Origin of polycyclic aromatic hydrocarbons and other organic pollutants in the air particles of subway stations in Barcelona

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HIGHLIGHTS
• PM2.5 levels in subway platforms are higher than those for urban outdoor.
• PAH levels at the platforms are similar to those in the outdoor ambient air.
• Maintenance works and inverse ventilation do not influence the indoor air quality for PAH.
• PSD and advanced ventilation systems reduce PM2.5 concentrations in the platform.
• 75% of the detected PAH concentrations in the platforms origin from outdoor air.

GRAPHICAL ABSTRACT

ABSTRACT

Underground subways transport large numbers of citizens in big cities, which must breathe air with limited ventilation. These atmospheric conditions may enhance the concentration of air pollutants from both outdoor and indoor air. The influence of ventilation conditions and maintenance activities on the concentrations of air pollutants have been studied. Particulate matter with aerodynamic diameter smaller than 2.5 μm (PM2.5) in indoor air was sampled in ten platforms of nine subway stations of the metropolitan area of Barcelona in 2015 and 2016. These particles were analyzed for polycyclic aromatic hydrocarbons (PAH) and organic tracer compounds. The concentrations of PAH were in the range of the street air levels with higher PAH values in the colder period. No influence of nighttime maintenance activities was observed on the platform air quality during daytime. Source apportionment analysis using the concentrations of hopanes, nicotine and levoglucosan as molecular tracer compounds showed that 75% of the detected PAH at the platforms have an outdoor PM origin. The modern subway stations, with advanced ventilation and platform screen doors that separate the subway system from the platform, showed lowest PAH and PM concentrations.

Keywords: Subway; PAH; PM2.5; Source apportionment; Air quality

1. Introduction

Underground subway is an important transport mode for citizens in large cities. They generate distinctive micro-environments with restricted ventilation conditions which may yield to high concentration of air pollutants from both outdoor and indoor air. Particulate matter (PM) in subways is of great concern since many people spend considerable time commuting on a daily basis, and the exposure to PM-bounded chemicals may involve adverse health effects (Bigert et al., 2008). Previous air quality studies in platforms of subways from Barcelona have reported PM concentrations that often were several times higher than

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outdoors (Martins et al., 2015, 2016; Querol et al., 2012). A major portion of the PM$_{2.5}$ (atmospheric particulate matter with an aerodynamic diameter <2.5 μm) in Barcelona’s metro stations consists of iron oxide (haematite) and carbonaceous particles (mostly elemental carbon) from the rail track, catenary system, and brakes which is in agreement with the observations in other subway systems (Martins et al., 2016; Querol et al., 2012).

In the molecular context, elevated to moderate concentrations of polycyclic aromatic hydrocarbons (PAH) have been observed in the Barcelona’s subway stations (Martins et al., 2016). PAH are produced by incomplete combustion of organic material, such as fossil fuels, and some of the PAH, such as benzo[a]pyrene, are genotoxic. Higher PM$_{2.5}$ and PAH concentrations were generally observed in the old subway systems and stations and lower PAH and PM$_{2.5}$ in the modern subway systems that are equipped with platform screen doors (PSD) that separate the rail track from the platform. Moreover, in these modern systems, trains are equipped with, computer-controlled driving systems to optimize speed, braking, and stopping processes. These first results indicated that outdoor air pollutants may influence the air quality of the subway platforms through the ventilation systems. On the other hand, rail track and catenary maintenance works, including adding new ballast to the rail track, usually performed during nighttime with diesel fueled engine trains could also be potential contributors to the overall air pollution of these restricted environments. It is unknown what the influence of these operations is on the air quality in the platforms during the daytime. In order to study the influence of maintenance works and ventilation on the platform air quality, several metro station platforms in the city of Barcelona were sampled on PM$_{2.5}$ and analyzed on PAH and outdoor combustion tracers, e.g. nicotine from cigarette smoke and levoglucosan from biomass burning, as well as hopanes from vehicle lubricant oils.

The Barcelona’s subway system comprises of eight lines stretching 103 km and including 140 stations (Fig. 1). On a daily base, over 125 million passengers commute in the subway system, which is about 50% of the urban commuting load. In the present study, PM$_{2.5}$ was sampled in platforms of ten metro stations of the metropolitan area of Barcelona during and outside periods of rail track maintenances as well as under diverse platform ventilation modes during 2015 and 2016. The stations cover a variety of structures (single tunnel or double tunnel subways) and periods of construction (from 1959 to 2016). Especially, the two platforms from the modern station (Collblanc) consist of PSD and an advanced ventilation system. Overall, the study encompasses 137 filter samples which were analyzed for seven PAH, among them benzo[a]pyrene, and nicotine, levoglucosan, 17(H)α-21(β)-29-norhopane and 17(H)α-21(β)-3-hopane. Seasonality, rail track maintenance activities and ventilation conditions were the main aspects influencing on the composition of these pollutants.

2. Materials and methods

2.1. Subway stations and PM$_{2.5}$ filter sampling

The subway stations were selected in the context of the IMPROVE LIFE project. The nine stations are located in different neighborhoods in the metropolitan area of Barcelona and have contrasting designs belonging to the different lines (Fig. 1, Table 1). Eight stations encompassed platforms in double tunneled subways that could be separated or not by a wall. They have a mechanical ventilation system that introduces outdoor air to the platforms, and extracts air outside through ventilation grids in the tunnels. The modern Collblanc station has the platforms along a single track in a single tunnel that is separated from the rail track by a PDS with independent ventilation systems for tunnel and platforms. PM$_{2.5}$ was collected on pre-cleaned quartz filters by means of a high volume sampler (HiVol, CAV-A/MSb, MCV) from 5 a.m. to midnight (subway operating hours) at a sampling rate of 30 m$^3$ h$^{-1}$. Field blanks were taken at each station. After sampling, the filters were stored in aluminum foil at 4°C before analysis. The HiVol samplers were placed at the end of the platforms behind a light screen for security protection.

2.2. Sample analysis

A quarter part of each PM$_{2.5}$ filter was used for organic analysis following the methodology described elsewhere (Martins et al., 2016). Briefly, filter samples were spiked with deuterated standards and extracted in a mixture of dichloromethane and methanol (2:1 v/v, 3 × 15 mL) using an ultrasonic bath. After each extraction, the extracts were filtered on glass fiber filters in a stainless steel filter holder.

Fig. 1. Map of subway system in Barcelona. The analyzed stations are indicated by stars in the map.
# Table 1

Characteristics of the analyzed subway platforms and concentrations (mean and standard deviation) of PM$_{2.5}$ and analyzed organic compounds (ng/m$^3$).

| City         | Metro line | Construction year | Depth (m. below surface) | Metro frequency (trains/h) | Metro year | Metro period | Sample number | Testing | Sample | Sample | Sample | Sample | Concentration (ng/m$^3$) |
|--------------|------------|-------------------|--------------------------|---------------------------|------------|--------------|---------------|---------|--------|--------|--------|--------|--------------------------|
| Tarragona    | L5         | 1959              | 11                       | 30                        | 2016       | 0-12         | 35            | Track works |        |        |        |        | 11.5 ± 3.2               |
| Sta Coloma   | L3         | 1975              | 14                       | 26                        | 2015       | 5-60         | 11            | Track works |        |        |        |        | 16.7 ± 4.4               |
| Joanic       | L3         | 1975              | 14                       | 26                        | 2015       | 5-60         | 13            | Track works |        |        |        |        | 13.6 ± 2.5               |
| Sant Cristina| L3         | 1975              | 14                       | 26                        | 2015       | 5-60         | 9             | Track works |        |        |        |        | 14.4 ± 1.9               |
| Metro line L5 | L1        | 1983              | 12                       | 26                        | 2015       | 5-60         | 13            | Track works |        |        |        |        | 12.2 ± 2.2               |
| L4           |            | 1973              | 8                        | 30                        | 2016       | 5-60         | 5             | Track works |        |        |        |        | 14.4 ± 4.8               |
| L5           |            | 1976              | 14                       | 26                        | 2015       | 5-60         | 9             | Track works |        |        |        |        | 14.4 ± 4.8               |
| L3           |            | 1975              | 14                       | 26                        | 2015       | 5-60         | 13            | Track works |        |        |        |        | 12.2 ± 2.2               |
| Palau Reial  | L9         | 2016              | 60                       | 9                         | 2017       | 9-60         | 4             | Track works |        |        |        |        | 6.6 ± 1.1                |
| Poble Sec    | L9         | 2017              | 60                       | 9                         | 2017       | 9-60         | 5             | Track works |        |        |        |        | 5.3 ± 0.2                |

PM$_{2.5}$ was weighted on the filters by a microbalance, while total carbon (TC) concentrations were measured on a quarter part of the filter by the Thermal-optical Transmittance method (Martins et al., 2016).

2.3. Complementary data

PM$_{2.5}$ was weighted on the filters by a microbalance, while total carbon (TC) concentrations were measured on a quarter part of the filter by the Thermal-optical Transmittance method (Martins et al., 2016).

2.4. Source apportionment

Insight on the contribution of potential outdoor and indoor sources on organic aerosol and PAH was obtained from multiple variance regression models using the concentrations of the analyzed tracer (Sartorius) using a glass syringe (Fortuna Optima) in order to eliminate particles from the extracts. The filtered extract was concentrated to 500 mL by vacuum rotary evaporation. An aliquot of 25 μL was evaporated under a gentle N$_2$-gas stream and 25 μL bis(trimethylsilyl) trifluoroacetamide (BSTFA) + trimethylchlorosilane (99:1) (Supelco) and 10 μL of pyridine (Merck) were added. These solutions were heated at 70 °C for 1 h in order to derivatize the hydroxyl groups to trimethylsilyl ethers. Twenty-five μL of 1-phenyldodecane in isooctane (30 ng) were added and levoglucosan and nicotine were analyzed by gas-chromatography coupled to mass-spectrometry (GC-MS).

The remaining extract (95%) was used for the analysis of PAH and hopanes. These solutions were fractionated by aluminum oxide column chromatography (1 g). Then, PAHs and hopanes were eluted by rinsing the column with 6 mL of dichloromethane and hexane (2:1 v/v). The collected fraction was concentrated by vacuum rotary evaporation to 0.5 mL transferred to a vial and further concentrated to 25 μL under a gentle N$_2$-gas stream. Before instrumental analysis the 1-phenyldodecane standard was added.

The sample extracts were injected into a Thermo GC–MS (Thermo Trace GC Ultra – DSQII) equipped either with a 60 m fused capillary column (Rxi-5Sil MS 0.25-mm × 25-μm film thickness (Restek) for the analysis of levoglucosan and nicotine, or a 30 m column for the analysis of PAH and hopanes. The oven temperature program started at 60 °C in the first case and 90 °C in the second (holding time 1 min). Then both programs heated to 120 °C at 12 °C/min and to 320 °C at 4 °C/min with a final holding time of 10 min. The injector, ion source, quadrupole and transfer line temperatures were 280 °C, 200 °C, 150 °C and 280 °C, respectively. Helium was used as carrier gas at 0.9 mL/s. The MS operated in electron impact mode (70 eV). The quadrupole was operated in fullscan (m/z 50–650) for the analysis of molecular organic tracers, e.g. levoglucosan and nicotine, and in SIM-mode for the PAH and hopanes.

Levoglucosan (LEV; biomass burning) and nicotine (NIC; tobacco smoke) were identified with ions m/z 204 and 84, respectively, and retention times. Quantification was performed with external standard calibration curves. The concentrations were corrected by the recoveries of the surrogate standard levoglucosan-d$_5$ (m/z 206) and field blank levels.

PAH and hopanes were identified by retention time comparison in the following ion fragmentograms: benzo[a]anthracene (BAA m/z 228), chrysene+triphénylene (CHR m/z 228), benzo[b + j + k]fluoranthene (BFL m/z 252), benzo[e]pyrene (BEP m/z 252), benzo[a]pyrene (BAP m/z 252), indeno[1,2,3-cd]pyrene (IP m/z 276), and benzo[ghi]perylene (BGP m/z 276). 17(α-H)α-21(H)-29-norhopane (norHOP) and 17(α-H)α-21(H)-β-hopane (HOP) were identified in the m/z 191 mass fragmentogram and the corresponding retention times. Quantification was also performed by the external standard method. The calculated concentrations were corrected for surrogate recoveries, which consisted of deuterated compounds for each individual PAH, except benzo[e]pyrene and the hopanes, which were corrected with benzo[a]pyrene-d$_{12}$. In all cases these surrogate standard recoveries were higher than 70%. Field blank levels were between 1% and 30% of the sample levels. All concentrations were corrected for blank levels. Limits of Quantification (LOQ) were calculated using the lowest measured levels in the standard calibration curves. They were 0.1 ng m$^{-3}$ for the organic molecular tracers and 5 pg m$^{-3}$ for PAHs and hopanes.
compounds. For this purpose, the multivariate curve resolution alternating least squares (MCR-ALS) method (Tauler, 1995) was used. This method has been applied successfully for environmental source apportionment of the urban organic aerosol (Alier et al., 2013; van Drooge and Grimalt, 2015). MCR-ALS is based on an alternating linear least squares optimization under non-negativity constraints which produces physically better profiles than Principle Component Analysis, generating results analogous to Positive Matrix Factorization (Terrado et al., 2009).

3. Results and discussion

3.1. PM2.5, and TC concentrations

Table 1 contains the mean concentrations (+standard deviation) of PM2.5, TC, and analyzed compounds at the subway station platforms. The concentrations of PM2.5 and TC measured at the platforms are moderately correlated ($R^2 = 0.69$; $p < 0.001$), with the TC encompassing about 20% of PM2.5. The highest concentrations were observed in the L3 subway platforms of Tarragona, Poble Sec and Palau Reial ($PM_{2.5} = 87 \mu g/m^3$ in a period when new ballast was being added), while lowest mass concentrations were measured at the platform of the modern L9 stations Collblanc ($36 \mu g/m^3$). The lower levels at the Collblanc platform can be attributed to the PSD installed in this station that prevents the PM from the tunnel entering into the platform (Querol et al., 2012). However, they also could be attributed to the lower frequency of trains at this station (9 per hour) compared to the other conventional stations (19–30 per hour, stations with two rail tracks) and the more advanced ventilation setup.

Generally, the PM2.5 measured in the platforms is higher than the average PM2.5 concentrations measured at traffic sites in the city (Fig. 2), with factors ranging from 2.7 to 6.1. The efficiency of the ventilation system in the Collblanc station was tested by switching it off on 5 days and comparing this with the other 9 days. The PM2.5 concentrations significantly increased from $24 \pm 5 \mu g/m^3$ to $58 \pm 6 \mu g/m^3$ when the ventilation was switched off, while the TC concentrations increased from $5 \pm 1 \mu g/m^3$ to $7 \pm 1 \mu g/m^3$, indicating that indoor PM accumulated to four times higher PM levels compared to the outdoor PM2.5 (Table S1a). Hence, when the ventilation system at Collblanc is switched off, the PM concentrations at the platform are similar to those observed in the conventional stations. For example, Tarragona station showed PM2.5 and TC concentrations around $70 \mu g/m^3$ and $14 \mu g/m^3$, respectively. The ventilation efficiency was also tested in Tarragona station by introducing tunnel air to the platforms and extracting air from the platforms to the outdoor air (reverse mode of normal ventilation). This action did not have a significant influence on the indoor air concentrations (Table S1a), showing that the open platform–trail track form of the conventional stations is dominating the indoor air, and that the direction of the air flow has little influence. None of the other variables tested, i.e. track works and ballast adding to track during nighttime, did not show significant influence on the PM2.5 and TC concentrations at the station platforms during daytime (Table S1b and c). These results indicate that a dominant part of the PM2.5 in metro stations consists of indoor PM in the form of iron oxide (hematite) and carbonaceous particles (mostly elemental carbon) from the rail track, catenary system, and brakes due to movements of the trains during the operating hours, which is in agreement with the previous study (Martins et al., 2016).

3.2. Organic tracer compound concentrations

Levoglucosan is the compound found in highest concentration, followed by nicotine, and hopanes. The individual PAH showed lower concentrations (Table 1).

In urban areas, the hopanes are molecular tracer compounds of mineral oil contributions (Schauer et al., 2008) and their presence at the platforms can be related to lubricant oils from road traffic that have penetrated to the indoor air through ventilation or from the trains in the subway system. The two hopanes analyzed, 17H[α-21(H)]β-29-norhopane and 17H[α-21(H)]β-hopane, were the most abundant hopanes and their concentrations showed a very strong correlation ($R^2 = 0.97$; $p < 0.001$) with a norhopane/hopane ratio of 1.2. The highest concentrations were observed in the L3 subway platforms of Poble Sec ($\Sigma$ hopanes = 5.8 ng/m3), Palau Reial (5.3 ng/m3) and Tarragona (4.8 ng/m3), the stations that also showed highest PM concentrations. The lowest hopane concentrations were measured at the platforms of the modern L9 station Collblanc 1 (1.3 ng/m3) with the PSD systems. The later concentrations at Collblanc were close to those observed in outdoor air (Alier et al., 2013; van Drooge et al., 2012), while the concentrations at the platforms of the conventional subway stations were two to five times higher than those generally observed in outdoor air, even in urban road sites (Alier et al., 2013). The $\Sigma$ hopane concentrations at the station platforms correlated with the observed measured PM2.5 and TC concentrations ($R^2 = 0.45$ and 0.54, respectively; $p < 0.01$) indicating that an important part of the hopanes at the platforms are more related to an indoor source than to an outdoor source. The nighttime rail track work or ballast adding did not change the daytime concentrations at the platforms of the stations (Table S1b, c). Also changes of ventilation modes at the platforms did not have any significant influence on the hopane concentrations (Table S1a). On the days that the ventilation was switched off in the modern Collblanc station the hopanes showed slightly lower concentrations compared to the days when the ventilation was functioning normally, which could indicate a reduced input of outdoor air PM, or that the PM from the tunnel has little influence on the platform PM. Since the PM2.5 increased significantly when the ventilation system was switched off, it is probable that these particles are mostly resuspended

Fig. 2. PM2.5 concentrations measured at the subway platforms of the different stations, and the mean outdoor PM2.5 concentrations of four urban traffic sites in Barcelona (i.e. Eixample, Sant Gervasi, Plaça Universitaria, Poble Nou).
from the platform instead of coming from the track, tunnel or from the outdoor air.

Levoglucosan is a molecular tracer compound for biomass burning (Simoneit, 2002), which is not expected to be emitted inside the subway system. The detected levoglucosan at the platforms has its origin in the outdoor air after penetration to the indoor air by ventilation. Levoglucosan was measured in substantial concentrations at the subway platforms of Joanic (88 ng/m³), Sagrera (66 ng/m³), Santa Coloma (59 ng/m³) and Sant Ildelfons (55 ng/m³), while lowest concentrations were measured at the platforms of the L3 line Palau Reial (5 ng/m³), Taragona (5 ng/m³), Maria Cristina (4 ng/m³) and the modern L9 platforms of Collblanc (3–7 ng/m³). The data shows a clear seasonal trend with higher concentrations measured in the samples that were collected in the colder periods of the sampling campaign (October to March; Table 1). For example, the mean levoglucosan concentration at the platform of Palau Reial in October was 33 ng/m³, while this was 5 ng/m³ in April. The period of higher levoglucosan concentrations from October to March coincided with the period that outdoor air concentrations were around 100 ng/m³ (van Drooge et al., 2014). The observed levoglucosan concentrations are typical for in outdoor ambient air in urban areas without local biomass burning (Puxbaum et al., 2007). In the platform they are in the same range, indicating outdoor to indoor mixing.

The contribution of this outdoor PM to the indoor PM_{2.5} or TC, is however not equally important for the different stations. The overall correlation between levoglucosan and TC is very weak (R² = 0.06), although a moderate correlation (R² = 0.41; p < 0.05) between these two variables was observed at the platform of Sagrera station. This station, compared to the other conventional stations, has relatively high levoglucosan concentrations, moderate TC concentrations, and relatively low hopane concentrations, resulting in a relatively higher contribution of outdoor air on the platform indoor PM in this station compared to the other conventional stations. The nighttime activities in the tunnels and rail tracks, or the ventilation setting has no significant influence on the platform concentrations of levoglucosan (Table S1a, b, c). The mean concentration in Sagrera station with no-rail track works almost duplicates those in stations with rail track works, but this difference is likely the result of collection of all five samples in winter (January) when the outdoor concentrations were generally higher. In any case, the mean concentrations on days with and without rail works were not statistically significantly different due to the large standard deviation.

Another outdoor molecular tracer compound marker is nicotine (Rogge et al., 1994; Bi et al., 2005) since cigarette smoking is not allowed at the platforms. This compound showed variable concentrations among the sampled stations. The highest mean concentration was measured at Poble Sec station (29 ng/m³) and the lowest in other L3 stations, Palau Reial (2 ng/m³), Maria Cristina (3 ng/m³), and at the modern platforms of the L9 station Collblanc (3 ng/m³). The concentration observed at the Poble Sec platform is similar to those measured at an urban roadside in Barcelona near the entrance of a subway, while the lower levels of other platforms are similar to urban background concentrations (Alier et al., 2013; Ladji et al., 2009; van Drooge and Grimalt, 2015). Higher nicotine concentrations coincide with samples from stations that were collected in the cold seasons, although this seasonal trend is not so well defined as in the case of levoglucosan. There was a moderate correlation between these two outdoor PM tracer compounds in the overall data (R² = 0.55; p < 0.01), with an exception of the data from the platform of Poble Sec (Fig. 3). Despite its prohibition, indoor cigarette smoking can sporadically be observed at the platform. The overall correlations between nicotine and PM_{2.5} or TC (R² = 0.08) were very weak, indicating that, as expected, cigarette smoking did not contribute much to the indoor PM mass concentrations at the platforms.

PAH are tracer compounds for incomplete organic matter combustions. In the studied urban area, combustion of fossil fuels from motorized vehicles is the major source for PAH (Alier et al., 2013; Mortanais et al., 2017). Highest ∑PAH concentrations were measured at the platforms of Joanic (4.2 ng/m³) and Sagrera (4.1 ng/m³), while the lowest were measured at the platforms of Collblanc (0.5–0.6 ng/m³). The relative composition of individual PAH was dominated by benzo[b + j + k] fluoranthene (BFL) followed by benzo[ghi]perylene (BGP), although in the samples collected at the platforms of Sagrera, Palau Reial and Poble Sec higher abundances of chrysene were observed. Benzo[a]pyrene (BaP), the only PAH that is regulated by law (EC, 2004) with an annual target value for outdoor PM of 1 ng/m³ and a recommended annual value of ≈0.12 ng/m³ (WHO, 2013), showed highest mean concentrations at the platform of Joanic (0.66 ng/m³) and Sagrera (0.31 ng/m³). The lowest concentrations, 0.04–0.08 ng/m³, were measured at the Collblanc platforms. The other stations showed intermediate BaP between 0.12 and 0.25 ng/m³. These levels are generally lower than the target value of outdoor PM and in the range of the recommended value for health safety for outdoor exposure. The observed BaP concentrations are very similar to those measured by local authorities in the outdoor PM in urban traffic sites in the city (Fig. 4) and comparable to those observed in indoor air in primary schools (Mortanais et al., 2015). Generally, the outdoor ambient air BaP concentrations are higher in the colder period (October to March) and are predominately related to fossil fueled engine vehicles (Alier et al., 2013; Reche et al., 2012). The sampling days and sites of outdoor BaP do not
coincides with those in the present study, but there is a good correlation between outdoor vs. indoor station platform BaP levels (Fig. 4; $R^2 = 0.81$; $p < 0.001$). Stations that were sampled in the colder period, i.e. Joanic and Sagrera, show highest outdoor and indoor platform BaP levels. In this study, the seasonal trend can be best observed in the sampling sequence at the platform of Sagrera station ($n = 35$) from half January until the end of March 2015. A substantial decrease of the BaP concentrations can be observed (Fig. 5). This compound correlates ($R^2 = 0.86$; $p < 0.001$) well with levoglucosan concentrations in the same samples (Fig. 4). In the complete data set (including all samples from all stations) this correlation is also significant ($R^2 = 0.55$; $p < 0.01$). The strong correlation of these compounds at the subway platforms does not automatically mean that BaP is linked to biomass burning, but it indicates that the outdoor air PM is a major pathway for BaP, and other PAH, to the indoor air at the platforms. The modern stations, constructed in 2016, show substantially lower concentrations of organic pollutants due to the more sophisticated ventilation systems and the summer sampling period.

No influence on the PAH concentrations could be observed from rail track works and ballast adding to the tracks during nighttime (Table S1b, c), suggesting again that outdoor PM is the major source for particle bounded PAH at the platforms. Nevertheless, the inverse ventilation of the platform in the station of Tarragona did not show any change in PAH concentrations (Table S1a). The modern station of Collblanc, with the PSD system, showed a slight decrease of the PAH concentrations when the ventilation was switched off (Table S1a). The changes are however not large, probably due to overall low outdoor PAH concentrations in the sampling period.

3.3. Source apportionment of organic aerosol

Assuming that levoglucosan and nicotine have an outdoor origin and hopanes a predominantly indoor origin, i.e. from the subway machinery and wagons, further assessment on the origin of the subway organic aerosol can be obtained. For this purpose, the concentrations of the analyzed tracer compounds were evaluated with a multivariate curve resolution alternating least squares (MCR-ALS) method.

A two-component solution explains 92.3% of the variance in the data set, and involves a clear separation between a potential indoor aerosol and outdoor aerosol (Fig. 6a). The loading of the indoor aerosol is represented by hopanes (98%), while the loading of the outdoor aerosol is represented by levoglucosan (100%). Nicotine contributions were divided equally between the two components. In this two-component resolution model about 75 ± 13% of the PAH is related to the outdoor aerosol component. The score values of the components were used to estimate the relative contribution to the organic aerosol (i.e. sum of indoor component + outdoor component). The contribution of the outdoor component to the organic aerosol is most relevant at the subway platforms of Sagrera (79% of the sum of scores), Joanic (70%) and Sant...
lledfons (82%), that were sampled in winter. In the other subway stations the organic aerosol was dominated by the indoor contributions (>65%). (Fig. 6b).

Addition of a third component (96.3% of explained variance) separates the loading of the outdoor aerosol, i.e. levoglucosan and higher molecular weight PAH, into two outdoor aerosol components (Fig. 6a), suggesting two different outdoor sources. In fact, the outdoor component that contains benz[a]anthracene and chrysene (outdoor_1; Fig. 6c) has higher contributions to the organic aerosol at the platform of Sagrera (Fig. 6d), while the other outdoor component (outdoor_2; Fig. 6c) is more dominating in the other stations, such as Joanic (Fig. 6d). The higher contributions of benz[a]anthracene and chrysene with respect to other PAH in Sagrera station could be due to a specific local outdoor source emission that influences this station in particular.

In the three-component resolution model, nicotine is still divided between indoor and outdoor_1 aerosols, and does not contribute to this third component (outdoor_2).

Addition of a fourth component (98.3% of explained variance) separates the contributions of nicotine (cigarette smoke) into a fourth component (68% of nicotine), which also contains 35% of the hopanes, but <10% of PAH (Fig. 6e). The relative contribution of this cigarette smoke component to the organic aerosol is important at the platform of the subway stations of Poble Sec (46%), and Tarragona (37%) (Fig. 6f). In other outdoor contributions the sums to component scores are ~23%. The higher contribution of this cigarette smoke component is probably related to indoor smoking, even if forbidden, especially in the station of Poble Sec where also the highest nicotine concentrations were found. However, in the resolution with four components, the independent indoor component does not contain any nicotine anymore, but it is still represented by hopanes (65%) and the score value of this component remains high in the L3 stations of Palau Reial, Tarragona and Poble Sec.

The scores values of the indoor component in the different stations shows the best correlation with TC concentrations (R² = 0.67; p < 0.001), indicating that the platforms in the stations with highest indoor contributions are exposed to carbonaceous particles from the subway system, while the subway stations of Colblanc and Sant Ildelfons experience the lowest exposures. In the case of the Colblanc station, these low contributions of indoor PM can be explained by the physical separation of the rail track with the platform by mains of the PSD screens. The outdoor sources are important in the stations that were sampled in winter and coincides with the period of higher outdoor PM and PAH concentrations. In fact, the two outdoor sources still represent 77 ± 7% of the detected PAH. Based on the ventilation tests, there are evidences that the modern station of Colblanc with the PSD system reduces the introduction of indoor PM from the tunnel and subway system to the platform. However, at this stage it is still unclear whether the PSD screen system would impede the introduction of outdoor PM and PAH onto the platforms under outdoor conditions with high PM and PAH concentrations (i.e. winter).

4. Conclusions

PM_{2.5} and TC concentrations at the platforms of the conventional subway stations are several times higher than the ones of outdoor ambient air, while the modern stations with PSD and advanced ventilation systems show concentrations similar to outdoor. Nighttime maintenance works and inverse ventilation in conventional subway systems do not influence the indoor air quality for PAH in the platform on the next day. If the ventilation is switched off in the modern stations the PM concentrations increase to levels that are observed in the conventional stations. Conventional stations are influenced by outdoor PM although the indoor PM from the subway system dominates. PAH concentration at the platforms are similar to those observed in the outdoor ambient air of Barcelona, with benz[a]pyrene concentrations in winter that are above the recommended concentration for outdoor air.

The analysis of the organic tracer compounds levoglucosan, nicotine and hopanes, allowed to estimate the source apportionment of a part of the organic particle matter at the subway platforms. At the platforms 75% of the detected PAH concentrations have their origin from outdoor air. Supplementary data to this article can be found online at https://doi.org/10.1016/j.sctotenv.2018.06.032.

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