An Application of Passive Samplers to Understand Atmospheric

Mercury Concentration and Dry Deposition Spatial Distributions

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1 Abstract

- 2 Two modified passive samplers were evaluated at multiple field locations. The sampling
- 3 rate (SR) of the modified polyurethane foam (PUF)-disk passive sampler for total
- 4 gaseous mercury (TGM) using gold-coated quartz fiber filters (GcQFF) and gaseous
- 5 oxidized mercury (GOM) using ion-exchange membranes (IEM) were 6.4 ± 1.4 and 15.3
- $6 \pm 0.3 \text{ m}^3 \text{ day}^{-1}$, respectively. The relative percent difference between TGM and GOM
- 7 concentrations measured by a Tekran system and the passive samplers averaged 19 ± 14
- 8 and $13 \pm 12\%$ and ranged between 4-44 and 1.5-41%, respectively. The GcQFF and IEM
- 9 substrates were also evaluated as collection media for surrogate surface dry deposition
- 10 measurements. Mercury (Hg) concentration and dry deposition gradients were observed
- 11 using these samplers at an urban/industrial site and compared to a rural/remote site. The
- 12 Hg dry deposition rates measured by the surrogate surfaces were always higher than
- 13 when calculated by a widely used inferential modeling method (1.3 50 fold). This Hg
- 14 dry deposition measured at urban and suburban sites were comparable to those calculated
- 15 from model. However, they were much different at a rural site, probably due to the low
- 16 concentration. Both methods are relatively low cost and will aid in understanding spatial
- 17 distributions of Hg ambient air concentrations and dry deposition.
- 18
- 19 Keyword: Mercury, air concentration, dry deposition, passive sampler, surrogate surface
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22 Introduction

23	Mercury (Hg) is classified as a hazardous air pollutant by the United States EPA 1 .
24	In the atmosphere, it exists as three important forms: gaseous elemental Hg (GEM),
25	gaseous oxidized Hg (GOM), and particulate-bound Hg (PBM) (Schroeder and Munthe,
26	1998). Concentrations of all three forms are influenced by nearby and distant sources,
27	atmospheric chemistry, and deposition ²⁻⁴ . Deposited Hg is a major input to ecosystems,
28	and generally dry and wet deposition are thought to contribute equally in locations not
29	impacted by significant anthropogenic sources ⁵⁻¹⁰ .
30	Hg wet deposition has been widely investigated in part due to measurements made
31	by the United States Mercury Deposition Network (MDN). Dry deposition is less well
32	understood, primarily due to the difficulty in making these measurements.
33	Micrometeorological techniques are one method to measure dry deposition to natural
34	surfaces ¹¹ . However, this approach is typically deployed during relatively short intensive
35	studies since it requires strict siting criteria, expensive instrumentation, careful oversight,
36	and works only under limited meteorological conditions. Another approach is using
37	surrogate surfaces to measure Hg dry deposition ^{8, 12-17} . Most surrogate surface studies
38	use one of two common aerodynamic designs, a knife-edge (KSS) and a frisbee-shape
39	(FSS) ¹⁸ . The surrogate surfaces used for Hg dry deposition measurements are generally
40	designed to capture gas and particle phase deposition and often have low surface
41	resistance; therefore, it is a challenge to extrapolate the measured data using these
42	surfaces to natural surfaces ¹⁴ . A multiple-resistance model (MRM) has been developed
43	to predict Hg dry deposition rates ¹⁹ and compared with measured Hg dry deposition rates
44	obtained with a surrogate surface ^{8, 10, 14} .

Ambient Hg concentrations of GEM, GOM, and PBM have been routinely monitored over the last decade using manual and automated sampling systems consisting of selective adsorption surfaces followed by thermal decomposition and analysis by cold vapor atomic fluorescence spectroscopy (CVAFS) ²⁰⁻²³. However, these systems are relatively expensive, requires maintenance by well-trained operators, supplies, and substantial sampling site infrastructure. Therefore, passive sampler will play an important role in remote, intensive spatial, and other focused studies.

52 Passive air samplers (PAS) for Hg are a low-cost and relatively simple method to 53 measure atmospheric concentrations and could be widely used to explore long-term Hg spatial distributions ²⁴⁻²⁷. Previous studies have also used bio-makers, such as lichen, tree 54 core, and moss to understand atmospheric Hg changes over longer time periods ²⁸⁻³⁰. 55 Although PASs have been widely used to measure concentrations of SO₂, NO₂, NH₄, and 56 semi-volatile organics in the atmosphere ³¹, Hg has rarely been measured using this 57 technology. Recently, Lyman et al.²⁵ made GOM concentration measurements using a 58 59 passive sampler containing a cation-exchange membrane, and the sampling rate (SR) was found to be weakly correlated with wind speed. 60

In this study, modified PASs containing gold-coated quartz fiber filters (GcQFF) and ion exchange membranes (IEM) were evaluated for their efficiency in measuring total gaseous Hg (TGM) and GOM concentrations at multiple sites in 2009. In addition, a KSS with various collection media was deployed to directly measure Hg dry deposition. An inferential MRM was used to estimate Hg dry deposition rates for comparison to the measured values. These devices have been previously evaluated in a wind tunnel and using computational fluid dynamics (CFD) ^{18, 32}.

68 Methods

69 Sampling sites

70 Hg concentrations were measured at three sites in northeast United States (Table 71 1). The first was a United States EPA designated non-attainment site for PM_{2.5} located in an urban/industrial location near Cleveland, Ohio (G.T. Craig (GTC), Ohio). The site is 72 located north of the Ohio industrial valley, 3 km south of downtown Cleveland, adjacent 73 74 to a large integrated iron and steel mill, and near the intersection of I-90 and I-77 (Figure 1). During the same period, the site was used as an intensive air quality monitoring site 75 76 by the United States EPA. Two Tekran speciation systems were run asynchronously to obtain continuous hourly average GEM, GOM, and PBM concentrations. At two other 77 sites located in New York, single Tekran speciation systems measured 2 hour integrated 78 79 Hg concentrations. The suburban site (Rochester (ROC), New York) was located in the 80 central New York, close to the intersection of I-490 and I-590, and 5-30 km southeast of 81 downtown and most industries. The rural site (Huntington Forest (HF), New York) was 82 located in the forest of Adirondacks of New York State Park. For this site, there were no significant point sources within a radius of 100 km; however, the site may be influenced 83 by local wood combustion during winter ^{33, 34} and forest fires from Quebec ³⁵. 84 Meteorological data, including wind speed at 10 m, temperature, solar radiation, and 85 relative humidity were also available at HF from United Sates EPA Clean Air Status and 86 Trends Network (CASTNET (site HWF 187)). For sites without detailed meteorological 87 data, friction velocity was calculated using Eta Data Assimilation System (EDAS) 40-km 88 from National Oceanic and Atmospheric Administration (NOAA). 89

90 Sampling Methods

91 <u>Automated Hg Monitoring</u>

A Tekran 1130, 1135, and 2537 ambient speciation system (Tekran Instruments Corporation, Knoxville, TN) was used to measure GEM, GOM, and fine PBM (PBM_{2.5}). The system was operated at a flow rate of 10 L min⁻¹. Sampling intervals were two-hours in suburban and rural sites and one-hour at the urban site followed, in all cases, by a onehour thermal desorption period. Additional details are given by Landis et al. ²³ and Choi et al. ³³. The uncertainties of GEM and GOM concentrations measured by the Tekran system are approximately 10 and 40%, respectively ³⁶.

99 <u>Passive Hg Monitoring</u>

100 The Tisch PAS (TE-200-PAS, Tisch Environmental Inc. Cleves, Ohio) containing 101 a polyurethane foam (PUF) disk has been used extensively and successfully for ambient air measurements of semi-volatile compounds ³¹. In this study, the PUF disk was replaced 102 103 with an acrylic plate (the same size as the PUF disk, $14 \text{ cm} \times 0.9 \text{ cm}$). Four filters were placed on the top and bottom of the plate in filter holders to ensure filters and the surface 104 105 of the plate were at the same level. GcQFF and IEM were used to collect TGM and GOM, 106 respectively. A detailed description as well as wind tunnel testing results and computational fluid dynamic simulations are available in May et al. ³². Ideally, the SR of 107 108 a passive sampler would be independent of external wind speed so that the captured mass 109 could be directly converted to an air concentration. However, most passive samplers allow air to enter the sampler and capture the chemicals by both diffusion and dispersion, 110 making SRs dependent on wind speed. For the commonly used PUF disk sampler, a 111 linear correlation has been found between external wind speed and SR ^{32, 37, 38}. SR is also 112 113 dependent on sampler orientation, with the lowest SR found if the PUF-disk sampler was

114	oriented 10° against the wind ³² . The PAS was deployed at GTC a times ranging from 8
115	hours to 5 days and at ROC and HF for 7 to 14 days based on the expected concentrations
116	at the different sites (the intent was for the samples to collect significantly higher Hg
117	mass than in the blanks, but not to exceed their maximum capacity) and site access. At
118	GTC, the filters were used to examine passivation and to determine suitable exposure
119	times for these surfaces. In general, three or four IEMs and two GcQFFs were deployed
120	for each sampling period. There were 27 (5 periods), 29 (9 periods), and 16 IEM (4
121	periods) samples collected using passive samplers at HF, ROC, and GTC, respectively.
122	Twenty-four GcQFFs were deployed at GTC during this intensive campaign.
123	Surrogate Surface Direct Hg Dry Deposition Measurements
124	Four circular KSSs holding GcQFF (47 mm), IEM (47 mm, Pall Life Science,
125	I.C.E. 450), deionized (DI) water, and 0.5% (v/v) acidified BrCl solution (BrCl) were
126	used to measure Hg dry deposition fluxes manually at GTC. At the ROC and HF sites,
127	IEMs on a KSS were deployed on an automated Hg dry deposition sampler which is
128	exactly the same dimension as the manual one but installed on a MIC-B with a
129	precipitation sensor. During precipitation, it will automatically cover the KSS; otherwise,
130	the KSS would be exposed the weather. Detailed information about these surrogate
131	surfaces including wind tunnel testing results and computational fluid dynamic
132	simulations are available in Huang et al. ¹⁸ . Field blanks were collected during every
133	sample deployment, and all samples were blank corrected using their corresponding
134	blanks.
135	A Hummer VI-A sputter coater (Anatech Ltd., Union City, CA) was used to coat
136	gold on QFFs at 215 Å min ⁻¹ rate for two minutes. Detailed analytical methods for

GcQFFs preparation and analysis can be found in Huang et al. ¹⁸, Lai et al. ¹⁴, and is
summarized in supporting information (SI). The detailed QA/QC procedures are also
included in the SI.

140 <u>Hg Dry Deposition Estimation Using a Multiple-Resistance Model (MRM)</u>

For comparison to the measured values dry deposition was estimated using models described in Zhang et al. ³⁹ for particles and Zhang et al. ¹⁹ for gaseous forms, as described in Zhang et al. ⁴⁰. The land usage category (LUC) for GTC and ROC were urban, and for HF was mixed wood forest.

145 Source of Modeling Uncertainty

Zhang et al.^{19,40-42} summarized the uncertainties of the inferential dry deposition 146 147 model. The uncertainties for aerodynamic and boundary layer resistances were relatively small (up to a 30% error during strongly stable conditions)¹⁹. Although Zhang et al.^{19,41}, 148 42 determined the air-surface exchange related parameters for O₃ and SO₂ for different 149 land usage categories, those parameters for Hg forms were calculated using their 150 corresponding chemical and physical properties ⁴¹, which are not well understood. The 151 calculated Hg dry deposition velocity was corrected for land usage based on Zhang et al. 152 ^{19, 39}; however, there are only general trends for these land usage categories and are not 153 154 easy to determine for specific sites.

The uncertainties associated with using the passive sampler and surrogate surface for Hg concentrations and dry deposition measurements has been investigated by Lai et al. ¹⁴, Huang et al. ¹⁸, and May et al. ³². For passive samples, the uncertainties arise from the sampler orientation (which influence the sampling rate, from -40 to 40%), the influence of wind speed on sampling rate, and the sampling rate conversion from one species to

another $(\sim 20\%)^{32}$. For surrogate surfaces, the uncertainties are caused by the sampler

161 orientation (30-50%), non-linear wind speed effects, low surface resistances, passivation,

and species competition ^{14, 18}. Both of these field measurements also include analytical

163 uncertainties, which are low (<10%) based on QA/QC results.

164 **Results and Discussion**

165 <u>Sampling Rate of Passive Air Samplers</u>

The SR of a passive sampler $(m^3 day^{-1})$ is the ambient air volume that contains the 166 167 mass of the pollutant taken up by the sorbent each day. Mathematically, it is equal to the mass transfer coefficient multiplied by the sorbent collection area. Since the mass transfer 168 coefficient is difficult to measure directly, the SR was calculated from the uptake rate 169 170 divided by ambient air concentration measured by the Tekran speciation system. The measured SR for TGM was $6.6 \pm 1.4 \text{ m}^3 \text{ day}^{-1}$ ($r^2 = 0.70$) at GTC (Figure 2) if two outliers 171 172 are not included. One of the outliers was a long exposure time sample (148 hrs), and the other one was exposed during a high pollutant episode (average TGM was 3.4 ng m^{-3} and 173 up to 6 ng m^{-3}). For these two samples, the Hg mass collected was still below the 174 175 maximum capacity (~15 ng) measured in the lab; however, the gold-surface may have been passivated by other species present in the air. The Hg mass of the field blanks (0.17 176 ± 0.08 ng filter⁻¹; mean \pm std dev; n = 16) were insignificant ($\alpha = 0.05$) relative to the 177 178 amount captured in ambient samples; however, all measurements were field-blank corrected. Note that the regression line was forced through the origin since all 179 180 measurements were field blank corrected.

In a previous wind tunnel study using the same modified PUF sampler, the
 measured TGM SR was approximately 10 m³ day⁻¹ at 3 m s⁻¹ external wind speed when

the sampler was oriented parallel to the flow ³². Previous studies reported a linear 183 correlation between wind speed and SR^{32, 37}. In this study, the average wind speed was 184 2.0 m s⁻¹ at GTC suggesting the SR of TGM should be less than 10 m³ dav⁻¹ consistent 185 186 with wind tunnel measurements. In addition, dew was usually observed in the early morning at the sampling site and is hypothesized to create another resistance layer for the 187 GcQFFs and reduce the SR of TGM. The gold surface might also be passivated by the 188 189 chemical constituents in dew, similar to the passivation of gold traps by other chemicals in KCl-coated denuders ²³. Gustin et al. ²⁴ also reported the gradual passivation of gold 190 surfaces used for Hg measurements in passive samplers that limited the ability to reuse 191 the gold coated surface. 192

Overall, the measured SR of GOM was $15.3 \pm 0.3 \text{ m}^3 \text{ day}^{-1}$ (r² = 0.99) (Figure 2, bottom) at all three sites. Based on a diffusivity conversion ³², the SR of GOM should be lower than that of TGM because of its higher molecular weight. However, for GOM, it is hypothesized that dew on the sampling media enhances the mass transfer rate between the atmosphere and collection surface because of GOM's high water solubility. Another potential reason for the SR of GOM to be too low is the underestimation of GOM concentrations using KCl-coated denuder ^{43, 44}.

The GOM SR measured in this study was more dependent on the external wind speed and sampler orientation than the sampler designed by Lyman et al. ²⁵. Unlike the Lyman et al. ²⁵ sampler which only allows a small amount of air to reach to the collection surface primarily via diffusion, the passive sampler used in this study was modified from a commercial sampler which allows more air flow to enter the sampler. For this sampler,

May et al. ³² reported an increasing SR when the sampler was facing or against the wind which resulted in increased turbulence inside the samplers.

In addition to greater dependence on wind speed, a larger SR would allow for 207 208 shorter sampling times to reach method detection limits (MDL) if blank levels are similar. 209 Based on the calculated sampling rates of TGM/GOM and the blank Hg mass for this 210 sampler, the MDLs (three times standard deviation of blanks) for TGM and GOM for two-week exposure times were 20 pg m⁻³ and 0.3 pg m⁻³, respectively. This MDL is 211 approximately ten times lower than that of Lyman's design which has an IEM that is 8.5 212 times larger than used in this study (107 vs. 12.6 cm^2) and a higher MDL (2 pg m⁻³). 213 Relative percent differences (RPD) between Hg concentrations measured from 214 Tekran systems and passive samplers were calculated as: 215 $RPD = \frac{|P-T|}{\pi}$ 216 Eq-3 where P and T are the Hg concentrations measured by passive samplers and Tekran 217 systems, respectively. The RPD for TGM and GOM were 4.0 - 44% and 1.5 - 41%. 218 219 respectively (Figure 3). Similar with what was found in a previous study; higher RPDs were observed at lower ambient concentrations. In general, the RPD is lower in this study 220 than in the previous study using a different sampler design²⁵. However, the RPD 221

measured by Lyman et al. 25 is around same level (40%) at GOM concentrations above 20 pg m⁻³.

Ambient TGM concentrations measured using the PAS at GTC were 1.9 ± 0.4 ng m⁻³, which are in the range of the TGM concentration measured in an urban (Detroit) and a rural Michigan site (Dexter) recently by Liu et al. ⁴⁵. GOM concentrations measured by the passive samplers at HF, ROC, and GTC were 1.9 ± 0.5 (mean ± standard deviation),

4.2 \pm 2.0, and 29.5 \pm 4.9 pg m⁻³, respectively. Since these measurements were taken at different periods during the year, a direct spatial comparison is not possible (Table 1). However, the concentration gradient for GOM from the industrial area to rural areas

- 231 observed is consistent with expectations.
- 232 <u>Mercury Dry Deposition Fluxes Measured at Different Sites</u>

During this study, different surrogate surfaces were deployed to quantify Hg dry deposition; GcQFFs, IEM, DI water, and BrCl were used to collect total Hg, GOM+PBM, GOM+PBM, and partial GEM+GOM+PBM, respectively. Total Hg dry deposition fluxes to GcQFFs at GTC were 110 ± 50 (n = 47) ng m⁻² h⁻¹. Lai et al. ¹⁴ reported that the Hg dry deposition measured by GcQFFs on a KSS were ~80 ng m⁻² h⁻¹ at a rural site in summer. While on the same order, the higher ambient dry deposition to GcQFF at GTC is due to higher Hg concentrations in the urban/industrial area.

Hg dry deposition to the IEM at GTC, ROC, and HF were 1.8 ± 0.5 (n = 12), 0.5 ± 0.3 (n = 9), and 0.1 ± 0.1 (n = 12) ng m⁻² h⁻¹, respectively. These values are lower than the Hg dry deposition to an IEM measured at rural (0.5-1.2 ng m⁻² h⁻¹) and suburban (0.1-4.5 ng m⁻² h⁻¹) sites in Nevada using downward facing surrogate surfaces ⁸. Higher GOM concentrations were observed in the western United States than in the eastern United States ⁴⁶ and likely cause the higher GOM dry deposition fluxes in Nevada. The values measured at ROC were similar to those measured in Maryland ¹³.

The Hg fluxes to DI water and BrCl at GTC were, 1.1 ± 0.8 ng m⁻² h⁻¹ (n = 6), and 4.6 ± 3.9 ng m⁻² h⁻¹ (n = 5), respectively. In rural areas, GEM is expected to be the dominant Hg form of dry deposition to water containing BrCl due to the low GOM concentration and the reaction between GEM and BrCl. In a previous study, the Hg dry

deposition flux to a BrCl solution was usually 10-30% of that to GcOFFs^{14, 18}. In 251 urban/industrial areas, where GOM concentrations can be significantly higher (300 pg m⁻ 252 ³, 30-fold higher than in rural areas), GOM and GEM dry deposition to a BrCl solution 253 254 may both be important. Although GOM dry deposition is expected to be higher at GTC 255 than in Potsdam due to its higher atmospheric concentration, the SO₂ concentration is 256 also much higher at GTC than in Potsdam, NY (BrCl solution was only used in Potsdam 257 for Hg dry deposition measurements; therefore, the data collected at GTC was compared to samples collected in Potsdam, NY). Reduction of Hg^{2+} by S (IV) in aqueous systems is 258 a fast first order reaction ⁴⁷ and the most important Hg reduction pathway. This reaction 259 would cause Hg reduction followed by GEM volatilization. If these processes are 260 occurring, they would result in a lower net dry deposition for GOM in urban/industrial 261 262 areas and may explain why Hg dry deposition to DI and BrCl solutions at the urban and 263 rural sites were similar.

264 <u>Modeled Hg Dry Deposition</u>

Average Hg (GOM+PBM) dry deposition fluxes to IEM (upward facing) at HF, 265 ROC, and GTC were 0.1, 0.5, and 2.0 ng m⁻² h⁻¹, respectively (Table 3). Modeled GOM 266 and PBM dry deposition fluxes (GOM+PBM_{2.5}+PBM_{coarse}) at these three sites were 0.03, 267 0.42, and 0.90 ng m⁻² h⁻¹, respectively (Table 4). In a previous study, Hg dry deposition 268 269 fluxes measured using the surrogate surfaces were usually higher (2- to 5-folds) than the 270 fluxes estimated from MRM (Lyman et al., 2007). The difference between measured and 271 modeled results could be due to sampler orientation, underestimated GOM concentrations by Tekran, and an underestimated coarse PBM flux by the MRM model (as is discussed 272 273 below). However, the large difference between measured and modeled fluxes at the rural

site is probably due to the relatively low flux (the Hg mass was 0.4-0.7 ng, only slightly
above the MDL (0.3 ng)). This finding suggests that surrogate surfaces should be
deployed with increased sampling times in rural locations so as to reliably measure Hg
dry deposition. Zhang et al. ⁴¹ concluded that the uncertainties in modeled dry deposition
are approximately a factor of two, similar to the difference in measured and calculated
Hg dry deposition fluxes at the GTC and ROC sites.

280 In this study, there was a significant difference (Wilcoxon Signed Rank Test, $\alpha =$ 0.05) between Hg dry deposition fluxes measured by upward facing $(2.0 \pm 0.5 \text{ ng m}^{-3} \text{ h}^{-1})$ 281 and downward facing $(1.7 \pm 0.6 \text{ ng m}^{-3} \text{ h}^{-1})$ IEMs at GTC. This difference is likely to be 282 due to PBM. Fine PBM can deposit on the downward facing filter due to diffusion; 283 however, Brownian motion has a small impact on coarse particles, and, therefore, gravity 284 and inertia control their movement ⁴⁸. Hence large particles would not be deposited to a 285 downward facing filter. The dry deposition fluxes of GOM, PBM_{2.5}, and coarse PBM 286 were calculated from their modeled dry deposition velocity multiplied by measured 287 288 atmospheric concentrations. Since only PBM_{2.5} was measured by the Tekran system, coarse PBM was estimated to be 30% of the total PBM, based on Landis et al. 49, with 289 mass median diameters of 0.68 and 3.78 μ m 50 . Unlike measured fluxes, this calculation 290 291 indicates only a 2% of difference should exist in fluxes between up (total PBM and GOM deposition) and down (fine PBM and GOM deposition) facing IEMs. This difference 292 between measurements and simulations is probably due to different size distribution of 293 294 PBM in the varying airsheds and suggests that coarse particle Hg deposition was important at the urban site. 295

296 The higher dry deposition on GcOFFs might reflect the high collection efficiency 297 of GEM on the gold surface and would be similar to other surfaces in which uptake is limited by diffusion through the boundary layer (no surface resistance) and would be the 298 299 upper limit of GEM dry deposition to natural surfaces. However, GOM dry depositions 300 measured by IEM are comparable to these calculated from model since for GOM surface 301 resistance is not very important. The total modeled Hg dry deposition at HF, ROC, and GTC based on their corresponding LUCs were 1.2 ± 1.2 , 3.2 ± 1.5 , and 4.5 ± 3.1 ng m⁻² 302 h^{-1} , respectively (Table 4). Although GOM usually has much higher dry deposition 303 velocity than GEM (average 1.2 cm s⁻¹ vs. average 0.05 cm s⁻¹), ambient air GEM 304 concentrations are 1000 times higher than GOM. Therefore, GEM is the dominant form 305 306 in Hg dry deposition in the modeled results. 307 The relative percentage of GOM dry deposition to total Hg dry deposition 308 decreased from GTC (14 %) to HF (1%). This implies GOM dry deposition is a 309 significant input to ecosystems in urban/industrial areas; however, in rural/remote areas 310 total Hg dry deposition is roughly equal to GEM dry deposition. In general, the dry 311 deposition flux of GEM in areas not impacted by large anthropogenic sources has been neglected in previous studies due to the low deposition velocity ⁵¹ and the belief that 312 313 deposited GEM revolatilizes into the atmosphere. However, a significant GEM

deposition flux was observed in this study, especially in forested ecosystems; therefore,

315 understanding GEM emissions from leaves, soil, and other surfaces is required to close

the Hg mass balance in these ecosystems. A recent study found that GEM dry deposition

dominates Hg dry deposition (from \sim 50 to >90%) even when the re-emission was

318 considered 10 .

319 Conclusions

320 Modified Hg passive air samplers provide a relatively simple and low-cost 321 alternative method to understand Hg dry deposition spatial distributions. The SR of TGM 322 and GOM measured in this study by passive samplers varied from those measured in 323 previous studies in a wind tunnel due to different wind speeds, sampler orientations, 324 surface conditions including dew formation, and Tekran uncertainty. Although the 325 relationship between sampling rate, wind speed, and sampler orientation have been explored in previous studies ^{32, 37}, little work has been done on the influence of wet 326 surface conditions on SR. Based on the measurements presented, the passive samplers 327 were able to measure a GOM concentration gradient from GTC to HF, probably due to its 328 329 rapid removal by deposition and the distance from the emission sources. Surrogate 330 surfaces were also used to measure Hg dry deposition and compared with modeled results 331 at three sites. Based on the results in this study, Hg dry deposition measured by surrogate 332 surfaces was found to be reasonable in urban/industrial areas using three day sampling 333 times. It was found that reliable measurements in rural/background locations required longer sampling periods (more than two weeks). This method should be deployed at 334 multiple sites for long-term measurements to examine the performance of the Hg dry 335 336 deposition sampler at various locations.

337 Acknowledgments

This work was funded wholly or in part by the U.S. Environmental Protection
Agency Office of Research and Development and the Office of Air Atmospheric Clean
Air Markets Division, NADP Hg Monitoring Network (EP08H000270 and

341 EP08H000271), and a NYS Energy Research and Development Authority (NYSERDA)

- 342 grant (Charles Driscoll, Syracuse University PI). It has been subjected to Agency review
- and approved for publication. Mention of trade names or commercial products do not
- 344 constitute an endorsement or recommendation for use. We gratefully acknowledge the
- 345 substantial assistance of NY DEC (Dirk Felton and Tom Everts) and SUNY-ESF
- 346 (Charlotte L. Demers), and Leiming Zhang (Environmental Canada) for the dry
- 347 deposition model.

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Figure List

- Figure 1 The map showing the locations of the sampling site at Huntington Forest, New York (HF), Rochester, New York (ROC), and Cleveland, Ohio (GTC). The negative number indicates longitude.
- Figure 2 The collection rates of TGM (Top)/GOM (Bottom) by passive samplers and their ambient air concentrations measured from Tekran system in HF (black squares), ROC (open circles), and GTC (grey dots). The error bar indicates a standard deviation with the triplicate measurements using different samplers. The slopes of regression curve represent the sampling rates of the samplers.
- Figure 3 The relative percent difference (RPD) of TGM (black dots) and GOM (open circles) concentrations measured by passive samplers and Tekran systems in HF, ROC, and GTC. RPD = abs [concentrations measured by PAS – concentrations measured by Tekran]/average.



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Table List

- Table 1 Brief description of the three sampling sites.
- Table 2 Blanks of different samples at different sites (ng per filter), mean $\pm 1\sigma$.
- Table 3 Hg dry deposition fluxes collected by different materials at different sites, mean $\pm 1\sigma$, using knife edge surrogate surfaces. n is the samples number. Up and down represent the direction the filter is facing.
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Table 1 – Brief description of the three sampling sites					
Location	Туре	Sampling methods	Location	Period	
	AMNet site ^a	Tekran speciation system	43° 58' 23.34" N	Apr, 2009 ~ May, 2009	
Huntington, NY(rural)		Passive air sampler (IEM)	74° 13' 21.76" W	Nov, 2009 ~ Jan, 2010	
		Automatic Hg dry deposition collectors	510 meters elevation		
		Tekran speciation system	43° 08' 46.09" N	Jan, 2009 ~ Feb, 2009	
Rochester, NY (suburban)	NY DEC site ^b	Passive air sampler (IEM)	77° 32' 53.62" W	June, 2009 ~ Nov, 2009	
		Automatic Hg dry deposition collectors	136 meters elevation		
	CMAPS, EPA ^c	Tekran speciation systems	41 ° 29' 31.47" N	Aug 5~Aug 15, 2009	
Cleveland, OH (urban)		Passive air sampler (GcQFF, QFF, and IEM)	81° 40' 42.60" W		
		Manual Hg dry deposition collectors	206 meters elevation		

a Atmospheric Mercury Network

b New York State, Department of Environmental Conservation

c G.T. Graig Site - Cleveland Multiple Air Pollutant Study

	HF	ROC	GTC
GcQFF			0.17 ± 0.08
IEM	0.02 ± 0.01	0.04 ± 0.03	0.03 ± 0.01
DI water			0.01 ± 0.01
BrCl			0.05 ± 0.05

Table 2 – Blanks of different samples at different sites (ng per filter), mean $\pm 1\sigma$

Table 3 – Hg dry deposition fluxes collected by different materials at different sites, mean $\pm 1\sigma$, using knife edge surrogate surfaces. n is the samples number. Up and down represent the direction the filter is facing.

	Location	Measured Dry deposition flux (ng m ⁻² h ⁻¹)	Comment
IEM (up)	HF	$0.1 \pm 0.1 (n = 12)$	GOM + PBM (automatic sampler)
IEM (up)	ROC	$0.5 \pm 0.3 \ (n = 9)$	GOM + PBM (automatic sampler)
IEM (down)		$1.7 \pm 0.6 \ (n = 6)$	GOM + PBM _{2.5} (manual sampler)
IEM (up)		$2.0 \pm 0.5 \ (n = 6)$	GOM + PBM (manual sampler)
DI water	GTC	$1.1 \pm 0.8 \ (n = 6)$	GOM + PBM (manual sampler)
BrCl		$4.6 \pm 3.9 \ (n = 5)$	GEM (partial) + GOM + PBM (manual sampler)
GcQFF (total)		$110 \pm 50 \ (n = 47)$	GEM + GOM +PBM (manual sampler)

Table 4 – Modeled Hg dry deposition fluxes, mean $\pm 1\sigma$, model Hg dry deposition velocities were calculated based on the model in Zhang et al. (2009). For PBM_{2.5} and coarse PBM, the particle sizes were assumed to be 0.68 and 3.8 µm, respectively. Their concentrations were assumed to be 70 and 30% of total PBM concentrations, respectively.

	Modeled Hg dry deposition flux (ng $m^{-2} h^{-1}$)					
	Total	GEM	GOM	PBM _{2.5}	Coarse PBM	
HF	1.2 ± 1.2	1.2 ± 1.1	0.02 ± 0.03	0.003 ± 0.003	0.004 ± 0.003	
ROC	3.2 ± 1.5	2.7 ± 1.3	0.40 ± 0.67	0.013 ± 0.011	0.005 ± 0.003	
GTC	4.5 ± 3.1	3.6 ± 3.0	0.86 ± 0.93	0.028 ± 0.035	0.016 ± 0.021	
	Modeled Hg dry deposition velocity (cm s ⁻¹)					
HF		0.02 ± 0.02	0.53 ± 0.47	0.03 ± 0.02	0.07 ± 0.01	
ROC		0.06 ± 0.02	1.63 ± 0.83	0.10 ± 0.05	0.09 ± 0.02	
GTC		0.05 ± 0.03	1.27 ± 0.85	0.07 ± 0.04	0.08 ± 0.01	

Supporting Information for

An Application of Passive Samplers to Understand Atmospheric Mercury Concentration and Dry Deposition Spatial Distributions

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Analytical Methods

Clean GcQFFs were stored in new acid-cleaned plastic Petri dishes sealed with parafilm and Teflon tape in double-zipped bags, stored in a freezer at –10°C. All GcQFFs used in this study were new and coated a week before use. After sampling, GcQFFs were returned to new acid-cleaned Petri dishes and frozen until analysis by thermal desorption CVAFS. Before heating, the Hg level in the chamber was verified to be below 0.5 ng m⁻³. After sampling, all IEMs were immersed into 45 mL DI water, and treated as aqueous samples (EPA method 1631 version E). Hg was quantified using a Tekran 2600 as described by Huang et al. (2011b).

Quality Assurance/Quality Control

The thermal desorption system was calibrated using saturated Hg vapor injections from a Tekran Model 2505 primary calibration standard. The injections were made using a Hamilton Company (Reno, NV) Model 1702RN National Institute of Standards and Technology (NIST) traceable airtight digital syringe. The calibration curve was validated using NIST standard reference materials (SRM) 1633b coal fly ash and diluted NIST1641d (aqueous Hg, HgCl₂). The Hg recovery from SRM 1633b and 1641d was 85 \pm 12 and 95 \pm 6%, respectively. SRM 1641d was also diluted to 0.5, 1, 5, 25, and 100 ppt to calibrate the Tekran 2600 (sample concentrations were 24 \pm 31 ppt). Recovery was 99%. The initial and on-going precision and recovery were measured after every twelve samples and ranged from 90 to 110%. Field blanks results were similar with those found in a previous study (Lai et al., 2011).

The relative percent difference of collocated GcQFF samples and the range of standard deviations of collocated IEM samples were $33 \pm 30\%$ and 13-32%, respectively (Figure 2). Lai et al. (2011) reported no significant ($\alpha = 0.05$) difference between collocated GcQFF measurements using the same surrogate surface. The Hg mass captured on GcQFFs samples ranged from 1.1-5.2 ng with two ~ 0.75 ng. The average field blank was 0.17 ± 0.08 ng. Therefore, the Hg mass on blanks was 23% of those collected on the lowest two samples. For IEMs, the blanks were less than 10%, 20-30%, and 20-50% of actual samples for the GTC, ROC, and HF sites (Table 2).

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