Speciated atmospheric mercury in the marine boundary layer of the Bohai Sea and Yellow Sea

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HIGHLIGHTS

- Atmospheric Hg (GEM, RGM, and Hg^P_{2.5}) were determined in the East Asia MBL.
- Hg^P_{2.5} concentrations in the offshore area were higher than those in the open sea.
- GEM and Hg^P_{2.5} levels over the BS were higher than those over the YS.
- RGM showed a homogeneous distribution both in spring and fall.
- RGM was correlated well with air temperature but inversely correlated with RH.

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ABSTRACT

The objectives of this study are to identify the spatial and temporal distributions of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and fine particulate mercury (Hg^P_{2.5}) in the marine boundary layer (MBL) of the Bohai Sea (BS) and Yellow Sea (YS), and to investigate the relationships between mercury species and meteorological parameters. The mean concentrations of GEM, RGM, and Hg^P_{2.5} were 2.03 ng m⁻³, 2.5 pg m⁻³, and 8.2 pg m⁻³ in spring, and 2.09 ng m⁻³, 4.3 pg m⁻³, and 8.3 pg m⁻³ in fall. Reactive mercury (RGM + Hg^P_{2.5}) represented < 1% of total atmospheric mercury (GEM + RGM + Hg^P_{2.5}), which indicated that most mercury export in the MBL was GEM and the direct outflow of reactive mercury was very small. Moreover, GEM concentrations over the BS were generally higher than those over the YS both in spring and fall. Although RGM showed a homogeneous distribution over the BS and YS both in spring and fall, the mean RGM concentration in fall was significantly higher than that in spring. In contrast, the spatial distribution of Hg^P_{2.5} generally reflected a gradient with high levels near the coast of China and low levels in the open sea, suggesting the significant atmospheric mercury outflow from China. Interestingly, the mean RGM concentrations during daytime were significantly higher than those during nighttime both in spring and fall, while the opposite results were observed for Hg^P_{2.5}. Additionally, RGM positively correlates with air temperature while negatively correlates with relative humidity. In conclusion, the elevated atmospheric mercury levels in the BS and YS compared to other open seas suggested that the human activities had a significant influence on the oceanic mercury cycle downwind of China.

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1. Introduction

The special characteristics of mercury (Hg), such as the long-range atmospheric transport, transformation and bio-magnification, and the role as a neurotoxin, make it a ubiquitous,

potent, and persistent pollutant of global concern (Schroeder and Munthe, 1998; Wang and Pehkonen, 2004). Hg is emitted into the atmosphere in different chemical and physical forms from a variety of natural (e.g., oceans, land, biomass burning, and volcanoes) (Ferrara et al., 2000; Pirrone et al., 2010; Strode et al., 2007) and anthropogenic sources (e.g., fossil fuel combustion, metal production, cement production, and waste incineration) (Pacyna et al., 2003, 2006, 2010; Pirrone et al., 2010; Schroeder and Munthe, 1998; Zhang et al., 2015). Once Hg is released into the

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atmosphere, its physical and chemical properties and transformation processes will determine its subsequent fate and transport. Hg can be transformed from one species to another via photo-oxidation, photo-reduction, reactions with halides, and other oxidation or reduction reactions (Choi et al., 2008).

Hg in the atmosphere exists in three major operationally defined forms: gaseous elemental Hg (GEM or Hg^0), reactive gaseous Hg (RGM), and particulate Hg (Hg^p) (Schroeder and Munthe, 1998). Each Hg species behaves differently in the atmosphere depending on their different physicochemical characteristics. Generally, more than 95% of the total atmospheric Hg ($\text{TAM} = \text{GEM} + \text{RGM} + \text{Hg}^p$) is presented as GEM, which is very stable in the atmosphere with a residence time of 0.3–1 year due to its high volatility, low solubility, and chemical stability (Radke et al., 2007; Selin et al., 2007; Weiss-Penzias et al., 2003). This enables GEM to undergo a long-range transport and makes it well-mixed on a global scale. The atmospheric lifetime of RGM is shorter (hours to several days) than that of GEM due to its higher solubility and lower volatility (Holmes et al., 2009; Laurier and Mason, 2007). The composition of RGM (e.g., HgBr_2 , HgCl_2 , HgBrOH) varies across space and time (Gustin et al., 2015). The lifetime of Hg^p is on the order of a day or week depending on the diameter of the particulate. The shorter atmospheric lifetime of RGM and Hg^p indicates that they are more rapidly deposited on local to regional scales through both wet and dry deposition. Therefore, Hg speciation determines its fate and transport in the atmosphere. RGM and Hg^p play an important role in Hg deposition though they generally account for < 5% of TAM, and atmospheric Hg (mainly RGM and Hg^p) deposition is identified as the dominant source of Hg to the ocean (Holmes et al., 2009; Mason and Sheu, 2002; Mason et al., 2012).

Atmospheric Hg emissions from East Asia were much higher than those from other continents in global emission inventories (Pacyna and Pacyna, 2002; Pacyna et al., 2006; 2010). Current estimates suggest that over 50% of the global anthropogenic Hg emissions are from Asia (Lin et al., 2010; Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010), while approximately 40% of the anthropogenic Hg in China is emitted in the forms of RGM and Hg^p (Zhang et al., 2015; Streets et al., 2005). China is the largest contributor to global atmospheric Hg, where anthropogenic Hg emissions are likely to further increase with the expansion of nonferrous production and coal combustion (Streets et al., 2005; Wu et al., 2006; Zhang et al., 2015). Higher Hg emissions in China may result in elevated atmospheric Hg concentrations and deposition levels, and then cause Hg pollution in the surrounding regions. But we have little knowledge on the atmospheric Hg speciation in the East Asia marine boundary layer (MBL).

Recently, speciated atmospheric Hg concentrations have been monitored at many locations with various site characteristics, such as remote oceans, Arctic and Antarctic, coastal, rural, and urban sites (Chand et al., 2008; Cheng et al., 2012, 2013a,b, 2014; Choi et al., 2008; Fu et al., 2011, 2012; Gabriel et al., 2005; Kim et al., 2009; Laurier and Mason, 2007; Liu et al., 2007, 2011, 2010; Soerensen et al., 2010; Valente et al., 2007; Wan et al., 2009; Xu et al., 2015; Zhang et al., 2012). However, study on the knowledge of the speciated atmospheric Hg over the East Asia MBL is limited. The objectives of this study are to characterize the levels of atmospheric Hg species as well as their spatial distributions in the MBL of the Bohai Sea (BS) and Yellow Sea (YS), and to ascertain the relationships between Hg species and meteorological parameters. Findings from this investigation are discussed in terms of better understanding the behavior and cycling of atmospheric Hg in the MBL.

2. Materials and methods

2.1. Study area

The study area includes the BS and YS, which is located in the downwind of the East Asia. The BS is an inner sea with an average depth of 18 m, which is surrounded by numerous economically-developed and industrialized provinces, such as Shandong, Liaoning, Hebei, Tianjin, and Beijing (Fig. 1). The low rate of water exchange favors the accumulation of pollutants in the BS. The YS is a semi-enclosed and representative shallow continental shelf sea located between mainland China and the Korean Peninsula (Fig. 1). For these reasons, the BS and YS are particularly vulnerable to anthropogenic pollutants originated from industrialized and densely populated East Asia. Hg enters the BS and YS through terrestrial runoff from the rivers (e.g., Yellow, Liao, Luanhe, Haihe, Yalu, Han, Taedong, and Geum Rivers) and atmospheric wet and dry deposition. Hg and its compounds may have a toxic impact on the ecosystem of these marine environments.

2.2. Experimental methods

Two open cruises were organized by Ocean University of China (OUC), and conducted from 27 April to 20 May 2014 (spring) and from 5 to 24 November 2014 (fall), respectively. The two expeditions (spring: Fig. 2a and fall: Fig. 2b) covered the majority areas of the BS and YS between latitudes 31°N and 40°N and longitudes 118°E and 125°E. The data and samples were collected onboard the R/V *DongfanghongII* (OUC). In this study, meteorological parameters, including wind speed, air temperature, and relative humidity (RH), were measured synchronously with GEM.

2.2.1. Atmospheric GEM measurements

GEM in the marine atmosphere was continuously measured using an automatic dual channel, single amalgamation cold vapor atomic fluorescence analyzer (Model 2537B, Tekran®, Inc., Toronto, Canada) with a 0.2 μm Teflon filter and a soda-lime trap just

Fig. 1. Location of the study area, including the BS and YS.

Fig. 2. Cruise tracks (black line) of the R/V during the spring (a) and fall (b) of 2014.

upstream to remove the atmospheric particulates and water. The soda lime was changed every 3 days during the cruises. The Tekran[®] instrument is based on the collection of Hg^0 amalgamation on gold traps, followed by thermal desorption and then detection of Hg^0 by cold vapor atomic fluorescence spectrometry (CVAFS) (Tekran, 2008). In this study, 5-min sampling interval was conducted with an air flow rate of 1.5 l min^{-1} . The detection limit of GEM was less than 0.1 ng m^{-3} .

2.2.2. Sampling of atmospheric RGM and Hg^{P}

The RGM and Hg^{P} were sampled using a manual system, which has been described in detail by Landis et al. (2002). The unit includes two KCl-coated quartz annular denuders, a 47 mm Teflon filter holder (URG Corporation), and a pump etc. (Landis et al., 2002; Liu et al., 2011). The Hg^{P} measured in this study was the Hg content in fine particulate matters (hereafter referred to as $\text{Hg}^{\text{P}}_{2.5}$). The quartz annular denuders were cleaned, coated, and conditioned prior to RGM sampling with a flow rate of 10 l min^{-1} (Landis et al., 2002). The $\text{Hg}^{\text{P}}_{2.5}$ samples were collected on quartz fiber filter (47 mm diameter, Whatman) housed in quartz denuders because the quartz filter had been widely used to collect Hg^{P} in the previous studies (Kim et al., 2012; Landis et al., 2002; Liu et al., 2011). The manual system for RGM and $\text{Hg}^{\text{P}}_{2.5}$ traps were positioned vertically, and the inlet was located at the front deck 1.3 m above the top deck of the R/V. During sampling, denuders were maintained at $20\text{--}30^\circ\text{C}$ above the ambient air temperature using a heating sleeve to prevent hydrolysis of the KCl coating surface as well as ensure quantitative transport of air through the inlet. Approximately 11–12 h $\text{Hg}^{\text{P}}_{2.5}$ samples were collected each day from 6:00 to 18:00 (daytime) and from 18:00 to 6:00 (next day) (nighttime) with a resulting sample volume of $6.6\text{--}7.2 \text{ m}^3$, but the RGM samples were collected every 6 h (6:00–12:00 and 12:00–18:00, local time) during daytime and 12 h during

nighttime. These campaigns were conducted to investigate the difference in phase partitioning and cycling of RGM and $\text{Hg}^{\text{P}}_{2.5}$ between day and night.

2.2.3. Analysis of atmospheric RGM and $\text{Hg}^{\text{P}}_{2.5}$

Upon completion of the sampling, the KCl coated annular denuder was thermally desorbed in a tube furnace (Model BTF-1200 C-S, Anhui BEQ Equipment Technology Co., Ltd, China) used at 500°C for RGM. A soda lime trap was used to protect the gold traps (Tekran[®] 2537B) from being passivated by non-Hg compound(s) collected by the denuder (Landis et al., 2002), and the resulting thermally decomposed Hg^0 in carrier gas (zero air, i.e. Hg-free air) was quantified using the Tekran[®] instrument. The analysis procedures employed for RGM pyrolysis were described by Landis et al. (2002). The method detection limit was calculated to be 0.90 pg m^{-3} for RGM based on 3 times the standard deviation of the blanks ($n = 110$) for the whole dataset, which was comparable to that measured by Liu et al. (2011). The third reading during the zero air flush at the beginning of every desorbing cycle was used as the system blank (Liu et al., 2007; Xu et al., 2015). All RGM concentrations presented in this study were blank corrected.

While after sampling, the preservation and analysis methods for Hg^{P} have been described in our previous study (Wang et al., 2016). The average blank value ($n = 6$) was 3.4 pg of Hg per filter (equivalent of $<0.5 \text{ pg m}^{-3}$ for a 12 h sample) in this study. The average field blank was subtracted from the samples. The detection limit was less than 1.5 pg m^{-3} based on 3 times the standard deviation of field blanks ($n = 6$). A recent work has suggested that the filter-based Hg^{P} has minimal positive artifact from uptake of RGM during sampling (Talbot et al., 2011). However, it is important to note that there are still some artifacts associated with Hg^{P} collection and interferences with the collection of RGM on KCl coated denuders (Gustin et al., 2015; Lyman et al., 2010; Malcolm and

Keeler, 2007; Rutter et al., 2008; Talbot et al., 2011).

2.3. Quality assurance and quality control

To maintain high standard measurements, the Tekran® instrument was calibrated every 25 h using the internal calibration source and these calibrations were checked against manual injections of known quantities of Hg^0 before and after the cruises. The relative percent difference between manual injections and automated calibrations was less than 5% and the analytical precision was < 3% ($n = 6$). To diminish the contamination from domestic waste and exhaust plume of the ship, we installed the Tekran® system inside the ship laboratory and mounted the sampling inlet at the front deck 2 m above the top deck using an unheated Teflon tube. The use of this Teflon tube might result in some adsorption of Hg^p and RGM to the Teflon tubing. This system was designed to capture only the GEM since Hg^p would be lost on the Teflon filter and the long unheated Teflon tube, and most of the RGM would be removed when passing the sampling tube, which was probably coated by sea salt during the sampling (Fu et al., 2010). Furthermore, the GEM was reported at a level at least 2 orders of magnitude higher than RGM in the MBL (Chand et al., 2008; Soerensen et al., 2010; Wang et al., 2016). Therefore, the atmospheric Hg measured using the Tekran® was referred to as GEM (Fu et al., 2010; Radke et al., 2007).

Before sampling, the KCl coated denuders and Hg^p quartz filters were pre-cleaned by pyrolysis at 500 °C for 1 h and 900 °C for 3 h respectively to obtain low operational blanks. Quality assurance and quality control for $\text{Hg}^p_{2.5}$ and RGM were conducted using duplicates and field blanks. The mean relative differences of duplicated $\text{Hg}^p_{2.5}$ and RGM samples ($n = 6$) were $15 \pm 9\%$ and $17 \pm 10\%$, respectively. The average field blank of denuders was 1.2 ± 0.6 pg ($n = 6$). The field blank filters were treated similarly to the other samples but not sampling. Routine maintenance practices (e.g. filter changes) were completed using particle free gloves and Teflon coated tweezers to reduce the possibility of contamination. Recent work has shown that heating of the inlet to 100 °C improves RGM collection (Huang and Gustin, 2015), and the KCl denuder oxidized Hg collection method may not be as robust as previously thought (Lyman et al., 2010). Although the KCl-coated denuder method has yet to be improved (Gustin et al., 2015; Huang and Gustin, 2015), this method has become a standard method for measurement of RGM and has been widely used to measure RGM (Chand et al., 2008; Cheng et al., 2013a,b, 2014; Fu et al., 2011, 2012; Holmes et al., 2009; Kim et al., 2009; Liu et al., 2011; Mao and Talbot, 2012; Mao et al., 2012; Xu et al., 2015).

3. Results and discussion

3.1. Speciated atmospheric Hg concentrations in the MBL

Fig. 3 shows the time series of GEM, RGM, $\text{Hg}^p_{2.5}$, and several meteorological parameters (e.g., RH, air temperature, and wind speed) during the spring and fall cruises of 2014. The mean GEM concentration during spring (2.03 ± 0.72 ng m^{-3} , $n = 5243$) was comparable to that during fall (2.09 ± 1.58 ng m^{-3} , $n = 4413$) (t -test, $p > 0.05$). The mean GEM level during the whole study period was 2.07 ± 1.16 ng m^{-3} , which was higher than those in some other open oceans (see Table 1), such as the Atlantic Ocean (Laurier and Mason, 2007; Soerensen et al., 2013), the equatorial Pacific Ocean (Soerensen et al., 2014), the Adriatic Sea (Sprovieri and Pirrone, 2008), and the Indian Ocean (Witt et al., 2010), even higher than those of rural coastal sites in Canada (Cheng et al., 2014), and was comparable to those of coastal sites, such as the Hedo Station (Chand et al., 2008) in Japan, and the Augusta basin (Bagnato et al.,

2013) in Italy, but lower than those reported in the northern South China Sea (Fu et al., 2010; Tseng et al., 2012).

The mean $\text{Hg}^p_{2.5}$ concentration during spring was 8.2 ± 6.3 pg m^{-3} ($n = 39$) (Table 1) with a range of 1.8–28.4 pg m^{-3} except the two samples measured at Jiaozhou Bay in Qingdao, Shandong Province, China (Fig. 2a and left panel of Fig. 3), while the mean $\text{Hg}^p_{2.5}$ concentration during fall was 8.3 ± 6.9 pg m^{-3} ($n = 32$) (Table 1) with a range of 1.0–31.3 pg m^{-3} except the two samples measured at Jiaozhou Bay (Fig. 2b and right panel of Fig. 3). The results showed that the average $\text{Hg}^p_{2.5}$ concentration in spring was comparable to that in fall (t -test, $p > 0.1$). This trend was consistent with the results obtained for GEM. The average $\text{Hg}^p_{2.5}$ concentration during the entire study period was 10.1 pg m^{-3} ($n = 75$), which was higher than those of other oceanic, coastal, and even rural environments (see Table 1), such as the Adriatic Sea (Sprovieri and Pirrone, 2008), the Ontario Lake (Cheng et al., 2012), the Okinawa Island in Japan (Chand et al., 2008), the CPO (Weiss-Penzias et al., 2003) and the Weeks Bay (Engle et al., 2008) in the US, but obviously lower than the average Hg^p_{10} concentration (15.6 pg m^{-3}) in the East Asia MBL (including the BS, YS, and East China Sea) (Wang et al., 2016), and considerably lower than those of Chinese rural sites, such as Waliguan (Fu et al., 2012) and Mt. Changbai (Wan et al., 2009).

The mean RGM concentration in spring (2.5 ± 1.7 pg m^{-3} with a range of 0.2–9.8 pg m^{-3} , $n = 60$) was significantly lower than that in fall (4.3 ± 2.5 pg m^{-3} with a range of 0.8–15.3 pg m^{-3} , $n = 50$) (t -test, $p < 0.01$). The mean concentration of RGM during the entire study period was 3.3 ± 2.3 pg m^{-3} ($n = 110$), which was comparable to the global mean concentration of RGM in the MBL (Soerensen et al., 2010), and somewhat higher than those of rural or coastal areas in North America (Table 1), such as the Ontario Lake (Cheng et al., 2012), several coastal sites in Nova Scotia (Cheng et al., 2013a, 2014), and slightly lower than those of other seas, such as the Mediterranean Sea (Sprovieri et al., 2003), the Weeks Bay (Engle et al., 2008), the Adriatic Sea (Sprovieri and Pirrone, 2008), the subtropical North Atlantic (Laurier and Mason, 2007), the Okinawa Island (Chand et al., 2008), and the North Pacific Ocean (Laurier et al., 2003). But RGM concentrations measured in this study area were much lower than those of urban or rural sites in China and South Korea, such as Guiyang (Fu et al., 2011; Liu et al., 2011), Xiamen (Xu et al., 2015), Mt. Changbai (Wan et al., 2009), and Seoul (Kim et al., 2009).

Overall, the higher concentrations and larger variability of GEM and $\text{Hg}^p_{2.5}$ over the BS compared to over the YS (Fig. 3) demonstrated that the BS was influenced by human activities more seriously than the YS. Moreover, the long-lived GEM showed smaller variability (especially over the YS) compared to the short-lived species like RGM and $\text{Hg}^p_{2.5}$, indicating that the RGM and $\text{Hg}^p_{2.5}$ were easily removed from the marine atmosphere because of their higher activity and solubility. Interestingly, it could be found that the average value of reactive Hg (RGM + $\text{Hg}^p_{2.5}$) (Rutter and Schauer, 2007) in spring was comparable to that in fall, and the reactive Hg constitutes less than 1% of TAM in the MBL, which was comparable to those observed in other remote sites, such as the two sites in the Bay St. François wetlands (Poissant et al., 2004), and the Okinawa Island (Chand et al., 2008). The results suggested that most Hg export in the BS and YS was GEM and the direct anthropogenic emission of reactive Hg was very small.

3.2. Spatial distributions of atmospheric Hg in the MBL

The spatial distributions of GEM during the spring and fall cruises can be found in our previous study (Wang et al., 2016). The spatial distributions of $\text{Hg}^p_{2.5}$ in the MBL of the BS and YS were illustrated in Fig. 4a and b. During spring, two higher $\text{Hg}^p_{2.5}$

Fig. 3. Time (local time) series of GEM, $\text{Hg}_{2.5}^{\text{P}}$, RGM, and some meteorological parameters, including RH, air temperature, and wind speed. The legends show the respective variables, the light gray areas represent the samples in the BS.

Table 1.

The GEM, $\text{Hg}_{2.5}^{\text{P}}$, and RGM concentrations in this study and values reported in other literature.

Location		Classification	Sampling time	GEM (ng m ⁻³)	Hg ^P _{2.5} (pg m ⁻³)	RGM (pg m ⁻³)	Reference
China	BS and YS	Sea	2014 (Spring)	2.03 ± 0.72	11.3 ± 18.5	2.5 ± 1.7	This study
	BS and YS	Sea	2014 (Fall)	2.09 ± 1.58	9.0 ± 9.0	4.3 ± 2.5	This study
	Mt. Changbai	Remote	2005–2006	3.58 ± 1.78	77 ± 136	65 ± 84	Wan et al., 2009
	Waliguan	Remote	2007–2008	1.98 ± 0.98	19.4 ± 18.1	7.4 ± 4.8	Fu et al., 2012
USA	CPO ^a	Coastal	2001–2002	1.55	0.5	<1.6	Weiss-Penzias et al., 2003
	Weeks Bay	Coastal	2005–2006	1.6 ± 0.3	2.7 ± 3.4	4.0 ± 7.5	Engle et al., 2008
Canada	Ontario Lake	Remote	2005–2006	1.57 ± 0.22	4.42 ± 3.67	0.99 ± 1.89	Cheng et al., 2012
	Nova Scotia	Coastal	2010–2011	1.67 ± 1.01	2.32 ± 3.09	2.07 ± 3.35	Cheng et al., 2013a
	Nova Scotia	Coastal-rural	2010–2011	1.38 ± 0.20	3.5 ± 4.5	0.4 ± 1.0	Cheng et al., 2014
	Nova Scotia	Coastal-urban	2010–2011	1.67 ± 1.01	2.3 ± 3.1	2.1 ± 3.4	Cheng et al., 2014
Korea	Seoul	Urban	2005–2006	3.22 ± 2.10	23.9 ± 19.6	27.2 ± 19.3	Kim et al., 2009
Japan	Okinawa Island	Coastal-rural	2004	2.04 ± 0.38	3.0 ± 2.5	4.5 ± 5.4	Chand et al., 2008
North Atlantic Ocean		Ocean	2003	1.63 ± 0.08	NA ^b	5.9 ± 4.9	Laurier and Mason, 2007
North Pacific Ocean		Ocean	2002	2.5	NA	9.5	Laurier et al., 2003
Mediterranean Sea		Ocean	2000	1.9 ± 1.0	NA	7.9	Sprovieri et al., 2003
Global Ocean		Ocean	2006–2007	1.53 ± 0.58	NA	3.1 ± 11.0	Soerensen et al., 2010
Adriatic Sea		Ocean	2004	1.6 ± 0.4	4.5 ± 8.0	6.7 ± 11.7	Sprovieri and Pirrone, 2008

^a CPO: Cheeka Peak Observatory.

^b NA: no data available.

concentrations (119.0 and 24.5 pg m^{-3}) were observed at Jiaozhou Bay during the daytime and nighttime on the day of 7 May 2014 presumably because of the local human activities, while the lowest $\text{Hg}_{2.5}^{\text{P}}$ concentration (1.8 pg m^{-3}) was observed in the northern YS during daytime on the day of 11 May 2014 (Fig. 4a). During fall, the maximum and minimum values of $\text{Hg}_{2.5}^{\text{P}}$ concentrations were observed in the BS and southern YS respectively (Fig. 4b). Fig. 4a and b show that the spatial distributions of $\text{Hg}_{2.5}^{\text{P}}$ generally reflected a gradient with high levels near the coast of East China and low levels in the open sea both in spring and fall, suggesting significant atmospheric $\text{Hg}_{2.5}^{\text{P}}$ outflow from China. Interestingly,

higher $\text{Hg}_{2.5}^{\text{P}}$ concentrations generally went with the higher GEM concentrations during the two cruises (especially over the BS), which could be found in Fig. 4a and b in this study and Fig. 2 in our previous study (Wang et al., 2016). This was probably due to the large anthropogenic Hg (including the GEM and Hg^{P}) emissions in China (Zhang et al., 2015).

However, there was large difference in $\text{Hg}_{2.5}^{\text{P}}$ concentration between the BS and YS. The average $\text{Hg}_{2.5}^{\text{P}}$ concentrations in the BS (spring: 15.5 pg m^{-3} , fall: 16.7 pg m^{-3}) were more than 2 times higher than those in the YS (spring: 6.7 pg m^{-3} , fall: 7.0 pg m^{-3}) both in spring (Fig. 4a) and fall (Fig. 4b). We speculate that the

Fig. 4. The concentrations and spatial distributions of $\text{Hg}^{2+}_{2.5}$ (a: spring, b: fall) and RGM (c: spring, d: fall) in the MBL of the BS and YS (units for both $\text{Hg}^{2+}_{2.5}$ and RGM: pg m^{-3}).

$\text{Hg}^{2+}_{2.5}$ in the BS mainly originated from the surrounding land areas due to the large emission of Hg^{P} . The BS was more susceptible to the anthropogenic pollutants than the YS due to its specific location. Additionally, it could be found that the $\text{Hg}^{2+}_{2.5}$ concentrations in the BS were comparable to those observed in Jiaozhou Bay, and $\text{Hg}^{2+}_{2.5}$

concentrations varied more markedly on the diel time scale in the BS compared to those in the YS (Fig. 4a and b), which further indicated that $\text{Hg}^{2+}_{2.5}$ in the BS was dramatically influenced by any local (e.g., marine oil exploration) or regional processes.

The spatial distributions of RGM over the BS and YS were plotted

in Fig. 4c and d. RGM showed homogeneous distributions over the study area both in spring and fall. The lower concentrations and homogeneous distributions of RGM indicated that the majority of the RGM presumably not originated from the land. Interestingly, the RGM concentrations during fall were generally higher than those during spring (see Fig. 4c and d), which maybe due to the difference in RH between spring and fall (RGM has strong water solubility and activity), and the detailed discussions can be found in the next section. In addition, there was no significant difference in RGM concentrations between the BS (spring: 3.1 pg m^{-3} , fall: 4.8 pg m^{-3}) and YS (spring: 2.6 pg m^{-3} , fall: 4.1 pg m^{-3}) both in spring (t -test, $p > 0.05$) and fall (t -test, $p > 0.05$).

3.3. Diurnal variation of speciated atmospheric Hg and the potential sources of RGM in the MBL

3.3.1. Diurnal variation of GEM in the MBL

The diurnal variation of GEM concentrations during the spring and fall cruises was illustrated in Fig. 5. The amplitude (difference between maxima and minima) of diurnal variation of GEM in the BS was much greater than that in the YS both in spring and fall. Actually, as shown in Fig. 1, the BS is surrounded by numerous industrial provinces, and the large emissions of Hg from China have seriously impacted the GEM distribution in the BS. The GEM concentrations over the BS dominantly fell in the range of $2.0\text{--}4.0 \text{ ng m}^{-3}$ (Fig. 5a and b), while they mainly fell in the range of $1.5\text{--}2.0 \text{ ng m}^{-3}$ over the YS (Fig. 5c and d). It could be found that GEM concentrations in spring were generally higher than those in fall in the YS (Fig. 5c and d), which was in contrast to the GEM results obtained in the BS (Fig. 5a and b). In the BS, GEM concentrations in the daytime were higher than those in the nighttime during spring (Fig. 5a), while opposite result was observed during

fall, just as illustrated in Fig. 5b, GEM suddenly decreased at 01:00 and then suddenly increased at 19:00 in fall, which demonstrated that the BS was seriously polluted by Hg pollutant. It was notable that there was no consistent diurnal pattern of GEM over the BS (Fig. 5a and b) presumably due to the significantly influence of human activities. In the YS, the mean GEM concentration in the daytime was significantly lower than that in the nighttime during spring (t -test, $p < 0.01$) (Fig. 5c). One probable reason was the oxidation of GEM in the daytime (Lindberg et al., 2002). Although the mean GEM concentration in the nighttime was comparable to that in the daytime, the GEM levels slowly decreased in the daytime during fall (especially after 10 a.m.) (Fig. 5d). The smaller variability and lower concentrations of GEM over the YS indicated that the YS suffered less influence of human activities. According to the previous study conducted in 2012, the GEM levels during the two cruises in the YS were similar (spring: $1.86 \pm 0.40 \text{ ng m}^{-3}$, fall: $1.84 \pm 0.50 \text{ ng m}^{-3}$) (Ci et al., 2015), which were comparable to those of our observations in the YS.

3.3.2. Diurnal variation of $\text{Hg}^{P_{2.5}}$ and RGM in the MBL

Fig. 6a shows the $\text{Hg}^{P_{2.5}}$ concentrations in the daytime and nighttime during the entire study period. During spring, the mean $\text{Hg}^{P_{2.5}}$ concentration in the nighttime ($9.0 \pm 5.2 \text{ pg m}^{-3}$, $n = 19$) was slightly higher than that in the daytime ($7.1 \pm 5.9 \text{ pg m}^{-3}$, $n = 20$) except the two samples in the Jiaozhou Bay. Similarly, during the fall cruise, the mean $\text{Hg}^{P_{2.5}}$ concentration in the nighttime ($10.3 \pm 8.3 \text{ pg m}^{-3}$) was also somewhat higher than that in the daytime ($6.6 \pm 4.7 \text{ pg m}^{-3}$). But in fact, with exception of the samples observed in the Jiaozhou Bay and BS, there was no significant difference in $\text{Hg}^{P_{2.5}}$ concentrations between day and night in the YS both in spring and fall (Fig. 6a), which was consistent with the GEM results in the YS (Fig. 5d). The results suggested that the YS

Fig. 5. Diurnal variation of atmospheric GEM concentrations (mean $\pm$ SD) over the BS (a: spring, b: fall) and YS (c: spring, d: fall).

Fig. 6. $\text{Hg}_{2.5}^{\text{P}}$ (a) and RGM (b) concentrations in the daytime and nighttime during the spring and fall cruises, the light gray areas represent the samples in the BS.

suffered less anthropogenic Hg^{P} as compared to the BS and the $\text{Hg}_{2.5}^{\text{P}}$ over the YS presumably originated from both the *in-situ* formation and anthropogenic emissions.

The time series of RGM concentrations in the daytime and nighttime were plotted in Fig. 6b. Generally, RGM showed a diurnal variation with higher levels in the daytime and lower levels in the nighttime during the entire study period. During spring, the average RGM concentration in the daytime ($3.2 \pm 1.9 \text{ pg m}^{-3}$) was significantly higher than that in the nighttime ($1.8 \pm 0.9 \text{ pg m}^{-3}$) (*t*-test, $p < 0.01$). We found a similar pattern during fall, and the mean RGM concentration in the daytime ($5.0 \pm 2.3 \text{ pg m}^{-3}$) was also significantly higher than that in the nighttime ($3.4 \pm 1.8 \text{ pg m}^{-3}$) (*t*-test, $p < 0.05$). Our results were consistent with the previous multiple-sites (e.g., coastal, oceanic, and urban sites) studies (Cheng et al., 2014; Engle et al., 2008; Laurier and Mason, 2007; Liu et al., 2007), which showed that the RGM typically followed a diurnal pattern with lower concentrations in the nighttime and higher concentrations in the daytime. Numerous field studies have shown that GEM in the MBL can be rapidly oxidized to form RGM *in-situ* (Chand et al., 2008; Hedgecock and Pirrone, 2001; Hedgecock et al., 2003; Laurier et al., 2003; Laurier and Mason, 2007; Soerensen et al., 2010; Sprovieri et al., 2003, 2010). In addition, the oxidation of GEM must be photochemical, as evidenced by the observed seasonal cycle of GEM (Selin et al., 2007) and the diurnal cycle of RGM (Laurier and Mason, 2007). For these reasons, we attribute the diurnal variation of RGM to the photochemical activity. We speculate that there are at least three main reasons for the lower RGM concentrations in the nighttime: (a) there is no solar radiation at night, and there is little RGM production; (b) the higher RH during nighttime is conducive to the removal of RGM; and (c) the lower air temperature during nighttime is beneficial to the partitioning of RGM from the gas to the particle phase (Amos et al., 2012; Rutter and Schauer, 2007), while more further studies are needed to verify these hypotheses.

Fig. 6b shows that there was large difference in RGM concentration between the beginnings of the two cruises. The RGM concentrations in the beginning of the spring cruise were far lower than those in the beginning of the fall cruise. According to our observations on the weather conditions, it was a rainy day on 28 April 2014, when the RH reached 100% and the wind speed was very high ($> 12 \text{ m s}^{-1}$) (see Fig. 3). The lower concentrations of $\text{Hg}_{2.5}^{\text{P}}$ and RGM (Fig. 6a and b) in the first day of the spring sampling time might be caused by wet scavenging since the first sampling day experienced precipitation, while it was a sunny day on 7 November 2014 with lower RH (40–50%) and wind speed ($< 7 \text{ m s}^{-1}$) (see Fig. 3). Moreover, it was obviously found that the RGM and $\text{Hg}_{2.5}^{\text{P}}$ concentrations were considerably lower in the rainy and heavy foggy weather than those in the fine days (e.g., 2–4 May 2014 and 7–10 November 2014) (see Fig. 6a and b), while we found lower RGM and relatively higher $\text{Hg}_{2.5}^{\text{P}}$ concentrations during the period of little fog. Therefore, we suggest that the solar radiation and RH have significant influence on the formation and removal of RGM in the MBL (Selin et al., 2007; Laurier and Mason, 2007; Soerensen et al., 2010).

3.3.3. Potential sources of RGM in the MBL

Previous studies suggested that RGM production is believed to primarily occur via ozone (O_3) and hydroxyl radical (OH) oxidation of Hg^0 (Calvert and Lindberg, 2005; Pal and Ariya, 2004a,b). Recently, both experimental and theoretical studies suggested that the gas phase recombination of Hg^0 with halogen atoms is sufficiently fast to initiate the oxidation process of Hg^0 (Auzmendi-Murua et al., 2014; Wang et al., 2015), and the oxidation of Hg^0 must be photochemical (Laurier and Mason, 2007; Selin et al., 2007). Numerous studies have suggested that reactive halogen species (Br, Cl, and BrO etc.) that generated from sea salt aerosols (Sander et al., 2003; Sheu and Mason, 2004; Soerensen et al., 2010) may be the dominant sources for the oxidation of Hg^0 in the MBL.

(Auzmendi-Murua et al., 2014; Holmes et al., 2010; Laurier et al., 2003; Seigneur and Lohman, 2008; Steffen et al., 2015), while this process may be limited in coastal environments because of the higher O_3 concentration (Laurier and Mason, 2007; Lyman et al., 2010). Holmes et al. (2009, 2010) studied the sources of RGM in the marine atmosphere, and they suggested that 80–95% of divalent Hg (Hg^{II}) in the MBL was present in sea salt aerosols rather than gas-phase and the RGM was mainly from the oxidation of Hg^0 by Br and O_3 . A recent study suggested that up to 100% conversion of GEM to RGM has been observed in the Arctic (Steffen et al., 2015).

It is now generally accepted, even though not fully understood, that Hg^0 oxidation and RGM production are closely related to photochemically induced heterogeneous and autocatalytic reactions involving sea-salt particles and reactive halogen species (Lindberg et al., 2002). The reactions with atomic Br and Cl have substantially larger rate constants (Ariya et al., 2002; Ariya and Ryzhkov, 2003; Wang et al., 2015) and therefore oxidation by these mechanisms may proceed faster than oxidation by O_3 and OH even though the concentrations of the halogen radicals in the MBL were substantially lower than that of O_3 . However, the results of spatial distributions of RGM (Fig. 4c and d) showed that higher RGM levels were often observed in the offshore areas, and the RGM concentrations in the BS were slightly higher than those in the YS, which indicated that a small portion of RGM presumably originated from the surrounding land or offshore oil exploitation (e.g., in the BS). Therefore, in this study, we speculate that the RGM in the open sea was mainly from the oxidation of Hg^0 by reactive halogen species, while the RGM in coastal environments was predominately from both the oxidation of Hg^0 and anthropogenic emissions. In addition, a little part of RGM probably originated from the free troposphere (Weiss-Penzias et al., 2009; Wang et al., 2015).

3.4. Relationships between speciated atmospheric Hg and meteorological parameters

The descriptive statistics for correlation coefficients for speciated atmospheric Hg and meteorological parameters during the two sampling campaigns were summarized in Table 2. The elevated GEM concentrations and the strong positive relationship between $Hg^{P}_{2.5}$ and GEM (Pearson's correlation coefficient) both in spring and fall suggested that the $Hg^{P}_{2.5}$ likely originated from the land, while the $Hg^{P}_{2.5}$ had no significant correlation with RH and air temperature (Table 2). There was no significant correlation between RGM and GEM during the whole study period, while significantly positive correlation between RGM and air temperature was found both in spring and fall (Table 2). One of the reasons could be related to an increase in atmospheric radical production (especially during daytime) and subsequent formation of RGM (Mao and Talbot, 2012; Mao et al., 2012). Besides, the higher air temperature was conducive to partitioning of RGM from the particle phase to the gaseous phase, and this trend has been demonstrated in the previous studies (Choi et al., 2008; Rutter and Schauer, 2007). Moreover, the correlations of RGM-wind speed and $Hg^{P}_{2.5}$ -wind

speed were not significant both in spring and fall (Table 2), which were consistent with the previous study conducted at two coastal sites (Cheng et al., 2014). Furthermore, a significantly negative correlation was observed between RGM and RH during the fall cruise (see Table 2), which demonstrated that elevated RH may facilitate the removal of RGM. However, the RGM-RH correlation was not significant during spring probably due to the much higher RH (generally > 80%). Our findings (negative correlation between RGM and RH, positive correlation between RGM and air temperature) were consistent with the previous studies conducted at the coastal and marine locations (Cheng et al., 2014; Mao et al., 2012). More efforts and research work are needed to account for such phenomenon. Cheng et al. (2014) had proposed two potential factors for the strong negative correlation between RGM and RH: (1) higher humidity increases particle growth and thus particle surface area which in turn increases partitioning of RGM to particles (by decreasing RGM); and (2) RGM positively correlates with air temperature while RH negatively correlates with air temperature under fixed water vapor content.

As show in Fig. 7, the RGM and $Hg^{P}_{2.5}$ predominately fell in the RH range of 70–100% during spring, while they dominantly fell in the range of 50–80% during fall. We found an interesting phenomenon that the higher the RH and the lower the RGM concentration both in spring and fall, but there was no distinct difference in $Hg^{P}_{2.5}$ concentration between higher and lower RH. Additionally, there was no significant correlation between RGM and $Hg^{P}_{2.5}$ both in spring and fall (see Table 2 and Fig. 7) probably due to their higher activity and deposition rates. Priorities for future research include identification of Hg^P and RGM compounds in ambient air and development of information on their chemical and physical properties (Gustin et al., 2015).

4. Conclusions

During the spring and fall cruises of 2014, speciated atmospheric Hg was determined in the MBL of the BS and YS downwind of the East Asia. Our observations of RGM and $Hg^{P}_{2.5}$ represent the first reported measurements in the BS and YS. The average concentrations of GEM and $Hg^{P}_{2.5}$ in spring were comparable to those in fall, while RGM concentrations were generally higher in fall than in spring. Moreover, the $Hg^{P}_{2.5}$ showed spatial distributions with higher concentrations in the offshore area and lower values in the open sea. The larger variability and higher concentrations of GEM, $Hg^{P}_{2.5}$, and RGM concentrations in the BS as compared to those in the YS demonstrated that the BS was more vulnerable to anthropogenic Hg. Our results suggested that reactive Hg (RGM + $Hg^{P}_{2.5}$) comprised < 1% of the TAM, indicating that most Hg export in the BS and YS was GEM. Inspection of the RGM and $Hg^{P}_{2.5}$ concentrations during daytime and nighttime, the RGM concentrations in the daytime were significantly higher than those in the nighttime during the entire study period, but opposite results for $Hg^{P}_{2.5}$ were observed. Correlation analysis showed that there was a significantly positive correlation between $Hg^{P}_{2.5}$ and GEM during the entire

Table 2.
Correlation coefficients for speciated atmospheric Hg concentrations and meteorological parameters (one asterisk denotes significant correlation in $p < 0.05$, double asterisks denotes significant correlation in $p < 0.01$).

Season	Speciation	GEM		$Hg^{P}_{2.5}$		Temperature		RH		Wind speed	
		p	r	p	r	p	r	p	r	p	r
Spring	RGM	0.881	−0.020	0.774	0.045	0.017	0.307*	0.443	−0.101	0.556	0.077
	$Hg^{P}_{2.5}$	<0.01	0.635**			0.182	0.208	0.873	−0.025	0.772	0.045
Fall	RGM	0.713	−0.053	0.225	0.191	0.031	0.305*	0.014	−0.344*	0.055	0.274
	$Hg^{P}_{2.5}$	<0.01	0.522**			0.983	−0.003	0.233	0.188	0.523	0.101

Fig. 7. Humidity compared with concentrations of RGM and $\text{Hg}_{2.5}^{\text{P}}$.

study period, the RGM-air temperature correlation was positive and the RGM-RH correlation was negative during the entire study period. Overall, the human activities in East Asia (mainly China) have a significant influence on the oceanic Hg cycle in the BS and YS. However, from what is currently known about the atmospheric chemistry of Hg in the East Asian MBL, short-term measurements are insufficient to determine the chemical mechanisms occurring and the long-term measurements concurrent with wet and dry deposition of Hg are essential in understanding the fate of Hg in the MBL.

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