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Comparison and calibration of methods for ambient reactive mercury quantification

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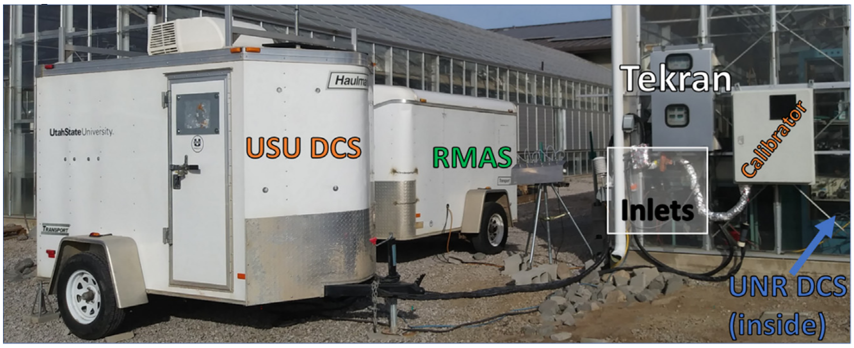
HIGHLIGHTS

- Historic methods for gaseous oxidized mercury (RM) measurements are inaccurate.
- New methods are being developed, lack intercomparison & demonstrated calibration.
- Four methods were co-located with a Tekran for intercomparison, one was calibrated.
- New methods performed similarly, and measured 80 % more GOM than the Tekran.
- DCS are accurate, precise, calibrated RM measurement methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Gaseous oxidized mercury (GOM) is the dominant form of atmospheric mercury (Hg) deposited and sequestered within ecosystems. Thus, accurate, calibrated measurements of GOM are needed. Here, two active membrane-based collection systems (RMAS) were used to determine GOM and particulate-bound Hg (PBM), as well as reactive Hg (RM = GOM + PBM), and compared with two dual-channel systems (DCS) and a Tekran 2537/1130 speciation system. The DCS measured operationally defined GOM by difference, using concentrations of gaseous elemental Hg (GEM) and total gaseous Hg. One DCS was linked to a custom-built, automated calibration system that permeated GEM, $HgBr_2$, or $HgCl_2$. The five systems were co-located for one-year to develop a dataset that would allow for understanding limitations of each system, and assessing measurement accuracy and long-term precision of the calibrator. The Tekran system measured ~14.5 % of the GOM measured by the other systems. The USU and UNR DCS and RMAS were significantly correlated, but the DCS was 50 and 30 % higher, respectively, than the RMAS. The calibrator performed consistently in the field and lab, and the DCS fully recovered GOM injected by the calibrator. Since the uncalibrated DCS measured the same concentrations as the calibrated DCS, they are both accurate methods for measuring RM and/or GOM. Some loss occurred from the RMAS membranes.

Synopsis: Accurate and calibrated measurements of atmospheric reactive mercury using membranes and two dual-channel systems.

Abbreviations: University of Nevada Reno, (UNR); Utah State University, (USU); mercury, (Hg); gaseous oxidized Hg, (GOM); particulate-bound Hg, (PBM); gaseous elemental Hg, (GEM); reactive Hg, (RM = GOM + PBM); total gaseous Hg, (TGM); dual-channel system, (DCS); cation exchange membrane, (CEM); polytetrafluoroethylene, (PTFE); RMAS system with upstream PTFE, (RMAS + P).

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1. Introduction

Accurate and precise measurements of ambient atmospheric reactive mercury (RM) compounds are a challenge for the mercury (Hg) research and monitoring communities. The standard instrument used to make these measurements, the Tekran® speciation system (Tekran Instruments Corporation, Toronto, Ontario, Canada), has been demonstrated to inaccurately measure gaseous oxidized Hg (GOM) and particulate-bound Hg (PBM) concentrations (Marusczak et al., 2017; McClure et al., 2014; Gustin et al., 2013; Talbot et al., 2011). In recent years, two alternate measurement systems have been developed, including high time resolution dual-channel systems (DCS) and a lower time resolution membrane sampling system.

DCS have been independently developed by several research teams (Tang et al. 2022; Lyman et al., 2020; Gustin et al., 2019; Ambrose et al., 2013; Winston Luke, personal communication). Each uses an elutriator or a filter at the inlet to prevent PBM of a certain size fraction from entering the system, and measures total gaseous Hg (TGM) and gaseous elemental Hg (GEM) using a bifurcated sampling line. One channel passes through a pyrolyzer to reduce all Hg forms to GEM – the TGM channel – and the other channel passes through a collection surface to collect GOM and any additional PBM, allowing only the GEM fraction to pass to the detector – the GEM channel. The amount of PBM entering the system is determined by the geometry and configuration of the inlet and the flow rate of the system. Potassium chloride denuders, quartz chips, and wool traps have been used in some DCS designs, all of which have been shown to not accurately capture and measure GOM and/or RM (RM = GOM + PBM) (Ambrose et al., 2015; Swartzendruber et al., 2009). Currently, cation exchange membranes (CEM) are used in the GEM channel as the collection surface. Operationally defined GOM is calculated as the difference between the Hg concentrations measured on each channel (TGM − GEM = GOM).

The membrane sampling system, the University of Nevada, Reno – Reactive Mercury Active System 2.0 (RMAS), has been developed to collect RM or GOM and PBM compounds for direct quantification and identification, depending on the membrane configuration (Gustin et al., 2019). Unlike the DCS, the RMAS allows for identification of RM and GOM compounds using thermal desorption from nylon membranes; however, it has been demonstrated the nylon membranes do not collect RM and GOM compounds with equal efficiency as the CEM (Gustin et al., 2021; Luippold et al., 2020a; Huang et al., 2013). Because the thermal desorption method can only qualitatively identify compounds, there is uncertainty as to the exact RM chemistry.

Another challenge is the lack of a commercially available, standardized calibrator for GOM and PBM measurements that can be used for field studies. This type of equipment is critical for the accurate measurement of atmospheric Hg compounds, validation of previous measurements, and standardization of measurements across studies and field locations. Most measurements of ambient GOM to date have been uncalibrated. Some researchers have designed and built their own permeation tube-based versions of a field calibration unit for GOM compounds that showed some promise (e.g., McClure et al., 2014; Finley et al., 2013; Winston Luke, personal communications). A custom-built automated permeation tube-based calibrator, designed by Lyman et al. (Lyman et al., 2020; Lyman et al., 2016), has been successfully used to check the collection efficiency of Tekran 1130 modules and DCS. Several calibrators have also been developed that rely on evaporation of Hg(II) from liquid solutions or pure Hg (II) compounds (Gačnik et al., 2021; Petrov et al., 2020; Sari et al., 2019), but these types of systems have not yet been demonstrated in field settings.

Here, two RMAS, two DCS, and a Tekran 2537/1130 speciation system were deployed along with an automated calibration system for one year. By co-locating multiple systems, direct comparison of their performance when sampling the same air mass was possible, eliminating possible variations in performance due to differences in sampling conditions (e.g., air chemistry, meteorology). The objectives of this comparison were to: 1) investigate differences in observations from the DCS and RMAS, and use this information to understand what the systems were measuring and limitations of the systems; 2) assess the accuracy and long-term precision of the custom-built calibrator for use as a field calibration technique for the DCS; and 3) learn what calibrated measurements can tell us about how well the RMAS is working.

2. Methods

2.1. Site description

All inlets for the systems used in this study were co-located outside at the University of Nevada, Reno's Valley Road Greenhouse Complex, USA (39.5375 N, 119.8047 W, 1367.6 masl). This site is located directly adjacent to a major interstate highway and is impacted by local mobile point-source emissions as well as regional and long-range transport of contaminants (Gustin et al., 2019). The systems were operated from November 21, 2019 to November 24, 2020; there were no breaks in sampling due to COVID-19 restrictions. Mercury sampling systems have been deployed at this site in previous studies (Gustin et al., 2019; Pierce et al., 2018).

2.2. Sampling systems

Five active systems were deployed in this intercomparison campaign, including: 1) a Tekran 2537/1130 speciation system; 2) the University of Nevada, Reno DCS (UNR DCS); 3) the Utah State University DCS (USU DCS); and 4) two RMAS. In a previous study, Gustin et al. (2019) compared the Tekran, the UNR DCS, and RMAS observations at this location. This study allowed for further evaluation of methods by comparing measurements with a calibrated DCS.

For this study, only the 1130 and 2537B modules of the Tekran speciation system were used, resulting in GOM and GEM measurements, respectively. The 1135 module, that measures PBM, was not used in this study. The Tekran speciation system was otherwise strictly operated and maintained following protocols used by the National Atmospheric Deposition Program's Atmospheric Mercury Network (AMNet).

The UNR DCS (Fig. S1A) was a custom-built sampling system designed to separate PBM from TGM at the inlet, and alternately quantified GEM and TGM in the two channels, resulting in measured GEM and calculated GOM concentrations (Gustin et al., 2019; Fig. S1A). At the system inlet was a polytetrafluoroethylene membrane (PTFE; Sartorius, 0.2 μm) that was used to remove PBM from air entering the system. The GEM channel (line 0) had an in-line dual-stage CEM filter pack (Pall Corporation, Mustang-S, 0.8 μm). These membranes have been shown to efficiently capture GOM compounds, only allowing GEM to pass through to the Tekran 2537A detector (Miller et al., 2021; Luippold et al., 2020a). The TGM channel (line 1) had a pyrolyzer (650 °C) that reduced all gaseous Hg forms to GEM for detection. GOM was calculated as the difference between the measurements in the GEM and TGM channels (see Eq. (5) in Gustin et al. (2019)). The total mass of Hg on each CEM and PTFE in the DCS was also quantified after digestion (EPA Method 1631) by cold vapor atomic fluorescence spectrometry (CVAFS; see discussion in SI). The CEM and inlet PTFE membranes were changed every 7 or 14 days, corresponding with the sampling duration of the RMAS. The analyzer was calibrated daily using the internal calibration source, and periodically with an external calibration source (Tekran 2505) to verify the daily calibrations were within +/− 5 % of the expected value. This system had a detection limit of 0.1 ng m^{-3} (manufacturer detection limit).

The USU DCS (Fig. S1B), originally described in Lyman et al. (2020), was similar to the UNR DCS, but had several key differences. First, the USU DCS was an automated system with custom-built switching units and operating software that utilized a Campbell CR1000X data logger to calculate peak heights from the detector in real time, improving sensitivity. Second, the system used an elutriator at the inlet instead of the PTFE membrane used by the UNR DCS. The elutriator was the same as the elutriator assembly used on the Tekran speciation system, but had a side-arm adapter that allowed for flushing air scrubbed of Hg with activated carbon into the sampling stream. The elutriator captures 50 % of 2.5 μm particulate matter (PM; URG Corporation, PN URG-2000-30 K). Third, the sampling lines were constantly heated to 120 °C. Fourth, the sampling line was longer than the UNR DCS (1.26 m), but was shortened during the campaign; the long line (6 m) was used from November 21, 2019 to September 23, 2020, and the short line (1.7 m) was used from September 23, 2020 to November 24, 2020. The USU DCS had an average detection limit of 55 pg m^{-3} during this study.

The RMAS has been demonstrated to consistently provide higher GOM and/or RM concentrations than the Tekran system (Luippold et al., 2020b) when averaged over the 7- to 14-day RMAS deployment periods. The RMAS was previously described in detail (Luippold et al., 2020a) and has been deployed at a variety of sites globally (e.g., Nevada, Utah, Hawaii, Florida, and Maryland, USA; Sydney, Australia; Svalbard, Norway; Amsterdam Island) (Gustin et al., 2021; Osterwalder et al., 2021; Luippold et al., 2020b; Huang et al., 2017). For this study, two RMAS systems with different configurations were used to measure RM or PBM and GOM concentrations. One RMAS had 6 dual-stage filter packs, with three housing 2 CEM and three housing 2 nylon membranes (Sartorius, 0.2 μm pore size); this configuration allowed for the collection of RM. The second RMAS (RMAS + P) was identical to the first system, but had an additional PTFE upstream of all nylon or CEM (3-membrane filter packs), allowing for the separation of PBM (> 0.2 μm) on the PTFE and GOM on the downstream CEM or nylon membranes. The two systems were operated identically. For more details, see the SI.

2.3. USU automated calibrator

The custom-built automated calibrator was capable of injecting GEM or oxidized Hg – in the form of either $HgBr_2$ or $HgCl_2$ – vapor into the sampling stream of an active sampler. The calibrator was an improved version compared to that described by Lyman et al. (2020) and Lyman et al. (2016), including valves and carrier gases. For detailed discussion of calibrator operation and changes made relative to the calibrator previously discussed in Lyman et al. (2020), see the SI. Permeation tubes were weighed weekly on a Mettler Toledo XS3DU microbalance after the study concluded to determine the rate of mass loss (Lyman et al., 2020). In addition, the calibrator was connected to a gas chromatograph mass spectrometer (GC–MS) after the study to determine the chemical speciation of the output of each permeation tube, following the method described by Jones et al. (2016).

2.4. Analyses of membranes

2.4.1. Total Hg analyses

Total Hg content on CEM, PTFE, and the downstream nylon membranes were quantified following EPA method 1631 Revision E and analysis on a CVAFS (Tekran 2600-IVS). For details, see the SI.

2.4.2. Thermal desorption and peak deconvolution

Luippold et al. (2020a) described procedures used to quantify and characterize RM compounds collected on the RMAS nylon membranes. For this study, the thermal desorption procedure was identical to that in Luippold et al. (2020a); however, the peak deconvolution procedure was further optimized. The updated deconvolution procedure used the peakfit (O'Haver, 2021) function in MATLAB R2021a to generate model fits to the thermal desorption data. The temperature ranges at which each oxidized Hg compound was thermally desorbed from the nylon membrane were slightly adjusted from previous publications (Gustin et al., 2021; Luippold et al., 2020a) to better bracket the peak of each oxidized Hg compound's standard profile peak. The adjusted temperature ranges used in this study were: 82.5–92.5 °C for [—O], 95–115 °C for [−Br/Cl], 117.5–127.5 °C for [—N], 130–147.5 °C for [—S], and 150–190 °C for methylmercury (MeHg) or organic-bound Hg compounds. The order of GOM compounds released from the membranes was similar to the order reported by other groups for thermal release of GOM compounds from coal-derived surfaces (Rumayor et al., 2015; Rumayor et al., 2013). This optimization allowed for the determination of each individual oxidized Hg compound in the thermal desorption data, without describing compound mixtures as previously reported. By constraining the model to the updated temperature ranges, the model output is more simplistic and representative of the thermal desorption data based on the standard profiles. As a result, the average coefficient of determination (R^2) for the models was 0.993 ± 0.011 (n = 38), with the lowest R^2 values occurring when the Hg concentrations were lowest. For details on the thermal desorption method, see the SI.

2.5. Ancillary measurements

$PM_{2.5}$ and PM_{10} data were downloaded from the EPA's air quality data archive. Site 320310016 was used for this study, since it is the closest monitoring station to the sampling location (1.4 km apart).

2.6. Data corrections and statistical analyses

The Tekran 2537 analyzers in each of the Tekran speciation system and both DCS measured ambient GEM from the same location. Despite following strict protocols and making significant efforts to calibrate the instruments, the GEM measurements varied between 0.1 and 48 % (mean = 19.4 %, as % difference) between the 3 analyzers. This discrepancy has been observed in other co-location intercomparison studies that utilized carefully calibrated instruments (c.f., Gustin et al., 2013), and could be due to the limited calibration of the instrument. Elemental Hg analyzers are typically only calibrated at one span point, usually significantly above the ambient range. Multiple calibration points in the ambient range would likely improve GEM intercomparability.

In this study, the Tekran analyzer-based GEM and GOM measurements were corrected in order to directly compare measurements between systems. For the data correction, the USU DCS was selected as the baseline analyzer, since it was calibrated by an external calibrator in addition to the protocol calibrations (e.g., internal source, bell jar spikes). Daily-averaged GEM measurements for the UNR DCS and Tekran speciation system were regressed against the USU DCS GEM measurements using reduced major axis (RMA) regressions, and the slope of the RMA regressions used to adjust the measured GEM concentrations of the UNR DCS (m = 0.979) and Tekran speciation system (m = 1.423). The same slope correction factor was applied to the GOM measurements for each system. Only the corrected values are presented and were used in statistical comparisons.

For analyses comparing Tekran-based systems (i.e., Tekran speciation system and DCS) and the RMAS, the data were averaged over the RMAS deployment period; data for each system were only used when the systems were collecting data >50 % of the deployment period (n = 22 for USU DCS, 32 for UNR DCS, 34 for Tekran, 37 for RMAS, of 37 total deployments for this study).

Statistical analyses, including correlations, regressions, and ANOVA, were performed in Microsoft Excel using the data analysis tool. Reduced major axis (RMA) regression was used for determining slopes between different datasets; RMA analyses were performed using the lmodel2 package (Legendre, 2018) in R (R Core Team, 2020).

3. Results & discussion

3.1. Comparison of GEM measurements

Overall, averaging the corrected measurements over the RMAS sampling duration of 1 or 2 weeks, the Tekran 2537s in the 2 DCS were well correlated (Fig. S2); the GEM measurements in the UNR DCS were the same as the USU DCS (UNR DCS GEM = 1.001 × USU DCS GEM; r = 0.90, $p < 0.001$). The USU DCS measurements were correlated with the Tekran speciation system GEM (Tekran GEM = 1.000 × USU DCS GEM; r = 0.83, $p < 0.001$).

3.2. Comparison of GOM and RM measurements

For this study, the RM measurements made by the UNR DCS, USU DCS, and Tekran speciation system were operationally defined as GOM. Since the PTFE membrane at the inlet of the UNR DCS has been demonstrated to collect PBM < 0.2 μm (Gustin et al., 2019) based on the pore size of the inlet membrane, the UNR DCS measurement is described as GOM. Since the Tekran and USU DCS systems used an elutriator at the inlets (50 % aerodynamic diameter cutpoint of 2.5 μm in both cases), some PBM was likely collected in these systems and the RM measurements for these systems represent GOM plus a component of fine PBM. Based on the RMAS PBM measurements, PBM ranged from 0 to 64 % of the RM during the sampling campaign, with a mean of 29 ± 16 % (1σ) of RM that was particulate-bound. The mean fraction of $PM_{2.5}$:PM_{10} was 0.25 ± 0.15, and ranged from 0.02 to 0.64, indicating variation in particle size distribution throughout the sampling campaign. No attempt was made to characterize atmospheric particle size distribution, so corrections for contributions of particles to Hg RM measurements is not possible. Together with the fact that each measurement system has a different cut size for particle removal, the likelihood that at least some of the PBM that made it past the elutriator was deposited on the denuder (Tekran speciation system) or tubing (USU DCS) surfaces without making it to the analyzer and reducing the effect of particulate-bound Hg compounds on downstream Hg measurements, and the fact that AMNet operationally defines measurements downstream of the elutriator as GOM, lead to the use of the term GOM for the Tekran and USU DCS systems in this study. Lastly, changing the length of the USU DCS sampling line did not affect measurements, due to the fact that the line was heated (Fig. S2); concentrations across systems and membranes were consistent before and after this change.

The Tekran speciation system GOM (Tekran GOM) measurements were consistently the lowest, with other systems measuring 5.9 to 6.8 times more GOM or RM (Fig. 1), on average, when averaged over a 7- to 14-day period. The USU DCS GOM was correlated with the Tekran GOM and UNR DCS GOM, and RMAS RM concentrations (Figs. 1,2). Developed relationships could provide a means of adjusting the Tekran 1130-derived data at this location. If similar comparisons were made at specific locations, this approach could be a means of adjusting historical datasets.

Comparison of the GOM measurements made with membranes in the DCS and the RMAS also exhibited strong relationships (Fig. 3). The RMAS + P RM (CEM + PTFE) measurements had a one-to-one correlation with the RMAS RM (the concentration of RM on the CEM) measurements. There was also a good correlation between the RMAS RM and the UNR DCS CEM GOM. The RMAS RM was also correlated with the USU DCS CEM GOM, except the DCS concentrations were lower. The reason for this could be removal of PBM/GOM by the elutriator, and/or volatilization of RM from the CEM over time due to heating and during periods when heated air from the pyrolyzer was routed to the CEM as a system check. The UNR DCS CEM GOM that had a PTFE membrane at the inlet (not impacted by GOM loss due to heating) measured 4.3 times more GOM than the Tekran 1130 module (r = 0.63, p = 0.002).

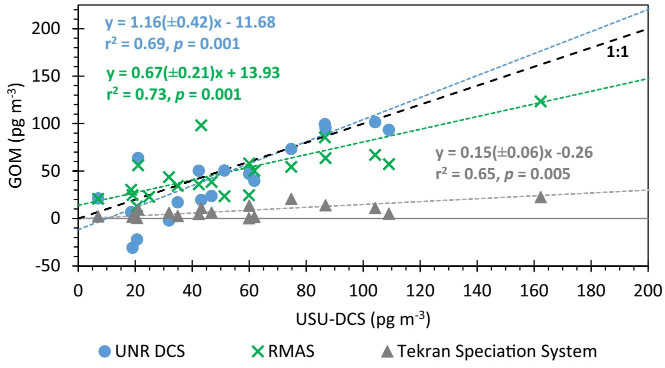

Fig. 1. GOM measurements for USU DCS versus other systems (i.e., UNR DCS and Tekran speciation system) and RMAS RM, averaged over RMAS collection periods. For all data, see Fig. S2. Trendline equations and statistics shown are RMA regressions; 95 % confidence intervals of RMA slopes are shown.

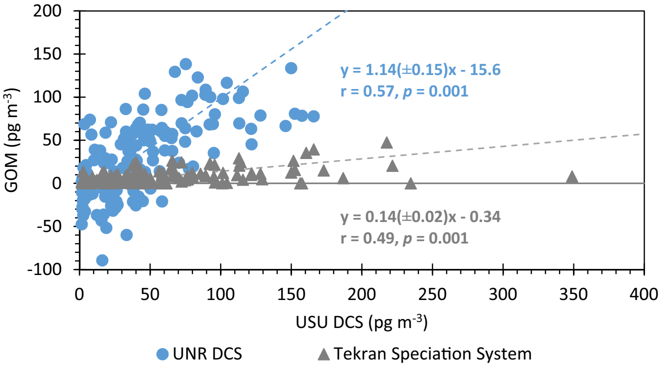

Fig. 2. Comparison of daily average Tekran-based GOM measurements in the DCS against the Tekran speciation system GOM measurements. Periods with <60 % data coverage were excluded. Trendline equations and statistics shown are for RMA regressions; 95 % confidence intervals of RMA slopes are shown.

3.3. RMAS performance

RMAS membranes followed similar trends as the automated systems (Figs. S3, S4). RMAS RM observations were ~1:1 correlated with the RMAS + P RM measurements and the UNR DCS membrane-based GOM concentrations (CEM + PTFE; $p < 0.001$). Measured GOM on the membranes in the USU DCS was 46 % lower than the RMAS RM. Similar to previous studies of the RMAS, the nylon membranes were 25 % less efficient at capturing Hg(II) than the CEM (Figs. 3, S3; Gustin et al., 2021; Luippold et al., 2020a). For details on the relative recovery of Hg(II) on the membranes and breakthrough, see the SI. Tekran-based GOM measurements in the DCS were significantly correlated with the RMAS RM, though the USU and UNR DCS were 50 and 30 % higher than the RMAS, respectively (Fig. S4).

Comparison of the RM and GOM chemistry of the RMAS and RMAS + P nylon membranes, respectively, demonstrated that GOM had more –O-based Hg(II) compounds and organic Hg(II) compounds than RM. Also, GOM infrequently had more –N-based Hg(II) compounds, and never had more –S-based Hg(II) compounds than RM (Fig. 4). This suggests that PBM and GOM had different chemistries. Further investigation into these trends will be discussed in a subsequent paper.

3.4. Calibrator assessment of USU DCS performance

Fig. S5 shows the average recoveries of GEM and GOM by the USU DCS when additions from the GEM, $HgBr_2$, $HgCl_2$, and blank permeation tubes

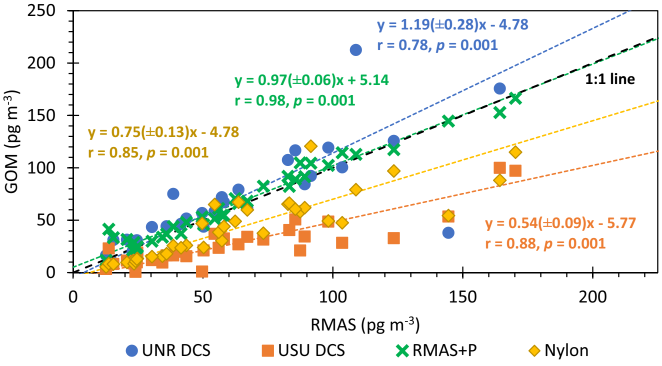

Fig. 3. Relationships between RMAS (THg on CEM in RMAS) and other membrane-based measurements. The UNR DCS and USU DCS measurements reflect the concentrations on the CEM + PTFE or CEM, respectively, in the instrument. The RMAS + P represents the concentration on the CEM plus that on the PTFE membrane in the RMAS + P. Nylon represents the RM on the nylon membranes in the RMAS (no upstream PTFE). Trendline equations and statistics shown are RMA regressions; 95 % confidence intervals of RMA slopes are shown.

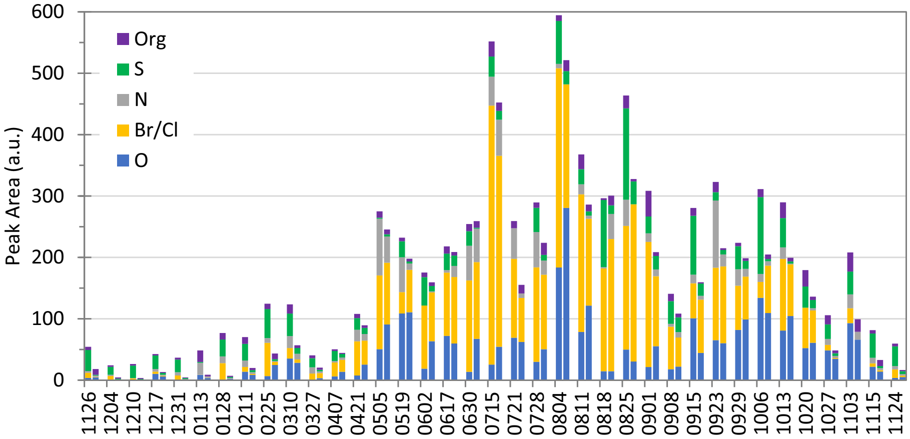

Fig. 4. Figure showing the peak area for the thermal desorption profiles for each sampling period, from November 2019 (left) to November 2020 (right); x-axis codes are harvest dates (MMDD). For each deployment period, the left bar represents the RM on the upstream nylon in the RMAS and the right bar represents the GOM on the upstream nylon behind the PTFE in the RMAS + P.

in the calibrator occurred. Fig. 5 shows a time series of the percent of recovered Hg that was GOM for each permeation tube. Variability shown in the figures could be the result of inconsistent permeation from the calibrator and/or inconsistent recovery by the analyzer.

Based on field injections, recovery of Hg from the blank permeation tube was low (0.08 ± 0.07 pg s^{-1}; average ± 95 % confidence interval), and was 91 ± 16 % GOM. Hg added from the blank permeation tube likely represents residual Hg in the calibrator from other injections that can be expected to be mostly $HgBr_2$ and/or $HgCl_2$ (Fig. S5). Recovery of Hg from the GEM permeation tube was 1.32 ± 0.16 pg s^{-1}, and was 6 ± 2 % GOM. Recovery of GOM from the GEM permeation tube was 0.07 ± 0.03 pg s^{-1}, similar to recovery from the blank permeation tube, and was probably due to emission of residual $HgBr_2$ and/or $HgCl_2$ in the calibration system. Recoveries of Hg from the $HgBr_2$ and $HgCl_2$ permeation tubes were similar (0.19 ± 0.03 pg s^{-1} and 0.23 ± 0.06 pg s^{-1}, respectively). The percent of recovered Hg that was GOM was similar for the $HgBr_2$ and $HgCl_2$ permeation tubes (70 ± 7 % and 68 ± 6 %, respectively), and within the expected range for the output of the calibrator (Fig. 5). Additional information about calibrator and permeation tube performance is available in the SI.

3.5. Implications

The Tekran speciation system exhibited the lowest (14.5 %) GOM observations of all the sampling systems, providing further evidence to the growing body of literature that this system is inadequate as a standard instrument for ambient RM measurements. However, since GOM data generated with the Tekran were correlated with the RMAS and DCS data, comparisons at specific locations could allow for adjusting historic Tekran datasets. The DCS performed similarly to each other. DCS GOM measurements were significantly correlated with RMAS RM and GOM data; however, the RMAS RM results were 30–50 % lower based on the slope of the regression equations comparing the two, indicating incomplete capture by the CEM, loss of RM to the RMAS filter pack holders, reduction of RM on the CEM, and/or generation of GOM within the DCS. Preliminary results indicate that <5 % of the total RM is adsorbed to the filter pack holders during the summer (Allen et al., *in preparation*), when RM at the sampling location is highest; thus, this possibility alone does not account for the complete discrepancy between the two system types. The shortened inlet did not significantly change the performance of the USU DCS, suggesting that a heated line efficiently transmits RM.

The RMAS is an inexpensive alternative to automated analyzer-based measurements methods (e.g., dual-channel systems) for ambient RM compounds, and currently provides more information about the Hg compounds collected on the membrane surfaces than the other systems. Nylon membranes have been demonstrated to not collect RM compounds with equal efficiency, especially nitrogen- and sulfur-based compounds (Gustin et al., 2021; Huang et al., 2013). Chemistry data showed differences in the GOM and PBM chemistry through the use of nylon membranes with and without an upstream PTFE. Better collection surface materials need to be

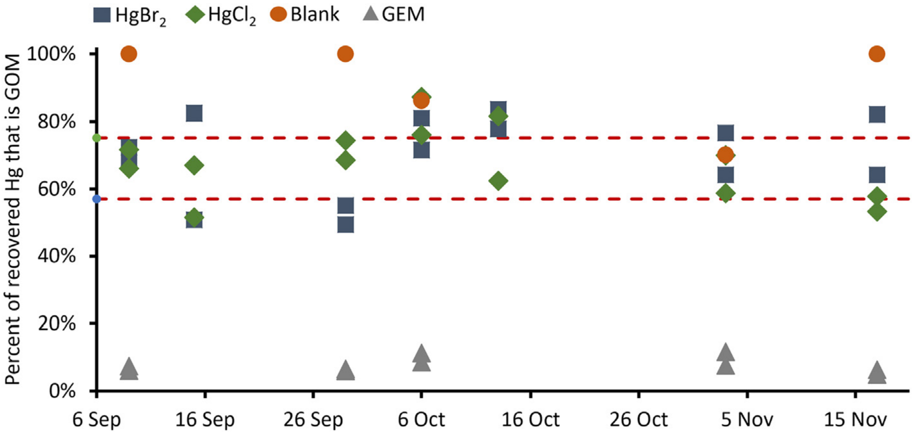

Fig. 5. Time series (2020) showing the percent of total Hg recovered by the USU DCS that was GOM in response to additions from $HgBr_2$, $HgCl_2$, GEM, and Hg-free blank permeation tubes. The dashed red lines indicate the upper and lower bounds of percent GOM recovery from similar calibrated $HgBr_2$ and $HgCl_2$ permeation tubes.

identified or developed that have higher Hg(II) collection efficiencies (e.g., less breakthrough) and equal efficiencies for all Hg(II) compounds; a collection surface should, at a minimum, meet these requirements, and ideally also be compatible with thermal desorption and other chemistry methods and be reusable. In addition, the time resolution for the RMAS is days to weeks, depending on the ambient RM concentration. Improving the temporal resolution would be useful for the Hg monitoring community.

The calibrator linked to the DCS allowed for assessing the accuracy of the measurement of the different systems, and demonstrated that both DCS were making accurate measurements using $HgBr_2$ permeation tubes, while RMAS concentrations were lower. To better serve the ambient Hg research community, these systems, and others, need to be tested in different environments to assess their robustness under a range of climate and air chemistry conditions.

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CRediT authorship contribution statement

Sarrah Dunham-Cheatham maintained instruments and collected RMAS samples during data collection. She analyzed the RMAS samples, compiled and processed the data, and wrote parts of and edited and revised the manuscript. Seth Lyman remotely controlled the USU DCS and calibrator. He compiled data obtained using these instruments, and wrote parts of and edited the manuscript. Mae Gustin decided how to configure the manuscript and wrote parts of and edited the manuscript. All worked on the statistical analyses of data.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.159219.

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