Use of membranes and detailed HYSPLIT analyses to understand atmospheric particulate, gaseous oxidized, and reactive mercury chemistry

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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 polytetrafluoroethylene (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), GOM, and PBM). Despite the coarse sampling resolution (1-to-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. Comparing 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.

Keywords: cation exchange membrane, nylon, criteria air pollutants, PTFE, thermal desorption, UNR-RMAS

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, HI, Reno, NV, Piney Creek Reservoir, MD, and Horsepool, UT, USA, corresponded well with projected source areas, meteorology, criteria air pollutants, and other ions collected on the membranes[7](for locations see graphical abstract).

Gustin et al. (2019)[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.(2019)[3] study was to compare four methods for measuring RM and

61 determine the potential for the three-membrane system applied here to provide a better
62 understanding of whether RM was gaseous or particle-bound. Detailed analyses of RM
63 chemistry and sources was not investigated in the 2019 study. For the present study, data were
64 collected in a transect across the United States with sampling sites on Hawai'i (HI) and in
65 Nevada (NV), Utah (UT), and Maryland (MD). Our main working hypothesis was that the three-
66 membrane system would provide a method of identification of GOM and PBM concentrations
67 and chemistry , and that the information developed would be useful for better understanding
68 atmospheric Hg chemistry. The second working hypothesis was since RM compounds present
69 are influenced by the oxidants in the air[7], detailed HYSPLIT analyses associated with each
70 location would allow us to discern sources of oxidants forming RM compounds. The efficiency
71 of the membranes for collection of RM/GOM/PBM was also investigated to determine the
72 robustness and limitations of this method. This was addressed through comparison of
73 concentrations from membranes with and without upstream polytetrafluoroethylene membranes
74 (PTFE), and concentrations and chemistry associated with each fraction (GOM and PBM).

75 **Methods**

76 Sampling locations

77 Field sites for this study were the same as those discussed in Luippold et al.[7], at which
78 only RM was measured. Locations included the Mauna Loa Observatory in Hawaii (HI) that is
79 operated by the National Oceanic and Atmospheric Administration (NOAA) (19.5392, -
80 155.5792; 3397 masl; 1 Aug 2019 to 2 Jan 2020, n = 10 2-week periods). The location in Reno,
81 Nevada (NV) was at the College of Agriculture, Biotechnology & Natural Resources Nevada
82 Agricultural Experiment Station Valley Road Greenhouse Complex (39.5375, -119.8047; 1371
83 masl; 1 Oct 2019 to 28 Jan 2020, n = 11 1-week periods and n = 4 2-week periods). The

Horsepool Monitoring Station, Utah (UT) (40.1434, -109.4689; 1567 m; 1 Aug 2019 to 6 Jan 2020, n = 11 2-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 Aug 2019 to 21 Nov 2019, n = 6 2-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, San Francisco and Sacramento, and the marine boundary layer[7-9]. UT is located in a remote area with oil and gas production occurring in the basin, 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.(2020)[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. Lastly, 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 6 filter packs. Sampling air velocity through each filter pack is regulated at 1 Lpm, using

106 critical flow orifices (Teledyne Technologies) and measured at the beginning and end of each
107 deployment. Two pumps (KNF P/N UN838KNI, these pumps were consistently used in this
108 project, but failed often and are not recommended for future use) were used so that if one pump
109 went offline, data were still being collected; the pumps were housed in a custom-designed pump
110 box. For more details, see Luippold et al. (2020)[6]. The RMAS typically houses triplicate two-in-
111 series CEM (Pall, 0.8 μm pore size) and nylon membranes (Sartorius, 0.2 μm pore size) in 6 total
112 dual-stage filter holders (Savillex). For this study, at the NV site two RMAS were used: one
113 following the traditional configuration, with 6 total dual-stage filter holders holding two-in-series
114 CEM (n = 3) and nylon membranes (n = 3). The second RMAS housed triple-stage filter holders
115 with a PTFE membrane (Sartorius, 0.2 μm pore size) upstream of the two-in-series CEM and
116 nylon membranes. This allowed for triplicate samples of all membrane measurements.

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

123 For this study, the two-in-series upstream and downstream CEM and nylon Hg
124 concentrations were added together and the blanks for that sampling time subtracted. Herein, the
125 terms “CEM RM” and “nylon RM” indicate data collected on these membranes with no
126 upstream PTFE; “CEM GOM” and “nylon GOM” are Hg concentrations on these membranes
127 with an upstream PTFE, while the PTFE membrane Hg data are considered PBM. CEM and
128 nylon GOM+PBM indicates the total Hg concentration for the PTFE plus the upstream and

129 downstream CEM and nylon membranes, respectively. Use of a single measurement for CEM
130 and nylon membranes was justified given the good replication observed in other studies using
131 this system[6, 7]. At the end of each deployment, membranes were stored in 50 mL polypropylene
132 centrifuge tubes (Falcon®, Corning Inc)[6] and shipped to UNR, frozen, and analyzed within two
133 weeks of receipt.

134 Blank membranes (n = 3) of each membrane type were collected at the start of each
135 deployment and kept in individual storage vessels at -20 ºC and analyzed at the same time as the
136 corresponding samples. Downstream membranes were used to quantify breakthrough, calculated
137 as follows:

138

140 $$\%\ \text{breakthrough} = \frac{(\text{downstream membrane} - \text{blank})}{[(\text{downstream membrane} - \text{blank}) + (\text{upstream membrane} - \text{blank})]} \times 100$$

139 Equation 1

141 Analyses of membranes

142 Total Hg concentrations of CEM, the downstream nylon membranes, and PTFE were
143 determined following EPA Method 1631 that consists of BrCl oxidation, SnCl reduction, and
144 analyses using cold vapor atomic fluorescence spectrometry. All samples were above the method
145 detection limit (40 pg Hg).

146 Upstream nylon membranes were thermally desorbed to determine the RM compounds
147 collected on the membranes. Details of the thermal desorption system can be found in Luippold
148 et al.[6] Briefly, a nylon membrane was placed inside a sealed Hg-free, temperature-controlled
149 oven and gradually heated from 50 to 200 ºC at a rate of 2 ºC min^{-1}. Volatilized RM compounds
150 are pulled through a pyrolyzer, to reduce all Hg compounds to elemental Hg, into a Tekran®
151 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 $HgBr_2$, $HgCl_2$, $HgN_2O_6•H_2O$, $HgSO_4$, and HgO, and elemental Hg, as well as methylmercury chloride directly added to membranes.[10-12]

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.(2020)[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 calculated using the NOAA Air Resources Laboratory GDAS 1º data archive and Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model[13,14]. Trajectories were analyzed using a gridded frequency distribution method[15], generating 216 trajectories per day or 51,840 hourly points. There is only one day (Jan 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 SI 1) used in this study included Eurasia, East Asia, the North Pacific Ocean, Canada, and continental United States. 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 Nevada[16] and over the marine boundary layer of the Pacific Ocean[16]. 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?nvunrc (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 Hg compounds due to its use in Hg samplers. If CEM and nylon membranes were collecting PBM, then they should have similar total Hg concentrations as the corresponding membrane type combined with the PTFE. Additionally, the

198 CEM and nylon GOM should be lower than the CEM and nylon alone if PBM is present. Nylon
199 and CEM RM and GOM followed the same trends for all locations (Figure S2).
200 At HI, CEM RM concentrations were 51 ± 10 % greater than the nylon membranes
201 (Table 1), based on the slope of the regression line throughout this sampling campaign. Based on
202 data presented in Gustin et al.(Year?)[12] comparing membrane data with those collected with the
203 Tekran system KCl denuder in clean air , CEM and nylon membranes collected 2.4 and 1.6 times
204 more $HgCl_2$ compounds, respectively. For $HgBr_2$ compounds, nylon and CEM concentrations
205 were 1.7 and 1.6 times that of the denuder, respectively. Based on these results, the 50%
206 disparity observed in this study can be best explained by the RM compounds being primarily
207 $HgCl_2$. Both nylon and CEM RM concentrations were highest in August and October then
208 decreased to ~35 and 150 pg m^{-3} through Novem m mber and December (Figure 1; Table S2).
209 This trend is similar to that reported in Luippold et al.(Year?)[7]. Nylon GOM concentrations were
210 not significantly different from the nylon GOM+PBM concentrations and CEM GOM+PBM
211 concentrations were not significantly different from CEM GOM, indicating that little PBM was
212 present at this sampling location during the sampling campaign. PBM concentrations between
213 the two membranes were not significantly different (p = 0.25, single factor ANOVA) and the
214 percent PBM of total RM measured on the PTFE in front of the CEM and nylon membrane was
215 3 ± 3% and 2 ± 2%, respectively.
216 In NV, nylon RM concentrations were 16% lower than the CEM RM, if the first three
217 deployment periods in October 2019 were removed from the dataset (Table 1, based on the
218 regression slope; Figure 1). In Figure 1, the NV-1 plot contains all of the data for the sampling
219 campaign, and the NV-2 plot only displays the data from October 28, 2019 onward to provide a
220 closer look at the data with the initial higher concentration samples removed. When using all the

data (NV-1), the nylon:CEM RM ratio was 1.95. Membrane Hg concentrations all followed similar trends, and the CEM GOM+PBM was, in general, similar to the CEM RM, while the CEM GOM data were 36% lower than the CEM RM (Figure S2; Table 1). The nylon GOM+PBM concentrations were 23% less than the CEM GOM+PBM concentrations, while the nylon GOM were 60% lower than the CEM GOM. PBM concentrations associated with CEM and nylon membranes were not significantly different, indicating that aerosol was being collected on the PTFE membranes. The difference between the CEM and nylon membranes (for NV 2 data) GOM and GOM+PBM were 60 versus 23 pg m^{-3}, respectively. The percent of PBM relative to the nylon and CEM GOM+PBM were significantly different (p = 0.04, one way ANOVA), and 57 ± 30 and 37 ± 19 % of total Hg concentrations measured on the membranes, 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.(Year?)[7] were similar to those observed in this study, with ~50 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 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 essentially the same; however this was not true for the nylon membrane losing GOM.

In MD, the nylon RM concentrations were 40% lower than CEM RM. CEM RM and CEM GOM+PBM concentrations were, similar to NV, the same, and CEM GOM concentrations

were 24% lower than CEM RM. Nylon GOM+PBM concentrations were 42% higher than the nylon RM and the nylon GOM was 13% higher than the nylon RM indicating 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 ± 34% for nylon and 48 ± 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.(Year?)[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 mercury 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 aerosol-based RM, 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[17], and retain generated RM compounds[12].

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[12], 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 previous work, Luippold et al.(Year?)[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 S3). 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 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 S3), indicating agreement between RM compounds and locally measured air pollutants. However, the same was not true for –O and –

290 Br/Cl compounds that are thought to be derived from long-range transport. Together, this
291 indicates global, regional and local air chemistry are producing RM observed in northern NV.
292 Using back trajectories (Table SI 4, https://scholarworks.unr.edu//handle/11714/7532), high –O
293 concentrations at both NV and UT were associated with times when long-range transport was
294 prevalent. In MD, halogenated compounds were present when air passed over the Pacific Ocean
295 to MD. Air during this time period was derived from the marine boundary layer and free
296 troposphere (Table SI 4, https://scholarworks.unr.edu//handle/11714/7532).

297 At HI, RM chemistry was dominated by halogenated compounds, with a small amount of
298 –O, –S and –N compounds (Figure 1). In general, nylon GOM concentrations were higher than
299 the nylon RM concentrations, indicating loss on the nylon membrane without the upstream PTFE
300 (Table SI 2).

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

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

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

317 HYSPLIT results

318 HYSPLIT analyses were performed to better understand the sources of air interacting
319 with each site and how, in detail, this was reflected in the RM chemistry. At HI, the air was
320 primarily sourced from the marine boundary and the free troposphere, where halogenated
321 compounds are dominant (Tables SI 3 and 4, https://scholarworks.unr.edu//handle/11714/7532;).
322 However, when air intersected with the continental US or Asia source boxes, some minor –O, –
323 N, –S, and organic compounds were present. For example, during the September 19th
324 deployment, 8% of the air sampled at the site was sourced from the continental US source box,
325 and –N was present as RM; however, –N was not detected as GOM, indicating –N compounds
326 were associated with the particulate fraction.

327 In NV, the first 4 sampling periods over the month of October had significant amounts of
328 –O, –N, and –S RM and GOM compounds (Table SI 4, Figure 1). During this time, trajectories
329 spent the majority of time over Eurasia, Asia, Canada, and the continental US (Table SI 4). For
330 the membranes collected November 19th, sampled air passed high over Eurasia and East Asia,
331 and then over the Pacific Ocean where 32% of the air mass coming into NV was < 2 km and
332 68% > 2 km. This air then subsided as it came into the United States. During this time, –O
333 compounds were present, as were halogens, –N, and – S compounds. The following week
334 (November 26th), the air mass intersecting NV spent much of its time at > 2 km above Eurasia,

335 Asia, and the Pacific Ocean, and more time at < 2 km when entering the continental US source
336 box; halogenated compounds were less abundant compared to the previous week. For the rest of
337 the sampling campaign at NV, the primary compounds were associated with anthropogenic
338 pollutants, and 10 to 32% of the air was associated with the Eurasian and Asian source boxes.

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

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

350 Figure 2 contains trajectories for similar time periods for each location and a summary of
351 the compounds on the membranes. For HI, the air resided over the Pacific Ocean and RM
352 compounds were halogenated GOM. The air impacting NV was not associated with the air
353 impacting HI, and most of the air passed over the North Pacific Ocean (in both the boundary
354 layer and above) and below the boundary layer for the United States. Compounds reflected these
355 sources, with –Br/Cl compounds being PBM, –O, –S, and organic compounds being GOM and
356 PBM, and –N/S being GOM. At UT, the sampled air had more halogenated compounds and
357 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 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 Supplemental Information Files (Tables SI 3 and 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 for these two membrane configurations were similar from October until November 11th, then breakthrough increased significantly, ranging for 6 to 35% for CEM RM and 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

381 measurement, indicating some –O compounds were aerosol and others were a gaseous form
382 (Figure 1). This suggests that –N and –S are not as efficiently retained by the CEM. Nylon GOM
383 percent breakthrough was often higher than for nylon RM, indicating the compounds collected
384 on the nylon membranes after the PTFE were less well retained.

385 At UT, breakthrough was not significantly different between the CEM and nylon
386 membrane RM and GOM concentrations. Breakthrough was higher from early October through
387 November, when there were –O, –N, –S, and organic compounds present. Comparable to other
388 sites and previous studies[3,7], less breakthrough was observed when halogenated compounds were
389 dominant.

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

395 Replication for this dataset

396 Investigation of replication is useful for understanding the ability of membranes to
397 consistently capture RM compounds. As documented in a previous study[6], the CV for RM
398 concentrations on the CEM and nylon membranes was good (8.2 ± 4.7% [n = 126] and 6.3 ±
399 5.0% [n = 103], respectively) with the RMAS. Overall, for this study the CEM CV for HI was
400 lowest (6%), while for NV, UT, and MD was 13, 10, and 18% respectively. For NV, where each
401 combination of membranes occurred in triplicate, the CEM GOM+PBM, CEM GOM, and nylon
402 RM CVs were 25, 30, and 9%, respectively. For nylon GOM+PBM, the variability was 11, 25,
403 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 combination of membranes occurred in triplicate, the CEM GOM+PBM, CEM GOM, and nylon RM CVs were 25, 30, and 9%, respectively For NV, where each sampling scenario occurred in triplicate, the CEM GOM+PBM, CEM GOM, and nylon RM, the location with the and 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

~~Here we~~ 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 and CEM GOM+PBM, the nylon membrane consistently lost –S, –N, and organic compounds, regardless of the presence of the PTFE. Good mass balances between the CEM RM and CEM GOM+PBM measurements demonstrated reactions were not associated with the CEM and both RM and GOM are retained on the CEM.

Despite long sampling durations (1 to 2 weeks), this work also demonstrated that PBM and GOM concentrations and chemistry vary across space and time. HYSPLIT analyses support that the chemistry of Hg compounds correspond 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 Hg concentrations were much higher. As we transition from west to east across the continental United States, depending on the speed of the air mass, Eurasia, Eastern Asia, and 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. (Year?)[12] 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 to 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 to 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 –N, -S, –O, and organic forms were present. Higher PBM concentrations were found at the NV location, that is adjacent to a highway and downwind of San Francisco and Sacramento[8]. The method developed in this study is a step forward for better differentiating between PBM and GOM concentrations and chemistry.

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Supplemental information consists of a document containing 5 tables and 2 figures, as well as HYSPLIT model results for each deployment period for each sampling location at the following URL: https://scholarworks.unr.edu//handle/11714/7532.

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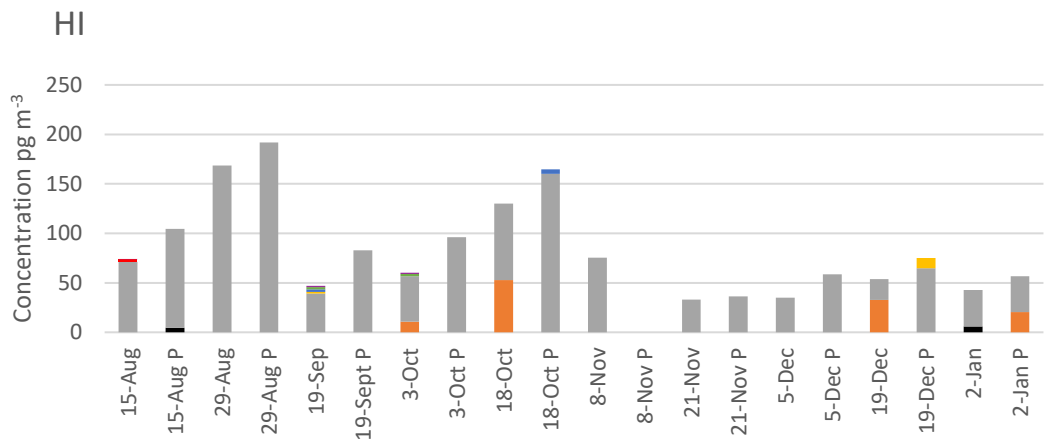
516

517

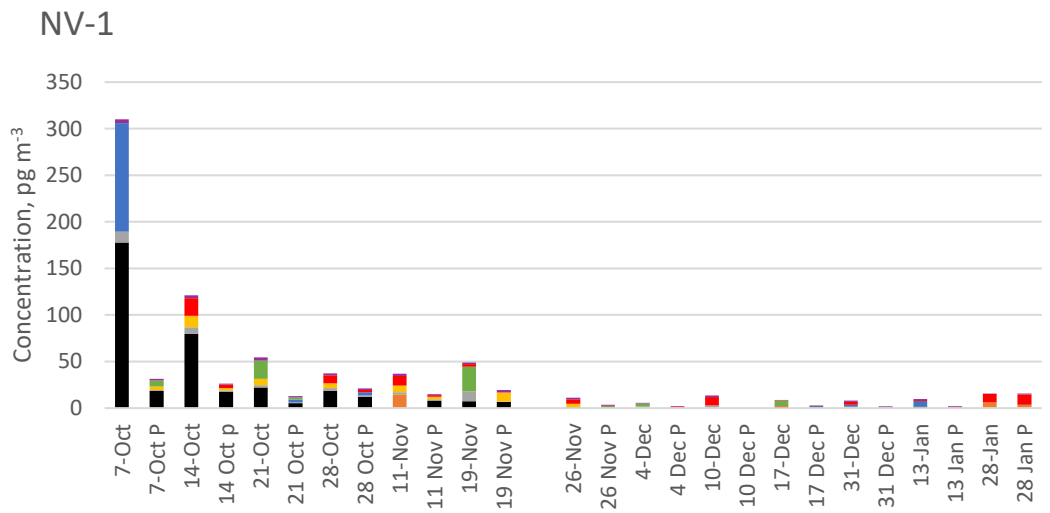
Table 1. Top panel is mean concentration on membranes for each field location for the entire campaign, in pg m^{-3}. Bottom panel is slope and r^2, in parenthesis, for the regression between various membrane configurations. CEM and nylon membrane measurements were made simultaneously.

Location	HI	HI-CV	NV	NV-CV	UT	UT-CV	MD	MD-CV
Number of samples	10		15		11		6	
			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 GOM+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	0.38
			Slope (r2) 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			0.84 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 (0.58)		0.53 (0.84)		0.53 (0.84)	

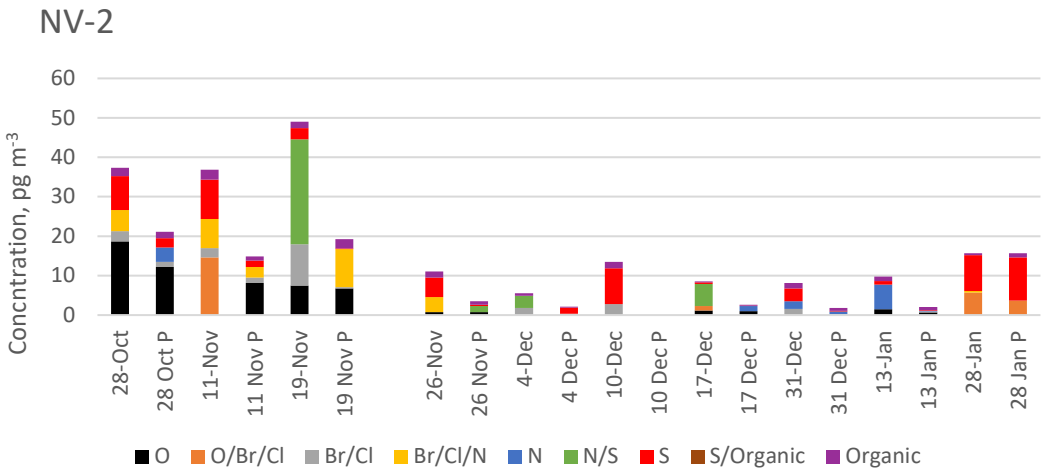
Note mean and std are mean of 2 to 3 membranes and mean of std associated replicates
All regressions are significant at $p<0.05$.
CV indicates the mean coefficient of variation for all samples.


HI
Concentration pg m-3
250
200
150
100
50
0
15-Aug
15-Aug P
29-Aug
29-Aug P
19-Sep
19-Sept P
3-Oct
3-Oct P
18-Oct
18-Oct P
8-Nov
8-Nov P
21-Nov
21-Nov P
5-Dec
5-Dec P
19-Dec
19-Dec P
2-Jan
2-Jan P

524


NV-1
Concentration, pg m-3
350
300
250
200
150
100
50
0
7-Oct
7-Oct P
14-Oct
14 Oct p
21-Oct
21 Oct P
28-Oct
28 Oct P
11-Nov
11 Nov P
19-Nov
19 Nov P
26-Nov
26 Nov P
4-Dec
4 Dec P
10-Dec
10 Dec P
17-Dec
17 Dec P
31-Dec
31 Dec P
13-Jan
13 Jan P
28-Jan
28 Jan P

525


NV-2
Concntration, pg m-3
60
50
40
30
20
10
0
28-Oct
28 Oct P
11-Nov
11 Nov P
19-Nov
19 Nov P
26-Nov
26 Nov P
4-Dec
4 Dec P
10-Dec
10 Dec P
17-Dec
17 Dec P
31-Dec
31 Dec P
13-Jan
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N
N/S
S
S/Organic
Organic

526

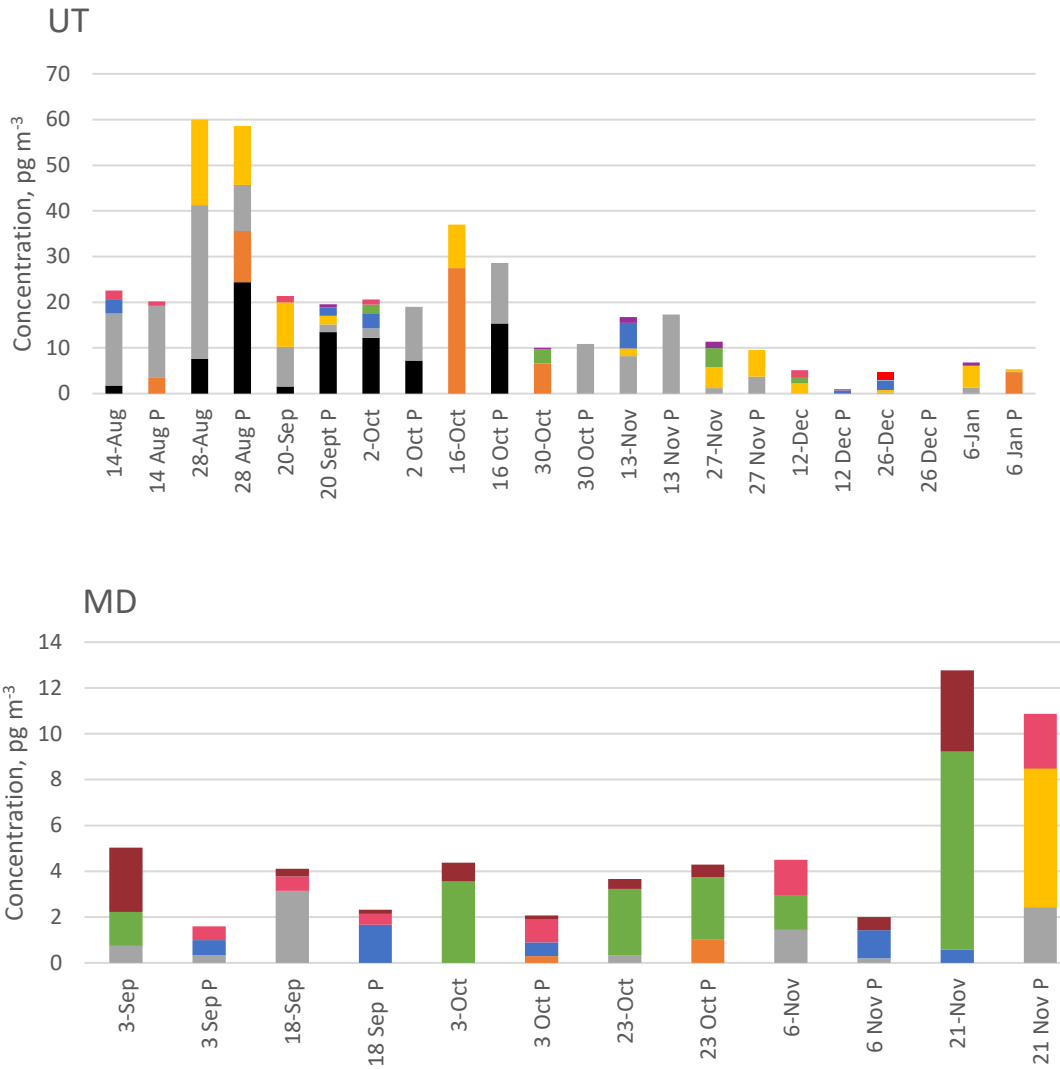
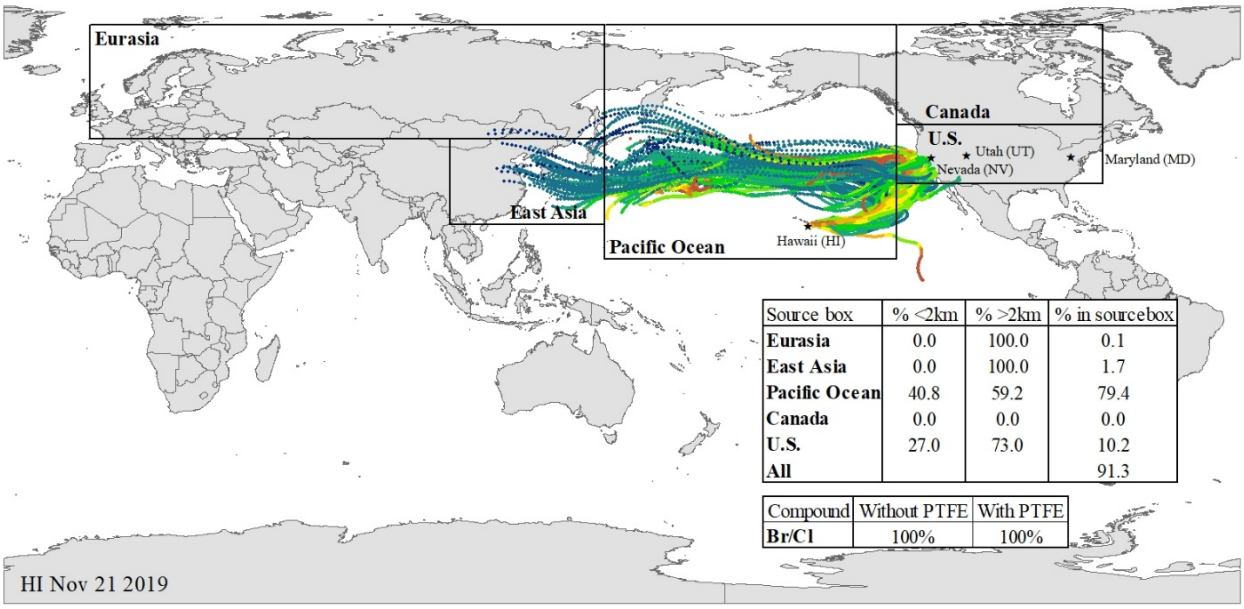


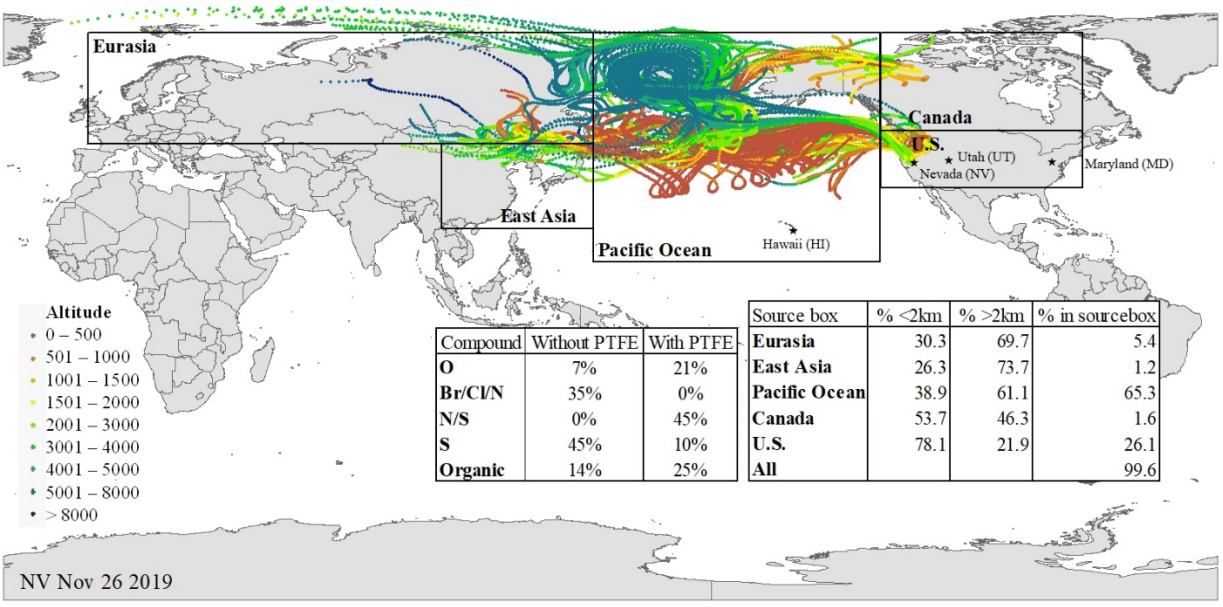
Figure 1. Concentrations of RM and GOM compounds on nylon membranes for each sampling deployment for each sampling location. Dates represent the end date of the deployment period. NV-2 shows the same data for NV-1, leaving out the 3 high initial sampling durations to provide a closer look at the remaining data.



Source box	% <2km	% >2km	% in sourcebox
Eurasia	0.0	100.0	0.1
East Asia	0.0	100.0	1.7
Pacific Ocean	40.8	59.2	79.4
Canada	0.0	0.0	0.0
U.S.	27.0	73.0	10.2
All			91.3

Compound	Without PTFE	With PTFE
Br/Cl	100%	100%

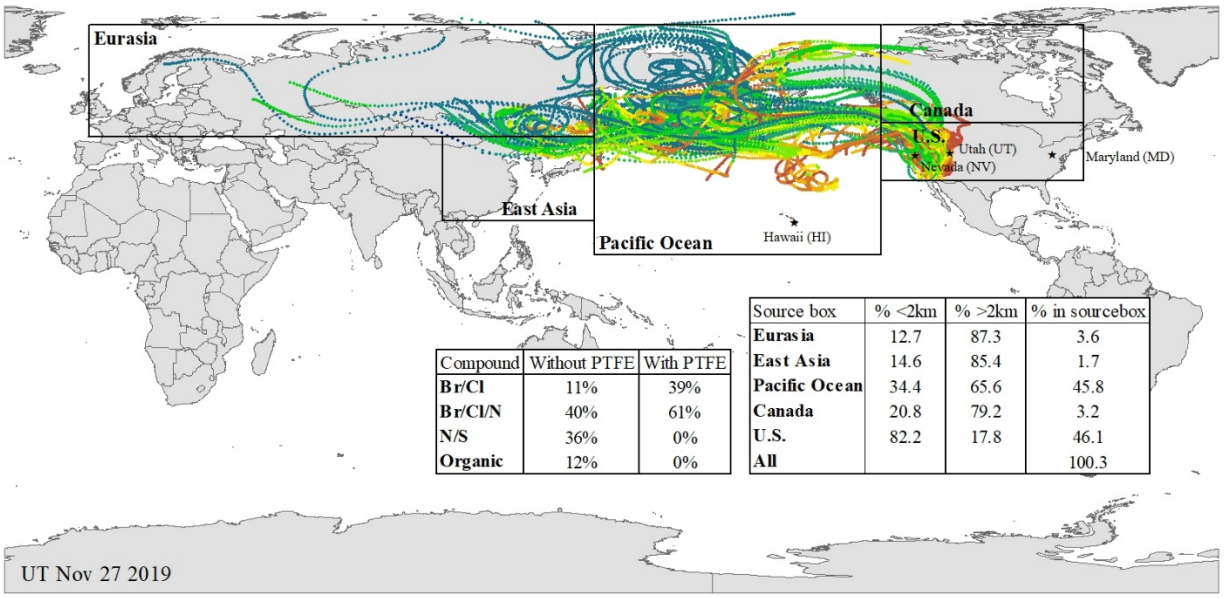
533



Compound	Without PTFE	With PTFE
O	7%	21%
Br/Cl/N	35%	0%
N/S	0%	45%
S	45%	10%
Organic	14%	25%

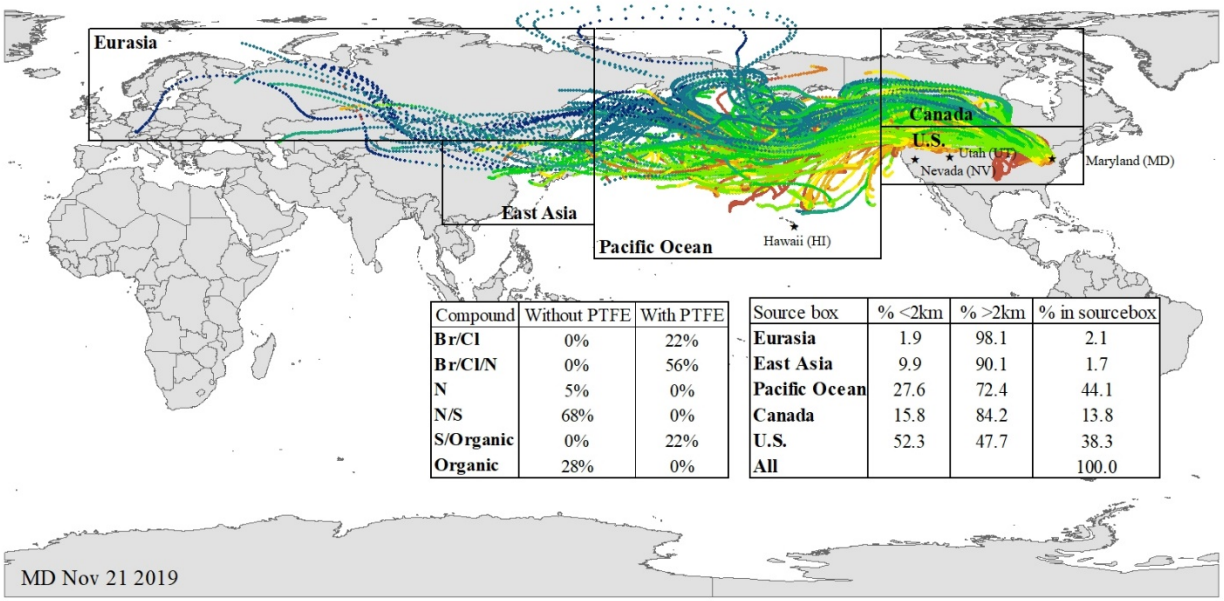
Source box	% <2km	% >2km	% in sourcebox
Eurasia	30.3	69.7	5.4
East Asia	26.3	73.7	1.2
Pacific Ocean	38.9	61.1	65.3
Canada	53.7	46.3	1.6
U.S.	78.1	21.9	26.1
All			99.6

534



Compound	Without PTFE	With PTFE
Br/Cl	11%	39%
Br/Cl/N	40%	61%
N/S	36%	0%
Organic	12%	0%

Source box	% <2km	% >2km	% in sourcebox
Eurasia	12.7	87.3	3.6
East Asia	14.6	85.4	1.7
Pacific Ocean	34.4	65.6	45.8
Canada	20.8	79.2	3.2
U.S.	82.2	17.8	46.1
All			100.3



Compound	Without PTFE	With PTFE
Br/Cl	0%	22%
Br/Cl/N	0%	56%
N	5%	0%
N/S	68%	0%
S/Organic	0%	22%
Organic	28%	0%

Source box	% <2km	% >2km	% in sourcebox
Eurasia	1.9	98.1	2.1
East Asia	9.9	90.1	1.7
Pacific Ocean	27.6	72.4	44.1
Canada	15.8	84.2	13.8
U.S.	52.3	47.7	38.3
All			100.0

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 occured outside of the source boxes.