Atmospheric iron particles in $PM_{2.5}$ from a subway station, Beijing, China

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Highlights:

- The majority of $PM_{2.5}$ in the subway's atmosphere are Fe-rich particles.
- Fe-rich particles are mainly derived from mechanical abrasion at the brake-wheel-rail interfaces.
- The Fe-rich particles typically exist as Fe-Mn alloy fragments.

Abstract:

Particulate matter pollution in the subway station's atmosphere can seriously influence the air quality and impacts on the health of subway workers and commuters. In this study, $PM_{2.5}$ samples were collected from different locations within a subway station in Beijing, and the individual particles were analyzed for morphology and composition by Transmission Electron Microscopy with Energy Dispersive X-ray Spectrometry (TEM-EDX). The results showed that the concentration of $PM_{2.5}$ in subway stations was affected by both indoor and outdoor sources. Particles generated by train-related sources such as resuspension, wheel, rail, brake and collector shoe abrasion were a significant source of airborne pollution in the subway atmosphere. Within the subway station $PM_{2.5}$, Fe was the dominant element, and was detected in more than 75% of all particles analyzed. The Fe-rich particles were identified in railway carriages (79.4%), station concourse (65.3%), and platforms (61.3%). The geometric mean diameter of Fe-rich particles was 0.34 μm, which was smaller than that of all detected particles. Cr, Mn and other metals were often detected in the Fe-rich particles, reflecting metal alloys used in the wheels and tracks. A better understanding of the particle distribution around different areas of the subway system and the physicochemical characteristics of these Fe-rich particles is critical in developing a meaningful assessment of the risk posed by particles in the subway atmosphere.

Keywords: Subway atmospheric pollution, $PM_{2.5}$, TEM-EDX, Individual particle analyses, Fe-alloy metals

1. Introduction

Globally, subways are crucial public transportation systems in megacities, because of their convenience, safety, efficiency, and large passenger capacity (Chang, et al., 2021). However, the subway environments are usually composed of confined and artificially ventilated spaces, resulting in restricted air flow and concentration of airborne pollutants within the station. The concentration of these pollutants will be a function of many factors such as operation times, depth, design style or the efficiency of ventilation system. A number of studies that have been conducted in subway stations showed that $PM_{2.5}$ might accumulate to 2-10 times higher levels than in the ambient air outside the stations (Reche et al., 2017; Chang et al., 2021). Cao et al. (2017) reported that the average $PM_{2.5}$ mass concentration at an underground platform of the Suzhou subway station in the southeastern Jiangsu Province of eastern China was 142 $\mu g/m^3$, which was higher than the second-level concentration limit for the ambient air (75$\mu g/m^3$) stipulated by the National Ambient Air Quality Standards (GB3095–2012). Martins et al. (2016) noted that in the Barcelona, Spain, subway system the average $PM_{2.5}$ concentrations in the subway platforms atmosphere were between 1.4 and 5.4 times higher than that found outdoors.

Many studies have shown that the chemical composition of $PM_{2.5}$ in subways consisted mainly of the metal elements including Fe, Mn, Mg, Pb, Na, Cr, K, Cu, Ca, Zn, Ba, Ni, V and the non-metallic elements such as C, O, S, and Si (Kamani et al., 2014; Moreno et al., 2014; Byeon et al., 2015). Among the metallic elements, Fe was the most common in the $PM_{2.5}$ of subways (Midander et al., 2012; Mohsen et al., 2018). When compared with local outdoor $PM_{2.5}$ pollution, the Fe content in the subway tunnel was almost twice that measured in the outdoor air (Pan et al., 2019). These iron particles from subway stations were discharged into the ambient atmosphere through the ventilation systems and might have an impact on human health and geochemical cycles (Li et al., 2017; Zhu et al., 2020).

Metal particles can pose potential respiratory health risks to commuters and workers in subway stations (Canu et al., 2021; Hwang et al., 2021). A study in Canada evaluated the exposure risk to the commuter in the subway, which indicated that the commuters were exposed to $PM_{2.5}$ containing several heavy metals in the subway system every day, especially to Fe that accounts for 80%-99% (Van Ryswyk et al., 2017). The metal components of $PM_{2.5}$ can be solubilized once respired, and generate Reactive Oxygen Species (ROS), which can induce oxidative stress and inflammation in the lungs and respiratory tract (Kumar et al., 2018; Palleschi et al., 2018). There is also a synergy between certain metals resulting in a toxic cocktail, which is more harmful than the toxic sum of the individual metals (Merolla and Richards, 2005). Gali et al. (2017) and Moreno et al. (2017) reported the oxidative potential of $PM_{2.5}$ samples collected from the subway system in Hong Kong and Barcelona. Their results indicated that subway PM toxicity might be affected by the presence of metal elements sourced from the alloys used in the mechanical components of the system.

Although several studies have reported the concentration, distribution and toxicity of metallic particles in the subway stations, these results cannot directly reveal the source of pollution and mechanism of toxicology (Kelly et al., 2012; Xiao et al., 2020; Ji et al., 2021; Saeedi et al., 2021). The morphology, elemental composition and size are the key factors determining the source and toxicity of particles (Li et al., 2020; Wang et al., 2022). However, no detailed targeted work has been done to characterize the physicochemical characteristics of Fe-rich particles. Individual particle analysis technology based on TEM-EDX which make up for the disadvantages of previous research, can obtain the morphology, element composition, and size of individual particle to analyze the surface elements occurrence state, and source of particles (Shao et al., 2022b).

In this study, individual particles were collected from different locations within the LiuDaoKou (LDK) subway station in northwestern urban Beijing, under different pollution conditions. The occurrence, form and spatial distribution of Fe-rich particles in $PM_{2.5}$ were studied by TEM-EDX, and the results provide important insights into the nature of the subway air pollution, and additionally data for risk assessments on the respiratory health of subway workers and commuters.

2. Material and methods

2.1 Study area

The LDK subway station of line 15 opened in 2014. The full height screen door is fitted between the platform and the tunnel. In this subway station, the air flow is separated by the screen door, except when the doors are open or the seals are broken. All the stations have air conditioning, which is connected to the surface ventilation shaft to exchange fresh air from outside with the station air. The LDK subway station is one of the newest types of stations in Beijing which has more advanced ventilation and screen doors than the older stations of line 1. Therefore, this study chose the LDK station as the sampling site.

The LDK station has two-level underground floors. The sampling sites at (A) carriage, (B) platforms, (C) concourse, and (D) exit are showed in Fig. 1.

A. Carriage: The sampling point is located in the middle of a train carriage, approximately 20 metres from the joints to the connecting carriages, and 2 metres from the door.

B. Platform: The sampling point is located in the center of the platform at the lower floor, approximately 3-4 metres from the platform screen doors and 100 metres from the escalators on both sides.

C. Concourse: The sampling point is located at the side of the concourse at the upper floor, approximately 50 metres from the main entrance and escalator.

D. Exit: The exit is located on the surface, connecting the station to the outside environment. The sampling point is located at the upper end of the exit escalator, approximately 10 metres from the escalator.

The sampling was undertaken during off-peak hours, and the average frequency of trains was every 3-4 minutes.

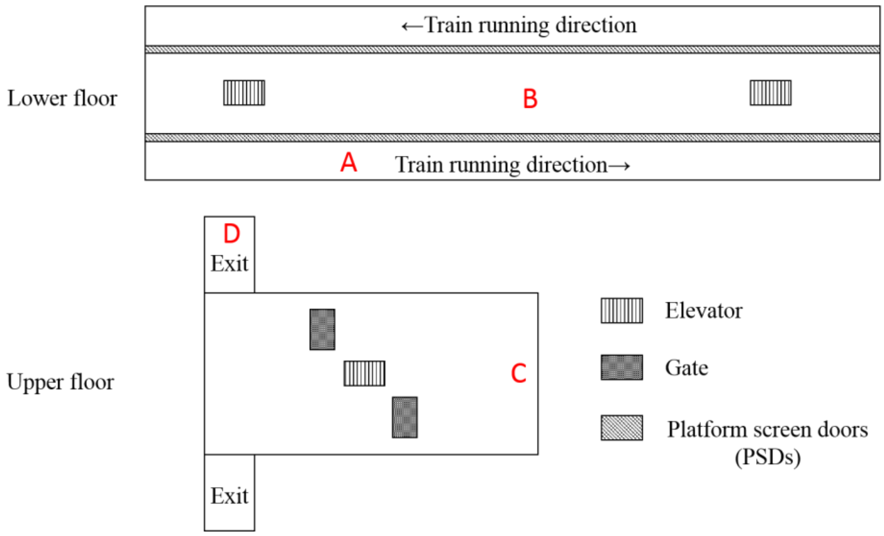

Fig.1. Plain view of two floors for the localities of the sampling sites (A: Carriage, B:

Platform, C: Concourse, D: Exit)

2.2 Aerosol sampling

A single-stage cascade PM sampler (DKL-2, Qingdao Jinshida Company, China) was used at a flow rate of 1.0 L/min to collect the particle samples under different pollution conditions in September 2018. According to the second-level concentration limit for the ambient air stipulated by the National Ambient Air Quality Standards (GB3095–2012), we defined the days with $PM_{2.5}$ concentrations higher than 75μg/m^3 as haze days and lower than 75μg/m^3 as non-haze days.

Copper TEM grids with carbon-coated organic film (300-mesh copper, T10023, Beijing Xinxingbairui Company, China), placed inside the PM sampler, were used. The Kestrel 5500 Pocket Weather Tracker (Nielsen-Kellerman Inc., Minneapolis, MN, USA) was synchronously used to measure the relative humidity (RH) and temperature (T).

A $PM_{2.5}$ detector (SDL301, China) was used to monitor the average real-time concentrations of $PM_{2.5}$ at the sites of the exit, concourse, platform and carriage inside the subway station. The time interval of collection was 1s, and more than 500 data points were collected from the same sampling sites.

The hourly average concentrations of $PM_{2.5}$, SO_2, NO_2 and O_3 in the ambient atmosphere outside the subway station were obtained from the Wanliu monitoring station (http://www.bjmemc.com.cn/) in Haidian district (116.287E, 39.987N; 5km from the subway station).

2.3 Individual-particle analysis

TEM-EDX (JEM2800, JEOL, Japan, 200 kV) was used to analyze the morphology and elemental composition of individual particles. Only elements with an atomic number larger than 5(B) were detected by the EDX . In order to ensure the collection of all possible elements and minimize the omission of volatile elements, the collection time of EDX spectra was 20-90s. Since the TEM grids are made of copper, Cu was excluded from the analysis.

To ensure that the analyzed particles were representative of the whole sample, at least 90 particles from 2-3 random areas were analyzed on each grid. Considering the collection efficiency of the impactor, particles smaller than 0.1 μm are not counted. An image processing system (Microscopic Particle Size of Digital Image Analysis System, UK) was used to measure the surface areas of particles. According to the circle area formula, the equivalent spherical diameter of a particle was calculated by sqrt(s/4π), where S was the surface area. To compare the size of different types of particles, the following formula was used to calculate the geometric mean diameter (D_{gm}) of particles:

$$D_{gm} = (D_1 \cdot D_2 \cdot D_3 \cdots D_n)^{\frac{1}{n}}$$

where n represents numbers of particles.

3. Results

3.1 Mass concentration of air pollutants

The results of the average real-time concentration of $PM_{2.5}$ at the different locations in the subway station and outside environment during haze and non-haze days are presented in Fig. 2.

On haze days, the average concentration of $PM_{2.5}$ in the atmosphere inside the subway station was 90±3μg/m^3 and was 22% lower than the outside environment $PM_{2.5}$ concentrations. The concentration of $PM_{2.5}$ at the exit site was the highest, being 101±1.8μg/m^3, and that at the carriage site was the lowest, being 76±3.8μg/m^3. The concentration of $PM_{2.5}$ at different locations in the station from high to low was exit > concourse > platform > carriage.

On non-haze day, the inside subway station atmosphere showed an average $PM_{2.5}$ concentration of 20±1μg/m^3 and was 1.2 times higher than the outside atmosphere $PM_{2.5}$ concentration. The concentration of $PM_{2.5}$ in the carriage was the highest, at 32±1.3μg/m^3 and in the exit the lowest at 11±0.9μg/m^3. The concentration of $PM_{2.5}$ at different locations in the station from high to low was carriage > platform > concourse > exit.

Overall, the results showed that the concentrations of $PM_{2.5}$ in the subway station were lower than that in the outside air during haze days. However, during non-haze days, the concentrations of $PM_{2.5}$ in the subway station were higher than those in outside air. This result was consistent with those reported by Pan et al. (2019) who concluded that the pollution in subway stations varies over a wide range compared with the outside environment.

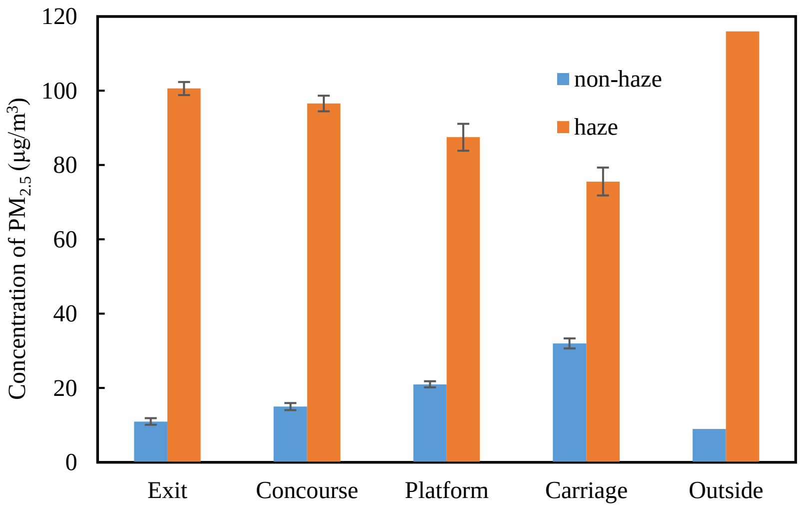

Fig. 2. The concentration of $PM_{2.5}$ at different locations in the subway station and outside environment during haze and non-haze days

3.2 Frequency of elements in individual particles

The particles collected in the subway station show complex compositions. TEM-EDX has detected more than 16 elements in the particles, including N, O, Na, Mg, Al, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, and Zn (Fig. 3).

In the subway station particles, except for O, Fe was the most abundant element, and was detected in more than 75% of all the analyzed particles. The abundance of Ca and S was next to Fe, and these elements were detected in more than 30% of all the analyzed particles. More than 75% of the particles contained metallic elements, including Fe, Mn, and Cr. Our results closely compared with those reported by Van Ryswyk et al. (2017) where Fe and Mn were the most abundant metals in the Toronto and Vancouver subway atmospheric pollution. Metallic elements have generally been identified as potentially hazardous components in the airborne particles (MohseniBandpi et al., 2018; Guo et al., 2021), and these particles present in subway station air could present health risks to the people commuting in the subway station.

Once these particles are discharged into the proximal surface atmosphere by the ventilation systems, they could further increase the health risk to people outside the subway.

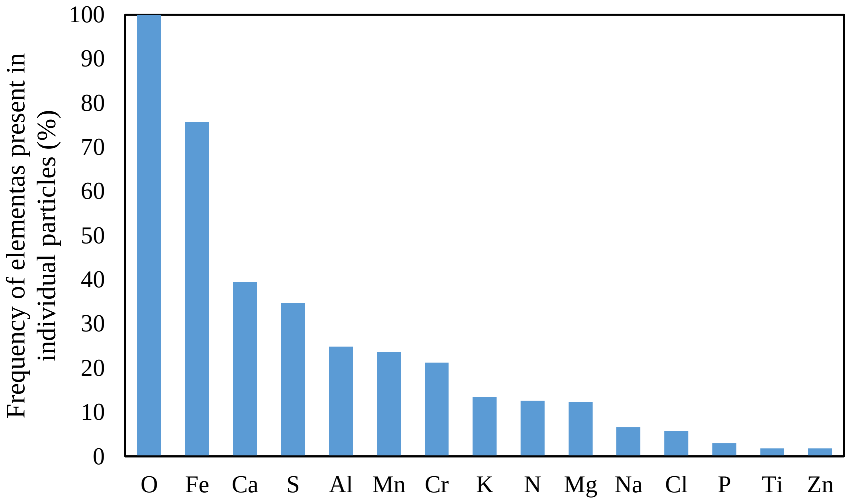

Fig. 3. Frequency of elements present in the collected aerosol particles in the subway station.

3.3 Classification and number fractions of individual particles

A total of 344 particles were analyzed from the subway station. Based on their morphology and elemental composition, the particles in subway station air were classified into types of metal, mineral, S-rich, organic and salt particles. Detailed characteristics of different types of individual particles are shown in Table 1.

Table 1: Types and characteristics of individual particles in subway station air

Particle types	Major elements	Possible source
Metal	Composed of Fe and O, and minor Cr and Zn	Rail, wheel, and brake wear (Minguillon et al., 2018; Salma et al., 2007)
Mineral	Composed of Si and O, and minor Ca, Mg, Al	Wear and resuspension of building materials in the subway system (Jung et al., 2010)
S-rich	Composed of S, N, O	Secondary formation in atmosphere (Shao et al., 2022b)

Organic	Composed of C and O, and minor S	Trains, escalators and passengers (Van Drooge et al., 2018; Shao et al., 2022a)
Mixture	Complex elemental composition	Secondary chemical reaction (Shao et al., 2022b)

Metal particles have irregular shapes, among which the Fe-rich particles (Fig. 4a, b, d, e) are the most common. The metal particles in the subway station are identified to be emitted from brake wear, rail-wheel' friction (Minguillon et al., 2018) and rubbing of bow sliding collectors and the electric conducting rail (Salma et al., 2007).

Mineral particles are irregular in shape (Fig. 4g) with the major elements such as Si, Al, and Ca (Fig. 4h), which are identified as crustal elements. Mineral particles are extremely stable and non-volatile under the strong electron beam. Mineral particles include a large number of silicate minerals, which are thought to have originated from wear and resuspension of building materials in the subway system and raised by the piston wind (Jung et al., 2010).

The S-rich particles mainly consist of ammonia sulfate and have irregular or spherical shapes (Fig. 4i), and these type of particles tend to be formed by the secondary chemical reactions in the atmosphere (Shao et al., 2022b). These sulfate particles, which easily volatilize under the electron beam have a 'foam-like' morphology after volatilizing.

Organic particles have spherical or nearly spherical shapes (Fig. 4k). Unlike S-rich particles, organic particles are extremely stable and non-volatile under the strong electron beam. Van Drooge et al. (2018) have reported that the majority of organic particles in the platforms originate from outdoor air. In the outside atmospheric environment, organic particles are mainly emitted from fossil fuels and biomass burning (Shao et al., 2022b). In addition to those transported from external environment, there are also a number of sources of organic particles from trains, escalators and passengers in subway system (Van Drooge et al., 2018; Shao et al., 2022a).

Particles in the atmosphere often don't exist as a single phase of chemical composition. For example, due to the high humidity in haze weather, the chemical reaction between particles is more intense than that in non-haze days (Shao et al., 2022b). Under these conditions, particles tend to appear in a mixed state by the secondary chemical reactions in the atmosphere (Xing et al., 2020). Mixed particles are irregular in shape and show inhomogeneous internal structures (Fig. 4m). Sulfate particles mixed with metal particles were the most common among all detected mixture particles in this study.

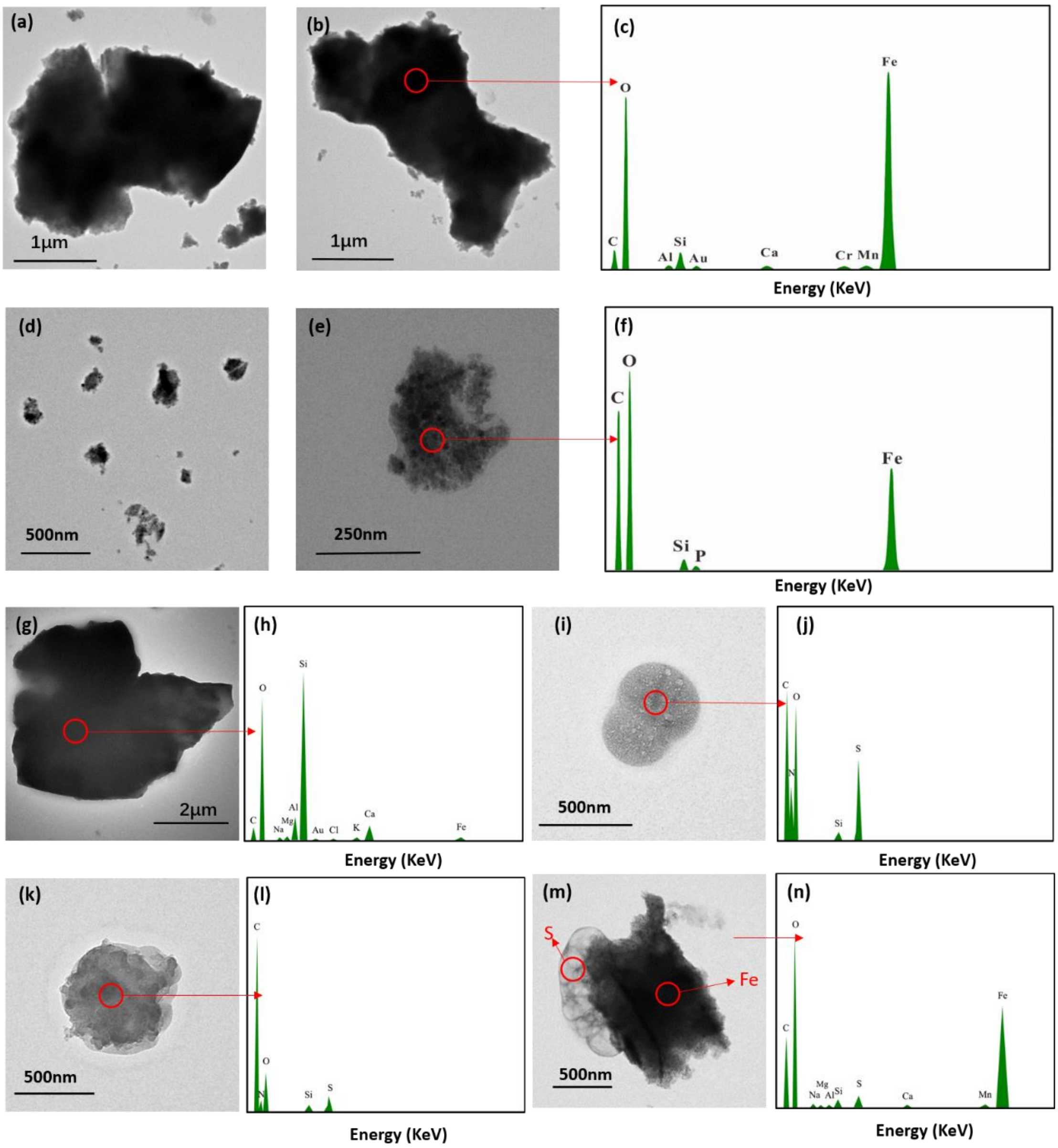

Fig. 4. Examples of morphologies under TEM, and mixing characteristics of individual particles in subway station. (a-b, d-e) Fe-rich particle, panels (c) and (f) are

EDX of (b) and (e); (g) Si-rich mineral particle, panel (h) is EDX of (g); (i) S-rich particle, panel (j) is EDX of (i); (k) organic particle, panel (l) is EDX of (k); (m) S-Fe mixture particle, panel (n) is EDX of (m)

The relative percentage of the different types of individual particle inside and outside the subway station is shown in Fig. 5.

The composition of $PM_{2.5}$ differed under the different pollution conditions. Metal particles were predominant in the subway station atmosphere during haze and non-haze days, accounting for 39.0% and 53.4% respectively. Inside the station, the relative percentages of metal particles were much higher than the outside atmosphere, and it has been reported by Shao et al. (2021) that the relative percentages of metal particles in outside ambient air during haze and non-haze day were 2.7% and 0.3% respectively. The S-rich particles were only found in the samples during the haze days, accounting for 30%. A number of studies have reported the high percentage of S-rich particles in the environmental atmosphere during haze days (Wang et al. 2022; Shao et al. 2021). Therefore, the S-rich particles detected in this study were mainly sourced from the outside environment.

The relative percentages of the different types of particles varied in different areas of the subway station. Metal particles were abundant at the carriages (79.4%), concourse (65.3%) and platform (61.3%). At the exit site, the mineral particles were the major particle type, accounting for 92.3%, which could be attributed to crustal dust resuspension.

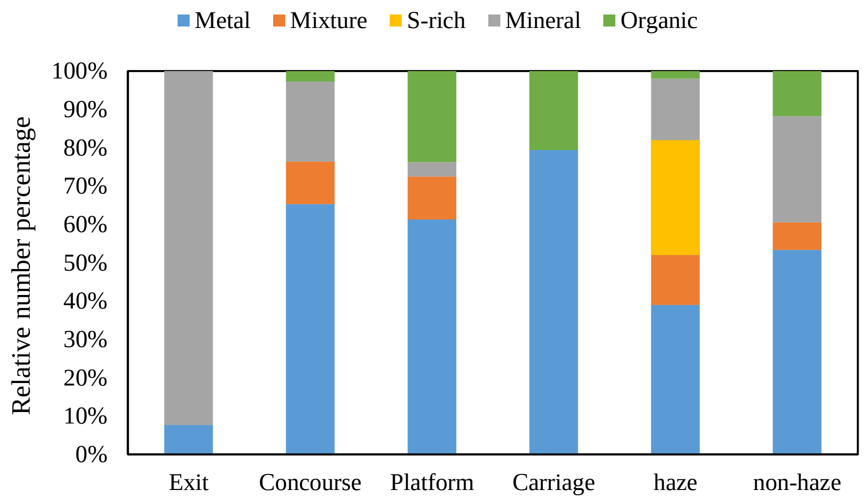

Fig. 5. Relative number percentages of individual particles in the subway station.

4. Discussion

4.1 Factors affecting $PM_{2.5}$ in the subway station

The $PM_{2.5}$ in the subway station is influenced by both indoor and ambient outdoor sources. Indoor sources include the resuspension of dust particles due to the passengers or train movements, and the mechanical abrasion emissions, such as between the train wheels and rails (Li et al., 2018). Ambient outdoor sources refer to the local air quality and pollution from vehicles, industry and combustion sources.

The pollution in the subway station varies over a wide range, as also seen with the outside atmospheric pollution (Zhao et al., 2017; Lee et al., 2018). In general, the concentrations of $PM_{2.5}$ were higher during the haze days than during non-haze days. During haze days the concentrations of $PM_{2.5}$ inside the subway station were lower than the those outside, which indicated that outside ambient sources were the main pollution contributors. On the contrary, during the non-haze days the indoor sources were the main components. Moreover, ranking the $PM_{2.5}$ concentrations of the different areas of the subway system during the non-haze days showed that carriage > platform > concourse > exit, which also indicated that the smaller distance to the rail track will be associated with the higher $PM_{2.5}$ concentrations in the subway station. This indicated that particles from train-related sources such as resuspension, wheel, rail, brake and collector shoe abrasion were the major factor causing environmental pollution inside the subway.

4.2 Morphology and chemistry of Fe-rich particles in subway air

From the high-resolution TEM images, it is shown that the Fe-rich particles mainly exist in two morphologies. The first is the homogeneous Fe-rich fragments (Fig. 4a and 4b), typically with torn and ragged edges. The second is the heterogeneous Fe-rich fragments, which interpreted as a large number of tiny Fe-rich fragments aggregate (Fig. 4d and 4e).

The two different morphologies may represent either an aging (oxidation) process or is a result of the mode of formation. A study by Moreno et al. (2015) suggested that Fe-rich flakes and splinters are released by mechanical wear at the brake-wheel and wheel-rail interfaces. The oxidation of these particles results in extensive alteration of the structure to more rounded aggregates, with iron metal flakes still preserved in some particle cores (Moreno et al., 2015). The presence of Mn is good evidence that the particles are largely generated from the train rails as Fe-Mn alloy, or 1084 rolled steel, is commonly used in railway tracks, and the addition of 0.7-1.0% Mn significantly improves the anti-wear properties (Dhar et al., 2020).

The analytical technique used in this study does not allow a determination of whether the Fe-rich particles are pure metal or metal oxide. The TEM-EDX spectra showed significant peaks for oxygen. This oxygen could be from the organic film used to support the particles for TEM, or also could come from metal oxides, predominantly Fe oxide. We can speculate that the Fe-rich particles may result from metal-on-metal abrasion. When the train brakes are applied, the resulting abrasion will generate minute Fe particles as well as heat (Martins et al., 2016; Moreno et al., 2017). Once generated, these particles will start to oxidize or rust, and they will either be directly suspended into the atmosphere by the strong air movements created by moving trains, or be deposited in the places proximal to the tracks where the potential of re-suspension into the atmosphere exists with every passing train (Jung et al., 2010). On some occasions, more aggressive braking can generate sparks, which are presumably the Fe-rich particles being instantly oxidized (Namgung et al., 2017). It is therefore likely that the

Fe-rich particles in the subway atmosphere will usually be “Fe oxide”-rich particles. Fe oxides are generally stable in the air as Fe_2O_3, which is the main component of hematite. It agrees with the conclusions reported by Moreno et al. (2015) that Fe-rich particles undergo progressive atmospheric oxidation from metal Fe to hematite.

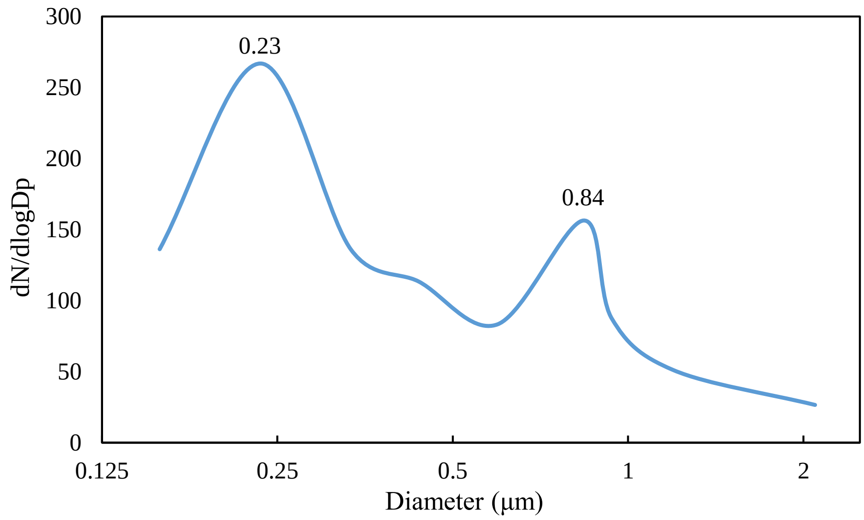

Fig. 6. Number-size distribution of Fe-rich particles in subway station air from the TEM analysis.

Fig. 6 illustrates the number (dN/dlogDp) - size distributions of Fe-rich particles in the subway station air, where N is the relative number fraction and Dp is the equivalent diameter. The Fe-rich particles were in the size range of 0.1-2.78 μm and displayed a bimodal distribution, with one peak at 0.23 μm and another at 0.84 μm. According to TEM analysis, the Fe-rich particles mainly exist in two morphologies, with the homogeneous Fe-rich fragments (Fig. 4a and 4b) and the heterogeneous Fe-rich fragments (Fig. 4d and 4e). The mean diameter of the homogeneous Fe-rich fragments was around 0.84 μm, while the heterogeneous Fe-rich fragments was around 0.23 μm. Therefore, the bimodal distribution of Fe-rich particles is consistent with the morphology characteristics.

In general, Fe-rich particles collected at different sites of the subway showed the consistent number-size distribution (Fig. S1). The geometric mean diameter of all Fe-rich particles was around 0.34 μm, which was smaller than all detected particles at 0.47 μm. Submicron particles (equivalent diameter less than 1 μm) accounted for 89.5% of all Fe-rich particles, indicating that most of the Fe-$PM_{2.5}$ in the subway air exists in smaller size ranges.

Several studies have shown that the form of metals in airborne particles can have important implications for human health (Zelikoff et al., 2002; Gilli et al., 2007; von Schneidemesser et al., 2010). Particles with smaller sizes are of more concern due to being more respirable, their relatively larger surface area and strong adsorption capacity (Al-Dabbous and Kumar, 2014; Olawoyin et al., 2018). Therefore, smaller respirable particles could present a higher health risk than larger particles (Feng et al., 2020; Pan et al., 2019). In addition, for the metal particles the detection frequency of Fe-Mn alloy particles is the highest (47.6%), which is consistent with the composition of manganese steel used in modern subway tracks (Dhar et al., 2020). Merolla and Richards (2005) have reported that when particulate matter contains multiple metals, the combined holistic toxic effects can exacerbate the health risk to human beings. Therefore, the large number of Fe-Mn alloy fragments with small particle size and potential toxicity in the subway system should attract our attention.

5. Conclusions

The concentration of $PM_{2.5}$ in subway stations was affected by both indoor generated and outdoor ambient sources. In this study, we noted that during the non-haze days, the concentrations of $PM_{2.5}$ inside subway station were higher than that found outside. However, during the haze days, the relationship was reversed. The train-related sources such as resuspension, wheel, rail, brake and collector shoe abrasion were the main cause of Fe-rich particulate pollution in the subway air.

Within the subway station, the Fe-rich particles were most abundant, and Fe was detected in more than 75% of all analyzed particles. The Fe-rich particles were abundant in the sites of carriages (79.4%), concourse (65.3%) and platform (61.3%).

The Fe-rich particles were in the size range of 0.1-2.78 μm, and the geometric mean diameter of the Fe-rich particles was around 0.34 μm, which was smaller than that for all detected particles, 0.47 μm. Cr and Mn were often detected with the Fe, which has implications for the potential respiratory toxicity of subway airborne particulate matter.

A better understanding of the particle distribution around different areas of the subway system and the physicochemical characteristic of these Fe-rich particles is critical in developing a meaningful assessment of the risk posed by particles in the subway atmosphere.

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Fig. S1. Size distribution of Fe-rich particles in different areas of subway station air from the TEM analysis.