Chemical Characterization of Outdoor and Subway Fine ($PM_{2.5-1.0}$) and Coarse ($PM_{10-2.5}$) Particulate Matter in Seoul Korea by Passive Sampling

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ABSTRACT: Outdoor and indoor (subway) samples were collected by passive sampling in urban Seoul and analyzed with computer-controlled scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (CCSEM-EDX). Soil/road dust particles accounted for 42-60% (by weight) of fine particulate matter larger than 1 micrometer ($PM_{2.5-1}$) in outdoor samples and 18% of $PM_{2.5-1}$ in subway samples. Iron-containing particles accounted for only 3-6% in outdoor samples but 69% in subway samples. Qualitatively similar results were found for coarse particulate matter ($PM_{10-2.5}$) with soil/road dust particles dominating outdoor samples (66-83%) and iron-containing particles contributing most to subway $PM_{10-2.5}$ (44%). As expected, soil/road dust particles comprised a greater mass fraction of $PM_{10-2.5}$ than $PM_{2.5-1}$. Also as expected, the mass fraction of iron-containing particles was substantially less in $PM_{10-2.5}$ than in $PM_{2.5-1}$. Results of this study are consistent with known emission sources in the area and with previous studies, which showed high concentrations of iron-containing particles in the subway compared to outdoor sites. Thus, passive sampling with CCSEM-EDX offers an inexpensive means to assess $PM_{2.5-1}$ and $PM_{10-2.5}$ simultaneously and by composition at multiple locations.

Key words: Subway, CCSEM, Particulate matter, Passive sampling, Indoor

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INTRODUCTION

Airborne particulate matter (PM) has been associated with adverse respiratory and cardiovascular health effects (Chen et al. 2004; Fung et al. 2006; Krewski and Rainham 2007). Understanding the chemical and physical properties of fine and coarse ambient particles is essential to the understanding of emission sources, transport, and deposition mechanisms as well as the health impact of particles deposited in the respiratory system (Mamane et al. 2001).

Numerous studies have focused on the biological effects of transition metals (iron, vanadium, nickel, chromium, copper and zinc) in PM because of their ability to generate reactive oxygen species (ROS) which can cause oxidative stress, cell death, biological aging and diseases(Carter et al. 1997; Costa and Dreher 1997; Goldsmith et al. 1998; Kodavanti et al. 1998; Ghio 2001; Li et al. 2003; Hetland et al. 2004; Valavanidis et al. 2005; Valavanidis et al. 2008; Chen and Lippmann 2009; Gualtieri et al. 2009; Akhtar et al. 2010; Wei et al. 2011; Ghio et al. 2012). Iron (Fe) is of particular interest in this study because of the high concentration of Fe-rich particles in subways and because iron is usually present at much higher concentrations in ambient air than other transition metals. The role of iron in mediating health effects from exposure to PM has been explored in a number of studies. Donaldson et al.(1997) and Valavanadis(2000) demonstrated that iron released from airborne PM can stimulate the generation of hydroxyl radicals by Fenton-type reactions, causing extensive oxidative damage to cellular macromolecules. Strong associations between iron and oxidative stress and pulmonary inflammation were also reported(Smith et al. 2000; Quinlan et al. 2002; Zelikoff et al. 2002; Zhang et al. 2008). ROS activity in rat alveolar macrophages exposed in vitro to Denver PM correlated highest (among nine distinct source types) with an unidentified iron source in the Denver airshed(Zhang and Napier-Munn 1995; Smith et al. 2000; Quinlan et al. 2002; Zelikoff et al. 2002; Zhang et al. 2008). Shafer et al.(2010) concluded that transition metals, particularly iron, are major factors mediating the ROS-activity of water extracts of PM collected in Lahore, Pakistan. In contrast to the above studies, Lay et al.(2001)studied the effects of inhaled iron oxide particles on alveolar epithelial permeability in healthy human subjects and found no appreciable alteration of alveolar epithelial permeability, lung diffusing capacity, or pulmonary function.

The US Environmental Protection Agency (EPA) currently regulates airborne concentrations of PM_{10} and $PM_{2.5}$ (particulate matter with aerodynamic diameter <10 µm and <2.5 µm, respectively). In 2006, the EPA proposed to replace the PM_{10} standard with $PM_{10-2.5}$, defined as the difference between PM_{10} and $PM_{2.5}$ ("coarse" particles). This change would have eliminated the duplication in regulation of particles <2.5 µm in both PM_{10} and $PM_{2.5}$ and may have prevented adverse health effects associated with exposure specifically to ambient coarse particles. Although the EPA ultimately retained the PM_{10} standard, there remains a need to understand the sources and composition of coarse PM and its potential health effects (Brunekreef and Forsberg 2005; Chang et al. 2011).

Traditionally, air quality studies have employed filter-based sampling and bulk analytical methods to determine ambient PM concentrations and average aerosol composition. However, computer-controlled scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (CCSEM-EDX) can provide information on the size, morphology, and elemental composition of individual particles, which can enable source identification. This technique was developed in the late 1970s and early 1980s and has been applied in numerous studies to characterize aerosols in the environment and for source apportionment (Kim and Hopke 1988; Dzubay and Mamane 1989; Vander Wood 1992; Johnson 1995; Katrinak et al. 1995; Jambers and Van Grieken 1997; Conner et al. 2001). Mamane et al.(2001) investigated how many particles are needed to statistically represent a sample and concluded that the major particle class abundances and average class compositions converged to within a few percent from final values after analyzing several hundred particles. Kang et al.(2008) and Jung et al.(2010) employed a variation of CCSEM-EDX called low-Z particle electron probe X-ray microanalysis (low-Z particle EPMA) to characterize aerosol composition in the Seoul, Korea subway system.

Passive sampling is an inexpensive way to measure particulate matter in many locations simultaneously and thus offers a way to improve exposure assessment (Noll et al. 1988; Brown et al. 1994; Vinzents 1996; Wagner and Leith 2001). Wagner and Leith, 2001 developed the UNC passive aerosol sampler in which ambient PM concentrations are estimated from 1) the surface loading of particles collected onto a substrate over time, and 2) knowledge of the flux, or rate of transfer, of these particles to the sampler. In the Wagner-Leith method, surface loading is determined by microscopy, by counting and sizing particles that have deposited on the substrate, and flux is estimated from a semi-empirical model that is a function of the aerodynamic diameter of a particle, d_a. Passive sampling combined with CCSEM-EDX has been used in recent studies in the U.S. to characterize particles in urban air sheds (Ault et al. 2012; Kumar et al. 2012; Mukerjee et al. 2012).

Concerns about the public health impact of subway aerosols(Chillrud et al. 2004; Karlsson et al. 2005; Seaton et al. 2005; Karlsson et al. 2006; Bachoual et al. 2007; Salma et al. 2007; Gustavsson et al. 2008; Karlsson et al. 2008), have motivated a number of air quality studies in subway systems around the world (Sitzmann et al. 1999; Furuya 2001; Chillrud et al. 2004; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007; Jung et al. 2010). Two of these studies (Kang et al. 2008; Jung et al. 2010) were conducted in the Seoul subway system: Kang et al.(2008) monitored particles in the Hyehwa subway station which are the most frequently encountered with relative abundances in the range of 61-79%., while Jung et al.(2010) characterized Fe-containing particles in four subway stations (Jegi, Chungmuro, Yangjae, and Seouldae) which decrease as the distance of sampling locations from the tunnel increases. Samples collected at the platform in subway stations with platform screen doors(PSDs) that limit airmixing between the platform and the tunnel showed marked decreases in relative abundances of Fe-containing particles, clearly indicating that Fe-containg subway particles are generated in the tunnel. Jung et al.(2010) collected particles with a three-stage PM_{10} sampler, obtaining particles in two size fractions: 10 µm to 2.5 µm; and 2.5 µm to 1 µm. Kang et al.(2008) used a 7-stage May cascade impactor with particles collected onto Ag foil. Disadvantages of these collection methods are that an air pump is needed to 'actively' pull air through the sampler and particles may bounce from collection substrates and pass erroneously to subsequent stages if substrates are not treated properly.

The goal of our study was to use passive sampling in conjunction with CCSEM-EDX to compare the chemical composition of fine and coarse particle matter in outdoor settings to that in the Jegi subway station in Seoul, South Korea. Passive sampling requires substantially less effort than active sampling. Thus, this technique may allow substantially more samples to be collected than 'active' sampling for similar or lower cost.

METHODS AND MEASUREMENTS

Passive samplers were deployed over seven-day periods in June 2010 in four locations (Dobong, Sungbuk, Guro and Jegi subway station) in Seoul, South Korea (Fig. 1). Dobong, Sungbuk and Guro are residential sites located along a line running northeast to southwest through the center of Seoul. Jegi is a subway station on Line 1 of Seoul's multiline subway system. A total of ten samples were collected, with two samples per location including two blanks. The Jegi samples were collected from the subway's platform which does not employ platform screen doors to limit mixing between the subway tunnel and the platform (Jung et al. 2010). The passive samplers used in this work were identical to those described by Ault et al. (2012). Briefly, particles were collected on polycarbonate substrates, which provide a flat, featureless substrate for CCSEM analysis. The substrates were mounted on an SEM stub below a protective mesh cap as described by Wagner and Leith (2001). The entire assembly was placed within a protective shelter (Ott et al. 2008b).

Collected particles were analyzed with the Personal SEM™ (PSEM) (Aspex Corporation, Delmont, PA) and with a Mira3 Field Emission SEM (Tescan USA Inc., Cranberry Township, PA). Both instruments are equipped with secondary and backscattered electron detectors and thin-window, energy-dispersive X-ray detectors (EDX) that enable X-ray detection of carbon and heavier elements. Both instruments use proprietary software to perform CCSEM analysis of the sample and to enable off-line review and processing of CCSEM data. More details on particle analysis by CCSEM are provided in Mamane et al. (2001).

For the present study, the PSEM software was configured to analyze particles between 1 and 18 μm (physical diameter) and to retain only those particles with aerodynamic diameter d_a between 1 and 10 μm. The d_a of each particle is estimated from the particle's physical diameter and EDX composition. The following SEM parameters were used: 20 kV accelerating voltage, magnification of 720X, 16 mm working distance, backscatter detection mode, and an EDX acquisition time of 2.5 seconds, sufficient to acquire a robust X-ray spectrum. CCSEM was conducted in the point analysis mode, whereby the electron beam was focused at the center of each particle while X-rays were acquired. The analysis time per sample was about 2-3 hours in which ~80% of the exposed collection area was analyzed. A total of 12,429 particles in the eight field samples were analyzed by CCSEM. The particles in each sample were classified using rules based on their elemental composition into 19 chemical classes or particle types shown in Table 1. (The class labeled “Others” contains several minor classes). Results of the CCSEM analysis were broken down by particle size into $PM_{2.5-1}$ (“fine” particles between 1 and 2.5 µm, aerodynamic diameter) and $PM_{10-2.5}$ (“coarse” particles between 2.5 and 10 µm).

RESULTS AND DISCUSSION

Results are summarized in Table 1 and Fig. 2 for fine particles ($PM_{2.5-1}$) and in Table 2 and Fig. 3 for coarse particles ($PM_{10-2.5}$). Following Jung et al. (2010), the chemical composition of the $PM_{2.5-1}$ samples was sorted into six major particle-type categories: soil/road dust, iron-containing, carbonaceous, aluminum, secondary nitrates/sulfates, and other. Soil/road dust included Al-Si, Al-Si-K, Al-Si-Mg, Ca/S, Ca/Si, Ca-Mg, Ca-rich, and Si-rich components. Particles in the iron-containing class had EDX spectra in which iron x-rays comprised at least 20% of the EDX spectrum. Carbon x-rays comprised at least 50% of the EDX spectrum for the carbonaceous class. Aluminum particles were distinguished from soil/road dust particles by their absence of silicon. Secondary nitrates/sulfates included Na/Cl, Na-rich and S-rich components.

As shown in Table 1, the order of abundance of these major particle types for the outdoor samples was: soil/road dust > carbonaceous > secondary nitrates/sulfates > others > iron-containing > aluminum. Soil/road dust particles were the greatest contributor to fine particle mass at the outdoor locations, accounting for 42% (Dobong) to 60% (Guro) of $PM_{2.5-1}$. Within the soil/road dust classification, aluminum silicate particles accounted for the greatest percentage by weight followed by calcium-containing particles and finally silicon-rich particles for both outdoor and subway samples. Carbonaceous particles accounted for 21~26%, secondary nitrates/sulfates were 4~21%, others were 4~5%, iron-containing were 3.5~5.8% and aluminum particles were 2~3%.

Some inter-site differences among the outdoor $PM_{2.5-1}$ samples are notable (Table 1). Guro aerosol had more soil/road dust by weight (60%) and less sodium/sulfur-rich mass (4%) compared to Dobong and Sungbuk. We attribute the similar composition of $PM_{2.5-1}$ aerosol samples in Sungbuk and Dobong to the relative proximity of these two sites (7.8 km), although several mountains are located around Dobong. Guro, however, is located south of the Han River at a distance of 16.7 km from Sungbuk. Many buildings were under construction within 1.0km of the Guro site during sampling which may account for the higher concentration of soil/road dust. The highest concentration of S-rich particles (presumably sulfate) was observed in Dobong (15%). The emission source for these particles is unknown but may originate from a garbage incineration plant located about 2.5 km from the sampling location.

The Na/Cl, Na/S and Na-rich content of $PM_{2.5-1}$ was substantially higher at Sungbuk compared to that observed at other sites. These particles may originate from road salt applied in the winter near the site

Particles collected in the Jegi subway station were strikingly different from those collected at the outdoor sites. The order of abundance of the major particle types for the Jegi subway samples was: iron-containing > soil/road dust > carbonaceous > others > aluminum > secondary nitrates/sulfates. These samples were dominated by iron-containing particles (69% of $PM_{2.5-1}$ by weight compared to 3-6% at the outdoor sites, a factor of 12 to 23 times higher).

These results are consistent with previous subway air quality studies in which iron-containing particles comprised the most abundant particle class by weight (Sitzmann et al. 1999; Furuya 2001; Chillrud et al. 2004; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007; Jung et al. 2010).

Seaton et al.,2005 reported that iron oxide particles comprised 67% by weight of $PM_{2.5}$ in samples collected in London Underground stations. In the Jegi subway station, Jung et al. (2010) found that 70.9% (± 8.0) of iron-containing particles by number were in the size range of 2.5 µm to 1 µm, which is in close agreement with our finding of 66% (± 9).

Iron-containing particles in subways are generated mainly from mechanical wear and friction processes at rail-wheel-brake interfaces, and at the interface between catenaries providing electricity to subway trains and pantographs attached to trains (Jung et al. 2010). Jung et al. characterized aerosol composition at different locations within Seoul subway stations to convincingly show that iron-containing subway particles are generated in the subway tunnels.

As shown in Table 2, the order of abundance of the major particle types for the three outdoor sites was soil/road dust > carbonaceous > others > iron-containing > aluminum > secondary nitrates/sulfates. As expected, soil/road dust particles were the greatest contributor to coarse particle mass in the outdoor samples, accounting for 66% to 83% of $PM_{10-2.5}$. Within the soil/road dust classification, aluminum silicate particles accounted for the greatest percentage by weight followed by calcium-containing particles and silicon-rich particles. Carbonaceous particles comprised 6~16% by mass, others were 4~7%, iron-containing were 3~5%, aluminum particles accounted for 2~3%, and secondary nitrates/sulfates were 1~3% by mass.

In outdoor samples, soil/road dust particles accounted for a higher proportion of mass for $PM_{10-2.5}$ than for $PM_{2.5-1}$. In contrast, secondary nitrates/sulfates and carbonaceous particles accounted for a higher proportion of mass for $PM_{2.5-1}$ than for $PM_{10-2.5}$. These observations are consistent with coarse mode particles being derived primarily from crustal material and fine mode having large portions of nitrates/sulfates and carbonaceous particles from other sources.

In contrast to fine particles, where abundances were most similar between the closest sites (Dobong and Sungbuk), abundances of coarse particles were most similar at the most distant sites(Sungbuk and Guro), while the Dobong samples had a higher weight percent of coarse carbonaceous particles. Compared to fine particles, coarse particles can have short atmospheric lifespans(Ott et al. 2008a); thus, differences among sites are not surprising. SEM-EDX analysis of the outdoor samples revealed more than a three-fold increase in the weight percent of pollens and plant debris particles (a subset of the carbonaceous class) in the Dobong samples relative to Sungbuk and Guro.

Subway samples showed a different order of abundance: iron-containing > soil/road dust > carbonaceous > others > aluminum > secondary nitrates/sulfates. Within the soil/road dust class in subway samples, particles containing aluminum silicates accounted for the greatest percentage by weight followed by calcium-rich particles and finally silicon-rich particles. Iron-containing and soil/road dust particles dominated coarse mass in the subway samples (44% and 36%, respectively).

In subway samples, iron-containing particles were the greatest contributor to mass for $PM_{2.5\text{-}1}$ (69%) and for $PM_{10\text{-}2.5}$ (44%). The smaller size fraction of particles showed a higher concentration of iron-containing particles. Also in the subway samples, the mass fraction of coarse soil/road dust particles abundance was twice the fine mode mass fraction .

Kang et al.(2009) reported that urban PM_{10} samples collected far away from subway stations contained 4.6% by number of iron-containing particles, which agrees with our number concentration of 4%, averaged over Sungbuk, Dobong, and Guro samples.

The most striking difference in PM composition between sites is the abundance of iron-containing particles in the Jegi subway site relative to the outdoor locations (Tables 1 and 2). Manual and computer-controlled SEM-EDX were used to investigate differences in iron particle composition and/or morphology between sites. The majority of Fe-rich particles were iron oxides as evidenced by the presence of oxygen in the EDX spectra (not shown).

Compared to the outdoor sites, samples collected in the Jegi subway had higher concentrations of stainless steel particles as well as particles rich in iron, calcium and silicon (Fe-Ca-Si class). Stainless steel particles from the subway station were typically larger than 10 µm and many showed surface features consistent with wear (Fig. 2). The source of these particles is unknown but may be attributable to wear from the subway cars.

The abundance of Fe-Ca-Si particles in subway samples, also noted by Jung et al. (2010), is attributed by Sitzmann et al.(1999) to friction between the train wheels and the brake blocks (composed of iron, glass fibers and $CaCO_3$). Figs. 3a and 3b show images and spectra of subway particles representing the Fe-Ca-Si class. The particle in Fig. 3a is decorated on its surface with many fine iron-rich particles smaller than a few hundred nanometers. Kang et al.(2008) hypothesized that nanosized particles on the surface of large Fe-containing particles are formed by the condensation of gaseous iron species from the sparking between the third rail and the electricity guide of subway trains, in a process similar to that of arc welding particles.

Electron micrographs and spectra of iron-containing particles found at the outdoor sites are provided in Fig. 4. The particle shown in Fig. 4a(Dobong) was identified as automotive brake wear from Dobong. That shown in Fig. 4b is a Fe-Ca-Si particle from Dobong of unknown origin, similar in composition to those identified in the subway. Lastly, the particle shown in Fig. 6c is an iron oxide sphere from Guro, presumed to originate from steel processing operations in the vicinity.

CONCLUSIONS

This study demonstrates the ability of low-cost passive sampling coupled with CCSEM-EDX analysis to identify differences in chemical composition of fine and coarse PM across multiple sites within an urban area. The chemical compositions of particles collected outdoors at three sites in Seoul, South Korea were similar. For $PM_{2.5\text{-}1}$ the similarities were greatest for the sites that were closer to each other, Dobong and Sungbuk. However, for $PM_{10\text{-}2.5}$, Sungbuk and Guro were most similar in composition. Soil/road dust particles dominated both $PM_{10\text{-}2.5}$ and $PM_{2.5\text{-}1}$ in outdoor samples, accounting for a larger fraction of $PM_{10\text{-}2.5}$ mass than $PM_{2.5\text{-}1}$ mass. The Jegi subway station aerosol was quite different in composition from the outdoor samples. Iron-containing particles accounted for only a small fraction of outdoor mass (3~6%) but represented a large fraction (44~69%) of mass in subway aerosol samples. Iron-containing particles accounted for a larger fraction of $PM_{2.5-1}$ than $PM_{10-2.5}$. Our results from the Jegi station agree with previous studies, which have reported enhanced concentrations of iron-containing particles in subway stations. Electron microscopy analysis of iron-containing particles in the outdoor and subway samples revealed enhanced concentrations in the subway of 1) large stainless steel particles consistent with wear and 2) iron-rich particles containing calcium and silicon, consistent with frictional wear between train wheels and brake blocks.

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Fig. 1. Passive sampling locations in Seoul, Korea

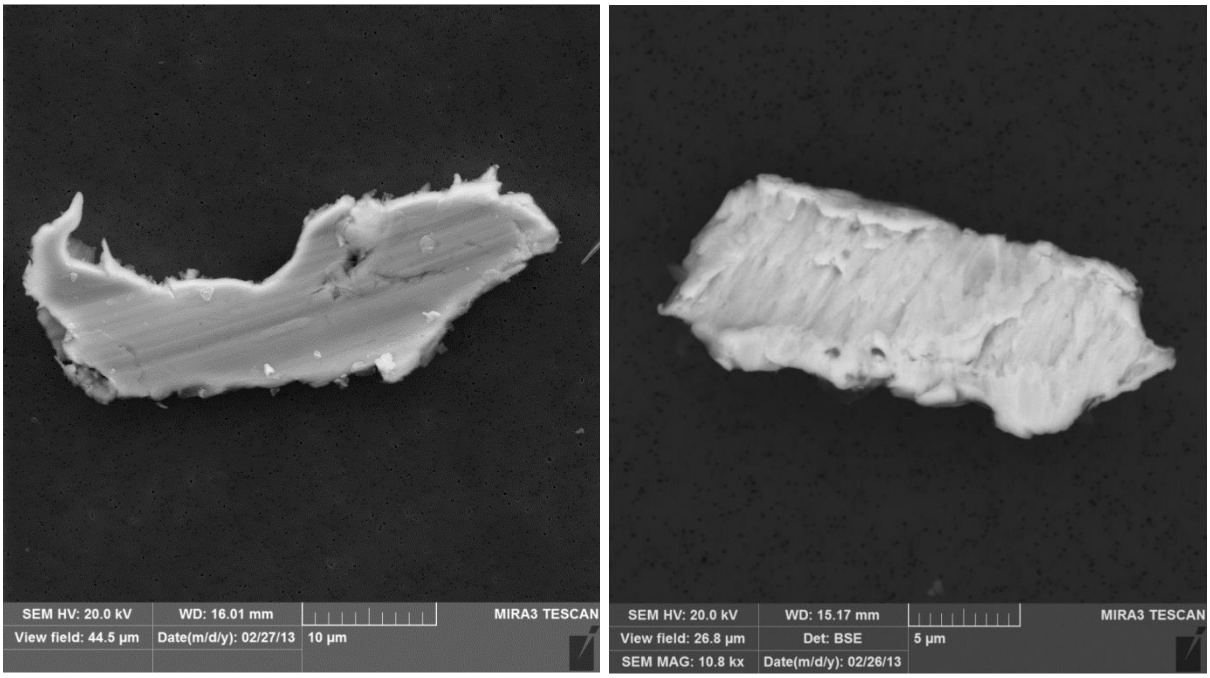
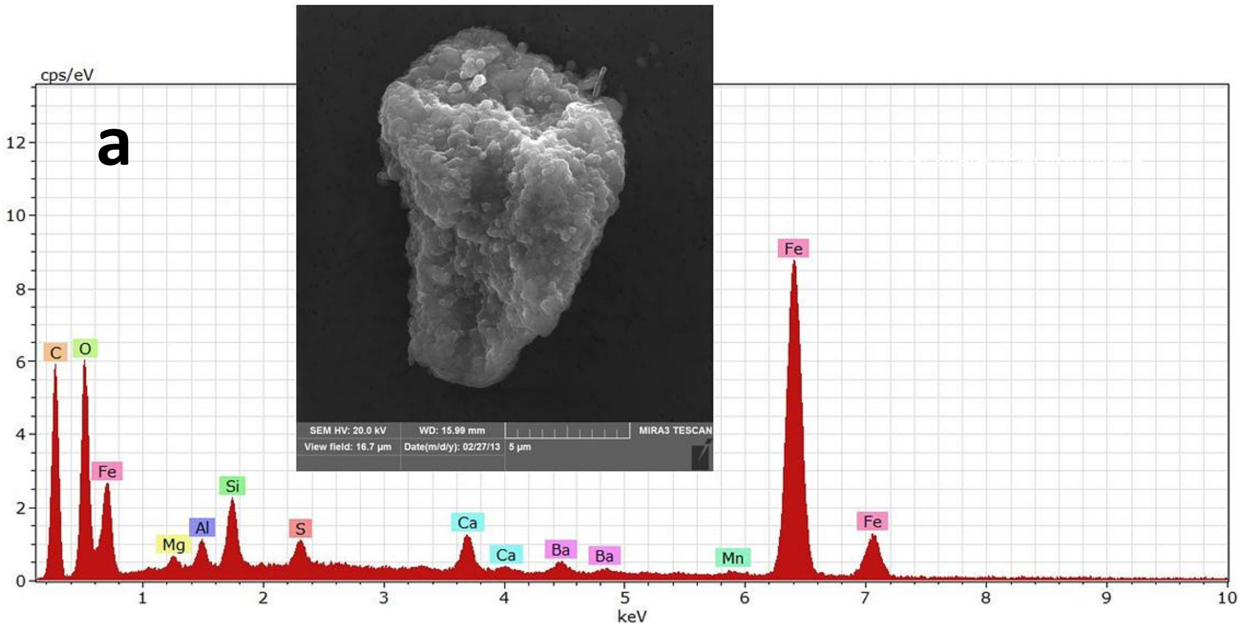


Fig. 2. Stainless steel particles collected in Jegi subway station showing surface features characteristic of wear processes**.** Such particles were typically larger than 10 µm and were unique to the Jegi site. The EDX spectra showed Fe, Cr, and Ni.



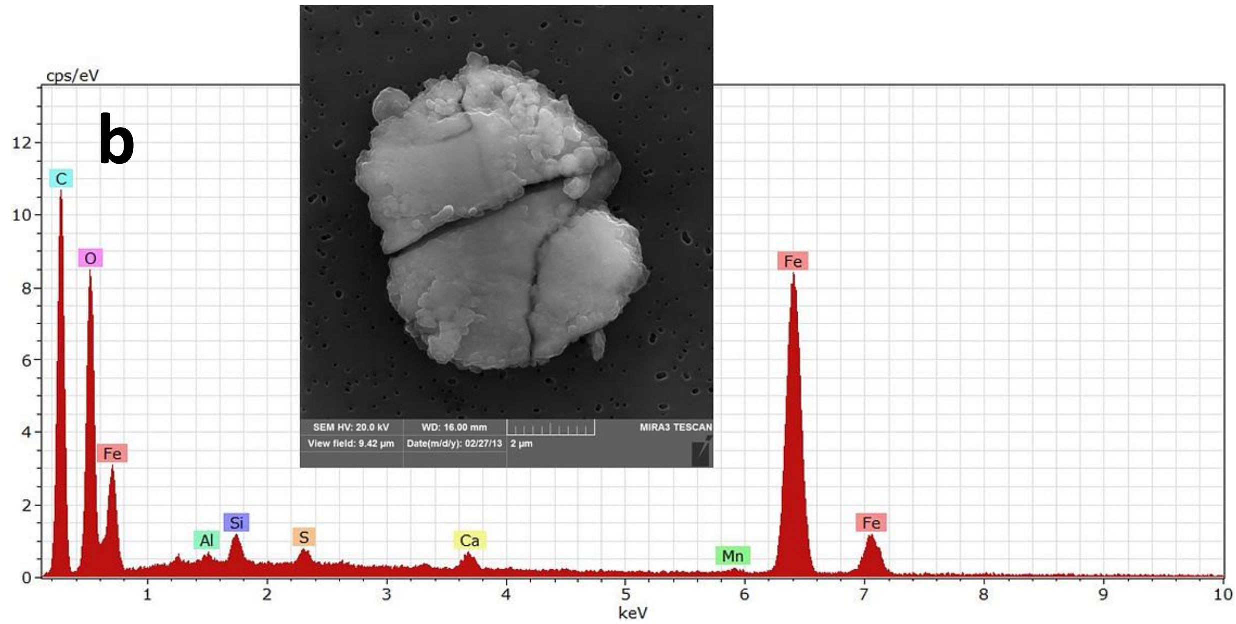


Fig. 3. Fe-Ca-Si particles from the Jegi subway station. Fe-Ca-Si particles were found in much higher concentration in the subway site compared to the outdoor sites. These particles may originate in friction between the brake block and the train wheels. The spectrum in Fig. 5a also shows sulfur, barium and manganese.

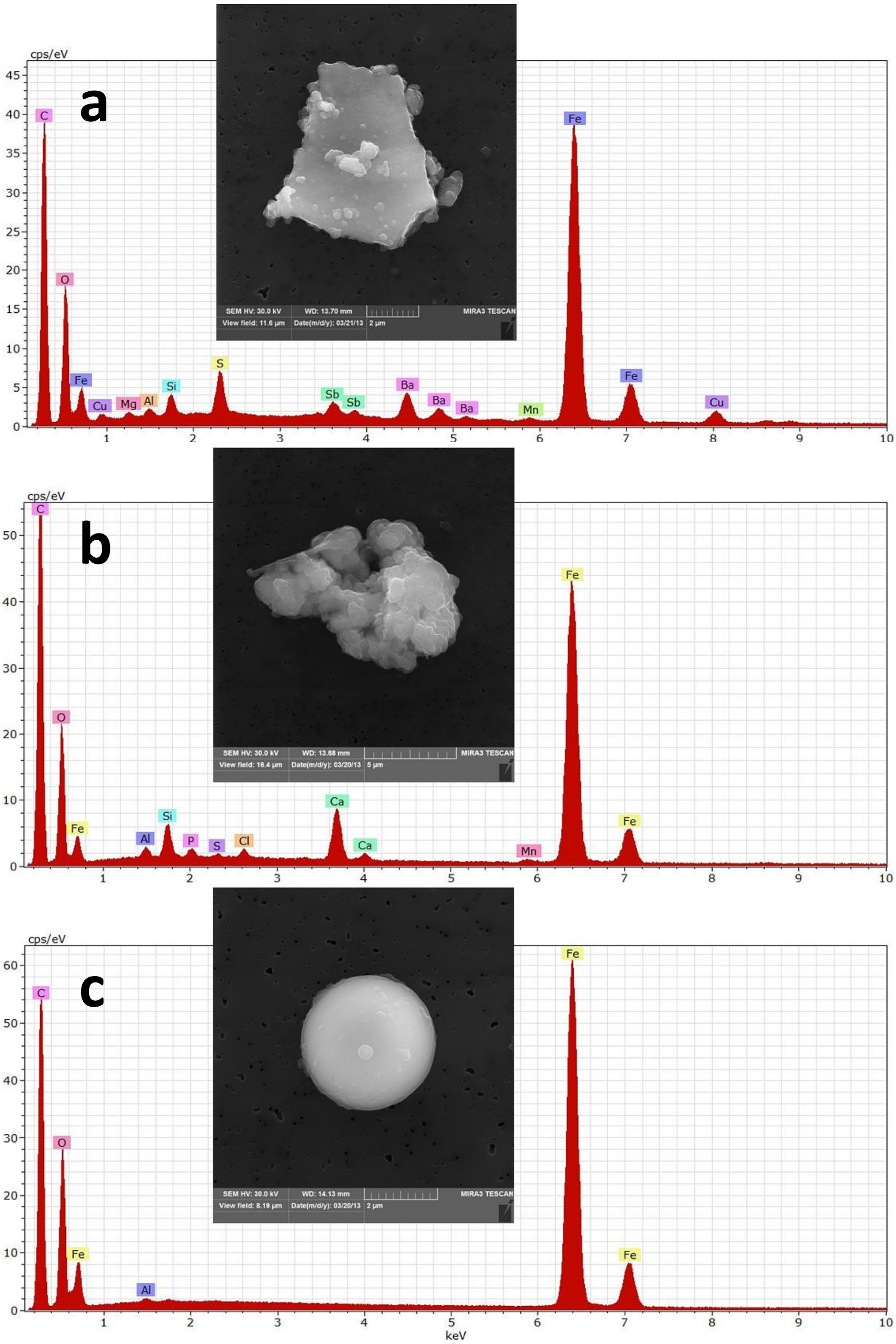


Fig. 4a. Likely automotive brake wear particle from Dobong with Ba, S, Sb, and Cu; **6b)** Fe-Ca-Si particle from Dobong, similar to those found in subway; **6c)** iron-oxide sphere from Guro, typically associated with steel production.

Table 1. Average relative abundances and standard deviations (weight %) of $PM_{2.5-1}$ composition by particle types from the outdoor and subway sites. Two samples were collected in each location. Values in italics indicate the abundance of individual particle types that were grouped into broader categories.

	Weight % (Std Dev)			
Particle type	**Dobong**	**Sungbuk**	**Guro**	**Jegi (subway)**
Soil/road dust, sum of:	42 (± 23)	49 (± 5)	60 (± 2)	18 (± 7)
Al-Si, Al-Si-K, Al-Si-Mg	*24*	*31*	*36*	*8*
Ca/S, Ca/Si, Ca-Mg, Ca-rich	*14*	*13*	*18*	*9*
Si-rich	*4*	*6*	*6*	*1*
Iron-containing	3 (± 0.4)	4 (± 0.1)	6 (± 0.1)	69 (± 8)
Carbonaceous	26 (± 5)	21 (± 1)	24 (± 2)	8 (± 1)
Aluminum	3 (± 2)	2 (± 0.1)	2 (± 1)	2 (± 1)
Secondary nitrates/sulfates, sum of:	21 (± 27)	18 (± 8)	4 (± 1)	0.3 (± 0.3)
Na/Cl, Na/S, Na-rich	*6*	*11*	*2*	*0*
S-rich	*15*	*7*	*2*	*0*
Others	4 (± 0.2)	5 (± 2)	4 (± 1)	3 (± 1)

Table 2. Average relative abundances and standard deviations (weight %) of $PM_{10-2.5}$ composition by particle types from the outdoor and subway sites. Two samples were collected in each location. Values in italics indicate the abundance of individual particle types that were grouped into broader categories.

Particle type	Weight % (Std Dev)			
	Dobong	**Sungbuk**	**Guro**	**Jegi (subway)**
Soil/road dust, sum of:	66 (± 1)	83 (± 2)	83 (± 4)	36 (± 2)
Al-Si, Al-Si-K, Al-Si-Mg	*51*	*59*	*66*	*23*
Ca/S, Ca/Si, Ca-Mg, Ca-rich	*12*	*18*	*10*	*12*
Si-rich	*4*	*5*	*6*	*1*
Iron-containing	5 (± 3)	4 (± 0.2)	3 (± 1)	44 (± 4)
Carbonaceous	16 (± 4)	6 (± 1)	7 (± 2)	8 (± 5)
Aluminum	3 (± 2)	2 (± 1)	3 (± 2)	5 (± 7)
Secondary nitrates/sulfates, sum of:	3 (± 1)	2 (± 0.3)	1 (± 1)	2 (± 1)
Na/Cl, Na/S, Na-rich	*1*	*1*	*1*	*1*
S-rich	*2*	*1*	*0*	*1*
Others	7 (± 5)	4 (± 1)	4 (± 2)	6 (± 1)