Ultrafine Metal Concentration in Atmospheric Aerosols in Urban Gwangju, Korea

K. Park*, Y. Heo, H. E. Putra

Research Center for Biomolecular Nanotechnology, Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea

Abstract

PM_{10}, PM_5, and ultrafine (< 0.132 μm) mass concentrations, and metals (As, Be, Ca, Cd, Fe, K, Mn, Ni, Pb, Sb, Se, and Zn) in ultrafine particles were determined in urban Gwangju, Korea during the sampling periods of 4/2/2007-4/20/2007 in spring, 8/2/2007-9/12/2007 in summer, 11/19/2007-12/2/2007 in fall, and 1/16/2008-2/3/2008 in winter. Data showed that PM_{10} mass concentration was the highest in spring due to the contribution of long-range transported and fugitive dust particles, whereas mass concentration of ultrafine particles had no seasonal variation and was not significantly affected by dust particles. Enrichment factor (EF) for each metal and Principal Component Analysis (PCA) among ultrafine metals were conducted to evaluate effects of anthropogenic and natural sources on ultrafine metals and to determine association among metals. We found that Fe, Ni, Zn, Sb, and K exhibited relatively higher fraction in ultrafine size and had higher EF values (i.e., anthropogenic). Results from wind-dependent metal concentrations suggested that Zn and Ni in ultrafine particles originated from metallurgical sources from a nearby industrial complex. We also found that during an Asian dust event, Ca concentration increased most significantly among ultrafine metals.

Keywords: Ultrafine particles; Metals; PM_{10}; Asian Dust.

INTRODUCTION

Combustion of fossil fuels and wood, natural metal aerosols (Buerki *et al*., 1989; Allen *et al*., 2001; Espinosa *et al*., 2001), exhaust emission from vehicles, industrial processes, and waste incineration can be anthropogenic sources for metal aerosols in the ambient atmosphere (Wang *et al*., 2008; Lin *et al*., 2008; Srivastava *et al*., 2008). Erosion, surface dusts, volcanic activity, oceans, and forest fires can contribute as well (Karanasiou *et al*., 2007; Zhang *et al*.,

* Corresponding author. Tel: 82-62-970-3279; Fax: 82-62-970-2434

E-mail address: kpark@gist.ac.kr

2008). High concentration and/or long exposure of metals may cause toxic effects on human health, even though they constitute a small fraction of PM (Berggren *et al*., 1990; Devries *et al*., 1996). Determination of metals composition of inhalable particles is important in determining their potential impact on human health (Allen *et al*., 2001).

Depending on emission sources, rates of wet and dry deposition, and physical/chemical transformation, concentration and size distributions of metal aerosols will vary (Gu *et al*., 2008). Long-range transport of aerosols will also affect concentration and size distribution of metals (Xu *et al*., 2008). Typically, particles in the accumulation mode have a long residence time and can be transported over a long distance affecting remote regions from sources. Therefore, size-resolved metal concentration will provide information on the toxicity level of metals, as well as on transport behavior in the ambient atmosphere and on inhalation characteristics of the human respiratory system. Recently, ultrafine particles in the ambient atmosphere have been of particular interest because they provide a high surface area-to-volume ratio, leading to higher toxicity and reactivity (Dockery *et al.*, 1994; Peters *et al.*, 1997; Oberdörster, 2000). However, there has been limited information on size-resolved metal concentration, especially in ultrafine fraction.

In this study, chemical speciation of metals in five different size intervals in submicron size fraction (< 0.071 μm, 0.071–0.132 μm, 0.132–0.213 μm, 0.213–0.241 μm, 0.241–5 μm) was conducted using a 4-stage low pressure cascade impactor with a backup filter at an urban location (Gwangju, Korea). Seasonal variation of metal in ultrafine mode (< 0.132 μm) was examined by sampling aerosols for about one month in each season. Enrichment Factor (EF) and Principal Component Analysis (PCA) were carried out to estimate sources for ultrafine metals. We also measured metal concentrations when Asian dusts were transported to our sampling site to investigate the effect of long-range transported aerosols on ultrafine metals.

Methods

The sampling site is located ~ 7.6 km north of downtown Gwangju city hall and ~ 4.2 km northeast of Hanam industrial complex. The site was also influenced by traffic from a nearby highway (~ 1.5 km away from the site), residential heating from residential/commercial areas (~ 0.6 km away from the site), and biomass burning from agricultural areas (~ 0.8 km away from the site). The main industrial activities in the Hanam industrial complex are metallurgy and chemical products. A map of the sampling site, including possible local sources for particulate matter, is shown in Fig. 1.

A low pressure cascade impactor with a conventional cyclone inlet having a cut-off diameter of 5 μm (Mogo *et al*., 2005; Lee *et al*., 2006). was placed on the roof of a four-story building located in the campus of

Gwangju Institute of Science and Technology (GIST). The impactor collected aerosol particles during the sampling periods of 4/2/2007-4/20/2007 in spring, 8/2/2007-9/12/2007 in summer, 11/19/2007-12/2/2007 in fall, and 1/16/2008-2/3/2008 in winter. The PM_5 inlet and impactor stages allowed collection of particles in five different size fractions (< 0.071 μm, 0.071–0.132 μm, 0.132–0.213 μm, 0.213–0.241 μm, and 0.241–5 μm). Also, we collected PM_{10} using a MiniVol sampler (Airmetrics, USA). Teflon filters with a 37 mm diameter and 2 μm pore size (TefloTM, Gelman Laboratory, USA) with particle collection efficiency of 99.7% for 0.3 μm-sized particles were used for collection of particles (Kodavanti *et al.*, 2005). Flow rates were checked before and after the sampling period (~ 24 hours) and did not significantly deviate from the initial value (9 L/min for the impactor and 5 L/min for the minivol sampler). The filters were weighed before and after the sampling using a microbalance (SartoriusTM, MC-5, USA) with 1 μg sensitivity to obtain the net mass of collected particles. The filters were equilibrated in desiccator with stabilized temperature (22−23ºC) and relative humidity (45–50%) for at least 24 hours before and after actual weighing. Meteorological data (wind speed, wind direction, temperature (T), relative humidity (RH), and solar radiation were also measured at the same place.

We followed the analytical procedure for determination of trace metals in filters shown in Work Assignment 5-03 (EPA,

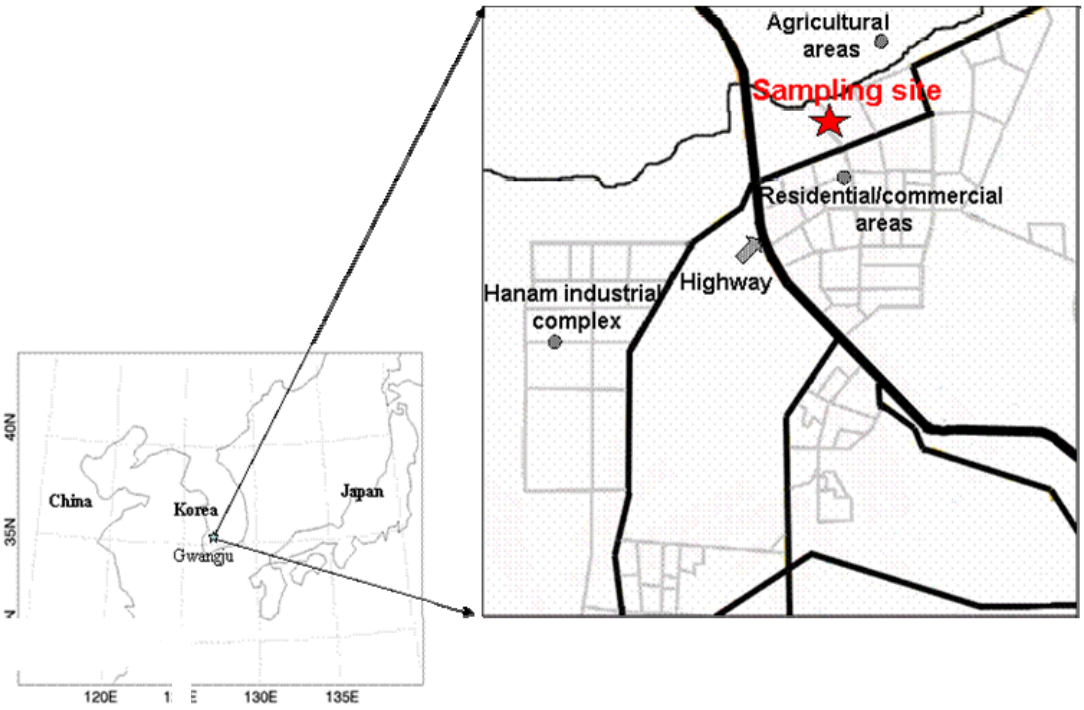

Fig. 1. Map of the sampling site including possible local sources.

2005) and SOP MLD061 (ARB, 2002). The collected filters were extracted in Teflon centrifuge tubes with 25 mL of the 4% nitric acid followed by ultrasonic treatment for 3 hours using a heated (69ºC) sonication bath. After sonication, the samples were allowed to cool down at room temperature. Samples were filtered by Whatman 541 filter paper and then diluted with clean DI water having a final volume of 50 mL prior to use of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Atomic Absorption Spectroscopy (AAS) to analysis of As, Be, Ca, Cd, Fe, K, Mn, Ni, Pb, Sb, Se, and Zn. The samples were stored in a refrigerator at -18ºC before analysis. Quantification was carried out by external calibration standards (ICP-MS standard metal solutions having 0-100 ppb) at concentration levels close to those of the samples during the ICP-MS and AAS running a set of external calibration standards before and after the ICP-MS and AAS analysis of the samples.

RESULTS AND DISCUSSION

PM_{10}, PM_5, and ultrafine mass concentrations

Daily mass concentrations of PM_{10}, PM_5, and ultrafine particles (defined as particles less than 0.132 μm in this study) during the whole sampling period are shown in Fig. 2. We observed an Asian dust event on March 2, 2008, having a PM_5 concentration of 167.4 μg/m^3, which exceeded its yearly average (36.7 μg/m^3) by a factor of 4.2. On the Asian dust event day, PM_{10} increased up to 228.9 μg/m^3. However, ultrafine mass did not have such an increase, suggesting that the Asian dust had little contribution to ultrafine particle mass.

Seasonal variations of PM_{10}, PM_5, and ultrafine particle mass concentrations are shown in Fig. 3. PM_{10} is the highest in spring and lowest in summer. Coarse-mode particles (5-10 μm) substantially contributed to the increase in PM_{10} in spring, whereas contribution of the coarse-mode particles was the smallest in summer. Long-range transported particles (e.g., Asian dust) and fugitive dust that occurred more often in spring substantially contributed to the increased PM_{10} (Choi *et al*., 2001; Kim *et al*., 2002; Senlin *et al*., 2007). However, we observed no significant variation of ultrafine particle mass concentration. Previously, particles substantially increased in summer in this area due to a strong photochemical activity (Park *et al*., 2008). Our PM data suggest that even when ultrafine particles exist in large number in summer, their contribution to PM_{10} mass is not significant.

Metal concentrations

Metal concentrations in PM_{10} averaged over the whole sampling period are shown in Fig. 4. Based on the field blank experiments, concentration of metals in the field blanks were less than 0-5 ng/m^3. The most abundant elements in the PM_{10} were Ca (1484.58 ng/m^3), Fe (691.67 ng/m^3), K (680.73 ng/m^3), and Zn (170.72 ng/m^3) followed by Pb, Mn, and Sb in 60–10 ng/m^3.

Concentrations of Be, Cd, and Se were below 5 ng/m^3. The Ni concentration exceeded the PM_{10} limit (~ 5 ng/m^3) established by the European Union. Metal concentrations in ultrafine particles are also included in Fig. 4. We observed that ultrafine fraction over PM_{10} for Ni, Sb, Zn, Fe, Ca, and K metals was greater than 15%. Anthropogenic sources such as combustion of fossil fuels and biofuels, exhaust emission from vehicles, and industrial processes are responsible for metal aerosols in ultrafine fraction, rather than natural sources such as erosion and surface dusts that would contribute to particles present in the larger particle size range (Espinosa *et al.*, 2001). Our sampling site is usually affected by multiple sources, such as Hanam industrial activities, traffic from a nearby highway, residential heating, and biomass burning. During the sampling period, western, southwestern, and south winds were dominant at our sampling site. The southwestern wind typically passed over the industrial complex before reaching our sampling site. To find possible emission sources for ultrafine metals, we examined their wind-direction dependent concentrations. As shown in Fig. 5, ultrafine Ni and Zn metals had a high concentration during days with prevailing southwest wind, while Fe and K did not have such dependence, suggesting that ultrafine Ni and Zn metals might be transported from the Hanam industrial complex (~ 4.2 km away).

Enrichments Factors (EFs) of metals can be used to evaluate the effects of anthropogenic and natural sources on metals, relative to the earth's crustal abundances. EFs of metals (M) were calculated by using Fe as a reference for crustal material and crustal fractions for the metals, given by:

$$EF = [M/Fe]_{air} / [M/Fe]_{crust}. \quad (1)$$

The EF should be much higher than a unit to consider sources of metals as anthropogenic origin. EFs of ultrafine metals as a function of ultrafine fraction are shown in Fig. 6. Se and Sb have the highest EF (~ 7000), which were not included in Fig. 6 for clarity. Ni, Pb, and Zn have high EFs (> 400) and ultrafine fractions (> 0.10), suggesting that these metals may originate from combustion-related anthropogenic sources. Cd has a high EF (> 700), but a low ultrafine fraction, suggesting that this metal might not be related to combustion sources.

We also conducted Principal Component Analysis (PCA) for ultrafine metals and their results are summarized in Table 1, which excludes the Asian dust event. The PCA is usually used to identify the patterns of correlations among observed elements (variables), and to reduce such large data sets into a small number of principal components (PCs) without losing significant information from the origin of the data. We conducted Varimax (orthogonal) rotation to determine principal components having an eigenvalue larger than 1. With the PCA method, we are able to infer whether metals come from a similar source or not. As, Be,

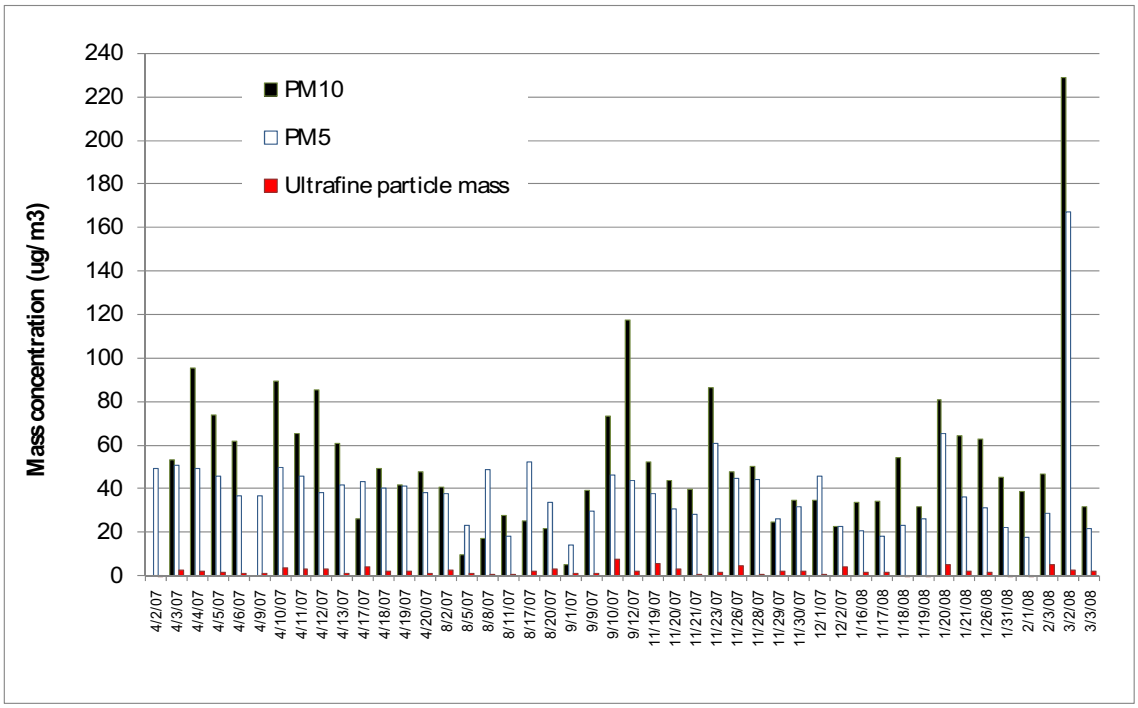

Fig. 2. Daily average of PM_{10}, PM_5, and ultrafine particle mass concentrations over the whole sampling period.

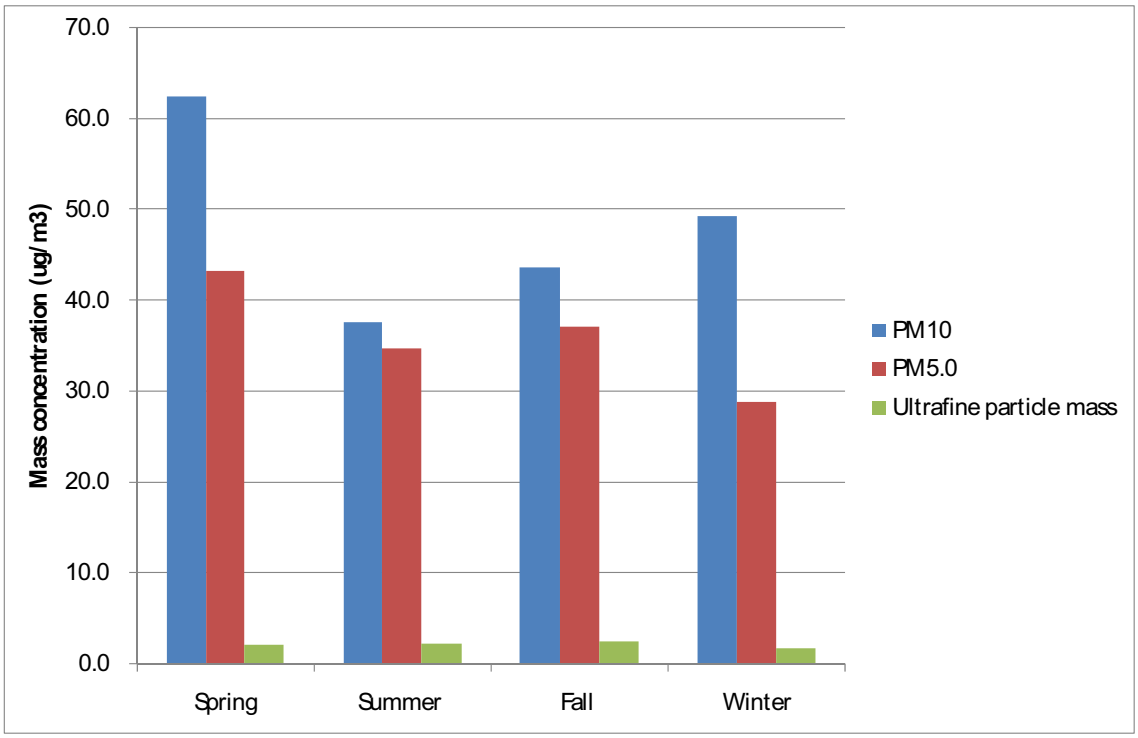

Fig. 3. Seasonal variation of PM_{10}, PM_5, and ultrafine particle mass concentrations.

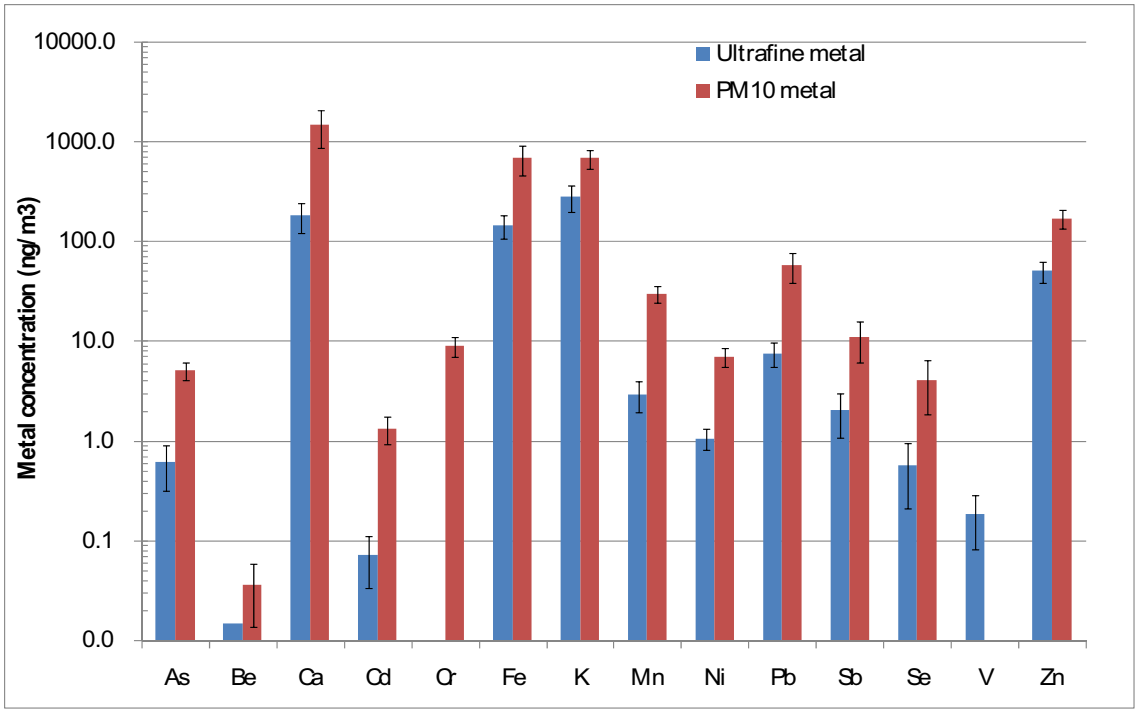

Fig. 4. Average metal concentrations of PM10 and ultrafine particles.

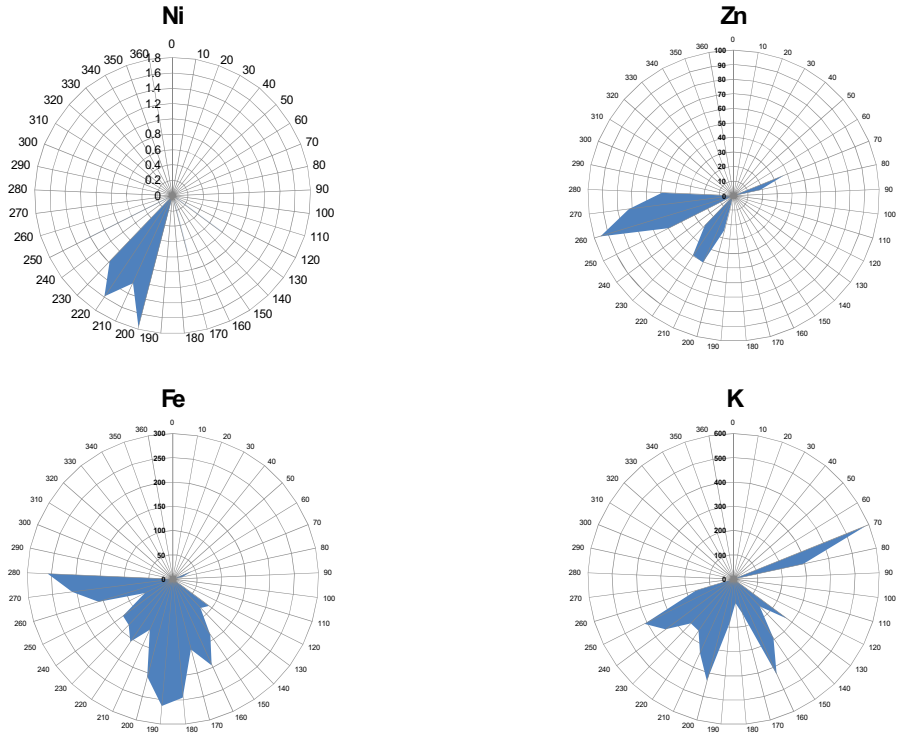

Fig. 5. Wind-direction dependent concentrations of ultrafine metals (Ni, Zn, Fe, and K).

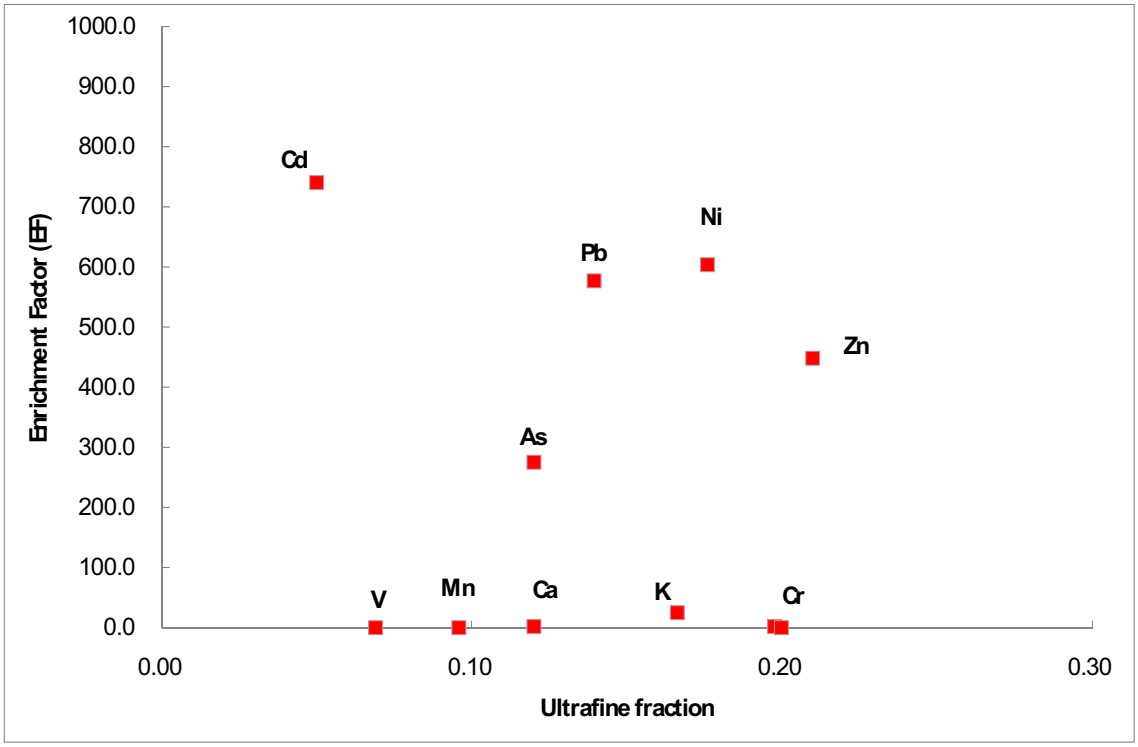

Fig. 6. Enrichment Factor (EF) of ultrafine metals as a function of ultrafine fraction in PM_{10}.

Table 1. Principal component analysis (PCA) for ultrafine metals.

	PC1	PC2	PC3
As	0.997	-0.018	0.013
Be	0.932	0.117	0.305
Ca	-0.944	0.222	-0.192
Cd	0.928	0.337	0.155
Fe	0.381	0.893	0.105
K	-0.169	-0.984	0.012
Mn	0.257	0.003	0.918
Ni	0.225	-0.786	0.536
Pb	-0.462	0.835	0.259
Sb	0.453	-0.540	0.614
Se	-0.056	-0.116	-0.920
Zn	-0.953	0.100	-0.182
Eigenvalue	5.24	3.57	2.62
Cum. (%)	43.64	73.41	95.23

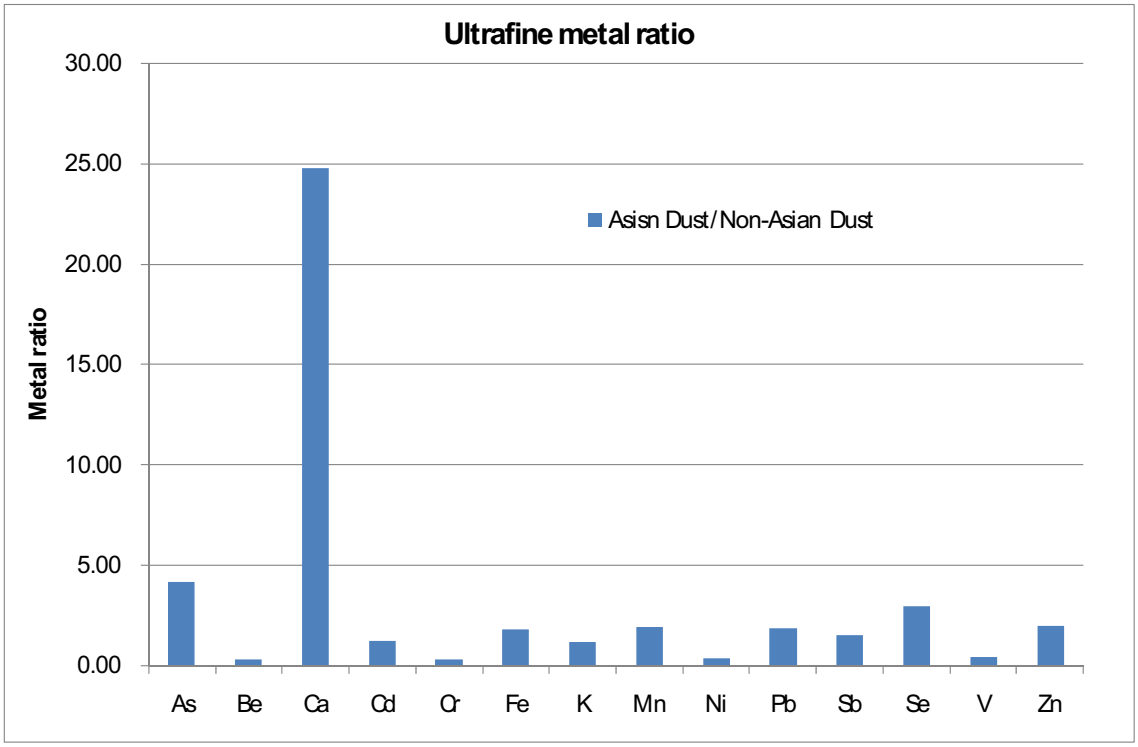

Fig. 7. Ratio of ultrafine metal concentration during the Asian dust event day (3/2/2008) to average ultrafine metal concentration.

and Cd have high values in principal component 1 (PC1), Fe and Pb in PC2, and Mn and Sb in PC3. The PC1 may originate from road traffic and combustion sources. To investigate the effect of Asian dust on ultrafine metal concentration, we obtained the ratio of ultrafine metal concentration during the Asian dust event day (3/2/2008) to average ultrafine metal concentration as shown in Fig. 7. Note that as shown previously, total mass of ultrafine particles little increased, but that metal mass somewhat increased. Among ultrafine metals, Ca concentration increased significantly by a factor of 25 on the day of Asian dust event (Fig. 7).

CONCLUSIONS

We determined PM_{10}, PM_5, and ultrafine (< 0.132 um) mass concentrations, and ultrafine metals (As, Be, Ca, Cd, Fe, K, Mn, Ni, Pb, Sb, Se, and Zn) in urban Gwangju, Korea during the sampling periods of 4/2/2007-4/20/2007 in spring, 8/2/2007-9/12/2007 in summer, 11/19/2007-12/2/2007 in fall, and 1/16/2008-2/3/2008 in winter. The PM_{10} mass was the highest in spring probably due to dust particles. However, mass of ultrafine particles had no seasonal variation. Additionally, the mass concentration of ultrafine particles exhibited no increase during an Asian dust event, although PM_{10} was significantly affected by the Asian dust event. During that event, Ca

concentration increased most significantly among ultrafine metals. Fe, Ni, Zn, Sb, and K metals existed in relatively higher fraction in ultrafine size and had high EF values, suggesting their origins were from anthropogenic combustion sources. Furthermore, wind-direction dependent concentration of ultrafine particles suggested that ultrafine Zn and Ni metals were transported from a near industrial complex which mainly consists of metallurgical activities (~ 4.2 km away).

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