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Mercury Concentration in Urban and Rural Atmospheres of Korea

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Abstract

The distribution of airborne mercury was investigated from several districts of Seoul, five other major cities and two rural areas during the period April, 1994 to March, 1995. The method used in this study involves absorption of gaseous mercury on Chromosorb^R A coated with gold and detection by cold vapor atomic absorption spectroscopy. The atmospheric mercury concentrations in Seoul ranged from N.D. to 120.17 ng m^{-3} (mean 27.01 ± 9.42 ng m^{-3}, N=139), while those in rural areas ranged from 1.72 to 8.24 ng m^{-3} (mean 4.57 ± 3.07 ng m^{-3}, N=5). The spatial distribution characteristics of mercury distribution in urban air were examined by comparing mercury levels as a function of the distance from the urban center. Temporal distribution trends of airborne mercury were also studied using the monthly mean mercury data of various districts in Seoul. The atmospheric mercury concentration around Mokdong wastes incinerator in Seoul were also investigated.

Key words : Total mercury; atmosphere; Seoul; rural; variation; gold amalgamation; AAS

INTRODUCTION

It is well known that mercury can be easily emitted into atmosphere due to its substantially high volatility. Environemntal mercury origins from both natural and anthropogenic sources. The major natural sources of mercury include both oceanic and terrestrial environments (Mason *et al.*, 1994). The anthropogenic sources that are estimated to reach about 75% of global mercury budget include: the burning of fossil fuels, discharges from power plants, paints, pesticides, batteries, lamps, mining, smelting and so on (Japanese Association of Chemistry, 1977). The amount of mercury discharged from human activities has been estimated to reach about 6,000-7,500 tons per year worldwide (Mason *et al.*, 1994). On account of the high volatilities of mercury compounds, most of mercury discharged is considered to remain in gaseous form in the atmosphere. The primary forms of interest are dimethyl mercury and elemental mercury. Only several percent of the total mercury from a point emission source deposit in its neighboring areas, while most of those released are dispersed over long distance.

During the past decades, large quantities of mercury have been consumed in Korea and released into the environment. We previously reported the amount of mercury released from fossil fuel combustion (Sohn, 1982a), mercury concentrations in biological samples (Sohn *et al.*, 1981, 1982b), background levels of mercury in soil (Sohn, 1979) and riverine environments in Korea (Sohn *et al.*, 1988). We have reported that results of airborn mercury during 1988~89 elsewhere (Sohn *et al.*, 1993). In this study, we conducted measurements of the atmospheric mercury concentrations in Seoul using atomic absorption spectrometry (Slemer *et al.*, 1979). In our continuing efforts of mer-

cury research, our data collected during April, 1994~March, 1995 are described in this paper.

MATERIALS AND METHODS

Equipment Air samples were collected using a sampling device which is independent from the analytical system. The ambient air was drawn into amalgamation trap by a suction pump. Our sampling trap was prepared as follows: Chromosorb^R A (40~60 mesh, Sigma, USA) was mixed with $HAuCl_4 \cdot 4H_2O$ (Wako Pure Chem., Ltd., Japan) at a weight ratio of 100:1. This mixture was then dried on a sand bath. Upon drying, gold was coated on the particles by heating at 800°C. This absorbent material was packed in a Pyrex tube (6 mm i.d. X 130 mm L.) and stoppered up with quartz wool. Prior to sample collection, the sampling tube was cleaned by heating at 800°C with a mercury-free air stream for 3~5 min to eliminate any source of contamination. This procedure ensured that blank was nearly zero. The openings of this pretreated sampling traps were sealed air-tight from both ends using Teflon^R film. For collecting the ambient air, the sampl-

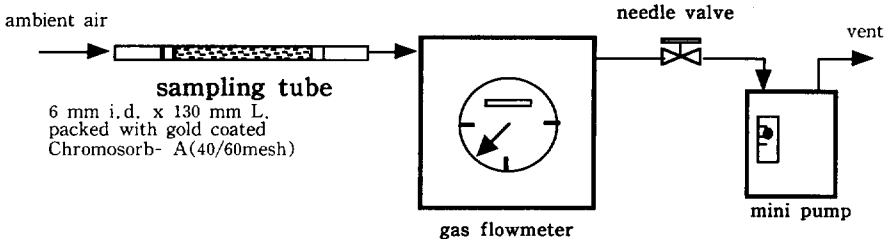

Fig. 1. Field sampling tube and an apparatus for atmospheric mercury determination.

Table 1. Time and place of ambient air sampling for mercury analysis.

Area	Radius*	Sampling stations	Sampling period	No. of samples	Sampling duration	Remarks
Seoul	5 km	Chongro 5-ga	April 19, 1994-Mar. 9, 1995	11	2-3	
		Chongyangri	April 19, 1994-Mar. 10, 1995	12	2-3	
	10 km	Kuro-dong	April 18, 1994-Mar. 5, 1995	12	2-3	to examine
		Kangnam	April 18, 1994-Mar. 9, 1995	12	2-3	mercury
		Chungang Univ	April 20, 1994-Mar. 12, 1995	15	2-4	distribution
	15 km	Bulkwang-dong	April 22, 1994-Mar. 12, 1995	11	2-3	as a function of
		Sillim-dong	April 20, 1994-Mar. 11, 1995	17	2-5	radial distance
		Konghang-dong	April 21, 1994-Mar. 11, 1995	17	2-4	
		Jungke-dong	April 21, 1994-Mar. 12, 1995	12	2-4	
		Mok-dong	Oct. 17, 1995-Oct. 21, 1995	10	2-3	around the
		Dangsan-dong	Oct. 17, 1995-Oct. 21, 1995	5	2-3	wastes
		Sillim-dong	Oct. 17, 1995-Oct. 21, 1995	5	2-3	incinerator
Other major cities		Daegu	Sept. 18, 1994-Sept. 19, 1994	3	3-4	For the
		Chuncheon	April 15, 1995-April 20, 1995	3	2-3	comparison
		Jeonju	April 6, 1995	1	2-3	with Seoul
		Iksan	Mar. 25, 1995	1	3	metropolitan
		Daejeon	May 4, 1995-May 5, 1995	2	3	area
Rural		Yangyang	Oct. 17, 1995-Oct. 21, 1995	3	14	background
		Yongin	Oct. 17, 1995-Oct. 21, 1995	2	6-8	

*Radius is the lineal distance from the center of the city; Kwanghwamun.

ing tube was connected to a gas-flow meter (NWK-1A, Shinagawa Seiki, Japan) and mini air pump (MP50-NC, MP-30CF, Shibata, Japan) as shown in Fig. 1. The flow rate was adjusted at 1.0 l/min and sampling was conducted for the total duration of 2 to 14 hrs depending on locations and their concentration of mercury.

Sampling During April, 1994 to March, 1995, ambient air was sampled at 9 sampling stations in Seoul. Sampling stations are classified into 3 groups: (1) within a radius of 5 km, (2) 10 km and (3) 15 km from the center of the city (Kwanghwamun). Sampling at Mokdong wastes' incinerator was also carried out for comparative purpose. Two rural areas and five major cities in Korea were also investigated. Table 1 shows the information of when and where sampling was made.

A map of the sampling stations is illustrated in Fig. 2.

Analysis Our analytical system for mercury analysis consists basically of a heating vaporization apparatus and atomic absorption spectrometer. Upon the completion of air sampling, the sampling tube was immediately detached from the sampling devive and sealed air-tight. For laboratory analysis, the tube was opened and connected to the analytical system. The tube was then inserted into the heating vaporization furnace and connected to a mercury-free air supplying system wherein mercury is desorbed by heating at 800°C for 3 min. The mercury vapor was then conveyed to the sam-

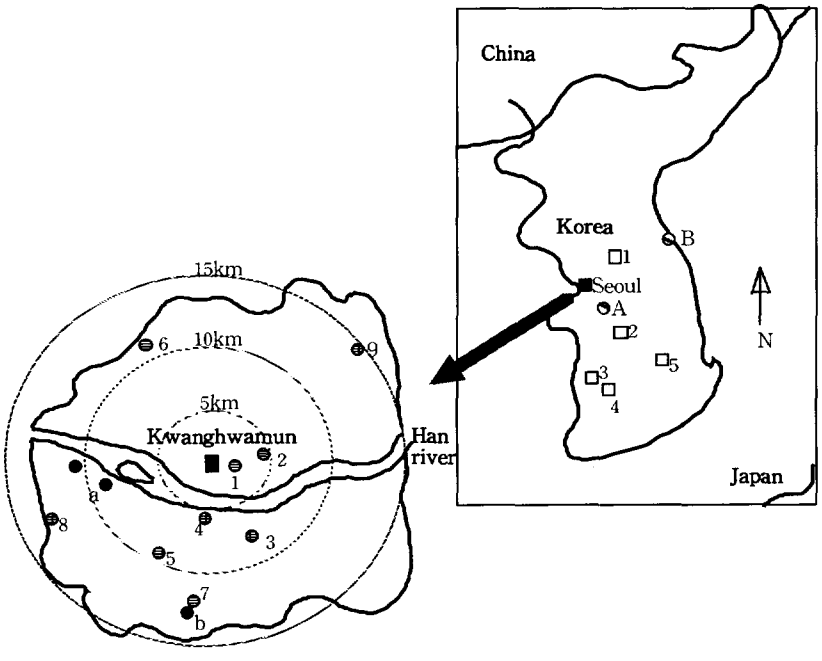

Fig. 2. A Map showing sampling stations.

■ Seoul ▦ other major cities; 1. Chuncheon, 2. Daejeon, 3. Iksan, 4. Jeonju 5. Daegu

⊘ rural area; A. Yongin, B. Yangyang

■ the center of Seoul (Kwanghwamun)

⊖ sampling points; 1. Chongro 5-ga, 2. Chongyangri, 3. Kangnam, 4. Chungang Univ., 5. Kuro-dong, 6. Bulkwang-dong, 7. Sillim-dong, 8. Konghang-dong, 9. Jungke-dong

● Mok-dong (near waste incinerator)

● comparison with wastes' incinerator; a. Dangsan-dong, b. Sillim-dong

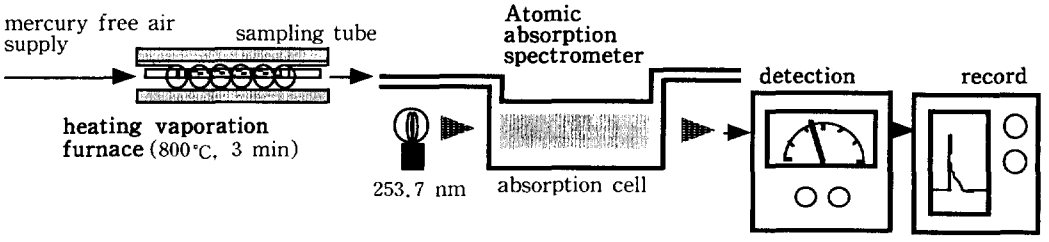

Fig. 3. A Diagram of heating vaporation system for mercury analysis using flameless cold-vapor atomic absorption spectrometry.

ple cell and measured by an atomic absorption spectrometer (MV-253, Beckman-Toshiba). A block diagram of the apparatus is shown in Fig. 3.

Assuming mercury vapor behaves like an ideal gas, we calibtated our system by injecting known amounts of mercury-saturated air onto a gas collecting system. Mercury-free air was filled in a gas collector and mercury was saturated at 24.2°C. This standard gas 0.1 ml (equivalent to 1.861 ng of mercury), 0.2 ml, 0.4 ml, 0.8 ml each was taken by gas-tight syringe and injected to the analytical device. The calibration curve was linearly constructed as $Y=3.069X+0.151$ ($\gamma=0.999$) from the amount injected and the response obtained (peak height). This sytem showed detection limit of mercury, 1.861 ng. The method to obtain this detection limit was according to our previous report (Fujita *et al.*, 1991). The detection limits of atmospheric mercury by this method were 2.21 ng m^{-3} (14 hrs' air sampling) to 15.5 ng m^{-3} (2 hrs' air sampling).

RESULTS AND DISCUSSION

Mercury in Rural Air as an Indicator of Back-ground Concentration In an effort to assess atmospheric mercury concentrations in background air, measurement were made from two rural sites. The results show ambient concentrations in the range of 1.72~8.24 ng m^{-3}. The average level of mercury is approximately 4.57±3.07 ng m^{-3} as shown in Table 2. Yongin showed comparably higher concentrations than those of Yangyang due to more anthropogenic sources. This average value seems remarkably consistent with the background levels of 1.0~5.0 ng m^{-3} reported by other researchers (Slemr *et al.*, 1979, Williston, 1978, Thrane, 1977) but higher than 2.0 ng m^{-3} which is accepted as precise worldwide background.

Atmospheric Mercury in Seoul Area Nine sampling stations in Seoul area were investigated. These stations were divided into 3 groups, each of which consist of three sampling stations. These stations were grouped as a function of their distance from the center of the city: wit-hin a radius of 5 km, 10 km and 15 km. A total of 119 samples were collected from April, 1994 to March, 1995. The results are summarized in Table 3.

The mean concentration of atmospheric mercury in Seoul area was 27.01±9.42 ng m^{-3} with the range of N.D. ~120.17 ng m^{-3}. This level is about the same or a little higher than our pre-

Table 2. Atmospheric mercury concentrations in rural areas.

Sampling point	Province	Temperature (°C)	Mercury concentration (ng m^{-3}) Mean±S.D.	Range
Yangyang	Kangwon	-11.6~1.3	2.35±0.46	1.72~2.81
Yongin	Kyungki	-1.5~0.3	7.88±0.35	7.53~8.24
	General mean		4.57±3.07 ng m^{-3}	

Sampling was carried out 2~3 times at each point.

Table 3. Atmospheric mercury concentrations in Seoul area.

Radius (km)	Sampling point	Temperature (°C) range	Mercury concentration (ng m^{-3}) Mean±S.D.	Range
5 km	Chongro 5-ga	−0.9~+37.5	36.62±19.31	18.10~ 78.05
	Chongyangri	−4.5~+35.3	25.28±16.51	9.70~ 67.37
10 km	Kuro-dong	−3.2~+33.5	18.78± 5.53	8.31~ 27.20
	Kangnam	−2.5~+36.7	34.21±22.33	13.41~ 81.56
	Chungang Univ	+1.5~+28.9	31.97±11.30	N.D. ~ 66.51
15 km	Bulkwang-dong	+2.1~+32.5	23.86±11.46	N.D. ~ 48.58
	Sillim-dong	−1.5~+38.7	32.28±29.64	11.36~ 120.17
	Konghang-dong	−2.4~+29.4	23.71± 8.18	9.25~ 39.92
	Jungke-dong	−2.4~+33.0	16.35± 5.86	8.75~ 30.33
		General mean	27.01±9.42 ng m^{-3}	N.D. ~120.17

vious measurment data during 1988~1989 (mean 25.10 ng m^{-3} Sohn *et al.*, 1993) and than a typical urban concentration of about 22 ng.m^{-3} (range 5.0~60.0 ng m^{-3} in Chicago: Wroblewski *et al.*, 1974). Our data indicate that mercury concentrations tend to decrease with increasing distance from the center of city (Fig. 4). The mean mercury concentrations for the above three groups decreased on the order: 30.95±5.67 ng m^{-3} (5 km), 28.21±6.80 ng m^{-3} (10 km) and 24.05±5.63 ng m^{-3} (15 km).

Monthly Variation in Atmospheric Mercury Concentration Fig. 5 shows the monthly variation of atmospheric mercury from nine sampling stations. From April to August, 1994, the concentration reached the maxima in compliance with the temperature rise and decreased thereafter. From these results, it can be interpreted that temperature is a major factor influencing the atmospheric mercury concentration as we previously reported the existence of strong correlation between atmospheric mercury and temperature (Sohn *et al.*, 1993).

Regional Differences in Mercury Distribution Behavior To investigate the regional differences in atmospheric mercury concentration, our data were divided into several categories; farmland region (Konghang-dong, n=17), apartment house region (Sillim-dong, Jungke-dong, n=29), unshared house region (Chonyangri, Chungang Univ., Bulkwang-dong, n=23) and

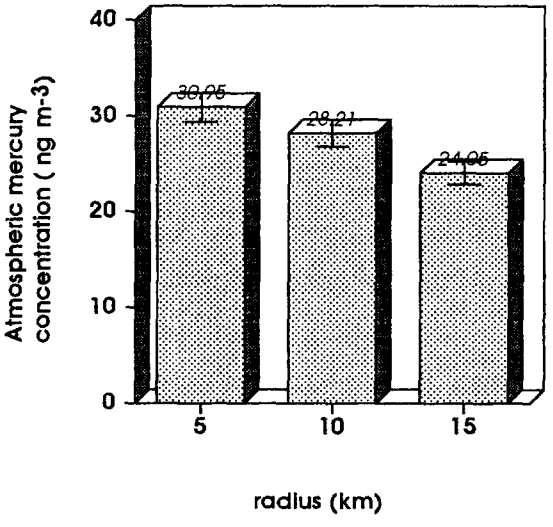

Fig. 4. Variation of atmospheric mercury concentration as a function of the distance from center of Seoul. The Data are mean±SD.

roadside commercial region (Kangnam, Chongro 5-ga, n=23). As shown in Fig. 6, the maximum concentration of mercury was found at the roadside commercial region. The difference between apartment house and unshared house region is thought to be the consequences of differencies in their fuel-consumption bahavior.

Atmospheric Mercury around Wastes' Incinerator Recently, dioxines exhausted from wastes incinerator is considered to be one of the threatening environmental pollutants. While these

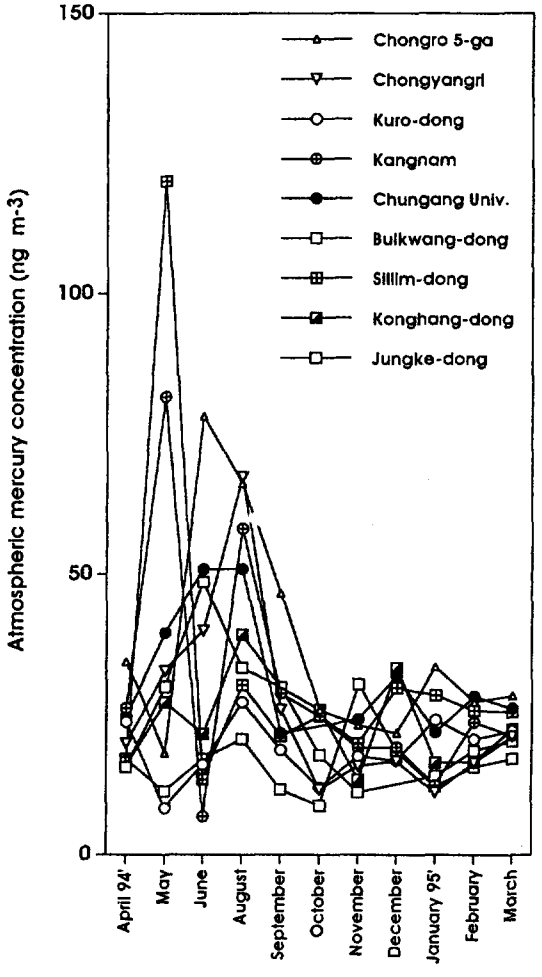

Fig. 5. Monthly variations in atmospheric mercury concentrations from 9 sampling stations in Seoul.

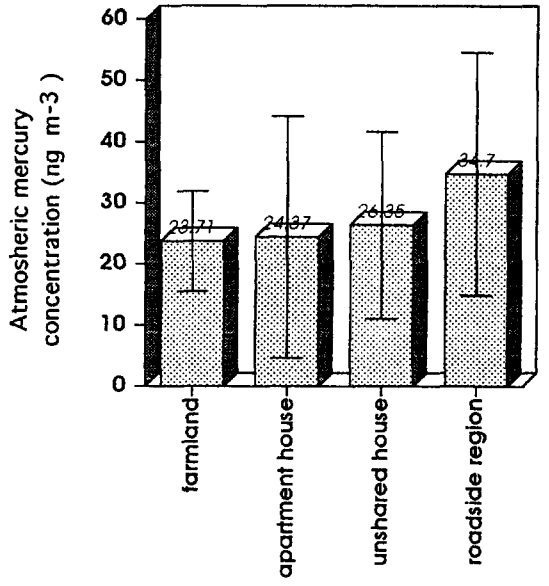

Fig. 6. Comparison of atmospheric mercury concentrations determined from agricultural, residential and commercial districts in Seoul. The Data are mean±SD.

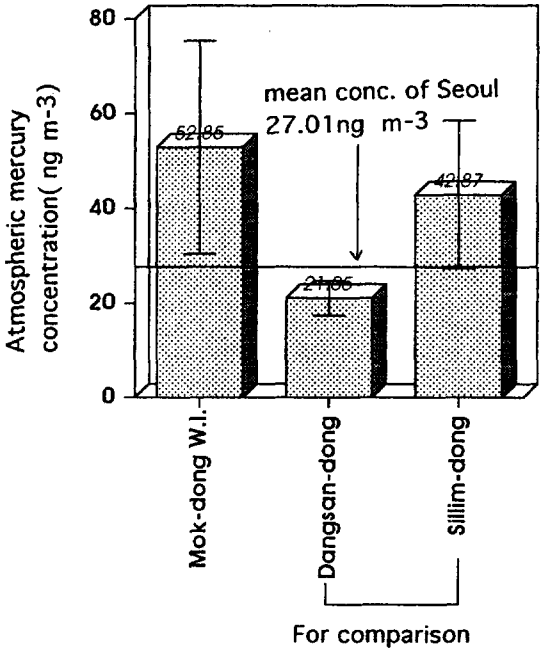

Fig. 7. Comparison of atmospheric mercury concentrations between Mok-dong waste incinerator and near-by districts. The Data are mean± SD.

secondary organic products have attracted a great deal of periods attention, mercuric compounds from wastes incinerator are also well-known for its potential for environmental deterioration. Mok-dong wastes incinerator disposes about 150 tons of wastes per day. The atmospheric mercury around Mok-dong wastes' incinerator and two other points in Seoul area were investigated for comparison. The atmospheric mercury around Mok-dong wastes' incinerator was 52.85 ± 22.50 ng m^{-3} which is about two times higher than the annual me-

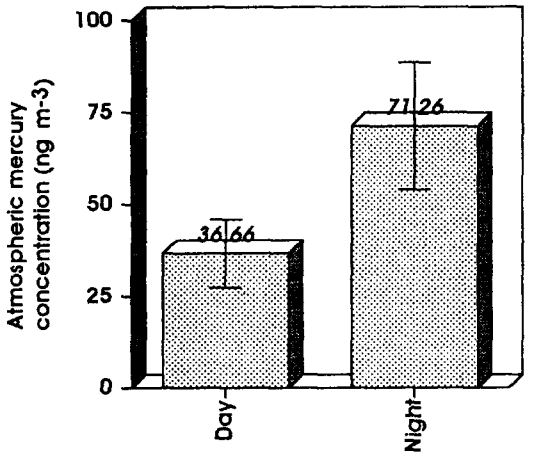

Fig. 8. Comparison of atmospheric mercury concentrations during daytime and nighttime around Mok-dong waste incinerator. The Data are mean±SD.

an of Seoul area. Dangsan-dong shows relative low concentartion. Sillim-dong where briquette is largely consumed showed 42.87±15.65 ng m^{-3}.

Diurnal Variation around Wastes' Incinerator During 5 day periods (October 17~21, 1995), samples were collected diurnally around Mok-dong wastes' incinerator. As shown in Fig. 8, mercury concentration at night time was about twice higher than those measured during day time. The reason for this diurnal trend is likely due to the fact that the facility is mainly operated during night time for heating.

Atmospheric Mercury in Five Major Cities For comparison with Seoul area, atmospheric mercury concentrations were analyzed at five other major cities in Korea and summarized in Table 4. The mean concentrations in these five cities were lower than that of Seoul. Only exception was found from Daegu city (36.73± 3.30 ng m^{-3}).

Table 4. Atmospheric mercury concentration in other cities.

City	Sampling point	Temperature (°C)	Mercury concentration (ng m^{-3})	
		range	Mean±S.D.	Range
Daegu	Gongpyung-dong	25.0~32.5	36.73±3.30	32.52~40.58
Chuncheon	Myung-dong	13.5~15.5	19.77±2.41	16.58~22.40
Jeonju	Chunang-dong	14.0	26.15	-
Iksan	Namjung-dong	10.3	15.64	-
Daejeon	Yongdu-dong	20.3~24.0	15.20±4.16	11.04~19.37
		General mean	24.17 ng m^{-3}	

CONCLUSIONS

From April, 1994 to March, 1995, the concentrations and distribution of atmospheric mercury were investigated from nine sampling stations in Seoul, five major cities and two rural areas. The concentrations of atmospheric mercury in 119 samples collected from Seoul was 27.01±9.42 ng m^{-3} (N.D.-120.17 ng m^{-3}), while those five samples from the two rural areas had the mean value of 4.57±3.07 ng m^{-3} (1.72 ~8.24 ng m^{-3}). The concentrations of atmospheric mercury in five major cities averaged 24.17±8.89 ng m^{-3} which were generally lower than the average value for Seoul. The atmospheric mercury of Seoul showed a decre-asing trend as a function of distance from the urban center, which reflect intense anthropogenic activities in the center of city. Our analysis of monthly variations in atmospheric mercury concentrations also indicated that temperature is acting as a major controlling factor of mercury distribution behavior. When mercury concentrations were compared depending on the locations of sampling, the maximum concentration of mercury was observed at the roadside commercial region. The atmospheric mercury around Mok-dong wastes' incinerator measured to be 52.85±22.50 ng m^{-3} which is about two times higher than the mean for Seoul area. Dangsan-dong showed relative low concentartion. Sillim-dong where briquette is largely consumed showed 42.87±15.65 ng m^{-3}. A diurnal variation of mercury concentration around wastes' incinerator was also observed. The mercury concentration at night time showed twice higher than that of day time. We suspect that this is because the facility is main-

ly being operated during night time for heating energy distribution. The disused fluorescent lamps and batteries containing mercury being intermixed with combustible wastes are thought to be a major source of atmospheric mercury.

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