

PA46) Temporal Variation and Enrichment Factor Analysis of Heavy Metals in Airborne Particulate Matter in Ulsan

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1. Introduction

Air pollution by particulate matter (PM) is considered as a serious environmental issue due to the presence of the hazardous materials such as toxic trace metals in the atmosphere (Shah et al., 2006). The increased anthropogenic emissions of heavy metals in the atmosphere have emerged as a major concern in recent years since these may influence urban as well as rural areas (Funasaka et al., 2003). Heavy metals are found in almost all atmospheric aerosol size fractions and, in general, fine PM carries a higher burden of heavy toxic metals than does coarse PM (Fang et al., 2000).

Ulsan is the largest industrial city in Korea with 60% of the total emissions from industrial emissions. In addition, the large population of 1.1 million people and high density of industrial activities have resulted in the dense traffic in the city. The objective of this study was to identify the concentrations and temporal characteristics of heavy metals in fine and coarse aerosols in an urban residential area of Ulsan for a year. Crustal enrichment factor calculation for these heavy metals was also shown in this study.

2. Methods

Size fractionated airborne PM was collected from a residential area of Ulsan city (Mugeo-dong office) during the period April 2008–January 2009. The sampling site with the height of 15m was adjacent to a highway of 6 lanes and a busy rotary. An ambient cascade impactor (Model 20-800, Tisch Environmental, Inc.) equipped with a 8-stage inertial impactor was employed. This sampler was operated at a constant flow rate of 28.3L/m³ for 24-h period. At the operational sampling conditions, collected particles were classified in the following size intervals: <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 μ m. Samples were collected on the glass fiber filters with diameter of 81 mm and a pore size of 2 μ m. All blanks and sample filters were kept for 48 h in a desiccator in a conditioned room at a relative humidity (RH) of 45 \pm 5% and temperature of 20 \pm 2 $^{\circ}$ C before weighing. PM concentrations of eight fractions were determined by a gravimetric analysis. To determine metal concentrations, filters were extracted with a mixture solution of 1.03M HNO₃ and 2.03M HCl (1:1) using ultrasonic water bath at 90 $^{\circ}$ C for 2h. Eight selected heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Fe and Zn) from the extracted solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

3. Results and Discussion

The average concentrations of heavy metals in the fine (PM_{2.1}) and coarse (PM_{2.1-10}) particles in the four seasons were presented in Fig. 1. The concentration of Fe was the highest and followed by Zn and Pb. For PM_{2.1}, the concentrations of Cd, Cr, Cu, Mn, Ni, Pb were higher in summer and winter, but their concentrations were lower in spring and fall; Fe and Zn had the highest concentrations in spring. For PM_{2.1-10}, most of heavy metals had the highest levels in winter, followed by summer or fall, except Fe and Mn which has highest levels in spring. Fe and Mn have high concentrations from soil, thus high level of them in spring time might be due to the effect of Asian dust in this period.

The remaining heavy metals are usually attributed to anthropogenic sources. In summer, the prevailing winds showed southeast and south-southeast winds which passed through the industrial (a petrochemical and non-ferrous industrial park in Ulsan) and traffic areas, resulting in the high metal concentrations. In winter, however, the direction of the prevailing wind was south which not passed through the areas with significant sources of pollutants. The high concentrations of metals in winter might be due to the increased energy uses for heating, dry weather conditions with low humidity, and the increased accumulation of metals on soil surface.

Calculation of the enrichment factor (EF) value helps to determine whether a certain element has additional sources other than its major natural source. The average element concentration data for the upper continental crust were obtained from Yaroshevsky (2006). Iron was used as a reference element assuming that its anthropogenic sources to the atmosphere are negligible. If the EF value approaches unity, then crustal sources are predominant. In general, $EF > 5$ indicates that a large fraction of the element can be attributed to non-crustal sources given to anthropogenic sources (Samara and Voutsas, 2005).

Table 1 shows the enrichment factors (EFs) of the aerosol samples in $PM_{2.1}$ and $PM_{2.1-10}$ in the four seasons. The EF values for Cd were the highest, followed by Pb, Zn and Cu for both PM sizes. EF value of Mn was lower than 5, it means most of Mn originated from soil, except for $PM_{2.1}$ in winter. Other metals such as Cd, Cr, Cu, Ni, Pb and Zn had much higher than 5, thus their origin were from anthropogenic sources. For $PM_{2.1}$, EF values of metals were the highest in fall even though their concentrations were the lowest. The prevailing winds in fall like summer mostly came from the industrial areas which have large anthropogenic sources. Therefore, the increased EFs in fall represent increased contribution of anthropogenic metals compared to other seasons. For $PM_{2.1-10}$, EF values in the four seasons were not very different from each other, except for spring. The EF values of metal were the lowest in spring, it means the crustal was the predominant source in spring compared to other seasons.

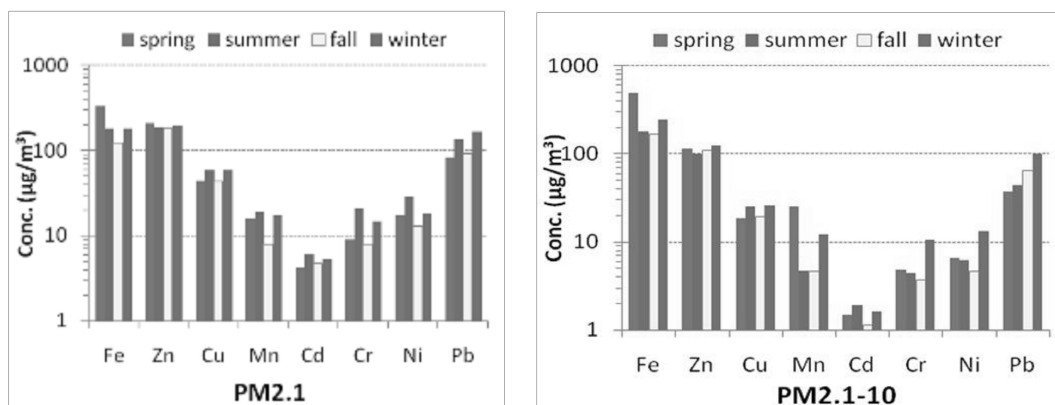


Fig. 1. Average metal concentrations in $PM_{2.1}$ and $PM_{2.1-10}$ in four seasons.

Table 1. Crustal enrichment factors (EF) of heavy metals in four seasons.

| | | Fe | Zn | Cu | Mn | Cd | Cr | Ni | Pb |
|----------------------|--------|-----|-------|-------|-----|---------|-------|-------|--------|
| PM _{2.1} | Spring | 1.0 | 379.3 | 287.3 | 2.8 | 3895.4 | 24.0 | 88.3 | 455.1 |
| | Summer | 1.0 | 614.7 | 705.2 | 6.2 | 9976.3 | 102.8 | 262.6 | 1385.9 |
| | Fall | 1.0 | 879.3 | 755.1 | 3.8 | 11625.6 | 56.4 | 177.0 | 1372.7 |
| | Winter | 1.0 | 644.3 | 702.9 | 5.6 | 8977.4 | 71.0 | 164.8 | 1676.2 |
| PM _{2.1-10} | Spring | 1.0 | 139.3 | 79.9 | 2.9 | 893.3 | 8.5 | 21.7 | 136.9 |
| | Summer | 1.0 | 334.0 | 304.1 | 1.5 | 3216.7 | 22.0 | 57.4 | 452.8 |
| | Fall | 1.0 | 383.9 | 248.7 | 1.6 | 2038.5 | 19.7 | 46.0 | 703.3 |
| | Winter | 1.0 | 302.1 | 230.6 | 2.9 | 2030.4 | 38.7 | 90.5 | 755.0 |

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