



# The effects of meteorological parameters and diffusive barrier reuse on the sampling rate of a passive air sampler for gaseous mercury

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**Abstract.** Passive air sampling of gaseous mercury (Hg) requires a high level of accuracy to discriminate small differences in atmospheric concentrations. Meteorological parameters have the potential to decrease this accuracy by impacting the sampling rate (SR), i.e., the volume of air that is effectively stripped of gaseous mercury per unit of time. We measured the SR of a recently calibrated passive air sampler for gaseous Hg in the laboratory under varying wind speeds (wind still to  $6 \text{ m s}^{-1}$ ), temperatures ( $-15$  to  $+35 \text{ }^\circ\text{C}$ ), and relative humidities (44 to 80 %). While relative humidity has no impact on SR, SR increases slightly with both wind speed ( $0.003 \text{ m}^3 \text{ day}^{-1}$  increase in SR or 2.5 % of the previously calibrated SR for every  $\text{m s}^{-1}$  increase for wind speeds  $> 1 \text{ m s}^{-1}$ , typical of outdoor deployments) and temperature ( $0.001 \text{ m}^3 \text{ day}^{-1}$  increase in SR or 0.7 % for every  $1 \text{ }^\circ\text{C}$  increase). The temperature dependence can be fully explained by the effect of temperature on the molecular diffusivity of gaseous mercury in air. Although these effects are relatively small, accuracy can be improved by adjusting SRs using measured or estimated temperature and wind speed data at or near sampling sites. We also assessed the possibility of reusing Radiello<sup>®</sup> diffusive barriers previously used in the passive air samplers. The mean rate of gaseous Hg uptake was not significantly different between new and previously used diffusive barriers in both lab and outdoor deployments, irrespective of the applied cleaning procedure. No memory effect from Radiellos<sup>®</sup> previously deployed in a high Hg atmosphere was observed. However, a loss in replicate precision for the dirtiest Radiellos<sup>®</sup> in the indoor experiment suggests that cleaning is advisable prior to reuse.

## 1 Introduction

Fine spatial resolution measurements of atmospheric contaminants are difficult and expensive, especially at remote locations and in developing countries. By allowing for simultaneous, cost-effective measurements at a multitude of sites, passive air samplers (PASs) are useful, complementary monitoring tools in atmospheric science. PASs can be deployed in high numbers, at sites away from sources of electricity, and in locations where the costs and logistics of active sampler deployments can be prohibitive (McLagan et al., 2016a). In order for a PAS to yield volumetric air concentration data, a sampling rate (SR), i.e., the volume of air that is effectively stripped of the contaminant of concern per unit of time, needs to be derived. This is done either in calibration experiments that deploy the PAS concurrently with reliable active sampling techniques or theoretically based on an understanding of the processes controlling mass transfer from atmosphere to PAS sorbent (Armitage et al., 2013; Gustin et al., 2011; Skov et al., 2007). Any uncertainty and bias in the SR is directly propagated to the volumetric air concentration derived from a PAS. Accordingly, a reliable PAS requires that the impact of various factors influencing the SR is, in order of preference, either eliminated, minimized, or quantifiable and predictable.

A common conceptual model of uptake in PASs assumes a stagnant air layer or air-side boundary layer (ASBL) around the sorbent, through which contaminant transfer occurs solely by molecular diffusion (McLagan et al., 2016a; Shoeib and Harner, 2002). Wind decreases the thickness of the ASBL, which in turn increases the SR (Bartkow et al., 2005; Moeckel et al., 2009; Pennequin-Cardinal et al., 2005). Diffusive barriers aim to reduce the influence of wind by

standardizing the molecular diffusion distance to the sorbent and thereby ensuring that the diffusive component of contaminant transfer is the rate limiting step (Huang et al., 2014; Lozano et al., 2009; McLagan et al., 2016a). For PASs with diffusive barriers the ASBL is shifted from the outside of the sorbent to the outside of the diffusive barrier (McLagan et al., 2016b). While a diffusive barrier thus reduces the relative contribution of the ASBL to the overall diffusion distance, it cannot entirely mitigate SR variability caused by wind (Pennequin-Cardinal et al., 2005; Plaisance et al., 2002; Skov et al., 2007). Protective shields around the sorbent or diffusive barrier are often employed to further reduce the influence of wind by reducing the face velocities at these surfaces. However, like diffusive barriers, they too are not likely to completely eliminate the influence of wind on the thickness of the ASBL (Huang et al., 2014).

Temperature has the potential to affect SR in two ways: (i) changing the rate of gas phase diffusion of the contaminant due to the temperature dependence of molecular diffusion coefficients (Armitage et al., 2013; Huang et al., 2014; Lozano et al., 2009) and (ii) shifting the partitioning equilibria between the sorbent and the gas phase (Armitage et al., 2013; Lozano et al., 2009; McLagan et al., 2016a). Relative humidity (RH) may affect SRs by influencing the sorptive properties of certain sorbents for target analytes (Huang et al., 2014). Other factors that may affect the sorption of contaminants to PAS sorbents include passivation of sorbents (interfering compounds blocking sorbent uptake sites or stripping analytes through reaction) (Brown et al., 2012; Gustin et al., 2011), degradation of the sorbent over time (Brown et al., 2011; McLagan et al., 2016a), and uptake of the contaminant to the sampler housing or diffusive barrier (Gustin et al., 2011; Huang et al., 2014; McLagan et al., 2016a).

Mercury is a persistent, bioaccumulative, and toxic contaminant of global concern that has come under greater international scrutiny with the adoption of the Minamata Convention (UNEP, 2013). A key stipulation under Article 19 of the convention “Research, Development and Monitoring” is the requirement of participating parties to improve current monitoring networks (UNEP, 2013). A PAS for measuring atmospheric Hg could play an important role in this context, if it can be shown to be suitable for monitoring long-term background concentrations, concentration gradients in and around Hg sources, and personal exposure levels (McLagan et al., 2016a). Gaseous elemental Hg (GEM) is generally the dominant form of atmospheric Hg (typically making up > 95 %), due to its high atmospheric residence time of ~ 1 year (Driscoll et al., 2013; Pirrone et al., 2010; Selin, 2009), especially at sites remote from combustion sources (McLagan et al., 2016a; Peterson et al., 2009; Rutter et al., 2009). The long atmospheric residence time of GEM results in relatively uniform background concentrations within each hemisphere, with much of the global atmosphere having levels within < 25 % of the hemispheric average (Gustin et al.,

2011). PASs capable of discriminating such small concentration variability require high accuracy and precision; i.e. SRs need to be well characterized and repeatable. Existing PASs for gaseous mercury have struggled to achieve the accuracy and precision necessary for background monitoring due to inadequate detection limits or highly variable SRs (Huang et al., 2014; McLagan et al., 2016a).

We recently introduced a PAS for gaseous Hg with a precision-based uncertainty of  $2\pm 1\%$  that uses an activated carbon sorbent and a Radiello<sup>®</sup> diffusive barrier (McLagan et al., 2016b). While it is believed that the sampler takes up predominantly GEM, we cannot rule out the possibility for gaseous oxidized Hg to also pass through the diffusive barrier (McLagan et al., 2016b). We therefore use the term gaseous Hg to define the target analyte. An earlier calibration of this PAS at one outdoor location yielded a SR of  $0.121\text{ m}^3\text{ day}^{-1}$  (McLagan et al., 2016b). Here we report on a series of laboratory experiments that quantified the effect of wind speed, temperature, and RH on the SR of that sampler. We additionally explored the possibility of reusing the Radiello<sup>®</sup> diffusive barrier in multiple deployments in order to further reduce the costs associated with the sampler’s use. During deployment, the inside of the Radiello<sup>®</sup> can become covered in sorbent dust. It is also possible that atmospheric components, e.g. atmospheric particulate matter and oxidants, sorb to or react with the diffusive barrier during deployment. Thus, in addition to meteorological impacts on the PAS’s SR, we also explored the effect of prior use and cleaning of the diffusive barrier on the uptake of Hg in the PAS.

## 2 Methods

### 2.1 Sampler design

The sampler consists of a porous stainless steel mesh cylinder, filled with ~ 0.7 g of sulfur-impregnated activated carbon sorbent (HGR-AC; Calgon Carbon Corp.), which is inserted into a Radiello<sup>®</sup> radial diffusive body (Sigma Aldrich), which itself is placed inside a polyethylene-terephthalate protective shield that also doubles as a storage container. During deployments the opening of the jar, covered with a polypropylene (PP) mesh screen, is facing down. After sampling the protective shield is sealed tightly with a PP cap, PTFE tape wrapped around the seal, and placed in double resealable plastic bags for transport and storage. McLagan et al. (2016b) provide more detail on the PAS design.

### 2.2 Study design

#### 2.2.1 Wind

PAS in four different configurations were exposed to different wind conditions in the laboratory at the University of Toronto Scarborough: (1) regular, white Radiello<sup>®</sup> with

protective shield; (2) white Radiello<sup>®</sup> without protective shield; (3) thick-walled, less porous, yellow Radiello<sup>®</sup> with protective shield; and (4) yellow Radiello<sup>®</sup> without protective shield. Adopting the experimental setup of Zhang et al. (2013), electronic fans (Delta Electronics Inc., model number: BFC1212B) were employed to generate wind for each individual sampler. The angle of wind incidence was always 90°; i.e. we simulated wind that is blowing parallel to the surface. Wind speeds of 1, 1.5, 2, 3, 4, 5, and 6 m s<sup>-1</sup> were achieved by manipulating the distance between PASs and fan (see Figs. S1 and S2 in the Supplement). For each wind speed triplicate PASs were deployed. Wind speeds for each individual PAS were measured every 5 s with a hot-wire anemometer/thermometer (Traceable<sup>®</sup>, VWR International) for 5 min before and 5 min after each deployment. As such, average wind speeds of individual samplers within each wind speed treatment varied slightly (Fig. 1). “Wind-still” experiments without fans were performed for comparison (with wind speed assumed to be 0.05 m s<sup>-1</sup>).

While experiments with white Radiellos (configuration 1 and 2) generally lasted 1 week, additional experiments lasting 2, 3, and 4 weeks were performed at selected wind speeds (3 and 6 m s<sup>-1</sup>). Experiments with yellow Radiellos (configurations 3 and 4) lasted 2 weeks (the lower SR of yellow Radiello<sup>®</sup> requires longer deployment times to reach detection limits) and were only performed at wind speeds of 3 and 6 m s<sup>-1</sup>, as well as without fans. Additionally, a 3-month uptake experiment under wind-still conditions was performed in order to obtain a precise SR of the PAS with a white Radiello deployed indoors with a protective shield. Eighteen samplers were deployed at the same time and triplicates were removed after 15, 28, 46, 56, 70, and 84 days. The earlier indoor calibration experiment described in McLagan et al. (2016b) had been performed without a protective shield.

Temperature and RH, monitored before, after, and periodically during each individual experiment, ranged from +21.9 to +24.2 °C and from 32 to 53 %. While there was some variation in the gaseous Hg concentration as recorded by the Tekran 2537A between deployments, the average concentration across all wind experiments was  $1.9 \pm 0.3 \text{ ng m}^{-3}$ .

### 2.2.2 Temperature and relative humidity

The regular PAS configuration (configuration 1) was exposed to eight different combinations of temperature and RH (Table 1) for 2-week periods in climate-controlled walk-in chambers located at the Biotron Facility of Western University in London, Ontario. Each treatment included five replicates, all deployed in the same chamber over the same time period. Samplers were attached to metal shelving units near the centre of the chambers where a continuous flow of air from the outflow of the climate control units of 1.1–2.3 m s<sup>-1</sup> was observed using the hot-wire anemometer over a 2 min period at the completion of each experiment. The average

actively measured gaseous Hg concentration across all temperature and RH experiments was  $2.2 \pm 0.9 \text{ ng m}^{-3}$ .

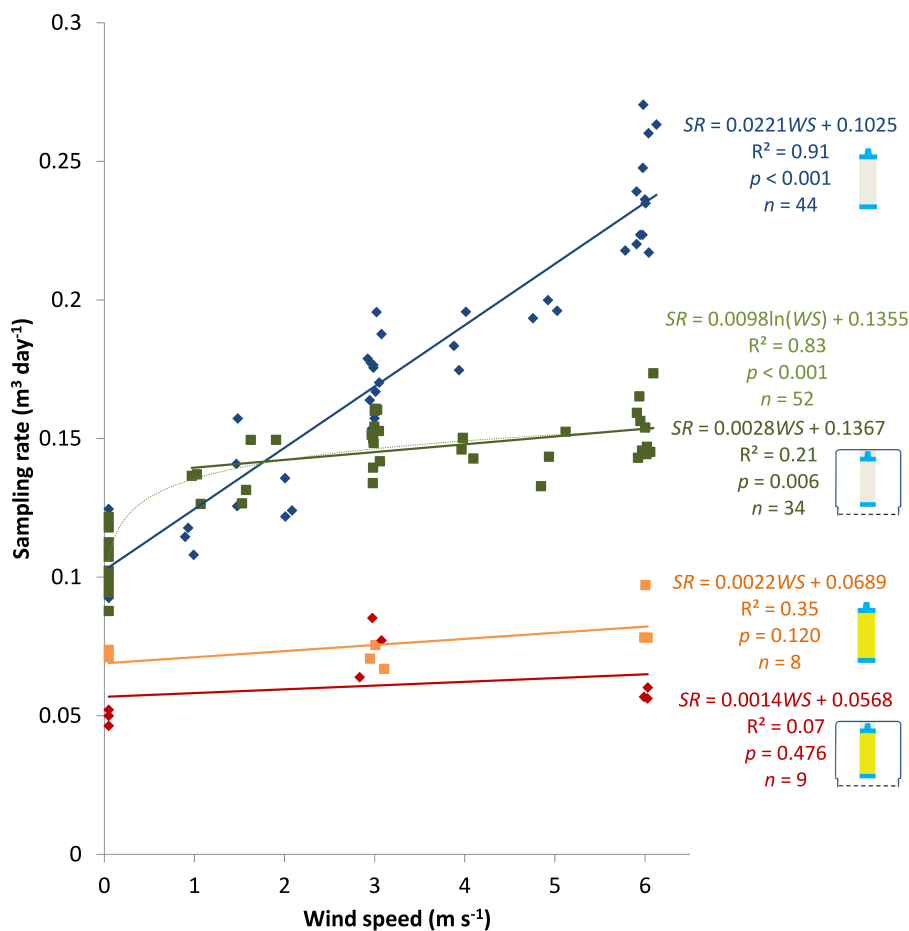
### 2.2.3 Radiello<sup>®</sup> reuse

The potential impacts of sorbent dust accumulation or atmospheric contamination during prolonged deployment periods on SRs and therefore on the ability to reuse the Radiello<sup>®</sup> diffusive barriers are unknown. Currently, new diffusive barriers are used for each deployment. In this experiment, previously used Radiellos<sup>®</sup> were redeployed after different cleaning procedures were applied. Six cleaning treatments were applied: “new” (unused Radiellos<sup>®</sup>), “uncleaned” (unaltered after previous deployments), “physical” (physical agitation with funnel brushes and compressed air blow down), “soap” (Citranox<sup>®</sup> detergent, cleaning brushes, and deionized water, compressed air blow down, deionized water rinse and sonication and air drying), “acid” (6-hour soak in 20 % HNO<sub>3</sub> bath, deionized water rinse, compressed air blow down, deionized water rinse and sonication, and air drying), and “heat-acid” (6-hour soak in 20 % HNO<sub>3</sub> bath at 40 °C, deionized water rinse, compressed air blow down, deionized water rinse and sonication and air drying). All Radiellos<sup>®</sup> in each cleaning treatment were cleaned once according to the aforementioned methods. Prior to cleaning, diffusive bodies were categorized based on the extent of visible dust coating using a five-point scale (0 – new, 1 – very low, 2 – low, 3 – moderate, 4 – high, and 5 – very high; see Fig. S3). To the extent this was possible with a limited stock of previously deployed Radiellos<sup>®</sup>, we evenly distributed Radiellos<sup>®</sup> of variable dust coating among the treatments (see Table S2 for details). We also tested Radiellos<sup>®</sup> previously deployed in contaminated environments with very high gaseous Hg concentrations ( $\sim 100\text{--}10\,000 \text{ ng m}^{-3}$ ) to assess whether such deployments led to a memory effect whereby sorbed Hg is released from the diffusive body during subsequent uses. All samplers from this “memory” treatment contained moderate dust coating and were not cleaned.

Five replicate samplers for each of the seven treatments were deployed for a period of 2 weeks in a laboratory with slightly elevated Hg concentrations (previously measured as  $\sim 5\text{--}10 \text{ ng m}^{-3}$ ) at the University of Toronto Scarborough. Additionally, five different replicate samplers for each of the three treatments new, uncleaned, and soap were exposed for 34 days outdoors on the campus of the University of Toronto Scarborough (43.78 714° N, 79.19 049° W). In this case, all previously used Radiellos<sup>®</sup> were heavily dust coated (category 4 or 5; see Table S3 for details). In both the indoor and outdoor experiment all samplers were deployed concurrently. Therefore, no active gaseous Hg measurements were necessary and the mass of sorbed Hg could be directly compared and was used in data analysis.

**Table 1.** Combinations of temperature and relative humidity during the eight experiments performed in climate-controlled chambers. The three relative humidity treatments were 44, 60, and 80 % while the temperature was held constant at 20 °C. All treatments were used for the temperature experiments.

Temp (°C)	−15.0 ± 0.1	5.0 ± 0.0	12.5 ± 0.1	19.9 ± 0.0	20.0 ± 0.1	20.0 ± 0.1	27.5 ± 0.0	35.0 ± 0.0
RH (%)	68 ± 1	77 ± 1	76 ± 2	44 ± 5	60 ± 1	80 ± 0	60 ± 1	45 ± 3



**Figure 1.** The effect of wind speed on the sampling rate of four different configurations of a passive air sampler for gaseous mercury. Configuration 1: white Radiello<sup>®</sup>, with protective shield (■, green); configuration 2: white Radiello<sup>®</sup>, without protective shield (◆, blue); configuration 3: yellow Radiello<sup>®</sup>, with protective shield (■, orange); configuration 4: white Radiello<sup>®</sup>, without protective shield (◆, red). Standard error of slope and y intercept are give in Table S1 in the Supplement.

## 2.2.4 Active gaseous mercury measurements

A Tekran 2537A (Tekran Instruments Corp.) was used to measure the gaseous Hg concentrations at 5 min intervals throughout all wind, temperature, and RH experiments. A sampling inlet that combined a 2 m Teflon tube connected to a 0.2 µm PTFE filter was used (detailed setup is given in Cole and Steffen, 2010; Steffen et al., 2008). Auto-calibrations were made using the internal Hg permeation unit every 25 h and these were verified through manual injections from a Tekran 2505 Mercury Vapor Primary Calibration Unit (Tekran Instruments Corp.) before and after each set

of experiments. Quality control and assurance of the Tekran 2537A data sets followed the Environment Canada Research Data Management and Quality Control system (Steffen et al., 2012).

## 2.2.5 Sampling rate calculation

SRs ( $\text{m}^3 \text{day}^{-1}$ ) were calculated using

$$\text{SR} = \frac{m}{(Ct)}, \quad (1)$$

where  $m$  is the mass of sorbed mercury (ng),  $C$  is the concentration of gaseous Hg measured by the Tekran 2537A

( $\text{ng m}^{-3}$ ), and  $t$  is the deployment time of the PAS (days). With the exception of the 3-month experiment, the SRs were derived from the sorbed Hg ( $m$ ) in individual PAS deployments using Eq. (1). SRs derived from a single deployment generally have a higher uncertainty than SRs derived from experiments involving multiple simultaneous deployments of variable length, such as those described in McLagan et al. (2016b). This uncertainty is further increased when deployment times are short and gaseous Hg concentrations are low, as  $m$  will be closer to quantification limits. In order to constrain the uncertainties from the experiments described here, we performed a high number of replications, which allows an average and SD for the SR of each deployment. In the wind experiments, true replication was not possible, as wind speed varied slightly between each deployment. While they cannot be called replicates, we performed a very large number of individual experiments, which allowed for the derivation of a robust relationship between SR and wind speed. Additionally, the variable length of the experiments at selected wind speeds not only added to the number of data points but also allowed us to assess if there was any effect of deployment time on SR.

### 2.3 Analyses

Total Hg in the activated carbon sorbent was quantified using thermal combustion, amalgamation, and atomic absorption spectroscopy in oxygen ( $\text{O}_2$ ) carrier gas (USEPA method 7473) using an AMA254 (Leco Instruments Ltd.) (USEPA, 2007). Because the sorbent in a PAS cannot be assumed to take up Hg homogeneously, the entire carbon from each PAS was analyzed in two aliquots of up to 0.45 g each. In order to increase the lifetime of AMA254 catalyst tubes while processing samples with high sulfur content, catalyst tubes were amended with 5 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\approx 0.15$  g of  $\text{Na}_2\text{CO}_3$  was added directly to each sample boat (McLagan et al., 2017). Samples were dried for 30 s at  $200^\circ\text{C}$  and thermally decomposed at  $750^\circ\text{C}$  for 330 s, while gaseous elemental Hg was trapped on the gold amalgamator. After combustion the system was purged for 60 s to ensure all pyrolysis gases were removed from the catalyst. Throughout the analysis the catalyst was heated to  $550^\circ\text{C}$ . After purging, the amalgamator was heated to  $900^\circ\text{C}$  for 12 s to release the trapped Hg into the cuvette where absorption at 253.65 nm was measured by dual detector cells for both low and high absolute amounts of Hg.

The instrument was calibrated by adding varying amounts of Hg liquid standard for AAS ( $1000 \pm 5 \text{ mg L}^{-1}$ ; in 10 % w/w HCl; Inorganic Ventures) to  $\approx 0.22$  g of clean (unexposed) HGR-AC. Approximately 0.15 g of  $\text{Na}_2\text{CO}_3$  was added on top of the liquid standard and HGR-AC. In all experiments absolute amounts of Hg were less than 20 ng and the high cell was therefore not required for quantification. The low cell calibration included standards of 0, 0.1, 0.25,

0.5, 1, 2.5, 5, 10, 15, and 20 ng of Hg (uncertainty in autotipette is  $1 \pm 0.004$  ng) fitted with a quadratic relationship.

### 2.4 Quality assurance and control

Both analytical and field blanks were included in all experiments. Analytical blanks represented analyses of clean HGR-AC with mean concentration of  $0.3 \pm 0.2 \text{ ng g}^{-1}$  of HGR-AC ( $n = 14$ ). Field blanks, taken both at the start and end of each experiment, were taken to the site, opened, deployed, and then immediately taken down, sealed with PTFE tape and stored for analysis in double resealable plastic bags. The mean field blank concentration for the wind experiments ( $n = 7$ ), the temperature/RH experiments ( $n = 5$ ), and the Radiello<sup>®</sup> reuse experiments ( $n = 4$ ) were  $0.5 \pm 0.2$ ,  $0.58 \pm 0.15$ , and  $0.38 \pm 0.08 \text{ ng g}^{-1}$  of HGR-AC, respectively. All results are blank adjusted by subtracting the mean field blank concentration for each experiment multiplied by the mass of HGR-AC in that sample from the sorbed Hg in each sample.

Analytical precision was monitored throughout the experiments (approximately every 10–15 instrumental runs) by analyzing 5 or 10 ng Hg liquid standards for AAS added to  $\approx 0.22$  g of HGR-AC. Recoveries for precision testing were  $100.1 \pm 1.6$  ( $n = 62$ ),  $100.0 \pm 1.3$  ( $n = 24$ ), and  $100.0 \pm 1.3$  ( $n = 21$ ) % for the wind, temperature/RH, and reuse experiments, respectively. Recovery was monitored throughout the experiments (approximately every 10–15 runs) by analyzing a high sulfur, bituminous coal standard reference material, NIST 2685c ( $S = 5 \text{ wt } \%$ ; National Institute of Standards and Technology), or our own in-house reference material, RM-HGR-AC1 (powdered HGR-AC loaded with Hg by exposure to air for 4 months then homogenized;  $23.1 \pm 0.8 \text{ ng g}^{-1}$  based on 198 analytical runs). Recoveries of NIST 2685c were  $101 \pm 3$  ( $n = 35$ ),  $102 \pm 3$  ( $n = 14$ ), and  $99 \pm 4$  ( $n = 10$ ) % for the wind, temperature/RH, and reuse experiments, respectively. Recoveries of RM-HGR-AC1 were  $98 \pm 3$  ( $n = 43$ ),  $97 \pm 2$  ( $n = 13$ ), and  $96 \pm 2$  ( $n = 10$ ) % for the wind, temperature/RH, and reuse experiments, respectively. All statistical tests were either performed by hand or using R v3.3.2 (R Foundation for Statistical Computing).

## 3 Results and discussion

### 3.1 Wind

The effect of wind speed on SR varied considerably across the four tested PAS configurations (Fig. 1). The greatest effect was observed for white Radiello<sup>®</sup> without protective shield (configuration 2), which is a configuration that is unlikely to be used in practice ( $r^2 = 0.91$ ;  $p < 0.001$ ;  $n = 44$ ). The positive linear relationship across the tested wind speed range (wind still to  $6 \text{ m s}^{-1}$ ) had a slope indicative of a  $0.022 \text{ m}^3 \text{ day}^{-1}$  (or 18 % of the calibrated SR) increase in SR for every  $1 \text{ m s}^{-1}$  increase in wind speed (Fig. 1). Previ-

ous investigators, using the white Radiello<sup>®</sup> (without protective shield) to monitor varying atmospheric contaminants, fitted logarithmic (Pennequin-Cardinal et al., 2005; Plaisance, 2011; Skov et al., 2007) or quadratic (Plaisance et al., 2004) relationships to data describing the effect of wind speed on SR. The SR was most sensitive at lower wind speed (typically  $< 1 \text{ m s}^{-1}$ ). However, due to the limited number or range of measured wind speeds, or high data uncertainty, a linear relationship fits some of these data equally well (McLagan et al., 2016a).

The addition of the protective shield (configuration 1), which is the current method of practice for the PAS, reduced the effect of wind speed on the SR, particularly at higher wind speeds. The best fit of the data was a logarithmic relationship (linear fit:  $r^2 = 0.83$ ;  $p < 0.001$  for exponentially transformed data;  $n = 52$ ) in which SR was most sensitive to wind speed between 0 and  $1 \text{ m s}^{-1}$  (Fig. 1). While average wind speeds of less than  $1 \text{ m s}^{-1}$  are common for indoor deployments, outdoors average wind speeds typically exceed  $1 \text{ m s}^{-1}$  (98.3 % of data from  $0^\circ 10'$  resolution global data set of monthly averaged wind speeds at 10 m a.g.l. between 1961 and 1990; New et al., 2002). When we consider only the data  $> 1 \text{ m s}^{-1}$  we observe a slight, but significant, positive linear relationship between SR and wind speed ( $r^2 = 0.21$ ;  $p = 0.006$ ;  $n = 34$ ) corresponding to a  $0.003 \text{ m}^3 \text{ day}^{-1}$  (or 2.5 % of the previously calibrated SR) increase in SR for every  $\text{m s}^{-1}$  increase in wind speed (Fig. 1). Neither configuration with the thicker, yellow Radiello<sup>®</sup> led to a significant effect ( $p > 0.05$ ) of wind speed on SR (Fig. 1). When the protective shield is in place the SR was approximately 10 % lower than without the protective shield for the yellow Radiello<sup>®</sup>. Plaisance (2011) also noted a negligible effect of wind speed on SR using a yellow Radiello<sup>®</sup> PAS without any protective shield when monitoring benzene.

The importance of a diffusive barrier is illustrated by the very strong effect of wind speed on the SR of another PAS for gaseous Hg that also utilizes an activated carbon sorbent, but has no diffusive barrier: the SR increased by  $0.126 \text{ m}^3 \text{ day}^{-1}$  (or 97 % of the calibrated SR) for every  $\text{m s}^{-1}$  increase in wind speed (Guo et al., 2014; Zhang et al., 2012). This information and the results here demonstrate the merit of employing both diffusive barriers and protective shields in reducing the effect of wind speed on SR. The diffusive path length of the PAS has three components: (1) the ASBL, (2) the diffusive barrier (adjusted for the porosity of the diffusive barrier), and (3) the internal airspace of the Radiello<sup>®</sup> (McLagan et al., 2016b). Employing a thicker, less porous diffusive barrier (yellow Radiello<sup>®</sup>) increases the diffusive path length of the diffusive barrier component, in turn reducing the SR. By reducing turbulence on the outside of the diffusive barrier, the protective shield essentially increases the thickness of the ASBL (McLagan et al., 2016b), leading to a reduction in SR.

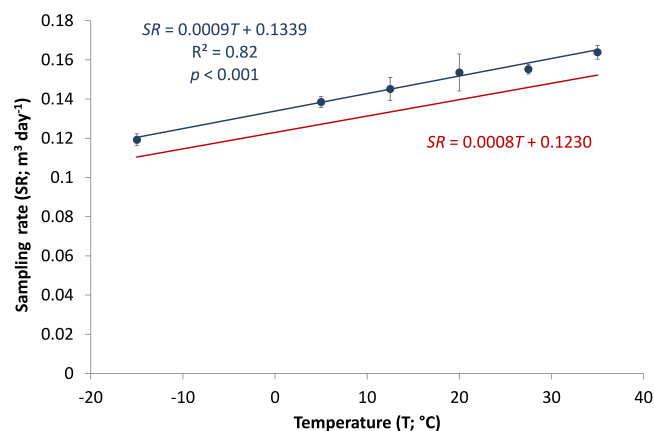
Because the samplers were not exposed to exactly the same wind speeds, it is not possible to construct up-

take curves from the experiments with variable deployment length. It is, however, possible to test whether the measured SRs depend on the length of each PAS deployment. The relationship between deployment length and SR was not significant ( $p > 0.05$ ), irrespective of the applied wind speed (wind still,  $\sim 3$ , and  $\sim 6 \text{ m s}^{-1}$ ) or configuration (1 and 2); see Fig. S4 for details. This confirms that the SRs derived from short 1-week deployments were neither biased high or low.

The 3-month uptake experiment under wind-still conditions produced a SR of  $0.106 \pm 0.009 \text{ m}^3 \text{ day}^{-1}$  when calculated as the average of each PAS deployment (see Fig. S5 for uptake curve). The slope of the regression of  $m$  against  $C \times t$  (McLagan et al., 2016b; Restrepo et al., 2015) gave a very similar SR of  $0.109 \pm 0.009 \text{ m}^3 \text{ day}^{-1}$ . Because the latter method is thought to give a slightly more reliable SR (McLagan et al., 2016b; Restrepo et al., 2015), we suggest using this SR for indoor deployments of the PAS using the white Radiello and a protective shield (configuration 1). This SR is 9.9 % lower than the SR obtained in an earlier outdoor calibration study, despite the higher temperature ( $\sim 23^\circ \text{C}$ ) indoors than outdoors (mean temperature across all deployments:  $7.6^\circ \text{C}$ ). Additionally, the replicate precision of samplers from this uptake experiment for the wind-still data with the protective shield ( $11 \pm 8 \%$ ) was significantly poorer ( $p < 0.001$ ) than in the outdoor calibration study with the same sampler setup ( $2 \pm 1.3 \%$ ; mean wind speed  $1.89 \text{ m s}^{-1}$ ) (McLagan et al., 2016b). Both the lower SR and the greater uncertainty of the SR are consistent with the effect of wind observed for this configuration (green markers in Fig. 1): at the low wind speeds of indoor deployments ( $< 1 \text{ m s}^{-1}$ ), the SR is expected to be both lower and more sensitive to changes in wind speed. Although, conditions for this experiment were labelled “wind still”, in reality any activity within the laboratory (movement of lab personnel, opening and closing of doors, etc.) will result in small variations in wind speeds around the PAS within the range where the SR is most sensitive to such variations (Zhang et al., 2013). Thus, for indoor deployments of the passive sampler, especially using the white Radiello<sup>®</sup>, we can expect somewhat less precise results. The effect of laboratory activity may also cause disturbances in the wind measured at higher wind speed treatments. Wind speeds could only be measured for 5 min before and after each experiment and there may be some difference between measured and actual average wind speed for each deployment. These issues may have contributed to the higher variability in the wind experiments compared to the temperature and relative humidity experiments (see below), which were conducted in closed chamber experiments.

### 3.2 Temperature and relative humidity

Relative humidity, tested at 44, 60, and 80 % and a stable temperature of  $20^\circ \text{C}$ , had no significant effect on SR ( $r^2 = 0.11$ ;  $p = 0.080$ ;  $n = 13$ ; see Fig. S6), which is sim-



**Figure 2.** The effect of temperature on the sampling rate of a passive air sampler for gaseous mercury as determined experimentally (blue) and as calculated using the diffusion model (red) by McLagan et al. (2016b). The measured and calculated temperature dependence, given by the slopes of the relationships, is not significantly different.

ilar to Guo et al. (2014), who also observed no effect from relative humidity on the SR of their PAS that uses the same sulfur-impregnated activated carbon sorbent. It is therefore appropriate to analyze the effect of temperature on SR despite small variations in RH at different temperatures. We observed a significant, positive, linear relationship between SR and temperature ( $r^2 = 0.82$ ;  $p < 0.001$ ;  $n = 36$ ; Fig. 2) corresponding to a  $0.001 \text{ m}^3 \text{ day}^{-1}$  increase in SR for every  $1^\circ\text{C}$  increase in temperature (or  $0.7\%$  of the calibrated SR). This relationship remained linear across the tested range from  $-15$  to  $35^\circ\text{C}$ .

Temperature can affect the SR because of its impact on (i) the partitioning equilibrium between the sorbent and the gas phase and (ii) the diffusion coefficient (McLagan et al., 2016a; Pennequin-Cardinal et al., 2005). The uptake capacity of the HGR-AC for gaseous Hg is extremely high and we suspect that any change in the sorption equilibrium caused by changing temperatures should have a negligible effect on the SR. The increase in diffusivity caused by an increase in temperature is easily quantified. Figure 2 also displays SR as a function of temperatures predicted with a previously described model based on Fick's first law of diffusion (McLagan et al., 2016b). While the predicted SRs are  $\sim 8\%$  lower than the measured ones, the slope of the relationship between SR and temperature is the same (no significant difference,  $z$  score test,  $p = 0.427$ ), confirming that the effect of temperature on the diffusivity of gaseous Hg is sufficient to explain the observed temperature dependence of the SR.

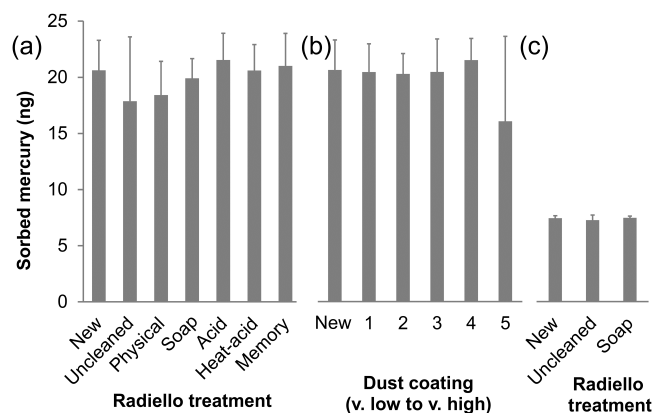
Earlier studies on PAS for gaseous Hg did not observe an effect of temperature on SR in laboratory chamber experiments. Guo et al. (2014) found no significant effect of temperature on the SR of their activated carbon-based PAS between  $-10$  and  $+35^\circ\text{C}$ . Similarly, there was no effect of

temperature on the SR of a PAS using a solid gold sorbent and a white Radiello<sup>®</sup> diffusive body (Skov et al., 2007). In neither case, however, was the precision of the measurement sufficient to detect the small dependence of SR on temperature caused by the effect of temperature on diffusivity. Such a small temperature effect can only be detected in a highly precise sampler.

### 3.3 Radiello<sup>®</sup> reuse

In the Radiello<sup>®</sup> reuse experiment conducted indoors, no significant difference in the amount of sorbed Hg was observed between new, uncleaned, or any of the cleaned Radiellos<sup>®</sup> (ANOVA,  $p = 0.467$ ; Fig. 3a). Similarly, when we ignore the effect of cleaning, no significant difference in the sorbed amount of Hg was observed between Radiellos<sup>®</sup> with different degrees of dust coatings, including the new Radiellos<sup>®</sup> (ANOVA,  $p = 0.841$ ; Fig. 3b). The cleaning treatments also did not differ in terms of the observed variances (Levene's test,  $p = 0.307$ ). However, the amount of Hg taken up in Radiellos<sup>®</sup> with the most dust (category 5) had a significantly higher variance than all other treatments ( $p = 0.004$ , Levene's test with Tukey's honest significant difference post hoc test). Although the differences between all Radiello<sup>®</sup> treatments in the indoor Radiello<sup>®</sup> reusability experiments are small, the significantly higher variability observed for Radiellos<sup>®</sup> with the highest dust coating suggests some form of cleaning would be better in maintaining the high level of precision of this PAS. Effect size, using Cohen's  $d$  value (see Sect. S5), was then applied to examine differences in treatments without the use of traditional binary hypotheses testing (See Table S4). In comparison to new Radiellos<sup>®</sup> soap, acid, and heat-acid were the most effective treatments. While there was no significant difference in means (ANOVA;  $p = 0.548$ ) or variances (Levene's test;  $p = 0.221$ ) for the outdoor experiment testing new, uncleaned, and soap Radiellos<sup>®</sup>, effect size analysis (see Sect. S5) confirmed that soap cleaning is an effective method in preparing used Radiellos<sup>®</sup> for redeployment (Fig. 3c).

Uptake of Hg in uncleaned Radiellos<sup>®</sup> previously deployed in gaseous Hg concentrations 2–4 orders of magnitude higher than the other Radiellos<sup>®</sup> (memory treatment) was also not significantly different from any of the other treatments in terms of mean (ANOVA:  $p = 0.499$ ) or variance (Levene's test:  $p = 0.307$ ; Fig. 3a). This implies that very little Hg was sorbed to the Radiello<sup>®</sup> and re-released during the subsequent deployment and that gaseous Hg has little affinity for the porous high-density polyethylene diffusive membrane of the Radiello<sup>®</sup>.



**Figure 3.** Mean sorbed mercury for differing Radiello® cleaning treatments and at varying degrees of HGR-AC dust coating inside the Radiello® (panel b) from indoor experiment. Cleaning treatments and degree of dust coating is described in Sect. 2.2.3. Panel (a) also includes the memory effect treatment, which were uncleaned Radiellos® from deployments in a high concentration environment. Panel (c) presents the mean sorbed mercury for differing Radiello® cleaning treatments from outdoor experiment.

#### 4 Recommendations and conclusions

While the SR of the PAS in its standard configuration (white Radiello® with protective shield) was found to depend on both wind speed and temperature, the effects are both small and predictable. The accuracy of volumetric air concentrations derived from the PAS can be improved by applying adjustment factors to the SR, especially for deployments at or close to background gaseous Hg concentrations. The SR of the standard configuration PAS (white Radiello® with shield) deployed outdoors of  $0.121 \text{ m}^3 \text{ day}^{-1}$  was obtained for a mean wind speed of  $1.89 \text{ m s}^{-1}$  and a mean temperature of  $7.6^\circ\text{C}$ .<sup>15</sup> We recommend to use the increments from Figs. 1 and 2, i.e.  $0.003 \text{ m}^3 \text{ day}^{-1}$  increase in SR for every  $\text{m s}^{-1}$  increase in wind speed and  $0.001 \text{ m}^3 \text{ day}^{-1}$  increase in SR for every  $1^\circ\text{C}$  increase in temperature to adjust the SR of  $0.121 \text{ m}^3 \text{ day}^{-1}$  to the average temperature and wind speed of each PAS deployment (See Sect. S6 for SR adjustment equation and sample calculation).

The experiments here predict a SR of  $0.142 \text{ m}^3 \text{ day}^{-1}$  for an average wind speed of  $1.89 \text{ m s}^{-1}$  (Fig. 1) and a SR of  $0.141 \text{ m}^3 \text{ day}^{-1}$  for an average temperature of  $7.6^\circ\text{C}$  (Fig. 2). Both these values are greater than the SR of  $0.121 \text{ m}^3 \text{ day}^{-1}$  from the calibration study (McLagan et al., 2016b). While we presently do not know the reason for this discrepancy, it may be related to the relatively short deployment periods used in the present experiments. As mentioned above, short deployment at background concentrations yield a SR with a higher uncertainty. Also, McLagan et al. (2016b) observed that SR for PAS deployed outdoors for less than 1–2 months were higher than the SR derived for the entire 1-year sampling period. Despite this slight discrepancy, we note that the  $y$  inter-

cepts of the relationships reported here (the magnitude of the SR) are less important than their slopes (i.e. the temperature and wind speed adjustment factors). An ongoing study measuring the uptake of gaseous Hg in PASs deployed at several locations with widely different temperature and wind speed conditions will help refine both the SR applicable to outdoor deployments and the validity of the laboratory derived adjustment factors for temperature and wind speed reported here.

When designing a PAS, there is a need to strike a balance between maximizing the SR and minimizing the variability in the SR caused by factors such as wind speed, objectives that are contradictory in nature (McLagan et al., 2016a). Although using a thicker, yellow Radiello® with or without a protective shield are the methods least affected by wind, the SR for these methods is approximately half that of the white Radiello® with a shield. A lower SR translates to lower amounts of sorbed Hg, which means that longer deployments are required to reach method quantification limits (MQL). The PAS configuration with white Radiello® and protective shield needs to be exposed to typical background concentrations of gaseous Hg ( $\sim 1.5\text{--}2 \text{ ng m}^{-3}$ ) for approximately 1 week to reach levels above MQL (McLagan et al., 2016b). A PAS with yellow Radiello would presumably require deployments twice as long. For either configuration, longer deployments of a month or more are likely to yield greater accuracy. Given the possibility of adjusting the SR for the slight effect caused by wind speeds above  $1 \text{ m s}^{-1}$  and the shorter minimum deployment times, we recommend the PAS configuration with a shielded white Radiello for most outdoor deployments. Nonetheless, there may be long deployments under highly variable winds that warrant the use of the yellow Radiello®. A full long-term calibration study outdoors would be advisable prior to using this configuration.

Finally, our results suggest that previously deployed Radiello® are indeed reusable as long as the Radiellos® are cleaned between deployments. Because the different cleaning methods were generally equally effective, we recommend the use of the soap method because of its overall ease and health, safety, and waste benefits over using acids (Anastas and Warner, 1998). Additionally, Gustin et al. (2011) suggested the porosity of high-density polyethylene diffusive barriers can be affected by cleaning with HCl. While in this study we used  $\text{HNO}_3$  for cleaning purposes, the possibility of porosity changes caused by acid cleaning is further incentive to clean previously used Radiellos® with soap rather than acid or heat-acid treatments.

*Data availability.* Data can be found in the paper, the Supplement, or via communication with the corresponding author.

**The Supplement related to this article is available online at <https://doi.org/10.5194/amt-10-3651-2017-supplement>.**



*Competing interests.* The authors declare that they have no conflicts of interest.

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