Atmospheric concentrations of GEM can be measured with well calibrated



analytical instruments, whereas the quantification of GOM and PBM has depended on operationally defined methods with demonstrably large uncertainty (Cheng and Zhang, 2017; Gustin et al., 2015; Gustin et al., 2013; Jaffe et al., 2014; Zhang et al., 2017).

Scientific understanding of the biogeochemical cycling of Hg is currently inadequate due to the large uncertainties in measurements, and general difficulty of research on atmospheric Hg chemistry (Jaffe et al., 2014). Atmospheric GEM is relatively inert, has a low deposition rate, and hence a relatively long atmospheric lifetime ranging from minutes to 1 year (Krabbenhoft and Sunderland, 2013; Zhang et al., 2009; Gustin et al., 2013). Observations of rapid depletion of GEM from the atmosphere suggests that deposition and re-emission on short time scales is an important process driving movement (Howard and Edwards, 2018; Lu et al., 2001; Schroeder et al., 1998). In contrast to GEM, GOM compounds have higher dry deposition velocities (Zhang et al., 2009). Knowledge of concentrations, chemistry, and processes forming atmospheric GOM is critical for understanding how Hg moves and impacts ecosystems globally. Recent research on GOM has demonstrated that compounds in air vary both spatially and temporally to a considerable extent, pointing to the need for extensive measurements of concentrations and identifying the specific compounds (Gustin et al., 2016; Huang and Gustin, 2015b; Huang et al., 2014; Huang et al., 2017).

Fluxes of total gaseous mercury (TGM) and GEM have been successfully measured in many environments, providing insights into air-surface exchange that is critical for understanding biogeochemical cycling of GEM (Yannick et al., 2016; Zhu et al., 2016). In contrast, there are few direct measurements of GOM air-surface exchange (Zhang et al., 2009). GOM fluxes reported in the literature are largely based on measurements made with the KCl denuder as the



69 GOM collection method, as well as a passive Hg dry deposition sampler (Brooks et al., 2008;
70 Castro et al., 2012; Engle et al., 2005; Lindberg et al., 2002; Lindberg and Stratton, 1998; Lyman
71 et al., 2009; Lyman et al., 2007; Malcolm and Keeler, 2002; Poissant et al., 2004; Rea et al.,
72 2000; Rothenberg et al., 2010; Sather et al., 2013; Skov et al., 2006; Zhang et al., 2005; Huang et
73 al., 2015b). The few direct GOM-specific air-surface exchange measurements using KCl
74 denuder-based approaches have been undertaken with mixed results (Brooks et al., 2008; Skov et
75 al., 2006). Moreover, recent evaluation of KCl denuder approaches show these methods tend to
76 underestimate GOM and are subject to interferences due to ozone and water vapor (Huang and
77 Gustin, 2015a; Lyman et al., 2010; McClure et al., 2014). Understanding GOM air-surface
78 exchange processes would facilitate the Hg scientific community's ability to move forward in
79 understanding the biogeochemical cycling of atmospheric Hg.

80 In this study, we developed and applied a novel experimental approach for direct measurement
81 of GOM fluxes using cation exchange membrane (CEM) filters. CEM filters have been
82 successfully deployed to measure GOM in ambient air in previous studies (Gustin et al., 2016;
83 Huang et al., 2017; Huang et al., 2013; Maruszczak et al., 2017; Pierce and Gustin, 2017), and
84 their use here was modified to allow for the determination of GOM air-surface exchange. A
85 recent study (Miller et al., 2018) and ongoing work (unpublished data) have demonstrated that
86 GEM is not collected by the CEM and it efficiently collects a variety of GOM compounds. Here
87 is described a series of experiments that were conducted to optimize the CEM/GOM flux
88 methodology, and then, the resulting method was subsequently applied to determine fluxes over
89 both background waste rock material and Hg enriched mining materials. Our research
90 hypothesis was the system developed would provide a means of determining if GOM is



91 deposited or emitted from substrates, and this system would allow us to develop an
92 understanding of GOM air-surface exchange.

93 **Methods**

94 **2.1 Materials**

95 Substrate materials used for measuring Hg flux were acquired from industrial scale, open pit
96 gold mines in central Nevada, and include waste rock, heap leach ore, and tailings. Materials
97 were obtained from 4 ongoing mining operations: Twin Creeks (TC) and Lone Tree (LT)
98 operated by Newmont Mining Corporation, and Cortez Pipeline (CP) and Gold Strike (GS)
99 operated by Barrick Gold Corporation (Fig. 1; Table 1). There were 3 types of materials: waste
100 rock called cap (C), heap leach material (L), and tailings (T or tails). (Waste rock is non-
101 mineralized low Hg overburden consisting of alluvium or hard rock that covered the ore body
102 prior to mining. For this study, materials were sampled from the waste rock piles specifically set
103 aside for future capping and site reclamation, and as such is referred to as cap material. Heap
104 leach is low-grade ore blasted from the mine wall and “heaped” on an impoundment for
105 irrigation with dilute cyanide leach solution for gold extraction. Tailings are the waste remnant
106 of high-grade ore that has been pulverized by mechanical ball milling and undergone
107 thermal/chemical treatment to extract gold. All mining substrate materials were collected in
108 September 2010, for measurements of GEM flux under controlled conditions (Miller and Gustin,
109 2013).

110 Each material was divided into replicate trays (50 x 50 x 7 cm³ plywood lined with 3mil
111 polyvinyl sheet) and stored inside a greenhouse bay at the University of Nevada Reno



112 Agricultural Experiment Complex. At the onset of the GOM flux experiments described in this
 113 paper, substrates were undisturbed for ~3 years, and were completely dry and well
 114 compacted/consolidated from previous watering experiments. A circular chamber footprint
 115 impression previously existed from prior experiments provided an excellent existing contact for
 116 the chamber base. Comparing GEM flux measurements made in this study with the previous
 117 measurements, an overall trend of decreasing GEM flux over time was observed. This fits a
 118 hypothesis suggested by Eckley et al. (2011b) of a long term reduction in GEM evasion from a
 119 mine substrate as time from disturbance increases.

120 **2.2 Methodology**

121 GOM flux was measured by modifying our existing GEM flux method consisting of a dynamic
 122 flux chamber (DFC) and an ambient air Hg analyzer (Tekran® 2537A) after the methods of
 123 Eckley et al. (2010; 2011a) and Miller et al. (2011).

124 Briefly, the GEM flux system used a 2537A in conjunction with a cylindrical DFC (footprint
 125 0.036 m^2) made of molded Teflon film (0.19 mm thick) over a rigid Teflon frame (1.5 mm
 126 thickness), with a total internal volume of 2.0 Liters (Fig. 2). Air enters the chamber through 24
 127 inlet holes (1 cm diameter) spaced 2.5 cm apart around the perimeter and 2.0 cm above the
 128 bottom edge. The sample outlet is 0.625 cm diameter PTFE tubing at the top-center of the
 129 chamber, and sample inlet air is measured through equivalent tubing at the height of the chamber
 130 inlet holes. A Tekran® Automated Dual Switching (TADS) unit was used to cycle the sample
 131 flow (1.0 Lpm) between the chamber inlet and outlet lines in sequential 10 min intervals (two 5
 132 min samples on each line). GEM in each 5 min sample volume was quantified automatically by
 133 the 2537A analyzer using pre-concentration on gold traps followed by thermal desorption (500



134 °C) and cold vapor atomic fluorescence spectrometry (CVAFS). The difference in Hg
 135 concentration between the outlet and inlet air ($C_o - C_i$) referred to as ΔC , and was used to
 136 calculate flux by Eq. 1:

$$137 \quad F = Q * (C_o - C_i) / A \quad (1)$$

138 where F is the net Hg flux ($\text{ng m}^{-2} \text{h}^{-1}$), Q is the flow rate through the chamber ($\text{m}^3 \text{h}^{-1}$), C_o is the
 139 mean concentration of two consecutive 5 min outlet air samples (ng m^{-3}), C_i is the mean
 140 concentration of inlet air in the samples before and after C_o , and A is the area of the substrate
 141 under the chamber (m^2). The sign of ΔC indicates the direction of flux with positive being
 142 emission and negative being deposition.

143 The two modified systems included fitting the DFC inlet and outlet sample lines with 2-stage
 144 disc filter assemblies (Savillex[®] 47 mm PFA Teflon Filter Holder) holding two inline
 145 polysulfone cation exchange membranes (CEM 0.8 μm , Mustang[®] S, Pall Corporation) (Fig. 2).
 146 CEMs preferentially capture GOM compounds while allowing GEM to pass freely (Miller et al.
 147 2018; unpublished data). The first upstream CEM served as the primary collection filter, while
 148 the second downstream CEM captured any Hg escaping from or missed by the first filter
 149 (referred to as breakthrough). With CEM filters deployed at the front of the sample lines, in
 150 conjunction with the 0.2 μm particulate filter at the rear sample inlet of the Tekran[®], GOM was
 151 scrubbed from the sample flow and all Hg measured downstream on the 2537A is in GEM form.

152 An additional set of CEM filters was deployed simultaneously, using sample pumps and mass
 153 flow controllers set to match the 2537A sample flow rate (1.0 Lpm, Fig. 2) at a height of 2 m



154 above the flux system. This was done to measure background ambient GOM concentrations in
155 the greenhouse.

156 With both the Tekran[®] and external pump controlling CEM sample lines at 1 Lpm, total flow
157 through the DFC was 2.0 Lpm that provides a chamber turn over time (TOT) of 1 minute. At this
158 flow rate, flow velocity through the chamber is laminar with no turbulent eddy formation, as
159 determined through computational fluid dynamic (CFD) modelling of the chamber geometry
160 performed by Eckley et al. (2010). Thus the chamber design of Eckley et al. (2010) is optimal in
161 terms of not disturbing the substrate being studied. With low velocity, non-turbulent flow,
162 particle entrainment from the substrate surfaces is not expected, especially for particle sizes
163 greater than the CEM filter pore size of 0.8 μm .

164 2.3 Analyses

165 After flux measurements, CEM filters were collected into sterile 50 mL polypropylene centrifuge
166 tubes, and frozen at -20 °C until analyses (within 14 days of collection). Filters were analyzed for
167 total Hg by aqueous digestion and cold vapor atomic fluorescence spectrometry (CVAFS, EPA
168 Method 1631, Rev. E) using a Tekran 2600 system, with total Hg operationally equivalent to
169 total GOM. The blank Hg mass that can be expected on an unused CEM filter (median = 68 pg, n
170 = 56) was determined from clean filters collected with every set of measurements, and the
171 median blank value was subtracted from all sample values. Breakthrough is defined as the
172 amount of Hg on the secondary filter as a percent of the total Hg collected on both filters (after
173 blank correction), and overall median breakthrough was low (4.2%, n = 222).



174 The GOM concentration in the inlet/outlet sample air was calculated by combining the blank-
 175 corrected primary and secondary filters into a total Hg mass per sample line and dividing by the
 176 respective sample air volume. The difference in GOM concentration between the inlet and outlet
 177 lines provided a ΔC_{GOM} , with this multiplied by sample flow providing the GOM emission rate
 178 (pg h^{-1}). Reactive Hg flux ($\text{pg m}^{-2} \text{ h}^{-1}$) was calculated with Eq. 1 using ΔC_{GOM} values, the flow
 179 rate ($1.0 \pm 0.005 \text{ Lpm}$) and the chamber footprint (0.036 m^2).

180 The GOM flux detection limit was determined by the minimum statistically resolvable difference
 181 between C_o and C_i , i.e. the smallest meaningful ΔC_{GOM} that could be measured (Fig. 3). The C_o
 182 and C_i concentrations were based on two measurements: total Hg on the CEM filters as
 183 determined by analysis on the Tekran® 2600 system, and total sample volume as determined by
 184 the mass flow-controlled sample rate and time. The MFC precision was $\pm 0.5\%$ ($\pm 0.005 \text{ Lpm}$ at
 185 1.0 Lpm) and the detection limit of the 2600 was 1 ppt, or $\sim 53 \text{ pg}$ per reagent blank in a clean 50
 186 mL collection tube. The median mass of Hg on the blank CEM filters was 68 pg and was used as
 187 the practical detection limit for the method. As the distribution of CEM blank values was non-
 188 normal and skewed heavily to the right (Fig. 3a), the 95% confidence interval around the median
 189 ($58 - 73 \text{ pg}$) was used to define a minimum detectable GOM concentration (Fig. 3b). For
 190 example, in a 24 h sample, the minimum detectable GOM concentration would be $\sim 3.5 \text{ pg m}^{-3}$ to
 191 exceed the upper 95% confidence limit of 73 pg. In a 24 h sample the minimum resolvable
 192 ΔC_{GOM} would be 13.5 pg m^{-3} (sum of upper + lower confidence intervals, + 3 pg m^{-3} to account
 193 for flow precision, converted to 24 h sample volume concentration). This was taken as the upper
 194 minimum ΔC_{GOM} value.



195 Chamber blanks were determined for each Teflon DFC (referred to as Chamber A and Chamber
 196 B) by measuring flux over a clean Teflon sheet. Chamber blank emission rates were measured
 197 immediately following chamber cleanings (24 h acid wash, 10% HNO₃), and then between
 198 substrate types (i.e. cap, leach, tailings). For the summer measurement period, the median
 199 chamber blank ΔC_{GOM} for both Chambers A and B ($A = 13 \text{ pg m}^{-3}$, $B = 14 \text{ pg m}^{-3}$, $n = 12$) was at
 200 the detection limit, so chamber blanks were not subtracted from material fluxes. This was due to
 201 high ambient GOM concentrations in the greenhouse. For the following winter measurement
 202 period, the median chamber blank ΔC_{GOM} for both chambers was significantly negative ($A = -60$
 203 pg m^{-3} , $B = -60 \text{ pg m}^{-3}$, $n = 6$), and the median chamber blank was $-215 \text{ pg m}^{-2} \text{ h}^{-1}$, indicating that
 204 the chamber and the blank Teflon sheet were acting as depositional surfaces for GOM. For these
 205 measurements, the chamber blanks were subtracted. For materials that demonstrated net GOM
 206 deposition, the deposition velocity ($V_d \text{ cm s}^{-1}$) was calculated using Eq. 2:

$$207 \quad V_d = \text{flux} (ng \text{ m}^{-2} \text{ h}^{-1}) / \text{air concentration} (ng \text{ m}^{-3}) * (100/3600)(2)$$

208 All fluxes were measured in the University of Nevada-Reno Agricultural Experiment Station
 209 greenhouse. Meteorological parameters were measured synchronously with flux and recorded in
 210 5 min averages, including temperature and relative humidity (HMP45C, Campbell Scientific®),
 211 substrate temperature (C107, Campbell Scientific®), and solar radiation (LI-200X, LiCor®).
 212 Rudimentary climate control was provided by ventilation fans pulling outside air across the
 213 greenhouse bay from intakes on the opposite side. Fluxes were measured on the “upwind” side
 214 of the bay in a variety of orientations (see below).
 215 Data was processed in Microsoft Excel (version 16.22) and RStudio® (version 3.2.2).



2.4 Development of the method

Two Tekran[®] 2537A analyzers with associated GOM filter systems were used to simultaneously measure flux from two replicate trays (one for each A and B system) of each sample material. The duplicated systems allowed a total of four GOM flux measurements to be collected each time a material was tested, two from the Tekran[®] sample lines and two from the external pump lines. The intention of the duplicate systems was to evaluate consistency and repeatability of the measurements. However, during the initial method testing it became apparent that the position of the trays and the inlet sample lines was an important variable. For example, strong GOM emission from an “upwind” tray could substantially increase the inlet GOM concentration of the “downwind” tray, resulting in a negative ΔC_{GOM} and apparent deposition. Such contradictory results compelled us to test a variety of orientations for the two systems. The best results were achieved in the final design by placing both trays all the way against the intake wall of the greenhouse bay, and separating them laterally by 1.5 m, with all equipment located downwind. This configuration provided the most uniform inlet air concentrations for both systems.

2.5 Limitations of method

The use of filter membranes in conjunction with a DFC to measure GOM flux has several limitations. Given the low concentrations of GOM, a relatively long sampling time of at least 24 h is required to capture a sufficient mass for quantification on low Hg containing substrates. Despite the limitations, this method moves us a step further for understanding GOM flux. The low temporal resolution limits analysis of the factors controlling GOM flux, since there will be changes on a diel cycle similar to observations of GEM flux (c.f. Gustin et al., 2013). In



237 addition, flow rate and surface area could be increased, but in order to change this method a
238 number of proof of concept tests would have to be done.

239 A necessary condition of the DFC method is the placement of flux chambers directly on a
240 material, resulting in artificial modification of surface conditions and a presumptive influence on
241 the magnitude of flux. In our study, this limitation is immaterial, as the entire experimental setup
242 constitutes an artificial environment, and we are more interested in 1) our ability to
243 experimentally detect measurable GOM flux, and 2) the qualitative direction of flux versus
244 absolute quantification. As the method develops, it will become necessary to more thoroughly
245 evaluate the effects of the DFC on GOM flux.

246 Lastly, CEM were analyzed within two weeks of collection. Pierce et al. (2017) demonstrated
247 that little HgCl_2 was lost from the membranes over this time period. This needs to be tested for
248 other GOM compounds thought to be present in the atmosphere (Huang et al., 2013; Gustin et
249 al., 2016).

250 **3 Results**

251 **3.1 GOM flux measurement repeatability**

252 The first test of the optimized configuration was a set of replicate measurements made on a
253 single material, to assess method repeatability. The material used for this test was a heap leach
254 ore of intermediate total Hg concentration (TCL, $13.2 \pm 2.0 \mu\text{g g}^{-1}$). Filters were deployed in
255 three consecutive sample sets of approximately 72 h each, for a total of 12 replicate filter flux
256 measurements (i.e. two GOM flux measurements on two separate replicate trays, three times).
257 The mean GEM flux from all samples was $167 \pm 57 \text{ ng m}^{-2} \text{ h}^{-1}$ ($n = 6$). The duplicate



measurements of background greenhouse GOM showed a mean concentration of $13 \pm 7 \text{ pg m}^{-3}$ ($n = 12$). The ΔC_{GOM} was well above detection for all measurements (median 97 pg m^{-3} , $n = 12$), and the mean GOM flux over all 12 samples was $370 \pm 80 \text{ pg m}^{-2} \text{ h}^{-1}$ ($n = 12$) and ranged from 240 to $490 \text{ pg m}^{-2} \text{ h}^{-1}$ (Fig. 4).

The mean relative percent difference (RPD) of GOM flux measured between Pump and Tekran sample lines on the same tray was $6.5 \pm 3.9\%$, and mean RPD between trays was 21.4%. These replicate measurements of a single material consistently showed the same direction and magnitude of GOM flux with good agreement.

3.2 GOM flux measurement replication over expanded range of materials: Summer

Following the triplicate measurement of TCL (May), follow up testing was conducted on a series of three additional materials (July – August): a low to intermediate Hg cap material and heap leach ore (TCC $0.2 \text{ } \mu\text{g g}^{-1}$, LTL $0.6 \text{ } \mu\text{g g}^{-1}$), and a high Hg tailings (TCT $36 \text{ } \mu\text{g g}^{-1}$). Measurement time was reduced to 48 h for this series of materials, as the previous deployments had total GOM loading well above detection. However, several of the LTL and TCC flux measurements resulted in insignificant ΔC_{GOM} values (Fig. 5). In these cases, GOM flux could not be discriminated, and these values were excluded from subsequent analysis.

A comparison of GOM flux measured by the replicate sample lines on each system (Tekran® sample flow and external pump sample flow) show a relationship of 1:1 (Fig. 6) that indicates that CEM filters on two independent flow channels were capturing equivalent amounts of GOM. This equivalency was true for both of the replicate systems (System A and B) that were each simultaneously measuring flux from replicate trays of the same material. The high level of



replication displayed by the system, both in general and in detail, for multiple substrate types, increases confidence that these measurements represent a real net surface exchange of GOM.

Positive GOM fluxes were associated with the higher substrate concentration materials (TCL, TCT). The low Hg TCC experienced net GOM deposition, with a mean V_d of $0.03 \pm 0.01 \text{ cm s}^{-1}$ ($n = 6$). The 3x higher Hg concentration LTL showed either no net flux or slightly positive GOM emission ($64 \pm 10 \text{ pg m}^{-2} \text{ h}^{-1}$, $n = 3$). The very high substrate Hg concentration TCT⁻ materials showed uniformly high GOM emission ($4060 \pm 1000 \text{ pg m}^{-2} \text{ h}^{-1}$, $n = 7$).

The mean ambient GOM in the greenhouse during this period was $130 \pm 55 \text{ pg m}^{-3}$ ($n = 24$); however, there was a distinct trend of increasing ambient GOM over the course of measurements. During the TCC measurements, ambient GOM concentration in the greenhouse was $70 \pm 20 \text{ pg m}^{-3}$ ($n = 8$). This increased to $150 \pm 20 \text{ pg m}^{-3}$ ($n = 8$) during the LTL measurements, and up to $180 \pm 40 \text{ pg m}^{-3}$ ($n = 8$) during the TCT measurement.

3.3 GOM flux measurement over complete range of materials: Winter

A full set of 24 h GOM flux measurements including all the available mining materials was made in the following winter period (January – March, 2016). Ambient GOM concentration in greenhouse air was 50 pg m^{-3} ($n = 16$), much lower than in the summer months. Mean RH and solar radiation were similar between the summer and winter periods, due to the attenuating effect of the greenhouse. However, mean air and substrate temperatures were significantly lower in the winter (Table 1).

All measured fluxes were above the ΔC_{GOM} detection limit (Fig. 7a). The relationship between GOM flux measured on the A and B systems was slightly less than 1:1 ($B = 0.87 \cdot A$) and not as



300 strong ($r^2 = 0.74$) as during the summer measurements. Without chamber blank correction, GOM
301 fluxes were uniformly negative for all materials except the very high Hg TCT (Fig. 7b, orange
302 shades). However, with the chamber blank correction applied, GOM flux from the cap materials
303 became ambiguous (i.e. both deposition and emission observed) and positive for all leach and
304 tailings materials except the LTT (Fig. 7c, green shades).

305 Three replicated materials had consistent fluxes, with or without blank correction: GS cap (GOM
306 deposition, $V_d = 0.02 - 0.04 \text{ cm s}^{-1}$, corrected), LTT (GOM deposition, $V_d = 0.01 - 0.05 \text{ cm s}^{-1}$,
307 corrected), and TCT (strong GOM emission). The GS mine exploits a predominantly
308 carbonaceous ore deposit, and much of the mine and surrounding areas are subject to carbon
309 loading from aerial dust deposition. The carbon in the GS waste rock and ore likely facilitate
310 deposition of Hg and GOM (c.f. Miller et al, 2013 ; Eckley et al., 2011), . The LTT material is
311 from a non-active tailings impoundment that was partially revegetated at the time of collection,
312 versus the entirely barren surface typical of active tailings. Although the LTT Hg concentration
313 was high ($11 \mu\text{g g}^{-1}$), the surface was old, and it is possible this material behaved more as a
314 background substrate. The TCT material was collected from an actively filling tailings
315 impoundment that collected process waste from a variety of ore types, from multiple mine sites,
316 and had the highest Hg concentration of the materials used in this study, which likely explains its
317 tendency to be a strong emitter of both GEM and GOM, a conclusion also made by Eckley et al.
318 (2011a).

319 An interesting point is that background (2 m and inlet GOM concentrations were very similar
320 during the summer measurements (Fig. 8a), but inlet concentrations were 3x higher than
321 background during the winter measurements (Fig. 8b). The lower winter background GOM (50



322 pg m^{-3}) compared to summer (110 pg m^{-3}) may partially explain this, however the distance
323 between the inlet and background sampling heights was only $\sim 1 \text{ m}$, which implies a strong
324 vertical gradient in GOM concentration in the greenhouse air. The explanation for this is less
325 well mixed air in the greenhouse bay during the winter, as the greenhouse circulation was shut
326 down at temperatures approaching 13°C , setting up stratified conditions. The relatively high
327 inlet level GOM concentrations during the winter also caused the higher deposition observed in
328 the chamber blank measurements during this time.

329 4 Conclusions

330 This study presents direct GOM flux measurements using a CEM filter technique and provides
331 an analysis of whether the necessary measurements of small differences in GOM concentration
332 were possible using a DFC method. Measurements of GOM flux were above calculated
333 detection limits in most cases, and both intra- (Tekran vs Pump sample) and inter- (A vs B)
334 system replicate measurements showed very good agreement. After initial trials at 72 h and 48 h,
335 a 24 h sample time was found to be generally sufficient for detecting GOM flux on the mining
336 materials used in this study, some of which were similar to background soils. It would be
337 possible to operate the system at higher flow rates, to decrease sample time and improve the
338 temporal resolution of the flux measurements. However, sample deployment and collection
339 require 20-30 min and to some extent perturbs the system, so ultimately the flux resolution is
340 limited by practical operational constraints. The 24 h measurement at least serves to capture net
341 flux over a full diel cycle without continuous interruptions.

342 We specifically refer to our measurement as GOM. This is because particulate Hg is not *emitted*
343 from a surface in the volatile sense, and particle entrainment was negligible at the low flow



344 velocities generated in the flux chambers. Thus GOM concentrations measured at the chamber
345 outlet CEM filters are dominated by GOM. If ambient air GOM concentrations were primarily
346 PBM, at a size fraction large enough to be captured by the CEM filters (i.e. $> 0.8 \mu\text{m}$), it will
347 undeniably be captured at the chamber inlet filters. However, PBM at this size would likely
348 deposit to the substrate surface within the chamber, thus deposition is GOM loading on the C_o
349 filters versus the C_i filters.

350 Here we have demonstrated that GOM can be deposited and emitted from a surface. It is unlikely
351 GOM was produced by oxidation of GEM given short time of air moving through the chamber
352 and the fact that strong oxidants were likely removed as air moved through air handlers into the
353 greenhouse. This is a unique scientific finding. Flux measured from low Hg, non-mineralized
354 cap materials for both GEM and GOM were low positive and negative values oscillating around
355 a net zero flux (Table 1). The observed GEM deposition velocities were typical of non-vegetated
356 surfaces, while GOM deposition occurred at V_d values ($0.01 - 0.07 \text{ cm s}^{-1}$) on the low end of the
357 suggested range (Zhang et al., 2009). The higher Hg concentration leach and tailings material
358 (except LT tails) showed net GEM and GOM emission in the summer, while deposition was
359 observed for both for most materials in the winter. The highest GOM emissions were
360 consistently observed for the highest Hg concentration substrate, TCT, in both summer and
361 winter conditions with fluxes higher in the summer during which time the greenhouse was better
362 mixed. The implications of these results are that GOM fluxes may be directly measured and that
363 contaminated areas such as mine tailings impoundments can act as a direct emission source of
364 GOM compounds to the atmosphere.

365

366 **Acknowledgements**



367 The authors would like to acknowledge funding from National Science Foundation Grant
368 629679, Barrick Gold Corp and Newmont Mining Corp for donating substrate materials, and Dr.
369 Ashley Pierce for invaluable assistance in preparing this manuscript.

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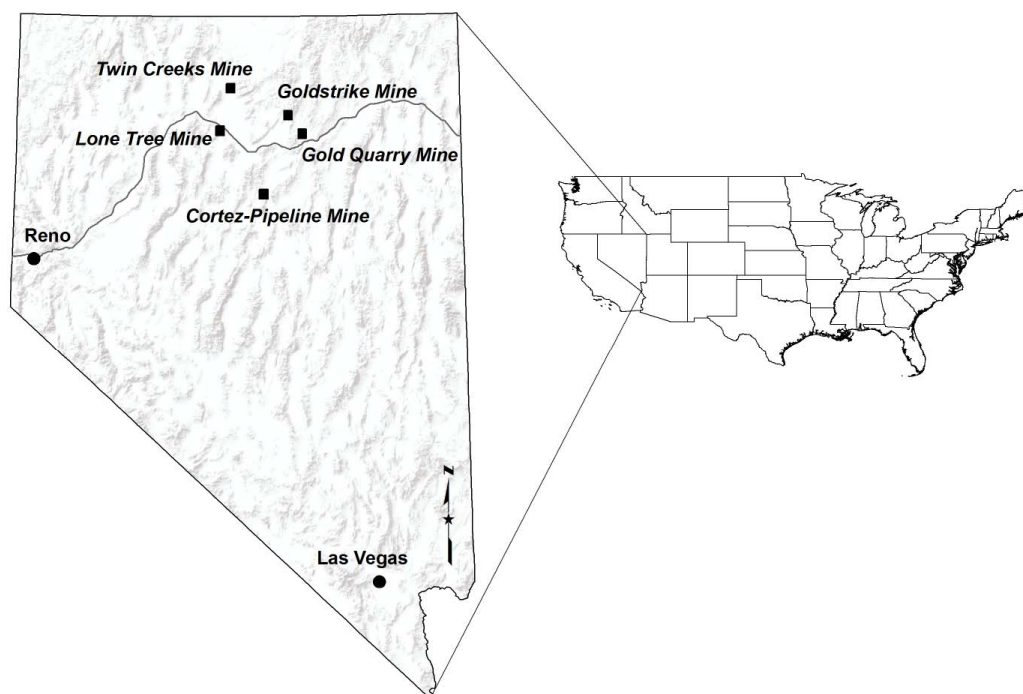


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Figure 1. Location map of study sites, Nevada, USA (From Miller and Gustin, 2013).

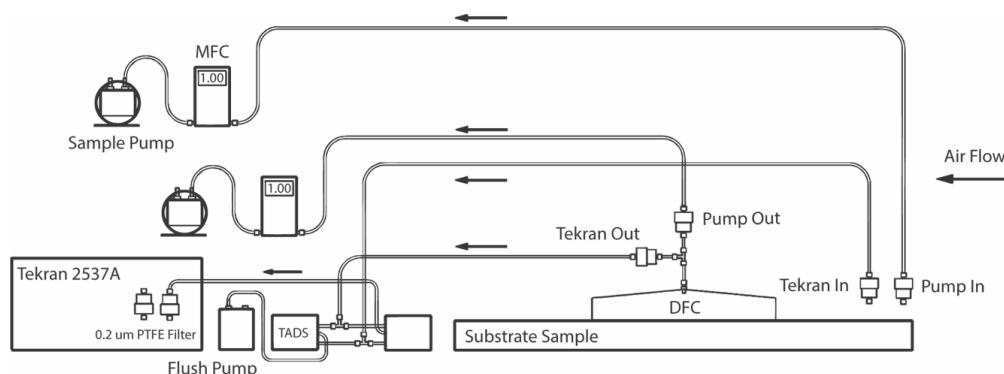


Figure 2. Diagram of one GOM filter-based flux system, deployed in duplicate as Systems A and B. Filter packs indicate the location of the CEM samples.

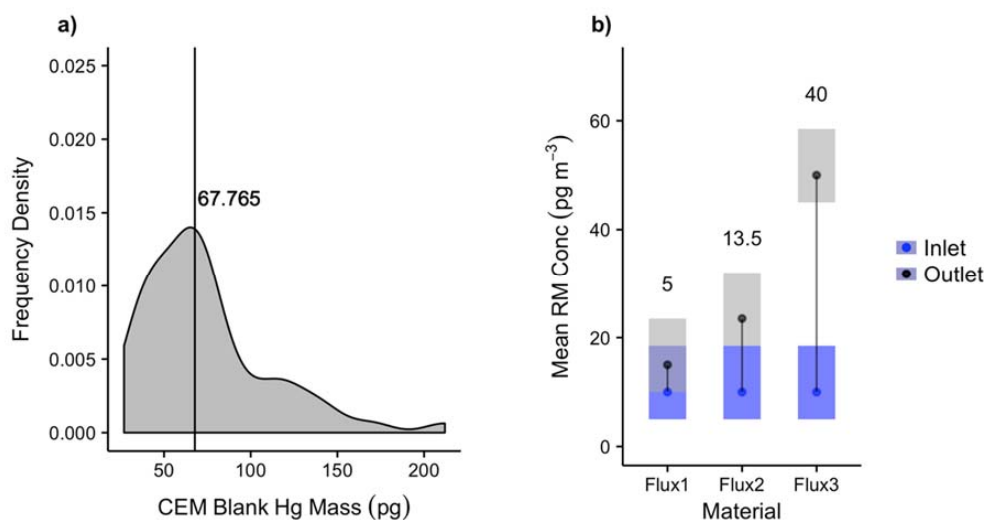
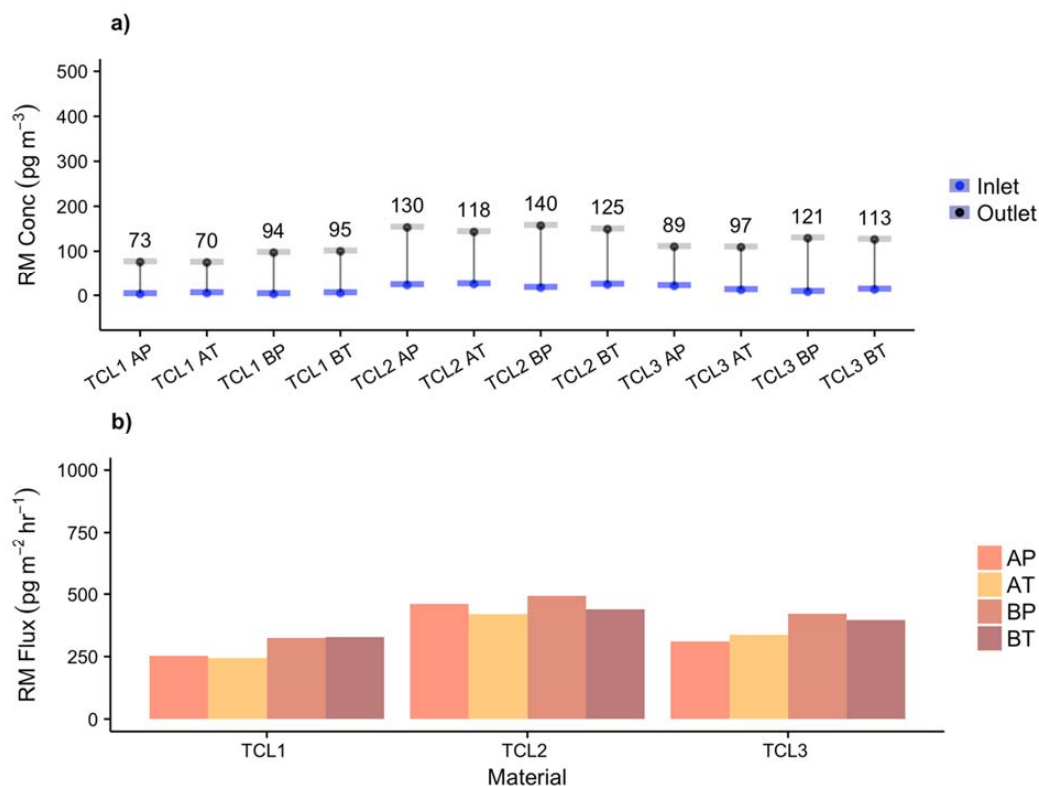


Figure 3. Determination of ΔC_{GOM} detection limit. a) Distribution of Hg mass on unused “blank” CEM filters (median = 68 pg) b) Hypothetical example of statistically detectable GOM flux criteria: shaded boxes represent the maximum uncertainty in concentration, based on 95% confidence interval around the median filter blank (58 – 73 pg), Flux1 represents an insufficiently resolvable ΔC_{GOM} in which the 95% confidence intervals around the median blank-corrected C_o and C_i values overlap, Flux2 represents the minimum detectable ΔC_{GOM} (13.5 pg m⁻³), and Flux3 represents an obviously resolvable ΔC_{GOM} .



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540 **Figure 4.** Test 72 h replicate measurements of TCL material. a) ΔC_{GOM} values: grey points indicate chamber
 541 concentration (C_o), blue points indicate inlet air concentration (C_i), and the numeric value of ΔC_{GOM} is shown above
 542 b) GOM flux from TCL material in three consecutive 72 h measurements, no chamber blank correction. Sample
 543 line labels: AP = Pump A, PB = Pump B, AT = Tekran A, BT = Tekran B.

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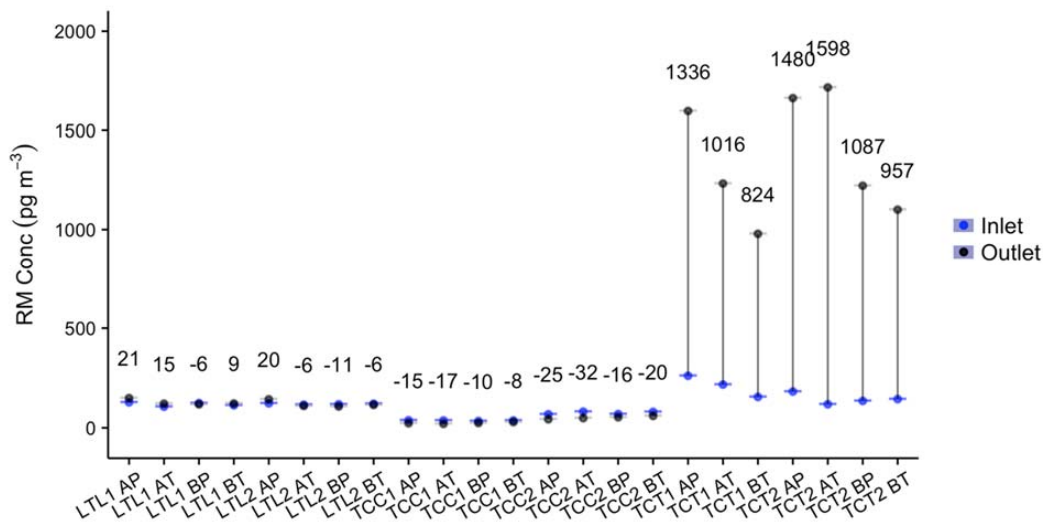


Figure 5. Expanded set of GOM flux measurements for select materials during summer. ΔC_{GOM} was below detection for 5 of 8 LTL measurements, and 2 of 8 TCC measurements, and these values were excluded.

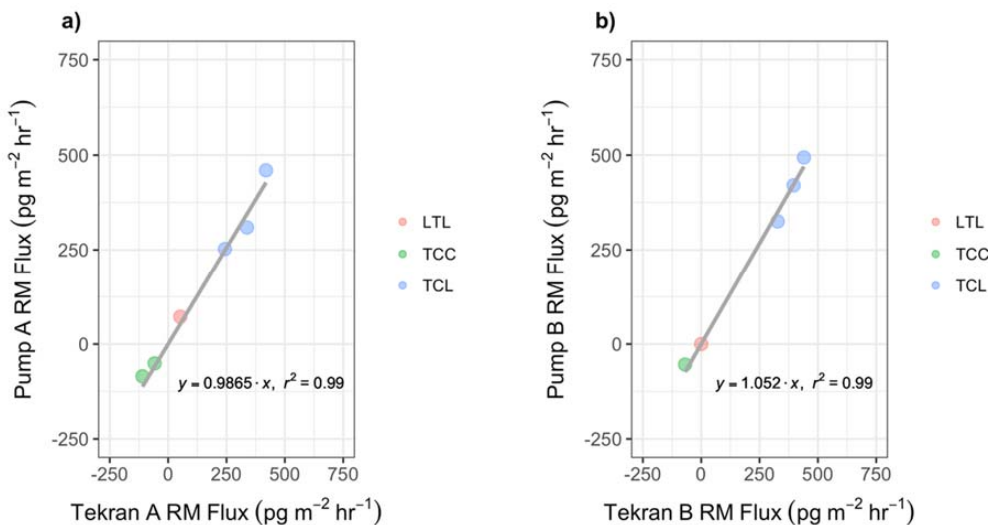
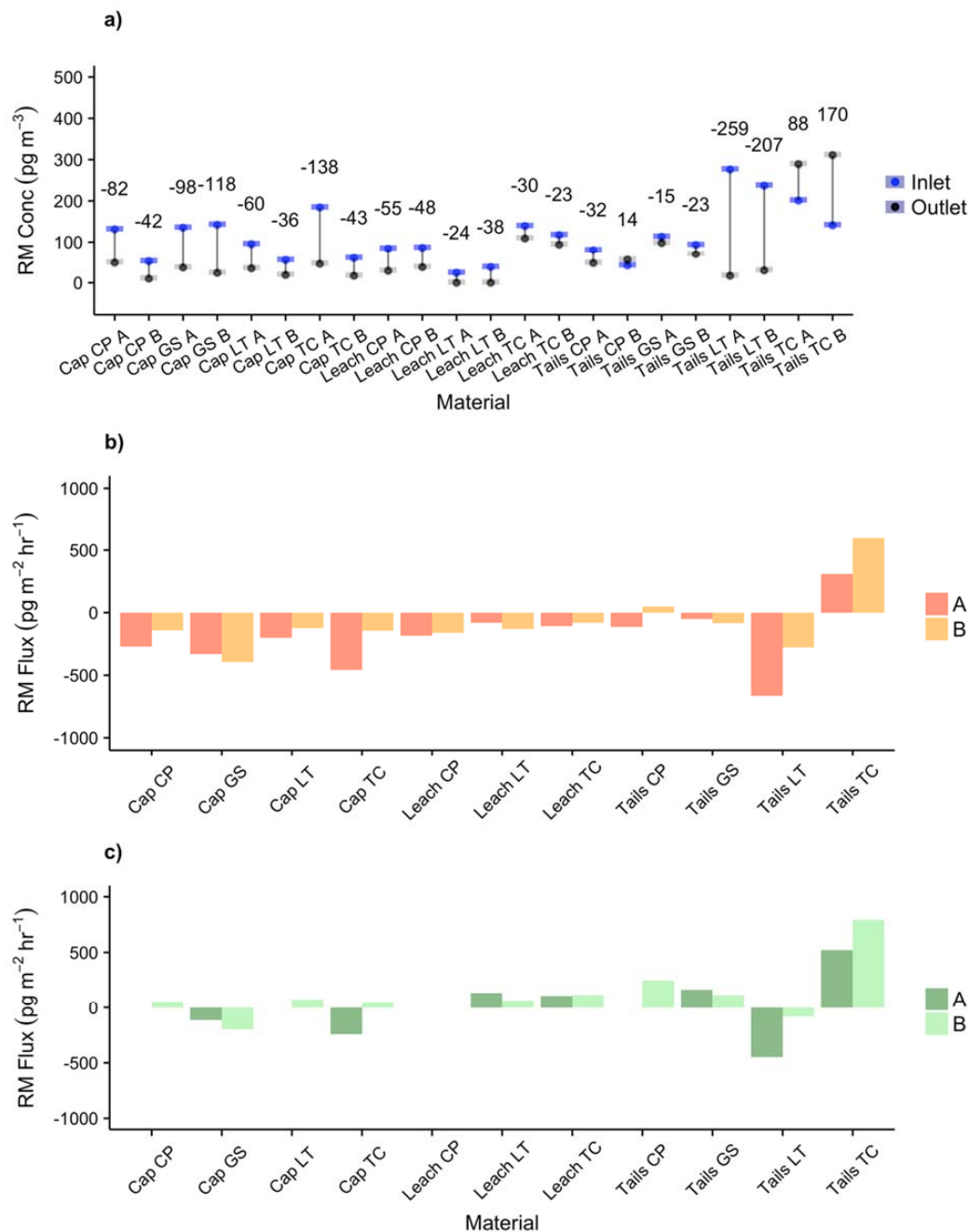


Figure 6. Comparison of GOM fluxes measured by Tekran controlled flow sample lines and external pump flow controlled sample lines, for a) System A and b) System B using TCL, TCC, LTL, and TCT summer measurements. Note TCT data not graphed, as fluxes were an order of magnitude higher and skew the regression r^2 towards 1.



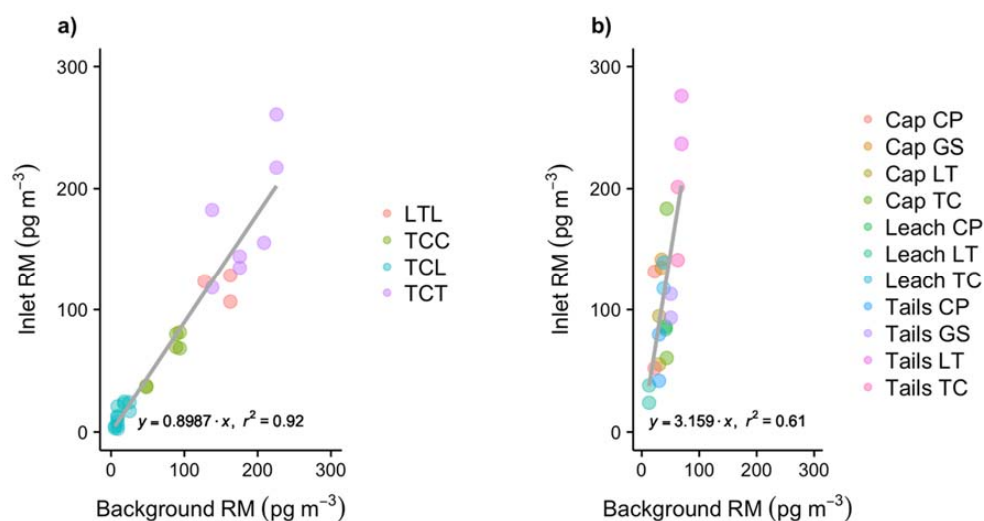
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Figure 7. GOM flux measurements for all materials, winter 2016. a) ΔC_{GOM} , above detection limit for all measurements b) GOM flux, no chamber blank correction (shaded orange) c) GOM flux, with chamber blank correction (shaded green).



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560 **Figure 8.** Comparison of ambient background GOM concentrations measured at 2 m height in the greenhouse, vs
 561 GOM concentrations measured at the chamber inlet, for a) Summer 2015, and b) Winter 2016. Background vs inlet
 562 concentrations were comparable during Summer measurements, but inlet concentrations were much higher relative
 563 to background in the winter.

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Table I.

Material	Sample	Date	Substrate Conc (ng g ⁻¹)	GEM Flux (ng m ⁻² h ⁻¹)	RM Flux (ng m ⁻² h ⁻¹)	RM Inlet (ng m ⁻³)	RM V_d (cm s ⁻¹)	Ambient RM (ng m ⁻³)	Temp (°C)	RH (%)	Solar (W m ⁻²)	Soil Temp (°C)
Leach	TCL1*	5/16-5/19	11900	134	0.29	0.01	-	0.01	na	na	na	na
	TCL2*	5/19-5/22		151	0.45	0.03	-	0.03				
	TCL3*	5/22-5/25		215	0.37	0.02	-	0.01				
Summer 2015	Cap	TCC1A P	230	10	-0.05	0.04	0.04	0.05	22.6	41.6	15.8	23.9
		TCC1A T			-0.06	0.04	0.04					
		TCC1B P		12	na	0.03	na					
		TCC1B T			na	0.04	na					
		TCC2A P		4	-0.09	0.07	0.03					
		TCC2A T			-0.11	0.08	0.04					
	Leach	TCC2B P	590	13	-0.05	0.07	0.02	0.09	24.8	28.7	15.8	26.4
		TCC2B T			-0.07	0.08	0.02					
		LTL1A P		105	0.07	0.13	-					
		LTL1A T			0.05	0.11	-					
		LTL1B P		87	na	0.12	na					
		LTL1B T			na	0.11	na					
	Tailings	LTL2A P	35750	100	0.07	0.12	-	0.16	23.4	24.1	17.3	25.6
		LTL2A T			na	0.12	na					
		LTL2B P		99	na	0.12	na					
		LTL2B T			na	0.12	na					
		TCT1A P		483	4.46	0.26	-					
		TCT1A T			3.37	0.22	-					
Winter 2016	Cap	TCT1B P	230	370	na	0.15	-	0.22	23.8	31.4	16.6	24.2
		TCT1B T			2.76	0.16	-					
		TCT2A P		702	5.02	0.18	-					
		TCT2A T			5.43	0.12	-					
		TCT2B P		457	3.02	0.13	-					
		TCT2B T			2.57	0.14	-					
	Leach	TCCA	11900	1	-0.24	0.18	0.07	0.04	15.0	37.6	2.7	14.5
		TCCB		1	0.05	0.06	-					
		LTCA		0	0.00	0.09	-					
		LTCB		-1	0.07	0.06	-					
		CPCA		-1	0.00	0.13	-					
		CPCB		na	0.06	0.05	-					
	Tailings	GSCA	21150	-1	-0.12	0.13	0.02	0.03	14.6	26.6	11.0	15.8
		GSCB		-1	-0.20	0.14	0.04					
		TCLA		29	0.11	0.14	-					
		TCLB		30	0.11	0.12	-					
		CPLA		-18	0.00	0.08	-					
		CPLB		-12	0.00	0.09	-					
	Leach	LTLA	21150	-4	0.13	0.02	-	0.01	11.7	25.5	14.6	14.2
		LTLB		-3	0.07	0.04	-					
		CPTA		4	0.00	0.08	-					
		CPTB		5	0.25	0.04	-					
		GSTA		16	0.16	0.11	-					
		GSTB		-1	0.11	0.09	-					
	Tailings	LTTA	35750	2	-0.45	0.28	0.05	0.07	19.8	23.1	31.0	22.3
		LTTB		2	-0.08	0.24	0.01					
		TCTA		51	0.52	0.20	-					
		TCTB		71	0.79	0.14	-					

Table I. Summary of GEM and GOM flux and ambient parameters for all measurements. Fluxes are chamber blank-corrected where applicable, and V_d values are based on corrected fluxes (- indicates no deposition, na indicates non-detectable flux).