Elemental mercury (Hg(0)) in air and surface waters of the Yellow Sea during late spring and late fall 2012: Concentration, spatial-temporal distribution and air/sea flux

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HIGHLIGHTS

- Elemental Hg in air and surface waters of the Yellow Sea were determined in two cruises.
- Elemental Hg flux at air/sea interface was estimated using a two-layer exchange model.
- The seasonality of elemental Hg and its air/sea flux was discussed.

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ABSTRACT

The Yellow Sea in East Asia receives great Hg input from regional emissions. However, Hg cycling in this marine system is poorly investigated. In late spring and late fall 2012, we determined gaseous elemental Hg (GEM or Hg(0)) in air and dissolved gaseous Hg (DGM, mainly Hg(0)) in surface waters to explore the spatial-temporal variations of Hg(0) and further to estimate the air/sea Hg(0) flux in the Yellow Sea. The results showed that the GEM concentrations in the two cruises were similar (spring: $1.86 \pm 0.40 \text{ ng m}^{-3}$; fall: $1.84 \pm 0.50 \text{ ng m}^{-3}$) and presented similar spatial variation pattern with elevated concentrations along the coast of China and lower concentrations in the open ocean. The DGM concentrations of the two cruises were also similar with $27.0 \pm 6.8 \text{ pg L}^{-1}$ in the spring cruise and $28.2 \pm 9.0 \text{ pg L}^{-1}$ in the fall cruise and showed substantial spatial variation. The air/sea Hg(0) fluxes in the spring cruise and fall cruise were estimated to be $1.06 \pm 0.86 \text{ ng m}^{-2} \text{ h}^{-1}$ and $2.53 \pm 2.12 \text{ ng m}^{-2} \text{ h}^{-1}$, respectively. The combination of this study and our previous summer cruise showed that the summer cruise presented enhanced values of GEM, DGM and air/sea Hg(0) flux. The possible reason for this trend was that high solar radiation in summer promoted Hg(0) formation in seawater, and the high wind speed during the summer cruise significantly increased Hg(0) emission from sea surface to atmosphere and subsequently enhanced the GEM levels.

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1. Introduction

Mercury (Hg) is a naturally occurring toxic element. In the past two centuries, human activities (e.g., coal combustion, mining and industry) have released a large amounts of Hg from long-term geologic storage into the biosphere (Pirrone and Mason, 2009; Pacyna et al., 2010). All kinds of Hg in the environment can convert to elemental Hg (Hg(0)). Because of its low solubility and high vapor pressure, Hg(0) formed in surface environments (e.g., water, soil and vegetable) emits to the overlaying air, and then transports to the global ecosystem via atmospheric circulation (Selin et al.,

2008; Selin, 2009; Pirrone and Mason, 2009). In aquatic environment, inorganic Hg can also convert to methylmercury (MMHg) (Fitzgerald et al., 2007), the most toxic Hg species that poses human and ecological health risks (Clarkson et al., 2003). Therefore, Hg is identified as a global pollutant (Pirrone and Mason, 2009).

Oceanic Hg cycle is one of the most important fractions of global Hg biogeochemical cycle (Fitzgerald et al., 2007; Strode et al., 2007; Soerensen et al., 2010b; Mason et al., 2012). Globally, atmospheric deposition is the dominant Hg input to the ocean (Mason and Sheu, 2002; Selin, 2009). In seawater Hg can reduce to Hg(0) via photochemistry and microbial activities (Amyot et al., 1997; Rolfhus and Fitzgerald, 2004; Fantozzi et al., 2009; Qureshi et al., 2010; Whalin et al., 2007; Monperrus et al., 2007) and then release

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from sea surface to atmosphere (Fitzgerald et al., 1984; Kuss and Schneider, 2007; Fu et al., 2010; Andersson et al., 2011; Ci et al., 2011a; Qureshi et al., 2012). Modeling studies showed that more than 80% of Hg deposited to oceans is reemitted to atmosphere as Hg(0) (e.g., Strode et al., 2007).

The marginal seas and coastal regions are special environments for Hg biogeochemistry (Horvat et al., 2003; Fitzgerald et al., 2007; Balcom et al., 2008). Because they connect with the terrestrial ecosystems, the coastal/marginal marine environments generally have high Hg load due to elevated atmospheric Hg deposition and watershed and coastal Hg input (Luo et al., 2010; Bratkič et al., 2013). The water column and sediments in coastal environments are hotspots for MMHg production since these regions have high nutrient concentrations and microbial activities, which are favorable factors for MMHg production (Hammerschmidt and Fitzgerald, 2004; Sunderland et al., 2006). Some studies also suggest that Hg(II) reduction to Hg(0) and subsequent emission is enhanced in marginal seas (e.g., Lanzillotta et al., 2002). Therefore, Hg biogeochemistry in coastal/marginal ecosystem has received increasing attentions over the past decade (Fitzgerald et al., 2007).

East Asia is the largest anthropogenic Hg emission source in the world due to the rapid industrial growth and growing energy consumption over the past five decades (Streets et al., 2005; Pacyna et al., 2006, 2010; Ci et al., 2012; Wu et al., 2006; Kim et al., 2010). Atmospheric Hg output from East Asia across the boundary has received much attentions (Jaffe et al., 2005; Ci et al., 2011b; Weiss-Penzias et al., 2007; Obrist et al., 2008; Sheu et al., 2010). The Yellow Sea is located on the western Asian continental margin. This marine system has great economic, climatic and ecologic importance for the half billion population living in its surrounding regions. As the downwind and downstream of East Asia, the Yellow Sea receives high Hg input from atmospheric deposition and river/wastewater discharge (Ci et al., 2011d). Many studies also highlight that the anthropogenic Hg emission from East Asia will continue to increase (e.g., Streets et al., 2009; Pacyna et al., 2010). In this context, the Hg loading in the Yellow Sea system will increase in the foreseeable future.

Previous studies have shown that the Yellow Sea ecosystem is suffering from serious Hg pollution. Hg concentrations in various environmental samples (e.g., water, sediment, and organism) are elevated and the Hg contamination has posed a serious risk to this marine ecosystem (Liang et al., 2003; Luo et al., 2012). Recently, many modeling efforts have been made to explore the Hg cycling in East Asia (Shetty et al., 2008; Lin et al., 2010). However, the accuracy of the modeling result is difficult to evaluate because of limited field data, especially those related to marine system (Jaffe and Strode, 2008; Ci et al., 2012). At present, most atmospheric Hg measurements focused on the coastal region of East Asia (e.g., Wang et al., 2007; Ci et al., 2011b; Nguyen et al., 2010; Xiu et al., 2009), but the investigations focusing on the open ocean are limited (Friedli et al., 2004; Ci et al., 2011d; Nguyen et al., 2011; Fu et al., 2010; Tseng et al., 2012; Sheu et al., 2013). The lack of Hg knowledge in the open ocean of East Asia has become a critical barrier to the current understanding of the regional and global Hg cycles (Jaffe and Strode, 2008; Ci et al., 2012).

The purpose of this study is to further improve the understanding of Hg cycling in the Yellow Sea combining our previous investigations in the same region (Ci et al., 2011a,c,d). The main goals of the present study include: (a) to determine the spatial and temporal variations of gaseous elemental Hg (GEM or Hg(0)) in air and dissolved gaseous Hg (DGM, mainly Hg(0)) in surface waters during spring and fall, (b) to estimate the air/sea Hg(0) fluxes, and (c) to explore factors influencing the spatial-temporal variations of GEM, DGM and air/sea Hg(0) exchange.

2. Experimental methods

2.1. Cruise information

Two research cruises covering the Yellow Sea were organized by the Ocean University of China (OUC) aboard the *R/V Dongfanghong II*. The general purposes of the two cruises were to investigate the effect of human activities and climate change on the eastern Asian marine ecosystems. The spring cruise and fall cruise was conducted in May 1–16 and November 2–17, 2012, respectively. The cruise track and water sampling stations are shown in Fig. 1.

2.2. Measurements of GEM in air

During the spring cruise, the GEM concentrations in air were determined using a Lumex RA-915+ Hg analyzer (Lumex, Inc., St. Petersburg, Russia), which is based on the differential Zeeman Atomic Absorption Spectrometry (ZAAS) with high-frequency modulation of light polarization and a multi-path analytical cell (Sholupov et al., 2004; Kim et al., 2006). The principle and set-up of the analyzer was given before in detail (Ci et al., 2011b,d). Briefly, the Lumex Hg analyzer was installed inside a ship laboratory and the ambient air was delivered via a Teflon tube. The air inlet was installed on 8 m above the upper deck to avoid the contamination from the *R/V* emission. The GEM concentrations were determined with a time resolution of 1 min and then were modified to hourly mean for analysis. Based on three times standard deviation of the system blank, the Lumex Hg analyzer has a detection limit of 0.30 ng m^{-3} (Ci et al., 2011a,d).

During the fall cruise, the atmospheric Hg concentrations were quantified using a Tekran 2537B Hg vapor analyzer (Tekran, Inc., Toronto, Canada). The detail of the principle of the Tekran Hg analyzer can be found in Munthe et al. (2001), Ebinghaus et al. (2002) and Weiss-Penzias et al. (2003, 2013). The Tekran Hg analyzer was installed inside the same laboratory and the ambient air was delivered via a Teflon tube. The analyzer determined the atmospheric Hg by amalgamation onto gold traps with subsequent thermal desorption and the Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS) detection. Since the particulate matter and reactive gaseous Hg (RGM) in the air stream are removed by a Teflon filter before they reach the gold trap, it is widely accepted that the Tekran Hg analyzer adopted with this procedure determines GEM in the air sample (Slemr et al., 2011; Weiss-Penzias et al., 2013). Air was sampled at 1.5 L min^{-1} and the GEM was pre-concentrated on the gold traps for 10 min. The analyzers were calibrated every 25 h with a built-in automatic permeation source injection. The detection limit for GEM in this operation mode is better than 0.10 ng m^{-3} . The inter-comparisons between the Lumex and Tekran Hg analyzer were consistent (Fu et al., 2011).

2.3. Measurements of DGM in surface waters

The details of the water sampling, DGM collection, quantification and QA/QC were presented in our previous studies (Ci et al., 2011a,d). Briefly, in the sampling station (see Fig. 1), 1 L of seawater was manually collected from sea surface (0.2–0.3 m) with an acid-cleaned 1 L borosilicate bottle and immediately decanted into a 1.5 L borosilicate bubbler. The water sample was purged for 30 min under the dark condition with Hg-free ambient air at 0.5 L min^{-1} . The released DGM was collected on gold trap and sealed with Teflon endcaps. Hg collected on the gold trap was quantified by a CVAFS detector (Model III, Brooks Rand, USA) using the two-stage gold amalgamation method (Fitzgerald and Gill,

Fig. 1. The tracks and sampling stations for (a) the spring cruise during May 2012 and (b) the fall cruise during November 2012 in the Yellow Sea.

1979; Ci et al., 2011a,d; Fantozzi et al., 2013). The analysis system was calibrated using a gas-tight microsyringe to inject Hg(0)-saturated air from a water bath and the analytical precision was <2% (Ci et al., 2011a,d).

2.4. Ancillary measurements

The *R/V Dongfanghong II* was equipped with comprehensive meteorological and oceanographic instrumentations. The meteorological data were obtained from an automatic meteorological station in the *R/V*. The surface water temperature and salinity were determined with a rosette-mounted Conductivity–Temperature–Depth (CTD) probe.

2.5. Back-trajectory model

We calculated 72-h back-trajectories of air mass transport using the NOAA–HYSPLIT model (Draxler and Rolph, 2003) to explore the influence of air mass movements on the temporal and spatial variations of GEM. Meteorological dataset from the National Centers for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS) was used as the model input (<http://www.emc.ncep.noaa.gov/gmb/gdas/>). The start height of back-trajectory was selected as 500 m above sea level, which generally represents the typical height of the marine boundary layer (MBL) in the Yellow Sea.

2.6. Model for air/sea Hg(0) exchange

The calculation of air/sea Hg(0) flux and the discussion of its uncertainties and limitations were given in Ci et al. (2011a,d) in detail. Briefly, air/sea Hg(0) flux was calculated with a two-layer gas exchange model (Liss and Slater, 1974): $F = K(C_w - C_a/H')$, where F is the Hg(0) flux ($\text{ng m}^{-2} \text{h}^{-1}$) and K is the gas transfer coefficient (m h^{-1}). C_w and C_a are Hg(0) concentrations in surface waters (DGM, pg L^{-1}) and in air (GEM, ng m^{-3}), respectively. H' is the dimensionless Henry's Law constant: $H' = \exp(-2404.3/T + 6.92)$ (Andersson et al., 2008a), where T is the surface water temperature (K).

In this study, the gas transfer parameterization of Wanninkhof (1992) is used to calculate the gas transfer coefficient: $K = 0.31u_{10}^2(Sc_{Hg}/660)^{-0.5}$, where u_{10} is the wind speed (m s^{-1}) at 10 m above the sea surface. Sc_{Hg} is the Schmidt number of Hg(0) for seawater: $Sc_{Hg} = \nu/D$, where ν is the kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) of sea water and D is the aqueous diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) of Hg(0). The ν and D is calculated according to the method described by Wanninkhof (1992) and Kuss et al. (2009), respectively.

The degree of saturation of Hg(0) in surface waters (DGM) with respect to the atmospheric Hg(0) (GEM) is defined as S_a : $S_a = C_w H'/C_a$, where C_w , H' , and C_a are as identical as described above. The S_a value greater than 1 indicates the supersaturation of Hg(0) in surface waters with respect to Hg(0) in air and subsequent Hg(0) emission from sea surface, otherwise under saturation is indicated and Hg(0) deposition from the atmosphere to the sea surface occurs.

3. Results and discussion

3.1. GEM in air

The GEM concentrations in the two cruises were similar (t -test, $P > 0.05$) with $1.86 \pm 0.40 \text{ ng m}^{-3}$ ($0.85\text{--}2.79 \text{ ng m}^{-3}$) in the spring cruise and $1.84 \pm 0.50 \text{ ng m}^{-3}$ ($0.93\text{--}5.09 \text{ ng m}^{-3}$) in the fall cruise. These GEM concentrations are statistically lower (t -test, $P < 0.05$) than our previous summer cruise (July 2010) covering the similar sea region ($2.61 \pm 0.50 \text{ ng m}^{-3}$, Ci et al., 2011d). The GEM data of the three cruises suggest the high concentrations during the summer cruise and low concentrations during the spring cruise and fall cruise. This seasonality is different from the ground measurements

in rural/coastal CST station of the Yellow Sea (Ci et al., 2011a, the location of CST station refers to Fig. 1), which showed high concentrations in cold seasons and low concentrations in warm seasons (Table 1). Notably, Tseng et al. (2012, 2013) reported a different seasonal variation of GEM in MBL of the northern South China Sea (SCS) with high concentrations in cold seasons and low concentrations in warm seasons during 2003–2005 (Table 1), although the SCS and the Yellow Sea have the similar climate condition and human activity strength. The GEM concentrations in the summer campaign in the SCS are comparable to those of the summer cruise in the Yellow Sea and the SCS (2.62 ng m^{-3}) by Fu et al. (2010). However, GEM concentrations in the SCS during the spring campaign and fall campaign are significantly higher than those of the spring cruise and fall cruise in the Yellow Sea, and also higher than those of rural/coastal CST station in the spring campaign and fall campaign. The mean GEM concentrations in the winter campaign in the SCS were significantly higher than those of the winter campaign in CST. Tseng et al. (2012, 2013) suggested that the air masses with elevated GEM in the SCS mainly originated from Eurasia with great anthropogenic Hg emissions. Interestingly, the mean GEM concentrations in the winter campaign in the SCS were similar to the instantaneous enhanced GEM levels during pollution events originated from North China in CST (Ci et al. 2011b), but generally higher than those of pollution events in our shipboard measurements (see discussion below and Figs. S2 and S3 in Supplementary material). Considering the short duration of measurements (<1 month) and the different cruise track and atmospheric condition for individual cruise, currently these shipboard measurements only can obtain the snapshot of GEM distribution in the MBL. More field measurements are needed to obtain a complete figure of the temporal/spatial variation of GEM in the MBL of East Asia.

The mean concentrations of GEM for the three cruises in the Yellow Sea were 2.13 ng m^{-3} , which are higher than the North Hemispheric background regions (e.g., $1.5\text{--}1.7 \text{ ng m}^{-3}$, Ebinghaus et al., 2002; Sprovieri et al., 2010) and slightly higher than Hedo Station in the open ocean of the East China Sea (2.04 ng m^{-3} , Jaffe et al., 2005). This indicates that the anthropogenic Hg emission has substantially enhanced the GEM concentration over the downwind region of East Asia. The GEM concentrations are comparable or lower compared to marine regions that impacted by direct human activities or historical Hg releases, such as the SCS ($2.8\text{--}5.7 \text{ ng m}^{-3}$, Fu et al., 2010; Tseng et al., 2012, 2013), the Mediterranean Sea ($1.5\text{--}2.1 \text{ ng m}^{-3}$, Sprovieri et al., 2003; Bagnato et al., 2013) and the Atlantic Ocean (2.26 ng m^{-3} , Soerensen et al., 2010a), but are significantly higher than remote oceans, such as the south-west Indian Ocean (1.2 ng m^{-3} , Witt et al., 2010) and

the oceans in the South Hemisphere ($1.0\text{--}1.5 \text{ ng m}^{-3}$, Soerensen et al., 2010a), and also higher than the coast of Central and Southern California in North America (1.40 ng m^{-3} , Weiss-Penzias et al., 2013).

Fig. 2 shows the spatial variation of GEM during the two cruises. The results present the similar spatial variation pattern with increased concentrations along the coast of the east of China and decreased concentrations in the open ocean, although the movements of air masses had important influence on the GEM concentrations (see discussion below). This pattern is consistent with our summer cruise (Ci et al., 2011d) and two shipboard measurements from Weihai and Qingdao in the Shandong Peninsula (China) to Incheon (South Korea) crossing the north of the Yellow Sea (Nguyen et al., 2011). The combination of this study and other measurements in the open ocean (Friedli et al., 2004; Ci et al., 2011d; Nguyen et al., 2011) and coastal regions (Nguyen et al., 2007; Ci et al., 2011a) suggests that the GEM concentrations in the Yellow Sea had a common spatial pattern with increased concentrations in the coastal region ($2.5\text{--}3.5 \text{ ng m}^{-3}$) and decreased concentrations in the open ocean ($1.3\text{--}1.7 \text{ ng m}^{-3}$). This phenomenon has also been successfully reproduced by modeling study (e.g., Lin et al., 2010). This indicates that the east of China has significant contribution to the atmospheric Hg pool downwind of East Asia.

During the two cruises, the prevailing wind direction was north to northwest, implying most of air masses sampled during the two cruises were generally originated from the Continental East Asia, especially in the sampling period of the south of the Yellow Sea, the GEM concentrations near the coast of the east of China were generally higher than the open ocean (Fig. 2). The back-trajectory analysis showed that most of air masses reaching the region of $32^\circ \text{ N}\text{--}36^\circ \text{ N}$, $120^\circ \text{ E}\text{--}124^\circ \text{ E}$ originated from the north of China (Fig. S1 in Supplementary material) with high anthropogenic Hg emission (see Fig. 6 in Pacyna et al. (2010) and Fig. 1 in Streets et al. (2005)). The spatial variation pattern of high concentrations near the coast and low concentrations in the open ocean reflected that the air dilution and the transformation from GEM to RGM during atmospheric transport may reduce the peak levels of GEM.

The movements of air masses also significantly influenced the GEM concentrations. For example, during the two cruises in the north of the Yellow Sea ($37^\circ \text{ N}\text{--}39^\circ \text{ N}$, $122^\circ \text{ E}\text{--}124^\circ \text{ E}$), the R/V navigated along the coast of China and the Korean Peninsula, where is the most important anthropogenic Hg emission source region in the world (Pacyna et al., 2010; Streets et al., 2005). However, the GEM concentration in this period generally fell in $1.2\text{--}1.7 \text{ ng m}^{-3}$, reflecting the regional background GEM concentration of East Asia (Jaffe et al., 2005; Ci et al., 2011a; Fu et al., 2010). The back-trajectory analysis showed that, in the spring cruise the air masses

Table 1
Summary of seasonal data related to air/sea Hg(0) flux in the open ocean and coastal/rural CST station of the Yellow Sea and the SEATS station in open ocean of the South China Sea (SCS).

Type	Season	DGM (pg L^{-1})	GEM (ng m^{-3})	Water T ($^\circ\text{C}$)	Wind speed (m s^{-1})	S_a	Hg(0) flux ($\text{ng m}^{-2} \text{ h}^{-1}$)	N	Reference
Open ocean in the Yellow Sea	Spring	27.0 ± 6.8	1.87 ± 0.42	12.6 ± 2.2	4.42 ± 1.80	3.40 ± 1.14	1.06 ± 0.86	53	This study
	Summer	63.9 ± 13.7	2.61 ± 0.50	24.0 ± 0.9	9.59 ± 3.36	7.80 ± 2.30	18.3 ± 11.8	40	Ci et al. (2011d)
	Fall	28.2 ± 9.0	1.81 ± 0.45	12.3 ± 4.5	6.72 ± 3.80	3.70 ± 1.57	2.53 ± 2.12	50	This study
CST station in the coast of the Yellow Sea	Spring	23.0 ± 8.7	2.38 ± 0.94	8.0 ± 0.5	3.2 ± 2.0	2.00 ± 0.98	0.32 ± 0.71	43	Ci et al. (2011a)
	Summer	69.0 ± 23.3	1.98 ± 0.97	19.0 ± 0.9	1.5 ± 1.0	11.0 ± 5.92	0.88 ± 1.38	47	
	Fall	27.0 ± 16.4	2.36 ± 0.66	18.8 ± 0.5	3.8 ± 1.9	3.50 ± 2.60	0.89 ± 1.84	41	
	Winter	16.0 ± 6.0	3.06 ± 0.95	2.4 ± 0.4	2.8 ± 2.1	0.96 ± 0.39	-0.06 ± 0.64	41	
SEATS station in the open ocean of the SCS	Spring	14 ± 8	3.2 ± 0.6	26.6 ± 1.7	5.3 ± 0.5		0.5 ± 1.3^a		Tseng et al. (2012, 2013)
	Summer	32 ± 8	2.8 ± 0.4	29.6 ± 0.3	5.5 ± 0.2		4.8 ± 1.0		
	Fall	24 ± 8	3.6 ± 0.6	27.8 ± 0.5	8.6 ± 1.5		6.1 ± 1.8		
	Winter	12 ± 6	4.5 ± 1.5	23.9 ± 0.5	9.6 ± 0.6		-1.5 ± 1.0		

^a Tseng et al. (2012, 2013) used the slightly different parameterization with this study to calculate the Hg(0) flux at air-sea interface.

Fig. 2. The spatial distribution of gaseous elemental mercury (GEM) during (a) the spring cruise and (b) the fall cruise in the Yellow Sea.

sampled from Station B01 to B19 originated from the Sea of Japan and crossed the Korea Strait and the north of the Yellow Sea before reaching the *R/V* (Fig. S2a in Supplementary material). This region has moderate and/or no anthropogenic Hg emission. The previous shipboard measurements also reported the low atmospheric Hg concentrations in this source region ($\sim 1.5 \text{ ng m}^{-3}$, Kang and Xie,

2011). During the fall cruise, the air masses reaching the *R/V* from Station BF3 to B30 generally originated from the east of Russia and passed over the northeast of China (Fig. S2b in Supplementary material). Although this region has the moderate or low anthropogenic Hg emission sources (Pacyna et al., 2010), the great wind speed and high traveling height of air masses (1000–2000 m) passing over the anthropogenic Hg emission source region (Fig. S2c–h in Supplementary material) did not favor the air masses to carry enhanced atmospheric Hg emitted from the surface. From Station B28 to B38 during the spring cruise and from Station B35 to B38 during the fall cruise, the GEM concentrations increased substantially, the back-trajectory analysis suggested that these air masses generally originated from high anthropogenic emission sources (e.g., the Shandong Peninsula, Fig. S2 in Supplementary material).

During the fall cruise, in the center of the south of the Yellow Sea the GEM concentrations increased from 1.71 ng m^{-3} in 123.7622° E , 34.2062° N (at 02:05 on 9 November, UTC + 0800) to 4.17 ng m^{-3} in 123.6562° E , 34.4928° N (at 03:45 on 9 November) and then decreased to 1.73 ng m^{-3} in 123.4942° E , 34.9908° N (at 06:55 on 9 November) in a very short time ($\sim 4 \text{ h}$). The back-trajectory analysis showed that these air masses reaching the *R/V* in this period had similar pathways with others in the open ocean (Fig. S3 in Supplementary material). We checked the direction of the *R/V* movement and found that the inlet of Hg analyzer always was upwind of the chimney of the *R/V* during this period. We suppose that the other ship emissions near the *R/V* may contribute to the high GEM concentrations.

Fig. 3 illustrates the diurnal variation of GEM in the MBL for the three cruises in the Yellow Sea. The GEM concentrations in the spring cruise and the fall cruise were no significantly diurnal variation (t -test, $P > 0.05$). This is different from the summer cruise, which showed a diurnal variation with increased concentrations in morning–midday and decreased concentrations in afternoon–nighttime (t -test, $P < 0.05$). The measurements in coastal/rural CST station also reported the similar pattern that the magnitude of diurnal variation (difference between maxima and minima of GEM concentrations) in the summer campaign was significantly higher than the spring and fall campaign. The combination of results in CST and the open ocean suggested that the great Hg(0) emission from sea surface to atmosphere during summer (see discussion in Section 3.4) may have significant contribution to atmospheric GEM pool in MBL in short time scale ($\sim$ several hours). For example, the measurements by Sigler et al. (2009) in coastal region of New England indicated, under the favorable conditions

Fig. 3. The diurnal variation of gaseous elemental mercury (GEM) for the spring cruise (this study), the summer cruise (data from Ci et al., 2011d) and the fall cruise (this study) in the Yellow Sea.

(e.g., the high wind speed), Hg(0) emission from the sea surface might have an important contribution to atmospheric GEM in the regional scale. Many other factors, such as the seasonal and diurnal variation of MBL height and GEM concentrations above the MBL, also have important influence on temporal variation of GEM in the MBL, but current study focused on these factors is very limited.

3.2. DGM in surface waters

The mean DGM concentrations of the surface water during the two cruises were also similar (t -test, $P > 0.05$) with $27.0 \pm 6.8 \text{ pg L}^{-1}$ ($n = 53$) in the spring cruise and $28.2 \pm 9.0 \text{ pg L}^{-1}$ ($n = 50$) in the fall cruise (Table 1). In the spring cruise, the highest DGM concentration (42.2 pg L^{-1}) was determined at Station H26 (at 10:17 on 5 May 2012, UTC + 0800) and lowest concentration (13.0 pg L^{-1}) at Station B15 (at 21:48 on 13 May 2012). During the fall cruise, the highest DGM concentration (53.3 pg L^{-1}) was determined at Station H03 (at 16:49 on 2 November 2012) and lowest concentration (14.7 pg L^{-1}) at Station B32 (at 23:43 on 15 November 2012). The concentrations are comparable to many coastal or marginal marine environments, such as the Chesapeake Bay (Mason et al., 1999), the Mediterranean Sea (Lanzillotta et al., 2002; Fantozzi et al., 2007, 2013; Andersson et al., 2007), the Baltic Sea (Wängberg et al., 2001), and higher than some recent measurements in Open Ocean, such as the Atlantic Ocean (Andersson et al., 2011; Kuss et al., 2011; Soerensen et al., 2013), but lower than the Arctic Ocean (Sommar et al., 2007; Andersson et al., 2008b). Notably, as listed in Table 1, the two cruises combining with the previous summer cruise (Ci et al., 2011d) show that the DGM concentrations in the open ocean were almost identical to those determined at coastal/rural CST station in the corresponding season campaign. Correspondingly, the seasonality of DGM in the open ocean was also identical to CST with high concentrations in warm seasons and low concentrations in cold seasons (Table 1). The similar seasonality also was widely reported in other marine environments, e.g., the Mediterranean Sea (Andersson et al., 2007), the Baltic Sea (Kuss and Schneider, 2007), the SCS (Tseng et al., 2013) and the West Atlantic Ocean (Soerensen et al., 2013). Previous laboratory studies and field measurements suggest that many factors, such as high solar radiation, elevated microbial activities, great Hg input to coastal region via river discharge and wet deposition, will promote the DGM formation in warm seasons (Amyot et al., 1997; Costa and Liss, 1999; Rolffhus and Fitzgerald, 2004; Lanzillotta et al., 2002; Ci et al., 2011a; Sommar et al., 2007; Tseng et al., 2013).

The three cruises data showed that the DGM was significantly positive (t -test, $P < 0.05$) correlated with the surface water temperature ($\text{DGM} = 0.2563 \cdot T + 278.75$, $R^2 = 0.62$, T is the surface water temperature (K)). Because Hg(0) emission from sea surface is the dominant sink of Hg(0) in surface water column, we assume that the Hg(0) formation rate in water column is equal to the Hg(0) emission rate from sea surface. The temperature dependence of Hg(0) formation in water column can be investigated by using the Arrhenius equation, $K_{\text{Hg}(0)} = Ae^{-E_a/RT}$, where $K_{\text{Hg}(0)}$ is the formation rate or emission rate of Hg(0) ($\text{mol m}^{-2} \text{ h}^{-1}$) and E_a is the activation energy of Hg(0) formation (kJ mol^{-1}). The value of E_a is obtained from the slope of the linear regression of the natural logarithm of Hg(0) emission rate versus $1/T$ (Xiao et al., 1991). The values of E_a were estimated to be $135 \pm 20 \text{ kJ mol}^{-1}$ at water temperatures of $\sim 3\text{--}25^\circ\text{C}$ for the three cruises. The values are comparable to those of surface waters in Swedish temperate lakes ($\sim 125 \pm 5 \text{ kJ mol}^{-1}$ at water temperatures of $0.5\text{--}23^\circ\text{C}$) (Xiao et al., 1991) and in Arctic lakes ($\sim 150 \pm 40 \text{ kJ mol}^{-1}$, $11\text{--}15^\circ\text{C}$) (Tseng et al., 2004) and in the SCS ($\sim 140 \pm 20 \text{ kJ mol}^{-1}$, $23\text{--}31^\circ\text{C}$, Tseng et al., 2013). Our result seems to further support the state-

ment of Tseng et al. (2013) that there is a universal value of E_a for Hg(0) formation in various type waters.

The relationship between DGM concentrations and salinity was negative, but not significant (t -test, $P > 0.05$). This is most probably due to the less variability in salinity ($\sim 29\text{--}33$). Complexation of Hg by chloride is believed to be important in seawater, however, its complexation by organic matter should not be ignored in marginal seas (e.g., the Yellow Sea) (Ravichandran, 2004; Lamborg et al., 2004). Although many studies have addressed that the interaction of Hg with organic matter and chloride significantly influences the broader biogeochemical cycle of Hg (including the Hg redox chemistry in aquatic environment), the knowledge of the speciation of Hg(II) complexes is limited because of the technical limitation (Ravichandran, 2004; Fitzgerald et al., 2007). At present, the information about Hg(II) speciation in the open ocean of the Yellow Sea is scarce. The measurements in the summer cruise showed that about 60% of Hg in water column was the reactive Hg (roughly equal to Hg(II)) (Ci et al., 2011d). However, this available data from current studies are not enough to deeply investigate the Hg redox chemistry in the Yellow Sea. More targeted research strategies should be considered in the future.

Fig. 4 shows a large spatial variation of DGM in surface waters during the two cruises. During the summer cruise, the mean DGM concentrations of stations near the coast were statistically higher than the open ocean stations (Ci et al., 2011d), suggesting the near-shore environment was favorable for DGM formation. However, this pattern was not found in the spring cruise and fall cruise. DGM concentrations in surface waters are the net effect of DGM formation/consumption and evasion/deposition, and vertical mixing of water. Various temporal variables, such as solar radiation, wind speed, water mixing and chemistry and so on, can alter the DGM levels of surface water in short time scales (e.g., several hours). Many field measurements also reported the large spatial and temporal variations of DGM in various marine environments (Andersson et al., 2007; Whalin et al., 2007; Fu et al., 2010; Ci et al., 2011d; Tseng et al., 2013; Fantozzi et al., 2013). More comprehensive data set should be collected to explore the spatial variation of DGM in the marginal marine system with complicated physical, chemical and biological properties.

Fig. 5 illustrates that there is no significantly (t -test, $P > 0.05$) diurnal variation of DGM in surface waters of the open ocean in the Yellow Sea during the three cruises periods. Many incubation studies have confirmed that photochemical reduction of Hg(II) is the primary pathway of Hg(0) formation in water column (Amyot et al., 1997; Whalin et al., 2007; Qureshi et al., 2010), meaning the enhanced DGM in surface waters in daytime should be expected. A number of field measurements in coastal regions have shown that the DGM commonly exhibits clear diurnal pattern with high concentrations in daytime and low concentrations in nighttime, especially in the day characterized by high solar radiation and low wind speed (e.g., Fantozzi et al., 2007; Ci et al., 2011a). Currently, there are limited studies focused on the diurnal variation of DGM in surface water of the open ocean. The field measurements by Soerensen et al. (2013) during six cruises in the West Atlantic Ocean also did not find any difference in DGM in daytime and nighttime. The difference between the coast and the open ocean suggests the controlling factors for DGM variations in the open ocean are more complicated than the coast. One of the possible reasons is that the wind speed in the open ocean generally is greater than the coastal region. The high wind speed promotes the air/sea Hg(0) exchange by enhancing turbulence in air/sea interface to reduce DGM in surface waters. Meanwhile, it also facilitates mixing with subsurface water that can provide additional DGM and Hg(II) for reduction to form DGM and then reduce the magnitude of diurnal DGM in open ocean.

Fig. 4. The spatial distribution of dissolved gaseous mercury (DGM) during (a) the spring cruise and (b) the fall cruise in the Yellow Sea.

3.3. Air/sea Hg(0) flux

The S_a values in the two cruises were similar (t -test, $P > 0.05$) with a range of 1.59–6.55 (mean $\pm$ SD: 3.40 ± 1.14) in the spring cruise and 1.30–8.97 (mean $\pm$ SD: 3.70 ± 2.12) in the fall cruise, respectively. As listed in Table 1, the S_a values in the two cruises are comparable to the corresponding season campaign in coastal

Fig. 5. The diurnal variation of dissolved gaseous mercury (DGM) for the spring cruise (this study), the summer cruise (data from Ci et al., 2011d) and the fall cruise (this study) in the Yellow Sea.

CST station but significantly lower than the summertime measurements in the open ocean and CST. The main reason for the elevated S_a values in summer is the high DGM concentration and high water temperature. The similar seasonal variation pattern has been extensively reported by many field measurements (e.g., Andersson et al., 2007; Rolffhus and Fitzgerald, 2001).

As mentioned above, S_a value greater than 1 indicates the supersaturation of Hg(0) in surface waters with respect to Hg(0) in air, subsequently inducing Hg(0) emission from sea surface to the atmosphere. In the two cruises all S_a values were greater than 1, indicating the surface water always was the potential Hg(0) source for the overlying air. According to the model described in Section 2.6, the mean Hg(0) emission fluxes were $1.06 \pm 0.86 \text{ ng m}^{-2} \text{ h}^{-1}$ with a range of 0.00 – $3.65 \text{ ng m}^{-2} \text{ h}^{-1}$ in the spring cruise and $2.53 \pm 2.12 \text{ ng m}^{-2} \text{ h}^{-1}$ with a range of 0.00 – $7.35 \text{ ng m}^{-2} \text{ h}^{-1}$ in the fall cruise, respectively. Although there are similar values of S_a for the spring cruise and fall cruise, the Hg(0) flux in the fall cruise was significantly higher than those of the spring cruise. The main reason is that the two-layer exchange model used to calculate air/water Hg(0) flux is very sensitive to the wind speed (Andersson et al., 2007; Ci et al., 2011a; Sharif et al., 2013). If the S_a values are greater than 1, under the condition with the similar S_a , the high wind speed will substantially promote the emission of Hg(0) from sea surface. The high variation of Hg(0) flux also was attributed from the highly temporal variation of wind speed.

The fluxes obtained in the two cruises were comparable to open regions of many other marine systems, such as the Pacific Ocean ($\sim 3 \text{ ng m}^{-2} \text{ h}^{-1}$, Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993), the Mediterranean Sea (1.52 – $4.92 \text{ ng m}^{-2} \text{ h}^{-1}$, Andersson et al., 2007; 4.2 – $7.9 \text{ ng m}^{-2} \text{ h}^{-1}$, Gårdfeldt et al., 2003; $2.2 \pm 1.5 \text{ ng m}^{-2} \text{ h}^{-1}$, Fantozzi et al., 2013), the Arctic Ocean ($2.4 \text{ ng m}^{-2} \text{ h}^{-1}$, Andersson et al., 2008b), the North Sea (~ 2 – $6 \text{ ng m}^{-2} \text{ h}^{-1}$, Baeyens and Leermakers, 1998) and the SCS (4.5 – $3.4 \text{ ng m}^{-2} \text{ h}^{-1}$, Fu et al., 2010), but significantly lower than those Hg-polluted region, such as the Adriatic Sea (10.0 – $165.5 \text{ ng m}^{-2} \text{ h}^{-1}$, Andersson et al., 2007), the Augusta Basin ($72 \text{ ng m}^{-2} \text{ h}^{-1}$, Bagnato et al., 2013). The fluxes were also comparable to the corresponding seasons in CST with similar S_a and wind speed but significantly lower (~ 5 – 10 times) than the summer cruise (Table 1) because the high S_a and great wind speed in the summer cruise substantially promoted the Hg(0) emission (Ci et al., 2011d). This seasonal air/sea Hg(0) exchange pattern with high flux in summer and low flux in other seasons were also widely reported in many other marine environments (e.g., Kuss and Schneider, 2007; Tseng et al., 2013).

Shetty et al. (2008) used a same two-layer exchange model with slightly different K algorithm and constant DGM concentrations in surface waters (40 pg L^{-1}) to estimate the air/water $\text{Hg}(0)$ flux for East Asia. The modeling results showed that the surface water was the source of $\text{Hg}(0)$ in air with high flux in cold months (ca. $3.0 \text{ ng m}^{-2} \text{ h}^{-1}$ in January and October) and low flux in warm months (ca. $2.0 \text{ ng m}^{-2} \text{ h}^{-1}$ in April and July). This seasonality was dominated by the high wind speed in January and October. The modeling fluxes for the spring and fall are comparable to the observations in this study, but the modeling flux for summer was significantly lower than the field observation by Ci et al. (2011d) in the summer cruise. The main reason for this difference is the DGM concentrations (63.9 pg L^{-1}) observed in the summer cruise were remarkably elevated than the modeling study (40 pg L^{-1}), which corresponds to high S_a and subsequent great $\text{Hg}(0)$ emission potential. These observations also highlight that an assumed constant DGM concentrations in the modeling study may lead to substantial uncertainties of air/sea $\text{Hg}(0)$ flux since the measurements presented the high temporal and spatial variation of DGM in surface waters. More reliable parameterization to describe the aquatic DGM production and consumption will significantly improve the modeling result (Strode et al., 2007; Soerensen et al., 2013).

4. Conclusions

The gaseous elemental Hg (GEM or $\text{Hg}(0)$) in air and dissolved gaseous Hg (DGM, largely $\text{Hg}(0)$) in surface waters in the Yellow Sea were determined during two cruises performed in late spring and late fall 2012, respectively. The GEM concentrations in the two cruises were slightly higher than the North Hemisphere background regions and generally showed the similar spatial variation pattern with high concentrations along the coast of the east of China and low concentrations in the open ocean, indicating that the anthropogenic Hg emission from the east of China has substantially enhanced the Hg concentrations in air over the downwind regions. The DGM concentrations, the saturation degrees of $\text{Hg}(0)$ in surface water respect to the atmosphere and the air/sea $\text{Hg}(0)$ fluxes for the spring cruise and fall cruise were similar and presented highly temporal and spatial variations. The combination of this study and previous summer shipboard measurements in the similar sea region suggested the enhanced GEM, DGM, the saturation degree of $\text{Hg}(0)$ in surface waters and $\text{Hg}(0)$ emission fluxes during the summer cruise. The deeper understanding of the air/sea $\text{Hg}(0)$ exchange and subsequent regional and global Hg cycle is likely to benefit from the close corporation among the laboratory scientists, field investigators and model developers.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.05.064>.

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