



Invited paper

Origin of inorganic and organic components of PM_{2.5} in subway stations of Barcelona, Spain



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ARTICLE INFO

Article history:

Received 23 April 2015

Received in revised form

30 June 2015

Accepted 1 July 2015

Available online 16 July 2015

Keywords:

Indoor air quality

Subway

PM_{2.5}

Chemical composition

PMF

Fe

ABSTRACT

The present work assesses indoor air quality in stations of the Barcelona subway system. PM_{2.5} concentrations on the platforms of 4 subway stations were measured during two different seasons and the chemical composition was determined. A Positive Matrix Factorization analysis was performed to identify and quantify the contributions of major PM_{2.5} sources in the subway stations. Mean PM_{2.5} concentrations varied according to the stations design and seasonal periods. PM_{2.5} was composed of haematite, carbonaceous aerosol, crustal matter, secondary inorganic compounds, trace elements, insoluble sulphate and halite. Organic compounds such as PAHs, nicotine, levoglucosan and aromatic musk compounds were also identified. Subway PM_{2.5} source comprised emissions from rails, wheels, catenaries, brake pads and pantographs. The subway source showed different chemical profiles for each station, but was always dominated by Fe. Control actions on the source are important for the achievement of better air quality in the subway environment.

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1. Introduction

People living in urban areas usually spend a considerable amount of their daily time commuting, with underground subway being one of the public transport modes most used in cities around the world. Several studies concerning the air quality in subway systems worldwide have been conducted, focussing mainly on the concentrations of particulate matter (PM) (Martins et al., 2015 and references therein), as the exposure to PM can be related to the occurrence of adverse health effects such as respiratory and cardiovascular diseases (e.g. Pope et al., 2004), and the subway emissions have been shown to contribute to personal exposure to PM (Bachoual et al., 2007; Bigert et al., 2008; Minguillón et al., 2012). However, other authors such as Gustavsson et al. (2008) found no increased lung cancer incidence among the subway drivers in Stockholm, and Seaton et al. (2005) stated that those principally at

risk from dust inhalation by working or travelling in the London Underground should not be seriously concerned. Studies indicate that PM may enter from outdoor ambient air in addition to that generated internally in the system by the motion of the trains, and the movement of passengers which promotes the mixing and resuspension of PM (Aarnio et al., 2005; Adams et al., 2001; Braniš, 2006; Cheng et al., 2008; Chillrud et al., 2004; Johansson and Johansson, 2003; Karlsson et al., 2005; Kim et al., 2008; Nieuwenhuijsen et al., 2007; Park and Ha, 2008; Ripanucci et al., 2006; Salma et al., 2007; Seaton et al., 2005). The less common manuscripts dealing with chemical composition of subway PM show that this consists mainly of Fe, which accounts between 40 and 80% of its mass fraction, as well as several other transition metals such as Cu, Ba, Cr, Si, Mn, and Zn (Aarnio et al., 2005; Jung et al., 2010; Loxham et al., 2013; Moreno et al., 2015; Mugica-Álvarez et al., 2012; Querol et al., 2012; Salma et al., 2007), which are reported as being mostly generated by the abrasion of rail tracks, wheels, catenaries, brake pads and pantographs produced by the motion of the trains (Chillrud et al., 2004; Jung et al., 2012, 2010; Park et al., 2012; Querol et al., 2012). There is a large variety of factors influencing the concentration and composition of PM

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in subway systems. These factors include differences in the depth and design of the stations and tunnels, system age, wheel and rail track materials and braking mechanisms, train speed and frequency, passenger densities, ventilation and air conditioning systems and cleaning frequencies (Moreno et al., 2014 and references therein). The results of different studies are not always directly comparable due to differences in sampling strategies, measurement methods, analytical procedures, and data analysis (Nieuwenhuijsen et al., 2007).

Most of the studies have investigated the PM composition in a reduced number of stations, limited number of samples and without quantifying the contribution of the potential sources. On the other hand, the study of the organic compounds contained in the subway PM is lacking. Therefore, there is a need for extensive studies of entire subway systems, covering stations of the vast diversity of lines, providing an overview of the overall characterization of PM in this environment.

With this in mind, the purpose of the present work was to study the PM_{2.5} chemical composition on the platforms of four different subway stations from four subway lines in the city of Barcelona, including a new line equipped with platform screen doors (PSDs). This chemical composition was obtained in terms of major and trace elements, ions, total carbon, and organic compounds. The measurements were performed during two seasonal periods, covering a high number of samples (approx. 240). Additionally, a source apportionment study was performed to identify and quantify the contributions of major PM_{2.5} sources in the subway stations, with the aim of identifying possible abatement measures.

2. Methodology

2.1. Field study

Barcelona's subway system (managed by Transports Metropolitans de Barcelona, TMB) comprises 8 lines stretching 102.6 km and including 140 stations (Fig. S1). Currently, over 1.25 million passengers commute in this subway system on a daily basis, absorbing around 50% of the urban commuting load (Querol et al., 2012). In this study, subway PM_{2.5} samples were collected at four underground stations with highly contrasting designs belonging to different lines (Fig. S1): Joanic (L4), Santa Coloma (L1), Tetuan (L2), and Llefià on the new line (L10). Each station has a different architectural design (Table S1): one wide tunnel with two rail tracks, separated by a middle wall in Joanic station and without middle wall in Santa Coloma, a single narrow tunnel with one rail track in Tetuan, and a single tunnel with one rail track separated from the platform by a glass wall with platform screen doors (PSDs) that are opened simultaneously with the train doors in Llefià. The PSDs new system includes advanced platform ventilation systems and driverless trains with computer-controlled driving system that optimises speed, braking and stopping processes. All trains are operated electrically with a frequency between 2 and 15 min, depending on the day (weekend or weekday), subway line and time of day. The mean train frequency on each of the four selected stations is displayed in Table S1. The braking system is electric when approaching the platform, changing to non-asbestos pneumatic braking when slowing down below a 5 km h⁻¹ velocity for all lines independently of the platform design, using either frontal or lateral brake pads.

The measurements were conducted continuously at each station during a month in two different periods: warmer (2 April – 30 July 2013) and colder (28 October 2013 – 10 March 2014) (Table S1). For comparison purposes, outdoor ambient PM concentrations were measured concurrently at the urban background station of Palau Reial which was used as a reference site (Fig. S1) (Rivas et al., 2014).

2.2. Sampling methodology

PM_{2.5} samples were collected on quartz microfiber filters by means of a high volume sampler (HVS, Model CAV-A/MSB, MCV), programmed to sample daily over a 19 h period (from 5 a.m. to midnight, subway operating hours) at a sampling flow rate of 30 m³ h⁻¹. A field filter blank per period was taken at each station. The aerosol samples (123 and 113 in the warmer and colder periods, respectively) and blank filters were placed in aluminium foil until analysis. The instrument was placed at the end of the platform corresponding to the train entry point, far from the commuters' access-to-platform point, and behind a light fence for security protection. This location was chosen as a compromise between meeting conditions for undisturbed measurement and minimizing the annoyance to commuters.

In the urban background station of Palau Reial the measurements were performed using the same protocol but working for 24 h every third day.

2.3. Sample analysis

2.3.1. PM_{2.5} concentrations

All filters were weighed before and after sampling by a microbalance (Model XP105DR, Mettler Toledo), after being stabilized for at least 48 h in a conditioned room (20 °C and 50% relative humidity) to determine PM_{2.5} mass concentrations by standard gravimetric procedures.

In order to have PM characterisation representative of the whole platform, the PM mass and chemical compounds concentrations reported here are those corrected for spatial variation at each platform, based on the measurements described in Martins et al. (2015), where the PM_{2.5} concentrations were measured at four different sites along the platforms.

2.3.2. Analysis of inorganic and organic compounds

One quarter of each filter was acid digested and subsequently analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES) and Mass Spectrometry (ICP–MS) to determine major and trace elements, respectively. A few milligrams of a standard reference material (NIST 1633b) were added to a fraction of a blank filter to check the accuracy of the analysis of the acid digestions. Another quarter of filter was water leached with de-ionized water to extract the soluble fraction and analysed by ion chromatography for determination of soluble anions (Cl⁻, SO₄²⁻, and NO₃⁻), and by specific electrode for ammonium (NH₄⁺). A third portion of filter (1.5 cm²) was used to measure total carbon (TC) using the Thermal – Optical Transmittance (TOT) method by means of a laboratory OC–EC Sunset instrument. A detailed description of the analytical methodology is given by Querol et al. (2012). Blank filters were analysed in the batches of their respective filter samples and the corresponding blank concentrations were subtracted from each sample in order to calculate the ambient concentrations. Uncertainties were calculated as described by Escrig et al. (2009).

In addition a quarter of 54 selected samples (6–7 per station and period) was extracted in a solvent mixture of methanol and dichloromethane. The usage of this organic solvent mixture allows the extraction of a wide range of organic compounds with different polarities. The extracts were analysed on a gas-chromatograph coupled to a mass-spectrometer (GC–MS) after derivation of COOH and OH groups into trimethylsilyl (TMS)-esters and TMS-ethers. The quantified compounds in the present study are polycyclic aromatic hydrocarbons (PAHs; phenanthrene, anthracene, fluoranthene, pyrene, retene, benz[a]anthracene, chrysene, benzo [b+j+k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno [123cd]pyrene, benzo[ghi]perylene, coronene), 17(H)α-21(H)β-29-

norhopane, 17(H) α -21(H) β -hopane, nicotine, levoglucosan, methyl-dihydrojasmonate, galaxolide, xylitol, α -glucose, β -glucose, mannitol, dibutyl phthalate (DBP) and di(ethylhexyl) phthalate (DEHP). Methyl-dihydrojasmonate, galaxolide, DBP, and DEHP were analysed for the first time in PM filter samples, while the applied method for the other compounds is described in more detail elsewhere (Alier et al., 2013). The new compounds were identified with authentic standards, retention times in the GC–MS and the following ions: methyl-dihydrojasmonate (m/z 153), galaxolide (m/z 243), DBP (m/z 149), and DEHP (m/z 149) in the fraction of the extract that was used for the analyses of TMS-derived compounds in scan mode. The limit of detection (LOD) was between 0.1 and 0.4 ng m⁻³ for these compounds. Methyl-dihydrojasmonate and galaxolide were under LOD in blank filters, while DBP and DEHP had blank levels of 1 and 0.8 ng m⁻³, respectively, representing maximum 5% of the concentration found in the samples. No corrections for blanks were applied on the sample concentrations.

2.4. Source apportionment

The source apportionment of the PM composition was carried out by means of a Positive Matrix Factorization (PMF; Paatero and Tapper, 1994), using US–EPA PMF 5.0 software. This multivariate receptor model factorizes the chemical composition matrix X , containing n samples (rows) with m species (columns), into two submatrices, the chemical profiles F and the time series G , so that p different sources of emissions or secondary components are identified and their contribution is quantified. The residual E matrix corresponds to the fraction of X not explained by the solution.

$$X = GF + E \quad (1)$$

The G and F matrices are adjusted until a minimum for the objective function Q for a given number of factors p is found:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \quad (2)$$

where e_{ij} is the residual associated with the j th species concentration measured in the i th sample, and σ_{ij} is the user defined uncertainty for the j th species in the i th sample.

PMF analyses were performed separately for each subway station with datasets including both seasonal periods. The source apportionment was applied using the sum of all chemical species analysed, as the total variable hence excluding the non-determined

mass due to humidity and heteroatoms. The selection of the species included in the model was done according to their signal to noise ratio, the percentage of samples above detection limit and the significance of the species (knowledge of its presence in possible PM sources).

3. Results and discussion

3.1. Mass concentrations

Mean PM_{2.5} concentrations in the warmer and colder periods were 31 and 70, 51 and 65, 40 and 93, and 21 and 32 $\mu\text{g m}^{-3}$, for Joanic, Santa Coloma, Tetuan and Llefia stations, respectively (Fig. 1).

The lower PM_{2.5} concentrations in Llefia station compared to the old conventional stations by a factor of around 2.0 and 2.4 in the warmer and colder periods, respectively, may be attributed to the PSDs installed in this station that prevent the air from the tunnel entering the platform, but also to the more advanced ventilation setup and the lower train frequency. Kim et al. (2012) and Querol et al. (2012) also reported that the PSDs were helpful reducing PM levels on the platform.

During the colder period, with constant ventilation efficiency, PM_{2.5} concentrations in the station with single narrow tunnel and one rail track (Tetuan) were on average higher than those in the station with one wide tunnel and two rail tracks separated by a middle wall (Joanic), probably due to the less efficient dispersion of air pollution. In the station with one wide tunnel and two rail tracks without middle wall (Santa Coloma) were observed PM_{2.5} concentrations much more variable (See interquartile range in Fig. 1). These results are in accordance with the concentrations measured in 24 stations with distinct designs (Martins et al., 2015).

Seasonal differences among the four stations showed that the values in the colder period were higher and also more variable than in the warmer period (Fig. 1), probably due to more intensive ventilation in the warmer period controlling the air quality of the subway system. Similar seasonal results were reported in other studies (Branis, 2006; Furuya et al., 2001; Querol et al., 2012).

The mean PM_{2.5} concentrations on the platforms were between 1.4 and 5.4 times higher than in the Barcelona's outdoor ambient air (measured at the urban background station of Palau Reial) (Fig. 1), which is similar to other studies (Adams et al., 2001; Colombi et al., 2013; Johansson and Johansson, 2003; Kamani et al., 2014; Querol et al., 2012). These results indicate the presence of indoor particulate sources in the underground stations, as will be discussed further below.

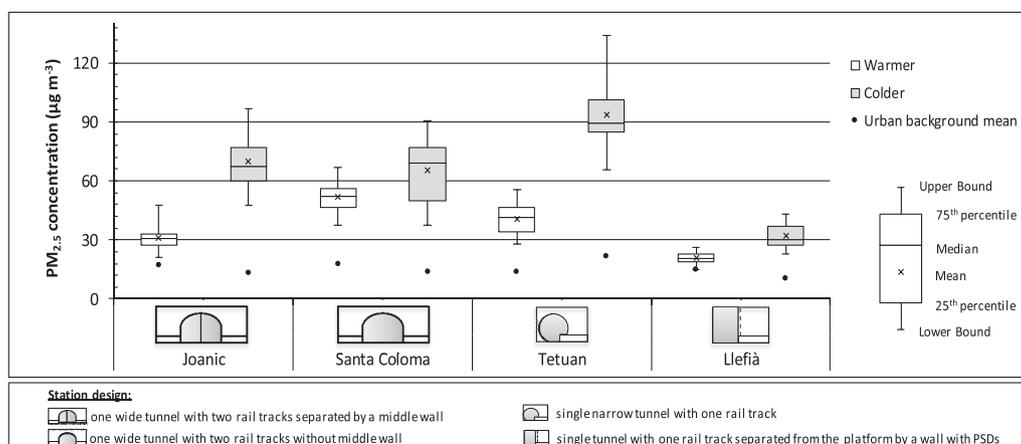


Fig. 1. PM_{2.5} concentrations in the four subway platforms and at the urban background station during the warmer and colder periods.

Table 1
Mean PM_{2.5} concentrations and the associated elemental components on the four subway platforms in both periods. (sd – standard deviation; TC – total carbon; ws – water soluble; CM – crustal matter; CA – carbonaceous aerosol; SIC – secondary inorganic compounds). The SiO₂ was estimated by multiplying Al₂O₃ by a factor of 3. The CO₃²⁻ was estimated by multiplying Ca by a factor of 1.5. (n ≈ 30 per station and period).

	Warmer period								Colder period								
	Joanic		Santa Coloma		Tetuan		Llefià		Joanic		Santa Coloma		Tetuan		Llefià		
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	
µg m⁻³																	
PM _{2.5}	30.9	6.7	51.5	7.5	40.3	7.3	20.7	2.9	69.6	13.0	65.3	15.2	93.2	18.3	32.0	6.1	
TC	7.5	1.9	9.5	1.5	6.8	1.8	3.2	0.9	10.2	2.4	17.1	5.3	16.4	4.3	6.9	2.6	
ws-Cl ⁻	0.2	0.2	0.1	0.1	0.3	0.2	0.1	0.1	0.3	0.1	0.3	0.2	0.5	0.2	0.4	0.2	
ws-NO ₃ ⁻	0.7	0.3	0.4	0.1	0.6	0.2	0.3	0.1	0.5	0.2	1.1	0.9	2.3	1.0	0.6	0.3	
ws-SO ₄ ²⁻	1.5	0.7	2.6	0.6	1.7	0.7	1.5	0.6	0.9	0.5	1.1	0.6	2.1	0.6	0.6	0.3	
ws-NH ₄ ⁺	0.4	0.2	0.6	0.2	0.3	0.2	0.4	0.1	0.1	0.1	0.2	0.2	0.5	0.3	0.2	0.1	
Ca	0.2	0.1	0.6	0.1	0.5	0.1	0.3	0.1	0.7	0.2	1.5	0.7	1.8	0.5	0.7	0.3	
Mg	0.1	<0.1	0.3	0.1	0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.4	0.1	0.3	0.1	0.1	<0.1	
Na	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1	
SO ₄ ²⁻	1.9	0.8	3.4	0.7	1.9	0.8	1.8	0.6	1.3	0.4	2.1	0.6	2.5	0.7	0.8	0.3	
Fe ₂ O ₃	8.6	2.7	22.8	4.2	19.0	3.9	6.9	1.9	45.4	11.7	24.9	6.9	52.4	12.5	15.5	3.9	
CO ₃ ²⁻	0.4	0.1	1.0	0.2	0.7	0.2	0.4	0.1	1.1	0.2	2.2	1.0	2.7	0.7	1.0	0.4	
Al ₂ O ₃	0.3	0.1	0.3	0.1	0.2	0.1	0.1	0.1	0.6	0.1	0.8	0.3	0.7	0.1	0.2	0.1	
SiO ₂	0.8	0.4	1.0	0.4	0.5	0.3	0.4	0.2	1.7	0.4	2.3	1.0	2.0	0.4	0.7	0.3	
K ₂ O	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	0.1	0.3	0.1	0.3	0.2	0.6	0.2	0.2	0.1	
TiO ₂	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
P ₂ O ₅	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1	
ng m⁻³																	
Ba	45.7	13.0	567.9	141.7	26.1	10.3	7.5	8.3	146.7	34.6	838.4	245.5	72.9	13.4	15.0	7.4	
Cu	113.1	36.2	98.3	21.0	84.8	27.3	21.1	6.2	465.3	146.5	104.1	31.1	231.2	45.2	41.4	13.3	
Mn	63.6	19.1	127.4	24.9	122.6	23.9	46.9	15.9	304.3	69.6	197.6	54.8	364.8	87.7	103.5	24.8	
Zn	92.8	27.9	129.7	29.5	64.2	19.4	37.4	25.3	266.2	64.0	198.2	60.8	193.8	86.8	71.2	25.0	
Cr	8.8	2.5	12.9	2.7	15.7	3.5	7.5	2.6	39.5	9.9	22.0	6.3	45.5	11.0	16.5	4.2	
Sr	1.6	0.7	13.9	3.2	2.1	0.6	1.2	1.3	4.1	0.8	19.1	5.3	8.5	2.9	1.7	0.6	
Zr	10.1	1.6	10.5	1.0	10.7	1.7	7.9	1.3	8.1	1.3	6.3	1.6	16.1	1.9	14.3	1.7	
Mo	17.6	6.8	16.1	3.9	11.5	6.3	6.8	7.7	18.3	6.4	24.6	11.7	10.1	4.9	16.1	4.1	
Sb	35.9	10.2	1.4	0.3	14.5	6.1	3.3	1.1	95.0	17.2	3.5	1.1	36.5	9.5	15.0	5.8	
Sn	4.0	1.8	5.2	1.1	3.5	1.2	2.1	0.7	7.9	1.6	8.0	2.2	9.7	2.2	3.4	1.3	
Ni	5.7	2.5	7.2	1.4	5.3	2.0	2.8	1.3	11.2	2.4	10.1	3.0	6.8	1.5	3.6	1.0	
As	0.8	0.2	1.2	0.2	0.8	0.2	0.4	0.1	2.6	0.6	1.5	0.4	1.9	0.4	0.7	0.3	
Pb	6.1	2.2	5.2	1.7	3.6	1.7	2.7	1.6	12.6	3.4	10.6	4.2	11.6	5.3	7.0	5.4	
V	4.8	4.9	6.0	2.0	6.2	5.2	4.7	2.3	3.5	2.2	4.5	1.5	5.4	2.8	2.6	1.4	
Co	0.5	0.2	0.9	0.2	0.6	0.1	0.2	0.1	1.9	0.4	1.1	0.3	1.5	0.3	0.5	0.1	
W	0.8	0.3	1.1	0.2	0.5	0.2	0.2	0.1	1.9	0.4	0.4	0.4	2.3	0.6	0.5	0.3	
Li	0.2	0.1	0.3	0.1	0.2	0.1	0.1	<0.1	0.3	0.1	0.5	0.2	0.6	0.1	0.2	0.1	
Hf	0.3	0.1	0.5	<0.1	0.5	0.1	0.3	0.1	0.4	0.1	0.2	0.1	0.7	0.1	0.7	0.1	
Rb	0.3	0.1	0.4	0.1	0.3	0.1	0.2	0.1	0.7	0.1	0.8	0.3	1.2	0.3	0.5	0.1	
Nb	0.4	0.2	0.9	0.1	0.3	0.1	0.2	0.1	0.6	0.2	0.8	0.4	1.4	0.3	0.3	0.1	
Ge	0.3	0.1	<0.1	0.1	0.3	0.1	0.1	0.2	0.4	0.1	0.7	0.3	0.6	0.1	0.4	0.2	
Ga	0.1	<0.1	0.2	<0.1	0.2	<0.1	0.1	<0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.1	<0.1	
U	0.3	0.2	0.1	<0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	<0.1	
Y	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.2	0.1	
Th	0.2	0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.1	0.1	0.2	<0.1	0.1	<0.1	
Cd	0.1	0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1	
Bi	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.3	0.2	0.1	0.9	1.5	0.5	0.2	0.6	1.5	
Se	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.3	0.1	0.3	0.1	
La	0.4	0.1	0.3	<0.1	0.2	0.1	0.1	<0.1	0.6	0.1	0.5	0.1	0.5	0.1	0.2	0.1	
Ce	0.8	0.2	0.5	0.1	0.5	0.1	0.2	0.1	1.2	0.2	1.0	0.3	1.1	0.2	0.4	0.2	
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	0.1	<0.1	<0.1	<0.1	
Nd	0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.2	0.1	0.2	<0.1	0.1	<0.1	
µg m⁻³																	
Fe ₂ O ₃	8.6	2.7	22.8	4.2	19.0	3.9	6.9	1.9	45.4	11.7	24.9	6.9	52.4	12.5	15.5	3.9	
CM	1.9	0.7	3.4	0.9	2.1	0.7	1.4	0.5	4.7	0.9	7.6	3.2	8.2	2.0	2.9	1.1	
CA	10.4	2.7	13.3	2.1	9.5	2.5	4.5	1.2	14.3	3.4	23.9	7.4	23.0	6.0	9.6	3.6	
Insoluble SO ₄ ²⁻	0.4	0.2	0.8	0.2	0.2	0.3	0.4	0.2	0.4	0.1	1.0	0.3	0.4	0.2	0.2	0.1	
SIC	2.7	1.1	3.5	0.8	2.6	1.1	2.1	0.8	1.4	0.7	2.4	1.4	5.0	1.8	1.4	0.6	
Halite	0.3	0.2	0.2	0.1	0.5	0.3	0.2	0.2	0.5	0.2	0.5	0.2	0.8	0.3	0.6	0.3	
Trace elements	0.4	0.1	1.0	0.2	0.4	0.1	0.2	<0.1	1.4	0.3	1.5	0.4	1.0	0.2	0.3	0.1	
% determined	80.1	4.9	87.4	3.7	85.1	6.0	75.6	5.8	98.1	5.0	94.6	4.4	97.4	5.3	95.3	4.1	

3.2. PM chemical composition

Mean elemental concentrations of PM_{2.5} collected at the four selected platforms are summarized in Table 1. Assuming that all the Fe is in the haematite oxidised form (Lu et al., 2015; Querol et al., 2012) and for a better mass closure, concentrations are reported

as Fe₂O₃, although magnetite and Fe metal can be still present as nanometric aggregates in much smaller proportion normally surrounded by haematite rims (Moreno et al., 2015). Subway particles were grouped into seven categories, based on their chemical composition: haematite (Fe₂O₃); crustal matter (CM, the sum of Ca, Mg, Al₂O₃, SiO₂, CO₃²⁻, K₂O, TiO₂ and P₂O₅); carbonaceous aerosol

(CA, calculated from the TC concentrations, assuming an elemental to organic carbon (EC/OC) ratio of 0.5 (Querol et al., 2013), and an organic matter to organic carbon (OM/OC) ratio of 1.6 (Minguillón et al., 2011) for Barcelona); insoluble sulphate (SO_4^{2-}); secondary inorganic compounds (SIC, the sum of water-soluble sulphate (ws-SO_4^{2-}), nitrate (ws-NO_3^-) and ammonium (ws-NH_4^+)); halite (the sum of Na and Cl) and trace elements.

The analysed chemical species accounted for 75.6–98.1% of the total $\text{PM}_{2.5}$ on the platforms (Table 1 and Table S2). The distributions of the chemical components were similar at the four subway stations (Fig. 2). The haematite was the most abundant species at all stations, accounting for 27.9–65.3% of $\text{PM}_{2.5}$, except for Joanic station in the warmer period, where the CA was the main component, closely followed by haematite. These results are in agreement with the high levels of iron reported in other subway systems (Aarnio et al., 2005; Adams et al., 2001; Chillrud et al., 2004; Furuya et al., 2001; Grass et al., 2010; Johansson and Johansson, 2003; Murrini et al., 2009; Nieuwenhuijsen et al., 2007; Raut et al., 2009; Ripanucci et al., 2006; Salma et al., 2007; Seaton et al., 2005). The mean concentration of haematite in Tetuan station in the colder period was the highest among the four stations (Fig. 2). This could be related to the weaker ventilation in the colder period, enhancing the accumulation of PM, which is more common in the stations with a single narrow tunnel (Martins et al., 2015; Moreno et al., 2014). Jung et al. (2010) reported the generation of Fe particles in the tunnels, indicating that at narrow platforms there is a larger dependence on strong ventilation to maintain relatively low PM concentrations. In Llefia station the haematite concentration was around 60% lower than in the conventional stations, which is probably attributable to the more advanced ventilation setup, the lower train frequency, and especially the presence of PSDs that restrict the air-exchange of Fe particles from the tunnel to the platform.

Some studies have reported EC and OC concentrations in subway environments (Aarnio et al., 2005; Kam et al., 2013, 2011; Midander et al., 2012). However, the iron acts as a catalyser for EC oxidation during the TOT analysis (Chow et al., 2001), and hence the high iron concentrations in the subway environment lead to artificially high OC/EC ratios (Querol et al., 2012). Therefore only TC concentrations were measured in the present study. The mean concentrations of CA ranged between 4.5 and 23.9 $\mu\text{g m}^{-3}$, representing the second largest component of $\text{PM}_{2.5}$. Highest concentrations were measured in Santa Coloma station in the colder period, although variations were not as large as for haematite (Table 1).

The crustal matter was the third most abundant chemical species on the subway platforms, with relative amounts in the range of 5.2–11.7% (Table S2), and mean concentrations ranging from 1.4 to 3.4 $\mu\text{g m}^{-3}$ in the warmer period and from 2.9 to 8.2 $\mu\text{g m}^{-3}$ in the colder period.

The SIC account for 2.0–10.2% of the total $\text{PM}_{2.5}$ concentrations (Table S2). The highest ws-SO_4^{2-} concentrations were recorded in the warmer period and the highest ws-NO_3^- were recorded in the colder period, according to the outdoor concentrations, which have a similar seasonal variation. The relative amount of SIC in the total $\text{PM}_{2.5}$ was higher (10.2%) in the new station, given that the indoor sources for this station were lower (Table 1). Concentrations of insoluble sulphate (SO_4^{2-}) were very low and very similar at both seasonal periods in each platform, with mean concentrations ranging between 0.2 and 1.0 $\mu\text{g m}^{-3}$ (Table 1). Higher relative amounts of insoluble SO_4^{2-} in the total $\text{PM}_{2.5}$ were observed in the warmer period (Table S2). The halite reached similar levels among the stations (0.2–0.8 $\mu\text{g m}^{-3}$), with higher values in the colder period (Table 1).

The highest concentration of trace elements was observed in

Santa Coloma station in both periods (Table 1) while the opposite was obtained in Llefia station. Fig. 3 shows the concentration of the more enriched trace elements in the aerosols collected in the warmer and colder periods, including Ba, Cu, Mn, Zn, Cr, Sr, Zr, Mo, Sb, Sn, Ni, Pb, V and Co. As expected, the trace elements concentrations in the colder period were higher than those in the warmer period due to the different ventilation programs, as previously stated. The elements with higher enrichment comparing to the simultaneous mean outdoor concentrations at Palau Reial (e.g. Ba, Mn, Cu, Cr, Sb, Sr) were those associated with the presence of particulate sources in the underground stations. It is worth to mention the following (Fig. 3):

- Ba was especially enriched in Santa Coloma station, with concentrations 165 and 171 times higher than outdoors, in the warmer and colder periods, respectively;
- The highest Sb and Cu concentrations were found in Joanic station, with concentrations of Sb 35 and 98, and of Cu 18 and 54 times higher than those at the urban background, in the warmer and colder periods, respectively;
- The lowest concentration of trace elements was observed in Llefia station;
- Mn, Cr, Zn, Zr, Sn, among other trace elements, showed similar concentrations among the stations.
- The Mo, Pb and V concentrations were similar among the subway stations and similar to simultaneous outdoor concentrations, implying that their sources can be located outdoors rather than being originated within the subway environment.

Differences in trace elements concentrations among stations are associated to the different chemical composition of wheels, rail tracks, catenaries (C-rich), brake pads (lateral vs frontal, of different composition) and pantographs (Cu vs C), which are different depending on the subway line, as observed in previous findings (TMB data not published). Therefore, a more intense ventilation and low metal specifications for any of the above components of the railway and trains would reduce considerably commuter's exposure to metals.

3.3. Particulate organic chemical composition

Polycyclic aromatic hydrocarbons (PAHs, 13 in total) were detected in all $\text{PM}_{2.5}$ analysed samples. Although it is possible that maintenance works during night-time can still affect daily platform concentrations, part of these compounds could enter the subway systems from outdoor air through ventilation. The highest concentrations were observed in the colder period in Tetuan station, where the mean $\sum\text{PAH}$ was 11 ng m^{-3} , in contrast to the moderated values found in other conventional stations (Joanic: $\sum\text{PAH}_{\text{colder}} = 4 \text{ ng m}^{-3}$, Santa Coloma: $\sum\text{PAH}_{\text{colder}} = 6 \text{ ng m}^{-3}$). The lowest colder time levels were observed in the station of the modern subway system, Llefia, where $\sum\text{PAH}_{\text{colder}} = 3 \text{ ng m}^{-3}$ and benzo[a]pyrene = 0.2 ng m^{-3} . The low cold-period PAHs concentrations found in Llefia are similar to those observed in the other stations during the warmer time (Table 2), while the levels in Llefia station in the warmer period were lower; $\text{PAH}_{\text{warmer}} = 1 \text{ ng m}^{-3}$. Hence the colder time concentrations were 2 times higher than those in the warmer time, similarly to the differences observed in the outdoor air in Barcelona (Reche et al., 2012). In general the subway PAHs concentrations are in the range of the ones observed in urban road traffic sites of the city, although the observed variation among the stations is probably caused by their different designs. The higher levels of PAHs in Tetuan station may be caused by the narrow single track structure of the station. The low concentration observed in the new Llefia station is probably a direct effect

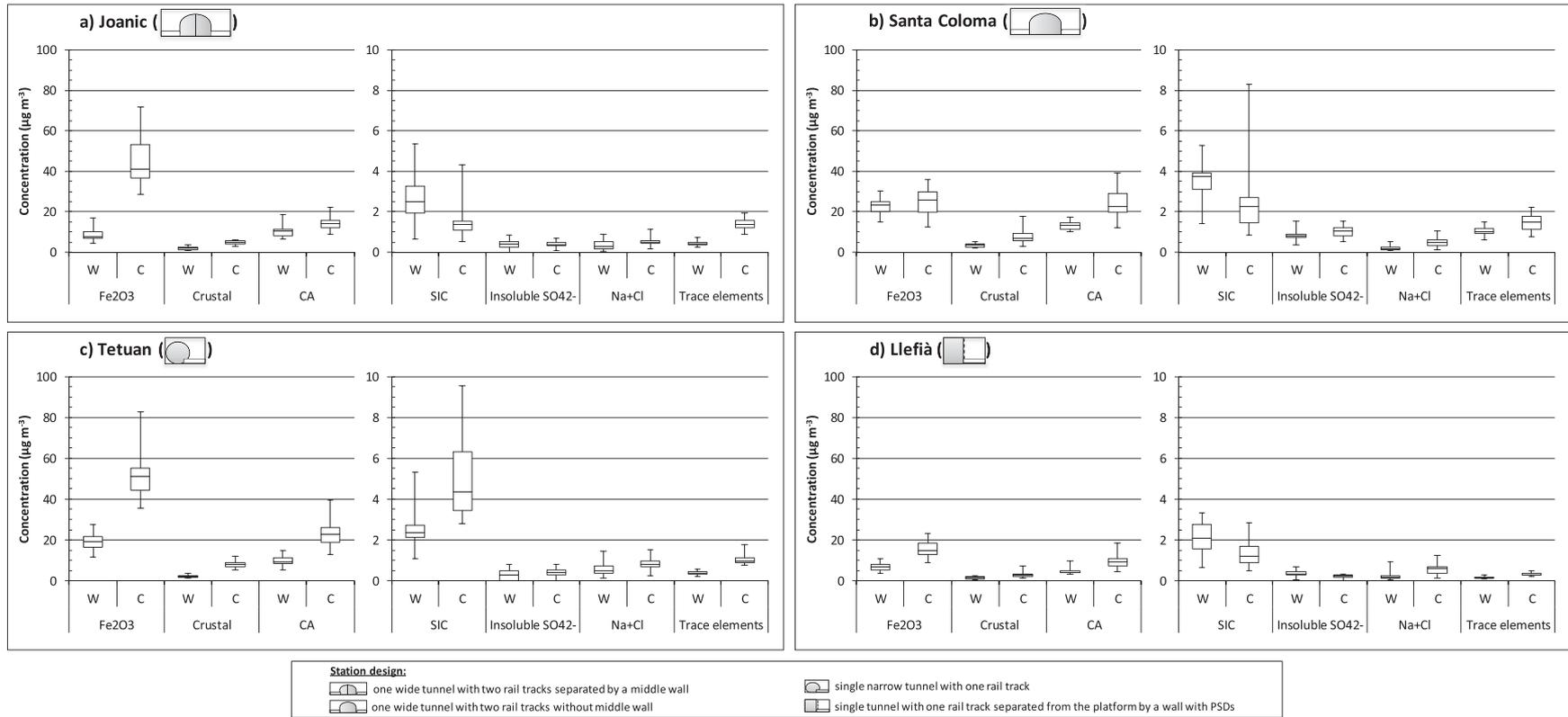


Fig. 2. PM_{2.5} chemical components concentrations during the warmer and colder periods in the subway stations: a) Joanic; b) Santa Coloma; c) Tetuan; d) Llefià (W — warmer period; C — colder period). The line within the box shows the median, while the box bottom and top represent the 25th and 75th percentile, respectively. The whiskers represent the lower and the upper bounds.

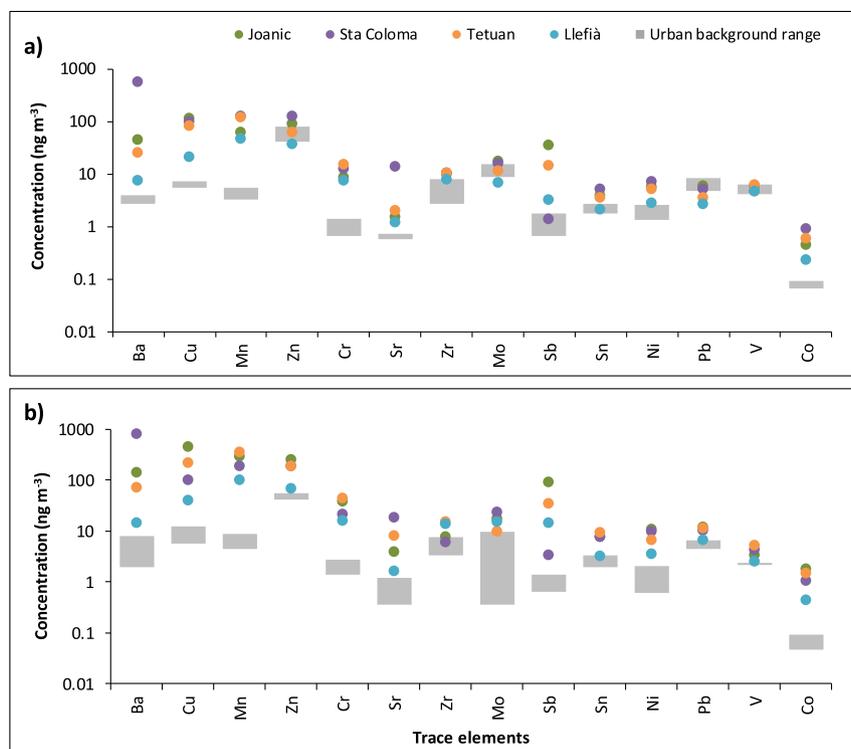


Fig. 3. Mean concentrations of trace elements (ng m^{-3}) for the four subway stations and the simultaneous urban background range (ambient site) a) in the warmer and b) in the colder periods.

of the isolation of the platform from the tunnel, and its more advanced ventilation setup.

The warmer time PAHs levels are correlated ($R^2 = 0.7$) with the detected hopanes (17(H) α -21(H) β -29-norhopane and 17(H) α -21(H)

β -hopane) in the four stations (Fig. 4a), with the lowest hopane levels in Llefia station. Hopanes are molecular markers for mineral oils, and their presence in PM can be related to lubricating oil residues from primary road traffic emissions penetrating indoor

Table 2

Mean concentrations of organic compounds (ng m^{-3}) and standard deviations (sd) on the four subway platforms in both periods. (n = 6–7 per station and period).

	Warmer period								Colder period							
	Joanic		Santa Coloma		Tetuan		Llefia		Joanic		Santa Coloma		Tetuan		Llefia	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
Phenanthrene	0.14	0.05	0.51	0.15	0.20	0.03	0.09	0.02	0.16	0.04	0.34	0.03	0.38	0.06	0.11	0.05
Anthracene	0.01	0.01	0.04	0.01	0.02	0.00	0.01	0.00	0.02	0.01	0.04	0.01	0.08	0.04	0.02	0.01
Fluoranthene	0.27	0.11	1.29	0.36	0.56	0.10	0.14	0.04	0.38	0.09	0.60	0.14	0.67	0.23	0.24	0.06
Pyrene	0.31	0.12	0.80	0.22	0.62	0.12	0.20	0.06	0.43	0.11	0.46	0.14	0.86	0.30	0.34	0.08
Retene	<LOD	–	<LOD	–	<LOD	–	<LOD	–	0.02	0.01	0.04	0.02	0.07	0.05	0.07	0.03
Benz[a]anthracene	0.12	0.06	0.09	0.02	0.17	0.03	0.04	0.01	0.16	0.03	0.23	0.08	0.61	0.11	0.19	0.08
Chrysene	0.25	0.10	0.31	0.07	0.35	0.05	0.11	0.03	0.33	0.07	0.37	0.20	0.99	0.15	0.35	0.12
Benzo[b+j+k]fluoranthene	0.46	0.21	0.82	0.22	0.73	0.28	0.33	0.11	0.78	0.32	1.20	0.17	2.75	0.46	0.60	0.25
Benzo[e]pyrene	0.43	0.21	0.40	0.12	0.54	0.12	0.19	0.07	0.49	0.21	0.53	0.09	1.35	0.18	0.31	0.13
Benzo[a]pyrene	0.26	0.14	0.17	0.08	0.26	0.05	0.08	0.02	0.34	0.11	0.38	0.10	1.07	0.16	0.23	0.13
Indeno[123cd]pyrene	0.02	0.02	0.02	0.01	0.04	0.03	0.02	0.01	0.17	0.06	0.33	0.09	0.55	0.22	0.23	0.11
Benzo[ghi]perylene	0.44	0.20	0.21	0.05	0.34	0.05	0.11	0.03	0.59	0.15	0.78	0.19	1.26	0.34	0.48	0.13
Coronene	0.08	0.03	0.04	0.01	0.07	0.02	0.02	0.01	0.19	0.06	0.33	0.14	0.39	0.11	0.19	0.08
PAHs	2.8	1.2	4.7	1.1	3.9	0.8	1.3	0.4	4.1	1.1	5.6	0.7	11.0	1.6	3.4	1.1
Norhopane	2.0	0.8	6.3	1.1	3.7	0.6	2.1	0.8	3.5	2.5	6.2	3.5	6.1	2.9	0.9	0.6
Hopane	1.9	0.8	6.2	1.4	3.2	0.5	1.5	0.6	2.8	1.8	3.5	1.7	4.9	2.3	0.7	0.3
Nicotine	6.1	2.0	6.4	1.7	4.2	1.7	1.3	0.5	8.0	2.3	8.9	1.0	12.2	2.4	2.4	1.1
Levogluconan	16.7	6.7	5.7	1.4	6.6	4.2	5.1	1.7	17.6	6.1	87.8	14.2	132.3	60.6	70.7	54.0
Methyl-dihydrojasmonate	44.2	21.7	6.4	3.4	44.4	13.4	5.5	6.2	99.5	101.1	109.7	81.1	42.5	26.7	9.6	3.0
Galaxolide	7.2	2.0	1.8	0.6	11.2	5.9	1.0	0.9	17.3	16.1	17.7	12.4	9.6	6.4	4.3	2.3
Xylitol	0.2	0.0	1.8	1.1	0.8	0.4	0.8	0.5	3.0	0.9	3.3	1.7	5.8	1.2	2.9	2.3
α -glucose	4.8	0.8	7.2	6.0	2.9	0.8	2.6	0.8	12.3	3.0	11.4	3.4	14.8	3.1	5.0	2.0
β -glucose	5.1	1.0	8.3	7.1	3.1	0.7	2.9	0.8	14.0	3.6	12.0	3.8	15.4	3.2	5.3	2.1
Mannitol	0.7	0.2	2.1	1.1	1.6	0.6	0.7	0.3	2.5	0.5	2.2	0.5	4.3	0.6	1.7	0.8
DBP	97.2	7.9	29.9	10.7	48.1	10.1	174.4	79.5	105.8	40.9	85.4	15.3	41.9	5.8	99.4	11.3
DEHP	29.7	5.0	81.1	15.2	30.7	5.0	44.3	8.1	71.2	14.7	40.9	5.4	34.1	2.5	30.7	3.3

LOD – limit of detection.

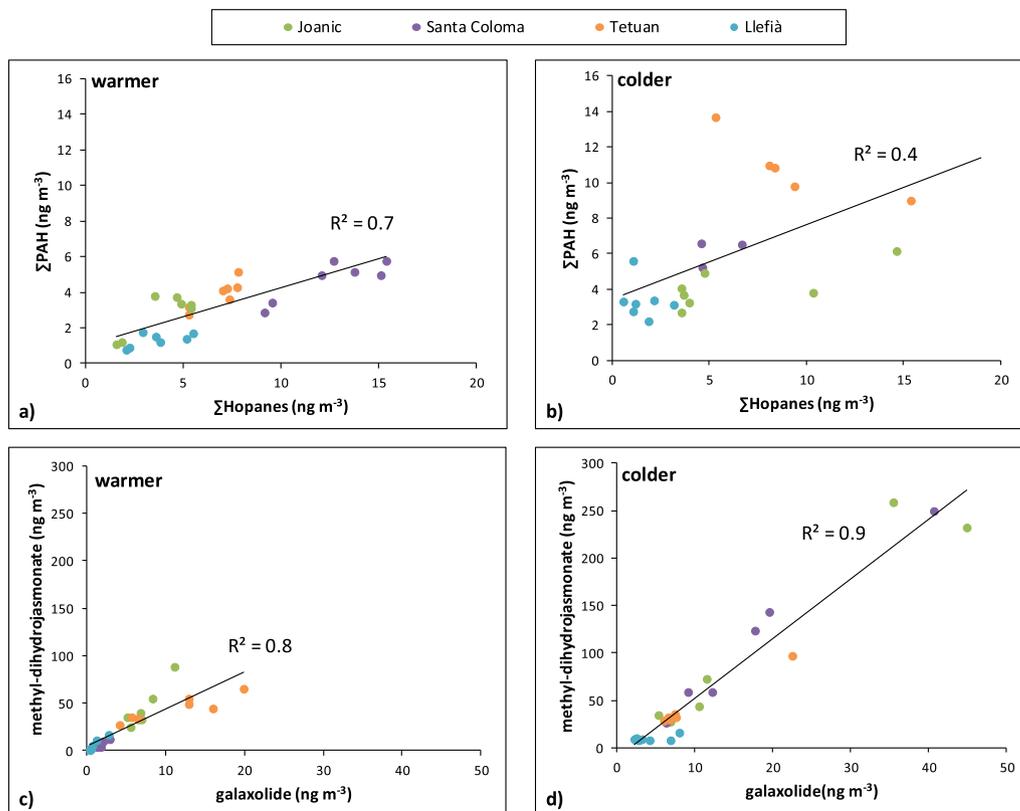


Fig. 4. Comparison of the analysed PAHs and Hopanes concentrations in the a) warmer and b) colder periods, and the methyl-dihydrojasmonate and galaxolide concentrations in the c) warmer and d) colder periods.

(Rogge et al., 1993; Schauer et al., 2007), but also the possible influence of night-time diesel trains for maintenance activities which can be still measured during daytime. In the colder time, hopane concentrations were similar to the ones observed in the warmer period (Table 2). Nevertheless, the correlation between PAHs and hopanes concentrations in the colder period is weaker, or they are even anti-correlated in Tetuan (Fig. 4b). In contrast to hopanes, PAHs are emitted during incomplete combustion and their emissions generally increase at lower ambient temperatures.

An indication for the potential influences of outdoor combustion sources in the subway environment could be the presence and abundance of tracer compounds for biomass burning or cigarette smoke, since these activities are not allowed in the subway system. Nicotine is an alkaloid present in high concentrations in environmental tobacco smoke and although it is mainly present in the gas-phase due to its relatively high volatility, it can be detected at trace levels on particulate urban samples (Alier et al., 2013; Bi et al., 2005; Rogge et al., 1994). Nicotine was detected in low concentrations on the platforms of all stations, ranging from 1.3 ng m^{-3} in Llefià station in the warmer period to 12 ng m^{-3} in Tetuan station in the colder period, which corresponds to the lower range of the outdoor concentrations measured in Barcelona (Alier et al., 2013). This suggests that active smoking is probably not an important source, but that the translocation of outdoor air to the subway environment may introduce the nicotine inside, although other sources, including the transport of nicotine on passenger cloths, skin, and hair can not be excluded.

Levogluconan is a monosaccharide anhydride generated by thermal alteration of cellulose, which is emitted in large quantities during biomass burning (Fine et al., 2004; Simoneit, 2002). The levels at the subway platforms ranged from 5 ng m^{-3} in Llefià

station in warmer time to 132 ng m^{-3} in Tetuan station in the colder period. This concentration is in the range of that observed in the outdoor atmosphere in Barcelona (around 100 ng m^{-3} ; van Drooge et al., 2014).

In both warmer and colder periods there were substantial correlations between the PAHs levels and the outdoor tracers for cigarette smoke (nicotine: $R^2_{\text{warmer}} = 0.5$; $R^2_{\text{colder}} = 0.6$ for data of all stations). In the colder period there was a substantial correlation of PAHs with the outdoor tracer for biomass burning (levoglucosan: $R^2_{\text{colder}} = 0.5$). These results indicate that a significant part of the detected PAHs in the subway systems could indeed have been generated by outdoor combustion sources.

Other organic compounds, such as aromatic musk compounds (methyl-dihydrojasmonate and galaxolide) are widely used as fragrance in cleaning agents, personal care and consumer products (Matamoros and Bayona, 2006) and may form part of the indoor atmosphere from desorption from its users and after subway and train cleaning operations. This study shows for the first time that these compounds can be detected in rather high concentrations on the platforms of subway stations, with the lowest concentrations in Llefià station in warmer time (methyl-dihydrojasmonate = 5 ng m^{-3} , galaxolide = 1 ng m^{-3}) and the highest in Santa Coloma station in the colder period (methyl-dihydrojasmonate = 110 ng m^{-3} , galaxolide = 18 ng m^{-3}). The Joanic and Tetuan stations, situated in the center of Barcelona, showed high levels in both warmer and colder periods. Overall, there were strong correlations between these two tracers for fragrances ($R^2_{\text{warmer}} = 0.8$; $R^2_{\text{colder}} = 0.9$ for data of all stations; Fig. 4(c and d), indicating similar mixtures, despite concentration variations. However, there were only moderate correlations between these compounds and primary saccharides in the colder period

Table 3Contribution ($\mu\text{g m}^{-3}$) of the different sources found in the $\text{PM}_{2.5}$ on the four subway platforms in both periods.

Subway station	Period	Sources					
		Secondary	Secondary warmer	Secondary colder	Sea salt	Fuel oil combustion	Subway
Joanic	Warmer	5.9	–	–	5.9	2.0	3.2
Joanic	Colder	0.6	–	–	6.2	0.8	43.0
Tetuan	Warmer	4.8	–	–	9.2	5.3	7.4
Tetuan	Colder	8.6	–	–	7.7	2.1	44.4
Santa Coloma	Warmer	–	23.2	1.4	–	–	20.8
Santa Coloma	Colder	–	0.9	19.6	–	–	20.3
Llefià	Warmer	–	9.7	0.9	2.8	–	2.7
Llefià	Colder	–	0.6	5.4	2.3	–	13.5

($R^2 = 0.3$), indicating that these tracers were rather independent and may be related to the amount of commuters passing the platforms and partially from local cleaning operations.

Primary saccharides: α - and β -glucose are an important fraction of organic matter in organic dust. These compounds can be emitted into the atmosphere as constituents in particles originating from wind erosion and up whirling of dust (Simoneit et al., 2004). At the subway platforms these dust particles can be originated from the air (wind) movements in the tunnels by the passing trains, and were also related to other compounds, such as alcohol saccharides (xylitol and mannitol), which are reduced saccharides and also constituents of organic matter in dust. Moreover, mannitol is related to fungi (Simoneit et al., 2004). These compounds were detected in moderate concentrations, compared to typical outdoor concentrations, with the lowest concentrations in Llefià station ($\sum \text{saccharides} = 7 \text{ ng m}^{-3}$). The concentrations were 3–5 times higher in the colder period, although the concentrations in Llefià increased only by a factor of 2, indicating that the isolation of the platform from the tunnel in Llefià station reduces also the influence of organic dust particles.

Dibutyl phthalate (DBP) and di(ethylhexyl) phthalate (DEHP) are phthalate esters that are widely used as plasticizers in furniture and building materials (Otake et al., 2001). Both DBP and DEHP were detected in all stations in high concentrations (ranging from 30 ng m^{-3} to 174 ng m^{-3} for DBP and from 30 ng m^{-3} to 81 ng m^{-3} for DEHP). Interestingly, the highest DBP concentration was recorded in the warmer period in Llefià station, and the DEHP concentration was also high (44 ng m^{-3}), which can be attributed to the application of new building material in this site, given that these compounds were not correlated with any of the other tracer compounds.

3.4. Source apportionment

The number of 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 (rail tracks, wheels, brake pads, catenaries and pantographs).

The outdoor $\text{PM}_{2.5}$ sources were secondary sources, sometimes split in two, one of them corresponding mainly to the colder period and the other one to the warmer period. The warmer secondary source is characterized by a high contribution of sulfate, whereas the colder secondary source is dominated by nitrate. The sea salt source was identified for three of the datasets (Joanic, Tetuan and Llefià stations), whereas it was merged with the secondary sources for the fourth dataset (Santa Coloma station). This source was mainly characterized by the presence of Na and Cl, with similar contributions in the warmer and the colder periods (Table 3). Moreover, a source dominated by V was identified for two datasets (Joanic and Tetuan stations), representing the fuel oil combustion (Agrawal et al., 2008), and otherwise merged with the secondary source for the warmer period. The differences among stations are attributed to the different influence of outdoor air, which is influenced by the time of the year, among other factors, and to the different characteristics for each station, leading to different influences of the subway emissions on the platform environment.

The subway source identified has a different chemical profile for each of the stations (Fig. 5). Whereas the Fe dominates the composition of this source at all stations, its content varies from 53% in Santa Coloma to 68% in Joanic, which would correspond to 76–86% if Fe_2O_3 is considered. Moreover, the relative abundance of specific elements varies from station to station. Thus, the Cu/Fe ratio varies from 0.004 to 0.007 in Llefià, Santa Coloma, and Tetuan to 0.013 in Joanic. This higher Cu/Fe ratio in Joanic reflects the influence of pantograph emissions, given that some of the trains operating in the subway line 4 are still equipped with pantographs containing Cu in their composition, in contrast with the rest of the lines where pantographs are C-rich (graphite). Another relevant difference is the Ba/Sr ratio, which varies from 8 to 10 in Tetuan and Llefià to 39–45 in Joanic and Santa Coloma. This probably reflects the differences in brakes composition used in the different subway lines. These differences evidence the relevance of the composition of the different elements present in the subway system, which is directly reflected in the ambient concentrations in the subway environment.

Table 3 summarizes the contribution of each source for each station and period. The subway contribution is much lower during

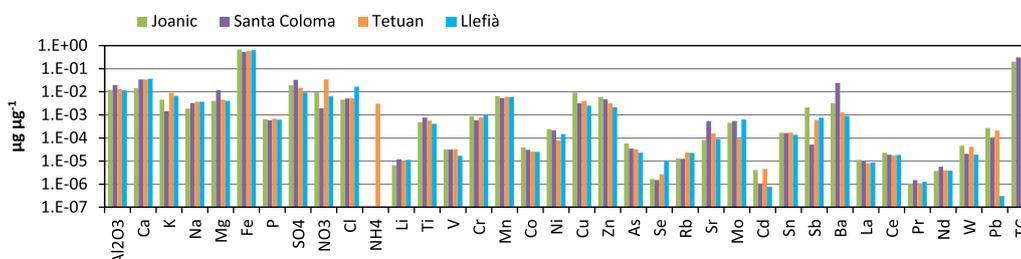


Fig. 5. Source profile of the subway source in Joanic, Santa Coloma, Tetuan and Llefià stations.

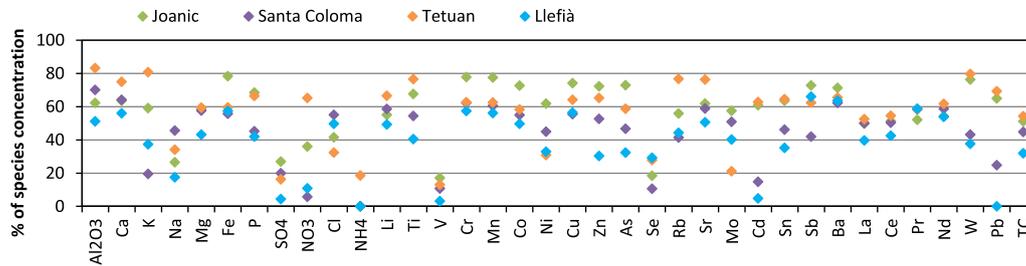


Fig. 6. Percent of species concentration apportioned by the subway source in Joanic, Santa Coloma, Tetuan and Llefia stations.

the warmer period, ranging from 9 to 17% of $PM_{2.5}$, than during the colder period, ranging from 41 to 58% of $PM_{2.5}$ for Joanic, Tetuan and Llefia. These differences are attributed to the different ventilation, which allows for a better dispersion of the subway emission in the warmer period. Santa Coloma station shows similar subway emissions contribution for both seasonal periods (29–32%), in agreement with the $PM_{2.5}$ concentrations, also similar for both periods, reflecting the relatively limited ventilation of this station compared to others. The contribution of this source to each of the species is shown in Fig. 6. The subway source is responsible for more than 50% to the concentration of Al_2O_3 , Ca, Fe, Cr, Mn, Cu, Sr, Ba, Pr, and Nd at all the stations, and also of Mg, Li, Ti, Co, Zn, and Ce for the old stations (Joanic, Tetuan and Santa Coloma).

4. Conclusions

The subway environment has been monitored in Barcelona on four distinct platforms of four different subway lines during two seasonal periods (warmer and colder), focusing on $PM_{2.5}$ mass concentration and chemical composition.

$PM_{2.5}$ mass concentrations were clearly lower in the new station (with PSDs) with respect to old conventional stations, but also a very significant reduction of the concentrations was observed by the different ventilation conditions in the warmer compared to colder period. The low concentrations observed in the PSDs-equipped station was probably a direct effect of the isolation of the platform from the tunnel, more advanced ventilation setup and the lower train frequency. Additionally, the mean $PM_{2.5}$ concentrations on the subway platforms were between 1.4 and 5.4 times higher than those outdoors.

Subway aerosol is a complex mixture of compounds characterized by high concentrations of haematite (mainly from the wearing of wheels and rail tracks) and carbonaceous aerosol. The relative abundance of particles of outdoor origin, such as SIC, varies somewhat among seasons, reflecting the differences in the ventilation and the outdoor concentrations. In the new station with PSDs the amount of haematite in the $PM_{2.5}$ mass was around 60% lower than in the old conventional stations, clearly indicating that these particles predominating in the subway stations are originated from the tunnel.

Particulate organic compounds such as PAHs were also detected in the subway stations. Similarly to the inorganic PM components, the highest concentrations of PAHs in the subway $PM_{2.5}$ were observed in the colder period and in the conventional stations. Aromatic musk compounds (methyl-dihydrojasmonate and galaxolide) used as fragrance in cleaning agents and personal care products were also identified for the first time on the platforms of subway stations.

The concentrations of the PM chemical components varied not only due to the different seasonal periods (warmer vs colder) but also to the distinct stations design and the chemical composition of rail tracks, wheels, brake pads, catenaries and pantographs.

Some trace elements (Ba, Mn, Cu, Cr, Sb, Sr, among others) were recorded in higher concentrations than outdoors, with higher levels in the colder time, and their concentrations varied among the subway stations. These differences are associated to the variations on ventilation intensity but also to the distinct components of rail tracks, wheels, catenaries, brake pads and pantographs, and to different characteristics of each station, influencing the subway emissions on the platform environment as shown by the source apportionment results. The subway $PM_{2.5}$ contribution obtained by receptor model was much lower during the warmer period than during the colder period and is responsible for more than 50% to the ambient concentrations of Al_2O_3 , Ca, Fe, Cr, Mn, Cu, Sr, Ba, Pr, and Nd at all the stations, with a common feature of being dominated by Fe (53%–68%).

This study provided a comprehensive assessment of $PM_{2.5}$ chemical characterization of subway transport environment. In addition, the results reported may be useful to help the control and improve the air quality in the subway systems. Thus, controlling the ventilation conditions and the composition of the subway components (brakes, pantographs, etc) may result in an improvement of the particle ambient concentrations in the subway environment.

Acknowledgement

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), and the IMPROVE LIFE project (LIFE13 ENV/ES/000263). Fulvio Amato is beneficiary of an AXA Research Fund postdoctoral grant. The authors would like to thank the Transports Metropolitans de Barcelona METRO staff who arranged the sampling campaign and contributed actively to this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.07.004>.

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