

Experimental investigation of the scavenging of gaseous mercury by sea salt aerosol

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Abstract Sea salt aerosol may be an important sink for reactive gaseous mercury (RGM) in the marine boundary layer, reducing ambient RGM concentrations and transferring the mercury (Hg) to the oceans and coastal ecosystems. The goal of this study was to determine the affinity of gaseous mercury for sea salt aerosol (SSA) by conducting adsorption experiments with sea salt-coated sampling denuders. In the first set of experiments, ambient outdoor air was passed through denuders coated with either KCl, as in the widely accepted method to sample RGM, or with NaCl, a primary component of sea salt aerosols. On the one sampling day in which RGM was above the MDL, the NaCl coated denuders removed Hg from the ambient air, equivalent to 87% of the RGM in the air (as determined by KCl denuders). For the second set of experiments HgCl₂ generated in the laboratory was passed through denuders coated with KCl and either NaCl or sea salt. The NaCl denuders collected an average of 99±16% of the mercury that the KCl denuders collected. Newly coated sea salt denuders collected 88±17% of the amount of mercury that the KCl denuders collected, but interestingly the sea salt denuders capacity decreased with repeated use. These experiments demonstrate that HgCl₂, a major component of RGM has a strong affinity for NaCl and sea salt and is therefore likely to be scavenged by SSA. This study adds to the growing evidence that RGM is scavenged by sea salt aerosols and therefore more quickly deposited to the ocean and coastal environment.

Keywords Gas-particle partitioning · Reactive gaseous mercury · Atmospheric mercury · Particulate mercury · Marine boundary layer · Sodium chloride

1 Introduction

Pioneering mercury research in lacustrine and forested watersheds demonstrated that mercury could be transported through the atmosphere on regional and global scales,

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affecting even remote locations. These studies led to the realization that an understanding of the atmospheric chemistry of mercury is necessary for predicting its atmospheric transport and deposition. In the last decade, many researchers have shifted attention to coastal and open ocean environments. What they have found is a unique and dynamic environment. The chemical cycling of atmospheric mercury is greatly influenced by the chemistry of the marine boundary layer (MBL), which includes many reactive halogen compounds. The halogen gas bromine, along with other photochemically produced oxidants (Lin and Pehkonen 1999; Seigneur and Lohman 2008; Selin 2009), rapidly convert some of the abundant, long lived elemental gaseous mercury (Hg_{g}^0) to oxidized gaseous forms of mercury, collectively known as reactive gaseous mercury (RGM). RGM is then quickly removed from the atmosphere through wet and dry deposition processes. Several recent modeling studies, field measurements, and laboratory experiments have begun to elucidate these processes and their importance for the local and global transport and deposition of mercury (For example see: Sprovieri and Pirrone 2008; Holmes et al. 2009; Engle et al. 2008). There is an additional importance to understanding mercury (Hg) cycling in the MBL because many people throughout the world are exposed to mercury through consumption of marine fish. The full impact of anthropogenic atmospheric emissions on the concentrations of mercury in seafood is just beginning to be understood (Sunderland et al. 2009; Kraepiel et al. 2003). This study adds to the growing evidence that RGM is scavenged by sea salt aerosols and therefore more quickly deposited to the ocean and coastal environment.

The chemical form of mercury affects its transport and deposition, so a complete understanding of atmospheric mercury's chemical and physical transformations is crucial to predicting the fate of mercury emissions. Three major forms of mercury exist in the atmosphere: elemental gaseous (Hg_{g}^0), reactive gaseous (RGM or $\text{Hg}_{\text{g}}^{\text{II}}$), and particulate phase (Hg_{p}). Hg_{g}^0 typically comprises over 95% of Hg in the atmosphere and is relatively inert, with a lifetime estimated to be 6 months to 1 year (Lin and Pehkonen 1999). Consequently, Hg_{g}^0 can be distributed on a global scale. RGM, on the other hand, is water-soluble and reactive with a high dry deposition velocity, causing it to be deposited to ecosystems close to its source (Lin and Pehkonen 1999; Schroeder and Munthe 1998). RGM is operationally defined, based on widely used sampling techniques; however, the separate chemical components of RGM have not been individually measured in the field. They are expected to include Hg(II) gases such as HgCl_2 , HgBr_2 and HgO . Hg_{p} is also readily deposited by wet or dry deposition mechanisms, dependent on the size and chemical properties of the aerosol particle.

Open ocean and coastal environments have high concentrations of sea salt aerosols (SSA), which are released from the ocean surface (Lewis and Schwartz 2004). Owing to high humidity in coastal environments and their hygroscopic nature, sea salt particles are typically deliquesced, having an associated aqueous phase that could facilitate mass transfer of RGM. Soluble gases like RGM preferentially partition into the aqueous phase, as evident by the Henry's Law Coefficient of HgCl_2 (3.7×10^{-5} Pa·m³/mol). In contrast, the Henry's Law Coefficient for the less soluble Hg_{g}^0 is 729 Pa·m³/mol. Consequently, RGM is expected to partition more rapidly into SSA. Based on the reactive nature of RGM gases, we predict that RGM has a large mass accommodation coefficient for deliquesced or dry sea salt particles, so that a large fraction of the RGM molecules striking a SSA will be captured and dissolve into the SSA. Through this process, we expect that SSA is an important sink for RGM in the marine boundary layer, significantly reducing ambient RGM concentrations. Such scavenging of Hg gases would cause Hg to be rapidly cycled at the atmosphere-ocean interface from gaseous, to aerosol, to oceanic forms. Deposition of

aerosol enriched in Hg via this process may constitute a significant global mercury flux to the oceans. This process may also increase local deposition in coastal cities where there are large sources of anthropogenic gaseous mercury and may also enhance deposition to manmade and natural surfaces that are coated with sea spray.

As artifact-free measurements of $\text{Hg}_{(p)}$ are difficult to obtain, much of what we know about the gas-particle partitioning of mercury comes from models and a select few field and laboratory studies. Modeling studies by Pirrone et al. (2000) and Hedgecock and Pirrone (2001) suggest that $\text{Hg}_{(p)}$ with high chloride content may play a role in oxidizing mercury, and then releasing $\text{HgCl}_{2(g)}$ to the atmosphere. A measurement study in Florida (Malcolm et al. 2003) suggested that some form of gaseous mercury may be incorporated into SSA, increasing the transfer of mercury from the atmosphere to ocean. Mercury concentrations in SSA were higher than could be explained by mercury in seawater alone. Calculations based on major cations in the aerosol revealed that $\text{Hg}_{(p)}$ concentrations were $3000\times$ greater than expected if seawater was the only source of the Hg to the aerosols. A hypothesized explanation for these observations was that mass transfer of RGM to existing SSA comprised most of the particulate Hg concentration. At sites along the US Gulf Coast, Engle et al. (2008) observed Hg bound to coarse aerosol, and hypothesized that some of this was Hg bound to sea salt aerosol.

Selin et al. (2007) found that their global mercury model could not reproduce the concentration and diurnal behavior of RGM over the Pacific Ocean without including uptake of RGM by SSA. Without this sink, the modeled RGM peak concentrations were too high and did not decrease quickly enough in the afternoon. In a laboratory study of gas-particle partitioning, Rutter and Schauer (2007) found that $\text{HgCl}_{2(g)}$ preferentially partitions to dry NaCl particles. Reactive gaseous mercury compounds also preferentially partitioned to particles of sodium nitrate and potassium chloride. Partitioning of reactive mercury shifted to the gas phase for ammonium sulfate and organic aerosols. Holmes et al. (2009) used a chemical box model to investigate the production and destruction of RGM in the MBL. They predicted that under typical MBL conditions about 85% of total Hg^{II} is partitioned into SSA at equilibrium. Deposition of these aerosols accounted for 65–90% of the total RGM loss for modeling scenarios over the Pacific and Atlantic Ocean.

The aim of this study was to determine the affinity of gaseous mercury for sea salt aerosol by conducting adsorption experiments with sodium chloride and sea salt-coated sampling surfaces. Adsorption of ambient RGM, HgCl_2 , and $\text{Hg}_{(g)}^0$ were evaluated.

2 Methods

For these experiments, denuders were coated with either sodium chloride or seawater, to simulate SSA. Air containing mercury was passed over the denuders' coated surfaces and adsorption by the salt was quantified. Experiments were done using both ambient, outdoor air and a N_2 carrier gas with $\text{HgCl}_{2(g)}$ addition. Several other RGM gases in addition to HgCl_2 have been predicted to occur in the atmosphere. HgCl_2 is often chosen as a representative species for laboratory experiments (Landis et al., 2002; Rutter and Schauer 2007).

2.1 Denuders

Diffusion denuders are a common sampling device used when reactive gases must be segregated from aerosols during collection. They typically consist of single or concentric

tubes, whose inner surfaces are coated with a sorbent or reactive trapping medium for the sampling gas. Large particles are removed upstream of the denuder with cyclones or impaction inlets, and the air stream is passed through the tube at a flow rate sufficient to ensure laminar flow. This prevents small particles from impacting on the coating surface, but allows the gas of interest to diffuse to and be retained by the coating. Thus by varying the denuder coating and geometry, denuders have been designed which selectively collect gases of interest, and minimize collection of particles and unwanted gases (Appel 1993).

Potassium chloride (KCl) coated quartz annular denuders have been shown in the laboratory to be an effective method for selectively collecting RGM without collection of $\text{Hg}_{(g)}$. Landis et al. (2002) demonstrated that their capture efficiency for HgCl_2 was greater than 97%. The denuders chosen for this study are identical to those used in Landis et al. (2002) (manufactured by URG Corporation). They are annular denuders and consist of an outer tube that contains an inner tube, or annulus (Landis et al. 2002). The inside of the outer tube and outside of the annulus are coated with KCl salts, so that when air is passed through the denuder, the RGM diffuses to the KCl coating. The RGM is then thermally desorbed for quantification. For these experiments, denuders were not only coated with the standard KCl solution, but also with sodium chloride (NaCl) solution and sea water.

The NaCl and sea water coatings were chosen to chemically simulate SSA. The chemical composition of newly formed SSA is similar to that of bulk seawater, with the following constituting most of the salinity: chloride (55.04%), sodium (30.61%), sulfate (7.68%), magnesium (3.69%), calcium (1.16%) and potassium (1.10%). Minor constituents, including other ions and organic compounds total less than 1% of seawater's salinity (Trujillo and Thurman 2008). As SSA age, their composition can change however, such as by reactions with acidic gases which can reduce the chlorine content and increase the sulfur content (Lewis and Schwartz 2004). NaCl was chosen as a coating for this study because it corresponds to the two primary ions of seawater (85%), it has a high melting and boiling point (801°C and 1413°C; CRC 2009) making it suitable for a thermal denuder, and it has been successfully used as a denuder coating for HNO_3 sampling (Appel 1993). Seawater was also chosen as a coating since its more complex chemical composition will more closely mimic real SSA.

Before coating, the denuders were rinsed twice with 3.5 M hydrochloric acid solution and three times with deionized water, then dried with activated carbon filtered air. Coating was accomplished by dipping the denuder into an aqueous solution of 2.4 M KCl, 2.4 M NaCl, or concentrated seawater. The inlet was dipped three times in deionized water to help reduce the formation of salt crystals. Care was taken during the whole process to prevent the introduction of liquids into the annulus of the denuder through the vent hole. The seawater was collected from the Atlantic Ocean at approximately 0.6 m from the shoreline in Virginia Beach, VA (36°50'43" N, 75°48'26"). The water was collected in acid cleaned bottles that were rinsed three times with seawater. The salinity of the seawater was measured using a refractometer and then concentrated by gently boiling with a hotplate to reach a concentration of approximately 2.4 M.

After coating, the denuders were dried by blowing mercury free air through them. The inlet was cleaned of any crystals with a Kimwipe wetted with deionized water. Before use, denuders were blanked by heating in a furnace to 525 °C for 30 min with mercury free air passing through. Denuder blanks were routinely measured for quality control as reported below.

2.2 Ambient experiments

Ambient outdoor air was passed through denuders coated with either KCl or NaCl for 6–24 hours. Experiments were conducted on the roof of the science building, Blocker Hall, on

the campus of Virginia Wesleyan College in Norfolk, Virginia. Experiments used either one KCl and one NaCl denuder side by side, or two of each denuder type (Fig. 1). Backup KCl denuders were also placed downstream of the NaCl denuders to capture any RGM not removed by the NaCl. Air was pulled through the denuders at a flow rate of about 10 lpm, and Teflon coated cyclones (URG Corporation) were used at the inlets to exclude large particles. Calibrated dry test meters (DTM) were employed for sample volume measurements, and rotameters were used to check flow rates before and after each sample was collected. Heat tape surrounded the denuders to maintain a temperature near 50°C. Ancillary meteorological measurements included relative humidity, temperature, and solar radiation (Davis Vantage Pro2).

2.3 Manifold experiments

Since ambient RGM concentrations were often below the detection limit during ambient experiments, a glass manifold system was designed so that a controlled, artificial source of RGM could be passed through the denuders. RGM was supplied by a permeation source constructed from Teflon tubing and loaded with mercuric chloride (HgCl_2). The manifold system and the denuders were warmed with heat tape, and N_2 , supplied by a compressed gas cylinder (ultra high purity grade), served as the carrier gas for HgCl_2 .

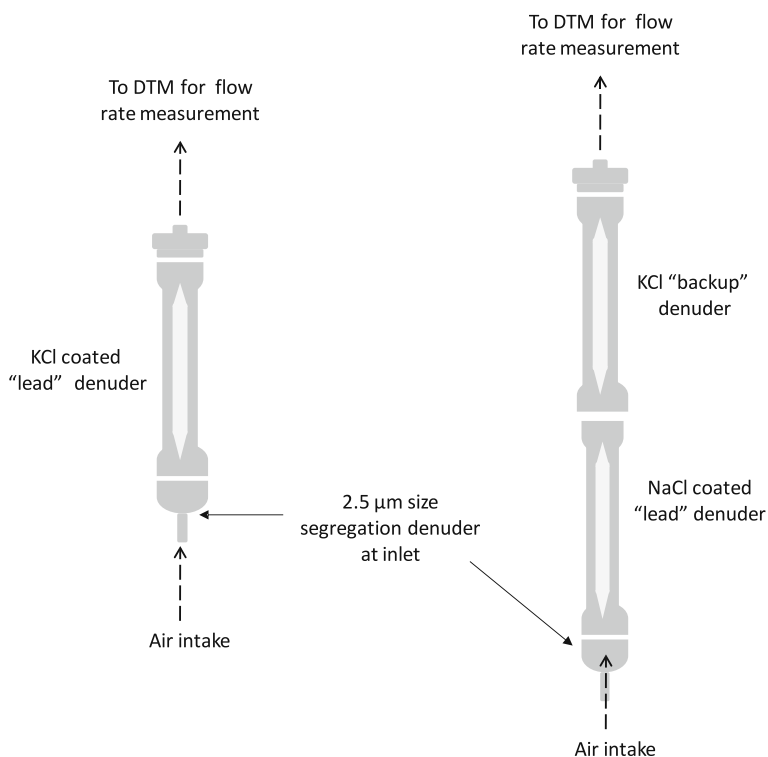


Fig. 1 Ambient outdoor sampling setup. Sampling train on the left consists of a lead KCl denuder. The sampling train on the right includes a lead NaCl denuder and a backup KCl denuder. For the June experiments, two of each sampling train were used simultaneously

The glass manifold and annular quartz denuder system was constructed and modified from the system used by Landis et al. (2002). Our setup consisted of a single piece glass manifold tube with five ports, denuder attachments, and a connected glass side arm with a Teflon tubing connection for N_2 gas (Fig. 2). All glass manifold components were coated with highly cross-linked Teflon (URG Corporation). A port within the sidearm held the $HgCl_2$ permeation tube inside the manifold. The permeation tube was mounted to the 0.64 cm end of the glass sidearm port by connecting a 12 cm piece of Teflon tubing (0.46 cm I.D.) to the port plug. A 4 cm length of quadruple-layered heat shrink Teflon tubing was used as the permeation tubing. It was loaded with 0.001 g of solid phase $HgCl_2$ that was contained in a centimeter space of the tube and was capped at both ends by two solid Teflon end plugs. Early attempts with more $HgCl_2$ introduced too much Hg to the system and caused contamination problems. After optimization, the amount delivered to each denuder port was within the range of 0.1–0.9 ng. This was enough Hg so that it was easily detected by our analyzer, within the range of standards for our calibration curve, and did not cause carryover or blank problems.

Each manifold experiment compared denuders coated with either 1) NaCl vs. KCl or 2) sea salt (SS) vs. KCl. Denuders were attached to ports on the manifold by Teflon-coated glass elutriators. The relative position of the denuders was varied among the experiments. Backup KCl denuders were also placed downstream of the NaCl and SS denuders to capture any RGM not removed by the NaCl. The downstream end of each KCl denuder was connected to a DTM to measure the flow rate through each of the four denuder setups. Both the manifold and denuders were heated to $50^\circ C \pm 5^\circ C$ by heat tape and covered with Reflectix brand insulation to help maintain a uniform temperature.

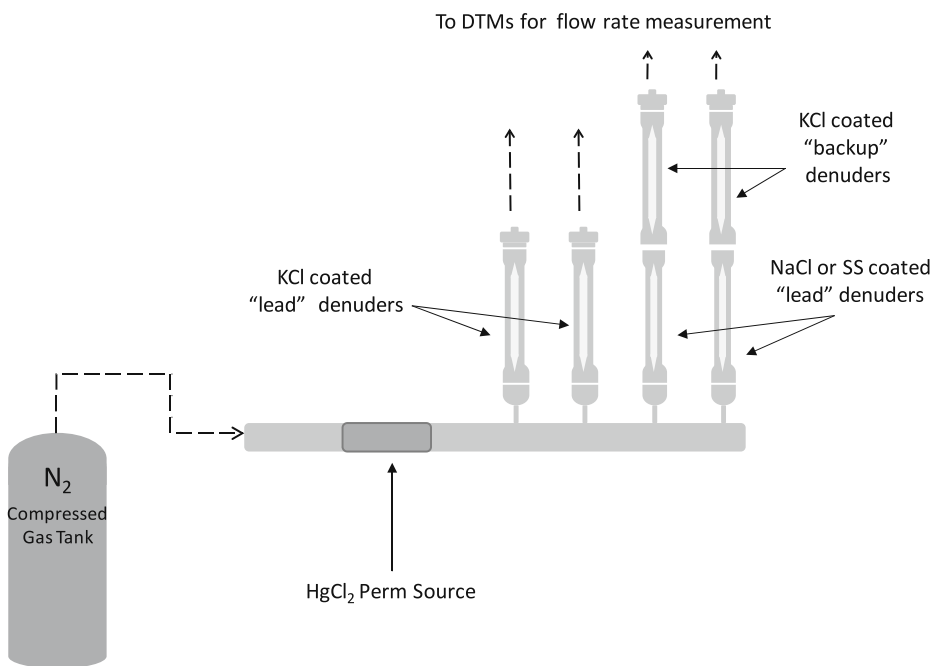


Fig. 2 Manifold laboratory sampling setup. Nitrogen was introduced as the carrier gas from a compressed gas cylinder. The nitrogen gas passes through the $HgCl_2$ permeation tube and four denuder ports. The relative location of the denuder sampling trains on the four ports was varied among experiment runs

In order to minimize the residual mercury in the manifold system before beginning an experiment, the permeation source sidearm was removed from the manifold while the entire system was flushed with N₂ gas for 30 min. During the flushing time, the heat tape on the manifold was turned on. Immediately following the flushing, the denuders (already wrapped in heat tape) were attached to their designated port and DTM. When all connections were complete, the heat tape on each denuder treatment was turned on. Temperature was monitored on the denuders and the manifold. Once all the denuder treatments and manifold were within the 50°C±5°C range, the sidearm containing the permeation source was reattached to the manifold and the N₂ gas was turned on. The N₂ flow rate for each experiment was between 5 and 12 lpm. The experiments were conducted for one to 6 min then the gas was turned off, and the sidearm was removed from the system. Next, the heat tapes were turned off and the DTM values were recorded for each denuder treatment. The denuders were then ready for analysis.

2.4 Denuder analysis

The Hg was thermally desorbed from the denuders onto gold coated sand traps (Brooks Rand) by heating to 525°C in a clamshell furnace (Landis et al. 2002). The heating time was a minimum of 15 min for KCl denuders and 30 min for NaCl and sea salt (SS) denuders. Two gold traps were used in sequence after the denuder in case of breakthrough of Hg through the first trap. The traps were then analyzed by cold vapor atomic fluorescence (CVAFS) on a Tekran 2600 analyzer with a Brooks Rand Amalgamation Control Module. Calibration was completed each analysis day by injection of Hg⁰ vapor standards onto gold coated sand traps (Brooks Rand Air Calibration Unit and traps) (Dumarey et al. 1985). The standard curve consisted of a minimum of 4 standards with an r² value of at least 0.999.

2.5 Quality control and calculations

Clean techniques were employed throughout the study. All sampling components were acid cleaned with 3.5 M HCl and dried in a High Efficiency Particulate Air (HEPA) filtered drying cabinet. In addition, particle-free gloves were worn at all times, and samples and sampling equipment were stored and transported in new zip top bags. Denuders were quantitatively blanked before each experiment to minimize contamination.

Denuder blanks were collected throughout the study for all denuder types. The mean ± standard deviation of the denuder blanks for the ambient study were 0.011±0.012 and 0.013±0.014 ng/denuder for the KCl and NaCl denuders, respectively ($n=23$, $n=11$). The mean±standard deviation of the denuder blanks for the manifold study were 0.016±0.015, 0.012±0.014, 0.007±0.005 ng for the KCl, NaCl and SS denuders respectively ($n=47$, 10, and 10). An ANOVA test showed no significant difference among all of these blank types ($p=0.210$), so the blanks were pooled to give an overall mean ± standard deviation of 0.013 ±0.013 ng ($n=101$). An estimate of the MDL for all experiments was calculated as 0.026 ng, based on the standard deviation of these pooled blanks times the student's t-value ($df=100$). All experimental values were blank corrected by subtracting the mean blank value of 0.013 ng. Since denuder measurements are reported as a mass and not a concentration, mass values were corrected for any differences in flow rate among denuders within each experiment. Uncertainty in denuder measurements was also estimated using the standard deviation of the blanks, 0.013 ng.

The manifold setup was tested and optimized before data collection began. This included two experiments in which four KCl denuders were attached to the ports. This comparison allowed for evaluation of the variability of Hg delivered to the different ports and captured by individual denuders. The mean \pm standard deviation of the each of the two tests was 0.229 ± 0.028 and 0.329 ± 0.026 ng. The standard deviation of these tests is roughly double that of the blanks, and may reflect the added variability from the experimental procedures using the manifold.

Mercury collected on the backup KCl denuders during the ambient experiments was similar to the denuder blank values (mean 0.013 ± 0.018 , $n=7$). Mercury collected on the backup KCl denuders during the manifold experiments was higher, suggesting some breakthrough from the NaCl and SS denuders at these higher concentrations (mean 0.62 ± 0.82 , $n=9$; one data point missing due to broken denuder). Backup denuders were not used behind the lead KCl denuders, so it is not known if a similar amount of breakthrough would occur for both types of denuders. Despite these higher values the mass on the backup denuders was always less than the mass on the lead denuder, with the exception of one denuder pair on 02/11/09 (see Results and Discussion).

Statistical analysis was done with the SPSS statistical package software.

3 Results and discussion

3.1 Ambient air experiments

The ambient air experiments were conducted by passing outdoor air through the denuders. At our sampling location the concentrations of RGM were found to be typically quite low (≤ 5.2 pg/m³) and below the detection limit most sample days. For the three sampling days in December, only one NaCl denuder and one KCl denuder were used, and the sampling time was approximately 10:00 – 17:00 local time. Only one denuder on one of these days collected a mass of mercury above the MDL (0.026 ng). This was the KCl denuder, which collected 0.032 ng of Hg on 12/1/05 (Fig. 3). Therefore on these days, low ambient RGM concentrations made comparison of KCl and NaCl denuders difficult.

In an effort to collect a greater mass of Hg than the MDL, the sampling time for subsequent experiments was increased to 24 h. Two NaCl denuders and two KCl denuders were co-located and sampled simultaneously. On 6/16/06 Hg mass from these four lead denuders were at or below the MDL (≤ 0.026 ng). Heavy rain during the second half of sampling is likely to have contributed to the low concentrations of RGM, which is easily scavenged by precipitation and wetted surfaces (Malcolm and Keeler 2002). On 6/28/06, the KCl denuders captured 0.049 and 0.043 ng Hg and the NaCl denuders captured 0.040 and 0.041 ng Hg (Fig. 1). On average the NaCl denuders collected 87% of the mercury that the KCl denuders collected for this day.

Although concentrations during all these experiments were below or close to MDL levels, the experiment on 6/28/06 suggests that NaCl did remove Hg from the ambient air. This implies that some RGM compounds have an affinity for sodium chloride, a hypothesis that was further tested by the manifold experiments. The unlikely possibility that the Hg collected by the NaCl was elemental gaseous mercury is discussed below.

3.2 Manifold experiments

RGM concentrations near the MDL in the ambient experiments led to the design of laboratory experiments, which were conducted by passing HgCl₂ through a manifold to

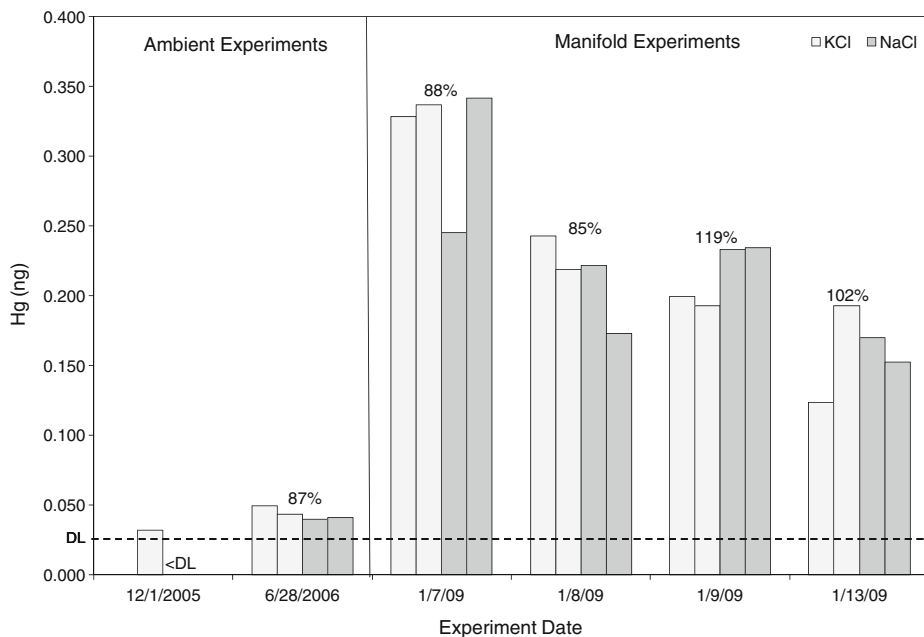


Fig. 3 Mass of mercury collected on KCl vs. NaCl denuders from ambient outdoor air experiments and manifold experiments using HgCl_2 . The detection limit is shown by the dashed lines. The average percent of mercury mass collected on the NaCl relative to the KCl denuders is shown above the bars. Only one KCl and one NaCl denuder were used each day for the December experiments. The mass of mercury on the NaCl denuder on 12/1/05 was below the detection limit. All denuder values were below the detection limit for experiments on 12/2/05, 12/3/05 and 6/16/05, and are not shown on the graph

which denuders were directly attached. Four connection ports were used on the manifold. A lead KCl denuder was attached to each of two ports. To the other two ports were attached either lead NaCl denuders or lead sea salt (SS) denuders (Fig. 2, Table 1). Higher concentrations of HgCl_2 were used in the manifold than the ambient air experiments to ensure concentrations were well above the detection limit. A total of four NaCl experiments and seven seawater experiments were conducted. We found that mercury capture was very similar when comparing the NaCl denuders to the KCl denuders (Fig. 3). On average the NaCl denuders collected 99% of the amount of mercury that the KCl denuders collected for these four experiments, with a range of 85–119% for individual experiments.

One unexpected finding was that the sea salt denuders apparently lost their efficacy with repeated use (Fig. 4, Table 1). This was not observed for the NaCl or the KCl denuders. For example, on 2/3/09 and 2/10/09 the average HgCl_2 collected by the pair of SS denuders relative to the corresponding KCl denuders was 94 and 81% respectively (Fig. 4). For the next three experiments (2/11/09, 2/14/09, 2/24/09) the collection efficiency varied from 47% to 59%. The SS denuders were then cleaned and recoated (with the same seawater sample), and a subsequent experiment (3/10/09) gave 89% collection. For the following experiment 2 weeks later, the two SS denuders only captured 63% of the HgCl_2 . One possible explanation is that a chemical present in the seawater coating either decreased HgCl_2 adsorption or reduced the release of Hg upon

Table 1 Summary of the results from all ambient outdoor and manifold laboratory experiments

Date	RGM source	NaCl or SS denuders used?	NaCl or SS denuder mean Hg collected (ng)	KCl denuder mean Hg collected (ng)	% Hg collected on NaCl or SS relative to KCl ^a
12/1/05 ^b	Ambient	NaCl	<MDL ^c	0.032	—
12/2/05 ^b	Ambient	NaCl	<MDL	<MDL	—
12/3/05 ^b	Ambient	NaCl	<MDL	<MDL	—
6/16/05	Ambient	NaCl	<MDL	<MDL	—
6/28/05	Ambient	NaCl	0.040	0.046	87±26
1/7/09	Manifold	NaCl	0.293	0.332	88±4
1/8/09	Manifold	NaCl	0.197	0.231	85±5
1/9/09	Manifold	NaCl	0.234	0.196	119±7
1/13/09	Manifold	NaCl	0.161	0.158	102±8
2/3/09	Manifold	SS	0.513	0.546	94±2
2/10/09	Manifold	SS	0.268	0.332	81±4
2/11/09	Manifold	SS	0.183	0.319	57±3
2/17/09	Manifold	SS	0.190	0.385	49±3
2/24/09	Manifold	SS	0.139	0.249	56±4
3/10/09 ^d	Manifold	SS	0.179	0.202	89±6
3/24/09	Manifold	SS	0.171	0.271	63±4

^a Uncertainty propagated from uncertainty on individual denuder measurements, which was estimated as one standard deviation of the Hg mass of the blanks (0.013 ng)

^b Only one NaCl and one KCl denuder used on these days

^c MDL=0.026 ng

^d SS denuders recoated before this experiment

heating of the denuder. The backup KCl denuders downstream of the SS denuders were only elevated on 2/11/09. On this day the backup denuders collected 0.088 and 0.187 ng of Hg. If the Hg from the backup denuders is added to the corresponding SS denuder, the SS/backup combination collected on average 100% of the Hg collected by the KCl denuders. Thus on 2/11/09, it appears that the SS denuders had a low capture efficiency of 57%. On the other 3 days however, the Hg on the backup denuders was very low, ranging from 0 to 0.026 ng, capturing at most 4% of the Hg on the lead KCl denuders. Based on these experiments, the cause and mechanism of reduced efficacy for the SS denuders is not clear. It may be a function of repeated heating at high temperatures, although there was no clear correspondence in number of times heated and reduced efficacy. If the problem is related to heating it would not have any real implication for SSA in the natural environment. Consequently, the low collection efficiency experiments (<80%) were discarded in the following statistical analyses. When considering these three SS denuder experiments with the fresher SS coatings, on average the seawater denuders collected 88% of the mercury that the KCl denuders collected (Fig. 5).

In order to compare the NaCl and SS experiments, the ratio of Hg collected on each NaCl to its paired KCl denuder and each SS to its paired KCl denuder was calculated for all experiments with results above the MDL (ambient and manifold; $n=10$ for NaCl/

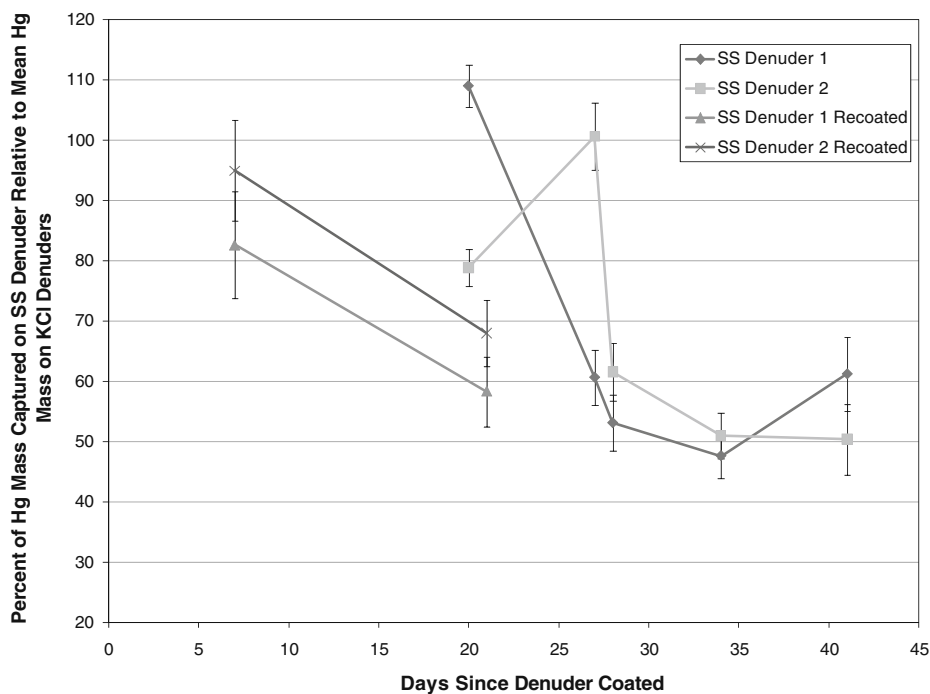


Fig. 4 Results of the manifold experiment using seawater (SS) coated denuders. Relative mass of Hg collected on each SS denuder relative to the mean mass of Hg collected on the KCl denuders from the same experiment. Data is shown relative to number of days since the SS denuder was coated, demonstrating an apparent loss of efficacy for the SS denuders over time

KCl, $n=6$ for SS/KCl; excluding low efficacy SS experiments noted above). A t-test showed no significant difference between the means of these two groups ($p=0.420$), suggesting similar HgCl_2 collection for NaCl and fresh SS. Given that there was no significant difference in means between the NaCl and SS data, they were pooled into one data set for further analysis. A paired t-test showed no significant difference between the mass of Hg collected on the KCl versus the corresponding NaCl or SS denuder ($p=0.173$, $n=16$), supporting the hypothesis that NaCl and SS have a high affinity for HgCl_2 , similar to that of KCl.

3.3 Does gaseous elemental mercury adsorb to NaCl?

Ambient elemental gaseous mercury (Hg^0) was not measured at our sampling location, but is expected to be about $1.5\text{--}2.5\text{ ng/m}^3$ based on data from similar locations (Lamborg et al. 2002; Schroeder and Munthe 1998). Therefore the $\text{Hg}^0_{(\text{g})}$ concentration should have been approximately $1000\times$ greater than that of RGM at our outdoor site. If Hg^0 did adsorb to the NaCl, we would have expected to measure much higher concentrations on the NaCl denuders, yet on 4 days, the Hg collected on the NaCl denuder was below the MDL. For example, on 6/16/06, the Hg collected by the two KCl and two NaCl denuders were all at or below the detection limit of 0.026 ng , or 1.2 pg/m^3 . This represents only about 0.1% of the $\text{Hg}^0_{(\text{g})}$ that was available for collection to the NaCl denuder. KCl denuders are selective for

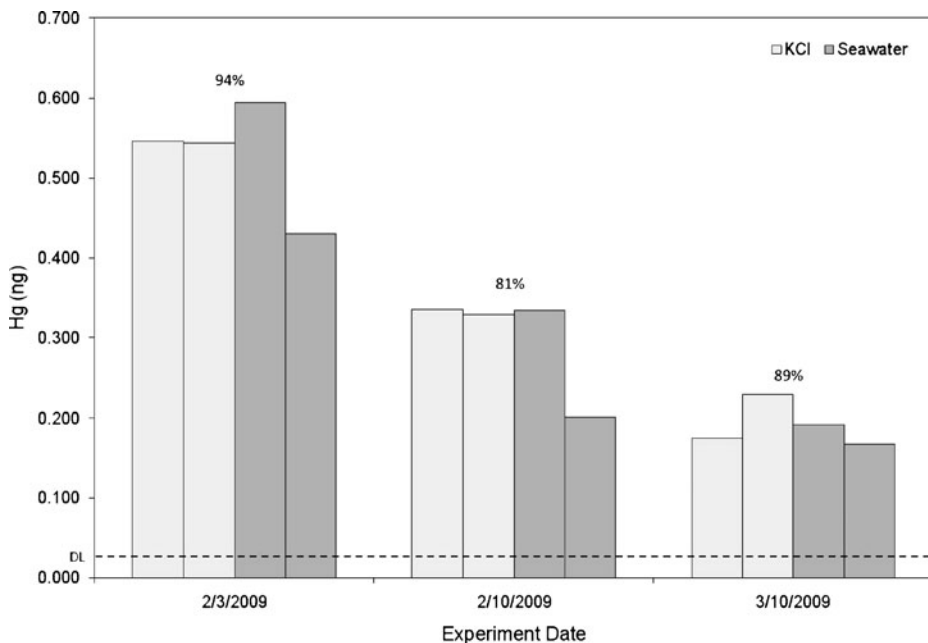


Fig. 5 Mass of laboratory generated HgCl_2 collected on denuders coated with KCl and seawater (SS) using the manifold system. The detection limit is shown by the dashed lines. The average percent of mercury mass collected on the SS relative to the KCl denuders is shown above the bars

RGM, and should not collect Hg^0 . The close match between the Hg collected on the KCl and NaCl denuders in the ambient experiment on 6/28/05 and in all of the HgCl_2 manifold experiments thus further supports the conclusion that the form of Hg collected in the ambient experiments was RGM. Therefore we can deduce that $\text{Hg}^0_{(g)}$ is not adsorbing to the NaCl denuders in our experiments.

3.4 Implications for mercury deposition and transport

The lifetime of SSA can range up to a few days and is a function of wind speed and particle size (Sander and Crutzen 1996). Sea salt penetration onto land is greatest in the first few kilometers but can exceed 50 km inland (Gustafsson and Franzen 2000). In some cases, sea salt particles may be transported to the free troposphere as well (Patterson et al. 1980). Aerosols may continue to scavenge Hg gases throughout their lifetime. Consequently, the effects of Hg scavenging by sea salt may be globally important, particularly to marine and coastal ecosystems. Models by Selin et al. (2007) and Holmes et al. (2009) demonstrated that a fast sink, like scavenging by SSA was required to reproduce RGM concentrations and diurnal patterns in the marine boundary layer. Holmes et al. (2009) further hypothesized that the uptake of RGM by SSA would be limited by mass transfer.

SSA can also serve as cloud condensation nuclei and be scavenged by wet deposition processes. Scavenging of RGM by SSA may thus indirectly increase wet deposition of mercury. In a recent modeling simulation, this process increased Hg wet deposition along the Northeastern U.S. coast (Selin and Jacob 2008). In the coastal environment, sea spray

and dry deposition of SSA will coat natural and manmade surfaces. Salts deposited to leaf surfaces have been shown to increase surface wetness, even at moderate relative humidity (Burkhardt and Eiden 1994). These sea salt coatings may enhance dry deposition of RGM to surfaces coated with dry salts or with aqueous films and dew.

3.5 Future studies

Direct measurements of mercury on SSA are difficult, due to the potential positive (Lynam and Keeler 2002) and negative sampling artifacts (Lynam and Keeler 2005; Malcolm and Keeler 2007). Consequently, many studies have focused on only fine fraction ($<2.5 \mu\text{m}$) aerosols. These studies underestimate the total concentration and dry deposition of $\text{Hg}_{(p)}$. In a study on the Atlantic coast of Florida for example, during periods of onshore airflow, the fine fraction $\text{Hg}_{(p)}$ ($<2.5 \mu\text{m}$) only accounted for 25% of the $\text{Hg}_{(p)}$ on aerosols less than $10 \mu\text{m}$ (Malcolm et al. 2003). The larger particles will deposit more quickly, while smaller particles can be transported further inland. Future studies should evaluate the role of SSA in all size fractions on local and regional deposition.

4 Summary

This is the first study to experimentally investigate the gas-particle partitioning of RGM to sea salt that has used ambient air or sea salt generated from seawater. These experiments demonstrate that HgCl_2 , a major component of RGM has a strong affinity for NaCl and fresh sea salt and is likely to be scavenged by SSA. This adds to the evidence that RGM is scavenged by sea salt aerosols, and thereby could be more quickly dry deposited.

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