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Isotopic composition of species-specific atmospheric Hg in a coastal environment

J.M. Rolison ^{a, b,*}, W.M. Landing ^a, W. Luke ^c, M. Cohen ^c, V.J.M. Salters ^{a, b}

^a Department of Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, FL 32306, USA

^b National High Magnetic Field Laboratory, Tallahassee, FL 32310, USA

^c NOAA Air Resources Laboratory, Silver Spring, MD 20910, USA

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ABSTRACT

The isotopic composition of species-specific atmospheric mercury (Hg) was investigated in the coastal environment of Grand Bay, Mississippi, USA. Atmospheric mercury species $(Hg^0_{(g)}, Hg^{II}_{(g)})$ and $Hg_{(p)})$ were collected individually, and analyzed for isotopic composition. Gaseous elemental Hg $(Hg^0_{(g)})$ displayed δ^{202} Hg ranging from -3.88% to -0.33%. Aerosol Hg $(Hg_{(p)})$ displayed intermediate δ^{202} Hg ranging from -1.61% to -0.12%, while reactive gaseous Hg $(Hg^{II}_{(g)})$ displayed positive δ^{202} Hg ranging from +0.51% to +1.61%. Significant positive mass-independent fractionation (MIF) was observed in Hg_(p) (Δ^{199} Hg = +0.36% to +1.36%), while Hg⁰_(g) displayed negative MIF (Δ^{199} Hg = -0.41% to -0.03%) and Hg^{II}_(g) displayed intermediate MIF (Δ^{199} Hg = -0.28% to 0.18%). Positive MIF of ¹⁹⁹Hg and ²⁰¹Hg measured in Hg_(p) is consistent with significant in-aerosol photoreduction. Significant MIF of ²⁰⁰Hg was observed in all Hg species with Hg⁰_(g) displaying negative Δ^{200} Hg values of -0.19% to -0.06% while Hg^{II}_(g) and Hg_(p) displayed positive Δ^{200} Hg values of +0.06% to +0.28%, which are similar to Δ^{200} Hg values reported by Gratz et al. (2010). These results suggest that isotope tracing of each atmospheric Hg species may be feasible during important atmospheric processes such as wet and dry deposition.

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1. Introduction

Mercury (Hg) is a naturally occurring toxic heavy metal whose global biogeochemical cycle has been significantly altered by human civilization. Centuries of mining and industrial activities have increased the total amount of Hg cycling through Earth's surface environment. Due to the increased load of atmospheric Hg, the current flux of Hg being deposited to the Earth's surface exceeds the pre-industrial deposition flux by approximately a factor of three (Mason and Sheu, 2002: Fitzgerald et al., 2005). Once deposited to terrestrial or aquatic ecosystems, the potential exists for conversion to toxic methylmercury, which bio-accumulates and threatens human health through consumption of contaminated organisms (EPA, 1997). Although industrial regulations in many countries now limit the production of goods containing Hg and require removal and filter systems, such as scrubbers on coal fired power plants, global Hg emissions remain elevated, with Asia accounting for nearly two-thirds of all anthropogenic mercury emissions (Pacyna et al., 2010; Pirrone, et al., 2010).

Our current understanding of the atmospheric cycling of Hg is based on observations of temporal variations in the concentrations of the relevant atmospheric Hg species which are gaseous elemental Hg (GEM; Hg⁰_(g)), gaseous oxidized Hg compounds (Hg^{II}_(g)) and particulate/aerosol bound Hg (Hg_(p)). Hg⁰_(g) is the dominant form of

E-mail address: rolison@magnet.fsu.edu (J.M. Rolison).

0009-2541/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.chemgeo.2012.10.007 atmospheric Hg and generally accounts for >95% of total Hg in uncontaminated air (Schroeder and Munthe, 1998; Liu et al., 2010). ${\rm Hg^0}_{(g)}$ is highly volatile and has limited solubility in water, hence ${\rm Hg^0}_{(g)}$ is not efficiently scavenged by either wet or dry deposition processes. As a result, the atmospheric residence time of $Hg^{0}_{(g)}$ is relatively long, 0.5 to 1 year, which allows for regional/global transport of $Hg^{0}_{(g)}$ emissions (Lindberg et al., 2007). $Hg^{0}_{(g)}$ is converted to $Hg^{II}_{(g)}$ compounds upon reactions with atmospheric oxidants, such as halogens, ozone, and OH radicals (Lin and Pehkomen, 1999; Holmes et al., 2009; Subir et al., 2011). Because Hg^{II}(g) is highly reactive and water soluble, local/regional deposition is expected in the vicinity of direct Hg^{II}_(g) emission sources. Hg^{II}_(g), and to a lesser extent $\mathrm{Hg}^{0}_{(g)}$, can become associated with aerosols and particulate matter to make $Hg_{(p)}$, which is also effectively removed from the atmosphere through wet and dry deposition. Both wet and dry deposition of atmospheric Hg are dominated by reactive gaseous Hg and aerosol Hg (Schroeder and Munthe, 1998; Guentzel et al., 2001).

Oxidized Hg and aerosol Hg species (i.e. $Hg^{II}_{(g)}$ and $Hg_{(p)}$) are typically present in the atmosphere at concentrations <10 pg/m³ in uncontaminated rural environments but can reach levels in excess of 300 pg/m³ in contaminated industrial areas and during atmospheric Hg depletion events (Lindberg et al., 2002; Sprovieri et al., 2002; Liu et al., 2010). $Hg^{II}_{(g)}$ and $Hg_{(p)}$ can account for a significant fraction of total atmospheric Hg emissions during industrial processes such as municipal waste incineration and fossil fuel combustion (Capri, 1996; Pirrone et al., 2001). Coal fired power plant plumes can transport direct emissions of $Hg^{II}_{(g)}$ compounds over distances

^{*} Corresponding author at: Department of Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, FL, USA.

greater than 100 km (Edgerton et al., 2006). Accordingly, elevated wet and dry deposition rates around large urban/industrial centers are expected and were observed during the Lake Michigan Mass Balance Study (Landis and Keeler, 2002). Furthermore, Landis et al. (2005) observed increasing levels of $Hg^{II}_{(g)}$ with altitude in the marine troposphere off the Atlantic coast of Florida, indicating oxidation of Hg⁰(g) at high altitude. Guentzel et al. (2001) hypothesized that tall (12-16 km) convective thunderstorms in Florida during the wet season can scavenge high altitude $Hg^{II}_{(g)}$ and $Hg_{(p)}$, thereby enhancing deposition rates. Source attribution of Hg deposition on a regional scale is challenging using concentration and speciation data only. This is because $Hg^{0}_{(g)}$ may be deposited, upon oxidation to $Hg^{II}_{(g)}$, far from its emission source(s), while direct $Hg_{(g)}^{II}$ and $Hg_{(p)}$ emissions will be deposited closer to their emission sources. Therefore, deposition on a regional scale represents a combination of multiple sources of Hg (global, regional, or local; natural or anthropogenic). Hg isotope ratio measurements could provide a valuable new tool for identifying sources of Hg deposition in a multiple source environment.

Over the last decade, development and implementation of analytical methods to precisely measure Hg isotope ratios have documented mass-dependent fractionation (MDF) of Hg isotopes during a variety of natural and industrial Hg transformations (Smith et al., 2005; Bergquist and Blum, 2007; Kritee et al., 2007; Zheng et al., 2007; Kritee et al., 2008; Estrade et al., 2009; Kritee et al., 2009; Laffont et al., 2009; Sonke et al., 2010). Additionally, the discovery of massindependent fractionation (MIF) of Hg isotopes has been documented during abiotic reduction, both photochemical and non-photochemical (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010b), and physical (Estrade et al., 2009) and chemical processes (Wiederhold et al., 2010). Such processes lead to differences in the Hg isotopic composition of different emission sources, both natural and anthropogenic. Therefore, Hg isotope ratios measured in ambient air could be used to trace the sources of atmospheric Hg. However, atmospheric processes (i.e. transportation, oxidation/reduction, deposition, and reemission) could induce additional Hg isotope fractionation, thereby changing the Hg isotopic composition relative to the source.

This study reports our attempts to measure the isotopic compositions of $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$, and $Hg_{(p)}$ collected concurrently in a coastal marine environment. The objectives of this work are 1) to establish methods to separate and collect $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$, and $Hg_{(p)}$ of sufficient quantity for isotope ratio analysis, 2) characterize the isotopic composition of $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$, and $Hg_{(p)}$, and 3) use the isotopic composition of $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$, and $Hg_{(p)}$ to describe atmospheric processes affecting Hg isotope fractionation and to perhaps identify sources of atmospheric Hg.

2. Experimental

2.1. Site descriptions

Daily atmospheric Hg samples were collected during a three-week field campaign (18-April-2011 to 9-May-2011) at the Grand Bay National Estuarine Research Reserve in Moss Point, MS (Lat: 30.43°N–Long: 88.43°W). Grand Bay (GB) is situated on the northern coast of the Gulf of Mexico and is often influenced by air masses coming from the marine environment, especially during the summer months. The GB site is semi-rural, surrounded by a sparsely populated suburban area. Possible local anthropogenic atmospheric Hg emission sources include a large oil refinery 10 km to the SW with an unknown Hg emission inventory and a coal fired power plant approximately 25 km to the NW. A large open field within the reserve, 5 km NW of the Gulf of Mexico, was selected as the site to deploy atmospheric sampling equipment.

Aerosol samples were also collected at a second site located 21 km NW of Pensacola, FL and 20 km N of the Gulf of Mexico (Lat: 30.55°N and Long: 87.38°W). The site, termed Outlying Landing Field (OLF), is located on the edge of large open field and is considered suburban. Plant Crist, a coal fired electrical facility, is located 15 km ENE of the site and is considered to be the dominant local source of atmospheric Hg emissions (Caffrey et al., 2010).

2.2. Sample collection process

 $Hg^{II}_{(g)}$ and $Hg_{(p)}$ were collected using a Tisch 5170V-BL high volume aerosol sampler (Tisch Environmental Inc., Ohio, USA). The system is equipped with a vacuum pump that creates a flow through filter of approximately 3 L/cm²-min. The area of the filter is approximately 406 cm², resulting in a total flow of 1.2 m³/min (± 0.1 m³/min). The total flow rate is dependent upon temperature, barometric pressure, and vacuum pressure behind the filter. ${\rm Hg}_{(p)}$ was collected on untreated quartz fiber filters (Whatman QMA). ${\rm Hg}^{\rm II}_{\rm (g)}$ was collected on quartz fiber filters treated with potassium chloride (KCl, Fisher Scientific, >99.9%). Treatment consisted of soaking the quartz fiber filters in 10% KCl solution (w/v, 1.34 M) until fully saturated at which time they were removed and allowed to air dry under a laminar flow hood. Untreated OMA and KCl-OMA (KCl treated guartz fiber filters) were pre-combusted at 550 °C for \geq 10 h to eliminate any trace of Hg prior to use. Immediately following pre-combustion, the filters were wrapped in pre-baked aluminum foil and then placed inside a sealed, clean plastic zipper-seal bag. The filters were deployed in a filter cartridge that was mounted in the aerosol sampler. After deployment, the filters were removed from the filter cartridge, placed back in the aluminum foil and plastic bag, and were kept frozen until further processing. The particle collection efficiency for QMA filters is similar to that of W41 filters (Pszenny et al., 1993) with efficiencies of 99% for aerosol dust (Savoie, 1984) and 95% for particles 0.18 µm or larger (Stafford and Ettinger, 1967).

At the GB site, untreated QMA filters and KCl-treated QMA filters were deployed simultaneously as a filter stack in a single filter cartridge for an interval of approximately 24 h. This allowed for collection of sufficient quantities of $Hg_{(p)}$ and $Hg^{II}_{(g)}$ required for isotope analyses (~3 ng Hg). The untreated QMA filter, on top of the stack, collected $Hg_{(p)}$ while $Hg^{II}_{(g)}$ was transmitted and collected on the KCl-QMA filter on the bottom of the stack, resulting in $Hg_{(p)}$ and $Hg^{II}_{(g)}$ being collected separately from the same air mass. At the OLF site, only untreated QMA filters were deployed during August 2010 for 72-hour intervals. Therefore, these filters were sectioned into thirds and subsequently extracted and analyzed as individual samples.

Hg⁰_(g) was collected and pre-concentrated using gold (Au) traps via gold-mercury amalgamation. Gold traps consisted of approximately 1 g of gold-coated ultra-pure silica sand secured in a quartz tube with quartz wool. Each gold trap was cleaned of residual Hg by baking at 500 °C for 1 h and then stored in a sealed glass test tube until use. A vacuum pump was used to pull air through the gold trap at approximately 2 L/min for 24-hour intervals. However, the flow rates through the gold traps were not monitored or controlled and cannot be assumed to be the same for each gold trap. Therefore, the total mass of Hg collected on each gold trap cannot be used to calculate the average Hg⁰_(g) concentration during the deployment interval. During one gold trap deployment, a second gold trap was placed in-line behind the first gold trap to test for potential breakthrough of $\mathrm{Hg^{0}}_{(\mathrm{g})}$. Breakthrough of $\mathrm{Hg^{0}}_{(\mathrm{g})}$ across the first trap proved to be negligible (i.e. similar to blanks, <50 pg Hg). While the gold traps were not heated, as is sometimes done to avoid condensation of water vapor and potential reduction of the Hg⁰_(g) trapping efficiency, the lack of significant breakthrough onto the second trap suggests that this was not a significant problem. Such breakthrough could result in mass-dependent fractionation of Hg isotopes (yielding more positive δ^{202} Hg values), but would not be expected to cause mass-independent fractionation.

The gold traps were deployed approximately 2 m above ground level. Since a pre-filter was not employed, gold traps collected Hg_T (Hg⁰_(g), Hg^{II}_(g), and Hg_(p)) rather than Hg⁰_{gas} solely. However, the ambient concentration of Hg⁰_(g) was typically 2–3 orders of magnitude higher than Hg^{II}_(g) and Hg_(p) during the field campaign. Therefore, the contribution of Hg^{II}_(g) and Hg_(p) to the total Hg sampled by the gold trap is believed to be negligible. While the gold traps were handled wearing clean nitrile gloves, the outsides of the traps were not cleaned prior to analysis. We assume that any particles that may have accumulated on the outside surface of the golf trap contributed negligibly to the total amount of Hg collected in the traps. Gold trap Hg samples will be referred to as Hg⁰_(g) in the following discussion.

2.3. Sample extraction

Fig. 1 illustrates the Hg combustion system used for extraction of Hg from gold traps and QMA filters (untreated and KCI-treated). The quartz tubes (OD 2.54 cm; ID 2.44 cm; length 61 cm) were fitted with threaded Teflon end caps used to connect the quartz tube to a supply of ultra high purity Ar and O₂ carrier gases and a Teflon impinger (30 mL microcolumn; 6.4 mm ID×9.6 mm OD×25 cm capillary; Savillex, Minnesota, USA) via Teflon tubing. The carrier gases were passed through gold traps to remove any trace Hg. Quartz tubes and Teflon connectors were cleaned by soaking in a 8 M HNO₃ solution for ≥48 h and rinsed thoroughly with high purity DI (18.2 MΩ.cm) water.

Quartz tubes loaded with gold traps and QMA filters were heated in a Lindberg/Blue M Mini-Mite programmable tube furnace. Hg_(P) on untreated QMA filters was liberated and volatilized using a multi-step heating routine. The first heating step ramped the temperature to 500 °C at 50 °C/min, the temperature then ramped to 800 °C at 25 °C/min. The temperature was then held at 800 °C for 15 min before cooling to room temperature. Volatilized Hg was transported out of the quartz tube in a stream of Ar (35 mL/min) and O_2 (15 mL/min) and was then captured in a KMnO₄ trapping solution. O₂ was used as a carrier gas during the combustion of untreated QMA filters to ensure that oxidation of any organic matter was complete. Gold traps and KCl-QMA filters were extracted using the same combustion oven technique with the following alterations to the method. Instead of using a mixed Ar/O₂ carrier gas, Ar was used solely at a flow rate of 50 mL/min. Both sample types were heated to 500 °C at 50 °C/min, held for 20 min at 500 °C, and then allowed to cool to room temperature. KCl melts at 771 °C and Rutter et al. (2008) reported evaporation and condensation of KCl at temperatures lower than 771 °C in a similar combustion system using KCl treated quartz fiber filters. Also, heating gold traps and KCl-QMA filters to temperatures above 500 °C did not release additional Hg. Thus, 500 °C was chosen as the maximum temperature for the gold traps and the KCI-treated QMA filters. Re-combustion of QMA filters, KCI-QMA filters, or gold traps did not release any additional Hg, indicating that these conditions are appropriate for quantitatively releasing the Hg from each sample type.

During combustion, volatilized Hg is primarily in the $Hg^{0}_{(g)}$ state and a strong oxidizing agent, such as potassium permanganate (KMnO₄), is required for trapping. During combustion, the carrier gas enters the impinger and is introduced to the trapping solution at which time gaseous Hg⁰ is oxidized to Hg^{II} and trapped in the solution. Different concentrations of KMnO₄ were tested to determine the optimal trapping solution. Using a cold vapor atomic fluorescence spectrometer (Model II, Brooks Rand Labs, Washington, USA) in conjunction with a gold trap, a 2.5 mM KMnO₄ in 1.13 M HNO₃ solution was deemed adequate because >99% trapping efficiency was achieved during elemental Hg vapor injections and combustion of standard reference materials (NIST SRM 1572), while minimizing the Hg blank associated with KMnO₄. The addition of O₂ helped the KMnO₄ solution to retain its oxidizing efficiency by oxidizing organic compounds evolved during combustion of aerosol filters that would otherwise be oxidized by the KMnO₄ solution. In the absence of O_2 , combustion of heavily loaded OMA filters consumed the KMnO₄ before the combustion routine was complete. O₂ was deemed unnecessary during combustion of gold traps and KCl-QMA filters because both sample types contained significantly less organic matter and therefore the trapping efficiency of the KMnO₄ solution was not compromised. Breakthrough of Hg during sample extractions, monitored via CV-AFS on all samples, was negligible (<20 pg).

2.4. Mass spectrometry

Hg standards and extracted samples were analyzed for Hg concentrations and isotope compositions using a cold-vapor introduction system interfaced to a multi-collector inductively coupled plasma mass spectrometer (CV-MC-ICP-MS). A CETAC HGX-200 continuous flow cold-vapor (CV) generator was coupled to a Thermo Finnigan Neptune MC-ICP-MS. Dissolved Hg^{II} was reduced by online mixing of 0.16 M SnCl₂ in 1.2 M HCl with the sample solution, generating a continuous flow of $Hg^{0}_{(g)}$. The flow rates of the sample solution and $SnCl_2$ solution were both approximately 0.8 mL/min. All standards and samples were partially reduced with 0.004 mL of 0.72 M NH₂OH·HCl per 1 mL of 2.5 mM KMnO₄ to dissolve manganese oxides immediately prior to analvsis. Drift in instrumental mass bias was corrected using the standardsample-standard bracketing technique. The international delta-0 Hg standard, NIST SRM 3133, was employed as the bracketing standard. Bracketing standards were matrix matched and concentration matched to within 10% of all samples and secondary standards. Mass limitations of samples restricted data acquisition time to 4 min (1 block, 60 cycles, and 4 s integrations). After each analysis, the introduction system was



Fig. 1. Schematic of the combustion/extraction system used for untreated QMA filters, KCI-treated QMA filters, and gold traps.

washed with 1.13 M HNO₃ until signal intensity on ²⁰²Hg achieved blank levels (≤ 0.005 V). Blank signals were always $\leq 1\%$ of sample signals. Standard operating conditions were optimized daily for signal intensity and stability. Estimating the Hg concentration in each sample by monitoring the signal intensity on ²⁰²Hg is not as accurate as making a separate concentration measurement on an aliquot of each trapping solution, and we have since modified our procedure to include this.

Hg isotope ratios are reported using the standard delta $\left(\delta\right)$ notation:

$$\delta^{\text{XXX}} \text{Hg} = \left| \frac{R_{\text{sample}}^{\text{XXX}/198}}{R_{\text{NIST3133}}^{\text{XXX}/198}} - 1 \right| * 1000\%$$
(1)

where xxx = 199, 200, 201, and 202. Any isotope composition that does not follow the theoretical mass-dependent fractionation (MDF) is considered an isotope anomaly caused by mass-independent

fractionation (MIF). MIF is reported using the "capital delta" (Δ) notation as the difference between the measured and the theoretical MDF value (Blum and Bergquist, 2007):

$$\Delta^{199} \text{Hg}(\%) = \delta^{199} \text{Hg} - \left(\delta^{202} \text{Hg} \times 0.2520\right)$$
(2)

$$\Delta^{200} Hg(\%) = \delta^{200} Hg - \left(\delta^{202} Hg \times 0.5024\right)$$
(3)

$$\Delta^{201} Hg(\%) = \delta^{201} Hg - \left(\delta^{202} Hg \times 0.7520\right)$$
(4)

$$\Delta^{204} Hg(\%) = \delta^{204} Hg - \left(\delta^{202} Hg \times 1.493\right). \tag{5}$$

A secondary reference material, UM-Almadén Hg standard, was analyzed during each analytical session to quantify the analytical reproducibility of CV-MC-ICP-MS isotope ratio analysis. It was prepared

Table 1

Hg isotope data from replicate analysis of the UM-Almadén Hg standard obtained during analytical sessions from May 2011 to October 2011, comparisons between digestion and combustion methods for three SRMs, and results from the analysis of gold traps loaded with an elemental Hg vapor sample. Reported Hg isotope data for the UM-Almadén Hg standard and the DORM-3 SRM are from Blum and Bergquist (2007) and Sherman and Blum (in press).

Sample		δ^{199} Hg	δ^{200} Hg	δ^{201} Hg	δ^{202} Hg	Δ^{199} Hg	Δ^{200} Hg	$\Delta^{201} Hg$		
		%	‰	‰	‰	%	%	‰		
UM-Almadén Standard (n = 30)										
Average		-0.18	-0.32	-0.54	-0.66	-0.01	0.01	-0.04		
2SD		0.08	0.07	0.09	0.09	0.07	0.06	0.07		
Reported		-0.16	-0.28	-0.46	-0.57	-0.02	0.01	-0.03		
		0.04	0.03	0.05	0.05	0.03	0.02	0.02		
Digestion										
DORM-3		1.89	0.45	1.99	0.84	1.68	0.03	1.36		
DORM-3		2.03	0.45	2.06	0.84	1.82	0.03	1.43		
Combustion										
DORM-3		1.67	0.40	1.47	0.58	1.52	0.11	1.03		
DORM-3		1.63	0.47	1.56	0.64	1.47	0.15	1.08		
	2SD	0.08	0.10	0.15	0.16	0.06	0.05	0.08		
Reported										
DORM-3		1 94	0.32	184	0.48	1.82	0.08	1 48		
Donan S	2SD	0.06	0.07	0.13	0.15	0.06	0.02	0.04		
Digestion										
MESS-3		-0.55	-1.26	- 1.85	-2.45	0.07	-0.03	-0.01		
MESS-3		-0.46	-1.14	-1.76	-2.32	0.12	0.02	-0.02		
Combustion										
MESS-3		-0.43	-1.11	-1.98	-2.44	0.18	0.11	-0.15		
MESS-3		-0.66	-1.22	-2.20	-2.57	-0.01	0.08	-0.26		
	2SD	0.08	0.10	0.15	0.16	0.06	0.05	0.08		
Direction										
DOLT-3		0.63	-0.29	0.18	-0.64	0 79	0.03	0.66		
DOLT-3		0.59	-0.36	0.13	-0.69	0.77	-0.01	0.65		
Combustion		0.62	0.44	0.05	0.05	0.01	0.01	0.00		
DULI-3		0.62	-0.44	0.05	-0.85	0.84	-0.01	0.69		
DOLI-3	260	0.60	-0.38	0.15	-0.68	0.77	-0.04	0.00		
	230	0.08	0.10	0.15	0.10	0.06	0.05	0.08		
Elemental Hg vapor injected directly into the KMnO ₄ trapping solution										
a		-0.19	-0.63	-0.87	-1.34	0.15	0.04	0.14		
b		-0.10	-0.55	-0.83	- 1.25	0.21	0.07	0.11		
с		-0.22	-0.70	-0.97	-1.42	0.14	0.02	0.10		
	Average	-0.17	-0.63	-0.89	- 1.34	0.16	0.04	0.12		
	2SD	0.12	0.14	0.14	0.17	0.08	0.06	0.04		
Gold traps loaded with	elemental Hg vapor, t	then combusted into	the KMnO ₄ trapping	solution						
a		-0.21	-0.64	-0.86	- 1.25	0.11	-0.01	0.08		
b		-0.15	-0.66	-0.85	- 1.28	0.17	-0.02	0.11		
с		-0.21	-0.68	-0.96	- 1.38	0.14	0.01	0.08		
	Average	-0.19	-0.66	-0.89	- 1.30	0.14	0.00	0.09		
	2SD	0.06	0.05	0.12	0.13	0.06	0.03	0.03		

in an identical KMnO₄ matrix and at concentrations similar to sample solutions (0.5 to 1.0 ppb). During the analysis period (May–Oct 2011) the UM-Almadén standard averaged δ^{202} Hg = $-0.66\% \pm 0.09\%$ (2SD, n = 30), Δ^{199} Hg = $-0.01\% \pm 0.07\%$ (2SD, n = 30), and Δ^{201} Hg = $-0.04\% \pm 0.07\%$ (2SD, n = 30) (Table 1), which is consistent with values reported by other laboratories (Blum and Bergquist, 2007; Sherman and Blum, in press). Replicate subsamples of untreated QMA filters collected at the OLF site were analyzed for Hg isotopic composition, as were gold traps loaded with an elemental Hg vapor standard. Analytical uncertainties are reported as the larger value of either 2SD of the reproducibility of the UM-Almadén standard or 2SD of procedural replicates (Table 1).

3. Results

3.1. Collection of $Hg^{0}_{(g)}$, $Hg_{(p)}$, and $Hg^{II}_{(g)}$

The effectiveness of KCl treated quartz fiber filters at capturing $Hg^{II}_{(g)}$ in this study was evaluated by comparison with hourly integrated $Hg^{II}_{(g)}$ concentration measurements made with two co-located

Tekran® 2537A/1130/1135 automated Hg speciation units operating asynchronously to provide continuous mercury species measurements (operated by W. Luke, NOAA/Air Resources Laboratory). Rutter et al. (2008) previously concluded that manual filtration using KCl-QMA filters and Tekran® speciation units compared well in terms of quantifying $Hg^{II}_{(g)}$. The Tekran® unit uses a KCl-coated annular denuder to collect $Hg^{II}_{(g)}$ species which are collectively operationally defined as reactive gaseous Hg (RGM) (Landis et al., 2002). Fine particulate Hg (FPM; particle size < 2.5 µm) was collected on a particulate filter and gaseous elemental Hg (GEM) was collected on an internal gold trap.

During the initial phase of the field campaign (18 April–27 April), RGM at GB did not reach concentrations above 10 pg/m³ and 24 h averages were typically ≤ 1 pg/m³ (Fig. 2a). Consequently, daily KCl-QMA filters deployed during this time interval collected less than 2 ng Hg per filter and precise isotope ratio measurements were not possible (Fig. 2b). During the final phase of the field campaign (28 April–9 May), RGM concentrations were elevated and displayed a strong diurnal cycle typical of the marine environment (Laurier et al., 2003; Holmes et al., 2009) with a maximum peak of ~70 pg/m³ and 24 h averages ≥ 5 pg/m³ (Fig. 2a). Daily KCl-QMA filters

Fig. 2. Time series of the concentrations of GEM, RGM, and FPM measured by dual Tekran® 2537A/1130/1135 automated Hg speciation analyzers (a) and the mass of Hg collected concurrently on gold traps, KCI-QMA quartz fiber filters, and untreated QMA quartz fiber filters (b) at the Grand Bay NERR site (data in Table 3).



deployed during this time interval were, on average, loaded with > 5 ng Hg per filter (Fig 2b). The FPM concentration shows a similar pattern to the RGM, with increased concentrations and a strong diurnal cycle during the final phase of the field campaign (Fig. 2a). Daily untreated QMA filters collected during the final phase of the field campaign were, on average, loaded with > 5 ng of Hg (Fig 2b). These variations in Hg^{II}_(g) and Hg_(p) concentrations are surely due to a variety of processes, including differences in meteorological conditions and impacts from different possible sources of these two atmospheric Hg species. Efforts to understand these factors are part of the broader goals of the Grand Bay sampling experiment, but are not the focus of this report which describes the sampling methods that we have developed to separate atmospheric Hg species and to demonstrate that these species can have significantly different Hg isotopic compositions.

Fig. 3 shows a comparison from the Grand Bay site between the Hg_(p) and Hg^{II}_(g) concentrations measured using the Tekran 2537A/ 1130/1135 automated atmospheric Hg speciation instruments and those measured on our high-volume untreated QMA and treated KCl-OMA filters. There are statistically significant linear relationships between the two sampling techniques for both $Hg_{(p)}$ (Fig. 3a) and Hg^{II}_(g) (Fig. 3b), although the regression slopes are on the order of 0.33-0.35. This indicates that the high-volume filters collect less of both species, and this could be due to several factors. Firstly, the intake for the Tekran unit is elevated (10 m) on a tower immediately adjacent to the sawgrass marsh close to the coast, while the high-volume sampler was located at ground level approximately 2.5 km inland at the Grand Bay NERR laboratory building. Secondly, the fetch between the tower and the NERR building is completely vegetated, and it is very possible that $Hg_{(p)}$ and $Hg_{(g)}^{II}$ would have been scavenged from the boundary layer between the two sites. We are conducting additional experiments to test for a variety of potential sampling artifacts including: adsorption of $\text{Hg}^{II}_{(g)}$ onto the $\text{Hg}_{(p)}$ that has accumulated on the untreated QMA filter; loss of volatile $Hg_{(p)}$



Fig. 3. Comparison between the concentrations of (a) FPM and (b) RGM measured by dual Tekran® 2537A/1130/1135 automated Hg speciation analyzers and the concentrations of $Hg_{(p)}$ and $Hg^{II}_{(g)}$ collected using our high-volume aerosol sampler filters at the Grand Bay NERR site.

(as $Hg^{II}_{(g)}$ or $Hg^{0}_{(g)}$) from an untreated QMA filter over 24-hour deployment periods; and loss of volatile $Hg^{II}_{(g)}$ from a treated KCI-QMA filter over 24-hour deployment periods.

GEM concentrations averaged 1.5 ng/m^3 over the duration of the field campaign (Fig. 2a). Daily gold traps, on average, were loaded with 3.3 ng of Hg. One gold trap was deployed for approximately 48 h (26 April–28 April) and collected 11 ng of Hg. As previously mentioned, the flow rates through the gold traps were not monitored or controlled, thus the average atmospheric concentration of Hg⁰_(g) could not be calculated from the amount of Hg collected on the gold traps.

Procedural blanks of gold traps and filters were collected and analyzed for Hg content by CV-AFS. Blank samples were prepared and stored identically to samples. Procedural gold trap blanks were transported to the field and briefly exposed to the atmosphere. Procedural filter blanks were loaded in a cassette transported to the field, installed on the aerosol sampler, then removed and stored identically to samples. Blank gold traps (n=3) averaged \leq 50 pg of Hg while blank untreated QMA filters (n=3) and KCI-QMA filters (n=3) averaged \leq 200 pg of Hg.

3.2. Hg isotopic compositions

To test for Hg isotopic fractionation during the combustion process, the DORM-3, MESS-3, and DOLT-3 SRMs were analyzed using the combustion technique and compared to results obtained from samples that were digested using hot concentrated nitric and sulfuric acids (Estrade et al., 2009), showing that both methods yield Hg isotope ratios that are not significantly different (Table 1). The reproducibility of the isotopic composition of mercury collected on gold traps was investigated with an elemental Hg vapor sample (from the head-space over a pool of Fisher Mercury Metal Redistilled) and the data are also reported in Table 1. While the true Hg isotope ratios for this Hg vapor sample are not known, the excellent precision of our measurements and the fact that no additional Hg was released from the traps when heated to higher temperatures suggests that we have recovered 100% of the Hg⁰(g) from the traps during the oven combustion step. In addition, there is excellent agreement among the Hg isotopic ratios measured on Hg vapor injected directly into the KMnO₄ trapping solution and for the same Hg vapor injected onto a gold trap (which was then combusted as described above). These results indicate that the combustion technique does not cause isotopic fractionation.

The Hg isotopic composition of replicate extractions of five untreated QMA filter samples from the OLF site is reported in Table 2. Each filter was deployed for three days, and the filters were therefore cut into equal thirds for analysis as replicate samples. The averages of the 2SD calculated for each set of three samples were used to approximate the reproducibility of the method, from collection through extraction and isotope ratio analysis for QMA filter samples. We did not collect any three-day integrated KCl-QMA filter samples at OLF and the analytical reproducibility for the KCl-QMA filter samples remains somewhat uncertain. Because the combustion/ trapping method employed for both the KCl-QMA and QMA filters was very similar, we assume that the reproducibility for the KCl-QMA filter analysis should be very similar to the reproducibility of the untreated QMA filter analysis. These species-specific uncertainties were applied to all analytical results unless the 2SD of the reproducibility of the UM-Almadén standard (Table 1) was larger. The minimum and maximum 2SD from these replicate analyses of untreated QMA filters are also reported in Table 2. Use of the maximum 2SD instead of the average 2SD does not affect our discussion or conclusions.

The isotopic compositions for samples collected at GB are summarized in Table 3. Hg⁰_(g) displayed the lowest δ^{202} Hg and a range of $-3.88\% \pm 0.13\%$ to $-0.33\% \pm 0.13\%$, (2SD). Aerosol Hg_(p) δ^{202} Hg displayed

Table 2

Replicate analysis of sectioned untreated quartz fiber filters deployed at the OLF site for approximately 72 h. Concentrations of Hg for each subsample were calculated from the CV-MC-ICPMS²⁰²Hg signals. One sample (OLF 4.c) suffered from low a carrier gas flow rate during the combustion process, which resulted in decreased recovery.

Sample	Deployment date	Recovery date	Hg/sample	$\delta^{199}\text{Hg}$	δ^{200} Hg	$\delta^{201} Hg$	$\delta^{202} Hg$	$\Delta^{199} Hg$	$\Delta^{200} \text{Hg}$	$\Delta^{201} Hg$
			ng	‰	‰	‰	%	%	‰	‰
OLF QMA-1	14-Aug-2010	17-Aug-2010								
a	-	-	5.22	0.03	-0.41	-0.46	-0.90	0.26	0.05	0.22
b			3.82	-0.06	-0.53	-0.65	-1.13	0.23	0.03	0.20
с			4.53	0.02	-0.46	-0.59	-1.09	0.30	0.09	0.23
			Average	0.00	-0.47	-0.57	-1.04	0.26	0.06	0.21
			2SD	0.10	0.13	0.19	0.24	0.07	0.07	0.04
OLFQMA-2	28-Aug-2010	31-Aug-2010								
a			6.65	-0.17	-0.38	-0.74	-1.05	0.09	0.15	0.04
b			8.38	-0.21	-0.48	-0.86	-1.14	0.08	0.09	-0.01
С			8.63	-0.05	-0.31	-0.72	-0.98	0.20	0.18	0.02
			Average	-0.14	-0.39	-0.77	-1.05	0.12	0.14	0.02
			2SD	0.17	0.17	0.15	0.15	0.13	0.09	0.05
OLF-QMA-3	31-Aug-2010	3-Sep-2010								
a			10.17	0.19	-0.20	-0.31	-0.75	0.38	0.18	0.26
b			11.22	0.21	-0.16	-0.24	-0.70	0.38	0.19	0.28
С			8.00	0.16	-0.22	-0.36	-0.78	0.36	0.18	0.23
			Average	0.18	-0.19	-0.30	-0.74	0.37	0.18	0.26
			2SD	0.05	0.05	0.12	0.09	0.03	0.01	0.06
OLF QMA-4	3-Sep-2010	6-Sep-2010								
a			9.65	0.41	0.08	0.17	-0.23	0.47	0.20	0.34
b			9.23	0.44	0.12	0.30	-0.11	0.46	0.18	0.38
С			2.58	0.48	0.13	0.21	-0.07	0.50	0.17	0.27
			Average	0.44	0.11	0.23	-0.14	0.48	0.18	0.33
			2SD	0.07	0.06	0.13	0.17	0.04	0.03	0.12
OLF QMA-5	6-Sep-2010	9-Sep-2010								
a			4.86	0.18	-0.18	-0.23	-0.60	0.33	0.12	0.22
b			5.44	0.20	-0.08	-0.07	-0.53	0.33	0.18	0.33
С			4.73	0.21	-0.09	-0.12	-0.46	-0.33	0.14	0.22
			Average	0.20	-0.12	-0.14	-0.53	0.33	0.15	0.26
			2SD	0.04	0.10	0.16	0.14	0.01	0.06	0.13
			Average 2SD	0.08	0.10	0.15	0.16	0.06	0.05	0.08
			Minimum 2SD	0.05	0.05	0.09	0.09	0.01	0.01	0.03
			Maximum 2SD	0.17	0.17	0.19	0.24	0.13	0.09	0.13

intermediate δ^{202} Hg values $(-1.61\% \pm 0.16$ to $-0.12\% \pm 0.16$, 2SD) and Hg^{II}_(g) displayed the highest δ^{202} Hg values $(+0.51\% \pm 0.16$ to $+1.61\% \pm 0.16$, 2SD). Significant mass-independent fractionation (MIF) of ¹⁹⁹Hg and ²⁰¹Hg in all samples is illustrated in Fig. 4 by plotting Δ^{199} Hg and Δ^{201} Hg (Δ^{199} Hg = $+0.36\% \pm 0.07\%$ to $+1.36\% \pm 0.07\%$, 2SD; Δ^{201} Hg = $+0.30\% \pm 0.08\%$ to $+1.20\% \pm 0.08\%$, 2SD), while Hg⁰_{gas} and Hg^{II}_{gas} display negative Δ^{199} Hg and Δ^{201} Hg values or values that are indistinguishable from zero, with the exception of the KCI-QMA sample collected on 05/07/11-05/08/11 (Δ^{199} Hg = $0.18\% \pm 0.07$, 2SD; Δ^{201} Hg = $0.19\% \pm 0.08$, 2SD) (Fig. 4). A linear regression of Δ^{199} Hg and Δ^{201} Hg for all samples yields a slope of 1.15 ± 0.02 (r² = 0.99) (Fig. 5).

Atmospheric Hg at Grand Bay displayed significant MIF of ²⁰⁰Hg (Fig. 6). Hg⁰_(g) was characterized by negative Δ^{200} Hg = $-0.19\% \pm 0.06\%$ to $-0.06\% \pm 0.06\%$ (2SD). Hg^{II}_(g) and Hg_(p) displayed positive Δ^{200} Hg of similar magnitude (Hg^{II}_(g) Δ^{200} Hg = $+0.08\% \pm 0.06\%$ to $+0.28\% \pm 0.06\%$, 2SD; Hg_(p) Δ^{200} Hg = $+0.06\% \pm 0.06\%$ to $+0.28\% \pm 0.06\%$, 2SD; Hg_(p) Δ^{200} Hg = $+0.06\% \pm 0.06\%$ to $+0.26\% \pm 0.06\%$, 2SD). Significant MIF of ²⁰⁰Hg was recently reported in atmospheric Hg in the Great Lakes regions of the U.S., including precipitation and Hg⁰_(g) (Gratz et al., 2010). Their observations are similar to ours in that their vapor phase Hg has low Δ^{200} Hg compared to the precipitation Hg, which is presumably composed of Hg^{II}_(g) and Hg_(p).

4. Discussion

4.1. Mass-dependent fractionation of $Hg^{0}_{(g)}$

Although Hg stable isotope geochemistry has been established as a powerful tool for studying the complex biogeochemical cycle of Hg, few studies have focused on direct isotope composition measurements of atmospheric Hg species (Zambardi et al., 2009; Gratz et al., 2010; Sherman et al., 2010; Chen et al., 2012; Sherman et al., 2012). Rather, the isotope composition of atmospheric Hg has been investigated indirectly by measuring the isotopic composition of Hg in reservoirs that are considered to be tracers of atmospheric Hg deposition such as lichens, moss, peat, coal, soils, and sediments (Biswas et al., 2008; Ghosh et al., 2008; Carignan et al., 2009; Estrade et al., 2010; Sonke et al., 2010). This is primarily due to the analytical challenges of measuring isotopic compositions of low-level atmospheric Hg species. The primary objective of this study was to separate and analyze the isotopic composition of the individual atmospheric Hg species.

Mass-dependent fractionation will be discussed in terms of δ^{202} Hg. δ^{202} Hg values reported here for Hg⁰_(g) are more negative than previous reports (Zambardi et al., 2009; Gratz et al., 2010; Sherman et al., 2010). However, the sampling locations were drastically different for each study. Zambardi et al. (2009) collected ${\rm Hg^0}_{\rm (g)}$ in a fumarole plume. Sherman et al. (2010) collected Hg⁰_{gas} in the Arctic and Gratz et al. (2010) collected Hg⁰_{gas} in the Great Lakes region of the United States. In our study, air masses were sampled at GB in a semi-rural coastal environment at ~2 m above sea level. It is expected that air masses originating offshore may contain significant Hg derived from long-range transport or emissions from surface waters (Strode et al., 2007). However, local anthropogenic sources may also be present in air masses that appear to originate offshore due to alternating wind directions during sea breeze and land breeze conditions. Therefore, potential sources of Hg⁰_(g) include long-range transport, Hg that has been emitted from Gulf of Mexico surface waters, local/regional anthropogenic emission sources, and possibly minor amounts of Hg⁰_(g) emitted from local soils and vegetation. Although the isotopic compositions of $Hg^{0}_{(g)}$ from long-range transport and from local/regional anthropogenic sources are unknown, the photoreduction of dissolved ${\rm Hg^{II}}_{(aq)}$ and subsequent volatilization of

Table 3

Isotopic composition of species-specific atmospheric Hg samples collected at Grand Bay, Mississippi (USA) during April-May, 2011. $Hg^{0}_{(g)}$ was collected on gold traps, $Hg^{II}_{(g)}$ was collected on KCl-treated quartz fiber filters, and $Hg_{(p)}$ was collected on untreated quartz fiber filters.

*	, O(p)		1							
Site	Deployment date	Recovery date	Hg/sample	δ ¹⁹⁹ Hg	δ ²⁰⁰ Hg	δ^{201} Hg	δ ²⁰² Hg	Δ^{199} Hg	Δ^{200} Hg	Δ^{201} Hg
			ng	‰	‰	‰	‰	‰	‰	‰
Cold traps $(Hg^0,)$										
GB	19-Apr-2011	20-Apr-2011	15							
GB	20-Apr-2011	21-Apr-2011	110							
GB	21-Apr-2011	22-Apr-2011	2.1							
GB	22-Apr-2011	24-Apr-2011								
GB	23-Apr-2011	25-Apr-2011	3.2							
GB	24-Apr-2011	25-Apr-2011								
GB	25-Apr-2011	26-Apr-2011	3.4	-0.81	- 1.32	-1.94	-2.39	-0.20	-0.12	-0.14
GB	26-Apr-2011	28-Apr-2011	11.0	-0.34	-0.23	-0.45	-0.33	-0.26	-0.06	-0.20
GB	28-Apr-2011	29-Apr-2011	2.7	-0.47	-0.74	-1.03	- 1.31	-0.14	-0.08	-0.05
GB	29-Apr-2011	30-Apr-2011	2.2	-1.18	-2.11	-3.12	- 3.88	-0.21	-0.16	-0.20
GB	30-Apr-2011	1-May-2011	2.6	-1.31	- 1.97	-3.01	- 3.58	-0.41	-0.17	-0.32
GB	1-May-2011	2-May-2011	3.9	-1.08	-1.75	-2.67	- 3.22	-0.27	-0.13	-0.25
GB	2-May-2011	3-May-2011	4.2	-1.01	- 1.55	-2.40	-2.88	-0.29	-0.10	-0.23
GB	3-May-2011	4-May-2011	2.8	-1.18	- 1.82	- 2.68	- 3.24	-0.37	-0.19	-0.25
GB	4-May-2011	5-May-2011	2.7	- 1.11	- 1./4	-2.75	- 3.28	-0.28	-0.09	-0.29
GB	5-May-2011	7 May 2011	2.3	-0.90	- 2.00	- 2.80	- 5.07	-0.05	-0.10	-0.04
CB	$7_M_{2V} = 2011$	7-May-2011 8-May-2011	2.4	- 0.92	- 1.65	-2.77	- 2.45	-0.20	-0.00	-0.18
GB	8-May-2011	9-May-2011	4.4	-0.52	-0.71	-1.20	- 1 27	-0.20	-0.03	-0.25
	0 Widy 2011	5 Widy 2011	-11	0.00	0.71	1.25	1,27	0.20	0.07	0.27
KCl-OMA Filters $(Hg^{II}_{(q)})$										
GB	19-Apr-2011	20-Apr-2011	1.3							
GB	20-Apr-2011	21-Apr-2011								
GB	21-Apr-2011	22-Apr-2011	1.6							
GB	22-Apr-2011	23-Apr-2011								
GB	23-Apr-2011	24-Apr-2011	1.3							
GB	24-Apr-2011	25-Apr-2011								
GB	25-Apr-2011	26-Apr-2011	0.9							
GB	26-Apr-2011	28-Apr-2011								
GB	28-Apr-2011	29-Apr-2011	4.4	0.28	0.98	1.03	1.41	-0.07	0.28	-0.03
GB	29-Apr-2011	30-Apr-2011	13.4	0.30	0.94	1.03	1.45	-0.07	0.21	-0.06
GB	30-Apr-2010	1-May-2010	2.8	0.23	0.73	0.92	1.29	-0.10	0.08	-0.04
GB	I-May-2010	2-May-2010	2.2	0.15	0.88	1.11	1.57	-0.24	0.09	-0.07
GB	2-May-2010	3-May-2010	0.6	0.10	0.41	0.27	0.51	0.02	0.10	0.02
GB	3-May-2010	4-May-2010	3.4	0.16	1.02	1.06	1.50	0.03	0.16	-0.02
GB CB	4-May-2010	5-May-2010	6.2	0.51	0.85	0.64	1.36	-0.09	0.24	-0.15
CB	$6_{May} = 2010$	$7_M_{2}^{-1}$	5.9	0.10	0.83	0.04	1.15	-0.20	0.20	-0.23
GB	7-May-2010	8-May-2010	11.1	0.05	0.05	0.70	0.79	0.18	0.18	0.25
GB	8-May-2010	9-May-2010	59	0.50	0.92	1.00	1.61	-0.28	0.10	-0.22
	0 May 2010	5 May 2010	5.5	0.15	0.52	1.00	1.01	0.20	0.11	0.22
Untreated QMA Filters $(Hg_{(p)})$										
GB	19-Apr-2011	20-Apr-2011	2.9							
GB	20-Apr-2011	21-Apr-2011								
GB	21-Apr-2011	22-Apr-2011	3.1							
GB	22-Apr-2011	23-Apr-2011								
GB	23-Apr-2011	24-Apr-2011	0.9							
GB	24-Apr-2011	25-Apr-2011								
GB	25-Apr-2011	26-Apr-2011	0.6							
GB	26-Apr-2011	28-Apr-2011	10.2	0.00	0.01	0.01	0.00	0.50	0.05	0.40
GB CD	28-Apr-2011	29-Apr-2011	10.2	0.33	-0.21	-0.21	- 0.92	0.56	0.25	0.48
GB CD	29-Apr-2011	30-Apr-2011	2.9	-0.01	-0.72	-0.84	- 1.61	0.39	0.09	0.37
	50-Apr-2011	1-IVIdy-2011 2 May 2011	3.3 1.9	0.80	0.00	0.72	- 0.12	0.89	0.12	0.66
	1-IVIdy-2011 2 May 2011	2-IVIdy-2011 2 May 2011	1.ð 1.0	0.51	-0.36	-0.07	- 0.98	0.75	0.13	0.66
GB	2-11/1ay-2011 3-May-2011	2-191ay-2011 2-May-2011	1.5	0.56	-0.49	_022	-110	0.86	0.12	0.68
GB	4-May-2011	-1-1v1ay-2011 5-May-2011	2.0 14.2	1.07	-0.40 -0.14	0.22	- 0.19	1 27	0.12	1 1 2
GB	5-May-2011	6-May-2011	69	0.50	-030	-0.02	-0.85	0.71	0.20	0.62
GB	6-May-2011	7-May-2011	8.1	1.09	0.05	0.80	-0.28	1 16	0.15	1 01
GB	7-May-2011	8-May-2011	5.5	1.00	-0.67	0.12	-1.44	1.36	0.06	1.20
GB	8-May-2011	9-May-2011	3.7	0.24	-0.14	-0.06	-0.49	0.36	0.10	0.30

the product, $Hg^{0}_{(g)}$, has been shown to follow mass-dependent fractionation, which predicts enrichment of light isotopes in product $Hg^{0}_{(g)}$ (Bergquist and Blum, 2007; Zheng et al., 2007; Zheng and Hintelmann, 2009). Therefore, the low $\delta^{202}Hg$ values reported here for $Hg^{0}_{(g)}$ suggest that the evasion flux of Hg from surface water may have contributed significantly to atmospheric $Hg^{0}_{(g)}$ along the northern coast of the Gulf of Mexico.

To examine this hypothesis, air mass back-trajectories were calculated for each sample using the NOAA HYSPLIT model (Draxler and Hess, 1998). Back-trajectories were started every 30 min for the duration of a given sample at a starting height equal to the midpoint of the time-dependent planetary boundary layer, and were simulated for 120 h using meteorological data with 12 km horizontal resolution (from NOAA's North American Mesoscale – "NAM" – Forecast System).



Fig. 4. Δ^{199} Hg (‰) versus δ^{202} Hg (‰) for atmospheric Hg samples collected at the Grand Bay NERR site during April–May, 2011. Data points represent Hg⁰_(g) (open squares), Hg_(p) (black triangles), and Hg^{II}_(g) (open circles). Uncertainties are determined by the reproducibility of the UM-Almadén standard and procedural replicates and standards (see text).

Thus, a 24-hour sample would have 48 associated back-trajectories, characterizing the paths that air masses took in arriving at the sampling site. The Hg⁰_(g) samples were divided into two groups: three samples (4/26-4/28, 4/28-4/29, and 5/8-5/9) with relatively high δ^{202} Hg values (>-2%) and the remaining samples, with relatively low δ^{202} Hg values (<-2%). For each trajectory group, the fractional residence time was computed for each grid square in a 0.1×0.1 grid. The locations, types, and magnitudes of large anthropogenic mercury point sources were assembled and added to these geographical distributions of backtrajectories. The geographical pattern of back-trajectory residence times for the low and high δ^{202} Hg groups of samples is shown in Fig. 7, along with the locations, types, and magnitudes of large anthropogenic mercury point sources in the region based on data from the US EPA's 2005 National Emissions Inventory. The back-trajectories for the low δ^{202} Hg group (Fig. 7a) show a strikingly uniform pattern of marine air masses, while the high δ^{202} Hg group (Fig. 7b) shows significant impacts from terrestrial and anthropogenic source regions. These results support the hypothesis that the low δ^{202} Hg values for Hg⁰_(g) found in this study reflect photo-reduction and evasion from the ocean, although it is equally possible that the sources of $Hg^{0}_{(g)}$ in the marine boundary layer arriving at the GB site simply started with low $\delta^{202}\text{Hg}$ values. For example, $\delta^{202}\text{Hg}$ values in $\text{Hg}^0_{(g)}$ could be driven more negative during long range transport by oxidation and subsequent deposition of isotopically heavy oxidized Hg species. Additionally,



Fig. 5. Δ^{199} Hg (‰) versus Δ^{201} Hg (‰) for atmospheric Hg samples collected at the Grand Bay NERR site during April–May, 2011. Data points represent Hg⁰_(g) (open squares), Hg_(p) (black triangles), and Hg^{II}_(g) (open circles). Uncertainties are determined by the reproducibility of the UM-Almadén standard and procedural replicates and standards (see text).



Fig. 6. Δ^{200} Hg (‰) versus δ^{202} Hg (‰) for atmospheric Hg samples collected at the Grand Bay NERR site during April–May, 2011. Data points represent Hg⁰_(g) (open squares), Hg_(p) (black triangles), and Hg^{II}_(g) (open circles). Uncertainties are determined by the reproducibility of the UM-Almadén standard and procedural replicates and standards (see text).

known local/regional anthropogenic emission sources contributing to the atmospheric Hg at GB include coal-fired power plants, which could possibly influence the observed Hg isotopic compositions (Sherman et al., 2012). Biswas et al. (2008) measured δ^{202} Hg values from -3% to -0.5% in a variety of United States coals. However, it is not known if, or to what extent, Hg isotopes are fractionated during combustion and emission. The use of pollution control devices, such as scrubbers, to remove Hg from emissions most likely induces significant fractionation of Hg during the combustion and emission processes. The range in atmospheric δ^{202} Hg values observed in the Hg⁰_(g) collected at GB must represent mixing of multiple natural and anthropogenic sources, and we cannot definitively conclude whether any particular source is dominant. Further study is obviously necessary to understand these various processes.

4.2. Mass-independent fractionation (MIF)

4.2.1. MIF mechanisms

MIF of ¹⁹⁹Hg and ²⁰¹Hg has been explained by at least two mechanisms: the magnetic isotope effect (MIE) and the nuclear volume effect (NVE). The NVE arises due to the non-linear increase between the Hg isotope number and the mean square nuclear charge radius, $\langle r^2 \rangle$. In particular, ¹⁹⁹Hg and ²⁰¹Hg are characterized by nuclear volume/shape distortions that give rise to smaller than expected $\langle r^2 \rangle$ (Schauble, 2007). The NVE mechanism has been documented during elemental Hg⁰ liquid–vapor equilibrium (Ghosh et al., in press; Estrade et al., 2009), abiotic non-photochemical Hg^{II}_(aq) reduction (Zheng and Hintelmann, 2009, 2010b), and equilibrium Hg^{II}_(aq)-thiol complexation (Wiederhold et al., 2010).

Odd isotopes of Hg have a nuclear spin and associated nuclear magnetic moment that can interact with magnetic moments of electrons (i.e. nuclear-electronic hyperfine coupling) and change a reaction from the spin-forbidden to a spin-allowed state or from the spin-allowed to spin-forbidden state. This effect results in different reaction rates between even and odd isotopes of Hg during reactions involving long-lived radical pairs (Buchachenko et al., 2004; Zheng and Hintelmann, 2009, 2010a; Epov, 2011). Thus, isotope fractionation during radical pair reactions involving Hg may be influenced by a parameter other than mass, resulting in mass-independent fractionation (MIF).

Theory and observations suggest that the NVE and MIE mechanisms yield significantly different relationships between Δ^{199} Hg and Δ^{201} Hg. All available theoretical and experimental evidence for NVE suggest a slope > 1.5 when Δ^{199} Hg is plotted against Δ^{201} Hg. Experimental evidence for the MIE mechanism results in a Δ^{199} Hg/ Δ^{201} Hg

slope in the range of 1.00–1.36 (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010a). In this study, all samples collected yielded a slope of Δ^{199} Hg/ Δ^{201} Hg = 1.15 ± 0.02 (Fig. 5), indicating that the MIF signature in atmospheric Hg is likely to have been produced by the MIE mechanism.

4.2.2. MIF in atmospheric Hg

Bergquist and Blum (2007) observed anomalous enrichments of ¹⁹⁹Hg and ²⁰¹Hg (i.e. positive MIF) in residual Hg^{II}_(aq) and methylmercury during laboratory experiments on Hg^{II}_(aq) photoreduction and methylmercury photodegradation in simulated natural waters. During a similar experiment, Zheng and Hintelmann (2009) showed the evading $Hg^{0}_{(g)}$ to be depleted in the odd isotopes more than would be expected by mass-dependent fractionation alone (i.e. negative MIF). Furthermore, Hg in fish, which is predominantly methylmercury, was shown to exhibit significant positive MIF (Bergquist and Blum, 2007; Das et al., 2009). Thus, it was predicted that atmospheric and aquatic reservoirs of Hg might contain complimentary MIF signatures (Bergquist and Blum, 2007; Carignan et al., 2009). However, direct measurements of atmospheric $Hg_{(g)}^{0}$ by Gratz et al. (2010) and Sherman et al. (2010) showed minor MIF (range of Δ^{199} Hg from -0.22% to 0.06%). Also, Hg^{II} in precipitation has significant positive Δ^{199} Hg ranging from +0.10% to +0.61% (Gratz et al., 2010). These observations question the importance of aquatic

photoreduction as a source of MIF in atmospheric $Hg^{0}_{(g)}$ (Gratz et al., 2010; Sonke, 2011).

In this study, the isotopic compositions of atmospheric Hg species $(\text{Hg}^{0}_{(\text{g})}, \text{Hg}^{\text{II}}_{(\text{g})}, \text{ and } \text{Hg}_{(\text{p})})$ were measured directly. Negative values were observed for $\text{Hg}^{0}_{(\text{g})} \Delta^{199}\text{Hg}$ (average = $-0.25\% \pm 0.09\%$, 1SD, n = 13) and Δ^{201} Hg (average = $-0.20\% \pm 0.09\%$, 1SD, n = 13). Hg⁰_(g) with negative MIF is expected to be associated with photoreduction of Hg^{II}_(aq) (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009). As discussed above, the low ${\rm Hg^0}_{(g)}\; \delta^{202} {\rm Hg}$ values and negative MIF in $Hg^{0}_{(g)}$ are consistent with the hypothesis that evasion of $Hg^{0}_{(g)}$ from surface waters could be a significant source of atmospheric $Hg^{0}_{(g)}$ along the northern coast of the Gulf of Mexico. However, a variety of U.S. coal deposits display similar MIF with Δ^{199} Hg and Δ^{201} Hg values ranging from -0.30% to +0.10% (Biswas et al., 2008; Lefticariu et al., 2011). It is unknown whether combustion of the coal and the subsequent scrubbing of the flue gasses introduce significant isotope fractionation of the mercury that enters the atmosphere. $\mathrm{Hg^{II}}_{(g)}$ showed variable MIF with average Δ^{199} Hg and Δ^{201} Hg values ranging from -0.28% to +0.18% (average $= -0.11\% \pm 0.14\%$; 1SD, n = 10) and -0.25% to +0.19% (average $= -0.09\% \pm 0.13$; 1SD, n = 10), respectively. If one assumes that the majority of the ${\rm Hg}^{\rm II}{}_{\rm (g)}$ we collected had been produced by oxidation of the ambient $Hg^{0}_{(g)}$, then the small differences between MIF measured in $Hg^{0}_{(g)}$ and $Hg^{II}_{(g)}$ may indicate that atmospheric oxidation reactions do not induce significant MIF of Hg isotopes. Since oxidation by ozone or halogen radicals is not a direct



Fig. 7. Gridded frequency analysis of 120-hour back trajectories from the Grand Bay NERR site for (a) $Hg_{(g)}^{0}$ samples showing $\delta^{202}Hg$ (‰) values more negative than -2.0 and (b) $Hg_{(g)}^{0}$ samples showing $\delta^{202}Hg$ (‰) values more positive than -2.0.



Fig. 7 (continued).

photochemical process, long-lived radical pairs are not produced and therefore no MIF from MIE is expected (Buchachenko, 2001; Zheng and Hintelmann, 2009, 2010a; Gratz et al., 2010). It is also quite possible that at least some of the ambient $\mathrm{Hg}^{\mathrm{II}}_{(\mathrm{g})}$ was derived from emission sources, such as coal-fired power plants in the region, and not from oxidation of the ambient ${\rm Hg}^0{}_{({\rm g})}.$ It is one of the broader goals of this project to investigate this possibility, and will be discussed in future papers. The most significant MIF was measured in $Hg_{(p)}$. Values of $\Delta^{199}Hg$ and Δ^{201} Hg range from +0.36‰ to +1.36‰ (average = 0.83 ± 0.35; 1SD, n = 10) and +0.30% to +1.20% (average $= 0.73 \pm 0.31$; 1SD, n =10), respectively. Gratz et al. (2010) suggested that photoreduction of Hg^{II} in cloud droplets containing organic matter may produce MIF similar to that observed in controlled photoreduction experiments and that cloud droplets would preferentially retain odd isotopes thereby becoming increasingly positive with respect to Δ^{199} Hg and Δ^{201} Hg. This prediction was invoked to explain positive Δ^{199} Hg and Δ^{201} Hg measured in precipitation (Gratz et al., 2010). Significant positive $Hg_{(p)} \Delta^{199}Hg$ and Δ^{201} Hg measured in this study supports this hypothesis.

4.2.3. Modeling in-aerosol photoreduction

Sonke (2011) constructed a global Hg MIF box-model to simulate observed MIF signatures in environmental reservoirs. Total fractionation factors $\alpha_{1001(0-11)}^{1000}$ are the product of mass-dependent and mass-

independent fractionation such that $\alpha_{\text{XXY}}^{\text{XXY}|98} = \alpha_{\text{XXY}}^{\text{XXY}|98} \times \alpha_{\text{XXY}}^{\text{XXY}|98}$. Sonke (2011) obtained optimum model results with in-aerosol MIF of magnitude $\alpha_{\text{aerosol}-\text{MIF}}^{199/198}$ = 0.993, which suggest the accumulation of significantly positive Hg_(p) Δ^{199} Hg directly resulting from in-aerosol photoreduction. The extent of in-aerosol photoreduction based on MIF can be modeled using a modified Rayleigh equation (Sonke, 2011):

$$10^{3} \times \ln \frac{\left(10^{-3} \times \Delta^{199} \text{Hg}_{t}^{\text{II}} + 1\right)}{(10^{-3} \times \Delta^{199} \text{Hg}_{t=0}^{\text{II}} + 1)} = \epsilon_{\text{aerosol-MIF}(0-\text{II})}^{199/198} \times \ln f$$
(6)

where Δ^{199} Hg^{II}_{t=0} and Δ^{199} Hg^{II} are the measured Hg^{II}_(p) Δ^{199} Hg at time t = 0 and time t, and f is the fraction of Hg^{II}_(p) remaining at time t. $\epsilon^{199/198}_{aerosol-MIF(0-II)}$ is the 'permil fractionation factor': $\epsilon^{199/198}_{aerosol-MIF(0-II)} = 10^3 \times (\alpha^{199/198}_{aerosol-MIF(0-II)} - 1)$. Therefore, $\epsilon^{199/198}_{aerosol-MIF(0-II)} = -0.7\%$ under optimal model conditions meaning that during photoreduction of Hg^{II}_(p), the production of Hg⁰ has a Δ^{199} Hg anomaly of -0.7%. (Sonke, 2011). Under the assumptions that no MIF takes place during Hg^{II}_(g) \rightarrow Hg^{II}_(p) and that Hg_(p) is derived completely from Hg^{II}_(g), then Hg^{II}_(g) Δ^{199} Hg can be used to estimate Hg^{II}_(p) Δ^{199} Hg at t=0. Solving Eq. (6) for f yields an estimate for the extent of photoreduction, Hg^{II}_(g) \rightarrow ^{hv} Hg⁰_(g), in the range of 46–87\%. This estimate is rather poorly constrained, however, since it is almost certainly true that the ambient Hg_(p). could have come from regional emission sources, and one would have to measure the Hg isotopic composition of such aerosols in order to improve the reliability of this assumption.

4.2.4. MIF of ²⁰⁰Hg

Significant MIF of ²⁰⁰Hg was recently reported in precipitation and $Hg^{0}_{(g)}$ collected in the Great Lakes region of the U.S. (Gratz et al., 2010). Our results support the findings of Gratz et al. (2010) with Δ^{200} Hg values greater than the 2SD uncertainty (0.06‰) measured in all $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$, and $Hg_{(p)}$ samples, with the exception of two. Procedural replicates show that the Δ^{200} Hg values measured in samples are reproducible. Furthermore, procedural standards do not show significant MIF of ²⁰⁰Hg. Because ²⁰⁰Hg has no nuclear spin, the MIE mechanism cannot induce MIF of ²⁰⁰Hg (Buchachenko et al., 2004). Schauble (2007) has calculated that the nuclear volume effect (NVE) can yield slight MIF of the even Hg isotopes. Significant MIF of ²⁰⁰Hg measured here and in other studies (Gratz et al., 2010), combined with uncertainties in the nuclear charge radii of Hg isotopes suggests that the magnitude of NVE may not be adequately estimated at this time.

5. Conclusions

The isotopic composition of species-specific atmospheric Hg has been measured in a coastal environment along the northern coast of the Gulf of Mexico. $Hg^{0}_{(g)}$, $Hg^{II}_{(g)}$ compounds, and $Hg_{(p)}$ were collected on gold traps, KCI-treated quartz fiber filters, and untreated quartz fiber filters, respectively. While inter-conversions from one species to another may alter the Hg isotope ratios, all three species in this study were isotopically distinct suggesting that isotope tracing of each species may be possible.

 ${\rm Hg}^0_{({\rm g})}$ samples collected at Grand Bay National Estuarine Research Reserve were isotopically similar to published analyses of ${\rm Hg}^0_{({\rm g})}$ at other sites and to a variety of U.S. coal deposits. However, photoreduction of ${\rm Hg}^{\rm II}_{({\rm aq})}$ in surface waters of the Gulf of Mexico could also produce ${\rm Hg}^0_{({\rm g})}$ with negative mass-dependent fractionation (MDF) and negative mass-independent fractionation (MIF). Source attribution of atmospheric ${\rm Hg}^0_{({\rm g})}$ at GB may be possible if the isotopic compositions of primary emission sources were significantly different from each other and from the global background. Diurnal variation observed in ${\rm Hg}^{\rm II}_{({\rm g})}$ and ${\rm Hg}_{({\rm p})}$ concentrations suggests that the primary source of ${\rm Hg}^{\rm II}_{({\rm g})}$ and ${\rm Hg}_{({\rm p})}$ at GB is the photochemical oxidation of ${\rm Hg}^0_{({\rm g})}$. Our observation of positive mass-independent fractionation in ${\rm Hg}_{({\rm p})}$ suggests that significant in-aerosol photochemical reduction of ${\rm Hg}^{\rm II}$ has taken place.

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