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PRELIMINARY MEASUREMENTS OF ATMOSPHERIC MERCURY IN MOUNTAINOUS REGIONS OF KOREA

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= Abstract =

We conducted preliminary measurements of airborne Hg concentrations from 13 remote mountainous sampling stations located in the Republic of Korea during the periods covering October 1987 through February 1993. The concentrations of atmospheric Hg determined from our field campaigns were found in the range of 1.48 to 8.00 ng m^{-3} with the dominant portions of them spanning between 2 to 5 ng m^{-3} (78%): the mean and 1SD for the whole data sets were 3.99±1.46 ng m^{-3}(N=32). When compared to a few datapoints reported previously for similar regions, the generally enhanced Hg levels and the wide spreadness of such trend suggest that Hg pollution in the Korean atmosphere may be a significant process. The results of correlation analysis between Hg concentrations and the simultaneously measured environmental parameters(which include: air temperature, RH, pressure, and wind speed) indicated several interesting features of its distribution behavior. Although the measured Hg levels were found to be weakly correlated with such important variable as temperature($r=0.2429$, $P < 0.20$, N=32), pressure exhibited a significant correlation with the Hg data($r=0.3654$, $P < 0.05$, N=32). This finding suggests that pressure, rather than temperature, may exert more sensitive influences on the Hg distribution at high altitudes.

INTRODUCTION

The important role of atmospheric Hg cycling is well recognized with progressive advances achieved in the determination of mercury (Hg) species in diverse environmental media.[1] In line with a growing recognition of its environmental significance, the frequency with which

measurements of airborne Hg concentrations and the associated upward/downward fluxes are made has been notably increasing over the past several years.[2,3] Although atmospheric Hg data are rich in quantity relative to other metal species of environmental interest, most of pre-existing ones are geographically confined to certain localities of the world such as western Europe and North America.[2,4] In turn, these limitations in database remain as one of the major obstacles to the accurate assessments of its global geochemical budget.[5]

With public's growing alertness to the environmental consequences of pollution, the distribution and behavior of various toxic air pollutants including a number of metal species became the common subjects of various research. Among a number of regions in the world, the Pacific rim (including China, Japan, and Korea) is well known for its rapid industrialization in concert with its contributions to the global budgets of major atmospheric pollutants.[6] Nevertheless, data for toxic pollutant species in background atmosphere of Pacific rim region is extremely scarce.

With this respect, Hg appears to be one of the poorest measured species, for most of previous studies were conducted under the urban atmospheres wherein its detection is unlikely to be restricted by the instruments.[7,8] Hence, extension of reliable Hg database in this region of the world is considered to be of urgent task.

In an effort to provide a basis for establishing the nationwide background concentrations of airborne Hg within Korea and to collaborate the extension of its database worldwide, we designed and performed preliminary measurements of Hg concentrations under background atmosphere of Korea. To this end, the concentrations of atmospheric Hg were analyzed from 13 remotely located mountainous sampling sites in various locations of Korea for the periods covering October 1987 through February 1993. Using our preliminary measurement data, the fundamental factors underlying geographical variabilities in the distribution of atmospheric Hg have been examined.

EXPERIMENTAL

All of our measurements were conducted from sampling stations located in the 13 individual mountainous sites of Korea, most of which are relatively well preserved as the National Parks. The geographical location and information concerning each study site are given in Figure 1 and Table 1.

The concentrations of atmospheric Hg were determined by sampling from a series of field trip and by the following laboratory analysis. We did our field trip for the measurements at intervals of one to two times per month basis, and each of our study sites was investigated during one field trip with a duration of one to two day periods. For each site investigated, field experiments were routinely conducted as a series of two to three consecutive runs.

Fig. 1. The locations of 13 individual sampling stations. Information of each station are provided in Table 1.

Table 1. Information of the 13 sampling stations investigated.

Station No.	Location	Elevation (m)	Time (Month/Year)
1*	So-Baik Mt.	1439	10/87
2	Kwan-Ak Mt.	600	10/87
3*	Do-Bong Mt.	716	11/87
4*	Sok-Ri Mt.	1029	1/88
5*	Nae-Jang Mt.	504	1/88
6*	Gye-Ryung Mt.	750	2/88
7*	Wall-Ak Mt.	1097	4/88
8*	Seorak Mt.	1708	6/88
9	Nam Mt.	232	6/88
10*	Ji-Ri Mt.	1915	10/88
11*	Oh-Dae Mt.	1563	11/88
12*	Ka-Ya Mt.	1430	12/92
13*	Chi-Ak Mt.	1248	2/93

* denotes National Park of Korea.

The procedures used in the determination of Hg vapor closely follow those used in previous studies of Kim et al.[7,8]: (1) preconcentration of vapor-phase Hg on traps filled with #32 mesh-sized, gold-coated Chromosorb P(AW) and (2) detection of the thermally desorbed Hg by cold-vapor atomic absorption spectrophotometry (CVAAS). For each field experiment, the air stream was drawn into the replicate Hg-collection traps at flow rates of approximately 1,000 cm^3 min^{-1} for sampling periods of 1 to 3 hr. The total amount of gaseous Hg was determined using the two-stage Au amalgamation gas-flow technique[9] which requires an 'analytical' amalgamation trap in addition to the field-sampling amalgamation trap. The wide use of this technique has been attributed to its effectiveness in separating interfering substances from Hg before its release to the detection system.[10] Because our field amalgamation trap collects total gaseous Hg, which exists predominantly (e.g., > 95%) in its elemental form,[11] the Hg collected will be referred hereafter as Hg°.

Laboratory analysis of the Hg° contained in each field sampling trap was performed in the following sequence: (1) thermal desorption of Hg° from the field trap (at 450℃), (2) retrapping of Hg° by an analytical trap, (3) thermal desorption of Hg° from the analytical trap, and (4) detection of Hg° by the CVAAS system. The analytical system was standardized by measuring known volumes of a Hg-saturated atmosphere via an airtight gas syringe.[12] The precision of our CVAAS system in analyzing replicate air samples was tested via calibration from multiple injections of Hg°-saturated standard air sample. The level of precision, if expressed in terms of relative standard error (RSE = standard error (SE)/mean), generally fell in the range of 0.4 to 2.0% with a mean of 0.8%. The working detection limit for the system is determined to be approximately 10 pg of Hg° (calculated as 3 standard deviation (SD) of typical gold trap blanks).

RESULTS AND DISCUSSION

The concentrations of atmospheric Hg measured during our field campaigns were found in the range of 1.48 to 8.00 ng m^{-3} (N=32) with a mean and 1 SD of 3.99±1.46 ng m^{-3}. Although more than 100 datapoints were obtained originally, we had to screen out dominant portions of our data for their high blank-to-sample (B/S) ratios. (We suspect the causes of such undesirable incidence to be the inexperience in field work at the initial stage and significantly reduced sensitivity of our instrumental system at the later stage.)

Upon screening out the data with the B/S ratio of above 0.2, 32 datapoints remained. Hence, we had to confine our interpretation of Hg distribution behavior to these 32 datapoints. As shown in the frequency plot for all of these data sets, a relatively wide scattering of Hg concentrations occurred (Figure 2). However, most of datapoints were found at concentrations in between 2 to 5 ng m^{-3} (78%).

To offer some insights into the distribution behavior of Hg, our data for the Hg concentrations in background air are compared with previously reported Hg concentrations in the Korean peninsula (Table 2). The levels of Hg found in our study are several times lower than the

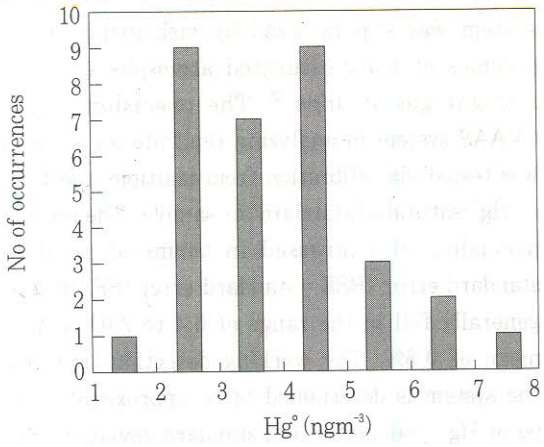

Fig. 2. Frequency plot of atmospheric Hg concentrations measured during our field campaign periods.

concentrations typically observed in urban atmospheres of Korea: through an extensive survey of Hg concentrations in Seoul metropolitan area(SMA), Kim et al.[8] found the concentrations of Hg to range from 4.73 to 112.8 ng m^{-3} with a mean of 14.7 ng m^{-3} (N=2513). In fact, the upper bound concentrations measured in our study(i.e., in the range of 5 to 8 ng m^{-3})are quite comparable to those previously measured in suburban areas of Korea[7]: they reported a mean and 1SD value of 5.91±1.26 ng m^{-3}(range: 3.63 to 11.28 ng m^{-3})from 140 measurements made in a suburban area surrounding the SMA.

Among others, the most meaningful comparison for our current data sets can be made with previous results of Sohn et al.[13] in which a few data for the background Hg concentrations were acquired. They were able to measure Hg concentrations from several spots of Mt. Seorak at the range of 0.7 to 1.8 with a mean of 1.2 ng m^{-3} (N=4). Interestingly, the site investigated by Sohn et al.[13] coincided with one of our sampling stations. By simple comparison of the data sets between the two studies (in terms of absolute magnitude), we can see that their values are approximately three-fold lower than our values.

The magnitude of previously measured data appear to be even lower than those typically reported as background concentratons of Europe or N. America.[2] However, the validity of the data reported by Sohn et al. is somewhat under question, as they might have suffered from similar sensitivity problems we experienced. With a lack of measurements over longer time scale and many uncertainties involved in previously measured data, it is difficult to derive meaningful interpretations for temporal trends in the distribution of Hg. However, our findings of the generally enhanced Hg levels (relative to previous

Table 2. A comparison of previously measured airborne Hg concentrations in urban and suburban atmospheres of Korea.

Location	Mean±1 SD (ng m^{-3})	Range	N	Time	Source
		A. Nonurban Atmosphere			
13 Mountainous Stations	4.47±1.82	1.48-8.77	32	10/87-2/93	ThisStudy
Seorak Mt.	1.20	0.7-1.80	4	8/85	(1)
Seoul Park (Kwa Chun)	5.91±1.26	3.63-11.28	140	8/87	(2)
		B. Urban Atmosphere			
Han Nam Dong (Seoul)	14.7	4.73-112.8	2513	8/87-10/88	(3)
Olympic Park	13.4±5.9	6.5-36.7	196	8/88	(3)
Olympic Park	8.2±2.79	4.4-23.7	194	9/88	(3)
Sports Complex	6.3±1.5	2.9-13.8	165	8/88	(3)
Sports Complex	7.7±2.93	4.4-25.5	190	9/88	(3)
Guro Industrial Complex	14.0±6.8	6.2-43.7	190	10/88	(3)

Sources: (1) Sohn et al.[13]; (2) Kim et al.[7]; (3) Kim et al.[8]

measured data) in concert with the wide spreadness of such trend suggest that Hg pollution in the Korean atmosphere may be a significant process.

To explore the mechanisms controlling the geographical variabilit-ies in Hg distribution, we examined relationships between Hg concentrations and the simultaneously measured environmental parameters (which include: air temperature, RH, pressure, and wind speed). The results of this analysis showed generally insignificant correlations between variables and the Hg content. While temperature is well-known for its correlation with the Hg concentration,[14] such correlation was found to be relatively insignificant from our data ($r=0.2429$, $P< 0.2$, $N=32$).

Instead, the best correlation was found in between pressure and airborne Hg levels ($r=0.3654$, $P < 0.05$, $N=32$: see Figure 3). Although it may not be directly relevant, there were some indications for the significant role of pressure in regulating Hg levels: Klusman and his colleagues have found that the barometric pressure was inversely correlated with the rate of Hg emissions.[14] However, this finding suggests that pressure, rather than temperature, may exert more sensitive influences on the Hg distribution at high altitudes.

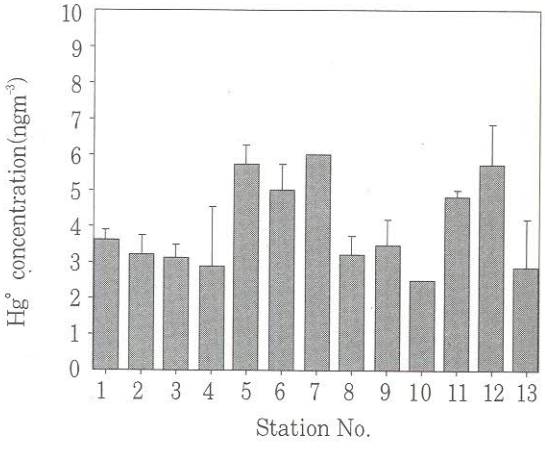

Fig. 3. The concentrations of atmospheric Hg determined from 13 individual sampling stations during October 1991 through December 1992. Error bars represent 1 standard errors for the mean values.

As explained above, we were able to make preliminary measurements of Hg concentratons in some remote locations of Korea. Although these data provide some fundamental features for Hg distribution behavior under the Korean atmosphere, we were confronted by significant analytical problems. Prior to the extention of Hg database over longer time scale or over wider areal scale, we strongly feel to improve our measurement techniques to obtain more reliable data for generally reduced Hg levels in the background environment.

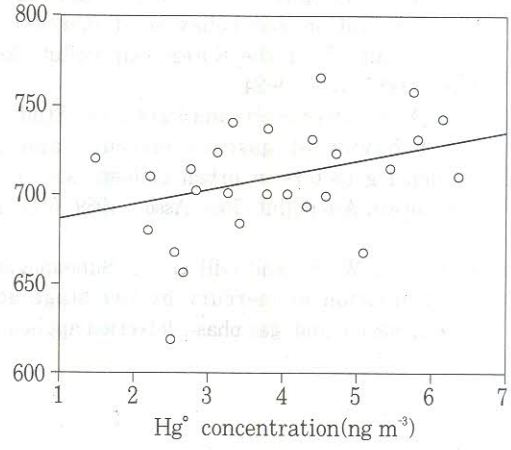

Fig. 4. Relationship between atmospheric Hg concentration and pressure.

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