ABSTRACT

Under a very tough situation that there has been increasing concern to the air quality in underground subway spaces, this study set sights on the thorough estimation of the chemical properties and source apportionment of particulate matter (PM) collected on an underground subway platform by a cooperative approach of semi-bulk and single particle analyses. The size-resolved PMs were intensively collected on the platform of Miasageori station on the Seoul Subway Line-4, and then, they were semi-bulkily analyzed by a PIXE and the TOR® method, and individually analyzed by a SEM-EDX. Overwhelmingly enriched iron was a notable feature of elemental concentration of PM$_{2.5}$. Source classification of iron in PM$_{10-2.5}$ and PM$_{2.5}$ performed along with their elemental concentrations, indicates that the railway originated iron accounts for 95.71% and 66.39% of total iron in PM$_{10-2.5}$ and PM$_{2.5}$, respectively. Via a stoichiometric categorization, Fe$_2$O$_3$, CaAl$_2$Si$_2$O$_8$, Al$_2$O$_3$, and CaCO$_3$ show more than 85% abundance ratio in individual coarse particles. The result of theoretical estimation of the subway derived organic carbon (OC$_{Subway}$) suggests that OC$_{Subway}$ in PM$_1$ and PM$_{2.5-1}$ account for 75.86% and 51.88% of total organic carbon, respectively.

Key words: Particulate matter, Subway, Individual particle, Element, Organic carbon, PIXE

1. INTRODUCTION

The concern over urban crowding and automotive air pollution has stimulated the construction and expansion of underground transportation system (i.e., subway transit system) in most metropolitan areas worldwide. In addition to the role of transportation, the space of subways, properly speaking, the courses of subway station tend to play parts in centers of daily activities such as various cultural events and commercial activities.

However, many underground spaces of a subway station (e.g., shopping mall, station office, and platform) are also the vulnerable areas for air pollution that may be caused by the pollutants both from the outside atmosphere and generated internally. Both gaseous and particulate air pollutants can be considered as indoor air pollutants exposed to millions of people (e.g., passengers, passers, merchants, and the ticket gate staff) daily. As one of gas-phase pollutants, volatile organic compounds (VOCs) with NO$_2$ emitted from vehicles on road can flow into subway station through ventilating openings or stairs (Son et al., 2011). Other VOCs can be generated by evaporation from a wide array of manufactured goods (e.g., varnishes, cosmetics, office equipment such as copiers and printers, and craft materials like glues, adhesives and permanent markers, etc.) displayed at shopping mall and dissipate into the indoor subway space. Chan et al. (2003) reported that although the exposure level of VOC in the subway was lower than that in roadway transports, the benzene measured in subway was 7.6 μg m$^{-3}$.

Moreover, railway systems are a great generator of particulate matter (PM), especially iron abundant particles at both submicron and coarse fractions. Very small PM can be generated by a high-temperature process when train is breaking. Meanwhile, relatively large-size particles such as splinters are most likely generated by mechanical abrasion (Lorenzo et al., 2006).

During braking, both the wheel-mounted disc and the brake pads often used in rail transport are worn, then, generate PM (Abbasi et al., 2011). A previous field study classified the airborne wear particles generated from railway brake as the ultra-fine particles with a size around 100 nm in diameter, the fine particles with a size around 350 nm in diameter, and the coarse particles with a size of 3-7 μm in diameter (Abbasi et
Particles, especially small-sized, float in air for a long time in semi-closed underground subway space and cause damage to human respiratory system (McDonnell et al., 2000).

To know the chemical properties and sources of PM in subway space is very important to realization of effective control and improvement of indoor air quality of underground subway.

The purpose of the research presented in this paper is to clarify the chemical properties and source profiles of PM collected on an underground subway platform.

2. EXPERIMENTAL METHODS

2.1 Description of Measurement Site

Miasageori station (37°36′48″N, 127°01′48″E) is a station on the Seoul Subway Line-4. Its name, i.e., Miasageori, means “four-way junction in Mia-dong, Gangbuk-gu, Seoul. Fig. 1 shows the schematic structure of Miasageori Station and the measurement point. This station has a side platform positioned to the side of a pair of tracks at a railway and screen doors are installed at each side of platform. Subway tunnel is mechanically ventilated by two ventilators. Daily running train number and passenger number are 494 and 69,601 people (getting on 38,373, getting off 31,228), respectively (Seoul Metro Subway homepage, 2014). Six-lane outdoor roads, with usually heavy traffic, are running above Miasageori station.

Fig. 1. Schematic structure and outline of Miasageori station.

2.2 Particle Sampling

Size-resolved PM sampling was intensively performed on the platform (L2) of Miasageori station (see Fig. 1) from 10:00 AM to 3:00 PM on Aug. 21st, 2012.

For the collection of size-resolved PM, two kinds of two-stage multi nozzle cascade impactor (MCI) samplers (Tokyo Dylec Co.) were synchronously operated. One MCI sampler collected coarse (PM10-2.5) and fine (PM2.5) fractions of PM separately on a prefilter and a back-up filter, respectively. The former and the latter MCI samplers loaded the Nuclepore® polycarbonate filters (GE Healthcare Whatman) with 0.2 μm pore size and quartz fiber filters (Whatman) on each stage for analysis of elements and carbonaceous components, respectively. The more details of particle cut-off and filter arrange have been described elsewhere (Ma et al., 2010). In order to exclude the direct influence of the stirring up of PM by passengers’ steps as well as to consider health effects of PM, two MCI samplers were installed at 1.6 m above platform surface.
2.3 Analyses of Elements and Carbon

2.3.1 Determination of Elemental Components in Semi-bulk PM

The reasonable determination of elemental concentration is the primary requisite to successful estimation of the chemical properties and source profiles of PM. In this study, both coarse fraction PM (PM$_{10-2.5}$) and fine fraction PM (PM$_{2.5}$) were the target of semi-bulk analysis using a Particle Induced X-ray Emission (PIXE). One of PM spots formed on the prefilter placed under the jet-nozzles of the MCI cascade impactor and a portion of backup filter loading PM$_{2.5}$ were irradiated by the proton beam of PIXE installed at the Cyclotron Research Center of Iwate Medical University. This PIXE analytical system has the great advantages such as an excellent sensitivity, a nondestructive technique for multielement with a wide range of elements (Z, atomic number $> 10$), and a short measuring time (3-10 minutes for typical environmental samples). The sensitivity, if defined by the ratio of (PIXE yield per unit dose)/(mass thickness), can be determined experimentally and theoretically for all objective elements. For instance, the sensitivity of calcium was calculated to be 1700 (counts · cm$^2$/μC · μg) with a detection limit of $9.4 \times 10^{-3}$ (μg/cm$^2$). The more detailed analytical procedures and experimental set-up used for PIXE analytical system were described elsewhere (Sera et al., 1999).

2.3.2 Morphological Observation and Elemental Analysis of Individual Particles

A Scanning Electron Microscope (SEM) (JEOL JSM-5400) equipped with an Energy Dispersive X-ray Detector (EDX) (Philips, EDAX DX-4) was employed on morphological observation as well as elemental analysis of the individual particles in PM$_{10-2.5}$. The pre-treated samples were placed inside the SEM’s vacuum column ($10^{-6}$ Torr) through an air-tight door. The randomly selected single particles were observed and analyzed under high resolution and 15-20 kV working conditions. The more details of instrumental feature and analytical processes of SEM-EDX employed in this study have been described elsewhere (Aboraia et al., 2013).

2.3.3 Analysis of Carbonaceous Component in PM$_{2.5-1}$ and PM$_{1}$

The concentration of carbonaceous compositions (i.e., organic carbon (OC) and elemental carbon (EC)) was determined using the TOR® (DRI) Method. This TOR® method is a well-accepted technique in which the sample is progressively pyrolyzed with continuous detection of evolved carbon. Two particle spots and two 0.64 cm$^2$ punches were taken from the 1st and 2nd stage quartz filters, and then, placed in the analyzer. OC was defined as all carbon that evolved from the sample without added oxygen when heated up to 550°C. Two additional temperature steps of 700°C and 800°C are made. EC was defined as all carbon that evolved from the sample when heated up to 800°C in 2% oxygen and 98% helium atmosphere after the OC was removed. A full detail of TOR® method was described in elsewhere (Chow et al., 1993).

3. RESULTS AND DISCUSSION

3.1 Quality Assurance (QA) for PIXE Data

Although, as mentioned previously, PIXE analysis is one of most advanced analytical techniques, it is a debatable point that PIXE analytical data of each particle spot and filter portion on MCI stage are identical because only two particle spots and portions from each filter were analyzed. To make clear this doubt, two different spots of MCI’s prefilter were analyzed under the same analytical conditions of PIXE.

Fig. 2 shows the correlation of elemental concentrations of two spots formed on the 1st stage of MCI sampler.

Fig. 3 displays the elemental concentration of PM$_{2.5}$. A notable feature is the enrichment of iron. It is well-
known that iron is the most abundant element in PM in indoor air of underground subway station. Iron in fine PM is mainly originated from the thermal metamorphism of train wheels (Lorenzo et al., 2006). The small size steel dusts are also produced from the mechanical friction of numerous train wheels roll, electrical wires, and train bodies through the subway tunnels. Iron might be also occurred as a result of accumulation in street dust of small rust particles.

Calcium and magnesium, as the next major components, were presumably derived from the cement used as common bridging underneath the railway tracks in Seoul subway (Institute of Environmental Research at Kangwon National Univ., 2006). Although, the quantity were very insignificant compare to upper 3-component, chromium (1183 ng m$^{-3}$) and manganese (175 ng m$^{-3}$) were also detected. These metals with together iron are produced by the friction erosion of subway rails, wheels and brushes and most enriched in subway (Chillrud et al., 2005). In spite of their low-levels, there is increasing interest in health effect (e.g., Parkinsonism and carcinogenesis) from long-term exposure (Aschner et al., 1999; Langard and Norseth, 1985).

3.3 Source Apportionment of Iron in PM$_{10-2.5}$ and PM$_{2.5}$

As mentioned above, iron containing particles are dominated in the particles collected on subway platform. Iron exposure together with other transition metals has been speculated to negative health effect related to its ability to generate free radicals in the body (Chillrud et al., 2005). It would therefore be absolutely necessary to make clear assessment about iron source for the improvement of indoor air quality in subway and making regulation strategies.

Source apportionment (i.e., railway sources and others) of iron in PM$_{10-2.5}$ and PM$_{2.5}$ was carried out by the iron concentration determined in this study and
referential data, and its result is shown in Fig. 4. The railway origin iron was estimated as below equation on the assumption that subway rails, wheels, and train bodies are potassium free (The center of research development for metallic materials, 1999).

$$Fe_{RAILWAY} = \frac{Fe_{PIXE}}{K_{PIXE}} \cdot \frac{Fe_{SOIL}}{K_{SOIL}}$$

where $Fe_{PIXE}$ and $K_{PIXE}$ are the concentrations of iron and potassium determined PIXE analysis in this study. $Fe_{SOIL}$ and $K_{SOIL}$ are the referential data for the concentrations of iron and potassium in soil (Wielopolski et al., 2005).

The railway originated iron accounts for 95.71% and 66.39% of total iron in PM$_{10-2.5}$ and PM$_{2.5}$, respectively. This means a large number of particles, especially coarse particles, containing iron are generated from railway system. Through a model calculation for indoor air quality in a subway station in Seoul, Song et al. (2004 and 2008) reported that ferrous related particles were thought to be the largest contributors to particle emissions on the platform.

Coarse fraction ferrous particles were most likely generated by the physical friction and mechanical abrasion (or collision) among train body, wheel, rail, and electric wire. And their shape is irregular as shown at the portion of bottom right in Fig. 5 that shows marked differences of SEM observation among individual particles. Meanwhile, the fine iron containing particle has a round shape as displayed at the upper right of Fig. 5. These size and morphology indicate that this small size steel dust was probably generated by a high-temperature process during train wheel and rail sparking. One of iron sources in the “Others” of PM$_{2.5}$ in Fig. 4, the small size particles generated through a thermal metamorphism of the ballast (indoor: cement, outdoor: feldspar and granite) can be assigned.

In order to stoichiometrically estimate the abundantly detected elements (Figs. 3 and 5) in particles on the subway platform, the classification of individual coarse particles was attempted.

The stoichiometric classification was carried out by the algorithm introduced by Lorenzo et al. (2006). They distinguished the PM$_{10}$ samples collected near a busy railway line using the net intensities of the EDX spectra.

In this study, iron, silica, aluminum, and calcium analyzed from the individual particles (in total approximately 1,000 randomly selected particles) of PM$_{10-2.5}$ were target of stoichiometric classification on the basis of spectra and net-count of SEM-EDX. The flow chart described in Fig. 6 explains the algorithm used to particle categorization. Abundance ratio of the stoichiometrically categorized 7-class particle types are also given in Fig. 6. As a result, Fe$_2$O$_3$, CaAl$_2$Si$_2$O$_8$, Al$_2$O$_3$, and CaCO$_3$ show the more than 85% abundance ratio.

Fig. 5. Elemental maps of SEM-EDX analysis for three individual particles.
3.4 Theoretical Calculation of Subway Origin OC

In the case of subway commuters in Boston, the contribution of subway exposures to total VOC exposures was about 10 to 13% (benzene 10%, toluene 12%, ethylbenzene 11%, m-/p-xylene 13%, and o-xylene 11%) (Chan et al., 2012). As mentioned earlier, since most underground subway stations are connected to above-ground transportation, gas-phase pollutants including volatile organic compounds (VOCs) exhausted from vehicles flow subsequently into subway stations through ventilating openings or stairs (Son et al., 2011). Original sources of VOCs in underground subway space might be considered. They are interior and exterior paints/adhesives in concourse and subway platform, and numerous goods displayed in stores of shoes, clothing, and other petrochemistry products in concourse. These VOCs released from various sources will exert a strong influence on the rises of organic carbon in subway microenvironments.

It is well known that particulate OC is emitted in primary particulate form and secondary formed (i.e., secondary OC) in the atmosphere through photochemical reactions. Underground space (e.g., concourse and platform) is, therefore, not favorable for the formation of secondary OC. However, low-volatility products from the gas-phase organics condense or absorb onto particle surfaces, or absorb into pre-existing particulate matter resulting in the addition of particulate OC to underground subway space. This is termed “OC_{Subway}” in this study.

We attempt to theoretically estimate the OC_{Subway}. The procedure of this novel try is displayed in Fig. 7. Assuming the OC_{Subway} exists in total OC (OC_{Total}), particulate OC_{Total} can be calculated by summing of primary OC (OC_{Pri}), secondary OC (OC_{Sec}), and subway origin OC (OC_{Subway}). Meanwhile, OC_{Pri} is comprised of both biological OC (OC_{Bio}) (e.g., pollens, micro-organisms, and small insects) and vehicle origin OC (OC_{Vehicle}). In this study, the subject of theoretical calculation of OC_{Subway} is PM_{1} and PM_{2.5-10}, therefore, OC_{Bio}, which is clearly much larger than 2.5 μm, can be disregarded. Then, OC_{Pri} in this study refers to only OC_{Vehicle}. OC_{Vehicle} can be calculated by a equation of (OC/EC)_{Vehicle} × EC_{Subway} (Park et al., 2005).

For the purpose of determining the carbonaceous components exhausted from automobile, Ma et al. (2004) carried out a field study at the center of Buk-Ak tunnel, which is one of heavily polluted tunnels in Seoul. The urban tunnel data obtained by their field
study were employed to estimate the ratio of OC to EC directly emitted from vehicles [(OC/EC)\textsubscript{Vehicle}].

The secondary OC (OC\textsubscript{Sec.}) formed at outdoor atmosphere by the gas-particle conversion of gaseous hydrocarbon precursors as a result of photochemical activity is also one of OC types in the space of underground subway station. This OC\textsubscript{Sec.} refers to the referential data (Ma, 2012) of the concentration of 6-kind water soluble organic acids in size-resolved particles collected in an urban city.

Finally, OC\textsubscript{Subway} can be estimated by subtraction the sum of OC\textsubscript{Bio.}, OC\textsubscript{Pri.}, and OC\textsubscript{Sec.} from OC\textsubscript{Total}. And it can be formulated as follows:

\[
\text{OC}\textsubscript{Subway} = \text{OC}\textsubscript{Total} - \left[ \text{OC}\textsubscript{Bio.} + \left( \frac{\text{OC}\textsubscript{Vehicle}}{\text{EC}\textsubscript{Vehicle}} \times \text{EC}\textsubscript{Subway} \right) + \text{OC}\textsubscript{Sec.} \right]
\]

Table 1 shows the measured OC\textsubscript{Total}, calculated OC\textsubscript{Pri.}, and OC\textsubscript{Sec.} concentrations, and the fraction of OC\textsubscript{Subway} to OC\textsubscript{Total}. The concentrations of OC\textsubscript{Subway} in PM\textsubscript{1} and PM\textsubscript{2.5-1} were 8.80 μg m\textsuperscript{-3} and 2.35 μg m\textsuperscript{-3}, respectively. And their fractions to OC\textsubscript{Total} were 75.86% and 51.88%, respectively. As shown in Table 1, OC\textsubscript{Subway} exhibits a predominant occurrence in PM\textsubscript{1}.

High OC\textsubscript{Subway} levels were probably attributed to the low rates of air exchange between the underground subway space, especially concourse, and outdoor environment.

Although, it is difficult to accurately measure the particulate OC concentrations because particulate OC lost due to volatilization (i.e. negative artifacts) and adsorption of gas-phase organics onto the filter (i.e. positive artifact) during and/or after sampling, our result demonstrates that the longer the subway commuters stayed underground, the higher their exposures of gaseous and particulate OC.

### 4. CONCLUSIONS

This study was carried out to clarify the chemical properties and source profiles of PM collected on an underground subway platform. The results of present study newly point out that “iron containing particles” generated from railway system were dominated in both coarse and fine mode PMs collected on subway platform. The concentration of OC\textsubscript{Subway} occupied a large portion of total organic carbon. It is therefore undeniable that although subway metro system has brought great convenience to the city’s travelling public, a lot of people who use subway spaces are exposed to harmful particulate substances. High levels of toxic particles in indoor subway space were probably attributed to the low rates of air exchange between the underground subway space, especially concourse, and outdoor environment. It would therefore be absolutely necessary to improve the ventilation system for a drastic betterment of indoor air quality in subway. In addition, both institutional improvement (i.e., reconsidering regulation strategies) and technical development on reduction of railway generated pollutants (e.g., particle generation from brake pads, mechanical abrasion, and thermal metamorphism) are urgently needed. In the current study, the spatial distribution of PM at subway platform was not discussed because, as mentioned earlier, a PM sampling was intensively done at a fixed point on subway platform. A more comprehensive assessment is being planned to make clear a spatial dissimilarity of PM concentration at subway microenvironment.

### ACKNOWLEDGEMENT

The work described in this paper was supported by research grants on the Railway Technology Research Project by Minister of Land, Infrastructure and Transport (14RTRP-B081249-01). We express our sincere thanks to the alumna of the Lab. of environmental inorganic chemistry of Dept. of Environmental Science, Fukuoka Women’s University for their experimental supports. The author expresses a sincere thank to staffs of the Seoul Metro Subway for their cooperation.

### REFERENCES

Abbasi, S., Wahlström, J., Olander, L., Larsson, C., Olofsson, U., Sellgren, U. (2011) A study of airborne wear particles generated from organic railway brake pads and brake discs. Wear 273, 93-99.
Aboraia, M.S., Wasly, S.H., Doheim, M.A., Abdalla, G.A., Mahmoud, A.E. (2013) Characterization of Al/(10%Al2O3-10%ZrO2) nanocomposite powders fabricated by high-energy ball milling. International Journal of Engineering Research and Applications 3, 474-482.

Aschner, M., Vrana, K.E., Zheng, W. (1999) Manganese uptake and distribution in the central nervous system (CNS). Neurotoxicology 20, 173-180.

Chan, C.C., Spengler, J.D., Ozkaynak, H., Lefkopoulou, M. (2012) Commuter exposures to VOCs in Boston, Massachusetts. Journal of the Air & Waste Management Association 41, 1594-1600.

Chan, L.Y., Lau, W.L., Wang, X.M., Tang, J.H. (2003) Preliminary measurements of aromatic VOCs in public transportation modes in Guangzhou, China. Environment International 29, 429-435.

Chillrud, S.N., Grass, D., Ross, J.M., Coulibaly, D., Slavkovich, V., Epstein, D., Sax, S.N., Pederson, D., Johnson, D., Spengler, J.D., Kinney, P.L., Simpson, H.J., Brandt-Rauf, P. (2005) Steel dust in the New York City subway system as a source of manganese, chromium, and iron exposures for transit workers. Journal of Urban Health 82, 33-42.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G. (1993) The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies. Atmospheric Environment 27A, 1185-1201.

Langard, W., Norseth, T. (1985) Handbook on Toxicology of Metals. Amsterdam: Elsevier, pp. 185-210.

Lorenzo, R., Kaegi, R., Gehrig, R., Grobéty, B. (2006) Particle emissions of a railway line determined by detailed single particle analysis. Atmospheric Environment 40, 7831-7841.

Ma, C.J. (2012) Quantification of water soluble organic acids in the highly time-resolved ambient particle using capillary electrophoresis method. Earth & Environmental Research 7, 1-7 (in Korean).

Ma, C.J., Kim, K.H., Kang, G.U. (2010) A case study of ionic components in the size-resolved ambient particles collected near the volcanic crater of Sakurajima. Japan. Asian Journal of Atmospheric Environment 4, 72-79.

Ma, C.J., Tohno, S., Kasahara, M. (2004) A case study of the single and size-resolved particles in roadway tunnel in Seoul, Korea. Atmospheric Environment 38, 6673-6677.

McDonnell, W.F., Nishino-Ishikawa, N., Petersen, F.F., Chen, L.H., Abbey, D.E. (2000) Relationships of mortality with the fine and coarse fractions of long-term ambient SPM concentrations in nonsmokers. Journal of Exposure Analysis and Environmental Epidemiology 10, 427-436.

Park, J.S., Kim, S.D., Han, J.S., Kim, T.S. (2005) Estimation of secondary component of carbon matters in particulate matters. Proceeding of the 40th Meeting of Korean Society for Atmospheric Environment, pp. 370-372.

Institute of Environmental Research at Kangwon National University (2006) Research report of air and soil pollution at cement company in Youngwoelgun, pp. 1-15.

Seoul Metro Subway homepage (2014) http://www.seoulmetro.co.kr.

Sera, K., Futatsugawa, S., Matsuda, K. (1999) Quantitative Analysis of Untreated Bio-samples. Nuclear Instruments and Methods in Physics Research B 150, 226-233.

Son, Y.S., Kang, Y.H., Chung, S.G., Park, H.J., Kim, J.C. (2011) Efficiency evaluation of adsorbents for the removal of VOC and NOx in an underground subway station. Asian Journal of Atmospheric Environment 5, 113-120.

Song, J.H., Lee, H.K., Kim, S.D. (2004) Model development for IAQ in a subway station. Air & Waste Management Association, p. 574.

Song, J.H., Lee, H.K., Kim, S.D., Kim, D.S. (2008) How about the IAQ in subway environment and its management? Asian Journal of Atmospheric Environment 2, 60-67.

The center of research development for metallic materials (1999) The impurities in iron scraps. Recycle of iron scrap 4, pp. 378.

Wielopolski, L., Song, Z., Orion, I., Hanson, A.L., Hendrey, G. (2005) Basic considerations for Monte Carlo calculations in soil. Applied Radiation and Isotopes 62, 97-107.

(Received 18 March 2015, revised 20 April 2015, accepted 12 May 2015)