

Monitoring of Atmospheric Mercury at a Global Atmospheric Watch (GAW) Site on An-Myun Island, Korea

Hang Thi Nguyen · Ki-Hyun Kim ·
Min-Young Kim · Sungmin Hong ·
Yong-Hoon Youn · Zang-Ho Shon ·
Jeong Soon Lee

Received: 6 December 2006 / Accepted: 17 May 2007 / Published online: 12 June 2007
© Springer Science + Business Media B.V. 2007

Abstract In order to investigate the regional background concentration levels of mercury (Hg), measurements were routinely recorded on An-Myun Island off

the coast of Korea (December 2004 to April 2006). The mean concentration of Hg computed from the entire measurement period was $4.61 \pm 2.21 \text{ ng m}^{-3}$ with a range of $0.10\text{--}25.4 \text{ ng m}^{-3}$ ($N=10,485$). Using these data, we inspected various aspects of Hg behavior from the relatively remote island of An-Myun in Korea. Inspection of the seasonal patterns of Hg indicated that its concentration levels generally peaked in spring, while reached a minimum in summer. The summertime deficiency of Hg along with the lack of diurnal variation suggests that the environmental behavior of Hg at the study site was strongly suppressed by heavy precipitation during specific period. The diurnal variations of Hg, typically characterized by a relative daytime dominance, are distinguishable between seasons so that such patterns disappear during the summer. The results of our analysis, when inspected in terms of long-range transport of airborne pollutants, imply that Hg concentration levels can be affected intensively by trans-boundary input processes over certain period of time. Its springtime dominance hence suggests the combined effects of various local source processes and the meteorological conditions favorable for the massive air mass transport phenomenon (such as Asian Dust storms) during that time period.

H. T. Nguyen · K.-H. Kim (✉)
Department of Earth and Environmental Sciences,
Sejong University, Seoul, South Korea
e-mail: khkim@sejong.ac.kr

M.-Y. Kim
Seoul Metropolitan Institute of Public
Health and Environment, Seoul, South Korea

S. Hong
Polar Environmental Research Division,
Korea Polar Research Institute, KORDI,
Inchon, South Korea

Y.-H. Youn
Marine Meteorology Division,
Korea Meteorological Administration,
Seoul, South Korea

Z.-H. Shon
Department of Environmental Engineering,
College of Engineering, Dong-Eui University,
995 Eomgwangno, Busanjin-gu,
Busan, South Korea

J. S. Lee
Environment Measurement Group, Korea Research
Institute of Standards and Science (KRISS),
1 Doryong Dong, Yuseong Gu,
Daejeon, South Korea

Keywords Mercury · Island · Long-range transport ·
Background · Monitoring

1 Introduction

Mercury (Hg) belongs to one of the toxic pollutant species emitted into the atmosphere by both natural and anthropogenic processes. Emissions due to industrial activities can contribute to Hg pollution, especially via combustion of fossil fuels. In Poland, fuel combustion is estimated to generate more than 75% of the atmospheric mercury countrywide (Pacyna et al. 2001). On the other hand, such environmental compartments as soil, water, and vegetation are known to be natural sources of mercury emission (Xu et al. 1999; Poissant et al. 2004). An inventory study of atmospheric mercury reports that both anthropogenic and natural (including re-emission) emissions of Hg decreased worldwide from 1990 to 1996 (Slemr et al. 2003). According to a global inventory of Hg as of the year 2000, two-thirds of anthropogenic emission (ca. 2,190 ton) came from the combustion of fossil fuels (Pacyna et al. 2006). The major chemical form of mercury emitted into the atmosphere is identified as gaseous elemental mercury (referred hereafter as GEM (Hg^0)) which accounts for up to 53% of the total emission followed by gaseous divalent mercury [$\text{Hg}(\text{II})$] (37%). The Hg emissions of particles [$\text{Hg}(\text{p})$], however, account for only about 10% of total emissions (Pacyna and Pacyna 2002). Mercury in the atmosphere, once emitted, is chemically transformed and eventually removed either by wet or dry deposition processes (Gbor et al. 2006).

Numerous studies have been made to investigate the behavior of Hg under various environmental conditions. It appears that emissions of mercury have been decreasing due to the application of efficient control equipment in many developed countries (Mukherjee et al. 2000; Pacyna et al. 2006). Although the temporal distribution of Hg often varies in a predictable manner across different time scales, it can also exhibit dramatic changes under the influence of strong man-made source processes (Kim and Kim 2000). In contrast, the spatial distribution of atmospheric Hg, being controlled by an interplay between chemistry, transport, and dispersion processes, can reflect the combined effects of such factors as its physicochemical properties and the rate of chemical transformation among different species [such as Hg^0 , $\text{Hg}(\text{II})$, and $\text{Hg}(\text{p})$] (Schroeder and Munthe 1997).

In order to extend our knowledge on the environmental behavior of Hg, its concentration was

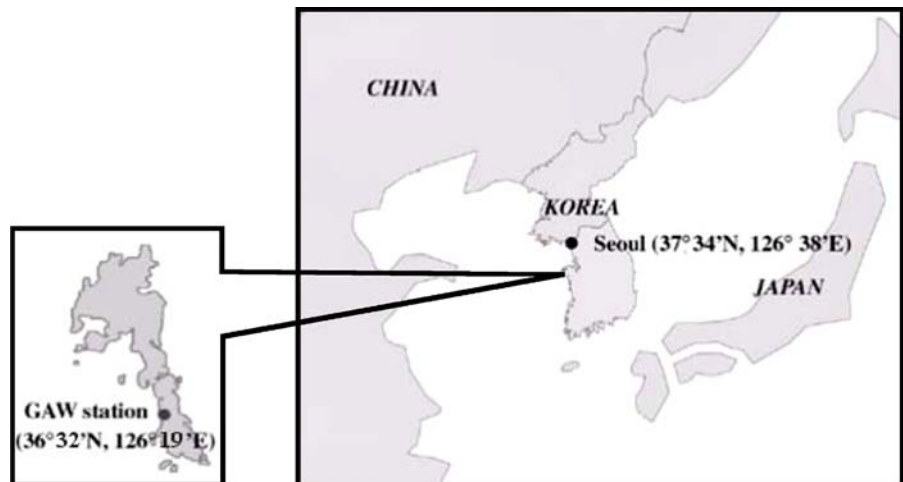
monitored on a routine basis on An-Myun Island located off the west coast of Korea for a 16-month period (16th December 2004 to 20th April 2006). The selected study site represents the ideal conditions for coastal locations in Korea. The results of our study are thus expected to offer valuable insight into the factors governing the behavior of Hg in local background areas that are moderately distant from strong man-made activities in Korea.

2 Materials and Methods

The concentrations of Hg in air were determined from the Korean Global Atmospheric Watch (K-GAW) station located on An-Myun (AM) Island, Korea. This GAW atmospheric observatory is located on the western coast of Korea ($36^{\circ}32'N$, $126^{\circ}19'E$) at 45.7 m above sea level (Fig. 1). The climate of the area is characterized by both summer Asian monsoons (with heat and humidity from the Northern Pacific air mass) and cold winter temperatures along with strong westerly winds from continental China (e.g., Oh et al. 2001). The AM station is also a World Meteorological Organization (WMO) global observation station, which transmits data to the WMO following a pre-arranged schedule. The environmental parameters routinely observed at monitoring station included criteria pollutants (SO_2 , NO_x , O_3 , and CO), greenhouse gases (CO_2 , CH_4 , CFCs, and N_2O), aerosols (PM_{10} and $\text{PM}_{2.5}$), and meteorological elements including solar and terrestrial radiation (Oh et al. 2001).

Hg concentration was measured every hour over the entire study period from the GAW station on AM island (actual sampling height=3 m above the observatory ground). For the analysis of Hg, air samples were drawn via a 2-m long sampling train made from Teflon tubing (30 mm diameter) into an on-line automatic Hg analyzer (AM-2 model, the Nippon Instrument Co., Japan) with an internally combined setting of both sampling and detection devices. As samples of Hg were collected without aerosol filter upstream of the analyzer, it can be more or less equivalent to total gaseous Hg (TGM). However, for the sake of simplicity, we referred to it as Hg or mercury, unless otherwise specified. At each hourly interval, Hg was collected by an Au–amalgam trap at a constant flow rate of 1.0 l min^{-1} , desorbed

Fig. 1 The geographical location of the study site (An-Myun (AM) island in Korea)



thermally, and detected at a wavelength of 253.7 nm by a non-dispersive double beam, flameless cold vapor atomic absorption spectrometry (CVAAS) system. The absolute detection limit of the system was ca. 1 pg of Hg. The precision of this analytical system, if evaluated in terms of relative standard error ($RSE=SE/mean \times 100$) of five replicate injection samples of vapor-phase standards (at three different concentration levels of 1, 2, and 3 ng m^{-3}), averaged 0.3–0.6% (e.g., Kim and Kim 2001). Although accuracy is an important parameter for defining the characteristics of our analytical system, we could not assess it directly because of the unavailability of certified vapor standards. When the system was calibrated against several NBS standards (e.g., NBS-1632a, 1568, and 1575), the values were generally estimated in the 3–5% range. The performance of our measurement technique has also been tested against other automated analyzers such as the Lumex system (Kim et al. 2006) or customary manual method (Pandey and Kim 2007). A reasonable amount of agreement was observed across these comparative tests.

3 Results and Discussion

3.1 The Fundamental Picture of Hg Distribution in the Study Area and the Environmental Conditions

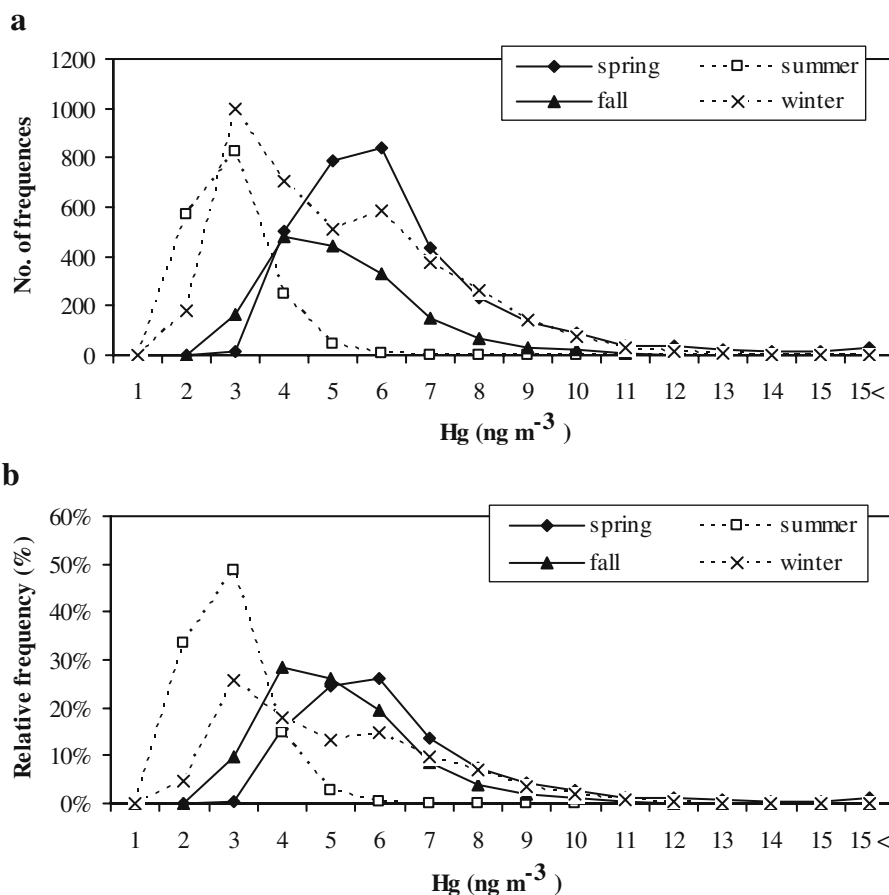
In this study, Hg concentration data were collected for approximately a year and a half (December

2004 to April 2006). The mean concentration of Hg for the entire study period was $4.61 \pm 2.21 \text{ ng m}^{-3}$ (median = 4.32 ng m^{-3}) with a range of 0.10–25.4 ng m^{-3} ($N=10,485$). The observed concentration levels of Hg were much higher than those observed in other remote island locations in Korea. For instance, on Kang Hwa Island, Hg concentrations were typically monitored at around 3 ng m^{-3} (Kim et al. 2003).

To explore the occurrence patterns of Hg at the study area, frequency distribution was also checked across seasonally divided data groups (Fig. 2). The results indicate that Hg concentration peaked in the 5–7 ng m^{-3} range during spring, while in the summer values were recorded at around 3 ng m^{-3} . The results of this frequency analysis have also been inspected in both absolute and relative terms. The patterns of such a comparison suggest the possibility of more prominent Hg source processes in spring than in other seasons (Fig. 2).

To facilitate the interpretation of Hg behavior at the island location, the basic environmental conditions of the study area were also examined using a few basic meteorological parameters that were measured concurrently (e.g., wind speed, temperature, and rainfall). According to this analysis, the study site can be classified as a temperate climate zone where the mean temperature in the summer reached $22.7 \pm 3.14^\circ\text{C}$, while, as expected, much lower values were observed in the winter ($-1.02 \pm 3.37^\circ\text{C}$). The amount of rainfall during the winter ($29.8 \pm 32.8 \text{ mm}$) was also significantly lower than in the other seasons [e.g., $73.8 \pm 84.8 \text{ mm}$ (spring), $156 \pm 203 \text{ mm}$ (summer), and $172 \pm$

Fig. 2 The frequency distribution patterns of Hg concentration data between four seasons (in both absolute and relative terms). **a** Absolute terms. **b** Relative terms



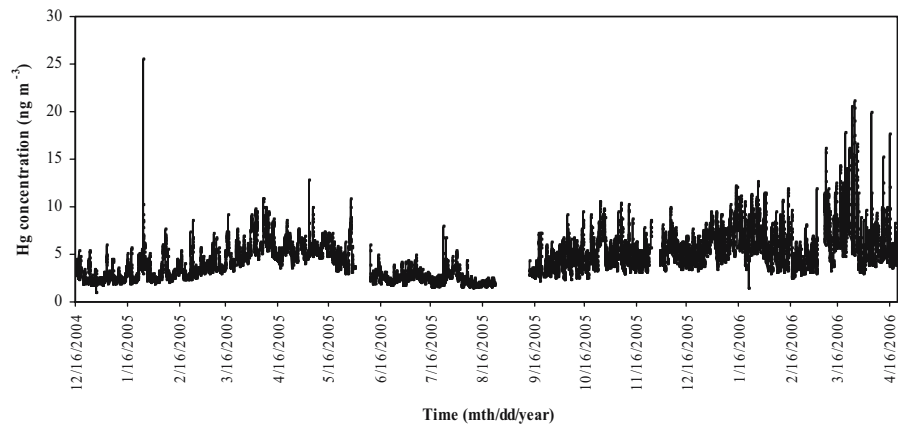
259 mm (fall)]. In addition to this general and cyclic trend, the windrose patterns at the site were inspected. Winds generally occurred from NNE (the first sector; between 0 and 22.5°) during most of the study period, with a relative frequency of 18.5% ($N=1823$). This was followed by SSW with a frequency of 15.7% ($N=1543$).

3.2 Seasonal Distributions of Hg on AM Island

The temporal pattern of Hg distribution plotted on a day-to-day basis can be seen in Fig. 3. The presence of generally enhanced Hg concentration levels at the site relative to fairly clean environments (e.g., 1.65 ± 0.42 ng m⁻³, St. Anicet, Quebec, Canada: Poissant et al. 2005) suggests the influence of man-made activities (e.g., burning of biomass in the spring) within or around the island. If the Hg data are inspected simply across the entire study period, there

is a notable enhancement in the Hg concentration levels for the second half of the study period relative to the first half. The highest Hg concentration value (25.4 ng m⁻³) occurred at 17:00 on 25th January, 2005 (Julian day (JD) 391; note the beginning time for JD counting for the entire study period between 350 and 840 days simply set on 1 January 2004). The lowest value of Hg (0.89 ng m⁻³), on the other hand, occurred at 20:00 on the 28th of December, 2004 (JD 363). The seasonal distribution of Hg was analyzed after grouping the data sets on a seasonal basis (Table 1). As shown in Fig. 4, Hg concentration peaked in spring with a mean value of 5.82 ± 2.25 ng m⁻³ (median= 5.44 ng m⁻³) in the range 2.81 – 21.0 ng m⁻³, $N=3208$. The Hg values then decreased slightly in the fall (4.69 ± 1.48 ng m⁻³, median= 4.46 ng m⁻³) and winter (4.54 ± 2.12 ng m⁻³, median= 3.12 ng m⁻³), reaching a minimum (2.43 ± 0.71 ng m⁻³) in the summer. The occurrence of the highest Hg values in

Fig. 3 A plot of the day-to-day variability of Hg measured on An Myun (AM) Island, Korea over the entire study period (December 2004 to April 2006)



the spring may be a combination of the effects of strong source processes, weak chemical loss process (chemical transformation), weak physicochemical processes (dry and wet depositions), and the possibly potent role of springtime environmental conditions which may facilitate the transport of pollutants along with massive air mass (such as Asian dust storms).

In fact, similar seasonal patterns of Hg have been observed in many previous studies. For example, in a study of the TGM at Mace Head, Ireland, the highest TGM value occurred during the spring and winter months ($\sim 1.8 \text{ ng m}^{-3}$), with the lowest value recorded during the summer months (1.65 ng m^{-3} ; Kock et al. 2005). The occurrence of the minimum value during

summer is a common pattern of trace gas distribution, as the strength of the source processes (such as fossil fuel burning) is weakened during summer (Kock et al. 2005). In addition, the minimum value during the summer at the AM site might result from suppressed source and strong sink (wet deposition due to Asian monsoons and photochemical reaction (e.g., $\text{Hg} + \text{O}_3$ and $\text{Hg} + \text{OH}$ reactions; Shon et al. 2007).

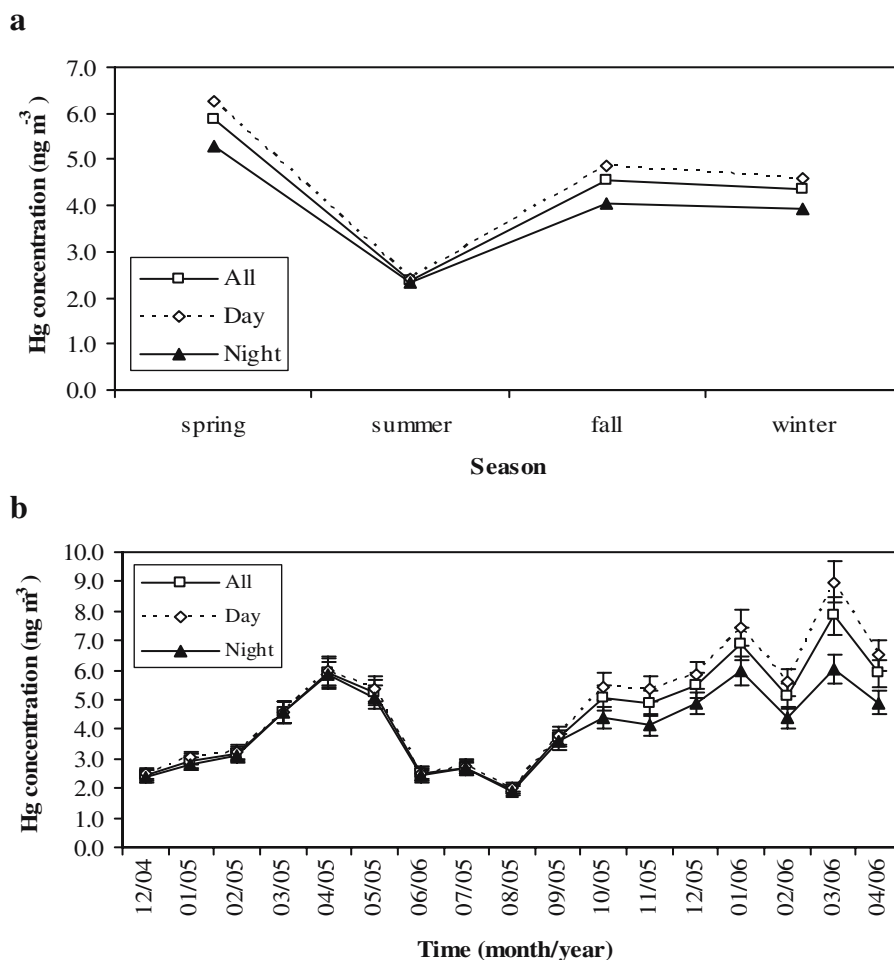
To examine the seasonal patterns of Hg in detail, Hg concentration data were examined at monthly intervals (Fig. 4b). The results confirm that the concentration levels of Hg reached a minimum value during the summer months and that the values increased during the fall through and spring months.

Table 1 A statistical summary of Hg concentration data and the basic environmental parameters measured during the entire study period

	All data	Spring	Summer	Fall	Winter
Hg (ng m^{-3})	4.61 ± 2.21 (4,32) 0.89~25.4 (10,484)	5.82 ± 2.25 (5,44) 2.81~21.0 (3,208)	2.43 ± 0.71 (2,28) 1.40~7.86 (1,698)	4.69 ± 1.48 (4,46) 2.07~10.5 (1,685)	4.54 ± 2.12 (3,12) 0.89~25.4 (3,893)
Wind speed ^a (m s^{-1})	4.09 ± 2.32 (3,60) 0.0~16.5 (8,600)	4.21 ± 2.60 (3,60) 0.0~16.5 (2,208)	3.95 ± 2.44 (3,50) 0.0~15.7 (2,200)	3.63 ± 1.99 (3,40) 0.0~14.3 (2,031)	4.53 ± 2.10 (4,20) 0.0~16.2 (2,160)
Temperature ^a ($^{\circ}\text{C}$)	11.7 ± 9.94 (12,9) -10.3~33.6 (8,600)	9.46 ± 5.92 (9,80) -3.90~23.6 (2,208)	22.7 ± 3.14 (22,7) 13.9~33.6 (2,200)	15.6 ± 5.76 (15,7) 1.60~28.5 (2,031)	1.02 ± 3.37 (-1,40) -10.3~12.9 (2,160)
Humidity ^a (%)	74.1 ± 16.7 (76,0) 30.0~100 (8,600)	72.8 ± 16.2 (75,0) 41.0~98.0 (2,208)	88.6 ± 9.26 (91,0) 50.0~100 (2,200)	69.6 ± 15.8 (68,0) 30.0~100 (2,031)	64.8 ± 14.2 (63,0) 32.0~97.0 (2,160)
Rainfall (mm)	110 ± 178 (35,0) 5.00~1150 (1,727)	73.8 ± 84.8 (25,0) 5.00~310 (421)	156 ± 203 (60,0) 5.00~945 (588)	172 ± 259 (70,0) 5.00~1150 (325)	29.8 ± 32.8 (15,0) 5.00~150 (393)
CO_2 ^a (ppm)	393 ± 8.98 (392) 350~420 (6,377)	394 ± 7.73 (393) 378~420 (1,647)	389 ± 9.18 (387) 366~419 (1,173)	393 ± 8.86 (392) 351~420 (1,584)	393 ± 9.42 (392) 350~420 (1,972)
CH_4 ^a (ppm)	1.89 ± 0.07 (1,87) 1.74~2.33 (6,259)	1.88 ± 0.04 (1,87) 1.79~2.21 (2,002)	1.89 ± 0.11 (1,87) 1.74~2.33 (1,345)	1.91 ± 0.08 (1,88) 1.76~2.32 (1,110)	1.89 ± 0.05 (1,87) 1.82~2.16 (1,801)

^aNote that the availability of some environmental parameters (CO_2 and CH_4) was confined to the year 2005.

Fig. 4 Comparison of temporal distribution patterns of Hg at mixed time intervals. **a** Comparison of both seasonal and diurnal patterns of Hg. **b** Month-to-month variation patterns of Hg



According to this comparative analysis, the maximum monthly mean value of Hg (7.85 ng m^{-3}) was found in May 2006. The minimum mean value (1.98 ng m^{-3}) was recorded in August 2005. As rainfall occurs most intensively in the late summer months, such a phenomenon might have led to the reduction of Hg concentration levels during summer. A clear increase in the Hg concentration levels from fall through winter may be explained as the direct effect of anthropogenic emissions (e.g., household heating). Moreover, it is also plausible that the low mixing depth during winter may contribute to the enhancement of Hg concentration relative to the other seasons.

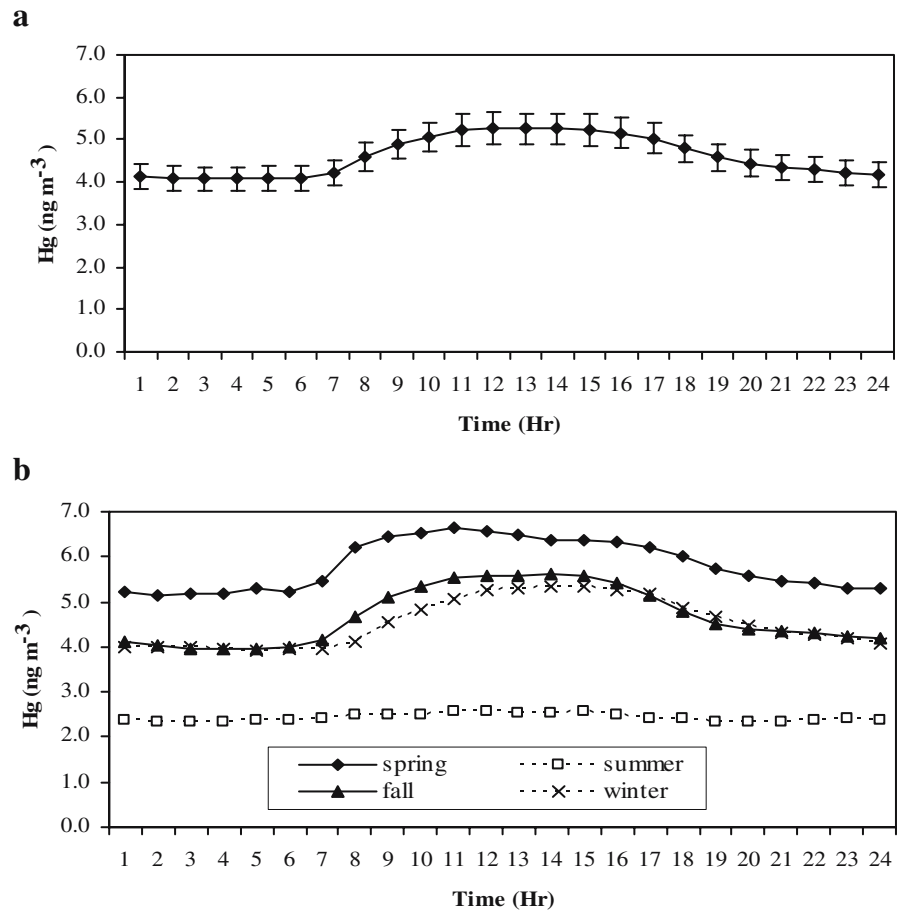
It should be addressed that there are certain environmental conditions under which Hg emission is facilitated. For instance, the effect of wet surface conditions

(and/or high temperature conditions) has been postulated to promote the emission of Hg (e.g., Wallschlager et al. 2000). Despite a line of evidence suggesting that Hg concentrations can rise under wet conditions (e.g., enhanced emission of Hg after the early rain event following a long dry period), we speculate that the summertime conditions for the present study site may have overridden such source effects as either wet surface or irradiation due to heavy precipitation with an efficient removal mechanism in an island area.

3.3 Short-term Variabilities of Hg Concentration

In Fig. 5, the diurnal variation patterns of Hg are plotted using hourly mean values for both the entire study period and seasonally divided data groups. The

Fig. 5 Plots of diurnal variability in Hg concentration. **a** Patterns derived using all measurements data. **b** Patterns for seasonally divided data sets



hourly mean concentration values generally lie in the range 4 to 5.5 ng m⁻³ with an amplitude of variation slightly exceeding 1 ng m⁻³. The overall pattern indicates that Hg concentrations during the daytime (0800–1700 hours) are high relative to the night concentrations. Relative dominance of Hg during the day may be explained by the mixed effects of such factors as: photo-induced biological processes (e.g., photosynthesis), an increase of surface emission by high surface temperature, etc (e.g., Denis et al. 2006). The results seen on AM island are thus quite compatible with those reported in many previous studies conducted in diverse locations such as islands, coasts, rural, and residential areas (Kim and Kim 1999; Munthe et al. 2003; Kellerhals et al. 2003). For instance, in the rural locations (e.g., Changping, Huairou County) in Beijing, China, Liu et al. (2002) observed enhanced Hg concentration levels during the daytime

(5.00 ng m⁻³) relative to nighttime (3.7 ng m⁻³). The pattern seen in this study also contrasts with some previous results. For instance, as seen from an inspection of Hg diurnal variability made at an urban area in Seoul, it was clearly indicated that the relative dominance of Hg was persistent during the nighttime (Kim and Kim 2001). These authors suggested that the use of fossil fuel, especially coal (as the major fuel for heating systems) during the winter nights was the chief cause of the higher concentration of nocturnal Hg during the late 1980s in Seoul.

Comparison of diurnal patterns across seasons, as shown in Fig. 5b, reveals that patterns can change significantly between seasons. The dominance of Hg during the day was recorded in the spring, fall, and winter months. However, in the case of the summer months, it changes quite considerably so that the differences between daytime and nighttime are almost

undistinguishable under most circumstances. It may thus be inferred that the effect of strong and frequent precipitation in summer may have acted to suppress the differences in Hg concentration levels across diurnal periods. The findings of the poor diurnal variability seen at AM island during the summer season suggest that Hg behavior can be significantly altered by changes in environmental conditions.

3.4 Factors Affecting the Environmental Behavior of Hg

As a simple means to assess the relationships between environmental conditions and Hg distribution, we investigated the effects of pollution rose pattern on Hg concentration levels. The mean concentrations of Hg, initially divided by season, were plotted in relation to each wind sector (Fig. 6). The results for summer were significantly different from those found during the other seasons. The existence of a strong homogeneity at relatively low Hg concentration values was seen persistently from almost all wind sectors during the summer. However,

in the other seasons, differences in Hg concentration levels tended to be more prominent across different wind sectors so that slightly enhanced Hg values commonly occurred from such directions as the SE or NNW (during winter) and NW (during fall).

To learn more about the factors governing Hg behavior, data were analyzed in terms of correlation analysis with other parameters measured concurrently. In Table 2, the results of correlation analysis made between Hg concentrations and a few relevant environmental parameters are shown for both (a) all data sets and (b) temporally divided data groups. The strength of correlation between data pairs were compared by arbitrarily dividing them into five categories of correlation strengths based on the magnitude of probability (P) such as: (1) no class (the weakest correlation strength range): $P \geq 10^{-2}$; (2) class I: $10^{-5} \leq P < 10^{-2}$; (3) class II: $10^{-10} \leq P < 10^{-5}$; (4) class III: $10^{-15} \leq P < 10^{-10}$; and (5) class IV (the strongest correlation range): $P < 10^{-15}$. When the results obtained using all Hg concentration data were examined, the existence of good correlation can be observed in most cases. For instance, results of correlation analyses between Hg concentration

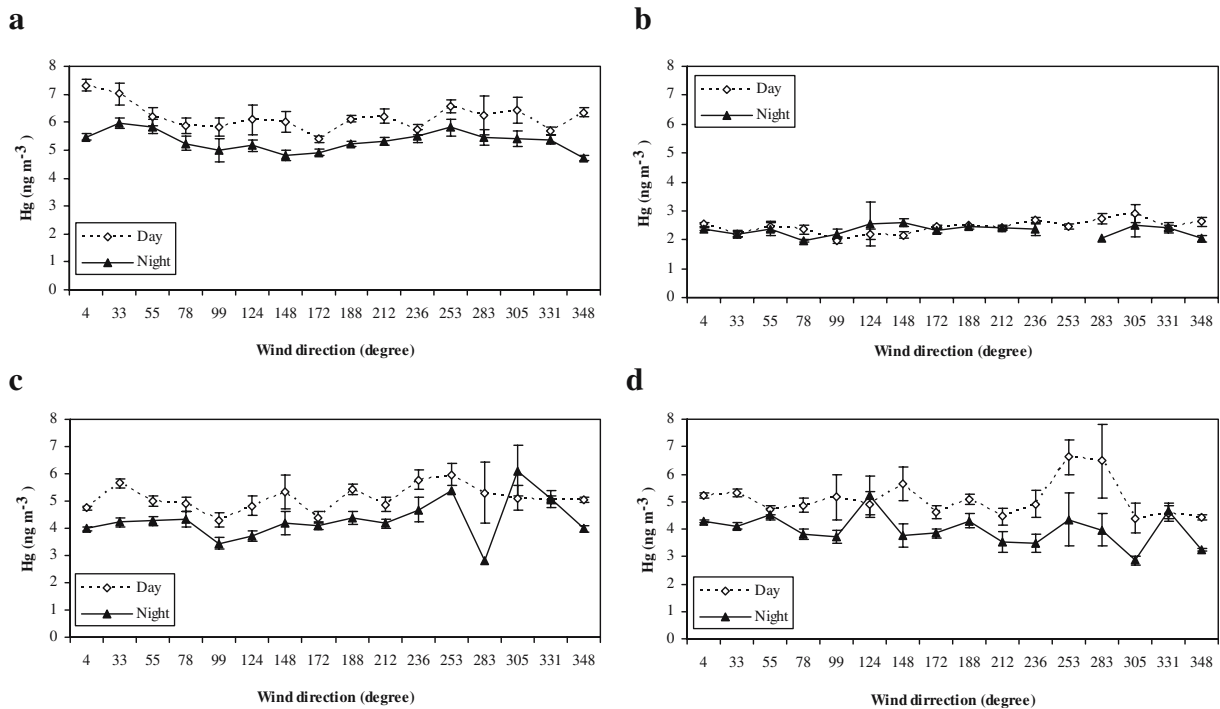


Fig. 6 The mean concentrations of Hg for each respective wind sector compared between day and night periods. Comparisons for each of the four seasons: **a** Spring, **b** Summer, **c** Fall, **d** Winter

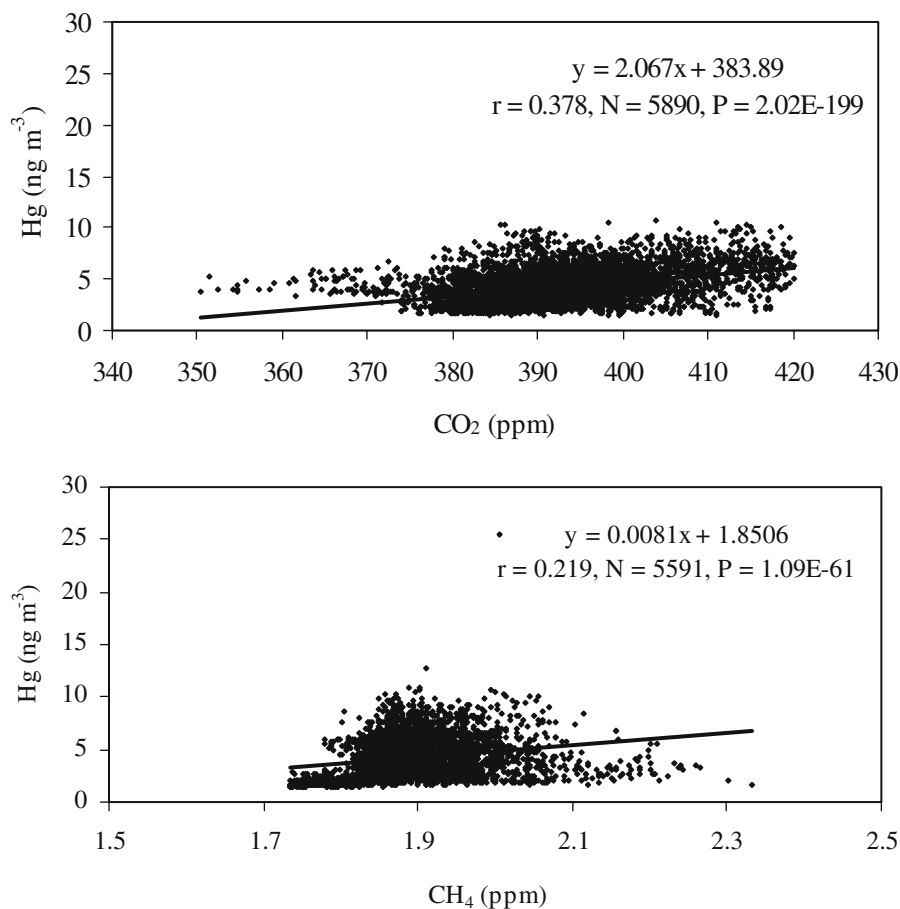
Table 2 Results of correlation analysis between Hg concentration and the relevant parameters

	All data			Spring			Summer			Fall			Winter		
	r	P	N	r	P	N	r	P	N	r	P	N	r	P	N
Using all data															
Wind speed ^a	-0.109 (IV)	2.58E-21	7,519	-0.011	6.11E-01	2,139	-0.133 (II)	3.78E-08	1,698	-0.181 (III)	6.42E-13	1,555	-0.251 (IV)	6.43E-32	2,127
Temperature ^a	-0.174 (IV)	3.46E-52	7,519	0.276 (IV)	1.06E-38	2,139	-0.126 (II)	1.90E-07	1,698	0.014	5.81E-01	1,555	0.23 (IV)	6.21E-27	2,127
Humidity ^a	-0.131 (IV)	3.88E-30	7,519	0.22 (IV)	7.40E-25	2,139	-0.035	1.49E-01	1,698	-0.014	5.81E-01	1,555	0.229 (IV)	1.04E-26	2,127
Rainfall	-0.154 (II)	1.89E-09	1,506	0.114	2.36E-02	394	0.159 (I)	4.71E-04	480	-0.166 (I)	8.54E-03	250	0.359 (III)	4.59E-13	382
CO ₂ ^a	0.378 (IV)	2.02E-199	5,890	0.319 (IV)	3.21E-39	1,602	0.088	1.01E-02	853	0.357 (IV)	3.88E-46	1,494	0.391 (IV)	6.37E-72	1,941
CH ₄ ^a	0.219 (IV)	1.09E-61	5,591	0.26 (IV)	2.60E-31	1,938	0.492 (IV)	3.94E-75	1,216	0.158 (I)	4.21E-05	666	0.358 (IV)	1.08E-54	1,771
Using the daytime measurement data during															
Wind speed ^a	-0.125 (IV)	6.98E-17	4,427	-0.008	7.84E-01	1,172	-0.16 (II)	1.19E-24	1,053	-0.187 (II)	3.66E-09	980	-0.262 (IV)	1.25E-20	1,222
Temperature ^a	-0.199 (IV)	8.95E-41	4,427	0.289 (IV)	5.54E-24	1,172	-0.121 (I)	8.28E-05	1,053	-0.037	2.47E-01	980	0.203 (III)	7.85E-13	1,222
Humidity ^a	-0.163 (IV)	9.74E-28	4,427	0.238 (IV)	1.48E-16	1,172	-0.05	1.05E-01	1,053	-0.032	3.17E-01	980	0.253 (IV)	2.67E-19	1,222
Rainfall	-0.197 (II)	7.44E-10	960	0.109	9.07E-02	242	0.143	1.14E-02	311	-0.267 (I)	3.68E-04	174	0.362 (II)	1.26E-08	233
CO ₂ ^a	0.398 (IV)	2.35E-131	3,451	0.342 (IV)	2.32E-25	873	0.108	1.35E-02	523	0.372 (IV)	3.98E-32	937	0.383 (IV)	2.23E-40	1,118
CH ₄ ^a	0.249 (IV)	1.26E-47	3,286	0.263 (IV)	2.62E-18	1,065	0.529 (IV)	1.56E-55	753	0.259 (II)	2.00E-08	456	0.358 (IV)	5.76E-32	1,012
Using the nighttime measurement data during															
Wind speed ^a	-0.093 (II)	2.21E-07	3,092	-0.029	3.68E-01	967	-0.105 (I)	7.61E-03	645	-0.169 (I)	4.64E-05	575	-0.241 (III)	2.00E-13	905
Temperature ^a	-0.164 (IV)	4.40E-20	3,092	0.247 (III)	6.59E-15	967	-0.191 (II)	1.03E-06	645	0	1.00E+00	575	0.232 (III)	1.59E-12	905
Humidity ^a	-0.051 (I)	4.56E-03	3,092	0.224 (III)	1.84E-12	967	0.067	8.91E-02	645	0.193 (II)	3.13E-06	575	0.251 (III)	1.81E-14	905
Rainfall	-0.067	1.18E-01	546	0.168	3.85E-02	152	0.191	1.29E-02	169	0.173	1.35E-01	76	0.383 (I)	1.42E-06	149
CO ₂ ^a	0.376 (IV)	9.31E-83	2,439	0.294 (IV)	5.30E-16	729	0.106	5.44E-02	330	0.524 (IV)	1.30E-40	557	0.415 (IV)	1.33E-35	823
CH ₄ ^a	0.168 (IV)	4.69E-16	2,305	0.253 (III)	3.24E-14	873	0.441 (IV)	1.85E-23	463	-0.076	2.73E-01	210	0.39 (IV)	5.54E-29	759

Refer to Table 1 for units of each parameter. The strengths of correlated cases are compared using five different categories set arbitrarily such as: No class: $P \geq 10^{-2}$; class I: $10^{-5} \leq P < 10^{-2}$; class II: $10^{-10} \leq P < 10^{-5}$; class III: $10^{-15} \leq P < 10^{-10}$; class IV: $P < 10^{-15}$

^a Refer to Table 1

Fig. 7 Results of correlation analyses between Hg concentration and other pollutants measured on An Myun Island



and CO₂ (or CH₄) concentration showed a fairly strong correlation with each other (Fig. 7). However, the results of this analysis, when compared across different seasons, indicates that the relative abundance of strongly correlated pairs is clearly distinguished between seasons. It is interesting to find that the results for the summer period show a relatively deficient pattern in all four seasons, while the large amount of strongly correlated cases peaks during winter followed by spring. It is also interesting to note that many strongly correlated cases exhibit an inverse relationship with the Hg data. This pattern is significant, especially with respect to the results derived using all data sets (refer to Table 2). Although many previous studies conducted in clean background environments demonstrated the existence of strong correlations between Hg concentration and temperature (e.g., Kim et al. 1995; Kim and Kim

2001; Poissant and Casimir 1998), the patterns noted in this study are quite complicated. According to our analysis, the abundance of strongly correlated cases changed between different seasonal data groups or between different parameters. For instance, although temperature exhibits a positive correlation with Hg during the winter season, it is not the case for the other seasons. As such, wind speed tends to maintain an inverse correlation consistently with Hg concentration with the exception of the fall season. The results of this analysis suggests that the occurrence of strong winds at the research site may generally have acted to dilute or diminish Hg concentration levels.

To further describe the effects of environmental conditions regulating the behavior of Hg, we also investigated data in relation to the movement patterns of air masses during the whole study period by using the hybrid single-particle Lagrangian integrated trajectories

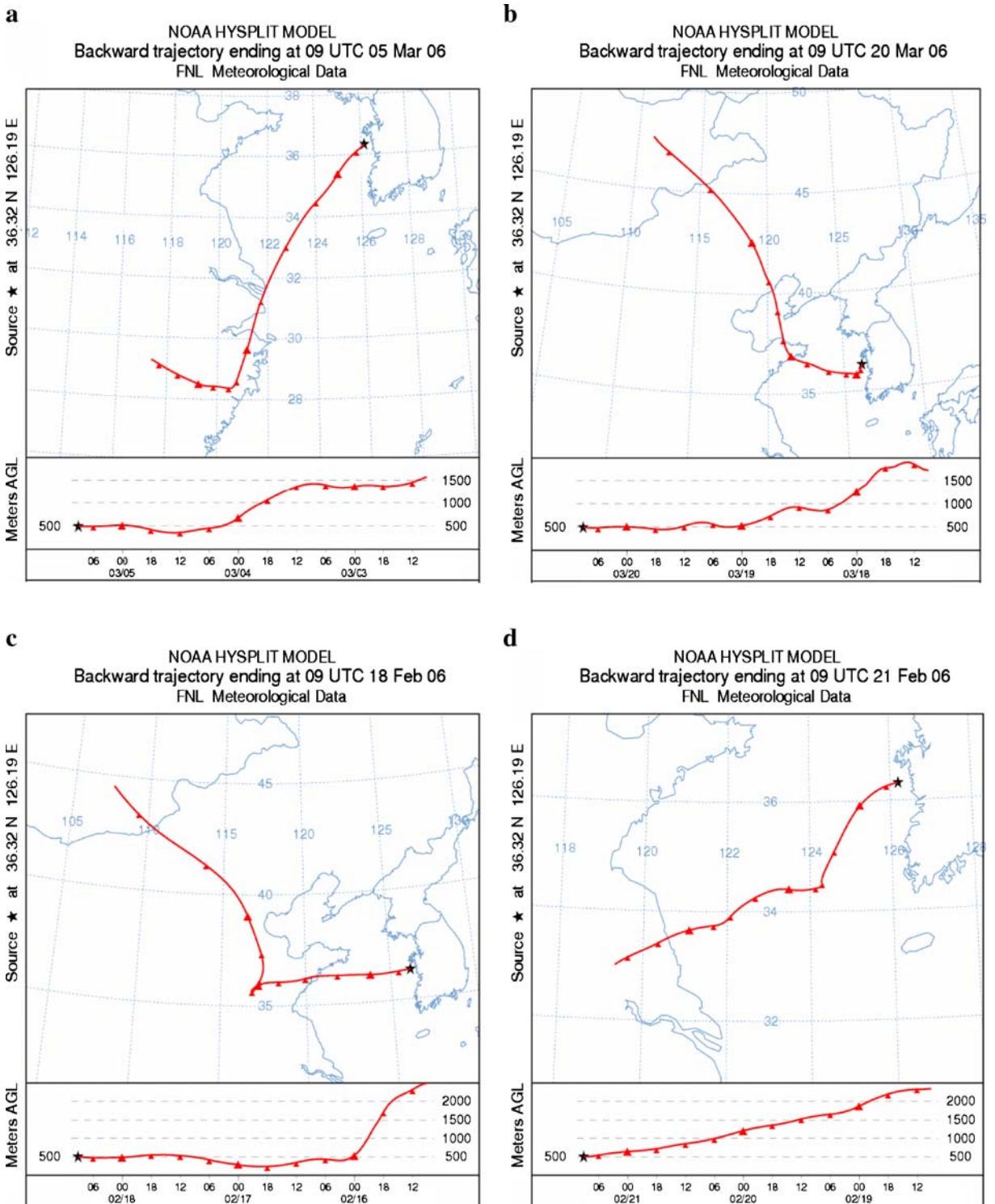


Fig. 8 Results of back-trajectory analysis showing 4 different pathway types of air mass transport: spring (route type **a**: passing from S. China and route type **b**: passing from N. China) and winter (route type **c**: passing from N. China and route type **d**: passing from S. China)

(HYSPLIT) model developed by National Oceanic and Atmospheric Administration/Air Resources Laboratory (NOAA/ARL) (Draxler 1996). Each trajectory was computed over a 72-h duration at midnight intervals (00:00 LTC or UTC+9:00). As input meteorological data to run the trajectory model, National Centers for Environmental Prediction (NCEP) model output (6-h interval, hemispheric 129 by 129 polar stereographic grids) was also used (Kanamitsu 1989). The altitude of the starting point for the trajectory model calculation was set at 500 m above mean sea level, which corresponded to the height within or across the planetary boundary layer. The back-trajectory analyses calculated for two characteristic trajectories of air masses in the spring and winter of 2006 are presented in Fig. 8: (1) South of China across the Yellow Sea during 3–5 of March (Fig. 8a) and during 19–21 of February (Fig. 8d); and (2) North of China across the Yellow Sea during 18–20 of March (Fig. 8b) and during 16–18 of February (Fig. 8c).

Considering the fact that Hg is a long-lived atmospheric pollutant, it is reasonable to suspect that the geographical distribution of Hg can be affected by such factors as long-range transport process. To check for such a possibility, Hg concentration data were plotted against information concerning the transport route of air masses for three days (i.e., 72 h) at upwind positions as representative of individual back trajectories. Similar approaches have been used previously in the study of CH₄ (Tohjima et al. 2002) and reduced sulfur compounds (Kim et al. 2004). To evaluate the significance of this effect, correlation analyses were conducted between Hg and geographical location data sets for seasonally divided data groups over a 3-year period (2004 to 2006), as shown

in Table 3. The results of this analysis indicated that the strongest correlations with longitudinal or latitudinal data were apparent in the spring of 2006. However, strong correlation was lacking in other seasons, especially during winter. In addition, relatively good correlations were found abundantly for longitude data sets. Although the signal of geographical dependence is not too strong in many cases, the patterns observed during the spring of 2006 suggest the possibly significant role of long range transport from China during that specific time period (Fig. 9). It is interesting that the highest Hg concentration (21 ng m⁻³) was in China (49°42'; 118°54') followed by 20.30 ng m⁻³ along the transport route (36°44'; 126°11') during this time.

3.5 Comparison with Previous Studies

To estimate the pollution status of Hg at the study site, we compared concentration levels with those reported previously from various locations around the globe (Table 4). For the purpose of this comparative analysis, the Hg concentration data representative of different continents, countries, and sources (e.g., urban, rural, and island areas) were simply compiled to derive the common patterns for both Asian and Western countries. According to this approach, the mean Hg concentrations in most Asian countries are significantly higher than those of the western countries. Evaluation of Hg concentrations in the Asian countries showed that the highest value (14.4 ng m⁻³) occurred in the Han Nam district of Seoul, Korea during 1987–1988 (Kim and Kim 2002). However, Hg concentration at that specific site has decreased significantly since then, reaching a

Table 3 Results of correlation analysis between Hg concentration level and geographical position: comparison is made using the locational data sets data obtained based on 72 h back trajectory analysis

Season	Year	Latitude					Longitude				
		SLOPE	Offset	<i>r</i>	<i>N</i>	<i>P</i>	Slope	Offset	<i>r</i>	<i>N</i>	<i>P</i>
Winter	2004	-0.0035	2.6105	0.0469	369	3.69E-01	0.0256	-0.6427	0.1758	369	6.94E-04
Spring	2005	-0.0055	5.4329	0.0283	2,208	1.84E-01	0.0385	0.5179	0.1565	2,208	1.41E-13
Summer	2005	-0.0109	2.7878	0.0825	2,207	1.04E-04	-0.0241	5.4521	0.1871	2,207	7.78E-19
Fall	2005	0.0488	2.7387	0.1934	2,170	9.90E-20	-0.0241	7.6438	0.1466	2,170	6.78E-12
Winter	2005	0.0104	3.4336	0.0424	2,160	4.88E-02	0.0090	2.8035	0.0387	2,160	7.21E-02
Winter	2006	0.0156	5.2571	0.0566	1,338	3.84E-02	0.0188	3.6935	0.0819	1,338	2.72E-03
Spring	2006	0.1164	2.1076	0.3064	1,147	2.34E-26	-0.0761	15.9190	0.2173	1,147	1.00E-13

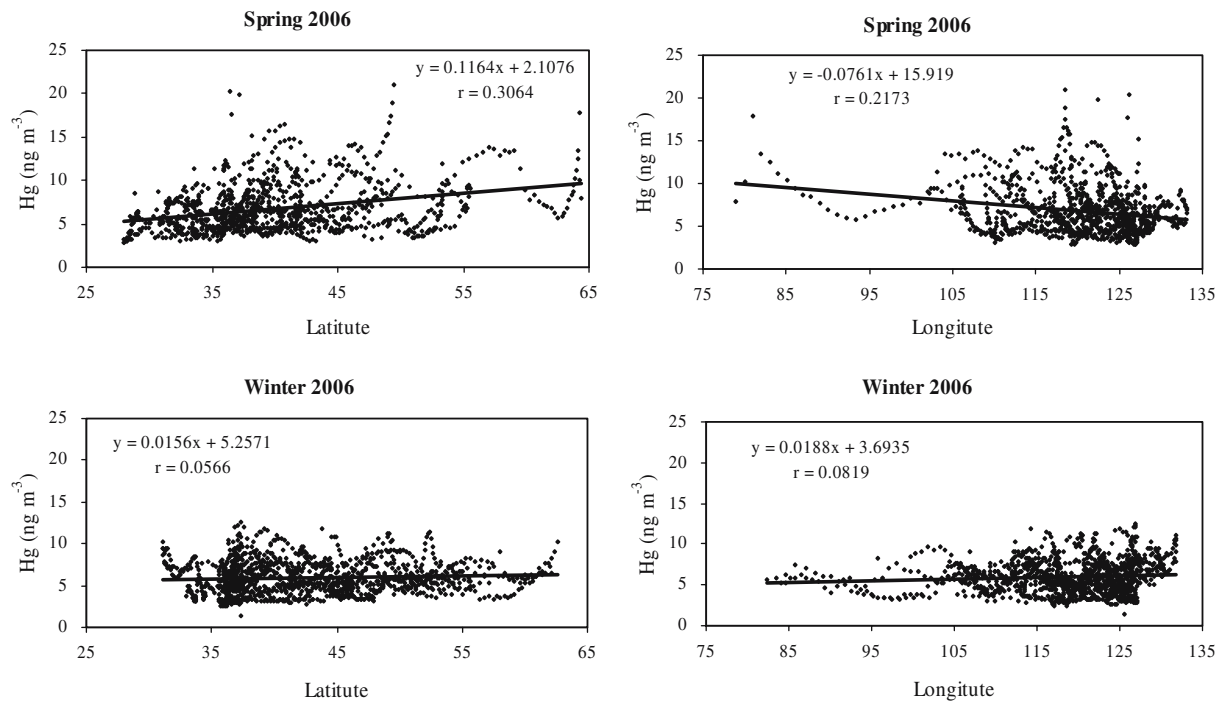


Fig. 9 The results of correlation analysis between Hg concentration and geographical position data in the spring and winter of 2006

mean of 5.34 ng m^{-3} during 1999–2000. In addition, an inspection of the most current Hg data sets in urban areas of Asia shows that fairly high Hg concentration (12.6 ng m^{-3}) was observed in Tiananmen Square, Beijing, China in the late 1990s (Liu et al. 2002). This was followed by Tokyo, Japan at 10.9 ng m^{-3} in the mid 1990s (Nakagawa and Hiromoto 1997). It is most likely that the present concentration levels of Hg in urban areas in Korea are comparable to or low relative to many other Asian locations. The high Hg concentration levels in the urban areas of Asian countries were explained as the consequence of weak control efforts on the anthropogenic source processes, especially with respect to the consumption of anthracite coal (a heating fuel for residential facilities). Nakagawa and Hiromoto (1997) further indicated the potent role of some natural source processes, as Japanese islands have many active volcanic zones. In fact, the geothermal field and/or some fumarole gases directly contribute to an increase in Hg concentration levels during high volcanic activity.

In Western countries, low Hg concentrations near $1\text{--}2 \text{ ng m}^{-3}$ are prevalent at most sites. The highest Hg concentrations measured in the background urban areas

of Western countries were found in Manhattan and Brooklyn (New York, USA) with values of 3.84 and 3.70 ng m^{-3} , respectively (Carpi and Chen 2002). Both measurement sites in the US are surrounded by highly commercialized areas with strong man-made activities. The results of this comparison thus suggest that control of Hg emissions may have been much more effective in many Western countries compared to Asian ones.

To evaluate the Hg concentration levels measured at AM Island, our Hg data were compared with those measured from other islands or clean air locations (such as rural and oceanic sites). The results of this comparison indicate that the Hg concentration at AM Island is the highest followed by the rural areas of Changping, Beijing, China (4.35 ng m^{-3} ; Liu et al. 2002) and Hari, Kang Hwa Island, Korea (3.49 ng m^{-3} ; Kim and Kim 2002). In contrast, significantly reduced Hg values (e.g., in the range of 1.33 to 1.58 ng m^{-3}) were seen from four sites of Canada, including a rural area of Kejimijuk, Canada (Kellerhals et al. 2003). The presence of such low Hg concentration levels at Canadian sites was ascribed to relatively insignificant anthropogenic activities in the remote rural sites (Kellerhals et al. 2003).

Table 4 Comparison of the Hg concentration data measured in urban, rural, and island locations between this study and previous studies

Ref. No.	Site	Land type	Study periods	Mean	SD	Min.	Max.	N	Source (author)
Asian countries									
Korea									
1	Han Nam, Seoul	Urban	1987–1988	14.4	9.56	4.73	113	2,714	Kim and Kim 2002
2	Han Nam, Seoul	Urban	1999–2000	5.34	3.92	0.56	80.1	2,576	Kim and Kim 2002
3	Hari, Kang Hwa	Island	Mar. 2001	3.49	0.87	2.02	8.04	165	Kim et al. 2003
4	An-Myun	Island	Dec. 2004–Apr. 2006	4.61	2.21	0.10	25.4	10,485	This study
Japan									
5	Tokyo	Urban	1995	10.9		6.70	29.0	25	Nakagawa and Hiromoto 1997
6	Okinawa	Suburban	1995	5.50		1.70	17.0	23	Nakagawa and Hiromoto 1997
7	Japan sea	Ocean	1991	1.80		1.70	1.80	2	Nakagawa and Hiromoto 1997
China									
8	Tiananmen Square, Beijing	Urban (city center)	Sep. 1998	12.6	3.10	6.70	19.6		Liu et al. 2002
9	Xuanwu, Beijing	Urban (residential)	Sep. 1998	10.1	4.85	4.90	25.3		Liu et al. 2002
10	Shijingshan, Beijing	Suburban	Sep. 1998	8.15	3.10	3.20	16.1		Liu et al. 2002
11	Changping, Beijing	Rural	Sep. 1998	4.35	1.65	2.10	7.40		Liu et al. 2002
Western countries									
USA									
12	Manhattan, New York	Urban (Central Park Station)	Jun. to Nov. 2000	3.84	0.10			1,740	Carpi and Chen 2002
13	Brooklyn, New York	Urban (LaGuardia Airport Station)	Aug. 2000	3.70	0.08			1,063	Carpi and Chen 2002
14	Queens, New York	Urban (JFK Airport Station)	Jul. 2000	2.69	0.03			1,270	Carpi and Chen 2002
Canada									
15	Toronto, Ontario	Urban	2001–2002	2.48	2.22	0.39	137	10,643	Denis et al. 2006
16	St. Andrews	Rural	1997–1999	1.43	0.20	0.68	2.64	15,866	Kellerhalsa et al. 2003
17	Kejmkujuk	Rural	1997–1999	1.33	0.25	0.26	2.69	15,730	Kellerhalsa et al. 2003
18	Burnt Island	Island	1997–1999	1.58	0.23	0.65	3.04	5,229	Kellerhalsa et al. 2003

All units are in ng m^{-3} .

4 Conclusions

The concentrations of atmospheric Hg were measured at An-Myun Island in Korea for a year and a half (December 2004 to April 2006). In order to investigate the distribution patterns of Hg and the factors affecting its environmental behavior, the Hg concentration data for the entire study period were examined in various ways. The mean value of Hg measured at $4.61 \pm 2.21 \text{ ng m}^{-3}$ was relatively high, if one considers that the site is distant from major cities on the peninsula. The analysis of seasonal patterns indicated that Hg concentration levels at the island generally decreased across the seasons on the order of spring, fall, winter, and summer. The occurrence of the highest Hg concentration in spring may be explained by the combined effects of various source processes with environmental conditions favorable for massive air mass transport (Asian Dust storms). The observation of low Hg concentration levels in summer was a consequence of efficient rainfall removal under weak wind conditions. Evaluation of diurnal variabilities of Hg on AM island showed that its concentration was higher during the daytime (4.91 ng m^{-3}) than the nighttime (4.17 ng m^{-3}). Although large differences in the Hg concentration values across diurnal periods were apparent in most cases, this was not the case for summer. The effects of strong and frequent precipitation during summer may have helped eliminate the causes of such diurnal differences.

To assess the fundamental factors affecting the environmental behavior of Hg, we examined our Hg data by means of correlation analysis. The results of this analysis generally confirmed that Hg tends to exhibit good correlations with temperature and wind speed. Although such patterns are apparent under most circumstances, the strengths of correlation diminished in the seasonally divided data groups. In addition, to evaluate the pollution status of Hg on An-Myun Island, Korea, our results were compared with previous data sets reported from various locations on the Asian continent as well as a number of Western countries. When the Hg data measured between different continents were compared with each other, the results suggested that Hg emissions in the Asian countries are more intense than for the Western countries. The Hg data were also inspected in terms of geographical dependence by comparing the Hg concentration data with air mass transport routes. The results of this comparative analysis

show the important role of long-range transport processes, especially during the spring by Asian Dust.

Acknowledgements This research was carried out with the financial support of the Korea Polar Research Institute, KORDI (Grant PP06010). Also, the authors would like to thank the Korea Research Foundation which provided grant that contributed to this research (KRF-2005-201-C00045). Many thanks also go to NOAA/ARL for providing the HYSPLIT model and meteorological data. Special thanks to two anonymous reviewers for their constructive comments.

References

- Carpi, A., & Chen, Y.-F. (2002). Gaseous elemental mercury fluxes in New York City. *Water, Air, and Soil Pollution*, *140*, 371–379.
- Denis, M. St., Song, X., Lu, J. Y., & Feng, X. (2006). Atmospheric gaseous elemental mercury in downtown Toronto. *Atmospheric Environment*, *40*, 4016–4024.
- Draxler, R. R. (1996). Boundary layer isentropic and kinematic trajectories during the August 1993 North Atlantic Regional Experiment Intensive. *Journal of Geophysical Research*, *101*(D22), 29255–29268.
- Gbor, P. K., Wen, D., Meng, F., Yang, F., Zhang, B., & Sloan, J. J. (2006). Improved model for mercury emission, transport and deposition. *Atmospheric Environment*, *40*, 973–983.
- Kanamitsu, M. (1989). Description of the NMC global data assimilation and forecast system. *Weather and Forecasting*, *4*, 335–342.
- Kellerhals, M., Beauchamp, S., Belzer, W., Blanchard, P., Froude, F., Harvey, B., et al. (2003). Temporal and spatial variability of total gaseous mercury in Canada: Results from the Canadian Atmospheric Mercury Measurement Network (CAMNet). *Atmospheric Environment*, *37*, 1003–1011.
- Kim, K. H., & Kim, M. Y. (1999). The exchange of gaseous mercury across soil–air interface in a residence area of Seoul, Korea. *Atmospheric Environment* *33*, 3153–3165.
- Kim, K. H., & Kim, M. Y. (2000). The effects of anthropogenic sources on temporal distribution characteristics of total gaseous mercury in Korea. *Atmospheric Environment*, *34*, 3337–3347.
- Kim, K. H., & Kim, M. Y. (2001). The temporal distribution characteristics of total gaseous mercury at an urban monitoring site in Seoul during 1999–2000. *Atmospheric Environment*, *35*, 4253–4263.
- Kim, K. H., & Kim, M.-Y. (2002). A decadal shift in total gaseous mercury concentration levels in Seoul, Korea: Changes between the late 1980s and the late 1990s. *Atmospheric Environment*, *36*, 663–675.
- Kim, K. H., Kim, M. Y., Kim, J., & Lee, G. (2003). Effects of changes in environmental conditions on atmospheric mercury exchange: Comparative analysis from a rice paddy field during the two spring periods of 2001 and 2002. *Journal of Geophysical Research*, *108*, 4607.
- Kim, K. H., Lindberg, S. E., & Meyers, T. P. (1995). Micrometeorological measurements of mercury vapor fluxes over background forest soils in Eastern Tennessee. *Atmospheric Environment*, *29*, 267–282.

- Kim, K.-H., Mishra, V. K., & Hong, S.-M. (2006). The rapid and continuous monitoring of gaseous elemental mercury (GEM) behavior in ambient air. *Atmospheric Environment*, *40*, 3281–3293.
- Kim, K.-H., Swan, H., Shon, Z.-H., Lee, G., Kim, J., & Kang C.-H. (2004). Monitoring of reduced sulfur compounds in the atmosphere of Gosan, Jeju during the Spring of 2001. *Chemosphere*, *54*(4), 515–526.
- Kock, H. H., Bieber, E., Ebinghaus, R., Spain, T. G., & Thees, B. (2005). Comparison of long-term trends and seasonal variations of atmospheric mercury concentrations at the two European coastal monitoring stations Mace head, Ireland, and Zingst, Germany. *Atmospheric Environment*, *39*, 7549–7556.
- Liu, S., Nadim, F., Perkins, C., Carley, R. J., Hoag, G. E., Lin, Y., et al. (2002). Atmospheric mercury monitoring survey in Beijing, China. *Chemosphere*, *48*, 97–107.
- Munthe, J., Wängberg, I., Iverfeldt, Å., Lindqvist, O., Strömberg, D., Sommar, J., et al. (2003). Distribution of atmospheric mercury species in Northern Europe: Final results from the MOE project. *Atmospheric Environment*, *37*, S9–S20.
- Mukherjee, A. B., Melanen, M., Ekqvist, M., & Verta, M. (2000). Assessment of atmospheric mercury emissions in Finland. *Science of the Total Environment*, *259*, 73–83.
- Nakagawa, R., & Hiromoto, M. (1997). Geographical distribution and background levels of total mercury in air in Japan and neighbouring countries. *Chemosphere*, *34*, 801–806.
- Oh, S. N., Youn, Y. H., Park, K. J., Min, H. K., & Schnell, R. C. (2001). Surface measurements of global warming causing atmospheric constituents in Korea. *Environmental Monitoring and Assessment*, *70*, 21–34.
- Pacyna, E. G., & Pacyna, J. M. (2002). Global emission of mercury from anthropogenic sources in 1995. *Water, Air, and Soil Pollution*, *137*, 149–165.
- Pacyna, E. G., Pacyna, J. M., & Pirrone, N. (2001). European emission of atmospheric mercury from anthropogenic sources in 1995. *Atmospheric Environment*, *35*, 2987–2996.
- Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., & Wilson, S. (2006). Global anthropogenic mercury emission inventory for 2000. *Atmospheric environment*, *40*, 4048–4063.
- Pandey S. K., & Kim K.-H. (Submitted) Experimental bias involved in the collection of gaseous elemental mercury by the gold amalgam method. *Environmental Engineering Science*.
- Poissant, L., & Casimir, A. (1998). Water–air and soil–air exchange rate of total gaseous mercury measured at background sites. *Atmospheric Environment*, *32*, 883–893.
- Poissant, L., Pilote, M., Xu, X., Zhang, H., & Beauvais, C. (2004). Atmospheric mercury speciation and deposition in the Bay St. Francois wetlands. *Journal of Geophysical Research*, *109*, D11301.
- Poissant, L., Pilote, M., Beauvais, C., Constant, P., & Zhang, H. H. (2005). A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hg_p) in southern Québec, Canada. *Atmospheric Environment*, *39*, 1275–1287.
- Schroeder, W. H., & Munthe, J. (1997). Atmospheric mercury – An overview. *Atmospheric Environment*, *32*, 809–822.
- Shon, Z.-H., Kim, K.-H., Song, S. K., Kim, M.-Y., & Lee J. S. (Submitted) Environmental fate of gaseous elemental mercury at an urban monitoring site based on long-term measurements in Korea (1997–2005). *Atmospheric Environment*.
- Slemr, F., Brunke, E.-G., Ebinghaus, R., Temme, C., Munthe, J., Wängberg, I., et al. (2003). Worldwide trend of atmospheric mercury since 1997. *Geophysical Research Letters*, *30*(10), 1516.
- Tohjima, Y., Machida, T., Utiyama, M., Katsumoto, M., & Fujinuma, Y. (2002). Analysis and presentation of in situ atmospheric methane measurements from Cape Ochi-ishi and Hateruma Island. *Journal of Geophysical Research*, *107*(D12), ACH 8(1)–8(11).
- Xu, X. H., Yang, X. S., Miller, D. R., Helble, J. J., & Carley, R. J. (1999). Formulation of bi-directional atmosphere surface exchanges of elemental mercury. *Atmospheric Environment*, *33*, 4345–4355.
- Wallschlager, D., Kock, H. H., Schroeder, W. H., Lindberg, S. E., Ebinghaus, R., & Wilken, R.-D. (2000). Mechanism and significance of mercury volatilization from contaminated floodplains of the German river Elbe. *Atmospheric Environment*, *34*, 3745–3755.