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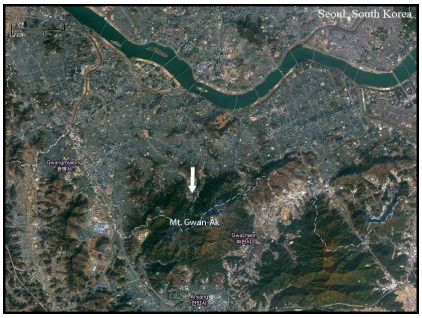

The study at Mt. Gwan-ak (Seoul, Korea) revealed that the behavior of Hg was strongly correlated with water vapor and CH_4 to suggest good similarities in their source characteristics.

Environmental Impact statement

The mean Hg level observed in this study is lower than those of other Asian locations. In contrast, the mean concentrations of the two important GHGs (CO_2 and CH_4) were moderately higher from those recorded from other locations across the World. The results indicate that the behavior of Hg is strongly correlated with water vapor and CH_4 in terms of source characteristics; however, diurnal patterns are quite different. The analyses of both frequency distribution and correlation indicated similarity of behavior for Hg and GHGs, in terms of their combined emissions from anthropogenic and environmental sources. In winter, ozone was probably acting as major sink for atmospheric Hg. The site shows moderate impact of anthropogenic sources for both Hg and GHGs.

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INVESTIGATION OF THE RELATIONSHIP BETWEEN ATMOSPHERIC MERCURY AND CONCENTRATIONS OF KEY GREENHOUSE GASES AT A MOUNTAINOUS MONITORING SITE

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Abstract

The concentration of total gaseous mercury (TGM) was monitored, together with some key greenhouse gases (GHGs: carbon dioxide (CO_2), methane (CH_4), and water (H_2O) vapor) over hourly intervals at a mountainous monitoring site close to the highly industrialized city of Seoul, Korea. Correlations between concentrations of Hg and these greenhouse gases were examined to assess their source characteristics and responses to changes in meteorological conditions. The mean Hg levels in this study (3.58 ± 2.13 ng m^{-3}) were considerably lower (e.g., 24.3%) than those measured from other comparable sites during 1999-2006 (4.73 ± 1.34 ng m^{-3}). Accordingly, such reduction in Hg levels suggests the effectiveness of the regulatory measures enforced over the years. The mean Hg level observed in this study is also lower (by approximately 5%) than those of other Asian locations. In contrast, the mean concentrations of the two most important GHGs (CO_2 and CH_4) were moderately higher than those recorded from other locations across the World (approximately 4 to 9%). The results of our analysis indicate that the behavior of Hg is strongly correlated with water vapor and CH_4 in terms of their source characteristics despite notable differences in their diurnal patterns.

***Key words**: Greenhouse gases, airborne mercury, mountain, Anthropogenic; climate change;*

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1. INTRODUCTION

Despite the many advances achieved in emission control technology, most man-made activities relying on fossil fuel combustion resulted in the net release of diverse gaseous pollutants (e.g., SO_x, NO_x, and CO)[1]. The environmental significance of such activities is not limited to increased air pollution but also to the exacerbation of climate change through increased emissions of greenhouse gases (GHGs) represented by CO_2[2]. Moreover, anthropogenic gaseous emissions are known to simultaneously affect the global budgets of other trace atmospheric components, especially gaseous volatile organics and vapor-phase metallic species like elemental mercury (Hg^o)[3,4]. As such, global warming, induced by diverse man-made activities, is expected to alter the biogeochemical cycle of diverse pollutants, especially highly volatile pollutant species like total gaseous mercury (TGM) across the air, soil, and water compartments.

Atmospheric mercury shares similar source processes, evasion mechanisms (from environmental sinks), and chemical properties (e.g., volatility) as common GHGs[5]. Hence, it is of interest to properly assess the key factors controlling the environmental fate and distribution characteristics of TGM in association with GHGs. It is estimated that the concentration levels of Hg in the troposphere have increased constantly over the past centuries, e.g., a three-fold increase since the industrial revolution[6]. Moreover, as the global temperature rises, emission of Hg to the atmosphere from various environmental reservoirs is expected to increase along with the activated transformation of inorganic Hg into far more toxic organic forms, e.g., methyl-mercury (CH_3Hg^+)[7]. Such changes are thus expected to pose a greater threat to human health and ecological systems.

In this study, the environmental behavior of Hg was investigated in relation to the key GHGs (including CO_2, CH_4, and H_2O vapor) from the Mt. Gwan-Ak monitoring station

located in Seoul, Korea.. To assess the relationship between Hg and GHGs, their temporal distribution patterns were examined in different temporal scales. In addition, the factors affecting their distributions were also examined based on diverse statistical analysis.

2. MATERIALS AND METHODS

2.1 Site description

As the capital of South Korea, Seoul has a carbon footprint of 1.59 metric tones per person[8]. The Seoul metropolitan area has 10 million inhabitants, while occupying only 0.6 percent of the country's land area. More than 80% of the total energy used in Seoul comes from fossil fuels, mostly coal, petroleum, and natural gas[8]. The city also maintains a large number of water and waste treatment plants along with landfills that may release large quantities of greenhouse gases[9-11].

In this study, concentration data for Hg and major GHGs (CO_2, CH_4, and H_2O vapor) were collected from an air quality monitoring station on the top of Mt. Gwan-ak (37º 26' 44" N, and 126º 57' 49"E). It is a relatively small mountain located at the southern district of Seoul, South Korea with the total area of 19,226,942 m^2 (Fig. 1). Mt. Gwan-ak is situated to overlap four different districts, namely: Gwanak-gu (11,412,035 m^2: 59.4%), Geumcheon-gu (2,120,595 m^2: 11%), and Gwacheon City - Anyang City of Gyeonggi-do (5,694,312 m^2: 29.6%). It has a steep topography with ravines running in all directions. Only a few species of needle-leaf trees (e.g., pine trees) grow, while a wide variety of deciduous broadleaved trees (e.g., black oaks) can be found on the mountain[12].

2.2 Data collection and analysis

In this study, concentrations of TGM were obtained from the Mt. Gwan-ak monitoring station, as shown in Fig. 1; operation of this station along with several others at the city boundary has been managed by the Seoul Metropolitan Research Institute of Public Health and Environment (SRIE). At this mountainous air quality monitoring site, hourly Hg data were collected continuously from June 1st to December 31st 2011.

The concentrations of Hg were measured by transporting outdoor air via sampling train (~2 m long) made of Teflon tubing (30 mm diameter) into an on-line automatic analytical system (AM-3 model, the Nippon Instrument Co., Japan). For each hourly interval, vapour phase Hg was collected by an Au-amalgam trap at a constant flow rate of 1.0 L min^{-1}, desorbed thermally, and detected at wavelength of 253.7 nm by a non-dispersive double beam, flameless atomic absorption system.

The analysis of the GHGs was made using a $CO_2/CH_4/H_2O$ analyzer[13]. Additionally, an automated air pollution monitoring system (Thermo, USA) is located at a height of 620 meters above mean sea level. The vertical height of sampling inlet from the monitoring station is 14 m, while the station itself is 9 m above the soil. Other key pollutants (NO_x, O_3, SO_2, and particulate matter) were also monitored. A list of meteorological parameters was also measured concurrently: (1) wind speed (WS) and wind direction (WD) (WM05103: R.M.Yong, U.S.A); (2) temperature (TEMP) and humidity (HUM) (HMP45A: VAISALA Co., Finland); and (3) solar radiation (LI200SZ: LI-COR Co., U.S.A). Statistical evaluation of the data including the Pearson correlation analysis, regression analysis, and student's t-test was made using the Microsoft excel software.

2.3 Quality assurance (QA) for the analysis of Hg and GHGs

The basic procedures used for sampling and analysis of Hg have been described in a number of our recent studies[3,4]. The results of relevant QA can be summarized as follows. For the analysis of Hg, the absolute detection limit of the system was approximately 1 - 2 pg of Hg. The precision of individual analytical systems, evaluated in terms of relative standard error (RSE = SE/mean x 100) of the five replicate injections of vapor-phase standards (at three different mass levels of 1, 2, and 3 ng), averaged 0.3-0.6%. Owing to the unavailability of certified vapor standards, the system was calibrated against certified reference materials of National Institute of Standards and Technology (NIST: NIST-SRM 1632d); the results revealed the values of the mean accuracy in the 3-5% range.

The instrument used to measure concentration of CO_2 is Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) Picarro G1301 analyzer[13]. This CRDS technique is a highly precise method measuring a spectral signature of the target molecule[13]. It is a real time, trace gas monitor capable of measuring gases at amount fractions of parts-per-billion (ppb). The instrument is capable of measuring CO_2 in the amount fraction range 0-1000 (parts-per-million) ppm, and CH_4 in the range 0-20 ppm. By following the procedure of Busch and Busch[14], the measurement precision was assessed by taking a spectral scan at every 5 min on a 380 ppm CO_2 standard at room temperature. The relative standard deviation (RSD %) was then estimated as 0.04%.

3. RESULTS AND DISCUSSION

3.1 Basic Properties of Hg and GHGs distribution in the study area

Data were collected during the period June-December 2011. The data sets are analyzed on various temporal scales such as hourly, daily, monthly, and seasonal basis (i.e., March-May (Spring), June-August (Summer) September to November (Fall), and

December to February (winter)). As shown in Table 1, the average concentration of Hg was 3.58 ± 2.13 ng m^{-3} and exhibited a wide range from 1.37 to 33.1 ng m^{-3}.

As shown in Fig 2, the Hg concentration data tend to occur most frequently in the 2-3 ng m^{-3} range (about 62 % of the total occurrences). The rest of the data was distributed as follows: about 13 % at or below the 2 ng m^{-3} range, about 17 % in the 3-5 ng m^{-3} range, and about 8 % in the 5-15 ng m^{-3} range. On a seasonal basis, the frequency range of peak values is different in the summer (3-4 ng m^{-3}) as compared to the other months, i.e., fall (around 2 ng m^{-3}) and winter (at or below 2 ng m^{-3}). Analyzed on relative percentage basis (the % occurrences out of total occurrences), most Hg concentrations lie below 4 ng m^{-3} (about 94 % and about 97 % for fall and winter, respectively). However, in summer, only about 75 % of data fell below 4 ng m^{-3} range. The occurrence of a few very high values (e.g., around 14 ng m^{-3}) can be ascribed to unidentified anthropogenic influences (e.g., local or trans-boundary sources) or to unusual meteorological factors (such as extreme temperature or solar intensity), and greater soil Hg evasion especially in summer[15].

With respect to the GHG data, the average CO_2 level (406 ± 14.5 ppm) at the site was moderately higher than its global mean of 389 ppm (WMO, 2012). In contrast to Hg, the highest CO_2 levels occurred in winter months, i.e., 412 ± 12.9 ppm, and were slightly reduced in summer (406 ± 15.5 ppm) and fall (401 ± 12.8 ppm). Similarly to CO_2, CH_4 also showed the highest value in winter (2.00 ± 0.05 ppm). This probably reflects the difference in the mean height of the boundary layer in summer and in winter. However, the concentration of H_2O peaked in summer (2.57 ± 0.56 ppm). O_3, concentrations in this Mountain site were very high (40.8 ± 20.0 ppb) compared to the urban background levels measured previously observed in Seoul (i.e., 14.0 ± 14.2 ppb) from 1996 to 2006[16].

3.2 Temporal distribution of Hg and GHGs

As Hg concentrations and GHGs were measured concurrently at hourly intervals, their data sets can also be analyzed on varying temporal scales. The plot of the daily Hg concentration data indicates the occurrence of unusually large concentrations during summer (Fig 3). These high episodic values (i.e., in between Julian day no. 225 to 229) are thought to be due to some anthropogenic sources under given environmental conditions[17]. GHGs like CH_4 and CO_2 generally showed moderate variations on a daily basis. In line with the general expectation, the day-to-day variations in H_2O and O_3 concentrations seem to be different across seasons, as they are more susceptible to changes in meteorological conditions such as precipitation, temperature, and UV radiation[18 and references therein].

If the data sets are examined on an hourly basis, the peak concentrations of Hg were generally observed in daytime (between 11 to 15 hrs). As shown in Fig 4, when the diurnal pattern is examined similar patterns were seen consistently between seasons. However, in the case of fall and winter, the variation in Hg concentration levels was not as evident as that in summer. This may be explained by differences in mechanisms affecting the short term variability of Hg such as the variation of boundary layer heights between day and night and also evasion of Hg from soil[19,20]. If this type of comparison is extended to the other air pollutants, CO_2 and CH_4 followed a very similar pattern of hourly variations (Fig 4). Moreover, when they were compared against Hg, these two key GHGs exhibited a very strong similarity until about11-12 am (Fig 4). This similarity indicates that Hg and these two GHGs may share similar evasion patterns from environmental reservoirs and are affected by the environmental conditions such as boundary layer height, ambient temperature, and dispersion conditions. In contrast, the slight differences observed for Hg during the rest of the day can be explained by the

187 additional combined effects of short-term environmental conditions and cycling of short-
188 lived mercury compounds in air[19,21].

189 Although there is a slight difference between the start of data acquisition for Hg (since
190 June 2011) and the other measurands (since May, 2011), they have both been measured
191 long enough to evaluate these temporal variations with some confidence. Hence, if
192 average concentrations of Hg and other air pollutants are compared across the seasons
193 (i.e., summer, fall, and winter) (Table 1), the means for Hg were: summer (4.59 ± 2.70
194 ng m^{-3}), fall (2.92 ± 1.13 ng m^{-3}), and winter (2.60 ± 0.90 ng m^{-3})). The results of a t-test
195 revealed highly significant variations across seasons (i.e., summer *vs.* winter ($P<0.001$),
196 summer *vs.* fall ($P<0.001$), and winter vs. fall ($P<0.001$). The significantly higher
197 summer concentrations may be ascribed to the strong influence of meteorological
198 conditions such as solar radiation, temperature, and humidity prevailing in the
199 mountainous area, increasing evasion from environmental reservoirs such as soil and
200 water[21,22].

201

202 *3.3 Factors affecting the distribution of Hg and GHGs*

203 To examine the factors controlling the distribution of Hg in the studied mountain area,
204 Pearson correlation analysis was conducted between Hg and the other parameters
205 determined concurrently (Table 2). The daily mean data for all variables were used to
206 assess the possible relationship between different parameters. If the analysis is performed
207 using all daily data acquired across the entire study period, Hg was positively correlated
208 with such parameters as H_2O ($P<0.001$), humidity ($P<0.001$), temperature ($P<0.001$), and
209 UV ($P<0.01$). Moreover, the O_3 data were also strongly correlated with Hg levels. On the
210 other hand, it showed an inverse correlation with NO and NO_2. These observations

211 suggest that Hg concentrations, similarly to H_2O and O_3 concentrations are sensitive to
212 prevailing local meteorological conditions.
213 In order to learn more about the factors controlling the behavior of Hg and GHGs
214 across seasons, the Pearson correlation was also applied to the data sets after grouping on
215 a seasonal basis (Table 2 B). The results indicate the presence of distinct seasonality in
216 many respects. For instance, in summer, there were only two significant cases of
217 correlation between Hg and GHGs (i.e., CH_4 and H_2O). However, if this comparison is
218 extended further, strong correlations with Hg occurred more frequently in fall with both
219 GHGs (CH_4, H_2O, and CO_2) and others (SO_2, NO_2, and O_3).
220 When we looked at the relationship with some meteorological parameters, especially
221 the effect of temperature, their relationship appeared to be more prominent in fall
222 ($P<0.001$) than in winter or summer (during which the impact of humidity differ greatly).
223 However, as the number of data for temperature was relatively low (n = 8 days) in winter,
224 validation of such seasonal dependence needs further examination. In winter, Hg tended
225 to exhibit relatively strong correlations with some GHGs (e.g., CO_2 ($P<0.001$), and CH_4
226 ($P<0.001$)). This observation may suggest that the effect of meteorological conditions for
227 Hg and GHGs should vary moderately between seasons, while they appear to be affected
228 by the similar source processes. Interestingly, it was also observed that there was a
229 strong inverse correlation between Hg and O_3 in winter ($P<0.001$). This suggests that in
230 winter, ozone may be acting as major sink for atmospheric Hg in the area[23].
231 In general, the observation of variable correlations between Hg and some GHGs across
232 the seasons can also be explained at least partially by the wind rose patterns (see SI Fig
233 1). The maximum percentage of wind was from the NE direction in both winter and fall.
234 This suggests that the transport of the air pollutants from the NE direction will have been
235 prominent. However, in case of summer season the wind rose pattern was mixed. Hence,

based on these observations, it can be inferred, from the wind direction and known local and regional sources, that the effect of anthropogenic sources was more dominant in winter and fall, while they were less significant in summer under more complicated conditions. If the results of these correlation analyses are assessed in more detail, both H_2O and CH_4 tend to exhibit significant correlations with Hg in all three seasons. This may be attributed at least in part to the effect of water vapor on the air-surface exchange of Hg[24-26]. Additionally, both Hg and H_2O experience similar evasion patterns from environmental compartments as a function of ambient temperature. For instance, Marsik and Keeler[27] reported an increase in the ambient concentrations of TGM within the surface layer with an increase in the water vapor (or latent heat) flux over a mixed Sawgrass vegetation area in Florida everglades. As the mountainous site investigated in the current study is also covered with arboreal vegetation, the increase of atmospheric Hg with water vapor is likely to be accompanied with biogenic emission and foliar exchange of Hg (a link between gaseous Hg emission and transpiration/photosynthesis). It is natural to expect that the behavior of CH_4 should also be affected by similar (biogenic) sources and processes[28].

3.4 Comparison of Hg and GHGs levels with previous studies

The data produced in this study was first compared with those measured from other sites on the Korean peninsula. The mean concentration level of Hg in this study (3.58 ± 2.13 ng m^{-3}) was moderately low when compared to those of our previous studies (4.73 ± 1.34 ng m^{-3}) conducted at a number of mountainous and background/remote locations in Korea during 1999-2006 (Table 3). However, considering the long time gap between the studies, the observed decline (~ 24.3 % in the year 2011) in the current Hg level should reflect the result of effective emissions control in recent years[29].

The comparison of Hg levels between this study and other published literature can be extended further to cover similar mountainous sites and background areas around the world (Table 3). To make comparison meaningfully, these data sets were initially grouped by continent[19,21,30-50]. The mean Hg level derived in this study was 2 to 3 times higher than some pristine locations in the world such as Polar Regions (i.e., Arctic (1.6 ng m^{-3}) and Antarctic (1.0 ng m^{-3}). Likewise, it was around 1.5 times higher than the mean values derived for those of the European (2.17 ± 1.06 ng m^{-3}) and North America region (2.39 ± 0.90 ng m^{-3}). In contrast to North America, Europe, and Asia, there is scarcity of data in South America and Africa (Table 3). The results obtained from the Amazonian basin showed the patterns that are almost comparable to this study. In contrast, the values derived from Africa are significantly lower than our results and more comparable to those of the pristine Polar Regions (Table 3).

Conversely, when the mean value determined in the current study (3.58 ± 2.13 ng m^{-3}) is compared with those derived across a number of urban-background and mountainous sites in Asia (3.76 ± 1.44 ng m^{-3}), it was found to be much comparable with each other. However, when the results are compared between individual sites, it was considerably lower than some of the Asian mountainous locations. Hence, it is reasonable to expect that the cycle of Hg in this Gwan Ak mountain site has been affected by the combined effects of both anthropogenic and local sources.

In addition to Hg, we can compare the concentration levels of other important GHGs such as CO_2 and CH_4 measured concurrently in this study to those observed recently from other locations in the Korean peninsula and the world. The mean concentration level of CO_2 in this study (406 ppm) was moderately higher (by about 3%) than those derived for the Korean peninsula (394.5 ppm) by the Global Atmospheric Watch report in 2010[51]. On the other hand, it was about 5% higher than the global mean of CO_2 as of

2011[52]. If such comparison is extended to the current CH_4 level (1.95 ppm) in this work, it was higher by 2 and 8% higher than the overall average of Korean peninsula in the year 2010[51] and the global CH_4 average in 2011[52], respectively. Hence, in general, the GHGs levels at our study site were moderately or slightly higher than other relevant references either locally or globally, indicating perhaps the enhanced role of anthropogenic sources at the study area.

4. CONCLUSIONS

In this study, the concentration of Hg was measured continuously at the Mt. Gwan-ak air quality monitoring station in Seoul, Korea in 2011. We investigated the factors affecting the environmental behavior of Hg in a number of respects. The concentration of Hg in the study area averaged 3.58 ng m^{-3}, which was lower than the levels recorded previously (1999-2006) from other comparable sites. As such, the results of the current study suggest the effectiveness of legislative and control measures adopted by the authorities in Seoul. Overall, the Hg concentration in this work was of an intermediate level, when compared to other mountainous/background locations on a worldwide basis.

The concentrations of GHGs (CO_2 and CH_4) were comparatively higher than the average concentrations across the Korean peninsula and the globe in the same time band. There were considerable seasonal variations in Hg in the area, showing the highest values in summer. The results of both frequency distribution and correlation analysis indicated strong similarities in the behavior of Hg and GHGs, in terms of their source processes. There was a slight variation between seasons. In winter, it is possible to suspect that ozone was acting as the major sink for atmospheric Hg in the area, while such evidence was not apparent in other seasons – presumably owing to the greater speed and availability of other photochemical reaction pathways during summer. Overall, the

311 mountainous site under investigation showed consistently the impact of anthropogenic
312 sources for both Hg and GHGs at moderate levels.
313

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429 Table 1. Statistical summary of TGM and relevant parameters measured at Gwan Ak mountain, Seoul, Korea in 2011.

Season	Hg	CO_2	CH_4	H_2O	SO_2	NO	NO_2	NO_x	O_3	WS[a]	TEMP[b]	HUM[C]	UV[d]
	ng m^{-3}	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	m sec^{-1}	$_oC$	%RH	mW cm^{-2}
All	3.58 ± 2.13 (3.05)[e]	406 ± 14.5 (406)	1.95 ± 0.08 (1.94)	1.68 ± 0.93 (1.60)	4.19 ± 2.55 (4.00)	4.42 ± 5.46 (3.00)	12.8 ± 9.20 (10.0)	17.2 ± 13.0 (13.0)	40.8 ± 20.0 (37.0)	3.39 ± 3.14 (2.40)	13.7 ± 9.02 (15.9)	65.5 ± 24.8 (73.0)	0.31 ± 0.58 (0.00)
	1.37-33.1 (5060)[f]	335-533 (5834)	1.38-2.52 (5834)	0.01-3.46 (5834)	1.00-47.0 (5798)	1.00-85.0 (5779)	1.00-68.0 (5779)	3.00-150 (5797)	2.00-151 (5797)	0.02-18.2 (5859)	-13.7-31.1(5859)	0.00-94.0 (5859)	0.00-4.13 (5859)
Spring	-	417 ± 7.90 (416)	1.93 ± 0.05 (1.93)	1.29 ± 0.47 (1.24)	4.91 ± 2.68 (4.00)	3.41 ± 2.65 (3.00)	12.1 ± 8.20 (10.0)	15.53 ± 9.96 (13.0)	59.02 ± 17.0 (59.0)	4.80 ± 3.96 (3.50)	14.73 ± 3.68 (14.7)	30.0 ± 28.9 (30.0)	0.42 ± 0.68 (0.03)
	-	402-453 (743)	1.82-2.21 (743)	0.40-2.80 (743)	2.00-47.0 (740)	2.00-36.0 (740)	3.00-51.0 (740)	5.00-75.0 (740)	8.00-112(740)	0.30-16.5 (743)	5.50-25.8(743)	0.00-34.0 (743)	0.00-2.73 (743)
Summer	4.59 ± 2.70 (3.89)	406 ± 15.5 (406)	1.92 ± 0.09 (1.90)	2.57 ± 0.56 (2.60)	3.03 ± 1.65 (2.00)	3.56 ± 2.76 (3.00)	11.0 ± 7.87 (9.00)	14.50 ± 9.45 (12.0)	44.4 ± 24.2 (41.0)	3.75 ± 3.23 (3.00)	20.7 ± 2.93 (20.9)	80.7 ± 15.8 (89.0)	0.39 ± 0.68 (0.03)
	1.37-33.1 (2156)	335-533 (2194)	1.38-2.52 (2194)	0.01-3.46 (2194)	1.00-23.0 (2195)	2.00-68.0 (2195)	1.00-61.0 (2195)	3.00-112 (2195)	4.00-151 (2195)	0.20-18.2 (2207)	12.0-31.1(2207)	29.0-94.0 (2207)	0.00-4.13 (2207)
Fall	2.92 ± 1.13 (2.77)	401 ± 12.8 (406)	1.97 ± 0.07 (1.95)	1.35 ± 0.62 (1.28)	4.43 ± 2.34 (4.00)	3.82 ± 4.81 (2.00)	12.9 ± 9.00 (10.0)	16.7 ± 12.0 (13.0)	37.2 ± 14.9 (36.0)	2.66 ± 2.79 (1.7)	12.4 ± 6.35 (12.6)	65.0 ± 18.0 (65.0)	0.26 ± 0.50 (0.00)
	1.47-22.3 (2162)	354-475 (2153)	1.38-2.50 (2153)	0.17-2.95 (2153)	2.00-24.0 (2148)	1.00-50.0 (2129)	1.00-68.0 (2129)	3.00-92.0 (2129)	2.00-93.0 (2147)	0.20-16.8 (2165)	-9.20-28.8(2165)	19.0-93.0 (2165)	0.00-2.70 (2165)
Winter	2.60 ± 0.90 (2.39)	412 ± 12.9 (408)	2.00 ± 0.05 (2.00)	0.41 ± 0.21 (0.37)	6.26 ± 3.37 (6.00)	9.94 ± 10.9 (5.00)	18.76 ± 11.7 (16.0)	28.7 ± 20.3 (23.0)	22.2 ± 8.18 (23.0)	3.000 ± 2.12 (2.8)	-4.00 ± 4.48 ('-3.60)	57.9 ± 18.2 (58.0)	0.09 ± 0.15 (0.00)
	1.37-6.46 (742)	393-517 (744)	1.90-2.35 (744)	0.08-0.94 (744)	2.00-25.0 (715)	1.00-85.0 (715)	2.00-68.0 (715)	3.00-150 (715)	2.00-44.0 (715)	0.20-9.90 (744)	-13.7-4.30(744)	7.00-89.0 (744)	0.00-0.68 (744)

430 Acronyms with superscripts a through d denote the following meteorological parameters as wind speed, temperature, humidity and ultraviolet, respectively. Superscript e
431 denotes mean + standard deviation and median in the parenthesis. Superscript f denotes range of data with the number of data in the parenthesis. Red colored values are
432 negative.

433 Table 2. Results of correlation analysis between Hg and relevant environmental parameters

434 [A] Correlation between all parameters using all measurement data sorted in daily intervals.

		Hg	CO_2	CH_4	H_2O	SO_2	NO	NO_2	NO_x	O_3	WS	TEMP	HUM
CO_2	r	-0.003											
	P	9.60E-01											
	n	211											
CH_4	r	0.073	0.285**										
	P	2.93E-01	6.07E-06										
	n	211	244										
H_2O	r	0.496**	-0.188**	-0.545**									
	P	1.75E-14	3.13E-03	2.77E-20									
	n	211	244	244									
SO_2	r	-0.126	0.394**	0.511**	-0.553**								
	P	6.77E-02	1.66E-10	1.18E-17	5.90E-21								
	n	212	244	244	244								
NO	r	-0.160*	0.333**	0.412**	-0.439**	0.367**							
	P	1.97E-02	1.00E-07	2.07E-11	6.08E-13	3.21E-09							
	n	212	244	244	244	245							
NO_2	r	-0.069	0.494**	0.700**	-0.431**	0.587**	0.677**						
	P	3.19E-01	1.99E-16	2.70E-37	1.81E-12	4.58E-24	3.30E-34						
	n	212	244	244	244	245	245						
NO_x	r	-0.143*	0.475**	0.643**	-0.478**	0.549**	0.857**	0.957**					
	P	3.88E-02	4.22E-15	1.08E-29	2.74E-15	1.55E-20	3.46E-71	4.38E-131					
	n	210	243	243	243	243	243	243					
O_3	r	0.280**	0.117	0.090	0.067	0.145*	-0.411**	-0.084	-0.220**				

	P	3.75E-05	6.90E-02	1.60E-01	3.01E-01	2.33E-02	2.29E-11	1.94E-01	5.56E-04				
	n	211	244	244	244	244	244	244	243				
WS	r	0.079	0.197**	-0.326**	0.119	0.098	-0.163*	-0.300**	-0.280**	0.045			
	P	2.51E-01	2.00E-03	2.06E-07	6.34E-02	1.25E-01	1.07E-02	1.84E-06	9.31E-06	4.81E-01			
	n	211	243	243	243	244	244	244	243	243			
TEMP	r	0.370**	-0.200**	-0.362**	0.805**	-0.362**	-0.340**	-0.302**	-0.353**	0.238**	-0.024		
	P	2.58E-07	3.25E-03	4.87E-08	3.38E-50	4.37E-08	2.94E-07	6.03E-06	1.07E-07	4.25E-04	7.25E-01		
	n	183	215	215	215	216	216	216	215	215	216		
HUM	r	0.380**	-0.198**	-0.247**	0.621**	-0.358**	-0.141*	-0.208**	-0.204**	-0.318**	0.090	0.322**	
	P	1.22E-08	1.94E-03	1.01E-04	2.85E-27	8.34E-09	2.78E-02	1.09E-03	1.37E-03	4.29E-07	1.59E-01	1.33E-06	
	n	211	243	243	243	244	244	244	243	243	244	216	
UV	r	0.198**	-0.231**	-0.181**	0.252**	-0.128*	-0.358**	-0.213**	-0.283**	0.588**	-0.185**	0.486**	-0.212**
	P	3.89E-03	2.88E-04	4.63E-03	7.33E-05	4.58E-02	9.09E-09	8.05E-04	7.31E-06	5.59E-24	3.78E-03	3.51E-14	8.80E-04
	n	211	243	243	243	244	244	244	243	243	244	216	244

435

436 [B] Hg and others in seasonally divided groups

Parameters		Summer	Fall	Winter
CO_2	r	-0.154	0.264**	0.790**
	P	1.47E-01	1.18E-02	1.26E-07
	n	90	90	31
CH_4	r	0.376**	0.460**	0.665**
	P	2.64E-04	5.18E-06	4.42E-05
	n	90	90	31
H_2O	r	0.210*	0.457**	0.410*
	P	4.71E-02	6.12E-06	2.18E-02
	n	90	90	31
SO_2	r	-0.009	0.360**	0.720**
	P	9.30E-01	4.56E-04	4.93E-06
	n	90	91	31
NO	r	-0.099	0.073	0.242
	P	3.54E-01	4.93E-01	1.90E-01
	n	90	91	31
NO_2	r	-0.007	0.309**	0.753**
	P	9.48E-01	2.92E-03	1.05E-06
	n	90	91	31
NO_x	r	-0.117	0.261*	0.592**
	P	2.74E-01	1.36E-02	4.47E-04
	n	90	89	31
O_3	r	0.136	0.300**	-0.645**
	P	2.02E-01	4.13E-03	9.04E-05
	n	90	90	31
WS	r	0.001	-0.090	-0.144
	P	9.89E-01	3.98E-01	4.39E-01
	n	90	90	31
TEMP	r	0.022	0.415**	-0.550
	P	8.35E-01	7.75E-05	1.58E-01
	n	90	85	8
HUM	r	0.159	0.283**	0.441*
	P	1.34E-01	6.86E-03	1.31E-02
	n	90	90	31
UV	r	-0.056	0.167	-0.034
	P	5.98E-01	1.16E-01	8.54E-01
	n	90	90	31

437

438 ** Correlation is significant at the p-value of less than 0.01 (2-tailed).

439 *Correlation is significant at the p-value of less than 0.05 (2-tailed).

440 Table 3. Comparison of TGM concentrations at mountainous/background regions across the
441 Globe

Major regions	Site	City (Province)/ Country	Study period	Concentration (ng m^{-3})	Reference
North America	Point Petre	Canada	1997-2000	1.93	30)
	Egbert	Canada	1997-2000	1.90	30
	Burnt Island	Canada	1998-2000	1.58	30)
	Toronto (U-BG)	Canada	2001-2002	2.48	31
	10 rural sites (CAMNet)	Canada	1995-1999	1.32-1.89	32
	Manhattan (U-BG)	New York, USA	2000	3.84	33
	Brooklyn (U-BG)	New York, USA	2000	3.70	33
	Queens (U-BG)	New York, USA	2000	2.89	33
	Great smoky mountain	Look Rock, Tennessee, USA	2004	1.65	34
	Rocky mountain	Colorado, USA	2006-2007	1.51	35
			Mean ± SD	2.39 ± 0.90	
South America	Rondonia (Amazon basin)	Brazil	1995	3.05	50
Europe	Wank Mountain (Bavarian Alps)	Southern Germany	1990-1996	1.82-2.97	19
	Champ sur Drac (Greenoble) (sub-urban)	Southereast France	1999-2000	3.40	36
	Wytham Wood (Rural)	UK	2004-2007	1.50	37 and references therein
	Ten rural sites (Rural)	UK	2004-2007	1.62	37 and references therein
			Mean ± SD	2.17 ± 1.06	
Asia	Seoul (U-BG)	South Korea	1999-2000	5.34	38
Korean Peninsula	13 mountainous sites	South Korea	1987-1993	3.99	39
	Hari	Kang Hwa Island, South korea	2001-2002	3.15	40
	GAW Station	An-Myun Island	2004-2006	4.16	41
	2 Mountains	South Korea	1997-1998	7.03	21
			Mean ± SD	4.73 ± 1.34	
Other regions	2 rural sites (Beizing)	China	1998	2.5-5.0	42
	Cape Hedo Station (Remote site)	Okinawa Island, Japan	2004	2.04	43
	Mt. Gongga	Tibetan Plateau, China	2005-2006	3.98 [a]	44
	Changbai mountain area	North-eastern China	2005-2006	3.58	45
	Cape Hedo Station,	Okinawa Island, Japan	2004	2.04	43
	Mt. Leigong	China	2008-2009	2.80	46
	Mt. Gongga	Tibetan Plateau, China	2006-2007	3.90	47
	Mountain sites	Guizhou	Unreported	3.35	48
			Mean ± SD	3.65 ± 1.51	

Africa	Overall	-	-	1.2-1.4	49
Polar regions	Arctic	Overall	-	1.60	49
	Antarctic	Overall	-	1.00	49

442

443 **Figure captions**

444 Fig. 1. Geographical location of Mt. Gwan-ak (GA) in Seoul, Korea.

445 a. Location of Seoul.

446 b. Location of Mt. Gwan-ak (GA).

447 Fig 2. Frequency distribution patterns of Hg concentration data measured at Gwan Ak

448 Mountain, Seoul, Korea in 2011.

449

450 Fig.3. Daily mean values of air pollutants at Gwan Ak Mountain, Seoul, Korea in 2011

451 (Julian days 121-365)

452

453 Fig. 4. Diurnal patterns of Hg, GHGs, and other air pollutants at Gwan Ak Mountain,

454 Seoul, Korea in 2011.

455

456

457

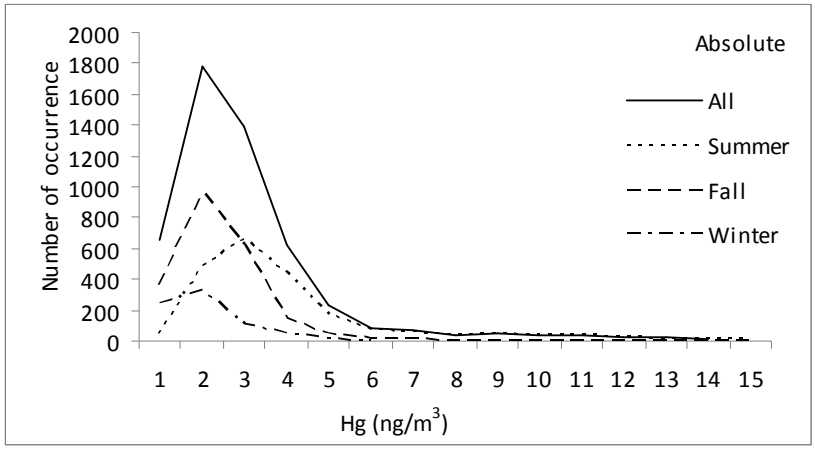
458

459 a. Location of Seoul.

460

461 b. Location of Mt. Gwan-ak (GA)

462 Fig 1. Geographical location of Mt. Gwan-ak (GA) in Seoul, Korea.



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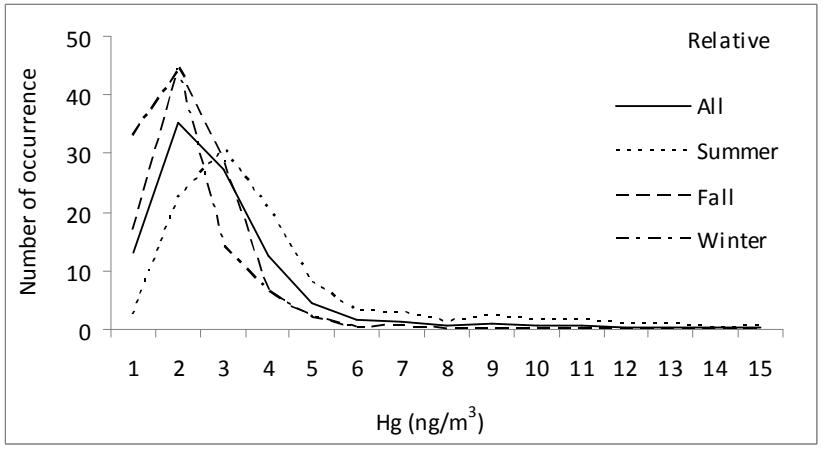
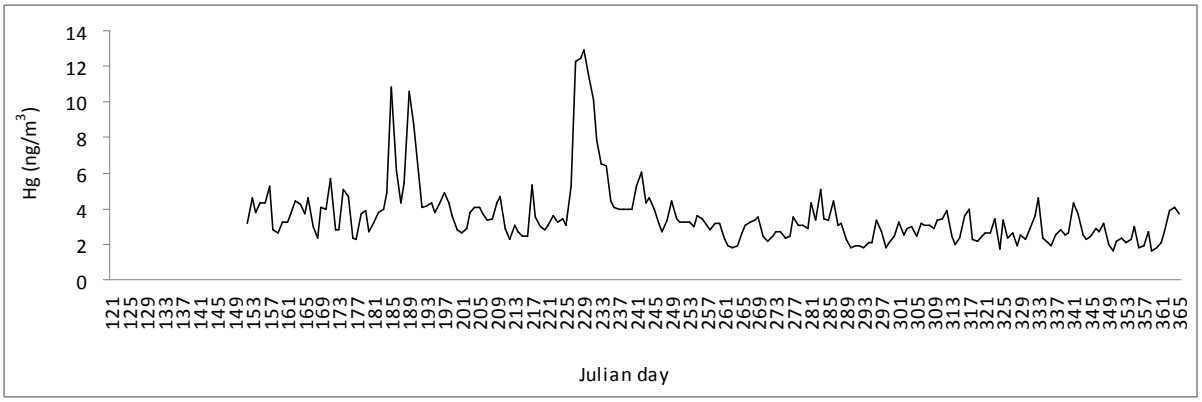


464

465 Fig.2. Frequency distribution patterns (in terms of % number of occurrences) of Hg

466 concentration data measured at Gwan Ak Mountain, Seoul, Korea in 2011.



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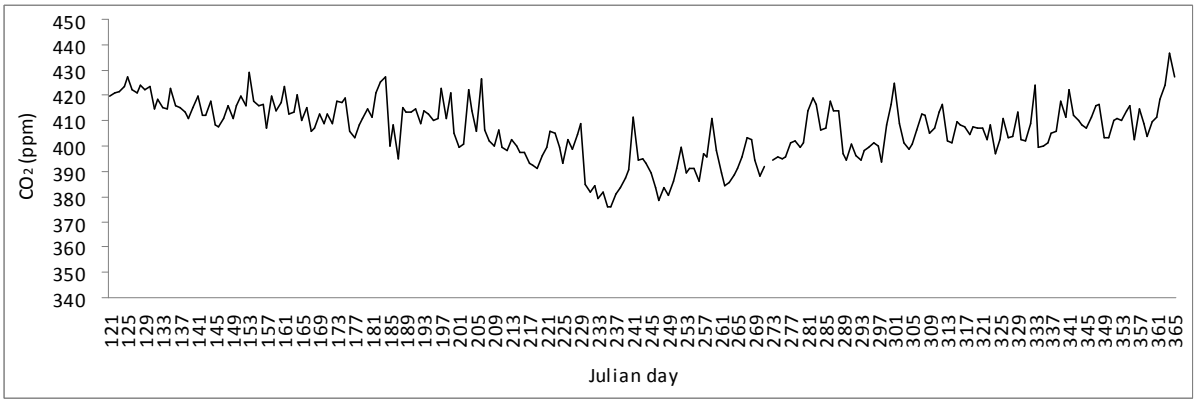

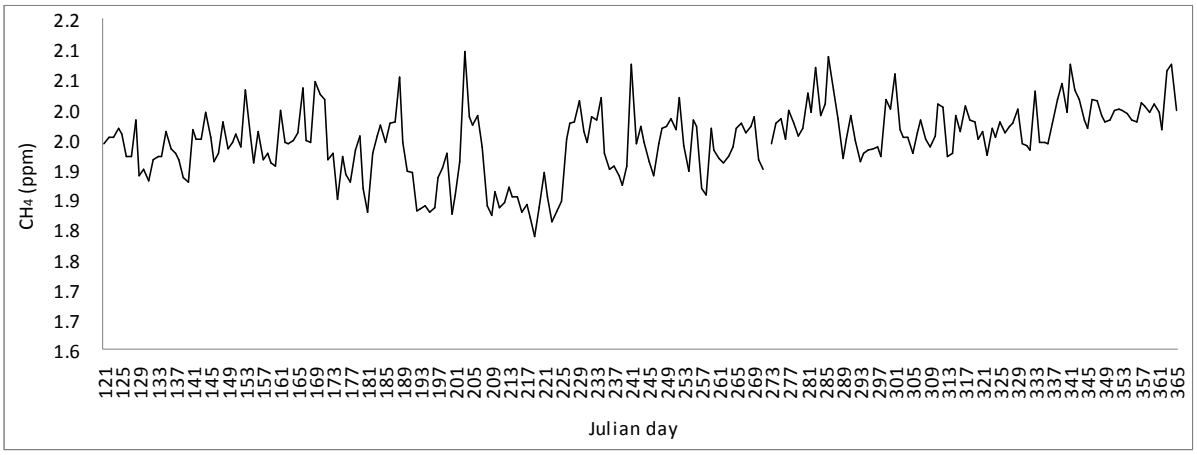

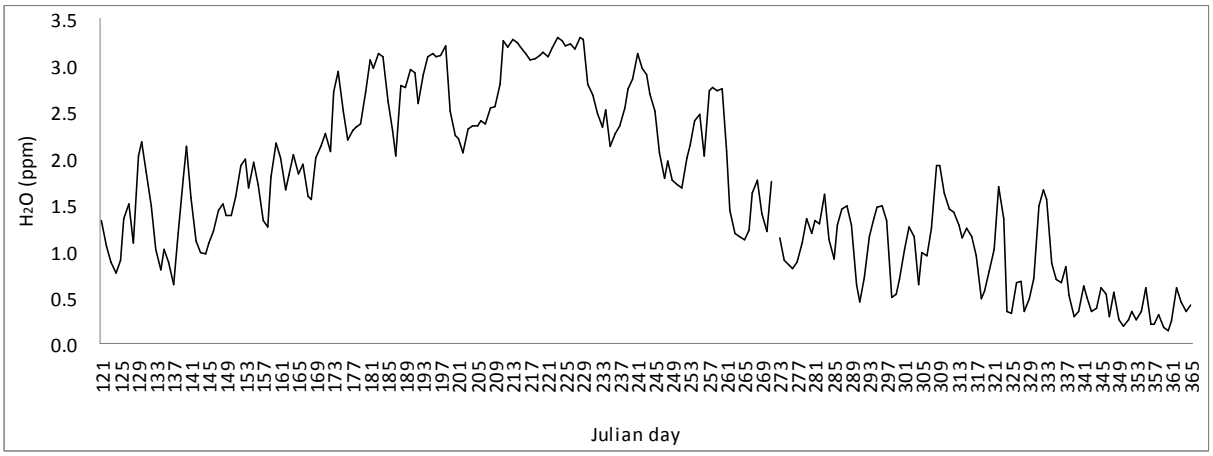

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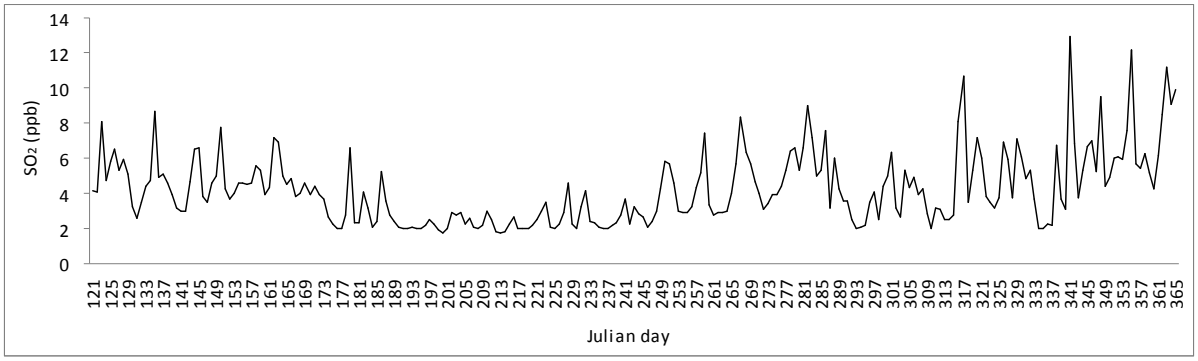

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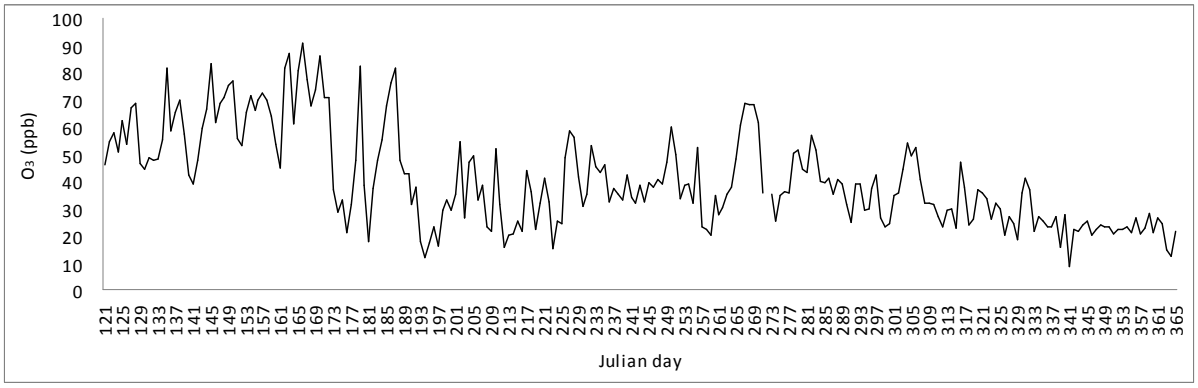

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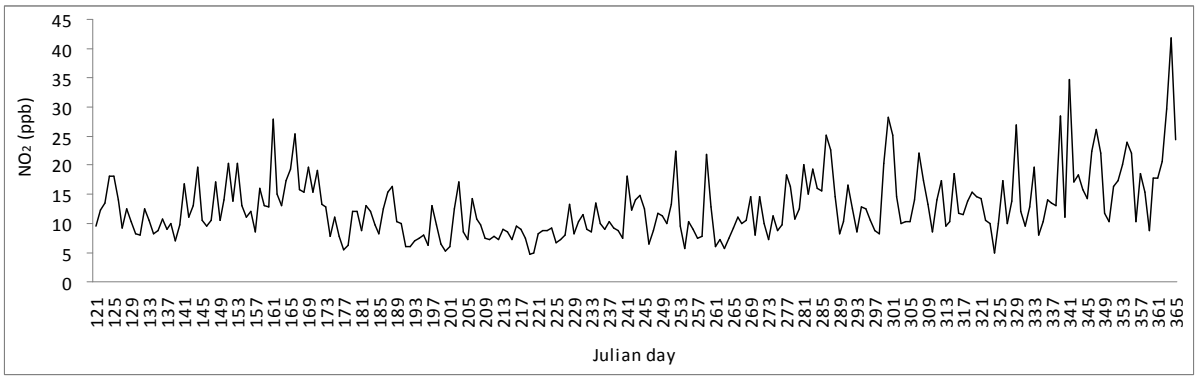

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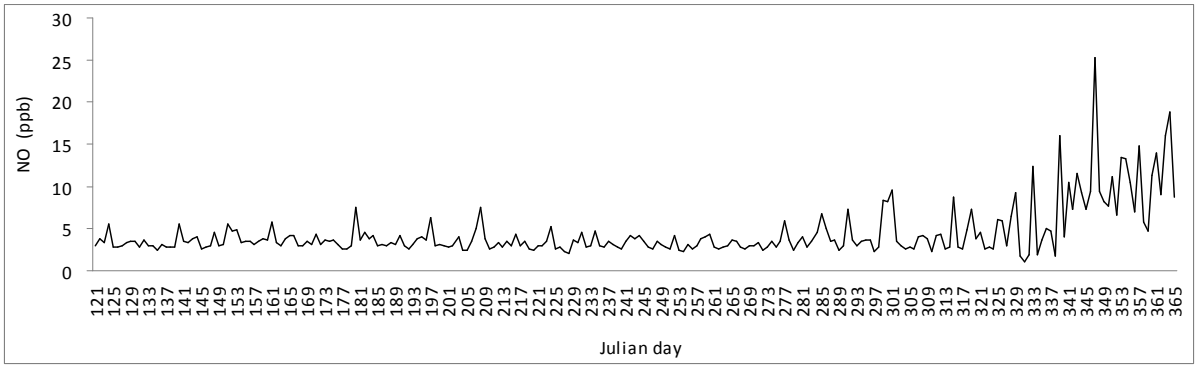
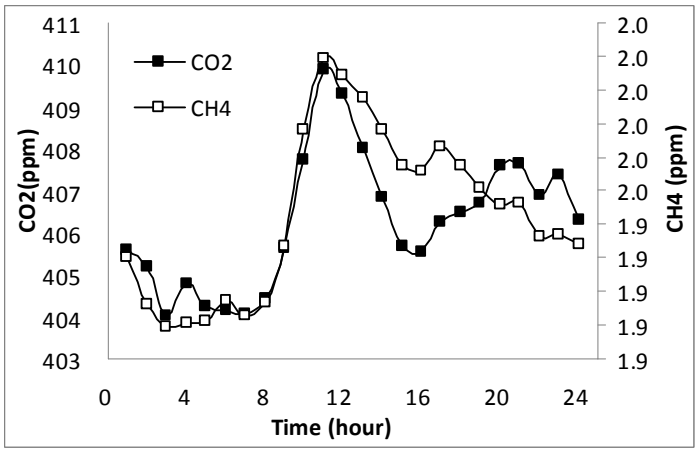
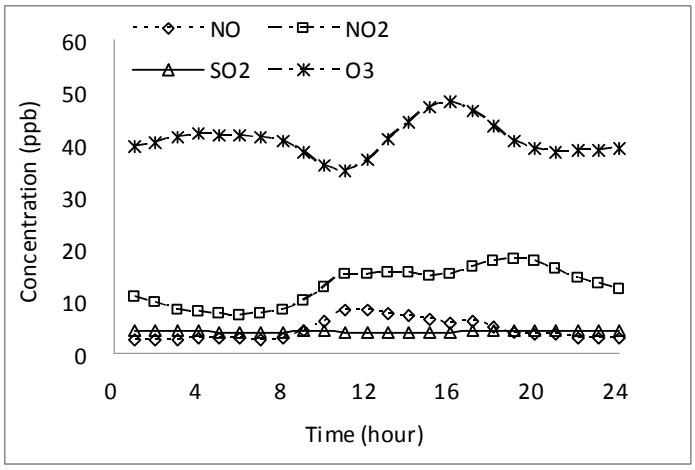


473

474 Fig.3. Daily mean values of air pollutants at Gwan Ak Mountain, Seoul, Korea in 2011

475 (Julian days 121-365)





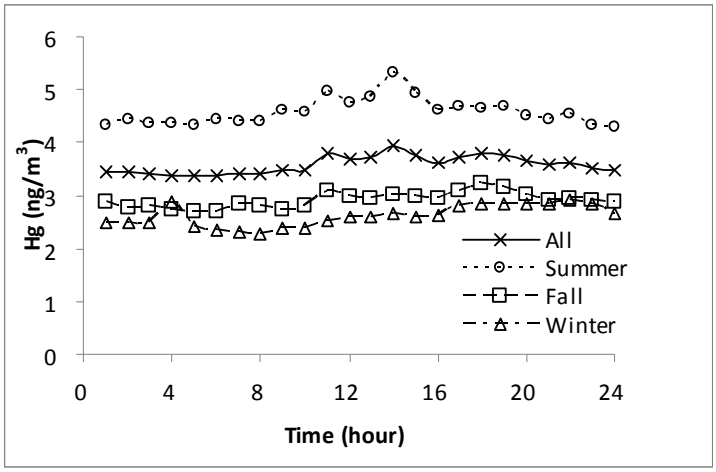


Fig 4. Diurnal patterns of Hg (broken down with respect to season) and GHGs and other air pollutants (annual average data only) at Gwan Ak Mountain, Seoul, Korea in 2011.