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Metallic elements in $PM_{2.5}$ in different functional areas of Korea: Concentrations and source identification

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ABSTRACT

Both $PM_{2.5}$ mass concentration and its chemical composition are a great concern to human health. In this study, the concentrations of $PM_{2.5}$ and their metallic elements were measured to identify the characteristics and to trace sources at two different functional areas, a residential and a cement industrial area. The average $PM_{2.5}$ concentrations were not significantly different between the two sites, but their chemical compositions were clearly different. Crustal elements in $PM_{2.5}$ were significantly higher in the residential area, while the concentrations of metals typically emitted from anthropogenic sources were generally higher in the cement industrial area. Crustal elements often increased during spring in the residential area due to the blustery weather with high wind speeds; however, most metallic elements were enhanced during winter in the cement industrial area. Principal component analysis was used to trace the sources. Soil re-suspension, traffic-related sources, and asphalt concrete production were identified as the main sources of $PM_{2.5}$ in the residential area, while the cement industry, Ni–Cr plating industry, and other industrial activities were identified in the cement industrial area.

1. Introduction

$PM_{2.5}$, defined as particles less than 2.5 μm, has been a great concern due to its significant adverse effects on human health. Many epidemiology studies have shown that respiratory and cardiovascular diseases and associated mortality are closely related with enhanced $PM_{2.5}$ concentrations (Bell et al., 2009; Ostro et al., 2009). Therefore, many countries, including Korea, have directed many efforts toward reducing atmospheric $PM_{2.5}$ concentrations. $PM_{2.5}$ is emitted from both natural sources, including soil and ocean, and anthropogenic sources, including automobiles, incineration, and power plants. The chemical and physical properties of the particles, such as predominant size, shape, and solubility, are greatly dependent on the source. Recent studies also showed that chemical composition can determine the health risk, and particles from combustion sources are associated with greater health risks than those from natural sources (Forsberg et al., 2005; Hong et al., 2010). In addition, $PM_{2.5}$ can either be directly emitted from sources or newly formed in ambient air through gas-particle conversions, making the establishment of appropriate $PM_{2.5}$ reduction strategies difficult.

Among the various components of $PM_{2.5}$, metallic elements can seriously influence human health, although their mass contributions are generally insignificant compared with other $PM_{2.5}$ components, such as ionic and carbonaceous compounds. The International Agency for Research on Cancer (IARC) of WHO (World Health Organization) classified the carcinogenicity of compounds into 5 classes. Arsenic (As) and As compounds, Cadmium (Cd) and Cd compounds, and Chromium (VI) are classified in Group 1 (carcinogenic to humans), and inorganic Lead (Pb) compounds are included in Group 2A (probably carcinogenic to humans). Metallic elements can be used as tracers for sources; As, Hg, and Se are emitted from coal

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combustion; Ca, Cd, K, Na, Pb, and Cl are emitted from steel mills; Cu, Mn, Fe, Zn, Ba, Sn, and Ni are emitted from vehicles (Fabretti et al., 2009; Gietl et al., 2010; Amato et al., 2011a,b); and Ni and V are emitted from oil combustion (Pey et al., 2010). Using the concentrations of trace metals in $PM_{2.5}$ as tracers of specific sources, possible source types have been identified in previous studies (Fabretti et al., 2009; Han et al., 2011; Amato and Hopke, 2012).

In Korea, while the concentrations of typical pollutants including carbon monoxide and sulfur dioxide have steadily decreased over the past few decades (Ministry of Environment, http://stat.me.go.kr/nesis), the $PM_{2.5}$ concentrations in ambient air have increased or been relatively consistent (Han et al., 2008; Kim et al., 2011). Relatively consistent $PM_{2.5}$ concentrations are derived from both local emission sources and regional sources from outside of Korea. Korea is adjacently situated east of China; hence, air pollutants, including $PM_{2.5}$, from China can transport over long ranges to Korea with the westerly winds (Kim et al., 2007; Han et al., 2011). According to PM_{10} and $PM_{2.5}$ measurement data provided by Environment Korea (http://www.airkorea.or.kr), PM_{10} concentrations in rural areas and even in background areas are often comparable with those measured in megacity and industrial areas, indicating that long-range transport from regional sources may be important.

In this study, the atmospheric concentrations of $PM_{2.5}$ and its metallic elements were measured in two different functional areas. One site represents a small city, mainly composed of residential areas, where no large industrial emission sources are located. The other site is a smaller city, but large cement and lime industries are located near; accordingly, serious issues on associated health effects including COPD (Chronic Obstructive Pulmonary Disease), lung cancer, and pneumoconiosis have been raised in this area since 2007 (Leem et al., 2010). In addition, the usage of wastes, including waste tire, sewage sludge, and refuse-derived fuel, as supplement fuel in the cement industry may cause more serious air pollution and associated health effects. This study was designed to identify the characteristics of $PM_{2.5}$ collected for more than one year at two different functional areas, to identify the differences in concentrations and trends of metallic elements of $PM_{2.5}$ at these two areas and to trace sources of $PM_{2.5}$ using principal component analysis.

2. Methods

2.1. Site description

In this study, $PM_{2.5}$ samples were collected in two cities in Korea, Chuncheon (CC) and Yeongwol (YW), from April 2012 to October 2013. CC is a relatively small town surrounded by mountains, which limit the transport of locally emitted air pollutants. CC is a city famous for leisure and tourism, and there are no large industries. According to the National Emissions Inventory in CAPSS (Clean Air Policy Support System) in 2009 (NIER, 2011), PM_{10} emissions were 588,491 kg yr^{-1} (note that $PM_{2.5}$ emissions are not estimated in Korea). However, CC is located approximately 100 km northeast of urban (Seoul) and industrial (Incheon) areas; therefore, the pollutants emitted in these areas can transport to CC with predominant westerly winds. The sampling site was the roof of the four-story Kangwon National University Natural Sciences building.

On the other hand, YW is a small town with two large cement industries, producing approximately 7,500,000 t yr^{-1} of cement. PM_{10} emissions from anthropogenic sources in YW were estimated to be 7,095,470 kg yr^{-1} in 2009, according to the National Emissions Inventory (NIER, 2011). The sampling site in YW was the roof of the town office, located approximately 600 m northeast of a cement production facility and 5.2 km north of another cement plant (Fig. 1). In addition, there are two other cement production facilities in the neighboring town, which are located approximately 4.2 km southeast and 23.8 km south from the sampling site; therefore, the $PM_{2.5}$ samples collected at YW site are likely to be affected by cement industries. The populations in CC and YW are 277,417 and 40,204, respectively, and the population densities are 248.5 km^{-2} and 35.7 km^{-2}, respectively.

2.2. Sampling and analysis

Sampling for $PM_{2.5}$ followed the procedures outlined in the US EPA Compendium Method IO-4.2 (U.S.EPA, 1999). For $PM_{2.5}$ mass monitoring, a 37 mm Teflon filter (Pall Life Sciences, Teflo) was placed in a clean Teflon filter pack (URG) after the cyclone (URG) at a flow rate of 16.7 L min^{-1} at the CC site, while a 47 mm Teflon filter was used for the $PM_{2.5}$ sequential sampler (PMS-103, APM Engineering) at a flow rate of 16.7 L min^{-1} at the YW site. Samples were taken every third day in CC and every two days in YW for 24 h (from 00:00 to 00:00). In total 130 and 169 $PM_{2.5}$ samples were collected over the sampling period at the CC and the YW sites, respectively. Teflon filters were stored under controlled conditions of temperature and relative humidity for at least 24 h before and after sampling and then passed through a static electricity remover (2U500) before being weighed at least twice using an analytical balance (Sartorius CP225D, readability $= 10^{-5}$ g, the acceptance % difference between two readings was 0.02%). The filters were then stored in a freezer before analysis using energy disperse X-ray fluorescence (XRF; Spectro X-Lab Pro) at Clarkson University, USA. The details of the XRF procedure are described in Sunder Raman et al. (2008), and the uncertainty of the analytical XRF results can be found in Rousseau (2001). In this study, 7 toxic metals, including Pb, Ni, Cd, Cr, Zn, As, and Cu, and 6 crustal metals, including Al, Si, Ca, Fe, Mn, and K, were analyzed by XRF.

2.3. QA/QC

All apparatuses were cleaned with Alconox and hexane, followed by deionized water, before sampling and analysis. Field blanks (FB) were collected every sixth samples ($n = 20$ and 25 for CC and YW, respectively), and the method detection limit (MDL) was calculated as 3 times the standard deviation of FB. Concentrations less than the MDL were substituted with 0.2 × MDL in this study, and all concentrations in the following sections were FB corrected. Analytical precision was calculated as the relative percent difference (RPD) from duplicates ($n = 10$ set for each site). MDL, RPD, and the percentage of the number of observations below the detection limit for all elements at the two sampling sites are shown in Table 1.