Seasonal Variation and Sources of Heavy Metals in Atmospheric Aerosols in a Residential Area of Ulsan, Korea

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ABSTRACT

This study investigated seasonal variations in mass concentrations of particulate matter (PM) and compositions of heavy metals in $PM_{2.5}$ and PM_{10} collected from a typical urban residential area in Ulsan, Korea. PM measurements were conducted during spring and summer of 2009. Mean concentrations of $PM_{2.5}$ in spring and summer were 23.2 and 18.1 $\mu g/m^3$, respectively. Mean concentrations of PM_{10} in spring and summer were 45.9 and 33.2 $\mu g/m^3$, respectively. The lower summer PM concentrations as compared to the spring ones are due to the increased rainfall precipitation. Airborne PM was analyzed for these heavy metals: Fe, Zn, Cd, Mn, Pb, Cu, Cr and Ni. All of the metals in $PM_{2.5}$ and PM_{10} had higher concentrations in spring than in summer, except Cr in PM_{10} which shows similar concentrations between spring and summer. Seasonal differences in the metal concentrations may be due to differences in wind directions with some winds passing through industry or traffic areas. Analysis of enrichment factors of heavy metals showed highly enriched Cd, Zn, Pb and Cu. Principal component analysis for the heavy metals in $PM_{2.5}$ and PM_{10} identified industrial emissions and road dust (soil and traffic) as major sources at the sampling site.

Keywords: Temporal variation; $PM_{2.5}$; PM_{10}; Heavy metals; Source identification.

INTRODUCTION

The association of particulate matter (PM) with adverse health effects has been recognized for a long time. Many studies have reported that people exposed to high concentrations of PM, particularly fine particles, show increased respiratory symptoms, outbreaks of cancer and even mortality rates (Dockery and Pope, 1994; Espinosa *et al.*, 2001; Shah *et al.*, 2006a). Size, concentration, composition and toxicity of PM are important factors which can greatly affect the possible human health problems associated with exposure to airborne PM. Ambient concentrations of total suspended particulates (TSP) and PM_{10} have been investigated (Samara *et al.*, 2003; Quiterio *et al.*, 2004; Shah *et al.*, 2006b; Pérez *et al.*, 2008), but recently, research of PM has focused on fine particles such as $PM_{1.0}$ and $PM_{2.5}$ because of strong correlations of PM to adverse health effects (Begum *et al.*, 2010). However, PM_{10} (thoracic size fractions) and $PM_{2.5}$ (alveolar size fractions) are usually selected as the monitoring parameters for evaluations of air quality (Bešlic *et al.*, 2004; Gehrig, 2007). $PM_{4.0}$ is known to "finer size fraction that could penetrate the conductive airways of the tracheobronchial tree that distributes the inhaled air to the gas-exchange airways in the lungs" (Mar *et al.*, 2004), and thus it is called a respirable size fraction. Also, some have argued that $PM_{1.0}$ could be substituted as a better standard cut-off point or more effective indicator for fine particles rather than $PM_{2.5}$ (Pérez *et al.*, 2008) because human respiratory symptoms are highly associated with $PM_{1.0}$ levels (Pope *et al.*, 2006). The detailed analysis of fine particles at certain level of interest areas can be crucial information for evaluating adverse health effects of PM exposure.

PM pollution is a serious environmental issue mainly due to the presence of toxic substances and trace metals in the atmosphere (Shah *et al.*, 2006b). Heavy metals associated with respirable particles have also been shown to increase lung or cardiopulmonary injuries caused by particulate air pollutant exposure (Espinosa *et al.*, 2001; Cancio *et al.*, 2008; Leili *et al.*, 2008). Natural emissions (crustal minerals, forest fires and oceans), traffic and industrial emissions (combustion of fossil fuel and industrial metallurgical processes) are the principal sources of heavy metals in the ambient air (Park *et al.*, 2008; Xu *et al.*, 2010; Cheung *et al.*, 2011). Traffic emissions also represent potential sources of trace heavy metals, including combustion products from fuel and oil, road construction materials, road dust and wear products from tires, brake linings and bearings (El-Fadel *et al.*, 2001; Kothai *et al.*, 2008). Naturally derived trace metals are usually found in coarse particles (Stone *et al.*, 2011). However, trace metals of anthropogenic origin

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are mainly distributed in fine particles which are able to carry more toxic chemicals to human beings and ecosystems than the coarse fractions (Fang *et al.*, 2000; Fang *et al.*, 2006; Zhao *et al.*, 2011).

Ulsan is the largest industrial city in Korea, thus its air quality is an important environmental issue. Air emissions from industrial activities may even affect residential areas at remote distances from industrial sectors. The objective of this study was to investigate temporal variation in mass concentrations and heavy metal components in thoracic and alveolar size fractions included in airborne particulate matter collected from the residential area in a typical industrial city of Korea. Also, this study aimed to identify possible sources of heavy metals associated with the atmospheric aerosols using enrichment factors (EFs) and principal component analysis (PCA).

MATERIALS AND METHODS

Site Description and Sampling

Ulsan is the largest industrial city with a population of 1.1 million and has two national scales of industrial complexes (ICs) including fine- and petro-chemical IC, non-ferrous metal IC, automobile and mechanical IC, and shipbuilding zones. Daily samples were collected on the roof (7.5 m height) of the Mugeo-dong office, which is in a typical residential area of the metropolitan city of Ulsan, Korea. The sampling site is located in a busy urban residential area which is in a part of the western center of the city. The sampling site was 700 m from a university campus, 120 m from a highway, 200 m from a busy traffic rotary, and approximately 6 to 8 km from the petrochemical industrial complex in Ulsan. 20 daily-airborne PM samples were collected simultaneously using a high volume PM_{10} sampler (Model 6070, Tisch Environmental, Inc., USA) and a PQ 200 $PM_{2.5}$ sampler from May to August 2009 (divided into spring and summer seasons). The high volume sampler (1.13 m^3/min) for PM_{10} measurements and PQ 200 (16.7 L/min) for $PM_{2.5}$ measurements were loaded with Whatman quartz fiber filters at a size of 203 × 254 mm and a diameter of 47 mm, respectively.

There might be a difference in $PM_{2.5}$ and PM_{10} value between the different measurement methods. Thus the $PM_{2.5}$ values obtained by the PQ 200 $PM_{2.5}$ sampler were compared by the $PM_{2.5}$ values retrieved by the cascade impactor from the same sampling sites. In the 12 repeated simultaneous measurements at the same sampling sites (6 from a residential site and 6 from a downtown site) during the spring sampling period, their average values (28.3 ± 17.4 and 28.3 ± 13.7 $\mu g/m^3$) were almost same. Even though there was a small difference in the $PM_{2.5}$ value each day, 12 repeated measurements also showed a very significant correlation ($r^2 = 0.919$) as shown in Fig. 1. Therefore, the $PM_{2.5}$ values obtained by PQ 200 $PM_{2.5}$ sampler and the cascade impactor (described in the following section) are acceptable. The PM_{10} values obtained by the high volume (hi-vol) PM_{10} sampler were also compared by the PM_{10} values retrieved by the β-ray attenuation method from the UNAPM) located in the same sampling site. In the 7 repeated simultaneous measurements at the same sampling site during the summer sampling period, there was a difference of 7.7% in the average PM_{10} values between the β-ray attenuation and the hi-vol methods ($r^2 = 0.923$, see Fig. 2). Even though there was a relatively large difference in the PM_{10} values on the first measurement day, the rest of 6 repeated measurements showed a very significant correlation ($r^2 = 0.954$). Therefore, the PM_{10} values obtained from the hi-vol sampler are acceptable for this study.

PM Concentration and Size Distribution Analysis

Before and after the sampling procedure, filters were kept for 48 h in desiccators in a environmentally conditioned room with a RH of 45 ± 5% and a temperature of 20 ± 2°C before being weighed by a microbalance (detectability of 1 μg). $PM_{2.5}$ and PM_{10} concentrations, collected by the PQ 200 and hi-vol samplers, were determined by gravimetric analysis using the weight difference of the filters before and after the sampling campaigns.
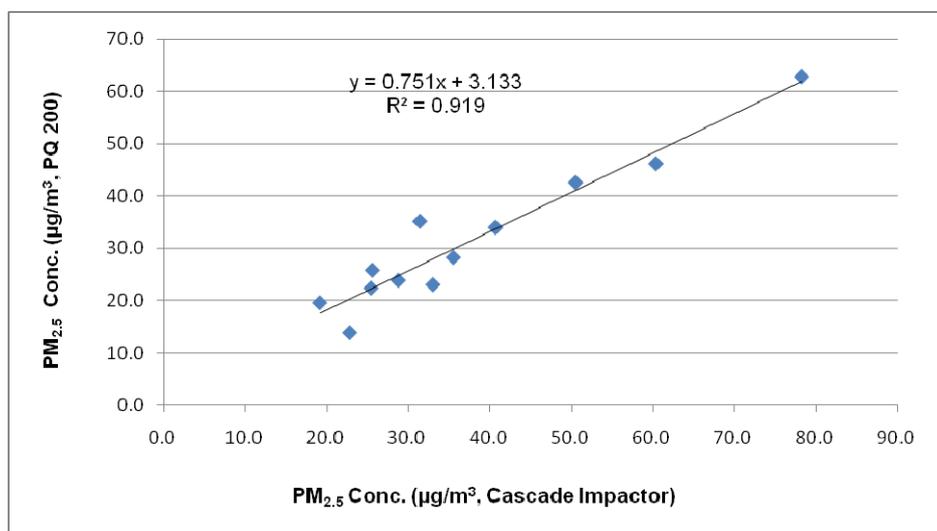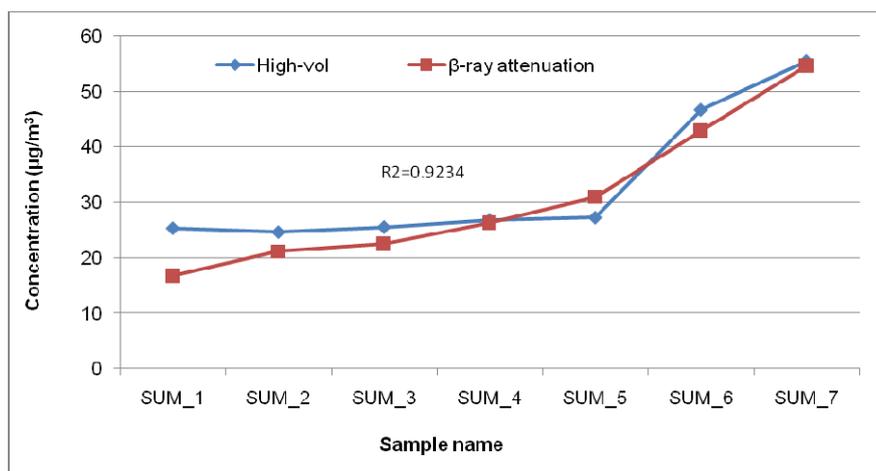

Fig. 1. Simultaneous $PM_{2.5}$ measurement by cascade impactor and $PM_{2.5}$ sampler (PQ 200) methods.

Fig. 2. Simultaneous PM_{10} measurement by high-volume sampler and β-ray attenuation methods.

This study analyzed seasonal PM concentration distributions for different size ranges of the particles collected by using an ambient cascade impactor (Model 20–800, Tisch Environmental, Inc.) and operating at the sampling site during both the spring and summer sampling periods. The cascade impactor had aerodynamic size cuts of 0.4, 0.7, 1.1, 2.1, 3.3, 4.7, 5.8, 9 and 10 µm. The cascade impactor was operated at a constant flow rate of 28.3 L/min and particulates were collected on glass fiber filters with diameters of 81 mm (Oh *et al.*, 2011). PM mass concentrations for nine particle size ranges, as previously separated by the cascade impactor, were determined by gravimetric analysis before and after PM sampling. The micro analytical electronic balance with a precision of ± 1 µg was used for gravimetric analysis after the glass fiber filters were kept for 48 h storage in desiccators in the environmentally controlled room described above. $PM_{2.5}$ concentrations from the cascade impactor were calculated by summing up the mass from backup stage (0.4 ≤ µm), stage 7 (0.4–0.7 ≤ µm), stage 6 (0.7–1.1 ≤ µm), stage 5 (1.1–2.1 ≤ µm), stage 5 (2.1–3.3 ≤ µm) x 0.84, and stage 4 (3.3–4.7 ≤ µm) × 0.13 ($PM_{2.5} = PM_{0–2.1} + 0.84$ x $PM_{2.1–3.3} + 0.13 × PM_{3.3–4.7}$). The multiplication values in the formula were obtained from the manufacturer of the cascade impactor. PM_{10} concentrations were also calculated by summing up the mass obtained from all the backup stages. This study also evaluated PM concentration distributions for the different size ranges, classified by the ambient cascade impactor, between a clear day and a rainy day in order to evaluate rain effect on the size-resolved particle concentrations.

Chemical Analysis

For analysis of metallic elements, filters were extracted with a mixture solution of 1.03 M HNO_3 and 2.03 M HCl (1:1) using an ultrasonic water bath at 90°C for 2 h. Samples were kept in a refrigerator at 4°C until analyzed. Extracted solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with related detection limits of Ni, Cd, Cr, Cu, Fe, Mn, Pb and Zn were 1.67, 0.33, 0.58, 1.52, 1.14, 0.26, 4.17 and 7.31

ng/mL, respectively. Relative standard deviations (RSD) were less than 2% for the concentrations of all of the elements measured using prepared standard solutions of reference materials accredited by the US National Institute of Science and Technology (NIST). The method for validating for accuracy and repeatability of metal analysis was conducted to analyze atmospheric particulate matter collected in urban area St. Louis, MO, USA from the standard reference material (SRM 1648a). The recovery analysis results of SRM 1648a was 103.2, 100.2, 3.4, 79.5, 79.9, 96.8, and 89.8% for Ni, Cd, Cr, Cu, Fe, Mn and Pb, respectively. Reproducibility of the elements was 1.25, 0.80, 1.52, 0.94, 0.84, 0.99, and 1.87% for Ni, Cd, Cr, Cu, Fe, Mn and Pb, respectively. One field blank with every 6 or 7 field samples was collected for monitoring purposes of background contamination. The field and filter blanks were analyzed using the same procedure as the samples. There was no significant difference between the filter and field blanks. The blank value of each heavy metal was subtracted from the analyzed values from the real samples.

Statistical Analysis

Source identification of the heavy metals in airborne particulates was performed by using a principal component analysis (SPSS version 13.0). Moreover, wind rose diagrams, including wind direction and wind speed during the sampling period, were obtained using Korean software for atmospheric dispersion modeling (Airmaster, version 2.0).

RESULTS AND DISCUSSION

Mass Concentrations of PM

Fig. 3 shows the median values with ranges of PM concentrations that were observed using PQ 200 $PM_{2.5}$ and hi-vol PM_{10} samplers over the study periods. Table 1 represents that the mean PM concentrations of $PM_{2.5}$, $PM_{2.5–10}$, and PM_{10} in spring were higher than those in summer. In general, higher PM concentrations in spring in Korea are blamed to the effects of Asian dust. Even after the main streams of Asian dust events passed through the region of interest, there were remaining fine particles which
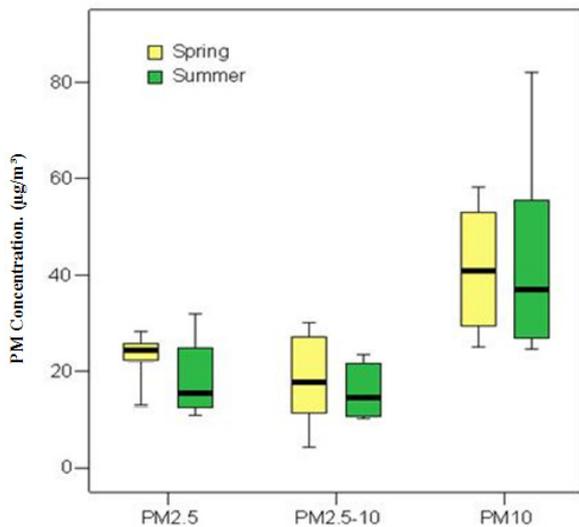
Fig. 3. PM concentration distribution in spring and summer.

contributed to increased local PM concentrations. In particular, Asian dust episodes can greatly increase PM concentrations of coarse particles (Lee *et al.*, 2005). However, this study did not take airborne PM samples during the Asian dust episodes. Only one sample might have been affected by remaining Asian dust. However, the PM concentration measured on that day was not that high as compared with other spring days. The ambient air temperature at the sampling site during the spring sampling periods in Ulsan was much lower than that during the summer ones (Table 2). The lower temperature leaded to more energy consumption for industrial purposes resulting in emitting more emissions of primary PM from the industrial sources. Also, dry atmospheric conditions in the spring season can produce more suspended particulate from surfaces of roads and soils. Also, increased pollens from plant surfaces can greatly contribute to increase in PM concentrations in the spring. Thus, the higher PM concentrations in the spring as compared to those in the summer could be due to the relatively cold weather, dry atmospheric conditions, and increased pollen levels in the spring season.

Within cities in Korea, average $PM_{2.5}$ and PM_{10} concentrations identified from Ulsan during the study periods were higher than those in Busan (winter average, 19.2 and 34.2 $\mu g/m^3$), but lower than in Seoul (winter average, 58 and 79.1 $\mu g/m^3$) (Kim *et al.*, 2006). Also, $PM_{2.5}$ and PM_{10} concentrations in Ulsan during the spring sampling periods were higher than the state of California standards (12 and 20 $\mu g/m^3$ for annual $PM_{2.5}$ and PM_{10}, respectively) in USA and the WHO standards (10 and 20 $\mu g/m^3$ for annual $PM_{2.5}$ and PM_{10}, respectively) (Krzyzanowski *et al.*, 2008).

Table 1 also shows the concentration ratios of fine particles

to coarse particles. Lower value in $PM_{2.5}/PM_{10}$ and higher value in $PM_{2.5}/PM_{2.5-10}$ in the spring as compared to those in the summer which indicates that spring has a higher coarse fraction. In general, weather conditions during spring periods in Korea are dry with lower humidity as compared to those in summer periods (Table 2). In 2009, the mean ratios $PM_{2.5}/PM_{10}$ during the spring and the summer sampling time were 0.54 and 0.59, respectively. This means the predominant component in PM_{10} was $PM_{2.5}$ in Ulsan. The average ratios of $PM_{2.5}/PM_{10}$ in this study were similar to that in Busan, Korea (0.56) (Kim *et al.*, 2006). However, the value of $PM_{2.5}/PM_{10}$ in Ulsan was much lower than those in Seoul, Korea (0.73), in Taichung, Taiwan (0.62), and in Basel, Switzerland (0.76) (Wu *et al.*, 2007; Fang *et al.*, 2008). This indicates that PM_{10} in the study area of Ulsan has a relatively increased fraction of coarse particles as compared other cities.

Seasonal PM Comparison

Fig. 4 shows a seasonal comparison of PM concentrations as a function of particle size between the spring and the summer sampling periods. The two seasons had different distribution patterns of PM concentrations for the particle size range classified by the cascade impactor analysis. The spring concentrations showed a distinct bimodal distribution with one peak in fine particles ($PM_{2.5}$) and the other peak in coarse particles ($PM_{4.7-10}$). However, the summer concentrations showed trimodal distribution with three peaks at $PM_{1.1}$, $PM_{1.1-4.7}$, and $PM_{4.7-10}$. The difference in meteorological conditions between the spring and the summer seasons could lead to the difference in size-resolved PM concentrations. Dry weather conditions in the spring may increase more PM concentrations over coarse particle ranges in the spring time than those in the summer. High concentrations that may exist in the fine particles, particularly ranged from 0.4 to 2.1 μm, in the spring may be due to the combination effects of traffic engine emissions and industrial emissions such as combustion of fossil fuels.

Summer seasons in Korea mostly include the monsoon period which usually has large amounts of precipitation and high relative humidity (Table 2). Fig. 5 shows a size distribution of particles collected from the sampling site on the clear day without wet precipitation activities, such as rain, and on the rain day with 5.5 mm precipitation/day in early June of 2009. Rain causes large decrease in all the analyzed particle size ranges, except for 0.4–0.7 μm, particularly showing large reduction in the size range of 0.7–2.1 μm and 9.0–10 μm. Thus, these meteorological conditions, such as increased rainfall and humidity, during the summer periods can greatly decrease PM concentrations in ambient air via rainout or washout mechanisms (Pillai *et al.*, 2002; Glavas *et al.*, 2008). Also, the size of particles

Table 1. PM concentrations ($\mu g/m^3$) and their ratios in spring and summer.

Year	Season	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}	$PM_{2.5}/PM_{10}$	$PM_{2.5}/PM_{2.5-10}$
	Spring	23.2	18.1	41.3	0.54	1.28
2009	Summer	18.1	15.1	33.2	0.59	1.20
	Average	20.6	16.6	37.2	0.57	1.24

Table 2. Meteorological conditions at the sampling site during sampling periods.

Meteorological parameter	Spring	Summer
Temperature (°C)	13.9 ± 2.7	23.3 ± 2.2
Humidity (RH) (%)	63.2 ± 12.9	77.5 ± 10.9
Wind speed (m/s)	1.1 ± 0.7	1.1 ± 0.5
Rain fall (mm)	155.2	722.4

exposed to high humidity or rain drops may increase removal processes of the particles, easily. Thus, the difference in PM concentrations between the spring and the summer periods can be explained by the difference in weather pattern or meteorological condition for each specific season.

Metallic Elements in PM

Fig. 6 shows the average concentrations of heavy metals in $PM_{2.5}$ and PM_{10} obtained from the ambient air in the residential area of the industrial city during the study periods. Among the analyzed heavy metal concentrations, Fe showed the highest concentration, followed by Zn and Pb.

Higher concentrations of Zn and Pb might be due to the combined effects of industrial emissions and vehicle exhaust from traffic areas. All of the heavy metal concentrations in $PM_{2.5}$ and PM_{10} in the spring were higher than those in the summer. However, Ni concentrations in PM_{10} between spring and summer sampling periods were similar each other. The prevailing winds of spring were southeast direction, which passed through industrial areas in Ulsan (Fig. 7). The city of Ulsan has national scale industrial complexes (ICs), including petrochemical IC and non-ferrous metallic IC, which were located 6–8 km away from the sampling site. Therefore, differences in wind direction were the main reason for higher concentrations of heavy metals in the spring. The prevailing winds of summer were south-southwest direction, which may not greatly include emission sources of heavy metals leading to relatively lower concentrations in trace metals in atmospheric PM (Fig. 7).

Enrichment Factor

Calculation of enrichment factor (EF) values helps to determine whether a certain element has additional or
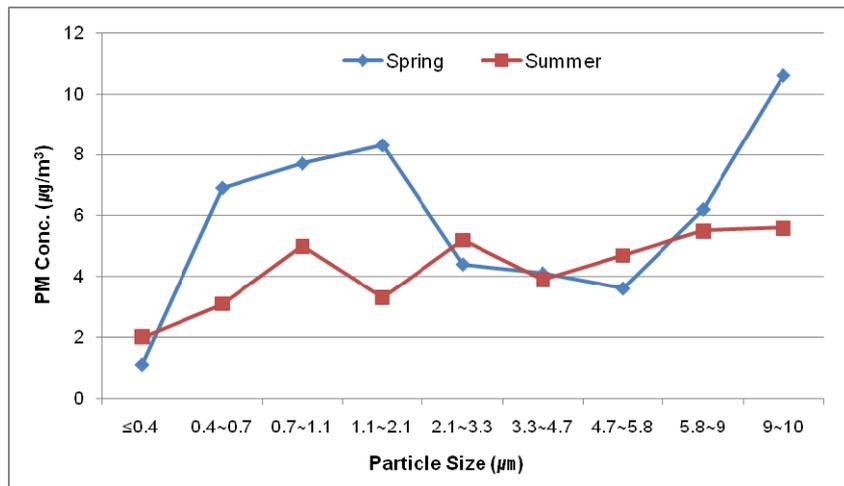
Fig. 4. Distribution of PM concentrations for size ranges classified by a cascade impactor between the spring and summer sampling periods.
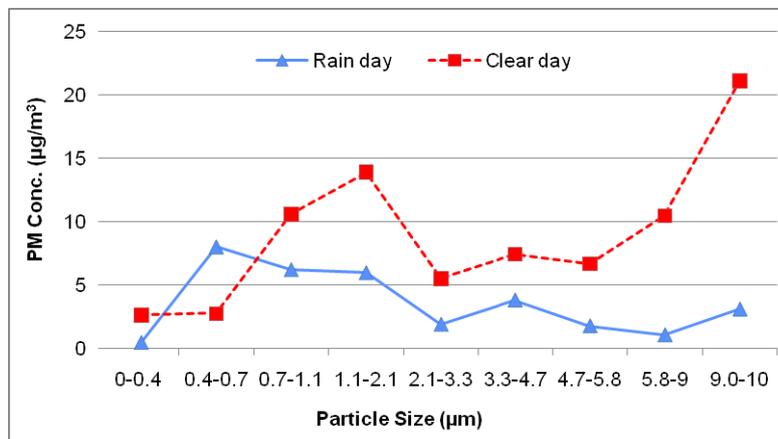
Fig. 5. Distribution of PM concentrations for size ranges classified by a cascade impactor on a clear day and a rain day at the sampling site.
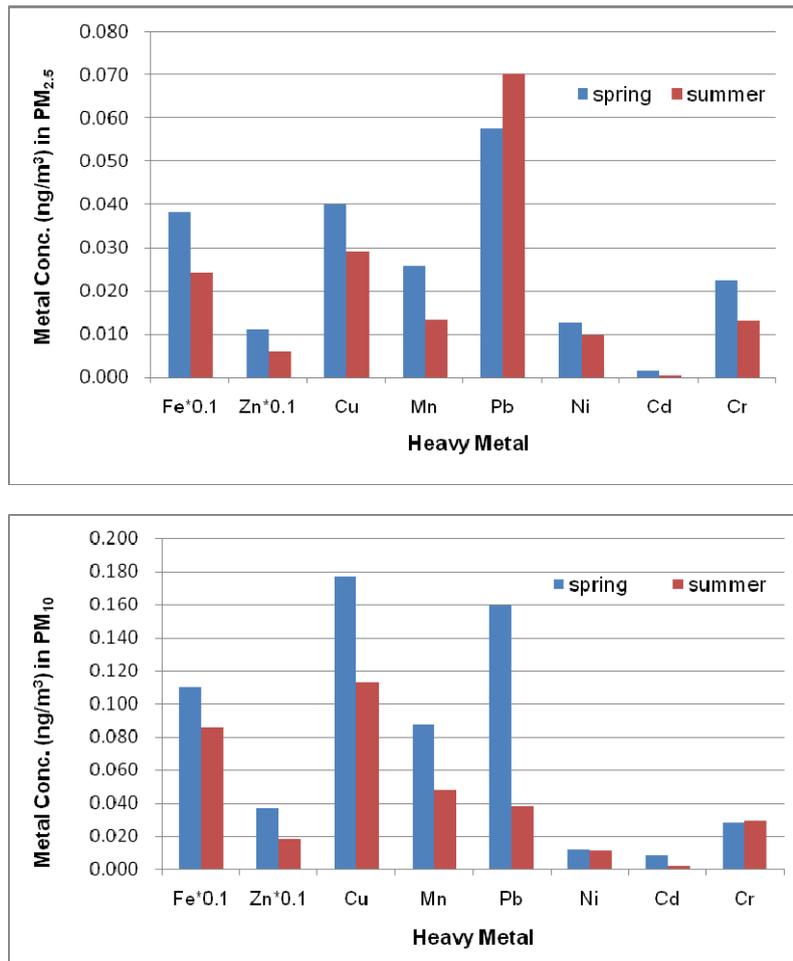
Fig. 6. Average concentrations of heavy metals in $PM_{2.5}$ and PM_{10} between spring and summer sampling periods.

| (a) | (b) |
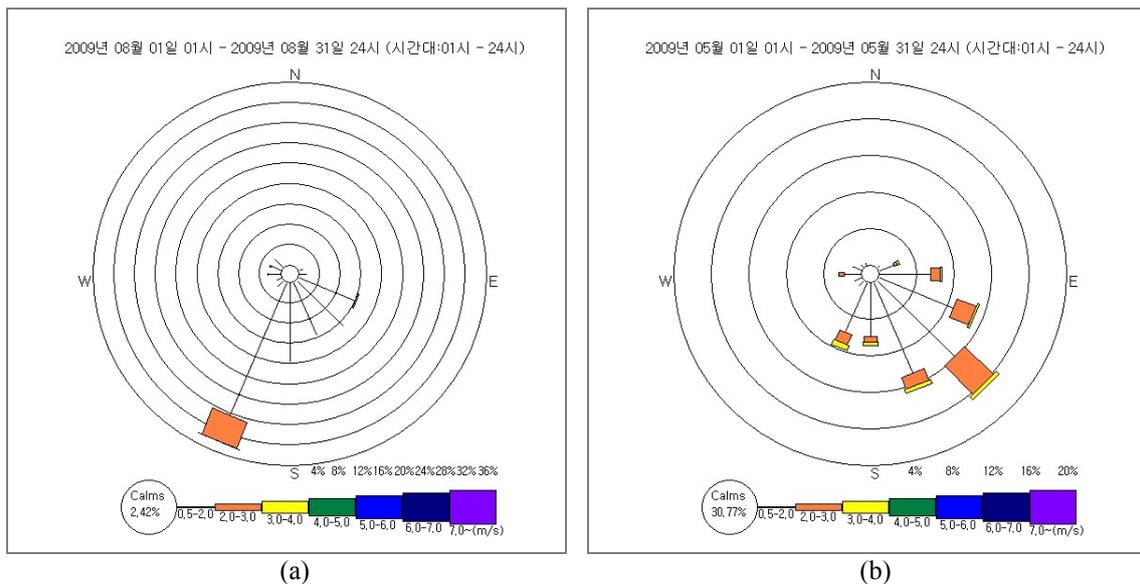
Fig. 7. Wind roses at the sampling site during (a) spring and (b) summer sampling periods.

anthropogenic sources other than its major natural sources. Since iron (Fe) has been used as a reference element for an EF evaluation, assuming that the contribution of its anthropogenic sources to the atmosphere is negligible

Yaroshevsky (2006), this study used the EF calculation formula as follows:

$$EF = (X/Fe)_{air}/(X/Fe)_{crust} \qquad (1)$$

If the EF value approaches unity, then crustal sources are predominant. In general, an EF > 5 indicates that a large fraction of the element can be attributed to non-crustal or anthropogenic sources (Wu *et al.*, 2007).

Table 3 shows the seasonal mean enrichment factors (EFs), based on average seasonal metal concentrations, of the heavy metals identified in $PM_{2.5}$ and PM_{10} collected from the residential site. EF values for Cd were the highest, followed by Pb, Zn and Ni, and their EFs were much higher than 5. This indicates that the collected PM fractions were extremely contaminated by anthropogenic Cd sources and were also heavily contaminated with anthropogenic Pb, Zn and Cu (Huang *et al.*, 2010).

Seasonal EF values of the heavy metals in $PM_{2.5}$ and PM_{10} showed similar trends between the spring and the summer seasons excluding Cd and Ni. Most of the heavy metals, except Cd and Ni, had higher EF values in the spring than those in the summer. Thus, the higher concentrations of trace metals in the spring were due to increased contributions of anthropogenic sources such as industrial emissions from the southeast direction (prevailing winds) during the spring season.

In comparison of EF values between $PM_{2.5}$ and PM_{10}, each metal shows different characteristics. The EF values of Cd, Pb, and Ni, which have mainly anthropogenic sources such as industrial emissions, in $PM_{2.5}$ were higher than those in PM_{10}. In particular, the EF values of Cd in $PM_{2.5}$ were 2.95 (spring) and 2.41 (summer) times higher than those in PM_{10}. The EF values of Ni and Pb in $PM_{2.5}$ were 2.35 and 1.05 times (spring) and 1.16 and 2.86 times (summer), respectively, higher than those in PM_{10}. This also indicates

that the exposure to fine particles in Ulsan can have more adverse health effects associated with Cd, Ni and Pb (Hieu and Lee, 2010). However, the EF values of Zn, Cu, Mn and Cr, which can be easily affected by traffic emissions (anthropogenic sources) and soil origins (natural sources), in $PM_{2.5}$ was lower than those in PM_{10}. These results indicate that metals in fine particles can be more affected by anthropogenic sources and those in coarse particles are affected by both anthropogenic and natural sources.

Source Identification

Table 4 shows the results of a principal component analysis (PCA) that was performed to identify common sources of heavy metals in daily $PM_{2.5}$ during spring and summer sampling time. PCA results of trace metals in $PM_{2.5}$ for spring showed three factors accounting for 91.4% of the overall variance. Factor 1 had high loadings for Zn, Mn, Pb, Cd and Ni which explained 54.5% of the total variance. This factor is associated with coal-oil combustion (Zn, Mn, Ni) and traffic emission sources (Zn, Pb, Cu, Cd, Cr, Mn and Ni) (Veron *et al.*, 1992; Manoli *et al.*, 2002; Samara and Voutsa, 2005; Viana *et al.*, 2008; Chang *et al.*, 2009). Thus, factor 1 can be identified as mixed sources of industrial activities from petrochemical IC and traffic emissions. Factor 2 explained 22.5% of the total variance and correlated with high loadings on Cu, Mn, and Ni. This factor represented Cu (or Zn) smelting sources (Viana *et al.*, 2008) located in the non-ferrous metal IC. Factor 3 explained 14.3% of the total variance and correlated with high loadings of Fe and Cr. Manoli *et al.* (2002) reported that road dust had high loadings on Fe, Mn, and Cr.

Table 3. Seasonal mean crustal enrichment factors (EF) of heavy metals based on average seasonal metal concentrations.

PM	Season	Fe	Zn	Cu	Mn	Pb	Cd	Cr	Ni
$PM_{2.5}$	Spring	1.0	174.8	227.3	4.0	275.8	9,940	3.3	97.8
	Summer	1.0	89.3	187.2	1.7	231.4	9,987	0.5	64.9
PM_{10}	Spring	1.0	198.8	347.3	4.6	263.3	3,366	6.9	41.7
	Summer	1.0	126.9	285.8	3.3	81.0	4,148	1.6	56.1
$PM_{2.5}/PM_{10}$	Spring	-	0.88	0.65	0.87	1.05	2.95	0.48	2.35
	Summer	-	0.70	0.66	0.52	2.86	2.41	0.31	1.16

Table 4. Rotated factor loading of heavy metals in $PM_{2.5}$.

Variable	Spring			Summer		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Fe		-	0.964	0.659	-	0.621
Zn	0.821	-	-	0.651	-	-
Cu	-	0.987	-	-	-	0.931
Mn	0.719	0.668	-	-	0.915	-
Pb	0.977	-	-	0.735	-	0.538
Cd	0.976	-	-	-	0.902	-
Cr	-	-	0.667	0.935		-
Ni	0.507	0.793	-	0.951	-	-
% of variance	54.5	22.5	14.3	44.4	23.8	19.9
Cumulative (%)	54.5	77	91.4	44.4	69.2	87.1
Main sources	Coal-oil combustion/ Road dust	Cu-Ni Smelting	Soil/Road dust	Road/Soil dust	Steel/Cd Industry	Soil dust

Natural soil dust such as Asian dust has also high loadings on Fe, Mn, and Cr (Lee *et al.*, 2004; Zhao *et al.*, 2011). Thus, factor 3 can be associated with soil/road dust.

In summer, three factors obtained in the PCA analysis of trace metals in $PM_{2.5}$ accounted for 87.1% of the overall variance. Factor 1 (44.4%) had high loadings for Fe, Zn, Pb, Cr and Ni which can be traffic emissions or road dust. Chang *et al.* (2009) reported that road dust near a steel plant had high loadings on Fe, Zn, and Pb. Also, high loading on Fe, Mn, and Cr reflects soil road dust (Manoli *et al.,* 2002). Thus factor 1 is assigned as road/soli dust. Steel production emissions show characteristic ratios of Mn/Cd and Mn/Ni and also high Mn emissions (Veron *et al.*, 1992). Factor 2 (23.8%) with very high loadings on Mn and Cd could be assigned as steel industry emissions in the automobile and mechanical IC and the shipbuilding zones. Factor 3 (19.9%) had high loading for Fe, Cu, and Pb, indicating emissions of soil dust.

Table 5 represents the PCA results used to identify common sources of heavy metals in daily PM_{10} during spring and summer sampling periods. PCA results of trace metals in PM_{10} for spring showed two factors, accounting for 88.1% of the overall variance. Factor 1 had high loadings for Zn, Mn, Pb, Ni, Cd and Cr which explained 73.5% of the total variance. This factor indicated a mixture of industrial emissions (Zn, Pb, Ni and Cd) (Yaroshevsky, 2006; Zabalza *et al.*, 2006; Querol *et al.*, 2007; Krzyzanowski and Cohen, 2008) and soil origins (Mn and Cr) (based on EF values shown in Table 3). Factor 2 (14.6%) was identified as a road dust source (Fe and Cu). In summer, two factors obtained in the PCA analysis of trace metals in PM_{10} accounted for 86.4% of the overall variance. Factor 1 accounted for 53.5% and had high loadings of Zn, Cu, Mn, Pb, Cd and Ni. This factor originated from vehicle emissions/oil combustion and resuspended road dust from urban areas with high traffic densities (Samara and Voutsa, 2005; Shah *et al.*, 2006b; Viana *et al.*, 2008). Factor 2 with 32.9% variance presented high loadings for Fe and Cr, indicating soil dust origins (based on EF values).

CONCLUSIONS

Based on the analysis of PM collected from a residential area of an industrial city in Korea, $PM_{2.5}$ and PM_{10} concentrations in spring were higher than those in summer. Increased energy uses and dry atmospheric conditions in the spring time contributed to increasing PM concentrations in spring period, while increased rainfall precipitation in summer time greatly contributed to decreasing PM levels in the summer period. The PM concentrations as a function of particle size distribution of PM in the spring showed a bimodal distribution with a peak in fine particles and another peak in coarse particles, while they showed three peak distributions in the summer. Rainfall decreased PM concentrations over all the analyzed particle size ranges, except for 0.4–0.7 m, with particularly a large concentration reduction in the size range of 0.7–2.1 μm and 9.0–10 μm.

All of the heavy metals in $PM_{2.5}$ and PM_{10} in the spring were higher than those in the summer. Increased concentrations of heavy metals in PM during the spring time could be attributed to increased contributions of industrial emissions, which could be transported by the prevailing winds during that time. Calculation of enrichment factors (EF) of the heavy metals showed high enrichment of Cd, Pb, Cu and Zn, indicating heavy contamination by anthropogenic sources. However, Mn and Cr had mostly crustal origins. The spring and summer EF values of Cd, Pb, and Ni in $PM_{2.5}$ were 2.95–2.41, 2.35–1.05, and 1.16–2.86 times, respectively, higher than those in PM_{10}. However, the EF values of Zn, Cu, Mn and Cr in $PM_{2.5}$ was lower than those in PM_{10}. Heavy metals in fine particles can be more affected by anthropogenic sources and those in coarse particles can be easily affected by both anthropogenic and natural sources. PCA results for $PM_{2.5}$ and PM_{10} showed industry emissions as the main sources of variance in the spring at the sampling site of Ulsan. However, major sources of variance for $PM_{2.5}$ and PM_{10} in the summer were road/soil dust and traffic emissions, respectively.

Table 5. Rotated factor loading of heavy metals in PM_{10}.

Variable	Spring		Summer	
	Factor 1	Factor 2	Factor 1	Factor 2
Fe	-	0.847	-	0.702
Zn	0.720	-	0.982	-
Cu	-	0.848	0.956	-
Mn	0.780	-	0.945	-
Pb	0.751	-	0.972	-
Cd	0.770	-	0.942	-
Cr	0.855	-	-	0.893
Ni	0.914	-	0.702	-
% of variance	73.5	14.6	53.5	32.9
Cumulative (%)	73.5	88.1	53.5	86.4
Main sources	Industry /Soil	Road dust	Traffic	Soil dust

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