## Response to Anonymous Referee #1

Review McLagan et al. This paper reports on work towards development of a passive sampler for gaseous Hg. The paper reports on tests to determine the impact of meteorological parameters on the sampler. They found that RH did not affect the sampling rate and it increased slightly with wind speed. They also assess the utility of reusing Radiello sampler housings. In general I do not think this paper is of sufficient quality and novelty to be considered for publication in AMT.

**Response:** The reviewer provides no evidence to support an assessment of insufficient quality or novelty. In our manuscript we describe tests on the effects of wind speed, temperature and relative humidity on the sampling rate of a previously published passive air sampler (PAS) for gaseous Hg (McLagan et al. 2016a). Quantifying the sampling rate variability caused by meteorological conditions is a critical step in validating any PAS. This work had not been previously done for this sampler, and we feel we have approached this with utmost rigor. Given AMT's mandate of "*validation of measurement instruments*" and "*advances in…measurement techniques for constituents…of the earth's atmosphere*", we feel strongly that this contribution fits well within the scope of this journal.

I do not really understand the part of the sentence that starts with "with" just does not make sense so I would eliminate.

**Response:** We do not know what the reviewer is referring to in this comment. There are two sentences in the entire manuscript that start with the word "with" (pg. 9, line 199 and pg. 12, line 278) and both are grammatically correct. In case the reviewer is referring to line 278, we rephrased the sentence to read: "***When*** *the protective shield* ***is*** *in place the SR was approximately 10% lower than without the protective shield* ***for the yellow Radiello®****."*

Also is the resolution of this sampler sufficient for collecting meaningful data around the globe given the limited variability in concentrations outside of contaminated areas?

**Response:** The replicate precision of this sampler is 2±1 % relative standard deviation (McLagan et al. 2016a). Whether this is sufficient "resolution" for discerning the relatively small concentration differences of gaseous mercury "outside of contaminated areas" depends to a large degree on the extent to which the sampling rate is variable between different deployments. In other words, the work described in the submission is a necessary step towards establishing whether the sampler has the requisite level of accuracy and precision to monitor background levels of gaseous Hg. Our study shows that the effect of wind speed, temperature and relative humidity on the sampling rate is small and quantifiable. While this is necessary, it not yet sufficient to establish the smallest concentration difference the sampler is able to detect. This will require the determination and comparison of sampling rates in the field at sites that vary widely in terms of meteorology. Such work is currently ongoing.

Pg 6 Methods section It appears they had no simultaneous replication and the experiment seems quite crude there is no n and just looking at parallel wind speed is not sufficient.

**Response:** We measured the sampling rate of the PAS with the white Radiello at eight different wind speeds (wind still, 1, 1.5, 2, 3, 4, 5, 6 m/s) and those for the yellow Radiello at three wind speeds (windstill, 3, 6 m/s). Each of these measurements was triplicated, for a total of 33 individual sampling rate determinations. The high *n* in our study is apparent from Figure 1. We believe that this is a sampling design that compares very favorably with any that had been adopted in previous studies examining the relationship between wind speed and sampling rate in PASs. The following statement (in red) has been added to line 126 on pg 6 to increase clarity:

"…the distance between 126 PASs and fan (see Fig. S1 and Fig. S2). For each wind speed triplicate PASs were deployed."

We do not report the average and standard deviation of the replicated measurements at different wind speeds, because it is impossible to **exactly** replicate exposure of PAS to wind in a sampling design (Zhang et al. 2012) that relies on individual electrical fans for each individual deployment (Lines 126-131 pg 6). Instead, we quantified the wind speeds at the front of the protective shield or diffusive housing of EACH individual sampler and used those individual data in the regressions displayed in Figure 1. The uncertainty of the sampling rate–wind speed relationships can be determined from the standard error of the slope of these relationships, which have been added to the revised manuscript.

Possibly the reviewer's reference to "parallel wind speed" not being sufficient, is meant to suggest that we should have also investigated the influence of the angle of wind incidence on the sampling rate. While this issue has not been investigated previously for any PAS for gaseous mercury or any PAS relying on the Radiello diffusive barrier, it has been studied in PAS for organic contaminants (May et al. 2011, Zhang et al. 2013, Gong et al. 2017). Because none of these PAS used a diffusive barrier, they are more susceptible to wind effects than our sampling design. Considering that our sampler design includes both a windshield and a diffusive barrier, we felt it not necessary to also include experiments with variable angles of wind incidence. However, that could be the subject of future experiments.

The temperature range tested is extremely low as is the relative humidity. Also, the temperature and relative humidity reported in the methods is not consistent with the abstract.

**Response:** The temperatures in our experiments ranged from -15 °C to +35 °C. This is not "extremely low" and covers the range of most average temperatures found on Earth. The relative humidity in our experiments ranged between 44 and 80 %. This was the maximum range achievable at the Biotron climate control chambers; increasing or decreasing relative humidity further while keeping temperature at 20 °C was not possible. While there are locations where relative humidity can be outside this range it does cover the mean range of relative humidity over land, 70-80% (Dai, 2006). We further note that the range of temperatures and relative humidity tested compares very favorably with those in other studies on the influence of meteorological conditions on the sampling rates of mercury passive samplers (Guo et al. 2014, Skov et al. 2007, Gustin et al. 2011, Brumbaugh et al. 2000).

The temperature and relative humidity ranges are not reported differently in the abstract, methods, or discussion, but to clarify the temperature range in the abstract (Line 18 pg 2) has been rewritten as: "-15 to +35 °C"

Also the caption of Table 1 has been updated to: "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."

Pg 7 I do not really understand what they mean by replicated 5 times. Were 5 samplers deployed or was one sampler deployed in the center of the chamber or are there 5 chambers with the exact same conditions?

**Response:** The sentence on line 149 pg 7 has been updated to the following: "Each treatment included five replicates, all deployed in the same chamber over the same time period."

Pg 9 line 268 needs a reference and R2 should be r2 and there should be a p value and n

**Response:** The sentence does require a reference to the initial calibration study. It has been updated in the manuscript for clarification purposes as follows: "The addition of the windshield to the white Radiello® (configuration 1), which is the current method used for outdoor deployments with this PAS (McLagan et al., 2016a), reduced the effect of wind speed on the SR, particularly at higher wind speeds."

$R^2$ has been changed to $r^2$ and n = 44 has been added, and *p*-value for the exponentially transformed data (since we cannot run a significance test on untransformed log data; this *p* – value has been added to the Figure). $r^2$, n and p-values have also been added to the other wind relationships (line 262, line 278)

P 14 line 337 self-citation in not appropriate here and in multiple other places in the paper. i.e. pg. 18 line 419

**Response:** We disagree and believe that citations to our earlier papers are appropriate, both in these two instances and elsewhere in the manuscript. On lines 337 and 419 we cite our earlier review paper (McLagan et al. 2016a), in which we discuss (i) the two different ways in which temperature can affect the sampling rate of a PAS, and (ii) the two conflicting design criteria affecting the sampling rate of a PAS.

Pg 16 line 373 porosity of sampler housings has been demonstrated to be impacted by acid cleaning. How many times were the samplers subjected to these treatments?

**Response:** The following statement has been added to the manuscript at the end of line 436 pg 18: "Additionally, Gustin et al., (2011) suggested the porosity of high density poly-ethylene diffusive barriers can be affected by cleaning with HCl. While in this study we used $HNO_3$ 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.*"

The Radiellos were cleaned once for each method following the description in the methods (i.e. acid baths were for 6 hours). The following has been added to line 169 pg 7: "…water rinse and sonication and air drying). All Radiellos in each cleaning treatment were cleaned once according to the aforementioned methods."

Sampling rates should be compared to those in other papers

**Response:** The relationships and uncertainty of these relationships have been compared to other samplers throughout the paper (e.g. Lines 265-267, Lines 280-281, Lines 290-293, lines 352-358). The actual SRs determined in this study in the various experiments were frequently compared to the SR of the original calibration study by McLagan et al., (2016a). In that study the calibrated rates were compared to the SRs of other studies, especially that of Skov et al, (2007) which is physically the most similar sampler to that of our own.

We did observe one comparison that was not included in the manuscript and lines 329-330 have been updated as follows: "Relative humidity, tested at 44, 60, and 80% and a stable temperature of 20 °C, had no significant effect on SR (p = 0.080; see Fig. S5), which is similar to

Guo et al., (2014) who also observed no effect from relative humidity on the SR of their PAS that uses the same sulphur-impregnated activated carbon sorbent."

## Response to Anonymous Referee #2

The manuscript by McLagan et al. presents interesting new data to assess performance of a novel passive method for gaseous mercury determination. This is currently a very important field of research and it may have beneficial applications in different environmental contexts all over the world, finding a large international audience.
Particularly worthy is the pursuit of the authors to adopt cost-effective procedures (i.e. Radiellos reuse) measuring their impact on the analytical quality of data. Indeed, it is essential for a passive sampling method to be low cost for being effective in pollution surveys with high spatial resolution and for supporting air quality management.
The paper by McLagan et al. is well written. The title is clear and informative; the abstract concisely reports well the rationale and the main results of the paper. Also, the introduction is correctly conceived with a logical and continuous development of the different points leading to the statement of the aim of the research. The result and discussion section is well organized and the data, although coming from multiple experiments of different design, are presented intelligibly through few figures (3).

**Response:** We thank the reviewer for their positive feedback.

However, there is room to improve caption of figure 1 (lines 283-289). It may be difficult for readers to get out of the symbols used which are of similar shape and color. Please check correspondence of colors and shapes of symbols in the figure with those reported in the legend in parentheses in the caption. In my opinion, the fact that similar colors are used for the relationships (reported irrespectively of the deployment length) of each configuration and the color symbols used for different deployment periods (weeks) may be confusing.

**Response:** We have removed the different colours for different deployment times.

At line 270 a $r^2$ of 0.66 is reported in apparent incoherence with those two $r^2$ reported in the figure 1 for the configuration 2.

**Response:** Thank you for picking up this discrepancy. The $r^2$ in text has been updated to 0.83 to match the value in the figure.

The Authors in this latter case should explain better in the text the difference of calculations. In the same sentence it is stated that "SR is most sensitive to wind speed between 0 and 1 m s-1" (lines 270-271) which may not be the same meaning of the previous sentence at the line 265 "The SR was most sensitive at lower wind speed". Although the latter sentence is understandable, it could be improved to make it clearer to the readers.

**Response:** We have clarified this sentence by adding the following in parenthesis to line 265: "The SR was most sensitive at lower wind speed (typically < 1 m $s^{-1}$)".

I have no remarks on analytical quality of data as the analyses have been carried through sound methodologies and reliable instrumentations (i.e. USEPA method; Leco Instrument) under verified quality control measures (i.e. SRMs, monitoring of analytical precision and recovery). Experiments seem to me well conceived and correctly implemented.
In the research Authors showed that the tested passive sampler provided very precise data for gaseous mercury which were little affected by variability of temperature over a large interval, reflecting different potential conditions of deployment in the field. More importantly it came up the robustness of data that can be obtained by the configuration for outdoor deployments (yellow Radiello® with windshield) which resulted very little affected by wind conditions. The potential reusability of radiello for multiple deployment cycles without detriment of the analytical performances, as tested in this research, is a key feature in the cost management of this passive sampler.
In my opinion, the manuscript provide novel information, well reported, which is essential to support a new methodology that is meeting actual needs for monitoring of gaseous mercury. This allow me to recommend the manuscript by McLagan et al. for publication in Atmospheric Measurement Techniques.

**Response:** Again we thank the reviewer for the support of the manuscript.

**References:**

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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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## 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 m $s^{-1}$), temperatures (-15 to +35 °C), and relative humidities (44 to 80 %). While relative humidity has no impact on *SR*, *SR* increases slightly with both wind speed (0.003 $m^3$ $day^{-1}$ increase in *SR* or 2.5 % of the previously calibrated *SR* for every m $s^{-1}$ increase for wind speeds > 1 m $s^{-1}$, typical of outdoor deployments) and temperature (0.001 $m^3$ $day^{-1}$ increase in *SR* or 0.7 % for every 1 °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 *SR*s using measured or estimated temperature and wind speed data at or near sampling sites. We also assessed the possibility of reusing Radiello® 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® previously deployed in a high Hg atmosphere was observed. However, a loss in replicate precision for the dirtiest Radiellos® in the indoor experiment suggests that cleaning is advisable prior to reuse.



## KEYWORDS

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


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## 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 *SR*s 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 fairly 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. *SR*s 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 ± 1 % that uses an activated carbon sorbent and a Radiello® 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 $m^3$ $day^{-1}$ (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® 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® 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 sulphur-impregnated activated carbon sorbent (HGR-AC; Calgon Carbon Corp.), which is inserted into a Radiello® radial diffusive body (Sigma Aldrich), which itself is placed inside a polyethylene-terephthalate protective jar. During deployments the opening of the jar, covered with a polypropylene (PP) mesh screen, is facing down. After sampling the jar is sealed tightly with a PP cap, PTFE tape wrapped around seal, and placed in double resealable plastic bags for transport and storage. McLagan et al. (2016b) provide more detail on the PAS design.

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## 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® with windshield, (2) white Radiello® without windshield, (3) thick-walled, less porous, yellow Radiello® with windshield, and (4) yellow Radiello® without windshield. 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 $s^{-1}$ were achieved by manipulating the distance between PASs and fan (see Fig. S1 and Fig. S2). For each wind speed triplicate PASs were deployed. Wind speeds for each individual PAS were measured every 5 seconds with a hot-wire Anemometer/Thermometer (Traceable®, VWR International) for five minutes before and five minutes 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 $s^{-1}$).

While experiments with white Radiellos (configuration 1 and 2) generally lasted one week, additional experiments lasting two, three, and four weeks were performed at selected wind speeds (3 and 6 m $s^{-1}$). Experiments with yellow Radiellos (configurations 3 and 4) lasted two weeks (the lower *SR* of yellow Radiello® requires longer deployment times to reach detection limits) and were only performed at wind speeds of 3 and 6 m $s^{-1}$, as well as without fans. Additionally, a 3 months 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 windshield.

Temperature and RH, monitored before, after, and periodically during each individual experiment, ranged from +21.9 to +24.2 °C and from 32 – 53 %. While there was some variation

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in the gaseous Hg concentration as recorded by the Tekran 2537A between deployments, the average concentration across all wind experiments was 1.9 ± 0.3 ng $m^{-3}$.

*2.2.2 TEMPERATURE & RELATIVE HUMIDITY.* The regular PAS configuration (configuration 1) was exposed to eight different combinations of temperature and RH (Table 1) for two weeks 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 $s^{-1}$ was observed using the hot-wire Anemometer over a two minute period at the completion of each experiment. The average actively measured gaseous Hg concentration across all temperature and RH experiments was 2.2 ± 0.9 ng $m^{-3}$.

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**Deleted:** Each experiment was replicated five times.

**Table 1: 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 |

*2.2.3 RADIELLO® REUSE.* The potential impacts of sorbent dust accumulation or atmospheric contamination during prolonged deployment periods on sampling rates and therefore on the ability to reuse the Radiello® diffusive barriers are unknown. Currently, new diffusive barriers are used for each deployment. In this experiment, previously used Radiellos® were redeployed after different cleaning procedures were applied. Six cleaning treatments were applied: *new* (unused Radiellos®), *uncleaned* (unaltered after previous deployments), *physical* (physical agitation with funnel brushes and compressed air blow down), *soap* (Citranox® detergent, cleaning brushes, and deionized water, compressed air blow down, deionized water rinse and sonication and air drying), *acid* (six hour soak in 20 % $HNO_3$ bath, deionized water rinse, compressed air blow down, deionized water rinse and sonication and air drying), and *heat-acid* (six hour soak in 20 % $HNO_3$ bath at 40 °C, deionized water rinse, compressed air blow down,

deionized water rinse and sonication and air drying). All Radiellos® 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 5-point scale (0 – new, 1 – very low, 2 – low, 3 – moderate, 4 – high, and 5 – very high). To the extent this was possible with a limited stock of previously deployed Radiellos®, we evenly distributed Radiellos® of variable dust coating among the treatments (see Table S2 for details). We also tested Radiellos® previously deployed in contaminated environments with very high gaseous Hg concentrations (~100 – 10000 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 7 treatments were deployed for a period of two weeks in a laboratory with slightly elevated Hg concentrations (previously measured as ~5-10 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 (43.78714 °N, 79.19049 °W). In this case, all previously used Radiellos® 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.

*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 hrs 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).

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

$$SR = {}^{m}/_{(C\ t)} \quad (1)$$

where *m* is the mass of sorbed mercury (ng), *C* is the concentration of gaseous Hg measured by the Tekran 2537A (ng $m^{-3}$), and *t* is the deployment time of the PAS (days). With the exception of the 3-months experiment, the *SRs* were derived from single point calibrations using Eq. (1). *SR*s derived from a single deployment have a higher uncertainty than *SR*s 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. To nevertheless constrain the uncertainties from the experiments described here, we performed a high number of replications. 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 (THg) in the activated carbon sorbent was quantified using thermal combustion, amalgamation, and atomic absorption spectroscopy in oxygen ($O_2$) 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 sulphur content, catalyst tubes were amended with 5 g of sodium carbonate ($Na_2CO_3$) and ≈0.15 g of $Na_2CO_3$ was added directly to each sample boat (McLagan et al., 2017). Samples were dried for 30 seconds at 200 °C and thermally decomposed at 750 °C for 330 seconds, while gaseous elemental Hg was trapped on the gold amalgamator. After combustion the system was purged for 60 seconds to ensure all

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pyrolysis gases were removed from the catalyst. Throughout the analysis the catalyst was heated to 550 °C. After purging, the amalgamator was heated to 900 °C for 12 seconds 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 ± 5 mg $l^{-1}$; in 10 % w/w HCl; Inorganic Ventures) to ≈0.22 g of clean (unexposed) HGR-AC. ≈0.15 g of $Na_2CO_3$ 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 autopipette is 1 ± 0.004 ng) fitted with a quadratic relationship.

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**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 ± 0.2 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® reuse experiments (n=4) were 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 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.

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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 ≈0.22 g of HGR-AC. Recoveries for precision testing were 100.1 ± 1.6 (n=62), 100.0 ± 1.3 (n=24), and 100.0 ± 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 sulphur, bituminous coal standard reference material, NIST 2685c (S = 5 wt %; National Institute of Standards and Technology), or our own in-house reference material, RM-HGR-AC1

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(powdered HGR-AC loaded with Hg by exposure to air for four months then homogenized; 23.1 ± 0.8 ng $g^{-1}$ based on 198 analytical runs). Recoveries of NIST 2685c were 101 ± 3 (n=35), 102 ± 3 (n=14), and 99 ± 4 (n=10) % for the wind, temperature/RH, and reuse experiments, respectively. Recoveries of RM-HGR-AC1 were 98 ± 3 (n=43), 97 ± 2 (n=13), and 96 ± 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® without windshield (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 m $s^{-1}$) had a slope indicative of a 0.022 $m^3$ $day^{-1}$ (or 18 % of the calibrated SR) increase in *SR* for every 1 m $s^{-1}$ increase in wind speed (Fig. 1). Previous investigators, using the white Radiello® (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 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 windshield (configuration 1), which is the current method of practice (McLagan et al., 2016a), 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 m $s^{-1}$ (Fig. 1). While average wind speeds of less than 1 m $s^{-1}$ are common for indoor deployments, outdoors average wind speeds typically exceed 1 m $s^{-1}$ (98.3 % of data from 0° 10' resolution global data set of monthly averaged wind speeds at 10 m above ground level

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between 1961 and 1990 (New et al., 2002)). When we consider only the data >1 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 $m^3$ $day^{-1}$ (or 2.5 % or the previously calibrated SR) increase in *SR* for every m $s^{-1}$ increase in wind speed (Fig. 1). Neither configuration with the thicker, yellow Radiello® 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®. Plaisance (2011) also noted a negligible effect of wind speed on *SR* using a yellow Radiello® PAS without any protective shield when monitoring benzene.

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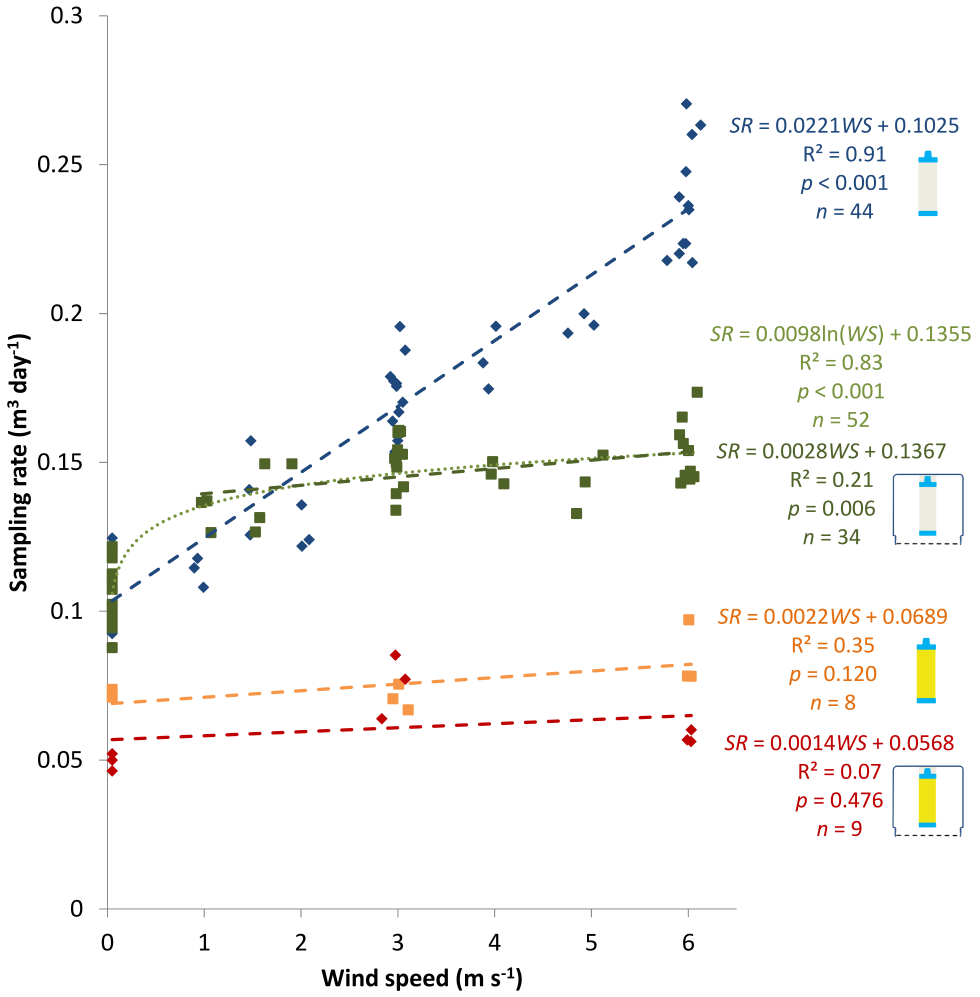


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313 **Figure 1: The effect of wind speed on the sampling rate of four different configurations of a passive air**
314 **sampler for gaseous mercury. Configuration 1: White Radiello®, with protective shield (■);**
315 **Configuration 2: White Radiello®, without protective shield ( ); Configuration 3: Yellow Radiello®,**
316 **with protective shield (■); Configuration 4: White Radiello®, without protective shield ( ). Standard**
317 **error of slope and y-intercept are give in Table S1.**

318 The importance of a diffusive barrier is illustrated by the very strong effect of wind speed on
319 the *SR* of another PAS for gaseous Hg that also utilizes an activated carbon sorbent, but has no
320 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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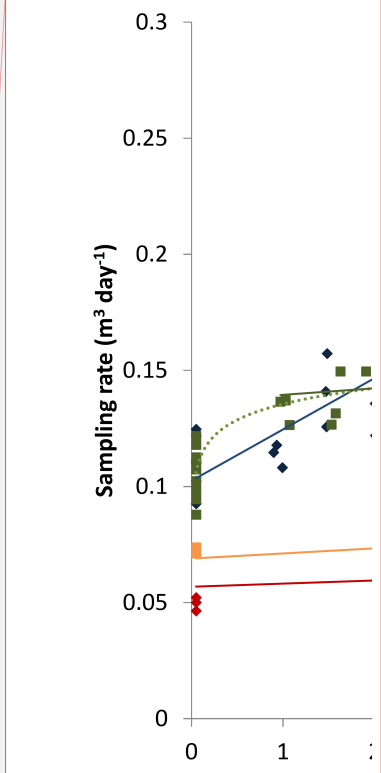


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329 [1] increase in wind speed (Guo et al., 2014; Zhang et al., 2012). This information and the results
330 here demonstrate the merit of employing both diffusive barriers and protective shield in
331 reducing the effect of wind speed on *SR*. The diffusive path length of the PAS has three
332 components: (1) the ASBL, (2) the diffusive barrier (adjusted for the porosity of the diffusive
333 barrier), and (3) the internal airspace of the Radiello® (McLagan et al., 2016b). Employing a
334 thicker, less porous diffusive barrier (yellow Radiello®) increases the diffusive path length of the
335 diffusive barrier component, in turn reducing the *SR*. By reducing turbulence on the outside of
336 the diffusive barrier, the protective shield essentially increases the thickness of the ASBL
337 (McLagan et al., 2016b), leading to a reduction in *SR*.

338 Because the samplers were not exposed to exactly the same wind speeds, it is not possible to
339 construct uptake curves from the experiments with variable deployment length. It is, however,
340 possible to test whether the measured *SR*s depend on the length of the single point
341 calibrations. The relationship between deployment length and *SR* was not significant ($p > 0.05$),
342 irrespective of the applied wind speed (wind-still, ~3 m $s^{-1}$, and ~6 m $s^{-1}$) or configuration (1 and
343 2); see Fig. S3 for details. This confirms that the *SR*s derived from short one-week deployments
344 were neither biased high or low.

345 The 3-month uptake experiment under wind-still conditions produced a *SR* of 0.106 ± 0.009 $m^3$
346 $day^{-1}$ when calculated as the average of single point calibrations (see Fig. S4 for uptake curve).
347 The slope of the regression of *m* against *C*t* (McLagan et al., 2016b; Restrepo et al., 2015) gave
348 a very similar *SR* of 0.109 ± 0.009 $m^3$ $day^{-1}$. Because the latter method is thought to give a
349 slightly more reliable *SR* (McLagan et al., 2016b; Restrepo et al., 2015), we suggest to use this
350 *SR* for indoor deployments of the PAS using the white Radiello and a windshield (configuration
351 1). This *SR* is 9.9 % lower than the *SR* obtained in an earlier outdoor calibration study, despite
352 the higher temperature (~23°C) indoors than outdoors (mean temperature across all
353 deployments: 7.6°C). Additionally, the replicate precision of samplers from this uptake
354 experiment for the wind-still data with the protective shield (11 ± 8 %) was significantly poorer
355 ($p < 0.001$) than in the outdoor calibration study with the same sampler setup (2 ± 1.3 %; mean
356 wind speed 1.89 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 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).

### 3.2 Temperature and relative humidity

Relative humidity, tested at 44, 60, and 80 % and a stable temperature of 20 °C, had no significant effect on *SR* ($p$ = 0.080; see Fig. S5). Relative humidity, tested at 44, 60, and 80 % and a stable temperature of 20 °C, had no significant effect on SR ($r^2$ = 0.11; $p$ = 0.080; $n$ = 13; see Fig. S5), which is similar to Guo et al., (2014) who also observed no effect from relative humidity on the SR of their PAS that uses the same sulphur-impregnated activated carbon sorbent. It is therefore appropriate to analyze the effect of temperature on *SR* despite small variations in RH at different temperature levels. 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 $m^3$ $day^{-1}$ increase in *SR* for every 1 °C increase in temperature (or 0.7 % of the calibrated *SR*). This relationship remained linear across the tested range from -15 to 35 °C.

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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. Fig. 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 *SR*s are ~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*.

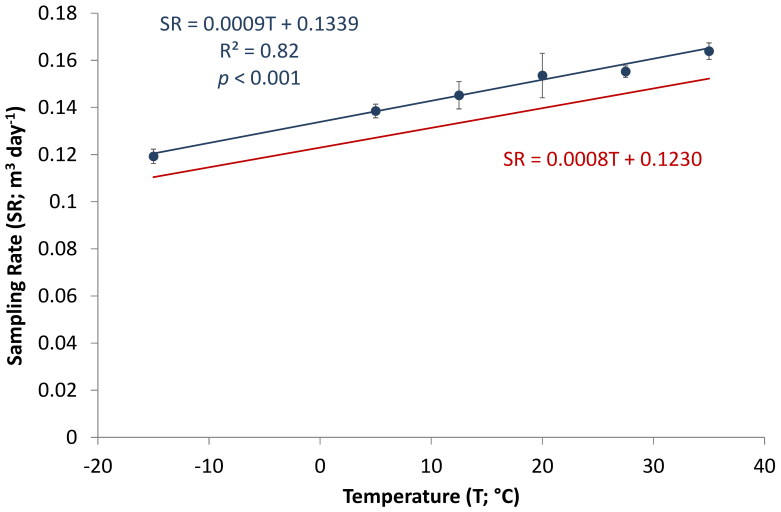


**Figure 2: The effect of temperature on the sampling rate of a passive air sampler for gaseous mercury as determined experimentally (blue) and as calculated using the diffusion model (red) by McLagan et al. (2016b). The measured and calculated temperature dependence, given by the slopes of the relationships,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

Earlier studies on PAS for gaseous Hg did not observe an effect of temperature on *SR*. Guo et al. (2014) found no significant effect of temperature on the *SR* of their activated carbon-based PAS between -10 and ±35 °C. Similarly, there was no effect of temperature on the *SR* of a PAS using a solid gold sorbent and a white Radiello® 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.

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### 3.3 Radiello® reuse

In the Radiello® reuse experiment conducted indoors, no significant difference in the amount of sorbed Hg was observed between *new*, *uncleaned*, or any of the cleaned Radiellos® (ANOVA, *p* = 0.467; Fig. 3(A)). Similarly, when we ignore the effect of cleaning, no significant difference in

the sorbed amount of Hg was observed between Radiellos® with different degrees of dust coatings, including the new Radiellos® (ANOVA, $p$ = 0.841; Fig. 3(B)). 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® 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® treatments in the indoor Radiello® reusability experiments are small, the significantly higher variability observed for Radiellos® 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 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® *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; $p$ = 0.221) for the outdoor experiment testing *new*, *uncleaned*, and *soap* Radiellos®, effect size analysis (see S5) confirmed that *soap* cleaning is an effective method in preparing used Radiellos® for redeployment (Fig. 4(C)).

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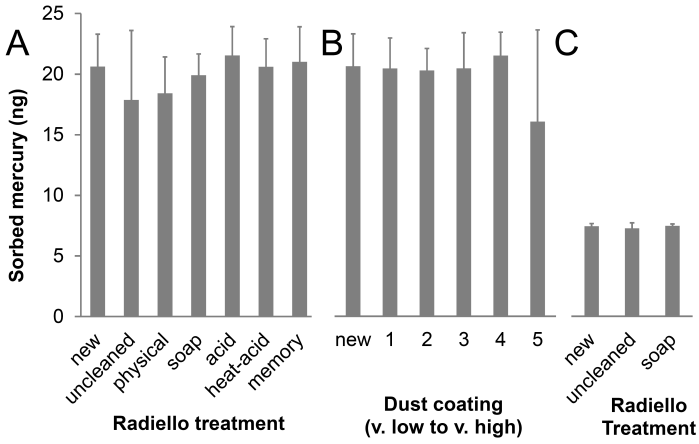


**Figure 3: Mean sorbed mercury for differing Radiello® cleaning treatments and at varying degrees of HGR-AC dust coating inside the Radiello® (Panel B) from indoor experiment. Cleaning treatments and degree of dust coating is described in Sect. 2.2.3. Panel A also includes the memory effect treatment, 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 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 and 0.001 $m^3$ $day^{-1}$ increase in *SR* for every 1 °C increase in temperature to adjust the *SR* of 0.121 $m^3$ $day^{-1}$ to the average temperature and wind speed of each PAS deployment (See S6 for SR adjustment equation and sample calculation).

The experiments here predict a *SR* of 0.142 $m^3$ $day^{-1}$ for an average wind speed of 1.89 m $s^{-1}$ (Fig. 1) and a *SR* of 0.141 $m^3$ $day^{-1}$ for an average temperature of 7.6°C (Fig. 2). Both these values are greater than the *SR* of 0.121 $m^3$ $day^{-1}$ 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 at al. (2016b) observed that *SR* for PAS deployed outdoors for less than 1-2 months were higher than the *SR* derived for the entire one-year sampling period. Despite this slight

discrepancy, we note that the y-intercepts 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 PAS 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 windshield needs to be exposed to typical background concentrations of gaseous Hg (~1.5 – 2 ng $m^{-3}$) for approximately one 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 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 poly-ethylene diffusive barriers can be affected by cleaning with HCl. While in this study we used HNO3 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 SI, or via communication with the corresponding author.

## Competing Interests

The authors declare that they have no conflicts of interest.

## Acknowledgements

We acknowledge funding from Strategic Project Grant #463265-14 by the Natural Sciences and Engineering Research Council of Canada (NSERC) and an NSERC Alexander Graham Bell Canada Graduate Scholarship. We thank S. Steffen of Environment and Climate Change Canada for the loan of the Tekran instrument and B. Branfireun, S. Bartlett, C. Hamilton, and A. Craig from Western University for providing access to the BIOTRON facility.

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