

**Supporting Information for:**

**A High Precision Passive Air Sampler for Gaseous Mercury**

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### SI1. Detailed Analytical Methodology, Calibration Setup and QA/QC

The stainless steel mesh cylinders, sieves and homogenisation vials were washed in a laboratory dishwasher, then heated to 250 °C for 3 hours to remove any residual mercury (Hg). In a preliminary experiment, sulphur-impregnated activated carbon (HGR-AC) as received from the supplier was exposed to temperatures between 50 and 200 °C for a period of 3 hours to ascertain whether this would reduce the amount of residual Hg present. No significant reduction in Hg concentration was observed ( $p > 0.05$  for all treatments; Figure S1) and the HGR-AC was used as provided.

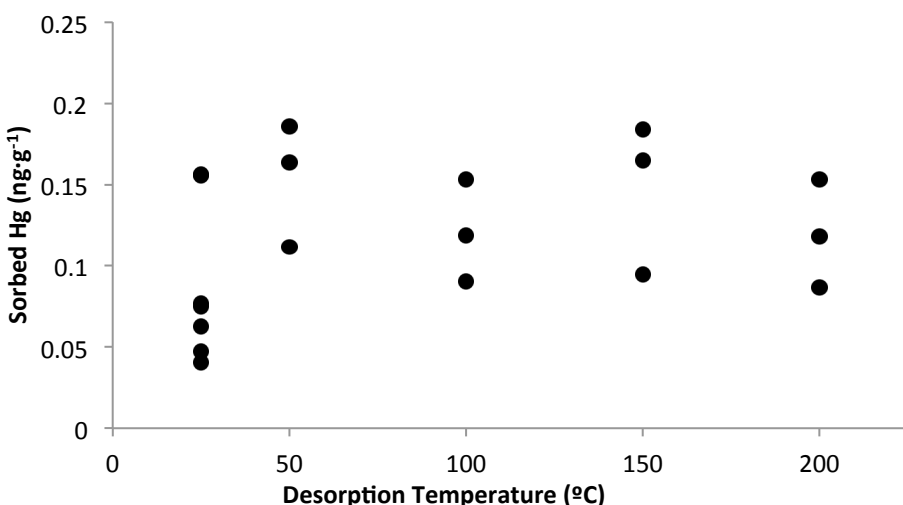


Figure S1 Amount of Hg quantified in HGR-AC exposed to different temperatures. Hg concentrations in HGR-AC that was not heated are shown at 25 °C.

The entire amount of HGR-AC within the sorbent cylinder of each PAS was analysed in order to remove uncertainty pertaining to sample homogeneity that may occur when analyzing one or two sample aliquots only. Since there is an upper limit to the size of a sample that can be analysed with the DMA-80, each HGR-AC sample was analyzed as four aliquots of ~170 mg. The amount in the four aliquots was then added to give the sorbed amount of Hg per sampler. The DMA-80 combustion method for dry samples had the following temperature program: 30 seconds at 200 °C, ramped to 750 °C over 2 minutes, held at 750 °C for 3 minutes. When analyzing the HGR-AC samples from the outdoor study, the catalyst tube of the DMA-80 had a fairly short life-time and needed to be replaced on a regular basis (approximately every 200-250

runs of HGR-AC samples). In an attempt to increase the life-time of the catalyst tubes ~200 mg of a 1:1 Fe<sub>2</sub>O<sub>3</sub> and ZnO mixture was added to each sampling boat on top of the HGR-AC from the indoor study. However, this method was not successful in increasing catalyst tube lifetime and investigation into alternatives is on-going.

Calibration curves were established by adding Fluka TraceCERT® Mercury Standard for AAS (1000 ± 4 mg·L<sup>-1</sup>; in 12% w/w HNO<sub>3</sub>; Sigma-Aldrich Production, Buchs, Switzerland; referred to as “Fluka Standard”) to sampling boats containing ~100 mg of clean HGR-AC. For the samples collected as part of the indoor experiment, 200 mg of the 1:1 Fe<sub>2</sub>O<sub>3</sub> and ZnO was added to the mixture. The curve included samples with 0, 1, 2, 5, 10, 15, and 20 ng of Hg (uncertainty in auto-pipette is 1±0.004 ng). The peak area of the 0 ng calibration point was subtracted from all other points and the quadratic curve was forced through zero. We tested whether there was an effect of the matrix on the signal obtained from a HGR-AC sample. This was the case, as calibration curves made by adding Fluka Standard to empty boats and those made by adding Fluka Standard to boats containing HGR-AC differed slightly (See Fig. S2 for an example).

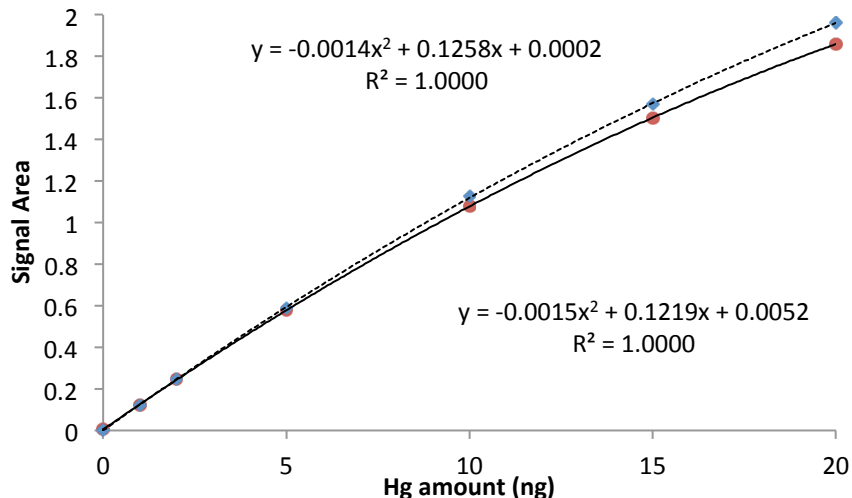


Figure S2 Example of calibration curves for Hg obtained with (red dots; solid trendline) and without (blue diamonds; dashed trendline) the addition of HGR-AC. Both calibration curves were made on the same day. These calibration points are the unadjusted data (peak area of 0 ng point not subtracted) and not forced through zero to demonstrate matrix effect.

This matrix effect was monitored throughout the life of each catalyst tube and varied slightly from one tube to the next. In general, calibration curves with HGR-AC gave a slightly higher signal for the 0 ng calibration point caused by residual amounts of Hg in unexposed HGR-AC. However, as the amount of added Hg increased, the signal of the HGR-AC curve became increasingly lower compared to the curve without HGR-AC.

Analytical precision was tested every 5-10 samples by adding Fluka Standard (5 or 10 ng of Hg) onto ~100 mg of clean HGR-AC (and ~200 mg of the Fe<sub>2</sub>O<sub>3</sub>/ZnO mixture for samples from the indoor experiment). Recoveries of the spiked standards were  $101 \pm 1.3\%$  ( $n=42$ ), and  $100 \pm 3\%$  ( $n=46$ ) for samples from the outdoor and indoor study, respectively.

Recovery was further tested every 10-15 samples by analyzing ~50-100 mg of Standard Reference Material (SRM) 2685c (National Institute of Standards and Technology, Gaithersburg, USA), a high sulphur (5% by mass) bituminous coal with a Hg concentration of  $149.4 \text{ ng}\cdot\text{g}^{-1}$ . When analyzing the SRM during the analysis of samples from the indoor study the Fe<sub>2</sub>O<sub>3</sub>/ZnO mixture was again added on top. Recoveries were  $99 \pm 3\%$  ( $n=44$ ) and  $99 \pm 3\%$  ( $n=24$ ) for samples from the outdoor and indoor study, respectively.

The analytical procedure included three types of blank samples: analytical (HGR-AC as supplied from Calgon;  $n=3$  for each experiment), lab (HGR-AC from PAS prepared in lab;  $n=3$  for each experiment) and field blanks (HGR-AC from PAS prepared in lab and opened, deployed, then immediately removed in the field;  $n=4$  for each experiment). Concentrations of Hg in analytical blanks (indoor =  $0.3 \pm 0.11 \text{ ng}\cdot\text{g}^{-1}$ ; outdoor =  $0.3 \pm 0.10 \text{ ng}\cdot\text{g}^{-1}$ ) were significantly lower ( $p < 0.05$ ) than lab blanks (indoor =  $0.4 \pm 0.11 \text{ ng}\cdot\text{g}^{-1}$ ; outdoor =  $0.4 \pm 0.14 \text{ ng}\cdot\text{g}^{-1}$ ). In turn lab blanks were significantly ( $p < 0.05$ ) lower than field blanks (indoor =  $0.6 \pm 0.10 \text{ ng}\cdot\text{g}^{-1}$ ; outdoor =  $0.46 \pm 0.04 \text{ ng}\cdot\text{g}^{-1}$ ) for both indoor and outdoor experiments. In order to allow determination of the concentration of Hg in analytical, lab, and field blanks, the calibration curves established without the addition of HGR-AC were used.

All actual samples were blank adjusted by subtracting the average Hg concentration in field blanks multiplied by the mass of HGR-AC in each PAS. The aforementioned uncertainty in field blanks added negligible increases to the uncertainty of Hg masses in the samples.

## SI2. Determination of Empirical Sampling Rates (SR)

Restrepo et al.<sup>1</sup> describe three methods for obtaining SRs from an uptake curve: (i) taking the average of the SRs of all individual samplers, which are calculated using eq. 1 in the main paper, (ii) calculating the slope of a linear regression of  $m$  against  $(C \cdot t)$ , and (iii) the difference method, which is calculated using Equation S1:

$$SR = [m_i - m_{i-1}] / [(C_i) \cdot (t_i - t_{i-1})] \quad (S1)$$

Where  $[m_i - m_{i-1}]$  is the difference of Hg sorbed by the  $i^{th}$  and  $i^{th} - 1$  PAS;  $(t_i - t_{i-1})$  is the difference in deployment times of the  $i^{th}$  and  $i^{th} - 1$  PASs;  $C_i$  is the mean actively measured concentration of gaseous Hg over time interval  $(t_i - t_{i-1})$ . Again, the SRs obtained for all time intervals are averaged. Table S1 lists the SRs obtained using the three methods.

Table S1 SRs ( $\text{m}^3 \cdot \text{day}^{-1}$ ) for gaseous Hg uptake in PASs obtained by the average, slope and difference methods. SRs are given both for the entire study period and the period when SR was constant (i.e., the relationship between SR and  $t$  was not significantly different from zero at the 5 % confidence levels).

	All data			Data from weeks 6 – 11 or months 4 - 12		
	average	slope	difference	average	slope	difference
indoor	$0.15 \pm 0.012$	$0.158 \pm 0.008$	$0.15 \pm 0.05$	$0.160 \pm 0.007$	$0.160 \pm 0.006$	$0.15 \pm 0.08$
outdoor	$0.13 \pm 0.011$	$0.121 \pm 0.006$	$0.13 \pm 0.04$	$0.121 \pm 0.005$	$0.120 \pm 0.003$	$0.12 \pm 0.03$

We chose to report the SRs calculated with the slope method in the main paper because of its generally lower estimated uncertainty. The substantially higher uncertainty in overall SR using the difference method is largely a result of calculations requiring input from two separate measurements, each with their own inherent uncertainty. This results in a propagation of error and hence greater uncertainty in the SR.

### SI3. Theoretical Sampling Rates

As described in the main paper the theoretical *SRs* were derived by modelling diffusion through an air-side boundary layer, the porous diffusive barrier and the internal airspace of the Radiello<sup>®</sup> (Figure S3). This model neglects the diffusion into the pores of the HGR-AC sorbent.

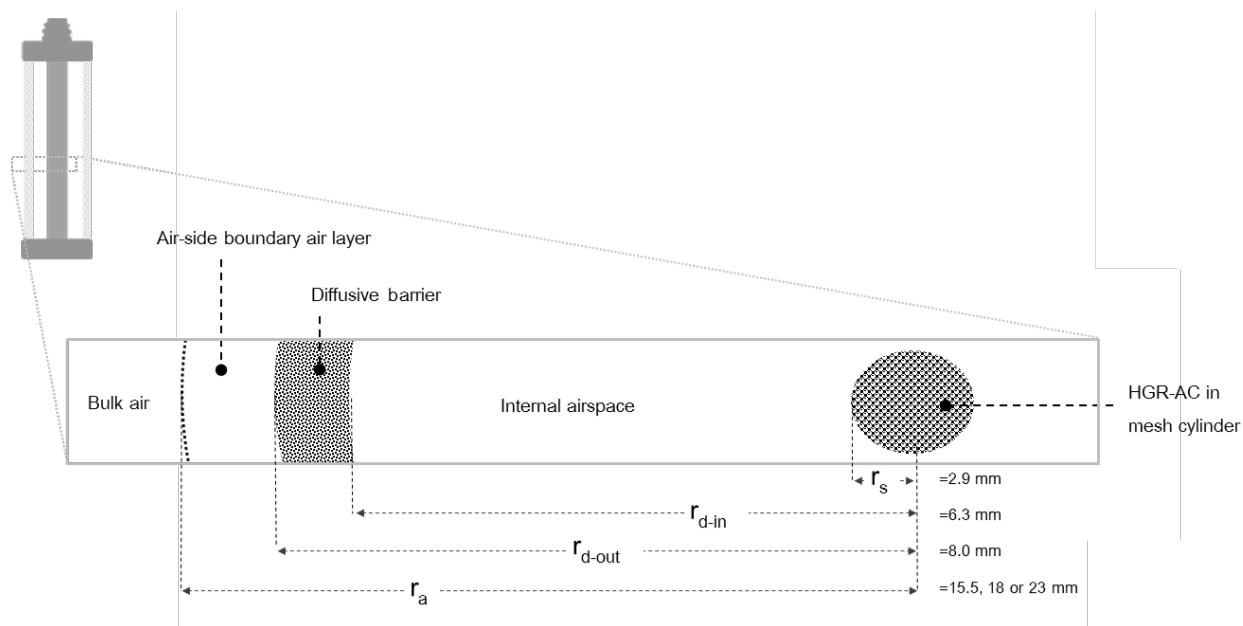


Figure S3 Top down cross-sectional view of the PAS showing parameters used to determine theoretical *SRs*.  $r_a$ ,  $r_{d-out}$ ,  $r_{d-in}$ , and  $r_s$  are the radii corresponding to the outside of the air-side boundary layer, the diffusive barrier, the internal air space, and the sorbent cylinder. The varying lengths given for  $r_a$  equate to air-side boundary layer thicknesses of 7.5, 10, and 15 mm. Diagram is not to scale.

#### SI4. Actively Measured Gaseous Hg Concentrations for Each Deployment Period

Table S2 lists the gaseous Hg concentrations measured at the University of Toronto Scarborough (UTSC) by the Tekran 2537B, averaged for each week of deployment and for the whole deployment period of each sampler, for both the indoor and outdoor study. The full actively measured gaseous Hg concentration data sets for each experiment can be seen in Figure S4.

Table S2 Actively measured gaseous Hg concentrations ( $\text{ng}\cdot\text{m}^{-3}$ ), averaged for each week or month of deployment and for the whole deployment period of each sampler (cumulative data). Temporal coverage is the percentage of the deployment period during which actively measured gaseous Hg concentrations were available.

Week	Indoor			Outdoor		
	Weekly	Cumulative	Temporal coverage (%)	Weekly or monthly	Cumulative	Temporal coverage (%)
1	$1.69 \pm 0.2$	$1.69 \pm 0.2$	100	$1.63 \pm 0.22$	$1.63 \pm 0.22$	100
2	$1.68 \pm 0.25$	$1.68 \pm 0.23$	100	$1.56 \pm 0.27$	$1.60 \pm 0.25$	100
3	$1.63 \pm 0.78$	$1.66 \pm 0.49$	100	$1.47 \pm 0.13$	$1.56 \pm 0.23$	100
4	$1.63 \pm 0.13$	$1.66 \pm 0.43$	100	$1.58 \pm 0.13$	$1.56 \pm 0.22$	83.4
5	$1.71 \pm 0.27$	$1.67 \pm 0.4$	100	$1.55 \pm 0.2$	$1.56 \pm 0.22$	69.8
6	$1.71 \pm 0.27$	$1.67 \pm 0.39$	96.3	$1.59 \pm 0.22$	$1.57 \pm 0.22$	74.8
7	$1.71 \pm 0.27$	$1.68 \pm 0.37$	96.8	$1.62 \pm 0.16$	$1.57 \pm 0.22$	65.3
8	$1.67 \pm 0.24$	$1.68 \pm 0.36$	97.2	$1.57 \pm 0.33$	$1.57 \pm 0.24$	66.8
9	$1.59 \pm 0.26$	$1.67 \pm 0.35$	97.5	$1.45 \pm 0.32$	$1.55 \pm 0.25$	70.5
10	$1.68 \pm 0.41$	$1.67 \pm 0.36$	97.8	$1.56 \pm 0.42$	$1.55 \pm 0.28$	73.4
11	$1.69 \pm 0.27$	$1.67 \pm 0.35$	98.0	$1.59 \pm 0.35$	$1.56 \pm 0.29$	75.8
12.14	-	-		$2.27 \pm 0.89$	$1.64 \pm 0.47$	78.1
16.43	-	-		$1.59 \pm 0.54$	$1.64 \pm 0.52$	83.8
21.14	-	-		$1.96 \pm 1.11$	$1.69 \pm 0.67$	79.7
26	-	-		-	$1.69 \pm 0.67$	66.4
30	-	-		$1.92 \pm 0.47$	$1.71 \pm 0.65$	63.1
34	-	-		$1.55 \pm 0.22$	$1.69 \pm 0.61$	64.1
38.86	-	-		$1.55 \pm 0.15$	$1.67 \pm 0.57$	67.9
43	-	-		$1.52 \pm 0.12$	$1.65 \pm 0.54$	67.4
46.86	-	-		$1.52 \pm 0.08$	$1.65 \pm 0.53$	63.5
51.86	-	-		-	$1.65 \pm 0.53$	58.2

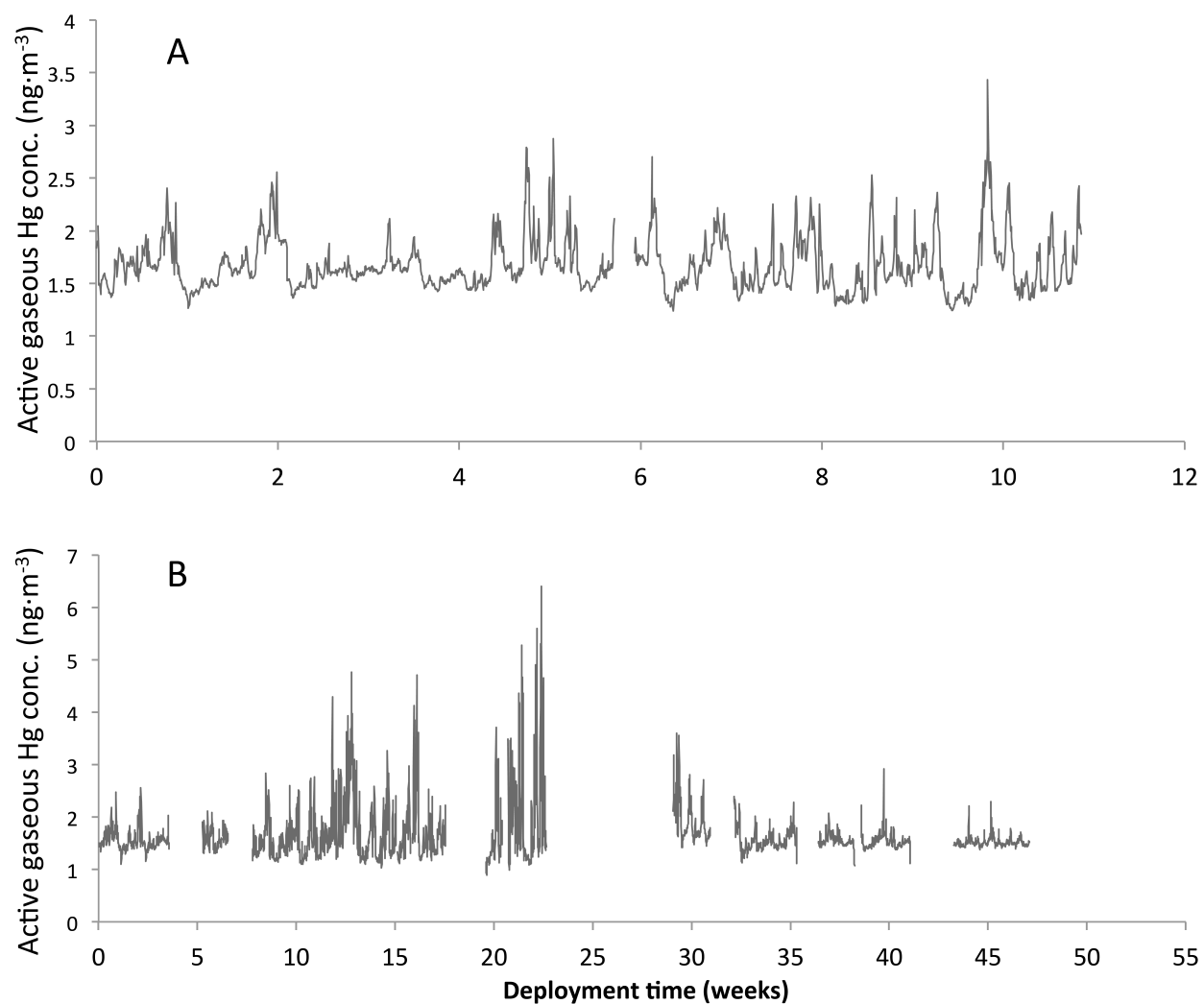


Figure S4      Hourly averages of actively measured gaseous Hg concentrations during the indoor (Panel A) and outdoor (Panel B) experiments.



## REFERENCE

1. Restrepo, A. R.; Hayward, S. J.; Armitage, J. M.; Wania, F., Evaluating the PAS-SIM model using a passive air sampler calibration study for pesticides. *Environ. Sci. Process. Impacts* **2015**, *17*, 1228-1237.