

The rapid and continuous monitoring of gaseous elemental mercury (GEM) behavior in ambient air

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Abstract

In order to examine the environmental behavior of elemental mercury (GEM or Hg⁰) at varying time scales, Hg concentration data were obtained at 1-s intervals using a rapid Hg monitoring system (Lumex Hg analyzer). The Hg data sets obtained from a total of 24 experiments were analyzed in two different manners—either as raw data (collected at 1-s intervals) or after modification into two arbitrarily extended intervals (i.e., 10 s and 1 min). To meaningfully interpret those rapidly monitored Hg data, we evaluated both the raw and modified data sets in varying respects. The environmental behavior of Hg, while exhibiting clear distinctions over diurnal and/or seasonal scales, was found to experience sharp changes for a very short time period, usually less than a few tens of seconds to a minute. During such a short duration, a five- to ten-fold increase in Hg concentration was commonly found. As a means to evaluate the temporal factors associated with Hg behavior, the correlation analysis was made using both the original and modified data sets between the various statistical parameters (mean, median, min, and max). The overall results of this study confirm that the temporal variability of Hg, while maintaining highly stable and systematic patterns (e.g., over diurnal or seasonal scale), can be dramatically dynamic over very short time intervals such as a few tens of seconds or minutes.

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1. Introduction

Mercury (Hg) is a highly toxic element of which accumulation can cause adverse effects on both human health and ecological systems (AMAP, 1998; EU, 2001). Like most toxic compounds in the environment, sources of Hg are found to include both natural and anthropogenic origins. The dominant form of mercury in the atmosphere is

identified as a gaseous elemental mercury (GEM: e.g., 98%) that is characterized by high stability, low solubility, high volatility, etc. (Schroeder and Munthe, 1998). (For the sake of simplicity, both GEM and Hg are used without distinction in this article, unless otherwise specified). It was estimated that the anthropogenic emissions of Hg are more significant, constituting 60% of the total budget (e.g., Pacyna, 1994). Some recent studies however were able to show a line of evidence that Hg concentration levels are decreasing through time (Pirrone et al., 1996). Similar to such finding, there were significant reductions in Hg concentrations

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which occurred from the late 80s (above 10 ng m^{-3}) to the late 90s ($\sim 5 \text{ ng m}^{-3}$) in Seoul, the capital city of Korea (Kim and Kim, 2000). Such a trend is in fact compatible with the estimates of its emission inventories. For instance in the case of Germany, changes in total Hg emissions occurred concurrently from 400 (1987/1988) to 113 tones per annum (1990) (Berdowski et al., 1997).

At present, the average concentrations of Hg are generally found to be between 1.5 and 5 ng m^{-3} in the Northern Hemisphere (NH), which are much lower than the critical load considered to exert harmful effects on human life (Kim et al., 2005). The establishment of the present Hg concentration levels may be attributable to the continuous efforts to reduce Hg emissions from major source processes. Because of the recognizable control on many major source types, the relative significance of diffused sources draws a great deal of attention (Billets, 2003). Diffusive emissions of Hg have been documented for various environmental reservoirs including soil, water, and vegetation surfaces (e.g., Poissant and Casimir, 1998). Nonetheless, to date, detailed information concerning the nature of diffuse sources is insufficient to account for their environmental significance.

As one simple means for accurately assessing the environmental behavior of Hg under varying environmental conditions, it may be desirable to describe its behavior at varying time scales. To meaningfully interpret Hg behavior from different temporal scales, we conducted a series of experiments using a fast-sensor type Hg monitoring system introduced recently; this system is advantageous in that it allows us to collect the Hg data as fast as 1-s intervals. Knowing that very few studies had previously attempted to collect the atmospheric Hg data at such short-time intervals (e.g., 1 s), the results of the present study can be used to provide some insights into the relationship between the environmental behavior of Hg and the temporal factors.

2. Materials and methods

2.1. Site characteristics

In the present article, the fundamental properties of Hg behavior were assessed by the data sets obtained using a rapid Hg monitoring system from a series of Hg measurement campaigns carried out in an urban monitoring station in Seoul, Korea

(September–November 2003); the general characteristics of the study site are given elsewhere (Kim et al., 2003). The collection of Hg data was made on the 4th floor of the Natural Science Building at Sejong University (height of 12 m from the ground); the site belongs to the Gwang Jin district of Seoul (mid-eastern region of the city) ($37^{\circ}32' \text{N}$ (latitude) and $127^{\circ}04' \text{E}$ (longitude)). This site represents a moderately developed, complex urban area surrounded by diverse urban facilities including a large-scale public park (E), a residential area (N and W), and a commercial area (S); it is hence expected to be influenced by the combined effects of various anthropogenic (and natural) source processes. There is however no known major sources of mercury emission other than a multitude of unidentified sources dispersed all across the urban area.

2.2. Performance of a rapid mercury monitoring system for AQM

The collection of GEM data in air was made using an RA-915+ Hg analyzer (Lumex, St Petersburg, Russia). The Hg analyzing system was essentially built to monitor GEM concentrations at 1-s intervals. The operation of the RA-915+ is based on differential Zeeman atomic-absorption spectrometry using a high-frequency modulation of light polarization (ZAAS-HFM). A radiation source (mercury lamp) is placed in a permanent magnetic field, and the mercury resonance line ($\lambda = 254 \text{ nm}$) is split into three polarized Zeeman components (π , σ -, and σ +). When radiation propagates along the direction of the magnetic field, a photo detector detects only the radiation of the σ - components (such as one of those falling within the absorption line profile and another lying outside). In the case that mercury vapor is absent from the analytical cell, the radiation intensities of both σ components are equal. As the absorbing atoms appear in the cell, the difference between the intensities of the σ components increases with the growth of mercury vapor content. The σ components are then separated in time by the polarization modulator. The spectral shift of the σ components is significantly smaller than the widths of the molecular absorption bands and scattering spectra; hence, background absorption (by interfering components) is not allowed to affect the reading values of Hg concentrations.

All of the measurements were made as a total of 24 experiments (hereafter, the term experiment(s) will be abbreviated as Exp(s)), which took place occasionally in the period between 17th September and 12th November 2003 (Fig. 1). The duration of each experiment ran from as little as 8 and up to 68 h (Table 1). Although all Hg measurements were made at 1 s intervals, the GEM concentrations were analyzed in two different manners to facilitate the data interpretation. First, all 1-s experiment data were analyzed as being obtained. Second, these data were also examined after modification into two arbitrarily extended intervals (i.e., between 10 s and 1 min). Knowing that Hg behavior can exhibit enhanced stability with elongated measurement duration, this modification procedure can facilitate the comparison of the original data (1-s data) with

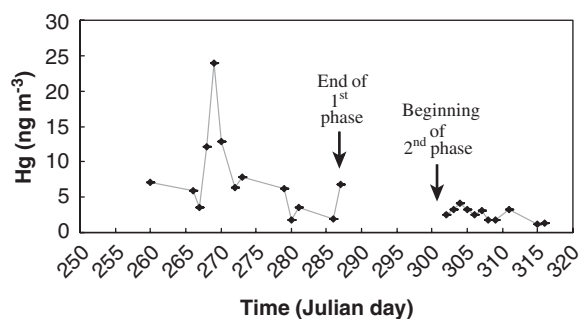


Fig. 1. Time series plot of daily Hg concentrations; the daily values were derived using all second-based measurement data from each of the individual 24 experiments (refer to Table 1). Julian days (JD) of 260 and 302 correspond to 17 September and 29 October 2003, respectively. JD 302 was selected arbitrarily as the starting point of the 2nd phase of the experiment due to the notable and consistent reduction in concentration levels.

Table 1

Summary of the fundamental experimental conditions for a total of 24 individual experiments conducted during the entire study period (September–November 2003)

Exp. no.	Start		End		JD start	Duration (hh:mm)	Number of data ^a		
	Date	Time	Date	Time			N_1	N_2	N_2/N_1^b
1	17/09/2003	10:48:36	17/09/2003	19:45:30	261	8:57	31081	297	0.96
2	23/09/2003	12:34:00	23/09/2003	20:34:39	266	8:01	22953	4322	18.8
3	24/09/2003	11:03:29	24/09/2003	19:04:08	267	8:01	24915	3142	12.6
4	25/09/2003	11:05:00	25/09/2003	21:36:41	268	11:32	29106	1849	6.35
5	26/09/2003	10:30:00	26/09/2003	22:28:50	269	11:59	36570	1022	2.79
6	27/09/2003	10:50:00	27/09/2003	18:50:39	271	8:01	24391	2672	11.0
7	29/09/2003	10:15:00	30/09/2003	2:10:30	273	15:56	48564	3879	7.99
8	30/09/2003	9:11:33	03/10/2003	5:12:30	274	68:01	122126	7796	6.38
9	06/10/2003	10:26:13	06/10/2003	18:26:52	280	8:01	26558	1529	5.76
10	07/10/2003	13:30:54	07/10/2003	21:31:33	281	8:01	23336	4723	20.2
11	08/10/2003	10:47:29	08/10/2003	18:48:08	282	8:01	24070	4005	16.6
12	13/10/2003	11:28:03	13/10/2003	19:28:42	287	8:00	24267	4573	18.8
13	14/10/2003	10:24:00	14/10/2003	18:24:38	288	8:00	27480	1359	4.95
14	29/10/2003	12:16:17	29/10/2003	20:16:26	303	8:00	24060	4750	19.7
15	30/10/2003	11:32:54	30/10/2003	19:33:00	304	8:00	20403	8407	41.2
16	31/10/2003	11:30:40	31/10/2003	19:30:49	305	8:00	25942	2868	11.1
17	01/11/2003	14:06:35	01/11/2003	22:07:04	306	8:00	27998	832	2.97
18	02/11/2003	13:15:06	02/11/2003	21:15:15	307	8:00	26636	2174	8.16
19	03/11/2003	10:41:18	03/11/2003	18:41:27	308	8:00	23015	5795	25.2
20	04/11/2003	13:34:52	04/11/2003	21:35:01	309	8:00	25574	3236	12.7
21	05/11/2003	10:26:20	05/11/2003	18:26:29	310	8:00	26928	1883	6.99
22	07/11/2003	11:33:33	07/11/2003	19:33:00	312	8:00	27733	1078	3.89
23	11/11/2003	12:05:12	11/11/2003	20:05:21	316	8:00	24026	4785	19.9
24	12/11/2003	13:51:14	12/11/2003	21:51:23	317	8:00	25437	3373	13.3
Sum							743169	80349	10.8
Mean							30965	3348	12.4

^aAs the fast Hg monitoring system can produce a small quantity of negative concentration data, the number of measurement data are presented in two different forms to consider such an effect: N_1 = total number of data, N_2 = number of data with negative concentration values.

^b N_2/N_1 ratio in percent value (%).

those elongated artificially (10 s or 1 min). In the latter case, all 1-s-based Hg data were combined into those modified intervals, and Hg values were derived artificially at those elongated intervals of 10 s or 1 min. For a proper interpretation of Hg data sets obtained at different intervals, the mean values for those three categories were computed and evaluated each other in Table 2.

Because of the unique instrumental setting of the rapid Hg monitoring system, it is not feasible to directly evaluate its analytical performance as is possible with the traditional system (CVAAS or CVAFS). Hence, as an alternative means to evaluate the analytical performance of the Lumex Hg analyzer, its relative performance was inspected against a traditional CVAAS-type Hg analyzer (WA-4 model, Nippon Instrument Corp. (NIC), Japan). Information concerning the analytical performance of such CVAAS systems is given in many of our previous works (Kim et al., 2001a, b). In the case of the CVAAS instrument, Hg is collected by the Au amalgam tube, liberated by heating up the tube, transferred to an absorption cell, and detected by atomic absorption at a wavelength of 253.7 nm by a non-dispersive double beam. The analytical cycle of this CVAAS system was set at hourly intervals with a detection limit (DL) of ca.1 pg. In contrast, the characterization of Lumex analyzer, based on the absorption of Hg atom resonance radiation with Zeeman correction for background absorption, requires highly delicate techniques under its unique operation condition (e.g., supply of air at 20 L min^{-1}) relative to traditional ones. It should be noted that its performance is relatively well elucidated for such matrices as soil and water, while relatively little is studied for air. Because of such technical limitations, we were not able to directly quantify its DL under normal operation conditions. However, in the manufacturer's performance report made as continuous vehicular survey (St. Petersburg, Russia, July 2001), the DL values of the system were shown to vary sensitively with the surveying speed of the vehicle such as 0.3 (fixed position or car stop) to 2.0 ng m^{-3} (vehicle speed of 30–60 km h^{-1}). As all of our monitoring was made at the same location in our laboratory, we expect that the Lumex system used in this study should have maintained the similar performance as that for the fixed position. As shown below, the results of comparative analysis made between this Lumex system and the traditional CVAAS method indicate that both systems

can exhibit a good compatibility even in the very low concentration ranges.

As an indirect means to validate the performance of the Lumex analyzer, the CVAAS system was also operated concurrently from time to time for the entire study period. Although the CVAAS system ran on a limited schedule such as on a few hours per day basis (during most of the study period), this comparison is still useful to assess the reliability of the rapid Hg monitoring system. The Lumex-based Hg data were thus compared against the CVAAS-based data collected for the entire study period; the results exhibited the presence of a very strong correlation between the two systems ($r = 0.94$, $P = 6.66\text{E-}16$, and $N = 26$) (Fig. 2). According to this comparative analysis, the Hg data obtained by the Lumex system were found to be compatible with those made by the traditional one. One should however be cautious about the negative concentration values generated by the Lumex analyzer. As it has an in-built baseline check-up system, the analyzer checks the baseline at 2 min intervals (for the duration of 20 s). The baseline correction is made by creating artificially the zero Hg vapor concentration in the analytical cell. Because of this routine procedure, the system attempts to detect the Hg level at or near its detection limit; this can lead to the production of a large quantity of negative concentration values. Hence, these negative values were manually removed at the time of data analysis. The occurrence patterns of those negative data were however found to vary significantly among different experiments, e.g., 0.96% (Exp. no. 1; 17th September) and 41.2% (Exp. no. 15; 30th October 2003) of the total observed Hg data for each experiment. This unique properties of the Lumex analyzer need to be investigated further for the proper application of this technique.

3. Results and discussion

3.1. The general pattern of Hg distributions at short-term intervals

In this study, the mean Hg concentration data, unless otherwise specified, denote the values derived from the original 1-s data sets for each experiment. However, for an in-depth analysis of these measurement data, the fundamental statistical terms were also derived for the two arbitrarily formed Hg data groups (i.e., after being grouped at intervals of 10 s and 1 min) (Table 2). To learn the effect of

Table 2
Statistical summary of Hg concentration data sets measured during the entire study period

Experiment no.	Start date	Hg (1 s)					Hg (10 s)					Hg (1 min)				
		Mean ±SD (Med)	Min	Max	N		Mean ±SD (Med)	Min	Max	N		Mean ±SD (Med)	Min	Max	N	
<i>A. The first period</i>																
1	17/09/2003	7.14 ± 4.67 (7.10)	1.00E-03	57.6	31081	7.11 ± 4.54 (7.19)	0.09	46.7	3076	7.08 ± 4.19 (7.43)	1.86	35.6	527			
2	23/09/2003	5.94 ± 18.6 (1.58)	1.30E-05	188	22953	7.11 ± 4.52 (1.36)	0.71	152	3130	5.26 ± 11.2 (1.32)	0.57	100	480			
3	24/09/2003	3.55 ± 7.03 (1.64)	1.00E-04	108	24915	3.32 ± 6.49 (1.65)	0.16	99.4	24915	3.33 ± 5.27 (1.44)	0.66	53.1	481			
4	25/09/2003	12.1 ± 20.5 (4.09)	1.90E-03	373	29106	10.2 ± 18.2 (3.75)	0.01	329	3657	10.2 ± 15.8 (3.83)	0.67	174	635			
5	26/09/2003	23.9 ± 28.2 (13.5)	2.20E-03	292	36570	23.7 ± 27.3 (13.5)	0.04	251	3728	23.7 ± 22.4 (16.8)	0.29	151	640			
6	27/09/2003	12.9 ± 30.7 (2.70)	2.00E-04	365	24391	16.1 ± 2.72 (2.20)	0.03	311	610	11.9 ± 23.4 (2.17)	0.67	225	480			
7	29/09/2003	6.35 ± 12.8 (2.52)	1.00E-04	322	48564	6.11 ± 13.2 (2.13)	0.05	275	3728	6.09 ± 9.55 (2.14)	0.61	104	895			
8	30/09/2003	7.85 ± 8.45 (3.32)	2.00E-04	387	224073	7.23 ± 7.59 (3.16)	0.08	207	23086	7.92 ± 6.26 (3.3)	0.57	132	4027			
9	06/10/2003	6.15 ± 7.47 (3.64)	3.80E-03	73.4	26558	6.11 ± 7.13 (3.36)	0.03	64.4	2769	5.98 ± 5.86 (3.78)	0.17	41.2	480			
10	07/10/2003	1.75 ± 1.60 (1.53)	5.00E-04	30.0	23336	1.67 ± 1.27 (1.50)	0.21	27.9	2775	1.67 ± 1.08 (1.51)	0.54	14.8	480			
11	08/10/2003	3.48 ± 7.78 (1.75)	3.00E-04	153	24070	3.22 ± 7.06 (1.67)	0.25	132	2781	3.25 ± 6.05 (1.68)	0.69	51.7	480			
12	13/10/2003	1.99 ± 1.41 (1.76)	2.16E-05	12.3	24267	1.91 ± 0.99 (1.68)	0.25	9.71	2884	1.96 ± 0.84 (1.71)	0.69	7.16	481			
13	14/10/2003	6.74 ± 7.12 (4.63)	9.00E-04	88.0	27480	6.50 ± 7.01 (4.30)	0.34	85.0	2884	6.59 ± 5.29 (5.05)	1.16	54.5	480			
Mean or sum		7.86 ± 10.2 (2.98)	1.30E-05	387	567364	7.44 ± 9.42 (2.74)	0.01	329	80023	7.77 ± 7.67 (2.94)	0.17	225	10566			
<i>B. The second period</i>																
14	29/10/2003	2.53 ± 2.63 (1.84)	2.00E-04	36.6	24060	2.30 ± 2.41 (1.64)	3.00E-03	30.9	2774	2.37 ± 1.97 (1.90)	0.07	15.6	478			
15	30/10/2003	3.19 ± 4.11 (1.93)	1.00E-04	42.1	20403	2.93 ± 3.77 (1.80)	1.36E-04	38.4	2352	3.09 ± 3.13 (1.95)	0.05	17.4	439			
16	31/10/2003	4.19 ± 3.61 (3.70)	3.00E-04	39.2	25942	4.04 ± 3.44 (3.59)	7.00E-03	33.8	2770	4.09 ± 2.96 (3.95)	0.01	20.8	476			
17	01/11/2003	3.21 ± 1.86 (2.91)	2.52E-05	25.1	27998	3.14 ± 1.74 (2.83)	1.60E-02	19.2	2883	3.18 ± 1.35 (2.92)	0.60	10.3	481			
18	02/11/2003	2.53 ± 2.57 (1.77)	3.00E-04	32.2	26636	2.43 ± 2.41 (1.64)	2.80E-02	27.5	2861	2.46 ± 1.94 (1.86)	0.23	15.3	481			
19	03/11/2003	3.03 ± 3.42 (2.03)	3.00E-04	63.4	23015	2.74 ± 3.03 (1.80)	4.00E-03	43.5	2693	2.87 ± 2.21 (2.28)	0.23	16.3	477			
20	04/11/2003	1.71 ± 2.17 (1.26)	4.00E-04	34.7	25574	1.61 ± 1.98 (1.20)	1.90E-02	32.4	2823	1.64 ± 1.58 (1.23)	0.10	13.2	477			
21	05/11/2003	1.81 ± 1.34 (1.53)	9.00E-04	13.1	26928	1.76 ± 1.20 (1.45)	2.00E-02	10.5	2875	1.77 ± 0.98 (1.53)	0.31	7.01	480			
22	07/11/2003	3.21 ± 0.93 (3.17)	1.60E-03	8.50	27733	3.16 ± 0.78 (3.13)	2.00E-03	7.29	2879	3.18 ± 0.66 (3.14)	0.17	5.77	481			
23	11/11/2003	1.14 ± 0.79 (1.03)	3.00E-04	10.7	24026	1.07 ± 0.58 (0.99)	3.00E-03	8.74	2820	1.08 ± 0.45 (1.05)	0.19	4.53	479			
24	12/11/2003	1.27 ± 0.92 (1.16)	5.03E-06	70.9	25437	1.21 ± 0.62 (1.09)	2.60E-02	8.10	2879	1.23 ± 0.47 (1.16)	0.35	3.27	480			
Mean or sum		2.59 ± 1.58 (1.78)	5.03E-06	70.9	277752	2.43 ± 1.47 (1.59)	1.36E-04	43.5	30609	2.48 ± 1.11 (1.82)	0.01	20.8	5229			
Grand mean or sum		5.56 ± 5.4 (3.52)	5.03E-06	387	845116	5.57 ± 5.59 (3.38)	1.00E-04	329	110632	5.35 ± 5.20 (3.22)	0.01	225	15795			

The main statistical terms for all Hg data (mean, SD, min, and max) were compared both as raw (1 s) and modified status (10 s and 1 min). All concentrations in ng m⁻³ unit.

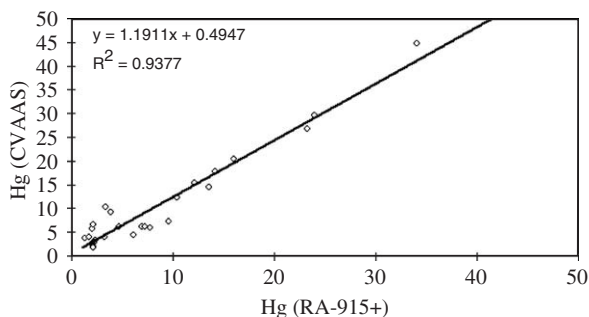


Fig. 2. Comparison of Hg data sets obtained by the two different Hg monitoring systems between the rapid Hg monitoring system (RA- 915+, Lumex, Russia) and traditional CVAAS technique (WA-4 model, Nippon Instrument Co., Japan): Comparison is made using the data sets obtained between 17th September and 13th October ($N = 36$). All concentrations in ng m^{-3} unit.

measurement duration on the Hg occurrence patterns and the related source processes, the frequency distribution patterns for all three data groups were compared using the results of the three different expts: 4th, 8th, and 20th Exp. (Refer to the Exp. number in Table 1); in the case of those three Exps, the relative portions of large concentrations (e.g., larger than 10 ng m^{-3}), when assessed by 1 min data sets, were found to constitute 30%, 59%, and 5% of each data set, respectively. This thus indicates that the proportion of Hg data can be distinguished at two opposing concentration ranges such as low (e.g., $< 5 \text{ ng m}^{-3}$) and high concentration values (e.g., $> 10 \text{ ng m}^{-3}$) (refer to Fig. 3). Considering the fact that the absolute number of data decreases significantly across three measurement intervals of 1 s, 10 s, and 1 min, relative occurrence patterns are also derived and compared in Fig. 3. The peak occurrence patterns of the 4th and 8th Hg measurement data hence appear to be quite compatible with those measured under strong anthropogenic source processes (e.g., Kim and Kim, 2000).

As shown in Fig. 1, the temporal distribution patterns of the Hg data can be compared across two distinct periods; the first (17/9–14/10) is characterized by generally enhanced Hg levels with relatively strong variability (the mean for Exps 1 through 13: 7.86 ng m^{-3}). In terms of the daily mean values, a wide variation was apparent during this period (1.75 and 23.9 ng m^{-3}). The second period (29/10–12/11), on the other hand, is characterized by consistently reduced values (mean 2.59 ng m^{-3}) with moderate change in its concentration levels. In fact, the daily

mean values in this period varied between 1.14 and 4.19 ng m^{-3} . It is however found that the grand mean of 5.56 ng m^{-3} , derived by combining both periods of I and II (Table 1), is highly comparable to the values typically observed from other Korean sites. The recent report of Hg concentration levels in a residential area of Seoul (Yang Jae: a southern-end district of Seoul) showed its mean concentration at 5.26 ng m^{-3} over a 20-month period from January 1999 to August 2000 (Kim and Kim, 2001a). The results obtained from other urban areas also showed that the Hg concentration level of around 5 ng m^{-3} could be considered a common value in the urban areas of Korea at present time (Kim and Kim, 2001b).

In the course of this study, Hg concentration data were also obtained during rain events on certain occasions; the results generally show the patterns that have been reported from many of previous studies. Except for the certain rain event when moderately low Hg levels were seen (11/11), the cases with 2–3 fold increases in its mean values were seen more frequently such as during on 30/9, 14/10 and 7/11. Considering that the period II was characterized as considerably low Hg levels relative to the period I, the results of 11/11 appear to reflect by and large the influence of low precipitation under reduced source strengths. Similar to the general pattern seen in this study, a notable increase in Hg concentration levels during precipitation period has been reported in a number of previous work (e.g., Schmolke et al., 1999). There is an indication that the emission of Hg can be activated under wet surface conditions. In fact, increased Hg fluxes have been found from soils after artificial irrigation with Hg-free water (Advokaat and Lindberg, 1996). Such an effect may be reproducible, by and large, since the high Hg flux appears to be stimulated by increased soil moisture (Wallschläger et al., 2000); these authors thus proposed a mechanistic model to ascribe increased Hg volatilization to rain events over contaminated soils. In the first step of their model, rainwater enters the soil to displace volatile Hg species contained in the soil air. This causes the first emission peak to appear before the rain events end. Thereafter, some Hg is mobilized into the aqueous phase from the soil to be transformed into volatile species either via biotic or abiotic processes. Consequently, they can evaporate to promote the second (larger and longer) flux events. Another potential explanation for the Hg flux increase during rain events was also sought from the

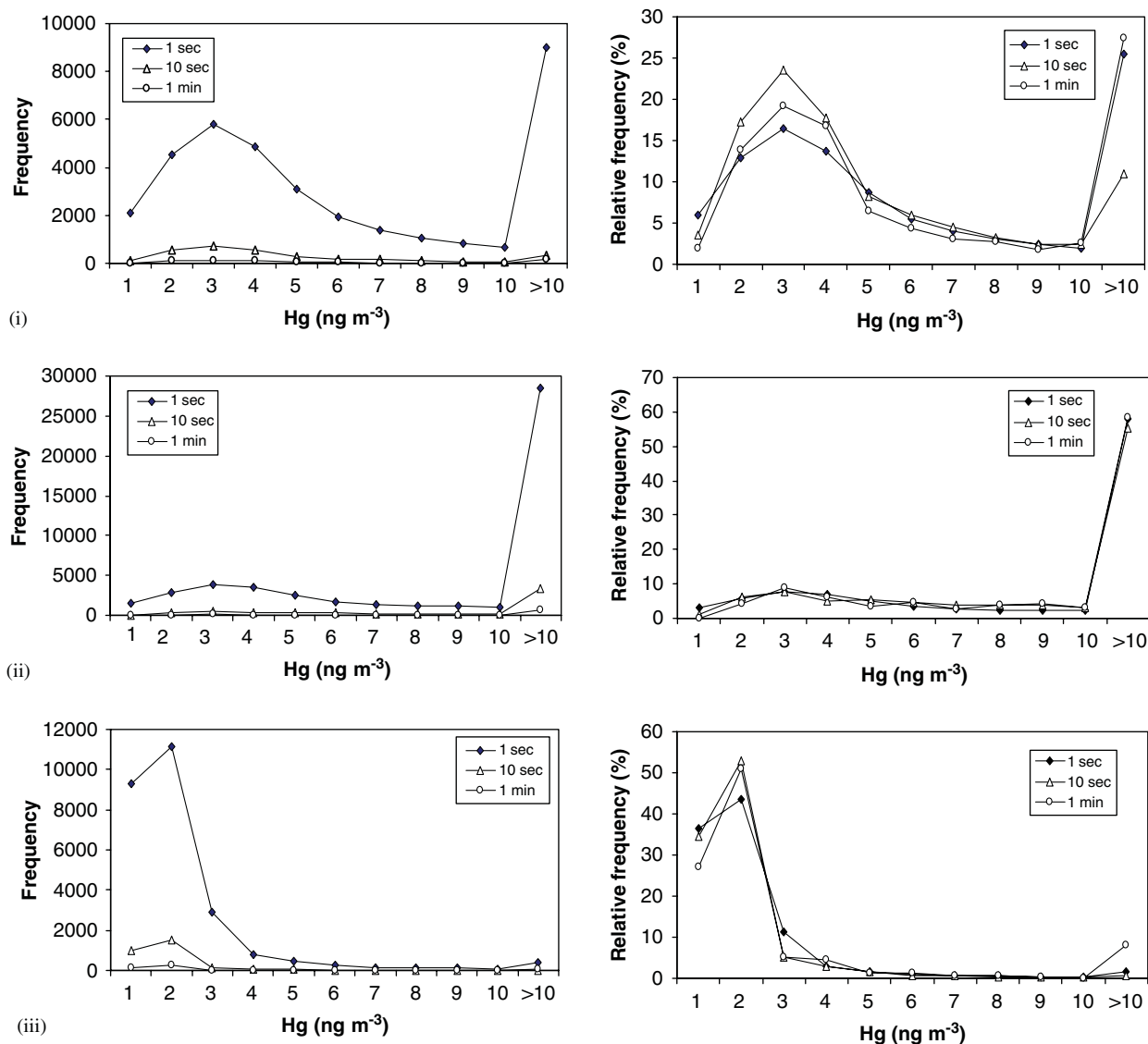


Fig. 3. Comparison of both absolute and relative occurrence patterns of Hg data is made using data sets collected from three experiments. All of these results are compared at three different data collection intervals of 1 s, 10 s, and 1 min. Both absolute (left hand) and relative (right hand) patterns are compared for the 4th, 8th and 20th experiment. (i) Frequency distribution of Hg concentration for the 4th exp (25th September). (ii) Frequency distribution of Hg concentration for the 8th exp (14th October). (iii) Frequency distribution of Hg concentration for the 20th exp (4th November).

spontaneous re-emission of Hg (e.g., Federer and Schirmer, 1990).

3.2. Comparison of Hg data sets among different time intervals

To meaningfully compare our Hg data, we compared them after confining into three different intervals of 1 s (i.e., use of the original data), 10 s, and 1 min (modified). To distinguish the influence of

selected intervals on the data interpretation, several different ratios were evaluated using both max and min concentrations of each Exp between different interval data groups (Table 3). These ratios appear to change dramatically among different groups in such a way that the highest mean value of $1.45E+07$ is obtained for the 1 s data group (Exp. no. 2), while that for the 1 min data group is 2084 (Exp. no. 16). The results of the 10-s data group on the other hand are much smaller than those of the

Table 3
The relationships of Hg concentration data obtained or modified at different measurement intervals

Exp. Date no.	Concentration variation ratio ^a						Comparison of minimum-to-minimum and maximum-to-maximum concentration ratios								
	Max/Min ratio			Max (10s)			Min (1min)			Max (10s)			Min (1s)		
	10 s	1 min	1 s	10 s	1 min	1 s	Min (10s)	Min (1min)	Min (1s)	Max (10s)	Max (1min)	Max (1s)	Min (10s)	Min (1min)	Min (1s)
1	17/09/2003	8.10	6.70	4.80	57600	518	19.1	90.0	20.7	1860	0.81	0.76	0.62	0.62	0.53
2	23/09/2003	32.0	21.3	19.0	14500000	214	175	23900	1.84	44000	0.91	0.58	0.53	0.53	0.49
3	24/09/2003	30.4	30.4	15.8	10800000	621	80.5	1600	4.13	6600	0.92	0.53	0.47	0.47	0.47
4	25/09/2003	31.0	32.0	17.0	196000	27400	259	6.32	55.8	353	0.88	0.53	0.52	0.52	0.52
5	26/09/2003	12.0	11.0	6.00	133000	5705	520	20.0	6.59	132	0.86	0.60	0.62	0.62	0.34
6	27/09/2003	28.0	19.3	19.0	1830000	10370	337	155	21.6	3350	0.04	14.7	0.62	0.62	0.34
7	29/09/2003	51.0	45.0	17.0	3220000	5288	170	520	11.7	6100	0.85	0.38	0.32	0.32	0.34
8	30/09/2003	48.4	28.6	16.7	1940000	2588	231	400	7.13	2850	0.53	0.64	0.64	0.64	0.56
9	06/10/2003	12.0	11.0	7.00	19300	2145	242	7.89	5.67	44.7	0.88	0.64	0.62	0.62	0.49
10	07/10/2003	17.1	16.6	8.50	60000	133	27.3	420	2.57	1080	0.93	0.53	0.49	0.49	0.34
11	08/10/2003	44.0	40.9	15.7	510000	528	74.9	833	2.76	2300	0.86	0.39	0.34	0.34	0.58
12	13/10/2003	6.10	5.00	3.30	569000	38.8	10.4	11600	2.76	31900	0.79	0.74	0.74	0.74	0.62
13	14/10/2003	13.1	13.0	8.10	97800	250	47.0	378	3.41	1290	0.97	0.64	0.62	0.62	0.43
14	29/10/2003	14.0	13.0	7.00	183000	10300	222	15.0	23.3	350	0.84	0.51	0.43	0.43	0.41
15	30/10/2003	13.0	13.0	6.00	421000	283000	348	1.36	368	500	0.91	0.45	0.41	0.41	0.53
16	31/10/2003	9.35	8.35	5.09	131000	4821	2084	23.3	1.43	33.3	0.86	0.62	0.53	0.53	0.41
17	01/11/2003	7.80	6.10	3.00	996000	1201	17.1	635	37.5	23800	0.77	0.53	0.41	0.41	0.47
18	02/11/2003	12.7	11.3	6.10	107000	982	66.4	93.3	8.21	767	0.85	0.56	0.47	0.47	0.38
19	03/11/2003	20.9	15.9	5.60	211000	10900	70.7	13.3	57.5	767	0.69	0.37	0.26	0.26	0.54
20	04/11/2003	20.0	20.0	8.00	86800	1704	131	47.5	5.26	250	0.93	0.41	0.38	0.38	0.68
21	05/11/2003	7.20	5.90	3.80	14600	524	22.6	22.2	15.5	344	0.8	0.67	0.54	0.54	0.68
22	07/11/2003	2.60	2.30	1.80	5310	3645	33.9	1.25	85.0	106	0.86	0.79	0.68	0.68	0.42
23	11/11/2003	9.40	8.20	4.00	35700	2913	23.8	10.0	63.3	633	0.82	0.52	0.42	0.42	0.05
24	12/11/2003	55.8	6.67	2.37	14100000	312	9.30	5160	13.5	69500	0.11	0.40	0.40	0.40	0.46
	Mean	21.1	16.3	8.8	1690000	15670	218	3179	308	8411	0.76	1.20	1.20	1.20	0.46

For this comparison, Hg concentration ratios are computed in various manners by combining the data sets categorized into three different intervals of 1 s, 10 s, and 1 min.

^aConcentration variation ratio: ((Max - Min)/Mean).

1-s data group by approximately 50 times ($\text{max}/\text{min} = 2.83\text{E}+05$) (Exp. no. 15). The presence of such extreme ratios in the original data sets (1-s interval) hence confirms that the Hg data can experience considerable variability at significantly short-term intervals. The wide variation in Hg data can also be explained from a different perspective. As shown in Table 3, the concentration variation ratios of Hg were computed for all three data groups such as $((\text{max}-\text{min})100/\text{mean})$. The extreme variation ratios in second-based values can be observed more clearly when the minimum concentration ratios are compared among the data sets of different intervals. For instance, the minimum (1 min)/minimum (1 s) ratios can be as high as $4.40\text{E}+04$ (Exp. no. 2). From these results, it can be concluded that the changes in the Hg behavior over a very short-term interval can be a highly significant process of Hg cycling.

In fact, an instant, but large-scale, fluctuation in Hg data (such as 5–10 fold shift) was observed commonly during a single experiment. This type of change, if occurring, generally lasted for 10 s–1 min; for instance, on 17th Sept., Hg concentrations changed abruptly from 7.82 (at 15:00:46) to 33.8 ng m^{-3} (at 15:00:47), and this enhanced level lasted till 15:01:30. Its concentration again dropped slowly to the value of around 10 ng m^{-3} at 15:01:34. Results of previous studies generally indicated that Hg concentration over a clean background soils are low and can vary within a very narrow band (Kim et al., 1995). However, such a pattern contrasted with that found from relatively polluted environments; under such conditions, Hg data generally exhibited large mean values with strong variations (Lindberg et al., 1995). The cause of such large variability in Hg distribution patterns has often been ascribed to certain factors such as source variation (e.g., reflected as wind-driven effect); the changes in Hg concentration can be tightly bound with the changes in wind direction (Lindberg et al., 1995). The pattern of strong fluctuations found in the present study may thus actually represent the potent roles of instantaneous processes such as volatilization from surrounding surfaces, occasional transport of Hg-rich air from source regions, chemical conversion, and surface deposition (e.g., Lindberg et al., 1995). Because our analyses are based on considerably short measurement intervals of 1 s, explanations for the observed patterns in this study cannot simply or directly be compared with those of previous studies based on

traditional method at measurement intervals of 15 min–1 h (e.g., Kim and Kim, 2001a,b).

The effect of selecting different measurement intervals on Hg monitoring was also examined in terms of correlation analysis (Table 4). The existence of correlations was examined between different statistical terms for each experiment (such as mean, median, min, and max). The results indicate that a strong correlation exists in the case of mean values, while such patterns are not so evident in minimum concentration data sets. Although significant differences in minimum concentration values (the weakest for 1-s data) were observed, the results for the other parameters were generally found to exhibit strong correlations with each other. In addition, it should be pointed that in compliance with the general expectation the strength of correlations between different parameters generally increases with extended measurement intervals for Hg (Table 4).

3.3. The signature of Hg temporal trends

As our measurements were made throughout a 3-month period (September–November 2003), the possible influence of seasonal factors on Hg distribution can be examined briefly. The concentration of Hg is found to have consistently decreased across those 3 months (Fig. 1). The observed temporal pattern may be explained partially by a moderate increase in Hg emissions during the first 2 months (a relatively warm period). Similar patterns of Hg distribution were commonly observed in previous studies (Tennessee, US: Kim et al., 1995). This is probably due to the influence of local Hg sources and their dependence on the air and soil temperature, such as enhanced Hg evasion under relatively high temperature conditions (Gustin et al., 2002). In addition, there is some possibility that construction activities at the monitoring site (during the early study period) might have facilitated Hg emissions leading to an increase in Hg concentration levels.

During the study period, the most extensive monitoring (in terms of the total duration) was made for the 8th experiment, which ran for four consecutive days (on 30/9–3/10). Hence, these data were analyzed to explore the diurnal variations of Hg (Fig. 4). If evaluated on a daily basis, patterns differed moderately across these days. It indicates that temporal patterns on the second day (30 September) were fairly constant throughout the

Table 4
Results of correlation analysis between various statistical parameters of Hg data sets; this comparison was made for the whole data groups representing each of the three different data collection intervals (1 s, 10 s, and 1 min)

	1 s-based data sets						10 s-based data sets						1 min-based data sets					
	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max		
	<i>r</i> ^a	1	0.91 ^{IIIb}	0.30 ^I	0.82 ^{III}	0.97 ^{III}	0.88 ^{III}	0.05	0.79 ^I	0.97 ^{III}	1.0 ^{III}	0.19	0.80 ^{III}	0.97 ^{III}	1.0 ^{III}	0.19	0.80 ^{III}	
<i>P</i>		1.24 E-20	2.60E-02	1.25E-20	1.25E-20	1.25E-20	8.17E-01	1.00E-03	1.25E-20	1.25E-20	3.65E-01	1.25E-20	1.25E-20	1.25E-20	3.65E-01	1.25E-20		
<i>N</i>		24	24	24	24	24	24	24	24	24	24	24	24	24	24	24		
Median		1	0.52 ^I	0.35	0.91 ^{III}	0.97 ^{III}	0.51	0.47	0.91 ^{III}	0.96 ^{III}	0.26	0.41	0.92 ^{III}	0.96 ^{III}	0.26	0.41		
<i>P</i>			9.00E-03	9.70E-02	1.25E-20	1.25E-20	4.97E-01	2.10E-02	1.25E-20	1.25E-20	2.19E-01	4.50E-02	1.25E-20	1.25E-20	2.19E-01	4.50E-02		
<i>N</i>			24	24	24	24	24	24	24	24	24	24	24	24	24	24		
Min			1	0.1	0.4	0.51	-0.08	0.28	0.4	0.51	-0.04	0.18	0.45	0.51	-0.04	0.18		
<i>P</i>				6.29E-01	5.30E-02	1.00E-02	7.09E-01	1.80E-01	5.30E-02	1.10E-02	8.58E-01	4.07E-01	2.70E-02	1.10E-02	8.58E-01	4.07E-01		
<i>N</i>				24	24	24	24	24	24	24	24	24	24	24	24	24		
Max				1	0.79 ^{III}	0.31	-0.001	0.92 ^{III}	0.79 ^{III}	0.3	0.21	0.90 ^{III}	0.77 ^{III}	0.3	0.21	0.90 ^{III}		
<i>P</i>					1.25E-20	1.37E-01	9.98E-01	1.25E-20	1.25E-20	1.57E-01	3.22E-01	1.25E-20	1.25E-20	1.57E-01	3.22E-01	1.25E-20		
<i>N</i>					24	24	24	24	24	24	24	24	24	24	24	24		
10 s-based data sets																		
Mean					1	0.92 ^{III}	0.078	0.54 ^I	1	0.95 ^{III}	0.2	0.76 ^{III}	0.95 ^{III}	0.90 ^{III}	0.2	0.76 ^{III}		
<i>P</i>						1.25E-20	7.18E-01	6.00E-03		1.25E-20	3.52E-01	1.25E-20	1.25E-20	1.25E-20	3.52E-01	1.25E-20		
<i>N</i>						24	24	24		24	24	24	24	24	24	24		
Median					1	1	0.16	0.45	1	0.89 ^{III}	0.26	0.38	0.89 ^{III}	0.95 ^{III}	0.26	0.38		
<i>P</i>							4.70E-01	2.80E-02		1.25E-20	2.12E-01	7.00E-02	1.25E-20	1.25E-20	2.12E-01	7.00E-02		
<i>N</i>							24	24		24	24	24	24	24	24	24		
Min							1	-0.07		0.05	0.71 ^{III}	0.05	0.11	0.71 ^{III}	0.05	0.05		
<i>P</i>								5.57E-03		1.14E-15	1.25E-20	8.04E-01	1.25E-20	1.25E-20	1.25E-20	8.04E-01		
<i>N</i>								24		24	24	24	24	24	24	24		
Max								1		0.72 ^I	0.18	0.65 ^I	0.44	0.44	0.18	0.65 ^I		
<i>P</i>										1.00E-03	4.02E-01	1.00E-03	3.30E-02	4.02E-01	1.00E-03	1.00E-03		
<i>N</i>										24	24	24	24	24	24	24		
1 min based data sets																		
Mean										1	0.19	0.79 ^{III}	1	0.94 ^{III}	0.19	0.79 ^{III}		
<i>P</i>											3.77E-01	1.25E-20	1.25E-20	3.77E-01	1.25E-20	1.25E-20		
<i>N</i>											24	24	24	24	24	24		
Median											0.6	0.36	1	0.6	0.36	0.36		
<i>P</i>											3.50E-01	8.20E-02	3.50E-01	8.20E-02	8.20E-02	8.20E-02		
<i>N</i>											24	24	24	24	24	24		
Min											1	0.27	1	0.27	0.27	0.27		
<i>P</i>												2.52E-01				2.52E-01		
<i>N</i>												24				24		

^a*r* and *P* denote correlation coefficient and probability of no correlation, respectively.

^bSuperscripts I, II, and III denote *P* values < 10⁻², 10⁻³, and 10⁻⁴, respectively.

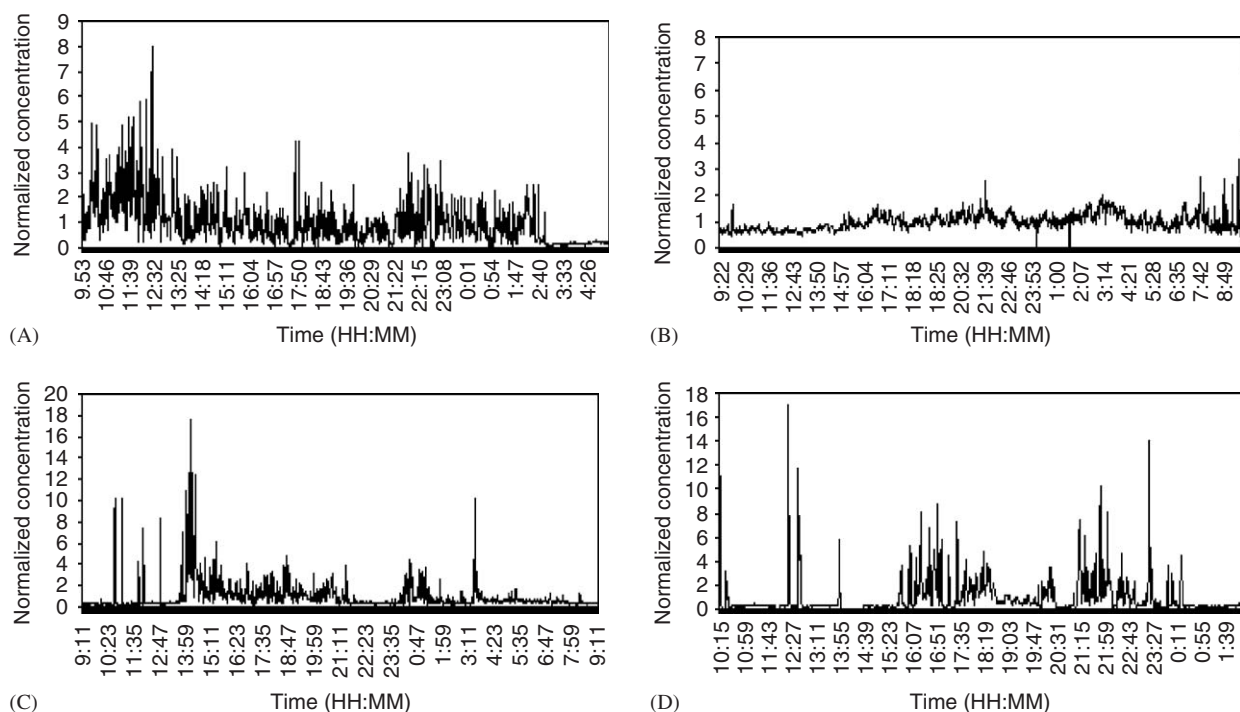


Fig. 4. Diurnal variabilities of Hg concentration data are examined using the mean values for 1-min intervals. The Hg data obtained continuously over 4 days periods (the 8th experiment: 29 September–2 October) were used for comparison. To minimize absolute concentration differences among different dates, all measurement data for each day were normalized by their respective daily mean values: (A) 29th September, (B) 30th September, (C) 1st October, and (D) 2nd October.

day. However, the results for the other days were quite variable with the occurrences of distinctive peak concentrations during certain period of the day; the peaks were observed during either early (11:00–12:00 on 29 September) or late afternoon (14:00–18:00 on 1 and 2 October). In fact, it was found that large-scale fluctuations in Hg concentration levels tend to occur during most of the daytime period with a continuous rise and fall within a matter of a few tens of seconds. Because of such variability, our examination of diurnal pattern was made using minute-based mean Hg values obtained throughout the whole 8th experiment.

The observations of remarkable diurnal periodicity between very high (during late afternoon) and low values (during early morning hours) suggest the possible influence of local diffuse emission of Hg. If air masses containing Hg are transported from a medium- or long-range distance, they are less likely to show such a stable pattern over a 24 h scale (Schmolke et al., 1999). In some studies, the peak Hg values were also observed during the daytime. The Hg measurements made in 10 rural sites across Canada (1997–1999) showed that seven of them

experienced a cyclic pattern with a maximum near solar noon (10:00–14:00 local standard time) and a minimum in the early morning (03:00–07:00) (Kellerhals et al., 2003). The continuous increase in Hg values from the morning into the early afternoon is likely to come from surface emission of Hg, affected by increasing solar radiation (Poissant and Casimir, 1998). The results of the extended monitoring study (Exp. no. 8) also indicated that the Hg levels tend to be at its lowest level during early morning hours (Fig. 4). On the 2nd of October, a sudden increase in Hg levels was observed abruptly from 2.1 (at 8:31:57) to 17.3 ng m^{-3} (at 8:32:09).

During the daytime, the enhancement of Hg levels must have been favored by strong sunlight, which may have facilitated the emission of Hg from soil. Gustin et al. (2002) reported that light is a dominant factor controlling Hg emissions from various substrates. The response of Hg flux to fluctuations in incident radiation is immediate and continuous over time. According to their regression analyses between in-situ Hg fluxes and light (and

temperature), light was found to be more important in controlling Hg emissions. These authors reported that the magnitude of light-enhanced emissions from natural substrates is 1.5–116 times higher than those measured in the dark under the same substrate temperature.

4. Conclusions

In order to examine the environmental behavior of Hg at varying time scales, Hg concentrations were measured at 1-s intervals using a rapid Hg monitoring system introduced by the Lumex. The results of the present study generally indicate that the temporal distribution of Hg can exhibit highly variable patterns in relation with monitoring intervals. The variation in ambient Hg levels was evident when the patterns were examined in terms of second intervals, which otherwise were not evident at hourly intervals.

In this study, sharp changes in Hg concentration levels were observed for a very short time duration (e.g., less than a few tens of seconds to a minute). During the period of such dramatic shift, a five- to ten-fold increase in Hg concentrations was routinely monitored. The occurrences of such sharp changes were seen almost consistently throughout the entire study period. These observations thus suggest a release of air containing a high quantity of Hg in batches which were dispersed immediately in the atmosphere (after its emission from its source(s)). After a few seconds of these events, the ambient concentration of Hg can again return to its previous level. In addition, the frequent occurrences of relatively high Hg concentrations during early (or late) afternoon period support the potential role of light (and temperature) in controlling Hg levels.

The frequency distribution pattern of Hg data sets showed that Hg data can occur most frequently at both low ($< 5 \text{ ng m}^{-3}$) and high concentration ranges ($> 10 \text{ ng m}^{-3}$), regardless of measurement intervals (1 s, 10 s, and 1 min). A series of the experiments made during the entire study period showed that the common values of Hg concentrations observed from the measurement site approached approximately 5 ng m^{-3} , as a good analogue to those reported previously from a number of urban locations in Korea. The measurement data made by the new Hg instrument (RA+915) assure the possibility that its performance can be as reasonable as the traditional one (e.g., CVAAS) in the application of ambient Hg

monitoring. Overall, the results of this investigation clearly indicate that Hg concentration changes over short-term intervals can be extremely diverse in relation with the highly dynamic nature of various source processes.

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