Environmental Research 146 (2016) 35–46

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Factors controlling air quality in different European subway systems

Vânia Martins [a,b,*], Teresa Moreno [a], Luís Mendes [c,d], Konstantinos Eleftheriadis [c], Evangelia Diapouli [c], Célia A. Alves [e], Márcio Duarte [e], Eladio de Miguel [f], Marta Capdevila [f], Xavier Querol [a], María Cruz Minguillón [a]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain
[c] Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, Environmental Radioactivity Lab, N.C.S.R. "Demokritos", Agia Paraskevi, 15310 Athens, Greece
[d] University of the Aegean, Department of Environment, 81100 Mytilene, Greece
[e] Centre for Environmental and Marine Studies (CESAM), Department of Environment, University of Aveiro, 3810-193 Aveiro, Portugal
[f] Transports Metropolitans de Barcelona, TMB Santa Eulàlia, Av. Del Metro s/n L'Hospitalet de Llobregat, 08902, Spain

ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form
2 December 2015
Accepted 8 December 2015
Available online 22 December 2015

Keywords:
Exposure
Subway stations
Trains
$PM_{2.5}$
Commuting

ABSTRACT

Sampling campaigns using the same equipment and methodology were conducted to assess and compare the air quality at three South European subway systems (Barcelona, Athens and Oporto), focusing on concentrations and chemical composition of $PM_{2.5}$ on subway platforms, as well as $PM_{2.5}$ concentrations inside trains. Experimental results showed that the mean $PM_{2.5}$ concentrations widely varied among the European subway systems, and even among different platforms within the same underground system, which might be associated to distinct station and tunnel designs and ventilation systems. In all cases $PM_{2.5}$ concentrations on the platforms were higher than those in the urban ambient air, evidencing that there is generation of $PM_{2.5}$ associated with the subway systems operation. Subway $PM_{2.5}$ consisted of elemental iron, total carbon, crustal matter, secondary inorganic compounds, insoluble sulphate, halite and trace elements. Of all metals, Fe was the most abundant, accounting for 29–43% of the total $PM_{2.5}$ mass (41–61% if Fe_2O_3 is considered), indicating the existence of an Fe source in the subway system, which could have its origin in mechanical friction and wear processes between rails, wheels and brakes. The trace elements with the highest enrichment in the subway $PM_{2.5}$ were Ba, Cu, Mn, Zn, Cr, Sb, Sr, Ni, Sn, Co, Zr and Mo. Similar $PM_{2.5}$ diurnal trends were observed on platforms from different subway systems, with higher concentrations during subway operating hours than during the transport service interruption, and lower levels on weekends than on weekdays. $PM_{2.5}$ concentrations depended largely on the operation and frequency of the trains and the ventilation system, and were lower inside the trains, when air conditioning system was operating properly, than on the platforms. However, the $PM_{2.5}$ concentrations increased considerably when the train windows were open. The $PM_{2.5}$ levels inside the trains decreased with the trains passage in aboveground sections.

1. Introduction

Underground subway is one of the major transportation modes in most metropolitan areas worldwide, due to its convenience, safety, efficiency, high speed, large transport capacity (in terms of number of commuters) and low emission system (electrical). Furthermore the shift from private transportation mode to subway system allows reducing road traffic congestion. It is also a distinctive microenvironment since it is a confined space poorly ventilated that may promote the concentration of pollutants both from the outside atmosphere and also generated internally (Nieuwenhuijsen et al., 2007).

Particulate matter (PM) in the underground subway microenvironments are of great concern since many people spend considerable time commuting on a daily basis, and the exposure to this pollutant in the subway systems has been linked to adverse human health effects (e.g. Bachoual et al., 2007; Bigert et al., 2008; Salma et al., 2009). Exposure studies in subways from different countries have reported concentrations of PM in subway systems usually several times higher than in the outdoor environments (see Martins et al., 2015b and references therein). Furthermore, there are some evidences that the PM of subway air is substantially different from the above outdoor air or other transport

* Corresponding author at: Institute of Environmental Assessment and Water Research (IDAEA), CSIC, C/ Jordi Girona 18-26, 08034 Barcelona, Spain.
E-mail address: vania.ferreira@idaea.csic.es (V. Martins).

http://dx.doi.org/10.1016/j.envres.2015.12.007

air, in terms of number, mass, size, concentration and chemical composition (e.g. Adams et al., 2001; Furuya et al., 2001; Martins et al., 2016; Moreno et al., 2015b; Querol et al., 2012; Salma et al., 2007).

Particles in the subway system are mainly generated by mechanical wear and friction processes at the rail–wheel–brake interfaces, and at the interface between power conductive materials providing electricity and the current collectors attached to trains, as well as by the erosion of construction material and resuspension (Jung et al., 2010; Loxham et al., 2013; Sundh et al., 2009). A railway is generally powered either by an overhead catenary with the current drawn through the contact material of the pantograph or by a third rail with the current drawn through the current-collecting component (contact shoe) on the train. Since PM emission sources in the underground subway systems are very different from those in the aboveground environment, the chemical composition of PM is also distinct. To know the chemical composition of PM on a subway platform is an essential prerequisite for understanding the indoor air quality of the subway system and subsequently to access on remediation measures. The air quality measurements at these microenvironments can also provide relevant information to evaluate the potential for health effects from exposures to PM as well as the effectiveness of ventilation systems (Martins et al., 2015a, 2015b and references therein). Several studies have reported Fe as the major chemical element constituting underground subway PM, while significant amounts of Mn, Si, Cr, Cu, Ba, Ca, Zn, Ni and K have been also observed (Aarnio et al., 2005; Chillrud et al., 2004; Martins et al., 2016; Murruni et al., 2009; Nieuwenhuijsen et al., 2007; Querol et al., 2012; Salma et al., 2009, 2007). Wear and friction processes initially produce iron-metal particles that react with oxygen in the air resulting in the formation of iron oxides (Guo et al., 2014; Jung et al., 2010; Moreno et al., 2015b). Moreover, the chemical composition of PM derived by sample analysis can be further utilised for the assessment of its source inventory (Martins et al., 2016; Park et al., 2014). The determination of the concentration of trace metals (Ba, Mn, Cr, Cu, Ni, Zn, etc.) is indispensable for risk assessment and although the trace metals represent only about 1% of the total PM, they can play a critical role in the source identification (Lim et al., 2010).

Concentration and chemical composition of subway particles depend on various factors, such as: outdoor air quality; differences in the depth and design of the stations and tunnels; system age; composition of wheels, rail tracks, brake pads and current supply materials; power system; braking mechanisms; train speed and frequency; passenger densities; ventilation and air conditioning systems; cleaning frequency; and other operational conditions (Johansson and Johansson, 2003; Kwon et al., 2015; Martins et al., 2016, 2015b; Moreno et al., 2014; Park and Ha, 2008; Ripanucci et al., 2006; Salma et al., 2007). Furthermore, results are not always directly comparable because of differences in sampling and measurement methods, data and sample analyses and the type of environment studied (Kim et al., 2008; Nieuwenhuijsen et al., 2007).

Starting from this consideration, the aim of this study was to assess the exposure concentrations and chemical composition of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) in the subway systems of three South European cities, including Barcelona (Spain), Athens (Greece) and Oporto (Portugal), to better understand the main factors controlling air quality in this environment. The study was based on air quality campaigns following the same sampling, measurement and analysis methods, and data treatment. Specific objectives of the study included: (1) determining concentrations of $PM_{2.5}$ and their chemical composition in selected subway stations; (2) comparing the levels of $PM_{2.5}$ and chemical elements among subway systems; (3) comparing $PM_{2.5}$ exposure levels on the subway platforms with outdoor levels; (4) studying the spatial and temporal variations in $PM_{2.5}$ in the subway stations; and (5) evaluating real-time variations in $PM_{2.5}$ levels inside trains.

2. Experimental section

2.1. Sampling methodology

The Barcelona subway system is one of the oldest underground transport systems in Europe, with its first line beginning operation in 1924. It comprises 8 lines, numbered L1 to L5 and L9 to L11, covering 102 km of route and 139 stations. The system carries around 376 million passengers a year and about 50% of people choose it as their mode of public transport in the city. The Athens Metro is a rapid-transit system in Greece. Line 1 was a conventional steam railway constructed in 1869, which was converted to electrical railway in 1904, and runs almost entirely aboveground. Lines 2 and 3 opened in 2000 and are underground. The entire system is 82.7 km long, with 61 stations (new stations are added continually) and is used by about 494 million passengers per year. The Oporto subway system is a light rail network with its first line opened in 2002. The network has 6 lines (LA, LB, LC, LD, LE and LF) and currently has a total of 81 operational stations across 67 km of double track commercial line. The system is underground in central Oporto (8 km of the network) and aboveground into the city's suburbs, carrying about 57 million passengers per year.

In the three South European subway systems (Barcelona, Athens and Oporto), aerosol measurements were performed both on the subway platforms and inside the trains. One station platform was selected from each of the subway systems to determine the exposure concentrations and chemical composition of $PM_{2.5}$. Additional real-time measurements were carried out on the platforms of 24 stations from Barcelona subway, and 5 stations from both Athens and Oporto subways. Inside the trains the samplings were performed in 5 lines in Barcelona, and 2 lines both in Athens and Oporto. Whereas the measurements performed in the Barcelona subway system have been published previously (Martins et al., 2016, 2015b), the measurement campaigns in Athens and Oporto were carried out exclusively for this study, as well as the simultaneous outdoor aerosol measurements performed at these two cities. Information on the subway systems, selected stations as well as the characteristics of the measurements carried out are summarised in Table 1.

2.1.1. Subway platforms

Continuous aerosol sampling and monitoring was performed on one station platform selected from each of the subway systems (Barcelona, Athens and Oporto). For comparison purposes, the measurements were performed on the platform of stations with the same architectural design: wide tunnel with two rail tracks in the middle with lateral platforms.

For the collection of $PM_{2.5}$ samples on the subway platforms different instruments were used among subway systems. In Barcelona and Athens campaigns the samplings were conducted using a High Volume Sampler (HVS, Model CAV-A/MSb, MCV S.A.) with a $PM_{2.5}$ head operating at an airflow rate of 30 $m^3\ h^{-1}$. In Oporto campaign a high volume sampler (TE-5200, Tisch Environmental Inc.) operating at 67.8 $m^3\ h^{-1}$ was used to collect coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) particles. However, for purposes of comparison among the three subway systems only the $PM_{2.5}$ data were used in this study. A comparison of $PM_{2.5}$ concentrations measured with both high volume samplers presented a squared Pearson correlation (R^2) equal to 0.91 and a linear regression with a slope close to unity. The particles were collected daily on quartz microfibre

Table 1
Sampling subway systems information.

Subway system	Barcelona	Athens	Oporto
Began operation	1924	1869	2002
Network extension (km)	102	83	67
Stations number	139	61 (41 are underground)	81 (only 14 stations are underground)
Ventilation	Forced and natural	Natural	Natural
Stations with ballast[a]	Yes	No	Yes
Lines	8	3	6
Operating hours	5:00 to 00:00	5:30 to 00:30	6:00 to 01:00
Passengers' number (million year^{-1})	375,7	493,8	56,9
Power supply (electric)	Overhead wire	Third rail[b]	Overhead wire
Wheels composition	Metal	Metal	Metal
Air-conditioned trains	Yes	Yes	Yes
Ability to open the windows in the trains	No	Yes	No
Sampling period	1 Jul–30 Jul 2013 10 Feb–10 Mar 2014	28 Apr–19 May 2014	27 Oct–14 Nov 2014
Selected station (building year)	Santa Coloma (1983)	Nomismatokopio (2009)	Bolhão (2002)[c]
Mean train frequency (trains h^{-1})[d]	29	21	37
Nº of additional selected platforms	24	5	5
Measurements inside trains (nº of lines)	5	2	2

[a] None of the selected stations have ballast.
[b] Third rail in the underground sections.
[c] Bolhão station is followed by an aboveground and an underground station in opposite extremes.
[d] Mean train frequency in the selected station.

filters during the subway operating hours (see Table 1). Field filter blanks were also collected. A real-time laser photometer (DustTrak, Model 8533, TSI) for the monitoring of $PM_{2.5}$ mass concentration was simultaneously operated at 5-minute time resolution during 24 h day^{-1}. $PM_{2.5}$ concentrations provided by DustTrak monitor were corrected against the in-situ and simultaneous gravimetric $PM_{2.5}$ measurements for each subway station. Fig. S1 displays the comparison of $PM_{2.5}$ concentrations measured with the DustTrak and those determined gravimetrically in the selected platform of each subway system.

The location of the sampling and monitoring devices was chosen as a compromise between meeting conditions for undisturbed measurement, obstructing pedestrian traffic as little as possible, and the availability of power supply. The aerosol inlets were placed at roughly 1.5 m above the ground level.

2.1.2. Additional platform measurements

Additional platforms were selected to study the temporal and spatial variations in the $PM_{2.5}$ concentrations. A total of 24 platforms from Barcelona subway system, 5 platforms from Athens subway system, and 5 platforms from Oporto subway system were studied. In Barcelona the platforms were those with the most common station designs present in the subway system: a wide tunnel with two rail tracks both with and without a middle wall, and a single narrow tunnel with one rail track both without and with a glass wall with platform screen doors (PSDs) separating the rail from the platform. The selected Athens subway stations have two different architectural designs: (i) a wide tunnel with two rail tracks in the middle with lateral platforms or (ii) a wide tunnel with two rail tracks with a central platform (only Monastiraki station selected with this design). In Oporto subway system all lines are double track with lateral platforms.

Measurements were performed at 4 positions approximately equidistant along the platform, during 1 h divided into periods of 15 min. Real-time $PM_{2.5}$ mass concentrations were registered using a DustTrak monitor set at 5-second time resolution. All measurements were carried out during weekdays after 9 a.m. The times of trains entering and departing the station were manually recorded. The described procedure was conducted twice at each subway platform, making a total 96 (48 at each period campaign) platform measurements in Barcelona and 10 platform measurements in each Athens and Oporto subway systems.

2.1.3. Inside the trains

Measurements inside the trains from 5 lines in Barcelona subway system (L1, L2, L3, L4 and L5), 2 lines in Athens (L2 and L3), and 2 lines in Oporto (LA and LD) were performed. Each of the lines was studied according to the following protocol: $PM_{2.5}$ concentrations were measured using a DustTrak monitor and CO_2 concentrations were monitored by means of an Indoor Air Quality meter (IAQ-Calc, Model 7545, TSI) in the middle of the central carriage of the train during a two-ways trip along the whole subway line. The total duration of the trip depended on the length of the line and ranged from 45 to 90 min approximately. Both instruments were set at 5-second time resolution. The instrumentation was transported in a bag with the air uptake inlet placed at shoulder height when sitting. The measurements were carried out after 10 a.m. on weekdays, and they were performed twice at each of the selected lines, making a total of 18 measurements. A manual record of the time when train doors open and close was performed. The effect of the carriage windows left open in the Athens lines and the differences between underground and aboveground sections in the Oporto lines were also analysed.

2.1.4. Outdoor environment

For comparison purposes, ambient $PM_{2.5}$ samples were collected concurrently at an urban station, which was used as a reference site. The Barcelona and Athens outdoor measurements were performed using a HVS in the sampling urban background stations of Palau Reial (Rivas et al., 2014) and Demokritos (Eleftheriadis et al., 2014), respectively. The measurements were carried out during 24 h every third day at Palau Reial station and 19 h (subway operating hours, see Table 1) every second day at Demokritos station. The Oporto outdoor measurements were conducted in the urban traffic station of Francisco Sá Carneiro – Campanhã with two low-volume Tecora samplers (TCR, Model 2.004.01) operating at a flow of 2.3 m^3 h^{-1}. $PM_{2.5}$ samples were collected onto quartz filters (47 mm diameter) in both TCR samplers simultaneously during 19 h (subway operating hours, see Table 1) every second day. This urban traffic station was selected because it is frequently used for air quality studies in Oporto (Amato et al., 2015). A map indicating the positions of the outdoor

sampling stations and the selected subway stations is shown in Fig. S2.

2.2. $PM_{2.5}$ mass concentrations and chemical composition

The filters were equilibrated for at least 48 h in a conditioned room (20 °C and 50% relative humidity) and then weighed before and after sampling to determine gravimetric $PM_{2.5}$ mass concentrations. Once the gravimetric determination was performed the filters were cut into several sections and analysed for the determination of the chemical composition of $PM_{2.5}$.

The first section was acid digested and subsequently analysed by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS) to determine major and trace elements, respectively. The second section was extracted using deionized water and the soluble fraction was dispensed for ion chromatography (IC) analysis to determine water-soluble anions (Cl^-, SO_4^{2-} and NO_3^-), and for specific electrode (SE) analysis to obtain the ammonium (NH_4^+) concentrations. Another portion was used to determine the total carbon (TC) concentration by means of thermal-optical methods using a Lab OC-EC Aerosol Analyser (Sunset Laboratory Inc.). The chemical species concentrations in $PM_{2.5}$ samples, blank filters, and standard samples were determined for quality control purposes under the same analytical conditions. The final concentrations were calculated after the subtraction of analytical blank values from the corresponding samples. A detailed description of analytical procedures and experimental set-up used for chemical analyses has been reported by Querol et al. (2012).

In order to have $PM_{2.5}$ characterisation representative of the whole platform, the $PM_{2.5}$ mass and chemical components concentrations reported in this study are those corrected for spatial variation at each selected platform (Santa Coloma, Nomismatokopio and Bolhão), based on the measurements described in Section 2.1.2., where the $PM_{2.5}$ concentrations were measured at 4 different positions along the platform. On the station platforms selected for carried out the continuous aerosol sampling and monitoring, one of the 4 measurement positions coincided with the sampling site (devices location). Hence, the concentrations measured at the selected platforms were multiplied by a $PM_{2.5}$ correction factor for spatial variation. These correction factors were obtained by dividing the average $PM_{2.5}$ concentrations along the platform (including the concentrations recorded at the 4 positions) by the average $PM_{2.5}$ concentrations at the selected sampling point for continuous measurements (gravimetric and chemical composition $PM_{2.5}$). In general, due to the station design, the concentration gradient along the platform was small (correction factors were very close to 1), since the air mixing is promoted by trains moving along the platform and by ventilation. Therefore, the concentrations measured at the sampling sites were very similar to the exposure levels of commuters waiting elsewhere along the platform.

3. Results and discussion

3.1. $PM_{2.5}$ mass concentrations on subway platforms

Mean $PM_{2.5}$ gravimetric concentrations and standard deviations (sd) on the subway platforms and in the corresponding outdoor ambient air are presented in Fig. 1. The lowest mean $PM_{2.5}$ concentration was found in Santa Coloma station with mean ± sd of $58.3 \pm 13.7\ \mu g\ m^{-3}$, while the highest $PM_{2.5}$ concentration was recorded in Bolhão station ($83.7 \pm 45.7\ \mu g\ m^{-3}$). In the Nomismatokopio station a mean $PM_{2.5}$ concentration of $68.3 \pm 11.3\ \mu g\ m^{-3}$ was obtained. These results may be associated to differences in the ventilation system among subway systems. Based on managers' information of each subway system, the Barcelona subway system is equipped with a ventilation system in all its length, whereas in both Athens and Oporto subway systems only natural ventilation occurs, with air exchange with the outdoor air happening mainly through draught relief outlets ("blast shafts") in the tunnels adjacent to the platform. Thus, the main ventilation flow of the platform was due to train movements through the tunnels to the platform. The forced ventilation is a relevant factor to improve the air quality within the subway system (Martins et al., 2015b). The majority of the underground sections in the Oporto subway system are composed by curved or/and sloping rail tracks, which may imply higher emissions from the rail–wheel–brake interfaces while trains are stopping on the platform (Jung et al., 2010) resulting on higher particle mass concentration on the platform. The frequency of train passages in the Oporto subway station is higher than in the stations of Barcelona and Athens, as trains from 5 different lines (LA, LB, LC, LE and LF) pass through Bolhão station using a common platform whereas in Barcelona and Athens subway systems only trains of one line circulate at each studied station.

Moreover, other factors not studied such as the differences in the engineering and power systems, braking mechanisms, technical and operational conditions, dimensions of the underground spaces, normal cleaning frequency, and passenger densities could also be reasons of differences in these results. For example, Mugica-Álvarez et al. (2012) and Johansson and Johansson (2003) reported that the subway cleaning operations decreased the mass concentrations of airborne particles in the Mexico city and Stockholm subway systems, respectively, due to the removal of deposited particles and hence the decrease in the resuspension of these particles with the consequent decrease in the ambient PM concentrations. Besides, the type of braking (either pneumatic or/and electric brakes) and power supply systems (overhead wire or third rail) have been considered as the major differences influencing the particulate air quality in some subway systems (Fromme et al., 1998; Ripanucci et al., 2006; Seaton et al., 2005).

The outdoor mean $PM_{2.5}$ concentrations were 15.7 ± 3.5, 9.9 ± 3.0 and $37.5 \pm 14.6\ \mu g\ m^{-3}$, for Barcelona, Athens and Oporto, respectively. Thus, the $PM_{2.5}$ concentrations on the platforms were on average 3.7, 6.9 and 2.2 times higher than those

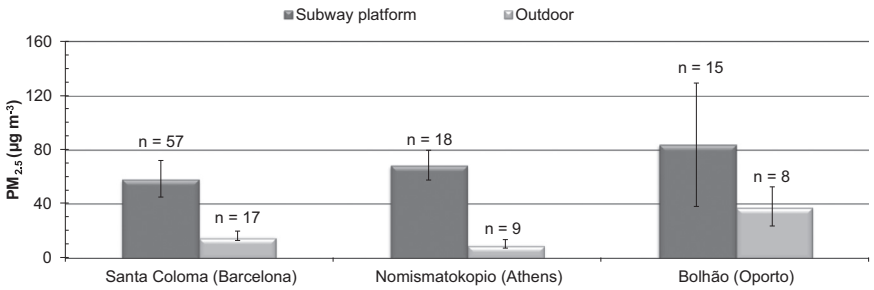

Fig. 1. Mean $PM_{2.5}$ gravimetric concentrations and standard deviations on the subway platforms and outdoor. (n – number of samples).

simultaneously recorded in ambient air, respectively (Fig. 1). Similar results have been reported in other subway systems, such as in London (Adams et al., 2001), Los Angeles (Kam et al., 2011), Milan (Colombi et al., 2013), Rome (Ripanucci et al., 2006), Stockholm (Johansson and Johansson, 2003) and Tehran (Kamani et al., 2014). The highest ambient $PM_{2.5}$ concentrations were found in Oporto because the measurements were conducted in an urban traffic station, whereas urban background stations were used in Barcelona and Athens.

The $PM_{2.5}$ mass concentrations in the subway stations and in ambient air were strongly correlated for Oporto (squared Pearson's correlation coefficient $R^2=0.74$) and Athens ($R^2=0.60$), indicating that the PM levels at the Bolhão and Nomismatokopio stations were markedly influenced by outdoor PM (see Fig. S3). Therefore, there is an important influence of airborne particles introduced through the ventilation grids, corridors and by commuters. The Bolhão station is followed by an aboveground station which favours the air exchange with outdoor environment. Hence, the highest $PM_{2.5}$ concentrations observed in the Bolhão station can also be explained with its location in the central area of the city (Fig. S2). Cheng et al. (2008) also suggested that PM can originate outside in ambient air and enter the stations via the subway tunnels and accumulate in the underground system, thereby inducing relatively high PM levels. In Barcelona there was no clear

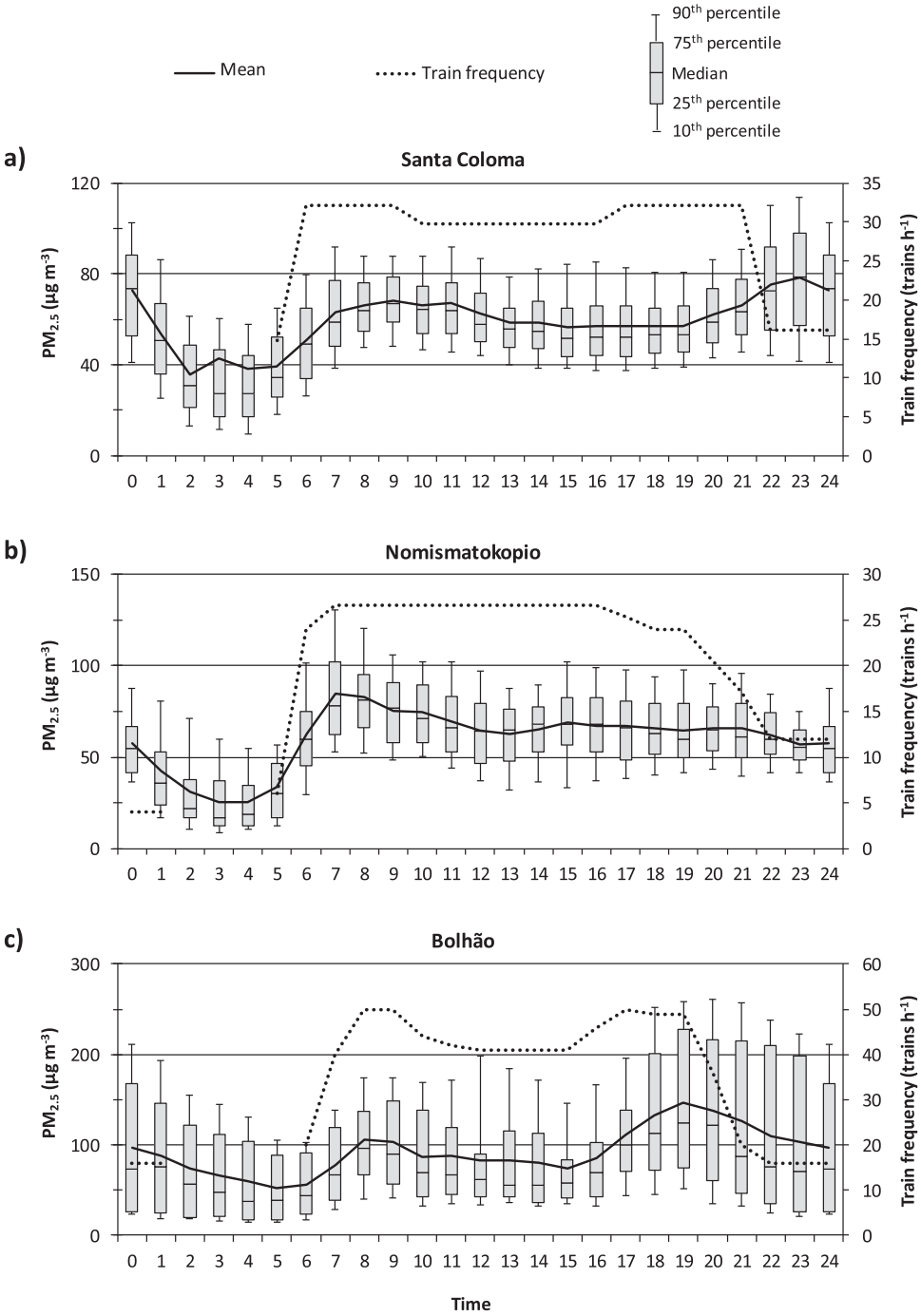

Fig. 2. Temporal variation of mean 1 h $PM_{2.5}$ mass concentrations and train frequency on the weekdays in the Santa Coloma (a), Nomismatokopio (b) and Bolhão (c) subway stations. The grey box represents the median, and the 25th and 75th percentile of hourly $PM_{2.5}$ concentrations. The whiskers show the 10th and 90th percentile of hourly $PM_{2.5}$ concentrations. Note the different scales for each of the three plots.

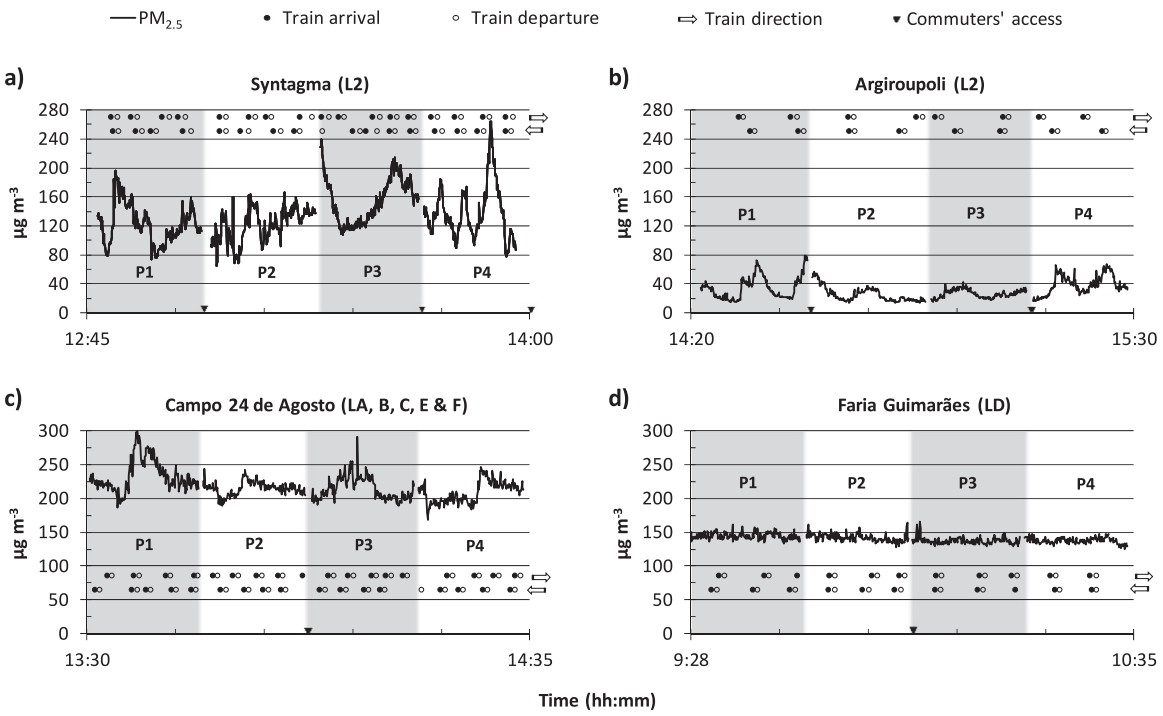

Fig. 3. Profiles of $PM_{2.5}$ concentrations (μg m^{-3}) on platforms from Athens subway (a and b) and Oporto subway (c and d) at 4 different positions (P1, P2, P3 and P4). Train arrival/departure and direction are indicated. Locations of commuters' accesses to platforms are represented either between two points (P) or in the extreme of a point. L is the line belonging to each station.

correlation (R^2=0.08), evidencing that in the Santa Coloma station the outdoor $PM_{2.5}$ concentrations do not drive the subway air quality, whereas the emissions generated within the subway system do.

3.1.1. Daily pattern

The $PM_{2.5}$ mass concentrations discussed in this section are those determined by the DustTrak monitor after being corrected against the gravimetric measurements (see Fig. S1). Fig. 2 shows the mean weekdays daily pattern for 1 h $PM_{2.5}$ mass concentrations and train frequency in the Santa Coloma (a), Nomismatokopio (b) and Bolhão (c) stations. Similar daily trends were observed among the subway platforms. The $PM_{2.5}$ mass concentration during the day varied largely depending on the train frequency. An increase in $PM_{2.5}$ mass concentration was marked in the morning rush hour period, between 07:00 and 10:00 h, which was attributable not only to the influx of commuters but also to the higher train frequency; the motion of the trains promotes the resuspension of $PM_{2.5}$ and their generation due to the abrasion of rail tracks, wheels, brake pads and current supply materials, and the movement of the commuters leads mainly to the $PM_{2.5}$ resuspension. Afterwards, $PM_{2.5}$ mass concentration varied slightly with relatively low levels until late afternoon. An increase in the $PM_{2.5}$ concentrations was registered during the evening rush hours (from 18:00 to 21:00 h) at both Santa Coloma and Bolhão stations. However, this phenomenon was much more pronounced in the Bolhão station where the increase in train frequency was higher (Fig. 2). In Nomismatokopio this trend was not observed because train frequency decreased during these hours. In the case of Santa Coloma station there was also a late peak (22:00–24:00 h) which was attributable to the changes in the ventilation settings (Martins et al., 2015b). During the night, there was a continuous decrease in $PM_{2.5}$ concentrations due to transport service interruption for several hours, which brought about settlement of a large quantity of $PM_{2.5}$. Salma et al. (2007) reported a similar behaviour in the continuous measurement of PM_{10} levels in the Budapest subway, where two peaks were observed, one at 7:00 h and other at 17:00 h approximately, with a substantial decrease during the night. In sum, the variations of $PM_{2.5}$ levels depend largely on the operation and frequency of the trains and the ventilation system, and therefore, the personal exposure to $PM_{2.5}$ concentrations is dependent on the time of the day used to commute.

Furthermore, the $PM_{2.5}$ concentrations among sampling days were much more variable in the Bolhão station than in the other two stations (see interpercentile range in Fig. 2), because during the sampling period the weather conditions and consequently the $PM_{2.5}$ concentrations in the ambient air were considerably variable (see Fig. S4). These factors are important because the air quality within the Bolhão station is markedly influenced by the outdoor air, as discussed previously.

Daily mean, standard deviation, minimum and maximum $PM_{2.5}$ concentrations for the 3 monitored European platforms during the subway operating hours are displayed in Table S1 for weekdays and weekends. The concentrations of $PM_{2.5}$ on the weekdays were on average 1.4 times higher than those on weekends, probably due to the lower number of commuters and frequency of trains. Similar results have been observed in studies conducted in other subway systems (Aarnio et al., 2005; Johansson and Johansson, 2003; Mugica-Álvarez et al., 2012; Raut et al., 2009). The difference between the weekdays and weekends in $PM_{2.5}$ concentrations were more pronounced in the Bolhão station and less in the Nomismatokopio station. In summary, the experimental results indicate the presence of $PM_{2.5}$ sources in the subway system, which lead to higher concentrations during train operating hours than at night when the system is closed and on weekdays more than on weekends.

3.1.2. Temporal–spatial variations

$PM_{2.5}$ concentrations measurements were performed at 4 different positions along the platforms in the 3 European subway systems. The results for Barcelona subway have been reported by

Martins et al. (2015b), and will only be summarised here. Experimentally, $PM_{2.5}$ concentrations in the stations of Barcelona subway system showed clear differences over time and location on the platform, reflecting the influence of the ventilation settings, passage and frequency of the trains, design of the stations and tunnels and location of passengers' access to the platforms.

Mean $PM_{2.5}$ concentrations and standard deviations at each studied station in Athens and Oporto subway systems, along the 4 different positions, are summarised in Table S2, whereas the specific cases are represented in Fig. 3. In some cases $PM_{2.5}$ concentrations on the platforms increased when the train entered the platform pushing in polluted air from the tunnel (by piston effect) and decrease when it departs as the train moves polluted air from the station, renewing the air on the platform (Fig. 3a–c). The same phenomenon was described for the Barcelona subway (Martins et al., 2015b). In some subway stations in Barcelona, higher $PM_{2.5}$ concentrations were observed in the train entry edges and in the areas closer to the commuters' access to the platforms. However, in the Athens and Oporto cases this was not clearly observed because there were day-to-day fluctuations in $PM_{2.5}$ concentrations along the platforms (see Table S2).

In the Syntagma station (Fig. 3a) $PM_{2.5}$ concentrations were

Table 2
Mean concentrations of $PM_{2.5}$ and elemental components on the subway platforms and in the corresponding outdoor ambient air. (sd – standard deviation; TC – total carbon; ws – water soluble).

	Barcelona				**Athens**				**Oporto**			
	Subway platform		**Outdoor**		**Subway platform**		**Outdoor**		**Subway platform**		**Outdoor**	
	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd
μg m^{-3}												
$PM_{2.5}$	58.3	13.7	11.0	3.5	68.3	11.3	9.9	3.0	83.7	45.7	37.5	14.6
TC	13.2	5.4	3.8	1.1	6.2	1.1	1.7	0.7	11.3	7.6	14.5	7.8
Fe	16.7	4.0	0.1	< 0.1	29.1	5.3	0.1	< 0.1	32.9	18.9	0.4	0.3
Crustal matter (μg m^{-3})												
Al_2O_3	0.6	0.3	0.1	0.1	0.6	0.1	0.2	0.1	1.0	0.8	0.4	0.5
SiO_2	1.7	1.0	0.4	0.3	1.8	0.4	0.5	0.2	2.9	2.5	1.2	1.4
Ca	1.1	0.6	0.1	< 0.1	1.2	0.3	0.3	0.2	0.4	0.3	0.1	0.1
Mg	0.4	0.1	< 0.1	< 0.1	0.2	< 0.1	0.1	< 0.1	0.2	0.1	0.1	< 0.1
CO_3^{2-}	1.6	1.0	0.1	0.1	1.9	0.5	0.5	0.3	0.7	0.4	0.2	0.2
Ti	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
K	0.2	0.2	0.1	< 0.1	0.2	< 0.1	0.1	< 0.1	0.6	0.4	0.3	0.3
P	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Secondary inorganic compounds (μg m^{-3})												
ws-NO_3^-	0.7	0.7	0.5	0.5	0.8	0.3	0.4	0.1	0.8	0.5	5.3	3.8
ws-SO_4^{2-}	1.8	0.9	2.4	1.7	2.8	1.5	2.7	1.5	1.5	0.6	3.5	4.5
ws-NH_4^+	0.4	0.3	1.0	0.6	0.7	0.5	0.8	0.6	0.2	0.2	3.7	2.1
Insoluble sulphate (μg m^{-3})												
SO_4^{2-}	0.9	0.3	0.1	0.1	0.7	0.3	0.1	0.1	0.4	0.4	0.7	0.5
Halite (μg m^{-3})												
Na	0.1	0.1	0.1	< 0.1	0.3	0.2	0.2	0.2	1.5	0.6	0.5	0.4
Cl	0.2	0.2	0.1	0.1	0.3	0.1	0.2	0.1	2.4	1.3	5.9	4.8
Trace elements (ng m^{-3})												
Ba	700.8	240.2	3.2	2.0	85.8	28.6	5.0	4.0	53.2	41.9	9.6	6.3
Cu	101.2	26.4	6.8	2.5	58.7	12.4	2.5	1.7	404.8	235.1	13.8	8.2
Mn	161.9	54.9	5.2	2.5	248.6	42.8	2.3	0.9	287.3	174.5	4.7	3.6
Zn	163.3	58.4	63.4	44.3	148.5	34.9	14.3	5.2	86.8	59.0	44.5	30.0
Cr	17.3	6.6	1.7	1.0	134.0	20.6	1.3	0.7	21.2	15.0	1.4	1.1
Sb	2.4	1.3	0.8	0.3	2.9	0.9	0.5	0.2	38.4	17.4	2.3	1.2
Sr	16.5	5.1	0.6	0.4	3.6	0.8	0.7	0.3	2.4	1.6	0.9	0.8
Mo	20.3	9.6	11.0	12.5	143.5	77.8	6.8	6.6	0.1	0.4	0.9	1.2
Zr	8.4	2.5	5.6	3.1	8.5	1.6	1.3	1.3	12.0	3.8	9.4	1.9
Ni	8.6	2.7	2.0	1.0	15.7	2.8	1.6	0.9	16.7	11.5	0.8	1.0
Pb	7.9	4.2	8.0	4.1	5.7	2.9	2.6	1.1	11.4	10.3	8.4	6.6
Sn	6.6	2.2	2.3	1.3	9.0	1.5	1.1	0.6	8.0	6.2	5.9	3.2
V	5.3	1.9	4.6	3.1	7.2	3.2	3.0	2.4	2.9	2.2	1.3	1.5
As	1.3	0.3	0.3	0.1	1.8	0.3	0.2	0.2	1.4	0.8	0.5	0.3
Co	1.0	0.3	0.1	< 0.1	1.7	0.3	0.1	< 0.1	1.1	0.8	0.1	0.1
Li	0.4	0.2	0.1	< 0.1	0.2	0.1	0.1	< 0.1	0.6	0.4	0.2	0.2
Ga	0.2	0.1	0.1	< 0.1	0.4	0.1	< 0.1	< 0.1	0.3	0.2	0.1	0.1
Ge	0.4	0.4	< 0.1	< 0.1	0.3	0.2	< 0.1	< 0.1	0.3	0.2	< 0.1	< 0.1
Se	0.3	0.1	0.2	0.2	0.3	0.2	0.3	0.1	0.3	0.2	< 0.1	0.1
Rb	0.6	0.3	0.2	0.1	0.5	0.1	0.2	0.1	1.6	1.1	0.9	0.7
Y	0.2	0.2	0.2	0.1	0.3	0.1	0.2	0.2	0.1	0.1	< 0.1	< 0.1
Nb	0.9	0.3	0.1	0.2	0.8	0.1	0.1	0.2	0.3	0.1	0.6	0.3
Cd	0.1	0.1	0.2	0.1	0.3	0.1	0.1	< 0.1	0.2	0.2	0.2	0.1
La	0.4	0.1	0.1	0.1	0.4	0.2	0.2	0.2	0.3	0.3	0.1	0.1
Ce	0.7	0.3	0.2	0.2	0.6	0.2	0.2	0.1	0.7	0.6	0.5	0.3
Pr	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	0.1
Nd	0.2	0.1	0.1	< 0.1	0.1	< 0.1	0.1	< 0.1	0.2	0.2	0.1	0.1
Hf	0.3	0.2	0.1	0.2	0.2	0.2	< 0.1	0.1	0.6	0.2	0.3	0.1
Bi	0.5	1.1	0.2	0.1	0.2	< 0.1	< 0.1	< 0.1	0.2	0.1	0.2	0.1
U	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	< 0.1
Accounted (μg m^{-3})	40.7	–	9.1	–	47.7	–	7.9	–	57.7	–	36.9	–
% Determined	**69.9**	–	**83.0**	–	**69.8**	–	**80.2**	–	**69.0**	–	**98.5**	–

higher than those in Argiroupoli station (Fig. 3b) even belonging to the same line (L2), which is probably attributable not only to the fact that Argiroupoli is a new station (opened in 2013), but also because it is located in the periphery of the line (out of the central area of the city) and the train frequency is lower (since some trains do not run the entire route). Measurements in the transfer station of Syntagma (Lines 2 and 3 intersect, see Table S2) showed that the $PM_{2.5}$ concentrations were higher in the Syntagma platform of Line 2 than that of Line 3, which may be related to the age of the lines and consequently the different materials used.

$PM_{2.5}$ mass concentrations were found to vary both spatially and temporally. The time scale for large variations was small, showing that commuters may be exposed to very high concentrations during very low time periods, which may have implications on health effects (Martins et al., 2015a). In some stations the levels were relatively constant throughout the time and the location on the platform (e.g. Faria Guimarães station in Fig. 3d). Therefore, in these cases the exposure levels of commuters were very similar when waiting anywhere along the platform. The $PM_{2.5}$ concentrations on the platforms in the Athens subway were generally more variable than in the Oporto platforms (see standard deviations in Table S2). The stations with passage of trains belonging to several lines (e.g. Campo 24 de Agosto in Fig. 3c) were associated with higher $PM_{2.5}$ concentrations.

In general, the air quality varies in time and space within a subway station. These features complicate the comprehensive characterisation and comparison of subway systems.

3.1.3. $PM_{2.5}$ chemical composition

Table 2 summarizes the mean chemical composition of $PM_{2.5}$ on the subway platforms and outdoors. The elemental species were grouped into seven different categories: (1) Elemental iron (Fe), (2) Total carbon (TC), (3) Crustal matter (CM, the sum of Ca, Mg, Al_2O_3, SiO_2, CO_3^{2-}, Ti, K and P), (4) Secondary inorganic compounds (SIC), the sum of water-soluble nitrate (ws-NO_3^-), sulphate (ws-SO_4^{2-}) and ammonium (ws-NH_4^+), (5) Halite (NaCl), (6) Insoluble sulphate and (7) Trace elements. As the oxidation state cannot be determined from the analysis performed, only elemental concentrations are shown in Table 2, but for the chemical mass balance, the oxide concentrations were calculated for Al_2O_3. Because silicon data were not acquired, SiO_2 was estimated by multiplying Al_2O_3 with a factor of 3, and CO_3^{2-} by multiplying Ca by a factor of 1.5 (Querol et al., 2001).

In the Barcelona, Athens and Oporto measurements, the analysed chemical elements accounted for, on average, 70%, 70% and 69% of the total $PM_{2.5}$ on the platform and 83%, 80% and 98% in the outdoor air, respectively. The unaccounted mass can be explained by the presence of oxide species, heteroatoms from the carbonaceous compounds and some water molecules (moisture, formation and crystallisation water).

The relative chemical composition of $PM_{2.5}$ was markedly different between subway platform and ambient air due to distinct emission source contributions. The percentage contributions of each group of chemical components to $PM_{2.5}$ are plotted in Fig. 4.

Fe was the most abundant element in $PM_{2.5}$ found in the subway stations, with relative contribution to the bulk $PM_{2.5}$ ranging from 29% to 43% (41–61% if Fe_2O_3 is considered). The considerable amount of Fe in the subway stations is mainly attributed to mechanical friction and wear processes between rails, wheels and brakes (Johansson and Johansson, 2003; Jung et al., 2010; Kam et al., 2013; Moreno et al., 2015a; Querol et al., 2012). High mass concentrations of Fe have also been found in other subway systems (Aarnio et al., 2005; Adams et al., 2001; Furuya et al., 2001; Johansson and Johansson, 2003; Mugica-Álvarez et al., 2012; Nieuwenhuijsen et al., 2007; Querol et al., 2012; Ripanucci et al., 2006; Salma et al., 2007; Seaton et al., 2005). Furthermore, the

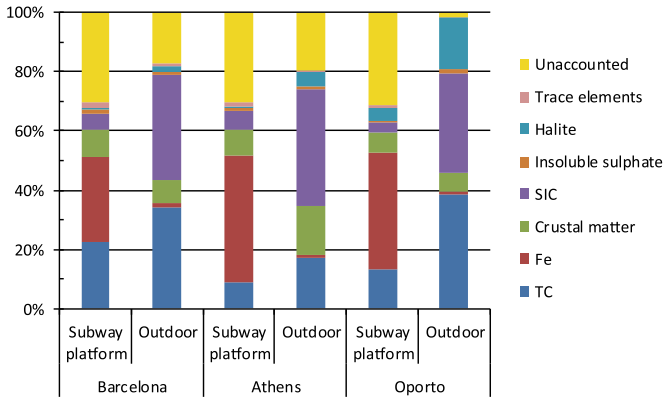

Fig. 4. Relative abundance of chemical components of $PM_{2.5}$ in the subway platforms and outdoor air. (SIC – secondary inorganic compounds; TC – total carbon).

relative abundance of Fe particles on the platform in the Santa Coloma station (17–36%) was much lower than that on the platforms in the Nomismatokopio (36–46%) and Bolhão (27–45%) stations. Considering that all three subway systems have metallic wheels, this marked decrease of abundance of Fe particles on the platform of Santa Coloma station might be attributable to the existence of forced ventilation in the subway system. The ventilation system promotes the outflow of particles, generated in the subway system (such as Fe), to the outdoor atmosphere. Outdoor aerosol samples contained less than 1% of Fe particles.

Total carbon (TC) particles represented the second largest component of the subway $PM_{2.5}$, with mean relative contributions ranging from 9% to 23%. In the ambient urban atmosphere, TC concentrations were generally lower, but their relative contribution to $PM_{2.5}$ was higher, accounting for 17–39%, due to the lower bulk $PM_{2.5}$ concentrations. It is important to note that in the three subway systems all trains are powered by electricity, thus, there are no combustion sources of TC, and hence it is somewhat unexpected to find relatively high levels of TC. However, in Barcelona and Athens the TC concentrations on the platforms (13.2 and 6.2 $\mu g\ m^{-3}$) were around 3.5 times higher than those in the associated outdoor air (Table 2). Possible sources of this TC are diesel-powered trains used for maintenance activities running at night, and the abrasion of C-bearing brake pads and current supply materials (Moreno et al., 2015a). In contrast, in Oporto the TC concentrations were very similar between the platform and the outdoor air, indicating the clear influence of outdoor air in the Bolhão station which is followed in the line by an aboveground station. These experimental results indicate that the carbonaceous particles on the platform can arise from the outdoor environment in addition to those generated inside. Hence, the outdoor concentrations of TC in Oporto (14.5 $\mu g\ m^{-3}$) were significantly higher than in Barcelona (3.8 $\mu g\ m^{-3}$) and Athens (1.7 $\mu g\ m^{-3}$) (Table 2) because the measurements were conducted in an urban traffic station, as stated previously.

Elements of crustal origin (Al, Ca, K, Ti, Mg and P) were found in higher concentrations in subway $PM_{2.5}$ samples in comparison to ambient air, with relative contributions of crustal matter in the range of 7–9% (Fig. 4). Crustal matter is expected to be present in outdoor PM samples, as these elements mainly derive from soil and urban mineral dust. This implies that the crustal particles found in the subway platforms flowed in from the outdoor environment by the commuters and by air-exchange between the indoor and outdoor environments. Moreover, crustal particles on the subway platforms could be originated from the resuspension of particles generated by wind erosion and weathering of construction material in both platform and tunnel, and can also be tracers of occasional construction works in the subway systems.

SIC particles were observed in subway aerosol samples, with their relative abundances ranging from 3% to 6%. In general, secondary particles (water-soluble nitrate, sulphate and ammonium) are one of the most abundant aerosol types in the outdoor atmosphere, accounting for 33–39% of the total $PM_{2.5}$, indicating that these particles in the subway environment might arise from the outdoor environment. Concentrations of insoluble sulphate were very low and very similar at both environments, with mean concentrations ranging between 0.1 and 0.9 μg m^{-3} (Table 2).

The halite present in the subway environment is expected to come from outdoors by both air and water infiltration. Its concentrations were similar at both Santa Coloma and Nomismatokopio stations, and comparable to the corresponding outdoor concentrations. In Oporto the halite concentrations were higher both in the subway environment and outdoors, possibly due to the location of the city next to the Atlantic Ocean.

Higher amounts of other metal particles in addition to Fe, such as Ba, Cu, Mn, Zn, Cr, Sb, Sr, Mo, Ni, Sn, As, Zr and Co (Table 2), were found in the subway $PM_{2.5}$ compared to the simultaneous outdoor samples, pointing towards the presence of metal particle sources in the subway stations. Concerning the enrichment of these trace metals on the subway platforms the following were observed:

1. the sum of trace metals concentrations were similar (0.9–1.2 μg m^{-3}) among the three subway platforms;
2. Ba was especially enriched in Santa Coloma station, with concentrations 217 times higher than outdoors, and 13 and 8 times higher than in Bolhão and Nomismatokio subway platforms;
3. Cu was the most enriched trace metal in the Bolhão station, with concentrations 29 times higher than in ambient air, and 7 and 4 times higher than in Nomismatokopio and Santa Coloma;
4. The mean concentrations of Mn were similar between the Nomismatokopio (248.6 ng m^{-3}) and Bolhão (287.3 ng m^{-3}), being about 1.7 higher than in Santa Coloma station (161.9 ng m^{-3});
5. The mean concentrations of Zn were similar between the Santa Coloma (163.3 ng m^{-3}) and Nomismatokopio (148.5 ng m^{-3}), being about 1.8 higher than in Bolhão station (86.8 ng m^{-3});
6. The highest Cr, Sn, Mo and As concentrations were found in Nomismatokopio station;
7. Cu, Mn, Sb and Ni were metals with the highest concentrations in Bolhão station.

Although the trace metals represent less than 2% of the total $PM_{2.5}$, they are important for source identification. Differences in the metal concentrations among the stations and subway systems might be associated to the different chemical composition of wheels and rails (Mn, Cr), brakes (Ba, Sb, Cu, Zn, Pb, Ni, Sr), and current supply materials (e.g. Cu-rich catenaries and Cu vs C pantographs) (Moreno et al., 2015a). The metals can be originated from mechanical wear and friction processes among these manufactured materials, as reported by other studies in subway systems (Furuya et al., 2001; Gustafsson et al., 2012; Martins et al., 2016; Querol et al., 2012). Therefore, a low metal specification for any of the above components of the railways and trains would reduce considerably commuters' exposure to metals.

The relative abundance of specific elements of the subway $PM_{2.5}$ varies from station to station. Representative cases are shown as example in Fig. 5a and b. The Ba/Sr ratio (both elements being present in brake pads) varied from 8 in Tetuan to 45 in Santa Coloma. All stations except Tetuan show close Ba/Sr ratios which can be interpreted as coming from a similar subway source (Fig. 5a). Another relevant difference was the Cu/Fe ratio, which varied from 0.001 in Nomismatokopio to 0.013 in Joanic. In this case Santa Coloma and Tetuan show comparable ratios (0.006–0.007, Fig. 5b). However, in the Bolhão station the Cu/Fe ratio was very variable among sampling days, which is probably attributable to the major influence of outdoor sources. It is also interesting to notice the relative lower concentrations of Cu in Nomismatokopio possibly due to the use of a third rail for power supply in the Athens subway system instead of the catenary used in Barcelona and Oporto.

The remaining trace elements (Zr, Pb, V, Li, Ga, Ge, Se, Rb, Y, Nb, Cd, La, Ce, Pr, Nd, Hf, Bi and U) represented a negligible amount ($<0.1\%$) of the total $PM_{2.5}$ and, in general, their mass concentrations in the subway $PM_{2.5}$ and in ambient $PM_{2.5}$ were similar, implying that subway concentrations are associated with the infiltration of ambient air in the subway systems.

3.2. $PM_{2.5}$ and CO_2 concentrations inside trains

The $PM_{2.5}$ and CO_2 concentration profiles during trips inside the trains showed dissimilar behaviours. The CO_2 concentrations were most probably driven by the number of passengers inside the train carriages. The maximum influx of people corresponds to stations located in the central area of each city. Average $PM_{2.5}$ concentrations are reported in Table S3.

Generally, the $PM_{2.5}$ concentrations along the lines presented a constant level, while short-term peaks were often observed after the train doors closed, probably due to turbulence and consequent PM resuspension produced by the movement of passengers inside the trains. The trains of the 3 subway systems are equipped with air conditioning system, and this can induce the relative constant and low $PM_{2.5}$ concentrations along the lines.

In the Athens subway system, carriage windows were usually open, despite the existence of air conditioning. This resulted in an increase in $PM_{2.5}$ concentrations inside trains when passing

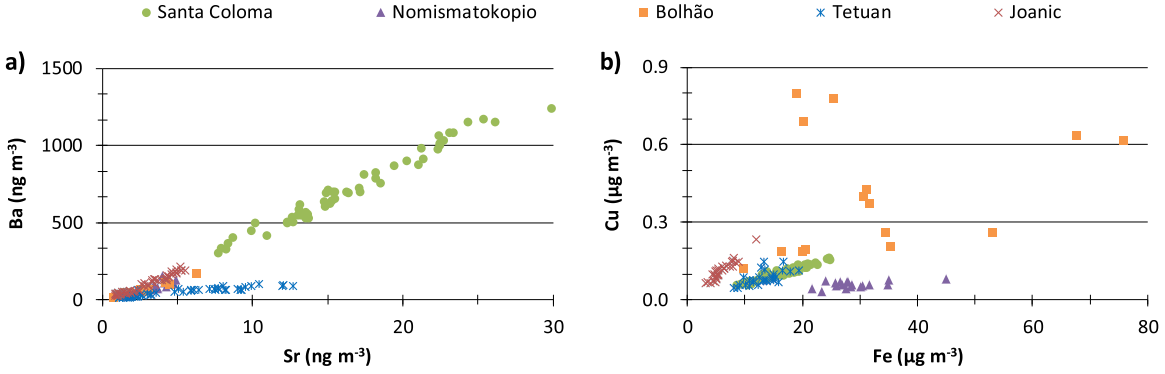

Fig. 5. Scatter plots of the concentrations of Ba vs. Sr (a) and Cu vs. Fe (b) in several subway stations. The results of Tetuan and Joanic stations have been reported by Martins et al. (2016).

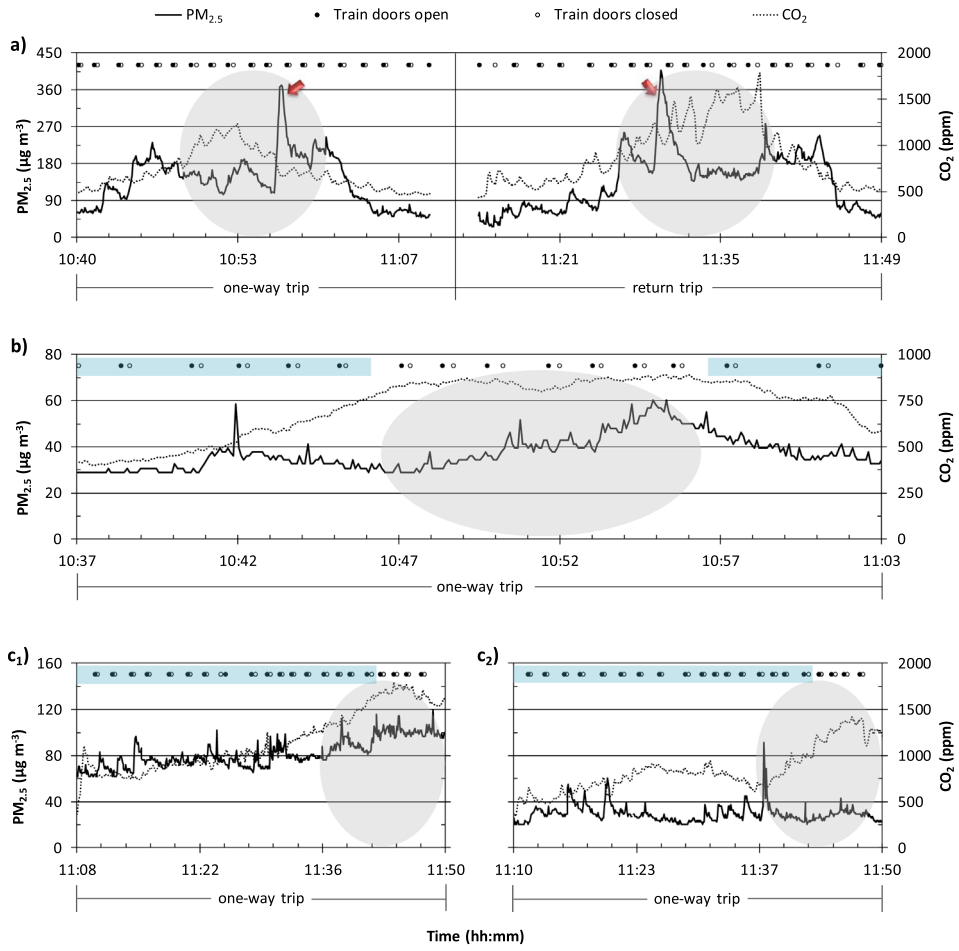

Fig. 6. $PM_{2.5}$ and CO_2 concentrations measured inside the train of Line 2 in the Athens subway system (a) and of Line D (b) and A in two different days (c_1 and c_2) in the Oporto subway system. The times of train doors open and closed are indicated. The central area of the city is grey shadowed. Arrows represent peaks in the $PM_{2.5}$ concentration registered while travelling in the same section of the tunnel. The aboveground sections of the lines are highlighted in blue. The mean daily outdoor $PM_{2.5}$ concentrations were 53.3 µg m^{-3} in c_1 and 17.3 µg m^{-3} in c_2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

through some tunnel sections between stations, due to the entrance of PM from the tunnel into the trains. An example is shown in Fig. 6a for Line 2, where a clear peak in the $PM_{2.5}$ concentration was registered while travelling inside a tunnel section in both directions (see arrows in Fig. 6a). The results indicate that the passengers might be exposed to higher $PM_{2.5}$ levels while the train is travelling in the subway tunnel because it is a more confined microenvironment and may present high $PM_{2.5}$ concentrations; tunnel particles can enter into the trains through the windows and be resuspended by the passengers' motion. When comparing the 3 subway systems, the highest $PM_{2.5}$ concentrations inside the trains were found in the lines belonging to Athens subway system (Table S3).

In general, in the Oporto subway system, the real-time measurements of PM levels inside the trains travelling both in aboveground and underground sections of lines LA and LD showed lower $PM_{2.5}$ and CO_2 concentrations while travelling in the aboveground section where clean air entering the trains produced an environmental "cleaning effect" (Fig. 6b and c_1, Table S4). Similar results have been reported in other subway systems, such as in Los Angeles (Kam et al., 2011) and Taipei (Cheng and Yan, 2011; Cheng et al., 2012). The $PM_{2.5}$ concentrations inside the trains of this subway system are greatly dependent on ambient air quality, as shown by the notably different levels of $PM_{2.5}$ concentrations inside the trains between the two days (Fig. 6c_1 and c_2) corresponding to high and low outdoor concentrations, respectively.

3.3. $PM_{2.5}$ concentrations on platforms vs inside trains

Comparing the $PM_{2.5}$ concentrations inside the trains (Table S3) with those found on the platforms (Fig. 1) corresponding to the same subway system, it was possible to observe that in the Barcelona and Oporto subway systems the concentrations inside the trains were in general lower than those on the platform, which may be attributed to the air conditioning system operating inside the trains, and in Oporto also by the predominance of aboveground stations along the lines (Table S4). In contrast, in Athens system, despite having also air conditioning, the concentrations inside the trains were higher than on the platform, since the trains run with most of the windows open, hence favouring the entrance of polluted tunnel and platform air into the trains. Therefore, the air conditioning system is not being effectively used, and safety, energy-saving and environmental awareness of the commuters should be applied.

In terms of personal exposure, a subject who commutes by subway typically spends some time of the day in the subway system, being most of this time spent inside the trains. Thus, the subway commuters are predominantly exposed to the relatively low $PM_{2.5}$ concentrations inside the trains, whereas the exposure

to higher $PM_{2.5}$ concentrations on the platforms lasts shorter.

Besides the time spent commuting in the subway, there are many other microenvironments to which the citizen is exposed at different times of the day, with the air quality of most of them being very different from that measured in the subway system. Thus, it is extremely important to consider this fact when estimating the daily exposure to $PM_{2.5}$ and subsequent deposition in the respiratory tract during breathing (Martins et al., 2015a). For instance, Moreno et al. (2015b) have studied the variations in urban air quality experienced during travelling on different modes of public transport (tram, subway and bus) and walking in Barcelona city, and they concluded that the air pollutant concentrations regularly inhaled by urban commuters vary greatly depending on the transportation mode used to travel.

4. Conclusions

Air quality sampling campaigns were conducted in 3 South European subway systems: Barcelona (Spain), Athens (Greece) and Oporto (Portugal), both on platforms and inside trains. The $PM_{2.5}$ concentration and their elemental composition were determined. The following main conclusions were drawn:

1. Mean $PM_{2.5}$ concentrations in the 3 subway stations were several times higher (between 2.2 and 6.9) than those in the corresponding ambient air. On the platforms the highest $PM_{2.5}$ concentrations were measured in the Bolhão station in the Oporto subway system, which is naturally ventilated and the frequency of train passages is higher than in the other 2 European subway stations.
2. $PM_{2.5}$ diurnal cycles showed higher concentrations during subway operating hours than during the night when the system is closed, and lower levels on weekends than on weekdays. $PM_{2.5}$ concentrations depended largely on the operation and frequency of the trains and the ventilation system.
3. In general, $PM_{2.5}$ concentrations varied in time and space within a subway platform. These features complicate the comprehensive characterisation and comparison of subway systems.
4. $PM_{2.5}$ differs substantially between the subway system and outside, not only in terms of mass concentration but also the chemical composition, owing to different PM emission sources.
5. Higher metal concentrations were found on the subway platforms compared to ambient air. Fe was the most abundant element, accounting for 29–43% of the total $PM_{2.5}$ mass (41–61% if Fe_2O_3 is considered).
6. The significant enrichment of metals present in the alloys used in the production of rails, wheels, brakes and current supply materials (Ba, Cu, Mn, Zn, Cr, Sb, Sr, Mo, Zr, Ni, among others), clearly suggests the wear of metal parts as the most important PM subway source.
7. The use of air conditioning inside the trains was responsible for reducing the $PM_{2.5}$ levels. Real-time measurements showed that $PM_{2.5}$ concentrations increase considerably when the train windows were open. The opposite effect happened in the aboveground section where clean air entering the trains produced an environmental “cleaning effect”.
8. Data from this study can be further used to assess health risks to improve policies and strategies for an indoor air quality management in the subway transportation system.

Acknowledgements

The present study was supported by the European Union Seventh Framework Programme (FP7/2007-2013) under Grant agreement no. 315760 HEXACOMM, the Spanish Ministry of Economy and Competitiveness and FEDER funds (METRO CGL2012-33066), the IMPROVE LIFE project (LIFE13 ENV/ES/000263), and the Generalitat de Catalunya 2014 SGR33. The authors also gratefully acknowledge the permission and collaboration from the Transports Metropolitans de Barcelona, the URBAN RAIL TRANSPORT S.A. for ATHENS Metro and the Metro do Porto S.A. to undertake this work. Special thanks are given to Dr Cristina Reche for supplying outdoor ambient data from Barcelona and to Catarina Silva for carried out the TC chemical analyses of Oporto subway samples.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2015.12.007.

References

Aarnio, P., Yli-Tuomi, T., Kousa, A., Mäkelä, T., Hirsikko, A., Hämeri, K., Räisänen, M., Hillamo, R., Koskentalo, T., Jantunen, M., 2005. The concentrations and composition of and exposure to fine particles (PM2.5) in the Helsinki subway system. Atmos. Environ. 39, 5059–5066. http://dx.doi.org/10.1016/j.atmosenv.2005.05.012.

Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., McMullen, M.A.S., Khandelwal, P., 2001. Fine particle (PM2.5) personal exposure levels in transport microenvironments, London, UK. Sci. Total Environ. 279, 29–44. http://dx.doi.org/10.1016/S0048-9697(01)00723-9.

Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Gianelle, V.L., Colombi, C., Alves, C., Custódio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillón, M.C., Manousakas, M., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X., 2015. AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in 5 Southern European cities. Atmos. Chem. Phys. Discuss. 15, 23989–24039. http://dx.doi.org/10.5194/acpd-15-23989-2015.

Bachoual, R., Boczkowski, J., Goven, D., Amara, N., Tabet, L., On, D., Leçon-Malas, V., Aubier, M., Lanone, S., 2007. Biological effects of particles from the Paris subway system. Chem. Res. Toxicol. 20, 1426–1433. http://dx.doi.org/10.1021/tx700093j.

Bigert, C., Alderling, M., Svartengren, M., Plato, N., de Faire, U., Gustavsson, P., 2008. Blood markers of inflammation and coagulation and exposure to airborne particles in employees in the Stockholm underground. Occup. Environ. Med. 65, 655–658. http://dx.doi.org/10.1136/oem.2007.038273.

Cheng, Y.-H., Lin, Y.-L., Liu, C.-C., 2008. Levels of PM10 and PM2.5 in taipei rapid transit system. Atmos. Environ. 42, 7242–7249. http://dx.doi.org/10.1016/j.atmosenv.2008.07.011.

Cheng, Y.-H., Liu, Z.-S., Yan, J.-W., 2012. Comparisons of PM10, PM2.5, particle number, and CO_2 levels inside metro trains between traveling in underground tunnels and on elevated tracks. Aerosol Air Qual. Res. 12, 879–891. http://dx.doi.org/10.4209/aaqr.2012.05.0127.

Cheng, Y.-H., Yan, J.-W., 2011. Comparisons of particulate matter, CO, and CO_2 levels in underground and ground-level stations in the Taipei mass rapid transit system. Atmos. Environ. 45, 4882–4891. http://dx.doi.org/10.1016/j.atmosenv.2011.06.011.

Chillrud, S.N., Epstein, D., Ross, J.M., Sax, S.N., 2004. Elevated airborne exposures to manganese, chromium and iron of teenagers from steel dust and New York City's subway system. Environ. Sci. Technol. 38, 732–737. http://dx.doi.org/10.1021/es034734y.

Colombi, C., Angius, S., Gianelle, V., Lazzarini, M., 2013. Particulate matter concentrations, physical characteristics and elemental composition in the Milan underground transport system. Atmos. Env. 70, 166–178. http://dx.doi.org/10.1016/j.atmosenv.2013.01.035.

Eleftheriadis, K., Ochsenkuhn, K.M., Lymperopoulou, T., Karanasiou, A., Razos, P., Ochsenkuhn-Petropoulou, M., 2014. Influence of local and regional sources on the observed spatial and temporal variability of size resolved atmospheric aerosol mass concentrations and water-soluble species in the Athens metropolitan area. Atmos. Env. 97, 252–261. http://dx.doi.org/10.1016/j.atmosenv.2014.08.013.

Fromme, H., Oddoy, A., Piloty, M., Krause, M., Lahrz, T., 1998. Polycyclic aromatic hydrocarbons (PAH) and diesel engine emission (elemental carbon) inside a car and a subway train. Sci. Total Environ. 217, 165–173. http://dx.doi.org/10.1016/S0048-9697(98)00189-2.

Furuya, K., Kudo, Y., Okinaga, K., Yamuki, M., Takahashi, S., Araki, Y., Hisamatsu, Y., 2001. Seasonal variation and their characterization of suspended particulate matter in the air of subway stations. J. Trace Microprobe Tech. 19, 469–485. http://dx.doi.org/10.1081/TMA-100107583.

Guo, L., Hu, Y., Hu, Q., Lin, J., Li, C., Chen, J., Li, L., Fu, H., 2014. Characteristics and

chemical compositions of particulate matter collected at the selected metro stations of Shanghai, China. Sci. Total Environ. 496, 443–452. http://dx.doi.org/10.1016/j.scitotenv.2014.07.055.
Gustafsson, M., Blomqvist, G., Swietlicki, E., Dahl, A., Gudmundsson, A., 2012. Inhalable railroad particles at ground level and subterranean stations – physical and chemical properties and relation to train traffic. Transp. Res. D: Transp. Environ. 17, 277–285. http://dx.doi.org/10.1016/j.trd.2011.12.006.
Johansson, C., Johansson, P.-A., 2003. Particulate matter in the underground of Stockholm. Atmos. Environ. 37, 3–9. http://dx.doi.org/10.1016/S1352-2310(02)00833-6.
Jung, H.-J., Kim, B., Ryu, J., Maskey, S., Kim, J.-C., Sohn, J., Ro, C.-U., 2010. Source identification of particulate matter collected at underground subway stations in Seoul, Korea using quantitative single-particle analysis. Atmos. Environ. 44, 2287–2293. http://dx.doi.org/10.1016/j.atmosenv.2010.04.003.
Kam, W., Cheung, K., Daher, N., Sioutas, C., 2011. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. Atmos. Environ. 45, 1506–1516. http://dx.doi.org/10.1016/j.atmosenv.2010.12.049.
Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2013. A comparative assessment of PM2.5 exposures in light-rail, subway, freeway, and surface street environments in Los Angeles and estimated lung cancer risk. Environ. Sci. Process. Impacts 15, 234–243. http://dx.doi.org/10.1039/c2em30495c.
Kamani, H., Hoseini, M., Seyedsalehi, M., Mahdavi, Y., Jaafari, J., Safari, G.H., 2014. Concentration and characterization of airborne particles in Tehran's subway system. Environ. Sci. Pollut. Res. 21, 7319–7328. http://dx.doi.org/10.1007/s11356-014-2659-4.
Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM10 and PM2.5) in Seoul Metropolitan Subway stations. J. Hazard. Mater. 154, 440–443. http://dx.doi.org/10.1016/j.jhazmat.2007.10.042.
Kwon, S.-B., Jeong, W., Park, D., Kim, K.-T., Cho, K.H., 2015. A multivariate study for characterizing particulate matter (PM10, PM2.5, and PM1) in Seoul metropolitan subway stations, Korea. J. Hazard. Mater. 297, 295–303. http://dx.doi.org/10.1016/j.jhazmat.2015.05.015.
Lim, J.-M., Lee, J.-H., Moon, J.-H., Chung, Y.-S., Kim, K.-H., 2010. Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization. Atmos. Res. 95, 88–100. http://dx.doi.org/10.1016/j.atmosres.2009.08.009.
Loxham, M., Cooper, M.J., Gerlofs-Nijland, M.E., Cassee, F.R., Davies, D.E., Palmer, M. R., Teagle, D. a H., 2013. Physicochemical characterization of airborne particulate matter at a mainline underground railway station. Environ. Sci. Technol. 47, 3614–3622. http://dx.doi.org/10.1021/es304481m.
Martins, V., Minguillón, M.C., Moreno, T., Querol, X., de Miguel, E., Capdevila, M., Centelles, S., Lazaridis, M., 2015a. Deposition of aerosol particles from a subway microenvironment in the human respiratory tract. J. Aerosol Sci. 90, 103–113. http://dx.doi.org/10.1016/j.jaerosci.2015.08.008.
Martins, V., Moreno, T., Minguillón, M.C., Amato, F., de Miguel, E., Capdevila, M., Querol, X., 2015b. Exposure to airborne particulate matter in the subway system. Sci. Total Environ. 511, 711–722. http://dx.doi.org/10.1016/j.scitotenv.2014.12.013.
Martins, V., Moreno, T., Minguillón, M.C., van Drooge, B.L., Amato, F., de Miguel, E., Capdevila, M., Centelles, S., Querol, X., 2016. Origin of inorganic and organic components of PM2.5 in subway stations of Barcelona, Spain. Environ. Pollut. 208, 125–136. http://dx.doi.org/10.1016/j.envpol.2015.07.004.
Moreno, T., Martins, V., Querol, X., Jones, T., BéruBé, K., Minguillón, M.C., Amato, F., Capdevila, M., de Miguel, E., Centelles, S., Gibbons, W., 2015a. A new look at inhalable metalliferous airborne particles on rail subway platforms. Sci. Total Environ. 505, 367–375. http://dx.doi.org/10.1016/j.scitotenv.2014.10.013.
Moreno, T., Pérez, N., Reche, C., Martins, V., de Miguel, E., Capdevila, M., Centelles, S., Minguillón, M.C., Amato, F., Alastuey, A., Querol, X., Gibbons, W., 2014. Subway platform air quality: assessing the influences of tunnel ventilation, train piston effect and station design. Atmos. Environ. 92, 461–468. http://dx.doi.org/10.1016/j.atmosenv.2014.04.043.
Moreno, T., Reche, C., Rivas, I., Minguillón, M.C., Martins, V., Vargas, C., Buonanno, G., Parga, J., Pandolfi, M., Brines, M., Ealo, M., Fonseca, A.S., Amato, F., Sosa, G., Capdevila, M., de Miguel, E., Querol, X., Gibbons, W., 2015b. Urban air quality comparison for bus, tram, subway and pedestrian commutes in Barcelona. Environ. Res. 142, 495–510. http://dx.doi.org/10.1016/j.envres.2015.07.022.
Mugica-Álvarez, V., Figueroa-Lara, J., Romero-Romo, M., Sepúlveda-Sánchez, J., López-Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. Atmos. Environ. 49, 284–293. http://dx.doi.org/10.1016/j.atmosenv.2011.11.038.
Murruni, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., Vázquez, M., Ozafrán, M., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. Atmos. Environ. 43, 4577–4583. http://dx.doi.org/10.1016/j.atmosenv.2009.06.025.
Nieuwenhuijsen, M.J., Gómez-Perales, J.E., Colvile, R.N., 2007. Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. Atmos. Environ. 41, 7995–8006. http://dx.doi.org/10.1016/j.atmosenv.2007.08.002.
Park, D., Lee, T., Hwang, D., Jung, W., Lee, Y., Cho, K., Kim, D., Lee, K., 2014. Identification of the sources of PM10 in a subway tunnel using positive matrix factorization. J. Air Waste Manag. Assoc. 64, 1361–1368. http://dx.doi.org/10.1080/10962247.2014.950766.
Park, D.-U., Ha, K.-C., 2008. Characteristics of PM10, PM2.5, CO2 and CO monitored in interiors and platforms of subway train in Seoul, Korea. Environ. Int. 34, 629–634. http://dx.doi.org/10.1016/j.envint.2007.12.007.
Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Mantilla, E., Ruiz, C.R., 2001. Monitoring of PM10 and PM2.5 around primary particulate anthropogenic emission sources. Atmos. Environ. 35, 845–858. http://dx.doi.org/10.1016/S1352-2310(00)00387-3.
Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., Capdevila, M., 2012. Variability of levels and composition of PM10 and PM2.5 in the Barcelona metro system. Atmos. Chem. Phys. 12, 5055–5076. http://dx.doi.org/10.5194/acp-12-5055-2012.
Raut, J.-C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. Atmos. Environ. 43, 860–868. http://dx.doi.org/10.1016/j.atmosenv.2008.10.038.
Ripanucci, G., Grana, M., Vicentini, L., Magrini, A., Bergamaschi, A., 2006. Dust in the underground railway tunnels of an italian town. J. Occup. Environ. Hyg. 3, 16–25. http://dx.doi.org/10.1080/15459620500444004.
Rivas, I., Viana, M., Moreno, T., Pandolfi, M., Amato, F., Reche, C., Bouso, L., Àlvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X., 2014. Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain. Environ. Int. 69, 200–212. http://dx.doi.org/10.1016/j.envint.2014.04.009.
Salma, I., Pósfai, M., Kovács, K., Kuzmann, E., Homonnay, Z., Posta, J., 2009. Properties and sources of individual particles and some chemical species in the aerosol of a metropolitan underground railway station. Atmos. Environ. 43, 3460–3466. http://dx.doi.org/10.1016/j.atmosenv.2009.04.042.
Salma, I., Weidinger, T., Maenhaut, W., 2007. Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. Atmos. Environ. 41, 8391–8405. http://dx.doi.org/10.1016/j.atmosenv.2007.06.017.
Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London Underground: dust and hazards to health. Occup. Environ. Med. 62, 355–362. http://dx.doi.org/10.1136/oem.2004.014332.
Sundh, J., Olofsson, U., Olander, L., Jansson, A., 2009. Wear rate testing in relation to airborne particles generated in a wheel – rail contact ‡. Lubr. Sci. 21, 135–150. http://dx.doi.org/10.1002/ls.80.