

Communication

Can the MerPAS Passive Air Sampler Discriminate Landscape, Seasonal, and Elevation Effects on Atmospheric Mercury? A Feasibility Study in Mississippi, USA

Byunggwon Jeon and James V. Cizdziel *

Department of Chemistry and Biochemistry, University of Mississippi, Oxford, MS 38677, USA;
bjeon@olemiss.edu

* Correspondence: cizdziel@olemiss.edu

Received: 16 August 2019; Accepted: 10 October 2019; Published: 12 October 2019



Abstract: Accurately measuring gaseous elemental mercury (GEM) concentrations in the atmosphere is important to understand its sources, cycling, distribution, and temporal trends. The MerPAS passive air sampler from Tekran Inc. (Toronto, ON, Canada) captures GEM on sulfur-impregnated activated carbon after it passes through a Radeillo diffusive barrier. Because they are small, relatively low in cost, and require no power, they can be deployed at multiple locations, yielding a much greater spatial resolution, albeit at coarser temporal resolution, compared to active sampling. In this study, we used the MerPAS to measure GEM concentration gradients at a mixed hardwood forest, wetland, pond, and a mowed (grass) field, all within close proximity (<500 m) to each other. Vertical profiles (0.5, 3.0, 5.5 m) were assessed during summer and winter. The sorbent was analyzed using a direct mercury analyzer. The samplers were captured between 0.90 to 2.2 ng over 2 weeks, well above the mean blank of 0.14 ng. We observed differences between the landscapes, elevation, and seasons. Nearest to the surface, GEM concentrations were lowest in the wetland (both seasons), where there was dense vegetation, and highest in the mowed field (both seasons). Generally, GEM levels increased with the elevation above the ground, except for the forest where the trend was slightly reversed. This suggests a possible net GEM deposition from the atmosphere to surfaces for three of the four landscapes. GEM concentrations were slightly higher in the winter than the summer at 5.5 m height where air masses were unimpeded by vegetation. Overall, we conclude that the MerPAS is indeed capable of measuring GEM gradients between landscapes, elevations, and seasons, if given sufficient collection time, good analytical precision, and low blank levels.

Keywords: passive sampler; gaseous mercury; forest; wetland; pond; mowed field; seasonal trend; vertical profile; outdoor air

1. Introduction

Mercury (Hg) is a widespread global contaminant that is distributed primarily through the atmosphere, where it exists in three common forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particle bound mercury (PBM) [1,2]. GEM is the predominant form of Hg in the atmosphere, typically comprising >95% of total gaseous mercury (TGM), often defined as GEM + GOM [1]. GEM has a relatively long residence time in the air (estimated from months to years), and thus it plays an important role in the global transport of Hg [3,4]. GEM is slowly converted by photochemical and other reactions to GOM, which, because of its solubility and particle-reactivity, has a relatively short lifespan in the atmosphere (estimated from days to weeks) depending on atmospheric conditions [1,4]. Likewise, PBM is scavenged from the atmosphere at shorter time-scales depending

on particle size and weather [5,6]. Each category of gaseous Hg can be deposited to terrestrial and aquatic surfaces through wet and dry deposition mechanisms [6,7]. Once deposited, inorganic Hg can be methylated by certain microorganisms to form methyl-Hg, a neurotoxin that can accumulate in biological tissues and concentrate up food chains [6].

To better describe the global biogeochemical cycling of Hg and to evaluate the effectiveness of the recent Minamata Convention, a global treaty to reduce Hg pollution and produce accurate measurements of Hg in the atmosphere are essential. However, reliably determining atmospheric Hg concentrations at ambient levels in the boundary layer is challenging because of its low background, which is on the order of 1–2 ng m⁻³ [1,7]. Most methods to measure airborne Hg rely on active sampling, drawing air at a known rate over a sorbent designed specifically to trap gaseous Hg species, typically using gold coated quartz [8]. The traps are subsequently heated, and the desorbed Hg is carried by argon gas into an atomic fluorescence instrument for analysis. Recently, an eddy covariance flux method was validated for direct Hg⁰ flux measurements [9]. Such setups are costly, require calibrated pumps, electrical power, trained operators, and have other constraints that limits their application [10,11].

An alternative approach to measure GEM uses passive air samplers (PASs), where gaseous Hg enters the sampler and diffuses at a known rate into a chamber where it is trapped on a sorbent. Compared to active sampling, the low-cost of passive sampling allows for a much larger number of samplers and thus a greater area coverage and spatial resolution, albeit at a coarser temporal resolution [10,12]. PASs can be deployed for extended periods without any need to revisit the site until they are removed for analysis, as long as the Hg sorbent capacity is not reached [10–13]. One PAS design for Hg uses sulfur-impregnated activated carbon as the sorbent, a Radiello diffusive barrier to constrain the sampling rate, and a protective shield for outdoors [14]. The amount of GEM taken up by this type of PAS, determined by a direct mercury analyzer (DMA), was shown to increase linearly with time, yielding outdoor sampling rates of ~0.135 m³ day⁻¹ and a replicate precision of 2 ± 1.3% [15]. Gaseous Hg concentrations are calculated by dividing the mass of sorbed Hg by the deployment time and the sampling rate. A critical review of passive air sampling of gaseous Hg revealed some shortcomings in the methodology (e.g., sampling rates that vary due to meteorological factors and manufacturing inconsistencies) but also discussed potential routes to overcome these difficulties [16].

Because GEM recycles between environmental compartments, it is necessary to quantify fluxes between the atmosphere and both terrestrial and aquatic surfaces [17]. However, GEM fluxes from the natural landscapes are relatively poorly characterized compared with many point sources of Hg, even though they can play a large role in influencing airborne Hg concentrations on local, regional, and global scales [1,4,18]. A variety of factors have been shown to influence GEM fluxes from natural surfaces, including the substrate's Hg concentration, sunlight, temperature, atmospheric turbulence, relative humidity, rain events, and vegetation cover [18,19]. Another important factor is reduction of oxidized divalent mercury (Hg²⁺) to Hg⁰ in both soil and aquatic environments, a process which is catalyzed by solar radiation [18,20].

Gradient fluxes of GEM from natural surfaces are typically measured using either enclosure (e.g., dynamic flux chamber (DFC)) or micrometeorological methods [4,21] but can also be estimated from vertical profiles of gaseous Hg determined by PASs [22]. Currently, Hg PASs are being used by the same University of Toronto research group that developed them to observe long term seasonal trends, the impact of wind speed, which can vary at different heights above the ground, at different sampling rates, and based on differences within and above the canopy. However, we are not aware of any studies comparing Hg concentrations between multiple landscapes in close proximity to each other, which is advantageous because weather and GEM carried by air masses entering the area are better constrained compared to landscapes separated by greater distances. It is worth noting that, while GEM fluxes vary diurnally, these fluctuations cannot be resolved by PASs due to the relatively long deployment times that they require (days to weeks, depending on concentrations).

We have previously examined GEM fluxes from different landscapes in Mississippi, USA using a dynamic flux chamber with active sampling [23]. The main goal of the current study was to test the feasibility of the MerPAS to measure GEM concentration gradients between some of these same landscapes, as well as by elevation (vertical profiles) and seasons. To address these goals, we deployed samplers in a mixed hardwood forest, wetland, pond and a mowed field, all within close proximity (~500 m) of each other. Vertical profiles (0.5, 3.0, 5.5 m) were assessed during both summer and winter. We report trends in our observed data based on the context of what is known from the literature; fully quantifying the factors that affect the GEM concentrations and GEM fluxes is beyond the scope of this feasibility study.

2. Materials and Methods

2.1. Study Site

The University of Mississippi Field Station (UMFS) is a 3 km² research and educational facility located 18 km northeast of the main campus of the University in North Central Mississippi, USA. It consists of mixed hardwood forest, wetlands, former pasture land, and 220 experimental ponds, with each type of landscape in close proximity (~500 m) of each other (Figure 1). The site lies within the Eocene Hills of the interior coastal plain of the southeastern U.S. and is characterized by sandy and sandy-loam soils. The area was row crops prior to 1947. The depth of the pond was ~1 m.

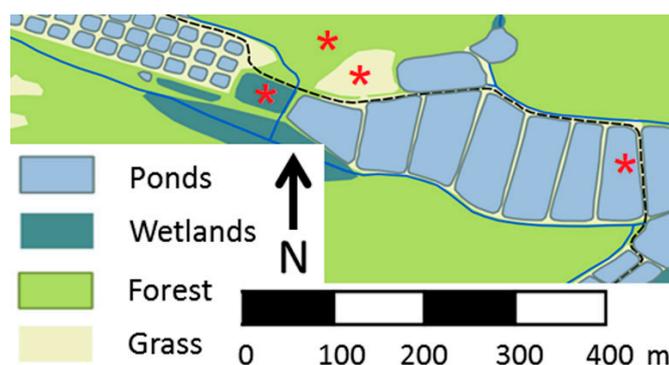


Figure 1. A map showing the proximity of the sampling locations (red stars) at the adjacent landscapes at the University of Mississippi Field Station.

2.2. Hg Passive Air Sampler

We used a commercially available Hg PAS called “MerPAS” (Tekran Inc., Toronto, ON, Canada) (Figure 2). The MerPAS is based on a design developed by researchers at the University of Toronto that has been described in detail in several papers [14–16]. Briefly, sulfur-impregnated activated carbon powder (HGR-AC, Calgon Carbon Corp., Pittsburg, PA, USA) housed in a stainless-steel mesh cylinder was inserted into a porous polyethylene diffusive barrier (White Radiello[®], Sigma Aldrich, St. Louis, MO, USA) that controls the rate of diffusion from the air to the sorbent. This diffusive barrier was then attached to the inside of a plastic (polyethylene terephthalate) protective shield to minimize and control the effects of wind, solar radiation, and precipitation on the rate of Hg uptake from the air [14]. The MerPAS is considered to be a GEM sampler because the diffusive barrier has been shown to prevent reactive gaseous mercury species (GOM) from passing through [24]. It is also worth recalling that GEM generally makes up >95% of the TGM at most locations not impacted by point sources [1].



Figure 2. Photos showing the Hg passive air sampler (MerPAS) with a White Radiello diffusive body inside a protective shield and the mesh cover in the background (**left**), as well as a close up of the diffusive body, stainless steel mesh screen, and sulfur-impregnated activated carbon sorbent (**right**).

In the present study, MerPAS samplers were loaded the day before deployment with freshly crushed and sieved HGR-AC (particles ranged in size between 250 and 1000 μm). The stainless steel mesh cylinder held 0.58 ± 0.02 g of the sorbent, with sufficient capacity to collect ambient levels of outdoor Hg for at least a year [21]. Prior to loading the stainless-steel cylinders, the sorbent was analyzed to assure that it met the low-blank criteria (<0.2 Hg ng/sampler). Diffusive barriers were re-used after inspection to make sure they were not visibly dirty; the mean rate of gaseous Hg uptake did not differ between new and previously used barriers if they remained clean [15,16].

2.3. Deployment of PAS

We deployed the PASs at the UMFS at three heights (0.5, 3.0, and 5.5 m) above a forest floor, a wetland, a mowed field, and a pond during the summer and winter of 2019 (Figure 3). Each site was within 500 m of the others. The samplers were mounted on a metal bracket attached to long wood (oak) boards purchased from a local hardware store (Figure 3). This sampling configuration was selected in part because there was a limited number of PASs to deploy at each site and other logistics. For instance, 5.5 m was the maximum height achievable by coupling two of the longest boards available from a local hardware store with a metal bracket; 0.5 m was selected as the lowest height to minimize water entering the samplers from splashing during rain events, and a middle height was selected to have three heights to assess vertical profiles.

To simplify the sampler's deployment and retrieval, a metal fence pole was driven into the ground such that the boards with samplers attached could readily be inserted for vertical deployment and later lifted out and laid on the ground to remove or replace the samplers. During the winter, we deployed 4 samplers at each height for a total of 48 samplers, while in the summer we deployed 3 samplers at each height for a total of 36 samplers, followed by a second summer sampling campaign targeting the pond and mowed field. The samplers were deployed concurrently at each location for 2 weeks and then retrieved, placed in a Ziplock bags, and transported to the laboratory, where they were stored in a clean room until analysis (within two days). The mean weather conditions at the nearest operational weather station (located 7 km to the southwest) during sampler deployment are reported in the Appendix A (Table A1).

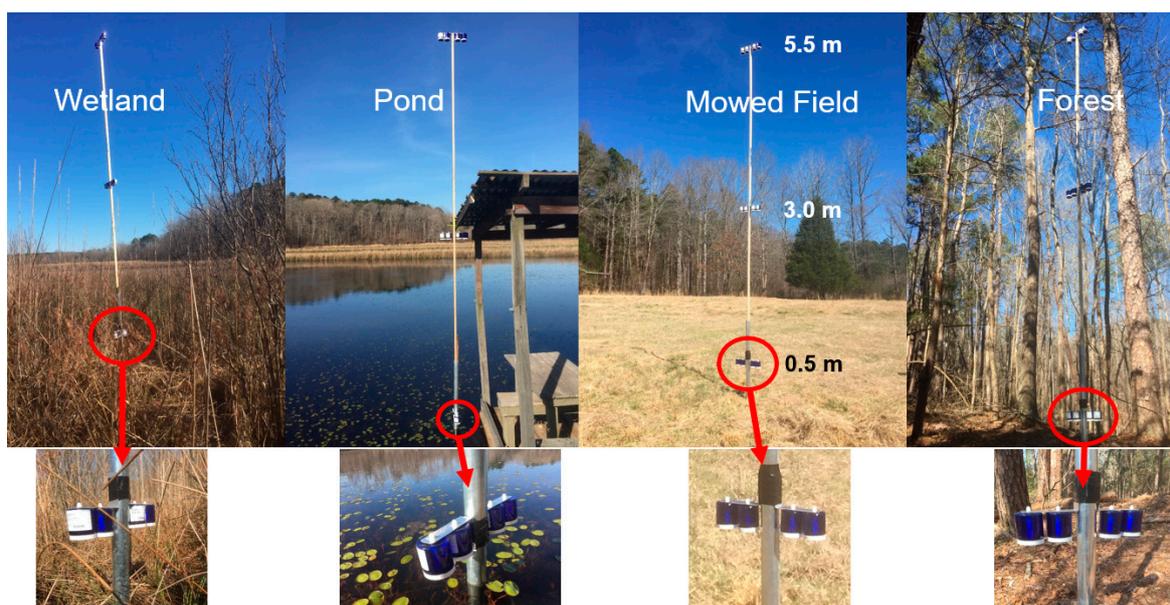


Figure 3. Deployment of Hg passive air samplers at the University of Mississippi Field Station during winter 2019.

2.4. Determination of Hg on the Sorbent and in the Soil and Sediment using a Direct Mercury Analyzer

Total-Hg in the samples was determined with a Direct Mercury Analyzer (DMA-80; Milestone Inc., Shelton, CT, USA) following the US EPA method 7473, with some modifications for the activated carbon (MerPAS) samples. This method is based on thermal decomposition-atomic absorption spectrometry, which has been widely used to measure Hg in a variety of complex matrices, including fish, sediment, and coal [25–27]. Here, we focus on the procedure for analyzing the PASs. After retrieving them from the field, the stainless steel cartridges containing the sorbent was removed in the laboratory and about half of its contents were carefully transferred into a pre-heated (blanked) quartz sample boat and recorded its weight. Then, ~0.2 g of Na_2CO_3 was added directly on top of the sorbent. This process was repeated using a second boat because the amount of sorbent exceeded the capacity of a single boat. Adding Na_2CO_3 has been shown to greatly increase the lifetime of the DMA catalyst by minimizing the SO_2 that reaches the catalyst [28]. When the sulfur-impregnated carbon sorbent is combusted, it produces SO_2 gas, which can poison the catalyst. Na_2CO_3 reacts with SO_2 to make Na_2SO_3 (s) along with CO_2 . We also amended the catalyst tube itself with 5 g of Na_2CO_3 powder.

The quartz boats with the PAS sorbent were loaded onto the auto-sampler, which sequentially inserts the boats into the decomposition furnace. There, samples are thermally decomposed at 750 °C, and the Hg released is carried by oxygen to the catalyst, where Hg species are reduced to gaseous elemental vapor (Hg^0). As other combustion gases are flushed from the system, Hg is trapped by amalgamation with gold. The trap is subsequently heated to 900 °C, and Hg is released and carried through an absorption cell where it is quantitatively measured at 253.7 nm. The instrument was set to collect the Hg from two quartz boats representing one PAS before heating the amalgamator to obtain one measurement per PAS.

The DMA instrument was calibrated using a series of standard Hg solutions prepared from a stock Hg standard solution from Spex Certiprep (Metuchen, NJ, USA). For quality control, coal fly ash standard reference material (NIST 1633C) was analyzed before the samplers and every ~20 boats thereafter. Recovery of the CRM was $97.5\% \pm 5.6\%$ (mean \pm SD). Sample boats were pre-heated to remove Hg and boat blanks were analyzed to assure there was a negligible contribution of Hg. The limit of detection (3 sigma criterion) was 0.014 ng of Hg.

2.5. Calculation of Atmospheric Hg Concentration

Concentrations of GEM were calculated by dividing the mass of sorbed Hg (ng) by the deployment time (days) and the sampling rate ($\text{m}^3 \text{ day}^{-1}$). The blank subtracted uptake (mass loading) of Hg from the atmosphere to the samplers ranged from 0.90 to 2.2 ng. Carbon blanks were <15% of this amount. We used a sampling rate of $0.111 \text{ m}^3 \text{ day}^{-1}$, modified slightly to reflect the mean temperature and wind speeds for each season [21]. The $0.111 \text{ m}^3 \text{ day}^{-1}$ base sampling rate was recommended by Tekran Inc., which has done a variety of inter-comparison studies to assess the MerPAS sampling rate (E. Prestbo, Tekran Inc., personal comm.). Our adjusted sampling rates were $0.115 \text{ m}^3 \text{ day}^{-1}$ in the summer and $0.103 \text{ m}^3 \text{ day}^{-1}$ in the winter. These, however, are slightly lower than the $0.135 \text{ m}^3 \text{ day}^{-1}$ determined by McLagan et al. [21], who deployed similar samplers worldwide, the Tekran MerPAS was reconfigured slightly from the earlier version for mass production, and it includes a screen that has slightly less open surface area than the earlier model (E. Prestbo, Tekran Inc., personal comm). Here, we are primarily concerned with the relative differences between landscapes, heights, and seasons, not the absolute concentrations. We are currently comparing the MerPAS with active sampling for Hg at Grand Bay, Mississippi (paper in progress).

2.6. Statistical Analysis

Data were analyzed using SPSS Version 25. Analysis of variance (ANOVA) was used to examine differences in the GEM between landscapes by season and the GEM between heights for each landscape. Tukey's tests were used to provide pairwise differences in the means among landscapes and heights. Differences were deemed significant at a $p < 0.05$ level.

3. Results and Discussion

3.1. Summary Statistics and Overall Trends

GEM concentrations by landscape, elevation, and season are shown Figure 4, with exact values in Table A2. The levels are at or below those generally accepted as the North American background ($1\text{--}2 \text{ ng m}^{-3}$) [1], but within this range, we have previously measured using active sampling in the area [23]. These relatively low concentrations indicate that there are no Hg point sources in the local area to affect the results. Total-Hg concentrations ($\text{ng g}^{-1} \pm \text{Standard Error}$) in the bulk soil and sediment (substrate) were forest (74.8 ± 2.8) > wetland (45.5 ± 1.9) > mowed field (21.2 ± 0.6) (Table A2). We observed several statistically significant differences ($p < 0.05$) between certain landscapes, between the 0.5 and 5.5 m elevations (within certain landscapes), and between seasons (for certain landscapes). Together, these data and observations (described below) suggest that the MerPAS is indeed capable of discriminating the effects that landscapes, elevation, and seasons have on atmospheric Hg; provided the sampler is given sufficient collection time, there is good analytical precision, and blank levels are low.

GEM concentrations ($\text{ng m}^{-3} \pm 1 \text{ Standard Error}$) nearest to the surface (0.5 m) ranged from 0.62 ± 0.04 at the wetland during the winter to 0.98 ± 0.10 at the forest during the winter. At the highest elevation (5.5 m), concentrations ranged from 0.75 ± 0.01 at the forest during the summer to 1.03 ± 0.11 at the mowed field during the winter. At the 0.5 m height, we observed statistically lower concentrations at the wetland (0.65 ± 0.03) compared with both the mowed field (0.88 ± 0.04) and the pond (0.83 ± 0.03) in the summer. Also, in the summer, the forest (5.5 m) had lower concentrations (0.75 ± 0.01) than both the mowed field (0.91 ± 0.03) and pond (0.88 ± 0.03). There were also statistical differences between elevations. During both the summer and winter, concentrations at the wetland were lower ($p < 0.01$) at the 0.5 m height compared to the 5.5 m height (Figure 4).

Seasonally, higher mean GEM concentrations were observed at the 5.5 m height in the winter compared to the summer at three of the landscapes, with the pond as an exception (Figure 4). GEM concentrations in air masses have also been reported to be higher in the winter compared to the summer, primarily due to the uptake of Hg by plants [1]. However, in the summer, there can be higher evasion fluxes from soil and other surfaces due to both higher temperatures and more intense solar radiation [29,30]. In our study, GEM concentrations in the forest were slightly lower in the summer, though not statistically different. Forests influence gaseous Hg differently, in part because of large changes in foliage and due to shade from the canopy, which influences Hg uptake and the penetration of solar radiation [31].

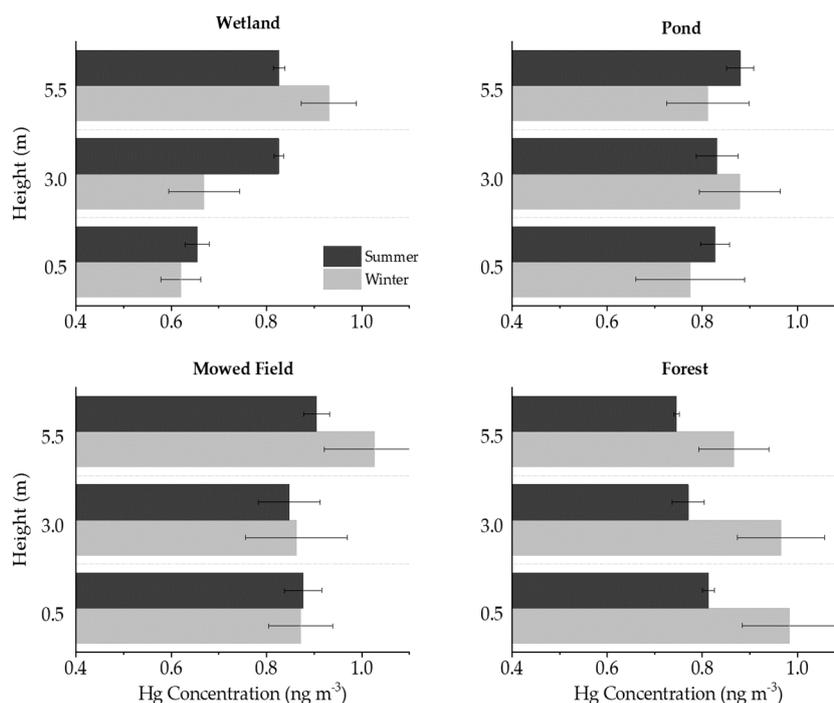


Figure 4. Mean concentrations ($\text{ng m}^{-3} \pm 1 \text{ S.E.}$) of gaseous elemental mercury determined with passive air samplers deployed at four adjacent landscapes in north-central Mississippi.

Trends for GEM concentrations with elevations above the surface were also evident. Concentrations were significantly greater for elevations in the wetland, and to lesser extent the mowed field, suggesting Hg deposition from the atmosphere to the surface (Figure 4). These landscapes have plants near and around the lower sampling height, which may be stripping some Hg from the atmosphere. Plants are known to be a sink for atmospheric Hg, and it has been hypothesized that Hg can migrate into leaf pores and, in some cases, traverse the cuticle until oxidized with organic acids and immobilized [32]. There was no apparent trend with height at the pond where air masses go unimpeded above the surface; however, there were relatively large uncertainties in the data for the samplers above the water. At the forest, the trend with height was opposite, with the mean concentrations decreasing slightly (statistically insignificant) for the elevation from the forest floor. As noted, the samplers were deployed below the canopy, so unlike the other sites where air masses could impinge on the top samplers unimpeded, the forest trees and foliage disrupt the flow of air at all sampling heights, as well as minimize the solar radiation reaching the soil.

It should be mentioned that Hg PAS sampling rates can vary with temperature and wind speed, so measuring these variables and including them in the calculations can improve accuracy [15,16]; however, we did not have the capability to deploy weather stations at each site, as this was beyond the scope of our feasibility study. A single weather station near the study site showed differences in temperature, wind speed, and precipitation between the summer and winter (Table A1). While impacting gaseous oxidized Hg and particle-bound Hg, rain affects GEM to a much lesser extent because GEM, which comprises >95% of the GEM, is not particularly soluble in water [1,7].

From the observed trends and statistical differences discussed above, we are confident that the MerPAS is capable of being used to differentiate patterns in GEM with seasons, landscapes, and, in some cases, by height. However, we acknowledge that there is room for improved precision. Some approaches to improving precision may be to deploy samplers for longer times (>2 weeks) to capture more Hg, to increase the number of samplers at each position, to thoroughly assess blank contributions, and to measure wind speed and other meteorological parameters at each location and at two or more heights. Below we present some further results for each landscape separately.

3.2. Wetland

The mean GEM concentration at the wetland was significantly higher at 5.5 m compared to 3.0 m and 0.5 m during both the summer and winter (Table A2). As noted, the wetland had dense plant growth in the summer that surrounded the lower sampling height. This maze of plants can impede air flow and influence airborne Hg concentrations through uptake by plants. GEM concentrations at the lower two heights were slightly different between the seasons, possibly reflecting differences in plant density and evasion fluxes. In contrast, GEM concentrations at the top (5.5 m) elevation, where there are no plant surfaces, were nearly the same in summer and winter.

3.3. Pond

At the pond, where there was no vegetation around the samplers, there was little difference between the different sampling heights and by season. Others have shown that dissolved gaseous Hg correlates with incident radiation due to photo-induced reduction in the water [33]. Because gaseous Hg is not particularly soluble in water and because solar intensity is highest during the summer, higher evasion fluxes can be expected in the summer. Another factor that promotes the reduction of dissolved metal ions like Hg^{+2} in natural waters is dissolved organic carbon (DOC); DOC can absorb light and transfer energy to an electron acceptor, thereby enhancing Hg^{+2} reduction and subsequent GEM emission in natural waters containing high DOC levels [34,35]. At the UMFS, there is high biological productivity and DOC levels in the ponds during the summer. However, the pond is also covered in lily pads that block much of the light from penetrating into the water. Also, unlike the other landscapes, there are no plants extending into the air to hinder the air flow or filter GEM above the water. If the pond was a significant source of Hg to the air, one might expect to see a concentration gradient with diminishing concentrations by elevation over the water. We did not observe this gradient, but it could have been masked by the relatively large uncertainty in some of the pond data.

3.4. Mowed Field

Mean GEM concentrations generally increased with height, with the greatest concentration at the highest elevation in both the summer and winter. Although the differences were not statistically significant, this trend is indicative of net emissions from the surface. We have previously measured GEM fluxes over a mowed field at the UMFS using a dynamic flux chamber, observing a net emission (mean $4.52 \pm 4.8 \text{ ng m}^{-2} \text{ h}^{-1}$). However, these data were limited to a couple of days during an earlier summer [23]. Others have observed relatively high GEM fluxes over grass, even at night [36]. Here, concentrations at the mowed field were statistically higher than those at the wetland during the summer ($p = 0.01$) at a 0.5 m height.

3.5. Forest

As previously discussed, there were some different trends observed at the forest site. Some of these differences may be attributed to the canopy, which can moderate temperatures and sunlight, thereby influencing Hg fluxes [37–40]; all our measurements were taken below the canopy. Moreover, the forest topography was different, with the samplers being situated on the side of a hill instead of on the valley floor, so wind and other meteorological conditions may vary somewhat. It is also known that leaves in the forest can uptake GEM, which can further influence local concentrations of GEM [37,38]. Forest soil, which is high in organic matter, had the highest concentration of total-Hg among the landscapes tested (Table A2). GEM concentrations in the forest generally decreased with height, suggesting a possible net emission from the soil's surface. Forest GEM concentrations were also slightly higher in the winter than in the summer. It has also been demonstrated that soil is a major contributor to atmospheric Hg and that solar radiation, which can reach the ground more frequently during the winter due to a decreased forest canopy, can impact emission fluxes [23,38,39].

4. Conclusions

The purpose of this research was to assess the feasibility of using the MerPAS to measure the vertical concentration gradients of GEM at different landscapes and by season. We observed differences between certain landscapes, elevations, and, to a lesser extent, seasons. Generally, we measured lower GEM concentrations near the surface where vegetation was abundant and greater concentrations at higher elevations where air masses were unimpeded. We conclude that, given sufficient collection time, good analytical precision, and low blank levels, the MerPAS is indeed capable of measuring GEM gradients in the environment at ambient (background) levels. However, the approach used in this study could benefit from improved precision to better quantify the factors affecting GEM concentrations and potentially to measure GEM fluxes. To that end, we recommend deploying the samplers for longer times (>2 weeks), increasing the number of samplers at each location, thoroughly assessing blank contributions, and measuring site-specific meteorological conditions including wind speeds at different heights. Because of their low cost and ease of deployment, PASs have the potential to open up research opportunities to improve the understanding of the many factors that influence GEM concentrations and GEM fluxes at disparate and under-studied landscapes. A follow-up study is underway.

Author Contributions: B.J. led the sampling and measurement campaign; B.J. and J.V.C. analyzed and interpreted the data and authored the manuscript; J.V.C. conceptualized, supervised, and administered the project.

Funding: This research was partially funded by the U.S. National Science Foundation, award #1632825.

Acknowledgments: We are grateful to Scott Knight and staff at the University of Mississippi Field Station for access to the site and for local meteorological data. We also thank Eric Prestbo and Lucas Hawkins at Tekran Inc. and Frank Wania and David McLagan at the University of Toronto for helpful information and suggestions on many aspects of Hg PASs.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Weather conditions near the study site during sampling.

Parameter	Winter	Summer
Mean Temperature (°C)	11.9	25.7
Mean Wind Speed (m/s)	0.16	0.08
Accumulated Precipitation (mm)	1.1	6.9

Table A2. Gaseous elemental mercury concentration (ng m^{-3}) at three different heights at adjacent landscapes in Mississippi, USA.

Landscape	Hg in Soil or Sediment (ng g^{-1} , dry weight, $n = 6$)	Height (m)	Summer		Winter	
			Mean ($n = 4$)	Standard Error	Mean ($n = 3$)	Standard Error
Wetland	45.5 \pm 1.9	5.5	0.83	0.01	0.93	0.06
		3.0	0.83	0.01	0.67	0.07
		0.5	0.65	0.03	0.62	0.04
Pond	Not Measured	5.5	0.88 ($n = 10$)	0.03	0.81	0.09
		3.0	0.83 ($n = 6$)	0.04	0.88	0.09
		0.5	0.83 ($n = 8$)	0.03	0.77	0.11
Mowed Field	21.2 \pm 0.6	5.5	0.91	0.03	1.03	0.10
		3.0	0.85 ($n = 7$)	0.06	0.86	0.10
		0.5	0.88 ($n = 6$)	0.04	0.87	0.07
Forest	74.8 \pm 2.8	5.5	0.75	0.01	0.87	0.07
		3.0	0.77	0.03	0.97	0.09
		0.5	0.81	0.01	0.98	0.10

References

- Schroeder, W.H.; Munthe, J. Atmospheric mercury—An overview. *Atmos. Environ.* **1998**, *32*, 809–822. [[CrossRef](#)]
- Valente, R.J.; Shea, C.; Humes, K.L.; Tanner, R.L. Atmospheric mercury in the Great Smoky Mountains compared to regional and global levels. *Atmos. Environ.* **2007**, *41*, 1861–1873. [[CrossRef](#)]
- Skov, H.; Christensen, J.H.; Goodsite, M.E.; Heidam, N.Z.; Jensen, B.; Wåhlin, P.; Geernaert, G. Fate of Elemental Mercury in the Arctic during Atmospheric Mercury Depletion Episodes and the Load of Atmospheric Mercury to the Arctic. *Environ. Sci. Technol.* **2004**, *38*, 2373–2382. [[CrossRef](#)] [[PubMed](#)]
- Gustin, M.; Jaffe, D. Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere. *Environ. Sci. Technol.* **2010**, *44*, 2222–2227. [[CrossRef](#)] [[PubMed](#)]
- Keeler, G.; Glinsorn, G.; Pirrone, N. Particulate mercury in the atmosphere: Its significance, transport, transformation and sources. *Water Air Soil Pollut.* **1995**, *80*, 159–168. [[CrossRef](#)]
- Driscoll, C.T.; Mason, R.P.; Chan, H.M.; Jacob, D.J.; Pirrone, N. Mercury as a Global Pollutant: Sources, Pathways, and Effects. *Environ. Sci. Technol.* **2013**, *47*, 4967–4983. [[CrossRef](#)] [[PubMed](#)]
- Lin, C.-J.; Pehkonen, S.O. The chemistry of atmospheric mercury: A review. *Atmos. Environ.* **1999**, *33*, 2067–2079. [[CrossRef](#)]
- Pandey, S.K.; Kim, K.-H.; Brown, R.J. Measurement techniques for mercury species in ambient air. *TrAC Trends Anal. Chem.* **2011**, *30*, 899–917. [[CrossRef](#)]
- Osterwalder, S.; Eugster, W.; Feigenwinter, I.; Jiskra, M. First eddy covariance flux measurements of gaseous elemental mercury (Hg^0) over a grassland. *Atmos. Meas. Tech. Discuss.* **2019**. in review. [[CrossRef](#)]
- Gustin, M.; Lyman, S.; Kilner, P.; Prestbo, E. Development of a passive sampler for gaseous mercury. *Atmos. Environ.* **2011**, *45*, 5805–5812. [[CrossRef](#)]
- Landis, M.S.; Stevens, R.K.; Schaedlich, F.; Prestbo, E.M. Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air. *Environ. Sci. Technol.* **2002**, *36*, 3000–3009. [[CrossRef](#)] [[PubMed](#)]
- Brumbaugh, W.; Petty, J.; May, T.; Huckins, J. A passive integrative sampler for mercury vapor in air and neutral mercury species in water. *Chemosphere Glob. Chang. Sci.* **2000**, *2*, 1–9. [[CrossRef](#)]
- Peterson, C.; Alishahi, M.; Gustin, M.S. Testing the use of passive sampling systems for understanding air mercury concentrations and dry deposition across Florida, USA. *Sci. Total Environ.* **2012**, *424*, 297–307. [[CrossRef](#)] [[PubMed](#)]
- McLagan, D.S.; Mitchell, C.P.J.; Huang, H.; Lei, Y.D.; Cole, A.S.; Steffen, A.; Hung, H.; Wania, F. A High-Precision Passive Air Sampler for Gaseous Mercury. *Environ. Sci. Technol. Lett.* **2016**, *3*, 24–29. [[CrossRef](#)]

15. McLagan, D.S.; Mitchell, C.P.J.; Huang, H.; Hussain, B.A.; Lei, Y.D.; Wania, F. The effects of meteorological parameters and diffusive barrier reuse on the sampling rate of a passive air sampler for gaseous mercury. *Atmos. Meas. Tech.* **2017**, *10*, 3651–3660. [[CrossRef](#)]
16. McLagan, D.S.; Mazur, M.E.E.; Mitchell, C.P.J.; Wania, F. Passive air sampling of gaseous elemental mercury: A critical review. *Atmos. Chem. Phys. Discuss.* **2016**, *16*, 3061–3076. [[CrossRef](#)]
17. Sommar, J.; Zhu, W.; Lin, C.-J.; Feng, X. Field Approaches to Measure Hg Exchange Between Natural Surfaces and the Atmosphere—A Review. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 1657–1739. [[CrossRef](#)]
18. Gustin, M.S.; Kolker, A.; Gårdfeldt, K. Transport and fate of mercury in the environment. *Appl. Geochem.* **2008**, *23*, 343–344. [[CrossRef](#)]
19. Choi, H.-D.; Holsen, T.M. Gaseous mercury fluxes from the forest floor of the Adirondacks. *Environ. Pollut.* **2009**, *157*, 592–600. [[CrossRef](#)]
20. Poissant, L.; Casimir, A. Water-air and soil-air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* **1998**, *32*, 883–893. [[CrossRef](#)]
21. McLagan, D.S.; Mitchell, C.P.J.; Steffen, A.; Hung, H.; Shin, C.; Stuppel, G.W.; Olson, M.L.; Luke, W.T.; Kelley, P.; Howard, D.; et al. Global evaluation and calibration of a passive air sampler for gaseous mercury. *Atmos. Chem. Phys. Discuss.* **2018**, *18*, 5905–5919. [[CrossRef](#)]
22. Feigis, M.; Mistry, S.; Snow, M.; Lei, Y.D.; Wania, F. Measuring Vertical Profiles of Gaseous Mercury Concentration using Passive Air Samplers. In Proceedings of the SETAC North America 39th Annual Meeting, Sacramento, CA, USA, 4–8 November 2018.
23. Cizdziel, J.V.; Zhang, Y.; Nallamotheu, D.; Brewer, J.S.; Gao, Z. Air/surface exchange of gaseous elemental mercury at different landscapes in Mississippi, USA. *Atmosphere* **2019**, *10*, 538. [[CrossRef](#)]
24. Stuppel, G.W.; McLagan, D.S.; Steffen, A. In situ reactive gaseous mercury uptake on Radiello diffusive barrier, cation exchange membrane and teflon filter membranes during atmospheric depletion events. In Proceedings of the International Conference on Mercury as a Global Pollutant, Krakow, Poland, 8–13 September 2019.
25. Antón, M.A.L.; Yuan, Y.; Perry, R.; Maroto-Valer, M.M. Analysis of mercury species present during coal combustion by thermal desorption. *Fuel* **2010**, *89*, 629–634. [[CrossRef](#)]
26. Cizdziel, J.V.; Hinnert, T.A.; Heithmar, E.M. Determination of Total Mercury in Fish Tissues using Combustion Atomic Absorption Spectrometry with Gold Amalgamation. *Water Air Soil Pollut.* **2002**, *135*, 355–370. [[CrossRef](#)]
27. Chen, J.; Chakravarty, P.; Davidson, G.R.; Wren, D.G.; Locke, M.A.; Zhou, Y.; Brown, G.; Cizdziel, J.V. Simultaneous determination of mercury and organic carbon in sediment and soils using a direct mercury analyzer based on thermal decomposition–atomic absorption spectrophotometry. *Anal. Chim. Acta* **2015**, *871*, 9–17. [[CrossRef](#)] [[PubMed](#)]
28. McLagan, D.S.; Huang, H.; Lei, Y.D.; Wania, F.; Mitchell, C.P. Application of sodium carbonate prevents sulphur poisoning of catalysts in automated total mercury analysis. *Spectrochim. Acta Part B Spectrosc.* **2017**, *133*, 60–62. [[CrossRef](#)]
29. Lindberg, S.E.; Dong, W.; Meyers, T. Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida. *Atmos. Environ.* **2002**, *36*, 5207–5219. [[CrossRef](#)]
30. Gustin, M.S.; Stamenković, J. Effect of Watering and Soil Moisture on Mercury Emissions from Soils. *Biogeochemistry* **2005**, *76*, 215–232. [[CrossRef](#)]
31. Kuiken, T.; Gustin, M.; Zhang, H.; Lindberg, S.; Sedinger, B. Mercury emission from terrestrial background surfaces in the eastern USA. II: Air/surface exchange of mercury within forests from South Carolina to New England. *Appl. Geochem.* **2008**, *23*, 356–368. [[CrossRef](#)]
32. Stamenkovic, J.; Gustin, M.S. Nonstomatal versus Stomatal Uptake of Atmospheric Mercury. *Environ. Sci. Technol.* **2009**, *43*, 1367–1372. [[CrossRef](#)]
33. Amyot, M.; McQueen, D.J.; Mierle, G.; Lean, D.R.S. Sunlight-Induced Formation of Dissolved Gaseous Mercury in Lake Waters. *Environ. Sci. Technol.* **1994**, *28*, 2366–2371. [[CrossRef](#)] [[PubMed](#)]
34. Zhu, J.; Wang, D.; Ma, M. Mercury release flux and its influencing factors at the air-water interface in paddy field in Chongqing, China. *Chin. Sci. Bull.* **2013**, *58*, 266–274. [[CrossRef](#)]
35. Nriagu, J.O. Mechanistic steps in the photoreduction of mercury in natural waters. *Sci. Total. Environ.* **1994**, *154*, 1–8. [[CrossRef](#)]
36. Ericksen, J.; Gustin, M.; Xin, M.; Weisberg, P.; Fernandez, G. Air–soil exchange of mercury from background soils in the United States. *Sci. Total. Environ.* **2006**, *366*, 851–863. [[CrossRef](#)] [[PubMed](#)]

37. Ericksen, J.; Gustin, M.; Schorran, D.; Johnson, D.; Lindberg, S.; Coleman, J. Accumulation of atmospheric mercury in forest foliage. *Atmos. Environ.* **2003**, *37*, 1613–1622. [[CrossRef](#)]
38. Gustin, M.S.; Ericksen, J.A.; Schorran, D.E.; Johnson, D.W.; Lindberg, S.E.; Coleman, J.S. Application of Controlled Mesocosms for Understanding Mercury Air–Soil–Plant Exchange. *Environ. Sci. Technol.* **2004**, *38*, 6044–6050. [[CrossRef](#)]
39. Feng, X.; Wang, S.; Qiu, G.; Hou, Y.; Tang, S. Total gaseous mercury emissions from soil in Guiyang, Guizhou, China: Mercury emission from soil in Guiyang. *J. Geophys. Res. Atmos.* **2005**, *110*. [[CrossRef](#)]
40. Mazur, M.; Mitchell, C.; Eckley, C.; Eggert, S.; Kolka, R.; Sebestyen, S.; Swain, E.; Sebestyen, S. Gaseous mercury fluxes from forest soils in response to forest harvesting intensity: A field manipulation experiment. *Sci. Total. Environ.* **2014**, *496*, 678–687. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).