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

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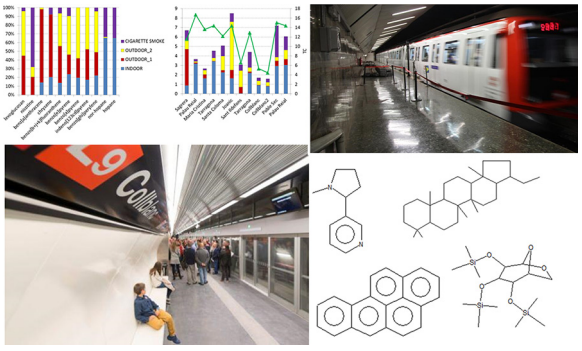
HIGHLIGHTS

- $PM_{2.5}$ 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 $PM_{2.5}$ concentrations in the platform.
- 75% of the detected PAH concentrations in the platforms origin from outdoor air.

GRAPHICAL ABSTRACT



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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 ($PM_{2.5}$) 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.

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 main 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(H)β-29-norhopane and 17(H)α-21(H)β-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 trough 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

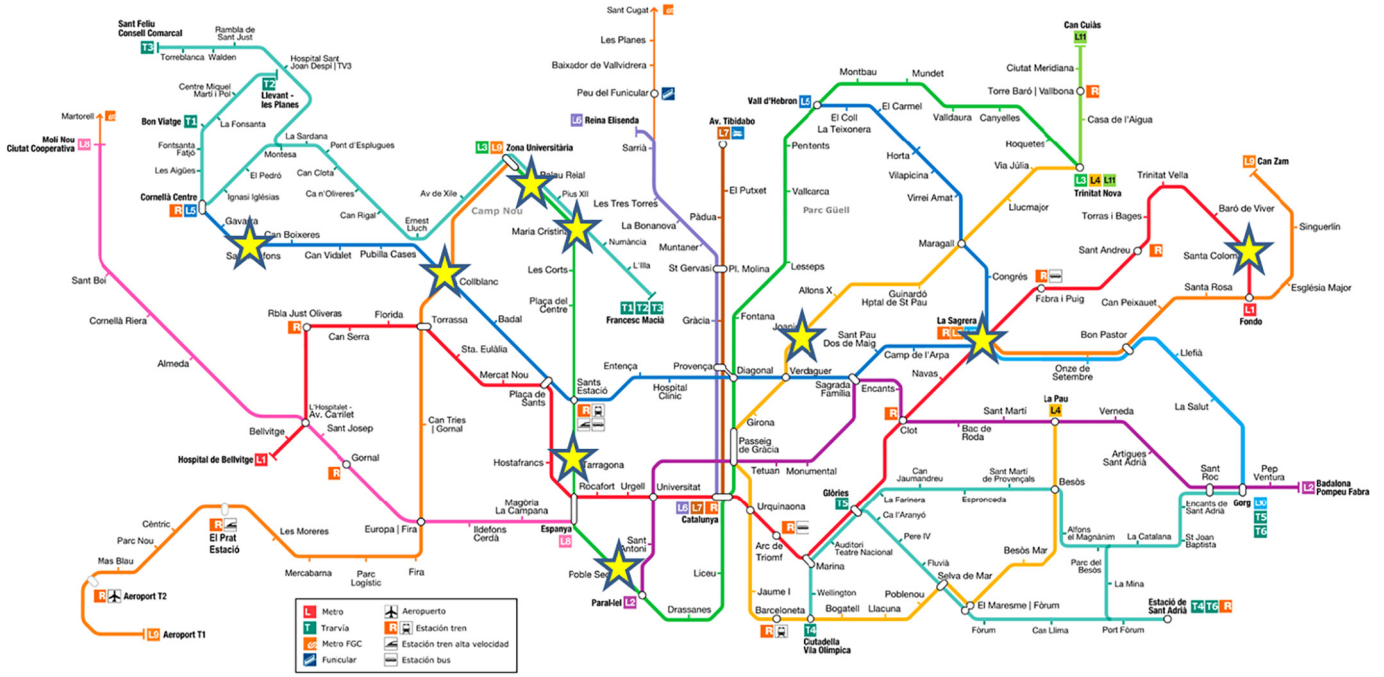

Fig. 1. Map of subway system in Barcelona. The analyzed stations are indicated by stars in the map.