



# Size Distribution and Source Identification of Airborne Particulate Matter and Metallic Elements in a Typical Industrial City

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## ABSTRACT

The size distribution of airborne particulate matter (PM) and the concentrations of associated metallic elements were investigated in a busy urban region of a typical Korean industrial city. The PM concentrations measured during the spring, except for those in the size range of 1.1 to 2.1  $\mu\text{m}$ , were slightly higher than the PM concentrations in the summer. Coarse particles contributed greatly to the variation in PM concentrations in the spring, while fine and sub-micron particles contributed largely to the variation in PM concentrations in the summer. The difference in size modes of the PM concentrations between spring and summer may be explained by the Asian dust effect and its accompanying wind direction and speed. Extremely high enrichment factors (EFs) values (6,971 to 60,966) for all of the size distributions in PM were identified for cadmium (Cd). High EFs values (12 to 907) were also identified for other heavy metals including Cr, Cu, Ni, Pb, Zn and Mn. Low EF values (0.29 to 8.61) were identified for Ca, K, Mg and Na. These results support the common hypothesis that most heavy metals in ambient PM have anthropogenic sources and most light metals have crustal sources. The results of principal components analyses and cluster analyses for heavy metals indicate that the principal sources of PM and metals were emissions from non-ferrous metal smelters, oil combustion, incinerators, vehicular traffic and road dust.

**Key words:** Size distribution, Metallic elements, PCA, Cluster analysis, Correlation

pollutants into the environment. Numerous studies have indicated an association between ambient PM concentrations and respiratory problems (Costa and Dreher, 1997; Hileman, 1981). Recent studies have shown that increased mortality and morbidity in the urban population is associated with increased PM and heavy metal concentrations in ambient air (Manoli *et al.*, 2002; Dockery and Pope, 1994). Different sizes and compositions of particles can be associated with adverse effects on the environment and human health. Concentrations of chemicals contained in anthropogenic PM ranging from 0.001 to 2  $\mu\text{m}$  in diameter have been proven to be responsible for acid rain (Ning, 1995). The efficiency of inhalation and respiratory deposition of PM is dependent on particle size (Hinds, 1999). PM less than 10  $\mu\text{m}$  in diameter has the potential to reach the lower respiratory tract, while particles more than 5  $\mu\text{m}$  in diameter are usually filtered out by the upper respiratory tract. Fine particles with a diameter of less than 2  $\mu\text{m}$  find their way deep into the alveolar regions of the human lung, affecting lung function, particularly if the particles contain toxic metals (Infante and Acosta, 1991). Therefore, analyzing the size distribution and components of PM helps to identify its risks to human health and inform appropriate methods for controlling PM emissions.

Analyses of the components of PM in ambient air have usually been limited to evaluation of total suspended particles (TSP) classified as  $\text{PM}_{10}$  (less than or equal to 10  $\mu\text{m}$ ) or  $\text{PM}_{2.5}$  (less than or equal to 2.5  $\mu\text{m}$ ). Studies conducted during the last two decades have evaluated the association between the size distribution of PM and metal concentrations in urban areas. In the past, many researchers in Europe have conducted experiments to study the size distributions of PM-based metals (Voutsas and Samara, 2002; Allen *et al.*, 2001; Fernandez Espinosa *et al.*, 2001). In Asia, research in this area is still evolving with a limited number of published studies on PM-based metal/elemental size distributions and concentrations (Srivastava *et al.*, 2009; Srivastava and Jain, 2006; Wang *et al.*, 2005;

## 1. INTRODUCTION

Elevated ambient concentrations of particulate matter (PM) and metals are considered a significant risk to human health especially in urban areas where many mobile and stationary sources emit large quantities of

Parmar *et al.*, 2001). However, these studies focused exclusively on the effects of PM size distribution on elemental concentrations.

A limited number of studies utilizing correlation analysis of size-based PM concentrations have been conducted. These included a study by Lundgren *et al.* (1996) that determined the relative concentrations of  $PM_{10}/PM_{2.5}/PM_1$  in the Phoenix, AZ area of the United States. Keywood *et al.* (1999) assessed the relationship between TSP,  $PM_{10}$ ,  $PM_{2.5}$ ,  $PM_1$  and ultra-fine particles ( $<0.1 \mu\text{m}$ ) at six urban sites in Australia and reported that  $PM_1$  comprised 50% of the  $PM_{10}$  on average. Recently, Lin and Lee (2004) documented the regression between  $PM_{10}$  and  $PM_1$ . However, there is limited data available on the association between PM concentrations and the size distribution of other fractions in urban areas, where most of the world population lives.

The purpose of this study was to identify the relationships between the concentrations of the nine PM fractions in a typical industrial city in Korea and to determine the effects of seasonal and meteorological factors on  $PM_{10}$  concentrations. An additional purpose of this study was to identify the possible sources of elemental PM using principle components analysis and cluster analysis.

## 2. METHODOLOGY

### 2.1 Study Area Descriptions

The metropolitan city of Ulsan, located in the southeastern part of the country, is the largest industrial city in Korea with a population of more than 1.1 million. There are three national-scale industrial complexes (ICs) in Ulsan, including a petrochemical IC, a non-ferrous metal IC and a mechanical and shipping IC, as well as four smaller local-scale ICs.

Airborne PM samples were collected from a residential area located within 100 to 120 m of an eight lane highway and a busy traffic rotary (Fig. 1). The average speed of the vehicles on the highway was 90 km/hr. The traffic rotary had an average traffic density of 5,000 vehicles/hr during the day. The rotary and the highway also had relatively high densities of diesel trucks and buses. There were many apartment complexes located within 100 to 200 m of the sampling site.

### 2.2 Sample Collection

The PM samples were obtained using an eight-stage cascade impactor (Tisch Environmental, Inc.) placed 12 m from the ground on the roof of a local official building and set with a constant flow rate of 28.1 L/min. Daily PM sampling was based on a 24 hr mea-

surement period and 16 daily samples were collected each month during the spring and summer (April to August, 2008). Glass fiber filters were used to collect particles in nine size intervals ( $<0.4$ , 0.4 to 0.7, 0.7 to 1.1, 1.1 to 2.1, 2.1 to 3.3, 3.3 to 4.7, 4.7 to 5.8, 5.8 to 9.0 and 9.0 to 10.0  $\mu\text{m}$ ).

### 2.3 Metal Analysis

The filters were stored in an environmentally controlled chamber ( $20^\circ\text{C} \pm 2^\circ\text{C}$ ,  $45 \pm 5\%$  RH) for 24 hrs prior to weighing before and after sampling. The weights of the filters were accepted only after triplicate consecutive weights within  $\pm 2 \mu\text{g}$  were obtained. The gravimetry of the samples was determined using an analytical balance with a precision of 1  $\mu\text{g}$ . In order to determine the concentrations of the metallic elements, a mixture of hydrochloric (HCl) and nitric acid ( $\text{HNO}_3$ ) was used to extract the metals from the filters. Each filter was cut into smaller pieces ( $0.5 \text{ mm} \times 2 \text{ mm}$ ) and put into a vial with 30 mL of the mixture (HCl :  $\text{HNO}_3 = 1 : 1$ ). Metallic elements were extracted using an ultrasonic bath at  $90^\circ\text{C}$  for 120 min. The extracts were filtered into beakers using a micro filter with 45  $\mu\text{m}$  pores and brought to a final volume of 50 mL using de-ionized water. The concentrations of 13 metals, including Al, Ca, Na, K, Mg, Mn, Cd, Ni, Cr, Pb, Zn, Cu and Fe, were analyzed using an Inductively Coupled Plasma-Atomic Emission Spectrophotometry (IPC-AES). The relative standard deviation (RSD) was less than 2% for the concentrations of all of the elements measured using the prepared standard solutions of the trace reference materials accredited by the US National Institute of Standards and Technology (NIST). Each solution was measured four times to obtain the concentrations of the elements. In addition, the detection limits of the metals were 1.67, 0.33, 0.58, 1.52, 1.14, 0.26 and 4.17 (ng/mL) for Ni, Cd, Cr, Cu, Fe, Mn and Pb, respectively, and 7.31, 0.03, 5.95, 1.64, 1.32 and 1.76 (ng/mL) for Al, Zn, K, Na, Mg and Ca, respectively. The reproducibility of the analyzed metals were 1.247, 0.797, 1.524, 0.941, 0.840, 0.990 and 1.867 (%) for Ni, Cd, Cr, Cu, Fe, Mn and Pb, respectively, and 0.639, 0.806, 0.817, 0.825, 0.887 and 0.697 (%) for Al, Zn, K, Na, Mg and Ca, respectively. Blank filters and dynamic blanks were exposed to the ambient air for approximately 10 sec at the sampling site and then were handled, stored and treated identically to the collected PM filters. Triplicate blank tests were conducted using the same analysis method as that for the actual samples.

### 2.4 Receptor Models

The enrichment factors (EF) of the metallic elements were utilized to identify the origin of the elements in



Fig. 1. A location map of the study area.

the atmosphere. Fe was selected as a reference element for the crust based on previous studies (Wang *et al.*, 2006; Samara and Voutsas, 2005; Manoli *et al.*, 2002). Natural sources contribute significantly to the composition of PM when the EF goes to unity and non-crustal sources are the predominant sources when the  $EF > 10$  (Wang *et al.*, 2006). The crustal average concentrations were obtained from Taylor's study (Taylor, 1996). The  $EF_{Crust}$  of element M in PM was obtained using the following formula:

$$EF_{Crust} = \frac{[M/Fe]_{Air}}{[M/Fe]_{Crust}}$$

where M equals the concentration of the metal of concern,  $[M/Fe]_{Air}$  is the concentration ratio of each metal depending on the size of each sample and  $[M/Fe]_{Crust}$  is the concentration ratio of each metal in the crust.

Principle components analysis (PCA) was used to obtain knowledge of emission inventories prior to this study (Chio *et al.*, 2004). In the present study, the number of factors was selected so that the cumulative percentage variance explained by all of the chosen factors was greater than 56% and only those factors with an eigenvalue greater than 1 were chosen. A varimax rotation that maximized the variance of the squared elements was completed using SPSS software (ver-

sion 13).

Cluster analysis (CA) was used to study the emitting sources of the different heavy metals found in the samples. Even though it is difficult to interpret dendrograms of unclear sample groups, we compared CA results with PCA results in order to be more confident in the final identification of sources. In this study, the groups were chosen based on dendrograms using Ward's method including the squared Euclidean distance and an agglomeration schedule.

### 3. RESULTS AND DISCUSSION

#### 3.1 Seasonal Size Distributions

Fig. 2 reveals seasonal changes in the average PM concentrations of nine fractions. The highest PM levels during the spring (April and May) were observed in the largest PM (9 to 10  $\mu\text{m}$ ) followed by the finest size (0.4 to 0.7  $\mu\text{m}$ ), one fine particle fraction (0.7 to 1.1  $\mu\text{m}$ ) and one coarse fraction (5.8 to 9.0  $\mu\text{m}$ ). In the summer (June to August), the highest PM levels were also observed in the size range of 9 to 10  $\mu\text{m}$  followed by the fine particle fractions (0.7 to 1.1 and 1.1 to 2.1  $\mu\text{m}$ ).

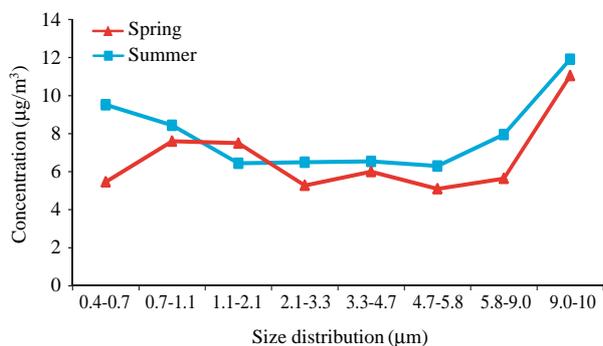
In a comparison of wind characteristics between the spring and summer sampling periods (Fig. 3), stronger

winds (with a wind speed of greater than 4 m/s) and more fractions of southern and southwestern wind series occurred during the spring. Therefore, the PM collected during the spring sampling period was expected originate from a greater variety of sources than the PM collected in the summer when a southeastern series of winds prevailed. In addition, the presence of some western series of winds during the spring indicated that the PM collected during the spring would be affected by the Asian dust that usually originates from the west or northwest of the sampling site. In a comparison of PM size distribution between the spring and

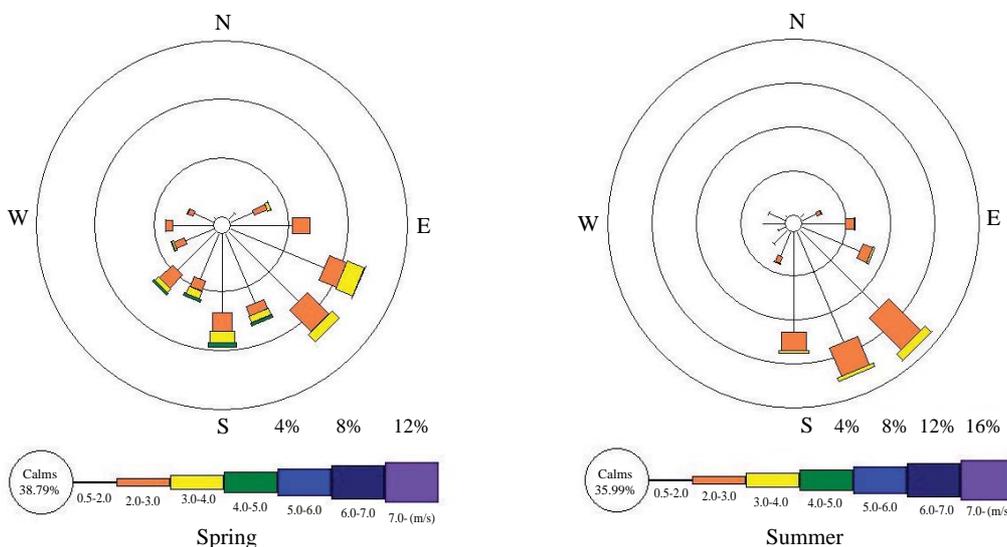
summer periods, the PM collected in the spring had increased concentrations of coarse particles due to the Asian dust. However, the PM collected in the summer would be affected more by the winds that pass through industrial areas.

### 3.2 Correlations between PM<sub>10</sub> and Other PM Sizes

Table 1 presents the coefficients of determination ( $r^2$ ) between each PM size fraction and the PM<sub>10</sub> concentrations during two seasons. In the spring, strong correlations existed between the PM<sub>10</sub> and coarse particles. In particular, the PM<sub>10</sub> concentrations and the coarse particles with concentrations in the range of 4.7 to 5.8  $\mu\text{m}$  showed the strongest correlation ( $r^2=0.87$ ). The weakest correlation ( $r^2=0.18$ ) was obtained between the submicron particles (0.4 to 0.7  $\mu\text{m}$ ) and PM<sub>10</sub>. These results suggest that coarse particles have a strong influence on the observed variability in PM<sub>10</sub> concentrations during the spring. While high correlations were obtained between most fine particles, the coefficients of determination between PM<sub>10</sub> concentrations and 0.7 to 1.1  $\mu\text{m}$  and 1.1 to 2.1  $\mu\text{m}$  particles in the summer were 0.76 and 0.73, respectively. The weakest correlation of concentration was between PM<sub>10</sub> and coarse particles in the range of 9 to 10  $\mu\text{m}$  ( $r^2=0.30$ ). These results revealed that fine particles



**Fig. 2.** PM concentrations for each size group during the spring and summer periods.



**Fig. 3.** Average wind rose at the sampling site during the spring and summer periods.

**Table 1.** Coefficients of determination ( $r^2$ ) between PM<sub>10</sub> and different fractions.

Season		0.4-0.7 $\mu\text{m}$	0.7-1.1 $\mu\text{m}$	1.1-2.1 $\mu\text{m}$	2.1-3.3 $\mu\text{m}$	3.3-4.7 $\mu\text{m}$	4.7-5.8 $\mu\text{m}$	5.8-9.0 $\mu\text{m}$	9.0-10 $\mu\text{m}$
Spring	PM <sub>10</sub>	0.18	0.57	0.55	0.67	0.51	0.87	0.65	0.70
Summer	PM <sub>10</sub>	0.60	0.76	0.73	0.57	0.56	0.44	0.48	0.30

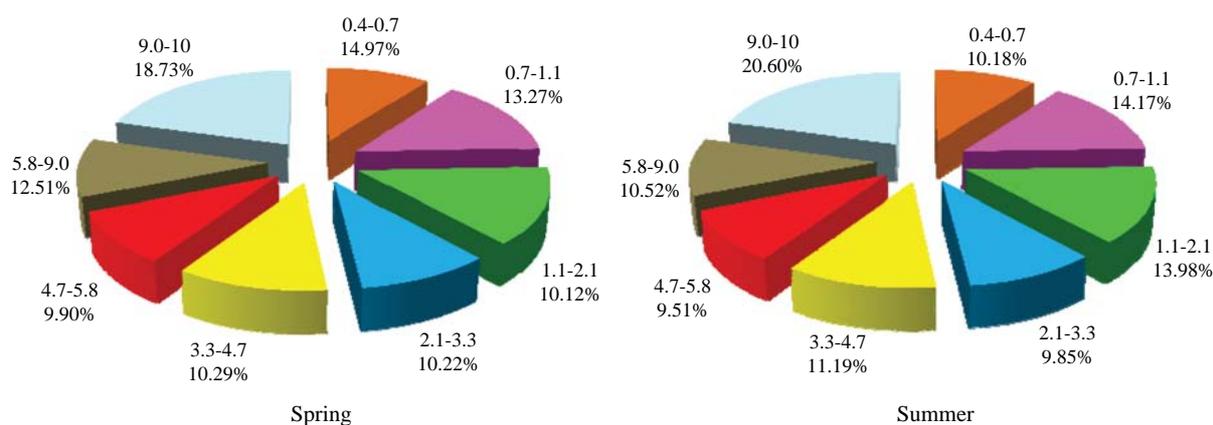


Fig. 4. Contribution of size-based PM components to PM<sub>10</sub>.

have a strong influence on the observed variability in PM<sub>10</sub> concentrations in the summer season.

Recent studies have indicated that PM<sub>2.5</sub> is the main component of PM<sub>10</sub> from urban locations. Harrison *et al.* (1997) found that up to 60% of PM<sub>10</sub> in Birmingham was composed of PM<sub>2.5</sub>. Clarke *et al.* (1999) reported that approximately 60 to 70% of urban PM<sub>10</sub> was composed of PM<sub>2.5</sub>. Kim *et al.* (2000a) and (2000b) studied variations in the PM<sub>2.5</sub> to PM<sub>10</sub> ratio within the south coast air basin of southern California and found that 52% to 59% of the PM<sub>10</sub> was composed of fine particles (PM<sub>2.5</sub>). Fernandez Espinosa *et al.* (2001) studied the size distribution of ambient aerosols in Seville, Spain, and found that PM<sub>2.5</sub> represented 72% of the PM<sub>10</sub>. In the current study, however, 41.4% and 41.2% of the PM<sub>10</sub> concentrations consisted of PM<sub>2.5</sub> in the spring and summer seasons, respectively (Fig. 4). The fractions of fine particles in this study were much lower than those in other studies. These results indicated that the fraction of coarse particles in the PM<sub>10</sub> was much higher than the fractions recorded in other studies. The increase in coarse fractions indicated higher contributions of crustal elements, particles from mechanical sources and suspended particles from the movement of vehicles. The PM collected at the site could easily be affected by traffic related sources such as the abrasion of brake systems, tires and road surfaces, since the sampling site was located near the highway and a busy traffic rotary area.

### 3.3 Source Identification for Size-based Particles

The PM correlations among different size fractions were determined by regression analysis as shown in Table 2. During the spring sampling period, there were strong correlations ( $r=0.60-0.90$ ,  $P<0.01$ ) between all of the coarse particles above 2.1 μm. However, all

of the fine particles below 2.1 μm and some of the coarse particles less than 3.3 μm were also highly correlated ( $r=0.57-0.87$ ,  $P<0.01$ ) during the summer sampling period. Previous studies (Li and Lin, 2003; Vallisu *et al.*, 2000) found that PM<sub>2.5</sub> and PM<sub>1</sub> were highly correlated and therefore could have similar sources. These results indicate that high correlation coefficients for various particle size groups can be related to the same sources. Therefore, these results indicate that there were common or similar PM sources among the coarse particles in the spring and among the fine particles in the summer. For both of the seasons, strong correlations were identified between the size group 5.8 to 9.0 μm and both fine particles (0.4 to 0.7 and 0.7 to 1.1 μm) and the size groups 1.1 to 2.1, 2.1 to 3.3 and 3.3 to 4.7 μm. However, very weak correlations ( $r=0.08-0.28$ ,  $P<0.01$ ) were noted in the summer between the size group of 9-10 μm and the other particle size groups. These results indicated that the particles in the 9-10 μm size group have different sources than the other PM size groups. The 9-10 μm size group showed strong correlations with coarse particles in the spring. These results indicated that there was a common source of coarse particles, such as Asian dust, in the spring.

Table 3 shows the results of a factor analysis of the size fractionated PM in PM<sub>10</sub>. In spring, factor 1 explains 61.24% of the variance with high loading (0.72) of a fraction of fine particles (1.1-2.1 μm) and also with high loading (0.82-0.96) of coarse particles (2.1 to 10 μm). Coarse particles have been used in the past as markers for road and soil dust (Houck *et al.*, 1990). Therefore, this factor can be identified as road dust and soil dust. Factor 2 explains 18.79% of the variance with high loading of submicron particles in the size groups of 0.4 to 0.7 μm (0.91) and 0.7 to 1.1 μm (0.85). Submicron particles are used as indicators

**Table 2.** Correlation coefficients (*r*) of different size fractions during two seasons.

Season	PM size	0.4-0.7 μm	0.7-1.1 μm	1.1-2.1 μm	2.1-3.3 μm	3.3-4.7 μm	4.7-5.8 μm	5.8-9 μm	9-10 μm
Spring	0.4-0.7 μm	1							
	0.7-1.1 μm	<b>0.63</b>	1						
	1.1-2.1 μm	0.11	0.52	1					
	2.1-3.3 μm	0.15	0.53	0.56	1				
	3.3-4.7 μm	0.05	0.21	0.41	<b>0.6</b>	1			
	4.7-5.8 μm	0.16	0.58	<b>0.74</b>	<b>0.9</b>	<b>0.77</b>	1		
	5.8-9 μm	-0.11	0.36	<b>0.67</b>	<b>0.72</b>	<b>0.77</b>	<b>0.88</b>	1	
	9-10 μm	0.1	0.39	0.59	<b>0.65</b>	<b>0.73</b>	<b>0.79</b>	<b>0.85</b>	1
Summer	0.4-0.7 μm	1							
	0.7-1.1 μm	<b>0.81</b>	1						
	1.1-2.1 μm	<b>0.69</b>	<b>0.87</b>	1					
	2.1-3.3 μm	<b>0.81</b>	<b>0.77</b>	<b>0.73</b>	1				
	3.3-4.7 μm	<b>0.57</b>	<b>0.65</b>	<b>0.7</b>	<b>0.64</b>	1			
	4.7-5.8 μm	0.5	0.43	0.51	0.42	<b>0.72</b>	1		
	5.8-9 μm	<b>0.64</b>	<b>0.6</b>	<b>0.62</b>	<b>0.62</b>	<b>0.65</b>	0.45	1	
	9-10 μm	0.13	0.26	0.2	0.08	0.12	0.28	0.1	1

**Table 3.** Factor analysis of size fractionated PM<sub>10</sub>.

Various sizes	Spring		Summer	
	F1	F2	F1	F2
0.4-0.7 μm		0.91	0.88	
0.7-1.1 μm		0.85	0.88	
1.1-2.1 μm	0.72		0.87	
2.1-3.3 μm	0.82		0.89	
3.3-4.7 μm	0.83		0.80	
4.7-5.8 μm	0.94		0.57	0.51
5.8-9 μm	0.96		0.79	
9-10 μm	0.88			0.94
Eigen values	4.90	1.50	4.91	1.04
% Variance	61.24	18.79	61.37	13.01

Note, F stands for a factor.

of emissions from diesel truck exhaust and oil combustion (Houck *et al.*, 1990). Therefore, this factor can be used to identify both diesel truck exhaust and oil combustion sources. Similarly, two factors were also found in the summer. Fuel combustion was responsible for high loading (0.79 to 0.88) of the fine particles (0.4 to 2.1 μm) and most of the coarse particles (2.1 to 9 μm), with the exception of the 9 to 10 μm size group (Kenneth *et al.*, 1998). Factor 2 only explained 13.01% of the variance with high loading of 9.0 to 10 μm (0.94) in the summer, indicating that the factor could be identified as road dust (Houck *et al.*, 1990).

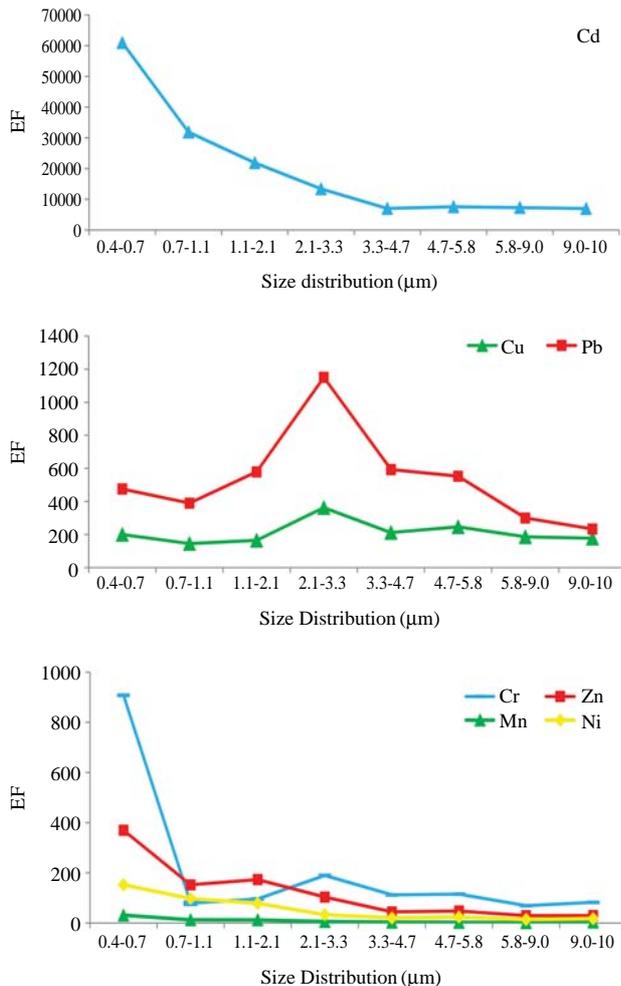
### 3.4 Enrichment Factors of Metallic Elements

Table 4 shows the EF of the light metals including each classified particle size. The EF values of the light metals (Al, Ca, K, Mg and Na) in all of the size fractions were less than 10. The lowest EF values were for Al (0.33 to 0.78) and Ca (0.66 to 1.8); these values were deficient compared to the minimal enrichment (Sutherland, 1999). K (1.14 to 3.14), Mg (0.55 to 2.48) and Na (3.16 to 8.61) had moderate EF values. EF values below 10 imply that crustal sources are predominant for those particles (Kao *et al.*, 1995). Manoli *et al.* (2002) reported that emissions from natural crustal sources were found mostly in coarse particle sizes. Wang *et al.* (2006) and Berg *et al.* (1994) reported the enrichment of Mg indicated a contribution from sea salts.

Most of the heavy metals (Cd, Pb, Zn, Cu, Cr and Ni) in all of the PM size fractions and Mn in the fine particle size fraction had very high EF values. Fig. 5 shows the change in the EF values of heavy metals as a function of particle size. The highest EF values for the heavy metals were observed within the fine particle size group of 0.4 to 0.7 μm, with the exceptions of Pb and Cu. The highest EFs for Pb and Cu were in the size group of 2.1 to 3.3 μm. The EF values generally decreased with increasing particle size. Cd (EF: 6,971-60,966) was the most enriched element in all of the particle size fractions, followed by Pb (EF: 233 to 1,151), Cr (EF: 69 to 908), Cu (EF: 145 to 362), Ni

**Table 4.** Enrichment factor (EF) values of light metals.

Metals	0.4-0.7 $\mu\text{m}$	0.7-1.1 $\mu\text{m}$	1.1-2.1 $\mu\text{m}$	2.1-3.3 $\mu\text{m}$	3.3-4.7 $\mu\text{m}$	4.7-5.8 $\mu\text{m}$	5.8-9 $\mu\text{m}$	9-10 $\mu\text{m}$
Al	0.36	0.29	0.39	0.78	0.41	0.46	0.33	0.33
Ca	0.69	0.60	0.66	1.57	1.02	1.07	1.53	1.80
K	1.43	1.17	1.52	3.14	1.67	1.81	1.14	1.15
Mg	1.17	0.96	1.23	2.48	1.32	1.44	0.55	0.57
Na	4.02	3.16	4.23	8.61	4.63	4.86	3.84	3.73

**Fig. 5.** Enrichment factors (EF) of heavy metals in PM as a function of the PM size.

(EF: 14 to 152) and Mn (EF: 12 to 31). In particular, the EF values of Cd in the fine particles that were smaller than 2.1  $\mu\text{m}$  ranged from 25,000 to 60,966, which indicated a very high level of enrichment. Therefore, urgent countermeasures should be provided to reduce Cd levels in the atmosphere. For the heavy metals noted above, non-crustal sources such as vehicular exhaust, fossil fuel combustion and several industrial processes are considered major emission sources

(Sabbioni and Zappia, 1993). Gao *et al.* (2002) also reported high EF values ranging from 200 to 20,000 for Cu, Pb, Zn and V in PM from the New York-New Jersey harbor estuary.

### 3.5 Source Identification of Heavy Metals

As indicated by the results of the EF analysis above, the EF values of the heavy metals Cd, Cr, Cu, Ni, Pb and Zn in all of the size fractions and Mn in the size fraction of 0.4 to 2.1  $\mu\text{m}$  were much higher than 10. The majority of these metals in the air came from the emissions of non-crustal sources such as anthropogenic sources. Therefore, we reanalyzed the anthropogenic origins using the principle component analysis and cluster analysis for these elements in the current study. A factor analysis method using the varimax rotated principal component was applied in order to identify the major sources of the heavy metals.

As shown in Table 5, three factors were identified in the PM<sub>3.3-10</sub> (coarse particles). Factor 1 explains 56.37% of the variance with high loading of Cd (0.94) and Cu (0.95). Cd, Pb and As have been used as marker compounds for non-ferrous metal smelters and automobile emissions (Eddie *et al.*, 1999; Fung *et al.*, 1995) and Cu has often been used as an indicator of air emissions from the smelting industry (Harrison *et al.*, 1997). Therefore, this factor can be identified as a non-ferrous metal smelter source. Factor 2 explains 22.15% of the variance and contains high loading of Mn (0.95), Cr (0.67) and Pb (0.65) which can indicate dust from traffic sources (Almeida *et al.*, 2006; Fang *et al.*, 2006). Factor 3 showed high loading of Ni (0.82) and Zn (0.88). Ni and V are used as indicators of emissions from oil combustion (Kowalczyk *et al.*, 1982; Zoller *et al.*, 1974). Zn has been used as a marker for heavy metals from waste combustion in incinerators (Wiles, 1996). Therefore, this factor can be identified as both oil combustion and incineration.

Three factors were also found in the case of PM<sub>1.1-3.3</sub> (fine and coarse particles) accounting for a total of 75.27% of the variance. Incineration and traffic dust were responsible for high loadings of Cr (0.88) and Zn (0.8) in factor 1 (Viana *et al.*, 2008; Fang *et al.*, 2006). Factor 2 in PM<sub>1.1-3.3</sub> could represent a non-ferrous metal smelter source which has a high loading of

**Table 5.** Factor loadings for the principal components analysis of metals in different PM fractions.

	PM <sub>0.4-1.1</sub>		PM <sub>1.1-3.3</sub>		F3	F1	PM <sub>3.3-10</sub>	
	F1	F2	F1	F2			F2	F3
Cd	<b>0.92</b>	-0.2	0.41	<b>0.7</b>	0.39	<b>0.94</b>	-0.03	0.28
Cr	<b>0.62</b>	<b>0.71</b>	<b>0.88</b>	0.03	0.14	0.32	<b>0.67</b>	0.52
Cu	<b>0.94</b>	-0.02	0.49	<b>0.74</b>	0.2	<b>0.95</b>	0.11	0.19
Mn	-0.19	<b>0.86</b>	0.46	- <b>0.75</b>	0.19	-0.19	<b>0.95</b>	0.05
Ni	0.42	-0.13	0.14	0.07	<b>0.72</b>	0.19	-0.09	<b>0.82</b>
Pb	0.31	- <b>0.74</b>	-0.01	0.06	<b>0.9</b>	0.51	<b>0.65</b>	-0.04
Zn	0.58	0.52	<b>0.8</b>	0.13	0.02	0.13	0.24	<b>0.88</b>
Eigen values	2.76	2.1	2.76	1.35	1.57	3.24	1.55	1.3
% of Variance	39.48	30.14	39.44	19.3	16.54	46.37	22.15	16.1

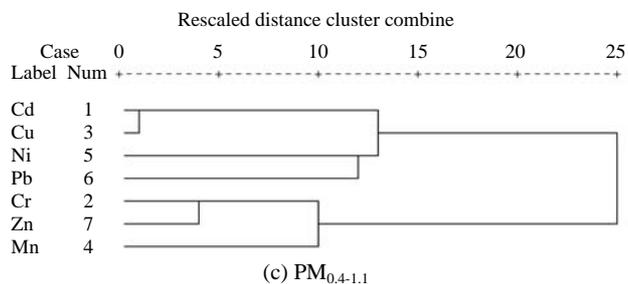
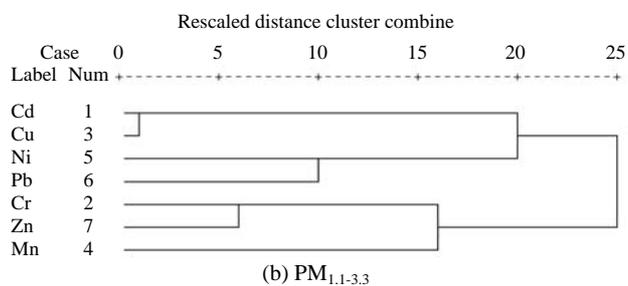
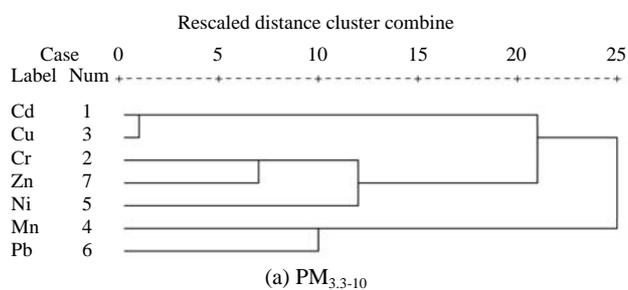
Note, F stands for a factor.

Cd (0.7), Cu (0.74) and Mn (-0.75) accounting for 19.30% of the total variance (Harrison *et al.*, 1997; Fung *et al.*, 1995). Factor 3 only explained 16.54% of the total variance with high loading of Pb (0.9) and Ni (0.72), suggesting that this factor can be identified as oil combustion and vehicle emissions (Balachandran *et al.*, 2000; Pio *et al.*, 1989).

For PM<sub>0.4-1.1</sub> (fine particles), two factors were obtained with eigenvalues that were greater than 1 and explained 69.62% of the total variance. Factor 1 explained 39.47% of the variance with high loading of Cd (0.92) and Cu (0.94). Non-ferrous metals smelting, such as that of Zn or Cu, was indicated as the source for this factor (Harrison *et al.*, 1997; Fung *et al.*, 1995). Factor 2 explained 30.14% of the total variance with a high loading of Cr (0.71), Mn (0.86) and Pb (-0.74). The dust from traffic sources was responsible for factor 2 (Fang *et al.*, 2006).

In this study, we tried to compare our cluster analysis results to our principal components analysis results in order to obtain more confident results for the source identification of heavy metals. Fig. 6 shows the dendrograms that resulted from using the Ward method for a cluster analysis of heavy metals. The results of the CA based on the dendrograms basically agreed with the results of the PCA. However, there was a slight difference between the two methods for the identification of the source groups (Table 6). For example, factor 2 in the CA included Cr, Ni and Zn (PM<sub>3.3-10</sub>) and factor 2 in the PCA only included Ni and Zn. In general, the PCA analysis reduced the number of variables while capturing as much as possible of the original information. Therefore, the variables in PCA, which have similar characteristics, could be arranged into the same factors (Fang *et al.*, 2004). For the cluster analysis, the variables which have short distances in the dendrograms could be basically classified into similar or the same source groups. Sometimes, it is difficult to interpret the CA results clearly. Even though

Dendrogram using ward method

**Fig. 6.** Cluster analysis of heavy metals in different size PM.

the variables look like a similar or the same group based on the CA dendrogram feature, they can be located in some distances which may not be considered as a similar source group. This case brings us unclear source identification. However, the CA classification

**Table 6.** Comparison between the results of principal components analysis (PCA) and cluster analysis (CA).

PM <sub>0.4-1.1</sub>		PM <sub>1.1-3.3</sub>		PM <sub>3.3-10</sub>	
PCA	CA	PCA	CA	PCA	CA
F1: Cd, Cu, Cr	G1: Cd, Cu, Ni, Pb	F1: Cr, Zn	G1: Cr, Mn, Zn	F1: Cd, Cu	G1: Cd, Cu
F2: Cr, Mn, Pb	G2: Cr, Zn, Mn	F2: Cd, Cu, Mn	G2: Cd, Cu	F2: Cr, Mn, Pb	G2: Mn, Pb
		F3: Ni, Pb	G3: Ni, Pb	F3: Ni, Zn	G3: Cr, Ni, Zn

Note, PCA and CA stand for principle component analysis and cluster analysis, respectively. F and G stand for a factor and a group, respectively.

can also provide simplicity when interpreting the relationship among the components using the distance information. Therefore, PCA and CA are both unique methods for the source identification of the materials of interest in terms of providing the possibility of various sources.

#### 4. CONCLUSIONS

Through the analysis of the size and concentration distribution of the airborne particles and associated metals in a busy, urban, residential area of a typical industrial city in Korea, we reached the following conclusions.

The PM concentrations of various size fractions in PM<sub>10</sub> were slightly higher in the spring than in summer. The PM<sub>10</sub> concentrations showed strong correlations with coarse particles in the spring and with fine particles in summer. Particles of the 9 to 10 µm size fraction did not show a strong correlation with the other sized particles in the summer.

Heavy metals were enriched in the PM we examined. In particular, Cd in PM was extremely enriched since it has an EF range of 6,971 to 60,966. The EF values of Pb, Cr, Cu and Ni were 233 to 1,151, 69 to 908, 145 to 362 and 14 to 152, respectively, indicating that they were the product of contamination by anthropogenic sources. The major sources of the heavy metals identified through principal components analysis and cluster analysis were air emissions from non-ferrous metal smelting, traffic, oil combustion and incineration.

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