Aerosol and Air Quality Research, 13: 13–23, 2013

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2012.05.0129

Tempospatial Variation and Partition of Atmospheric Mercury during Wet and Dry Seasons at Sensitivity Sites within a Heavily Polluted Industrial City

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ABSTRACT

This study investigated the seasonal variation and spatial distribution of total gaseous mercury (TGM) and particulate mercury (Hg_p) in the ambient atmosphere of Kaohsiung City, the largest industrial city in Taiwan, located at the coastal region of southern Taiwan. TGM and Hg_p were measured at six sensitivity sites and one coastal background site, from June to December, 2010. Field measurement results showed that the seasonal averaged concentrations of TGM and Hg_p were in the range of 2.38–9.41 and 0.02–0.59 ng/m^3 with the highest concentrations of 9.41 and 0.59 ng/m^3, respectively. Moreover, the partition of atmospheric mercury was found to be 92.71–99.17% TGM and 0.83–7.29% Hg_p. As a whole, the concentrations of mercury species in the dry season were higher than those in the wet season, for both TGM or Hg_p concentrations. The TGM and Hg_p concentrations at the Hsiao-kang site was the highest in Kaohsiung City. Hot spots of atmospheric mercury were found at two regions in Kaohsiung City, including a steel industrial complex in the south and a petrochemical industrial complex in the north. The correlation of atmospheric mercury with meteorological parameters (e.g., ambient temperature, relative humidity, and UV intensity) and air pollutants (e.g., CO, SO_2, NO_x, and O_3) was further discussed. The results indicated that TGM and Hg_p concentrations correlated positively with SO_2, NO_x, CO, ambient temperature, and UV_B, and negatively with relative humidity, O_3, and wind speed.

Keywords: Atmospheric mercury; Industrial city; Sampling and analysis; Tempospatial variation; Gas-particle partition; Correlation coefficients.

INTRODUCTION

Mercury is a persistent, toxic, and bio-accumulative heavy metal that exists primarily in three forms in the atmosphere: gaseous mercury including elemental and reactive mercury, and particulate mercury (Schroeder *et al.*, 1998; Lin *et al.*, 1999). Some factors (e.g., emission sources, regional atmospheric chemistry, near-ground micrometeorological conditions) may influence the distribution of atmospheric mercury speciation and deposition (Poissant *et al.*, 2004). Gaseous mercury could be transformed back and forth between two gaseous forms (i.e., elemental and reactive mercury), of which gaseous elemental mercury (GEM) is the major species in the atmosphere. Among them, elemental mercury has high volatility, low chemical reactivity, and low solubility in water, which accounts for more than 95% of gaseous elemental mercury (GEM) and has a residence time of 1–2 years in the atmosphere, which can transport over great distances across continents, while reactive gaseous mercury (RGM) and particulate mercury (Hg_p) is relatively abundant in the particulate phase and has a residence time of several days or a few weeks (Lanborg *et al.*, 1985; Slemr *et al.*, 1985; Boening *et al.*, 2000; Fu *et al.*, 2008). Mercury and its derivatives can be mitted from two major sources, including natural and anthropogenic sources (Schroeder *et al.*, 1998; Lin *et al.*, 1999; Fu *et al.*, 2008). The emission of mercury from natural sources is about 2,000 tons/yr; while the emission of mercury from anthropogenic sources, mainly coal-fired power plants and waste incinerators, accounts for approximately 4,000 tons/yr (UNEP, 2002). According to the estimates of global mercury budget, 6,000 and 10,800 tons of mercury are currently present in the troposphere and in the water bodies, respectively (Mason *et al.*, 1994).

Natural mercury sources as arising from changes in the crust, such as volcanic eruptions, rock weathering, forest fires, lakes, mercury mining and evaporation from oceans. The major anthropogenic mercury sources as arising from steel plants, coal-fired power plants, and industrial and municipal waste incinerators. Emission sources, regional

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atmospheric chemistry, and near-ground micrometeorological conditions may influence the temporal variation and spatial distribution of atmospheric mercury speciation, concentration, and deposition flux (Johnson *et al.*, 1974; Poissant *et al.*, 2004, 2005). Gaseous elemental mercury is mainly emitted from anthropogenic sources (Nelson, 2007) and mercury associated with airborne particulate matter is also largely of anthropogenic origin (Xiao *et al.*, 1991). Major anthropogenic mercury emission sources include point sources (e.g., municipal and industrial waste incinerators, fossil-fuel combustion, iron/steel smelting plants, petroleum refineries, cement plants) and area sources (e.g., industrialized region, mercury-contaminated site).

The concentrations of mercury in global atmosphere, water bodies, and soil have increased about three times since industrial revolution period, especially for those areas around industrial regions (UNEP, 2003). The concern of mercury pollution arises from the health effects caused by the existences of elemental mercury and its derivatives in the atmosphere and in the water bodies (Schroeder *et al.*, 1998; Lin *et al.*, 1999). Elemental mercury and most of its derivatives are metabolic poisons causing neurological and reproductive damage in terrestrial and aquatic organisms (USEPA, 1999). To date, many field studies have been conducted for atmospheric mercury measurements (Mason *et al.*, 2000; Malcolm *et al.*, 2002; Friedli *et al.*, 2003; Golubeva *et al.*, 2003; Poissant *et al.*, 2004, 2005; Kuo, *et al.*, 2006; Shon *et al.*, 2008; Sheu *et al.*, 2009; Fang *et al.*, 2010, 2012), yet none have been done for measuring atmospheric mercury speciation and concentration around the boundary of iron/steel or petrochemical industrial area. In this study, field measurement of atmospheric mercury was designated to investigate the tempospatial variation and partition of gaseous and particulate mercury during wet and dry seasons, and further correlated atmospheric mercury with meteorological parameters and air pollutants in Kaohsiung City, the largest industrial city in Taiwan, located at the coastal region of southern Taiwan.

EXPERIMENTAL METHODS

Selection and Description of Sampling Sites

Field measurement of atmospheric mercury speciation and concentration was conducted at a coastal background site and six sensitivity sites in Kaohsiung City, including Nan-zhi (22°44'00" North latitude, 120°19'41" East longitude, S1), Ren-wu (22°41'20" North latitude, 120°19'57" East longitude, S2), Zuo-ying (22°40'29" North latitude, 120°17'34" East longitude, S3), Cia-jin (23°37'56" North latitude, 120°17'16" East longitude, S4), Cian-jhen (22°36'18" North latitude, 120°18'30" East longitude, S5), and Hsiao-kang (22°33'57" North latitude, 120°20'15" East longitude, S6). The coastal background site along coastline far away from emission sources is located at the campus of National Sun Yat-Sen University (22°37'38" North latitude, 120°16'01" East longitude). The location of six sensitivity sites for TGM and Hg_p sampling in Kaohsiung City is shown in Fig. 1.

These sensitivity sites were mainly located at the air quality monitoring stations in Kaohsiung City. Among them, sites S5 to S6 were nearby a steel industrial complex in southern Kaohsiung, sites S1 and S2 were close to a petrochemical industrial complex in northern Kaohsiung. Active sampling of TGM and Hg_p were consecutively conducted at each site for 24 hours in wet and dry seasons from June to December of 2010 in Kaohsiung City. Among them, wet season started from June to September, while dry season started from October to December. This study intended to investigate the seasonal variation, spatial distribution, and partition of TGM and Hg_p at the coastal background site and six sensitivity sites of an industrial city.

Sampling of TGM and Hg_p

In this study, a method for sampling and analysis of atmospheric mercury issued by Taiwan EPA (NIEA A304.10C), mainly adopted from USEPA Method IO-5, was applied to measure the concentration of total gaseous mercury (TGM) and particulate mercury (Hg_p) and their

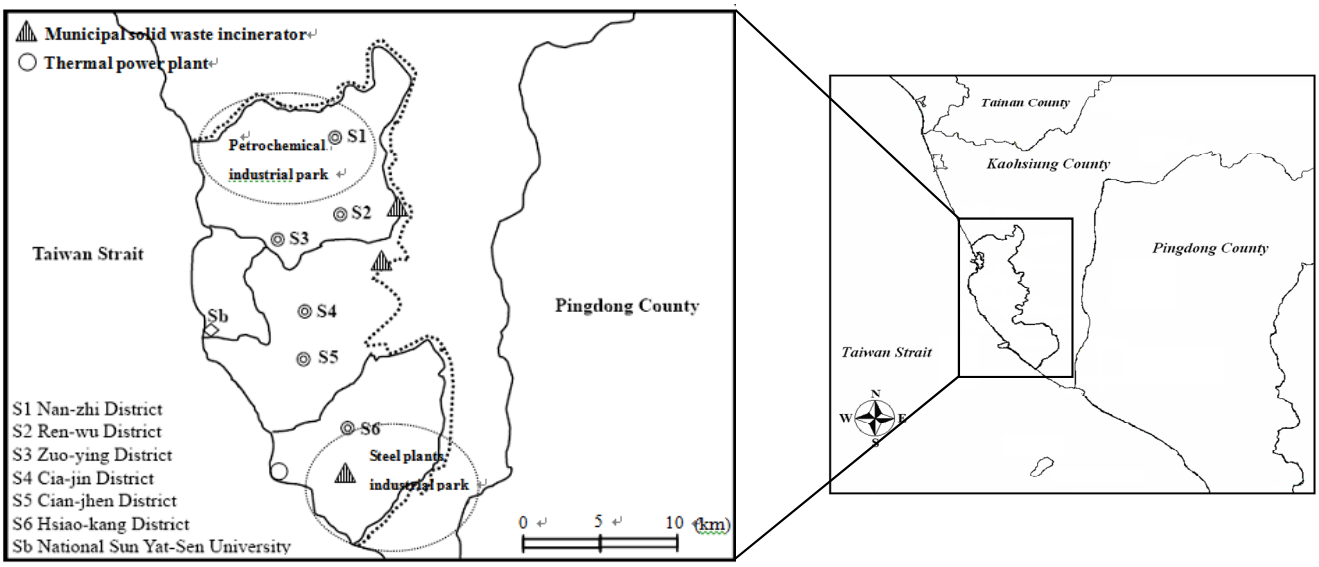

Fig. 1. The location of six sensitivity sites and the coastal site for TGM and Hg_p sampling in Kaohsiung City.

partition. The schematic diagram of a parallel sampling system used to collect ambient TGM and Hg_p is illustrated in Fig. 2. TGM was collected by two gold-coated sand traps connected in series through amalgamation with a constant air flow of 0.3 L/min. A close-faced Teflon filter pack with a glass-fiber filter was placed in front of the traps was used to remove particles from the inlet air. The filtered air was then heated at 30–40°C to remove moisture which could cause serious interferences for adsorbing TGM on the gold-coated sands.

Particulate mercury was collected by using a 47 mm glass-fiber filter in an open-faced Teflon filter pack, with a constant air flow of 30 L/min. Both TGM and Hg_p was continuously sampled for 24 hours at the sampling sites. Besides, the amalgamation of TGM is characterized as physical adsorption, thus it needs to sample air at a lower air flow rate for a longer time to allow mercury molecules to be fully adsorbed by the gold traps. To collect sufficient mercury for analysis, particulate matter was sampled at a relatively high air flow rate. Consequently, TGM and Hg_p were sampled parallel with different air flaw rates.

Analytical Methods of TGM and Hg_p

Determination of TGM and Hg_p in the ambient atmosphere was accomplished by using the dual-amalgamation of a cold-vapor atomic fluorescence spectrometry (CVAFS), manufactured by Brooks Rand (Model III, U.S.A.). The Hg^0 was further liberated from the gold-coated trap by carrying with inert $Ar_{(g)}$, and the desorption temperature was 600°C. Finally, Hg^0 was further measured with a CVAFS. The method detection limits (MDL) achieved by using NIEA A304.10C were 0.030 and 0.045 ng/m^3 for TGM and Hg_p, respectively, determined as triple standard deviation (SD) of the instrumental blank values. Repeated injections of TGM standards can be used to assess the analytical precision of less than 5% for the methods described. Hg_p should be less than 10%, and the correlation coefficient (r) should be 0.995 or higher and each of the points on the calibration curve should be predicted by the slope within 5% differentia of their actual values.

For TGM, samples were analyzed in duplicate. Hg_p collected on the glass-fiber filters was initially extracted in a nitric acid solution using microwave digestion to yield acid-extractable mercury prior to analysis. The concentration of nitric acid is 1.6 M, which is the level of trace metals grade (< 0.0000005% Hg). The extract was then oxidized with BrCl to convert all forms of Hg to Hg^{2+}, and $SnCl_2$ was added to the extract to reduce Hg^{2+} to Hg^0. The Hg^0 was further liberated from the extract by purging with inert $Ar_{(g)}$ and collected on the surface of gold-coated sands. The amount of mercury collected on the gold-coated sands was then determined with the CVAFS. The calibration curves of TGM and Hg_p had correlation coefficients (R) of 0.9998 and 0.9979, respectively. Moreover, the percentages of differences for the repeated injections of TGM and Hg_p was 2.5% and 5.5%, respectively, which could be used to assess the analytical precision of Method NIEA A304.10C. In this study, the blank tests of TGM and TPM during the sampling works were about 93.9 ± 5.8 pg and 47.3 ± 5.1 pg, respectively. While the blank tests of TGM and TPM in the analytical works at the Lab. were about 35.0 ± 3.5 pg and 38.0 ± 1.3 pg, respectively.

Additionally, in order to understand the correlation of atmospheric mercury with meteorological parameters and air pollutants, this study collected the meteorological and air pollutant data from six air quality monitoring stations, nearby the six sampling sites in Kaohsiung City. The meteorological parameters included ambient temperature (Temp), relative humidity (RH), wind speed (WS), wind direction (WD), and ultra-violet radiation (UV_B), while air pollutants included CO, SO_2, NO_X, and O_3.

RESULTS AND DISCUSSION

Seasonal Variation and Partition of TGM and Hg_p

Fig. 3 illustrates the seasonal variation of TGM and Hg_p concentrations at the northern and southern Kaohsiung as well as the coastal background site during the wet and dry

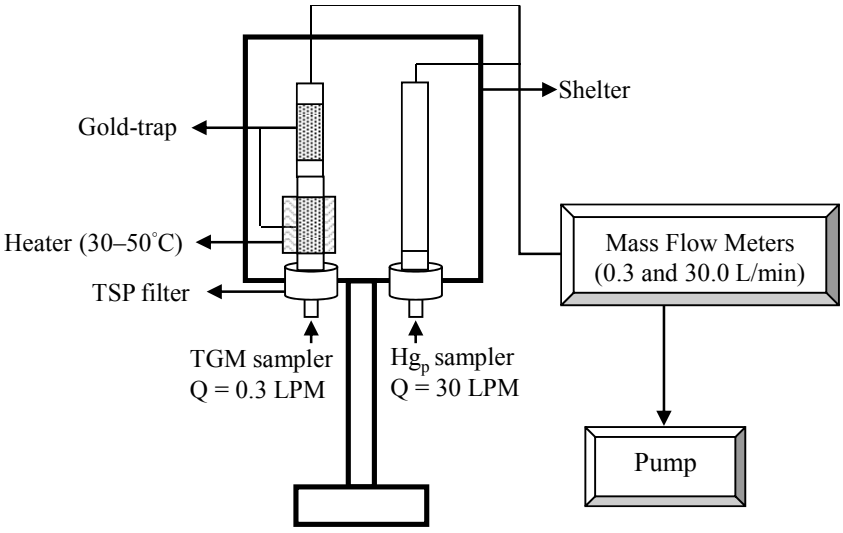

Fig. 2. Schematic diagram of the parallel TGM and Hg_p sampling system.

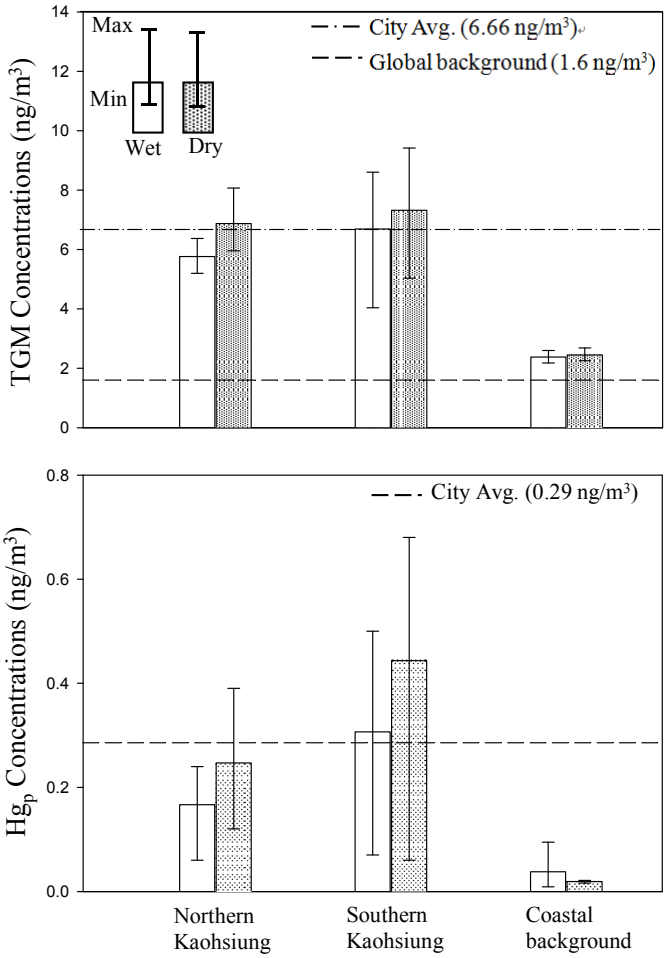

Fig. 3. Tempospatial variation of TGM and Hg_p concentrations during the wet and dry seasons at the northern and southern Kaohsiung sites and the coastal site.

seasons. The field measured meteorological data are listed in Table 1, and the field measurement data with mean, standard deviation (SD), and partition of TGM and Hg_p are summarized in Table 2. The meteorological condition of Kaohsiung City from June to December were gathered to decide the wet season, starting from June to September (early summer to early fall) and the dry season, starting from October to December (middle fall to early winter). During the wet season, ambient temperature, relative humidity, wind speed, and UV_B were 28.9 ± 0.7°C, 78.3 ± 1.7%, 2.2 ± 0.2 m/s, and 3.4 ± 0.5 UVI, respectively, which were mostly higher than those during the dry season. In addition, the prevailing wind direction was SW and NE during the dry season, and the prevailing wind blew from NW and NE during the wet season. It was mainly attributed to the fact that sea-land breezes were frequently blown in Kaohsiung City. However, the wet season is the heat convection season (i.e., hurricane season), in which the rainfall was about 427.9 ± 305.1 mm and the rainy days (rainfall ≥ 0.01 mm) were about 50 days. The dry season blew the northeast monsoon, in which the rainfall and rainy days were much less than those during the wet season. Therefore, the aforementioned meteorological condition can be considered as the differentiation between the dry and wet seasons in Kaohsiung City.

The results obtained from the seasonal variation of atmospheric mercury concentrations during the dry and wet seasons showed that the concentrations of TGM and Hg_p were 6.23 ± 1.62 ng/m^3 and 0.23 ± 0.17 ng/m^3, respectively, during the wet season, while the concentrations of TGM and Hg_p were 7.09 ± 1.57 ng/m^3 and 0.35 ± 0.25 ng/m^3, respectively, during the dry season in Kaohsiung City. The concentrations of atmospheric mercury during the dry season were obviously higher than those during the wet season. It showed that meteorological condition and atmospheric dispersion played a critical role on the seasonal variation of atmospheric mercury concentration. However, the seasonal concentrations of TGM and Hg_p did not vary much at the coastal background site, thus the seasonal variation had insignificant influences on regions where atmospheric mercury concentrations were high. The atmospheric mercury concentrations of southern Kaohsiung were mostly higher than those of northern Kaohsiung during the wet and dry seasons, and their average concentrations were respectively 1.12 and 1.79 times of those at the northern Kaohsiung. As a whole, the average concentrations of TGM and Hg_p in Kaohsiung City were about 2.94 and 11.7 times, respectively, higher than those at the coastal background site during the

Table 1. Meteorological parameters monitored in Kaohsiung City during the atmospheric mercury sampling periods for wet and dry seasons.

Seasons	Temp. (°C)	RH (%)	Rainfall (mm)	Rainy days	WS (m/s)	UV_B (UVI)	WD
Wet	28.9 ± 0.7	78.3 ± 1.7	427.9 ± 305.1	50	2.2 ± 0.2	3.4 ± 0.5	SW, NE
Dry	23.7 ± 3.4	73.3 ± 3.1	63.0 ± 97.6	12	1.9 ± 0.1	2.1 ± 0.3	NW, NE

Temp.: ambient temperature (°C); RH: relative humidity (%); Rainy day: days with rainfall ≥ 0.01 mm (day); WS: wind speed (m/s); WD: wind direction; UV_B: ultra-violet radiation (UVI).

Table 2. Seasonal variation of TGM and Hg_p concentrations at six sensitivity sites and the coastal site in Kaohsiung City.

Seasons	Types of mercury	Northern Kaohsiung sites			Southern Kaohsiung sites			Coastal background site
		S1	S2	S3	S4	S5	S6	Sb
Wet (n = 12)	TGM (ng/m^3)	5.72	6.37	5.20	4.04	7.42	8.60	2.38
	Hg_p (ng/m^3)	0.20	0.24	0.06	0.05	0.35	0.50	0.02
	Mean ± SD (ng/m^3)			6.23 ± 1.62 0.23 ± 0.17				
Dry (n = 12)	TGM (ng/m^3)	5.95	8.06	6.59	5.03	7.50	9.41	2.44
	Hg_p (ng/m^3)	0.23	0.39	0.12	0.08	0.59	0.68	0.03
	Mean ± SD (ng/m^3)			7.09 ± 1.57 0.35 ± 0.25				
Mean ± SD of atmospheric mercury (ng/m^3)				6.66 ± 1.42 0.29 ± 0.21				2.41 ± 0.04 0.03 ± 0.01

S1: Nan-zhi site; S2: Ren-wu site; S3: Zuo-ying site; S4: Cia-jin site; S5: Cian-jhen site; S6: Hsiao-kang site; Sb: coastal site at National Sun Yat-Sen University.

wet season and were about 2.6 and 11.5 times, respectively, during the dry season. The average TGM and Hg_p concentrations were 6.66 ± 1.42 and 0.29 ± 0.21 ng/m^3, respectively, in Kaohsiung City. The TGM concentration in Kaohsiung City was about 4.2 times and 2.8 times higher than the background TGM concentration of in the Northern Hemisphere (1.6 ng/m^3) and at the coastal site concentration in Kaohsiung City (2.4 ng/m^3), respectively. It showed that Kaohsiung City as a heavy industrial city was highly polluted with atmospheric mercury.

Fig. 4 illustrates the partition of Hg_p during the wet and dry seasons in Kaohsiung City. The results showed that TGM was the main mercury species, accounting for 94.56–99.59% of atmospheric mercury during the wet season, and 92.71–99.37% of atmospheric mercury during the dry season. Furthermore, Hg_p concentration had a tendency to increase with the distance from the emission sources. A maximum partition of Hg_p up to 20–40% of TAM has been observed in the ambient air (Lamborg *et al.*, 1995; Hladikova *et al.*, 2001). The partition of Hg_p is generally lower than 1% of TAM in the rural areas, about 1–3% in the metropolitan areas, and beyond 5% in the industrial areas (Feng *et al.*, 2003; Poissant *et al.*, 2005; Fu *et al.*, 2008). As shown in Fig. 5, site Sb was in the rural areas, sites S3 and S4 were in the metropolitan areas, and other sites were in the industrial areas in Kaohsiung City. Moreover, the partition of Hg_p during the dry season was generally higher than that during the wet season. It implied that the amount of rainfall, the number of rainy days, and relative humidity might correlate to the partition of Hg_p.

Spatial Distribution of TGM and Hg_p

The concentrations of TGM and Hg_p measured at each site are summarized in Table 2. As far as the spatial distribution of atmospheric mercury during the wet and dry seasons in Kaohsiung City was concerned, the atmospheric mercury concentrations (TGM of 6.37 ng/m^3; Hg_p of 0.24 ng/m^3) at site S2 was the highest and followed by sites S1 and S3 in northern Kaohsiung, while those (TGM of 8.60 ng/m^3; Hg_p of 0.50 ng/m^3) at site S6 was the highest and followed by sites S5 and S4 in southern Kaohsiung. During the dry season, the atmospheric mercury concentrations (TGM of 8.06 ng/m^3; Hg_p of 0.39 ng/m^3) at site S2 was also the highest and followed by sites S3 and S1 in northern Kaohsiung, while those (TGM of 9.41 ng/m^3; Hg_p of 0.50 ng/m^3) at site S6 was the highest and followed by sites S5 and S4 in southern Kaohsiung. Fig. 5 illustrates the variation of TGM and Hg_p concentrations at different mercury emission sources in Kaohsiung City (Jen *et al.*, 2010, 2011), sites S6 and S5 were located closely to a steel manufacturing complex, a coal-fired power plant, and an export processing district. In addition to the mercury emission sources, the tail gas exhausted from heavy-duty trucks also affected the concentration of atmospheric mercury in this region. Although sites S1 and S2 were close to a petrochemical industrial district, the consumption of fossil fuels (i.e., coal, petroleum, and gas), combustible wastes, and etc. in southern Kaohsiung were far higher than those in northern Kaohsiung, resulting in higher atmospheric mercury concentrations in southern Kaohsiung. Moreover, TGM and Hg_p concentrations at sites S3 and S4 were lower than other sites since these two sites, far from the mercury emission sources, were mainly influenced by traffic exhausts and cross-boundary transportation.

In this study, the mapping software (SURFER) was used for drawing the concentration contour of atmospheric

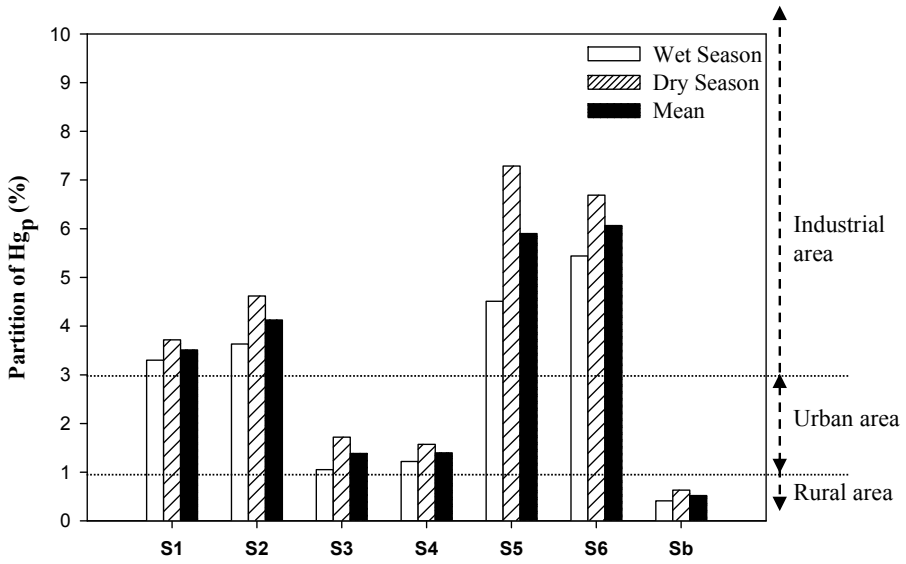

Fig. 4. Partition of Hg_p during the wet and dry seasons at six sensitivity sites (S1–S6) and the coastal background site (Sb).

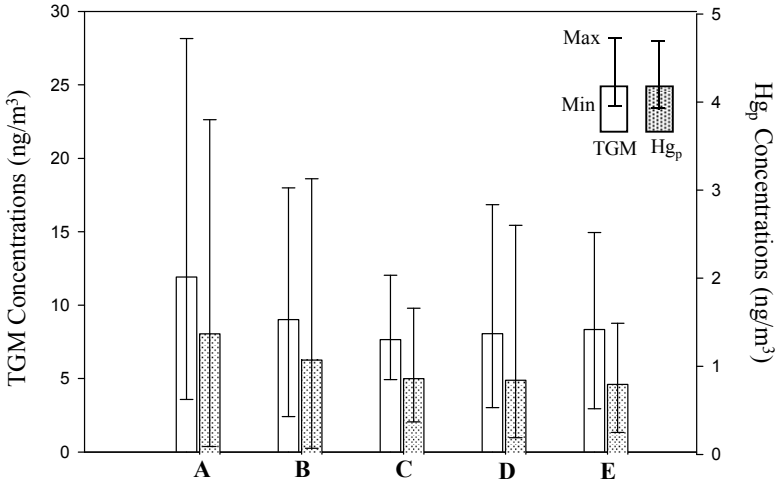

Fig. 5. Variation of TGM and Hgp concentrations in the atmosphere of major emission sources in Kaohsiung City. (A is the steelwork, B is the arc furnace factory, C is the petroleum refinery, D is the coal-fired power plant, E is the waste incinerator).

mercury in Kaohsiung City. The principle of this software is to use the grid difference as the calcuation basis, and interpolarate the data of atmospheric mercury concentration obtained from each sampling site into the map of Kaohsiung City. This study aimed to understand the spatial distribution of atmospheric mercury concentration in Kaohsiung City. As shown in Fig. 6, the atmospheric mercury concentrations of the northern and southern Kaohsiung were obviously affected by the mercury emission sources. Two major high mercury concetration regions in Kaohsiung City concurred with the petrochemical inudstrial district in northern Kaohsiung and the steel manufactoying complex in southern Kaohsiung. The main emission sources in northern Kaohsiung were petrochemcial manufatarung district, municipal and industral waste incinerators, cremators, and etc. In southern Kaohsiung, mercury was mainly emitted from steel smelters, arc furnance plants, cement plants, oil refineries, coal-fired power plants, municipal waste incinerators, and etc. Consequently, the atmospheric mercury concnetration in southern Kaohsiung was higher than that in northern Kaohsiung, which is attributed to higher mercury emission in southern Kaohsiung than that in northern Kaohsiung.

As a whole, the air quality of Kaohsiung City was highly influenced by the heavily densed industreis, thus the concentration of atmospheric mercury in the metropolition area was much higher than the background level during the wet and dry seasons. Both the emission sources and the consumption of fossil fuels in southern Kaohsiung were higher than those in northern Kaohsiung. Consequently, the atmospheric mercury concentration in southern Kaohsiung was generally higher than that in northern Kaohsiung.

Correlation of Atmospheric Mercury with Meteorological Parameters and Air Pollutants

The correlation of atmospheric mercury concentration, meteorological parameters and air pollutants affecting the

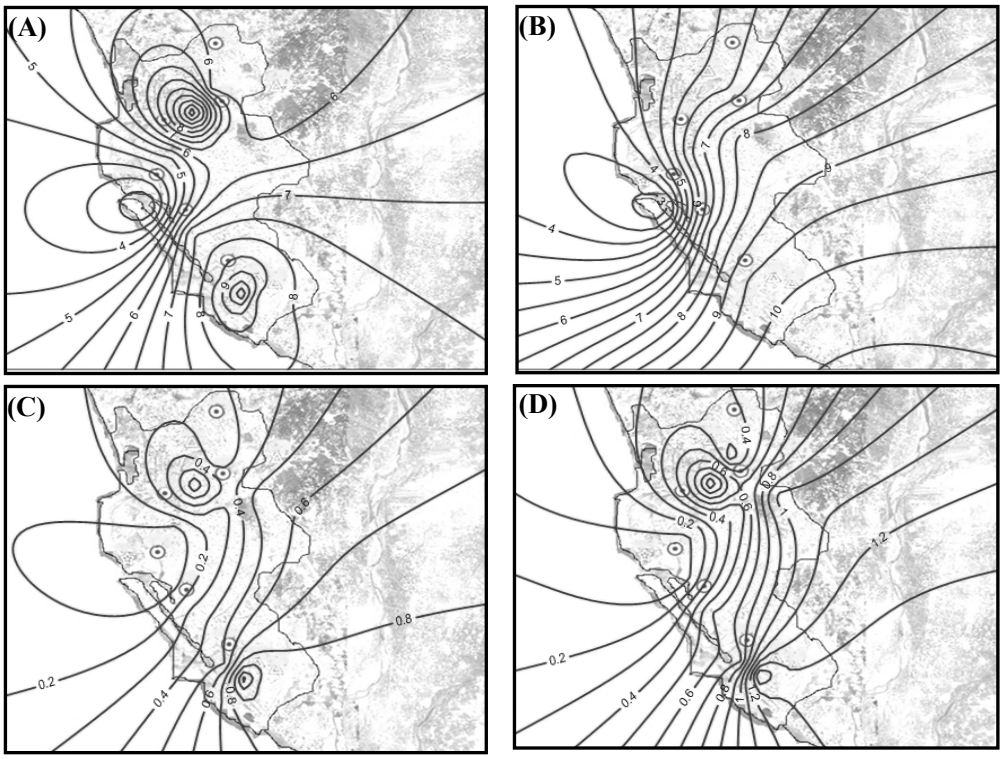

Fig. 6. Spatial distribution of atmospheric mercury in Kaohsiung City. (A) TGM concentration during the dry season, (B) TGM concentration during the wet season, (C) Hg_p concentration during the dry season, (D) Hg_p concentration during the wet season.

atmospheric mercury concentration is summarized in Table 3. This study revealed that TGM concentration correlated positively with Hg_p (R = 0.95), SO_2 (R = 0.75), NO_x (R = 0.66), UV_B (R = 0.51) and negatively with O_3 (R = –0.78), ambient temperature (R = –0.63), relative humidity (R = –0.69), and wind speed (R = –0.85), while Hg_p concentration correlated positively with SO_2 (R = 0.70) and NO_x (R = 0.79) and negatively with ambient temperature (R = –0.69), relative humidity (R = –0.92), and wind speed (R = –0.80). The burning of coal and fuel oil could increase the concentration of atmospheric mercury, SO_2, and NO_x in the air, which indicated that the concentration of atmospheric mercury increased as the amount of the emission from stationary and mobile sources increased in Kaohsiung City. Among them, as the concentration of NO_x became higher, O_3 concentration would be also increased by photochemical reactions. Thus, NO_x had a positive correlation with O_3 (R = 0.64). However, a negative correlation of TGM with O_3 was due to the oxidation of Hg^0 to Hg^+ and Hg^{2+} by O_3, which can be adsorbed onto the atmospheric aerosols. As O_3 concentration became higher, the concentration of TGM tended to decrease. Previous studies showed that CO could reduce Hg^+ and Hg^{2+} to Hg^0 (Feng *et al.*, 2002; Fu *et al.*, 2010), thus TGM concentration would be higher as CO concentration increased (Schroeder *et al.*, 1998). A low correlation coefficient of TGM versus CO suggested that TGM concentration was not solely influenced by CO reduction. Other factors such as the emission sources of high temperature combustion (e.g., coal-fired power plant, waste incinerators, steel plant) could also influence the variation of TGM concentration.

Atmospheric mercury concentration and meteorological parameters had negative correlation with ambient temperature, since the mixing height during the dry season (fall and winter) was relatively low and hence hinder atmospheric dispersion, thus the atmospheric mercury concentration showed an increase trend. During the wet season (summer), the ambient temperature was higher than those during the dry season, but the rainy days became longer, thus air pollutants could be scavenged below cloud by washout, and the atmospheric mercury concentration decreased as relative humidity became higher. High ultraviolet radiation could lead photochemical reactions and hence reduced Hg^+ and Hg^{2+} to Hg^0. The higher the wind speed is, the better the effect of atmospheric dispersion will be, which resulted in the reduction of atmospheric mercury concentration. Besides, the oxidized mercury in the atmospheric particles would be more stable if the relative humidity became higher, and only small amount of elemental mercury could be scavenged by water molecules (or droplets???), especially when O_3 concentration was higher.

Comparison of TGM and Hg_p Concentrations in the Major of Taiwan and Other Countries

Table 4 compares the concentration of atmospheric mercury measured in Kaohsiung City with other major cities in Taiwan. The results showed that the concentrations of TGM and Hg_p in the atmosphere of Kaohsiung City were generally higher than those of other cities in Taiwan during the wet and dry seasons. Of these, TGM concentration was

Table 3. Correlation of TGM and Hg_p concentrations with air pollutants and meteorological parameters.

	TGM	Hg_p	SO_2	NO_x	CO	O_3	TEMP	UV_B	RH	WS
TGM	1.00									
Hg_p	0.95	1.00								
SO_2	0.75	0.70	1.00							
NO_x	0.66	0.79	0.94	1.00						
CO	0.32	0.28	0.29	0.38	1.00					
O_3	–0.78	0.42	–0.53	0.64	–0.08	1.00				
TEMP	–0.63	–0.69	–0.52	–0.69	0.09	0.22	1.00			
UV_B	0.51	–0.35	0.08	–0.10	–0.33	0.70	0.18	1.00		
RH	–0.69	–0.92	–0.63	–0.69	0.03	0.13	0.78	0.10	1.00	
WS	–0.85	–0.80	–0.51	–0.65	–0.73	0.45	–0.12	0.07	–0.13	1.00

Table 4. Comparison of TGM and Hg_p concentrations for wet and dry seasons at major cities in Taiwan.

Cities	TGM (ng/m^3)		Hg_p (ng/m^3)		Dry/Wet Ratios	
	Dry	Wet	Dry	Wet	TGM	Hg_p
Taipei	2.86	3.90	0.07	0.15	0.73	0.47
Hsinchu	2.69	3.73	0.07	0.18	0.72	0.39
Taichung	3.27	4.58	0.10	0.15	0.71	0.67
Yunlin	2.65	3.13	0.07	0.11	0.85	0.64
Tainan	2.85	3.24	0.10	0.25	0.88	0.40
Kaohsiung	6.23	7.09	0.23	0.35	0.88	0.66
Hualian	2.67	3.08	0.08	0.15	0.87	0.53
Taiwan Overall	3.32 ± 1.30	4.11 ± 1.42	0.10 ± 0.06	0.19 ± 0.08	0.81 ± 0.08	0.54 ± 0.12

Wet season: June–September, 2010; Dry season: October–December, 2010.

about 1.6 to 2.3 times, while the Hg_p concentration was about 1.7 to 3.2 times, higher than other Taiwanese cities. It showed that Kaohsiung City was seriously polluted by atmospheric mercury year round. The dry/wet ratios of TGM concentrations ranged from 0.71 to 0.73 in northern Taiwan (i.e., Taipei, Hsinchu, and Taichung), which were higher than those measured in southern Taiwan. This phenomenon is mainly attributed to the fact that the weather changes frequently in northern Taiwan and its rainfall and rainy days are much higher and longer than those in southern Taiwan. Moreover, Kaohsiung City is the major industrial city in southern Taiwan, which has stronger activities in industrial areas (i.e., steel plant, coal-fired power plant, waste incinerator), thus the concentration of Hg_p in the dry season was high, resulting in a higher dry/wet ratio of 0.66 than other cities in Taiwan except Taichung. As a whole, the TGM concentrations were 4.11 ± 1.42 and 3.32 ± 1.30 ng/m^3, while the Hg_p concentrations were 0.19 ± 0.08 and 0.10 ± 0.06 ng/m^3, respectively, for the wet and dry seasons. The concentration ratios of the dry and wet seasons were 0.81 ± 0.08 and 0.54 ± 0.12 ng/m^3 for TGM and Hg_p, respectively.

Furthermore, the average concentrations of TGM collected from several major cities in East Asia (including Japan, Korea and China), Europe, and North America are compared in Table 5. The TGM and Hg_p concentrations of North America and Europe were 1.5–4.1 ng/m^3 and 0.11–26 pg/m^3, respectively. While the TGM and Hg_p concentrations of East Asia were 2.0–18.4 ng/m^3 and 3.0–1180 pg/m^3, respectively. However, America and Europe have enforced the best available technologies and the strictest regulations for mercury control, for approximately 20 years earlier than East Asia. Consequently, both the concentrations of TGM and Hg_p in the atmosphere of America and Europe are much lower than in East Asia.

The lowest TGM concentration in East Asia was observed in Tokyo, and the lowest Hg_p concentration was found in Seoul. These two cities might have better strategies for mercury control, thus the atmospheric mercury concentrations in Tokyo and Seoul were lower than other cities in East Asia. Generally, the highest mercury concentrations were observed in China (i.e., Changchun, Beijing, Guangzhou, Guiyang, and Chongqing), ranging from 6.7 to 18.4 ng/m^3 and from 276.0 to 1180.0 pg/m^3 for TGM and Hg_p, respectively. Overall speaking, the concentration of atmospheric mercury is not only affected by the amount of mercury emission, but also affected by the synoptic weather. Coal burning for space heating in winter season causes China the highest mercury emission country in the world, particularly in North China. Among them, the TGM concentration in Shanghai is only 2.7 ± 1.7 ng/m^2, but the Hg_p concentration goes up to 560 ± 220 pg/m^3 in urban area (Friedli *et al.*, 2010), suggesting that the TGM concentrations in Shanghai might be underestimated. Particularly, Guizhou ranks the highest mercury emission in China, since it accounts for 78% of gross amount of mercury mining in China (Fu *et al.*, 2011). Although the TGM concentration in Guiyang is a little bite lower than that in Beijing, the average TGM concentration up to 60 ng/m^3 is observed around the mining region in Guiyang (Feng *et al.*, 2003). The results showed that, in China, mercury emitted from natural sources had significant influences on atmospheric mercury concentration except for anthropogenic emission sources.

Table 5. Comparison of TGM and Hg_p concentrations in major cities of Asia, Europe, and North America.

Countries	Cities	TGM (ng/m^3)	Hg_p (pg/m^3)	References
USA	Detroit	2.5 ± 1.4	18.1 ± 61.0	Liu *et al.*, 2010
USA	Tuscaloosa	4.1 ± 1.28	16.4 ± 19.5	Gabriel *et al.*, 2005
USA	Reno	2.0 ± 0.7	7.0 ± 7.0	Lyman *et al.*, 2009
USA	Idaho	1.6 ± 0.6	–	Abbott *et al.*, 2008
USA	Houston	1.5-4.0	2.5 ± 5.2	Brooks *et al.*, 2010
USA	Toronto	4.5 ± 3.1	14.2 ± 13.2	Cheng, *et al.*, 2009
USA	Milwaukee	2.5 ± 1.7	11.8 ± 0.3	Rutter *et al.*, 2007
USA	St. Louis	4.05 ± 1.28	16.4 ± 19.5	Manolopoulos *et al.*, 2007
EU	Poland	1.63 ± 0.35	0.11 ± 0.05	Zielonka *et al.*, 2005
EU	Sweden	1.6 ± 0.2	12.50 ± 5.88	Li *et al.*, 2008
Canada	Quebec	1.7 ± 0.4	26.0 ± 54.0	Poissant *et al.*, 2005
Mexico	Metropolitan	7.2 ± 4.8	187.0 ± 300.0	Rutter *et al.*, 2009
Japan	Tokyo	2.7 ± 3.6	98.0 ± 51.0	Sakata, *et al.*, 2002
Koera	Seoul	3.2 ± 2.1	23.9 ± 19.6	Kim *et al.*, 2009
China	Changchun	18.4	276.0	Fang *et al.*, 2004
China	Beijing	9.7	1180	Wang *et al.*, 2006
China	Shanghai	2.7 ± 1.7	560.0 ± 220.0	Xiu *et al.*, 2009; Friedli *et al.*, 2010
China	Chongqing	6.7 ± 0.4	–	Yang *et al.*, 2009
China	Guangzhou	13.5 ± 7.1	–	Wang *et al.*, 2007
China	Guiyang	9.7 ± 10.2	368.0 ± 676.0	Fu *et al.*, 2011
Taiwan	Taichung	6.1 ± 3.9	71.1 ± 46.1	Huang *et al.*, 2012
Taiwan	Kaohsiung	6.7 ± 1.4	290.0 ± 210.0	This study

Overall, the TGM concentrations measured in major cities of Taiwan were generally higher than Tokyo and Seoul, and substantially lower than China. However, the Hg_p concentration in Kaohsiung City was a bit lower than Changchun, but closed to Guiyang. The results showed that Kaohsiung City was the highest mercury polluted city in Taiwan. Moreover, Japan, Korea, and Taiwan are located under the leeward of mainland China during the monsoon prevailing seasons, as one of the polluted air parcel transportation routes, it could blow atmospheric mercury downward and thus resulted in the increase of atmospheric TGM and Hg_p concentrations in East Asia.

CONCLUSIONS

The tempospatial variation and partition of gaseous and particulate mercury were investigated in Kaohsiung City. This study revealed that the average TGM concentration in Kaohsiung City was 6.66 ± 1.42 ng/m^3 and the average Hg_p concentration was 0.29 ± 0.21 ng/m^3, which was about 4.1 times higher than the TGM background concentration of 1.6 ng/m^3 in the North Hemisphere. The partition of TGM ranged from 94.56% to 99.59%, and from 92.71% to 99.37%, in the wet and dry seasons, respectively. The variation of spatial distribution showed that there were two major regions of high mercury concetration in Kaohsiung City, concurring well with the petrochemical complex in northern Kaohsiung and the steel manufacturing complex in southern Kaohsiung, respectively. The correlation of atmospheric mercury revealed that the TGM concentration correlated positively with Hg_p, SO_2, NO_x, and UV_B, and negatively with O_3, ambient temperature, relative humidity, and wind speed, while the Hg_p concentration correlated positively with SO_2 and NO_x, and negatively with ambient temperature, relative humidity, and wind speed.

This study compared the atmospheric mercury concentrations in Kaohsiung City with several major cities in East Asia, Europe, and North America. The results showed that TGM and Hg_p concentrations in Kaohsiung City were generally higher than those of other Taiwanese cities during the wet and dry seasons. Besides, the concentrations of TGM measured in the cities of Taiwan were higher than Tokyo and Seoul, however, lower than other cities in China. Coal burning for space heating in winter season causes China the highest mercury emission country in the world. Moreover, Japan, Korea, and Taiwan are under the leeward of mainland China, and are located at the major atmospheric mercury transportation routes. When the northeast monsoon prevailed, the concentrations of TGM and Hg_p increased in most major cities of East Asia.

ACKNOWLEDGMENTS

This study was performed under the auspices from the Environmental Protection Bureau of Kaohsiung City (KSEPB) in Taiwan through project grants NO. 99038. The authors would like to express their sincere appreciation for its financial support to accomplish this study.

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Received for review, May 14, 2012
Accepted, August 6, 2012