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# Comparison of 4 Methods for Measurement of Reactive, Gaseous Oxidized, and Particulate Bound Mercury

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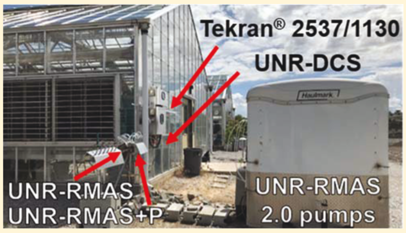
Supporting Information

**ABSTRACT:** The atmosphere is an important (1) pathway by which mercury (Hg) is transported around the globe and (2) source of Hg to ecosystems. Thus, understanding Hg atmospheric chemistry is critical for understanding the biogeochemical cycle and impacts to human and ecosystem health. Work over the past 13 years has demonstrated that the standard instrument used to measure atmospheric Hg does not accurately quantify gaseous oxidized mercury (GOM) or particulate bound mercury (PBM). This study focused on comparing four methods for quantifying atmospheric Hg and identifying Hg(II) compounds. Data from two automated systems, the Tekran 2537/1130 system and the University of Nevada, Reno-Dual Channel System (DCS), were compared with two University of Nevada, Reno-Reactive Mercury Active Systems (RMAS 2.0). One RMAS 2.0 included cation exchange membranes (CEMs) and nylon membranes, and the second included a polytetrafluoroethylene (PTFE) membrane upstream of the CEM and nylon membranes. The Tekran system and the DCS underestimated GOM concentrations with respect to that measured using the RMAS 2.0. The RMAS 2.0 with the upstream PTFE provided a means of distinguishing GOM and PBM. Thermal desorption of nylon membrane data identified a variety of GOM and PBM compounds present.



## INTRODUCTION

Over the past 13 years there has been increasing evidence that the standard instrument used to measure atmospheric mercury (Hg) suffers from bias and artefacts with respect to measurement of gaseous oxidized mercury (GOM) and particulate bound mercury (PBM).[1−7] The Tekran 2537/1130/1135 was designed to measure the 3 forms of Hg in the air using operationally defined procedures. These include gaseous elemental mercury (GEM), GOM, and PBM. The 2537 unit is thought to measure total gaseous mercury (TGM). However, this assumption is impacted by multiple factors, such as the inlet configuration,[3,8] temperature of gold cartridge desorption,[3] and potential for GOM compounds to not be collected.[8] The Tekran 2537 is thought to measure gaseous elemental mercury (GEM) when the 1130 and 1135 units are used simultaneously. However, because the 1130 unit does not collect all GOM and the 1135 may collect GEM (see below), the 2537 measurement with the 1130/1135 units may not represent GEM.

In addition, there is analytical uncertainty associated with processing the raw Hg atomic fluorescence signal. Ambrose[9] demonstrated that signal processing uncertainties were >5% for GEM and TGM at air concentrations of 1 to 2 ng $m^{-3}$. This results in a significantly low bias at concentrations of 1 to 2 ng $m^{-3}$ and also impacts GOM and PBM measurements that are often <5 pg.[10] However, given the artefacts and issues with the GOM and PBM measurements, this would not help correct these data. This issue for the GEM measurement can be solved by manually integrating the peaks.[9]

The 1130 unit consists of a KCl-coated denuder reported to capture GOM that is thermally desorbed and quantified as GEM by the 2537 unit. The 1135 component was designed to collect PBM on quartz chips that are subsequently desorbed and measured as GEM. There are no calibrations for the GOM and PBM measurements, and work has demonstrated that the KCl-coated denuder does not collect all forms of GOM with equal efficiency and has interferences with ozone and water vapor.[2,5,7,9] The PBM measurement is highly uncertain with GOM that is not collected by the denuder being collected as PBM,[3] lack of measurement,[11] and potential conversion of GEM to fine particulate Hg (Winston Luke, NOAA, personal communication 2 April 2019).

Recent work has demonstrated that cation exchange membranes (CEMs) are a reasonable alternative method for collection of reactive Hg (RM = GOM + PBM). In general, CEM measurements are higher than the KCl-coated denuder by 1.3- to 12- times, depending on the compounds in air, and membranes have been demonstrated to efficiently collect multiple forms of GOM,[4] and not GEM.[8]

An alternative system developed for the measurement of GOM was the University of Washington Detector for the Oxidized Mercury System (DOHGS).[12] This unit was deployed during the Reno Atmospheric Hg Intercomparison

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eXperiment (RAMIX).[3] During RAMIX, this system consisted of two cold vapor atomic fluorescence spectrometers (CVAFS; Tekran Instruments, Inc., model 2537B Hg vapor analyzer). Air was sampled from one sample line and then bifurcated, with one Tekran 2537 sampling air through a quartz pyrolyzer tube packed with quartz wool and heated to 650 °C to convert all sampled Hg to GEM to provide a measurement of TGM. The second Tekran 2537 pulled air through a quartz wool-filled tube designed to collect RM at ambient temperatures, and was thought to measure GEM. This method then compared the difference between the TGM and GEM measurements to determine GOM. Unfortunately, the unheated quartz wool was affected by relative humidity and some GOM collected was lost as GEM.[3] Despite limitations, this system demonstrated that the Tekran 1130 measurement was biased low.[11] An additional limitation of this system was the need to use two perfectly calibrated Tekran 2537 analyzers, requiring constant attention to instrument operation.

Here, we present the development of a modification of the DOHGS for measurement of TGM, GOM, and PBM using one Tekran analyzer with air passing first through a polytetrafluoroethylene (PTFE) membrane and then bifurcated to have equal flow in two lines, one with 2 CEMs and the second with a pyrolyzer (University of Nevada, Reno-Dual Channel System, DCS). Our goal was to develop an instrument that those with a Tekran 2537 could use to measure TGM, GOM, and PBM with time resolution sufficient for investigation of diel trends. Data collected with the DCS was compared with (1) two improved University of Nevada, Reno-Reactive Mercury Active Systems (RMAS 2.0; Luippold et al., submitted) that determined RM, GOM, and PBM concentrations, as well as the chemistry of RM compounds using nylon membranes and (2) Hg collected using a Tekran 2537/1130 system.

## ■ METHODS

**System Descriptions.** The 4 systems were deployed adjacent to each other outside the University of Nevada, Reno (UNR) College of Agriculture, Biotechnology, and Natural Resources Valley Road Greenhouse Facility in Reno, Nevada, USA (1377 m above sea level, 39° 32′ 14.87″ N, 119° 48′ 16.93″ W, adjacent to US Interstate 80), and sampled air at the same height (see graphical abstract).

**UNR-DCS.** The DCS method utilized a Tekran 2537A analyzer that has a set of dual gold cartridges that collect Hg. While one cartridge was being heated and the amalgamated Hg thermally desorbed into a CVAFS, the other was collecting Hg from ambient air. This allowed for continuous collection in this study at 5 to 10 min intervals. At the inlet of the sample line was a PTFE membrane in a single stage perfluoroalkoxy alkane (PFA) filter holder to collect particles with a pore size of 0.2 μm (Figure 1). Ambient air was collected through a sampling line that was bifurcated, with half of the air passing through a pyrolyzer (line 1) and half through a 2-stage filter holder containing 2 inline CEM (line 0). The total air flow through the DCS inlet was 2 Lpm. A Tekran 1110 2-port switching unit was installed downstream of the pyrolyzer and CEM filter holder to alternate air entering the Tekran 2537 (Figure 1). To avoid unbalanced flows and backflow through the lines, an auxiliary pump was used downstream of the switching unit so that the line that was not being sampled by the Tekran 2537 was also flowing at 1 Lpm. The flow of the auxiliary pump was maintained using a mass flow controller.

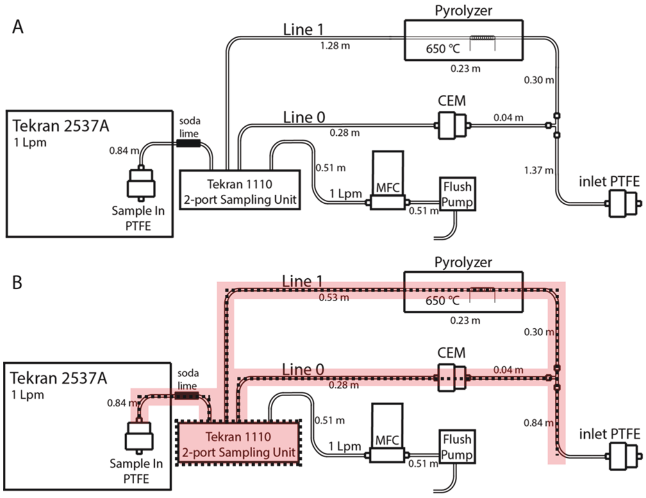

**Figure 1.** Schematic of the DCS configurations. Panel A illustrates the system for configurations 1 and 2, and panel B illustrates the system for configurations 3 and 4. The dashed lines with red-shading in panel B indicate the sections of the system that were heated to 100 °C during configuration 4. All tubing was 1/4" O.D. PTFE, and all connectors and fittings were PFA.

The pyrolyzed line (line 1) measurement was considered to represent TGM, while the CEM measurement (line 0) was considered to be GEM. It has been demonstrated in laboratory experiments that when the CEM is inline, <20% of the GOM makes it to the Tekran 2537,[11] and in most cases is 0%.[8] After passing through the 2-port switching unit, air entering the Tekran 2537 passed first through a soda lime trap (1/2" OD PFA tubing with PFA fittings, quartz wool plugs on either end, and filled with 10 cm length of 4−8 mesh soda lime (Alfa Aesar)), and then through a PTFE membrane (Figure 1). The Tekran 2537 was calibrated daily to monitor for trap bias.

The pyrolyzer consisted of a 25.4 cm long quartz tube (custom, OD 0.625 cm and ID 0.420 cm; URG Corporation) with 3 cm of quartz wool in the middle; the tube was wrapped with a 16 AWG nichrome wire (8 loops, 25.4 cm total length). The quartz tube and wire assembly were contained within 2.5 cm thick quartz fiber insulation housed in a 1.6 mm aluminum casing. The temperature was maintained at 650 °C using a thermocouple adjacent to the coil inside of the insulation that was connected to a solid state relay.

Several configurations of the DCS were investigated to optimize the system (Figure 1). These include the following, performed sequentially: (1) air collected through a 1.37 m unheated sampling line, through the pyrolyzer (line 1) for 5 min on each of the gold cartridges, then the CEM (line 0) on the gold cartridges; (2) air collected for 10 min on each cartridge, alternating lines with each cartridge [i.e., through the pyrolyzer (10 min), then through the CEM (10 min)]; (3) the system inlet line was shortened to 0.84 m, and the line between the pyrolyzer and the switching unit was shortened by 0.75 m, maintaining alternating sampling on lines 0 and 1 at 10 min intervals; (4) the shortened system from configuration 3 was heated to 100 °C for 5 weeks; and back to configuration (3) for 4 weeks. The 10 min collection time used in configurations 2 to 4 was chosen to improve the detection limit for GOM and allowed 30 min resolution.

**UNR-Reactive Mercury Active System 2.0 (RMAS 2.0).** Simultaneously, the RMAS 2.0 sampled ambient air at one-week intervals. A description of the RMAS 2.0 system can be

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found in the Supporting Information and Luippold et al. (submitted). Briefly, the RMAS 2.0 sampled air through 3 two-in-series nylon and 3 two-in-series CEM membranes held in multistage filter holders at a flow of 1 Lpm. Starting 3/5/2019, two RMAS 2.0 systems were deployed, one with PTFE membranes directly upstream of the CEM and nylon membranes (RMAS + PTFE), and one without upstream PTFE membranes (RMAS no PTFE). In the RMAS + PTFE and DCS, PTFE membranes were used to capture and measure PBM resulting in a measurement of GOM. PTFE membranes have been demonstrated to collect GOM when deployed as a surrogate surface.[13] PTFE tubing has been shown to adsorb GOM and re-emit as GEM.[3,8] Based on limited tests, PTFE membranes do not significantly sorb permeated gaseous GOM (see below). More work is needed to understand PTFE GEM/GOM/PBM interactions.

**Tekran System.** A Tekran system using the 2537 and 1130 components (Tekran 2537/1130) was deployed adjacent to the two RMAS 2.0 and the DCS (see graphical abstract). The sampling resolution was 2 h for GOM and 5 min for GEM (method 30-2L5, Tekran Instruments, Inc.). The system was maintained according to the National Atmospheric Deposition Program (NADP) Atmospheric Mercury Network (AMNet) protocols (http://nadp.slh.wisc.edu/lib/manuals/AMNet_Operations_Manual_v1-2.pdf). These protocols do not address the sample processing low bias. Air entering this system first passed through an elutriator designed to remove particles >2.5 μm, then through a KCl-coated denuder in the 1130 unit followed by a short line into a glass fiber filter, and then through a heated line (50 °C; 7.6 m) at 5.5 Lpm. The lower flow rate does not affect denuder performance, but it does increase the aerodynamic diameter cut point of the impactor from 2.5 to 3.0 μm.[14,15] An aliquot of this air was then directed through a soda lime trap, a PTFE membrane, and then into a Tekran 2537B analyzer at 1 Lpm.[16]

Comparison of TGM measurements from the Tekran 2537s analyzers in both the Tekran 1130/2537 and the DCS systems was done by pulling air through a PTFE membrane at the DCS system inlet directly to the Tekran 2537 system, through the 1130 quartz fiber filter after the 1130 unit, and through the heated line directly to the Tekran 2537 (with the system pump module idling to avoid biasing the flow in the system). These configurations represent the direct measurement of ambient air TGM for each system, without influence from the additional system components (e.g., CEM and pyrolyzer in DCS, denuder in Tekran 2537/1130 system). Differences between the DCS Tekran 2537A and the Tekran 2537/1130 2537B were −0.06 ± 0.18 ng $m^{-3}$ ($n$ = 852 5 min measurements, CV = 31%), 0.16 ± 0.04 ($n$ = 10 10 min measurements, CV = 23%), 0.106 ± 0.04 ($n$ = 14 10 min measurements, CV = 45%), and 0.124 ± 0.06 ($n$ = 20 10 min measurements, CV = 50%) on 12/7/2018, 4/29/2019, 5/13/2019, and 6/3/2019, respectively. This demonstrates the variability that can exist between two instruments, and is influenced by the efficiency of the gold cartridges and the internal permeation unit.

## ■ MATERIALS

Membrane materials used in this study have been described in detail elsewhere.[7,8] The CEM was a polyether sulfone membrane proprietarily treated for selective sorption of cations and has a reported pore size of 0.8 μm (Mustang S; Pall Corporation). Nylon membranes were made of a nylon polyamide material (pore size 0.2 μm; Sartorius Stedim). PTFE membranes had a 0.2 μm pore size (P/N 11807—47—N; Sartorius Stedim). All membranes were 47 mm in diameter and housed in a 1-, 2-, or 3-stage PFA filter holders (Savillex Corporation). Membranes in the 2- and 3-stage filter holders were 5 mm apart. Filter packs were tightened with wrenches to ensure no air leaks between pieces within the filter holder assembly. PTFE membranes associated with the DCS were analyzed starting 04/09/2019, and the concentration divided by 2 as samples on the PTFE were collected while measuring through both line 0 and line 1.

**Sample Collection.** Membranes were collected every 7 days from the two RMAS 2.0 systems and the DCS. To minimize system contamination during sample collection and processing from the DCS, a PFA union was used to replace the CEM filter holder and connect the upstream and downstream tubing, and a temporary PTFE filter pack was added to the system inlet. Contamination to the RMAS 2.0 systems was avoided by turning off the pumps during sample collection and processing. Membranes were removed from the filter holders using tweezers freshly wrapped with PTFE tape and each placed in a new 50 mL centrifuge tube (Falcon brand) and closed tightly. New membranes were placed in the filter holders using newly wrapped tweezers, and the filter holders were replaced in both systems. During membrane collection, triplicate nondeployed blank membranes of each material type were also collected to quantify how much Hg was on the membranes prior to deployment. All membranes were stored in centrifuge tubes in double-zipper bags in a freezer at −20 °C until analyzed (less than 4 weeks).

**Measurement of Total Hg Concentrations on Membranes.** CEM and PTFE membranes from the RMAS 2.0 and DCS systems were digested in the centrifuge tubes in which they were collected and stored. Total Hg concentrations on membranes were quantified following EPA Method 1631 and analyzed using CVAFS. The method detection limit (MDL) for this analysis was 40 pg Hg; all analyzed samples were above the MDL. The digestion efficiency for Hg on the PTFE membranes was checked by collecting ambient PBM on 12 membranes in the RMAS 2.0 for 7 days and analyzing 6 of the membranes using a modified EPA Method 1631 digestion procedure that uses 5.6% bromine monochloride (BrCl, EPA Method 1631 recommends ≤1%), and the other 6 were analyzed using 10% BrCl. Recovered Hg concentrations were not statistically significantly different between digestion BrCl concentrations ($p$ = 0.49); 5.6% BrCl was used for all membrane analyses.

Blank membranes ($n$ = 3) were collected in centrifuge tubes at the end of each deployment. These consisted of membranes stored in the same jars as those that held the sample membranes. Average concentrations of the blank membranes were subtracted from sample membrane concentrations for each deployment. All reagents used were of ACS grade or better, and were certified as suitable for Hg determination. Optima HCl and 18.1 + MΩ·cm water were used for all reagent and sample preparation.

**Nylon Membranes and Thermal Desorption Profiles.** Simultaneously with measurement of RM on the CEM in the RMAS and GOM in the RMAS + PTFE, the same was done with nylon membranes. These membranes were thermally desorbed using a temperature-controlled tube furnace (see Supporting Information for details and Luippold et al., submitted). The CEM cannot be used in thermal desorption analyzes because these membranes melt and passivate the gold cartridges in the Tekran 2537. With a new temperature ramp developed for the tube furnace relative to that presented in Huang et al. (2013) and careful calibration of the tube furnace, profile peaks have shifted to the left by ∼15 °C relative to those discussed in earlier papers.[17,18] Reference GOM profiles were generated from solid phase mercury compounds ($HgBr_2$, $HgCl_2$, $HgN_2O_6{\cdot}H_2O$, $HgSO_4$, and HgO) and elemental Hg, as well as methylmercury chloride directly added to the membranes (Alfa Aesar; $CH_3HgCl$ 1000 ppm in water).[17] Based on the new method, profiles have been updated and the peak temperatures for different GOM compounds are now 80−85 °C for [O], 90−110 °C for [Br/Cl], 125−135 °C for [N], 150−155 °C for [S], and 180−190 °C for methylmercury (MeHg) or what are considered organic mercury compounds.

Thermal desorption profiles, which are composite peaks from a combination of individual GOM compound signals, were deconvoluted to identify and quantify the collected GOM compounds on each membrane. The curve fitting function in MATLAB R2018a was used to split the thermal desorption profiles into different peaks with peak temperatures fixed in relatively small ranges, assuming the shape of a peak signal from one GOM compound can be considered as a Gaussian peak. The integral of the area of each peak (unit: $°C{\cdot}ng{\cdot}m^{-3}$) was obtained. These data can then be converted to Hg concentration data (unit: $pg{\cdot}m^{-3}$) using the Hg release rate ($pg{\cdot}min^{-1}$) based on the Tekran 2537 sampling rate (1 $L{\cdot}min^{-1}$), the temperature increasing rate (2 $°C{\cdot}min^{-1}$), and the total sampling volume (unit: $m^3$). This was done for RMAS and RMAS + PTFE nylon data to compare the composition of RM and GOM compounds.

**Ancillary Data and Data Analyses.** Meteorological data were collected adjacent to the system sampling inlets and at the greenhouse facility by the Western Regional Climate Center (https://wrcc.dri.edu/CLIMATEDATA.html). The two data sets were comparable. Parameters included temperature, relative humidity, solar radiation, and precipitation. Absolute humidity was calculated by first calculating the saturation vapor pressure

$$\text{Saturation vapor pressure} = 6.11 \times 10^{(7.5 \times T/237.3 + T)} \tag{1}$$

where $T$ is in °C. Then, the actual vapor pressure was calculated

$$\text{Actual vapor pressure} = \frac{\text{relative humidity} \times \text{saturated vapor pressure}}{100} \tag{2}$$

Lastly, absolute humidity, that is the density of water vapor in the air (kg $m^{-3}$) and independent of solar radiation, was calculated using the actual vapor pressure in Pa and the ideal gas law

$$\text{Absolute humidity} = \frac{\text{actual vapor pressure}}{T \times R} \tag{3}$$

where absolute humidity is in kg $m^{-3}$, actual vapor pressure is in Pa, $T$ is in K, and $R$ is the gas constant (461.5 J $kg^{-1}$ $K^{-1}$).

**Calculation of GOM Concentrations in the DCS System.** Because there was a PTFE membrane in front of the DCS, which was assumed to remove PBM, data derived represent GOM. Assuming the pyrolyzer (line 1) values were TGM and the CEM (line 0) GEM, TGM − GEM = GOM. Calculations of GOM concentrations in the DCS were made by using the TGM data obtained using the pyrolyzer line concentrations measured prior to and after the CEM line measurement that represents GEM. Thus, the concentration was calculated using eq 4 for the 5 min measurements on each cartridge, and eq 5 for the 10 min measurements on each cartridge.

$$\begin{aligned} \text{GOM}_{5\text{min}} = {} & \frac{\{\text{pyrolyzer prior to CEM (5 min)} + \text{pyrolyzer after CEM (5 min)}\}}{2} \\ & - \text{mean of 2 CEM measurements between pyrolyzer measurements} \\ & \text{(10 min)} \end{aligned} \tag{4}$$

$$\begin{aligned} \text{GOM}_{10\text{min}} = {} & \frac{\{\text{pyrolyzer prior to CEM (10 min)} + \text{pyrolyzer after CEM (10 min)}\}}{2} \\ & - \text{CEM} \quad \text{(10 min)} \end{aligned} \tag{5}$$

Note for configuration 1, which had 5 min Tekran 2537 cycles, the resolution for eq 4 was 20 min. For configurations 2 to 4, where Hg was collected on each cartridge for 10 min, eq 5 represents GOM concentrations of over 30 min. GOM concentrations were calculated in 2 ways. First, with no changes (Table S1). Second, with the following adjustments made prior to the calculation for both eqs 4 and 5 (1) negative calculated values were removed, as these indicated that GEM was greater than TGM and that is impossible and (2) if the concentration measured by the Tekran 2537 was less than 0.1 ng $m^{-3}$, the MDL for the Tekran 2537 the Tekran 2537 measurement was set to zero prior to calculations. Although there may have been some Hg in the air the Tekran could not measure it, justifying this decision. When assessing these data, it must be kept in mind that the results are small numbers derived from large numbers.

All statistical analyses were performed using Microsoft Excel and significant relationships ($\alpha$ = 0.05) are shown. Comparison of thermal desorption profiles for nylons in the RMAS and RMAS + PTFE systems were performed using the aov function in $R$[22] (version 3.6.0).

## RESULTS AND DISCUSSION

**UNR-DCS.** The GOM DCS values were not correlated with GOM measured using CEM in the RMAS + PTFE ($p$ = 0.18; Figure S1). Concentrations of GOM on the DCS-CEM were correlated with RM measured with the RMAS no PTFE ($p$ = 0.00) and GOM collected on the CEM in the RMAS + PTFE ($p$ = 0.00), with both being higher than the GOM measured by the DCS-CEM (Figure S2). GOM on the CEM in the DCS were comparable, but lower than that measured using the RMAS 2.0 systems. These results indicated that the reactions were occurring in the sampling line and converting GOM to GEM, similar to that observed during RAMIX.[3]

**UNR-Reactive Mercury Active System 2.0.** RM values from the RMAS systems were correlated, with RMAS + PTFE = 0.83 ± 0.10 RMAS ($r^2$ = 0.80, $p$ = 0.00, $n$ = 14; Figure S3). In addition, GOM measured using the CEM in the RMAS + PTFE was significantly lower than the RM measured using the RMAS by 12% ($p$ = 0.00). Total Hg concentrations measured on the PTFE in the DCS were lower than those on the RMAS + PTFE (DCS−PTFE = 0.64 ± 0.30 RMAS + PTFE − PTFE, $r^2$ = 0.74, $p$ = 0.00, $n$ = 9), with the difference between the two systems being the flow rate (DCS at 2 Lpm and RMAS at 1 Lpm; Figure S4). The similarity between the RM measured by the RMAS 2.0 systems indicated that the systems were measuring comparable values and that GOM was not being

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lost because of the presence of the PTFE membrane, indicating that this system is a viable method for quantitatively measuring RM, GOM, and PBM.

Ancillary data showed: (1) solar radiation was not correlated with absolute humidity; (2) RM collected by the RMAS was positively correlated with solar radiation ($p = 0.00$) and with the CEM in the DCS ($p = 0.00$), and negatively correlated with the GOM calculated for the DCS ($p = 0.02$); and (3) absolute humidity was not correlated with any of the above (Figure 2; see Figure S5 for trends). These results indicated that when solar radiation was greater, more GOM was produced by oxidants in the atmosphere and water vapor calculated as absolute humidity was not influencing any measurements.

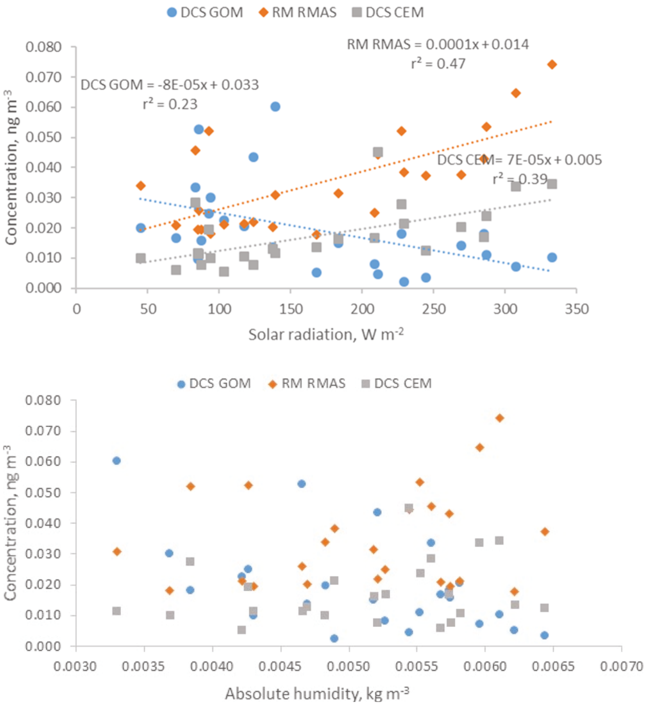

**Figure 2.** Measured solar radiation and absolute humidity vs concentrations of (1) GOM calculated for the DCS online (blue circles), (2) RM measured using the RMAS 2.0 (orange diamonds), and (3) GOM on the CEM in the DCS (grey squares).

Photochemical oxidation can occur in the gas phase, on aerosols, and in cloud water.[19] Deng et al.[20] demonstrated that Hg(II) on particles can be reduced to GEM and that reduction was more likely to happen when relative humidity was high. Saiz-Lopez et al.[21] indicated that fast gas-phase Hg(II) photolysis can promote atmospheric mercury reduction. These papers demonstrate the complexity of atmospheric Hg chemistry. The negative correlation between GOM calculated for the DCS and solar radiation is likely the result of GOM being converted to GEM because of photoreduction in the sampling line because it was exposed to sunlight, as was also observed during RAMIX.[3]

**Comparison of all Methods.** When comparing all methods, the uncertainties and limitations associated with each method needs to be considered. For the Tekran system, there is low bias because of data processing, lack of calibration for GOM and PBM, and interferences and artefacts associated with measurements. For the DCS, uncertainties also arise because of the low bias and the need for precisely calibrated gold cartridges. Limitations for both systems include the long sampling line facilitating oxidation and reduction reactions.[3] Uncertainties associated with the RMAS systems include the potential for reactions to occur in ambient air on the different collection surfaces (these are being investigated).

Weekly averaged data are presented in Table S2. GEM concentrations measured by the Tekran 2537s in the DCS and the Tekran 2537/1130 system were significantly correlated (Tekran 2537 = 0.86 ± 0.09 DCS GEM, $r^2 = 0.81$, $p = 0.00$, $n = 23$; Figure S6). Measurements from the Tekran 2537/1130 system were lower than those reported by the DCS by 10%. The lack of agreement is due to the two Tekran analyzers not being precisely calibrated, as was shown by the side-by-side comparison.

RMAS RM measurements were 3.7 ± 0.65 times higher than, and correlated with, the Tekran 2537/1130 GOM measurements ($r^2 = 0.6$, $p < 0.001$). Tekran 1130 GOM data were correlated with the GOM measured on the CEM in the RMAS + PTFE system Tekran GOM = 2.2 ± 0.45 * GOM DCS, $r^2 = 0.51$, $p < 0.001$, and not correlated with the DCS GOM calculated values. This indicated that the RMAS + PTFE and Tekran systems were measuring similar GOM/RM concentrations, through a different magnitude of values. This suggests that RMAS data may be used to correct Tekran GOM values if seasonal RMAS data is available for the sampling location.

With the long system, the DCS GOM and RMAS RM concentrations were different, and the DCS GOM was significantly greater than the Tekran 2537/1130 GOM measurement ($p = 0.00$; Figure 3). With the shortened system, the DCS GOM was significantly less than the RMAS 2.0 RM ($p = 0.00$). With the initial shortening of the DCS line, the Tekran 2537/1130 and the DCS GOM data were significantly different ($p = 0.00$). However, when the line was heated they were not different ($p = 0.95$) and this was also true for the final sampling time period when the line was unheated (May 7 to May 28, 2019; $p = 0.59$). Peaks in concentration, in general,

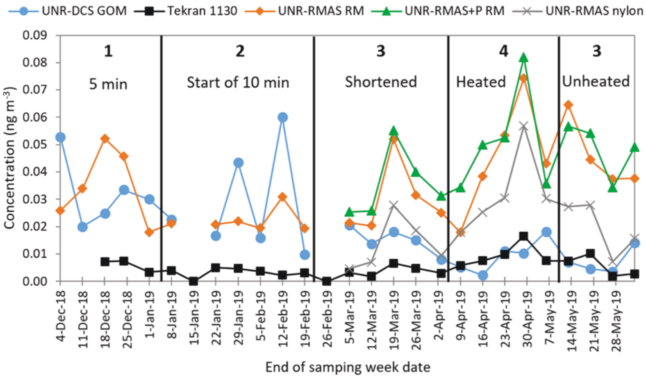

**Figure 3.** Time series of GOM and RM collected by the 4 methods over 1 week intervals, including GOM calculated for the DCS online (blue circles) and measured by the Tekran 1130 unit (black squares), and RM measured by the RMAS 2.0 (orange diamonds) and RMAS 2.0 + PTFE (CEM + PTFE, green triangles). RM concentrations from the RMAS 2.0 nylon membranes are also presented (grey Xs). The DCS configuration number for each time period, indicated by vertical black lines, is denoted at the top of each section, as well as the main change made to the system for the given time period. During the heating experiment the lines were heated to 100 °C.

corresponded with high solar radiation conditions, except for April 2nd, for which there is no clear explanation. Periods of measureable precipitation in general corresponded with decreased concentrations of GOM. This is expected as precipitation events readily remove GOM from air. For the DCS calculated GOM and Tekran 2537/1130 GOM, no clear relationship with solar radiation was observed. The temperature did not show any effect on observations. These relationships demonstrate that similar to the Tekran 2537/1130, the DCS does not accurately quantify GOM because of the reactions occurring in the tubing.

RMAS RM and RMAS + PTFE RM showed similar trends, with the latter having lower concentrations. The lower concentrations on nylon membranes as compared to CEM have been demonstrated in several studies.[14,18] The relationship between the RM measured by the CEM and the nylon membrane was nylon RM = 0.57 RMAS RM ($r^2$ = 0.69, $p$ < 0.001), while that for the GOM measurement was nylon GOM = 0.48 RMAS GOM ($r^2$ = 0.65, $p$ < 0.001). This shows that there was a fairly consistent relationship between the two measurements, and this will vary depending on the location and the chemistry of RM.

**Thermal Desorption Data.** GOM concentrations on nylon membranes in the RMAS + PTFE system were lower than the GOM measured without the PTFE system by 30% (Figure S7). For comparison, RM concentrations in the RMAS were higher than GOM measured on the CEM in the RMAS + PTFE system by 20% (Figure S3). Based on measurements from the nylon membranes in the RMAS + PTFE system, GOM concentrations were 48 to 77% of the RM, and PBM ranged from 22 to 52% (Table S3).

Thermal desorption profiles for nylon membranes in the RMAS and RMAS + PTFE systems were compared from the weeks ending 3/5/2019 until 6/3/2019 (Figure S8). For all time periods except one, the profiles were statistically significantly different ($p$ < 0.05). Quantitative assessment of the GOM compounds using peak deconvolution and integration revealed mixtures of compounds that were located between the defined peaks. These included peaks between (A) 88 to 92 °C that could be HgBrOH or HgClOH; (B) 115 to 120 °C that could be $HgBrNO_3$ or $HgClNO_3$; and (C) 140 to 145 °C that could be $NO_3{-}Hg{-}SO_4{-}Hg{-}NO_3$ or other unidentified compounds. Peaks at A and C were common in the RMAS, and those associated with A and B were found more commonly in the RMAS + PTFE. Hg(II) compounds were not always the same for the nylon membranes in the RMAS and RMAS + PTFE systems (Figure 4). Heterogeneous reactions on the PTFE could be affecting the compounds observed because of the interaction with particles. Mixtures of GOM compounds were more prevalent on the nylon membranes in the RMAS + PTFE. MeHg or other organic Hg compounds occurred at 180−190 °C in every GOM and RM sample with RM > GOM. Nitrogen and sulfur compounds were more prevalent in RM samples, which would reflect the aerosol compounds associated with highway pollution. Hg oxide related peaks were associated with both RM and GOM measurements. There was no clear relationship between % RM on the nylon membrane/CEM as would be expected because the nylon membrane does not appear to collect all ambient compounds with equal efficiency and the CEM is a quantitative measurement of RM.[5]

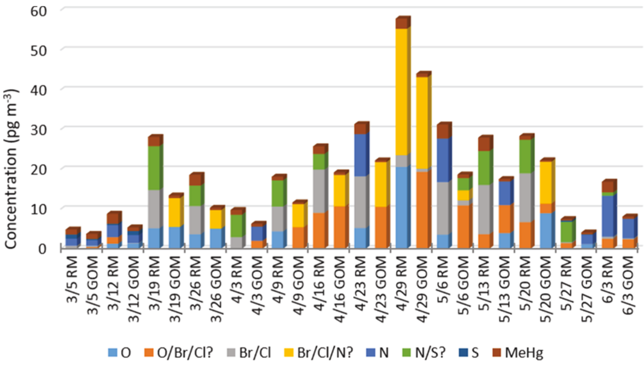

**Figure 4.** GOM compounds as determined by thermal desorption and peak deconvolution. For each sampling period, the RM on the nylon membrane from the RMAS is compared with the GOM compound on the RMAS + PTFE−nylon membrane representing GOM. Dates indicate the collection date.

**Implications and Limitations of These Systems.** GOM data generated using the DCS were similar to those measured by the Tekran 2537/1130 unit in that not all GOM was captured. For the DCS, this was because of the long uncovered sampling line and effects of relative humidity promoting transformation of GOM to GEM. For the Tekran 1130 unit, low recovery was because of a lack of capture by the KCl-coated denuder and the sampling design in general. Because of the reactions in the tubing, a short inlet, such as that associated with the RMAS 2.0, is needed to quantitatively measure RM. Adding a PTFE membrane in front of the RMAS 2.0 system resulted in the quantification of less RM on the downstream membranes, and use of the two RMAS 2.0 systems, with and without PTFE membranes, provided a means of measurement of RM, GOM, and PBM. Nylon membrane thermal desorption profiles demonstrated that a variety of Hg compounds existed at this site. Use of the PTFE in front of the nylon membranes in the RMAS + PTFE provided a means of understanding the chemistry of PBM versus GOM. GOM and PBM compounds varied spatially and temporally. Additional work is needed to further understand membrane results. Lastly, the RMAS 2.0 system is a viable system for quantifying RM, GOM, and PBM, as well as identifying GOM compounds, and outperforms the Tekran 1130/2537 and DCS for these measurements.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b04648.

Summary of 1-week data; concentration of different GOM compounds; comparison of the M calculated using the DCS versus the GOM measured on the RMAS +PTFE CEM, CEM GOM concentrations in the DCS versus the RM measurements from the RMAS 2.0 systems, UNR-RMAS 2.0 RM concentrations, with RMAS CEM concentrations on the x-axis and RMAS +PTFE concentrations on the y-axis, mean total Hg concentration from the RMAS+PTFE and the DCS PTFE, GEM measured by the DCS with the GEM measured by the Tekran 2537/1130 system, and RM concentrations on the nylons in the UNR-RMAS 2.0 systems; trends in one-week meteorological parameters; and thermal desorption profiles for nylon membranes in the RMAS (blue diamonds) and RMAS+PTFE (red squares) systems (PDF)

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### Notes

The authors declare no competing financial interest.

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