

Interaction of reactive mercury with surfaces and implications for atmospheric mercury speciation measurements

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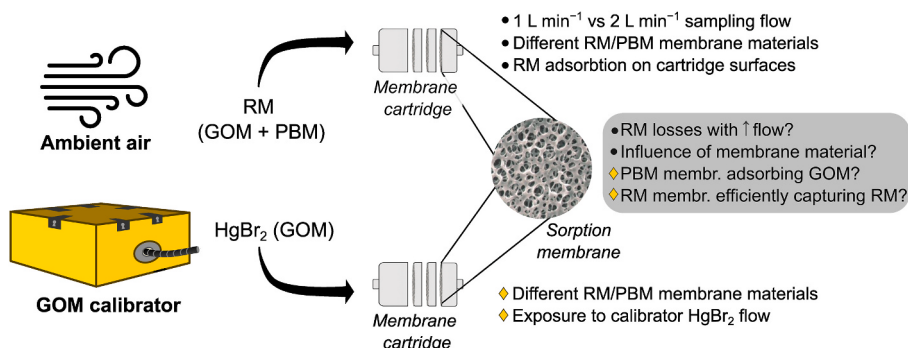
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HIGHLIGHTS

- Investigation of methods used to collect reactive atmospheric Hg is needed.
- Increased sample flow rate resulted in a seasonal decrease of [RM] measured by CEM.
- Flow rate had no effect on RM chemistry/concentration measured by nylon membranes.
- Historically used membrane materials outperformed alternative membrane materials.
- PBM membranes retain GOM.

GRAPHICAL ABSTRACT



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ABSTRACT

Accurate measurement of atmospheric reactive mercury (RM) presents analytical challenges due to its reactivity and ultra-trace concentrations. In the last decade, use of the University of Nevada, Reno – Reactive Mercury Active System (RMAS) for RM measurements has increased, since it has been shown to be more accurate than the industry standard, the Tekran 2537/1130/1135 system. However, RMAS measurements also have limitations, including long time resolution and sampling biases associated with membranes used for RM sampling. We therefore investigated the use of higher sampling flow rates to reduce sampling time and tested alternative membrane materials using both ambient air sampling and controlled laboratory experiments with a gaseous oxidized mercury (GOM) calibrator. Results indicated that increasing the RMAS sampling flow had a negative impact on determined RM concentrations. RM concentrations at 2 L min⁻¹ were 10% and 30–50% lower than at 1 L min⁻¹ in spring/summer and winter, respectively. However, the chemical composition of RM captured on membranes was not impacted by the increased flow rate. Membranes currently used in the RMAS performed better than numerous alternatives with similar composition, retaining Hg more efficiently. Both ambient air sampling and laboratory experiments revealed that membranes designed to retain only particulate-bound mercury (PBM) also retained significant amounts of GOM. PBM membranes based on borosilicate glass designs retained more than 70% of GOM.

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1. Introduction

Measurement of atmospheric reactive mercury (RM) concentrations and chemistry remains a challenge. Gaseous elemental mercury (GEM) is relatively inert, while gaseous oxidized (GOM) and particulate-bound (PBM) mercury together comprise reactive mercury ($RM = GOM + PBM$) that is formed by oxidation reactions and readily reduced (Lyman et al., 2020a). Atmospheric RM measurement methods were developed in the late 1990s and early 2000s (Landis et al., 2002; Munthe et al., 2001; Sheu and Mason, 2001). Potassium chloride (KCl)-coated denuders and a downstream quartz fiber membrane filter that reportedly selectively sorbed GOM and PBM, respectively, became the most widely used method of measuring atmospheric RM. Denuder and quartz fiber membranes were incorporated into the standard instrument used for atmospheric Hg measurements, the Tekran 2537/1130/1135 speciation system (Landis et al., 2002). The standard instrument has been shown to be subject to bias, with loss of GOM from the denuder as a function of ambient air chemistry and the chemical form of Hg present (Gustin et al., 2013; Huang et al., 2013; Lyman et al., 2010).

The need for more accurate measurements led to the development of alternative methods for measuring RM, including the use of membranes and dual-channel systems (DCSs). Membrane-based collection of RM is the basis of measurements used in the University of Nevada, Reno – Reactive Mercury Active System (RMAS). The RMAS is an active sampling system that was intended to provide a means of quantifying RM, PBM, and GOM concentrations and qualitatively identifying RM chemistry (Luippold et al., 2020b). The implementation of different types of membranes in the RMAS enables measurements of RM or GOM using cation-exchange membranes (CEM), estimation of RM or GOM chemistry using nylon membranes, and PBM measurements using a polytetrafluoroethylene (PTFE) membrane located upstream of CEM or nylon membranes (i.e., the RMAS + P) (Dunham-Cheatham et al., 2020). The forms of Hg as determined by membranes are operationally defined, with the terms RM, GOM, and PBM referring to the form retained by a specific sequence of different membrane types. Direct measurements of atmospheric Hg^{II} chemistry are currently not possible, although new promising methods are emerging that measure Hg^{II} directly by mass spectrometry (Deeds et al., 2015; Jones et al., 2016).

DCSs use a Tekran 2537 module to quantify total gaseous mercury (TGM) and GEM using two channels. One channel reduces TGM in sample air to GEM using a thermolyzer, resulting in a TGM measurement in the downstream Tekran 2537. The second channel contains a CEM to remove GOM and PBM ($>0.8 \mu m$), allowing just GEM to be measured. RM concentrations are calculated by difference (TGM – GEM) (Lyman et al., 2020b). Both alternative methods (DCSs and RMAS) measured 2- to 3-fold higher RM concentrations than the Tekran speciation system (Gustin et al., 2013).

However, the alternative RM measurement systems (RMAS and DCSs) are not without limitations. For example, DCSs are complex and require technical expertise to operate and the RMAS requires a long sampling deployment (1–2 weeks) to collect quantifiable masses of Hg on the membranes. Additionally, RMAS membranes have been historically purchased from two vendors, and membrane inefficiencies have been identified: nylon membranes have decreased RM retention under increasing ambient humidity and ozone (Huang and Gustin, 2015), and do not retain nitrogen-containing RM compounds well (Luippold et al., 2020a); and PTFE membranes most likely retain some GOM (Gustin et al., 2015). A recent study by Mao and Khalizov (2021) showed that GOM adsorbed to a polyethersulfone cation exchange membranes (PES, Cole-Parmer, 90 mm Diameter, pore size of $0.45 \mu m$) was subject to exchange interactions with co-adsorbed GOM and other chemical compounds. However, Mao and Khalizov's (2021) results were obtained using GOM concentrations that were 5-orders of magnitude higher than ambient background concentrations. More testing is necessary to determine whether and how RMAS membrane materials influence RM retention. Lastly, a recent RM sampling system intercomparison

demonstrated that the Utah State University (USU) and University of Nevada, Reno DCSs measurements of GOM were 50 and 30% higher, respectively, than RM measured by the RMAS (Dunham-Cheatham et al., 2023). The lack of agreement needs to be better understood.

For this study, since the required RMAS sampling resolution can be up to two weeks for pristine areas at a flow rate of $1 L min^{-1}$, the effect of increasing the flow rate on Hg measurements was investigated. In addition, the limitations of the membranes used in the RMAS discussed above indicates new sorption surfaces need to be identified. Thus, several alternative commercial membranes (of the same material, but from different vendors, or of a completely different material) were deployed to check their performance relative to the historically used membranes. Also, the question as to whether adsorption of RM to the RMAS membrane cartridge accounts for the RM concentration discrepancies observed between the RMAS and DCS was addressed. Lastly, PBM membranes were exposed to GOM ($HgBr_2$) produced by an automated calibrator to assess whether PBM membranes collect GOM, in addition to PBM.

2. Methods

2.1. University of Nevada, Reno – Reactive Mercury Active System (RMAS)

Three RMAS were used to perform experiments. The RMAS is an active sampling system with pumps that pull air through 47 mm two- or three-staged perfluoroalkoxyalkane membrane cartridges (Saville) at $1-2 L min^{-1}$ for one- or two-week sampling deployments. Additional description of the RMAS is available in the Supplementary material (Text S1) and elsewhere (Luippold et al., 2020b). In general, different atmospheric Hg forms can be measured using different sequences of membrane materials. Membranes historically used to measure RM and PBM concentrations include CEM (Pall Corporation, Mustang S; $0.8 \mu m$ pore size) and PTFE membranes (Sartorius Stedium Biotech, 1180747N; $0.2 \mu m$ pore size), respectively. The CEM material is a polyethersulfone (PES) membrane proprietarily treated to preferentially sorb cations, purchased in sheets that were cut into 47 mm diameter discs using a steel cutting die. Nylon (polyamide) membranes are used for qualitative determination of operationally defined RM chemistry (Sartorius Stedium Biotech, 2500747N; $0.2 \mu m$ pore size).

Within each membrane cartridge, two CEM or two nylon membranes were deployed. The membrane closest to the sampling inlet was considered the upstream membrane, and the subsequent membrane, the downstream membrane. The downstream membrane was used to measure breakthrough of Hg from the upstream membrane. In the RMAS + P configuration, a third membrane (i.e., PTFE membrane) was placed upstream of the two membranes to capture PBM ($>0.2 \mu m$), while the two downstream membranes then captured GOM. For all experiments in this study, triplicate blank samples of each membrane type were collected at the beginning of each sampling deployment, and the mean of the blank samples was subtracted from the mass of Hg quantified on each sample membrane. Data were removed when the downstream membrane measured higher RM than the upstream membrane, as this was indicative of an upstream membrane that was not flush with the support stage in the membrane cartridge; this occurred in less than 1% of samples.

2.2. Sampling location

All experiments were performed at the UNR College of Agriculture, Biotechnology & Natural Resources Agricultural Experiment Station Valley Road Greenhouse Complex (39.5375, -119.8047 , 1.37 km above sea level) (Fig. S1). This sampling location was the setting for previous RMAS experiments (Dunham-Cheatham et al., 2020; Luippold et al., 2020b). The site is impacted by vehicle emissions, as it is located adjacent (100 m distance) to Interstate-80, and long-range transport of

pollutants (Gustin et al., 2021b; Luippold et al., 2020a). Spring and summer deployments were characterized by high temperatures ($>20^{\circ}\text{C}$) and solar radiation ($\sim 300\text{ W m}^{-2}$), and low relative humidity ($<35\%$), conditions favoring GEM oxidation to RM (Gustin et al., 2023). Lower ambient temperatures ($<15^{\circ}\text{C}$) and solar radiation ($\sim 150\text{ W m}^{-2}$) and increased precipitation and relative humidity ($\sim 50\%$) were observed through the fall and winter deployments (Gustin et al., 2023). Although Hg sources and chemistry are not the focus of this study, the description of ambient air influences is important for data interpretation.

2.3. RMAS experiments

RMAS experiments were performed for at least five, one-week long deployments ($\pm 1\text{--}2$ days) and included comparing RMAS data collected at two flow rates, an intercomparison of historical RMAS and alternative membrane measurements, and an experiment to determine whether adsorption of RM to the membrane cartridges was occurring. Table S1 presents when each experiment occurred and for how long.

2.3.1. Flow rate variation

Experiments to investigate whether the time resolution of RMAS measurements can be improved were done by comparing RM concentrations and chemistry for samples collected at 1 and 2 L min^{-1} . For each deployment, triplicate dual-staged membrane cartridges with CEM or nylon membranes were installed on two co-located RMAS shields. Flow rates were controlled by critical flow orifices (Teledyne API, 941100 - 1 L min^{-1} and 941700 - 2 L min^{-1}).

2.3.2. Alternative membrane comparisons

Different membranes have previously been deployed to measure RM (quantitative analysis with PES membranes and their modifications, qualitative analysis with nylon membranes) (Araujo et al., 2022; Gustin et al., 2021b; Maruszczak et al., 2017; Sheu and Mason, 2001) and PBM (glass, quartz, and cellulose membranes) (Gustin et al., 2015; Lu and Schroeder, 1999), but have not been extensively compared. Therefore, alternative commercially available membrane materials were identified to assess whether the membranes measure similar concentrations and/or chemistry to the membranes historically used in the RMAS. Two- and three-staged membrane cartridges with historical and alternative membrane types were installed on co-located RMASs, all sampling at a flow rate of 2 L min^{-1} . Information on all membranes is listed in Table S2. Tested CEM membrane alternatives (RM quantitative analysis) were PES membranes that consisted of Sterlitech (PES0847100; $0.8\text{ }\mu\text{m}$) and Cole-Parmer (361-3811-CP; $0.45\text{ }\mu\text{m}$, 90 mm diameter cut to 47 mm). Tested nylon membrane alternatives (RM qualitative analysis) consisted of Sterlitech (Sterlitech $0.2\text{ }\mu\text{m}$; NY0247100 and Sterlitech $0.8\text{ }\mu\text{m}$; NY0847100) and Whatman nylon membranes (Whatman $0.2\text{ }\mu\text{m}$; 7402-004 and Whatman $0.8\text{ }\mu\text{m}$; 7408-004). The alternative PBM membranes consisted of VWR borosilicate glass filters (VWR part number: 28333-139, directly purchased from Tekran, Tekran part number: 90-13110-100; $1.0\text{ }\mu\text{m}$), and Whatman borosilicate glass microfiber (3827-047; $1.5\text{ }\mu\text{m}$) membranes, upstream of two nylon membranes (RMAS + P configuration). Nylon membranes were selected as the downstream membranes for the RMAS + P configuration to determine whether the upstream PBM membranes contributed to the alteration of downstream GOM chemistry during the experiment.

2.4. PBM membranes selectivity and RM membranes GOM capture efficiency

Membranes used for capturing PBM have been suggested to also collect GOM (Gustin et al., 2015). If true, the selectivity of PBM membranes for just PBM compounds would be poor, leading to biases in measurement systems collecting PBM. To test the potential for this, PBM membranes in single-stage filter cartridges were exposed to gaseous HgBr_2 as a GOM surrogate. A known amount of gaseous HgBr_2 was

produced continuously by the automated GOM calibrator whose permeation rate was 1.59 pg s^{-1} , determined both gravimetrically and using a dual-channel system. The calibrator design was an improvement on the design used by Dunham-Cheatham et al. (2023), main differences: i) no valves were present, Sulfinert® coated lines (both changes lowering HgBr_2 adsorption), ii) flow dilution system enabled the use of different concentration ranges, iii) outlet flow was measured using a Venturi-based flow measurement, iv) permeation tube was heated to 50°C , v) lines were heated to 150°C , and vi) permeation oven was made of 1.3 cm thick aluminum to increase temperature stability. Additional detailed information will be available elsewhere (Elgiar et al. in prep; Lyman et al. in prep). Previous research using GC-MS measurements gives confidence that HgBr_2 is the predominant compound in the calibrator output under the operating conditions (Dunham-Cheatham et al., 2023; Jones et al., 2016).

For this experiment, laboratory air was pulled through filter cartridges containing a single PBM membrane at a flow of 1 L min^{-1} ; the calibrator outlet was inserted directly into the filter cartridge $\sim 2\text{ cm}$ away from the PBM membrane to minimize potential HgBr_2 adsorption to the filter cartridge. The connection between the filter cartridge and the calibrator outlet was not airtight to prevent pressure issues within the calibrator that could cause instabilities in the HgBr_2 permeation rate. Consequently, a small amount of GOM/PBM (negligible in comparison to the GOM permeating from the calibrator) was drawn through the membranes from the laboratory air. This was accounted for by subtracting method blanks made by drawing laboratory air through the filter cartridge without exposure to the flow of HgBr_2 from the calibrator and doing so for the same amount of time as the duration of the experiment. Three method blanks were used for each PBM membrane type. Experiments lasted for 10 min , during which 954 pg of HgBr_2 was pulled through the PBM membrane when the membrane was exposed to the flow of HgBr_2 from the calibrator. The amount of GOM (HgBr_2) sorbed by PBM membranes was calculated relative to the amount of GOM sorbed by CEM, since CEM were shown to sorb GOM quantitatively (Dunham-Cheatham et al., 2020). To further investigate whether CEM is the most efficient material for capturing GOM out of the RMAS membranes, the exact same procedure was done for three RM membranes: Pall CEM, Sterlitech PES, and Sartorius nylon (Table S2).

Additionally, the selectivity of PBM membranes (ability to retain only PBM and not GOM), was tested after collecting ambient air for 1-week using the RMAS at 2 L min^{-1} flow. After the 1-week RMAS sampling, three PBM membranes of each type were used for blank subtraction (accounting for the accumulated Hg during sampling). The rest of PBM membranes after sampling underwent the same experimental procedure for loading GOM as described in the above paragraph.

2.5. Tekran PBM membranes selectivity

Experimental conditions for selectivity tests of membranes used for PBM sampling in the industry standard Tekran 1130/1135/2537 system were modified compared to other PBM membrane selectivity tests to reproduce sampling conditions similar to the actual sampling conditions used in the Tekran system. The Tekran PBM membranes were quartz fiber filter (Tekran part number: 90-13500-25, $0.1\text{ }\mu\text{m}$ pore size, 21 mm diameter). Tekran PBM membranes were cleaned by heating at 600°C for 20 min before conducting experiments to remove any Hg that was potentially adsorbed to the membranes. Laboratory air was pulled through glassware used in the Tekran 1135 module (regenerative particulate filter – RPF) containing a single Tekran PBM membrane at a flow of 9 L min^{-1} ; the calibrator outlet was inserted directly into the 1135 glassware $\sim 2\text{ cm}$ away from the PBM membrane to minimize potential HgBr_2 adsorption to the glassware. The glassware upstream and at the filter was heated to $\sim 50^{\circ}\text{C}$ by applying a heat tape; the amount of used heat tape controlled the achieved temperature. Temperature was measured with a thermocouple inside the glassware at the location of the filter and upstream of the Tekran 2537 PBM filter. Similarly, as for

other PBM membranes, a small amount of GOM/PBM was drawn through the membranes from the laboratory air; this was accounted for by subtracting method blanks made by drawing laboratory air through the filter cartridge without exposure to the flow of HgBr_2 from the calibrator and doing so for the same amount of time as the duration of the experiment. Three method blanks were used for this experiment. Experiments lasted for 10 min, during which 954 pg of HgBr_2 was pulled through the PBM membrane, when the membrane was exposed to the flow of HgBr_2 from the calibrator.

Additionally, the selectivity of Tekran PBM membranes was tested after collecting ambient air. Ambient air was drawn through the RPF containing a single PBM membrane at 9 L min^{-1} for 1.5 h and RPF was heated to $\sim 50^\circ\text{C}$ using a heat tape (as described in the above paragraph). This was repeated 12 times during a span of two days. A total of 12 Tekran PBM membranes were exposed to ambient air, 3 of them were used for blank subtraction (accounting for the accumulated Hg during sampling). The remaining 9 PBM membranes after sampling underwent the same experimental procedure for loading GOM as described in the above paragraph.

2.6. Cartridge adsorption test

CEM membranes deployed in the RMAS were recently shown to measure 50 and 30% less RM than a concurrently operating USU and UNR DCS, respectively, at the same location (Dunham-Cheatham et al., 2023). One explanation could be retention of RM by the RMAS membrane cartridge. To test whether adsorption of RM to the membrane cartridge was occurring, two-stage membrane cartridges with and without CEM were deployed when RM concentrations are highest at the sampling location (i.e., summer). The test was conducted using 2 L min^{-1} flow and Pall CEM membranes, no variation of flow and membrane materials were tested. After the deployment, cartridges were washed using 5% hydrochloric acid solution to remove the RM adsorbed during the deployment. The acid solution was measured for total Hg content as described for membrane analyses in section 2.7. The detailed washing procedure is described in Supplementary material (Text S2).

2.7. Membrane analyses, data processing, and ancillary data

The total Hg content of all upstream and downstream membranes, except for the upstream nylon membranes, was quantified using a modified EPA method 1631 Revision E (U.S. Environmental Protection Agency, 2002) with subsequent analysis by cold vapor atomic fluorescence spectrometry using a Tekran 2600-IVS. Upstream nylon membranes were analyzed using the thermal desorption method described by Dunham-Cheatham et al. (2023) to identify and quantify RM compounds. For more details about the analytical methods, see the Supplementary material (Text S3, S4).

Regression analyses were performed in RStudio, version 4.2.1 (R Core Team, 2021). Reduced major axis regression (RMA), using the *lmodel2* package (Legendre, 2018), was used to report slope, coefficient of determination (r^2), and p-values. The y-intercept was set to zero for all modeled regressions, because the x value (RM concentration) is expected to be zero when the y value (another RM concentration) is zero, and blank membrane Hg concentrations were subtracted from all samples. When the normality assumption of RMA was violated (non-normal data), ordinary least squares regression (OLS) was used (using *lmodel2* package), and correlation coefficient (r^2) and p-values were reported. Normality was violated only for 2 correlations, and even in those instances the RMA and OLS regression coefficients were within 5 % difference. The Grubbs' test was used to assess and remove outlier data (Komsta, 2006). T-tests were used to test statistical similarity of seasonal absolute humidity, and of cartridge adsorption results. T-tests were performed in Excel using the *t*-Test: Two-Sample Assuming Unequal Variances from the DataAnalysis ToolPack. For all statistical tests, $\alpha = 0.05$. Statistical similarity for thermal desorption data was tested by

one-way repeated measures multivariate analysis of variance (MANOVA, using MANOVA.RM package) (Friedrich et al., 2019) in combination with post-hoc Friedman tests (non-parametric repeated measures analysis of variance by ranks). RStudio code for regression and MANOVA analyses is available in Supplementary material (Text S5).

Meteorological data were downloaded from the Western Regional Climate Center's website for the Reno (UNR Campus) Station. Parameters included precipitation (mm), wind speed (m s^{-1}), mean air temperature ($^\circ\text{C}$), relative humidity (%), and solar radiation (W m^{-2}). The mean of every ancillary data parameter during each RMAS experiment was calculated and is presented in Table S3.

3. Results and discussion

3.1. Flow rate variation

During summer 2021, RM concentrations measured using nylon membranes at 1 versus 2 L min^{-1} were similar (2% difference), while RM concentrations measured using CEM were 10% less at 2 L min^{-1} than at 1 L min^{-1} (Fig. 1a). In winter 2021, nylon membrane concentrations at 2 L min^{-1} were 10% higher than at 1 L min^{-1} , and concentrations on the CEM were lower by 50% at 2 L min^{-1} (Fig. 1b). This experiment was redone in winter 2022, and nylon membrane concentrations at 2 L min^{-1} were 10% lower, while CEM concentrations were lower by 30% at 2 L min^{-1} (Fig. 1c). Results for spring 2023 were comparable to the results for summer 2021; RM concentrations measured using nylon membranes were similar for both flow rates (4% difference), while RM concentrations measured using CEM were 10% less at 2 L min^{-1} than at 1 L min^{-1} (Fig. 1d).

The difference between RM concentrations measured at 2 L min^{-1} and 1 L min^{-1} flow rate was higher during winter than in spring/summer. Gustin et al. (2023) observed that the air in Reno is affected by regional pollution in fall/winter, while during spring/summer air from free troposphere was more important. These seasonal differences and the different chemistry of RM could explain the higher difference between the RM concentrations measured at two flows in winter than in spring and summer. The summer/spring versus winter difference could also be in part explained by the higher particulate matter (PM) concentration during winter (PM < $2.5 \mu\text{m}$ diameter, average values of $4\text{--}8 \mu\text{g m}^{-3}$), than during spring/summer (PM < $2.5 \mu\text{m}$ diameter, average values of $3\text{--}4 \mu\text{g m}^{-3}$) (Pierce et al., 2019; US Environmental Protection Agency, 2022) that occurs due to temperature inversion. Elevated PM could influence the chemistry of RM and therefore the retention of specific RM compounds. The influence of relative humidity (RH) was also investigated; the average RH values were 28%, 67%, 70%, and 48% for summer 2021, winter 2021, winter 2022, and spring 2023, respectively. RH variation between fall/winter and spring/summer could have had an influence on our results. Higher RH could lead to a thicker aqueous film on CEM membranes and occurrence of deliquesced aerosol particles, which was previously speculated to increase the CEM capture rate (Huang et al., 2013). Since our results indicate the opposite – decreased capture rate at 2 L min^{-1} during winter at elevated RH – our results cannot be explained by RH.

An example of nylon RM chemistry is shown for summer 2021 in Fig. 1e; full results (summer 2021 to spring 2023) for nylon chemistry are shown in Fig. S2. RM chemistry was not statistically different when comparing all data pairs and compounds (–O, –Cl/Br, –N, –S, and organic RM compounds) for 1 vs 2 L min^{-1} flows (MANOVA, $p > 0.05$). Post-hoc statistical analyses (Friedman) for each separate compound revealed that only the amount of organic RM compounds was statistically different for 1 vs 2 L min^{-1} flows ($p < 0.05$), while other RM compounds were not statistically different ($p > 0.05$). Overall, results indicated that nylon membranes are not susceptible to significant biases when increasing sampling flow rates, since both the RM concentrations and chemistry of retained RM compounds were not significantly influenced.

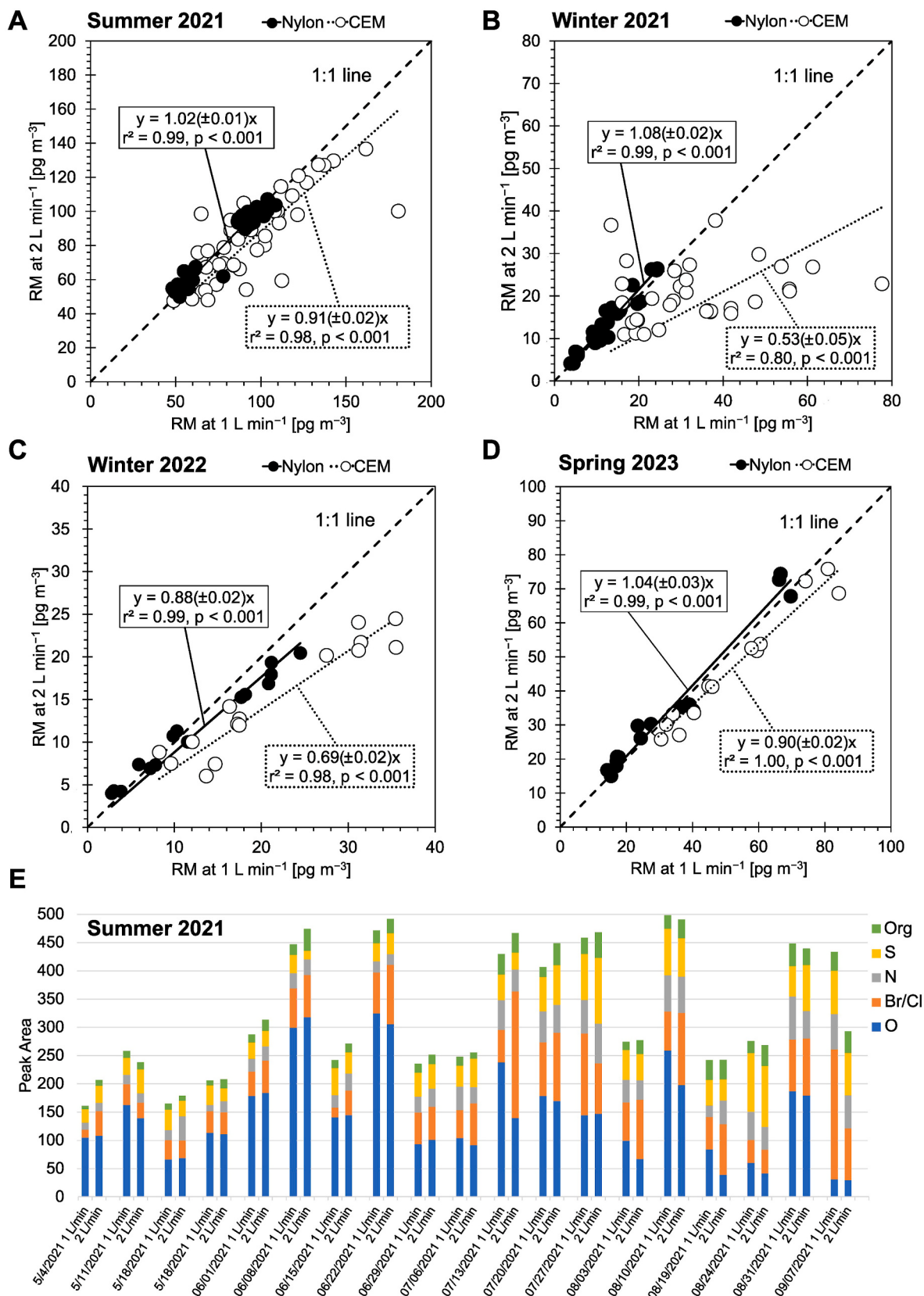


Fig. 1. Quantitative flow variation results (RM concentrations) for a) summer 2021, b) winter 2021, c) winter 2022, and d) spring 2023. Qualitative flow variation results (RM chemistry) are shown in e) summer 2021. The dates represent sample harvest date (MM/DD/YYYY).

3.2. Alternative membrane comparisons

All of the alternate membrane materials retained less RM than the historically used RMA membranes (Pall CEM, Sartorius Nylon, and Sartorius PTFE; Fig. 2). Weekly averages and standard deviations for all used membrane materials for the alternate membrane comparison experiment are shown in Fig. S3. Results for alternative RM membrane materials (Fig. 2a) showed that Sterlitech and Cole-Parmer PES membranes collected 23 and 14% less RM than the Pall CEM, respectively. We acknowledge that RM losses could have occurred for Pall CEM, similarly as discussed in previous section (2 L min⁻¹ flow rate was used); however, it is evident that even if RM losses occurred, Pall CEM was still the membrane material that performed best. Breakthrough values for each RM membrane material are available in Supplementary material (Fig. S4). Breakthrough values of Pall CEM, Sterlitech PES, and Cole-Parmer PES were statistically different when comparing all data pairs (MANOVA, $p < 0.05$), in the following order of average breakthrough values: Cole-Parmer PES > Pall CEM > Sterlitech PES. Interestingly, breakthrough values were significantly greater in winter, when RM concentrations were relatively low in comparison to late summer/autumn when RM concentrations were relatively high (MANOVA, $p <$

0.05). The cause for this occurrence can be explained similarly as for the summer versus winter variation discussed in the previous section (Fig. 1).

Experiments using alternative nylon materials showed RM concentrations using Sterlitech 0.2 μm and 0.8 μm were 8 and 3% lower than historical Sartorius (0.2 μm) membrane RM concentrations (Fig. 2b), respectively. Whatman 0.2 μm and 0.8 μm nylon membranes retained 33 and 43% less RM than the Sartorius (0.2 μm) membranes, respectively. Alternative nylon membrane thermal desorption profiles were not compared statistically, because the alternative nylon membranes have not been loaded with known Hg compounds (standards), therefore we cannot predict what the modeled profiles represented. However, the profiles were visually different from the historical Sartorius membrane (Fig. S5).

Alternative PBM membrane materials, Whatman and VWR glass filters, retained 19 and 23% less PBM than the Sartorius PTFE membranes, respectively (Fig. 2c). When comparing alternative PBM membrane materials from the standpoint of the GOM retained on downstream nylon membranes, 22 and 91% less GOM was retained when using upstream Whatman and VWR membranes, respectively (Fig. 2d). The low GOM amounts on membranes downstream of alternative PBM

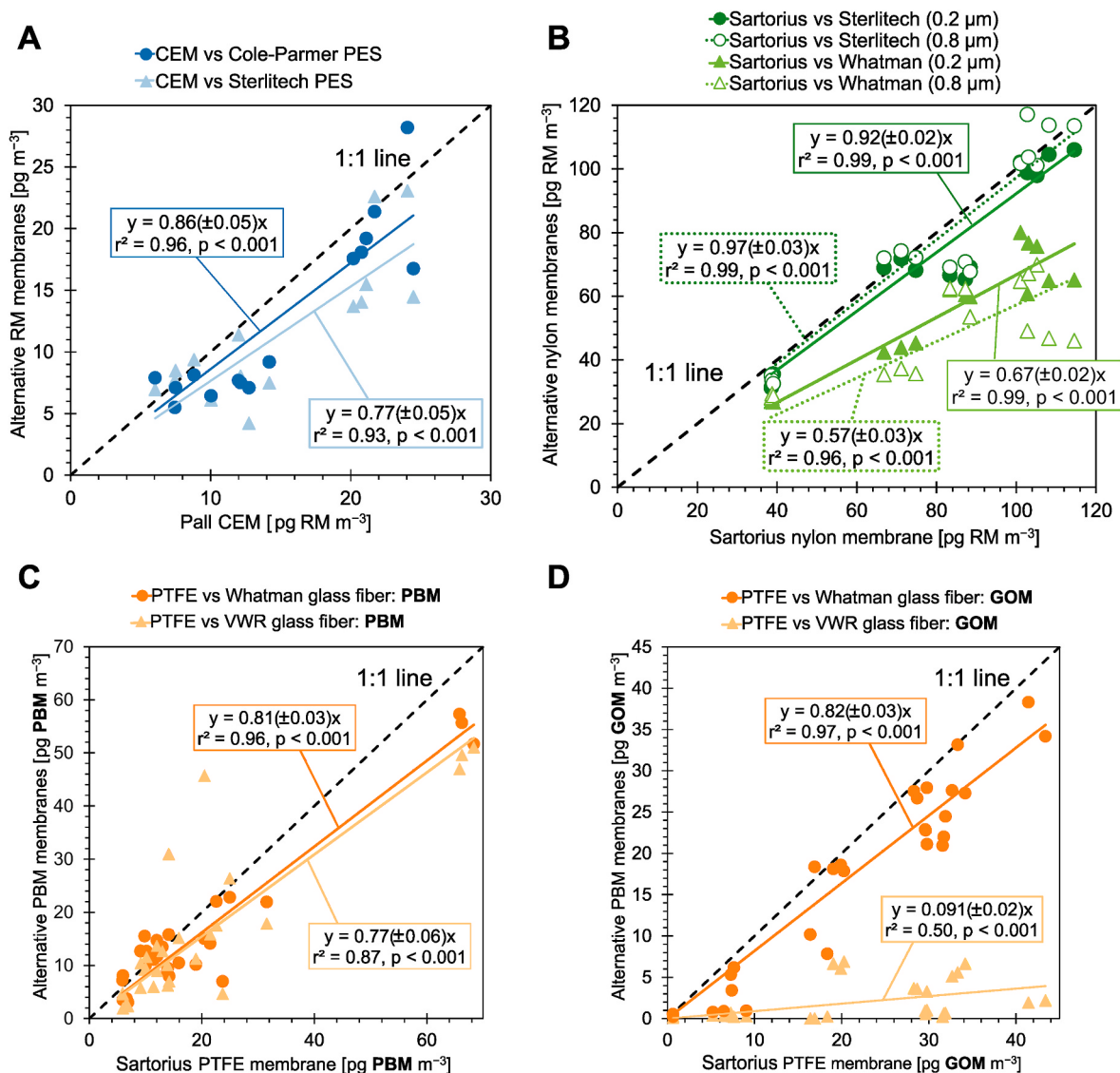


Fig. 2. Tests of alternative membrane materials in comparison with historically used RMA membrane materials: a) Pall CEM membrane alternatives (RM); b) Sartorius nylon membrane alternatives (RM); c) Sartorius PTFE membrane alternatives with regards to upstream PBM; and d) Sartorius PTFE membrane alternatives with regards to downstream GOM (measured by nylon membranes).

membranes can be explained by GOM degradation on borosilicate glass membranes, as suggested by Gustin et al. (2013). In our case, we hypothesized that the Whatman and VWR membranes likely contributed to the reduction of GOM to GEM, and the GEM passed through membrane filters (Tang et al., 2022), resulting in the low amount of GOM collected by the downstream nylon membranes. The explanation for the significant difference between the two borosilicate glass membrane producers is unclear and likely originates from unspecified manufacturing differences.

Nylon thermal desorption profiles of RMA5 (RM) and RMA5 + P (GOM) were statistically different (Fig. S6) when comparing all data pairs for all Hg compounds (MANOVA, $p < 0.05$), and also when comparing all data pairs for individual Hg compounds (Friedman, $p < 0.05$). This result was expected, as RM and GOM chemical compositions are likely different, although the exact composition of these operationally defined forms is unknown (Subir et al., 2012). Additionally, the influence of different upstream PBM membrane materials in the RMA5 + P configuration on the chemistry of the downstream GOM on nylon membranes was examined (Fig. S7). GOM compounds captured on nylon membranes were different when comparing all data pairs for all Hg compounds (MANOVA, $p < 0.05$), and also when comparing all data pairs for individual Hg compounds (Friedman, $p < 0.05$). The difference was most evident when using upstream VWR membranes, since there was very little GOM captured on downstream nylon membranes. These results indicated that the use of different PBM membrane materials significantly influences the chemistry of the GOM that is captured downstream. Our results could also be affected by exchange interactions of co-adsorbed GOM as shown by Mao and Khalizov (2021), however our study used ambient background concentrations that are 5-orders of magnitude lower than those in Mao and Khalizov (2021). More testing is necessary to determine whether and how RMA5 membrane materials influence RM retention.

In general, historically used membranes performed the best for RM, GOM, and PBM retention, indicating that the current membrane materials used in the RMA5 system are the best currently. These observations carry implications not only for the RMA5 system, but also for any system that employs membranes for capturing atmospheric RM compounds. Most notably, the observation that upstream PBM membranes influence both the concentration and the chemistry of GOM captured downstream implies that large biases can occur in measurement instrumentation that use PBM membranes. The concerns regarding performance of PBM membranes were further elaborated in controlled laboratory studies that are discussed below.

3.3. PBM membranes selectivity and RM membranes GOM capture efficiency

Results of controlled laboratory studies for exposure of PBM and RM membranes to GOM (gaseous HgBr_2 permeated from an automated calibrator) are shown in Table 1. PBM membranes that were exposed to only permeated GOM and then immediately analyzed ("immediate

exposure") revealed that both types of borosilicate glass PBM membranes (VWR and Whatman) retained large amounts of GOM (92 and 62 %, respectively), while the quartz Tekran PBM membranes retained smaller, although still significant amounts of GOM (44%). This was not the case for the Sartorius PTFE PBM membranes, as they retained comparatively negligible amounts of GOM (4% of total permeated GOM). On the other hand, all types of PBM membranes that were deployed in the RMA5 for 1 week (to collect atmospheric particulate matter) prior to exposure to permeated GOM ("exposure after 1-week") retained large amounts of GOM. The difference between immediate exposure and exposure after 1-week PBM sampling was most evident for Sartorius PTFE membranes, as 50% more GOM was retained in the latter exposure. These results indicated that GOM does not sorb to PTFE alone, and that GOM does sorb to particulate matter (PM) accumulated on PTFE surface. Thus, particles provide an active surface area for GOM retention. The extent of GOM binding to the active surface area of PM could be dependent on the chemical characteristics of PM, since PM composition has previously been shown to affect the gas-particle partitioning of reactive mercury (Rutter and Schauer, 2007). This essentially means that the selectivity of PBM membranes during real-time sampling of PBM is likely dependent on the PM composition.

Out of RM membrane materials, Pall CEM captured GOM most efficiently, with <1% GOM breakthrough. This is why the results obtained with CEM were used as the reference against which all other membrane results were compared. The breakthrough value for Pall CEM was much lower for this experiment (<1%) compared to ambient air sampling using RMA5 (<25%). This was because the laboratory test was much shorter (10 min) than ambient air sampling using RMA5 (1 week). Sterlitech PES and nylon membranes retained approximately 30% less than Pall CEM, confirming that CEM is the most appropriate material for RM quantification of all the materials tested to date.

As the name suggests, PBM membranes should be PBM-specific. The retention of GOM by PBM membranes is therefore undesirable, causing biases in atmospheric Hg speciation measurements. The results presented in this study cast doubt on the feasibility of all tested membranes to be used as accurate PBM sampling methods for atmospheric Hg speciation, further confirming findings from section 3.2. PTFE membranes performed best, but only when free from particulates. As some atmospheric Hg speciation methods use different membrane filters to separate the PBM from GOM, the validity of many PBM measurements performed in the last decades could be inaccurate. Even though certain instruments such as the Tekran 1130/1135 module and the DCS used by Tang et al. (2022) capture GOM using a denuder upstream of the quartz PBM membrane filter (Landis et al., 2002; Tang et al., 2022), thereby potentially avoiding the problem of GOM retention by PBM membranes, the denuder has been shown to be subject to GOM losses of more than 70% under certain sampling conditions (Huang et al., 2013; Lyman et al., 2010). GOM that is not retained by the denuder can then be retained by the downstream quartz PBM filter, causing biases in atmospheric mercury speciation measurements. However, more work done on these specific configurations is needed to fully confirm our

Table 1

Undesirable sorption of GOM by PBM membranes (PBM membranes selectivity) and GOM capture efficiency of RM membranes. Gaseous HgBr_2 obtained from an automated permeation calibrator was used as the GOM surrogate. Values are given relative to Pall CEM, as these membranes were shown to capture GOM quantitatively.

PBM membrane material	Immediate exposure to GOM (n = 9)				Exposure to GOM after PBM sampling (n = 9)			
	VWR glass	Sartorius PTFE	Whatman glass	Tekran quartz	VWR glass	Sartorius PTFE	Whatman glass	Tekran quartz
Rel. % GOM sorption ^a , AVG ± SD	92 ± 9.3%	4.0 ± 2.2%	62 ± 9.9%	44 ± 17%	69 ± 9.9%	55 ± 8.4%	67 ± 6.6%	35 ± 8.3%
RM membrane material	Sterlitech PES	Sartorius nylon						
Rel. % GOM sorption ^a , AVG ± SD	70 ± 7.2%	64 ± 7.5%						

^a Rel. % GOM sorption = $\frac{\text{GOM sorbed by membrane material}}{\text{GOM sorbed by Pall CEM}}$.

hypothesis. Since the separation of GOM and PBM seems challenging for the currently available methodology, measuring them cumulatively as RM would provide more reliable measurement data (Gustin et al., 2021a). The separation is challenging not only due to sorption of GOM on PBM filters, but also due to analytical challenges with certain methods used for GOM retention, such as denuders (Dunham-Cheatham et al., 2023; Huang et al., 2013; Jaffe et al., 2014). However, we do note that HgBr_2 does not represent all of the oxidized Hg compounds comprising GOM, and the results for different oxidized Hg compounds (e.g., HgCl_2 , HgO , etc.) might differ from our HgBr_2 observations.

PBM membranes selectivity results also have implications for atmospheric Hg analysis when only the Tekran 2537 module is used for measuring TGM/GEM, without the 1130/1135 modules for GOM and PBM measurement. Since a PTFE filter is used upstream of the 2537 analyzer, this means that some GOM will be retained by the PTFE filter, that is used to prevent particulates from entering the analyzer. The 2537 module therefore measures an atmospheric Hg fraction that is somewhere between TGM and GEM, unless an upstream thermolyzer or a filter capturing RM is used for measuring TGM and GEM, respectively. Detailed tests of GOM interaction with the 2537 analyzer and gold traps used in the same analyzer will be shown elsewhere (Gačnik et al. in prep).

3.4. Membrane cartridge adsorption

Overall, less than 5% of the RM that was captured by the CEM was retained on the inside surfaces of the membrane cartridge. The amount of RM that was adsorbed to the inlet piece of the membrane cartridge ($4 \pm 1 \text{ pg m}^{-3}$) with a CEM was greater than the RM adsorbed to the outlet ($0.2 \pm 0.2 \text{ pg m}^{-3}$) (*t*-test, $p < 0.05$). This difference is due to RM being in contact with cartridge only upstream of the CEM (inlet) and not downstream of the CEM (outlet), indicating that the CEM retained RM and minimal RM passed through to be able to interact with the outlet piece. Thus, membrane cartridge adsorption of RM cannot be considered a contributing factor to the RM concentration discrepancies seen between the RMA and DCSs in Dunham-Cheatham et al. (2023) (Fig. S8).

4. Conclusions

The presented work highlights that the selection of operating conditions of atmospheric Hg speciation systems should not be arbitrary, as demonstrated by the low RM concentrations determined using the RMA at increased sampling flows. The seasonal variation of the observed differences (larger discrepancies between low and high flows in winter than in spring/summer) is likely due to particulate matter and differing chemistry/sources of atmospheric RM. In addition, the evaluation of alternative RMA membrane materials demonstrated that some materials perform better than others; the choice of membrane material is particularly important for the temperature desorption profiles and qualitative analysis of RM compounds. Overall, the historically used membrane materials (Pall CEM and Sartorius nylon membranes for RM, and Sartorius PTFE for PBM) outperformed tested membrane alternatives, giving confidence to historical RM measurements using the RMA.

Adsorption of Hg onto the membrane cartridge was negligible, and thus, does not solely contribute to the discrepancies observed between RM measurements made with the RMA and the two DCSs in Dunham-Cheatham et al. (2023).

Ambient air sampling combined with laboratory results using the GOM calibrator revealed that there is a two-fold issue associated with the use of PBM membranes: i) PBM membranes are not selective for PBM due to additional retention of large amounts of GOM; and ii) GOM retained on specific PBM membranes is assumed to be largely reduced to elemental mercury (based on comparisons with literature findings). This two-fold issue was most pronounced for borosilicate glass membranes; the Tekran instrument and certain DCS systems could also be subject to this problem. Since denuder losses of GOM have been reported in the

literature, GOM that is not retained by the denuder can then be retained by the downstream PBM filter, causing biases in measurement of different atmospheric mercury forms. For this reason, new surfaces and/or methods need to be identified or developed for PBM measurements. The Hg community needs a calibrated standard measurement technique for atmospheric RM concentrations.

CRedit authorship contribution statement

Natalie Allen: Investigation, Writing – original draft, Data curation, Validation, Visualization. **Jan Gačnik:** Investigation, Writing – original draft, Conceptualization, Visualization. **Sarah M. Dunham-Cheatham:** Investigation, Conceptualization, Supervision, Writing – review & editing. **Mae Sexauer Gustin:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

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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.2023.120240>.

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