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Characterisation of Airborne Particulate Matter in Different European Subway Systems

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65364

Abstract

Air quality sampling campaigns in three European subway systems (Barcelona, Athens and Oporto) were conducted in order to characterise particulate matter (PM) to better understand the main factors controlling it. PM mass concentrations varied among the European subway platforms, and also within the same underground system, this being mainly associated to differences in the design of the stations and tunnels, system age, train frequency, ventilation and air-conditioning systems, commuter's density, rails geometry and outdoor air quality. PM concentrations displayed clear diurnal patterns, depending largely on the operation and frequency of the trains and the ventilation system. Chemically, subway PM_{2.5} on the platforms consisted of iron, carbonaceous material, crustal matter, secondary inorganic compounds, insoluble sulphate, halite and trace elements. Fe was the most abundant element, accounting for 19-46% of the bulk PM_{2.5}, which is generated mainly from mechanical wear at rail-wheel-brake interfaces. A source apportionment analysis allowed the identification of outdoor (sea salt, fuel-oil combustion and secondary aerosol) and subway sources on platforms. The use of airconditioning inside the trains was an effective approach to reduce exposure concentrations, being more efficient removing coarser particles. PM concentrations inside the trains were greatly affected by the surrounding (i.e. platforms and tunnels) air quality conditions.

Keywords: metro, platforms, trains, subway aerosol, indoor air quality, exposure, commuting



1. Introduction

Urban air quality plans incentivise the use of public transport to abate atmospheric emissions from road vehicles. In this context, underground subway systems with electric trains are especially desirable as they are energetically efficient and contribute to relieve surface traffic congestion; hence, it is considered one of the cleanest public transport systems. The subway system is one of the major transport modes in most metropolitan areas worldwide, due to its convenience, safety and high speed. Its high capacity in terms of the number of daily commuters makes it an environmentally friendly alternative.

Particulate matter (PM) in the underground subway microenvironments is 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 health effects [1–3]. Studies have indicated, with few exceptions, that PM concentrations are usually higher in these underground environments than in outdoor ambient air, as these environments are a confined space poorly ventilated promoting the concentration of PM entering from the outside atmosphere in addition to that generated internally in the system [[4] and references therein]. Particles in the subway system are mainly generated by the motion of trains, movement of commuters and subway staff, air ventilation, and works of maintenance and construction. Most particles in this environment are produced at the rail-wheel-brake interfaces by friction and mechanical wear processes, and at the interface between the current collectors attached to trains and the power-conductive materials providing electricity. Additional PM sources are provided by the erosion of construction materials and their subsequent resuspension [5–9]. Subway trains are typically powered either by an overhead catenary, involving the electrical current being drawn through the contact material of the pantograph, or by a third rail in which the current passes to the train via a contact shoe. Both coarse and fine particles are produced during shearing between wheels, rails and brakes, and ultrafine particles can be generated during the high temperatures resulting from friction at interfaces between these components, in some cases leading to vaporisation of the materials [7, 10].

Perhaps, more interesting than the bulk mass concentration of PM is the fact that these particles have peculiar physico-chemical characteristics specific to the subway environment, being loaded with ferruginous particles commonly accompanied by other elements such as Mn, Si, Cr, Cu, Ba, Ca, Zn, Ni and K [4–6, 11–16]. The considerable amount of Fe in the subway stations is mainly generated from mechanical friction and wear processes between rails, wheels and brakes [5, 15, 17, 18]. Wear and friction processes initially produce iron-metal particles that react with oxygen in the air resulting in the formation of iron oxides [5, 15, 19].

In any case, the 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, rails, brakes and power supply materials; braking mechanisms; power system; train speed and frequency; passenger densities; ventilation and air-conditioning systems; cleaning frequency and other operational conditions [23]: [16, 17, 20–23]. Knowing the chemical composition of PM in a subway platform is an essential prerequisite for understanding the indoor air quality of the subway system and subsequently

to assess remediation measures. Moreover, the chemical composition of PM derived by sample analysis can be further utilised for risk-assessment studies and although components such as the trace metals represent typically only about 1% of the total PM, they can play a critical role in the source identification [24, 25].

The aim of this study was to characterise personal exposure to PM while commuting, including the waiting time on the platform and travelling inside the trains, in the subway systems of three European cities, to better understand the main factors controlling air quality in this environment. The work was based on air quality campaigns following the same sampling, measurement and analytical methods, and data treatment.

2. Studied subway systems

Three European subway systems were selected: Barcelona (Spain), Athens (Greece) and Oporto (Portugal), although with main focus on Barcelona.

The Barcelona subway system is an extensive network of electrified railway lines that runs mostly underground. The network has 8 lines (numbered L1–L5 and L9–L11), 139 stations, 102.6 km of track (January 2016), carries around 376 million passengers each year, and is managed by *Transports Metropolitans de Barcelona* (TMB) [8, 15]. The platforms and tunnels are equipped with mechanical forced ventilation which favours the air exchange between the indoor and outdoor environments. All trains are operated using a rigid overhead catenary for power supply and run from 5:00 h until midnight every day, with additional services on Friday nights (finishing at 2:00 h of Saturday) and Saturday nights (running all night long), with a frequency between 2 and 15 min, depending on the day (weekend or weekday), subway line and time of day. Trains from all lines are equipped with an efficient air-conditioning system that works continuously throughout the year to maintain a comfortable temperature, but with higher intensity during the warmer period.

The Athens subway system is run by *Urban Rail Transport S.A.* and is used for the transportation of nearly 494 million passengers per year in the city of Athens. Line 1 was a conventional steam railway constructed in 1869, which was converted to electrical railway in 1904, and runs almost entirely above ground. Lines 2 and 3 opened in 2000 and are mostly underground (a portion of the L3 is a suburban rail line that runs above ground). The total length of the network is 82.7 km and includes 61 stations (January 2016). Trains run from around 5:30 until 00:30 h, with a frequency of 4–5 min during the rush hours and 7–15 min in the off-hours. The trains are provided with air-conditioning system and there is the ability to open the windows. The network uses electric trains equipped by both contact shoes and pantographs, which in the underground sections runs on third rail and in the above ground uses overhead catenaries.

The Oporto subway system is part of the public transport system of Oporto. *Metro do Porto, S.A.*, is engaged in the operation and maintenance of the subway system. The network has 6 lines (LA, LB, LC, LD, LE and LF) with the first line being opened in 2002. Currently, the system has an extension of 67 km with a total of 81 operational stations, 14 of which are underground

(January 2016). The system is underground in central Oporto (8 km of the network) and above ground into the city's suburbs, carrying about 57 million passengers per year. Trains run every day from 6:00 until 1:00 h with a frequency from 5 to 19 min, and are equipped with air-conditioning system. The power supply system is a solid overhead catenary line.

3. Experimental methods

3.1. Platform measurements

3.1.1. Intensive campaigns

In the case of the Barcelona subway study, four stations with distinct designs belonging to different lines were selected for the intensive campaigns: Joanic (L4), Santa Coloma (L1), Tetuan (L2) and Llefià (L10). The architectural design of the stations and tunnels is different for each station. In both Joanic and Santa Coloma stations, there is one wide tunnel with two central rails served by lateral platforms, although in Joanic the two rails are separated by a middle wall. In the case of Tetuan and Llefià, there is a narrower tunnel with just one platform and one rail, although with the major difference that in the more modern Llefià station the platform is separated from the rail by a glass wall within which is embedded a platform screen door (PSD) system (**Table 1**).

Two 1-month intensive campaigns were carried out at each of the stations during two periods: warmer (2 April–30 July 2013) and colder (28 October 2013–10 March 2014). Ventilation protocols were different in the warmer and the colder periods, which allowed to ascertain seasonal differences (**Table 1**).

 $PM_{2.5}$ samples were collected with a high-volume sampler (30 m³ h⁻¹, HVS, Model CAV-A/MSb, MCV) on quartz microfibre filters. Sampling was done daily for 19 h according to the subway working hours (5:00–24:00). Continuous measurements (24 h day⁻¹) with a 5-min time resolution were performed using a light-scattering laser photometer (DustTrak, Model 8533, TSI) for $PM_{1.7}$ $PM_{2.5}$ and PM_{10} mass concentrations and an indoor air quality meter (IAQ-Calc, Model 7545, TSI) for CO_2 and CO concentrations, temperature and relative humidity (RH).

In the case of the Athens and Oporto subway studies, the intensive sampling campaign was carried out at one station in each system, namely Nomismatokopio and Bolhão, respectively. For comparison purposes, the chosen stations had similar platform design: wide tunnel with two rails in the middle, one for each direction, with lateral platforms (**Table 1**). In Athens campaign, $PM_{2.5}$ samples were collected using a high-volume sampler, similar to the one used in Barcelona. In Oporto campaign, a high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 67.8 m³ h⁻¹ was used to collect coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) particles, although only the $PM_{2.5}$ data were used in this study. The particles were collected daily on quartz microfibre filters during the subway operating hours (from 5:30 to 00:30 h in Athens and from 6:00 to 01:00 h in Oporto). Field-filter blanks were also collected. A DustTrak and an indoor air quality meter were simultaneously operated at a 5-min time resolution during 24 h day⁻¹, as in Barcelona's campaign.

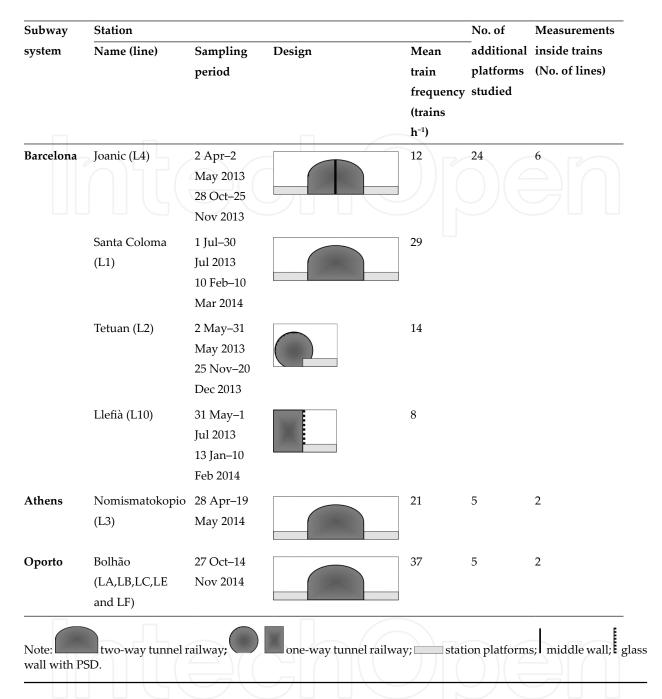


Table 1. Sampling campaigns information.

 $PM_{2.5}$ concentrations provided by DustTrak monitor were corrected against the in situ and simultaneous gravimetric $PM_{2.5}$ for each station. Concentrations of PM_1 and PM_{10} were corrected using the same correction factors obtained for $PM_{2.5}$. Therefore, in this study only the $PM_{2.5}$ concentrations are used in absolute terms, whereas the PM_1 and PM_{10} concentrations are only used to assess relative variations.

In the three subway studies, sampling and monitoring devices were placed at a distance from the commuters' access-to-platform point and behind a light fence for safety protection. The exact location chosen on each platform was typically a compromise between the availability of power supply, the need not to obstruct passenger movement and the preference to make the equipment as inconspicuous as possible.

3.1.2. Additional monitoring

Additional platforms were selected to study the temporal and spatial variations in the PM_X concentrations along the platforms. A total of 24 platforms from Barcelona subway system, 5 from Athens subway system, and 5 from Oporto subway system were studied (**Table 1**). Note that these stations include the aforementioned stations selected for the intensive campaigns (four in Barcelona, one in Athens and one in Oporto). Out of the 24 stations in Barcelona, 4 were new stations (line 10) and the remaining were old stations (lines 1–5), with a preference being given to selecting the most common station designs. This station selection included both those with double rail tracks with (4 stations) and without (14 stations) a middle wall, and a single rail track with (4 stations) and without (2 stations) a PSD system [8]. The subway stations chosen in Athens both have wide tunnels and two rail tracks, although one has a central platform and the others have two lateral platforms. In Oporto subway system, all stations are double track with lateral platforms.

Measurements were performed at 4 positions approximately equidistant along each platform, during a total of 1 h divided into periods of 15 min (at each of the 4 positions). Additionally, the sampling in the first point was repeated for 5 min after the 4 positions as a control. Real-time PM_1 , $PM_{2.5}$ and PM_{10} mass concentrations were registered using a DustTrak monitor set at 5-s time resolution, enabling us to see the effect of trains and commuter's movements. All measurements were carried out during weekdays after 9:00 h to avoid rush hours. The times of trains entering and departing the station were manually recorded to assess possible correlations with the variability of the registered concentrations. The described procedure was conducted twice at each subway platform in Athens and Oporto, and four times in Barcelona (twice during each seasonal period).

3.2. Train measurements

In addition to measuring air quality on platforms, data were also collected from inside trains. In the case of Barcelona, this involved measurements in six different subway lines (L1–L5 and L10), as compared to two lines in both Athens (L2 and L3) and Oporto (LA and LD) (**Table 1**). In each case, the same sampling protocol was adopted. PM_1 , $PM_{2.5}$ and PM_{10} mass concentrations were measured using a DustTrak monitor and CO_2 concentrations were monitored by means of an indoor air quality meter in the middle of the central carriage of the train during a two-way trip along the whole length of the subway line [8]. Both instruments were set at a 5-s 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 10:00 h on weekdays, and they were performed twice at each of the selected lines in Athens and Oporto, while they were performed four times in Barcelona (twice during each seasonal period). During the colder period of the Barcelona campaign, the measurements were carried out along the whole length of the line with and without air-conditioning (not possible during warmer period due to passenger's comfort requirements), so that the effect of it on the air quality could

be assessed. During each sampling session, a written record was made of each journey, making observations such as when doors opened and closed or (for Athens) if windows were open, or (for Oporto) if the train was travelling above or below ground.

3.3. Outdoor measurements

For comparison purposes, outdoor ambient PM_{2.5} samples were collected concurrently at an urban station at each city. The Barcelona and Athens outdoor measurements were performed using a HVS in the urban background stations of Palau Reial and Demokritos, respectively. The station of Palau Reial is located in the garden of the IDAEA-CSIC at the North-West of the city (41°23′14″ N, 02°06′56″E, 78 m.a.s.l). The Demokritos station is located in NCSR 'Demokritos' campus (37°99′50″ N, 23°81′60″ E, 270 m.a.s.l), at the North-East corner of the Greater Athens Metropolitan Area. The measurements were carried out for 24 h every third day at Palau Reial station, and 19 h (subway operating hours) every second day at Demokritos station. The Oporto outdoor measurements were conducted in the urban traffic station of Francisco Sá Carneiro-Campanhã (41°09′46.10″ N, 08°35′26.95″ W, 147 m.a.s.l), with two low-volume Tecora samplers (TCR, Model 2.004.01) operating a flow of 2.3 m³ h⁻¹. PM_{2.5} samples were collected by both TCR samplers simultaneously for 19 h (coinciding with the subway operating hours) every second day.

4. Sample treatment and analyses

4.1. Filters treatment and weight

Before sampling, quartz microfibre filters were heated in an oven at 200°C for a minimum of 4 h to eliminate the volatile impurities. 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 by means of a microbalance (Model XP105DR, Mettler Toledo). The gravimetric $PM_{2.5}$ mass concentrations were determined dividing the weight difference between the blank and the sampled filter by the volume of air sampled. Once the gravimetric determination was performed, the filters were cut into several sections for subsequent chemical analyses.

4.2. Chemical analyses

The first section of each filter was acid digested and then analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-mass spectroscopy (ICP-MS) to obtain concentrations of major and trace elements, respectively. In addition, the standard reference material NIST 1633b was also analysed in a blank filter to check the accuracy of the analysis. The second section was water leached with de-ionised water to extract the soluble fraction and analysed by ion chromatography for determination of soluble anions (Cl⁻, SO₄²⁻ and NO₃⁻), and by selective electrode for ammonium (NH₄⁺). A third portion of the filters was used to measure total carbon (TC) using a thermal-optical method. A detailed description of the analytical methodology has been reported by Querol et al. (2012) [15].

The final ambient air concentrations were calculated after the subtraction of analytical blank values from the corresponding sample concentrations. Detection limits and uncertainties of the determined species concentrations were calculated from the standard deviations from the blank filters analyses alongside the analytical uncertainties [26].

4.3. Source apportionment

After the complete chemical characterisation of PM_{2.5}, a receptor model was applied in order to determine and quantify the sources of atmospheric PM_{2.5} for the Barcelona subway study. The source apportionment was carried out by means of the positive matrix factorisation (PMF) [27] using the US Environmental Protection Agency (US-EPA) PMF 5.0 software. This multivariate receptor model provides estimates of the chemical composition of PM associated with different sources and the mass contribution attributed to each source.

PMF analyses were performed separately for each subway station from the Barcelona system with datasets including both seasonal periods. The species uncertainties were calculated according to Escrig et al. (2009) [26]. For the analysis, all chemical species analysed were summed as the total variable, not taking into account the non-determined mass due to humidity and heteroatoms. Species included in the model were selected based on their signal-to-noise ratio, the percentage of samples above detection limit and their significance (considering their possible presence in this environment).

5. PM mass concentrations

5.1. On platforms

From the extensive characterisation of 24 stations with distinct designs of the Barcelona subway system, a substantial variation in $PM_{2.5}$ concentrations among the stations was observed (hourly averages ranging from 13 to 154 μg m⁻³) [28]. This variation might be related to the differences in the design of the stations and tunnels, variations in the train frequency, passenger densities and ventilation systems, among other factors, as discussed below. Large variations were also observed in the Athens (22–158 μg m⁻³; five stations) and Oporto (65–265 μg m⁻³; five stations) subway systems [8].

In the Barcelona study, the stations composed by a single tunnel with one rail separated from the platform by a wall with PSD (new stations) showed on average lower $PM_{2.5}$ concentrations (around 50%) in comparison with the old conventional stations, which is related to a combination of factors such as (i) the PSD preventing the air from the tunnel entering the platform, (ii) the more advanced ventilation setup and (iii) the lower train frequency [28]. Within the conventional system, the stations with single narrow tunnel and one rail showed on average $PM_{2.5}$ concentrations higher than in stations with one wide tunnel and two rails separated by a middle wall, most probably due to the less efficient dispersion of air pollution, enhancing the accumulation of PM. In the stations with one wide tunnel and two rails without a middle wall, $PM_{2.5}$ concentrations were much more variable. Similarly, Jung et al. [5] reported that at

narrow stations there is a larger dependence on strong ventilation to maintain relatively low PM concentrations. Regarding Athens subway system, the $PM_{2.5}$ concentrations in a central station were higher than in a peripheral station (out of the central area of the city), even when both stations belong to the same line (L2), which is probably attributable not only to the age (new station opened in 2013) and location of the station but also to the train frequency (some trains do not run the entire line) and lower number of passengers. Furthermore, measurements in a transfer station (lines 2 and 3 intersect) showed that the $PM_{2.5}$ concentrations were higher in the station platform of L2 than that of L3, probably related to the age of the lines [8].

To compare the three subway systems among them, three stations with similar platform design were selected to minimise other factors influencing the variation of PM_{2.5} concentrations: Santa Coloma in Barcelona, Nomismatokopio in Athens and Bolhão in Oporto. The lowest mean PM_{2.5} concentration (± standard deviation of daily concentrations) was found in Santa Coloma station (58.3 \pm 13.7 μ g m⁻³) while the highest mean PM_{2.5} concentration was recorded in Bolhão station (83.7 \pm 45.7 μ g m⁻³) (**Figure 1a**). In the Nomismatokopio station, a mean PM_{2.5} concentration of $68.3 \pm 11.3 \,\mu g \, m^{-3}$ was obtained (**Figure 1a**). This range of results may be associated to different ventilation systems, since the Barcelona subway is equipped with mechanical forced ventilation in all its length, whereas in both Athens and Oporto subways only natural ventilation occurs, with air exchange with the outdoor air happening mainly through blast shafts. The mechanical forced ventilation is a relevant factor to improve the air quality within the subway system, as explained below. Moreover, the majority of the underground sections in the Oporto subway system are composed of curved and/or sloping rails, which may imply higher emissions from the rail-wheel-brake interfaces while trains are stopping on the platform and thus producing increased concentrations on the platforms. Train frequency at the sampling site in the Oporto subway is higher than those of both Barcelona and Athens (Table 1), as trains from five different lines (LA, LB, LC, LE and LF) converge on Bolhão station using a common platform, whereas in Barcelona and Athens only trains of one line serve each station and consequently the train frequency at the platform is lower [8]. Furthermore, the daily average PM_{2.5} concentrations were much more variable in the Bolhão station than in the other two stations, due to the variable weather conditions, and consequently the PM_{2.5} concentrations in the outdoor ambient air were considerably variable during the sampling period in Oporto. The PM concentrations in the Bolhão station may be particularly affected by the outdoor conditions, since it is followed by an above ground station which favours the air exchange with the exterior.

In general, the mean $PM_{2.5}$ concentrations on the subway platforms were notably higher (between 1.4 and 6.9 times) than those simultaneously recorded in the outdoor ambient air, indicating the presence of indoor particulate sources in the underground stations (**Figure 1a**).

During weekdays, the $PM_{2.5}$ concentrations on the station platforms were considerably higher (1.2–1.5 times) than those measured during weekends, due to the higher number of both commuters and trains. Similar results have been observed in other subway systems [11, 13, 17, 29]. However, considering the three subway systems this difference between the weekdays and weekends in $PM_{2.5}$ concentrations was more pronounced in Bolhão station (Oporto) and less in Nomismatokopio station (Athens), possibly again favoured by the busy environment of Bolhão station with the passage of trains of five lines.

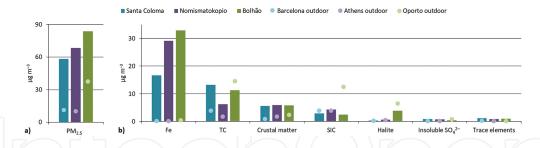


Figure 1. Mean concentrations of PM_{2.5} (a) and their elemental components (b) in Santa Coloma, Nomismatokopio and Bolhão and in the simultaneous outdoor ambient air (TC, total carbon; SIC, secondary inorganic compounds).

5.1.1. Influence of different ventilation settings

During the extensive campaign in Barcelona where different ventilation protocols were tested, mean $PM_{2.5}$ concentrations on Joanic, Santa Coloma, Tetuan and Llefià subway platforms ranged between 21 and 51 μ g m⁻³ in the warmer period, and between 32 and 93 μ g m⁻³ in the colder period (**Figure 2**). Seasonal differences among the four stations showed that the concentrations in the colder period were higher and generally more variable than in the warmer period, mainly due to the stronger ventilation in the warmer period that affects the air quality of the subway system, as the weaker ventilation enhances the accumulation of particles in the stations. These results were observed in all the additional platform measurements [28]. Regarding the PM size distribution, the PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ ratios were higher in the warmer period, indicating that the ventilation of the subway system was more efficient removing coarser particles. Thus, PM_1 was the major size fraction composing the PM in the subway system, especially during the warmer period.

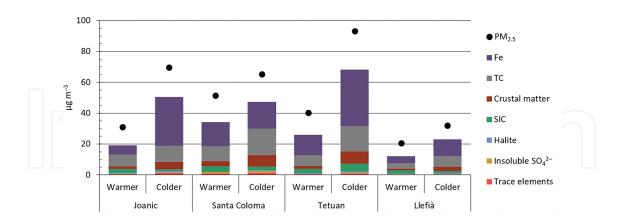


Figure 2. Mean concentrations of PM_{2.5} and the associated elemental components on the Joanic, Santa Coloma, Tetuan and Llefià platforms during the warmer and colder periods (TC, total carbon; SIC, secondary inorganic compounds).

5.1.2. Daily patterns

Similar daily trends were observed among the subway platforms of the three subway systems (**Figure 3**). The $PM_{2.5}$ daily pattern presented a concentration increase in the morning with the

arrival of the first trains showing a peak in the morning rush-hour period, which was attributable not only to the influx of commuters (CO₂ generated through exhalation) but also to the higher train frequency; the movement of the commuters leads to the PM resuspension, and the train movement promotes the resuspension of PM and its generation due to the abrasion of rails, wheels, brakes and power supply materials. Afterwards, PM_{2.5} concentration decreased towards a stable concentration until late afternoon. An increase in the PM_{2.5} concentrations was registered again during the evening rush hours, especially in the Bolhão station where the rise in train frequency was very important (increasing approx. 10 trains h⁻¹). In Nomismatokopio, there was no increase in PM_{2.5} concentrations in the evening because both train frequency and influx of commuters decreased during these hours. During the night, there was a continuous decrease in PM_{2.5} concentrations due to transport service interruption for several hours. However, in the Barcelona subway system some outliers during night-time series were generally identified in the conventional stations (Joanic, Santa Coloma and Tetuan), associated with occasional maintenance or cleaning operations (only Santa Coloma is shown as an example in **Figure 3**). The daily patterns evidence that the personal exposure to $PM_{2.5}$ concentrations is dependent on the time of the day used to commute.

In addition to the influence of the train frequency, in the Barcelona subway system, the changes of the ventilation settings along the day had considerable effect in the variations of the $PM_{2.5}$ concentrations on the platforms, particularly in the warmer period, when the ventilation is more intense [28]. It is evident that the impact of train frequency on $PM_{2.5}$ levels only becomes relevant in the absence of strong ventilation. Hence, the daily pattern of $PM_{2.5}$ concentrations in the Barcelona subway system was primarily influenced by the ventilation settings and secondarily by the train frequency [28].

5.1.3. Temporal and spatial variations

Although there were generally day-to-day fluctuations in $PM_{2.5}$ concentrations on the platforms, some temporal and spatial trends were observed along the platforms due to the influence of the ventilation settings but also to the design of the stations and tunnels, location of passengers' access to the platforms, commuter density, as well as to the effect of the passage and frequency of the trains.

The $PM_{2.5}$ concentrations on some platforms varied significantly in short time scales (e.g. an increase of a factor of 3 in less than 30 s), especially in the case of Athens and Barcelona subways [8, 28]. In some cases, the high time resolution measurements evidenced that $PM_{2.5}$ concentrations on the platform increased when the train entered the platform and decreased when it departed. Each train pushes into the station polluted air from the tunnel (by the piston effect) and $PM_{2.5}$ generated by resuspension, and when the train leaves the station the reverse piston effect moves polluted air out of the station, renewing the air on the platform. This effect of passage of trains was especially strong in the new stations (with PSD) and old stations with single rail, although in some stations with two rails without a middle wall this pattern was also observed [28]. The results showed that the PSD in the new stations do not prevent completely PM exchange between the railway and the platform.

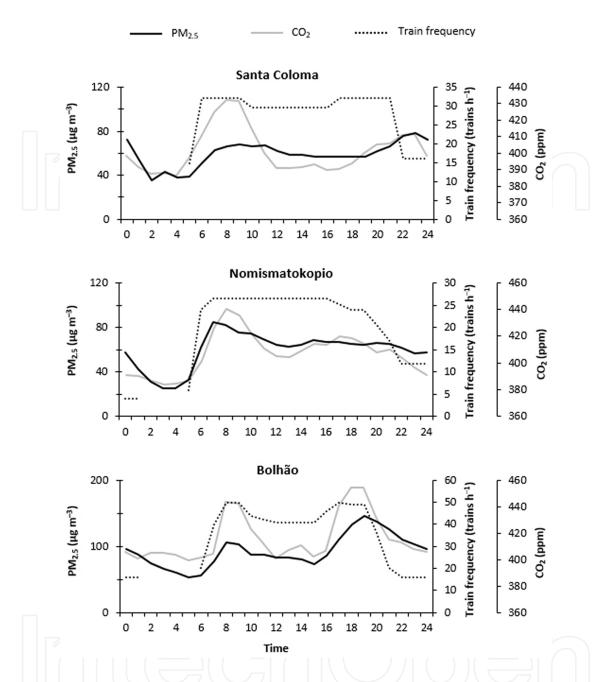


Figure 3. Temporal variation of mean hourly $PM_{2.5}$ and CO_2 concentrations and train frequency in the Santa Coloma, Nomismatokopio and Bolhão subway stations.

In some subway stations in Barcelona, higher $PM_{2.5}$ mass concentrations, especially of coarse particles, were recorded in the train-entry locations and in the areas closer to the commuters' access to the platforms, in comparison with other points on the platform [28]. However, in the Athens and Oporto cases this spatial variation was not clearly observed. Such a variation can be attributed to the turbulence generated by the train's entry, due to the wind blasts produced. In the areas closer to the passengers' access to the platforms, there is also a high probability of $PM_{2.5}$ resuspension, created by the commuters walking and the air flowing in and out of the station.

Moreover, $PM_{2.5}$ concentrations were relatively constant in time and along the platform of some stations. Therefore, in these cases the exposure levels of commuters were very similar when waiting anywhere along the platform.

5.2. Inside trains

The PM_X and CO_2 concentration profiles during trips inside the trains showed dissimilar behaviours. The CO_2 concentrations were clearly driven by the number of passengers inside the train carriages due to exhalation with the maximum influx of people corresponding to stations located in the central area of each city. An increase in the CO_2 concentrations inside the train was sometimes observed when the doors closed and a rapid drop was recorded when the doors opened.

The trains in the three subway systems are equipped with air-conditioning system. The mean PM_{2.5} concentration ranges inside the trains were 19–75, 78–135 and 29–79 µg m⁻³ in Barcelona (six lines), Athens (two lines) and Oporto (two lines), respectively. The study of the use of air-conditioning inside the trains of the Barcelona system evidenced that the airconditioning provided a clear abatement of PM concentrations, resulting in lower PM_x concentrations (by around 30% for PM_{2.5}) and finer particles (PM₁/PM₁₀ was around 15% higher), as well as lower variability of PM_x concentrations, than when the air-conditioning was switched off. Additionally, CO₂ exhaled by commuters accumulated inside the trains when air-conditioning was switched off and was less easily removed by the ventilation system compared to PM_x . Generally, the PM_x concentrations along the lines were relatively constant, while short-term peaks were observed after the train doors closed in a number of cases, probably due to turbulence and consequent PM resuspension produced by the movement of passengers inside the trains. In the Athens subway system, carriage windows were usually open, despite the existence of air-conditioning, resulting in an increase in PM_X concentrations inside the trains as they passed through some of the tunnel sections [8]. And thus, the highest PM_{χ} concentrations inside the trains from the three systems were found in the lines belonging to Athens subway system [8]. In the Oporto subway system, the PM_x and CO₂ concentrations inside the trains were generally higher while travelling in the underground than in the above ground sections, where outdoor ambient air entering the trains produced an environmental 'cleaning effect' [8]. Therefore, the PM_x concentrations inside the trains of this subway system are greatly dependent on outdoor ambient air quality.

The PM_X concentrations inside the trains were in general lower than those on the corresponding platforms in the Barcelona and Oporto subway systems, which may be attributed to the air-conditioning system operating inside the trains, and in Oporto also to the predominance of above ground stations along the lines. By contrast, in Athens system, the PM_X concentrations inside the trains were in general higher than those on the platforms since, as stated above, the trains run with most windows open, favouring the entrance of polluted air from tunnels into the trains.

In the Barcelona subway system, the $PM_{2.5}$ concentrations inside the trains in the new line (L10 with PSD) were on average around 50% lower than in the oldest lines (lines 1–5). Thus, the lowest PM_X concentrations were found in the new line both on the platforms and inside the

trains, because it is a technologically advanced line with more efficient mechanical ventilation system. Moreover, comparing the real-time measurements performed on the 24 stations with the measurements inside the trains of the six lines, there was the evidence that PM_{χ} levels inside the trains were affected by the surrounding conditions, that is, those on the platforms. **Figure 4** shows that the $PM_{2.5}$ concentrations inside the trains were strongly correlated with the $PM_{2.5}$ concentrations on the corresponding platforms ($R^2 = 0.75$). The lines with high PM concentrations were the first lines in operation and are the busiest ones because they run through the downtown area.

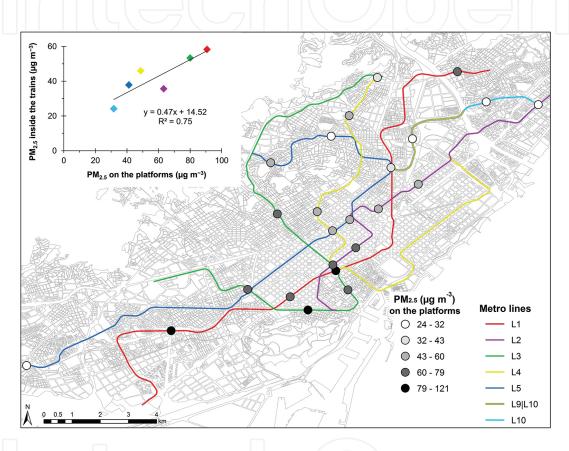


Figure 4. Relation between PM_{2.5} concentrations on the platforms and inside the trains in the Barcelona subway system.

6. Chemical composition of PM_{2.5}

The species present in the $PM_{2.5}$ samples can be broadly grouped into seven categories, namely (1) elemental iron (Fe), (2) total carbon (TC), (3) mineral or 'crustal' matter (CM; the sum of Ca, Mg, Al_2O_3 , SiO2, CO_3^{2-} , Ti, K and P), (4) secondary inorganic compounds (SIC; the sum of water-soluble sulphate, nitrate and ammonium), (5) halite (NaCl), (6) insoluble sulphate and (7) trace elements. The analysed chemical species accounted for, on average, 59–73% of the total $PM_{2.5}$ on the platforms (**Figures 1** and **2**) and 80–98% in the outdoor ambient 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) that have not been determined. The relative chemical composition of $PM_{2.5}$ was markedly different between subway platform and outdoor ambient air due to distinct emission source contributions, whereas the distributions of the chemical components were similar in the three subway systems studied.

Iron 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 19 to 46% (Figures 1 and 2). The considerable amount of Fe in the subway stations is mainly attributed to mechanical friction and wear processes at rail-wheel-brake interfaces [9, 18, 30]. However, wear and friction processes initially produce Fe metal particles, and the surface of the primary particles must be reactive enough with oxygen in the air to easily react on the metallic surface, resulting in the formation of iron oxides [5]. Previous studies have reported Fe as the most abundant species in other subway systems [11–13, 16, 17, 31, 32]. Furthermore, the relative abundance of Fe in PM_{2.5} on the platforms in the Barcelona subway system during the warmer period (19–33%) was lower than that measured on the platforms in Nomismatokopio (36-46%) and Bolhão (27-45%) stations [8]. Given that all three of these subway systems use trains with metallic wheels, this lower relative abundance of Fe in PM_{2.5} on the platforms of Barcelona could be attributable to the presence of strong forced ventilation in the subway system in the warmer period, since in the colder period the Fe abundance was similar (27–46%) to that in Oporto and Athens subway systems. By comparison, aerosol samples collected outdoors contained less than 1% of Fe mass concentration.

The second largest chemical component of the subway PM_{2.5} samples was that of total carbon, with mean relative contributions of this important subgroup ranging from 9 to 26% [8]. By comparison, in the outdoor urban air, TC concentrations were generally lower, although their relative contribution was higher (accounting for 17–39% of PM_{2.5}) due to the lower bulk PM_{2.5} concentrations (**Figures 1** and **2**). 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. However, in Barcelona and Athens the TC concentrations on the platforms were around three times higher than those in the associated outdoor ambient air (**Figure 1b**). Possible sources of this TC are diesel-powered trains used for maintenance activities running at night, and especially the abrasion of C-bearing brakes and catenary power supply materials [8, 9, 33]. By 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 above ground station. Hence, the carbonaceous particles on the platform can arise from the outdoor environment in addition to those generated inside.

Elements of crustal origin were found in higher concentrations in subway $PM_{2.5}$ samples in comparison to outdoor ambient air, with relative contributions of crustal matter in the range of 5–12%, representing the third most abundant chemical component on the subway platforms (**Figures 1** and **2**). CM is present in outdoor $PM_{2.5}$ samples, as it derives from soil and urban mineral dust, although in $PM_{2.5}$ a low contribution is expected given the dominantly coarse mode of mineral matter. It is probable that some of these inhalable mineral particles measured on the subway platforms were brought in from the outdoor environment by the commuting passengers and by air exchange between the indoor and outdoor environments.

In addition, however, an important local source of crustal particles present on subway platforms will result from the resuspension of particles generated by weathering and erosion of ballast and construction materials, sometimes enhanced by occasional construction works in the subway systems.

Secondary inorganic compounds accounted for 2–10% of the total PM_{2.5} subway concentrations. In general, SIC are one of the most abundant components in the outdoor atmosphere, accounting for 19–39% of the total PM_{2.5} (**Figures 1** and **2**), indicating that these particles in the subway environment might arise from the outdoor environment. Moreover, the highest ws-SO₄²⁻ concentrations were recorded in the warmer period and the highest ws-NO₃⁻ were recorded in the colder period in Barcelona, according to the outdoor concentrations, which have a similar seasonal variation [34]. The relative amount of SIC in the total PM_{2.5} was higher (10%) in the new station, given that the indoor sources for this station were lower.

The halite present in the subway environment is expected to come from outdoors by both air and water infiltration, the latter related to the evaporation of water and subsequent resuspension of halite minerals. The concentrations of NaCl were broadly similar at both Barcelona and Athens stations, and comparable to concentrations outdoors. By contrast, Oporto halite concentrations were notably higher in both the subway environment and outdoors, reflecting the Atlantic location of the city (**Figure 1b**).

Mean concentrations of insoluble sulphate ranged between 0.1 and 1.0 μ g m⁻³ associated with the use of barite (highly water insoluble, BaSO₄) as a bulk material (as mineral filler) in the fabrication of brakes in trains [11].

In addition to the characteristically high Fe loading of subway particles, several other metals showed enhanced levels as compared to normal concentrations outdoors. These subwayenhanced trace metals included Ba, Cu, Mn, Zn, Cr, Sb, Sr, Zr, Ni, Sn, As and Co, indicating the presence of metal particle sources specific to the underground system (Figure 5). As expected, in the Barcelona study the trace elements concentrations in the colder period were higher than those in the warmer period due to the different ventilation programmes, as previously stated. Among all the studied stations of the three subway systems, the lowest concentration of trace elements was observed in the new Llefià station. Although these trace elements comprise less than 2% of the total PM_{2.5}, they are potentially useful for source identification, given the fact that they likely relate to chemical differences between rails and wheels (Mn, Cr), brakes (Ba, Sb, Cu, Zn, Pb, Ni, Sr) and power supply materials (e.g. Cu-rich catenaries and Cu vs. C pantographs) [9, 33]. Metalliferous particles released from these materials originate from mechanical wear and friction processes, as reported by other studies in subway systems [15, 31, 35, 36]. Improved ventilation, perhaps combined with changes in the mix of trace metals used in these subway materials, would potentially reduce commuter exposure to the trace metals.

Other trace elements identified in the chemical analyses (Pb, V, Li, Zr, Se, Rb, Y, Cd, La, Ce, Pr, Nd, Hf, Bi and U) together comprise a negligible amount (<0.1%) of the total PM_{2.5}. Such elements are not especially characteristic of the subway environment, being present in similar

concentrations both below and above ground, and are probably associated with the infiltration of ambient city air in the subway systems.

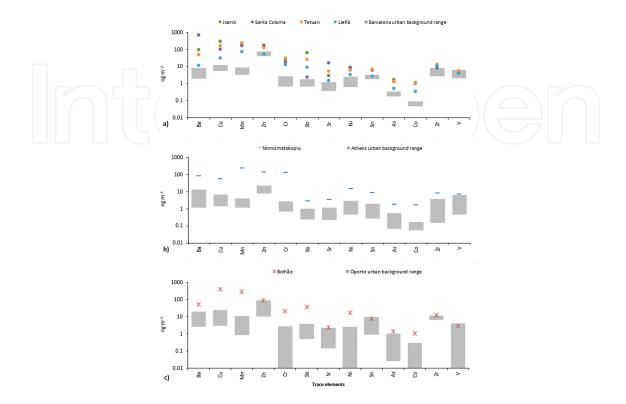


Figure 5. The mean concentration of trace elements (ng m⁻³) on the platforms and the simultaneous urban background range (ambient site) in Barcelona (a), Athens (b) and Oporto (c).

7. Source contributions

For the Barcelona subway study, the number of $PM_{2.5}$ sources identified by PMF analysis varied from one station to another, but they can be grouped into outdoor and subway sources, the latter including all emissions generated by the circulation of trains (rails, wheels, brakes, catenaries and pantographs). The main differences among stations are attributed to (i) the different characteristics for each station, leading to different influences of the subway emissions on the platform environment, (ii) the different chemical composition of rails, wheels, brakes and power supply materials and (iii) the different influence of outdoor air, which is affected by the time of the year, among other factors.

The outdoor PM_{2.5} sources found in the subway environment included secondary aerosol, sea salt and fuel-oil combustion. In the warmer period, the secondary source was characterised by a high contribution of sulphate, whereas in the colder it was dominated by nitrate. The sea salt source (mainly characterised by the presence of Na and Cl) had similar contributions in the warmer and colder periods. Moreover, a source characterised by V was identified, representing fuel-oil combustion [37].

The identified subway source had a different chemical profile for each of the stations. Although it was dominated by Fe at all stations, its content varies among stations (53–68%). Moreover, the relative abundance of other specific elements (e.g. Cu, Ba and Sr) of the subway $PM_{2.5}$ varied from station to station [9]. This source is identified as including over half of the Al_2O_3 , Ca, Fe, Cr, Mn, Cu, Sr, Ba, Pr and Nd concentrations measured in all stations sampled (as well as over half of the Mg, Li, Ti, Co, Zn and Ce measured in the older stations of Joanic, Tetuan and Santa Coloma) [9].

The subway contribution was much lower during the warmer period (9–29%) than during the colder period (32–58%), this being attributed to the different ventilation, which allows for a better dispersion of the subway emissions in the warmer period.

8. Conclusions

This work is based on a large dataset from intensive and extensive measurement campaigns, aiming to characterise the air quality in terms of PM in three European subway systems (Barcelona, Athens and Oporto), both on platforms and inside trains.

There are important factors influencing PM concentrations in the subway systems, such as differences in the design of the stations and tunnels, rails geometry (curved vs. straight and sloped vs. levelled), system age, train frequency, ventilation and air-conditioning systems, passenger densities and outdoor air quality.

PM concentrations in subway platforms display clear diurnal patterns driven by the train frequency and the ventilation settings, with higher concentrations during subway operating hours. Moreover, in some cases the PM_X concentrations show temporal and spatial variations along the platforms, influenced in addition to the ventilation settings, by the design of the stations and tunnels, location of passengers' access to the platforms, commuter densities, and the effect of the passage and frequency of the trains.

 PM_X concentrations inside the trains are very dependent on air-conditioning system, windows open/close, travelling above/underground, and PM_X concentrations on platforms and tunnels, showing short-time variations when doors open.

Subway aerosol is a complex mixture of components including iron, total carbon, crustal matter, secondary inorganic compounds, insoluble sulphate, halite and trace elements. Subway PM_{2.5} is characterised by high concentrations of Fe (relative contribution to the bulk PM_{2.5} ranging from 19 to 46%) in the three subway systems studied, generated mainly from mechanical wear and friction processes at rail-wheel-brake interfaces. Other trace elements with high enrichment in the subway PM_{2.5} are Ba, Cu, Mn, Zn, Cr, Sb, Sr, Ni, Sn, As, Co and Zr. All metals present in the alloys used in the production of rails, wheels, brakes and power supply materials clearly suggest the wear of metal parts as the most important PM_{2.5} subway source. In addition to the subway source, the contributions of secondary aerosol, sea salt and fuel-oil combustion sources can also be quantified.

This work expects to serve as a tool to establish the actions towards an effective control and to improve the air quality in subway systems, by identifying and encouraging the application of practical and focused air pollution mitigation strategies, appropriate for subway systems.

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 (LIFE13 ENV/ES/000263) and the AGAUR 2014 SGR33 grant from the Generalitat de Catalunya. Special thanks are also mentioned to Transports Metropolitans de Barcelona, the Urban Rail Transport S.A. (Athens Metro) and the Metro do Porto S.A.

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