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Characteristics and chemical compositions of particulate matter collected at the selected metro stations of Shanghai, China

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HIGHLIGHTS

- Low $PM_{2.5}$ and PM_1 levels were observed in younger underground environment compared to the older aboveground environment.
- TEM-EDS and XRD analyses revealed important aspects of mineralogy of metro dusts.
- Iron distributions and species were firstly determined by STXM and XANES analyses.

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ABSTRACT

A campaign was conducted to assess and compare the air quality at the different metro platforms at Shanghai City, focusing on particulate matter (PM) levels, chemical compositions, morphology and mineralogy, as well as species of iron. Our results indicated that the average $PM_{2.5}$ concentrations for the three metro lines were 177.7 $\mu g/m^3$, 105.7 $\mu g/m^3$ and 82.5 $\mu g/m^3$, respectively, and the average PM_1 concentrations for the three lines were 122.3 $\mu g/m^3$, 84.1 $\mu g/m^3$ and 59.6 $\mu g/m^3$, respectively. Fe, Mn, Cr, Cu, Sr, Ba and Pb concentrations in all of the sampling sites were significantly higher than that in the urban ambient air, implicating that these trace metals may be associated with the metro systems working. Individual airborne dusts were studied for morphology and mineralogy characteristics. The results revealed that the presence of most individual particles were with no definite shape and most of them were with a large metal content. Furthermore, Fe-rich particles had significantly higher abundance in the metro systems, which were more frequently encountered in the underground lines than the aboveground line. The 2D distribution map of an interested Fe-rich particle showed an uneven Fe distribution, implying that a hollow or core of other substance exists in the particle center during the formation process. Cluster analysis revealed that Fe-rich particles were possibly a mixture of Fe species. Fitting of X-ray absorption near-edge fine structure spectra (XANES) showed the main iron species within the particles collected from the three contrasting metro lines of Shanghai to be hematite, magnetite, iron-metal and mineral Fe. Hematite and mineral Fe were all found in three lines, while magnetite only existed in aboveground metro line. Iron-metal was determined in both the older and younger underground lines, based on the X-ray diffraction (XRD) analysis. As diverse Fe species have different physical–chemical characteristics and toxicity, the speciation of Fe-containing metro particles is important in the context of public health and control measures.

1. Introduction

Metro system is an important transportation mode in many megacities around the world due to its convenience, safety, efficiency and large transport capacity. It is also a peculiar microenvironment since it is closed, poorly ventilated and devoid of sunlight, where passengers suffer both continuous recirculation and resuspension of PM (Kang et al., 2008). Studies have shown that respirable metro air can be substantially different than corresponding ground-level or other transport air in terms of mass concentrations of variable PM size ranges. In Tokyo, the concentrations of suspended PM by mass were higher at the subway stations than those in the aboveground throughout the seasons (Furuya et al., 2001). Adams et al. (2001) have shown that personal exposure levels of $PM_{2.5}$ were eight times higher on the underground rail of London than other typical transport microenvironments. The same conclusion could be proposed on the basis of the measurements on the metro systems in Stockholm, Prague, Helsinki and Budapest (Johansson and Johansson, 2003; Branis, 2006; Aarnio et al., 2005; Salma et al., 2007). In contrast, lower concentrations of PM in the metro systems were observed as compared to that of the other modes of transport and/or street canyons in some other cities, including

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Guangzhou, Mexico, and Barcelona City (Chan et al., 2002; Gomez-Perales et al., 2007; Querol et al., 2012). In the comprehensive review by Nieuwenhuijsen et al. (2007), such differences may be attributed to different electric brakes, air-conditioning systems, and/or rubber tires used to operate trains.

Besides PM, a wide range of pollutants (metals, VOCs, PAHs, OC/EC, CO, et al.) associated with subways have been suggested in the metro systems. It has well been documented that the metals in the metro systems are the predominant pollutant of concern because of their abundance and carcinogenicity (Chan et al., 2002, 2003; Fromme et al., 1998; McNabola et al., 2008). The high proportion of atmospheric iron present in underground steel wheel metro systems has already been documented. In the Seoul subway, four major particle types were encountered. Among of them, Fe-containing particles were the most prevalent one with the relative abundance of 29–87% (Jung et al., 2012). In the case of Los Angeles, iron in the coarse PM makes up 27%, 6%, and 2% of gravimetric mass for the underground line, the aboveground line, and urban ambient condition, respectively. In fine PM it makes up 32%, 3%, and 1% (Kam et al., 2011a). Furthermore, sedimental dusts at the underground platform in Shanghai have the enriched Fe and Mn contents, but the lower Al and Ti contents relative to that of the floated PM in the subway atmosphere (Zhang et al., 2011). It was proposed that steel dust in subway system was the dominant source of elevated airborne exposures to iron, manganese, and chromium for many young people (Chillrud et al., 2004). Fe-containing subway particles almost always existed either as partially or as fully oxidized forms in underground subway microenvironments (Kang et al., 2008). In Budapest, Salam et al. (2009) found that the particles were mostly made up of Fe-bearing particles in the $PM_{2.0}$ size fraction, which typically consisted of aggregates of nano-sized hematite crystals that were randomly oriented, had round shapes and diameters in the range of 5–15 nm. In addition to hematite, a minor fraction of Fe-rich particles also contained magnetite, ferrite, carbides and FeOOH (Salma et al., 2009). By magnetic measurements with other geochemical analysis, Zhang et al. (2011) found that the magnetic mineralogy of the subway platform dusts was dominated by iron scraps, hematite and magnetite in Shanghai City. In the Barcelona subway, laminar hematite was found to be the dominant particle type, which may be mainly originated by mechanical abrasion of the rail track and wheels (Querol et al., 2012).

Few toxicological studies, primarily in vitro, have been conducted on the health impacts of metro particles. But according to several researchers, metro PM are more genotoxic and induce more oxidative stress than street particles (Karlsson et al., 2005; Bachoual et al., 2007; Karlsson et al., 2008). Seaton et al. (2005) found that particles sampled from three London metro stations had greater inflammatory potential and greater capacity to induce DNA damage in cultured human epithelial cells than aboveground particles. Although relatively little is known about the specific chemical constituents responsible for adverse effects on human health, particle-bound metals are implicated in a number of studies. Soluble Fe and Zn have been found to play an important role in the production of highly deleterious hydroxyl radicals in the lung fluid via the Fenton reaction, and are hypothesized to cause cellular inflammation (Baltrusaitis et al., 2012). Indeed, the dusts in the metro system were reported to be more toxic than ambient airborne particles possibly due to the enrichment of Fe components (Karlsson et al., 2005). Recently, as Fe is the most enrich metal in the metro systems, iron species in subway particles is of prime interest because of their different toxicity and magnetic properties according to the iron species (Eom et al., 2013).

Metro system in Shanghai plays a vital role among general mass transportations. There are already 13 metro lines and a growing number of metro lines are under construction. The total length of the Shanghai subway is reported to be 425 km with 282 stations at the end of 2011 and average 5.2 million commuters traveling daily (Ying, 2011). Especially, the subway was the dominant mode for commuting in the city (about 40% of trips) in the 2010 Shanghai World Expo (Ying, 2011). Particulate air pollution in the subway microenvironments of Shanghai has got more and more concerns. Some studies on the air quality of Shanghai metro microenvironments, especially underground subway stations, have already been reported (Zhang et al., 2011; Feng et al., 2010; Zhang et al., 2012). However, to the best of our knowledge, seldom studies on the characteristics of PM in different subway microenvironments have been reported. In Shanghai, as the subway systems were built in different ages and regions, several lines are completely built in the underground and others are built on the aboveground. Besides, the platform screen doors in some new lines are installed for security reasons, while the ones were not considered in the case of some old lines, resulting in the different microenvironments, and thus the different air quality. The platform screen door system has been installed in many current metropolitan subway systems (e.g. Brazil, Canada, Demark, Korea, Japan, USA, and United Kingdom) to help reduce the risk of accidents from high speed service trains passing through the stations and also for more effective temperature and ventilation controls on the platform. In Korea, Kim et al.'s (2011) study has proved that the mean PM levels have a significantly noticeable shift after platform screen door installation in a Korean subway station.

In the present study, three contrasting lines of the metro systems were selected for airborne PM measurements: Line 2 (an underground heavy-rail subway line without automatic door), Line 3 (a typical ground-level light-rail line), and Line 10 (an emblematical underground heavy-rail subway line with automatic door, newly operated in April, 2010). We compared the differences of PM pollution and the elemental compositions of the three contrasting lines. Morphology and mineralogy analyses of the metro dusts were determined by the transmission electron microscope (TEM) and the XRD analyses. Scanning transmission X-ray microscopy (STXM), near edge X-ray absorption fine structure (NEXAFS) and XANES analyses were also applied to identify the iron speciation as well as the Fe distribution within the particles collected from the Shanghai subway.

2. Experimental section

2.1. Sampling methodology

Two types of the samples were collected from the Shanghai subway system: one type was floated airborne particles and the other one was sedimental dusts. All of the samples were collected from several platforms of three highly contrasting metro lines, including Line 2 (L2), Line 3 (L3) and Line 10 (L10). The three metro lines represented three different metro microenvironments: L2 represents one of the oldest underground heavy-rail lines in the system, L3 represents one of the oldest and busiest typical aboveground light-rail line, and L10 represents part of the youngest and more advanced metro line, which has been installed with advanced ventilation systems and automatic platform screen door systems separating rail track from the platform. Airborne particles were sampled to assess the personal PM exposure of passengers who ride the L2, L3 and L10. Two samples were collected on the East Nanjing road station of Line 2. One sample was collected on the Jiangwan park station of Line 10 and one sample was collected on the Hongkou Stadium station of Line 3. All of the airborne samples were collected for 10 h at a flow rate of 9 L per minute for the measurements of the PM concentrations. For comparison, the sample was collected at a fixed site at Fudan University (FDU), which was used to represent an urban ambient environment. Personal sampling was carried out using a portable, battery-operated Leland Legacy pump (SKC) with a 5-stage cascade impactor (the personal-size Sioutas Impactor for the highly efficient collection of airborne particles in five size ranges: >2.5 μm, 1.0 to 2.5 μm, 0.5 to 1.0 μm, 0.25 to 0.5 μm, and <0.25 μm). All of the 5-stage particle samples were collected on Teflon filters (25 mm diameter, 1.2 μm pore size, and the 5th stage 37 mm PTEF with PMP ring, 1.2 μm pore). After sampling the filters were folded in a piece of parchment paper and stored in a freezer at −4 °C until chemical analysis. For the TEM analysis, particles were collected directly onto the 300-mesh copper TEM grids coated