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Chemical speciation of size-segregated floor dusts and airborne magnetic particles collected at underground subway stations in Seoul, Korea

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ABSTRACT

Previous studies have reported the major chemical species of underground subway particles to be Fe-containing species that are generated from wear and friction processes at rail–wheel–brake and catenaries–pantographs interfaces. To examine chemical composition of Fe-containing particles in more details, floor dusts were collected at five sampling locations of an underground subway station. Size-segregated floor dusts were separated into magnetic and non-magnetic fractions using a permanent magnet. Using X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX), iron metal, which is relatively harmless, was found to be the dominating chemical species in the floor dusts of the <25 μm size fractions with minor fractions of Mg, Al, Si, Ca, S, and C. From SEM analysis, the floor dusts of the <25 μm size fractions collected on railroad ties appeared to be smaller than 10 μm, indicating that their characteristics should somewhat reflect the characteristics of airborne particles in the tunnel and the platform. As most floor dusts are magnetic, PM levels at underground subway stations can be controlled by removing magnetic indoor particles using magnets. In addition, airborne subway particles, most of which were smaller than 10 μm, were collected using permanent magnets at two underground subway stations, namely Jegi and Yangjae stations, in Seoul, Korea. XRD and SEM/EDX analyses showed that most of the magnetic aerosol particles collected at Jegi station was iron metal, whereas those at Yangjae station contained a small amount of Fe mixed with Na, Mg, Al, Si, S, Ca, and C. The difference in composition of the Fe-containing particles between the two subway stations was attributed to the different ballast tracks used.

1. Introduction

People spend most of their time indoors, either at home, in the workplace, or in transit, and there is increasing concern over the air quality of indoor microenvironments and its effect on public health. Among the various types of indoor microenvironments, underground subway stations have some unique characteristics in that they are somewhat closed spaces with strong indoor particle emission sources. Subway aerosol particles, which are generated mainly by the movement of trains and passengers, can accumulate in a closed environment, resulting in high concentrations of indoor particulate matter (PM), as has been reported in many subway systems worldwide [1–10]. As many people within metropolitan areas worldwide commute using underground subway transportation, and spend considerable time in the underground subway environment on a daily basis, there has been increasing concern regarding the air quality in underground subway systems because of its possible adverse effects on public health [5,11–18].

As trains frequently run in partially closed underground subway systems, the characteristics of subway particles are unique and quite different from those in the aboveground urban atmosphere. Several studies have reported that the major chemical elements constituting underground subway particles are Fe and Si, with small amounts of Mn, Cr, Cu, Ca, and K [4,5,11,18,19]. In Tokyo, the PM_{10} concentrations in underground subway stations were reported to be 30–120 μg/m^3 throughout the year, and the iron concentrations in the subway PM_{10}, being the highest level of chemical element, were 30–60 times higher than those in the aboveground PM_{10} [1]. In Zürich (Switzerland), the iron mass concentration was estimated to be 6.9–108 ng/m^3 at a 10 m distance from outdoor railway [20], and iron metal concentrations measured in two stations in the Buenos Aires underground subway system were reported to range

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from 5 μg/m^3 to 102 μg/m^3 [10]. In our previous work [21], an extensive study was performed on the chemical compositions of subway particles collected at four different locations (in the tunnel, at the platform, near the ticket office, and outdoors) of four underground subway stations in Seoul, Korea. Four major types of subway particles were identified: Fe-containing; soil derived; carbonaceous; and secondary nitrate and/or sulfate particles. Among them, Fe-containing particles were found to be the most abundant in a subway environment. In particular, in the tunnel and platform, Fe-containing particles were encountered most commonly with relative abundances of 75–80%, indicating that most aerosol particles in the tunnel and at the platform were Fe-containing ones. In addition, most of the Fe-containing particles in underground subway microenvironments exist as the oxidized forms.

When the genotoxicity of different particle types collected from wood and pellet combustion, tire-road wear, an urban street, and subway stations was compared, the particles from the subway stations were found to be the most genotoxic [13]. Other studies reported that underground subway particles have cytotoxic and inflammatory potential and transient biological effects [5,14,15], and the toxicity of subway particles was attributed to the high iron content [22]. Fe-containing subway particles can be in the form of iron metal, hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and/or magnetite (Fe_3O_4), which have different toxic and magnetic properties. Subway particles collected in a subway station in Stockholm, Sweden, were found to be eight times more genotoxic than urban street particles because Fe-containing subway particles were in the form of magnetite, which has adverse health effects [12]. However, the authors just claimed that the observation of the magnetite was made by X-ray diffraction (XRD) measurements without showing any XRD patterns of the subway particle samples. On the other hand, major iron oxide particles collected at a subway station in Budapest, Hungary, were reported to be mostly relatively harmless hematite with small amounts of magnetite, where the iron speciation was performed by selected-area electron diffraction analysis of single subway particles [18]. These two different results have been the only ones reported on iron speciation of airborne subway particles up until now.

Hematite is antiferromagnetic, whereas iron metal is ferromagnetic and maghemite and magnetite are ferrimagnetic. If Fe-containing subway particles would be magnetic such as iron metal, maghemite, and magnetite, then the levels of subway PM could be reduced effectively using magnets. Therefore, the speciation of Fe-containing subway particles is important in the context of public health and control measures. Several studies on magnetic properties of a range of airborne particles, such as coal-fired power plant fly ash, Asian dust, and road dust, have been reported [23–26]. However, up until now, there has been just one report on iron species of floor dust particles based on magnetic measurements and geochemical analysis [27]. In their work, magnetic measurements revealed that the floor dusts collected at subway platforms in Shanghai, China, had extremely strong magnetic signatures. Also, XRD analysis clearly confirmed the presence of iron metal and magnetite in the magnetic extracts, although their XRD analysis was purely qualitative.

As just a few and limited studies have been reported for iron speciation of floor dusts and subway particles, it is imperative to elucidate the iron species generated in underground subway system. Firstly, this study investigated floor dusts collected at different locations of an underground subway station, Seoul, Korea, because a significant amount of particle samples was needed for iron speciation using XRD and magnetic measurements, and it was believed that the characteristics of the floor dusts would roughly reflect those of airborne subway particles. Secondly, airborne subway particles collected using permanent magnets at different locations of two underground subway stations in Seoul, Korea, were examined because most of floor dusts were found to be magnetic. XRD, scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX), and vibrating sample magnetometer (VSM) measurements for the speciation of the size-segregated floor dust and airborne magnetic particles were performed in this work.

2. Experimental

2.1. Samples

Seoul, the capital of Korea, is a densely populated megacity (population 10.3 million, area 605 km^2). The Seoul subway system contains 9 lines with a total of 358 stations. According to the statistics provided from the Seoul metro transportation center (http://www.seoulmetro.co.kr), approximately 6.7 million commuters use the Seoul subway system on a daily basis. In this study, floor dust samples were collected at five different locations of an underground subway station ("Jegi" station): on the railroad ties in the tunnel and in front of the platform, at the platform, near the ticket office, and at the outdoor ventilation opening (the samples collected at the five sampling locations are denoted as samples F1–F5, respectively). The railroad ties in the tunnel for sample F1 were located 50 m inside from the platform of the station. The platform and ticket office were two and one floor below the urban street level, respectively. The outdoor ventilation opening was located 3 m above the street level, and dust deposited on it was considered to be mostly from the underground subway station as the ventilation opening is connected to the ceiling of the platform. The samples were collected using a vacuum cleaner during 2–5 am on January 15, 2009 when trains had stopped running and the station was closed to the public (see Table 1 for the sampling durations, areas, and sample masses). To collect an appropriate sample quantity for iron speciation, the sampling durations and areas differed according to the sampling locations. Samples F1 and F2 were collected at the floor areas on railroad ties (6.56 m^2), and samples F3–F5 were collected at the floor areas of 31.2, 31.2, and 2.7 m^2, respectively.

Airborne subway particles were collected on permanent magnets of 4000 Oe by placing them on the walls near the rail track and of the platform in two underground subway stations, namely "Jegi" and "Yangjae" stations (the samples collected on the walls near the rail track and of the platform in Jegi station are denoted as samples A1 and A2, respectively, and the samples on the walls near the rail track and of the platform in Yangjae station are samples A3 and A4, respectively) for 3 days (July 22–24, 2009 in Jegi station and October 11–13, 2009 in Yangjae station). Hereafter, the particles collected on the magnets are designated "magnetic particles".

2.2. Size-segregated magnetic floor dusts

The floor dust was segregated in size using stainless steel sieves with 25 μm, 63 μm, 100 μm, and 200 μm mesh sizes, producing four size-segregated samples with <25 μm, 25–63 μm, 63–100 μm, and 100–200 μm size ranges. Each separation was performed using a sieve shaker with a sieving time of 1 h. The magnetic and non-magnetic fractions of the size-segregated samples were separated using a permanent magnet of 5000 Oe. Herein, the magnetic particles are defined as those attracted to the magnet. The permanent magnet wrapped with a weighing paper was rubbed softly over floor dust particles in a Petri dish to allow particles stick to the weighing paper. The magnet was then removed from the weighing paper to release the attached particles into another Petri dish. Non-magnetic dust particles could be in contact with the neighboring magnetic particles and be attracted to the magnet together with the magnetic particles. After shaking the particles released from the magnet vigorously, the extraction procedure was repeated

Table 1
Sampling durations, areas, and sample masses for floor dust and airborne magnetic aerosol samples collected at different sampling locations.

Floor dust samples				
Sampling site	Sampling location	Sampling duration (min)	Sampling area (m^2)	Mass of floor dust (g)
Jegi station	Sample F1: railroad ties in the tunnel	20	6.56	0.23
	Sample F2: railroad ties in the platform	20	6.56	5.61
	Sample F3: platform	40	31.20	1.61
	Sample F4: ticket office	40	31.20	4.62
	Sample F5: outdoor ventilation opening	10	2.73	3.01

Airborne magnetic aerosol samples			
Sampling site	Sampling location	Sampling duration	Mass of sample (mg)
Jegi station	Sample A1: on the wall under the platform (near rail track)	3 days	135.89
	Sample A2: on the wall of the platform	3 days	15.58
Yangjae station	Sample A3: on the wall under the platform (near rail track)	3 days	40.36
	Sample A4: on the wall of the platform	3 days	0.98

three times to ensure the complete segregation of the magnetic and non-magnetic particles.

2.3. XRD of the magnetic particle samples

To determine the chemical species of the magnetic particles, XRD (Rigaku DMAX-2500) was performed using Cu Kα radiation. The 2θ scanning range was 10–100°, the scanning speed was 3°/min, and the step size was 0.02° 2θ. The structures were identified using standard powders and the JCPDS card database. The standard powders included iron metal (Sigma–Aldrich, <212 μm, ≥99%), hematite (α-Fe_2O_3, Sigma–Aldrich, <5 μm, ≥99%), maghemite (γ-Fe_2O_3, Kojundo, <1 μm, 99%), magnetite (Fe_3O_4, Sigma–Aldrich, <5 μm, 98%), SiO_2 (Sigma–Aldrich, ≥99.995%), $CaCO_3$ (Sigma–Aldrich, ≥99.995%), and TiO_2 (Sigma–Aldrich, 99.99%).

2.4. SEM/EDX measurement for single particle analysis

Quantitative SEM/EDX single particle analysis, called low-*Z* particle EPMA, was applied to obtain morphological and elemental compositional information on the individual magnetic particles. The measurements were carried out on a JEOL JSM-6390 scanning electron microscope equipped with an Oxford Link SATW ultrathin window EDX detector with a resolution of 133 eV for Mn–Kα X-rays. The X-ray spectra were recorded under the control of EMAX Oxford software. A 10 kV accelerating voltage was chosen to achieve the optimal experimental conditions, such as a low background level in the spectra and high sensitivity for low-*Z* element analysis. The beam current was 1.0 nA for all measurements. A typical measuring time of 15 s was used to obtain a sufficient count in the EDX spectra while limiting the amount of beam damage to sensitive particles. A more detailed discussion on the measurement conditions is reported elsewhere [28]. EDX data acquisition for individual particles was carried out manually in point analysis mode, whereby the electron beam was focused on the center of each particle and X-rays were acquired while the beam remained fixed on this single spot. Some 300 particles for each sample were analyzed, totaling 2700 particles for the magnetic floor dust and airborne particle samples.

The net X-ray intensities for the elements were obtained by non-linear least-squares fitting of the spectra collected using the AXIL program [29]. The elemental concentrations of the individual particles were determined from their X-ray intensities using a Monte Carlo calculation combined with reverse successive approximations [30,31]. The quantification procedure provided results accurate within the 12% relative deviations between the calculated and nominal elemental concentrations when the method was applied to various standard particles, such as NaCl, Al_2O_3, $CaSO_4{\cdot}2H_2O$, Fe_2O_3, $CaCO_3$, and KNO_3 [31–33].

2.5. Magnetic property analysis

The magnetization versus applied magnetic field curves (*M*–*H* curves) at room temperature were measured using a commercial vibrating sample magnetometer (VSM, Quantum Design V525) in physical property measurement system (PPMS, Quantum Design 6000), with a maximum applied field of 5000 Oe. From the *M*–*H* curves, the saturation magnetization (M_s) and coercivity (H_c) data were used to determine the iron speciation of the magnetic particles. The saturation magnetization is defined as the saturation state where the increase in applied external magnetizing field no longer increases the magnetization of the sample. The H_c value is the intensity of the applied magnetic field needed to reduce the magnetization of the sample to zero after the magnetization of the sample reached saturation. To measure the magnetic properties of the magnetic floor dust and airborne samples, a few milligrams of the samples were attached to 5 mm × 5 mm glass slides. Iron metal, maghemite, and magnetite standard powders were measured for a comparison with real samples. The M_s values for the iron metal, magnetite, and maghemite standards were 193.7 emu/g, 80.2 emu/g, and 73.9 emu/g, respectively. The H_c values for the iron metal, magnetite, and maghemite standards were 10.5 Oe, 83.7 Oe, and 312.6 Oe, respectively. Those M_s and H_c values obtained for the standard particles are comparable to previously reported ones [34,35]. Although iron metal and hematite can be clearly differentiated from and magnetite and maghemite based on their XRD patterns, the strongest peaks of magnetite and maghemite are close and mostly too broad for real samples to distinguish between magnetite and maghemite by XRD. However, as the H_c values of magnetite and maghemite are quite different, this magnetic measurement is expect to clearly distinguish between magnetite and maghemite, if present in real samples.

3. Results and discussion

3.1. Floor dust particles

3.1.1. Particle size distributions and fractions of magnetic floor dust particles

Table 2 lists the size distributions of the floor dust collected at five different locations at Jegi subway station. Particles in the 25–63 μm size range are the most abundant of all samples, except for sample F2, where particles in the 63–100 μm range were most common. As the rails in the platform are curved with <140°, railhead lubricators are installed on the rail ballast in the platform,

Table 2
Size distributions and fractions of the magnetic particles in the floor dust samples.

Particle size	Size distribution					Fraction of magnetic particles				
	Sample F1	Sample F2	Sample F3	Sample F4	Sample F5	Sample F1	Sample F2	Sample F3	Sample F4	Sample F5
<25 μm	3%	7%	8%	4%	11%	100%	100%	100%	100%	98%
25–63 μm	50%	14%	54%	53%	77%	100%	100%	66%	97%	100%
63–100 μm	34%	76%	15%	24%	9%	100%	100%	33%	44%	48%
100–200 μm	13%	4%	23%	19%	3%	100%	100%	36%	28%	34%
Sum	100%	100%	100%	100%	100%	–	–	–	–	–

and grease is sprayed to reduce the level of friction, noise, and vibration between the rails and wheels when the trains arrive at the platform. The observation of larger sized particles in the F2 sample collected on railroad ties in the front of the platform is probably due to the agglomeration of particles by grease. As shown in Table 1, although samples F1 and F2 were collected at the same areas for the same sampling durations, the mass of sample F2 was 24.4 times larger than that of sample F1 collected on railroad ties in the tunnel because subway particles are largely emitted from the rail–wheel–brake interfaces when the trains are stopping in the platform.

Inhalable particles, <25 μm in size, can remain in the air and travel long distances, constituting most of the airborne particles. The fractions of such particles were the smallest among the four size fractions, with 3%, 7%, 8%, 4%, and 11% for samples F1–F5, respectively. Although the fraction of the inhalable particles is the smallest, it is the most important as the airborne particles can be inhaled into the human body. Fig. 1 shows the size distributions of the particles of <25 μm in size for samples F1–F5. The particle size distributions were obtained by the size measurements from secondary electron images (SEIs) of all the individual particles analyzed by low-*Z* particle EPMA. For samples F1 and F2, most of the particles are smaller than 10 μm, indicating that the characteristics of floor dust particles in the size fraction of <25 μm collected on railroad ties should somewhat reflect the characteristics of airborne particles in the tunnel and the platform. On the other hand, the floor dust particles of samples F3–F5 are bigger, indicating the big floor dust particles can be from outdoors.

As listed in Table 2, all the floor dust particles of samples F1 and F2 were magnetic, indicating that the sources of the magnetic subway particles are present near the rails. These magnetic particles are most likely Fe-containing particles, which are generated mainly from mechanical wear and friction processes at the rail–wheel–brake interfaces [3,19,21,36]. For samples F3–F5, the fractions of magnetic particles were in the range of 28–100%, strongly indicating that subway particles can be removed easily from the subway microenvironment using magnets. Almost all particles <25 μm in size for samples F3–F5 were magnetic, suggesting that the inhalable airborne particles might be magnetic. These small magnetic particles appear to be distributed from the rails to other areas, such as the platform, ticket office, and outdoor ventilation opening by train wind due to their agility.

3.1.2. XRD analysis of magnetic floor dust particles

The size-segregated bulk magnetic samples showed two different XRD patterns, i.e., with and without iron metal peaks, as shown in Fig. 2, which shows two XRD patterns for the size fractions of <25 μm of samples F1 and F3. The XRD patterns of all size-segregated samples from the same locations were similar. Also, the XRD patterns for all the size-segregated samples of samples F1 and F2 were similar to that shown in Fig. 2(A) and those for samples F3–F5 were similar to that shown in Fig. 2(B).

Fig. 2(A) shows that the major chemical species are SiO_2 (its strongest peak is at 26.64° 2θ), $CaCO_3$ (its strongest peak at 29.40° 2θ), iron metal (its strongest peak at 44.67° 2θ), and magnetite and/or maghemite (their strongest peaks at 35.42° 2θ and 35.63° 2θ, respectively). The peaks at 34.9–36.0° 2θ in Fig. 2(A) were too broad to clearly distinguish between magnetite and maghemite. Among these major chemical species, iron metal and magnetite/maghemite are chemical species with magnetic properties. The strongest XRD peak intensities of the standard SiO_2, $CaCO_3$, iron metal, maghemite, and magnetite powders, which

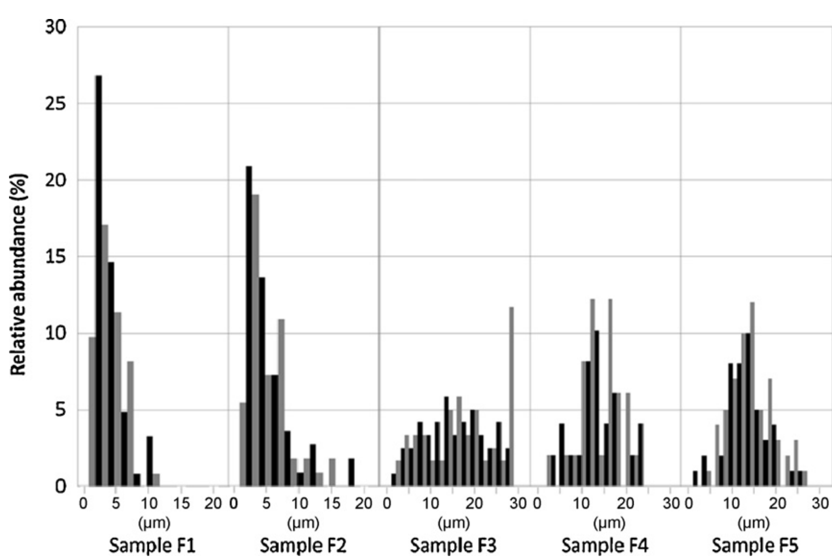

Fig. 1. Size distributions of magnetic floor dust particles, <25 μm in size, collected on the railroad ties in the tunnel (sample F1), on the railroad ties in front of the platform (sample F2), at the platform (sample F3), near the ticket office (sample F4), and at the outdoor ventilation opening (sample F5) of an underground subway station.

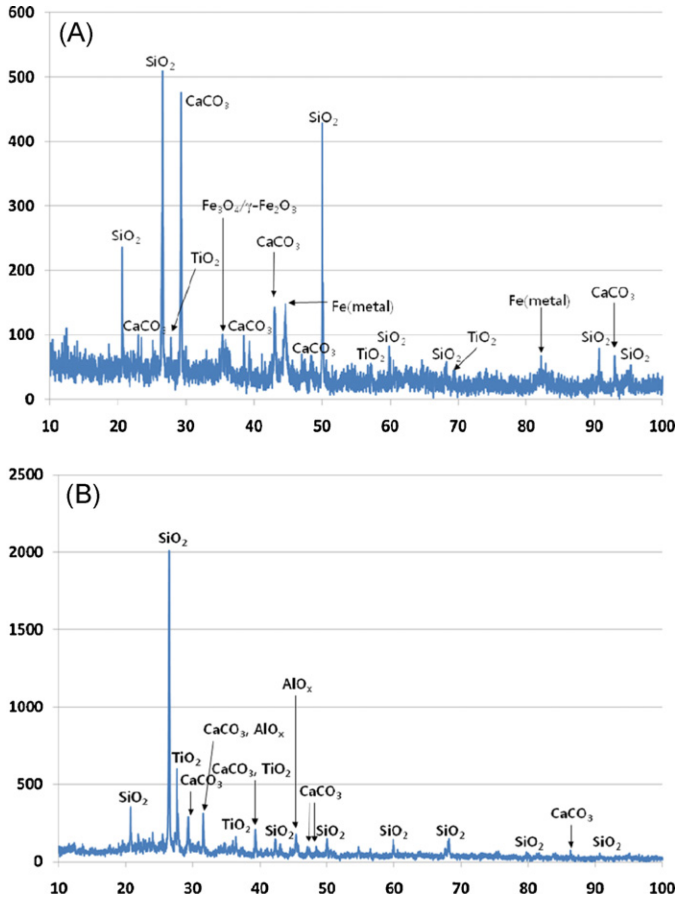

Fig. 2. XRD patterns of magnetic fractions of floor dust samples, <25 μm in size, collected (A) on railroad ties in the tunnel and (B) at the ticket office.

were obtained under the same analytical conditions, were ∼5600, ∼2930, ∼510, ∼530, and ∼590 cps, respectively. Based on their XRD sensitivities, SiO_2, $CaCO_3$, iron metal, and magnetite/maghemite contents were calculated to the first approximation to be 13%, 23%, 41%, and 24%, respectively. The contents of iron metal and magnetite/maghemite for the size-segregated samples of samples F1 and F2 were in the range of 41–53% and 24–37%, respectively, which strongly suggests that the Fe-containing particles are the major component in floor dust samples collected at railroad ties.

For all the size-segregated samples of samples F3–F5, no XRD peaks for Fe species were observed, but peaks for SiO_2, $CaCO_3$, TiO_2 (its strongest peak is at 27.51° 2θ), and AlO_x (its strongest peak at 45.20° 2θ) were noted, as shown in Fig. 2(B). As these major chemical species are not magnetic, the absence of peaks for Fe species indicates that the small amount of magnetic Fe species is below the detection limit of XRD due to their relatively low sensitivities. The detection limit of XRD for iron metal was estimated by the measurement of XRD peak intensities for standard iron metals mixed with SiO_2 at different weight concentrations of 1, 5, 10, 30, 50, 70, 90, and 100 wt%. The peaks for iron metal at 5 wt% or higher were observed, with a signal-to-noise (S/N) ratio of 3.8 for the 5 wt% sample. On the other hand, for real samples, where the peaks have more noise and are broader than the standard samples, as shown in Fig. 2(A), and the S/N ratio of the peak for iron metal of 41 wt% is only ∼12, the detection limit for iron metal in the real samples appears to be higher than 5 wt%. The reason why magnetic Fe species are not the major in the size-segregated magnetic samples collected at the platform, near the ticket office, and the outdoor ventilation opening is most likely due to the ubiquitous presence of magnetic Fe species in the particles with major non-magnetic chemical species because Fe vapor can be generated under high temperature conditions at the rail–wheel–brake interfaces and magnetic Fe species can be adsorbed on the surface of the particles containing non-magnetic chemical species. Although magnetic species were minor components in the floor dust particles of samples F3–F5, the presence of magnetic species appears to be sufficient for the particles to be attracted by a magnet.

3.1.3. Single particle analysis of magnetic floor dust particles

The individual magnetic floor dust particles were classified into different particle types based on the morphological and chemical compositional data from SEIs and X-ray spectra, respectively. Fig. 3 shows the typical SEIs of magnetic particles from the <25 μm fractions. The SEIs for samples F1, F3, and F5 are presented because those for samples F1 and F3 are similar to samples F2 and F4, respectively. A unique notation was devised to describe the chemical species of individual particles, e.g., the notation "Fe/FeO_x/Si/S/Ca/C" for a particle in Fig. 3(A) indicates that the particle is iron metal and iron oxides mixed internally with Si, S, Ca, and C at >5 at.%.

For samples F1 and F2 of the <25 μm size fractions, most of the particles were Fe-containing ones, i.e., iron metal, iron oxides, and Fe-containing particles mixed with Mg, Al, Si, S, Ca, and/or C, as shown in Fig. 3(A). Among the Fe-containing particles, the Fe/FeO_x/C and Fe/FeO_x/Si/Ca/C particles were the most common, which are similar to Fe-containing particles observed for airborne subway particles in previous studies [21,36,37]. On the other hand, compared to airborne subway particles, iron metal particles were encountered more frequently in the floor dust samples because relatively large and heavy iron metal particles are not suspended easily in the air and settle quickly to the floor from the air. Relatively small iron oxide particles, <2 μm in size, were also observed abundantly in the floor dust samples, as shown in Fig. 3(A). For samples F3–F5, the encountering frequency of iron metal particles was reduced significantly, and the particles with chemical species of a soil origin (aluminosilicates (hereafter notated as AlSi), SiO_2, $CaCO_3$, etc.) and/or sulfate were observed abundantly, as shown in Fig. 3(B and C). Nevertheless, almost all particles, regardless of their major chemical species, were mixed with a small amount of Fe as a minor element. These findings are well matched with those by XRD, where Fe species were the major components in samples F1 and F2 and no peaks for Fe species were observed for samples F3–F5.

Iron metal particles appear dark and sliced in shape, whereas iron oxides appear bright and angular, as shown in Fig. 4(A and B), which show iron metal particles agglomerated with a number of small iron oxide particles. These types of particles are abundant, particularly in samples F1 and F2. The different brightness between iron metal and oxides on their SEIs results mainly from the different secondary electron yields between conducting metal and insulating oxide particles, whereby the insulating oxide particles develop a negative voltage due to the accumulation of primary electrons, resulting in a bright contrast from the larger emission of secondary electrons by repulsion [38]. The sliced form and large size of iron metal particles are because they were generated by scraps broken off from the train wheels or rails. Fe-containing subway particles are generated mainly from mechanical wear and friction processes at the rail–wheel–brake interfaces and at the interface between the catenaries and pantographs. Wear and friction processes initially produce iron metal particles. The surface of the primary particles must be sufficiently reactive, particularly for small particles, for the oxygen in air to react easily on the metallic surface and form iron oxides. Almost all iron metal particles were observed to be agglomerated with iron oxides, strongly suggesting that the sources of iron

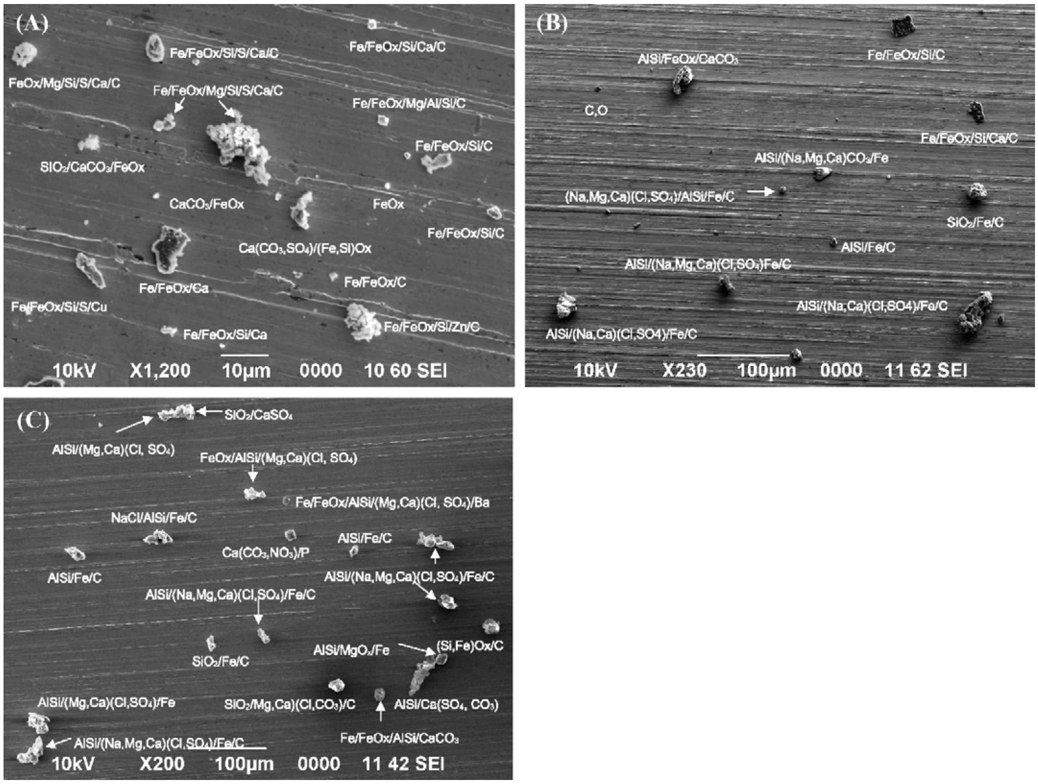

Fig. 3. Typical secondary electron images of the magnetic floor dust particles, <25 μm in size, collected (A) on the railroad ties in the tunnel, (B) at the platform, and (C) at the outdoor ventilation opening.

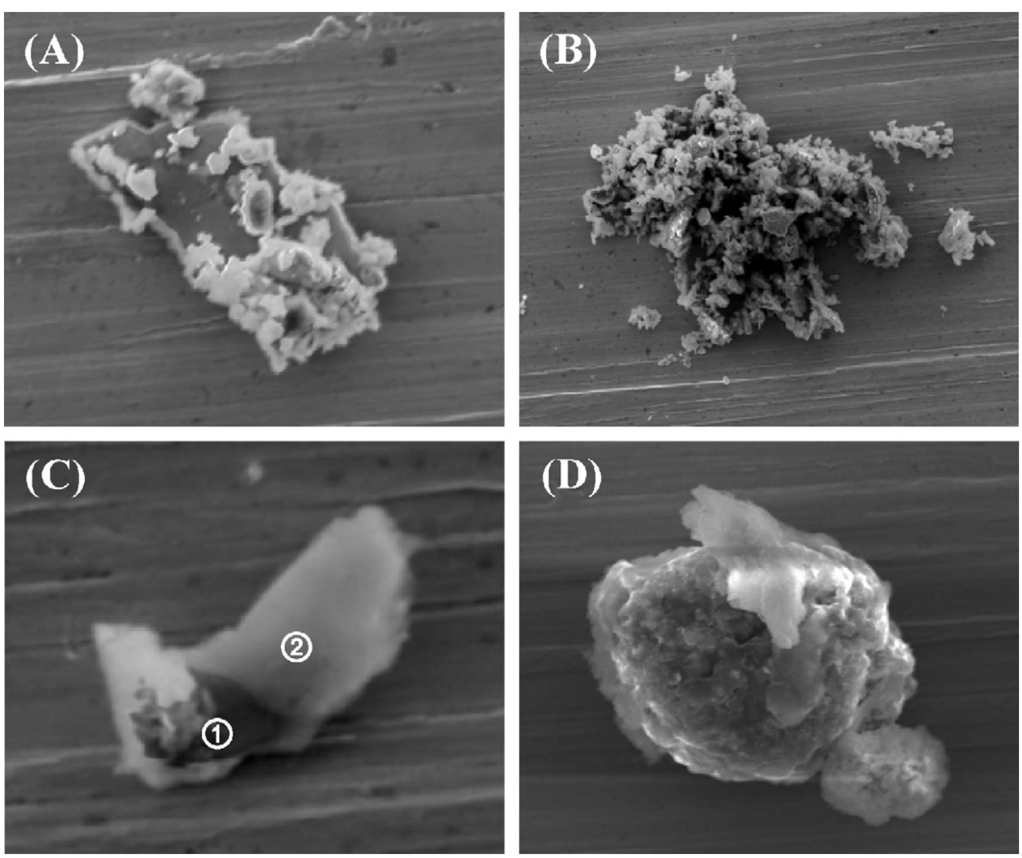

Fig. 4. Typical secondary electron images of floor dust particles: (A) and (B) iron metal particles agglomerated with a number of small iron oxide particles, (C) a particle internally mixed with iron metal and AlSi/K/C, and (D) a mixture particle of AlSi, (Na, Mg, Ca)(Cl, SO_4), and carbon.

metal and iron oxides are the same and that iron oxides are ferrimagnetic like maghemite and/or magnetite so that they can stick strongly to iron metal particles. As stated before, it is important to distinguish between maghemite and magnetite due to their different toxicity, but no X-ray spectral analysis can clearly differentiate them.

Fig. 4(C) shows a particle internally mixed with iron metal and AlSi/K/C, inferred from the elemental concentration data obtained at points 1 and 2, respectively, and also from the dark contrast of the area around point 1, which is specific to iron metal. This particle clearly shows that Fe species can be mixed with other particles because gaseous and/or reactive Fe species are generated at the rail–wheel–brake and catenaries–pantograph interfaces. These types of Fe-containing particles shown in Fig. 4(A–C) were mostly observed in samples F1 and F2. For samples F3–F5 of the <25 μm size fractions, the Fe-containing particles were minor. As a typical example, Fig. 4(D) presents a mixture particle of AlSi, (Na, Mg, Ca)(Cl, SO_4), and carbon. This particle was not classified as a Fe-containing particle as this particle contains only a small amount of Fe species (∼1 at.%). The abundant existence of this type of particle in samples F3–F5 explains why Fe species were not detected by XRD. These particles were attracted to a magnet due to the presence of a small amount of magnetic Fe species, too small to be detected by XRD.

Table 3 lists the relative abundances of the particle types encountered in the <25 μm size fractions of the floor dust collected at five locations. The relative abundance of each particle type was the number of particles encountered divided by the total number of particles analyzed. Fe-containing, soil-derived, carbonaceous, nitrate, and sulfate particles are the major particle types. Fe-containing particles were encountered most frequently in samples F1 and F2 with relative abundances of 70.1–70.9%, whereas they are not the major components in samples F3–F5 (14.2–20.4%). This strongly suggests that Fe-containing particles are generated near railroads.

Soil-derived particles, such as AlSi, AlSi/C, $CaCO_3$, $CaCO_3$/C, SiO_2, and SiO_2/C, are observed frequently in floor dust samples and their distributions are different among the samples collected at different locations, i.e., 19.5%, 20.0%, 33.3%, 38.8%, and 41.0% for samples F1–F5, respectively. The relative abundances of the soil-derived particles decreased with increasing distances of the sampling locations from the outdoors, indicating that they are mainly from the outdoor environment. Sulfate and/or nitrate particles, such as Ca(NO_3, SO_4), (Na, Mg)(NO_3, SO_4), and AlSi/(Na, Mg, Ca)(Cl, SO_4) were encountered, mostly as sulfate particles. For samples F1 and F2, the relative abundance of these sulfate and/or nitrate particles was relatively low, but the relative abundance was significant for samples F3–F5, indicating that they have an outdoor origin.

3.1.4. Magnetization analysis of Fe species using VSM

The magnetization analysis based on the *M*–*H* curves of the magnetic floor dust samples supports the XRD and low-*Z* particle EPMA data, i.e., iron metal is a major magnetic compound in magnetic floor dust. The H_c values of the magnetic floor dust particles were similar to those of iron metal with H_c less than several dozen Oe. The H_c values of samples F1–F5 were in the range of 2.9–45.8 Oe, indicating that the magnetic floor dust particles consist mainly of metallic iron. For samples F1 and F2, the M_s values were in the range of 30.9–45.6 emu/g and those for samples F3–F5 were 1.5–7.6 emu/g. As the M_s values for samples F3–F5 were lower than those for samples F1 and F2, the amounts of magnetic compounds in samples F3–F5 were significantly lower than those in samples F1 and F2, which also supports the results from XRD and low-*Z* particle EPMA.

3.2. Airborne magnetic subway particles

3.2.1. Masses and size distributions of airborne magnetic particles collected by magnets

Four airborne magnetic particle samples were collected using permanent magnets of 4000 Oe by placing them for 3 days on the walls near the rail track and of the platform in underground Jegi and Yangjae stations (samples A1–A4). As the magnets were placed vertically on the walls, the particles were attracted to the magnets mostly by a magnetic force. As shown in Table 1, the collected amounts of magnetic particles were different, even though sampling in both Jegi and Yangjae stations was performed for the same durations using the same magnets. For Jegi station, the amounts of samples A1 and A2 collected on the walls near the rail track and of the platform were 135.89 mg and 15.58 mg, respectively. For Yangjae station, those of samples A3 and A4 were 40.36 mg and 0.98 mg, respectively. The amounts of samples collected on the walls near the rail track in both stations were higher than those on the walls of the platform, i.e., 8.7 and 41.2 times more in Jegi and Yangjae stations, respectively, indicating that the sources of the magnetic subway particles are close to the rail tracks. The airborne magnetic particle samples collected were 3.4 and 15.9 times higher in Jegi station than in Yangjae station on the walls near the rail track and of the platform, respectively. In Yangjae station, platform screen doors (PSDs; full-height barriers between the station floor and ceiling) were installed between the tunnel and platform, which effectively limit air-mixing between the platform and tunnel. According to our previous study, the subway microenvironment in subway stations with PSDs has lower PM concentrations and lower contents of Fe-containing particles than in those without PSDs [21]. Therefore, the very small amount of airborne magnetic particles collected on the platform wall in Yangjae station is due mainly to the presence of PSDs. The smaller amount of samples collected in Yangjae station than in Jegi station can be attributed to water cleaning of the tunnel and platform walls performed during the sampling period. Different types of ballast tracks, i.e., concrete and gravel ballast, are used in Jegi and Yangjae stations, respectively, which affect the chemical compositions of the airborne magnetic particles, as will be discussed in the next section.

The particle size distributions of samples A1–A4 were obtained by the size measurements from SEIs of all the individual particles analyzed by low-*Z* particle EPMA. Indeed, as shown in Fig. 5, most of the particles for samples A1–A4 are smaller than 10 μm, as they were airborne particles, although the bigger particles were encountered in samples A3 and A4. The somewhat different size distributions of the magnetic airborne particles between two subway stations might also be the use of the different types of ballast tracks.

3.2.2. XRD analysis of airborne magnetic particles

Fig. 6 shows the XRD patterns of samples A1 and A3, which were collected on the walls near the rail track in Jegi and Yangjae stations, respectively. The XRD patterns of samples A2 and A4, which were collected on the walls of the platform in Jegi and Yangjae stations, respectively, were similar to those of samples A1 and A3, respectively. Airborne magnetic samples A1 and A2 showed strong iron metal peaks, whereas samples A3 and A4 collected at Yangjae station showed peaks for non-magnetic chemical components, such as $CaCO_3$, TiO_2, and SiO_2 without any observable iron metal peaks (see Fig. 6). The difference in results between the two stations is due likely to the different ballast tracks used, i.e., concrete and gravel ballast in Jegi and Yangjae stations, respectively. Concrete ballast induces higher noise and vibrations by the train running and requires higher first installation cost. On the other hand, it produces smaller amounts of dust during train running than gravel ballast (http://www.seoulmetro.co.kr). The samples collected in Jegi

Table 3
Relative abundances of significantly encountered particle types for magnetic floor dust samples, <25 μm in size, and airborne magnetic aerosol samples.

Particle types	Sample F1	Sample F2	Sample F3	Sample F4	Sample F5	Sample A1	Sample A2	Sample A3	Sample A4
Iron-containing	70.1%	70.9%	14.2%	20.4%	15.2%	95.0%	90.1%	78.7%	64.9%
Soil-derived (sum)	19.5%	20.0%	33.3%	38.8%	41.0%	4.0%	6.9%	18.0%	35.1%
Aluminosilicates	0.0%	0.0%	1.7%	0.0%	5.7%	1.0%	1.0%	4.5%	16.2%
Aluminosilicates/C	2.4%	4.5%	9.2%	16.3%	11.4%	0.0%	0.0%	0.0%	0.0%
$CaCO_3$	0.0%	0.0%	0.8%	0.0%	1.0%	0.0%	1.0%	3.4%	1.8%
$CaCO_3$/C	8.8%	5.5%	9.2%	4.1%	4.8%	1.0%	0.0%	5.6%	6.3%
SiO_2	0.8%	0.9%	0.0%	2.0%	1.9%	0.0%	0.0%	1.1%	1.8%
SiO_2/C	7.5%	9.1%	12.5%	16.3%	16.2%	2.0%	5.0%	3.4%	9.0%
Carbonaceous	4.5%	0.9%	14.2%	6.1%	1.9%	0.0%	1.0%	0.0%	0.0%
Secondary nitrates/sulfates (sum)	4.9%	5.5%	36.7%	34.7%	40.0%	0.0%	1.0%	0.0%	0.0%
$Ca(NO_3,SO_4)$	1.6%	0.0%	1.7%	4.1%	3.8%	0.0%	1.0%	0.0%	0.0%
$(Na,Mg)(NO_3,SO_4)$	0.8%	0.0%	4.2%	4.1%	1.0%	0.0%	0.0%	0.0%	0.0%
$AlSi/(Na,Mg,Ca)(Cl,SO_4)$	2.4%	5.5%	30.8%	26.5%	35.2%	0.0%	0.0%	0.0%	0.0%
Others	1.0%	2.7%	1.7%	0.0%	1.9%	1.0%	1.0%	3.4%	0.0%
Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

station contained mainly Fe-metal generated by mechanical wear and friction processes at the rail–wheel–brake interfaces, whereas in Yangjae station, an assortment of non-magnetic components were also generated from the gravel ballast.

3.2.3. Single particle analysis of airborne magnetic particles

Some 300 particles for each airborne magnetic particle sample were analyzed, totaling ~1200 particles. As shown in Table 3, the particles most frequently encountered in samples A1–A4 contained Fe. In particular, samples A1 and A2, which were collected in Jegi station, contain Fe-containing particles with relative abundances of >90%, for which only iron metal peaks were observed by XRD. For samples A1 and A2, most of the iron metal was quite large, and iron oxide particles are small. The small Fe-containing particles could be oxidized more easily because of their larger surface-to-volume ratio. The surfaces of metallic iron were also oxidized. For samples A3 and A4 collected in Yangjae station, Fe-containing particles were the major component, even though their contents were lower than those of samples A1 and A2. No peaks for Fe species were observed by XRD. Most of the magnetic particles contained Fe species as well as various non-magnetic species, such as Na, Mg, Al, Si, S, and Ca. The difference between the samples collected in Jegi and Yangjae stations is due likely to the different ballast types used, as mentioned above.

3.2.4. Magnetization analysis of Fe species using VSM

The magnetization analysis based on the *M–H* curves provided M_s and H_c values of 131.4 emu/g and 7.3 Oe for sample A1, respectively, which are similar to those of the iron metal standard powders with a M_s and H_c of 193.7 emu/g and 10.5 Oe, respectively, indicating that magnetic subway particles collected in Jegi station consist mostly of iron metal. The M_s and H_c values for sample A2 were 66.2 emu/g and 3.1 Oe, respectively, which are also similar to those of the iron metal standard sample. The amount of magnetic compounds in sample A2 is believed to be lower than that in sample A1 because sample A2 had a lower M_s value than sample A1.

Magnetization analysis of samples A3 and A4 collected at two sampling locations in Yangjae station indicates that magnetic airborne subway particles consist of iron metal because the H_c values for samples A3 and A4 were 11.9 Oe and 1.7 Oe, respectively. The M_s values of samples A3 and A4 were 68.8 emu/g and 30.8 emu/g, respectively, which are much smaller than those of samples collected in Jegi station. This means that the amounts of magnetic compounds in the samples collected in Yangjae station are

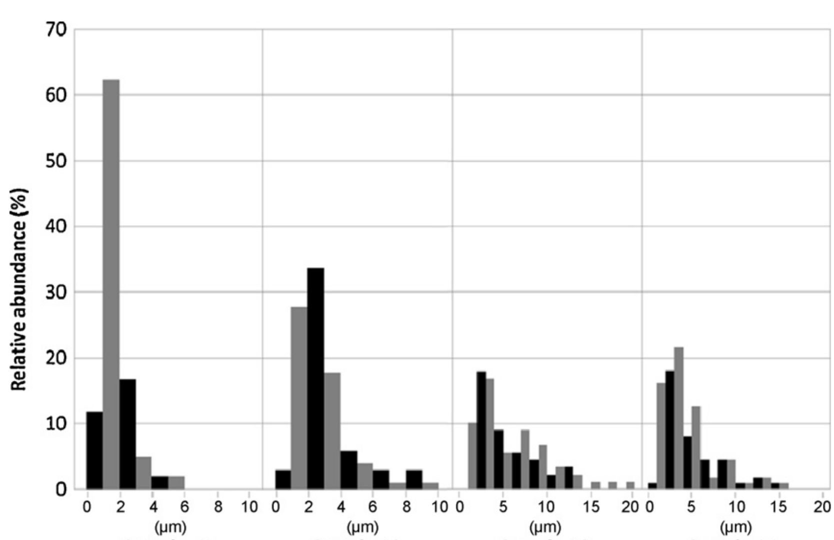

Fig. 5. Size distributions of airborne magnetic particles collected on permanent magnets placed on the walls near the rail track and of the platform in “Jegi” station (samples A1 and A2) and “Yangjae” station (samples A3 and A4).

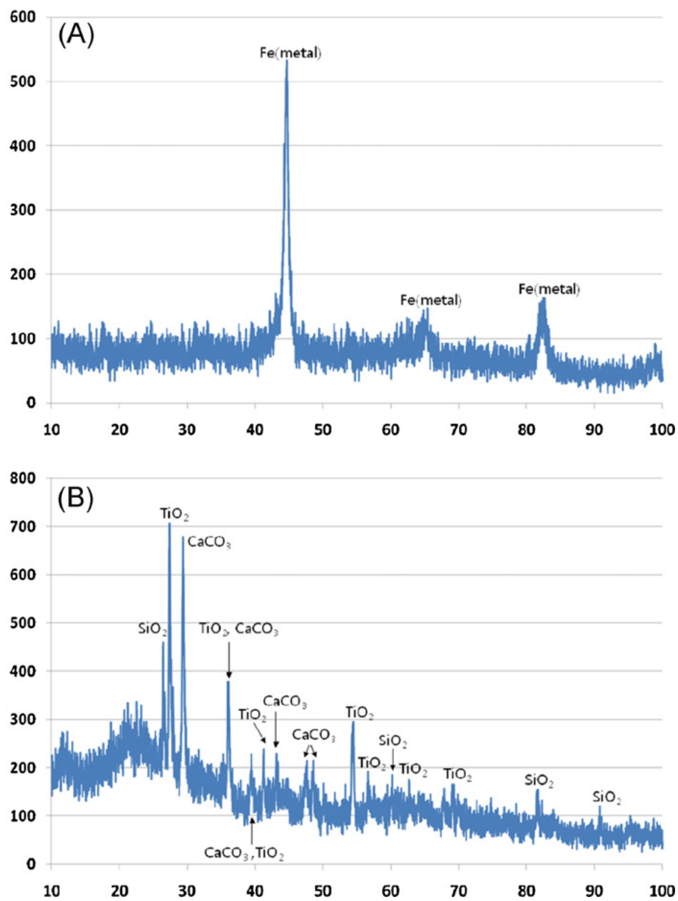

Fig. 6. XRD patterns of airborne magnetic particles collected on the walls near rail track in (A) Jegi and (B) Yangjae stations.

significantly lower than those collected in Jegi station, supporting the results of XRD and low-*Z* particle EPMA.

4. Conclusions

The speciation of underground Fe-containing subway particles is important in the context of public health and control measures; i.e., only magnetite among various iron species is reported to be toxic, and the major iron species, except hematite, are magnetic. As just a few and limited studies have been reported for iron speciation of floor dusts and subway particles, the elucidation of the iron species generated in underground subway system was performed in this work. Firstly, this study investigated floor dusts collected at different locations of an underground subway station in Seoul, Korea. Size-segregated floor dusts were separated into magnetic and non-magnetic fractions using a permanent magnet and it appeared that almost all of the inhalable floor dust particles, <25 μm in size, are magnetic. The size-segregated magnetic fractions of the floor dusts were examined by XRD, low-*Z* particle EPMA, and VMS. The majority of the magnetic floor dust particles of the <25 μm size fractions were iron metal, which is relatively harmless. Secondly, after confirming that the inhalable floor dusts are magnetic, airborne subway particles were collected using permanent magnets at different locations of two underground subway stations in Seoul, Korea, which were also examined by XRD, low-*Z* particle EPMA, and VMS. The majority of the magnetic airborne subway particles, particularly those collected at Jegi station, were iron metal, similar to the floor dusts collected at the same station, whereas those collected in Yangjae station contained a small amount of Fe mixed with Na, Mg, Al, Si, S, Ca, and C. The difference in composition of the Fe-containing particles between the two subway stations is due likely to the different ballast types used, i.e., gravel and concrete ballast in Jegi and Yangjae stations, respectively. It is expected that the PM levels in subway stations can be controlled by removing Fe-containing magnetic particles using magnets.

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