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Research Paper

Metal-enriched nanoparticles and black carbon: A perspective from the Brazil railway system air pollution

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ABSTRACT

Having a better understanding of air pollutants in railway systems is crucial to ensure a clean public transport. This study measured, for the first time in Brazil, nanoparticles (NPs) and black carbon (BC) on two ground-level platforms and inside trains of the Metropolitan Area of Porto Alegre (MAPA). An intense sampling campaign during thirteen consecutive months was carried out and the chemical composition of NPs was examined by advanced microscopy techniques. The results showed that highest concentrations of the pollutants occur in colder seasons and influenced by variables such as frequency of the trains and passenger densities. Also, internal and external sources of pollution at the stations were identified. The predominance of NPs enriched with metals that increase oxidative stress like Cd, Fe, Pb, Cr, Zn, Ni, V, Hg, Sn, and Ba both on the platforms and inside trains, including Fe-minerals as hematite and magnetite, represents a critical risk to the health of passengers and employees of the system. This interdisciplinary and multi-analytical study aims to provide an improved understanding of reported adverse health effects induced by railway system aerosols.

1. Introduction

The population of urban centers is daily exposed to air pollutants in several environments, including the outdoor air and microenvironments such as household, workplace, schools, and particularly during commuting (Martins et al., 2015). Transport system emissions are a large contributor of fine particles ($PM_{2.5}$: aerosols with aerodynamic diameters < 2.5 μm) and nanoparticles (NPs: aerosols with diameters < 100 nm) (Jeong et al., 2017; Kumar et al., 2019), which deteriorate urban air quality inducing a range of health problems such as cardiovascular and respiratory pathologies (Knibbs et al., 2011; Heal et al., 2012).

Most studies have focused on particulates emitted by road traffic combustion processes (Kumar et al., 2011), and few studies were conducted to investigate the presence of particulate matter in rail transportation (Chen et al., 2020; Shakya et al., 2020). This is because rail is usually considered a green mode of transport compared with air and road (Givoni et al., 2009). However, some studies have reported significant concentrations of NPs (Abbasi et al., 2011; Moreno et al., 2015), black carbon (BC) (Vilcassim et al., 2014; Jeong et al., 2017), and $PM_{2.5}$ (Cusack et al., 2015; Font et al., 2020) in railway environments. Therefore, the emission of particles, including both exhaust and non-exhaust ones, are considered a drawback of rail transport (Abbasi et al., 2013). In general soot is formed through incomplete combustion of carbonaceous fuels and emitted as particles into the atmosphere. Elemental carbon (EC) and BC have been measured in the subway where the soot was believed to originate from road traffic aerosols that enter via the ventilation system, or is generated by repair diesel trains driven in the subway at night (Aarnio and Yli-Tuomi, 2005). Diesel exhaust has been linked to several forms of cancer in epidemiological studies; lung cancer (Garshick et al., 2008), bladder cancer and colon cancer. An increased risk for cardiovascular diseases has been shown (Lundbäck, 2009). Diesel exhaust can also exacerbate asthma and is also suspected of actually causing asthma (Ris, 2007).

Having a better understanding of air pollutants in railway systems is relevant to consolidate a sustainable public transport (Cerletti et al.,

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2020). Urban sustainability includes planning green mobility infrastructure to improve public health and quality of life for citizens (Kumar et al., 2019; Zhao et al., 2020). Consequently, identifying the chemical characteristics of the airborne particles in these microenvironments is a crucial aspect to recognize the origin of the pollutants and ensure cleaner railway environments, free of potentially toxic compounds. This is of special interest to cities in developing countries which often have outdated infrastructure, becoming sources of air pollutants.

In the railway system, several factors affect the concentration and chemical composition of airborne particles. Some of these are the air quality to the surroundings, depth and architecture of the stations, conservation of the structure, composition of the wheels, type of rails, power supply materials, braking mechanisms, speed and frequency of trains, passenger density, power systems, ventilation and air conditioning, cleaning frequency, and other operating conditions (Johansson and Johansson, 2003; Ripanucci et al., 2006; Salma et al., 2007; Park and Ha, 2008; Kwon et al., 2015; Martins et al., 2015). One of the main concerns is the wide range of sizes from nanoparticles to coarse particles, as well as the metal-enriched nature and its level of toxicity (Cha et al., 2018). According to Lee et al. (2018), the brake system and the wheel-rail contact are the major sources of airborne wear particles that are harmful to human health because they include potential hazardous elements (PHEs) like Cr, Fe, Mn, Ba, Mo, Sn, Ni, Co, and Cd. Bolognin et al. (2009) reported that NPs associated with trace metals affect the neurological system, increasing oxidative stress and neuronal damage. Other pollutants such as NO_2, SO_2, and BC from vehicular traffic and industrial activities located near the stations can be introduced to railway environment. Several studies observed the adverse effects of BC to human lungs (Reche et al., 2015) and suggested that BC particles play an indirect key role in toxicity, carrying metals toxic compounds connected to their surface (WHO, 2013). As concentrations and properties of particles affect exposure of people on railway stations and in vehicles, studies on NPs and BC to reduce emissions are imperative.

Epidemiological studies have demonstrated positive associations between elevated PM2.5 concentrations and increased incidence of respiratory disease (Pun et al., 2015), impairment of lung function (Rice et al., 2013), increased number of hospital admissions (Tian et al., 2019) and mortality rates (Liu et al., 2019). These studies applied ambient concentrations as a proxy for population exposures, which neglected the variation in personal exposure related to individual activities (Richmond-Bryant and Long, 2020). Traffic-related air pollution is one of the primary sources of $PM_{2.5}$ in urban areas, which vary widely in space and time (Krall et al., 2018). Also, traffic-related $PM_{2.5}$ comprise a highly heterogeneous mixture containing different particle-bound constituents, including EC, also known as BC) (Chen et al., 2014), elemental components (Minguillon et al., 2018), and polycyclic aromatic hydrocarbons. Commuting activities constitute a considerable part of daily personal $PM_{2.5}$ exposure in urban areas (Ham et al., 2017). Also, commuter exposures are highly individualized to the unique transport systems (Krall et al., 2018), with chemical compositions (e.g., crustal matter, transition metals) different from those in the outdoor air (Minguillon et al., 2018). These studies demonstrated that exposure levels in transport microenvironments depended on the time of the day, urban morphology, traffic route, transport mode, traffic intensity, and meteorological condition (Tan et al., 2017).

Emissions associated with urban transport systems have been identified as the main source of urban particulate matter in different regions, including Brazil (Karagulian et al., 2015). Taking into account that a large part of the vehicles still dates from the 1990s and 2000s in Rio Grande do Sul state (RS), Southern Brazil, keeping road traffic as a relevant source of air pollution, the railway transportation is considered the cleanest system as it uses electric power. The railway system is also desirable because of its safety, high speed, and large transport capacity in terms of number of passengers (Martins, 2016). However, to the authors' knowledge, no studies on airborne particles at the railway stations have been carried out so far in Brazil, a country with a 1125-km-long electric rail system (CNT, 2014). Therefore, there is no information on air quality in this apparently clean transportation system. Consequently, the aim of the present study was to assess concentrations and chemical characteristics of NPs and BC sampled on two ground-level railway stations and inside trains of Metropolitan Area of Porto Alegre (MAPA) for thirteen consecutive months.

2. Materials and methods

2.1. Study area

Aerosol ultra-fine and nano-particles were continuously monitored and sampled in terms of number, surface area concentration and size distribution during daytime at different time-periods. The MAPA is located in the East-Central zone of RS, an urbanized region with relatively flat topography. This metropolitan area is at sea level and has humid subtropical climate according to the Koppen System of International Climate classification (Teixeira et al., 2012). The region has well-distributed rainfall throughout the year and monthly averages ranging from between 80 mm and 137 mm (de Miranda et al., 2011), as well a high influence of cold air masses from polar regions. During the day, the minimum wind speed occurs at the early morning, whereas the maximum speed is during the late afternoon. The direction of the wind has seasonal variations and is the result of interactions of meso-scale phenomena, with *E*-SE origin prevalent during summer/spring and the W-NW in the winter/fall months. Overall, seasons are reasonably defined, averaging a temperature of 25 °C in summer and 15 °C in winter (Teixeira et al., 2012).

The MAPA railway system is the biggest of the state, with its first line beginning operation in 1984. Currently, the system has a total length of 43.8 km, including 22 ground-level stations in six cities (Fig. 1). Two stations with natural ventilation were selected for sampling because of their large number of passengers and localization. The selected stations were the Rodoviária station (30°01′20.5” S and 51°13′13.3” W) located next to the bus station in the center of Porto Alegre City, and the Fátima station (29°56′19.0” S and 51°10′37.8” W) located in the Canoas City, close to several industrial activities (e.g. chemical and metallurgical sectors) and a Military Air Base. Both platforms are 200 m long in the middle of two sets of rail tracks, one for each direction.

2.2. On-line measurements

The measurements were performed both on the ground-level platforms and inside the trains, which always operate with closed windows, having the air conditioning with automatic adjustment as the only ventilation system. Trains commence at 4:00 am and the last train leaves the terminus station at 11:20 pm, with a frequency between 3 and 15 min depending on the time of day. The study was conducted for thirteen months (23 August 2018–23 September 2019) and all seasons were analyzed using the same devices.

Particle number concentration and size distributions of NPs were measured using a NanoScan scanning mobility particle sizer (SMPS model 3910, TSI Inc.). The instrument setting has a 0.75 L/min inlet flow and a 0.25 L/min CPC flow. This device used isopropyl alcohol as condensation liquid and considered particles of sizes 10–420 nm distributed across 13 channels, as described in previous studies (De Paoli et al., 2018). The BC measurements were carried out using a MicroAeth AE51 (Aethlabs Inc.) with a flowrate of 150 ml/min. This device measured BC (in $\mu g/m^3$) derived from absorption values at the wavelength of 880 nm (MAC = 16.6 m^2/g) transmitted in a Teflon-coated glass filter T60. The effect of filter loading was reduced by replacing the filter strips during every day of measurement. Both instruments were performed with a frequency of 60 s and the inlets were placed at 1.5 m above the ground level. The measurements were organized in three-day campaigns, twice a month, during the study period as follows: two days for 8 h daily in the platforms (9 h to 17 h UTC-3) and the third day inside

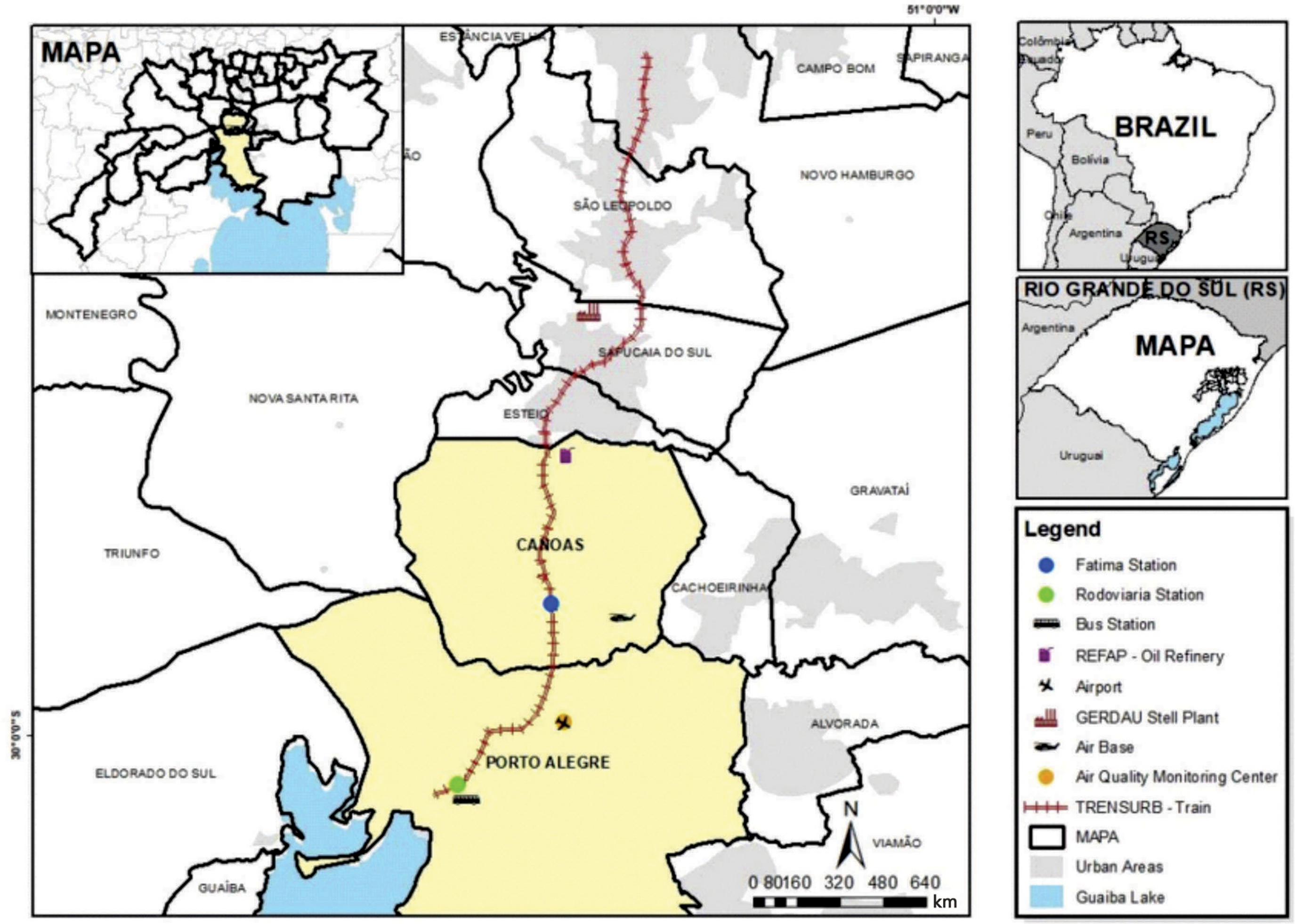


Fig. 1. Localization of the MAPA's railway system and the studied stations.

the first car of the train, during a trip along the whole length of the line (10 h to 13 h UTC-3). The samplings were performed on weekdays and the equipment was placed at the end of the platform in order to minimize obstruction of the commuter's path.

Meteorological parameters such as ambient temperature (AT, in °C), relative humidity (RH, in %), atmospheric pressure (AP, in hPa), wind speed (WS, in m/s), and solar radiation (SR, in W/m^2) were obtained from the Salgado Filho International Airport meteorological station. The NO, NO_2, SO_2, PM_{10} (in $\mu g/m^3$), and CO (in ppm) data were obtained from the Alberto Pasqualini Refinery (REFAP) and the CMPC Cellulose Industry air quality monitoring stations.

Statistical software SPSS® was performed for all statistics analysis, including the Kolmogorov-Smirnov (K-S) test to verify normality of the data and Spearman's correlation.

2.3. Off-line sampling and analytical procedures

The self-made passive sampler contained a PVC tube with one internal pin stub covered with carbon tape as previously reported by Silva et al. (2020), where the particles could be accumulated naturally according to the wind and the environment (Morillas et al., 2016). The samplers were mounted in the platforms at the air level breathed by the commuters (about 1.65 m above the platform floor). The T60 filters used in the BC measurements by the AE51 device were collected for evaluating particles inside trains. Several analytical tools were applied to characterize sampled subway particle fractions including Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) for morphological information, combined with Energy Dispersive Spectroscopy (EDS) for elemental information of discrete particles. Geochemical compositional analysis of the outermost surface was analyzed by means of X-ray Photoelectron Spectroscopy (XPS).

Advanced microscopy techniques are widely used for morphological and structural characterization of particles (Silva et al., 2020). The samples were air-dried and coated with platinum for better conductivity. The morphology and elemental composition of NPs were analyzed by Field Emission Scanning Electron Microscope (FE-SEM) (Zeiss Model Ultra plus FE-SEM with charge compensation) equipped with an Energy-dispersive X-ray Spectrometer (EDS) and Raman spectroscopy (Renishaw Invia Reflex Raman system), operated in the confocal mode. The structure of amorphous and mineral aggregates was further investigated using High-resolution Transmission Electron Microscope (HR-TEM) (200-keV HR-TEM JEOL-2010F) with Selected Area Electron Diffraction (SAED), Scanning Transmission Electron Microscopy (STEM), and Fast Fourier Transformation (FFT). Procedures of extraction by sonification were followed in the T60 filters as described by Rojas et al. (2019). The samples from the passive samplers were separated in alcohol through ultrasonic-sound suspension and subsequently pipetted into Lacy Carbon films supported by Cu grids (Quispe et al., 2012). EDS spectra recorded in FE-SEM and HR- TEM images mode were quantified using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into weight percentages (Ribeiro et al., 2010).

3. Results and discussion

3.1. Particle concentration and size

In spite of the use of electricity, there are several sources of particles related to the operation of trains, such as mechanical parts subjected to high temperatures, including brake pads and electric motors (Mendes et al., 2018). The highest levels of NPs and BC were found in the Fátima station, with medians of 6.66 × 104 cm^{-3} and 3.38 μg/m^3, respectively, while the lowest concentrations were recorded in the Rodoviária station (2.99 × 104 cm^{-3} and 1.97 μg/m^3, respectively). In the Fátima station, located at an industrial area, the NPs distribution had a bimodal behavior with higher concentrations in Nucleation and Aitken modes that is around of 15.4–27.4 nm (Fig. 2). In the Rodoviária station, located at an urban area, and inside the train, higher concentrations were observed around 27.4–36.5 nm, corresponding to the Aitken mode. Similar results were reported by Salma et al. (2007), who observed maximum concentrations between 10 and 50 nm in Budapest railway stations.

The emission of airborne wear particles varies according to speed, contact surface pressure, and state of rail and wheel materials (Lee et al., 2018). Also, operational factors, rail structure, and type of energy transmission can impact the size of NPs at railway environments (Sundh et al., 2009; Abbasi et al., 2013). Based on the information from the manager of the MAPA system, both stations have the same technical and operational conditions such as power supply system, rail composition, and cleaning frequency. According to the data obtained, the NPs concentrations at the Fátima station were 3.5-times those of the Rodoviária platform, whereas the concentrations of particles with a size above 100 nm were similar on the two platforms (Fig. 2). This suggests that NPs may have been influenced by emissions from external sources while the larger particles (> 100 nm) were originating primarily within the rail system.

Some authors have reported that NPs concentration inside the railway system is influenced by outdoor air (Cartenì et al., 2015). However, the ventilation system is a factor with the potential to deteriorate indoor air quality. Particle concentrations at Fátima and Rodoviária stations may be associated with the lack of an efficient ventilation mechanism, since railway stations with a natural ventilation have a low dilution factor of air pollutants (Kwon et al., 2010), which makes it easy to receive contributions from external sources. This coincides with the studies that measured higher NPs levels in old ground-level stations than in new underground stations with modern ventilation models (Xu and Hao, 2017). It is possible to notice the disadvantage caused by the lack of an appropriate ventilation system in the studied stations, since the NPs concentrations in both platforms were higher than that found in newly built underground stations in Prague (11.4×10^{3}cm^{-3}) (Cusack et al., 2015) and Athens (1.2×10^{4}cm^{-3}) (Mendes et al., 2018).

No significant BC concentrations are usually expected in railway environments with electric system. However, graphite connections between the third rail and the trains has been identified as the main source of BC in railway environments (Van Ryswyk et al., 2017). In addition, several studies have identified diesel-powered night maintenance devices in railway systems (Vilcassim et al., 2014), which is consistent with MAPA's railway conditions. Fátima and Rodoviária stations have diesel generator sets for emergency power supply and other repairs, which may contribute to the accumulation of BC on trains and platforms. Contributions from external sources, such as vehicular and industrial emissions, as well as activities of the passengers themselves such as smoking could also contribute to BC levels. The BC values observed in Fátima and Rodoviária platforms were below the values measured in China, where Li et al. (2015) reported an average of 9.43 μg/m^3 inside trains, and in the United States, the concentrations are between 5 and 23 μg/m^3 in platforms (Vilcassim et al.,2014). The BC and NPs data were positively correlated for all sites, obtaining ρ=0.45 for the Fátima station, ρ=0.53 for inside trains, and ρ=0.72 for the Rodoviária station. The strongest correlation in the platform close to the bus station could be related to a higher influence of external combustion processes, since BC particles have a tendency to mix with ultrafine particles (Wang et al., 2011).

Inside the train, a median of NPs was obtained (3.00×10^{4}cm^{-3}) which is almost equal to that found in the Rodoviária station. Further, the BC concentration was higher inside (3.14 μg/m^3), which indicates a low efficacy of air conditioning as a resource for improving indoor air quality during trips. The highest concentration of NPs on trains with value of 36.5 nm (Fig. 2), is probably a result of mechanical wear (Tokarek and Bernis, 2006) or external contributions from the station, such as gasoline-powered vehicle emissions (Morawska et al., 2008). Some studies about railway environments air quality have reported that the worse the air quality on the platform, the severe the air quality will be inside the trains (Wang et al., 2016). The strong correlations between inside train NPs and platforms NPs (ρ = 0.86 for the Fátima station and ρ = 0.98 for the Rodoviária station) suggests that indoor

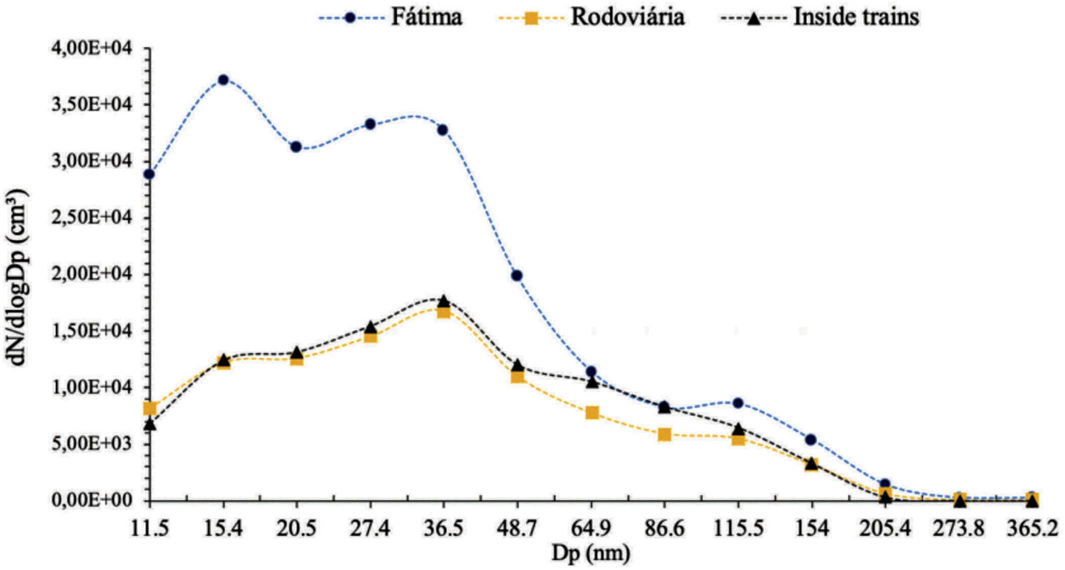


Fig. 2. Particle size distribution in the study area.

particles were strongly associated with stations particles, and are mainly introduced by commuters. In addition to the entry of NPs and BC from the platforms through the opening of doors, special attention should be paid to the accumulation of particles and other pollutants in the air conditioning system (Wang et al., 2016). According to employees of the rail system, train's air conditioning filters are not replaced frequently, leading to deterioration of the indoor air quality. Unlike underground systems where opened windows cause an increase in particle concentration inside trains by infiltration, the ground-level systems face a different situation, with the circulation of air from abroad can reduce indoor concentrations by producing an effect of "environmental washing" (Cartenì et al., 2015). Therefore, keeping windows closed during trips seem to contribute in worsening indoor air quality in the MAPA railway system.

The Spearman's coefficients between NPs and BC obtained on platforms and inside trains, and PM_{10}, SO_2, O_3, NO, NO_2, and CO levels measured in outdoor stations are shown in Supplementary Data (Table SD1). The BC concentrations were positively correlated with PM_{10}, NO, and CO, suggesting that both platforms were influenced by external local emissions such as traffic-related emissions (Cepeda et al., 2017). In the Rodoviária station, the positive correlation of BC and NPs with NO and NO_2 indicate that exhaust vehicular emissions from outdoor environment contributed to air pollution levels at the platform, which is a typical characteristic of urban areas affected by primary emissions (Johansson et al., 2007). Diesel exhaust particles are an important source of nanoparticles at street level. Nanoparticles in the studied areas are fewer than at street level and may to some extent be formed in stations from wear and spark discharges, but may also originate from diesel particles entering via the ventilation system.

3.2. Temporal variation

The highest levels of NPs and BC were observed between 9 and 11 h on both platforms (Fig. 3), when the urban activities were more intense around the stations and trains had a frequency of 3–5 min. This pattern agrees with previously studies that claimed that a higher frequency of trains leads to large levels of particles on platforms (Salma et al., 2007; Cartenì et al., 2015; Cusack et al., 2015) and a larger air pollutants concentrations commonly occur in the morning due to the intense vehicular emissions (Wang et al., 2010).

In the Rodoviária station, the maximum concentrations of NPs and BC coincided, both at 10 h (3.89×10^4 cm^{-3} and 3.03 μg/m^3, respectively), highlighting the strong association among these (Fig. 3). In the Fátima station, the NPs (8.77×10^4 cm^{-3}) and BC (5.50 μg/m^3) peaks were recorded at 11 h and 9 h, respectively. Inside trains, the levels were very similar to those found in the Rodoviária platform. The highest NPs and BC concentrations (3.22×10^4 cm^{-3} and 3.91 μg/m^3, respectively) were measured at 10–11 h when there was a noticeable passenger density. The indoor BC concentrations decreased by a factor of 2.7 and NPs concentrations by a factor of 1.3 when the trains became empty at 12 h.

In the early afternoon hours, both NPs and BC concentrations decreased in the Fátima station, which can be attributed to the low movement of commuters and longer interval of trains (10–15 min). A lower train frequency could represent a reduction in BC levels because production by mechanical processes, resuspension by turbulence, and transport of BC from the tunnels to the platforms declined (Cusack et al., 2015; Li et al., 2015). In contrast to the Fátima platform, the BC and NPs concentrations of the Rodoviária station remained relatively stable over the whole day despite changes in trains frequency and passenger density. The lowest NPs concentration ($4.94 \times 10^4 cm^{-3}$) was registered around at 16 h in the station, which could be related to less urban activity and a notable decrease in passenger density. The NPs concentration increased slightly at 17 h, influenced by the rise of commuters.

The NPs and BC concentrations in the warmer (October to March) and the cooler (April to September) seasons are shown in Fig. 4. Higher levels were observed for all sites during the colder season, which was consistent with similar studies (Kwon et al., 2015; Minguillón et al., 2018; Islam et al., 2019). Considering that the data were influenced by external pollutants, this pattern could be associated with a stable atmosphere (Young et al., 2012), a low wind speed, and a deficient pollutant dispersion during wintertime (Zhu et al., 2006). In addition, the gaseous-compound precursors of particles by condensation were more diluted in the heated day, accordingly the growth rate of particles was lower and the time of permanency of gaseous in the atmosphere

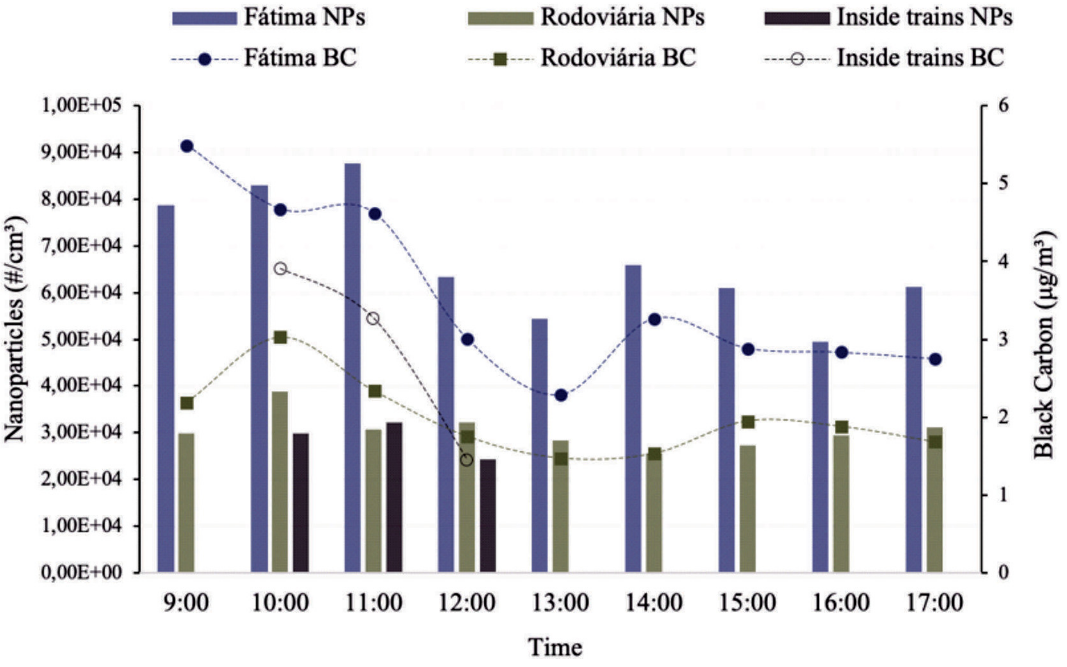


Fig. 3. Hourly concentrations of NPs and BC on both platforms and inside trains.

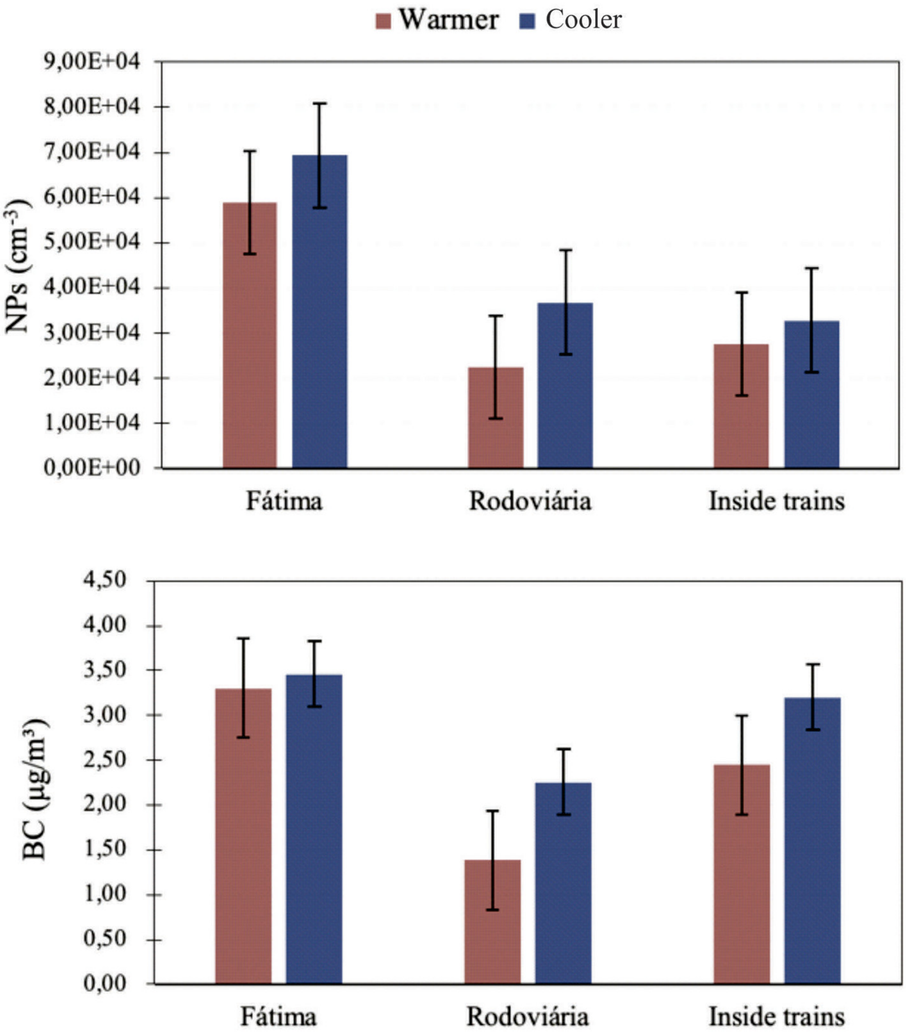


Fig. 4. NPs and BC median concentrations in the warmer and colder periods.

was higher in summertime, causing a reduction in NPs concentrations (Agudelo-Castañeda et al., 2016). Further, vehicle traffic and the use of the railway system tend to decrease during the warmer season, since a large part of the population traveled to the seaside, which implied a reduction in pollution levels on holidays. The Spearman's coefficient between particle levels on platforms and inside trains, and meteorological variables of the study are shown in Table SD2.

3.3. Chemical composition

3.3.1. Elemental compounds

Most of the particles collected at the two stations and inside trains occur in the form of irregular aggregates, with rare isolated apparitions. A common characteristic of aggregates is heterogeneity (Civeira et al., 2016), as result of a growth and/or development of particles under different environmental conditions. In the Rodoviária station, 47 NPs were analyzed by FE-SEM, HR-TEM, EDS, and RAMAN, and the results show that 75% were tubular in shape. About 80% of NPs were composed primarily of carbon (Fig. 5a), which is common in diesel railway environments (Abbasi et al., 2013). In electrical railway systems, carbonaceous particles come from the high-resistance commutator brushes in the electric motor and train pantographs connecting to the catenary (Moreno et al., 2015). However, a large number of carbonaceous particles could suggest a high influence of external traffic emissions. Carbonaceous complexes between 2 nm and 48 nm contained PHEs such as Pb, V, Cd, As, Hg, Se, Cr, Zn, and Ni were also identified (Fig. 5b). The presence of a large number of different elements has been reported in the literature with suggested origin from many different sources such as wear processes at rail-wheel-brake interfaces, current collectors and conductor rail, diesel, human activities, building materials and soil-derived atmospheric pollutants.

Several studies have reported similar carbonaceous complexes in railway stations, associating Cr with the wheels and rails composition (Querol et al., 2012); Fe, Cu, Al, Cr, Co, Sb, and Zn with the brakes (Abbasi et al., 2011); Cu with the trains operation (Cusack et al., 2015; Mohsen et al., 2018); and as with the catenary (Font et al., 2019). Mercury and Se could be released by fossil fuels combustion, consequently their presence associated with carbonaceous particles is common in urban environments (Pacyna and Pacyna, 2001). The PHEs associated with carbonaceous particles means a high toxicity of NPs since the reactivity in human body could be larger than that of only metallic particles. The metals observed (e.g. Cu, Ni, V, Zn, and Pb) are on the list of NPs emerging contaminants and have been considered to be toxic components (Kelly and Fussell, 2012; Rahim et al., 2019).

The abundance of carbonaceous NPs contrasted with the BC concentration measured in the Rodoviária station, which was the lowest in comparison with the Fatima station and inside the trains. The above results indicate the presence of other types of carbon particles such as secondary carbon, elemental carbon (EC), organic carbon (OC), among others, which could not be detected by aethalometer but were obtained

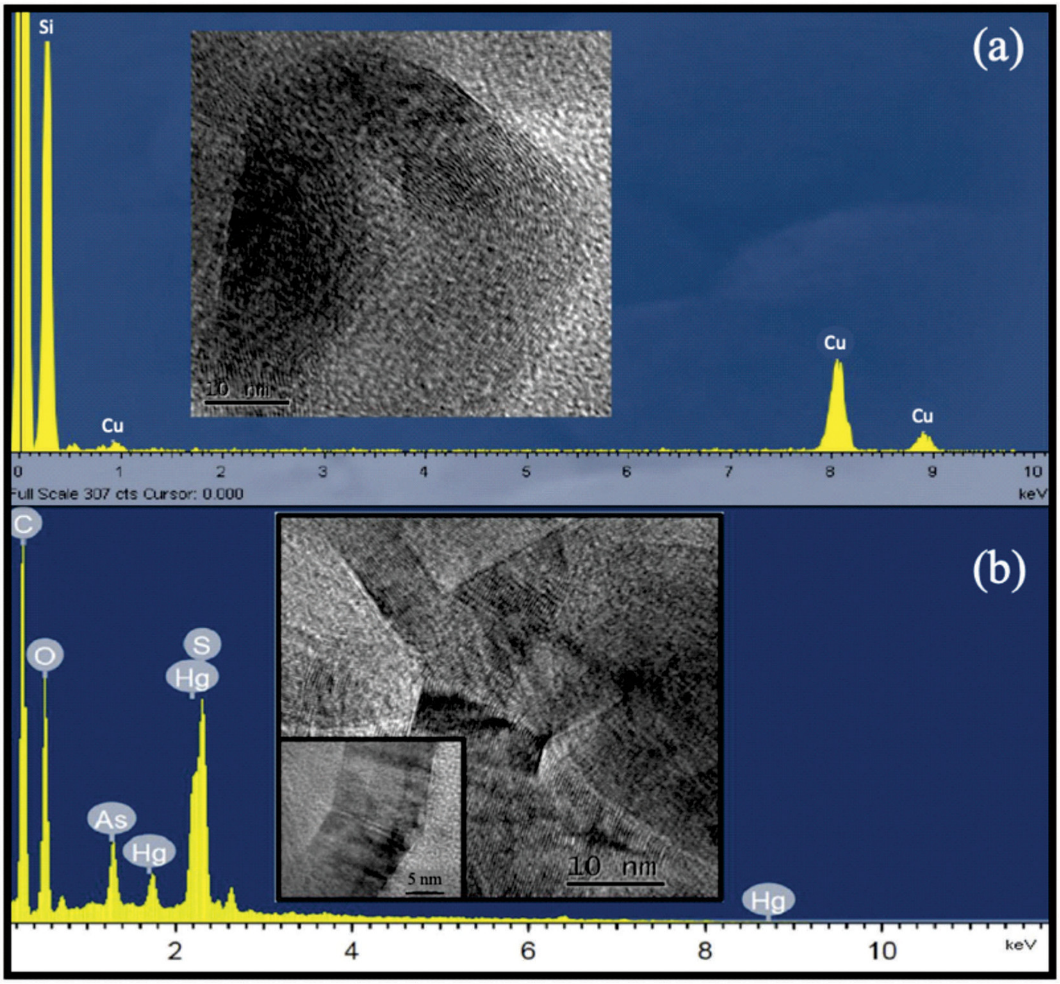


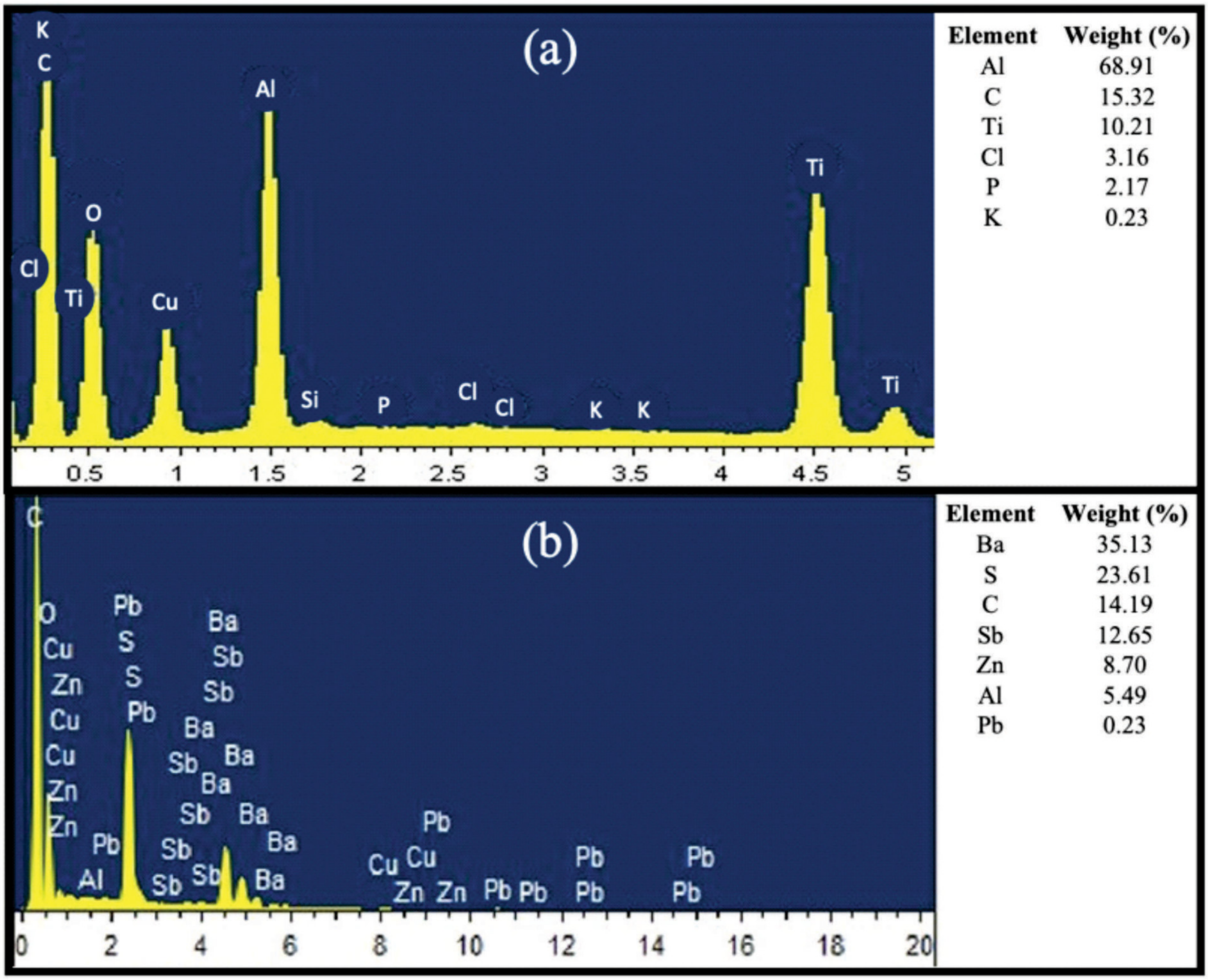
Fig. 5. (a) NPs composed primarily of carbon and (b) carbonaceous NPs complexes containing PHEs obtained at the Rodoviária station.

by Electron Microscopy and Raman Spectroscopy (note the differences between carbon particles and their properties as extensively discussed by Petzold et al., 2013). Previous studies have reported high concentrations of total carbon (EC + OC) in railway stations (Cusack et al., 2015; Lee et al., 2018). Point elemental analysis by means of FIB/FE-SEM/EDS showed that clusters of nanoparticles contained relatively higher amounts of carbon compared with larger sized particles. Elemental analysis was also conducted on single nanosized particles sampled on TEM grids by means of TEM/EDS. Nanoparticles of different elemental composition were identified, some containing Fe, Cr, NI, Zr, and many others metals. Diesel particles primarily composed of carbon and other particles containing elements like silicon, potassium, sulfur, sodium, phosphor, calcium and aluminum were in addition identified.

In the Fátima station, aggregates with slightly rounded formats were obtained. Particles from emissions without exhaust are usually spherical or semispherical, and the differences between the wear mechanisms are responsible for the format variations (Abbasi et al., 2011). A total of 95 NPs was analyzed in the station and the results reveal that mostly were typical inorganic elements, such as Al, C, Ti, Cl, P, Ca, Mg, Na, Mn, S, Si, and K, from soils, construction activities, and road dust (Fig. 6a). The presence of Al, Ca, and Mg could be associated with tunnel and platform building materials (Kang et al., 2008). Aluminum, as well as Mn, Na and S, could also be emitted by the rail tracks, brakes wear, and resuspension of the soil below the tracks (Rojas et al., 2019).

A higher metallic enrichment was observed in the Fátima station compared to the Rodoviária station, with significant proportions of Ba, Sb, Zn, Pb, Cr, Sn, Ti, and Fe detected in about 35% of the NPs (Fig. 6b). Barium, Sb and Sn are braking tracers usually found in railway environments (Moreno et al., 2014). The source of Ti may be the electric motor and the rail metals (Font et al., 2019), but also can be due to the pigments of wall paintings and products for oil removal (Tezza et al., 2015). Previous studies have identified the use of Zn, Pb, Cd, and Cu for metallurgy applications in Canoas city, which could also help with the metallic NPs enrichment in the Fátima station (Rojas et al., 2019). Although Fe was detected as NPs, the element was not the most abundant on platforms as revealed in several studies (Moreno et al., 2015). Although Fe has been recognized as a tracer of train circulation-related sources, Reche et al. (2017) claimed that it does not seem to have as much contribution in NPs as it has in coarse particles, which is consistent with our results.

Given the impossibility of fixing passive samplers inside trains, the T60 filters from BC measurements were analyzed. Among the 63 NPs studied, only 11 contained carbon traces, and most of these are morphologically and chemically similar to those found in the Fátima station. High levels of Cd, N, O, S, and Sn were markedly associated in nine amorphous NPs with a size between 21 nm and 57 nm (Fig. 7a). The presence of Cd is crucial because is one of the most significant toxic PHEs to the health, acting on the central nervous system (Silva et al., 2020). Other studies have reported that high concentrations of Cd-NPs lead to



Element	Weight (%)
Al	68.91
C	15.32
Ti	10.21
Cl	3.16
P	2.17
K	0.23

Element	Weight (%)
Ba	35.13
S	23.61
C	14.19
Sb	12.65
Zn	8.70
Al	5.49
Pb	0.23

Fig. 6. (a) Major elements and (b) metallic enriched NPs obtained at the Fátima station.

cough, asthma, vascular problems, and cancer (WHO, 2013). The strongest association was obtained between Cd and Sn.

Over 40% of the NPs obtained inside trains contained PHEs such as Cr, Pb, Ca, Mg, P, Cr, Sn, Cd, Zn, S, Ti, and Co which are highly correlated (Fig. 7b), with Pb being the only one that was not always present. Zinc oxides probably released from the abrasives and lubricants (Font et al., 2019) were also identified. In all cases, NPs were characterized by complex mixtures of amorphous material and some minerals in smaller quantity. The main concern about higher concentrations of PHEs in indoor NPs is the lack of natural ventilation and the use of air-conditioning with no maintenance. Karlsson et al. (2008) noted that people exposed to air pollution in railway systems have higher genome toxic effects due to the elevated oxidative capacity of NPs than those people exposed to emissions from vehicles or wood combustion. The train company estimated that for most commuters the average daily time waiting for the train on the platforms was 20 min and the round trip lasted 1 h. Considering this time during five weekdays, the average time of exposure to PHEs on the platforms and inside trains was approximately 13 days per year.

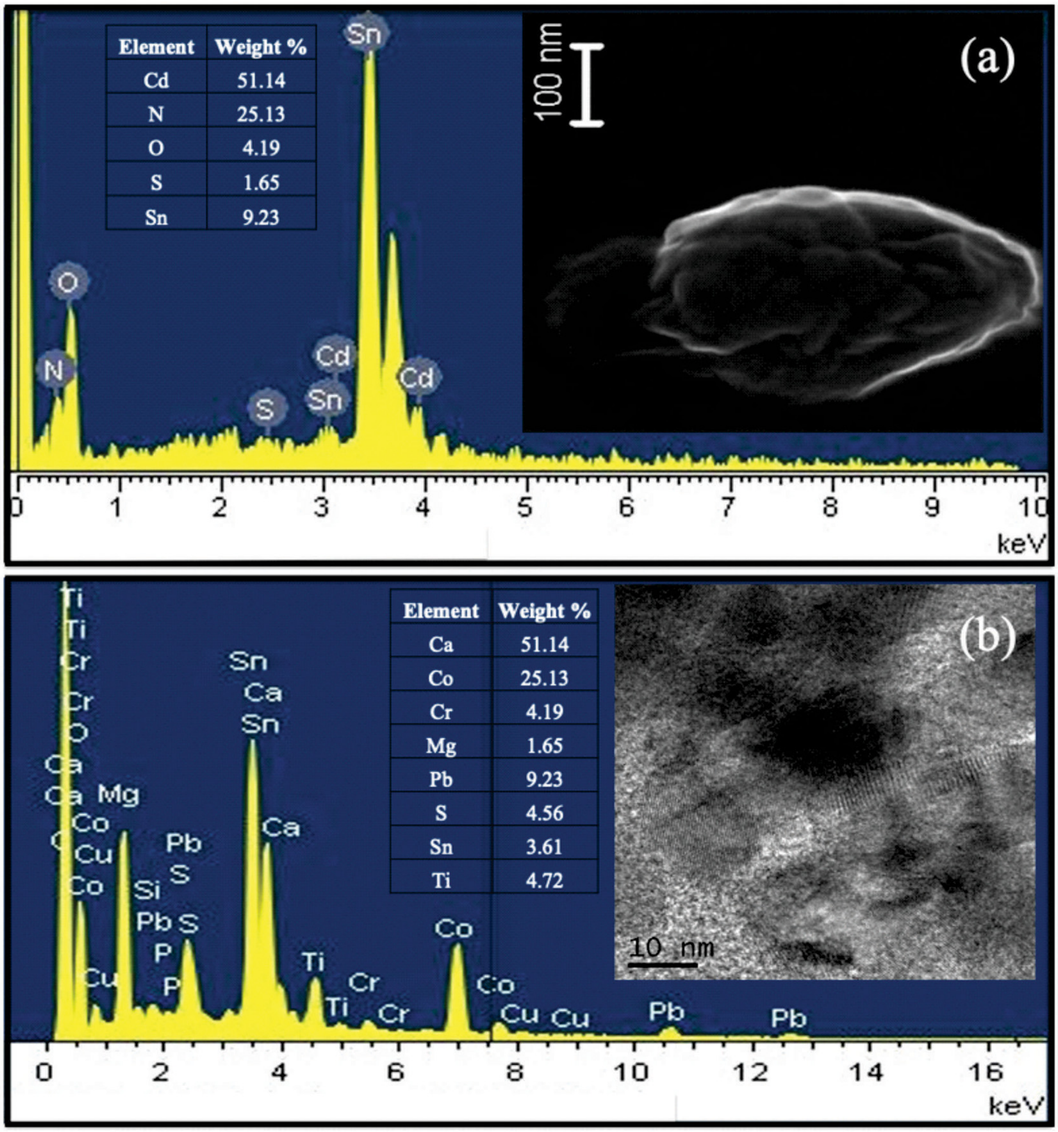
3.3.2. *Mineral fractions*

Although there was predominance of amorphous material, a variety of mineral fractions was detected by techniques applied, as shown in Table 1.

Mineral fractions from geological sources such as quartz, calcium carbonates (calcite and dolomite), and calcium sulphates (gypsum) are typical from soil resuspension and construction activities. They were found in both stations and inside trains, except for dolomite that was only found on the platforms. The toxic effect of quartz in the human organism is well established in the literature (Ross et al., 1993), consequently it has been classified as carcinogen by IARC (Guha et al., 2011). Phyllosilicates such as chlorite were found only inside the trains, and the presence of barite can be attributed to braking since flakes released from brakes are commonly Ba-rich (Moreno et al., 2015).

Fe-metal is less common than oxidized species as magnetite and hematite in railway environments (Moreno et al., 2015). In agreement with that, while metallic Fe concentrations were found in the NPs, Fe appears under different oxidation states in oxides, hydroxide and sulfate forms. Metallic Fe originated from the wear of Fe-rich materials throughout the system was oxidized to a magnetic oxide specie (magnetite) and finally to non-magnetic hematite during abrasion by air and thermal oxidation (Moreno et al., 2015). Among the crystalline forms of Fe detected, hematite is the most abundant both on platforms and inside trains. Magnetite, melanterite, and goethite were also found in all sites while jarosite was present only in the Fátima station and on trains. Previous studies have been reported similar results, both in ground-level and underground railway systems (Moreno et al., 2015; Lee et al., 2018; Font et al., 2019).

Iron oxides are recognized as the NPs class that receive most attention from environmental researchers due to their large adsorption capacity (Waychunas et al., 2005). Metals such As and Cr are easily



Element	Weight %
Cd	51.14
N	25.13
O	4.19
S	1.65
Sn	9.23

Element	Weight %
Ca	51.14
Co	25.13
Cr	4.19
Mg	1.65
Pb	9.23
S	4.56
Sn	3.61
Ti	4.72

Fig. 7. (a) NPs with abundance of Cd and (b) several PHEs identified inside trains.

adsorbed by these oxides, as well as other hazardous elements (Mohan and Pittman, 2007; Ramírez et al., 2020). Nanomagnetites were always associated with Ni, Si, and other metals at a lower frequency in the analyzed samples (Fig. 8a). Nanominerals of the same chemical formula as rutile and anatase (TiO_2) were easily distinguished by SAED, FFT, and STEM. However, anatase was detected in only one of the 31 nanoparticles containing Ti. Although more than 70% of the detected rutile particles contained Ti-amorphous, in none of the Ti-rutile was Ni detected by EDS. The only phase of Ti-NPs with Ni was anatase confirmed by SAED and FFT (Fig. 8b).

4. Conclusions

The present study was conducted to understand the concentration and chemical composition of NPs and BC to which commuters and employees of a metropolitan railway system are exposed. The concentrations of these pollutants on platforms and inside trains, in addition to their chemical composition based on metallic elements such as Cd, Pb, Hg, Fe, Sn, Ni, and Zn in amorphous and crystalline forms, constitute a risk factor for human health. The NPs and BC could come both from mechanical processes inside the stations (brake, rail and wheel wear) and from external sources (traffic-related emissions and industrial sector). Further, the concentrations of pollutants showed differences over time and location on platforms, reflecting the influence of variables such as frequency of the trains and passenger densities. The use of air-conditioning proved to be not effective in improving the indoor air quality on trains, acting as a cumulative factor because the filters were not changed frequently. Therefore, it is necessary to implement a ventilation system on the platforms and more efficient maintenance mechanisms for conditioned air to improve the air quality inside trains. To the authors' knowledge, studies in railway environments measuring the concentration of BC and NPs were not previously carried out in Brazil. Therefore, this study provides a useful approach in evaluating the air quality in rail public transport, opening new possibilities to achieve cleaner and more sustainable transport systems. Considering the high level of particulate matter at the studied stations and the large number of people exposed on a daily basis,

Table 1
Minerals detected by (a) Raman, (b) FE-SEM, and (c) HR-TEM.

Elements	Fátima	Rodoviária	Inside trains
Amorphous phases	a,b,c	a,b,c	a,b,c
Silicates			
Quartz, SiO_2	a,b,c	a,b,c	a,b,c
Microcline, $KAlSi_3O_8$	c	c	c
Zircon, $ZrSiO_4$	c	a,c	
Clay Minerals			
Kaolilite, $Al_2Si_2O_5(OH)_4$	a,b,c	a,b,c	a,c
Illite, $K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$	c	a,c	c
Chlorite, $Na_{0.5}Al_6(Si,Al)_8O_{20}(OH)_{10}.H_2O$			c
Sulphides		c	
Galena, PbS			
Sphalerite, ZnS		c	c
Carbonates	a,b,c	a,b,c	a,b,c
Calcite, $CaCO_3$			
Dolomite, $CaMg(CO_3)_2$	c	c	
Sulphates	a,b,c	a,b,c	a,b,c
Gypsum, $Ca[SO_4]\cdot 2H_2O$			
Barite, $BaSO_4$	b,c	b,c	c
Jarosite, $KFe_3^{3+}(SO_4)_2(OH)_6$	c		b,c
Hexahydrite, $MgSO_4\cdot 6H_2O$	c	b,c	b,c
Alunogen, $Al_2(SO_4)_3.17H_2O$	b	a,b	b
Oxides and hydroxides	c		
Anatase, TiO_2			
Brucite, $Mg(OH)_3$		c	
Goethite, $Fe(OH)_3$	c	c	a,b,c
Gibbsite, $Al(OH)_3$		c	
Hematite, Fe_2O_3	c	a,b,c	b,c
Magnetite, Fe_2O_3	a,b,c	a,b,c	a,b,c
Rutile, TiO_2	a,c	a,b,c	b,c

regular monitoring of air quality at studied stations is recommended to monitor and improve the air quality. Though commuters may be exposed for a short period of time, workers can be exposed to high PM concentrations depending on work schedule and railway system locations. Regular monitoring of indoor air quality is recommended to monitor and identify stations with the worst air quality. Ventilation system improvement, station redesign, regular cleaning, and proper maintenance should be done at such stations to improve the indoor air quality of railway system and to prevent health risks for railway system commuters and workers. Improvement in subway design to increase the ventilation, application of materials and technologies (e.g. rubber wheel systems and electric braking systems), installation of platform screen doors, regular cleaning of indoor environment of subway stations can all help to improve indoor air quality at railway system.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2020.12.010.

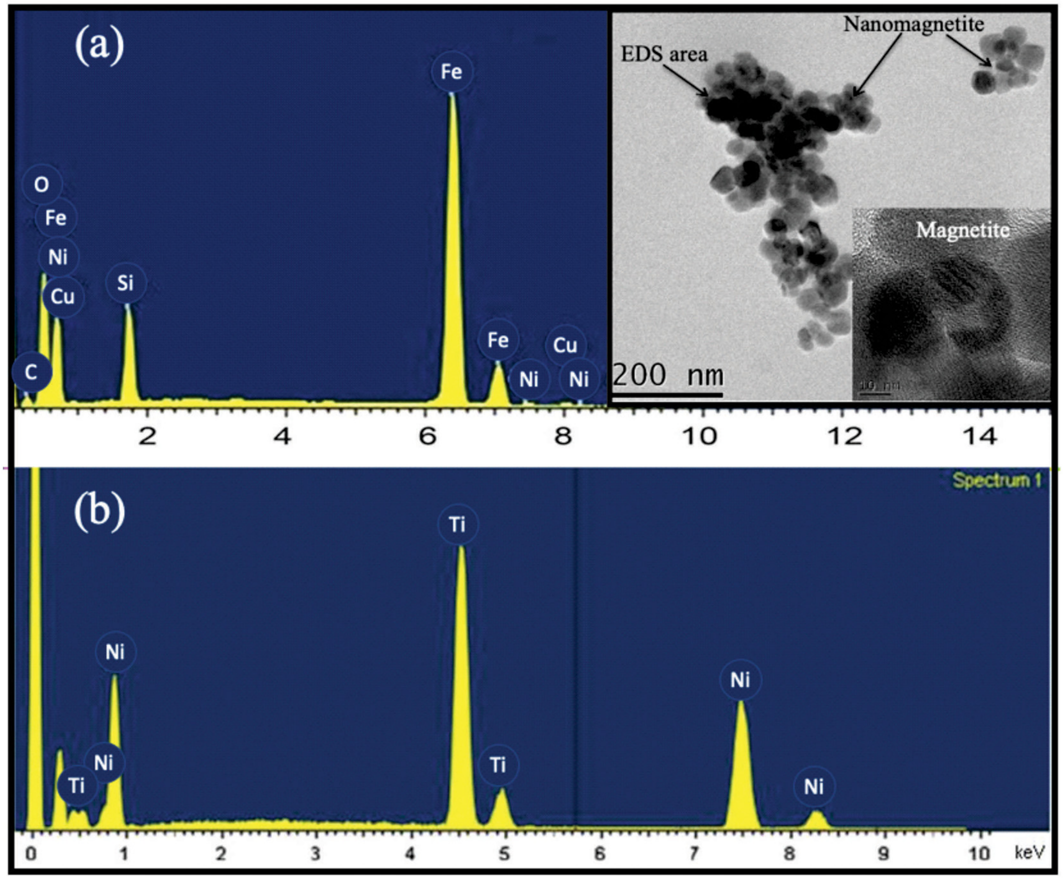

Fig. 8. (a) Nanomagnetites associated with Ni, Si, and metals obtained in the Rodoviária station and (b) Anatase (Ti-NPs with Ni) obtained in the Fátima station.

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