



Size Distribution of Airborne Particulate Matter and Associated Metallic Elements in an Urban Area of an Industrial City in Korea

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ABSTRACT

This study analyzed the size distribution of airborne particulate matter (PM) and 13 metallic elements associated with it. PM samples were collected using an eight-stage cascade impactor in a busy urban area of an industrial city, Korea during four seasons. Most of the fine and coarse particle mass was concentrated in the size range of 0.7–1.1 μm and 9–10 μm , respectively. PM mass showed two peaks in spring: The first peak was observed for the smallest particles ($< 0.7 \mu\text{m}$) and the second one was found in the coarse particles (2.1–10 μm). However, fine particles (0.7–2.1 μm) showed the highest PM concentrations in winter.

In the distribution analysis of 13 metals in PM, three main groups were determined: (i) heavy metals (Cd, Zn, Mn, Ni and Cr) which were present in high concentrations in fine particles ($< 2.1 \mu\text{m}$) particularly at the size of 0.4–0.7 μm , (ii) light metals (Na, Ca, K, Al) and Fe which had high concentrations in coarse particles, and (iii) other heavy metals (Pb, Mg and Cu) showing high concentrations at sizes larger than 5.8 μm . The concentrations of Cd, Mn and Ni in the size range of 0.4–0.7 μm of the airborne particles and their total levels obtained by summing up the concentrations of the 8 classified size groups were exceeded the proposed thresholds or tolerance levels of the toxic heavy metals. The mass concentrations of Cd, Mn and Ni decreased with increasing particle size, except the size range of 9–10 μm , in PM_{10} . The levels of Pb in PM_{10} did not show the size characteristics shown in Cd, Mn and Ni and also was below its tolerance level. Principal sources of 13 metallic elements in PM included natural sources and local anthropogenic sources such as non-ferrous metal smelting, oil combustion, welding, vehicular traffic and road dust.

Keywords: Size distribution; Metals; Seasonal PM; PCA; Enrichment factor.

INTRODUCTION

Airborne particulate matter (PM) consists of many organic and inorganic compounds with a variety of size and component characteristics (Cheng and Lin, 2010). Long-term exposure to high levels of PM can cause significant risk to human health. Different sizes and compositions of particles cause different adverse health effects. Larger sizes are easy to eliminate from the respiratory system through coughing, sneezing and swallowing, while particles less than 5 μm can reach the pharynx tract. Fine particles with a diameter less than 2.5 μm or ultra-fine particles can travel deep into the lungs with the potential to penetrate tissue and undergo interstitialization (GradeASteel, 2011). Fine particles are not easily removed and can be deposited on the respiratory tracks from the body, causing lung and heart problems, particularly if the particles contain toxic

components such as heavy metals and polycyclic aromatic hydrocarbon (PAHs). Inhalable particles can also deliver harmful species such as heavy metals to the blood system (McCormac, 1971; Infante *et al.*, 1991).

Metallic elements from natural sources such as soil/crustal and marine areas are generally found in coarse particles, while the metals in fine particles are related to anthropogenic sources (Seinfeld, 1986). Dockery and Pope (1994) reported that increased mortality and morbidity in urban populations can be associated with increased PM exposure. The potential of adverse health effects from PM varies by particle size, composition, toxicity and exposure level.

Recent studies of health effects of PM associated with heavy metals have mainly investigated the concentration of metals in total suspended particles (TSP), PM_{10} (less than or equal to 10 μm) and $\text{PM}_{2.5}$ (less than or equal to 2.5 μm). There have been a few studies to evaluate the association between the size distribution of PM and elemental concentrations in urban areas (Fang *et al.*, 2000, 2006). In the past, some researchers in Europe and Asia have analyzed the size distribution of heavy metals in TSP and roadside environments. Espinosa *et al.* (2001) and Allen *et al.* (2001) studied size distribution of metals in urban

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aerosols (Fang *et al.*, 2006; Sabbagh-Kupelwieser *et al.*, 2010). Recently, several investigations have been made on the measurements of size distribution of aerosols and associated elemental concentrations in urban areas (Salma *et al.*, 2002, 2005; Karanasiou *et al.*, 2007; Held *et al.*, 2008; Wagner *et al.*, 2008). Size distribution and anthropogenic apportionment of airborne trace metals were carried out in Kanazawa, Japan by Wang *et al.* (2006). Srivastava *et al.* (2009) studied winter-time size distribution and source apportionment of TSP and associated metals in Delhi, India and Begum *et al.* (2010) identified sources of fine and coarse PM in Dhaka, Bangladesh. However, there have been almost no studies to evaluate size distribution of PM and associated heavy metals from an industrial city.

Even though Ulsan is the largest industrial city in Korea, many urban residential areas are located close to industrial facilities which emit large amounts of toxic substances. Thus, people who live near industrial facilities or complexes may be exposed to toxic pollutants. Different sizes of airborne particles affect different regions of the respiratory system including 0.4–0.7 μm (alveolar), 0.7–1.1 μm (alveo-bronchial), 1.1–2.1 μm (bronchial), 4.7–5.8 μm (trachea-bronchial) and 5.8–10 μm (extrathoracic) as classified in this study.

The purpose of this study was to evaluate the size distribution of airborne PM in an urban residential area of a typical industrial city of Korea. Also, this study aimed to identify the size distribution of metallic elements in PM and to investigate seasonal and source characteristics of PM and its associated metals. Size characteristics of PM and its associated metals obtained in this study are expected to be important information for PM and metal control strategies.

MATERIALS AND METHODS

Area Description

Ulsan city is a typical industrial city which has the largest single-unit factories in the world related to automobile manufacturing and ship building. The city of Ulsan also has two national-scale industrial complexes (ICs) including one of the largest petrochemical and non-ferrous metal facilities in the world. Unfortunately, these industrial facilities are located near urban residential areas. The metropolitan city of Ulsan has a population over 1.1 million. Ulsan has a heavy traffic density due to the large population and operation of the large-scale industrial facilities. The general population has worried about the potential adverse health effects due to long-term exposure to toxic PM and heavy metals in urban aerosols of Ulsan.

Airborne PM samples were collected from an urban residential area in Ulsan. An eight-lane highway was about 150 m from the sampling site and a busy traffic rotary was within a distance of 180 m (Fig. 1). The rotary and the highway have a relatively high density of diesel trucks and buses with an average traffic density around 5,000 vehicles/hr during the day. The speed of vehicles running on the highway was around 90 km/hr.

Particulate Matter Sampling

Daily airborne PM samples (total 82 samples including 16, 34, 22, and 10 samples in spring, summer, fall, and winter, respectively) were collected with an eight-stage cascade impactor (Tisch Environmental, Inc) during 4 seasons (April 2008–January 2009). The cascade impactor system was placed on the roof of a local official building at a height of 12 m from ground. The air flow rate of the

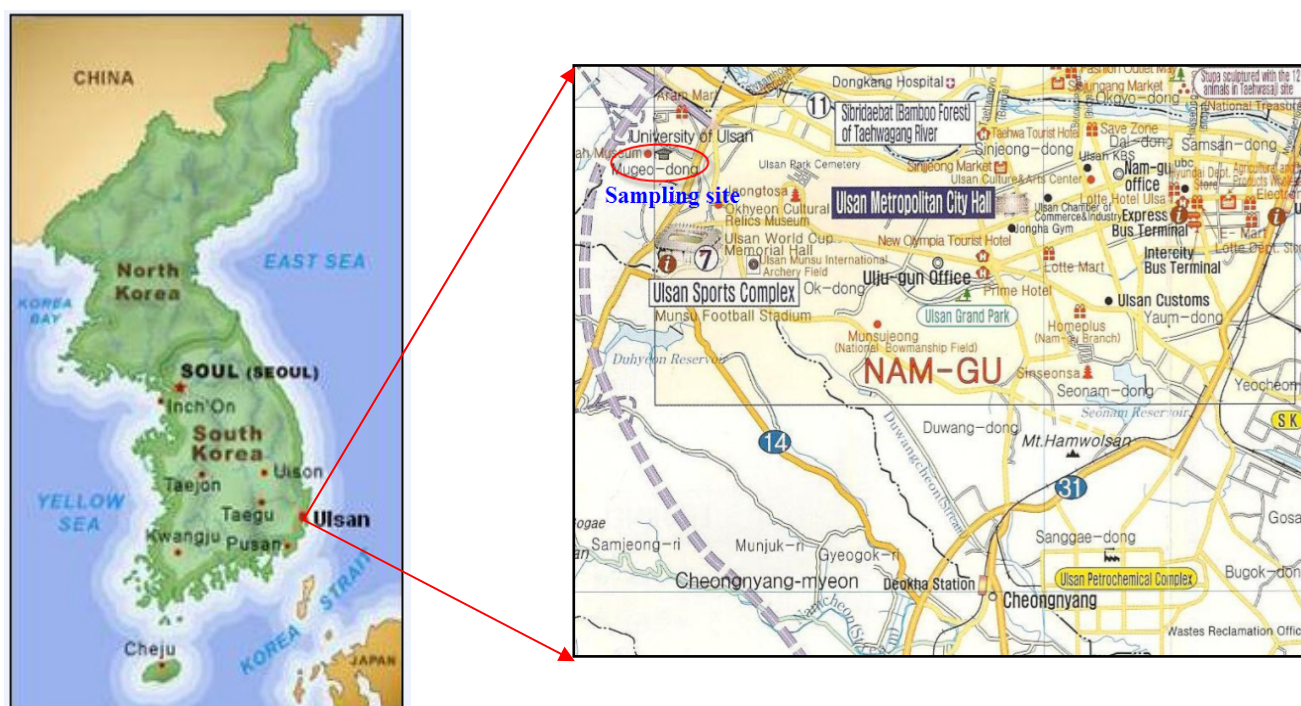


Fig. 1. Map of the Ulsan area with the sampling site marked.

impactor system was set at a value of 28.1 l/m. Glass fiber filters for PM sampling were used to collect particles in nine size fragments (< 0.4, 0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and 9.0–10.0 μm). Filters were weighed before and after sampling using a micro analytical electronic balance with a precision of $\pm 1 \mu\text{g}$ after 48 h storage in desiccators in a room with controlled relative humidity ($45 \pm 5\%$) and temperature ($20 \pm 2^\circ\text{C}$). Filters were considered to be valid after triplicate consecutive weighing within $\pm 2 \mu\text{g}$. PM concentrations of each stage with different particle size ranges were calculated gravimetrically three times measuring consecutive within 2 μg . An air monitoring network system, utilizing β -ray attenuation method, established at the same sampling site was used for a comparison purpose of PM_{10} data obtained from the cascade impactor. In a comparison of PM_{10} values simultaneously measured (20 times) by β -ray attenuator and the cascade impactor at the same site, the difference in the average PM_{10} concentrations was only 3.3% and the linearity of the PM_{10} values identified between the two methods was very high ($r^2 = 0.815$).

Chemical Analysis

To evaluate the concentration of metals in PM, filters were analyzed individually. Each filter was extracted with a mixture of hydrochloric (HCl) and nitric acid (HNO_3) ($\text{HCl}:\text{HNO}_3 = 1:3$, v/v) using an ultrasonic bath at 100°C for 60 min (Harper *et al.*, 1983). Extracts were filtered using a micro filter with a pore of 45 μm in beakers and adjusted to a final volume of 50 ml using de-ionized water. Concentrations of 13 metals, Al, Ca, Na, K, Mg, Mn, Cd, Ni, Cr, Pb, Zn, Cu and Fe, were determined with inductively coupled plasma-atomic emission spectrophotometry (ICP-AES). Relative standard deviations (RSD) in concentrations of all metallic elements were measured using prepared standard solutions of the trace reference materials (SRM 1648a) accredited by US NIST. RSDs were less than 2%. Each analysis solution was measured four times to obtain concentration values of the elements. The information of the method detection limit, quantification limit, precision (standard deviation), and reproducibility of each element was given in Table 1. Blank analyses were performed for about 10% of all field samples according to standard operating procedures. Triplicate blank tests were conducted with the same analysis method as the actual samples.

RESULTS AND DISCUSSION

Seasonal Size Distribution of PM

Seasonal changes in average mass concentrations of PM ($\text{PM}_{x-y} = \text{PM}_y - \text{PM}_x$, where PM_x or PM_y represents a sum of mass concentrations of all particle size groups $\leq x$ or $y \mu\text{m}$ at $x < y$) at the nine size fractions ($x \mu\text{m} < \text{size range} \leq y \mu\text{m}$) are shown in Fig. 2. For three of the seasons except spring, the highest concentrations of fine particles were observed at sizes between 0.7 and 1.1 μm followed by 1.1–2.1 μm . The highest concentrations of coarse particles (2.1 $\mu\text{m} < \text{particle size} \leq 10 \mu\text{m}$) were identified in the size range of 9–10 μm . The fine particles in spring showed the highest concentration in the size range of 0.4–0.7 μm . Fall and winter showed similar size distribution patterns.

Fig. 3 shows the distribution of mass concentrations of four particle size groups (≤ 0.7 , 0.7–2.1, 2.1–5.8 and 5.8–10 μm) during the four seasons. The particle size groups $\leq 0.7 \mu\text{m}$ and 0.7–2.1 μm can closely represent a transient nuclei (or Aitken nuclei) range and an accumulation range in fine particles, respectively. The particle size groups 2.1–5.8 μm and 5.8–10 μm can be a part of mechanically generated aerosol range or coarse particle fractions. In particular, since the size ranges of 2.1–5.8 μm contain a large fraction of respirable particles and thus were separated from the size ranges of 5.8–10 μm . The highest PM levels for all the size ranges (groups) except 0.7–2.1 μm were observed in spring. These high PM concentrations in spring can be explained by the frequent southeastern winds which pass through industrial areas. One of fine particle sizes, 0.7 to 2.1 μm (alveo-bronchial and bronchial regions), had the highest PM concentration in the winter period followed by the fall, spring and summer seasons. For coarse particles, spring showed the second highest levels of PM concentrations. There was a slight increase in average fine particles ($\text{PM}_{2.1}$) concentrations in the winter season ($25.2 \mu\text{g}/\text{m}^3$) as compared the fall value ($24.6 \mu\text{g}/\text{m}^3$). Also, a little more increase in average coarse particle ($\text{PM}_{2.1-10}$) concentration was observed in the winter ($37.0 \mu\text{g}/\text{m}^3$) than that in the fall ($35.1 \mu\text{g}/\text{m}^3$). This increase in fine and coarse particles resulted in increasing in $2.6 \mu\text{g}/\text{m}^3$ of average PM_{10} concentration in the winter as compared the fall (Table 2).

The size distribution of aerosol may be variable with time depending upon changes in source strengths and/or in the aerosol dynamics. Concentrations of PM collected during the spring period would be affected by various PM sources and wind directions, including Asian dust (contributing mostly coarse particles) usually from the west or northwest directions, traffic emissions (contributing fine particles) from southwestern winds, industrial emissions (providing

Table 1. Method detection limit, quantification limit, precision (standard deviation), and reproducibility of each element.

	Ni	Cd	Cr	Cu	Fe	Mn	Pb	Al	Zn	K	Na	Mg	Ca
MDL (ng/mL)	1.6685	0.3307	0.5795	1.5201	1.1361	0.2632	4.1725	7.3141	0.0311	5.9528	1.6473	1.3202	1.7632
QL (ng/mL)	5.3136	1.0531	1.8456	4.8411	3.6182	0.8383	13.2882	23.2934	0.0990	18.9578	5.2463	4.2044	5.6154
SD	0.0014	0.0004	0.0008	0.0025	0.0048	0.0026	0.0049	0.0330	0.0422	0.0829	0.0851	0.0940	0.0738
CV (RSD) (%)	1.2470	0.7965	1.5246	0.9411	0.8402	0.9898	1.8679	0.6391	0.8063	0.8166	0.8254	0.8875	0.6973

*MDL, QL, SD, CV(RSD) stand for method detection limit, quantification limit, standard deviation, and coefficient of variation (relative standard deviation), respectively.

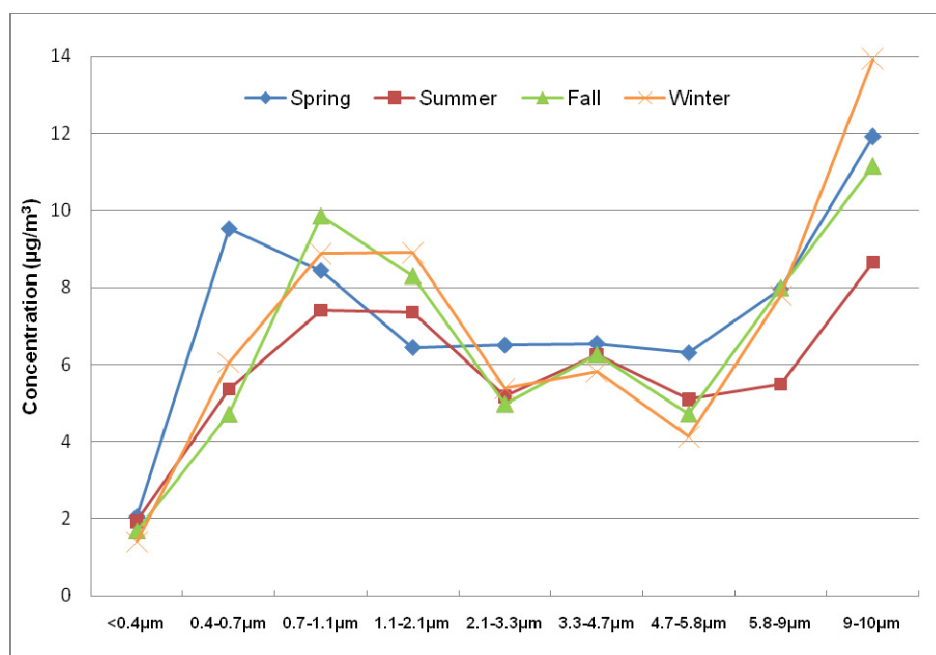


Fig. 2. Mass concentration distribution of different size groups of PM.

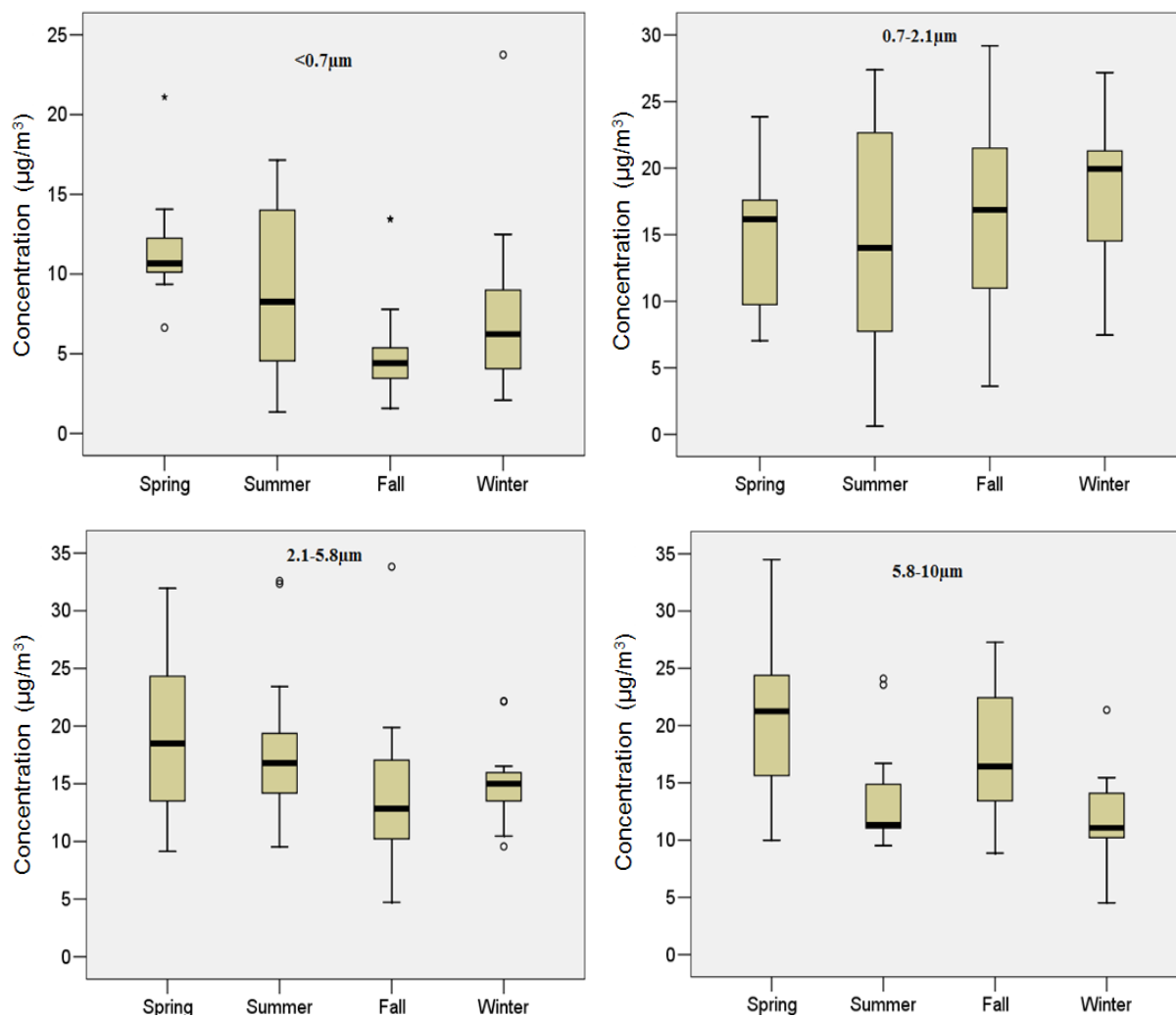


Fig. 3. Box plots of seasonal concentrations of PM in four size intervals.

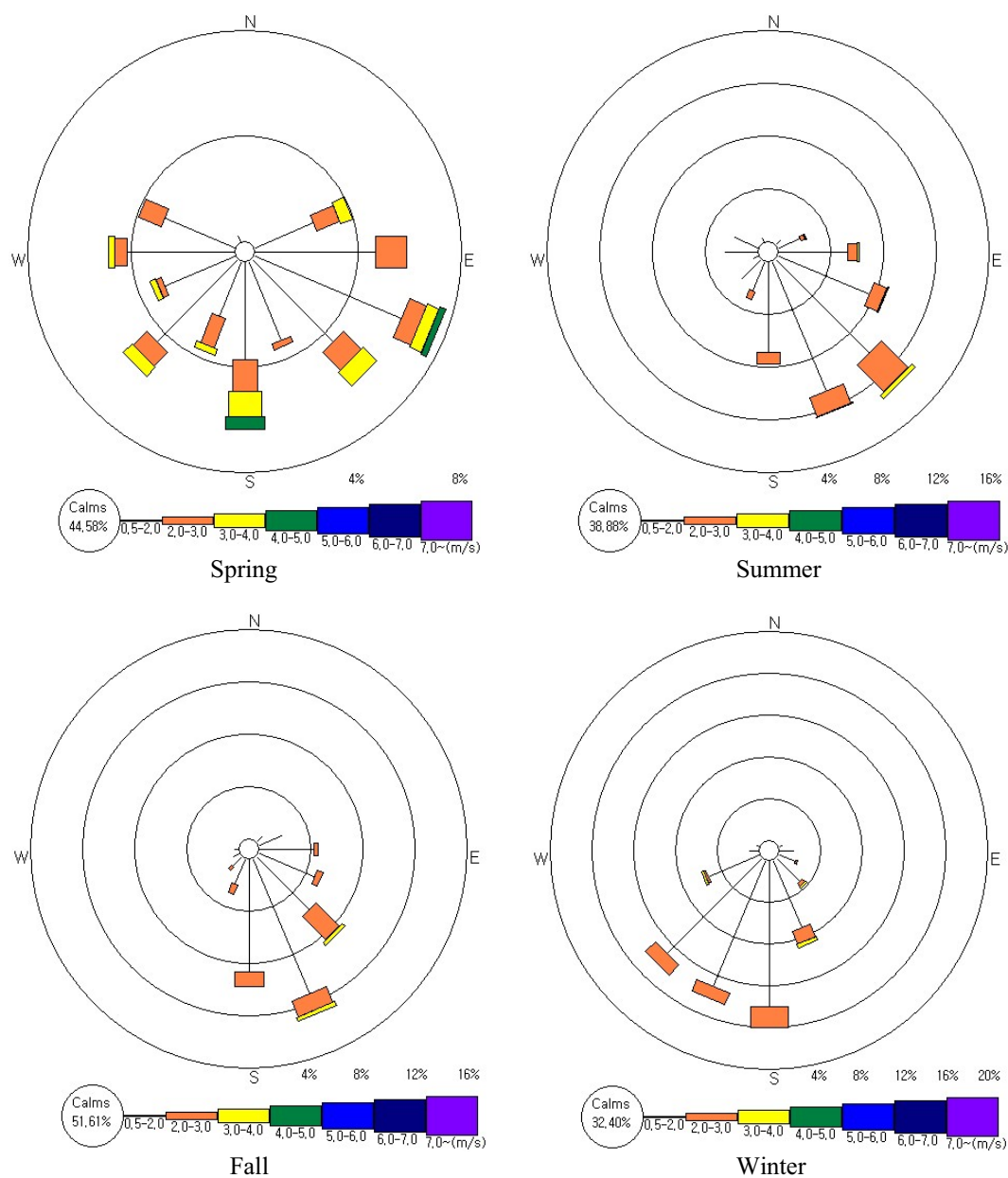
Table 2. Seasonal average concentrations ($\mu\text{g}/\text{m}^3$) of $\text{PM}_{0.7}$, $\text{PM}_{0.7-2.1}$, $\text{PM}_{2.1}$, $\text{PM}_{2.1-5.8}$, $\text{PM}_{5.8-10}$, and PM_{10} .

	$\text{PM}_{0.7}$	$\text{PM}_{0.7-2.1}$	$\text{PM}_{2.1}$	$\text{PM}_{2.1-5.8}$	$\text{PM}_{5.8-10}$	PM_{10}
Spring	11.6	14.9	26.3	19.3	19.9	65.5
Summer	7.3	14.8	22.0	16.5	14.1	52.7
Fall	6.4	18.2	24.6	16.0	19.2	59.7
Winter	7.5	17.8	25.2	15.3	11.9	62.3

Note: $\text{PM}_{x-y} = \text{PM}_y - \text{PM}_x$, where PM_x or PM_y represents a sum of mass concentrations of all particle size groups $\leq x$ or y μm at $x < y$.

mostly fine particles) from southeastern winds which pass through industrial areas, and downtown area emissions (providing mostly fine particles) from eastern winds (Fig. 4). The sampling site can be affected by many sources in spring, which could explain why the spring averages of PM concentrations at all sizes (< 0.7 , $2.1-5.8$, and $5.8-10$ μm),

except for the size fraction of $0.7-2.1$ μm , were higher than other seasonal average values (Table 2). The spring sampling period partly included the sandstorms in the Asian continent. The increased concentrations of coarse particles ($2.1-10$ μm) in spring may be partly associated with the particles transported from the Asian continent.

**Fig. 4.** Wind roses calculated for the different seasons at the sampling site.

The winter PM is affected by frequent south or southwestern winds which include more emissions from traffic activities. Traffic emissions usually contain high concentrations of fine particles, resulting in the highest concentration of PM at the size range of 0.7–2.1 μm in winter (Fig. 3). Also, the lower wind speeds in winter would contribute to increasing in the PM_{10} concentration which is the second highest among four seasons. However, spring showed the highest wind speeds among four seasons with a considerable fraction of 4–5 m/s strong winds passing through industrial sectors (Fig. 4). Also, the more contribution of PM by the industrial emissions could increase in concentrations of fine particles ($\text{PM}_{2.5}$) in spring.

Thus one cause of the difference in the PM concentrations of the size groups mentioned above between spring and other seasons is also due to differences in wind direction and speed through the sampling site. Thus seasonal PM with different wind characteristics will have different source and dispersion characteristics.

Size Distribution of Metals

Size distributions of individual metallic elements are presented in Fig. 5. Even though size distributions of the metals followed similar trends, there were important differences between groups of metals. The metals were divided into 3 groups based on concentration patterns as a

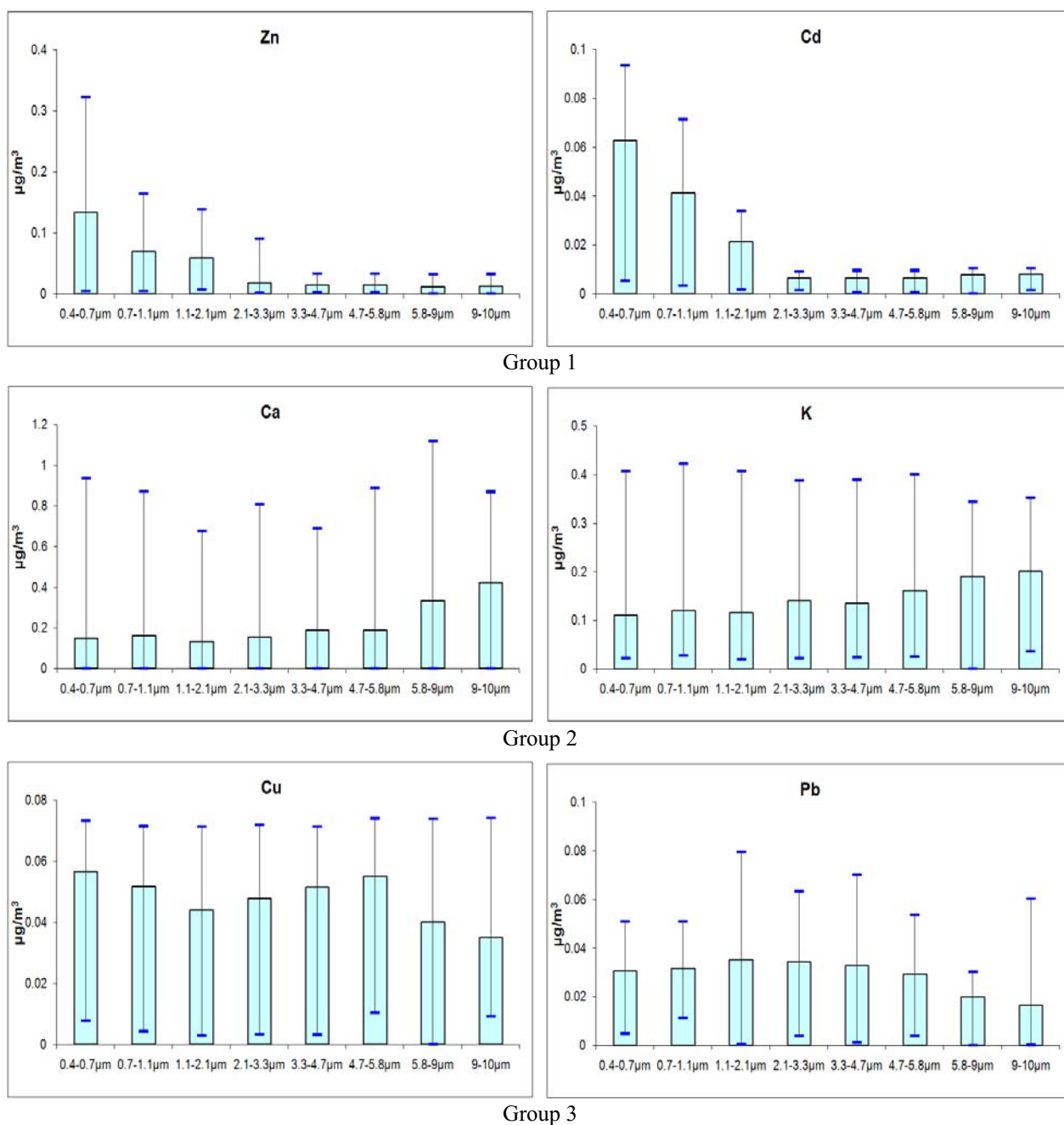


Fig. 5. Elemental mass concentrations in eight size intervals.

function of particle size. Metals (Cd, Zn, Mn, Ni and Cr) in Group 1 had much higher concentrations in fine particles ($< 2.1 \mu\text{m}$) as compared in coarse particles ($> 2.1 \mu\text{m}$) and the metal concentrations decreased with increasing size of particles within the fine size mode. As a typical example of size distribution trend of Group 1 metal, the concentrations of Zn ranged from 0.058 to 0.132 $\mu\text{g}/\text{m}^3$, with the highest level at the smallest size group (0.4–0.7 μm), in fine particles. However, Zn concentrations ranged from 0.006 to 0.008 $\mu\text{g}/\text{m}^3$ in coarse particles. These size trends of the metal concentrations were almost matched with the size distribution characteristics of metals in urban aerosol studies by in the Karanasiou *et al.* (2007) and Espinosa *et al.* (2001). The analysis of the metals classified into Group 1 category suggests that anthropogenic sources were the dominant contributors to the formation of fine particles. Concentrations of Mn, Cd, and Ni in fine particles less than 2.1 μm accounted for 62, 78, and 63%, which are less than the values reported in the previously studies (Espinosa *et al.*, 2001; Karanasiou *et al.*, 2007), of their total concentrations in PM_{10} , respectively, while 59% of the Cr concentration in PM_{10} was from submicron particles (0.4–0.7 μm). The presence of these toxic metals in the fine particles, which can reach deeply into the alveolar region in the lungs, might increase respiratory symptoms or diseases via long term exposure. The concentration of Zn in the fine particles identified in this study was much higher than the 13–25% obtained by Janssen *et al.* (1997) and lower than 52% determined by Wang *et al.* (2006).

Group 2, including light metals (Na, Ca, Al and K) and Fe, showed increased concentrations with increase in particle size, which is well matched with the size characteristics identified in the previously studies (Espinosa *et al.*, 2001; Karanasiou *et al.*, 2007). Group 2 metals represented a strong contribution to the coarse particles particularly for particles larger than 5.8 μm and mainly originated from crustal sources (Wang *et al.*, 2006). The sampling period included a few sandstorm events in the Asian Continent. Some metals derived from crustal sources may be indicative of particles transported from the Asian Dust events. Al, K, Ca and Fe showed high concentrations in the particle size range of 9–10 μm , while Na showed a peak in the particle size range of 4.7–5.8 μm .

The metals in group 3 (Pb, Mg and Cu) showed increasing concentrations in the size range of 1.1–5.8 μm , but decreasing concentrations in the size group above 5.8 μm . The size distribution trend of Pb concentration was roughly matched with the study result by Karanasiou *et al.* (2007). Higher concentrations of Cu, Pb and Mg were observed in the size range less than 5.8 μm suggesting that

these elements come from both crustal and anthropogenic sources. In particular, Cu had a bimodal distribution, including one peak at the submicron size range 0.4–0.7 μm and the other at 4.7–5.8 μm . Pb showed a peak in the size range of 1.1–2.1 μm which occupied 57% of the concentration in the fine particles.

Concentrations and Enrichment Factors of Heavy Metals

Table 3 shows the average concentrations of the toxic heavy metals (Cd, Mn, Ni and Pb) identified in 8 size groups (0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and 9.0–10.0 μm) of the PM collected in this study. All the mean levels of Cd in eight size fractions were exceeded the assessment thresholds (5 ng/m^3) proposed in the Directive of the European Parliament and of the Council (CEC, 2003). In particular, the Cd concentrations in the fine particles less than 2.1 μm were extremely high: 62.6, 41.2, 21.2 ng/m^3 for the size range of 0.4–0.7, 0.7–1.1 and 1.1–2.1 μm , respectively. Thus the Cd concentrations in $\text{PM}_{0.4-0.7}$, $\text{PM}_{0.7-1.1}$, and $\text{PM}_{1.1-2.1}$ in the ambient air were much higher (ranging from 4 to 12 times) as compared the proposed assessment threshold. The Cd concentrations in each size group over the coarse particle range were also exceeded the proposed threshold. The mean concentrations of Ni at the size larger than 2.1 μm (coarse particles) were lower than the proposed assessment threshold. However, the levels of Ni in fine particles less than 2.1 μm also exceeded the proposed assessment threshold (20 ng/m^3) (CEC, 2003). The mean concentration (153.1 ng/m^3) of Mn only at the smallest size 0.4–0.7 μm was observed to exceed the annual tolerance concentration (150 ng/m^3) included in the WHO Air Quality Guidelines) (CEC, 2003). The total concentrations of Cd, Mn and Ni obtained by summing up the concentrations of the 8 size groups were exceeded the proposed ambient assessment thresholds or air quality guidelines of them (WHO, 2002; CEC, 2003). This reveals that airborne particulate matter, containing high concentrations of Cd, Mn, and Ni, may pose a health risk for the local people who spend longer time in the urban area of the industrial city. However, the total mean concentration of Pb in was below the annual air quality standard (500 ng/m^3) specified in the EU) (EC, 1999).

Table 4 shows the enrichment factor (EF) values obtained based on the Fe value as a reference element of the heavy metals identified in the 4 classified size groups (Zoller *et al.*, 1974; Bilos *et al.*, 2001; Manoli *et al.*, 2002). Most of the heavy metals such as Cd, Pb, Zn, Cu, Cr and Ni showed very high EF values for all the sizes of particles. For these heavy metals with very high EF values, non-crustal sources, such as smelting, vehicular exhausts, fossil

Table 3. Average concentrations of heavy metals in 8 size groups of airborne particulate matter.

Size (μm)	Metal concentration (ng/m^3) in particle size group								Metal standard
	0.4–0.7	0.7–1.1	1.1–2.1	2.1–3.3	3.3–4.7	4.7–5.8	5.8–9.0	9–10	
Cd	62.57	41.21	21.29	6.42	6.21	6.42	7.69	7.86	5 (CEC, 2003)
Ni	58.59	47.33	28.52	5.97	6.74	7.57	5.61	7.37	20 (CEC, 2003)
Mn	153.10	79.69	57.81	13.82	14.44	10.61	7.31	21.72	150 (WHO, 2000)
Pb	30.49	31.52	35.07	34.41	32.80	29.20	19.69	16.48	500 (EC, 1999)

Table 4. Enrichment factor (EF) values calculated for different size fractions.

Size	Mn	Ni	Cu	Zn	Pb	Cr	Cd
< 0.7 μm	61.2	278.3	398.1	790.8	1025.2	1859.0	77959.5
0.7–2.1 μm	14.7	103.0	177.1	173.3	542.7	99.5	31821.7
2.1–5.8 μm	3.4	22.2	230.9	49.7	635.2	118.4	7828.6
5.8–10 μm	2.0	11.5	90.3	19.9	191.7	54.9	5149.8

fuel combustions and several industrial processes, are considered the major emissions sources to the ambient air (Sabbioni *et al.*, 1993). Mn showed high EF values for only fine particles less than 2.1 μm , which indicates non-crustal sources for Mn only in fine mode. EF values of heavy metals generally increased with decreasing particle size, suggesting stronger contributions of non-crustal sources to the finest particles. Gao's study in the New York-New Jersey harbor estuary also reported high EF values of 200 to 20,000 for Cu, Pb, Zn and V (Gao *et al.*, 2002).

The EF values of Cd ranged from 5,150 to 77,960 indicating extreme contamination by non-crustal or anthropogenic sources such as non-ferrous metal (Cu, Zn, etc) smelting for all the size groups. Based on the EF values of Cd in PM collected from the urban residential area of the industrial city, it is necessary to identify the sources of the Cd in airborne PM and implement proper control strategies for Cd level reduction. Also, EF values of Pb and Cr, particularly in the finest size fraction (< 0.7 μm), were still very high and will require similar countermeasures as Cd. The EF values of Cu, Pb and Cr at sizes from 2.1 to 5.8 μm were higher than those at sizes from 0.7 to 2.1 μm . Therefore, heavy metals can originate from vehicle and industrial emissions for the fine particles as well as from suspended road dust for the medium particles (2.1–5.8 μm) due to vehicle movements. Suspended road dust can also contain Cu, Pb and Cr via atmospheric deposition of particles with these metallic elements.

Source Identification of Metals

To identify and estimate possible sources of different size fractions of metallic elements, this study used Principal Component Analysis (PCA) using Varimax rotation and retention of principle components with eigenvalues >1 (SPSS 13). The PCA analysis reduced the number of variables (13 metals) while retaining as much as possible of the original information. Hence, variables with similar characteristics could be rearranged into the same factors (Fang *et al.*, 2004). The impactor size ranges were divided in the following categories: fraction 1 (< 0.7 μm : alveolar) refers to the sum of the concentration of stages 1–2, fraction 2 (0.7–2.1 μm : bronchial) represents the sum of stages 3–4, fraction 3 (2.1–5.8 μm : tracheo-bronchial) corresponds to stages 5–7 and fraction 4 (5.8–10 μm : extrathoracic) is the sum of stages 8–9.

Four factors for each size group were identified and they explained a total variance of almost 84%. Table 5 shows the factor analysis of metallic element concentrations for the four size groups of particle samples (20 sample sets for each size group) collected during the spring and summer seasons. PCA results indicate that four factors explain most of the data variance. In all the size groups, factor 1 presented high loading on Al, Ca, K, Mg, Fe, Zn and Cr. Al, Ca, Mg and Fe can be interpreted as the mineral source. Vehicle exhaust can include Fe, Zn and Cr. Since the sampling site was located near a busy traffic rotary and a highway, vehicular movement generated suspensions of soil/road dust, thus road dust with around 40% of the

Table 5. Varimax rotated principal component loadings for the size fractionated aerosol collected at the Ulsan metropolitan area.

Metals	< 0.7 μm		0.7–2.1 μm			
	F1	F2	F1	F2	F3	F4
Al	0.93	-	0.90	-	-	-
Ca	-	-	-	0.61	-	-
Cd	-	0.94	-	0.86	-	-
Cr	0.67	-	0.68	-	-	-
Cu	-	0.94	-	0.86	-	-
Fe	0.56	-	-	-	0.85	-
K	0.97	-	0.96	-	-	-
Mg	0.88	-	0.92	-	-	-
Mn	-	-	-	-	0.88	-
Na	-	0.97	-	0.88	-	-
Ni	-	-	-	-	-	0.86
Pb	-	-	-	-	-	-
Zn	0.95	-	0.95	-	-	-
% of Variance	43.4	23.4	40.3	23.2	13.5	8.9
Cumulative %	43.4	66.8	40.3	63.5	77.0	85.9
Origin	Road dust	Smelting/Marine	Road dust	Smelting/Marine	Crustal	Oil combustion

Table 5. (continued).

Metals	2.1–5.8 μm				5.8–10 μm			
	F1	F2	F3	F4	F1	F2	F3	F4
Al	0.95	-	-	-	0.92	-	-	-
Ca	-0.62	-	-	-	-0.61	0.64	-	-
Cd	-	0.91	-	-	-	0.90	-	-
Cr	0.62	-	-	-	-	-	-	0.82
Cu	-	0.91	-	-	-	0.97	-	-
Fe	0.85	-	-	-	-	-	0.83	-
K	0.95	-	-	-	0.94	-	-	-
Mg	0.92	-	-	-	-	-	0.84	-
Mn	-	-	-	0.97	-	-	-	0.91
Na	-	0.95	-	-	-	0.90	-	-
Ni	-	-	0.84	-	0.78	-	-	-
Pb	-	-	0.76	-	-	-	0.70	-
Zn	0.89	-	-	-	0.96	-	-	-
% of Variance	43.8	24.5	8.9	7.8	39.8	26.0	15.4	9.3
Cumulative%	43.8	68.3	77.2	85.0	39.8	65.8	81.2	90.5
Origin	Road dust	Smelting/ Marine	Traffic/Oil combustion	Shipbuilding	Road dust	Smelting/ Marine	Traffic/ Crustal	Shipbuilding

variance was dominantly associated with factor 1. Factor 2 ranged from 23.2 to 26% of variance with high loadings of Cd, Cu and Na. Cd, Pb and As have been used as tracers for non-ferrous metal smelters and automobile emissions and Cu has been often used as an indicator of air emissions from smelting industry (Fung *et al.*, 1995; Harrison *et al.*, 1996; Eddie *et al.*, 1999). Na is a component of marine sea salts. Hence, this factor was identified as a mixture of non-ferrous metal smelting and marine sources.

For factor 3, there was a slight indication of different sources among the different size fractions. For the medium size range (2.1–5.8 μm), the third factor with a high loading of Pb and Ni contributed percentage variance around 9–10%. Since Pb can come mainly from automobile exhaust and Ni is an indicator for oil combustion (Viana *et al.*, 2008), factor 3 for these sizes (2.1–5.8 μm) may indicate mixed sources of traffic and oil combustion. Factor 3 at the fine particle fraction (0.7–2.1 μm) showed high loadings of Fe and Mn (with a variance of 13.5%). Both natural and anthropogenic sources emit Mn (Kowalczyk *et al.*, 1982; Marcazzan *et al.*, 2001; Chao *et al.*, 2002). Mn and Fe correlated with the size fraction (0.7–2.1 μm), thus this factor can be the influence of industry (welding activities). Factor 3 of the coarse particles (5.8–10 μm) can be identified as a mix of traffic and crustal sources because of high loadings of Fe (0.83), Mg (0.84) and Pb (0.70). For fine particles less than 2.1 μm , the fourth factor had a high loading for only Ni with a variance around 8%. Ni is a marker for oil combustion (Zoller *et al.*, 1974; Kowalczyk *et al.*, 1982). Thus, factor 4 was identified as an oil combustion source. For the coarse particles (2.1–10 μm), factor 4 explained 8–9% of the total variance with high loadings of Mn and Cr. Welding is essential in the shipbuilding industry, one of three major industry categories in Ulsan. Welding activities produce large amounts of welding fumes and dust and also thermal degradation products from coated surfaces in the hull

assembly for shipbuilding. Welding fumes and dust include Mn. Thermal degradation products include Cr (Lee, 2009). Thus, factor 4 was associated with shipbuilding activities.

CONCLUSIONS

In the analysis of the size distribution and source apportionment of 13 metals in airborne particulate matter from an urban residential area of the largest industrial city in Korea, the following conclusions were reached:

- 1) Most of the fine particle mass was centered at the sizes between 0.7 and 1.1 μm . Coarse particle mass was mainly distributed in the size range of 9–10 μm . The highest PM levels were observed in the finest size range (< 0.7 μm) and in coarse particles (2.1–10 μm) in the spring. Fine particles (0.7–2.1 μm) had the highest PM concentrations in winter.
- 2) In the analysis of the size distribution characteristics of 13 metals, the following three groups were identified: (i) heavy metals (Cd, Zn, Mn, Ni and Cr) were present at high concentrations in fine particles (< 2.1 μm) and particularly at the size range of 0.4–0.7 μm , (ii) light metals (Na, Ca, K, Al) and Fe had strong contributions to coarse particles (2.1–10 μm), and (iii) the other metals (Pb, Cu and Mg) had high concentrations for sizes larger than 5.8 μm .
- 3) The predominance of toxic heavy metals, such as Cd, Ni and Mn, in the alveolar particle fraction (< 0.7 μm) and fine particles (< 2.1 μm) being deeply inhaled in the lungs, may increase the risk of adverse health effects particularly for the individuals who spend long time in the urban area of the industrial city.
- 4) EF values of Al, Ca, K, Mg, Na were less than 10, implying that crustal sources were predominant for these light metals. Most of the heavy metals such as Cd, Pb, Zn, Cu, Cr and Ni showed very high EF values at all particle sizes, suggesting that there were stronger

contributions of non-crustal sources to the finest particles. In particular, Cd in PM had extremely high EF values of 5,150–77,960 indicating extreme contamination by anthropogenic Cd sources. Based on the EF values of Cd in PM collected from the urban residential area of the industrial city, it is necessary to identify the sources of the Cd in airborne PM and implement proper control strategies for Cd level reduction.

- 5) Results of principal components analyses for 13 metals indicate that the principal sources were natural sources including soil/crustal elements and marine sources and local anthropogenic sources such as non-ferrous metal smelting, oil combustion, welding for shipbuilding, vehicular exhaust, and traffic and road dust.

REFERENCES

- Allen, A.G., Nemitz, E., Shi, J.P., Harrison R.M. and Greenwood, J.C. (2001). Size Distributions of Trace Metals in Atmospheric Aerosols in the United Kingdom. *Atmos. Environ.* 35: 4581–4591.
- Begum, B.A., Biswas, S.K., Markwitz, A. and Hopke, P.K. (2010). Identification of Sources of Fine and Coarse Particulate Matter in Dhaka, Bangladesh. *Aerosol Air Qual. Res.* 10: 345–353.
- Bilos, C., Colombo, J.C., Skorupka, C.N. and Presa, M.J.R. (2001). Sources, Distribution and Variability of Airborne Trace Metals in La Plata City area, Argentina. *Environ. Pollut.* 111: 149–158.
- Cheng, Y.H. and Lin, Y.L. (2010). Measurement of Particle Mass Concentrations and Size Distributions in an Underground Station. *Aerosol Air Qual. Res.* 10: 22–29.
- CEC (2003). *Proposal for a Directive of the European Parliament and of the Council, Relating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons in Ambient Air*, Commission of the European Communities, Brussels. Available from: http://europa.eu.int/eur-lex/en/com/pdf/2003/com2003_0423en01.pdf.
- Chao, C.Y. and Wong, K.K. (2002). Residential Indoor PM₁₀ and PM_{2.5} in Hong Kong and the Elemental Composition. *Atmos. Environ.* 36: 265–277.
- Dockery, D.W. and Pope, C.A. (1994). Acute Respiratory Effects of Particulate Air Pollution. *Aun. Rev. Publ. Health.* 15: 107–132.
- EC (1999). Council Directive 1999/30/EC Relating to Limit Values for Sulphur Dioxide, Nitrogen Dioxide and Oxides of Nitrogen, Particulate Matter and Lead in Ambient Air. Official Journal of the European Communities, L163.
- Eddie, L., Chan, C.K. and Paatero, P. (1999). Application of Positive Matrix Factorization in Source Apportionment of Particulate Pollutants in Hong Kong. *Atmos. Environ.* 33: 3201–3212.
- Espinosa, A.J.F., Rodriguez, M.T., Rosa, F.J.B. and Sanchez, J.C.J. (2001). Size Distribution of Metals in Urban Aerosols in Seville (Spain). *Atmos. Environ.* 35: 2595–2601.
- Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.P.C., Yang, I.L. and Chen, M.H. (2004). Characterization, Identification of Ambient Air and Road Dust Polycyclic Aromatic Hydrocarbons in Central Taiwan, Taichung. *Sci. Total Environ.* 327: 135–146.
- Fang, G.C., Chang, C.N., Wu, Y.S., Wang, V., Fu, P.P.C., Yang, D.G., Chen, S.C. and Chu, C.C. (2000). The Study of Fine and Coarse Particles, and Metallic Elements for the Daytime and Night-time in a Suburban Area of Central Taiwan, Taichung. *Chemosphere* 41: 639–644.
- Fang, G.C., Wu, Y.S., Chang, S.Y., Huang, S.H. and Rau, J.Y. (2006). Size Distributions of Ambient Air Particles and Enrichment Factor Analyses of Metallic Elements at Taichung Harbor near the Taiwan Strait. *Atmos. Res.* 81: 320–333.
- Fung, Y.S. and Wong, L.W.Y. (1995). Apportionment of Air Pollution Sources by Receptor Models in Hong Kong. *Atmos. Environ.* 29: 2041–2048.
- Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van, D.A., Glenn, T.R. and Eisenreich, S.J. (2002). Characterization of Atmospheric Trace Elements on PM_{2.5} Particulate Matter over the New York-New Jersey Harbor Estuary. *Atmos. Environ.* 36: 1077–1086.
- GradeASteel (2011). Ultrafine Particles: Encyclopedia. www.gradeasteel.com/Ultrafine_particles/encyclopedia.htm.
- Harper, S.L., Walling, J.F., Holland, D.M. and Pranger, L.J. (1983). Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particulates. *Anal. Chem.* 55: 1553–1557.
- Harrison, R.M., Smith, D.T.J. and Luhana, L. (1996). Source Apportionment of Atmospheric Polycyclic Aromatic Hydrocarbons Collected from an Urban Location in Birmingham, UK. *Environ. Sci. Technol.* 30: 825–832.
- Held, A., Zerrath, A., McKeon, U., Fehrenbach, T., Niessner, R., Plass-Dülmer, C., Kaminski, U., Berresheim, H. and Pöschl, H. (2008). Aerosol Size Distributions Measured in Urban, Rural and High-alpine Air with an Electrical Low Pressure Impactor (ELPI). *Atmos. Environ.* 42: 8502–8512.
- Infante, R. and Acosta, I.L. (1991). Size Distribution of Trace metals in Ponce, Puerto Rico Air Particulate Matter. *Atmos. Environ.* 25B: 121–131.
- Janssen, N.A.H., VanMansom, D.F.M., Van, D.J.K., Harssema, H. and Hoeck, G. (1997). Mass Concentration and Elemental Composition of Airborne Particulate Matter at Street and Background Locations. *Atmos. Environ.* 31: 1185–1193.
- Karanasiou, A.A., Sitaras, I.E., Siskos, P.A. and Eleftheriadis, K. (2007). Size Distribution and Sources of Trace Metals and n-alkanes in the Athens Urban Aerosol during Summer. *Atmos. Environ.* 41: 2368 – 2381.
- Kowalczyk, G.S. and Gordon, G.E. and Rheingrover, S.W. (1982). Identification of Atmospheric Particulate Sources in Washington, DC, Using Chemical Element Balances. *Environ. Sci. Technol.* 16: 79–90.
- Lee, J.H. (2009). A Study on Component Analysis and Reduction of Welding Fume and Dust from the Hull Assembly in Shipbuilding Industries, M.S. Thesis of the University of Ulsan, Korea.

- Manoli, E., Voutsas, D. and Samara, C. (2002). Chemical Characterization and Source Identification Apportionment of Fine and Coarse Air Particles in Thessaloniki, Greece. *Atmos. Environ.* 36: 949–961.
- Marcazzan, G.M., Vaccaro, S., Valli, G. and Vecchi, R. (2001). Characterisation of PM₁₀ and PM_{2.5} Particulate Matter in the Ambient Air of Milan (Italy). *Atmos. Environ.* 35: 4639–4650.
- McCormac, B.H. (1971). *Introduction to the Scientific Study of Atmospheric Pollution*, Reide Dordrecht, Holland.
- Sabbagh-Kupelwieser, N., Horvath, H., Szymanski, W.W. (2010). Urban Aerosol Studies of PM₁ Size Fraction with Reference to Ambient Conditions and Visibility. *Aerosol Air Qual. Res.* 10: 425–432.
- Sabbioni, C. and Zappia, G. (1993). Characterization of Particles Emitted by Domestic Heating Units Fuelled by Distilled Oil. *Atmos. Environ.* 27A: 1331–1338.
- Salma, I., Maenhaut, W. and Gyula Záray, G. (2002). Comparative Study of Elemental Mass Size Distributions in Urban Atmospheric Aerosol. *J. Aerosol Sci.* 33: 339–356.
- Salma, I., Ocskay, R., Raes, N. and Maenhaut, W. (2005). Fine Structure of Mass Size Distributions in an Urban Environment. *Atmos. Environ.* 39: 5363–5374.
- Samara, C. and Voutsas, D. (2004). Size Distribution of Airborne Particulate Matter and Associated Heavy Metals in the Roadside Environment. *Chemosphere* 59: 1197–1206.
- Seinfeld, J.H. (1986). *Atmospheric Chemistry and Physics of Air Pollution*, John Willey, New York.
- Srivastava, A., Gupta, S. and Jain, V.K. (2009). Winter-time Size Distribution and Source Apportionment of Total Suspended Particulate Matter and Associated Metals in Delhi. *Atmos. Res.* 92: 88–99.
- Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W. and Hitzenberger, R. (2008). Source Apportionment of Particulate Matter in Europe: A Review of Methods and Results. *J. Aerosol Sci.* 39: 827–849.
- Wang, X., Sato, T. and Xing, B. (2006). Size Distribution and Anthropogenic Sources Apportionment of Airborne Trace Metals in Kanazawa, Japan. *Chemosphere* 65: 2440–2448.
- Wagner, A., Boman, J. and Gatari, M.J. (2008). Elemental Analysis of Size-fractionated Particulate Matter Sampled in Göteborg, Sweden. *Spectrochim. Acta, Part B* 63: 1426–1431.
- World Health Organization (WHO) (2000). Air Quality Guidelines for Europe. WHO Regional Publications, Eur. Ser. No91. Regional Office for Europe, Copenhagen, Denmark.
- Zoller, W.H., Gladney, E.S. and Duce, R.A. (1974). Atmospheric Concentration and Sources of Trace Metals in the South Pole. *Science* 183: 198–200.

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