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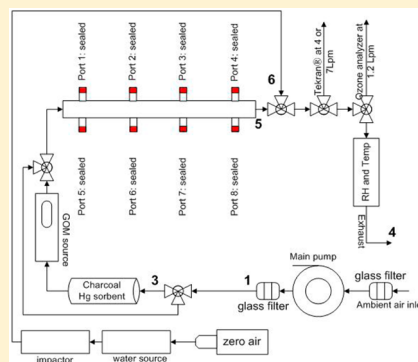
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# Uncertainties of Gaseous Oxidized Mercury Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes: Humidity Influences

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**ABSTRACT:** Quantifying the concentration of gaseous oxidized mercury (GOM) and identifying the chemical compounds in the atmosphere are important for developing accurate local, regional, and global biogeochemical cycles. The major hypothesis driving this work was that relative humidity affects collection of GOM on KCl-coated denuders and nylon membranes, both currently being applied to measure GOM. Using a laboratory manifold system and ambient air, GOM capture efficiency on 3 different collection surfaces, including KCl-coated denuders, nylon membranes, and cation-exchange membranes, was investigated at relative humidity ranging from 25 to 75%. Recovery of permeated  $\text{HgBr}_2$  on KCl-coated denuders declined by 4–60% during spikes of relative humidity (25 to 75%). When spikes were turned off GOM recoveries returned to  $60 \pm 19\%$  of permeated levels. In some cases, KCl-coated denuders were gradually passivated over time after additional humidity was applied. In this study, GOM recovery on nylon membranes decreased with high humidity and ozone concentrations. However, additional humidity enhanced GOM recovery on cation-exchange membranes. In addition, reduction and oxidation of elemental mercury during experiments was observed. The findings in this study can help to explain field observations in previous studies.



## INTRODUCTION

Understanding the global mercury (Hg) cycle is important due to the adverse health effects for humans and wildlife.<sup>1</sup> In the atmosphere, Hg is measured as 3 operational defined forms: gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particulate-bound Hg (PBM).<sup>2–4</sup> Measurement of GEM is reliable; however, uncertainties associated with GOM measurements are high.<sup>5,6</sup> GOM is the major Hg form involved in deposition processes that transfer Hg from the atmosphere to ecosystems.<sup>4</sup> The chemical composition of GOM is not understood, and varies with location and season.<sup>6–9</sup> Field investigations have identified potential GOM compounds including  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{HgSO}_4$ , and  $\text{HgO}$  based on comparison with thermal desorption profiles of Hg evolved from high purity permeation tubes;<sup>7,10</sup> however, the exact chemistry of the GOM compounds volatilized from these permeation tubes has not been identified.<sup>7,9</sup>

Methods for measurement of atmospheric GOM include KCl-coated denuders (manual and automatic system), mist chambers, the University of Nevada-Reno (UNR) active system with nylon and cation-exchange membranes, membrane filter packs including Teflon, quartz, cation-exchange membranes, and a differential method that quantifies total gaseous Hg (TGM) and GEM (the Detector for Oxidized Hg system (DOGHS)).<sup>3,6,7,11–15</sup> After field intercomparisons,<sup>3,12</sup> the mist chamber was discounted due to a potential positive artifact related to PBM, and the membrane pack measurement is influenced by upstream filters.<sup>6,9</sup> KCl-coated annular denuders

within the Tekran automatic system have been the most popular method for ambient GOM measurements, and is applied in the North America—Atmospheric Mercury Network (AMNet), and the Global Mercury Observation System (GMOS).<sup>16,17</sup>

However, concerns regarding the use of the Tekran system for GOM and PBM measurements have risen since 2009. In summary, a significant mass balance discrepancy between GOM and GEM was observed during daytime when atmospheric oxidation would occur in Nevada.<sup>18</sup> This led to uncertainties regarding the denuder; and a mismatch of GOM temporal trends using the Tekran system and passive samplers in Florida was observed,<sup>19</sup> again indicating potential uncertainties. Swartzendruber et al.<sup>20</sup> also pointed to disagreement of GOM measurements in the free troposphere using the KCl-coated denuders and a precursor to the current DOHGS instrument that determines the TGM and GEM, and then calculates reactive Hg ( $\text{RM} = \text{GOM} + \text{PBM}$ ) by difference. The effect of ozone on GOM collection by the KCl-coated denuder was investigated by Lyman et al.<sup>21</sup> Results indicated GOM loss from denuders loaded with  $\text{HgCl}_2$  and ambient air GOM collected in Nevada during ozone exposures. The UNR active system was compared with Tekran system using a laboratory

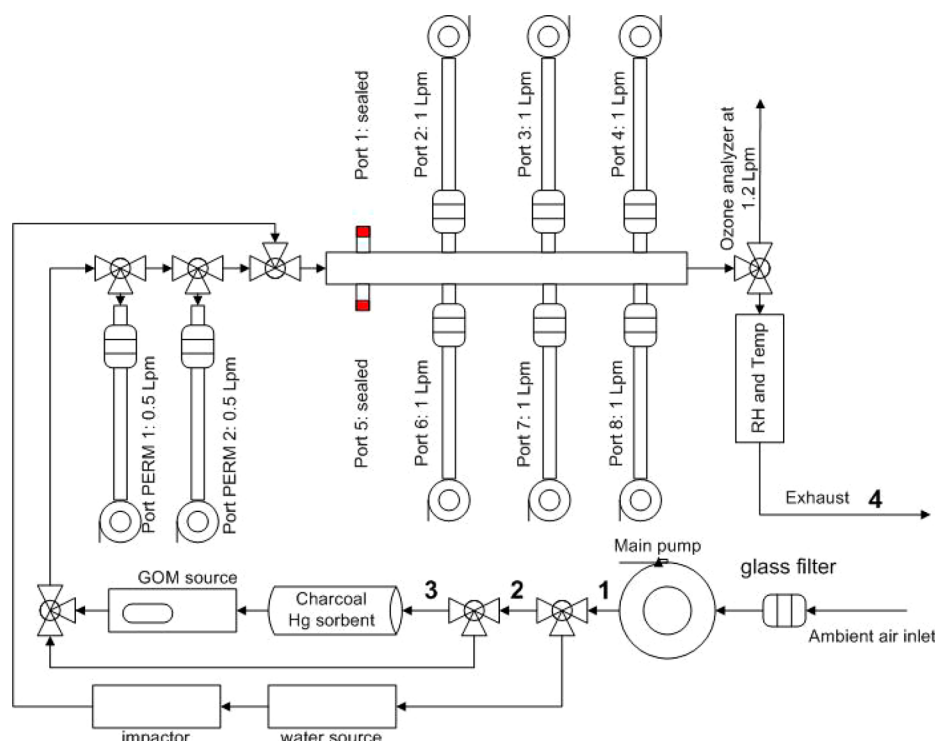
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**Figure 2.** Configuration of manifold system for 8-h humidity and  $\text{HgBr}_2$  exposures using the cation-exchange and nylon membranes in Experiment 2. Port PERM indicates the sampling location upstream of the water vapor source used to determine the concentration being permeated.

week, respectively. Weekly external calibrations showed that the recovery of the 2537 was  $102 \pm 3\%$ . Concentrations of GOM were calculated from the sum of GOM cycles which are flagged as 3 in the Tekran system and then the numbers were subtracted by Tekran blanks (the last flush which was flagged as 1 in Tekran after the denuder heating, the blank was considered when it higher than GOM number). Without GOM spikes the manifold blanks were below  $20 \text{ pg m}^{-3}$  with Tekran system blank below  $1 \text{ pg m}^{-3}$  (usually zero). However, at high concentrations, GOM spikes the Tekran system blank could be up to  $100 \text{ pg m}^{-3}$ . We still used it as a Tekran flush blank, although this could be an actual measurement of GOM. KCl-coated denuder, in-line filters, and soda-lime traps were replaced every batch experiment. According to AMNet protocol, the entire system is flushed and cleaned every six-month and the inlet temperature was set at  $50^\circ\text{C}$ . The system was operated within 1-h sampling mode and 40 min desorption mode. Detail information can be found in Huang et al.<sup>7</sup>

Because of the different flow rates, GOM concentrations were corrected to represent the values in the manifold using the equation below:

$$C_{\text{man.}} = \frac{C_{\text{Tekran}} \times (Q_{\text{man.}} + Q_{\text{ws}})}{Q_{\text{man.}}} \quad (1)$$

where  $C_{\text{man.}}$  and  $C_{\text{Tekran}}$  are the concentrations in manifold and Tekran system,  $Q_{\text{man.}}$  is the flow rate at position 5 (Graphical abstract), and  $Q_{\text{ws}}$  is the water source flow rate at position 6 (Graphical abstract).

**Membrane System.** Cation-exchange (polyethersulfone) membrane, Mustang S, Pall Corporation, NY, U.S.A.) and nylon membranes ( $0.2 \mu\text{m}$  pore size, Cole-Parmer, IL, U.S.A.) were used in this study to collect GOM from the manifold. Two membranes were deployed in-series as a membrane pack

with the second membrane used to check break-through,<sup>7</sup> and there was no break-through observed in this study.

For experiment 2, two sets of cation-exchange membranes were placed upstream of the water port and used to determine recovery of the membranes downstream of the port (Figure 2, Port PERM 1 and 2) during humidity exposures. Twelve membranes (6 cation-exchange and 6 nylon membranes 2 in-series) were placed downstream of the water port (Figure 2). Membranes in these 8 ports were deployed and collected at same time.

All membranes were stored in acid clean jars within double Ziploc bags at  $-20^\circ\text{C}$  until analyzed. Cation-exchange membranes were analyzed using EPA Method 1631 E<sup>25</sup> and nylon membranes were analyzed using thermal desorption and then EPA Method 1631 E. Detail information can be found in Huang et al.<sup>7</sup> Because of the different flow rates, GOM concentrations were corrected to represent the values in the manifold using the equation below:

$$C_{\text{man.}} = \frac{C_{\text{prem.}} \times Q_{\text{prem.}}}{Q_{\text{prem.}} + Q_{\text{makeup}}} \quad (2)$$

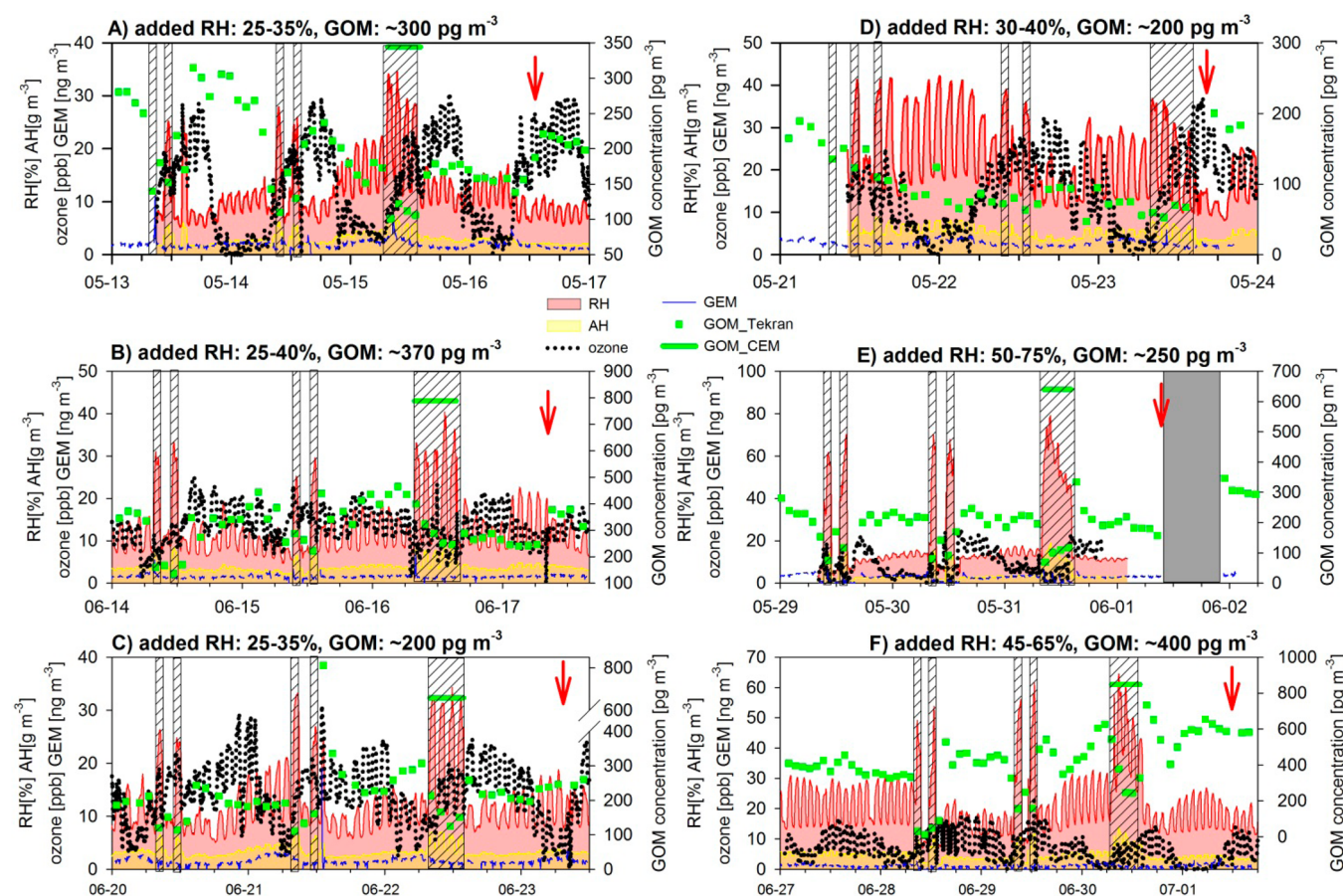
where  $C_{\text{man.}}$  and  $C_{\text{prem.}}$  are the concentrations in manifold and premanifold,  $Q_{\text{prem.}}$  is the flow rate at position 2 (Figure 2), and  $Q_{\text{makeup}}$  is the flow rate difference between position 1 and 2 (Figure 2).

Cation-exchange and nylon membranes blanks were  $0.26 \pm 0.16$  and  $0.03 \pm 0.04 \text{ ng}$  per membrane, respectively. Hg amounts on membrane were  $\sim 0.5$  to  $\sim 5$  and  $\sim 0.3$  to  $\sim 4 \text{ ng}$ , respectively. Air temperature and RH in the manifold were recorded using Campbell Scientific CS 500 L at end of the system with data logger CR10X (Graphical abstract, Figures 1 and 2). For Thermo 49C the detection limit is  $1.0 \text{ ppb}$ . Ozone calibrations (4 span and 1 zero, done by 2B ozone calibrator)



Table 1. Daily Average Mixing Ratio of Criteria Air Pollutants in Downtown Reno

	CO (ppm)	ozone (ppb)	NO <sub>x</sub> (ppb)	SO <sub>2</sub> (ppm)
5/13/2014–5/17/2014	0.18–0.25	34–56	11.3–20.8	<DL–0.28
5/21/2014–5/24/2014	0.13–0.20	31–46	6.6–13.8	0.01–0.07
5/29/2015–6/2/2014	0.14–0.17	37–58	6.2–12.0	0.14–0.49
6/14/2014–6/17/2014	0.08–0.10	32–48	4.0–5.8	0.06–0.25
6/20/2014–6/23/2014	0.10–0.13	47–52	4.9–8.8	0.28–0.35
6/28/2014–7/1/2014	0.14–0.17	34–53	7.9–15.8	0.24–0.40



**Figure 3.** Humidity tests on KCl-coated denuders, the hatch areas indicate when water was applied, and the gray area indicates unexpected power outage and no data were recorded. The red arrows indicate when the KCl-coated denuders were replaced. CEM represents cation-exchange membrane.

were done every three months for the whole year. This instrument was used only for manifold experiments; calibrated recovery ranged from 93 to 107%; and was very stable. Relative humidity generated using pure DI water in the manifold was lower than 90%, and the all significant droplets were removed using impactor before entering the manifold. A soda lime trap was used and replaced after each experiment upstream of Tekran 2537. The detector was also manually calibrated before and after each experiment. The results were good (102 "3 % recovery"). Therefore, the detector was not influenced by humidity.

**Data Analysis.** Sigmaplot 12.0 (Systat Software Inc. CA, U.S.A.) and Minitab 15 (Minitab Inc. PA, U.S.A.) were used for data analyses.

Absolute humidity was calculated from the RH and temperature:<sup>26</sup>

$$AH = \frac{P_{H_2O}^0 \times \frac{RH}{100} \times 18 \frac{g}{mol}}{R \times T} \quad (3)$$

where

$$P_{H_2O}^0 = 1013.25 \exp(13.3185A - 1.92A^2 - 0.6445A^3 - 0.1299A^4)$$

$$A = 1 - \frac{373.15}{T}$$

where AH = absolute humidity ( $g\ m^{-3}$ ), RH = relative humidity, R = ideal gas law constant, T = temperature (K).

## RESULTS AND DISCUSSION

**Experiment 1: Tekran Results.** It is important to note that a goal of this experiment was to make measurements in ambient air, and ambient RH and ozone concentrations

changed daily, and from day to day. Daily average criteria air pollutant mixing ratios in ambient air are listed in Table 1. Concentrations of ozone were significantly reduced relative to ambient air (cf. Figure 1). This is likely the case for other reactive pollutants. Although ozone concentrations varied among scenarios, similar patterns were observed in the 6 investigations being higher during the day than the night. The concentrations of GOM in the beginning and end of the measurement were different by approximately 30% (Figure 3, the highest E and F), and the GOM blank in the manifold was low. Measurements of GOM concentrations in the manifold were very stable ( $\sim 30\%$ , variation); however, in some cases, denuders were passivated. From Table 2 illustrates the fact

**Table 2. GOM Concentrations in the Manifold before Any Water Applications Using the Tekran System**

	GOM concentrations before humidity tests ( $\mu\text{g m}^{-3}$ )
5/12/2014–5/13/2014	$280 \pm 27$ ( $n = 5$ )
5/20/2014–5/21/2014	$181 \pm 12$ ( $n = 7$ )
5/28/2015–5/29/2015	$255 \pm 25$ ( $n = 6$ )
6/13/2014–6/14/2014	$357 \pm 27$ ( $n = 6$ )
6/19/2014–6/20/2014	$207 \pm 19$ ( $n = 6$ )
6/27/2014–6/28/2014	$341 \pm 11$ ( $n = 6$ )

GOM concentrations before any water applied were very stable. During this experiment that tested KCl-coated denuders within a Tekran system the background RH varied by  $\sim 10\%$  over the course of the day, and the additional humidity spikes caused humidity to increase up to 75%, (Figure 3). The oscillation in the RH observed in Figure 3 is due to increased flow of ambient air through the manifold during the desorption cycle of the Tekran 1130 unit holding the KCl-coated denuder due to flushing of zero air into the denuder by the pump module that controls flows. The impact of the humidity spikes during days 1 and 2 reduced collection of GOM captured by the denuder when the humidity spikes were on for an hour. During the low water vapor spikes (25–35%, Figure 3), GOM capture efficiency was reduced by 4–37% (Wilcoxon Signed Rank,  $p$ -value  $< 0.001$ ). However, at high water vapor spikes ( $> 35\%$ ), GOM not captured or reduced on the denuder wall was 10–60% (Wilcoxon Signed Rank,  $p$ -value  $< 0.001$ ). Loss was correlated with humidity (RH, 21.5–62.2%:  $r^2 = 0.49$ ,  $p$ -value  $< 0.01$ , and absolute humidity, 5.2–13.6  $\text{g m}^{-3}$ :  $r^2 = 0.45$ ,  $p$ -value  $< 0.01$ ). In some cases (three of six), GOM concentrations measured by KCl-coated denuders (Tekran system) decreased gradually; and recovered after the denuders were replaced with a new KCl-coated denuder, to the values before additional humidity was applied. Especially for scenario A, B, and D (Figure 3), GOM concentrations measured the first day of permeation were significantly higher than the last day ( $t$  test,  $p < 0.0001$ ). However, the difference is not significant for scenario E and F ( $p \approx 0.01$ ), and there is no significant difference for C ( $p = 0.129$ ). However, the reason is not clear. The last consistent pattern was GOM concentrations measured by cation-exchange membranes that were exposed to humidity in the manifold were 3–6 times higher than those measured by KCl-coated denuders (Tekran system, during the 8 h humidity spikes).

In the first two exposure experiments, GEM concentrations were negatively correlated with humidity (Table 3); however, in other experiments, correlations were not significant. If we

**Table 3. Pearson's Correlations between Hourly GEM Concentrations and Hourly Relative Humidity (RH), Ozone, and Absolute Humidity (AH)<sup>a</sup>**

		RH	ozone	AH
20140512	GEM	0.62	−0.56	0.61
	GOM	−0.66	insignificant	−0.63
20140521	GEM	0.56	−0.76	0.58
	GOM	−0.45	insignificant	insignificant
20140529	GEM	insignificant	insignificant	insignificant
	GOM	−0.43	insignificant	−0.45
20140614	GEM	insignificant	−0.045	insignificant
	GOM	−0.34	insignificant	insignificant
20140620	GEM	insignificant	−0.64	insignificant
	GOM	−0.35	insignificant	−0.37
20140627	GEM	insignificant	−0.69	insignificant
	GOM	−0.30	−0.31	−0.34

<sup>a</sup>“Insignificant” indicates the correlation is not significant ( $p$  value  $> 0.01$ ).

look at the data in detail, then GEM concentrations with water spikes off ( $x$ ) were  $\sim 0.5$  times of those when the water on ( $y$ ) (next hour measurement,  $y = 0.505x + 1.03$   $r^2 = 0.2$ ,  $p < 0.001$ ). These higher GEM values during water spikes imply that reduction occurs in Tekran system as suggested by McClure et al.<sup>22</sup> Negative correlation between GEM and ozone was found during all experiments; this is due to the chemistry in the manifold system (GEM being oxidized to GOM—see discussion of chemistry in the Supporting Information of Gustin et al.<sup>27</sup>). If oxidation reactions occurred in the system, then a positive correlation between GOM and ozone should be observed. However, Lyman et al.<sup>21</sup> reported ozone reduced the capture efficiency of GOM on KCl-coated denuders. The effect of ozone on production of GOM could be canceled out due to reactions on the denuder or GOM deposition to the walls (c.f. Gustin et al.,<sup>6</sup>). Because of this, the correlation was insignificant.

Total Hg in the gas phase was calculated as GEM +  $3 \times$  GOM measured by Tekran system (based on the inefficient capture of GOM by the denuder). On the basis of this assumption and calculation, total Hg concentrations were higher during water spikes ( $x$ ) than without water spikes ( $y$ ) ( $y = 0.63x + 0.89$   $r^2 = 0.38$ ,  $p < 0.001$ ). The inlet of Tekran speciation system was maintained at 50 °C, and this would result in GOM deposition on the inlet wall before water spikes. Thus, during the water addition deposited GOM is reduced to GEM resulting in higher values than expected.

McClure et al.<sup>22</sup> found reduction of GOM collection efficiency on KCl-coated denuders within the Tekran system was low (1.3–14.4%) in zero air with water vapor spikes, and stated that lost GOM was converted to GEM. Enhanced GEM concentrations (15–180%) were also observed in this study while additional humidity was applied. Two major differences between the McClure et al. (2014) study and this study were the inlet temperature and carrier air. The inlet was heated to 100 °C in McClure et al.;<sup>22</sup> however, in this study, we followed the standard operation procedure from AMNet and kept the inlet temperature at 50 °C. Feng et al.<sup>23</sup> reported this inlet setting (an impactor at 50 °C) would cause 30%  $\text{HgCl}_2$  loss. Furthermore, in this study, filtered ambient air was used as the air stream which may have consisted of atmospheric oxidants, and these might have synergistic or antagonistic influences on

Table 4. Comparison of GOM Collected on the Cation-Exchange and Nylon Membranes during Experiment 2<sup>c</sup>

date collected	humidity [%]	ozone [ppb]	air temperature [°C]	GOM cation exchange membrane PERM [pg m <sup>-3</sup> ]	GOM cation exchange membrane [pg m <sup>-3</sup> ]	GOM nylon membrane [pg m <sup>-3</sup> ]
2014/09/24	21 ± 1	17 ± 9	27 ± 1	1615 ± 42	868 ± 379 (54%)	729 ± 73 (45%)
2014/09/23	21 ± 5	14 ± 8	28 ± 2	1334 ± 350	827 ± 267 (64%)	726 ± 36 (54%)
2014/10/06	23 ± 5	8 ± 7	29 ± 2	12859 <sup>a</sup>	11727 ± 717 (91%)	8256 ± 411 (64%)
2014/10/08	23 ± 5	4 ± 5	29 ± 1	969 ± 243	879 ± 73 (91%)	760 ± 46 (78%)
2014/09/22	25 ± 3	10 ± 6	28 ± 2	1553 ± 59	1402 ± 355 (90%)	711 ± 38 (46%)
2014/10/07	25 ± 5	7 ± 2	29 ± 2	1844 ± 245	NA <sup>b</sup>	1031 ± 52 (56%)
2014/09/21	32 ± 2	15 ± 2	26 ± 1	1849 ± 241	885 ± 141 (51%)	738 ± 146 (43%)
2014/09/29	45 ± 12	0.2 ± 0.5	29 ± 2	3137 ± 558	3365 ± 316 (107%)	1124 ± 499 (42%)
2014/10/01	45 ± 13	11 ± 3	29 ± 2	1847 ± 123	1794 ± 1146 (97%)	770 ± 83 (36%)
2014/09/30	47 ± 14	1.5 ± 1.6	28 ± 3	2037 ± 25	1627 ± 383 (73%)	910 ± 134 (41%)

<sup>a</sup>Only one sample available. <sup>b</sup>NA: no data available. <sup>c</sup>Data are presented as mean and standard deviation of humidity, ozone, and temperature during the experiments. GOM cation-exchange membrane PERM indicates the concentration permeated based on the cation-exchange membrane before the manifold. Numbers in parentheses indicate the % captured by the membrane during exposure to relative humidity relative to that measured at the inlet prior to the water source.

the KCl surface. For example, ozone can cause negative artifact on GOM collection related to KCl-coated denuder.<sup>21</sup>

**Experiment 2: Membrane Results.** At low RH (no water spikes, 21–23%, 4 sets), recovery of GOM concentrations measured on the cation-exchange membranes downstream of water vapor injection port was 74 ± 19% relative to that measured upstream (Table 4). With moderate water vapor spikes (RH 25–32%, 2 sets), the recovery was 71 ± 27%. However, the recovery increased to 91 ± 18% at high RH (~45%, 3 sets). Although the membrane was visually dry when collected, condensation on the membrane surface could occur. This could create a water layer that enhances the GOM uptake rate on membrane as discussed in Huang et al.<sup>28</sup> and Huang et al.,<sup>7</sup> or liquid water with GOM was captured by membranes in manifold. However, if we look at the data in detail, then this difference could also due to ozone concentrations. In all cases, recovery of GOM from the cation-exchange membranes in manifold was low when average ozone concentrations were higher than 13 ppbv.

Humidity reduced the recovery of GOM measured by nylon membrane (no spike: 64 ± 14%, moderate water spike: 48 ± 7%, and high water spike: 39 ± 3%). Results were similar to the conclusion made by Huang et al.,<sup>7,10</sup> and this indicates that during humid conditions the nylon membrane is passivated by gaseous and/or liquid water. Additionally, recovery of GOM by the nylon membrane was influenced by ozone mixing ratios. If we separate the experiment into different groups based on water vapor spike (none, moderate, and high as defined above), then the lowest recovery of nylon was always found at the highest ozone mixing ratio (11–17 ppb). Overall, recovery of nylon membrane was high at low RH and ozone mixing ratio (such as 2014/10/06 and 2014/10/08), and the difference between GOM concentrations measured by nylon membranes in manifold was less 15–35% relative to those measured by cation-exchange membranes. Huang et al.<sup>7</sup> stated capture efficiencies of HgBr<sub>2</sub> on cation-exchange and nylon membranes were similar in zero air. Therefore, if the low ozone and humidity are considered, the measured GOM concentrations agree.

## ■ IMPLICATIONS

KCl-coated denuders have been reported to underestimate GOM concentrations at high ozone and humid conditions.<sup>21,22</sup> This study demonstrated interferences with ozone and

humidity on the GOM collection efficiency of KCl-coated denuder within the Tekran system. The capture efficiency of the KCl-coated denuder immediately decreased as additional humidity was applied, and, in some cases, KCl-coated denuders were gradually passivated by water vapor over time. Humidity has a positive artifact on cation-exchange membrane for GOM measurement; however, it reduces the capturing efficiency of GOM on nylon. Furthermore, nylon membrane can also be passivated by ozone based on the limited data in this study.

The entire investigation in this study supports the findings and provides the evidence for hypotheses in previous work.<sup>7,22</sup> During field measurements, because of the influences of ozone and humidity on KCl-coated surface and nylon membranes, GOM concentrations measured by cation-exchange membranes were always much higher than the values measured by other two materials.<sup>7</sup> Nylon membranes with thermal desorption are useful for qualitatively defining the GOM compounds in the atmosphere;<sup>9</sup> however, this material underestimates ambient GOM concentrations. Furthermore, the investigation in this study only applied HgBr<sub>2</sub> as the GOM permeation source and different GOM compounds might have different affinities on various materials.<sup>7,9</sup> Therefore, the influences from ozone and humidity on these materials with different GOM compounds need to be investigated.

McClure et al.<sup>22</sup> measured good GOM recovery of the KCl denuder (Tekran system) in zero air; however, Huang et al.<sup>7</sup> observed the underestimation of GOM measurements using KCl-coated denuder (Tekran system) compared to cation-exchange membranes. The GOM loss with water spikes in McClure et al.<sup>22</sup> was much lower than the values observed in this study. One is the different carrier gas (zero air and filtered ambient air), and the other reason is the temperature of Tekran inlet. Currently, the temperature of Tekran inlet is suggested to be 50 °C by the manufacture and AMNet. Feng et al.<sup>23</sup> reported the 30% loss of HgCl<sub>2</sub> on the inlet impactor of Tekran system. Detail investigation of Tekran inlet temperature and the wall loss of GOM are needed; this will help clarify a source of underestimation of GOM concentrations using the Tekran system, and could help to recalibrate data obtained in previous studies.



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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) UNEP. *Global Mercury Assessment 2013-Sources, Emissions, Releases, and Environmental Transport*; UNEP Division of Technology, Industry and Economics, Chemicals Branch International Environment House, 2013.
- (2) Schroeder, W. H.; Munthe, J. Atmospheric mercury—An overview. *Atmos. Environ.* **1998**, *32* (5), 809–822.
- (3) 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* (13), 3000–3009.
- (4) Lindberg, S. E.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *AMBIO* **2007**, *36*, 19–32.
- (5) Gustin, M.; Jaffe, D. Reducing the uncertainty in measurement and understanding of mercury in the atmosphere. *Environ. Sci. Technol.* **2010**, *44* (7), 2222–2227.
- (6) Gustin, M. S.; Huang, J.; Miller, M. B.; Peterson, C.; Jaffe, D. A.; Ambrose, J.; Finley, B. D.; Lyman, S. N.; Call, K.; Talbot, R.; Feddersen, D.; Mao, H.; Lindberg, S. E. Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX. *Environ. Sci. Technol.* **2013**, *47* (13), 7295–7306.
- (7) Huang, J.; Miller, M. B.; Weiss-Penzias, P.; Gustin, M. S. Comparison of gaseous oxidized Hg measured by KCl-coated denuders, and nylon and cation exchange membranes. *Environ. Sci. Technol.* **2013**, *47* (13), 7307–7316.
- (8) Huang, J.; Gustin, M. Use of passive sampling methods and models to understand sources of mercury deposition to high elevation sites in the Western United States. *Environ. Sci. Technol.* **2015**, *49*, 432–441.
- (9) Gustin, M.; Amos, H. M.; Huang, J.; Miller, M.; Heidecorn, K. Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level. *Atmos. Chem. Phys. Discuss.* **2015**, *15*, 3777–3821.
- (10) Huang, J.; Miller, M. B.; Edgerton, E. S.; Gustin, M. Use of criteria pollutants, active and passive mercury sampling, and receptor modeling to understand the chemical forms of gaseous oxidized mercury in Florida. *Atmos. Chem. Phys. Discuss.* *accepted*.
- (11) Ambrose, J. L.; Lyman, S. N.; Huang, J.; Gustin, M. S.; Jaffe, D. A. Fast time resolution oxidized mercury measurements during the Reno atmospheric mercury intercomparison experiment (RAMIX). *Environ. Sci. Technol.* **2013**, *47* (13), 7285–7294.
- (12) Sheu, G.-R.; Mason, R. P. An examination of methods for the measurements of reactive gaseous mercury in the atmosphere. *Environ. Sci. Technol.* **2001**, *35* (6), 1209–1216.
- (13) Landis, M. S.; Ryan, J. V.; ter Schure, A. F. H.; Laudal, D. Behavior of mercury emissions from a commercial coal-fired power plant: The relationship between stack speciation and near-field plume measurements. *Environ. Sci. Technol.* **2014**, *48* (22), 13540–13548.
- (14) Lindberg, S. E.; Stratton, W. J. Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **1998**, *32* (1), 49–57.
- (15) Mason, R. P.; Lawson, N. M.; Sullivan, K. A. The concentration, speciation and sources of mercury in Chesapeake Bay precipitation. *Atmos. Environ.* **1997**, *31* (21), 3541–3550.
- (16) Gay, D. A.; Schmeltz, D.; Prestbo, E.; Olson, M. L.; Sharac, T.; Tordon, R. The atmospheric mercury network: measurement and initial examination of an ongoing atmospheric mercury record across North America. *Atmos. Chem. Phys.* **2013**, *13*, 11339–11349.
- (17) System, G. M. O. <http://www.gmos.eu/>.
- (18) Weiss-Penzias, P.; Gustin, M.; Lyman, S. N. Observations of speciated atmospheric mercury at three sites in Nevada, USA: evidence for a free tropospheric source of reactive gaseous mercury. *J. Geophys. Res.* **2009**, *114* (14), 14302.
- (19) Peterson, C.; Alishahi, M.; Gustin, M. S. Testing the use of passive sampling systems for understanding air mercury concentrations and dry deposition across Florida, U.S.A. *Sci. Total Environ.* **2012**, *424* (0), 297–307.
- (20) Swartzendruber, P. C.; Jaffe, D. A.; Finley, B. Development and first results of an aircraft-based, high time resolution technique for gaseous elemental and reactive (oxidized) gaseous mercury. *Environ. Sci. Technol.* **2009**, *43* (19), 7484–7489.
- (21) Lyman, S. N.; Jaffe, D. A.; Gustin, M. S. Release of mercury halides from KCl denuders in the presence of ozone. *Atmos. Chem. Phys.* **2010**, *10*, 8197–8204.
- (22) McClure, C. D.; Jaffe, D. A.; Edgerton, E. S. Evaluation of the KCl denuder method for gaseous oxidized mercury using HgBr<sub>2</sub> at an in-service AMNet site. *Environ. Sci. Technol.* **2014**, *48* (19), 11437–11444.
- (23) Feng, X.; Lu, J.; Hao, Y.; Banic, C. M. Evaluation and applications of a gaseous mercuric chloride source. *Anal. Bioanal. Chem.* **2003**, *376*, 1137–1140.
- (24) Gustin, M.; Weiss-Penzias, P.; Peterson, C. Investigating sources of gaseous oxidized mercury in dry deposition at three sites across Florida, U.S.A. *Atmos. Chem. Phys.* **2012**, *12*, 9201–9219.
- (25) Lyman, S. N.; Gustin, M. S.; Prestbo, E. M. A passive sampler for ambient gaseous oxidized mercury concentrations. *Atmos. Environ.* **2010**, *44* (2), 246–252.
- (26) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; John Wiley & Sons, Inc.: Hoboken, NJ, 2006.
- (27) Gustin, M.; Amos, H. M.; Huang, J.; Jaffe, D.; Miller, M.; Heidecorn, K. Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level: a critical review. *Atmos. Chem. Phys. Discuss.* **2014**, *15*, 3777–3821.
- (28) Huang, J.; Choi, H.-D.; Landis, M. S.; Holsen, T. M. An application of passive samplers to understand atmospheric mercury concentration and dry deposition spatial distributions. *J. Environ. Monitor.* **2012**, *14* (11), 2976–2982.