REFEREE COMMENT: I think this is a well-written paper that reports on a well-designed set of experiments. It provides new and valuable information for those who might wish to use the mercury passive sampling method developed by this research group. I think it deserves publication in AMT.

AUTHOR RESPONSE: We appreciate the support of the presented research.

REFEREE COMMENT: I only have a few comments beyond those that have already been brought up by the other reviewers: At the end the authors talk about how the observed sampling rate was lower in their laboratory experiments than they observed in the field, and they offer a number of explanations for this. One possibility I think they should consider is that the sampler behaves differently in outdoor environments because of gas-phase and particle-phase constituents of ambient air that exist at much lower concentrations in a laboratory environment.

AUTHOR RESPONSE: The sampling rate derived from the laboratory experiments presented in the manuscript (0.141-0.142 m^3 day^{-1}) was actually **higher** (not lower) than the sampling rate measured outdoors in the previous calibration study (0.121 m^3 day^{-1}) (1). While we concede that it is conceivable, though not very likely, that the presence of other air atmospheric constituents is influencing the kinetics of mercury uptake in the sampler, that presence would need to explain a decrease in sampling rate rather than an increase.

REFEREE COMMENT: It is possible that some gases in the atmosphere react with mercury or mercury compounds on or in the charcoal sorbent, or perhaps take up active sites on the charcoal, driving mercury back into the gas phase.

AUTHOR RESPONSE: The form of mercury originally sorbed to the carbon (gaseous Hg, most likely elemental Hg) is the most volatile form of Hg. Any reaction that sorbed Hg might undergo with atmospheric gases, thus would presumably yield less volatile, oxidised Hg species that are less likely to be lost from the carbon.

The sulphur impregnated activated carbon has a very high capacity for gaseous Hg. The carbon can sorb up to ≈15, 45 and 120 µg Hg g^{-1} carbon when in equilibrium with high gas-phase Hg concentrations of 110, 380 and 1080 µg m^{-3}, respectively (2). In our own year-long deployment experiment, conducted in an urban atmosphere presumably abundant in other air pollutants, uptake remained linear for an entire 1 year with a total of ≈100 ng Hg g^{-1} carbon (1). In unpublished work, uptake in the sampler remained linear after a week of sampling at concentrations of ≈7.5 µg m^{-3} and the carbon took up ≈7.2 µg Hg g^{-1} carbon. All of this indicates that during the outdoor deployment that yielded a sampling rate of 0.121 m^3 day^{-1}, the carbon was extremely far from saturation, i.e. far from having all active sites taken up.

Overall, we believe the weight of evidence supports the assertion that (1) Hg, once sorbed to the carbon in the sampler, will remain sorbed, and (2) that the uptake kinetics of the sampler is not limited by its uptake capacity.

REFEREE COMMENT: It is also possible (and more likely, I think) that particulate matter deposits in the pores of the Radiello sampler body, closing off the diffusive pathway and reducing the uptake rate (or sorbing Hg before it can make it to the sorbent cartridge). Figure 3 shows that uncleaned Radiellos had a lower mean mercury loading than new or cleaned Radiellos. The variability was high, so the difference was not significant, but statistical noise may be covering up an important behavior of the sampler that needs to be investigated in future studies.

AUTHOR COMMENT: We suggest that caution is required when trying to interpret the results displayed in Figure 3 in terms of the influence of atmospheric particulate matter on uptake kinetics. The amount

of particulate matter that has been deposited on the Radiellos via dust from the carbon far outweighs that from atmospheric aerosols. We were able to visibly see the dust-related particulate matter inside the Radiellos *[to demonstrate this an additional section has been added to the SI, showing how we graded the various dust coatings of the Radiellos for the experiments]*. Thus, the very high dust coatings represent an extreme scenario that is not likely to occur during routine sampling, especially not as a result of deposition of airborne particulate matter.

While the referee correctly notes the high variance in the indoor experiments, we note that the second highest dust-coated Radiello grouping actually had a slightly higher amount of sorbed Hg (although not significant) than the new Radiellos. It was only at the highest coating (extremely dirty Radiellos) that particles appeared to reduce the porosity of the Radiello. Also, these experiments were conducted indoors in a small lab with only one ventilation unit and under slightly elevated gaseous Hg conditions (5-10 ng m^{-3}). Airflow within this room is not consistent and hence gaseous Hg concentrations are likely not entirely homogenous, which is likely to have contributed to some of the higher variance. This can be seen more clearly in comparison to the outdoor component of this experiment (Fig 3 C), where the variance is much lower and the *uncleaned* Radiellos are only very marginally (and not significantly) lower than the *new* or *soap* treatments.

REFEREE COMMENT: I am confused by the sentence that starts on line 309. I don't understand how the authors calculated the sampling rate "as the average of single point calibrations." My guess about what they mean is that they calculated the sampling rate of several samplers by comparing against the Tekran, and then averaged those values. I think it would be good to reword this.

AUTHOR COMMENT: To improve clarity, we have made changes in the three places in the manuscript that referred to "single point calibrations":

Line 202: "With the exception of the 3-months experiment, the *SRs* were derived from *the sorbed Hg (m) in individual PAS deployments* using Eq. (1)."

Line 309: "It is, however, possible to test whether the measured *SRs* depend on the length of *each PAS deployment*."

Line 315: "The 3-month uptake experiment under wind-still conditions produced a *SR* of 0.106 ± 0.009 m^3 day^{-1} when calculated as the average of *each PAS deployment* (see Fig. S4 for uptake curve)."

An addition to Line 208 was also made for further clarification: *"Nevertheless, to constrain the uncertainties from the experiments described here, we performed a high number of replications, which allows an average and standard deviation for the SR of each deployment"*

REFEREE COMMENT: The authors point out that Hg passive samplers developed by others have greater variability, obscuring the temperature relationship this paper was able to show. However, if the other studies the authors mention used measurements collected in outdoor conditions to look for temperature relationships, their results would likely contain more variability than the controlled indoor conditions used in this study, so the comparison would be unjustified.

AUTHOR COMMENT: Both the instances of the variability in other samplers caused by temperature mentioned (Guo et al.(3) and Skov et al.(4)) were determined from indoor deployments of their passive samplers in chamber experiments at various temperature treatments. To clarify this the following has been added to line 360: "Earlier studies on PAS for gaseous Hg did not observe an effect of temperature on *SR in laboratory chamber experiments.*"

REFEREE COMMENT: I am struck by the very low variability in Figure 2 compared to the apparently much higher variability in Figure 1. I think the authors don't comment enough on the high variability in their wind experiments. My best guess about what is going on is that the wind speed was not constant over time in the wind experiments. Since wind speed was only measured for 5 minutes at the beginning and again at the end of each weeks-long experiment, the real wind speed during these experiments in not known with a great deal of certainty. I think it would be useful to add a bit more discussion of the highly variable wind measurements.

AUTHOR COMMENT: To improve clarity, the following statement has been added to line 335: "*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 mins 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 SRs in the wind experiments compared to the temperature and relative humidity experiments (see below), which were conducted in closed chamber experiments*."

REFEREE COMMENT: The authors touch on the high sensitivity of the sampling rate to wind speeds below 1 m/s, but they didn't make measurements in that range. Passive samplers, including the Radiello, are often used in indoor environments. I would like to see the authors include an explicit statement about this limitation of the sampler when it is used in indoor environments.

AUTHOR COMMENT: The following has statement been added to line 333: "*Thus, for indoor deployments of the passive sampler, especially using the white Radiello®, we can expect somewhat less precise results*."

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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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12 **ABSTRACT**

13 Passive air sampling of gaseous mercury (Hg) requires a high level of accuracy to discriminate

14 small differences in atmospheric concentrations. Meteorological parameters have the potential

15 to decrease this accuracy by impacting the sampling rate (*SR*), i.e., the volume of air that is

16 effectively stripped of gaseous mercury per unit of time. We measured the *SR* of a recently

17 calibrated passive air sampler for gaseous Hg in the laboratory under varying wind speeds

18 (wind-still to 6 m s^{-1}), temperatures (-15 to +35 °C), and relative humidities (44 to 80 %). While

19 relative humidity has no impact on *SR*, *SR* increases slightly with both wind speed (0.003 m^3

20 day^{-1} increase in *SR* or 2.5 % of the previously calibrated *SR* for every m s^{-1} increase for wind

21 speeds > 1 m s^{-1}, typical of outdoor deployments) and temperature (0.001 m^3 day^{-1} increase in

22 *SR* or 0.7 % for every 1 °C increase). The temperature dependence can be fully explained by the

23 effect of temperature on the molecular diffusivity of gaseous mercury in air. Although these

24 effects are relatively small, accuracy can be improved by adjusting *SR*s using measured or

25 estimated temperature and wind speed data at or near sampling sites. We also assessed the

26 possibility of reusing Radiello® diffusive barriers previously used in the passive air samplers. The

27 mean rate of gaseous Hg uptake was not significantly different between new and previously

28 used diffusive barriers in both lab and outdoor deployments, irrespective of the applied

29 cleaning procedure. No memory effect from Radiellos® previously deployed in a high Hg

30 atmosphere was observed. However, a loss in replicate precision for the dirtiest Radiellos® in

31 the indoor experiment suggests that cleaning is advisable prior to reuse.

32 **KEYWORDS**

33 Passive air sampling, Hg, atmosphere, calibration, green chemistry

2

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

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62   diffusive barrier are often employed to further reduce the influence of wind by reducing the

63   face velocities at these surfaces. However, like diffusive barriers, they too are not likely to

64   completely eliminate the influence of wind on the thickness of the ASBL (Huang et al., 2014).

65   Temperature has the potential to affect *SR* in two ways: (i) changing the rate of gas phase

66   diffusion of the contaminant due to the temperature dependence of molecular diffusion

67   coefficients (Armitage et al., 2013; Huang et al., 2014; Lozano et al., 2009); and (ii) shifting the

68   partitioning equilibria between the sorbent and the gas phase (Armitage et al., 2013; Lozano et

69   al., 2009; McLagan et al., 2016a). Relative humidity (RH) may affect *SR*s by influencing the

70   sorptive properties of certain sorbents for target analytes (Huang et al., 2014). Other factors

71   that may affect the sorption of contaminants to PAS sorbents include passivation of sorbents

72   (interfering compounds blocking sorbent uptake sites or stripping analytes through reaction)

73   (Brown et al., 2012; Gustin et al., 2011), degradation of the sorbent over time (Brown et al.,

74   2011; McLagan et al., 2016a), and uptake of the contaminant to the sampler housing or

75   diffusive barrier (Gustin et al., 2011; Huang et al., 2014; McLagan et al., 2016a).

76   Mercury is a persistent, bioaccumulative, and toxic contaminant of global concern that has

77   come under greater international scrutiny with the adoption of the Minamata Convention

78   (UNEP, 2013). A key stipulation under Article 19 of the convention "Research, Development and

79   Monitoring" is the requirement of participating parties to improve current monitoring networks

80   (UNEP, 2013). A PAS for measuring atmospheric Hg could play an important role in this context,

81   if it can be shown to be suitable for monitoring long-term background concentrations,

82   concentration gradients in and around Hg sources, and personal exposure levels (McLagan et

83   al., 2016a). Gaseous elemental Hg (GEM) is generally the dominant form of atmospheric Hg

84   (typically making up >95 %), due to its high atmospheric residence time of ~1 year (Driscoll et

85   al., 2013; Pirrone et al., 2010; Selin, 2009), especially at sites remote from combustion sources

86   (McLagan et al., 2016a; Peterson et al., 2009; Rutter et al., 2009). The long atmospheric

87   residence time of GEM results in fairly uniform background concentrations within each

88   hemisphere, with much of the global atmosphere having levels within <25 % of the hemispheric

89   average (Gustin et al., 2011). PASs capable of discriminating such small concentration variability

90 require high accuracy and precision, i.e. *SR*s need to be well characterized and repeatable.
91 Existing PASs for gaseous mercury have struggled to achieve the accuracy and precision
92 necessary for background monitoring due to inadequate detection limits or highly variable SRs
93 (Huang et al., 2014; McLagan et al., 2016a).

94 We recently introduced a PAS for gaseous Hg with a precision based uncertainty of 2 ± 1 % that
95 uses an activated carbon sorbent and a Radiello® diffusive barrier (McLagan et al., 2016b).
96 While it is believed that the sampler takes up predominantly GEM, we cannot rule out the
97 possibility for gaseous oxidized Hg to also pass through the diffusive barrier (McLagan et al.,
98 2016b). We therefore use the term gaseous Hg to define the target analyte. An earlier
99 calibration of this PAS at one outdoor location yielded a *SR* of 0.121 m^3 day^{-1} (McLagan et al.,
100 2016b). Here we report on a series of laboratory experiments that quantified the effect of wind
101 speed, temperature, and RH on the *SR* of that sampler. We additionally explored the possibility
102 of reusing the Radiello® diffusive barrier in multiple deployments in order to further reduce the
103 costs associated with the sampler's use. During deployment, the inside of the Radiello® can
104 become covered in sorbent dust. It is also possible that atmospheric components, e.g.
105 atmospheric particulate matter and oxidants, sorb to or react with the diffusive barrier during
106 deployment. Thus, in addition to meteorological impacts on the PAS's SR, we also explored the
107 effect of prior use and cleaning of the diffusive barrier on the uptake of Hg in the PAS.

108 **2. METHODS**

109 **2.1 Sampler Design**

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

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2.2 Study Design

118 *2.2.1 WIND.* PAS in four different configurations were exposed to different wind conditions in

119 the laboratory at the University of Toronto Scarborough: (1) regular, white Radiello® with

120 windshield, (2) white Radiello® without windshield, (3) thick-walled, less porous, yellow

121 Radiello® with windshield, and (4) yellow Radiello® without windshield. Adopting the

122 experimental setup of Zhang et al. (2013), electronic fans (Delta Electronics Inc., model number:

123 BFC1212B) were employed to generate wind for each individual sampler. The angle of wind

124 incidence was always 90°, i.e. we simulated wind that is blowing parallel to the surface. Wind

125 speeds of 1, 1.5, 2, 3, 4, 5, and 6 m s^{-1} were achieved by manipulating the distance between

126 PASs and fan (see Fig. S1 and Fig. S2). For each wind speed triplicate PASs were deployed. Wind

127 speeds for each individual PAS were measured every 5 seconds with a hot-wire

128 Anemometer/Thermometer (Traceable®, VWR International) for five minutes before and five

129 minutes after each deployment. As such, average wind speeds of individual samplers within

130 each wind speed treatment varied slightly (Fig. 1). "Wind-still" experiments without fans were

131 performed for comparison (with wind speed assumed to be 0.05 m s^{-1}).

132 While experiments with white Radiellos (configuration 1 and 2) generally lasted one week,

133 additional experiments lasting two, three, and four weeks were performed at selected wind

134 speeds (3 and 6 m s^{-1}). Experiments with yellow Radiellos (configurations 3 and 4) lasted two

135 weeks (the lower *SR* of yellow Radiello® requires longer deployment times to reach detection

136 limits) and were only performed at wind speeds of 3 and 6 m s^{-1}, as well as without fans.

137 Additionally, a 3 months uptake experiment under wind-still conditions was performed in order

138 to obtain a precise *SR* of the PAS with a white Radiello deployed indoors with a protective

139 shield. Eighteen samplers were deployed at the same time and triplicates were removed after

140 15, 28, 46, 56, 70 and 84 days. The earlier indoor calibration experiment described in McLagan

141 et al. (2016b) had been performed without a windshield.

142 Temperature and RH, monitored before, after, and periodically during each individual

143 experiment, ranged from +21.9 to +24.2 °C and from 32 – 53 %. While there was some variation

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144   in the gaseous Hg concentration as recorded by the Tekran 2537A between deployments, the

145   average concentration across all wind experiments was 1.9 ± 0.3 ng m^{-3}.

146   *2.2.2 TEMPERATURE & RELATIVE HUMIDITY.* The regular PAS configuration (configuration 1)

147   was exposed to eight different combinations of temperature and RH (Table 1) for two weeks

148   periods in climate controlled walk-in chambers located at the Biotron Facility of Western

149   University in London, Ontario. Each treatment included five replicates, all deployed in the same

150   chamber over the same time period. Samplers were attached to metal shelving units near the

151   centre of the chambers where a continuous flow of air from the outflow of the climate control

152   units of $1.1 - 2.3$ m s^{-1} was observed using the hot-wire Anemometer over a two minute period

153   at the completion of each experiment. The average actively measured gaseous Hg

154   concentration across all temperature and RH experiments was 2.2 ± 0.9 ng m^{-3}.

155   **Table 1: Table 1: Combinations of temperature and relative humidity during the eight experiments**
156   **performed in climate-controlled chambers. The three relative humidity treatments were 44, 60, and**
157   **80 % while the temperature was held constant at 20 °C. All treatments were used for the temperature**
158   **experiments**

Temp (°C)	$-15.0_{\pm0.1}$	$5.0_{\pm0.0}$	$12.5_{\pm0.1}$	$19.9_{\pm0.0}$	$20.0_{\pm0.1}$	$20.0_{\pm0.1}$	$27.5_{\pm0.0}$	$35.0_{\pm0.0}$
RH (%)	$68_{\pm1}$	$77_{\pm1}$	$76_{\pm2}$	$44_{\pm5}$	$60_{\pm1}$	$80_{\pm0}$	$60_{\pm1}$	$45_{\pm3}$

159   *2.2.3 RADIELLO® REUSE.* The potential impacts of sorbent dust accumulation or atmospheric

160   contamination during prolonged deployment periods on sampling rates and therefore on the

161   ability to reuse the Radiello® diffusive barriers are unknown. Currently, new diffusive barriers

162   are used for each deployment. In this experiment, previously used Radiellos® were redeployed

163   after different cleaning procedures were applied. Six cleaning treatments were applied: *new*

164   (unused Radiellos®), *uncleaned* (unaltered after previous deployments), *physical* (physical

165   agitation with funnel brushes and compressed air blow down), *soap* (Citranox® detergent,

166   cleaning brushes, and deionized water, compressed air blow down, deionized water rinse and

167   sonication and air drying), *acid* (six hour soak in 20 % HNO$_3$ bath, deionized water rinse,

168   compressed air blow down, deionized water rinse and sonication and air drying), and *heat-acid*

169   (six hour soak in 20 % HNO$_3$ bath at 40 °C, deionized water rinse, compressed air blow down,

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170   deionized water rinse and sonication and air drying). All Radiellos® in each cleaning treatment

171   were cleaned once according to the aforementioned methods. Prior to cleaning, diffusive

172   bodies were categorized based on the extent of visible dust coating using a 5-point scale (0 –

173   new, 1 – very low, 2 – low, 3 – moderate, 4 – high, and 5 – very high; see Fig. S3). To the extent

174   this was possible with a limited stock of previously deployed Radiellos®, we evenly distributed

175   Radiellos® of variable dust coating among the treatments (see Table S2 for details). We also

176   tested Radiellos® previously deployed in contaminated environments with very high gaseous Hg

177   concentrations (~100 – 10000 ng m^{-3}) to assess whether such deployments led to a memory

178   effect whereby sorbed Hg is released from the diffusive body during subsequent uses. All

179   samplers from this *memory* treatment contained moderate dust coating and were not cleaned.

180   Five replicate samplers for each of the 7 treatments were deployed for a period of two weeks in

181   a laboratory with slightly elevated Hg concentrations (previously measured as ~5-10 ng m^{-3}) at

182   the University of Toronto Scarborough. Additionally, five different replicate samplers for each

183   of the three treatments *new*, *uncleaned*, and *soap* were exposed for 34 days outdoors on the

184   campus of the University of Toronto Scarborough (43.78714 °N, 79.19049 °W). In this case, all

185   previously used Radiellos® were heavily dust coated (category 4 or 5, see Table S3 for details).

186   In both the indoor and outdoor experiment all samplers were deployed concurrently.

187   Therefore, no active gaseous Hg measurements were necessary and the mass of sorbed Hg

188   could be directly compared and was used in data analysis.

189   *2.2.4 ACTIVE GASEOUS MERCURY MEASUREMENTS.* A Tekran 2537A (Tekran Instruments Corp.)

190   was used to measure the gaseous Hg concentrations at 5 min intervals throughout all wind,

191   temperature and RH experiments. A sampling inlet that combined a 2 m Teflon tube connected

192   to a 0.2 µm PTFE filter was used (detailed setup is given in: (Cole and Steffen, 2010; Steffen et

193   al., 2008)). Auto-calibrations were made using the internal Hg permeation unit every 25 hrs and

194   these were verified through manual injections from a Tekran 2505 Mercury Vapor Primary

195   Calibration Unit (Tekran Instruments Corp.) before and after each set of experiments. Quality

196   control and assurance of the Tekran 2537A data sets followed the Environment Canada

197   Research Data Management and Quality Control system (Steffen et al., 2012).

198 *2.2.5 SAMPLING RATE CALCULATION. SRs* (m^3 day^{-1}) were calculated using:

199 $$SR = {}^{m}\!/_{(C\,t)} \qquad\qquad\qquad\qquad (1)$$

200 where *m* is the mass of sorbed mercury (ng), *C* is the concentration of gaseous Hg measured by

201 the Tekran 2537A (ng m^{-3}), and *t* is the deployment time of the PAS (days). With the exception

202 of the 3-months experiment, the *SRs* were derived from the sorbed Hg (*m*) in individual PAS

203 deployments using Eq. (1). *SR*s derived from a single deployment generally have a higher

204 uncertainty than *SR*s derived from experiments involving multiple simultaneous deployments of

205 variable length, such as those described in McLagan et al. (2016b). This uncertainty is further

206 increased when deployment times are short and gaseous Hg concentrations are low, as *m* will

207 be closer to quantification limits. Nevertheless, to constrain the uncertainties from the

208 experiments described here, we performed a high number of replications, which allows an

209 average and standard deviation for the *SR* of each deployment. In the wind experiments, true

210 replication was not possible, as wind speed varied slightly between each deployment. While

211 they cannot be called replicates, we performed a very large number of individual experiments,

212 which allowed for the derivation of a robust relationship between *SR* and wind speed.

213 Additionally, the variable length of the experiments at selected wind speeds not only added to

214 the number of data points, but also allowed us to assess if there was any effect of deployment

215 time on *SR*.

2.3 Analyses

217 Total Hg (THg) in the activated carbon sorbent was quantified using thermal combustion,

218 amalgamation, and atomic absorption spectroscopy in oxygen (O$_2$) carrier gas (USEPA Method

219 7473) using an AMA254 (Leco Instruments Ltd.) (USEPA, 2007). Because the sorbent in a PAS

220 cannot be assumed to take up Hg homogeneously, the entire carbon from each PAS was

221 analyzed in two aliquots of up to 0.45 g each. In order to increase the lifetime of AMA254

222 catalyst tubes while processing samples with high sulphur content, catalyst tubes were

223 amended with 5 g of sodium carbonate (Na$_2$CO$_3$) and ≈0.15 g of Na$_2$CO$_3$ was added directly to

224 each sample boat (McLagan et al., 2017). Samples were dried for 30 seconds at 200 °C and

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Deleted: point calibrations

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226 thermally decomposed at 750 °C for 330 seconds, while gaseous elemental Hg was trapped on
227 the gold amalgamator. After combustion the system was purged for 60 seconds to ensure all
228 pyrolysis gases were removed from the catalyst. Throughout the analysis the catalyst was
229 heated to 550 °C. After purging, the amalgamator was heated to 900 °C for 12 seconds to
230 release the trapped Hg into the cuvette where absorption at 253.65 nm was measured by dual
231 detector cells for both low and high absolute amounts of Hg.

232 The instrument was calibrated by adding varying amounts of Hg liquid standard for AAS (1000 ±
233 5 mg l^{-1}; in 10 % w/w HCl; Inorganic Ventures) to ≈0.22 g of clean (unexposed) HGR-AC. ≈0.15 g
234 of Na_2CO_3 was added on top of the liquid standard and HGR-AC. In all experiments absolute
235 amounts of Hg were less than 20 ng and the high cell was therefore not required for
236 quantification. The low cell calibration included standards of 0, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 15,
237 and 20 ng of Hg (uncertainty in autopipette is 1 ± 0.004 ng) fitted with a quadratic relationship.

238 **2.4 Quality Assurance and Control**

239 Both analytical and field blanks were included in all experiments. Analytical blanks represented
240 analyses of clean HGR-AC with mean concentration of 0.3 ± 0.2 ng g^{-1} of HGR-AC (n=14). Field
241 blanks, taken both at the start and end of each experiment, were taken to the site, opened,
242 deployed, and then immediately taken down, sealed with PTFE tape and stored for analysis in
243 double resealable plastic bags. The mean field blank concentration for the wind experiments
244 (n=7), the temperature/RH experiments (n=5), and the Radiello® reuse experiments (n=4) were
245 0.5 ± 0.2 ng g^{-1}, 0.58 ± 0.15 ng g^{-1} and 0.38 ± 0.08 ng g^{-1} of HGR-AC, respectively. All results are
246 blank adjusted by subtracting the mean field blank concentration for each experiment
247 multiplied by the mass of HGR-AC in that sample from the sorbed Hg in each sample.

248 Analytical precision was monitored throughout the experiments (approximately every 10-15
249 instrumental runs) by analyzing 5 or 10 ng Hg liquid Standards for AAS added to ≈0.22 g of HGR-
250 AC. Recoveries for precision testing were 100.1 ± 1.6 (n=62), 100.0 ± 1.3 (n=24), and 100.0 ± 1.3
251 (n=21) % for the wind, temperature/RH, and reuse experiments, respectively. Recovery was
252 monitored throughout the experiments (approximately every 10-15 runs) by analyzing a high

253　sulphur, bituminous coal standard reference material, NIST 2685c (S = 5 wt %; National Institute

254　of Standards and Technology), or our own in-house reference material, RM-HGR-AC1

255　(powdered HGR-AC loaded with Hg by exposure to air for four months then homogenized; 23.1

256　± 0.8 ng g^{-1} based on 198 analytical runs). Recoveries of NIST 2685c were 101 ± 3 (n=35), 102 ±

257　3 (n=14), and 99 ± 4 (n=10) % for the wind, temperature/RH, and reuse experiments,

258　respectively. Recoveries of RM-HGR-AC1 were 98 ± 3 (n=43), 97 ± 2 (n=13), and 96 ± 2 (n=10) %

259　for the wind, temperature/RH, and reuse experiments, respectively. All statistical tests were

260　either performed by hand or using R v3.3.2 (R Foundation for Statistical Computing).

261　**3.　RESULTS AND DISCUSSION**

262　**3.1 Wind**

263　The effect of wind speed on *SR* varied considerably across the four tested PAS configurations

264　(Fig. 1). The greatest effect was observed for white Radiello® without windshield (configuration

265　2), which is a configuration that is unlikely to be used in practice (r^2 = 0.91; *p* < 0.001; *n* = 44).

266　The positive linear relationship across the tested wind speed range (wind still to 6 m s^{-1}) had a

267　slope indicative of a 0.022 m^3 day^{-1} (or 18 % of the calibrated SR) increase in *SR* for every 1 m s^{-1}

268　increase in wind speed (Fig. 1). Previous investigators, using the white Radiello® (without

269　protective shield) to monitor varying atmospheric contaminants, fitted logarithmic (Pennequin-

270　Cardinal et al., 2005; Plaisance, 2011; Skov et al., 2007) or quadratic (Plaisance et al., 2004)

271　relationships to data describing the effect of wind speed on *SR*. The SR was most sensitive at lower

272　wind speed (typically < 1 m s^{-1}). However, due to the limited number or range of measured wind

273　speeds, or high data uncertainty, a linear relationship fits some of these data equally well

274　(McLagan et al., 2016a).

275　The addition of the windshield (configuration 1), which is the current method of practice,

276　reduced the effect of wind speed on the *SR*, particularly at higher wind speeds. The best fit of

277　the data was a logarithmic relationship (linear fit: r^2 = 0.83; *p* < 0.001 for exponentially

278　transformed data; *n* = 52) in which *SR* was most sensitive to wind speed between 0 and 1 m s^{-1}

279　(Fig. 1). While average wind speeds of less than 1 m s^{-1} are common for indoor deployments,

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280 outdoors average wind speeds typically exceed 1 m s^{-1} (98.3 % of data from 0° 10' resolution

281 global data set of monthly averaged wind speeds at 10 m above ground level between 1961

282 and 1990 (New et al., 2002)). When we consider only the data >1 m s^{-1} we observe a slight, but

283 significant, positive linear relationship between *SR* and wind speed (r^2 = 0.21; *p* = 0.006; *n* = 34)

284 corresponding to a 0.003 m^3 day^{-1} (or 2.5 % or the previously calibrated SR) increase in *SR* for

285 every m s^{-1} increase in wind speed (Fig. 1). Neither configuration with the thicker, yellow

286 Radiello® led to a significant effect (*p* > 0.05) of wind speed on *SR* (Fig. 1). When the protective

287 shield is in place the *SR* was approximately 10 % lower than without the protective shield for

288 the yellow Radiello®. Plaisance (2011) also noted a negligible effect of wind speed on *SR* using a

289 yellow Radiello® PAS without any protective shield when monitoring benzene.
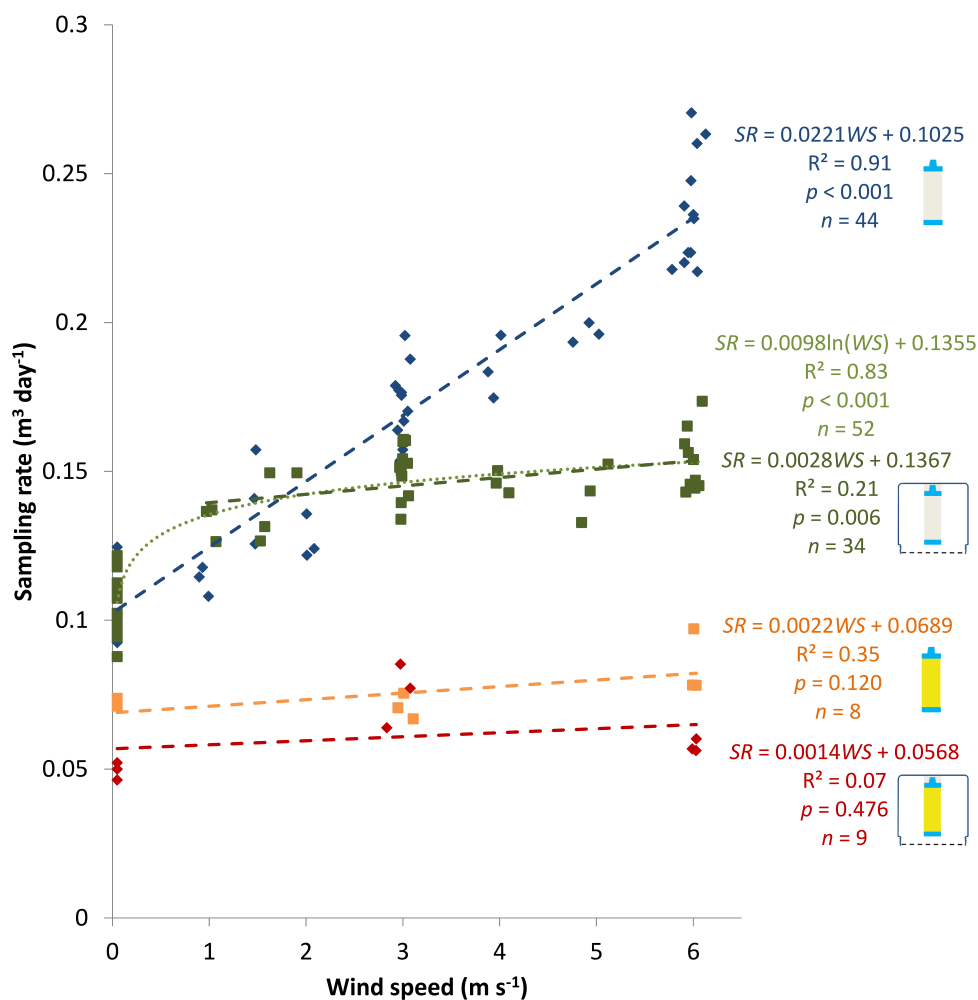
Figure 1: The effect of wind speed on the sampling rate of four different configurations of a passive air sampler for gaseous mercury. Configuration 1: White Radiello®, with protective shield (▪); Configuration 2: White Radiello®, without protective shield ( ); Configuration 3: Yellow Radiello®, with protective shield (▪); Configuration 4: White Radiello®, without protective shield ( ). Standard error of slope and y-intercept are give in Table S1.

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 m^3 day^{-1} (or 97 % of the calibrated SR) for every m s^{-}

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299 [1] increase in wind speed (Guo et al., 2014; Zhang et al., 2012). This information and the results

300 here demonstrate the merit of employing both diffusive barriers and protective shield in

301 reducing the effect of wind speed on SR. The diffusive path length of the PAS has three

302 components: (1) the ASBL, (2) the diffusive barrier (adjusted for the porosity of the diffusive

303 barrier), and (3) the internal airspace of the Radiello® (McLagan et al., 2016b). Employing a

304 thicker, less porous diffusive barrier (yellow Radiello®) increases the diffusive path length of the

305 diffusive barrier component, in turn reducing the SR. By reducing turbulence on the outside of

306 the diffusive barrier, the protective shield essentially increases the thickness of the ASBL

307 (McLagan et al., 2016b), leading to a reduction in SR.

308 Because the samplers were not exposed to exactly the same wind speeds, it is not possible to

309 construct uptake curves from the experiments with variable deployment length. It is, however,

310 possible to test whether the measured SRs depend on the length of each PAS deployment. The

311 relationship between deployment length and SR was not significant ($p > 0.05$), irrespective of

312 the applied wind speed (wind-still, ~3 m s^{-1}, and ~6 m s^{-1}) or configuration (1 and 2); see Fig. S4

313 for details. This confirms that the SRs derived from short one-week deployments were neither

314 biased high or low.

315 The 3-month uptake experiment under wind-still conditions produced a SR of 0.106 ± 0.009 m^3

316 day^{-1} when calculated as the average of each PAS deployment (see Fig. S5 for uptake curve).

317 The slope of the regression of m against $C*t$ (McLagan et al., 2016b; Restrepo et al., 2015) gave

318 a very similar SR of 0.109 ± 0.009 m^3 day^{-1}. Because the latter method is thought to give a

319 slightly more reliable SR (McLagan et al., 2016b; Restrepo et al., 2015), we suggest to use this

320 SR for indoor deployments of the PAS using the white Radiello and a windshield (configuration

321 1). This SR is 9.9 % lower than the SR obtained in an earlier outdoor calibration study, despite

322 the higher temperature (~23°C) indoors than outdoors (mean temperature across all

323 deployments: 7.6°C). Additionally, the replicate precision of samplers from this uptake

324 experiment for the wind-still data with the protective shield (11 ± 8 %) was significantly poorer

325 ($p < 0.001$) than in the outdoor calibration study with the same sampler setup (2 ± 1.3 %; mean

326 wind speed 1.89 m s^{-1}) (McLagan et al., 2016b). Both the lower SR and the greater uncertainty

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329 of the *SR* are consistent with the effect of wind observed for this configuration (green markers
330 in Fig. 1): At the low wind speeds of indoor deployments (< 1 m s^{-1}), the *SR* is expected to be
331 both lower and more sensitive to changes in wind speed. Although, conditions for this
332 experiment were labelled "wind-still", in reality any activity within the laboratory (movement of
333 lab personnel, opening and closing of doors, etc.) will result in small variations in wind speeds
334 around the PAS within the range where the *SR* is most sensitive to such variations (Zhang et al.,
335 2013). Thus, for indoor deployments of the passive sampler, especially using the white
336 Radiello®, we can expect somewhat less precise results. The effect of laboratory activity may
337 also cause disturbances in the wind measured at higher wind speed treatments. Wind speeds
338 could only be measured for 5 mins before and after each experiment and there may be some
339 difference between measured and actual average wind speed for each deployment. These
340 issues may have contributed to the higher variability in the wind experiments compared to the
341 temperature and relative humidity experiments (see below), which were conducted in closed
342 chamber experiments.

343 **3.2 Temperature and relative humidity**

344 Relative humidity, tested at 44, 60, and 80 % and a stable temperature of 20 °C, had no
345 significant effect on *SR* (p = 0.080; see Fig. S6). Relative humidity, tested at 44, 60, and 80 % and
346 a stable temperature of 20 °C, had no significant effect on SR (r^2 = 0.11; p = 0.080; n = 13; see
347 Fig. S6), which is similar to Guo et al., (2014) who also observed no effect from relative humidity
348 on the SR of their PAS that uses the same sulphur-impregnated activated carbon sorbent. It is
349 therefore appropriate to analyze the effect of temperature on *SR* despite small variations in RH
350 at different temperature levels. We observed a significant, positive, linear relationship between
351 *SR* and temperature (r^2 = 0.82; p < 0.001; n = 36; Fig. 2) corresponding to a 0.001 m^3 day^{-1}
352 increase in *SR* for every 1 °C increase in temperature (or 0.7 % of the calibrated *SR*). This
353 relationship remained linear across the tested range from -15 to 35 °C.

354 Temperature can affect the *SR* because of its impact on (i) the partitioning equilibrium between
355 the sorbent and the gas phase and (ii) the diffusion coefficient (McLagan et al., 2016a;
356 Pennequin-Cardinal et al., 2005). The uptake capacity of the HGR-AC for gaseous Hg is

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357 extremely high and we suspect that any change in the sorption equilibrium caused by changing

358 temperatures should have a negligible effect on the SR. The increase in diffusivity caused by an

359 increase in temperature is easily quantified. Fig. 2 also displays *SR* as a function of temperatures

360 predicted with a previously described model based on Fick's first law of diffusion (McLagan et

361 al., 2016b). While the predicted *SR*s are ~8 % lower than the measured ones, the slope of the

362 relationship between *SR* and temperature is the same (no significant difference, z-score test, *p*

363 = 0.427), confirming that the effect of temperature on the diffusivity of gaseous Hg is sufficient

364 to explain the observed temperature dependence of the *SR*.
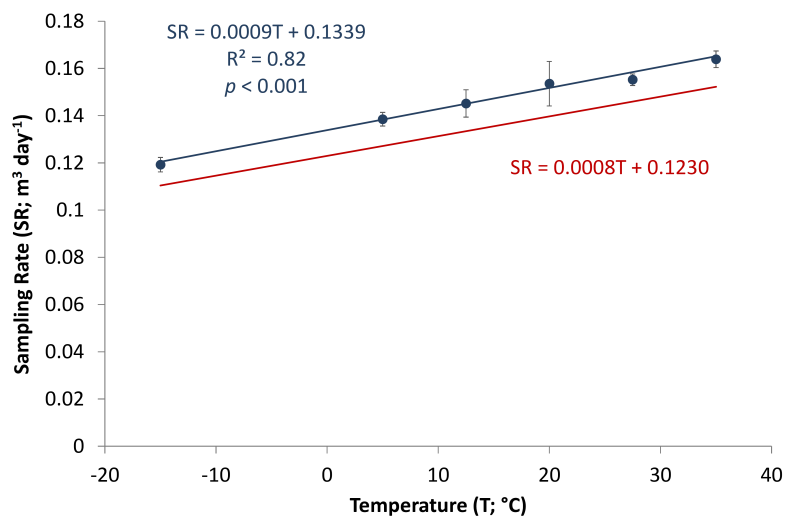
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366 **Figure 2: The effect of temperature on the sampling rate of a passive air sampler for gaseous mercury**
367 **as determined experimentally (blue) and as calculated using the diffusion model (red) by McLagan et**
368 **al. (2016b). The measured and calculated temperature dependence, given by the slopes of the**
369 **relationships, are not significantly different.**

370 Earlier studies on PAS for gaseous Hg did not observe an effect of temperature on *SR* in

371 laboratory chamber experiments. Guo et al. (2014) found no significant effect of temperature

372 on the *SR* of their activated carbon-based PAS between -10 and +35 °C. Similarly, there was no

373 effect of temperature on the *SR* of a PAS using a solid gold sorbent and a white Radiello®

374 diffusive body (Skov et al., 2007). In neither case, however, was the precision of the

375 measurement sufficient to detect the small dependence of *SR* on temperature caused by the

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376 effect of temperature on diffusivity. Such a small temperature effect can only be detected in a
377 highly precise sampler.

378 **3.3 Radiello® reuse**

379 In the Radiello® reuse experiment conducted indoors, no significant difference in the amount of
380 sorbed Hg was observed between *new*, *uncleaned*, or any of the cleaned Radiellos® (ANOVA, *p*
381 = 0.467; Fig. 3(A)). Similarly, when we ignore the effect of cleaning, no significant difference in
382 the sorbed amount of Hg was observed between Radiellos® with different degrees of dust
383 coatings, including the new Radiellos® (ANOVA, *p* = 0.841; Fig. 3(B)). The cleaning treatments
384 also did not differ in terms of the observed variances (Levene's Test, *p* = 0.307). However, the
385 amount of Hg taken up in Radiellos® with the most dust (category 5) had a significantly higher
386 variance than all other treatments (*p* = 0.004, Levene's Test with Tukey's Honest Significant
387 Difference post hoc test). Although the differences between all Radiello® treatments in the
388 indoor Radiello® reusability experiments are small, the significantly higher variability observed
389 for Radiellos® with the highest dust coating suggests some form of cleaning would be better in
390 maintaining the high level of precision of this PAS. Effect size, using Cohen's d value (see S5),
391 was then applied to examine differences in treatments without the use of traditional binary
392 hypotheses testing (See Table S4). In comparison to new Radiellos® *soap*, *acid*, and *heat-acid*
393 were the most effective treatments. While there was no significant difference in means
394 (ANOVA; *p* = 0.548) or variances (Levene's; *p* = 0.221) for the outdoor experiment testing *new*,
395 *uncleaned*, and *soap* Radiellos®, effect size analysis (see S5) confirmed that *soap* cleaning is an
396 effective method in preparing used Radiellos® for redeployment (Fig. 3(C)).
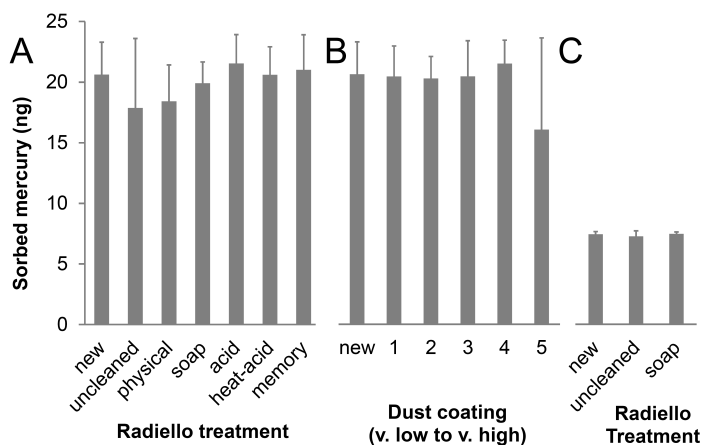
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Figure 3: Mean sorbed mercury for differing Radiello® cleaning treatments and at varying degrees of HGR-AC dust coating inside the Radiello® (Panel B) from indoor experiment. Cleaning treatments and degree of dust coating is described in Sect. 2.2.3. 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.

Uptake of Hg in uncleaned Radiellos® previously deployed in gaseous Hg concentrations 2 – 4 orders of magnitude higher than the other Radiellos® (*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: p = 0.307; Fig. 3(A)). This implies that very little Hg was sorbed to the Radiello® 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®.

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 m^3 day^{-1} was obtained for a mean wind speed of 1.89 m s^{-1} and a mean temperature of 7.6°C.[15] We recommend to use the increments

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418   from Fig. 1 and Fig. 2, i.e. 0.003 m^3 day^{-1} increase in *SR* for every m s^{-1} increase in wind speed

419   and 0.001 m^3 day^{-1} increase in *SR* for every 1 °C increase in temperature to adjust the *SR* of

420   0.121 m^3 day^{-1} to the average temperature and wind speed of each PAS deployment (See S6 for

421   SR adjustment equation and sample calculation).

422   The experiments here predict a *SR* of 0.142 m^3 day^{-1} for an average wind speed of 1.89 m s^{-1}

423   (Fig. 1) and a *SR* of 0.141 m^3 day^{-1} for an average temperature of 7.6°C (Fig. 2). Both these

424   values are greater than the *SR* of 0.121 m^3 day^{-1} from the calibration study (McLagan et al.,

425   2016b). While we presently do not know the reason for this discrepancy, it may be related to

426   the relatively short deployment periods used in the present experiments. As mentioned above,

427   short deployment at background concentrations yield a *SR* with a higher uncertainty. Also,

428   McLagan at al. (2016b) observed that *SR* for PAS deployed outdoors for less than 1-2 months

429   were higher than the *SR* derived for the entire one-year sampling period. Despite this slight

430   discrepancy, we note that the y-intercepts of the relationships reported here (the magnitude of

431   the *SR*) are less important than their slopes (i.e. the temperature and wind speed adjustment

432   factors). An ongoing study measuring the uptake of gaseous Hg in PAS deployed at several

433   locations with widely different temperature and wind speed conditions will help refine both the

434   *SR* applicable to outdoor deployments and the validity of the laboratory derived adjustment

435   factors for temperature and wind speed reported here.

436   When designing a PAS, there is a need to strike a balance between maximizing the *SR* and

437   minimizing the variability in the *SR* caused by factors such as wind speed, objectives that are

438   contradictory in nature (McLagan et al., 2016a). Although using a thicker, yellow Radiello® with

439   or without a protective shield are the methods least affected by wind, the *SR* for these methods

440   is approximately half that of the white Radiello® with a shield. A lower *SR* translates to lower

441   amounts of sorbed Hg, which means that longer deployments are required to reach method

442   quantification limits (MQL). The PAS configuration with white Radiello® and windshield needs

443   to be exposed to typical background concentrations of gaseous Hg (~1.5 – 2 ng m^{-3}) for

444   approximately one week to reach levels above MQL (McLagan et al., 2016b). A PAS with yellow

445   Radiello would presumably require deployments twice as long. For either configuration, longer

446   deployments of a month or more are likely to yield greater accuracy. Given the possibility of
447   adjusting the *SR* for the slight effect caused by wind speeds above 1 m s^{-1} and the shorter
448   minimum deployment times, we recommend the PAS configuration with a shielded white
449   Radiello for most outdoor deployments. Nonetheless, there may be long deployments under
450   highly variable winds that warrant the use of the yellow Radiello®. A full long-term calibration
451   study outdoors would be advisable prior to using this configuration.

452   Finally, our results suggest that previously deployed Radiello® are indeed reusable as long as
453   the Radiellos® are cleaned between deployments. Because the different cleaning methods were
454   generally equally effective, we recommend the use of the *soap* method because of its overall
455   ease and health, safety and waste benefits over using acids (Anastas and Warner, 1998).
456   Additionally, Gustin et al., (2011) suggested the porosity of high density poly-ethylene diffusive
457   barriers can be affected by cleaning with HCl. While in this study we used HNO3 for cleaning
458   purposes, the possibility of porosity changes caused by acid cleaning is further incentive to
459   clean previously used Radiellos® with *soap* rather than *acid* or *heat-acid* treatments.

460   **Data Availability**

461   Data can be found in the paper, the SI, or via communication with the corresponding author.

462   **Competing Interests**

463   The authors declare that they have no conflicts of interest.

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