

Release of mercury halides from KCl denuders in the presence of ozone

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Abstract. KCl-coated denuders have become a standard method for measurement of gaseous oxidized mercury, but their performance has not been exhaustively evaluated, especially in field conditions. In this study, KCl-coated and uncoated quartz denuders loaded with HgCl₂ and HgBr₂ lost 29–55% of these compounds, apparently as elemental mercury, when exposed to ozone (range of 6–100 ppb tested). This effect was also observed for denuders loaded with gaseous oxidized mercury at a field site in Nevada (3–37% of oxidized mercury lost). In addition, collection efficiency decreased by 12–30% for denuders exposed to 50 ppb ozone during collection of HgCl₂. While data presented were obtained from laboratory tests and as such do not exactly simulate field sampling conditions, these results indicate that the KCl denuder oxidized mercury collection method may not be as robust as previously thought. This work highlights needs for further testing of this method, clear identification of gaseous oxidized mercury compounds in the atmosphere, and development of field calibration methods for these compounds.

1 Introduction

The atmosphere is a major pathway by which mercury pollution reaches ecosystems (Fitzgerald et al., 1998). Since different atmospheric mercury forms exhibit different chemical and physical behavior (Schroeder and Munthe, 1998), accurate measurements of all forms are critical to understanding this pathway. Gaseous elemental mercury (GEM), particle-bound mercury (PBM), and gaseous oxidized mercury (GOM, a.k.a. RGM) are generally recognized as forms of significance (Landis et al., 2002). Though not the most

abundant atmospheric form, GOM is particularly important because it has a higher deposition velocity (Schroeder and Munthe, 1998) and is more directly bioavailable (Ullrich et al., 2001) than other forms. Although the chemical forms of GOM are not known, they are thought to include compounds such as HgCl₂ (Lindberg and Stratton, 1998), HgBr₂ (Holmes et al., 2006), HgO (Lin et al., 2006), and/or others. The importance of measuring oxidized mercury compounds separately from total gaseous mercury has been recognized since the 1970s (Braman and Johnson, 1974; Johnson and Braman, 1974), but no method for measurement of GOM was widely accepted until the early 2000s (a history of GOM measurement methods is given in Landis et al., 2002).

In 2002 Landis et al. published an article detailing a method, commercialized by Tekran Instruments Corporation, to measure GEM, PBM, and GOM. This method utilized quartz denuders constructed with an outer tube and an inner annulus, and a portion of the tube and annulus were frosted and coated with a KCl solution (Landis et al., 2002). It is presumed that GOM collects on KCl denuders because of a chemical interaction with the KCl surface. Previous work also utilized KCl denuders and showed that this surface collected HgCl₂ efficiently without interference from GEM in a lab setting (Xiao et al., 1997). Landis et al. (2002) analyzed denuders by heating them to release sorbed GOM as GEM, which was then analyzed by atomic fluorescence spectrometry (performed with a Tekran 2537 mercury analyzer). Laboratory and field tests described by Landis et al. (2002) showed that KCl denuders had lower blanks and better precision than other existing GOM measurement methods.

Since the development of this method well over 100 peer-reviewed publications utilizing KCl denuders for GOM measurements have been published and few competing methods have emerged (exceptions include Rutter et al., 2008; Lyman et al., 2009; Deeds et al., 2009). We emphasize, however, that although KCl denuders are in wide use, they have not been exhaustively evaluated. Experiments testing the collection



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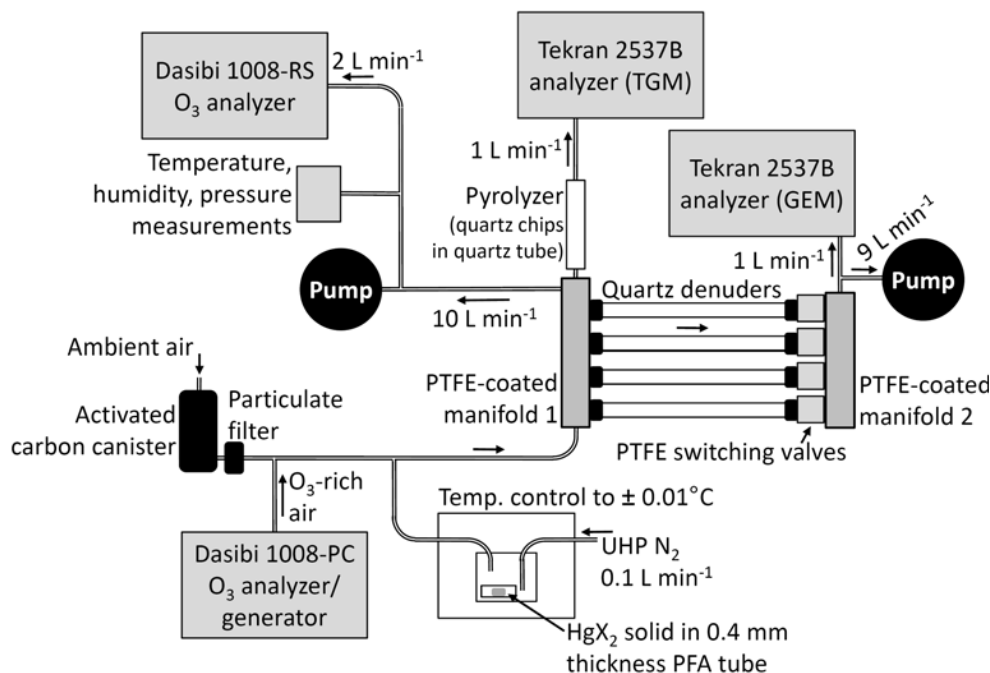


Fig. 1. Schematic of sampling system. All sample lines and the manifold upstream of the quartz denuders and pyrolyzer were heated to 100 °C. Sample lines were constructed of 0.64 cm PFA tubing. Denuders were connected to manifold 1 via Delrin couplers. The pyrolyzer was heated to 500 °C and denuders were heated to 50 °C. Switching valves allowed only one denuder to sample at a time. Mass flows are shown (STP of 0 °C, 1013 mb). The Dasibi 1008-PC was supplied with ambient air that had passed through an activated carbon canister.

efficiency of KCl denuders have been performed in laboratory settings with purified air and a single GOM compound (HgCl_2 ; e.g. Landis et al., 2002 and Xiao et al., 1997). Denuder performance in field settings has only been evaluated in a relative sense via intercomparisons of identical denuder systems or comparisons of KCl denuders with alternative GOM methods (Munthe et al., 2001; Sheu and Mason, 2001; Landis et al., 2002; Aspö et al., 2005; Lyman et al., 2009). Additionally, no robust calibration technique exists for GOM measurements.

In a departure from accepted methods, Swartzendruber et al. (2009a) recently reported measurements of GOM from aircraft using a dual channel system wherein total atmospheric mercury (TAM) was measured by a Tekran 2537 that pulled sample air through a pyrolyzer, and GEM was measured with another Tekran 2537 that pulled sample air through a KCl denuder and a particulate filter. High time resolution measurements of GOM were determined as TAM minus GEM (PBM was below detection in most cases). While this setup was unique, it still relied on KCl denuders to capture GOM. The results of this study were promising, and our group has continued field and laboratory work to characterize and improve this system. However, during multiple laboratory tests with HgCl_2 and HgBr_2 (i.e. HgX_2) added to ambient air, we noticed that the collection efficiency of KCl denuders was inversely related to ambient concentrations of

ozone in sampled air. We present here the results of experiments designed to 1) demonstrate whether HgX_2 compounds and ambient gaseous oxidized mercury loaded onto denuders are released when exposed to ozone and 2) show whether denuders that sample GOM in the presence of ozone have lower collection efficiency than denuders that sample in ozone-free air.

2 Methods

Three experimental designs were applied: In the first, denuders were exposed to ozone after being loaded with HgX_2 in the laboratory to explore the effects of ozone on sorbed HgX_2 . In the second, denuders were exposed to ozone after being loaded with ambient GOM at a field site in Nevada to determine whether ozone affected ambient GOM compounds. In the third, denuders were loaded with HgCl_2 in the laboratory in the presence or absence of ozone to simulate ozone exposure during field denuder sampling conditions.

2.1 Laboratory system for loading denuders with HgX_2

The system used for loading denuders with HgX_2 in the laboratory was adapted from that of Swartzendruber et al. (2009a), and is shown in Fig. 1. Mercury halides used for permeation were purchased from Sigma Aldrich and were

99.999% and 99.998% pure HgCl_2 and HgBr_2 , respectively. The permeation rate for HgX_2 was controlled by adjusting the temperature and/or permeable area of the permeation tube. The stability of the permeation rate was 8% (derived from replicate denuder samples), and there was no observable trend over time ($p = 0.74$). The Tekran 2537B analyzers shown in Fig. 1 measured TGM concentrations in air that passed through the pyrolyzer and GEM concentrations in air that passed through a denuder at 2.5 min resolution. GOM concentrations were calculated based on the difference between these and from denuders directly.

Sample lines were kept at 100°C to minimize wall loss of HgCl_2 and HgBr_2 . The standard inlet temperature for KCl denuder sampling has been 50°C (Landis et al., 2002), but we found that at 50°C sample lines quickly became contaminated by the permeated HgX_2 . The rates of some chemical reactions, such as ozone decomposition, may have been accelerated by the higher temperature and could have slightly changed the chemistry of sample air. Significant thermal decomposition of mercury halides at this temperature is unlikely, since the theoretical reaction rate for HgCl_2 decomposition at 100°C is $\sim 1 \times 10^{-26} \text{ s}^{-1}$ (Wilcox and Blowers, 2004), and since the residence time of sample air in the heated portion of the system was $\sim 0.4 \text{ s}$.

The KCl-coated quartz denuders used in this study were identical to the denuders for manual sampling described by Landis et al. (2002) and were cleaned and coated according to the methods of Landis et al. (2002). Denuders consisted of an outer tube and an inner annulus, with a 25 cm etched active surface length and 1 mm of space between the outer tube and annulus. Coating was accomplished by drawing a 2.4 M KCl solution to the top of the active surface, drying the denuder, then conditioning the active surface at 500°C for 1 h. Denuders were blanked less than 24 h before loading by heating to 500°C for 30 min. In laboratory experiments air samples were collected for 1 h unless otherwise specified. The PTFE-coated manifolds in Fig. 1 accommodated up to four denuders, and typically valid samples were collected on three denuders, while the fourth was used during quality control checks. Denuder HgX_2 concentrations did not depend on their position on the PTFE-coated manifold ($p = 0.94$). One additional denuder was left uncapped during installation of sample denuders, and afterwards was re-capped and stored, then analyzed along with sample denuders as a blank.

2.2 Denuder analysis system

Denuders loaded with GOM were analyzed using the system shown in Fig. 2, which allowed control of ozone concentration, water vapor concentration, and denuder temperature. Ozone concentration was controlled by regulating the intensity of the ozone-generating UV lamp within the Dasibi 1008-PC. The Tekran 2537B measured the amount of mercury released from denuders with 2.5 min resolution. Soda lime traps were not used. This setup was able to produce air

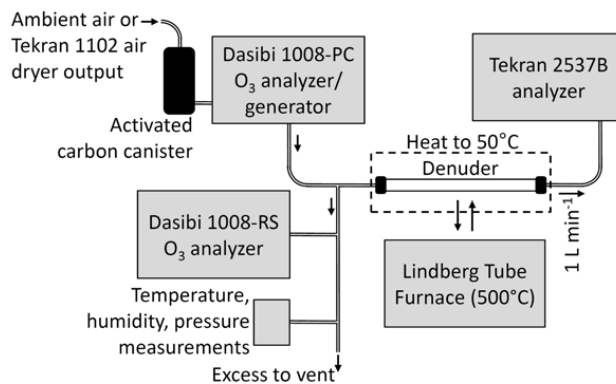


Fig. 2. Schematic of analytical system for quartz denuders. Tubing shown is 0.64 cm outer diameter PFA. Denuders were coupled to tubing via PTFE-lined thermoplastic caps. Mass flow is shown (STP of 0°C , 1013 mb).

with a mercury concentration below the detection limit of the 2537B, and, if no denuder was in place, the mercury concentration was not dependent on the ozone concentration.

Denuders loaded in the laboratory were analyzed within 24 h, and field denuders were analyzed within 2–4 days. During analysis, a denuder was installed on the system, then the Tekran 2537B pulled mercury-free air through it for 5 min to establish a baseline or zero value. Denuders were then either heated for 30 min or first subjected to a constant ozone concentration for 30 min, then heated for 30 min (no ozone during heating). During ozonation, denuders were kept at 50°C . The amount of mercury collected by denuders was calculated as the sum of all the 2.5 min Tekran 2537B outputs during ozonation and/or heating (in pg), and was blank corrected using values from the initial 5 min of zeroing ($\ll 1\%$ of total mercury on denuders).

2.3 Experimental design 1: ozonation after loading with HgX_2 in lab

In the laboratory, three sets of three KCl-coated denuders were loaded with HgBr_2 , four sets were loaded with HgCl_2 , and one set of uncoated (i.e. no KCl) denuders was loaded with HgCl_2 . For each set, two denuders and the accompanying blank were ozonated for 30 min then heated for 30 min, and one denuder was heated for 30 min without prior ozonation. Varying ozone and water vapor concentrations were used during these analyses.

In two additional tests with KCl denuders loaded with HgCl_2 , a blank KCl denuder was added immediately downstream from the sample denuder during analysis (via a Delrin coupler) to examine the nature of HgCl_2 loss during ozonation.

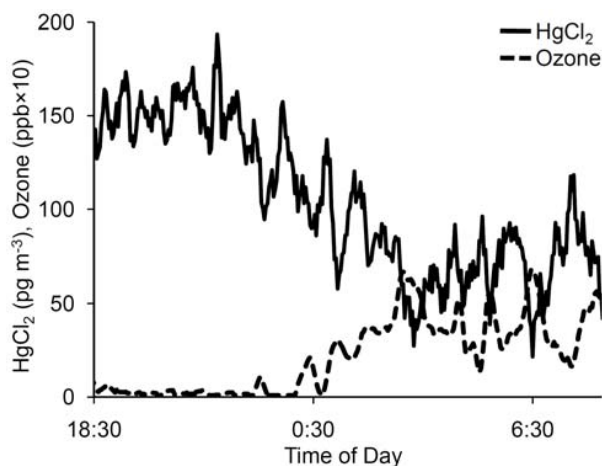


Fig. 3. Moving average (of five 2.5 min measurements) of HgCl_2 concentration (measured as the difference between TGM and GEM) and ozone concentration. HgCl_2 was added at a constant rate to particulate-filtered ambient air in a setup similar to that shown in Fig. 1, but the measured HgCl_2 concentration decreased as ambient ozone increased. Note that the 2.5 min detection limit for HgCl_2 concentration was 76 pg m^{-3} , while the 30 min detection limit was $\sim 30 \text{ pg m}^{-3}$.

2.4 Experimental design 2: ozonation of field denuders

Ambient GOM was collected onto three sets of KCl denuders at a field site established for measuring atmospheric mercury in Reno, Nevada (39.51° latitude, -119.72° longitude, elevation 1340 m; Lyman and Gustin, 2009). Air was pulled at $10 \text{ standard L min}^{-1}$ (standard conditions of 25°C and 1013 mb) through triplicate denuders at 4 m above ground level and maintained at 50°C . Impactors with $2.5 \mu\text{m}$ cut-points were placed upstream of denuders to remove coarse particles. Field denuders were analyzed as described in Sect. 2.2.

2.5 Experimental design 3: ozonation during collection of HgCl_2

To determine whether the presence of ozone during collection of HgCl_2 influenced collection efficiency, HgCl_2 was loaded onto two denuders sequentially, one in the presence of 50 ppb ozone and one in ozone-free air (this was done for three sets of two denuders). After collection, both denuders and a blank were analyzed by heating for 30 min (no ozone).

2.6 Quality control and data processing

Tekran 2537B analyzers were calibrated before and after each analysis period using their internal temperature-controlled permeation sources. Instrument performance was verified weekly by multiple injections of a known quantity

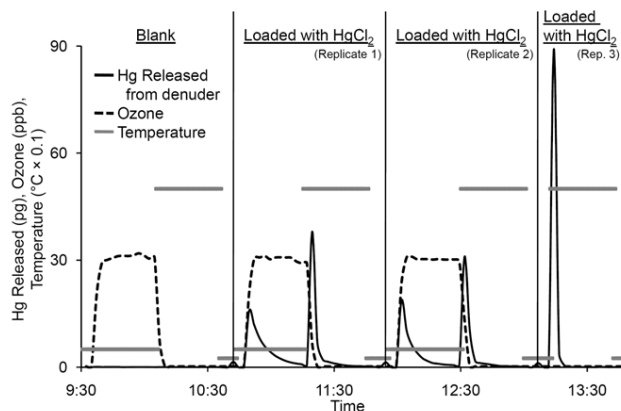


Fig. 4. Mercury released from replicate denuders subjected to 30 ppb ozone and/or heat, measured in pg released per 2.5 min sample period of the Tekran 2537B analyzer. The blank denuder was prepared as described in Sect. 2.1, and the denuders with HgCl_2 were loaded as described in Sect. 2.1. The last denuder in the series was analyzed by heating without ozone.

of GEM from a temperature controlled source (Tekran 2505) into sample air via an external injection port. Permeation sources were checked quarterly by injections of a known quantity of GEM into mercury-free air.

As discussed by Swartzendruber et al. (2009b), the detection limit for Tekran 2537 analyzers can be improved by determining mercury mass from peak height instead of the default automated peak area integration method. In this work, mercury mass per 2.5 min sample (pg) and mercury concentration (pg m^{-3}) were obtained by 1) processing the raw peak output of 2537B analyzers using a custom Matlab script to obtain peak heights, 2) determining a linear regression curve for mass loadings during internal calibrations (including zeros) versus peak height, 3) using the regression equation to determine pg mercury for each sample, and 4) dividing that value by the sample volume (at standard conditions of 0°C and 1013 mb) to determine concentrations.

At the start of each experiment, the 2537B analyzers sampled mercury-free air for at least 30 min, and detection limits for GEM, TGM, and GOM by difference were calculated as three times the standard deviation of concentrations measured during this period. Detection limits were $0.09 \pm 0.03 \text{ pg}$ ($34 \pm 12 \text{ pg m}^{-3}$; mean \pm standard deviation), $0.16 \pm 0.03 \text{ pg}$ ($64 \pm 12 \text{ pg m}^{-3}$), and $0.19 \pm 0.04 \text{ pg}$ ($76 \pm 15 \text{ pg m}^{-3}$), respectively. Denuder blanks were $0.9 \pm 0.3 \text{ pg}$, and the detection limit for GOM measured by denuders was 0.9 pg (1.5 pg m^{-3}), calculated as three times the standard deviation of blanks.

Table 1. Results of experiments in which denuders were loaded with HgX₂, then analyzed via 30 min ozone followed by 30 min heating at 500 °C with no ozone. The right-most columns show mean ± standard deviation for two replicate denuders.

Experimental design 1: ozonation after loading with HgX ₂ in Lab						
HgX ₂	Denuder	O ₃ During	H ₂ O During	Total Hg per	% Hg lost in	% Hg lost in
Compound	Type	Anlys. (ppb)	Anlys. (g/kg)	Denuder (pg)	2.5 min O ₃	30 min O ₃
HgBr ₂	KCl	100	0.1	345 ± 31	24 ± 3%	48 ± 4%
HgBr ₂	KCl	29	0.5	95 ± 9	11 ± 3%	55 ± 3%
HgBr ₂	KCl	30	6.0	69 ± 2	16 ± 0%	53 ± 8%
HgCl ₂	KCl	29	0.1	94 ± 2	22 ± 4%	40 ± 3%
HgCl ₂	KCl	6	0.1	96 ± 2	5 ± 2%	33 ± 0%
HgCl ₂	KCl	30	3.8	102 ± 10	17 ± 4%	51 ± 1%
HgCl ₂	KCl	29	0.3	11 ± 1	26 ± 0%	37 ± 1%
HgCl ₂	uncoated	29	0.1	95 ± 3	10 ± 2%	29 ± 7%

Table 2. Results of experiments in which denuders sampled ambient GOM at the Nevada field site. Denuders were analyzed via 30 min of ozone followed by 30 min of heating at 500 °C with no ozone.

Experimental design 2: ozonation of field denuders									
During Deployment at Field Site					During Analysis				
Date	Deploy	O ₃	Temp.	Humidity	O ₃	H ₂ O	Total Hg Per	% Hg lost in	% Hg lost in
Collected	Length (h)	(ppb)	(°C)	(%)	(ppb)	(g/kg)	Denuder (pg)	2.5 min O ₃	30 min O ₃
2010/2/16	5.5	26 ± 11	11.5 ± 2.9	50 ± 8	30	0.1	45 ± 33	2 ± 1%	3 ± 2%
2010/2/25	6.0	40 ± 5	7.7 ± 2.1	53 ± 9	30	0.3	15 ± 9	11 ± 4%	14 ± 3%
2010/3/15	6.8	42 ± 6	11.3 ± 3.6	24 ± 6	30	0.1	40 ± 16	20 ± 3%	37 ± 10%

3 Results and discussion

Figure 3 shows an example of the multiple observations that prompted this investigation. These initial experiments (described in the Introduction) were performed using a system similar to that shown in Fig. 1. They were carried out with the intention of performing quality control checks on the system described by Swartzendruber et al. (2009a). In Fig. 3 when the ambient ozone concentration was near zero ppb, the HgCl₂ concentration measured as the difference between TGM and GEM was about 150 pg m⁻³, but as the ozone concentration increased to about 5 ppb the measured HgCl₂ concentration dropped to about half its original value, resulting in an anticorrelation between HgCl₂ concentration and ozone ($r = -0.70$, $p < 0.001$). Experimental Designs 1–3 (Sects. 2.3–2.5; results below) were designed to determine whether the change in HgCl₂ concentration could be explained by the change in ozone concentration.

Table 1 shows that denuders loaded with HgX₂ in the laboratory and then ozonated for 30 min released 29–55% of the HgX₂ originally present on denuders. A representative analysis of a set of loaded denuders is shown in Fig. 4. The percentages of HgX₂ released in 30 min of ozonation were not significantly different for different ozone or water vapor concentrations, different HgX₂ concentrations or species, or presence or absence of KCl coatings (possibly due to small sample sizes; $n = 2$ for each condition). However, the percentages of HgX₂ released in the first 2.5 min were significantly different for 30 versus 6 ppb ozone ($p = 0.03$), for KCl-coated versus uncoated denuders ($p = 0.02$), and for denuders loaded with HgCl₂ versus HgBr₂ ($p = 0.04$). The percentages of HgX₂ released from denuders in the presence of high versus low water vapor concentrations were marginally significant for denuders loaded with HgBr₂ ($p = 0.07$), and insignificant for denuders loaded with HgCl₂ ($p = 0.25$). The percentage of HgCl₂ lost from denuders did not depend on the amount of HgCl₂ they contained ($p = 0.34$). Note

Table 3. Mercury collected by KCl denuders loaded with HgCl₂ in the presence of 50 ppb ozone or no ozone.

Experimental design 3: ozonation during collection of HgCl ₂				
Denuder with Ozone During Loading		Denuder without Ozone During Loading		Difference (%)
O ₃ Conc. (ppb)	Total Hg on Denuder (pg)	O ₃ Conc. (ppb)	Total Hg on Denuder (pg)	
50	85	0	110	23%
50	89	0	101	12%
50	86	0	123	30%

that the precision of replicate KCl denuder measurements is on the order of 15% (Landis et al., 2002).

While it is possible that the ozone generator produced reactive compounds other than ozone that influenced these results, it is likely that ozone was the dominant reactant. A literature search and inquiries to manufacturers were unable to produce evidence for the production of significant amounts of non-ozone reactive compounds by UV lamp-based ozone generators. Blank denuders released 0.5 ± 0.5 pg mercury when exposed to ozone, less than 1% of the amount released from loaded denuders, indicating that the ozone generator was not a significant mercury source.

We note that the analytical system employed for the above experiments is different from typical sampling conditions for KCl denuders in that 1) the flow rate through denuders was lower during ozonation; 2) the denuders were exposed to ozone after collection of oxidized mercury, instead of during collection; 3) mercury halides were used as surrogates for ambient GOM compounds, the chemical speciation of which is unknown; 4) denuders were exposed to ozone in activated carbon-scrubbed air, not ambient air. Due to these differences, the amount of oxidized mercury lost from denuders in these experiments is likely not quantitatively representative of any bias caused by ozone in typical field conditions.

Table 2 shows that denuders loaded with GOM at the Nevada field site also lost mercury in the presence of ozone, though the percent loss was more variable. While variability was high among different sample sets, the amount of ozone-mediated mercury loss within each sample set was quite consistent, indicating good experimental control. This shows that ozone can remove oxidized mercury compounds collected from the ambient atmosphere, though more comprehensive research is clearly merited. The cause of variability among field denuder sample sets may be due to differences in atmospheric composition during collection that caused GOM on denuders to respond differently to ozone. Alternatively, since the amount of mercury released from denuders in Experimental Design 1 was different for HgCl₂ and HgBr₂ for the first 2.5 min of ozonation, it is possible that differences in

the chemical speciation of GOM at the field site contributed to the variability of results. The observed variability in these results and those from laboratory denuders may also be due to other factors such as small variations in the KCl coating or geometry of denuders, or other factors that are as yet unknown.

Table 3 shows that the amount of HgCl₂ collected by denuders in the presence of 50 ppb ozone was $21 \pm 9\%$ less than the amount collected by denuders in ozone-free air (10 L min⁻¹ sampling rate). At the same time, GEM concentrations measured downstream of denuders were higher in 50 ppb ozone than in ozone-free air ($p = 0.07$), which was likely due to mercury released from denuders during sampling of HgCl₂ in the presence of ozone.

When newly blanked denuders were placed downstream from denuders loaded with HgCl₂ and 30 ppb ozone was added, the downstream denuders collected 0.07 ± 0.02 pg mercury, a value that was less than denuder blanks ($p = 0.02$) and less than 1% of the ozone-induced loss of HgCl₂ from the upstream denuders. We expect that little ozone was experienced by the downstream denuders in this setup, since Lynam and Keeler (2005b) showed that at an ambient ozone concentration of 29 ppb, 95% of ozone in sample air is destroyed as it passes through KCl denuders. Thus, mercury released from denuders in the presence of ozone was in a form that was not captured by the downstream KCl denuder or the subsequent sample lines and particulate filter of the 2537B analyzer. This suggests that the liberated mercury may have been GEM.

The HgCl₂ concentration derived from KCl denuders was not different from the concentration derived from uncoated denuders ($p = 0.81$), indicating that uncoated denuders collected HgCl₂ as efficiently as KCl-coated denuders. What is more, in preliminary experiments with a modified version of the setup in Fig. 1, we sampled HgCl₂ at 10 L min⁻¹ with an uncoated denuder followed by a KCl denuder coupled immediately downstream with a Delrin coupler (both denuders were kept at 50 °C). In these experiments ($n = 2$), breakthrough from the uncoated denuder to the KCl denuder was $0.5 \pm 0.1\%$, less than the breakthrough for KCl denuders determined in a similar experiment by our group (2.1%), and less than the breakthrough reported by others for KCl denuders (3.9% by Feng et al., 2000; 6% by Landis et al., 2002). While our experiments with uncoated denuders involved only HgCl₂, these lines of evidence indicate that some GOM compounds may not require KCl or any other chemical coating for efficient collection, provided no ozone is present.

4 Implications

These findings show that GOM measurements made with KCl denuders may be biased low in the presence of ozone, and the extent of the bias may depend on ambient ozone concentrations. While the different experiments performed

yielded different rates of oxidized mercury loss from KCl denuders, all experimental designs demonstrated a significant loss of mercury when denuders were exposed to ozone, showing that this effect is consistent for ambient (Fig. 3) and lab-produced ozone (Table 1), ambient (Table 2) and lab-produced oxidized mercury compounds (Table 1), and in idealized (Table 1) and more typical sampling conditions (Table 3).

We note that our findings corroborate those of Engle et al. (2005), which showed that ozone increased the flux of mercury from HgCl₂-enriched soils, though they reported that both GEM and GOM were released. Zhang et al. (2008), Watras et al. (2009), and Gustin and Ladwig (2010) also point to daytime atmospheric oxidants as drivers of mercury release from soils, laboratory surfaces, and coal combustion waste products, respectively. Our research shows that oxidized mercury compounds on inert surfaces (uncoated quartz denuders) can be removed in the presence of ozone, pointing to a possible mechanism for this phenomenon.

Several studies have reported a positive correlation between ambient ozone and GOM concentrations (e.g. Swartzendruber et al., 2006; Lynam and Keeler, 2005a; Choi et al., 2008; Peterson et al., 2009), but these do not constitute opposing evidence, since the effects of an ozone-induced bias on GOM measurements could feasibly be outweighed by a temporal relationship between the two compounds in the atmosphere. Note also that in a sampling setup which measures GEM downstream of a KCl denuder (e.g. the Tekran 1130 system) any oxidized mercury lost from denuders during sampling can be expected to be measured as GEM. In other words, while ozone may bias GOM measurements low, TGM (i.e. GEM + GOM) is likely unaffected.

The results presented here show that a bias exists under controlled conditions for HgX₂ compounds, but they do not show the quantitative extent of the bias for field GOM measurements. Quantification of the extent of any ozone-induced bias on KCl denuder measurements in the real atmosphere will require the development of a robust field calibration/spike method for representative GOM compounds. Indeed, because of the labile nature of mercury compounds, and because of the uncertainty inherent in the pre-concentration step required for trace mercury measurements, we feel that regular matrix spikes of representative gas-phase mercury compounds into ambient sample air should be an integral part of all atmospheric mercury measurements.

This work highlights the incompleteness of our understanding of GOM in the atmosphere and the need for further characterization of the KCl denuder method. Since almost all GOM measurements made in the past decade have utilized KCl denuders, confirmation of the existence and significance of an ozone-induced bias would likely have a broad impact on scientific understanding of GOM distribution and cycling. We recommend research in the following areas to increase our understanding of GOM in the atmosphere (as

have others, e.g. Lindberg et al., 2007; Pirrone et al., 2008; Gustin and Jaffe, 2010):

1. Identification of the chemical forms of GOM,
2. Comprehensive evaluation of the KCl denuder method (and/or alternative methods), including its response to specific compounds and possible interferences, and
3. Development of a stable and traceable calibration method for a variety of oxidized mercury compounds that can be readily deployed during field measurements.

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