

Letter

A High Precision Passive Air Sampler for Gaseous Mercury

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1 A High Precision Passive Air Sampler for Gaseous Mercury

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10 ABSTRACT

Passive air samplers provide an opportunity to improve the spatial range and resolution of 11 gaseous mercury (Hg) measurements. Here, we propose a sampler design that combines a 12 13 sulphur-impregnated activated carbon sorbent, a Radiello® diffusive barrier, and a protective shield for outdoor deployments. The amount of gaseous Hg taken up by the sampler increased 14 linearly with time for both an 11-week indoor ($r^2=0.990$) and 12-month outdoor deployment 15 (r^2 =0.996), yielding sampling rates of 0.158±0.008 m³·day⁻¹ indoors and 0.121±0.005 m³·day⁻¹ 16 outdoors. These sampling rates were close to modelled estimates of 0.166 m³·dav⁻¹ indoors and 17 0.129 m³·day⁻¹ outdoors. Replicate precision was lower than for all previous PASs for gaseous 18 19 Hg, especially during outdoor deployments $(2\pm1.3\%)$. Such low precision is essential for 20 discriminating the relatively small concentration variations occurring at background sites. 21 Deployment times for obtaining reliable time-averaged atmospheric gaseous Hg concentrations 22 range from a week to at least one year.

23 INTRODUCTION

24 Atmospheric mercury (Hg) can be found in three forms: gaseous elemental Hg (GEM), gaseous 25 oxidised Hg (GOM) and particle-bound Hg. The most persistent of these atmospheric forms is GEM (atmospheric residence time of ~1 year).¹⁻³ As such, long-range atmospheric transport of 26 GEM is the primary mechanism for distributing Hg globally.^{1,4} GEM typically makes up >95 % of 27 total gaseous Hg (TGM; made up of GEM + GOM) at most sampling locations.⁵⁻⁷ Coastal polar 28 29 sites during springtime are an exception, as rapid oxidation of GEM to GOM during atmospheric Hg depletion events (AMDEs) can cause GOM to contribute up to 100% of TGM for short 30 periods of time (hours to days).⁸ Recently, Gustin et al. hypothesized that uncertainties 31 associated with some GEM, GOM, and/or TGM measurements conceal that GOM may 32 contribute up to 25% of TGM at both inland and coastal sites in the USA.⁹ Empirical 33 34 confirmation through actual measurements of elevated GOM concentrations relative to 35 concurrently measured GEM concentrations will be required to substantiate this hypothesis. In 36 the meantime, we use the term gaseous Hg, when it is uncertain whether a measurement 37 records GEM or TGM concentrations.

Mean annual gaseous Hg concentrations at remote background sites range from 1.5 to 1.7 38 $ng \cdot m^{-3}$ and from 1.1 to 1.3 $ng \cdot m^{-3}$ in the Northern and Southern hemispheres, respectively,^{10,11} 39 with significantly higher concentrations in areas impacted by, but distant from point sources.¹²⁻ 40 ¹⁴ Given that these long term average concentrations typically vary within a fairly narrow range 41 (<0.5 $ng \cdot m^{-3}$ at remote background sites, a few $ng \cdot m^{-3}$ at background sites within source 42 regions),¹⁰ atmospheric gaseous Hg monitoring seeking to discriminate such differences needs 43 to be very precise.^{10,15} The recent introduction of the Minamata Convention to reduce global 44 45 mercury Hg emissions will require precise, long-term monitoring of Hg across the globe to assess its effectiveness.¹⁶ 46

The current spatial resolution and range of global gaseous Hg concentration data is limited due to high costs associated with instruments, energy and gas, and the technical training requirements needed for automated monitoring techniques.^{11,15,17} While not able to produce data at the fine temporal resolution as the automated techniques, passive air samplers (PASs)

that require no electrical energy, are low cost and are easy to deploy, have the potential to
substantially improve the spatial resolution of gaseous Hg data.^{15,17,18}

Several PAS prototypes for gaseous Hg have been proposed over the years to meet the stated 53 need for "a standard accurate calibrated passive sampling method".¹⁸ However, recent reviews 54 concluded that their accuracy and precision is insufficient for long-term monitoring of gaseous 55 Hg at sites removed from major atmospheric Hg sources.^{15,18} Here, we present a novel PAS 56 57 design for precisely monitoring background concentrations of gaseous Hg across a wide range 58 of effective deployment times. We note that, as with many other sampling techniques, the 59 exact species of gaseous Hg sampled by the PAS is uncertain. The use of a diffusive barrier in 60 our sampler design will prevent sampling of particulate-bound Hg. While the reactive nature of 61 GOM is likely to prevent it too from passing through the diffusive barrier this is yet to be 62 proven.

63 **METHODS**

64 Passive Sampler Design. The PAS presented here combines elements of previously reported PASs for gaseous Hg, namely the use of (i) a commercially available, bituminous coal-derived, 65 66 sulphur-impregnated activated carbon (HGR-AC) as the sorbent (Product number: 2300; Calgon Carbon Corporation),¹⁹ (ii) radial diffusion through a micro-porous diffusive body to constrain 67 the rate of sampling,^{10,20} and (iii) a protective shield to protect the sampler from wind and 68 precipitation (Figure 1).¹⁰ Specifically, a mesh cylinder (stainless steel, height 60 mm, diameter 69 70 5.8 mm, mesh size 165, 47 % open area, open at the top, closed at the bottom with a 0.1mm 71 stainless steel plate) is filled with 0.662±0.043 g of HGR-AC that has been crushed using a 72 laboratory grinder and sieved to mesh size 25 x 50 (particle diameter 300 to 710 µm). The open 73 end of the cylinder is then capped with a polytetrafluoro-ethylene (PTFE) stopper and placed 74 within a commercially available, white Radiello® diffusive body (high-density polyethylene, 75 height of the porous section 47 mm, thickness of porous barrier 1.7 mm, diameter 16 mm). This 76 diffusive body is then screwed into a PTFE cap, which in turn is glued to the interior of a 77 polyethylene terephthalate (PET) jar (height 75 mm, diameter 72 mm). During deployment a 78 polypropylene (PP) lid fitted with a PP mesh screen (diamond openings: 5 mm height, 4 mm

width) is used on the bottom of the jar to block entry of animals. Gaseous Hg enters the sampler, undergoing radial molecular diffusion through the diffusive barrier, the internal airspace of the sampler, and into the sorbent.

82 Study Design. In order to derive sampling rates (SRs), Hg uptake in the sampler was measured 83 for an 11-week period inside a laboratory and for a 12-month period in the field. The SR 84 represents the volume of air that is effectively stripped of Hg per unit time. During both studies, 85 gaseous Hg air concentrations were recorded at 5-minute intervals using a Tekran 2537B with 2m Teflon[®] tubing connected to a 0.2µm PTFE filter as the sampler inlet (details are given in 86 Cole and Steffen²¹). The Tekran 2537B was calibrated at 25 hour intervals using the internal Hg 87 88 permeation source of the system. Manual Hg injections from an external Hg source were made 89 before and after the experiments to verify calibrations.

90 During the indoor study, 33 samplers without a protective shield were deployed upright on a 91 bench in a small laboratory. Three randomly selected replicates were removed weekly for 11 92 weeks. To prevent further Hg uptake after retrieval, the Radiello® diffusive bodies were 93 wrapped in PTFE tape and replicates were placed in a PP container, which was sealed with PTFE 94 tape. Room ventilation as well as opening and closing of doors and movement of lab personnel 95 will have generated some air turbulence in the vicinity of the samplers. However, wind speed, 96 measured at the end of the study, was below the detection limit of the hotwire anemometer (<0.1 m \cdot s⁻¹). Air temperature was 21 to 23 °C throughout the study. 97

98 For the outdoor study, 63 PASs were deployed on April 8, 2014 at the University of Toronto 99 Scarborough (43.7836° N, 79.1856° W). Samplers were placed at 1.5 m above ground level by 100 attaching them to a fence. Three randomly selected PASs were removed weekly for the first 12 101 weeks and then monthly for an additional nine months. To prevent further Hg uptake, the open 102 mesh lids were removed and exchanged for a solid PP lid, which was sealed, wrapped with PTFE 103 tape, and stored in a resealable bag at room temperature. Wind speed, wind direction, and 104 temperature were monitored during the year of deployment at a site on top of a nearby 105 building (~10 m above ground level, ~50 m away). Temperature and wind speed (averaged on an hourly basis) ranged from -25.9 to 29.7 °C and 0.1 to 6.7 m \cdot s⁻¹, respectively. 106

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107 Total Hg concentrations in the HGR-AC were determined by thermal desorption, amalgamation 108 and atomic absorption spectroscopy (USEPA Method 7473)²² using a DMA-80 (Milestone Inc; 109 see SI1 for details of instrumental parameters, calibration setup and QA/QC). Statistical tests 110 were run using WinSTAT v5.0 (WinSTAT, R. Fitch Software) with an α value of 0.05 in all tests.

111 **Empirical Sampling Rate Determination.** Restrepo et al.²³ discuss different approaches for 112 deriving a SR (m³·day⁻¹). One method relies on the calculation of a SR for each individual PAS 113 using:

$$114 \quad SR = \frac{m}{(C \cdot t)} \tag{1}$$

where *m* is the amount of analyte collected by the PAS (ng), *C* is the mean actively measured concentration over the sampling period $(ng \cdot m^{-3})$, and *t* is the deployment time (days). The overall *SR* is then the average of these individual *SR* values. Alternatively, equation 1 can be rewritten as $m = SR \cdot C \cdot t$ and *SR* derived as the slope of a linear regression between *m* and *C* \cdot *t*. Since all Hg concentrations in samples are blank-corrected (see SI1), the regression was forced through zero. The final reported values for the *SR*s were derived using this slope method which has a lower uncertainty (see SI2 for details).

Theoretical Sampling Rate Estimation. We also estimated the *SR* theoretically. Agreement between theoretical and empirical *SR*s is a prerequisite for claiming a quantitative understanding of the processes involved in the uptake of Hg in the PAS. The assumption underlying the theoretical estimation is that gaseous Hg must undergo three sequential molecular diffusion steps, through: (i) an air-side boundary layer, (ii) the pore space of the diffusive barrier, and (iii) the internal air-space of the Radiello[®]. Accounting for the radial geometry of each of these steps, the *SR* can be calculated as:

129
$$SR = \frac{D(T,P) \cdot 2 \cdot \pi \cdot h}{\left[\ln \left(\frac{r_a}{r_{d-out}} \right) + v^{-1.33} \cdot \ln \left(\frac{r_{d-out}}{r_{d-in}} \right) + \ln \left(\frac{r_{d-in}}{r_s} \right) \right]$$
(3)

where D(T,P) is the molecular diffusion coefficient of GEM (the dominant fraction of gaseous Hg) in air (m²·day⁻¹), which is a function of temperature *T* and pressure *P*, *h* is the height of the diffusive barrier (m), and r_a , r_{d-out} , r_{d-in} , and r_s are the radii corresponding to the outside of the air-side boundary layer, the diffusive barrier, the internal air space, and the sorbent cylinder (m), respectively. The term $v^{-1.33}$ accounts for the tortuous path through the porous diffusive barrier, with *v* being the porosity (unitless).²⁴ A porosity of 0.496±0.001 for the Radiello[®] diffusive barrier was determined via Hg intrusion porosimetry (Quantachrome Material Characterization Laboratory,). A cross sectional diagram of this system is presented in SI3.

138 **RESULTS AND DISCUSSION**

139 Agreement Between Replicates. Figure 2 shows the amount of sorbed Hg as a function of deployment time for both the indoor (panel B) and outdoor (panel D) studies. The mean 140 141 relative standard deviation (RSD) of sorbed Hg between triplicate samplers was 4±2 % and 2±1 142 % for the indoor and outdoor experiments, respectively. This replicate precision, in particular 143 for the outdoor study, was considerably smaller than the RSDs reported for other PASs attempting to monitor background concentrations of gaseous Hg. In other studies, the lowest 144 mean RSDs between sampler replicates were reported to be 7.7%,²⁰ but more often it was 145 larger than 10%,^{19,25} or not reported at all.^{10,26} The RSD was smaller for the PASs deployed 146 147 outdoors, even though one might expect more stable conditions indoors. The smaller 148 uncertainty outdoors is most likely related to the stabilizing influence of the protective shield, 149 which was not used indoors. Furthermore, the effect of air turbulence on uptake is expected to be largest if that turbulence is low.^{20,27,28} For example, uptake of organic contaminants in a PAS 150 151 was more variable indoors than outdoors, which was attributed to the greater sensitivity of SRs to wind at low wind speeds.²⁹ 152

153 Uptake Curves and Longest Deployment Times. The uptake curves (Figure 2) demonstrate the 154 highly linear relationship between sorbed Hg and deployment time for both the indoor and outdoor studies ($R^2 > 0.99$). This linearity indicates that the sorbent had not approached its 155 156 equilibrium uptake capacity during deployment and that the variability on the time scale of 157 weeks to months in the atmospheric concentration of gaseous Hg during deployment was very 158 small. The latter is confirmed by the gaseous Hg concentration measured by the Tekran 2537B. 159 Over the course of the experiments the range of daily average concentrations was 1.35 to 2.16 ng·m⁻³ (mean: 1.65 ng·m⁻³) indoors and 1.17 to 3.29 ng·m⁻³ (mean: 1.68 ng·m⁻³) outdoors (see 160 SI4). Furthermore, the mean concentrations during each sampling period of all individual PASs 161

were, as expected, even less variable (indoor range: 1.67 to 1.69 ng·m⁻³; outdoor range: 1.55 to 163 1.71 ng·m⁻³, see also Figure 2 Panel A and C, respectively and SI4). The uncertainty of 164 measurements with the Tekran 2537 systems has previously been estimated to be 5-10%.³⁰ 165 Given that there was no indication that uptake slowed toward the end of the 12-month 166 outdoor experiment, the PAS can effectively be deployed to monitor gaseous Hg at background 167 concentrations over time periods as long as at least one year.

168 Detection Limit, Quantification Limit and Shortest Deployment Times. A method detection 169 limit (MDL) for the PAS of 0.26 ng Hg was derived by multiplying 3x the standard deviation of the field blank concentrations from both experiments (0.51±0.13 ng·g⁻¹) with the mean mass of 170 HGR-AC in each PAS (0.662 g). The method quantification limit (MQL) of 0.86 ng Hg was 171 172 similarly derived using 10x the standard deviation of the field blanks. Assuming a background gaseous Hg concentration of 1.5 ng·m⁻³ and using the calibrated SRs listed below this MDL 173 translates to a minimum deployment time for the PAS of approximately two days. Based on the 174 175 MQL, deployments of approximately five days are advisable to assure reliable quantification. At 176 sites with elevated gaseous Hg concentrations, deployment times can, of course, be much 177 shorter.

Empirically Determined Sampling Rates. When using the slope method, *SRs* of 0.158 ± 0.008 m³·day⁻¹ and 0.121 ± 0.005 m³·day⁻¹ were obtained from the indoor and outdoor study, respectively. We suggest two key factors may have contributed to the lower *SR* observed outdoors: (i) the protective shield added a kinetic resistance to Hg uptake in the sampler, presumably because reduced air turbulence inside the shelter increases the thickness of the stagnant boundary layer around the diffusive barrier, and (ii) the temperature dependence of the diffusivity coefficient for Hg.

Figure 2 also displays the *SRs* calculated for each individual sampler using eq. 1, as a function of deployment time (black circles). These data reveal that despite the strong linearity of the uptake curves, there was a slight increase in *SRs* during the first six weeks of the indoor experiment, whereas the *SRs* outdoors decreased during the first 16 weeks of the outdoor experiment. It is possible to envisage reasons why in the first period after deployment, *SRs* may

190 deviate from the long term average SR. For example, initially lower SRs could occur if gaseous 191 Hg is sorbed to the HDPE of the diffusive barrier. Once gaseous Hg establishes equilibrium between the HDPE and the gas phase, the SR would stabilise. Initially higher SR, sometimes 192 referred to as a two-stage uptake mechanism in the literature,^{31,32} may occur if the gaseous Hg 193 sorbs to sites at the outside of the carbon-filled cylinder first, but then has to diffuse through 194 the pores between and within the carbon particles to reach internal sorption sites.³³ The latter 195 would be consistent with reports that the rate-limiting step for removal of vapour phase Hg by 196 197 HGR-AC in industrial applications was diffusion of Hg into internal binding sites once exterior binding sites became saturated.³⁴ It is, however, difficult to explain why the former phenomena 198 should occur indoors, while the latter outdoors. 199

200 After the first six weeks in the indoor experiment and after the first four months of outdoor deployment, the SRs were no longer dependent on deployment time, i.e. the slope of a linear 201 202 regression between SR and t was not significantly different from zero. The SRs derived from the 203 slope method using only the data from weeks 6 to 11 (indoor) and months 4 to 12 (outdoor) were 0.160 \pm 0.006 m³·day⁻¹ and 0.120 \pm 0.004 m³·day⁻¹, respectively. These values are within 1 % 204 205 of the SRs obtained when all data were included, suggesting that the initial deviations in the SRs 206 have very little impact on the SR applicable over deployments lasting more than 1 or 2 months. 207 For shorter deployments, it may be feasible to estimate deployment time specific SRs using the 208 linear relationships included in Figure 2. However, for deployment at sites of elevated gaseous 209 Hg concentrations this is unlikely to be necessary, because faster uptake of gaseous Hg should 210 shorten the time required for the SR to stabilise.

Theoretically Derived Sampling Rates. With the exception of r_a , all of the parameters in eq. (3) 211 are known or can be determined with high precision. When testing the performance of a model 212 estimating SRs in a PAS for organic vapours, Armitage et al.³⁵ obtained good agreement with 213 214 empirical data when assuming an air-side boundary layer thickness of 10 mm (range 7.5 to 15 mm). Adopting a similar range of values for r_{a} - r_{d-out} and using a molecular diffusivity of gaseous 215 Hg either adjusted to the indoor temperature (22 °C) or to the average temperatures during the 216 outdoor study (7.6 °C),³⁶ the theoretical SR of the PAS is estimated to be 0.156 m³·day⁻¹ indoors 217 (range 0.166 to 0.141 $\text{m}^3 \cdot \text{day}^{-1}$) and 0.142 $\text{m}^3 \cdot \text{day}^{-1}$ outdoors (range 0.152 to 0.129 $\text{m}^3 \cdot \text{day}^{-1}$). 218

These values compare favourably with the *SR*s determined indoors (0.158 m³·day⁻¹) and outdoors (0.121 m³·day⁻¹), and in particular confirm that the lower *SRs* outdoors may be, in part, due to slower diffusion at lower temperatures. The remaining difference between outdoor and indoor *SR*s is likely due to a thicker air boundary layer around a diffusive barrier that is caused by the use of a protective shield.

224 Looking Forward. A major strength of this new sampler design is its low precision-based 225 uncertainty, which will assure that the uncertainty of mercury concentrations determined with 226 this sampler depends on the variability of the SRs between deployments. Here we could show 227 that SRs during two deployments under very different conditions only deviate by 23 % from 228 each other. Furthermore, we could explain most of that discrepancy. However, the experiments 229 described here do yet not allow for a full assessment of the uncertainty of concentrations 230 determined with this sampler, because the actively measured air concentrations were used in 231 the derivation of the SRs and can therefore not be used for comparison with air concentrations 232 obtained from PAS data. Therefore, in order to determine the full variability of SRs expected in 233 outdoor deployments and the extent to which this variability can be explained by our 234 understanding of the uptake process, we are currently measuring uptake curves in PASs 235 deployed at a number of sites with ongoing active sampling across a wide range of climatic 236 conditions. This includes sampling sites where atmospheric Hg depletion events are known to 237 occur, potentially allowing for a determination of whether the PAS also takes up GOM. In 238 addition to testing the suitability of the design within a variety of environments, this will allow 239 for a determination of the accuracy-based uncertainty. The relatively small difference in SRs observed between sheltered sampler deployed outdoors and unsheltered samplers deployed 240 241 indoors suggests that at a minimum the samplers can reliably distinguish places with concentrations at background levels (1.5 ng/m³) from those that have only slightly elevated 242 levels (>3 ng/m^3). If it should be feasible to determine the sorption coefficient of gaseous Hg 243 onto HGR-AC and the kinetics of this sorption process, mass transfer processes within the 244 carbon-filled cylinder can be added to the theoretical uptake model.³³ It is anticipated that 245 246 additional measurements and an expanded model will lead to an improved understanding of 247 the trends in the SR that may occur during shorter deployments.

248 ASSOCIATED CONTENT

Supporting Information Available: Detailed description of experimental methodologies, determination of *SRs*, and the actively measured gaseous Hg concentrations for each separate deployment period. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

AUTHOR INFORMATION

254 The authors declare no competing financial interest

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Figure 1: Technical drawing of passive air sampler for monitoring gaseous Hg. A –
Polytetrafluoroethylene screw cap. B – Stainless steel mesh cylinder containing HGR-AC
sorbent. C – Microporous diffusive barrier made from high-density polyethylene. D – Protective
shield made from polyethylene terephthalate. E – Open polypropylene lid with mesh screen,
replaced with closed lid for storage and transport. Diagram is to scale.



Figure 2: Uptake curve (solid diamonds; left axes) and SR (open circles; right axes) of individual 373 374 samplers for indoor (Panel B) and outdoor (Panel D) uptake studies. Linear relationships 375 between initial SRs and time were determined by sequentially eliminating weekly replicates until the linear fit was not significantly different from zero. From this point on the sampling rate 376 377 was considered stable. Actively measured gaseous Hg concentrations for each deployment period are given in Panel A and Panel C for the indoor and outdoor experiments, respectively. 378 Whiskers represent 5th and 95th percentiles, box represents 1st and 3rd guartiles, and marker is 379 380 the median of actively measured hourly averaged gaseous Hg data.

381 TOC Graphic



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