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Evaluation of sorption surface materials for reactive mercury compounds

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ABSTRACT

Sorption surfaces are commonly used to collect atmospheric mercury compounds, with a range of materials used by the mercury research community that have different levels of performance. Here, five polymer-based membranes were loaded with ambient reactive mercury and compared to 2 widely used sorption surface materials: nylon and cation exchange membranes. Only 1 tested material, polyethersulfone, performed similarly to the cation exchange membrane; the remaining tested materials sorbed significantly less mercury and many had significantly higher blank mercury amounts than the cation exchange membrane. Nylon was the only material that is compatible with thermal desorption analysis, as the remaining materials physically degrade or negatively affected the analyzer; however, it is not amenable for quantitative analyses under all ambient conditions. Additional testing of the nylon and cation exchange membrane demonstrated that ambient reactive mercury compounds were more stable on both materials than high concentrations of single-source gaseous oxidized mercury compounds. Single-source gaseous oxidized mercury compounds were significantly lost and/or transformed within less than 80 days of storage, whereas reactive mercury compounds were stable on nylon and cation exchange membranes after 190 days of storage. However, minimizing sampling and storage duration, along with exposure of sampled membranes to ambient air, to reduce biasing results is prudent.

1. Introduction

Mercury is a ubiquitous heavy metal in the environment that is readily transported via the atmosphere. Residence time in the atmosphere depends on the chemical form of mercury, with elemental mercury persisting for days to years, resulting in long-range transport. Oxidized mercury compounds, however, deposit quickly to surfaces (Gustin et al., 2013; Schroeder and Munthe, 1998). Due to its higher deposition rate to environments and conversion to methylmercury and toxicity to environments, it is critical to accurately measure atmospheric oxidized mercury to better understand concentrations and composition.

Sorption surfaces have been widely used as the preferred method for collection of atmospheric oxidized mercury, ranging from membrane materials to coated denuders to traps with sorbent materials (Luippold et al., 2020a; Gustin et al., 2019; Castro et al., 2012; Lyman et al., 2010; Caldwell et al., 2006; Feng et al., 2000). Effective sorption surfaces must produce reliable, repeatable measurements, have high sorption efficiencies with low breakthrough rates, be selective for a variety of oxidized mercury compounds, and have low background amounts of mercury, as well as be commercially available and economical. Studies have demonstrated that the current leading method for measuring atmospheric oxidized mercury, a KCl-coated denuder used in the 1130 Tekran® speciation unit, does not meet some of these requirements (Marusczak et al., 2017; Ariya et al., 2015; Gustin et al. 2013, Gustin et al., 2015; McClure et al., 2014; Talbot et al., 2011).

For this study, potential sorption surface materials were identified and tested to determine their viability for use in atmospheric reactive mercury (RM = gaseous oxidized mercury + particulate-bound mercury) research. To be deemed a feasible material for continued investigation, the tested material must have similar or better sorption efficiencies relative to standard materials used in past and current studies (i.e., nylon and cation exchange membranes) and not cause any analytical biases or problems. Ideally, feasible materials would also be compatible with thermal desorption methods and retain sorbed mercury without any loss, gain, or transformations through time. The research questions addressed in this study were: 1) How do the mercury sorption behaviors of a variety of commonly used, commercially available, potential feasible, and novel sorption surface materials compare to widely used materials? 2) Can the sorption surface materials be used with thermal desorption methods? 3) Do the materials sorb mercury linearly, or do they have a low capacity for mercury compounds that is likely to

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be reached during typical atmospheric sampling? 4) Can the sampling duration be reduced by increasing the material surface area? 5) Is mercury retained on the materials when loaded, or does the sorbed mercury volatilize from the material during storage? This question has been briefly addressed in other papers but with limited data (Pierce and Gustin, 2017; Lyman et al., 2010). 6) Do sorbed mercury compounds undergo transformations on the sorption surface material?

2. Materials and methods

2.1. Sorption surface material descriptions

The two reference materials used in this study were nylon membranes and cation exchange membranes (CEM) that have been used extensively in previous atmospheric mercury research (Gustin et al., 2019; Miller et al., 2019; Marusczak et al., 2017; Castro et al., 2012; Huang et al., 2012; Caldwell et al., 2006; Ebinghaus et al., 1999). Additional materials were selected to test whether alternative sorption surfaces sorb mercury compounds from ambient air similarly to the reference materials, and were selected based on their chemical and physical attributes. The polyethersulfone membrane (PES) was selected because it is the same material as the CEM, but without any additional treatment to preferentially sorb cations like the CEM. This membrane material has been used in previous studies to collect RM (Marusczak et al., 2017; Enrico et al., 2016). The anion exchange membrane (AEM) is the same material as both the CEM and PES, but is treated using a proprietary method to preferentially sorb anions; this membrane was selected to test whether the membrane treatment significantly affects mercury sorption to the polyethersulfone material. Two polycarbonate membranes were selected because some polycarbonates are similar in structure to polyethersulfone, but without the sulfone group; because mercury has a strong affinity for sulfur, comparing the results of the sulfone-bearing polyethersulfone materials (i.e., PES, CEM, AEM) and the sulfone-free polycarbonate determine if mercury is dominantly sorbing to the hydrocarbon structure of the sulfur group. Different brands of the polycarbonate membranes, Nuclepore™ (Nucle) and Isopore™ (Iso), were chosen to test if different brands of the same material perform similarly. A polypropylene membrane (PP) was selected to test whether polypropylene, a common laboratory membrane material, behaved similarly to the reference materials. Additional details for each membrane material used in this study are summarized in Table S1.

In addition to membrane materials, a multi-capillary polydimethylsiloxane (PDMS) denuder was used to test an alternative sorption surface and geometry to membranes. The PDMS denuders used in this study have been used successfully for thermally extracting semi-volatile organics sampled from the atmosphere (Rowe and Perlinger, 2010a,b). The denuders used in this study are described in detail in Rowe and Perlinger (2010a,b).

2.2. Thermal desorption system description and viability testing of materials

Each material described above was tested in a thermal desorption oven to determine if it was a viable material to be used for thermal desorption and mercury speciation analyses. The thermal desorption system used to test the materials has been previously described in detail (Luippold et al., 2020a). Briefly, ambient laboratory air was pulled at a rate of 1 Lpm through a Tekran® zero air cartridge (Tekran Instrument Corporation, Toronto, Canada) to ensure all downstream Hg measurements resulted from thermal release from the sample. The mercury-free air was then pulled through a quartz tube inside of a programmable tube furnace into a 350 ± 10 °C pyrolyzer with a quartz wool plug and finally into a Tekran® 2537 A, where total mercury concentrations were measured in 150 s intervals; see Luippold et al. (2020a) for complete details about system optimization. During a thermal desorption analysis, the tube furnace temperature increased from 50 to 200 °C with a 2 °C min^{-1} step. As the temperature of the furnace and the sample inside the furnace increased, mercury compounds were released from the sorption surface into the gas phase and were subsequently measured downstream (Luippold et al., 2020a; Huang et al., 2013). The pyrolyzer was used to thermally reduce any oxidized gaseous mercury compounds to gaseous elemental mercury (GEM), and the quartz wool acted as a reaction surface to mediate reduction.

Viability of materials for utilization in the thermal desorption system was determined in two stages. First, tests were conducted to determine whether the material could physically withstand the thermal desorption cycle from 50 to 200 °C. Second, tests were conducted to determine whether the material negatively affected the performance of the downstream Tekran® 2537 analyzer. For the first step, a sample of the material was placed inside the tube furnace so that it lay flush against the tube wall and was positioned in the center of the furnace. The furnace was attached to a Tekran® 1100 mercury zero air generator that pumped mercury-free air at a rate of 1 Lpm on the upstream side of the furnace and to an exhaust line that vented the air outside of the laboratory on the downstream side. The material was then evaluated after the completion of one thermal desorption cycle. If the material had significant physical alterations and no longer resembled the original material (e.g., melted, charred), then the material was deemed not viable for thermal desorption analyses. If the material did not appear to have significant physical alterations (e.g., faint discoloration, marginal desiccation), then the material proceeded to the next step. For the second step, a new sample of the material was exposed to a thermal desorption cycle in the complete thermal desorption system, including the downstream Tekran® 2537. The performance of the Tekran® 2537 was evaluated by comparing the gold cartridge response factors from repeat internal calibrations before and after a material test. If the response factors for each cartridge varied more than 5% between repeat measurements, indicating potential passivation of the cartridge, it was deemed that the material had a negative effect on the Tekran® 2537 and was considered not viable for thermal desorption analyses. If the response factors varied less than 5%, the test was repeated with new samples of the material to ensure that repeat analyses did not have a longer-term effect. If the response factors from the internal calibration prior to the first test and calibration after replicate desorption cycles did not vary more than 5%, the material was deemed to be viable for thermal desorption analyses.

2.3. Loading sorption surfaces in UNR-RMAS 2.0

The University of Nevada, Reno-Reactive Mercury Active System (UNR-RMAS) 2.0 was designed to actively sample RM in ambient air. Samples were generated by pulling ambient air through 2-stage membrane filter packs at a rate of 1 Lpm for 1–2 weeks. A full description of the system can be found in Luippold et al. (2020a). Previous and ongoing studies have used the UNR-RMAS and UNR-RMAS 2.0 systems to sample ambient RM at a variety of locations (e.g., Nevada, Utah, Maryland, Hawaii, Australia, Arctic Circle) and have used nylon membranes and CEM for analyses (Luippold et al., 2020b; Gustin et al., 2019; Miller et al., 2018).

The UNR-RMAS 2.0 was used to load the sorption surface materials to compare them to results obtained for the same sampling period and location from nylon membranes and CEM to determine if other materials sorb more ambient RM than the commonly used membrane materials. Membrane materials (PES, AEM, Nucle, Iso, PP) were deployed in a UNR-RMAS 2.0 at the Valley Road Greenhouse Complex at the University of Nevada, Reno. This site is located directly adjacent to a heavily trafficked interstate highway and is impacted by vehicle emissions, in addition to urban sources and long-range transport, and has variable air chemistry through time (Luippold et al., 2020b; Gustin et al., 2016). Membranes were deployed in triplicate 2-stage filter packs for 7 days alongside triplicate filter packs of each nylon membranes and CEM that were deployed in a second UNR-RMAS 2.0. Replicate deployments (n = 3–10) were conducted for each material tested to assess the membrane performance under different atmospheric chemistry conditions through time. Loaded membranes were collected in 50 mL centrifuge tubes and frozen (−20 °C) pending analysis. Total mercury on the loaded membrane sorption surfaces were quantified using a modified EPA Method 1631 (see Luippold et al., 2020a for more details) and analyzed using a Tekran® 2600 IVS.

Additionally, larger (90 mm diameter) CEM were deployed alongside standard 47 mm diameter CEM to assess whether using a larger collection surface area could reduce the sampling duration needed to collect sufficient RM to be accurately quantified. Triplicate single-stage filter packs for each membrane size were deployed for each of 3 separate 7-day sampling periods at the same flow rate (1 Lpm) as the 47 mm CEM. Loaded membranes were collected and analyzed following the same procedure described above.

2.4. Loading sorption surfaces in high-concentration permeation system

A custom-built high concentration permeation system was used in this study to load sorption surfaces with a single-source GOM compound. Single-source GOM vapor was generated from a 3.8 cm permeation tube made from ¼ in O.D. polytetrafluoroethylene (PTFE) tubing, 0.2 mm wall thickness, containing 0.01 ± 0.005 g oxidized mercury compound and sealed with PTFE plugs to produce a permeation length of 2 mm; the permeation tube was placed in an airtight PTFE vessel and held at a constant temperature in a refrigerated bath to ensure a stable permeation rate. Oxidized mercury compounds used in this study included: $HgBr_2$ (Sigma Aldrich, P/N 83,353), $HgCl_2$ (Sigma Aldrich, P/N 203,777), HgO (Sigma Aldrich, P/N 21908532), $Hg(NO_3)_2{\cdot}H_2O$ (Sigma Aldrich, P/N 516,953), and $HgSO_4$ (Sigma Aldrich, P/N 10,029). Additionally, a permeation tube made using the same specifications above containing a small bead of elemental mercury was used to load sorption surfaces with GEM. The permeation system used in this study was connected to a downstream Tekran® 2537 A and was described in detail in Miller et al. (2019) and is illustrated in Fig. 1 (without the PDMS denuder inline). Continuous downstream mercury measurements were made during each permeation in alternating 300 s intervals, switching between Line 0 that contained a 2-stage membrane filter pack with the sorption surface being tested and Line 1 that contained a pyrolyzer. The sorption surface was 30 cm downstream of the permeation tube during permeation.

CEM were loaded with $HgBr_2$ or $HgCl_2$ in the permeation system for various durations, from 1 to 16 h, to determine if the sorption surface materials have a maximum capacity for sorbed mercury compounds. Concentrations of $HgBr_2$ ranged from 0.14 to 2.8 ng Hg, and $HgCl_2$ ranged from 0.39 to 10.5 ng Hg during the loading durations; the $HgCl_2$ concentrations were higher due to a higher permeation rate relative to the $HgBr_2$ permeation rate. Loaded CEM were analyzed for total mercury amounts using the modified EPA Method 1631. High total mercury amounts were intentionally added to the CEM to test the performance of the material at concentrations throughout and above the range typical of ambient air samples.

2.5. Evaluating mercury retention on loaded surface materials

To evaluate whether mercury compounds are retained on sample surfaces over time, we loaded replicate membranes with either ambient RM or high concentrations of a single-source GOM compound. To assess the retention of a single-source GOM compound, replicate CEM (n = 28) were loaded with $HgBr_2$ in the permeation system described above. The effect of storage temperature, storage duration, and traveling to other field sites were investigated. Total Hg on the membranes were quantified on subsets of membranes that were: (1) analyzed 1 day after loading, (2) stored at room temperature inside a sealed opaque cardboard box for 72 days, (3) stored in a −20 °C freezer for 72 days, or (4) shipped to collaborators in Utah, Maryland, and Hawai'i, held at room temperature inside an opaque box, and then shipped back for analysis 72 days later. Replicate blank membranes (n = 18) were collected throughout the duration of the loading experiment and subsets of the blank membranes received the same treatments as the loaded membranes. The total Hg amounts on all membranes were quantified using the modified EPA Method 1631.

Retention of ambient RM was assessed by loading replicate nylon membranes and CEM in the UNR-RMAS 2.0. Replicate CEM (n = 18) or nylon membranes (n = 18) were loaded for 7 days, with 3 replicate deployments per sorption surface material. Loaded sample membranes and replicate (n = 18) blank membranes were immediately stored at −20 °C. Three loaded sample and 3 blank membranes were analyzed the day of collection for total mercury (CEM) or thermal desorption profile (nylon membranes) to determine the initial total mercury amount or ambient RM compounds present in the samples. Repli-

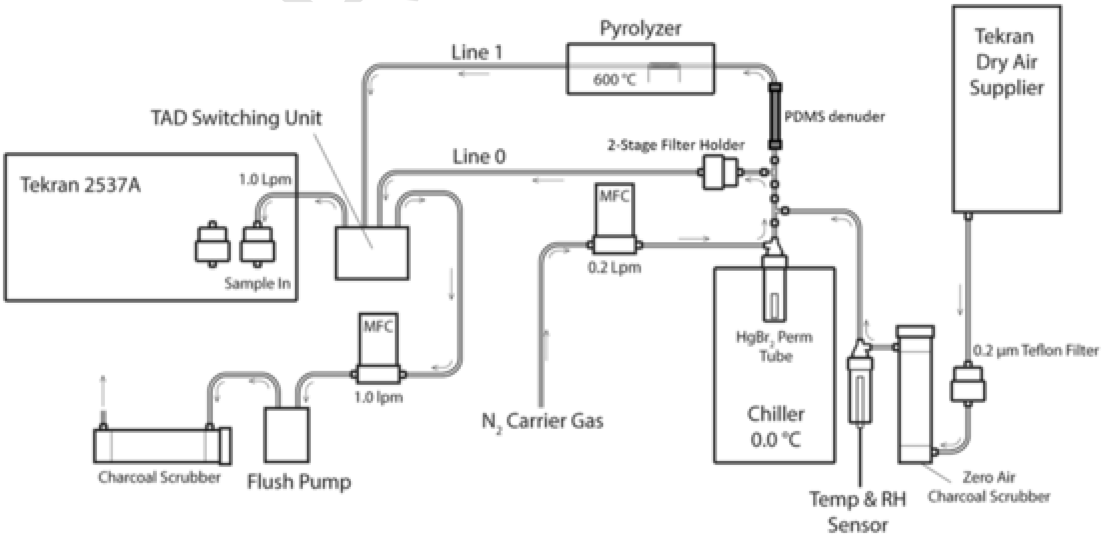

Fig. 1. Schematic of permeation system used to load the sorption surfaces (Line 0) or PDMS denuder (Line 1) with GOM compounds (indicated here by "$HgBr_2$ Perm Tube"). The schematic is adapted from Fig. 1c in Miller et al. (2019).

cate loaded and blanks membranes (n = 3 each) were analyzed after 1, 2, 3, and 6 months of storage.

2.6. Transformations of single-source GOM compounds and ambient RM on sample surfaces

Nylon membranes were loaded with a single-source GOM compound in the permeation system then either exposed to ambient air for 1 or 7 days or stored for up to 6 months to determine if transformations of sorbed mercury compounds occur on sorption surfaces. For the first test, to assess whether sorbed single-source GOM compounds transform during sampling, replicate (n = 7) nylon membranes were loaded in the permeation system described above with the same concentration of one single-source GOM compound. One membrane was immediately analyzed in the thermal desorption system to determine the initial thermal desorption profile, and 2 membranes were stored at −20 °C to be used as controls. The remaining 4 membranes were deployed in single-stage filter packs in the UNR-RMAS 2.0 for 1 (n = 2) or 7 (n = 2) days. Upon collection, the samples, along with 1 control, were analyzed to determine the thermal desorption profiles. For the second test, the thermal desorption profiles from the nylon membranes loaded with ambient RM and stored for 1–6 months, described above, were used to assess whether sorbed ambient RM compounds transform during long-term storage. Any changes to the thermal desorption profile (i.e., changes to profile shape or decrease in amount of Hg) indicate transformation of the RM compounds.

2.7. Evaluation of PDMS denuder

The PDMS denuder was loaded with mercury to test the sorption and thermal desorption efficiencies of the denuder for mercury compounds. The denuder was installed in the permeation system (Fig. 1) using deactivated fused silica-coated stainless steel compression fittings to connect the denuder to the system's PTFE tubing and loaded with 1.07 ng of Hg, as $HgBr_2$. Continuous downstream mercury measurements were made during the permeation, switching between Line 0 that contained a 2-stage CEM filter pack, and Line 1 that contained the denuder with a downstream pyrolyzer. Sorption efficiency was determined as the percent of Hg retained in the denuder, calculated as the total amount of Hg permeated into the denuder minus the amount of Hg that passed through the denuder as measured by the downstream Tekran® 2537, relative to the total amount of Hg permeated into the denuder.

The mercury-loaded denuder was placed directly into the tube furnace in the thermal desorption system. The denuder was installed inline in the system, replacing the tube furnace quartz tube in the desorption system. To avoid direct contact of the metallic denuder with the heating coils in the tube furnace and prevent uneven heating, the denuder was placed on a thin (~5 mm) layer of fiberglass insulation. The denuder was then exposed to a complete thermal desorption cycle and/or a constant temperature to desorb the mercury. In some tests, the tube connecting the Tekran® zero air cartridge to the upstream end of the denuder was heated to 100 °C using a heating tape (Glas-Col, Terre Haute, Indiana, USA) to promote isothermal air conditions inside the denuder.

3. Results & discussion

3.1. Comparing potential vs. standard sorption surface materials

Largely, the potential sorption surface materials did not perform as well as the standard materials (Fig. 2). Potential sorption surface materials were loaded with ambient RM in the UNR-RMAS 2.0 for replicate 7-day deployment periods, alongside two commonly used sorption surface materials: CEM and nylon membranes. Overall, the PES membrane was the only tested material that performed similarly to the CEM, based on total mercury amounts, with no significant difference (α = 0.05) between the two materials for 8 of 10 deployments and no significant difference between the breakthrough between the two materials in any of the 10 deployments (Table S2); breakthrough is the percent of mercury measured on the downstream membrane relative to the total mercury measured on both the up- and downstream membranes, and is used as a proxy for the collection efficiency of a sorption surface material. The remaining materials (i.e., AEM, Nucle, Iso, PP) sorbed significantly less mercury than the CEM for the majority of their deployments (Fig. 2, Table S2), indicating these materials are not as efficient at capturing ambient RM as CEM. Additionally, the total mercury amounts on blank Nucle, Iso, and PP membranes were significantly higher than on blank CEM. Similar to previous studies (Luippold et al., 2020a,b; Gustin et al., 2019; Gustin et al., 2016), the nylon membranes sorbed less ambient RM than CEM during most deployments, ranging from 10 to 100% of the RM sorbed by CEM (Fig. 2); results from Luippold et al. (2020b) indicate that this range

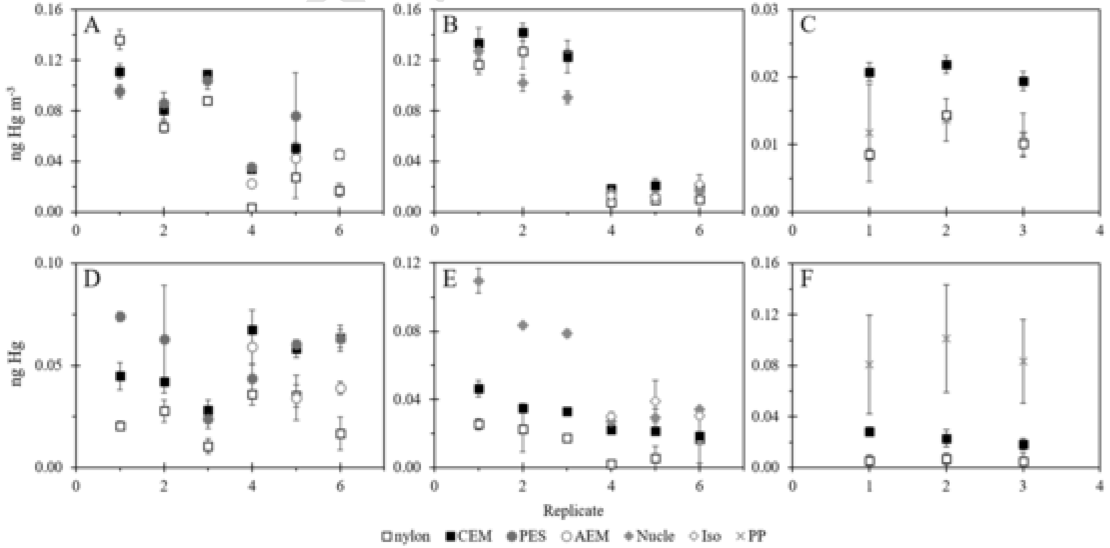

Fig. 2. Hg concentrations (ng Hg m^{-3}) on membrane materials loaded in the UNR-RMAS (A, B, C) and the total Hg amounts (ng Hg) on blank membranes (D, E, F) compared to the commonly used materials, nylon and CEM. Each symbol represents the mean of triplicate membranes and the error bars represent 1σ; some error bars are too small to see. Abbreviations: CEM = cation exchange membrane, PES = polyethersulfone, AEM = anion exchange membrane, Nucle = Nuclepore™, Iso = Isopore™, PP = polypropylene.

of discrepancy is likely due to varying RM chemistry and membrane sorption efficiency for different RM compounds. Together, with high background mercury amounts and low collection efficiency compared to CEM, the Nucle, Iso, and PP membranes are not recommended as sorption surfaces for ambient RM measurements.

The proprietary treatment of the polyethersulfone material did not make a significant impact on ambient RM collection efficiency. The PES, CEM, and AEM materials all start with the same base compound – polyethersulfone. The PES material is the base compound that is untreated, whereas the CEM is PES material that is proprietarily treated to selectively sorb cations and the AEM is PES material that is proprietarily treated to sorb anions. The ambient RM collection on the untreated PES and the treated CEM were not significantly different (Table S2). It is thus likely that ambient RM sorbs dominantly to the polyethersulfone base compound in the CEM material and not to the treatment. However, AEM ambient RM collection was significantly less than CEM and PES, indicating that only the treatment on the AEM material significantly affected ambient RM sorption to the polyethersulfone-based materials (Table S2). Additionally, the lower ambient RM collection on the polycarbonate materials (i.e., Nucle, Iso) compared to the PES and CEM suggests that the ambient RM is likely dominantly sorbing to the sulfone groups in the polyethersulfone base compound. Further studies are needed to verify that ambient RM compounds are associated with the sulfone groups and not another site(s) in the polyethersulfone.

Of the materials tested, only the nylon material was viable for thermal desorption analyses. During the first step of testing, both polycarbonate materials (i.e., Nucle and Iso) and the PP material melted, and thus, were not deemed viable for thermal desorption analyses. The CEM, AEM, and PES materials were faintly tan in color after a desorption cycle as contrasted to their initial white coloration; despite this physical change, the materials were considered for the second step of the thermal desorption testing. After one desorption cycle of a PES sample in the complete thermal desorption system, the gold cartridges in the Tekran® 2537 were passivated, as evidenced by a greater than 80% decrease in response factor of each cartridge after just one desorption cycle, and had to be replaced. Even though the material appeared to be unchanged, heating of the PES material during the desorption cycle likely resulted in the release of volatile compounds that reacted with the gold in the cartridges. Because the gold cartridges are expensive and critical to the analytical operation of the Tekran® 2537, the polyethersulfone-based materials were classified as not viable for thermal desorption analysis.

The multi-capillary PDMS denuder is not a good collection surface for single-source GOM compounds nor viable for thermal desorption analysis. When loaded with $HgBr_2$ in the permeation system the denuder passivated rapidly, with increased breakthrough during the 2-h permeation (Pearson correlation coefficient $r = 0.82$). During the permeation, the denuder had a sorption efficiency of 90% and sorbed 1.07 ng Hg. When thermally desorbed using the standard desorption cycle parameters, only 0.5% of the sorbed GOM compound was released from the denuder. When held at 200 °C for 5 h, only 13.2% of the sorbed GOM compound was released. The denuder performance is limited by low melting point of the PDMS material used to coat the inside of the denuder; increasing the desorption temperature may result in the fluidization of the PMDS material, allowing it to flow in and clog the capillaries. Another limitation is the geometry of the denuder, that is densely packed with capillary tubes. The density of the tubes throughout the denuder prevented isothermal conditions throughout the tube, which may have caused the inefficient thermal desorption of the sorbed GOM compound from the denuder. Lastly, heating of the PDMS material resulted in the passivation of the gold cartridges in the Tekran® 2537, similar to the polyethersulfone-based materials. For these reasons, the PDMS denuder, in its current configuration, is not recommended as a mercury collection surface.

CEM sorbed the highest amount of ambient RM and has the lowest background mercury amount, and the nylon material is the only tested material that is compatible with the thermal desorption system. These are promising characteristics of sorption surface materials for mercury research, though results using these materials may be limited by the inability to cross-compare the results from each material type and low sorption efficiency of the nylon membranes. Having alternative materials that could be used in the thermal desorption system could corroborate the nylon thermal desorption results and make the results more robust. Alternatively, a method that could allow for the determination of oxidized mercury compounds on the CEM could also help support the nylon thermal desorption results. Identification and testing of alternate materials and methods could increase confidence in the results collected from this and previous studies.

3.2. Mercury sorption capacity and sampling resolution

For both $HgBr_2$ and $HgCl_2$ GOM compounds, sorption is linear for both nylon and CEM membranes up to 3 ng of Hg for $HgBr_2$ and 10 ng of Hg for $HgCl_2$ (Fig. 3). In the UNR-RMAS 2.0 systems, the highest amount of mercury measured on CEM during a 2-week deployment was 7.1 ng Hg, and the mercury compounds were dominated by –Br and –Cl (Luippold et al., 2020b). Typically, the mercury amount measured on CEM during 1- and 2-week deployments are less than 3 ng Hg (Luippold et al., 2020b; Gustin et al., 2019). Total mercury amounts on nylon membranes were lower than on CEM for the same GOM compound at the same permeation rate (Fig. 3), consistent with the results discussed above and previous studies, and were increas-

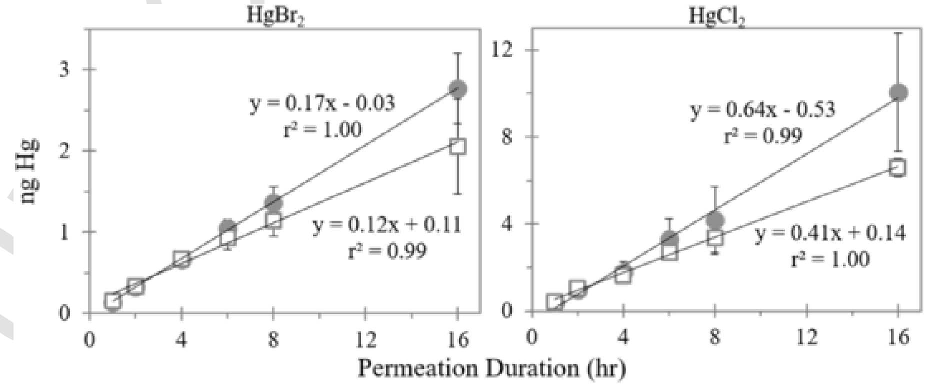

Fig. 3. Total mercury amounts, in ng Hg, on CEM (solid blue circles) and nylon membranes (open green squares) after being permeated with $HgBr_2$ (left) or $HgCl_2$ (right) for 1–16 h. A linear trendline and Pearson correlation coefficient (r) are reported for each model. Error bars represent standard deviation of replicate (n = 4) measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

ingly lower as the total mercury on the material increases. Because the two materials are being exposed to the same compound at the same concentration and the amount on the membrane with longer exposure durations continues to be linear, the lower amount on the nylon membranes is likely due to a lower sorption efficiency of nylon for mercury compounds and not to a lower sorption capacity of the material compared to CEM. Though mercury sorption to sorption surface materials may become less linear at higher loadings as the material reaches its capacity for mercury, for typical applications of these materials the total mercury amount is not expected to exceed 10 ng Hg and reaching a sorption capacity for these materials, resulting in increased breakthrough and loss of target compounds, is likely not a major concern.

It is desirable to minimize the discrepancy between the CEM and nylon membrane mercury amounts when used as sorption surfaces for ambient RM to ensure the results from each material better represent each other. Based on these results, it is clear that maintaining lower mercury amounts on the materials is best. This can be easily achieved by reducing sampling duration in areas with relatively high ambient RM concentrations, reducing the flow rate of air passing through actively sampled surfaces if longer sampling durations are required, or perhaps increasing the sampling surface area. However, there must be enough mercury on the materials to accurately quantify based on available analytical methods.

Increasing sampling surface area does not lead to lower mercury amounts nor the ability to decrease sampling duration. CEM of two different sizes, 47 and 90 mm diameters, with the same sampling durations and flow rates did not have significantly different total mercury amounts (Table S3). The larger membranes had significantly higher blank membrane amounts and higher relative deviations than the smaller membranes; the increased variability in the larger membranes may be due to increased handling needed to manipulate the larger membrane. These results indicate that materials with larger surface areas do not sorb more mercury at the same flow rate and may be less useful than the same material with a smaller surface area. Instead of surface area, the total volume of air passed through the sorption surface may be more important in controlling how much mercury is captured on the sorption surface. Increased flow rates may accumulate more mercury on the sorption surface faster, requiring a short sampling duration to sorb sufficient mercury for quantification; however, higher flow rates may lead to increased breakthrough of mercury compounds.

3.3. Mercury retention and transformations on sorption surfaces

The selection of the correct sorption surface material is important to ensure that the analytical results accurately represent the mercury compounds in the sampled air. Loss, gain, or transformations of mercury compounds on sorption surfaces due to reactions on the surface during sampling and storage may bias results and lead to incorrect interpretations. For example, Lyman et al. (2010) investigated whether the mercury amount on blank sorption surfaces held in a custom-built passive sampler, but away from air (sealed in jars), changed as a function of storage time (0–4 weeks) and temperature (2–40 °C). The authors demonstrated that mercury amounts on the blank membranes increased with increased storage time and temperature, indicating that contamination from the sampler body was occurring. However, this study does not represent typical storage conditions for many mercury samples and the results should be cautiously applied to other study designs. Unfortunately to date there has been very little supporting evidence for the quantitative retention and lack of transformations of mercury compounds on sorption surfaces during storage.

The standard sorption surface materials in this study quantitatively retained ambient RM, but not single-source GOM compounds, during long-term storage. The mercury amounts on CEM and nylon membranes loaded with ambient RM were not significantly different between samples analyzed immediately and after 190 days of storage at −20 °C (t-tests, $p > 0.05$). CEM and nylon membranes loaded with $HgBr_2$ in the permeation system were stored for up to 80 days under various temperature (−20 or 20 °C) and light (i.e., completely dark or set in a window, exposed to diurnal daylight patterns) conditions. Storage time was the most significant factor for single-source GOM compound retention on CEM samples and blanks, with a significant decrease, ranging from 36 to 46%, in mercury after just 72 days of storage for both blank (t-tests, $p = 0.001$) and sample membranes (t-tests, $p = 0.004$). Samples stored at −20 and + 20 °C did not have significantly different mercury amounts after 72 days of storage (t-tests, $p = 0.34$), nor did samples stored under different light conditions after 80 days of storage (t-tests, $p = 0.76$) or samples shipped to collaborators and shipped back for analysis after 72 days ($0.47 < p < 0.91$). Together, these results indicate that storage duration is the most critical factor to consider when generating and storing permeated single-source GOM compound samples, but may be less critical for ambient RM samples. Other GOM compounds may behave differently, and additional testing is required to better understand the mechanism of loss of mercury compounds from sorption surface materials.

Transformations of single-source GOM compounds occur on the sorption surface when exposed to ambient air or stored, but transformations of ambient RM compounds do not occur during long-term storage. Chemical transformations of sorbed single-source GOM compounds occurred on the nylon membrane surface when exposed to ambient air (Fig. 4, S1). Changes in the desorption profiles between the controls and sample membranes exposed to ambient air for either 1 or 7 days, along with a decrease in the area under the desorption profile curve with increased exposure time (Table S4), suggest that the single-source GOM compounds loaded on the membranes were transformed (i.e., shifting peaks) and lost from the sorption surface. This is likely a result of the single-source GOM compounds reacting with reducing compounds in the air that convert oxidized mercury to elemental mercury, that has been demonstrated to not sorb to the standard sorption surface materials (Miller et al., 2019). It should be noted that the thermal desorption profiles for the control membranes for each of the single-source GOM compounds are similar, with peaks around 80–100 °C (–O, –Br, and –Cl compounds) and 145–150 °C (–S compounds). Thermal desorption profiles of single-source GOM compounds in similar permeation systems have been previously published (Gustin et al. 2015, 2016; Huang et al., 2013) and exhibit a unimodal profile. It is possible that the compounds emitted from the permeation tubes and/or permeation system in this study were contaminated with –S compounds; the cause of the second –S peak is unknown and under investigation. Another potential cause of this discrepancy is a suspected change, based on other results not presented here, in the manufacturing of the nylon membrane product between older thermal desorption analyses of single-source GOM compounds and this study; the authors reached out to the manufacturer to determine if a change was made to the material production and/or processing but did not receive an answer. Regardless, the changes exhibited in the profiles of samples using the same nylon membrane material and mercury compounds demonstrate that the single-source GOM compound(s) are less stable on the sorption surface. Thermal desorption profiles of nylon membranes loaded with compounds emitted from a $HgBr_2$ permeation tube and stored, thus not exposed to ambient air, demonstrated that transformations and loss of a GOM compound occurs on the membranes during just 37 days of storage (Fig. S2). However, nylon membranes loaded with ambient RM did not demonstrate loss nor transformation of mercury compounds, even after 190 days of storage at −20 °C (Fig. 5, S3).

Sorption surfaces loaded with ambient RM demonstrate more quantitative retention and less transformation of mercury compounds during long-term storage compared with single-source GOM compounds. The sorption surface materials tested in this study are therefore best

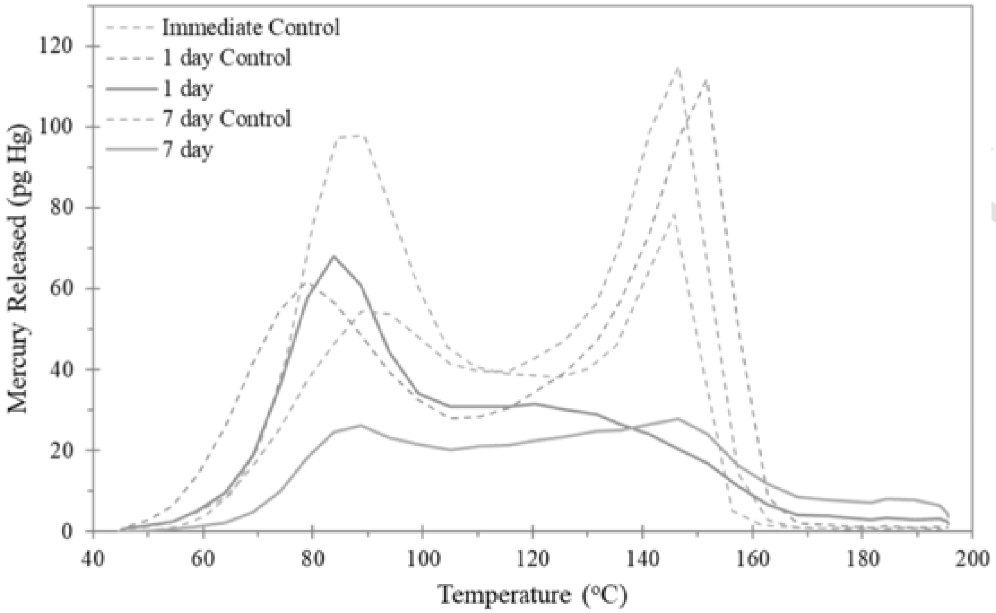

Fig. 4. Thermal desorption profiles for nylon membranes loaded with HgO in the permeation system and deployed in the UNR-RMAS 2.0 for 1 or 7 days. Solid lines represent the average profile of 2 samples and dashed lines represent the profile for 1 non-deployed control sample held for 0, 1, or 7 days.

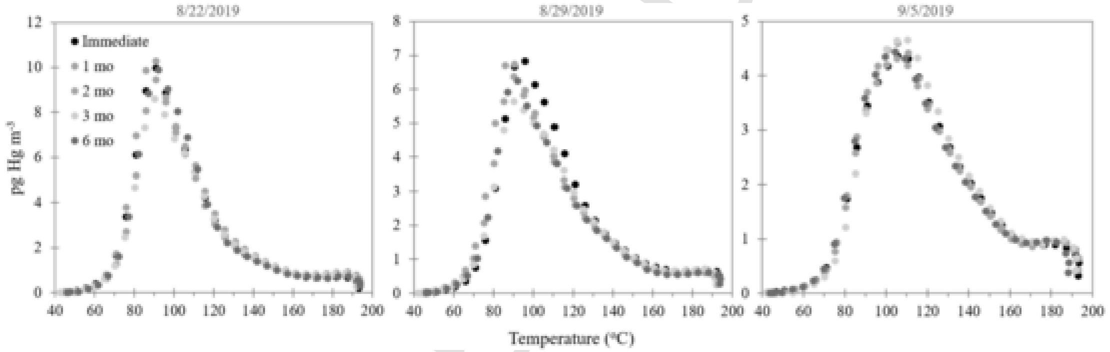

Fig. 5. Thermal desorption profiles for nylon membranes loaded with ambient RM in the UNR-RMAS 2.0 for 7 days then analyzed immediately (Immediate) or stored for 1–6 months prior to analysis. Panels represent results from 3 replicate deployments, with the collection dates at the top of each panel. Each symbol represents the mean of triplicate nylon membrane samples. Examples of standard deviation around the mean for replicate samples are presented in Fig. S3.

used for ambient RM research. Studies using these materials for high concentration single-source GOM research should proceed cautiously and test the materials extensively, especially if the materials will be stored for any substantial amount of time prior to analysis.

4. Conclusions

Several commercially available materials were tested for their viability as sorption surfaces for the quantitative retention of ambient RM. Of the tested materials, CEM and PES sorbed the highest amount of mercury and nylon was the only material that was compatible with thermal desorption analysis. These materials have been widely used in RM studies, though this is the first study to directly compare performance between CEM and PES. Though no significant differences were observed between the materials in these experiments, more studies are needed that compare the performance of the materials under a variety of conditions (e.g., humidity, air chemistry) before researchers switch from one material to the other. Additionally, identifying alternative materials will be important for corroborating results from these standard materials and being able to compare results from CEM (total mercury) and nylon membranes (RM compounds) for past and future studies.

Based on the experiments in this study, AEM, polycarbonate, and polypropylene materials should not be used for RM research, and PMDS should not be used in the configuration of a multi-capillary tube, though may be useful for RM research in other configurations. CEM and PES materials are good selections for ambient RM concentrations, but may be limited when used as sorption surfaces for high concentration GOM experiments. Nylon is good for identifying GOM compounds that comprise sorbed ambient RM, but should not be used as a quantitative sorption surface. Overall, the results of this study indicate that balancing sampling duration with total sorbed mercury amounts, minimizing storage of samples prior to analysis, and minimizing exposure of loaded surfaces with ambient air will reduce bias in analytical results and interpretation.

CRediT authorship contribution statement

Sarrah M. Dunham-Cheatham: Conceptualization, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Seth Lyman:** Conceptualization, Writing - review & editing. **Mae Sexauer Gustin:** Conceptualization, Investigation, Writing - review & editing, Supervision.

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.atmosenv.2020.117836.

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