



Field evaluation of a near–real time elemental monitor and identification of element sources observed at an air monitoring supersite in Korea

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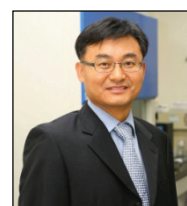
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ABSTRACT

Ambient measurements of elemental species concentrations were made using an online elemental monitor at an air pollution monitoring station in Gwangju, Korea to evaluate the performance of the monitor for near–real time PM_{2.5} elemental monitoring and identify possible sources of the observed elements. This study also demonstrates the utility of integrating hourly elemental data with the meteorological data to better understand the sources of elements. Good agreement between the online and filter–based measurements was obtained for the elements studied, with an R^2 of 0.73–0.97 and regression slopes of 0.84–2.37, suggesting the potential use of the online monitor to observe temporal variations in anthropogenic aerosol particles. Atmospheric element concentration levels varied were 2–20 times greater than their background levels when pollution plumes coming from industrial areas had impacted the site. Examination of the elements data revealed several short spikes of elements that are associated with local industrial emissions and road dusts. For the haze episodes observed over the study period, the element K was significantly influenced by biomass burning emissions with some impacts from soil dusts and industrial activities. Based on the wind direction and wind speed data, As/Se, Se/SO₄²⁻, and correlations among Se, As, Pb, SO₂, and SO₄²⁻, it is suggested that the observed As and Se were significantly impacted by local anthropogenic sources and long–range transport of aerosols, rather than local coal combustion or coke emissions. Conditional probability functions were applied to identify likely local emission source locations of the elements observed at the site, indicating that the elements contributions were from the southwest and northeast directions, where two industrial areas and an express highway are located. Results from principal component analysis indicate that the observed concentrations of the element species were likely attributed to road dust/local industrial emissions, oil combustion, and metal processing.

Keywords: Near–real time elemental monitor, elements, As/Se and Se/SO₄²⁻ ratios, industrial emissions, principal component analysis

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1. Introduction

It has been recognized that the exposure to elevated concentrations of particulate matter (PM) is associated with adverse human health effects (Dockery and Pope, 1994; Pope and Dockery, 2006). In particular, fine particles (PM_{2.5}) are more closely related to mortality and morbidity than coarse particles (PM_{2.5–10}) (Schwartz et al., 1996; Laden et al., 2000; Pope et al., 2002). Ambient PM is a complex mixture consisting of a number of chemical constituents such as carbonaceous, ionic, and elemental species.

Elemental species measurements of ambient aerosol particles, which are derived from anthropogenic (industrial facilities, incineration, vehicle exhaust, power plants, domestic heating, etc.) and natural (often crustal) sources, have been conducted for health and source apportionment studies. Elements including As, Sb, Cd, Cr, Hg, Pb and Be, have been identified as toxic air pollutants (Baird, 1995). It has also been suggested that some elements modulate the expression of pulmonary cytokines (Prieditis and Adamson, 2002; Schaumann et al., 2004) and are associated with oxidative stress in cell systems (Cheung et al., 2012). Elemental species are not significant contributors of PM_{2.5} mass, but as the chemical composition of raw materials is reflected in the aerosol particles emitted, characteristic elements, which are called

“marker species”, have been employed to identify and apportion the source contributions to ambient aerosol (Kidwell and Ondov, 2004; Pancras et al., 2006; Snyder et al., 2009; Smyth et al., 2013). For example, Se is a unique tracer of primary particles from coal combustion (Morawska and Zhang, 2002), As is a tracer of metals–ore processing aerosol (Pancras et al., 2006; Park et al., 2006), Ni and V are tracers for oil combustion emissions (Ogulei et al., 2005), Fe and Mn are markers for steel mill emissions (Pancras et al., 2006), Sb is closely associated with brake wear emissions (Bukowiecki et al., 2009), and Cd, Zn and Cl are markers for municipal incinerator emissions (Ondov and Wexler, 1998; Suarez and Ondov, 2002).

Due to the reasons above, accurate measurements of the elemental composition of ambient aerosol particles are of much interest. Once the characteristic elements are associated with particular emission sources, real–time measurements can be made which provide detailed information about the emission characteristics of those sources. In addition, identification of short duration spikes in ambient concentrations of elemental species has been shown to indicate local sources of the emitted compounds (Pancras et al., 2006; Park et al., 2006; de Foy et al., 2012; Smyth et al., 2013). To provide improved temporal resolution of elemental species concentrations, sampling devices performing sub–hourly or hourly collection of ambient aerosol particles for subsequent

laboratory analysis have been developed and utilized in the field (Cahill and Wakabayashi, 1993; Kidwell and Ondov, 2001; Kidwell and Ondov, 2004; Lee et al., 2011; Park et al., 2012). These include the Davis Rotating-drum Unit for Monitoring (DRUM; Cahill et al., 1985), Semi-continuous Elements in Aerosol Sampler (SEAS; Kidwell and Ondov, 2001), and a Korean version of SEAS (KSEAS; Lee et al., 2011). All provide improved temporal resolution of elemental composition but require a large commitment of analytical time. To address the large analytical time commitment from semi-continuous sampling systems, online semi-continuous measurement systems such as Aerosol Time-of-Flight Mass Spectrometry (TSI ATOFMS, Shoreview, MN) and near-real time Xact 620 field XRF analyzer (Cooper Environmental Services, CES) have been developed and commercialized for rapid detection of the ambient aerosol particle's elemental composition. CES has reported the Xact 620 multi-elemental monitor with 1-hr sampling yielded equal to or better PM₁₀ Pb measurements than 24-hr samples collected with PM₁₀ FRM samplers and laboratory XRF analysis (www.cooperenvironmental.com). However the Xact elements monitor needs to be tested in more complex source environments to improve its performance.

Recently the Korean EPA has deployed intensive air pollution monitoring stations, which are similar to the U.S. EPA PM Supersites, to develop effective control strategies to reduce the impacts of atmospheric PM including Asian dusts and long-range transported aerosols. Details of Korean PM Supersites are described in Park et al. (2013). Currently the online field XRF monitors are being operated to observe temporal variations of elemental species at four air monitoring stations. A CES field XRF analyzer with hourly time-resolution was utilized to observe the temporal profiles of PM_{2.5} elemental species during February of 2011 at a South Area Supersite in Gwangju, Korea. The objectives of this study are to (i) explore the accuracy of time-resolved CES multi-elements monitor by comparing with filter-based measurements, (ii) investigate the utility of integrating hourly elements data with meteorological data to provide a better understanding of the sources, and (iii) identify probable emission sources of the observed elemental species using a principle component analysis.

2. Methodology

2.1. Site description

The South Area Supersite (latitude 35.23°N, longitude 126.85°E) in Gwangju is located in the southern part of Korea, as depicted in Figure S1 of the Supporting Material (SM). A detailed description of the site can be found in Park et al. (2013). The site is located in a commercial and residential area which is surrounded by agricultural lands and traffic roads. The nearest major traffic road is approximately 0.3 km from the site, and an express highway is located 1.5–2.0 km southwest of the site. There is an industrial complex located 3–8 km southwest of the site (200–250°) and a high-tech industrial area located 1.0–1.5 km northeast (30–100°) of the site. It is important to note that there are no coal combustion boilers or industries that use coal within the industrial areas. The high-tech industrial area has a number of manufacturing companies, metallurgical companies, and chemical industries which account for 61.9%, 20.0%, and 3.4% of the total industries, respectively. Photonics and semi-conductor industries are also distributed within the complex. The industrial complex (southwest of the site) consists of approximately 1 000 industries of which 39.6 and 13.3% corresponded to metallurgical and chemical industries, respectively. Several large-scale companies producing household electric appliances are also distributed within the complex. There are also many small-scale companies producing car parts and metal coatings. Emissions from these industrial complex regions impacting the monitoring site could be resolved during typical southwestern and northeastern flow regimes. Meteorological data was monitored at the Gwangju regional meteorological station, located 7 km south of the site.

Time-resolved measurements of PM_{2.5}, organic and elemental carbon (OC and EC), ionic species, and elemental species were conducted at the Gwangju Supersite at 1-hr intervals during February 01–28, 2011. Only online XRF measurement results are discussed in this study. Water-soluble K⁺ and SO₄²⁻ data are used as ancillary data to explore probable emissions sources of the elements studied.

2.2. 24-hr filter-based and hourly elemental species measurements

Twenty-four hour integrated filter-based PM_{2.5} samples were collected between midnight and midnight with a sequential PM_{2.5} sampler (PMS103, APM Korea) and then were analyzed by Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer (Epsilon 5, PANalytical) for 29 elements (Si, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Cd, Sn, Sb, Te, Cs, Ba, Hg, Pb, and Bi). The Teflon filters (Teflon membrane, 2.0 μm pore size, R2PJ047, PALL Science, USA) were weighed before and after sample collections with a microbalance (1 μg sensitivity). In EDXRF, samples are energized by irradiation with X-rays, resulting in the emission of fluorescent X-rays with discrete energies characteristic of the elements present. The EDXRF spectrometer has an X-ray tube (Power_{max}=600 W, V_{max}=100 kV, Gd-anode), 3-dimensional polarization optics (Cartesian geometry), and Ge detector. The primary beam from the X-ray tube irradiates a polarizing target (secondary target) placed along the first axis of the optical path. After scattering at 90° the X-rays travel along the second axis to the filter sample. The spectrum of the sample is recorded by a detector placed along the third axis. By using secondary targets of different materials it is possible to optimize the excitation source for the elements of interest. In this study, we used eight secondary targets. The secondary targets, X-ray current and voltage were CaF₂: 17 mA and 35 kV; Ti: 8.5 mA and 70 kV; Fe: 7.5 mA and 80 kV; Ge: 7 mA and 85 kV; Zr: 6 mA and 100 kV; Mo: 6 mA and 100 kV; Ag: 6 mA and 100 kV; and Al₂O₃: 6 mA and 100 kV. X-ray counting time depends on the secondary target, ranging from 600 to 1 000 sec. The instrument was calibrated using thin film calibration standards (Micromatter – polycarbonate aerosol membranes, USA). The analytical target of analysis defines the necessary sample preparation technique. Diversity of sample type and measurement range is accommodated easily by the instrument. In this study filter samples were directly placed into the instrument. The quantifications of elements in the filter samples were carried out using an Auto Quantify routine based on fundamental parameters method. While a spectrum peak search and match routine facilitates qualitative analysis. Spectrum evaluation was done by non-linear least squares fitting, based on the AXIL algorithm developed at the University of Antwerp, Belgium. The analysis time per filter sample was approximately 140 min. The filter blanks were also analyzed, and the average filter blank value was used as a background subtraction for each sample filter. Precision, defined as the relative standard deviation, was less than 10% for all elements. Minimum detection limit for each element analyzed by EDXRF was determined as three times the standard counting error of the background intensity, ranging from 0.25 to 5.98 ng/m³.

Hourly PM_{2.5} elemental concentrations of (K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Ba, Ag, Tl, and Pb) were measured with an ambient elemental monitor (model: Xact™ 620, Cooper Environmental Services (CES), USA). The online Xact 620 monitor uses reel-to-reel filter tape sampling and nondestructive XRF analysis to measure ambient air particles. The air was introduced through a PM_{2.5} inlet at a sampling flow rate of 16.7 L/min and drawn through the filter tape. The resulting PM_{2.5} deposit was automatically advanced and analyzed by XRF for selected elemental species as the next sample was being collected. Sampling and analysis were performed continuously and simultaneously, except during advancement of the tape (~20 sec) and during daily automated quality assurance checks. The online Xact 620 monitor was calibrated using thin film standards for each

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