Pollution sources for indoor PM2.5 at the platform in subway station using a positive matrix factorization and an instrumental neutron activation analysis

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1. Introduction

Airborne particulate matters, especially the PM2.5 (aerodynamic equivalent diameter, AED, less than 2.5 μm) fraction has been important. This is because of their potential for deposition on to the human respiratory system being accompanied by many harmful trace metals (such as As, Cd, Cr, Cu, Mn, Pb, Se, and Zn) [1]. As most people spend more than 80% of their time indoors, indoor air quality (IAQ) can exert a considerable impact on the inhalation condition of toxic substances. Therefore, assessment of the absolute concentration levels and elemental composition of PM in an indoor environment such as subway station can be used as a practical barometer of IAQ. The contaminants originated from the indoor pollution sources as well as various outdoor sources are easily accumulated in indoor environment dissimilar to the outdoor. Especially, since the natural ventilation is nearly impossible in the subway station, its pollution status can be worsened under the circumstance that contaminants are constantly originated and circulated inside of station by the repetitive action of subway trains. In this study, a total of 60 PM2.5 samples were collected for 4 seasonal campaigns in 2009 with a low-volume air sampler at one subway station in Daejeon, Korea. We undertook the measurements of up to 25 elements in PM2.5 using an instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF). And inorganic ion species (SO_4^{2-}, NO_3^-, NH_4^+) also were determined by ion chromatography (IC). Next, sources at indoor/outdoor environment were identified and the contributions of each source were quantified by positive matrix factorization (PMF).

2. Experimental

2.1 Sampling site and sampling

The collection of PM2.5 samples was made simultaneously with low volume air samplers from one subway station in Daejeon city, Korea. The Daejoen city subway (approximately 94,000 passengers per day) has one line of about 22.6 km tunnel path that passes through the center of the city. The screen door was equipped in the platform to prevent the intrusion of the pollutants from the tunnel. The target sampling station (Yuseong spa station) is surrounded by a populated residential and commercial sector in Yuseong hot spring region. A total of 60 samples were collected in the spring (22 April - 5 May), summer (1 July - 15 July), fall (22 September - 10 October), and winter season (7 December - 21 December) in 2009. For the collection of PM samples, annular denuder air sampler (URG, 3000C model) with polycarbonate filter (47 mm, 0.4 μm pore size, Nuclepore) were used. The air flows for each sampler were adjusted to the rate of 16.7 L min^{-1} at the beginning of sampling on a 24 hour basis.

2.2 Elemental analysis

In the course of this research, a total of 25 trace elemental species were analyzed quantitatively from the both PM samples using INAA and XRF. The PM-bound concentrations of elements (Al, As, Ba, Br, Cl, Co, Cr, Cu, Fe, I, In, K, La, Mg, Mn, Na, Sb, Sc, Se, Si, Th, Ti, V, and Zn) were analyzed by INAA. The XRF (SEA2220A model, SII SEIKO Instruments Inc.) analysis was done before INAA procedure for the determination of the concentrations of Ca and Si. The PM2.5 samples were irradiated using thermal neutrons using the Pneumatic Transfer System (PTS, Φ_{th} = 2.95 x 10^{13} $cm^{-2}s^{-1}$, R_{cd}= 250) at the HANARO research reactor at the Korea Atomic Energy Research Institute. The measurements were carried out using a high-purity Ge detector with a relative efficiency of 25%. This measuring system has a resolution of 1.9 keV (FWHM) at 1332.5 keV of ^{60}Co with a peak-to-Compton ratio of 45:1.

2.3 Positive matrix factorization [2]

PMF is a new model that addresses such negative value problems by restricting the common factor and factor loading to have only a positive value, considering the standard deviation of measured data. Basic equation of the PMF model is shown equation (1). The method is to obtain the unknown matrix, G and F by the solution of a least square method iteratively:

$$X = GF + E \qquad (1)$$

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij} / s_{ij})^2 \qquad (2)$$

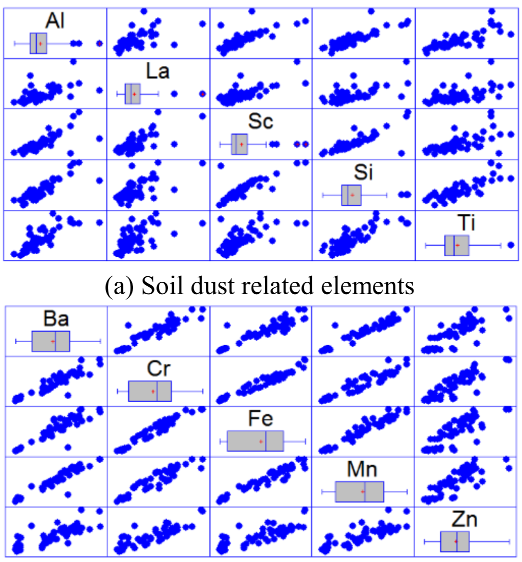
Where, X(m×n) is the data matrix consisting of the m chemical components analyzed in n samples, G(n×p) is the source contribution to the each sample. F(p×m) is the matrix of source profile. E presents the residual matrix of calculation, and the main process of the PMF is minimizing the Q-value, which is defined in the equation (2) below as the sum of square of the residuals (e_{ij}) weighted inversely with error estimates (s_{ij}) of the data point.

3. Results and discussions

3.1 PM2.5 and elemental concentration

The PM2.5 concentrations in the subway station varied in the range of 16.1 to 72.7 μg m^{-3} with average (± standard deviation) of 36.9 ± 12.4 μg m^{-3}. To describe the distribution patterns of 25 elements, their concentration data were further assessed by their magnitude. The concentrations of As, Cr, Mn, and Zn in PM2.5 averaged as 1.63±0.87, 25.5±11.7, 175.5±38.3, and 135.4±51.6 ng m^{-3}, respectively. It was found that the concentrations of Fe in PM2.5 were substantially larger than all other elements. One may note that Fe is generally the most abundant elements of indoor PM2.5 constituents in subway station. The Fe concentrations in PM2.5 varied in the range of 0.7 to 16.0 μg m^{-3} with average (± standard deviation) of 8.1 ± 8.9 μg m^{-3}. The Fe concentrations were apportioned by about 22% of the PM2.5. Thus Fe is the single predominant element, which trends to occur in the form of magnetite (Fe_3O_4), as they are released by the friction of steel.

The higher correlation coefficient imply that origins of specific species are influenced each other. If the correlation coefficients among elements with possible specific sources (e.g., soil dust or rail dust) are examined, strong relationships (r > 0.8) were found from both soil dust related elements (such as Al, La, Sc, Si, and Ti) and rail dust related elements (such as Ba, Cr, Fe, Mn, and Zn).



(a) Soil dust related elements

(b) Rail dust related elements

Fig. 1. Correlation analysis between elements from the possible sources and rail dust at the platform of Yuseong-Spa subway station

3.2 Source apportionment

The sources were classified into four categories by using PMF based on PM2.5 and elemental data collected in a subway station. The results of the correlation analysis using the observed versus predicted PM2.5 mass concentrations indicated that the resolved factors effectively accounted for the total mass. Correlation coefficient between the reconstructed and measured data sets was about 0.80. On average, the extracted factors from the data accounted for 99% with respect to the corresponding measured PM2.5 concentrations. Generally, because Ba, Cr, Fe, Ba, and Mn can be classified into crustal origin elements, their enrichment in subway station could be accounted for by resuspension of crustal particulates (introduced by penetration of outdoor APM) through incoming passengers as well as anthropogenic sources in subway station (steel friction of railway and wheel).

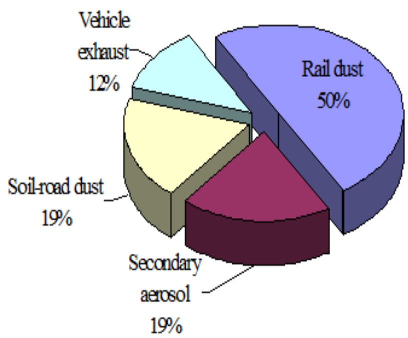


Fig. 2. Average source contribution estimate analyzed by PMF for indoor PM2.5 at platform in the subway station

The dominant five sources at the platform of the subway station were estimated and the contribution of each source was quantified by PMF receptor model; rail dust (18.0±12.4 μg m^{-3}, 50%), secondary aerosol (7.0±7.1 μg m^{-3}, 19%), soil-road dust (6.8±5.0 μg m^{-3}, 19%), and vehicle exhaust (4.3±4.7 μg m^{-3}, 12%). Excluding the rail dust generated by the friction of a rail and wheel, the PM2.5 at the subway platform were originated from the outdoor pollution sources (e.g., secondary aerosol, soil-road dust and vehicle exhaust). Therefore, the quantity of PM2.5 infiltrated from outdoor PM2.5 sources was estimated to be about 50% at the subway platform.

REFERENCES

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