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Particle Size Distribution of Heavy Metals in the Urban Air of Seoul, Korea

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Abstract□Atmospheric particulate matters (A.P.M.) were collected on quartz-fiber filters from March 1985 to May 1986, using the Andersen high-volume air sampler and contents of six heavy metals (Fe, Mn, Cu, Zn, Pb, Ni) in the A.P.M. were determined by atomic absorption spectrophotometry. These heavy metals were divided into the three groups with respect to their particle size distribution. Fe and Mn were mainly associated with coarse particles (diameter $>2.0\,\mu m$), but Pb and Ni were related fine particles (diameter $<2.0\,\mu m$). Cu and Zn had mixed size distributions in both of them. In the seasonal variation of heavy metals, the contents of Fe and Mn in spring and Ni and Pb in winter were higher than any other season. There were high mutual correlation between Fe and Mn in coarse particles, and between Pb and Ni in fine particles.

Keywords□Particle size distribution, heavy metal, urban air, atmospheric particulate matters.

The particulate matters in urban air contain many metals classified as toxic to human health. Because the concentration of metals in ambient air has increased with industrialization, this situtation has been given attention in many countries. The atmospheric behavior of particulate matters are mainly determined by the particle size[1]. Therefore, in order to properly assess the pollutants in particulate matters, it is necessary to study about the particle size distributions as well as contents of them.

Moreover, particle size distribution can give some information regarding the type of emission sources. Condensations in high temperature process are likely to produce small particles, whereas dispersion type sources emit large or giant particles[2]. Finally, information about the particle size distribution has a toxicological importance. Whether a particle is inhaled and retained in the lung or not, primarily depends on the particle size. Specially, the particles, in which the diameter is below 1.1 μm, are seriously toxic since they are able to penetrate deep into the lung.

To date, a number of studies report that the typical particle size distribution of particulate matters has been bimodal distribution[3,4], of which mass concentration was lowest at 2.0 μm and was almost equal at above or below 2.0 μm. This is consistent with the results from many countries. However, the concentrations and particle size distributions of pollutants vary with the kind of emission sources and pollutants. In this study, we collected the particulate matters according to the aerodynamic diameter and determined the concentrations and the particle size distributions of six heavy metals in them.

MATERIALS AND METHODS

Sampling

The particulate matters were collected on quartz-fiber filters using the Andersen high-volume air sampler (Sibata Dylec, Model HVC-1000) for 48 hours every month from March 1985 to May 1986 on the roof of Chung-Ang University (Seoul, Korea), located in a residential area near by a main road. The Andersen high-volume air sampler consisted five stages; Stage 1($>7.0\,\mu m$), Stage 2(3.3 -7.0 μm), Stage 3(2.0 - 3.3 μm), Stage 4(1.1 - 2.0 μm) and the Back-up stage($<1.1\,\mu m$). Stage 1 through Stage 4 filters were circular (Type 25000

Table I. Concentrations of A.P.M. and Heavy Metals (Sum of five stage)

Sampling date	A.P.M. ($\mu g/m^3$)	Concentration (ng/m^3)					
		Fe	Zn	Pb	Cu	Mn	Ni
850320	216.41	4343.80	1123.33	316.46	—*	170.44	58.25
850515	189.62	4320.86	1816.11	289.42	190.23	154.25	86.34
850619	146.80	1620.35	707.21	593.09	143.78	80.78	27.91
850717	96.74	1724.55	1278.71	886.63	194.35	30.64	64.31
850918	47.54	1943.26	1323.52	571.97	29.38	62.40	50.88
851016	235.05	6751.55	1880.50	758.46	270.61	144.12	71.89
851120	98.11	1936.02	983.05	577.54	21.15	52.91	48.29
851221	222.56	3651.02	1366.50	1136.47	102.85	109.26	88.10
860122	195.81	2257.95	1499.23	1749.57	54.70	163.11	63.40
860319	277.24	3124.70	2259.53	622.62	284.81	163.45	37.29
860416	426.64	6266.78	2159.97	946.03	111.01	266.60	86.82
860521	196.38	2679.44	1052.41	1186.85	353.45	127.74	30.38
Mean	195.58	3385.07	1454.17	802.76	159.67	127.14	59.49
C.V.%	50	51	51	69	33	51	36

*—: not dertermined.

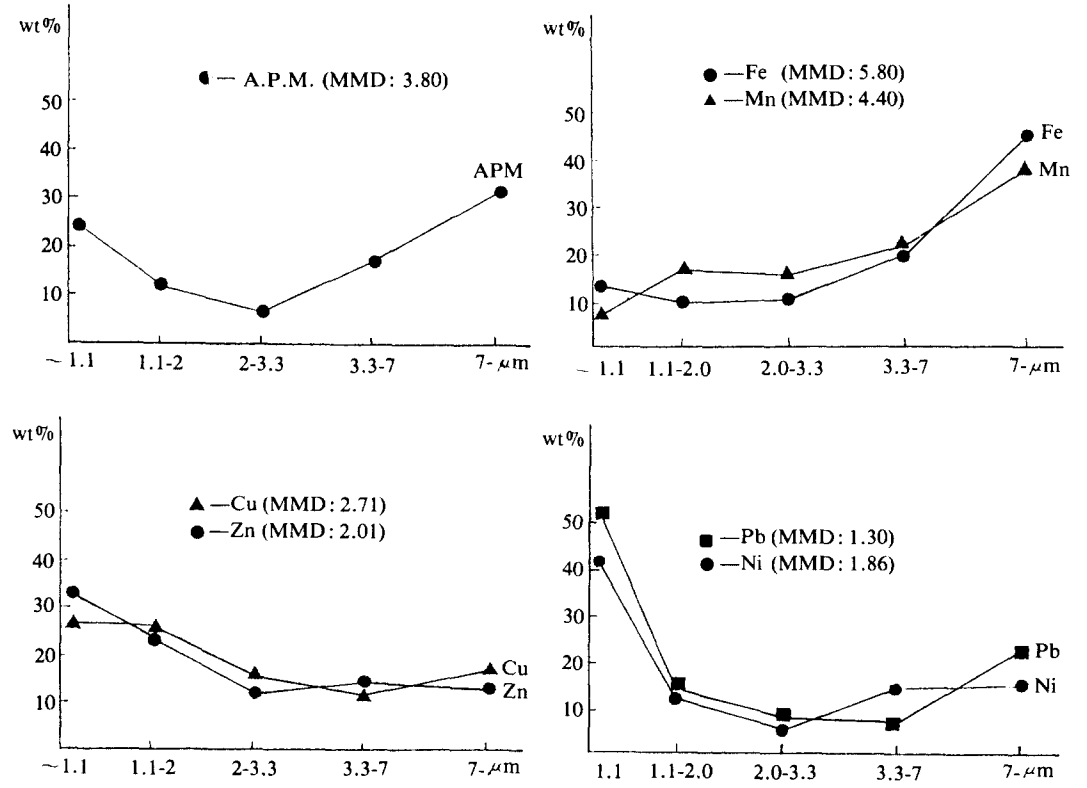


Fig. 1. The variations of weight percent and Mass Median Diameters of each heavy metals according to particle size range.

*MMD: Mass Median Diameter

* Weight percent =(Amount of each stage/Amount of whole stage)× 100

QAST, 30 cm in diameter) and the Back-up filter was rectangular (Type AHQ-630, 20×25 cm). Before and after each sampling period, the filters were conditioned under the constant relative humidity (50±2%) and temperature (20±2 °C) for 24 hours and weighed to obtain the weight of particulate matters.

Extraction and Analysis of Heavy Metals

One eighth of the circular filters and the double belt-punched portion (2 cm in diameter) of the Back-up filter were used for extraction of metals. Before extraction, filters were ashed by the plasma asher (Model PC-103, Yamato Co.) on the conditions of high frequency output 200w and oxygen flow 100 ml/min. Then they were extracted with 10% HNO_3 (For harmful metals analysis: Hayashi Pure Chemical Industries Ltd.). The filtrates were adjusted to 50 ml with 0.5N HNO_3. Concentrations of Fe, Mn, Cu, Zn, Pb and Ni were determined by the atomic absorption spectrophotometer (Perkin Elmer, Model 2308).

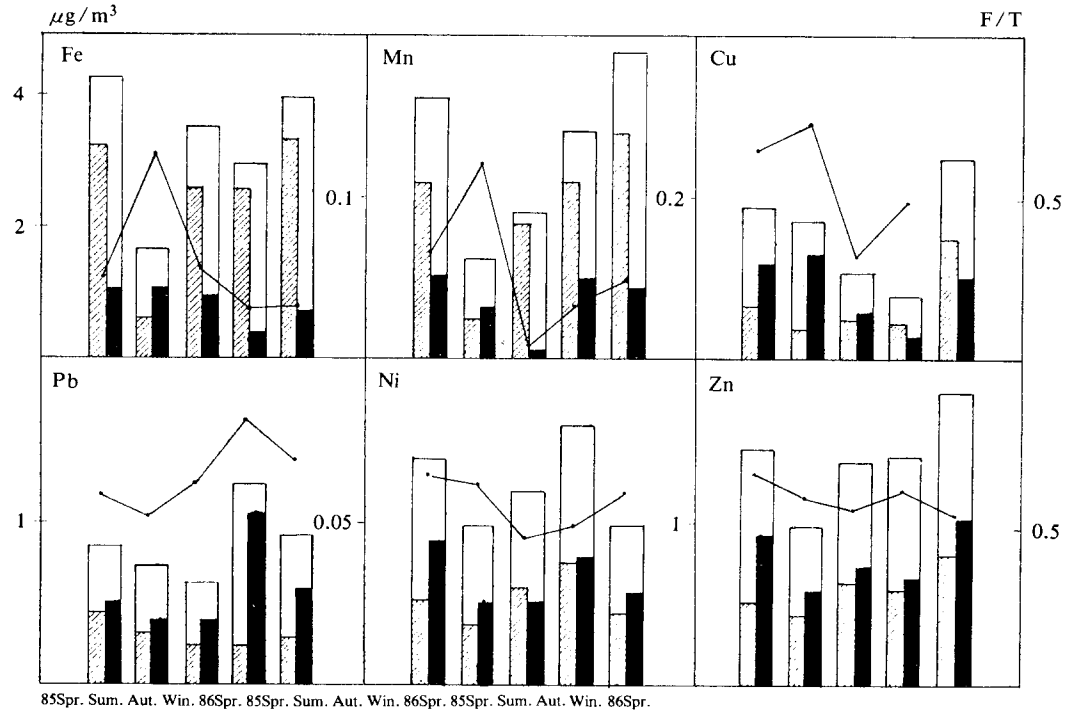
RESULTS AND DISCUSSION

Concentrations of A.P.M. and Heavy Metals

As shown in Table 1, concentrations of A.P.M. had a range of 47.54 to 425.64 $\mu g/m^3$ and the arithmetic mean was 195.57 $\mu g/m^3$. It is similar to the data reported by Korea National Institute of Environmental Research in Seoul, 1982 (185 $\mu g/m^3$).

Contents of heavy metals in A.P.M. decreased in the order Fe > Zn > Pb > Cu > Mn > Ni. We found that Pb and Zn, known to be mainly emitted from anthropogenic sources such as automobile exhausts, home heater, and other oil combustions, had a higher concentration than other metals. Since the sampling site was a residential area, contents of Cu, Mn and Ni were relatively low. In general, Cu and Mn were mainly emitted from the industrial area, and Ni was mainly emitted from the combustion of heavy oils[5].

Particle Size Distributions of Heavy Metals in A.P.M.



$$*F/T\ Ratio = \frac{[Fine\ Particle]}{[Fine\ Particle] + [Coarse\ particle]}$$

Fig. 2. Seasonal variations of heavy metals in A.P.M. (Spring '85-Spring '86).

The variations of weight percent (amount of each stage/amount of whole stage) with respect to particle size range, and Mass Median Diameter (M.M.D.) of each metals are given in Fig. 1. Mass Median Diameter, defined as the diameter at which half the mass is above and half below, was estimated by assuming the mass distributions that are lognormally distributed and by plotting the cumulative mass percent against the impactor cut-off diameter on lognormal probability paper[6].

As shown in Fig. 1, A.P.M. shows bimodal size distribution with a minimum abundance on Stage 3 (2.0-3.3 μm). It is generally accepted that the atmosperic size distributions of particulate matters are bimodal with a minimum at about 2.0 μm aerodiameter, and that the particles above this diameter are usually derived from natural erosion processes and reentrained dust. This agrees well with our results for A.P.M.. However, it has also been suggested that partices below 2.0 μm are mainly generated by combustions or high temperature processes in polluted environments as well as by secondary aerosol formation[7].

Particles, bearing Fe and Mn, are predominant in coarse particle. The most likely sources of coarse particle are fly ash particles from coal combustion and windblown dust from soil[8]. The distributions of Fe and Mn are so similar to each other that they surely originate from the same sources in about the same relative proportions.

The distribution curves of Pb and Ni have shapes which strongly favor fine particle in contrast to those of Fe and Mn. As can be seen from Fig. 1, a large part of the measured Pb and Ni was found in diameter below 1.1 μm. Such distribution can be regarded as normal. The Pb and Ni found in the fine particles probably comes from leaded gasoline combustion and oil-fired plant effluents, respectively[9].

Cu and Zn had mixed size distributions, indicating that each of those metals originates from two or more processes of comparable magnitude. The recent studies of trace element emissions from refuse incineration has identified large amounts of Cu and Zu released in fine particle form[10,11]. Friedlander and Lee *et al.* has suggested tire dust as a major sources of Zn in urban air[12,13]. Since tire dust is surely created by abrasion, Zn may be in coarse particles.

From the above results, these metals were divided into three groups according to the general shapes of their size distributions- *i.e.* those that favor coarse particle, those attached to fine particle, and those having both coarse and fine particle components.

Seasonal variations of Heavy Metals and Correlation analysis

Seasonal mean concentrations and F/T ratios of metals are shown in Fig. 2. The lowest concentrations for almost all elements in coarse particle were

Table II. Correlation coefficients between A.P.M. and Heavy Metals.

	APM	Fe	Mn	Cu	Zn	Pb	Ni
APM							
Fe	.81609					In coarse particle	
Mn	.79532	.90336					
Cu	.44577	.17923	.26795				
Zn	.57506	.58729	.54788	.40870			
Pb	.12764	.10939	.00278	-.14849	-.23196		
Ni	.09673	.53354	.37816	-.28218	.17826	-.25997	
APM							
Fe	-.19653					In fine particle	
Mn	.59425	.22167					
Cu	-.14382	.45030	-.02337				
Zn	.76482	.06377	.44244	.15477			
Pb	.35071	-.04196	.47940	-.25499	.30149		
Ni	.52133	.36824	.39417	.04814	.66014	.66377	

CRITICAL VALUE (1-TAIL, .05) = + Or -.49932
CRITICAL VALUE (2-TAIL, .05) = + /-.57400

found during the summer. In general, the scarvenging effect by rain is much more effective against the large air particles. Most of the metals emitted from anthropogenic source show a substantial seasional dependence with highest values in the winter, while most of the soil-derived metals have a well-known seasonal variation in Korea with the highest values during the spring. It was established that dusts from China frequently cross to Korea and often reach Hawaii, especially during the spring[14]. The high ratio of winter to summer concentrations can be explained as principally due to meteorological factors particularly great vertical dispersion in the summer, perhaps combined with somewhat higher emission rates of metals associated with the fossil-fuel combustion. The matrix of correlation coefficients for all elemental pairs are given in Table II. The use of correlation coefficients allows a quantitative estimate of similarity of the temporal variations of any two species. Highly correlated species may come from the same primary sources or secondary thansformation processes, or the correlation may indicate the species are carried together in the same air mass. Table II indicates high mutual correlations between Fe and Mn in coarse particle, and between Pb and Ni in fine particle. Fine air particles show a moderately high correlation with Ni, Mn and Zn. On the other hand, coarse air particles have a high correlation with Fe and Mn, which are abundant in soil.

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