

Use of Membranes and Detailed HYSPLIT Analyses to Understand Atmospheric Particulate, Gaseous Oxidized, and Reactive Mercury Chemistry

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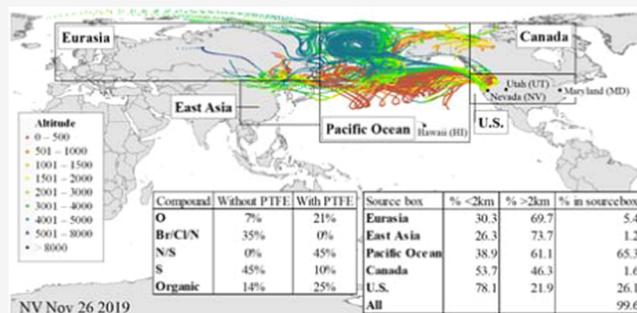


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ABSTRACT: The atmosphere is the primary pathway by which mercury enters ecosystems. Despite the importance of atmospheric deposition, concentrations and chemistry of gaseous oxidized (GOM) and particulate-bound (PBM) mercury are poorly characterized. Here, three membranes (cation exchange (CEM), nylon, and poly(tetrafluoroethylene) (PTFE) membranes) were used as a means for quantification of concentrations and identification of the chemistry of GOM and PBM. Detailed HYSPLIT analyses were used to determine sources of oxidants forming reactive mercury (RM = PBM + GOM). Despite the coarse sampling resolution (1–2 weeks), a gradient in chemistry was observed, with halogenated compounds dominating over the Pacific Ocean, and continued influence from the marine boundary layer in Nevada and Utah with a periodic occurrence in Maryland. Oxide-based RM compounds arrived at continental locations via long-range transport. Nitrogen, sulfur, and organic RM compounds correlated with regional and local air masses. RM concentrations were highest over the ocean and decreased moving from west to east across the United States. Comparison of membrane concentrations demonstrated that the CEM provided a quantitative measure of RM concentrations and PTFE membranes were useful for collecting PBM. Nylon membranes do not retain all compounds with equal efficiency in ambient air, and an alternate desorption surface is needed.



INTRODUCTION

The atmosphere is the primary pathway by which mercury (Hg) is deposited to ecosystems, and this occurs via dry deposition of both gaseous elemental (GEM) and gaseous oxidized (GOM) Hg compounds, with GOM being the dominant compound in wet deposition. It has been demonstrated that the Tekran speciation system, the only commercially available Hg monitoring instrument for ambient air sampling, does not accurately measure GOM and particulate-bound (PBM) Hg, and underestimates reactive mercury (RM = GOM + PBM) by up to 13 times.^{1–5} Thus, the Hg research community needs a method that allows for the accurate quantification and identification of RM compounds.

The University of Nevada, Reno-Reactive Hg Active System 2.0 (RMAS) is a promising technology for measuring reactive Hg (RM = GOM + PBM), GOM, and PBM in ambient air using membranes as collection surfaces.^{3,6} Membranes used in this system include cation exchange membranes (CEM) for quantification of RM and GOM concentrations, and nylon membranes for determination of RM and GOM chemistry. The RMAS has been applied for measurement of RM across multiple sampling locations, and numerous lines of evidence (meteorology, chemistry of compounds on membranes, back

trajectory analyses, anion chemistry, criteria air pollutants) have demonstrated the chemistry of RM compounds measured at Mauna Loa, Hawai'i (HI), Reno, Nevada (NV), Piney Creek Reservoir, Maryland (MD), and Horsepool, Utah (UT), USA, corresponded well with projected source areas, meteorology, criteria air pollutants, and other ions collected on the membranes⁷ (for locations, see graphical abstract).

Gustin et al.³ described a method whereby use of the three membranes could allow for separating the components of RM, that is GOM and PBM (>0.2 μm). The primary focus of the Gustin et al.³ study was to compare four methods for measuring RM, and to determine the potential for the three-membrane system applied here to provide a better understanding of whether RM was gaseous or particle-bound. Detailed analyses of RM chemistry and sources were not

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investigated in the 2019 study.³ For the present study, data were collected in a transect across the United States with sampling sites on Hawai'i (HI) and in Nevada (NV), Utah (UT), and Maryland (MD). Our main working hypothesis was that the three-membrane system would provide a method of identification of GOM and PBM concentrations and chemistry, and that the information developed would be useful for better understanding atmospheric Hg chemistry. The second working hypothesis was since RM compounds present are influenced by the oxidants in the air,⁷ detailed HYSPLIT analyses associated with each location would allow us to discern sources of oxidants forming RM compounds. The efficiency of the membranes for collection of RM/GOM/PBM was also investigated to determine the robustness and limitations of this method. This was done through comparison of (1) concentrations from membranes with and without upstream poly(tetrafluoroethylene) membranes (PTFE), and (2) concentrations and chemistry associated with each fraction (GOM and PBM).

METHODS

Sampling Locations. Field sites for this study were the same as those discussed in Luippold et al.,⁷ at which only RM was measured. Locations included the Mauna Loa Observatory (HI) that is operated by the National Oceanic and Atmospheric Administration (NOAA) (19.5392, -155.5792; 3397 masl; 1 August 2019 to 2 January 2020, $n = 10$ two-week periods). The location in Reno, Nevada (NV), was at the College of Agriculture, Biotechnology & Natural Resources Nevada Agricultural Experiment Station Valley Road Greenhouse Complex (39.5375, -119.8047; 1371 masl; 1 October 2019 to 28 January 2020, $n = 11$ one-week periods and $n = 4$ two-week periods). The Horsepool Monitoring Station, Utah (UT) (40.1434, -109.4689; 1567 m; 1 August 2019 to 6 January 2020, $n = 11$ two-week periods), operated by Utah State University, is south of Vernal, Utah, and Dinosaur National Monument in the Uintah Basin. The Piney Creek Reservoir location (MD) is northeast of Frostburg, Maryland (39.7053, -79.0122; 769 masl; 15 August 2019 to 21 November 2019, $n = 6$ two-week periods), and is operated by the University of Maryland Center for Environmental Science.

The HI site is primarily influenced by air from the free troposphere and the marine boundary layer.⁷ The NV location is 50 m from I-80, a major interstate highway within the city of Reno, and is also impacted by air from the free troposphere, Reno, San Francisco and Sacramento, and the marine boundary layer.⁷⁻⁹ The UT site is located in a remote area with oil and gas production occurring in the basin that has winter inversions, and inputs of air from the free troposphere. The MD location is in a forested area downwind of coal-fired power plants.⁷

Based on work by Luippold et al.,⁷ RM concentrations at HI > NV > UT > MD. The RM chemistry at HI was dominated by halogen-based compounds, while in NV, halogen, -N, and -S Hg compounds were abundant with some -O-containing compounds present. At UT, compounds included halogenated compounds along with -N- and -O-containing compounds. Finally, in MD, -N and -S RM compounds were dominant in the winter, while in the summer, organic compounds were more abundant.

Sampling System. Samples were collected from August 2019 to January 2020. The RMAS consists of a custom-

designed anodized aluminum weather shield (Deluxe Welding, Reno, Nevada) that houses six filter packs. Sampling air velocity through each filter pack is controlled at 1 L/min, using critical flow orifices (Teledyne Technologies) and flow rates are physically measured at the beginning and end of each deployment. Two pumps (KNF P/N UN838KNI, these pumps were consistently used in this project, but failed often and are not recommended for future use) were used so that if one pump went offline, data were still being collected; the pumps were housed in a custom-designed pump box. For more details, see Luippold et al.⁶ The RMAS typically houses triplicate two-in-series CEM (Pall, 0.8 μm pore size) and nylon membranes (Sartorius, 0.2 μm pore size) in six total dual-stage filter holders (Savillex). For this study, at the NV site two RMAS were used; one following the traditional configuration, with six total dual-stage filter holders holding two-in-series CEM ($n = 3$) and nylon membranes ($n = 3$). The second RMAS housed triple-stage filter holders with a PTFE membrane (Sartorius, 0.2 μm pore size) upstream of the two-in-series CEM and nylon membranes. This allowed for triplicate samples of all membrane measurements.

At HI, UT, and MD, one RMAS was used and configured so that two CEM and one nylon membrane dual-stage filter packs were deployed without a PTFE, and one CEM and two nylon membrane dual-stage filter packs had upstream PTFE membranes (Figure SI 1). This did not allow for replication of all measurements and provided duplicate measurements for the nylon membrane with the upstream PTFE and for the CEM without the upstream PTFE, and one measurement for the nylon without the PTFE and for the CEM with the PTFE.

Concentrations on the two-in-series upstream and downstream CEM and nylon Hg were added together for the second membrane reflects breakthrough, and the mean blank concentrations for that sampling time subtracted. Herein, the terms "CEM RM" and "nylon RM" indicate data collected on these membranes with no upstream PTFE; "CEM GOM" and "nylon GOM" are Hg concentrations on these membranes with an upstream PTFE, while the PTFE membrane Hg data are considered PBM. CEM and nylon GOM + PBM indicate the total Hg concentration for the PTFE plus the upstream and downstream CEM and nylon membranes, respectively. Use of a single measurement for CEM and nylon membranes was justified given the good replication observed in other studies using this system.^{6,7} At the end of each deployment, membranes were stored in 50 mL polypropylene centrifuge tubes (Falcon, Corning, Inc.)⁶ and shipped to UNR, frozen, and analyzed within 2 weeks of receipt.

Blank membranes ($n = 3$) of each membrane type were collected at the start of each deployment and kept in individual storage vessels at $-20\text{ }^\circ\text{C}$ and analyzed at the same time as the corresponding samples. Downstream membranes were used to quantify breakthrough, calculated as follows

$$\% \text{ breakthrough} = \frac{(M_{\text{down}} - \text{blank})}{[(M_{\text{down}} - \text{blank}) + (M_{\text{up}} - \text{blank})]} 100 \quad (1)$$

where M_{down} represents the downstream membrane and M_{up} represents the upstream membrane.

Analyses of Membranes. Total Hg concentrations on CEMs, downstream nylon membranes, and PTFE membranes were determined following EPA Method 1631 that consists of oxidation in an acidic solution containing BrCl, SnCl reduction, and analyses using cold vapor atomic fluorescence

Table 1. (Top) Mean Concentration on Membranes for Each Field Location for the Entire Campaign, in pg m^{-3} and (Bottom) Slope and r^2 , in Parenthesis, for the Regression between Various Membrane Configurations^{a,b,c,d,b,d}

location number of samples	HI 10	HI-CV	NV 15	NV-CV	UT 11	UT-CV	MD 6	MD-CV
	Mean (std) Concentration for Entire Campaign							
CEM RM	158 ± 9	0.06	32 ± 4	0.13	40 ± 4	0.10	11 ± 2	0.18
CEM GOM + PBM	168		36 ± 9	0.25	28		8	
CEM GOM	172		23 ± 7	0.30	32		12	
NYL RM	71		23 ± 2	0.09	19		5.7	
NYL GOIVH – PBM	102 ± 11	0.11	12 ± 3	0.25	17 ± 1	0.06	4 ± 3	0.75
NYL GOM	106 ± 11	0.10	25 ± 7	0.28	25 ± 7	0.28	8 ± 3	0.35
Slope (r^2) with Intercept Set to Zero								
CEM GOM + PM:CEM RM	1.10 (0.92)		1.1 (0.55)		0.90 (0.95)		0.98 (0.94)	
CEM GOM:CEM RM	1.09 (0.91)		0.70 (0.66)		0.66 (0.89)		0.76 (0.95)	
NYL RM:CEM RM	0.49 (0.82)		1.95 (0.3)		0.58 (0.86)		0.40 (0.69)	
NV 2 RM outliers removed			0.54 (0.66)					
NYL GOM + PBM:CEM RM	0.69 (0.78)		0.77 (0.84)		0.82 (0.92)		0.82 (0.92)	
NYL GOM:CEM RM	0.67 (0.81)		0.40 (0.53)		0.53 (0.84)		0.53 (0.84)	

^aCEM and nylon membrane measurements were made simultaneously. ^bNote mean and std are an average of all membrane concentrations for the whole sampling period. ^cAll regressions are significant at $p < 0.05$. ^dCV indicates the mean coefficient of variation for all samples.

spectrometry. All samples were above the method detection limit (40 pg Hg).

Upstream nylon membranes were thermally desorbed to determine the RM compounds collected on the membranes. The CEM cannot be used for thermal desorption for they melt. Details of the thermal desorption system can be found in Luippold et al.⁶ Briefly, a nylon membrane was placed inside a sealed Hg-free, temperature-controlled oven and gradually heated from 50 to 200 °C at a rate of 2 °C min⁻¹. Volatilized RM compounds are pulled through a pyrolyzer, to reduce all Hg compounds to elemental Hg that is quantified by a Tekran 2537. RM compounds are released from the membrane at different temperatures (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 organic Hg compounds), allowing for separation and determination of compounds as the sample is gradually heated. Resulting thermal desorption profiles were compared to those generated by thermally desorbing permeated pure GOM compounds. Solid compounds for which profiles have been developed include HgBr₂, HgCl₂, HgN₂O₆·H₂O, HgSO₄, and HgO, and elemental Hg, as well as methylmercury chloride directly added to membranes.^{8–10}

Thermal desorption profiles were deconvoluted using the assumption that profiles for specific compounds are Gaussian and compared to profiles generated from standard compounds (see Luippold et al.,⁷ Supplemental Information). Compound concentrations were calculated using the integral of peak area (unit: pg) divided by the sampling volume. Compounds were identified as those associated with –O, –Br/Cl, –N, –S, and –organics based on desorption temperatures of the standard GOM compounds. In some cases, peaks overlapped and these are designated as multiple compounds. These data must be used with the caveat that the exact compounds are unknown, and it is likely there are compounds with complex formulas that exhibit similar thermal desorption behavior compared to the pure compounds used here.

Back Trajectories and Statistical Analyses. Two hundred and forty-hour back trajectory simulations were conducted using the NOAA Air Resources Laboratory GDAS 1° data archive and Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.^{11,12} Trajectories

were analyzed using a gridded frequency distribution method,¹⁵ generating 216 trajectories per day or 51 840 hourly points. There is only 1 day (January 2) that trajectories went back 8 days instead of 10, producing 41 472 points using the same 216 trajectories. This was done because the software does not work when crossing over into a different calendar year.

Use of a large number of trajectories gives a general indication of source region and representation of air mass transport. Trajectory residence times were calculated as the percentage of total hourly trajectory points that resided in a three-dimensional source box. Defined source boxes (Table S1) used in this study included Eurasia, East Asia, the North Pacific Ocean, Canada, and continental US. In addition, the percentage of trajectory points below the boundary layer within each source box was designated as <2 km masl. The 2 km cutoff was used based on data collected in Nevada¹³ and over the marine boundary layer of the Pacific Ocean.¹⁴ Model output was visualized in ArcMap.

Microsoft Excel 2016 was used to calculate the source box residence times and the % < and > the boundary layer, and to perform statistical analyses. At each location, the coefficient of variation (CV = standard deviation ÷ mean) was calculated for replicate membrane data for each deployment, as well as for the whole campaign for each membrane type. Air quality data used in statistical analyses for the NV location was obtained from <https://wrcc.dri.edu/cgi-bin/rawMAIN2.pl?nvuncrc> (site 320310016 for 2019 and site 320310031 for December 2019 onward, as the site location was moved).

RESULTS AND DISCUSSION

General Trends. One of the major questions for this research was whether GOM versus PBM could be differentiated using the three membranes. To address this question, CEM and nylon membranes were deployed with an upstream PTFE; it was assumed that the PTFE was only acting as a particle filter and not selectively sorbing gaseous Hg compounds due to its use in Hg samplers. If CEM and nylon RM measurements were collecting PBM, then they should have similar total Hg concentrations as the corresponding membrane type GOM combined with the PTFE PBM.

Additionally, the CEM and nylon GOM should be lower than the CEM and nylon alone, if PBM is present. It must be realized that this exercise is qualitative. For example, it is not known whether GOM sticks to the PTFE or if captured PBM is revolatilized as GOM and captured in the CEM. Nylon and CEM RM and GOM followed the same trends for all locations (Figure SI 2).

At HI, CEM RM concentrations were $51 \pm 10\%$ greater than the nylon membranes (Table 1), based on the slope of the regression line throughout this sampling campaign. For the thermal desorption analyses, it is difficult to separate $-\text{Br}$ and $-\text{Cl}$ compounds. Based on data presented in Gustin et al.¹⁰ comparing membrane data with those collected with the Tekran system KCl denuder in clean air, CEM and nylon membranes collected 2.4 and 1.6 times more HgCl_2 compounds, respectively. For HgBr_2 compounds, nylon and CEM concentrations were 1.7 and 1.6 times that of the denuder, respectively. Based on these results, the 50% disparity observed in this study can be best explained by the RM compounds being primarily HgCl_2 . Both nylon and CEM RM concentrations were highest in August and October then decreased to ~ 35 and 150 pg m^{-3} through November and December (Figure 1 and Table SI 2). This trend is similar to that reported in Luippold et al.⁷ Nylon GOM concentrations were not significantly different from the nylon GOM + PBM concentrations, and CEM GOM + PBM concentrations were not significantly different from CEM GOM, indicating that little PBM was present at this sampling location during the sampling campaign. PBM concentrations between the two membranes were not significantly different ($p = 0.25$, single-factor ANOVA), and the percent PBM values of total RM measured on the PTFE in front of the CEM and nylon membrane were 3 ± 3 and $2 \pm 2\%$, respectively.

In NV, nylon RM concentrations were 16% lower than the CEM RM, if the first two deployment periods in October 2019 were removed from the dataset (Table 1, based on the regression slope; Figure 1). In Figure 1, the NV-1 plot contains all of the data for the sampling campaign, and the NV-2 plot only displays the data from October 28, 2019, onward to provide a closer look at the data with the initial higher-concentration samples removed. When using all of the data (NV-1), the nylon:CEM RM ratio was 1.95 due to two high nylon membrane concentrations in October. Membrane Hg concentrations all followed similar trends, and the CEM GOM + PBM was similar to the CEM RM, while the CEM GOM data were 30% lower than the CEM RM (Figure SI 2 and Table 1). The nylon GOM + PBM concentrations were 23% less than the CEM RM concentrations. Nylon GOM concentrations were 60% lower than the CEM GOM. PBM concentrations associated with CEM and nylon membranes were not significantly different, indicating that particulates were being collected on the PTFE membranes. The differences between the CEM and nylon membranes (for NV 2 data) GOM and GOM + PBM were 60 and 23 pg m^{-3} , respectively. The reason for the greater percentage of PBM on nylon membranes relative to the CEM was due to loss of RM compounds from the nylon membranes. Concentrations and trends for RM reported in Luippold et al.⁷ were similar to those observed in this study, with $\sim 50 \text{ pg m}^{-3}$ CEM RM, nylon RM concentrations 16% less than CEM RM, and concentrations declining into the winter.

In UT, nylon RM concentrations were 58% lower than the CEM RM (Table 1). The CEM GOM + PBM was 10% lower

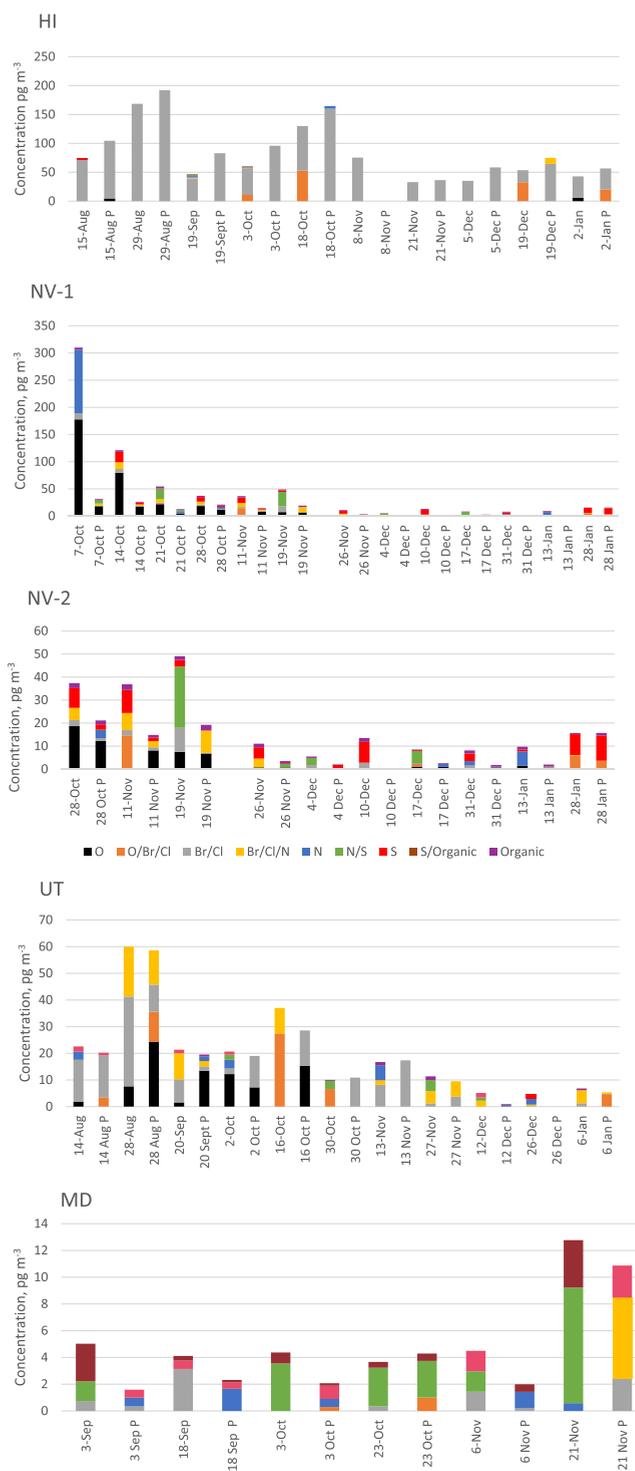


Figure 1. Concentrations of RM and GOM compounds on nylon membranes for each sampling deployment for each sampling location. Concentrations associated with dates only represent data from nylon membranes without PTFE in front. Concentrations associated with nylon membranes with the nylon membranes with PTFE in front are denoted as the date with a P. Dates represent the end date of the deployment period. NV-2 shows the same data for NV-1, leaving out the three high initial sampling durations to provide a closer look at the remaining data.

than the CEM RM, and GOM concentrations were 34% less than the CEM RM. Nylon PBM and CEM PBM concentrations were similar, except for the October 16th,

October 30th, and November 13th deployments, when the nylon PBM concentration was higher. This indicates that the CEM RM and CEM GOM + PBM were quite similar; however, this was not true for the nylon membranes that lost GOM.

In MD, the nylon RM concentrations were 60% lower than CEM RM. CEM RM and CEM GOM + PBM concentrations were the same. CEM GOM concentrations were 24% lower than CEM RM. Nylon GOM + PBM concentrations were 18% lower than the CEM RM and the nylon GOM was 47% lower than the CEM RM. These relationships indicate better retention of the compounds on the nylon membrane with the PTFE in front. The percentage of PBM relative to the total GOM + PBM concentration on the nylon and CEM were not significantly different ($p = 0.99$), with $49 \pm 34\%$ for nylon and $48 \pm 32\%$ for CEM. These values are variable given the complex chemistry occurring over the sampling period.

The nylon:CEM RM concentration ratios reported in Luippold et al.⁷ for HI, NV, UT, and MD were 0.58, 0.73, 0.44, and 0.5, respectively, similar to this study (Table 1). In general, for all locations except HI, PBM was collected on the PTFE (Table SI 2). It is noteworthy that, on average, the nylon GOM + PBM concentrations, except for HI, were higher than nylon RM by 37, 29, and 29% for NV, UT, and MD, indicating better retention of GOM compounds on the nylon membrane when the PTFE was in place; HI nylon GOM + PBM concentrations were not significantly different than nylon RM. Mean Hg concentrations on the nylon membrane decreased from west to east due to the fact that Hg air chemistry was more complex at the eastern sampling locations, with $-O$, $-N$, $-S$, and organic compounds that are not efficiently retained on the nylon membrane.⁷ The difference between the CEM RM and nylon GOM + PBM also increased from west to east due to greater loss of GOM from the nylon membranes. CEM RM and CEM GOM + PBM were similar across the sampling gradient, indicating that the PTFE membrane was quantitatively retaining PBM, as was the CEM without the upstream PTFE. RM measurements using CEM are thought to be accurate since they compared well with a calibrated dual channel system used to measure GOM concentrations,¹⁵ and they retained calibrated permeated RM compounds.¹⁰

Thermal Desorption Profiles. Thermal desorption data must be viewed within the limitations of the current method. Only select commercially available standard oxidized Hg compounds exist that can be used to generate standard desorption profiles, and the resulting profiles overlap. The deconvolution method allows for separating specific compounds, but the chemistry is complex and there are likely multiple compounds with similar behaviors. In addition, since nylon membranes do not appear to retain all compounds in ambient air with equal efficiency, though they do in charcoal-scrubbed air,¹⁰ the Hg chemistry derived from the method may not fully reflect actual RM chemistry and concentrations. However, that said, this work provides a platform for better understanding GOM and PBM chemistry that has not been possible with conventional methods, given their limitations.

In a previous work, Luippold et al.⁷ demonstrated that RM compounds at: HI were predominantly $-Br$ and $-Cl$; NV were $-Br/Cl$, $-N$, $-S$, and organic; UT were $-Br/Cl$, or $-O$, $-N$, and $-Br/Cl$; and MD were $-N$, $-S$, and organic. In this study, the compounds at HI were the same (Table SI 3). In NV, the % of $-O$ compounds was higher; otherwise, the same compounds were observed in both studies. At UT, $-O$

compounds were present from August to October, similar to NV where $-O$ compounds were abundant in the autumn months. In October in UT, the RM chemistry transitioned to halogenated compounds dominating, with some $-N$, $-S$, and organics present as well. The same transition happened in NV at the end of November and was associated with a shift from inputs from Eurasian sources to source areas from the Pacific Ocean, the continental US, and Canada. Criteria air pollutant data for NV showed high concentrations of NO_2 and SO_2 when $-N$ and $-S$ compounds were predominant on the nylon membranes (November 19, 2019, December 10, 2019, and January 13, 2020) (Figure SI 3), indicating agreement between RM compounds and locally measured air pollutants. However, the same was not true for $-O$ and $-Br/Cl$ compounds that are thought to be derived from long-range transport. Together, this indicates that global, regional, and local air chemistries are producing RM observed in northern NV. Using back trajectories (Table SI 4, <https://scholarworks.unr.edu/handle/11714/7532>), high $-O$ concentrations at both NV and UT were associated with times when long-range transport was prevalent. In MD, halogenated compounds were present when air passed over the Pacific Ocean to MD. Air during this time period was derived from the marine boundary layer and free troposphere (Table SI 4, <https://scholarworks.unr.edu/handle/11714/7532>). At HI, RM chemistry was dominated by halogenated compounds, with a small amount of $-O$, $-S$, and $-N$ compounds (Figure 1).

RM concentrations on the CEM and nylon membranes in NV were similar to the GOM + PBM (Table SI 2). Based on the deconvoluted thermal desorption profile data, during October, there was a significant amount of $-O$, $-N$, and $-S$ compounds with lesser amounts of halogenated and organic compounds (Figure 1). After this time compounds were predominantly $-S$, $-N$, and organic for both nylon RM and GOM compounds. In January, $-O$ compounds became prevalent again and were observed as nylon RM and GOM compounds. $-O$, $-N$, and $-S$ compounds were prevalent as PBM.

At UT, PBM concentrations were low ($<10 \text{ pg m}^{-3}$) and similar for the CEM and nylon membranes (Figure SI 2). Nitrogen and $-S$ compounds were predominant at this location throughout the sampling campaign. When $-N$ and organic compounds were present, they were found mostly in the RM measurements, indicating these compounds were present as PBM and not GOM (cf. October and November data).

In MD, nylon GOM + PBM concentrations were higher than nylon GOM. CEM GOM + PBM concentrations were higher than the nylon RM and nylon GOM + PBM concentrations, but this varied, indicating reactions or loss occurring on the nylon membrane alone. RM chemistry at this location was complex and RM compounds were not always present as GOM. Data suggest that PBM consisted mostly of $-O$, $-N$, and halogenated compounds.

HYSPLIT Results. HYSPLIT analyses were performed to better understand the sources of air interacting with each site and how, in detail, this was reflected in the RM chemistry. At HI, the air was primarily sourced from the marine boundary and the free troposphere, where halogenated compounds are dominant (Tables SI 3 and SI 4, <https://scholarworks.unr.edu/handle/11714/7532>). However, when air intersected with the continental US or Asia source boxes, some minor $-O$, $-N$, $-S$, and organic compounds were present. For example,

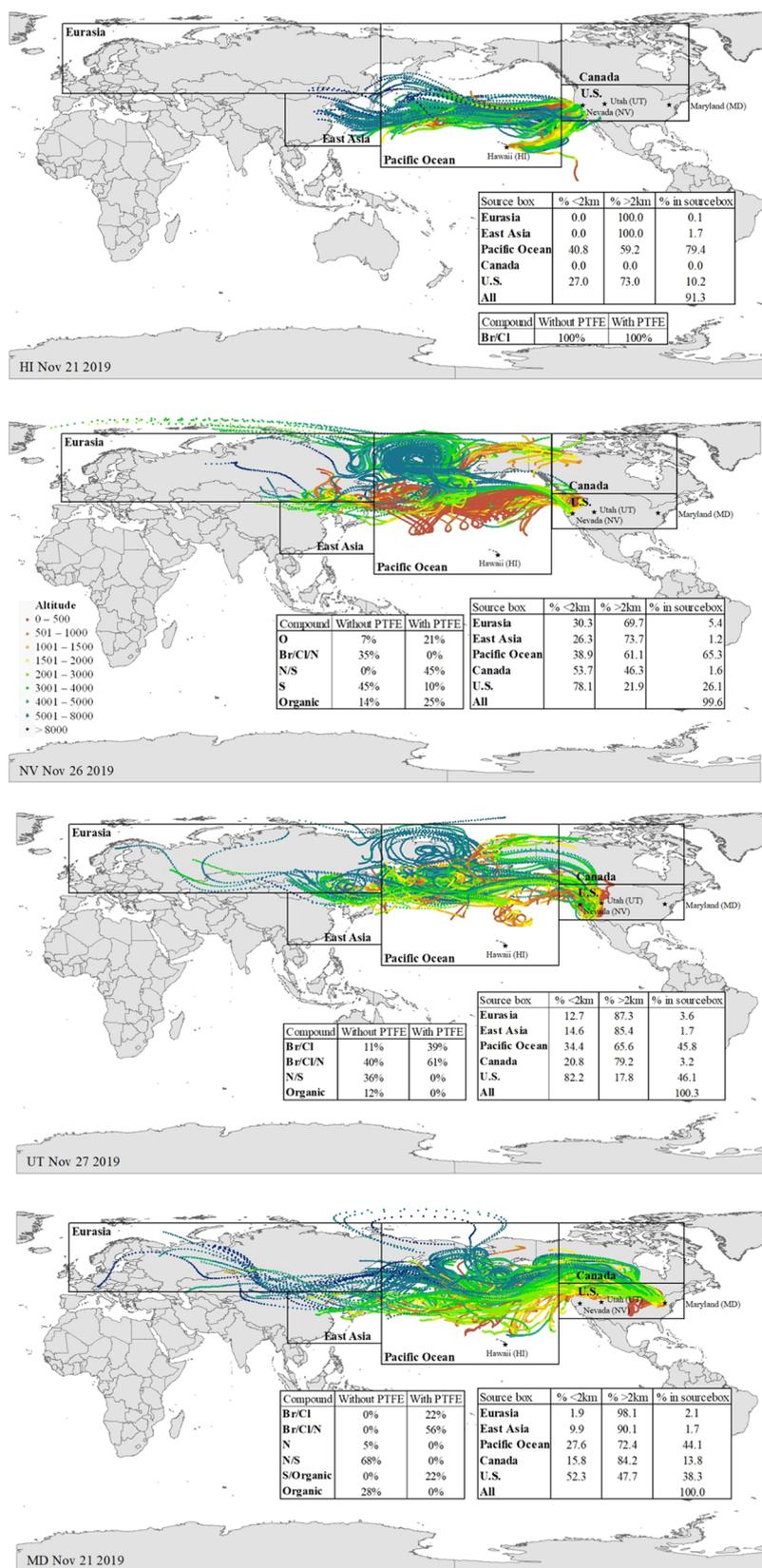


Figure 2. HYSPLIT trajectory analyses for the four sampling locations during a time period with overlap (see harvest dates on each map). Compounds on nylon membranes without (RM) and with (GOM) PTFE membranes are identified, as well as percent time in specific source boxes and the time above and below 2 km. The total percentage in all source boxes <100% indicates trajectory points occurred outside of the source boxes.

during the September 19th deployment, 8% of the air sampled at the site was sourced from the continental US source box, and -N was present as RM; however, -N was not detected as GOM, indicating -N compounds were associated with the particulate fraction.

In NV, the first four sampling periods over the month of October had significant amounts of -O, -N, and -S RM and GOM compounds (Table SI 4 and Figure 1). During this time, trajectories spent the majority of time over Eurasia, Asia, Canada, and the continental US (Table SI 4). For the membranes collected November 19th, sampled air passed high over Eurasia and East Asia, and then over the Pacific Ocean where 32% of the air mass coming into NV was <2 km and 68% >2 km. This air then subsided as it came into the United States. During this time, -O compounds were present, as were halogens, -N, and -S compounds. The following week (November 26th), the air mass intersecting NV spent much of its time at >2 km above Eurasia, Asia, and the Pacific Ocean, and more time at <2 km when entering the continental US source box; halogenated compounds were less abundant compared to the previous week. For the rest of the sampling campaign at NV, the primary compounds were associated with anthropogenic pollutants, and 10–32% of the air was associated with the Eurasian and Asian source boxes.

Air coming into UT primarily passed >2 km over the Pacific Ocean and below the boundary layer in the United States. Typically air sampled at this location spent <10% of time over Canada; however, on October 31st the sampled air spent 42% of time over Canada, and RM compounds were -O/Br/Cl and -N, while GOM compounds were primarily -Br/Cl (Table SI 4, <https://scholarworks.unr.edu/handle/11714/7532>).

At MD, a small component of the RM was composed of halogenated compounds for each sampling period, except October 3rd when the air resided primarily <2 km over the United States, and compounds were primarily -N, -S, and organic. During the other time periods, the sampled air was impacted by long-range transport, with up to 6% of the trajectories originating over Eurasia and East Asia, 21–52% over the Pacific Ocean, and 30–70% over Canada and the United States.

Figure 2 contains trajectories for similar time periods for each location and a summary of the compounds on the membranes. For HI, the air resided over the Pacific Ocean and RM compounds were halogenated GOM. The air impacting NV was not associated with the air impacting HI, and most of the air passed over the North Pacific Ocean (in both the boundary layer and above) and below the boundary layer for the United States. Compounds reflected these sources, with -Br/Cl compounds being PBM, -O, -S, and organic compounds being GOM and PBM, and -N/S being GOM. At UT, the sampled air had more halogenated compounds and more air sourced from the marine boundary layer and free troposphere. RM compounds included -Br, -Cl, -N, -S, and organic, while GOM compounds were primarily -Br- and -Cl-based. This indicates for NV and UT, -N and -S compounds were primarily PBM. At MD, trajectories were similar in direction to NV and UT, indicating this was a fast traveling air mass that affected the entire United States. At MD, RM compounds were -N, -S, and organic, while GOM compounds were halogen-based with some -S and organic compounds. This demonstrates that halogenated compounds were present that were most likely derived from the free troposphere and marine boundary layer. In addition, -N, -S,

and organic RM compounds were PBM and likely derived from regional and/or local pollution. For similar data presentation for all sites and deployments, see the Supporting Information (Tables SI 3 and SI 4, <https://scholarworks.unr.edu/handle/11714/7532>).

Breakthrough. Percent breakthrough at HI was lowest relative to the other sampling sites, with mean values of 6.4% for CEM RM, 3.7% for CEM GOM, and similar values of 1.7 and 1.9% (not significantly different) for the nylon membranes RM and GOM, respectively. Based on thermal desorption profiles, this indicated that halogenated compounds are most efficiently collected by the nylon membranes. Percent breakthrough was not significantly correlated with concentrations on the membranes. Less breakthrough was observed for the CEM GOM (Table SI 5).

In NV, breakthrough on average was 14% for the CEM RM and 28% for CEM GOM + PBM. The % breakthrough values for these two membrane configurations were similar from October until November 11th, then breakthrough increased significantly, ranging from 6 to 35% for CEM RM and from 18 to 56% for CEM GOM + PBM. The highest percentage of breakthrough occurred when -N and -S compounds were present. During October to November, there was a high percent of -O compounds; more were associated with the nylon RM than the nylon GOM measurement, indicating some -O compounds were aerosol and others were a gaseous form (Figure 1). This suggests that -N and -S are not as efficiently retained by the CEM. Nylon GOM percent breakthrough was often higher than for nylon RM, indicating the compounds collected on the nylon membranes after the PTFE was less well retained.

At UT, breakthrough was not significantly different between the CEM and nylon membrane RM and GOM concentrations. Breakthrough was higher from early October through November, when there were -O, -N, -S, and organic compounds present. Comparable to other sites and previous studies,^{3,7} less breakthrough was observed when halogenated compounds were dominant.

Nylon GOM concentrations were greater than the nylon RM concentrations for four of the six samples at MD. For these sampling periods, the chemistry was dominated by -N, -S, and organic RM compounds, indicating that the nylon membrane does not have good collection efficiency for these compounds. These results are further evidence to support the need for development of an alternate surface for understanding RM chemistry.

Replication for this Dataset. Investigation of replication is useful for understanding the ability of membranes to consistently capture RM compounds. As documented in a previous study,⁶ the CV for RM concentrations on the CEM and nylon membranes was good ($8.2 \pm 4.7\%$ [$n = 126$] and $6.3 \pm 5.0\%$ [$n = 103$], respectively) with the RMAS. Overall, for this study, the CEM CV for HI was lowest (6%), while for NV, UT, and MD, it was 13, 10, and 18%, respectively. For NV, where each combination of membranes occurred in triplicate, the CEM GOM + PBM, CEM GOM, and nylon RM CVs were 25, 30, and 9%, respectively. For nylon GOM + PBM, the variability was 11, 25, 6, and 75% for HI, NV, UT, and MD, respectively; for nylon GOM, the values were 10, 28, 28, and 38%, respectively. For NV, where each sampling scenario occurred in triplicate, the CEM GOM + PBM, CEM GOM, and nylon RM CVs were 25, 30, and 9%, respectively. The lowest CVs were observed for HI that has simple chemistry

and little PBM, and higher CVs were associated with sampling locations with more complex chemistry and/or a limited number of samples.

Implications. This study demonstrated the use of the three-membrane system allows for the quantification of PBM and GOM concentrations and identification of RM and GOM chemistry, something that had not been previously possible. PBM concentrations on the PTFE upstream of CEM and nylon membranes were the same, except in Nevada where the chemistry was much more complex. Based on the comparison of the CEM RM with the nylon membrane, the latter consistently lost $-S$, $-N$, and organic compounds, regardless of the presence of the PTFE. Good mass balances ($\pm 10\%$) between the CEM RM and CEM GOM + PBM measurements demonstrated that there could be some reactions associated with the CEM, and both RM and GOM are retained on the CEM.

Despite long sampling durations (1–2 weeks), this work demonstrated that PBM and GOM concentrations and chemistry vary across space and time. HYSPLIT analyses support that the chemistry of Hg compounds corresponded with air masses associated with each location. PBM concentrations, in general, were highest at NV, followed by MD > UT > HI; the high PBM concentrations at NV correspond with its proximity to a major highway. The results of these analyses are important for modelers trying to understand Hg deposition and provides information that will be useful for expanding the chemical reactions in the models.

HYSPLIT analyses and comparison with compounds on membranes at the different locations indicate that to understand RM chemistry we need to look beyond local oxidants and understand the total air mass chemistry interacting with a site. As would be expected, RM chemistry over the ocean was much less complex than over the continent; and RM concentrations were much higher over the ocean. As we transition from west to east across the continental US, depending on the speed of the air mass, Eurasia, Eastern Asia, and Pacific oceanic air can impact the entire continent.

This work demonstrated that the nylon membrane is not ideal for collecting and retaining RM and GOM compounds, and thus an alternate surface is needed for thermal desorption. Gustin et al.¹⁰ demonstrated that in charcoal-scrubbed air a linear relationship existed between uptake by nylon membranes and KCl denuders, with retention being similar across all compounds. Nylon membrane concentrations were 1.4–1.9 times higher than the denuder indicating consistent, but higher uptake. In contrast, there was significant variability associated with the CEM concentrations being higher than that measured by the denuder by 1.6–12.6 times. This indicates that in charcoal-scrubbed air, the nylon membranes retained a consistent amount of each compound, while in ambient air the retention of $-N$, $-S$, and organic-based compounds was less. PTFE membranes collected similar concentrations of PBM whether in front of the nylon or CEM. PBM measurements indicated that $-Br/Cl$, $-N$, $-S$, $-O$, and organic forms were present. The method developed in this study is a step forward for better differentiating between PBM and GOM concentrations and chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c07876>.

Source boxes for HYSPLIT analyses (Table SI 1); mean concentration on the membranes for each deployment (Table SI 2); percentage of RM and GOM compounds (Table SI 3); trajectory residence times in source boxes (Table SI 4); percent breakthrough for the in-series CEM and nylon membranes (Table SI 5); schematic of the RMAS membrane deployment method (Figure SI 1); time series of CEM and nylon membrane data for each sampling location (Figure SI 2); criteria air pollutant data from Washoe County Air Quality Division (Figure SI 3); and HYSPLIT model results for each deployment period for each sampling location at <https://scholarworks.unr.edu/handle/11714/7532> (PDF)

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Notes

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