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Air quality in subway systems: particulate matter concentrations, chemical composition, sources and personal exposure

Vânia Ferreira Martins

Programa de doctorat en Química Analítica del Medi Ambient i la Pol·lució

AIR QUALITY IN SUBWAY SYSTEMS: particulate matter concentrations, chemical composition, sources and personal exposure

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Vânia Ferreira Martins

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Supervisors:

Dr. Teresa Moreno

Dr. María Cruz Minguillón

Consejo Superior de Investigaciones Científicas (CSIC)

Institute of Environmental Assessment and Water Research (IDAEA)

Tutor:

Dr. Miquel Esteban Cortada

Universitat de Barcelona

Departament de Química Analítica

To my parents, my sister and to Luís.

"The whole of science is nothing more than a refinement of everyday thinking."

— Albert Einstein

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ABSTRACT

Air quality plans incentivise the use of public transport to abate atmospheric emissions from private road vehicles in cities. In this context, rail subway systems are especially desirable as they are based on electric trains, are energetically/environmentally efficient, and help to relieve surface traffic congestion. 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 worldwide. Despite the undoubted efficiency of subway travel, a number of studies have revealed poor air quality underground, especially concerning levels of particulate matter (PM). Interestingly, some subway systems appear to be worse than others in terms of PM loading, and it is clearly necessary to identify the main factors controlling air quality in this environment. When considering indoor air quality in underground subway systems, two aspects should be examined: the air quality on the platforms of the stations and the air quality inside the trains. Surveys on the concentrations and characteristics of inhalable particles existing in this indoor environment are of extreme interest, since they have been shown to cause adverse health effects.

The overall aim of this thesis is to fully characterise passenger exposure to PM while commuting (including waiting time on the platform and travelling inside the trains) in three European subway systems (Barcelona, Athens and Oporto). The Barcelona subway system comprises 8 lines, covering 102 km of route and 139 stations. The new stations have platforms separated from the rail track by a wall with mechanical doors, known as platform screen door systems (PSDs). The Athens subway system comprises 3 lines in 83 km long, with 61 stations. The Oporto subway system has 6 lines and 81 operational stations across 67 km of double track commercial line.

Air quality sampling campaigns both on platforms (focusing on concentrations and chemical composition of PM with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$)) and inside trains (measuring real-time PM concentrations) were conducted in order to characterise PM, investigating its variability, to better understand the main factors controlling it, and therefore the way to improve air quality. An intensive measurement campaign in the Barcelona subway system was performed in two one-month periods at

each of the four selected stations with different designs: Joanic, Santa Coloma, Tetuan and Llefià. The study was conducted in a warmer (2 April – 30 July 2013) and a colder (28 October 2013 – 10 March 2014) period, according to Transports Metropolitans de Barcelona (TMB) ventilation protocols to ascertain seasonal differences. In the case of the Athens and Oporto subway studies, 3-weeks intensive measurement campaigns were carried out at one station in each system, namely Nomismatokopio (28 April – 19 May 2014) and Bolhão (27 October – 14 November 2014), respectively. The campaigns were performed following a similar methodology, therefore results from the different subway systems are comparable. Outdoor ambient PM concentrations were measured concurrently at an urban station in each city, which was used as a reference site. The $PM_{2.5}$ chemical composition was obtained in terms of major and trace elements, inorganic ions and total carbon (TC). Additionally, in the Barcelona study the organic compounds were analysed; a Positive Matrix Factorization (PMF) analysis was performed to identify and quantify the contributions of major $PM_{2.5}$ sources; and a study to determine the dose of inhaled subway particles in the human respiratory tract (HRT) was performed using the ExDoM dosimetry model. Additional real-time measurements on the platforms of 24 stations from Barcelona subway, 5 stations from Athens subway and 5 stations from Oporto subway were carried out, to observe possible spatial and temporal variations in the PM concentrations along the platforms. Measurements inside the trains were performed in 6 lines in Barcelona, and 2 lines both in Athens and Oporto, during a return trip along the whole length of the subway line. In Barcelona, during the colder period of the campaign, measurements inside the trains were carried out with and without air-conditioning.

Results showed that PM concentrations varied among the European subway platforms, and also within the same underground system. This might be associated to differences in the design of the stations and tunnels; system age; train frequency; ventilation and air-conditioning systems; passenger densities; power system (catenary vs. third rail); composition of wheels, rail tracks, brake pads and power supply materials; rail tracks geometry (curved vs. straight and sloped vs. levelled); and outdoor air quality.

In the Barcelona subway system, the new stations showed on average lower $PM_{2.5}$ concentrations (around 50%) than those in the old conventional stations, mainly related to the stations design (with PSDs), but also due to the lower train frequency and more

advanced ventilation setup. Furthermore, PM concentrations on the platforms in the colder period were higher and also more variable than in the warmer period. This is mainly due to seasonal changes in the ventilation, which is stronger during the warmer period, controlling the air quality in the subway system. The ventilation was more efficient removing coarser particles. In Athens, the mean PM concentrations in a new station located in the periphery of the line (out of the central area of the city) were lower than in a central station, attributed not only to the age and location of the station, but also to the train frequency (some trains do not run the entire line).

Measurements carried out in the three subway systems performed on stations with similar platform design were compared. The highest $PM_{2.5}$ concentrations were observed in the Oporto subway station because the line is composed by curved and/or sloping rail tracks (resulting in a higher emission of rail wear particles) and it has a higher train frequency. Furthermore, mechanical forced ventilation is inexistent in this subway system.

The mean $PM_{2.5}$ concentrations on the platforms were notably higher (between 1.4 and 6.9 times) than those in the corresponding ambient air, evidencing the presence of indoor particulate sources in the underground stations.

PM concentrations displayed clear diurnal patterns among the three European subway platforms, depending largely on the operation and frequency of the trains and the ventilation system. During weekdays the PM concentrations on the platforms were 1.2 – 1.5 times higher than those measured during weekends, probably due to the lower frequency of trains. Moreover, in some cases the PM concentrations showed temporal and spatial variations on the platforms, probably due to the influence of the ventilation settings, design of the stations and tunnels, location of passengers' access to the platforms, commuter density, as well as to the effect of the passage and frequency of the trains.

PM concentrations inside the trains depend on air-conditioning system, windows open/close, travelling above/underground, and PM concentrations on platforms and tunnels, with short time variations when opening the train doors. The use of air-conditioning inside the trains was an effective approach to reduce exposure levels, being more efficient removing coarser particles. Having the carriage windows open

promotes the entrance of polluted air from tunnels and platforms into the trains. Nevertheless, even when the carriage windows are closed and the air conditioning system is switched on, the $PM_{2.5}$ concentrations inside the trains continue to be greatly affected by the surrounding air quality conditions.

The total and regional doses of particles in the HRT of a healthy adult male were estimated for the Barcelona study. The deposited mass of the $PM_{2.5}$ during a subway commuting travel was calculated assuming a typical exposure time of 5 min on the platforms and 15 min inside the trains. Particle deposition was proportional to the exposure concentrations. However, despite the lower $PM_{2.5}$ concentrations with respect to those on station platforms, the highest dose was observed inside the trains due to the longer exposure time. Overall, during a subway commuting travel, roughly 80% of the inhaled mass of subway $PM_{2.5}$ was deposited in the HRT. The highest amount of the inhaled particles was deposited in the extrathoracic region (68%), whereas the deposition was much smaller in the alveolar-interstitial region (10%) and tracheobronchial tree (4%). Individual's daily exposure to $PM_{2.5}$ and dose were estimated, considering a typical time-activity pattern of an adult male who lives in Barcelona and commutes by subway. While a subject typically spends approx. 3% of the day in the subway system, this microenvironment may account for up to 47% of the total $PM_{2.5}$ daily dose, hence accounting for the highest dose received per time unit during the day when considering no indoor sources at home and workplace and no spatial variability of outdoor aerosols. The dose, and its distribution on the different regions of the HRT, is mainly dependent on the particle size and exposure concentrations.

Chemically, subway $PM_{2.5}$ on the platforms is comprised of iron, total carbon, crustal matter, secondary inorganic compounds, insoluble sulphate, halite and trace elements. Organic compounds such as polycyclic aromatic hydrocarbons (PAHs), nicotine, levoglucosan and aromatic musk compounds were also identified on the platforms of the Barcelona subway system. The distributions of the relative contributions of the different components to the bulk $PM_{2.5}$ were similar at the stations of the three European subway systems. Fe was the most abundant element in $PM_{2.5}$ found on the platforms, with relative contribution to the bulk $PM_{2.5}$ ranging from 19 to 46%, which is generated mainly from mechanical wear and friction processes at rail-wheel-brake

interfaces. The trace elements with highest enrichment in the subway $PM_{2.5}$ were Ba, Cu, Mn, Zn, Cr, Sb, Sr, Ni, Sn, As, Co and Zr. Differences in metal concentrations in PM among the stations and subway systems might be associated to the different chemical composition of wheels, rails, brakes, and power supply materials. The metals can be originated from mechanical wear and friction processes among these manufactured materials.

For the Barcelona subway study, a source apportionment analysis by PMF allowed the identification of outdoor (sea salt, fuel oil combustion and secondary) and subway sources, the latter including all emissions generated within the subway system. The subway source was always dominated by Fe (53 to 68%) and comprises emissions from rails, wheels, catenaries, brake pads and pantographs. The subway source contribution to platform $PM_{2.5}$ was lower during the warmer period (9 to 29%) than during the colder period (32 to 58%) and was responsible for more than 50% of the concentrations of Al_2O_3, Ca, Fe, Cr, Mn, Cu, Sr, Ba, Pr, and Nd. Hence, control actions on this source are essential to achieve better air quality in the subway environment.

This thesis provides a comprehensive assessment on PM characterisation in the subway transport environment. The results reported here are valuable to support air quality improvement measures and policies in the subway systems worldwide.

CONTENTS

Chapter 1

Introduction

1. INTRODUCTION

Today there is a growing interest in improving air quality by both the general public and individual governments. This interest has prompted an important increase in atmospheric pollution research, which is a complex task requiring knowledge of all the factors and processes involved: the emission of pollutants into the atmosphere by natural and/or anthropogenic sources, the transport, the chemical and physical transformations and deposition of the pollutants, and, finally, their effects. Among the various atmospheric pollutants (O_3, NO_X, SO_X, CO, VOCs (volatile organic compounds), PAHs (polycyclic aromatic hydrocarbons), etc.), particulate matter (PM) is of particular interest. Particles in the atmospheric environment constitute a major class of pollutants, in addition to those occurring in gaseous form (Morawska and Salthammer, 2003). The growing scientific interest in atmospheric aerosols is due to their high importance for both environmental and health policies. In fact, ambient particles affect air quality and, in turn, human and ecosystem well-being.

1.1. Atmospheric Aerosols

Aerosols are a suspension of solid and/or liquid particles in a fluid. In the case of atmospheric aerosols, this fluid is the air (Seinfeld and Pandis, 2006). These particles, also known as particulate matter, can be originated from a wide variety of anthropogenic stationary and mobile sources as well as natural sources. Particles may be directly emitted (primary aerosols) or formed in the atmosphere (secondary aerosols) as a result of chemical reactions between gaseous components (gas-to-particle conversion), between gaseous components and pre-existing particles, or between different pre-existing particles (Warneck, 1988). The chemical and physical properties of PM vary greatly with time, region, climate/meteorology, and source category. The atmosphere contains particles of size ranging from a few nanometres (nm) up to hundreds of micrometres (μm) in diameter, which consist of a variety of chemical compounds (Hinds, 1999). Depending on their lifetime, the particles observed at a location can be both of local origin or the product of the transport over distances of

hundreds to thousands kilometres. Ambient particles can adversely affect human health (WHO, 2013) and drive many key aspects of the atmospheric and climate systems, such as cloud formation (IPCC, 2013). Moreover, the primary parameters that determine their role in atmospheric processes and their environmental and health effects are their concentration, size, structure, chemical composition, density, surface area, and optical properties (Finlayson-Pitts and Pitts, 2000; Pöschl, 2005).

1.1.1. Emission sources

Both primary and secondary aerosols may have a natural or anthropogenic origin (Warneck, 1988). Ambient particles may have their origin in both indoor and outdoor sources. The air exchange between the indoor and outdoor environments leads to interactions between all these emissions (Chen and Zhao, 2011). The examples listed in Table 1.1 distinguish between indoor versus outdoor, and natural versus anthropogenic sources.

Table 1.1 Sources of atmospheric particulate matter (non-exhaustive list).

Outdoor sources:	**Indoor sources:**
Natural • Biological materials (plant fragments, microorganisms, pollen, etc.) • Wildfires • Sea spray • Volcanic eruptions • Wind-driven resuspension of road, soil, and mineral dust • Lightning	• Human occupants, i.e. skin, hair, etc. • Plants, pets • Cleaning and vacuuming • Building materials • Combustion (biomass burning, candles, incense, smoking) • Cooking • Maintenance products
Anthropogenic • Fuel combustion and industrial processes • Transportation • Road traffic (exhaust and non-exhaust emissions) • Industrial activities • Construction and demolition activities • Farming activities	

In the atmosphere, the interactions of aerosols derived from varying sources are inevitable (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006). The natural and anthropogenic sources releasing primary PM to the atmosphere are many and varied, and these sources determine the physical characteristics of aerosols (size, density, surface, etc.) and their chemical composition (Calvo et al., 2013). As a result of this

wide range of possible primary sources and of the various formation mechanisms of secondary aerosols, PM is a combination of particles of different origins, composition and size distribution (Calvo et al., 2013). Thus, separating and apportioning measured ambient aerosol to a source is a difficult task. Furthermore, it is important to identify and quantify aerosol sources, but also to understand the complex interplay of the aerosols of different sources in the atmosphere if effective mitigation strategies for air pollution and climate are to be devised (Pöschl, 2005). Thus although there is a direct relationship between the emission of primary pollutants and their ambient concentrations, a reduction of a precursor does not automatically lead to a proportional decrease in the concentration of a secondary pollutant (Bernstein et al., 2004).

1.1.2. Size distribution

Particle size depends on the aerosol source and formation mechanism and is one of the most important parameters for characterising the behaviour of aerosols. The source and size affect the particle impacts on health, environment, and climate (Finlayson-Pitts and Pitts, 2000; Hinds, 1999; Seinfeld and Pandis, 2006). Some means of expressing the size of such particles is essential for many important properties of the particles such as volume, mass, and settling velocity (Finlayson-Pitts and Pitts, 2000).

Particles in the atmosphere have widely variable shapes that cannot be accurately described by a simple particle geometric diameter (D_g). In practice, the size of such irregularly shaped particles is expressed in terms of an equivalent diameter that depends on a physical, rather than a geometrical, property. An equivalent diameter is defined as the diameter of the sphere that would have the same value of a particular physical property as that of the irregular particle (Finlayson-Pitts and Pitts, 2000; Hinds, 1999). There are different types of equivalent diameters. One of the most commonly used is the particle aerodynamic diameter, D_a, which is defined as the diameter of a spherical particle of unit density (ρ_0, 1 g cm^{-3}) with equal settling velocity in air as the particle under consideration, normalizing particles of different shapes and densities. The particle aerodynamic diameter is given by Equation 1.1.

$$D_a = D_g \, k \sqrt{\frac{\rho_p}{\rho_0}}$$ **Equation 1.1**

where ρ_p is the density of the particle and k is the dynamic shape factor, which is 1 in the case of a sphere. Because of the effect of particle density on the aerodynamic diameter, a spherical particle of high density will have a larger aerodynamic diameter than its geometric diameter. In this thesis, particle size or diameter will be consistently referred as particle aerodynamic diameter.

A particle size distribution gives the number, surface-area, volume, or mass concentrations of particles as a function of diameter (Jacobson, 2005). Particle mass, number, volume, and surface area display different size distributions and are important for different applications; for instance, health standards of particles are defined in terms of mass, while volume and surface area considerations are essential in controlling reactions of gases with particles (Finlayson-Pitts and Pitts, 2000). Size distribution of particles is plotted in Figure 1.1a where the number and volume of particles are normalized as a function of the particle size diameter. Particle number is dominated by small particles, while particle volume, and hence mass, becomes more important at larger sizes.

Particles can be classified into 2 categories according to their size (Figure 1.1b): particles with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) are generally referred as fine and those greater than 2.5 μm in diameter as coarse (Seinfeld and Pandis, 2006). The fine particles are also categorised as nanoparticles (<0.05 μm) and ultrafine particles (<0.1 μm) (Figure 1.1b). The distinction between fine and coarse particles is a fundamental issue in terms of physics, chemistry, measurement, or health effects of aerosols, since fine and coarse particles, in general, are originated and transformed separately, are removed from the atmosphere by different mechanisms, have different chemical composition and optical properties, and differ significantly in their deposition patterns in the respiratory tract (Seinfeld and Pandis, 2006). The mixture of aerosols found in the atmosphere is polydisperse, meaning that it includes a large range of particles sizes, as opposed to a monodisperse aerosol, which would comprise single size particles (Kulkarni et al., 2011).

The aerosol size distribution is usually a result of one or several particle modes, which can be related with distinct particle formation mechanisms (Figure 1.1c). Fine particles can often be divided roughly into three modes (Seinfeld and Pandis, 2006): the *nucleation* (or *nuclei*) *mode*, the *Aitken mode* and the *accumulation mode* (Figure 1.1d).

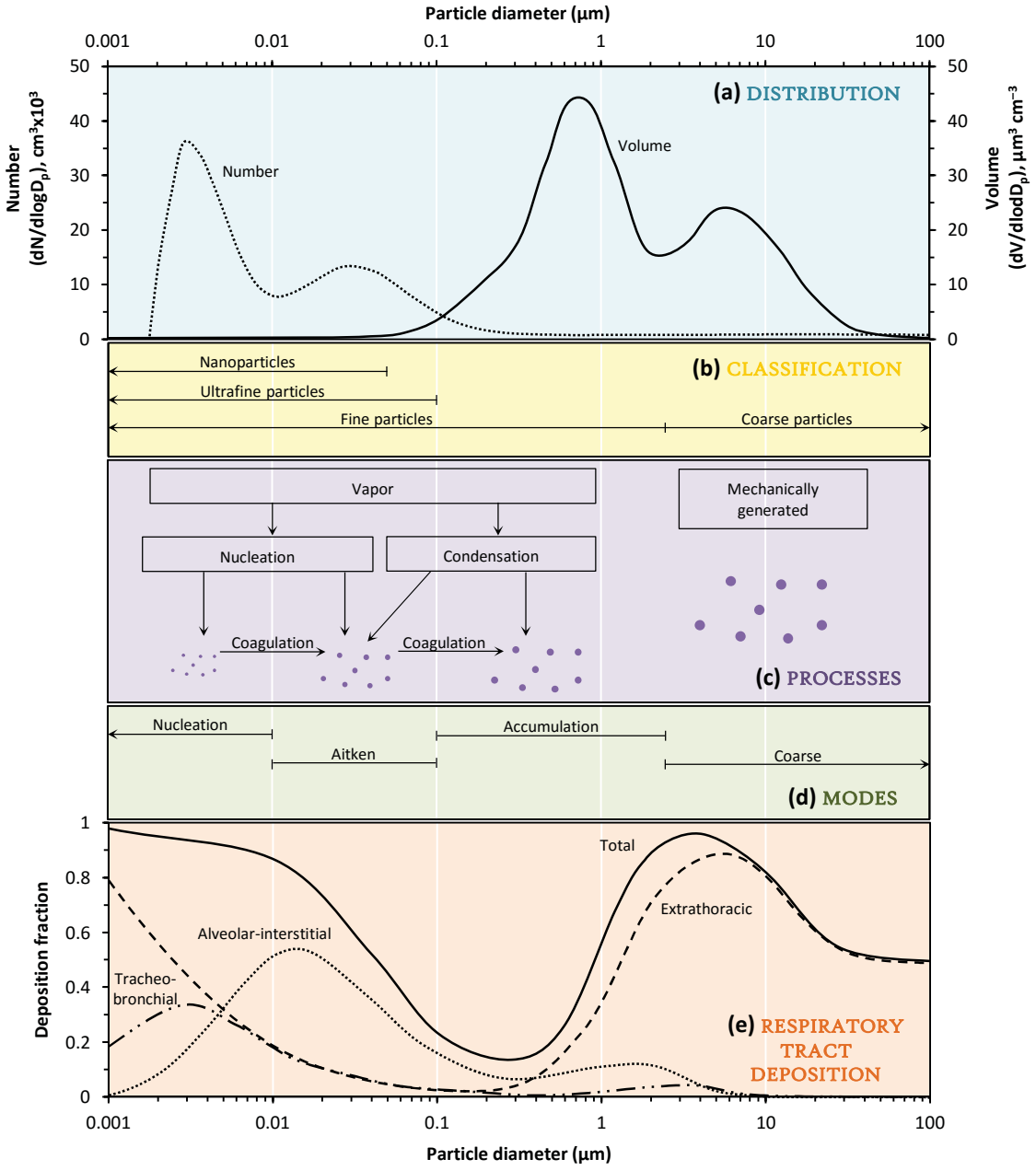


Figure 1.1 Composite picture of (a) typical atmospheric aerosol particle number and volume distributions (adapted from Seinfeld and Pandis, 2006) (b) particles classification, (c) formation processes of particles, (d) particles modes and (e) fractional deposition of inhaled particles in the human respiratory tract (adapted from ICRP, 1994) as a function of particle diameter.

The *nucleation mode* comprises particles with diameters up to about 0.01 μm. The *Aitken mode* spans the size range from about 0.01 to 0.1 μm in diameter. These two modes account for the preponderance of particles by number; although, because of their small size, these particles rarely account for more than a few percent of the total mass of airborne particles (Seinfeld and Pandis, 2006). The *accumulation mode*, extending from 0.1 to about 2.5 μm in diameter (upper value also listed as 1 μm or 2 μm in the literature), usually accounts for most of the aerosol surface area and a substantial part of the aerosol mass (Seinfeld and Pandis, 2006). Particles larger than 2.5 μm are normally classified into the coarse mode.

1.1.3. Formation processes

The physical (size distribution, shape, density, etc.) and chemical (composition) characteristics of aerosols may vary due to a number of formation processes (Mészáros, 1999). Fine and coarse particles generally have distinct sources and formation mechanisms, although there is some overlap. Fine particles are typically produced in high energy processes such as combustion, gas-to-particle conversion, nucleation processes or photochemical processes (Kulmala et al., 2004). By contrast, coarse particles are usually produced by mechanical processes such as cutting, grinding, breaking, and wear of material, as well as dust resuspension, meaning they are generally emitted from their source directly as particles (Finlayson-Pitts and Pitts, 2000; Holmes, 2007; Kulkarni et al., 2011; Seinfeld and Pandis, 2006). The formation and growth of fine particles are influenced by three processes (Hinds, 1999; Holmes, 2007; Kulmala, 2003; Seinfeld and Pandis, 2006): (1) nucleation of new particles from low-vapour pressure gases emitted from sources or formed in the atmosphere by chemical reactions; (2) condensation of low-vapour pressure gases on existing particles; and (3) coagulation of particles, the weak bonding of two or more particles into one larger particle. Gas phase material condenses preferentially on smaller particles since they have the greatest surface area, and the rate constant for coagulation of two particles decreases as the particle size increases (Holmes, 2007; Kulmala et al., 2004). Because a particle from a given source is likely to be composed of a mixture of chemical components and because particles from different sources may coagulate to form a new

particle, atmospheric particles may be considered a mixture of components. The composition and behaviour of particles are fundamentally linked with those of the surrounding gas. Figure 1.1c shows the formation and growth mechanisms of atmospheric particles. A brief description of the formation mechanisms for the particles modes is exposed hereinafter:

- *Nucleation mode* (<0.01 μm): Particles are directly emitted into the atmosphere or formed there by gas-to-particle conversion (Holmes, 2007; Kulmala, 2003). Because of their high number concentration, especially near their source, these nanoparticles coagulate rapidly with each other or grow by condensing secondary particles, resulting in coarser particles (Kulmala and Kerminen, 2008; Place Jr. et al., 2010; Rodríguez et al., 2005). Consequently, nucleation particles have relatively short lifetimes in the atmosphere.
- *Aitken mode* (0.01–0.1 μm): Particles of the nucleation mode, under favourable abiotic conditions, can rapidly agglomerate to larger clusters that characterize the Aitken mode (Nøjgaard et al., 2012). They originate from vapour nucleation or growth of pre-existing particles due to condensation. Particles typically have short lifetimes by acting as nuclei for condensation of low-vapour-pressure gases and growing into the accumulation mode, and/or undergoing rapid coagulation processes.
- *Accumulation mode* (0.1–2.5 μm): Particles are originated from primary emissions as well as through gas-to-particle conversion, chemical reactions, condensation of low-volatility vapours, and coagulation of multiple small particles. Particles in this mode tend to have considerably longer atmospheric residence times than those in either the nucleation or coarse mode and are typically removed by cloud activation and precipitation processes, as they are too small for sedimentation.
- *Coarse mode* (> 2.5 μm): Particles are generated by mechanical processes and usually consists of human-made and mineral dust or sea salt particles. Coarse particles have sufficiently large sedimentation velocities to be settled out of the atmosphere in a reasonably short time.

An idealized aerosol size distribution is illustrated in Figure 1.1a, together with the different particle modes (Figure 1.1d).

1.1.4. Chemical composition

The chemical composition of particles is wide-ranging, complex, varies with location and atmospheric conditions, and mostly depends on particle sources as well as post-formation processes (Finlayson-Pitts and Pitts, 2000; Kolb and Worsnop, 2012; Seinfeld and Pandis, 2006). Particles are composed of many different inorganic and organic compounds. Atmospheric particles are made up of mineral dust, sea salt, secondary inorganic compounds (SIC), carbonaceous aerosol and trace elements (e.g. Putaud et al., 2010), and contain a considerable mass fraction of water (e.g. Ervens et al., 2011). The predominance of any of these major components depends heavily on the principal emission source and the formation mechanism of the particles.

Mineral dust (or crustal matter) is typically comprised of primary particles and its chemical composition varies depending on local geology, soil mineralogy and anthropogenic activities, being mostly dominated by Si, Al, Fe, Ca, Ti, Mg and K (Goudie and Middleton, 2006). Mineralogically, this composition relates to dominance of quartz, carbonates, magnetite/hematite, clay minerals and feldspars (Alastuey et al., 2005; Coz et al., 2009; Goudie and Middleton, 2006). Ginoux et al. (2012) attribute 75% of the global dust emissions to natural origin (wind action), while 25% are related to anthropogenic (primarily agricultural) emissions. One of the largest sources of natural mineral dust is the Sahara desert (Prospero et al., 2002).

Sea salt is formed predominantly by Na^+ and Cl^-, with smaller amounts of other components such as SO_4^{2-}, Mg^{2+}, Ca^{2+} and K^+ (White, 2008). The ocean is the main source of atmospheric Na^+ and Cl^- in coastal areas (Claeys et al., 2010). However, it can be transported long distances (Pósfai and Molnár, 2012).

Secondary inorganic compounds refer to the main inorganic compounds in the atmosphere: sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), that are generated through a series of chemical reactions and physical processes involving precursor gases emitted from natural (e.g. marine dimethyl-sulphide and volcanic SO_2) or anthropogenic (e.g. nitrogen oxides (NO_X), sulphur dioxide (SO_2), ammonia (NH_3)) sources (Giere and Querol, 2010; Squizzato et al., 2013). Sulphate component is derived mostly from the atmospheric oxidation of anthropogenic and natural sulphur-

containing compounds such as SO_2 and dimethyl-sulphide (Lucas and Prinn, 2005). Nitrate is formed predominantly from the oxidation of atmospheric NO_2. Sulphate and nitrate initially occur as sulphuric (H_2SO_4) and nitric (HNO_3) acids, but are progressively neutralised by atmospheric NH_3 forming the corresponding ammonium salts (Stockwell et al., 2003). Oceans can be a significant source of NH_4^+. The neutralisation of H_2SO_4 generally prevails on the neutralisation of HNO_3 (Seinfeld and Pandis, 2006), but the production of secondary sulphates and/or nitrates strongly depends on several chemical and micro-meteorological factors, such as the levels of gaseous precursors, insolation, the concentrations of atmospheric oxidants, the characteristics of pre-existing aerosols, and the air temperature and humidity (Baek et al., 2004; Pathak et al., 2009).

Carbonaceous aerosol consists of a complex mixture of substances containing carbon atoms, usually classified in two major fractions as organic carbon (OC) and elemental carbon (EC) (Engling and Gelencsér, 2010). Frequently, OC is converted to organic matter (OM) in order to include all the elements (hydrogen, oxygen, nitrogen, etc.) that are components of organic compounds, not just carbon (Aiken et al., 2008; Turpin and Lim, 2001). OM is a complex mixture of many different organic compounds (Mikuška et al., 2015; van Drooge et al., 2012; Yang et al., 2016), such as carboxylic acids, hydrocarbons, alcohols, ethers, aldehydes, ketones, esters, among others, covering a wide range of chemical and thermodynamic properties (Seinfeld and Pandis, 2006). OM is a major part of submicron particles (Jimenez et al., 2009) and can be primary (e.g. from biomass burning and combustion processes) or can result from the atmospheric transformation of gaseous organic species that make up secondary organic aerosol (SOA) (Kroll and Seinfeld, 2008). EC, also called black carbon (BC) according to its optical properties, and graphitic carbon, is emitted directly into the atmosphere, predominantly from incomplete fuel combustions (Seinfeld and Pandis, 2006).

Trace elements in atmospheric particles may be diagnostic of specific sources and can therefore aid in source apportionment (Grobéty et al., 2010; Lim et al., 2010; Querol et al., 2007; Sternbeck et al., 2002; Thorpe and Harrison, 2008). Although trace elements constitute only a small proportion of PM mass, their negative impacts on human health

and ecosystems have attracted considerable attention because of their toxicity and bioaccumulation by inhalation and deposition (Kampa and Castanas, 2008; Pan and Wang, 2015). For example, stationary fossil fuel combustion is a major source of Cr, Hg, Mn, Sb, Se and Sn, whereas V and Ni are commonly attributed to the combustion of fuel oil and petroleum coke (Pacyna and Pacyna, 2001). The largest source of atmospheric As, Cd, Cu, and Zn is the non-ferrous metal production (Pacyna and Pacyna, 2001). Cu, Sb, and Ba in urban PM indicate that the particles are derived from abraded vehicle brake pads (Sternbeck et al., 2002).

The composition of fine and coarse particles is usually different. The mineral dust and the sea salt aerosols are dominantly in the coarse mode, whereas OC, EC, SO_4^{2-}, NO_3^- and NH_4^+ particles are mainly observed in the fine mode, although NO_3^- and SO_4^{2-} can interact with NaCl or mineral particles and therefore they are also present in the coarse mode. Trace elements can be observed both in fine and coarse particles depending to their sources.

1.1.5. Fate and transport

Once in the ambient air, the particles undergo a range of physical and chemical processes, which change their chemical composition, physical characteristics, and concentration in the atmosphere. Fine and coarse particles typically exhibit different behaviour in the atmosphere.

Particles can be removed from the atmosphere and deposited onto the Earth's surface by dry and/or wet deposition. Dry deposition rates are governed by meteorological variables (wind velocity or relative humidity), properties of the particles (size and shape) and variables of the surface on which the particles are deposited (friction velocity, microscale roughness, and surface temperature) (Jonsson et al., 2008; Zufall and Davidson, 1998). Wet deposition comprises processes in which particles might either serve as condensation nuclei for atmospheric water and be incorporated into the formed droplet or collide with an existing droplet, and subsequently be transferred to the Earth' surface. If these processes take place within a cloud (by colliding with droplets), they are named in-cloud scavenging or rainout. If they occur below the cloud

(by falling raindrops or snow), they are called below-cloud scavenging or washout (Seinfeld and Pandis, 2006).

The residence time of atmospheric particles in ambient air depends on their size, hygroscopicity and the nature of the processes in which they are involved. The removal mechanisms are more efficient for coarse and hygroscopic particles. The longest residence time corresponds to the particles in the accumulation mode.

1.1.6. Environmental and health effects

Particles in the atmosphere have impacts on visibility (Yuan et al., 2006; Zhao et al., 2015), ecosystems (Grantz et al., 2003; Katul et al., 2011), building materials (Costa et al., 2009), climate (Andreae et al., 2005; Das and Jayaraman, 2012; IPCC, 2013; Lohmann and Feichter, 2005; Mahowald et al., 2011; Zhuang et al., 2013) and human health (Dockery, 2009; Rückerl et al., 2011; Schleicher et al., 2011). The significance of these impacts depends strongly on the particle properties including concentration, size, composition, hygroscopicity, and mixing state (e.g. Karydis et al., 2011; Valavanidis et al., 2008; Wang et al., 2010; Yu, 2011). Thus, understanding the formation, composition and behaviour of aerosol particles is of critical importance in order to better quantify the effects of aerosols.

Effects on visibility

Visibility impairment has become an important environmental issue receiving considerable attention from the scientific community (Chen and Xie, 2012; Wang et al., 2009; Zhang et al., 2010) and the general public. The reduction of visibility has commonly been used as a visual indicator of ambient air quality (Watson, 2002), since it is mainly attributed to the scattering and absorption of visible light by particles and gaseous pollutants (e.g. NO_2) in the atmosphere (Deng et al., 2008; Zhao et al., 2015). The fine particles are major contributors to this phenomenon because of their highly efficient light scattering properties (Yuan et al., 2006). The absorbing aerosol particles (such as EC) also play important roles in the reduction of visibility (Deng et al., 2008). In terms of the aerosol composition, sulphate, nitrate, organics and elemental carbon are the major species that impair visibility (Cao et al., 2012; Yuan et al., 2006).

Ecological effects

PM can have physical effects on ecosystems caused by high levels of PM being deposited directly onto vegetative surfaces, or more importantly, from chemical effects resulting from constituents of PM deposited directly onto vegetative surfaces or acting indirectly through deposition into terrestrial and/or aquatic environments (Grantz et al., 2003; Lovett et al., 2009). Coating with particles may be associated with the reduction in light required for photosynthesis, an increase in leaf temperature due to changed surface optical properties, leaf tissues injury owing the presence of acidic and alkaline materials, and interference with the diffusion of gases into and out of leaves (Grantz et al., 2003; Prajapati, 2012; Vardaka et al., 1995). Moreover, particle deposition is also responsible for delivering loads of various compounds to the ecosystems: particles containing SO_4^{2-}, NO_3^- and NH_4^+ that contribute to potential acidification and eutrophication of the ecosystems; natural or anthropogenic radioactive particles; base cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} that influence the nutrient cycling in soil and ecosystems; and toxic heavy metals, such as Pb, Cd and Zn (Petroff et al., 2008; Prajapati, 2012; Ruijgrok et al., 1995).

Effects on materials

PM causes soiling and erosion damage to structures, including culturally important objects such as artwork, historic monuments and statues (e.g. Costa et al., 2009; Ferm et al., 2006; Tzanis et al., 2011; Watt et al., 2008). The degree of material damage is influenced by the optical properties and chemical composition of airborne particles (Jimoda, 2012). Soiling is an optical effect which is essentially the darkening of reflectance that results from the deposition of airborne PM to external building surfaces (Ghedini et al., 2000; Hamilton and Mansfield, 1993; Watt et al., 2008). Chemical degradation of materials due to deposition of atmospheric acid particles is an important aspect of material damage (Jimoda, 2012; Okochi et al., 2000).

Effects on climate

Aerosols have effects on radiative forcing of the climate system. In climate science, radiative forcing is defined as the change imposed by certain forcing agents (such as

greenhouse gases and aerosol particles) in the energy balance of the Earth (in units of Wm^{-2}) that eventually changes regional and global temperature (IPCC, 2013). Particles influence the climate directly by scattering (reflection) and absorbing the incoming solar radiation and the outgoing terrestrial radiation, and acting as cloud condensation nuclei (CCN) or ice nuclei (IN) and thereby indirectly affecting the radiative properties, formation and lifetime of clouds (Andreae and Rosenfeld, 2008; IPCC, 2013; Regayre et al., 2015; Tao et al., 2012). Negative radiative forcing such as the scattering and reflection of solar radiation by aerosols and clouds leads to a cooling effect, whereas positive radiative forcing such as the absorption of terrestrial radiation by greenhouse gases and clouds exerts a warming effect (greenhouse effect) (IPCC, 2013; Joos and Spahni, 2008; Mahowald et al., 2011; Zhuang et al., 2013). The relationship among aerosols, solar radiation, clouds and precipitation influences the regional and global radiative energy balance, as well as the temperature, dynamics, and general circulation of the atmosphere and oceans (Andreae et al., 2005).

Health effects

Particulate matter is an issue of increasing importance in pollution studies due to its noticeable effects on human health (e.g. Dominici et al., 2006; Katsouyanni et al., 2001; Lepeule et al., 2012; Pope and Dockery, 2006; Russell and Brunekreef, 2009; Schikowski et al., 2007; Shaughnessy et al., 2015; Valavanidis et al., 2008; Zhou et al., 2015), including decreased lung function, increased respiratory symptoms such as cough, shortness of breath, wheezing, and asthma attacks, as well as chronic obstructive pulmonary disease, cardiovascular diseases, and lung cancer (e.g. Anderson et al., 2012; Dockery, 2009; Kim et al., 2015; Rückerl et al., 2011; and references therein). Particular attention is being paid to the fine-sized particles ($PM_{2.5}$) due to their ability of being inhaled and reaching the gas exchange region of the lungs, as will be explained in section 1.1.7. There is strong evidence that $PM_{2.5}$ plays a significant role in the observed health effects even at very low levels of exposure (Dominici et al., 2006; Pope and Dockery, 2006). $PM_{2.5}$ composition may better predict health effects than PM mass or size (Rohr and Wyzga, 2012; Stanek et al., 2011; and references therein). Indeed, the harmful potential of particles is related to their ability in crossing human respiratory system, depositing in the deepest and most defenceless regions of the lung and

carrying with them a number of toxic compounds. Moreover, a fraction of the ultrafine particles may translocate from lung to the cardiovascular system (WHO, 2013). Toxicological studies suggest that several elements, including Al, Si, V, Pb, Ni and Zn, are most closely associated with health impacts, although many other components, such as EC and OC, have also been implicated (Chen and Lippmann, 2009; Rohr and Wyzga, 2012). The adverse health effects are related to both short-term (acute) and long-term (chronic) exposures to PM, and can range from relatively minor, such as increased symptoms, to very severe effects, including increased risk of premature mortality and decreased life expectancy from long-term exposure (Bentayeb et al., 2015; Cesaroni et al., 2013; Rückerl et al., 2011; Thurston and Lippmann, 2015). Numerous studies suggest that health effects can occur at particulate levels that are at or below the levels permitted under national and international air quality standards. The population groups most sensitive to the effects of PM include individuals with pre-existing chronic obstructive pulmonary or cardiovascular disease or influenza, genetic susceptibility, asthmatics, the elderly and children (Sacks et al., 2011).

1.1.7. Dosimetry

A large majority of the epidemiological and toxicological studies relate health effects to PM exposure (the inhaled concentration), although the negative outcomes are mainly caused by the subsequent deposition of PM in the respiratory tract (RT) during breathing (Salma et al., 2002). Hence, in order to understand the mechanisms behind the health responses, it is crucial to determine the respiratory tract deposition fraction (DF) of aerosol particles, which is their probability to deposit, and the dose (amount of inhaled particles deposited in the RT) (Löndahl et al., 2009). For aerosols this dose can be given as, for example, number, surface area or mass of the deposited particles.

Structure of the human respiratory tract

The detailed structure of the human respiratory tract (HRT) is illustrated in Figure 1.2. For dosimetry purposes, the respiratory tract is commonly divided into three major regions (ICRP, 1994): extrathoracic (ET, also called upper airways), tracheobronchial (TB), and alveolar-interstitial (AI). The ET region represents the areas through which

inhaled air first passes and consists of anterior nasal passages (ET_1) and the posterior nasal passages, oral passages, pharynx and larynx (ET_2). Inhalation can occur through either the nose or the mouth (or both, known as oronasal breathing) (Vincent, 2005). Most humans are oronasal breathers who breathe through the nose when at rest and increasingly through the mouth with increasing activity level. From the ET region, inhaled air enters the TB region at the trachea. From the level of the trachea, the conducting airways then undergo dichotomous branching for a number of generations. The TB region is composed by trachea and bronchi (BB) and the bronchiolar region (bb). The terminal bronchiole is the most peripheral of the distal conducting airways and leads to the AI region, which consists of respiratory bronchioles, alveolar ducts, alveolar sacs, and alveoli (the gas exchange region of the lungs). The term lower airways is used to refer to the intrathoracic airways (i.e. the combination of the TB and AI regions).

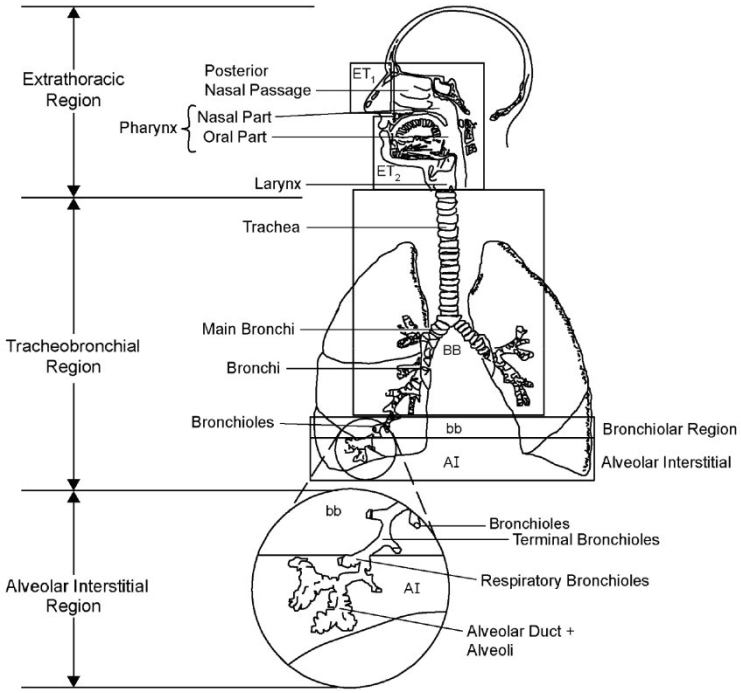


Figure 1.2 Anatomical regions of human respiratory tract. Abbreviations: ET_1: anterior nasal passages; ET_2: posterior nasal passages, oral passages, pharynx and larynx; BB: bronchial region, including trachea and bronchi; bb: bronchiolar region consisting of bronchioles and terminal bronchioles; AI: alveolar-interstitial region, consisting of respiratory bronchioles, alveolar ducts and sacs surrounded by alveoli.

Adapted from ICRP, 1994.

Size characterization of inhaled particles

Particle size is an important determinant of the fraction of inhaled particles deposited in the various regions of the RT. This means that the constituent particles within an aerosol have a range of sizes and are more appropriately described in terms of size distribution parameters. The distribution of particle sizes in an aerosol shows typically a lognormal distribution (e.g. Castro et al., 2010), described by the geometric mean (median) and the geometric standard deviation (GSD). The median of a distribution based on particle mass in an aerosol is the mass median diameter (MMD). When using aerodynamic diameters, a term that is encountered frequently is mass median aerodynamic diameter (MMAD), which is the median of the distribution of mass with respect to aerodynamic equivalent diameter. In most cases, the aerosols to which people are naturally exposed are polydisperse. By contrast, most experimental studies of particle deposition in the HRT use monodisperse particles.

Particle deposition

Inhaled particles may be either exhaled or deposited in the ET, TB, or AI region. The main mechanism for intake of airborne particles by the HRT is through their inhalation and consequent deposition. The deposition of inhaled particles in the HRT depends on a number of factors, including exposure concentration, physicochemical characteristics of PM (e.g. size distribution, density, shape and chemical composition), exposure duration, and exposed subject characteristics, as age, gender, race, health status, lung morphometry, and breathing parameters, among others (Broday and Agnon, 2007; Glytsos et al., 2010; Heyder, 2004; Hofmann, 2011; ICRP, 1994; Lazaridis et al., 2001; Löndahl et al., 2007; Patterson et al., 2014).

Lippmann et al. (1980) reported that the nasal passages are a more efficient particle filter than the oral ones, thus, persistent mouth breathers deposit more particles in their respiratory system than those breathing entirely through the nose. Additionally, Löndahl et al. (2007) conducted an intensive study determining that the amount of deposited particles in the HRT varied remarkably between genders, increasing substantially for the male subjects, because of their higher breathing rate values. The lung of a child differs significantly from that of adults in terms of airway dimensions

and breathing rate (Ménache et al., 2008). Due to the combination of smaller airway sizes, smaller tidal volumes, but higher breathing frequencies, the total deposition fraction in children is generally higher than in adults (Asgharian et al., 2004). The dose is generally higher in subjects with lung problems (such as asthma, obstructive lung diseases, etc.) than healthy subjects (e.g. Anderson et al., 1990; Chalupa et al., 2004; Kim and Kang, 1997). Brand et al. (1999) reported that for all particle sizes, the particle dose for each region of the HRT increases with increasing breathing rate. Increasing the breathing rate demonstrates the effect of inertial impaction in larger particle size, by increasing deposition in the upper respiratory tract and consequently increasing the DF in the extrathoracic region. For smaller particle size, increasing the amount of aerosol inhaled due to high air velocity promotes an increase of particle deposition in the deeper lung.

Inhaled particles are carried with the tidal air through the respiratory system. However, when travelling along an airway, particles will be exposed to different physical mechanisms forcing them to displace off the streamlines of the inhaled air volume and eventually depositing on the surrounding airway surfaces. The most important mechanisms acting upon the inhaled particles are inertial impaction, sedimentation (gravitational settling), diffusion (Brownian motion), interception, and electrostatic charging (Hofmann, 2011; Hussain et al., 2011; Löndahl et al., 2014). Coarse particles ($PM_{2.5-10}$) are mainly deposited in the upper airways of the HRT due to impaction, interception, gravitational settling, as well as turbulent dispersion. Fine particles ($PM_{2.5}$) have a high probability of deposition in deeper parts (lower airways), due to their high diffusivities (Vincent, 2005).

Deposition fraction is defined as the amount of particles deposited in the tissue divided by the amount of the particles inhaled. Figure 1.1e demonstrates the fractional deposition of inhaled particles in the HRT under conditions of nose breathing during light exercise, based on a predictive mathematical model (International Commission on Radiological Protection, 1994). Depending on their ability to enter specific regions of the HRT, the particles are inhalable (those that enter and deposit to the upper respiratory system), thoracic (those which can penetrate the trachea and bronchi), or

respirable (the fraction of thoracic particles that penetrates into the alveolar region of the lung) (Lazaridis, 2011; Vincent, 2005).

The dose of atmospheric aerosols in the HRT is measured by monitoring the inhaled and exhaled particle concentrations (Chalupa et al., 2004; Löndahl et al., 2008; Montoya et al., 2004; Morawska et al., 2005; Rosati et al., 2002). Due to experimental limitations, the regional dose in the respiratory system is typically estimated by means of mathematical models. Over the years, a large number of studies have been conducted to investigate particle deposition in the HRT, with a somewhat larger number focused on dosimetry modelling than on the experimental determination of the deposition (Aleksandropoulou and Lazaridis, 2013; Asgharian, 2004; Georgopoulos and Lioy, 2006; Heyder and Rudolf, 1984; ICRP, 1994; Klepeis, 2006; Koblinger and Hofmann, 1990; Lazaridis et al., 2001; Mitsakou et al., 2007; Rudolf et al., 1990; Sturm, 2007; Yeh and Schum, 1980). Reasonable correlation has been obtained between model predictions and experimental studies (Asgharian and Price, 2007; Löndahl et al., 2008; Stuart, 1984). An understanding of the mechanisms of particle deposition and the ability to quantify the deposition in individual regions of the HRT is of fundamental importance for dose assessment from inhalation of particles, which can then be used for risk assessment.

The clearance mechanisms are a natural defence of the human body and operate in different regions of the lungs to eliminate the trapped foreign material (Hussain et al., 2011). Furthermore, when comparing same mass deposits of large and small particles, the latter contains a much higher number of particles that need to be cleared (Carvalho et al., 2011).

1.1.8. Air quality regulations

The objective of environmental legislation is to protect human health and the environment as a whole. Concentration of PM in ambient air is currently legislated in most countries to maintain the quality of air, keeping pollutant concentrations under threshold levels to limit their impacts on human health. The European Union (EU) has set air quality guidelines to provide uniform targets for ambient air PM and other

pollutants. According to the EU legislation (Directive 2008/50/EC), the European standards for PM_{10} levels were set to 50 μg m^{-3} (24h average, not to be exceeded more than 35 times per year) and 40 μg m^{-3} (annual average) and to 25 μg m^{-3} (annual average) for $PM_{2.5}$. In 2006, the World Health Organization (WHO) released new air quality guidelines with dramatically lower standards for levels of pollutants by reducing PM_{10} to 20 μg m^{-3}, and $PM_{2.5}$ to 10 μg m^{-3} for annual mean levels (WHO, 2006).

However, there are no mandatory limit values established by the European Commission for indoor air quality. Thus, the WHO in 2010 discussed that "*There is no convincing evidence of a difference in the hazardous nature of PM from indoor sources as compared with those from outdoors and that the indoor levels of PM_{10} and $PM_{2.5}$, in the presence of indoor sources of PM, are usually higher than the outdoor PM levels*". Therefore, the WHO experts committee reported that the air quality guidelines for PM recommended by the global update 2005 (WHO, 2006) were also applicable to indoor spaces and that a new review of the evidence is not necessary at present (WHO, 2010).

1.2. Indoor Particulate Air Pollution

Numerous personal exposure studies have revealed poor correlations between ambient (outdoor) $PM_{2.5}$ concentrations and personal exposure measurements (e.g. Morawska et al., 2013). In fact, the personal exposure includes not only contributions from ambient PM sources, but also contributions from indoor, commuting and leisure activities, which depend on the lifestyle of each individual and the different microenvironments frequented, such as home, workplace, commuting type, etc. (Buonanno et al., 2013, 2011; Meng et al., 2005). Since people spend most of their time (80 – 90%) indoors, it is widely recognized that a significant portion of total personal exposure to ambient PM occurs in indoor environments (Klepeis et al., 2001).

Typically, particles encountered in indoor environment consists of primary particles emitted indoors, outdoor particles that enter indoors through natural and mechanical air exchange and infiltration, and secondary particles formed indoors through reactions of gas-phase precursors emitted both indoors and outdoors (Chen and Zhao,

2011; Meng et al., 2005; Morawska and Salthammer, 2003; Uhde and Salthammer, 2007; Wallace, 2006). Therefore, the composition and toxicity of indoor particles is very complex, with similarities but also differences to outdoor aerosols. A summary of the most significant outdoor and indoor particle sources is displayed in Table 1.1. The infiltration rate (fraction of outdoor particles that penetrate in a given indoor environment) can be assessed by the indoor to outdoor ratios for particle concentration (I/O) in the absence of indoor sources. Morawska and Salthammer (2003) concluded that, for naturally ventilated buildings in the absence of indoor sources, I/O ratios for PM_{10} and $PM_{2.5}$ ranged from 0.5 to 0.98 (with a median value of 0.7) and 0.54 to 1.08 (median, 0.91), respectively. This highlights the importance of the contribution of outdoor air as a source of particles encountered in indoor environments. However, when indoor sources are present, Morawska and Salthammer (2003) registered I/O ratios from 1.14 to 3.91 for PM_{10} and from 1 to 2.4 for $PM_{2.5}$, demonstrating the significance of indoor source contributions. Nevertheless, these I/O ratios can be even higher depending on the environment.

Health, environmental, and other effects caused by particles are the reasons for controlling their presence in the indoor environment. Particles generated either by indoor sources or infiltrated from outside will eventually be removed from the indoor environment through various mechanisms, including ventilation and deposition (Lai, 2004).

1.3. Particulate Air Pollution in Subway Systems

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

Studies have indicated, with few exceptions, that PM concentrations are usually higher in these underground environments than those in outdoor ambient air, as they are a confined space poorly ventilated that promotes the concentration of PM entering from the outside atmosphere in addition to that generated internally in the system (Nieuwenhuijsen et al., 2007 and references therein). Furthermore, there are some evidences that the PM characteristics in subway air are substantially different from the outdoor air, in terms of number, mass, size, concentration and chemical composition (Adams et al., 2001; Furuya et al., 2001; Querol et al., 2012; Salma et al., 2007). Concentration and chemical composition of subway particles depend on various factors, such as: outdoor air quality; differences in the depth and design of the stations and tunnels; system age; composition of wheels, rail tracks, brake pads, and power supply materials; braking mechanisms; power system; train speed and frequency; passenger densities; ventilation and air conditioning systems; cleaning frequency; and other operational conditions (Johansson and Johansson, 2003; Kwon et al., 2015; Moreno et al., 2014; Park and Ha, 2008; Ripanucci et al., 2006; Salma et al., 2007). Furthermore, results are not always directly comparable because of differences in sampling and measurement methods, data and sample analyses and the type of environment studied (Kim et al., 2008; Nieuwenhuijsen et al., 2007).

1.3.1. Particle sources

Particles in the subway system are mainly generated by the motion of trains, movement and activities of commuters and subway staff, air ventilation, and various stationary processes (Table 1.2). Most particles in this environment are produced by mechanical wear and friction processes at the rail-wheel-brake interfaces, and at the interface between power conductive materials providing electricity and the current collectors attached to trains, as well as by the erosion of construction material and resuspension (Jung et al., 2010; Loxham et al., 2013; Sundh et al., 2009). A railway is generally powered either by an overhead catenary with the current drawn through the contact material of the pantograph or by a third rail with the current drawn through the current-collecting component (contact shoe) on the train. Although abrasive forces between wheels, rails, and brakes can generate coarse and fine particles due to

shearing, there is evidence to suggest that ultrafine particles can be generated via the high temperatures of friction at interfaces between these components, with subsequent vaporisation of the substrate (Sundh et al., 2009; Zimmer and Maynard, 2002).

Table 1.2 Summary of subway PM sources.

Sources	Sub-category	Examples
Trains	Non-exhaust emissions	Wheel-rail contact Braking process Interaction between pantographs and catenary (overhead wire) or between third rail and contact shoe Erosion by air turbulence caused by the subway motion (piston effect)
	Indirect	Volatilization of oil and other lubricants
Stationary processes (maintenance and construction)	Direct	Cleaning (e.g. sweeping) Rail cutting Rail welding Ballast changing
	Indirect	Volatilization of cleaning material
	Exhaust emissions	Diesel exhaust (maintenance machinery engines)
Air ventilation	Natural and/or forced	Moving and transferring particle emissions from outdoor Natural erosion of masonry structure
Commuters and subway staff	Human activities	Smoking on platforms Resuspension of deposited particles
	Other	Particles shed by commuters' clothes Degraded perishable materials and garbage

1.3.2. Particle chemical composition

More interesting than the bulk mass concentration of PM is the fact that these particles have peculiar physicochemical characteristics specific to the subway environment, being loaded with ferruginous particles (FePM) commonly accompanied by other elements such as Mn, Si, Cr, Cu, Ba, Ca, Zn, Ni and K (e.g. Aarnio et al., 2005; Chillrud et al., 2004; Jung et al., 2010; Loxham et al., 2013; Mugica-Álvarez et al., 2012; Murruni et al., 2009; Nieuwenhuijsen et al., 2007; Querol et al., 2012; Salma et al., 2007). The considerable amount of Fe in the subway stations is mainly generated from mechanical friction and wear processes between rails, wheels and brakes (Johansson and Johansson, 2003; Jung et al., 2010; Kam et al., 2013; Querol et al., 2012). Kim B.-W. et al. (2010) and Şahin et al. (2012) reported that the PM concentration and the relative abundance of Fe particles increased with the decrease of the distance between the sampling sites and the tunnel, suggesting that most Fe particles are generated in the tunnel. Wear and friction processes initially produce iron-metal particles that react

with oxygen in the air resulting in the formation of iron oxides (Guo et al., 2014; Jung et al., 2010; Querol et al., 2012). To know the chemical composition of PM in a subway platform is an essential prerequisite for understanding the indoor air quality of the subway system and subsequently to assess remediation measures.

Moreover, the chemical composition of PM derived by sample analysis can be further utilized for risk assessment studies and although components such as the trace metals represent typically only about 1% of the total PM, they can play a critical role in the source identification (Lim et al., 2010; Park D. et al., 2014).

1.3.3. Health implications

PM in the underground subway microenvironments is of great concern since many people spend considerable time commuting on a daily basis, and the exposure to this pollutant in the subway systems has been linked to adverse health effects (e.g. Bachoual et al., 2007; Bigert et al., 2008; Salma et al., 2009). Some studies have reported that subway particles have a higher oxidative potential than outdoor particles. For example, Steenhof et al. (2011) investigated the in-vitro toxicity of PM collected at different sites in the Netherlands and concluded that the underground samples, characterized by a high content of transition metals, showed the largest decrease of metabolic activity in macrophages compared to traffic and urban background sites. In the Paris subway system, Bachoual et al. (2007) reported that PM has transient biological effects and that inflammatory and oxidative effects could be targets of subway PM exposure. These effects are similar to those described with PM from the London and Stockholm subway systems (Karlsson et al., 2005; Seaton et al., 2005). In addition, Karlsson et al. (2008) also investigated the bioreactivity of subway particles, revealing an apparently higher genotoxicity than several other particles (i.e. particles from a street, pure tire-road wear particles, and particles from wood and diesel combustion), and concluded that genotoxicity of subway particles was due to redox-active iron on the particles surface. Salma et al. (2009) also suggested that the enhanced genotoxicity of subway particles with respect to ambient outdoor particles is also linked to the differences in the oxidation states, surface properties or morphologies. In addition, potentially higher mobile part of toxic elements was found in the subway

tunnel compared to the road tunnel sample (Sysalova and Szakova, 2006). Of key interest here is FePM morphology and speciation of the inhalable ferruginous material, as some iron species are reported to be more toxic than others (Park E.-J. et al., 2014). Jung et al. (2012) reported levels of PAHs in a subway tunnel and they suggested that additive or synergistic effects by unidentified chemicals as well as PAHs contained in organic extracts of subway PM_{10} may induce genotoxic effects. It has also been argued that the metalliferous character of the particles produced by subway system has a considerable potential capacity to stimulate reactive oxygen species (ROS) generation and cause DNA damage (Jung et al., 2012). Klepczyńska-Nyström et al. (2012) reported that airway inflammatory responses after exposure in the subway environment of Stockholm differ between asthmatic and healthy human.

1.3.4. Subway studies literature

The first comprehensive subway commuters' exposure study was conducted in Boston at the end of the 1980s (Chan et al., 1991), focused on exposure to gasoline-related VOCs, and was followed by further studies assessing levels of air pollution in subway systems. After more than a decade of research, different air pollutants such as PM (e.g. Aarnio et al., 2005; Kam et al., 2011a; Mugica-Álvarez et al., 2012; Querol et al., 2012; Salma et al., 2007), PAHs (Fromme et al., 1998; Furuya et al., 2001), CO (Cheng and Yan, 2011; Gómez-Perales et al., 2004), O_3 (Awad, 2002), metals (Jung et al., 2010; Loxham et al., 2013; Mugica-Álvarez et al., 2012; Querol et al., 2012; Salma et al., 2007), and different biological pollutants (Awad, 2002; Hwang et al., 2010) have by now been measured in subway systems.

A number of studies have been conducted to assess the levels of PM and its chemical composition in subway systems. A summarised literature review of the previous recent studies conducted in subway systems worldwide is shown in Appendix, and summarised as a database in Table 1.3, which includes information on the subway city, time duration of the study, microenvironment measured (on platforms or/and inside train), identification of the measurement type (real-time or off-line), the characteristics of the measurements (e.g. time resolution, size fraction, number of samples), as well as the species analysed when as performed the chemical composition, with focus on

particulate matter. A total of 64 studies (articles in scientific journals), carried out in 26 different cities, have been compiled and considered in this literature review.

The levels of PM are not always directly comparable between the different studies because some studies used off-line monitors to measure the PM concentrations, whereas others used personal exposure equipment. Furthermore, different particle size fractions were measured and even where the same size fractions were measured they may not be directly comparable. One of the difficulties in these types of studies is the necessity of high sampling time or volume to collect sufficient PM for analyses. Furthermore, when conducting personal exposure monitoring during actual journeys the sampling duration could be relatively short. That is one of the reasons why some studies have opted for off-line sampling, even though this does not provide samples directly equivalent to personal exposure, but further interpretation of the data is required. Moreover, the data given by real-time monitors should be corrected against reference methods to provide reliable short term monitoring, however this is not always performed.

Table 1.3 Summarised literature review of subway studies.

City	Time duration	Measurements on platfom							Measurements inside train				Study reference
		Real–time			Off–line				Real–time			Off–line	
		Stations number	Time resolution	Size fraction	Stations number	Size fraction	Samples number	Species analysed	Lines number	Time resolution	Size fraction	Samples number	
Amsterdam (Netherlands)	3 days	–	–	–	1	<0.18, <2.5, 2.5–10 μm	3	NO_3^-, SO_4^{2-}, Cl^-, Fe, Cu, As, Mn, Zr, Mo, Sn, V, Cr, Ni, Nb, Hf, Ca, Mg, Zn, Ba, Sb, Rb, Cd, Pb, Al, Ti, Sr, Sc, La, Hg, Li, B, Na	–	–	–	–	Loxham et al. (2013)
Barcelona (Spain)	21 days	2	5 min	<1, <2.5, <10 μm	2	<2.5 (11 days); <10 μm (10 days)	20 (PM_{10}) + 19 ($PM_{2.5}$)	Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, OC, EC, Fe, Ca, Al, Ba, Mg, Cu, Mn, Zn, Na, K, Ti, Cr, Sr, Zr, Mo, Sb, Sn, Ni, As, Pb, V, Co, P, W, Li, Hf, Rb, Nb, Ge, Ga, U, Y, Th, Ta, Cd, Bi	3	30 s	<1, <2.5, <10 μm	–	Querol et al. (2012)
Barcelona (Spain)	13 days	10	15 min	<1, <3, <10 μm	–	–	–	–	–	–	–	–	Moreno et al. (2014)
Barcelona (Spain)	32 days	–	–	–	4	<10 μm	4 (1/station)	C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Zn, As, Sn, Sb, Ba	–	–	–	–	Moreno et al. (2015)
Boston (USA)	–	–	–	0.02–1, <2.5 μm	–	1 μm	–	PAHs	–	–	–	–	Levy et al. (2002)
Budapest (Hungary)	1 day	1	30 s	<10 μm	1	<2, 2–10 μm	4	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Pb	–	–	–	–	Salma et al. (2007, 2009)
Buenos Aires (Argentina)	30 days (5 days/station)	–	–	–	6	TSP	30 (5/station)	Fe, Zn, Cu	–	–	–	–	Murruni et al. (2009)
Cairo (Egypt)	7 days	–	–	–	–	TSP	–	–	–	–	–	–	Awad (2002)
Helsinki (Finland)	16 days	1	1 min	<2.5 μm	2	<2.5 μm	12 (6/station)	Al, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, P, Pb, S, Si, Ti, V, Zn, OC, EC	–	–		5 $PM_{2.5}$ samples	Aarnio et al. (2005)
Hong Kong (China)	–	–	–	–	–	–	–	–	–	–	<2.5, <10 μm	–	Chan et al. (2002)
Istanbul (Turkey)	35 days	6	15 min	<10 μm	6	<0.4, 0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9, >9 μm	–	Cu, Fe	–	–	–	–	Şahin et al. (2012)
Istanbul (Turkey)	–	–	–	–	–	–	–	–	–	30 s	<2.5 μm	–	Onat and Stakeeva, (2013)
London (UK)	15 days	–	–	–	–	–	–	–	–	–	–	56 $PM_{2.5}$ (personal samples)	Adams et al. (2001)
London (UK)	3 days	3	–	<2.5 μm	3	<2.5, <3.5, <10 μm	–	Fe, Cr, Cu, Zn, Mn	3	–	<2.5 μm	–	Seaton et al. (2005)

Table 1.3 Continued.

City	Time duration	Measurements on platfom							Measurements inside train				Study reference
		Real–time			Off–line				Real–time			Off–line	
		Stations number	Time resolution	Size fraction	Stations number	Size fraction	Samples number	Species analysed	Lines number	Time resolution	Size fraction	Samples number	
Los Angeles (USA)	75 days	27	30 s	<2.5, <10 μm	–	<2.5, 2.5–10 μm	–	Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, NH_4^+, K, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba, Eu, OC, EC, PAHs, hopanes, steranes	2 (1 UG; 1 AG)	30 s	<2.5, <10 μm	–	Kam et al. (2011a, 2011b, 2013)
Mexico city (Mexico)	4 weeks	–	–	–	–	<2.5 μm	18 (personal samples)	Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Pb, TC, OC, EC	–	–	–	–	Gómez–Perales et al. (2004)
Mexico city (Mexico)	21 days	–	–	–	1	<2.5, <10 μm	42 (1/day – each size)	Al_2O_3, SiO_2, Ca, Fe, Ba, Mg, Cu, Co, Cr, Mn, Ni, Pb V, Zn, Na, K, S	–	–	–	–	Mugica–Álvarez et al. (2012)
Milan (Italy)	54 days (9/station)	–	–	–	6	<10 μm	162 (3/day)	Al, Si, S, Cl, K, Ca, Ti, Mn, Ni, Cu, Zn, Br, Rb, Pb, Fe, Ba, Sb , Sr, Sn	–	–	–	–	Colombi et al. (2013)
Naples (Italy)	5 days	7 (1 AG; 6 UG)	120 s	<2.5, <10 μm	–	–	–	–	1	120 s	<2.5, <10 μm	–	Carteni et al. (2015)
New York (USA)	8 hours	–	–	–	–	<2.5 μm	2 personal samples (5h each)	Fe, Mn, Cr	–	–	–	2 $PM_{2.5}$ personal samples (3h each)	Chillrud et al. (2004)
New York (USA)	–	–	1 min	<2.5 μm	–	–	–	–	–	–	–	–	Morabia et al. (2009)
New York (USA)	4 months	–	–	–	–	<2.5 μm	39 personal samples	Fe, Cr, Mn	–	–	–	–	Grass et al. (2010)
Paris (France)	15 days	–	–	–	2	<10 μm	–	Fe, Mn, Ca, Cu, S, Si	–	–	–	–	Bachoual et al. (2007)
Paris (France)	11 days	1	1 min	<2.5, <10 μm	1	<2.5, 2.5–10 μm	18	Na^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, BC, OC	–	–	–	–	Raut et al. (2009)
Prague (Czech Republic)	1 year	–	1 min	<10 μm	–	–	–	–	–	–	–	–	Braniš et al. (2006)
Prague (Czech Republic)	24 h	1	3 min	14–637 nm 0.5–20 μm	1	<1, <2.5, <10 μm	–	TC, SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Fe, Ca, Al, Ba, Mg, Cu, Mn, Zn, Na, K, Ti, Cr, Sr, Mo, Sb, Sn, Ni, As, Pb, V, Co, W, Li, Rb, Cd, Bi	–	–	–	–	Cusack et al. (2015)
Rome (Italy)	–	–	–	–	–	<10 μm	–	Fe, Cu, Zn, Mn, Pb, Sb, Ni, Cr, rare earth, Sn, Th, Zr, Co, As, Y, Bi, Cd	–	–	–	–	Ripanucci et al. (2006)
Rome (Italy)	25 days	1	–	0.3–0.5, 0.5–0.7, 0.7–1.0, 1–2, 2–3, 3–5, 5–10, >10 μm	1	<10 μm	5	Al, Ca, Fe, K, Mg, Na, Si, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, As, Ba, Be, Cd, Ce, Co, Cu, Fe, La, Mn, Ni, Pb, Sb, Sn, Sr, Ti, V, Zn, OC, EC (*)	–	–	–	10 PM_{10} samples (5 with AC; 5 without AC)	Perrino et al. (2015)

Table 1.3 Continued.

City	Time duration	Measurements on platfom							Measurements inside train				Study reference
		Real–time			Off–line				Real–time			Off–line	
		Stations number	Time resolution	Size fraction	Stations number	Size fraction	Samples number	Species analysed	Lines number	Time resolution	Size fraction	Samples number	
Rotterdam (Netherlands)	1 day	–	–	–	1	<0.18, 0.18–2.5, 2.5–10 μm	1	Al, Cu, Fe, Ni, V, Zn, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, EC, OC, PAHs	–	–	–	–	Steenhof et al. (2011)
Seoul (Korea)	–	–	–	–	5	–	90	–	–	–	–	–	Cho et al. (2006)
Seoul (Korea)	–	22 (8 AG; 14 UG)	–	<2.5, <10 μm	–	–	–	–	4	–	<2.5, <10 μm	–	Kim et al. (2008)
Seoul (Korea)	8 days	–	–	–	1	2–1, 2–4, 4–8, 8–16, >16 μm	8	Fe, C, N, Mg, Al, Si, S, Ca, Ti, Cr, Mn, Ni, Cu, Zn, Ba	–	–	–	–	Kang et al. (2008)
Seoul (Korea)	3 days	–	–	–	2	1–2.5, 2.5–10 μm	6 (3/station)	Fe, C, Ca, Mg, Si, Ba, Al, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Cu	–	–	–	–	Kim B.-W. et al. (2010)
Seoul (Korea)	6 days	–	–	–	6	TSP	3–5/station	Fe, Cu, K, Ca, Zn, Ni, Na, Mn, Mg, Cr, Cd, Ba, Pb	–	–	–	–	Kim C.-H. et al. (2010)
Seoul (Korea)	–	–	–	–	–	TAB	67	–	–	–	–	–	Hwang et al. (2010)
Seoul (Korea)	–	–	–	–	–	<10 μm	–	PAHs	–	–	–	–	Jung et al. (2012)
Seoul (Korea)	–	–	–	–	1	<2.5, <10 μm	–	–	–	–	–	–	Kim et al. (2012)
Seoul (Korea)	80 h (40h/tunnel)	–	–	–	2 (tunnel samples)	<10 μm	23	–	–	–	–	–	Eom et al. (2013)
Seoul (Korea)	4 days	–	–	–	–	–	–	–	2	30 s	<2.5, <10 μm	–	Kim et al. (2014)
Seoul (Korea)	32 hours	1 (tunnel)	–	<1, <2.5, <10 μm	–	–	–	–	–	–	–	–	Son et al. (2014)
Seoul (Korea)	3 weeks (3 seasons)	6	1 min	<1, <2.5, <10 μm	–	–	–	–	–	–	–	–	Kwon et al. (2015)
Seoul (Korea)	–	–	–	–	16	platform floor samples	66	–	–	–	–	–	Hwang and Park (2014)
Seoul (Korea)	12 days	–	–	–	4	1–2.5, 2.5–10, <10 μm	12 (3/station)	Fe, C, N, Mg, Al, Si, S, Ca, Ti, Cr, Mn, Ni, Cu, Zn, Ba	–	–	–	–	Jung et al. (2010)
Seoul (Korea)	30 days	–	–	–	–	–	–	Mg, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb, NO_3^-, SO_4^{2-}, Cl^- (*)	1	6 s	<10 μm	30 PM_{10} samples	Park et al. (2012)
Seoul (Korea)	12 days	–	–	–	4 points in a tunnel	<10 μm	44	Mg^{2+}, Al, Si, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}	–	–	–	–	Park D. et al. (2014)
Shanghai (China)	–	16	5 s	<1, <2.5, <10 μm	–	–	–	–	–	–	–	–	Ye et al. (2010)

Table 1.3 Continued.

City	Time duration	Measurements on platfom							Measurements inside train				Study reference
		Real–time			Off–line				Real–time			Off–line	
		Stations number	Time resolution	Size fraction	Stations number	Size fraction	Samples number	Species analysed	Lines number	Time resolution	Size fraction	Samples number	
Shanghai (China)	–	–	–	–	56 (29 UG; 27 AG)	Total dust samples	56 (1/station)	Al, Fe, Ca, Na, Ti, Mn, Cr, Cu, Ni	–	–	–	–	Zhang et al. (2011)
Shanghai (China)	–	–	–	–	5	–	45	VOCs (monocyclic aromatic hydrocarbons, PAHs)	–	–	–	–	Zhang et al. (2012)
Shanghai (China)	–	–	–	–	–	<1, <2.5 μm	4	Mg, Al, Na, K, Ca, Ti, V, Cu, Cr, Mn, Fe, Ni, Zn, Sr, Mo, Ba, Pb	–	–	–	–	Guo et al. (2014)
Shanghai (China)	46 days	–	–	–	3	<2.5 μm	15 (5/station)	Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sc, Rb, Sr, Ag, Cd, Cs, Ba, Tl, Pb, Bi, Th, U	–	–	–	–	Lu et al. (2015)
St. Petersburg (Russia)	4 months	–	–	–	–	–	200	–	–	–	–	–	Bogomolova et al. (2009)
Stockholm (Sweden)	2 weeks	1	–	<2.5, <10 μm	–	–	–	–	–	–	–	–	Johansson and Johansson (2003)
Stockholm (Sweden)	–	–	5 min	14–330 nm	–	<2.5, <10 μm	–	EC, OC, Fe, C, Ca, Al, Mg, Cl, Tl, Cu, Ag, Cr, Ni, Zr, Ce, Si, K, S, Na, P, VOCs	–	–	–	–	Midander et al. (2012)
Stockholm (Sweden)	–	–	–	–	–	<10 μm	–	–	–	–	–	–	Karlsson et al. (2008)
Stockholm (Sweden)	–	–	–	–	–	<2.5, <10 μm	personal samples	Fe, Ba, Mn, Cu	–	–	–	–	Klepczyńska–Nyström et al. (2012)
Taipei (Taiwan)	–	5	1 min	<2.5, <10 μm	–	–	–	–	4 routes	1 min	<2.5, <10 μm	–	Cheng et al. (2008)
Taipei (Taiwan)	84 days	3 (1 UG, 2 AG)	1 min	<2.5, <10 μm	–	–	–	–	–	–	–	–	Cheng and Yan (2011)
Taipei (Taiwan)	–	1	–	0.23–20 μm	–	–	–	–	–	–	–	–	Cheng and Lin (2010)
Taipei (Taiwan)	–	–	–	–	–	–	–	–	2 routes (1 AG and 1 UG)	1 min	<2.5, <10μm	–	Cheng et al. (2012)
Tokyo (Japan)	4 days	–	–	–	3	TSP	–	Fe, Si, Ba, Cl, Ca, S, K, Cu, Zn, Cr, Ni, Mg, P, PAHs	–	–	–	–	Furuya et al. (2001)
Washington D.C. (USA)	6 days	–	–	–	–	<1 μm	–	–	–	–	–	–	Birenzvige et al. (2003)

Notes: TSP – total suspended particles; UG – underground; AG – aboveground; AC – air-conditioning system; TAB – total airborne bacteria; (*) species analysed in the PM_{10} samples collected on the platform and inside the trains; (**) species analysed in the PM_{10} samples collected inside the trains.

The key parameters examined by the considered research studies in terms of PM have been as follows: mass and number concentration, chemical composition (inorganic and organic components), number size distribution, absorption, identification of contaminant source, morphology, mineralogy, bioreactivity/toxicity, microorganisms and biomarkers. The number of studies on different parameters characterised in each subway system have been grouped by city in Table 1.4, considering data from platform, inside trains and tunnel measurements, chemical composition obtained both by chemical analyses (concentration) and microscopy methods (elemental weight %), number size distribution and quantitative identification of contaminant source (source apportionment). Most of the considered studies have focused on particle mass concentration (in 88% of the studies) although in a reduced number of stations and during a short period of time (Table 1.3). Only 15 of them have measured air quality inside trains. In the more frequent measurements on subway platforms half of studies have chemically characterised PM samples, although only 7 have analysed organic components. PM chemical composition is obtained by chemical analyses or microscopy methods. The number of samples collected is very variable, most commonly in the 2–50 range, with only 6 studies having a number of samples above 50 (Table 1.3). The characterisation of the particle number concentration is less frequent (22% of the studies). Particle morphology and mineralogy are also important issues, as they not only influence the severity of adverse health effects, but also convey information on factors contributing to particle formation (Abbasi et al., 2013). A research article on morphology and mineralogy of aerosol collected in the Barcelona subway system has been published with data derived from the work of this thesis (Moreno et al., 2015).

Although all scientific publications discuss the possible sources emitting airborne particles within the subway environment, only 2 subway studies show quantitative data on the contribution of each source to the total PM mass, using Positive Matrix Factorization analyses. The sources identified in these studies were: mineral dust; rail, wheel, and brake wear; electric cable wear; secondary aerosols and oil combustion.

Mean $PM_{2.5}$ mass concentrations and elemental composition for various underground subway systems are summarised in Table 1.5 (mean ranges are presented when available). There are substantial differences in the concentrations among the studies

and within a given subway system. This could be partly explained by the differences in the methodological approaches and experimental circumstances, such as, in the measuring locations selected, stationary or mobile types of the measurements, season, duration and timing of the measurements, or in the boundary conditions for averaging (Table 1.3). The monitoring equipment used varied and may have led to different reporting and makes it more difficult to compare results between subway systems. In general, the studies have highlighted that PM concentrations vary widely due to differences in the age of the rail system, tunnel ventilation, wheel type, braking system, and operating mode, measurement instruments and methods, chemical and size characteristics of PM and type of environment investigated. The studies available in the literature conclude that the PM mass concentrations at underground station platforms are consistently higher, usually several-fold, than at the outdoor ambient air, with $PM_{2.5}$ levels on platforms ranging approximately between 16 and 480 $\mu g\ m^{-3}$. Although in some cities, such as Hong Kong or Mexico city, the ordinary outdoor ambient mass concentrations can be higher than in their subway systems (Chan et al., 2002; Gómez-Perales et al., 2007). $PM_{2.5}$ concentrations inside the trains ranged from 15 to 250 $\mu g\ m^{-3}$ approximately. Comparing the results shown in Table 1.5 it is evident that particle concentrations are generally higher on platforms than inside the trains. In air-conditioned trains, PM mean concentrations are generally 15–20% lower than the levels for platforms, suggesting that filtration provided by air-conditioners is an effective way in reducing (coarse) PM concentrations (Salma, 2009).

Of the various elements measured in subway $PM_{2.5}$, Fe is present with the highest concentrations. Fe is a major component in all underground railways (except for Mexico City where the steel wheels are lined by rubber). The main explanation given by the authors was that Fe may have originated from wear of steel during friction between wheels and rail, wear of breaks, and metal emissions from sparking (e.g. Johansson and Johansson, 2003). For other elements present in the subway environment, such as Cu, Cr or Zn, the concentrations may vary up to one order of magnitude between different subway systems.

Table 1.4 Number of studies in each subway system, according to the PM parameters characterised.

City	Mass concentration	Chemical composition	Organic species	Absorption	Number concentration	Number size distribution	Source apportionment	Morphology	Mineralogy	Bioreactivity/Toxicity	Microorganisms	Biomarkers
Amsterdam (Netherlands)	1	1	–	–	–	–	–	1	–	1	–	–
Barcelona (Spain)	3	2	–	1	–	–	–	2	2	–	–	–
Boston (USA)	1	–	1	–	1	–	–	–	–	–	–	–
Budapest (Hungary)	1	1	–	–	–	–	–	1	1	–	–	–
Buenos Aires (Argentina)	1	1	–	–	–	–	–	1	–	–	–	–
Cairo (Egypt)	–	–	–	–	–	–	–	–	–	–	1	–
Helsinki (Finland)	2	1	–	1	1	1	–	–	–	–	–	–
Hong Kong (China)	2	–	–	–	–	–	–	–	–	–	–	–
Istanbul (Turkey)	3	1	–	–	1	1	–	–	–	–	–	–
London (UK)	3	1	–	–	1	1	–	–	–	1	–	–
Los Angeles (USA)	2	1	1	1	–	–	–	–	–	1	–	–
Mexico city (Mexico)	3	2	–	1	–	–	–	1	1	–	–	–
Milan (Italy)	1	1	–	–	1	1	–	–	–	–	–	–
Naples (Italy)	1	–	–	–	–	–	–	–	–	–	–	–
New York (USA)	4	2	–	–	–	1	–	–	–	–	–	1
Paris (France)	2	2	–	1	1	–	–	–	–	1	–	–
Prague (Czech Republic)	2	1	–	1	1	1	–	–	–	–	–	–
Rome (Italy)	2	2	–	1	–	–	–	2	1	–	–	–
Rotterdam (Netherlands)	1	1	1	1	1	–	–	–	–	1	–	–
Seoul (Korea)	10	6	1	–	1	1	2	4	2	2	3	–
Shanghai (China)	3	3	1	–	–	1	–	3	3	–	–	–
St. Petersburg (Russia)	–	–	–	–	–	–	–	–	–	–	1	–
Stockholm (Sweden)	3	2	1	1	1	1	–	1	–	2	–	–
Taipei (Taiwan)	4	–	–	–	2	1	–	–	–	–	–	–
Tokyo (Japan)	1	1	1	–	1	1	–	–	–	–	–	–
Washington D.C. (USA)	–	–	–	–	1	–	–	–	–	–	1	–
Total	**56**	**32**	**7**	**9**	**14**	**11**	**2**	**16**	**10**	**9**	**6**	**1**
% studies	**88**	**50**	**11**	**14**	**22**	**17**	**3**	**25**	**16**	**14**	**9**	**2**

Table 1.5 Mean $PM_{2.5}$ and elemental mass concentrations on platforms and $PM_{2.5}$ mass concentrations inside trains in various underground subway systems.

City (Country)	On platforms																							Inside trains	Study reference
	$PM_{2.5}$	Fe	Al	Ca	Mg	Ti	P	K	Cl	Ba	Cu	Mn	Zn	Cr	Sb	Sr	Zr	Ni	Pb	Sn	V	As	Co	$PM_{2.5}$	
	$\mu g\ m^{-3}$									$ng\ m^{-3}$														$\mu g\ m^{-3}$	
Amsterdam (Netherlands)	75																								Loxham et al. (2013)
Barcelona (Spain)	46[1]–125	32–56	0.4–0.7	1.2–1.8	0.1–0.9	0.02–0.05		0.08–0.10	0.4–0.7	20–2200	100–600	300–500	100–500	40–60	27–30	3–44	8–42	6–16	3–11	5–18	4–7	1.4–13	1.3–3.2	15–25	Querol et al. (2012)
Boston (USA)	67																								Levy et al. (2002)
Budapest (Hungary) [2]	33	15.5	0.09	0.41	0.13	0.025		0.13	0.104		190	148	50	15				8	21						Salma et al. (2007, 2009)
Helsinki (Finland)	47–60	21–29	0.27–0.28	0.14–0.33		0.02–0.04	0.04	0.15–0.23	0.09–0.105		117–173	234–311	34–124	42–59				23–34	10–13		5–8			21	Aarnio et al. (2005)
Hong Kong (China)																								21–48	Chan et al. (2002)
Istanbul (Turkey)																								40–45	Onat and Stakeeva. (2013)
London (UK)																								157–247	Adams et al. (2001)
London (UK)	270–480																							130–200	Seaton et al. (2005)
Los Angeles (USA)	57[3]	10.6	0.15	0.19	0.06	0.012		0.06		216	65	85	30	23				12					1.2	24[3]	Kam et al. (2011a, 2011b, 2013)
Mexico city (Mexico)	61[4]																								Gómez-Perales et al. (2004)
Mexico city (Mexico)	48	2.6	0.6	0.9	0.13					30	220	26	131.2	17				6	60		17		1.6		Mugica-Álvarez et al. (2012)
Naples (Italy)	45–60																							18-36	Cartenì et al. (2015)
New York (USA)	62	26										240		84											Chillrud et al. (2004)
New York (USA)	31[4]																								Morabia et al. (2009)
Paris (France)	35–93																								Raut et al. (2009)
Prague (Czech Republic)	94	26	0.2	0.3	0.1	0.01		0.4		70	70	270	110	30	3.4	2		5	23	4	1	9	1.8		Cusack et al (2015)
Seoul (Korea)	129																							126	Kim et al. (2008)
Seoul (Korea)	58[5]–66[6]																								Kim et al. (2012)
Seoul (Korea)																								58[7]–81[8]	Kim et al. (2014)
Seoul (Korea)	129[9]–219[10]																								Son et al. (2014)
Seoul (Korea)	52–83																								Kwon et al. (2015)
Shanghai (China)	287																								Ye et al. (2010)
Shanghai (China)	82–178	1.1–48	0.7–1.3	1.2–3.8	0.1–0.3	0.02–0.05		0.3–1.4		50–1947	38–240	36–420	20–400	24–570		0.9–69		6–30	1.1–37		4–10				Guo et al. (2014)
Shanghai (China)	49–66	6.6	1.6	0.24	0.25			0.45		119	48	84	127	26		10		34	21		5	2.0	1.3		Lu et al. (2015)
Stockholm (Sweden)	258																								Johansson and Johansson (2003)
Stockholm (Sweden)	60																								Midander et al. (2012)
Taipei (Taiwan)	35																							32	Cheng et al. (2008)
Taipei (Taiwan)	25–40[11]																								Cheng and Yan (2011)
Taipei (Taiwan)	16																								Cheng and Lin (2010)
Taipei (Taiwan)																								28[12]	Cheng et al. (2012)

Notes: [1] PSDs station; [2] PM_1; [3] only underground subway line data; [4] Commuting; [5] after PSDs; [6] before PSDs; [7] after subway cabin air purifier; [8] before subway cabin air purifier; [9] after using magnetic filters (tunnel samples); [10] before using magnetic filters (tunnel samples); [11] underground ticket hall and platform; [12] underground route.

1.3.5. Gaps in current knowledge

The studies described in section 1.3.4 have contributed to characterise the airborne PM in underground subway systems. The key parameters covered were: mass and number concentration, chemical composition (inorganic and organic components), size distribution, absorption, identification of contaminant source, morphology, mineralogy, bioreactivity/toxicity, microorganisms and biomarkers. Notwithstanding, certain gaps in the current knowledge have been identified:

- Despite the number of studies, most of them focused on the variations in PM mass concentration on platforms for a short period of time and in a reduced number of stations. Therefore, there is a need for extensive studies of entire subway systems, covering the vast diversity of lines, trains and stations and different seasonal periods to provide an overview of the overall exposure to PM in this environment. Moreover, the studies characterising the airborne PM in stations with different characteristics (design, depth, ventilation, number and location of connections with outdoor level and transfer stations, and train frequency) are rare and the existing studies are incomplete, being often based exclusively on stations design and depth.

- The number of studies including air quality inside trains (where the passengers spend most of the time) is relatively scarce, and the investigation of factors affecting PM, such as the use of air-conditioning or train windows open, is lacking in the literature.

- Most of the studies have investigated the PM chemical composition in a limited number of samples and focusing only in a few elements, while the study of the organic compounds in the subway PM is very limited.

- Very little is known about PM source contribution in subway environments in quantitative terms.

- Concentration and chemical composition of subway particles among different studies are not always directly comparable because of methodological issues. Studies following the same methodology applied to different subway systems are required.

- The exposure to PM in the subway environment has been associated with adverse health effects. Nevertheless, although these epidemiological and toxicological studies relate health effects to PM exposure (the inhaled concentration), the negative outcomes are mainly caused by the subsequent deposition of PM in the human respiratory tract during breathing. Hence, it is crucial to determine the amount of inhaled particles deposited in the HRT through their deposition fraction. To date, there are no studies on the deposition of subway PM in the human respiratory tract.

1.4. Objectives

The identification of the previous knowledge gaps led to define the main objective of this thesis, to extend and improve knowledge on air quality in underground subway systems. Thus, the specific objectives are:

- To determine the relationship between pollutant levels and the characteristics of the subway stations.
- To identify the factors affecting the concentrations of PM inside trains.
- To better understand the chemical composition and contribution of each source of airborne particles in the subway environment.
- To compare different subway systems understanding the main factors controlling air quality in this environment.
- To calculate the total and regional doses in the respiratory tract based on the $PM_{2.5}$ exposure during subway commutes.

1.5. Thesis Outline

This thesis has been organised in different sections. The introductory section consists of a review on general properties of aerosols with particular focus on particulate air pollution in subway systems, as well as the description of the aims of this thesis. A methodology section describes the monitoring sites, and outlines the measurement and

analysis methods as well as the description of the instruments used and data treatment applied. Results are presented in four scientific research articles published in peer-reviewed journals on atmospheric sciences. A discussion section includes the main findings explained in the different articles, and how the findings relate to each other, complemented by additional findings not included in the aforementioned research articles. The conclusion section highlights the main conclusions extracted from the study and is followed by a brief section identifying future research directions. Finally, the bibliographic references, and the abbreviations and symbols are listed. An appendix is presented with a subway literature review.

This thesis is based on the following scientific research articles:

Article 1: **Martins V.**, Moreno T., Minguillón M.C., Amato F., de Miguel E., Capdevila M. and Querol X. (2015). Exposure to airborne particulate matter in the subway system. *Science of the Total Environment* 511, 711–722. doi:10.1016/j.scitotenv.2014.12.013.

Article 2: **Martins V.**, Moreno T., Minguillón M.C., van Drooge B.L., Reche, C., Amato F., de Miguel E., Capdevila M., Centelles S. and Querol X. (2016). Origin of inorganic and organic components of $PM_{2.5}$ in subway stations of Barcelona, Spain. *Environmental Pollution* 208, 125–136. doi:10.1016/j.envpol.2015.07.004.

Article 3: **Martins V.**, Moreno T., Mendes L., Eleftheriadis K., Diapouli E., Alves C.A., Duarte M., de Miguel E., Capdevila M., Querol X. and Minguillón M.C. (2016). Factors controlling air quality in different European subway systems. *Environmental Research* 146, 35–46. doi:10.1016/j.envres.2015.12.007.

Article 4: **Martins V.**, Minguillón M.C., Moreno T., Querol X., de Miguel E., Capdevila M., Centelles S. and Lazaridis M. (2015). Deposition of aerosol particles from a subway microenvironment in the human respiratory tract. *Journal of Aerosol Science* 90, 103–113. doi:10.1016/j.jaerosci.2015.08.008.

Chapter 2

Methodology

2. METHODOLOGY

The methodology is divided into five subsections. Firstly, there is a description of the study areas and the sampling sites where air quality campaigns were carried out. Subsequently, detailed information about measurement techniques and instrumentation used is presented. Finally, a description of the chemical analyses and data treatment tools applied is provided.

2.1. Monitoring sites

The study was performed on three South European subway systems: Barcelona (Spain), Athens (Greece) and Oporto (Portugal), although with main focus on Barcelona. An urban station at each city was also used as a reference site for ambient air quality measurements.

2.1.1. Barcelona subway system

The Barcelona subway system is an extensive network of rapid transit electrified railway lines that run mostly underground in central Barcelona (Spain) and into the city's suburbs. The network is managed by Transports Metropolitans de Barcelona (TMB) and comprises 8 lines (numbered L1 to L5 and L9 to L11), covering 102.6 km of route and 139 stations (January 2016). The red line (L1) started operating in 1924, and the green (L3), blue (L5), yellow (L4), purple (L2), bright green (L11), orange (L9) and light blue (L10) lines have progressively been built since 1928 to 2010. The system carries around 376 million passengers a year and is chosen by about 50% of people as their mode of public transport in the city.

The following types of station designs are present in the network:

- Wide tunnel with two rail tracks in the centre running in parallel, one for each direction with lateral platforms. Some of these stations have the rail tracks separated by a middle wall.
- Wide tunnel with two rail tracks separated by a centre platform.
- Single narrow tunnel with one rail track and one platform.

- New lines L9 and L10 have single platforms separated from the tunnel by a glass wall with mechanical doors that are opened simultaneously with the train doors (known as platform screen door systems–PSDs).

The platforms have a specific ventilation system that introduces outdoor air to renew the air throughout lateral ventilation outlets across the platform and extracts the aged air through a vertical well. Furthermore, the ventilation system in the tunnels also consists of vertical wells that introduce outdoor air into the tunnel or remove indoor air towards the outdoor environment. The PSDs new system includes advanced ventilation system with more and stronger fans.

All trains are operated using a rigid overhead catenary electric power supply and run from 05:00 h until midnight every day, with additional services on Friday nights (finishing at 2:00 h of Saturday) and Saturday nights (running all night long), with a frequency between 2 and 15 min, depending on the day (weekend or weekday), subway line and time of day. Trains from all lines are equipped with an efficient air conditioning system that works continuously throughout the year to maintain a comfort temperature, but with higher intensity during the warmer period. 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 station design, using either frontal or lateral brake pads. Three new lines (L9, L10 and L11) on the network have driverless trains with computer-controlled driving system that optimises speed, braking and stopping processes. Night maintenance works involving diesel vehicles or yielding operations are occasional but can have impact on the platform air quality.

Urban background air quality monitoring station of Palau Reial

The station of Palau Reial is located in the garden of the IDAEA-CSIC at the North-West of the city (41°23′14″ N, 02°06′56″E, 78 m.a.s.l, Figure 2.1) and even though it represents urban background conditions, it is exposed to road traffic emissions from the Diagonal Avenue (approximately 200 m away), one of the largest thoroughfares in Barcelona that crosses the city from East to West and is primarily used by commuters. This station is co-operated jointly by CSIC and Generalitat de Catalunya (Spain).

2.1.2. Athens subway system

The Athens subway system is run by Urban Rail Transport S.A. and is used for the transportation of nearly 494 million passengers per year in the city of Athens (Greece). Line 1 was a conventional steam railway constructed in 1869, which was converted to electrical railway in 1904, and runs almost entirely aboveground. Lines 2 and 3 opened in 2000 and are mostly underground (a portion of the Line 3 is a suburban rail line that runs aboveground). The total length of the network is 82.7 km and includes 61 stations (January 2016). Most stations usually have two rail tracks in the centre of the station serving both directions with lateral platforms. Some stations have a tunnel with two rail tracks separated by a single island platform in the middle. Trains run from around 5:30 until 00:30 h, with a frequency of 4 – 5 min during the rush hours and 7 – 15 min in the off hours. The trains are provided with air-conditioning system and there is the ability to open the windows. The network uses standard gauge electric trains which in the underground places run on third rail, but the aboveground sections are provided with trains which use overhead catenaries.

Urban background air quality monitoring station of Demokritos

The Demokritos station is part of the Global Atmosphere Watch network (GAW-DEM) and is located in NCSR "Demokritos" campus (37°99′50″ N, 23°81′60″ E, Figure 2.2), at the North East corner of the Greater Athens Metropolitan Area and at an altitude of 270 m.a.s.l. This urban site is away from direct emission sources in a vegetated area (pine), being considered an urban background station.

2.1.3. Oporto subway system

The Oporto subway system, part of the public transport system of Oporto, Portugal, is a light rail network that runs underground in central Oporto and aboveground into the city's suburbs. The subway network currently serves 6 municipalities within the metropolitan area of Oporto: Oporto, Gondomar, Maia, Matosinhos, Póvoa de Varzim, Vila do Conde and Vila Nova de Gaia, covering a 586 km^2 territory.

Metro do Porto, S.A. is engaged in the operation and maintenance of light rail systems. The network has 6 lines (LA, LB, LC, LD, LE and LF) with the first line opened in 2002. Currently, the system has an extension of 67 km with a total of 81 operational stations, 14 of which are underground (January 2016). The system is underground in central Oporto (8 km of the network) and aboveground into the city's suburbs, carrying about 57 million passengers per year. All stations are built with two side platforms with a double track commercial line in the middle. Trains run every day from 6:00 until 1:00 h with a frequency from 5 to 19 min, and are equipped with air-conditioning system. Train compositions may be coupled in sets of two, depending on the line and the time of day. As in the Barcelona subway system, the power supply system is a solid overhead catenary line.

Urban air quality monitoring station of Francisco Sá Carneiro – Campanhã

The Francisco Sá Carneiro – Campanhã station is an urban traffic station located in Praça Francisco Sá Carneiro (41°09′46.10″ N, 08°35′26.95″ W, 147 m.a.s.l, Figure 2.3) and is part of the National Air Quality Network, QualAir. It is located in the eastern side of Porto city, next to the Fernão de Magalhães Avenue and at 600 m from the Inner Circular Motorway.

2.2. Sampling methods

2.2.1. Platform measurements

Platform measurements were carried out in the three subway systems in selected stations. Two types of measurements were performed: intensive campaigns and additional platform measurements.

Intensive campaigns

In the case of the Barcelona subway study, four stations with distinct designs belonging to different lines were selected for the intensive campaigns: Joanic (L4), Santa Coloma (L1), Tetuan (L2), and Llefià (L10). A map indicating the positions of the monitoring subway stations is shown in Figure 2.1. The architectural design of the

stations and tunnels is different for each station: one wide tunnel with lateral platforms and two rail tracks in the centre, one for each direction, separated by a middle wall in Joanic station and without middle wall in Santa Coloma, a single narrow tunnel with one platform and one rail track in Tetuan, and a single tunnel with one rail track separated from the platform by a glass wall with PSDs in Llefià.

Figure 2.1 Location of the monitoring subway and urban stations in Barcelona.

Two one-month intensive campaigns were carried out at each of the stations during two periods: warmer (2 April – 30 July 2013) and colder (28 October 2013 – 10 March 2014), according to TMB ventilation protocols to ascertain seasonal differences. The platform ventilation conditions in the stations are regulated by introducing outdoor air into the tunnel and/or platform (impulsion) and removing indoor air towards the outdoor environment (extraction). The mechanical ventilation settings, with strong or low impulsion and/or extraction of air between the platform stations and tunnels, were

adjusted for this study according to different TMB protocols during the sampling periods in order to evaluate the influence in PM concentrations and to determine the best operating conditions for air quality on the platform. Each selected ventilation setting was maintained at least during one week.

$PM_{2.5}$ samples were collected on quartz microfibre filters by means of a high volume sampler (HVS, Model CAV-A/MSb, MCV), programmed to sample daily over a 19 h period (from 5:00 h to midnight, subway operating hours). A field filter blank per period was taken at each station. Continuous measurements (24 h day^{-1}) with a 5-minute time resolution were performed using a light-scattering laser photometer (DustTrak, Model 8533, TSI) for PM_1, $PM_{2.5}$ and PM_{10} concentrations, an optical particle sizer (OPS, Model 3330, TSI) measuring particle number size distribution from 0.3 to 10 μm and an indoor air quality meter (IAQ-Calc, Model 7545, TSI) for CO_2 and CO concentrations, temperature and relative humidity (RH). CO concentrations were always below the detection limit (3 ppm) and hence they will not be further mentioned in this study. Additionally, in the warmer period PM_{10} was collected on polyurethane foam (PUF) substrates during 8 consecutive days using an Airborne Sample Analysis Platform system (ASAP; Model 2800 Thermo, USA).

In the case of the Athens and Oporto subway studies, the intensive sampling campaign was carried out at one station in each system, namely Nomismatokopio and Bolhão, respectively (Figure 2.2 and 2.3 for Athens and Oporto, respectively). For comparison purposes, the chosen stations had similar platform design: wide tunnel with two rail tracks in the middle, one for each direction, with lateral platforms. In Athens campaign, $PM_{2.5}$ samples were collected using a High Volume Sampler, similar to the one used in Barcelona. In Oporto campaign, a high volume sampler (TE-5200, Tisch Environmental Inc.) was used to collect coarse ($PM_{2.5–10}$) and fine ($PM_{2.5}$) particles, although only the $PM_{2.5}$ data were used in this study. The particles were collected daily on quartz microfibre filters during the subway operating hours (from 5:30 to 00:30 h in Athens and from 6:00 to 01:00 h in Oporto). Field filters blanks were also collected. A light-scattering laser photometer (DustTrak, Model 8533, TSI) for the monitoring of $PM_{2.5}$ mass concentration was simultaneously operated at 5-minute time resolution during 24 h day^{-1}, as in Barcelona's campaign.

Figure 2.2 Location of the monitoring subway and urban stations in Athens.

In the three subway studies, sampling and monitoring devices were placed far from the commuters' access-to-platform point and behind a light fence for safety protection. This location was chosen as a compromise between meeting conditions for undisturbed measurement, obstructing commuter's path as little as possible, and the availability of power supply. The aerosol inlets were placed at roughly 1.5 m above the ground level.

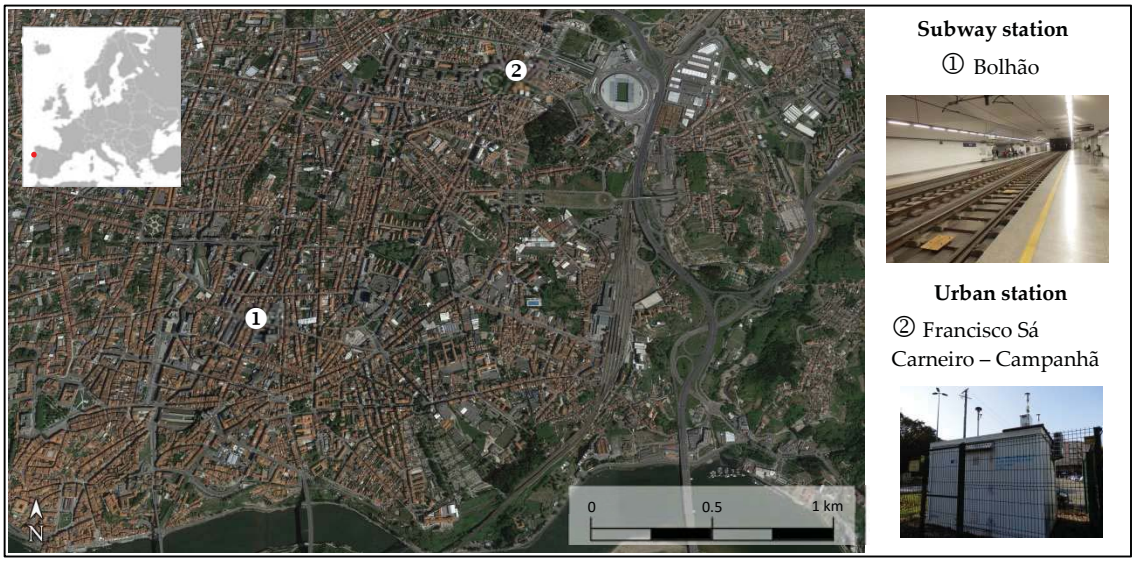
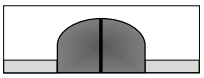
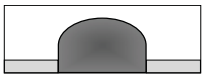
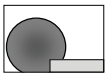
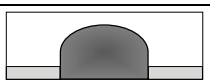
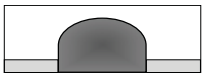


Figure 2.3 Location of the monitoring subway and urban stations in Oporto.

Information on the selected monitoring stations, sampling periods as well as the characteristics of the measurements carried out is summarised in Table 2.1.

Table 2.1 Sampling campaigns information.

Subway system	Station				No. of additional platforms studied	Measurements inside trains (No. of lines)
	Name (line)	Sampling period	Design	Mean train frequency (trains h^{-1})		
Barcelona	Joanic (L4)	2 Apr–2 May 2013 28 Oct–25 Nov 2013		12	24	6
	Santa Coloma (L1)	1 Jul–30 Jul 2013 10 Feb–10 Mar 2014		29		
	Tetuan (L2)	2 May–31 May 2013 25 Nov–20 Dec 2013		14		
	Llefià (L10)	31 May–1 Jul 2013 13 Jan–10 Feb 2014		8		
Athens	Nomismatokopio (L3)	28 Apr–19 May 2014		21	5	2
Oporto	Bolhão (LA,LB,LC,LE and LF)	27 Oct–14 Nov 2014		37	5	2

Note:  two-ways tunnel railway;  one-way tunnel railway; station platforms; middle wall; glass wall with PSDs.

Additional measurements

Additional platforms were selected to study the temporal and spatial variations in the PMx concentrations along the platforms. A total of 24 platforms from Barcelona subway system, 5 platforms from Athens subway system, and 5 platforms from Oporto subway system were studied (Table 2.1). Note that these stations include the aforementioned stations selected for the intensive campaigns (4 in Barcelona, 1 in Athens and 1 in Oporto). Out of the 24 stations in Barcelona, 4 were new stations (line 10) and the remaining were old stations (lines 1–5). In Barcelona the platforms were those with the most common station designs present in the subway system: a wide tunnel with two rail tracks both with (4 stations) and without (14 stations) a middle wall, and a single narrow tunnel with one rail track both without (2 stations) and with (4 stations) a glass wall with PSDs separating the rail from the platform. The selected Athens subway stations have two different architectural designs: i) a wide tunnel with two rail tracks in the middle with lateral platforms or ii) a wide tunnel with two rail

tracks with a central platform (only Monastiraki station selected with this design). In Oporto subway system all stations are double track with lateral platforms.

Measurements were performed at 4 positions approximately equidistant along the platform, during 1 h divided into periods of 15 min. Additionally, the sampling in the first point was repeated during 5 min after the 4 positions as a control in the colder period in Barcelona and in the Athens and Oporto campaigns. Real-time $PM_{2.5}$ mass concentrations were registered using a DustTrak monitor set at 5-second time resolution, enabling us to see the effect of trains and commuter's movements. All measurements were carried out during weekdays after 9:00 h. The times of trains entering and departing the station were manually recorded to assess possible correlations with the variability of the registered concentrations. The described procedure was conducted twice at each subway platform in Athens and Oporto, and four times in Barcelona (twice during each seasonal period), making a total of 96 platform measurements in Barcelona (48 in each sampling period) and 10 platform measurements in each Athens and Oporto subway systems. In addition, in 12 old stations of the Barcelona subway system, in the colder period, measurements were performed once more to study the influence of the piston effect on the air quality of the platforms.

Information on the number of aerosol samples collected and number of days with continuous measurements of PM_X in the intensive campaigns, as well as the number of measurements performed on additional platforms at each subway system is shown in Table 2.2.

2.2.2. Train measurements

Measurements inside the trains from 6 subway lines in Barcelona subway system (L1, L2, L3, L4, L5 and L10), 2 lines in Athens (L2 and L3), and 2 lines in Oporto (LA and LD) were performed (Table 2.1). Each of the lines was studied according to the following protocol: PM_X concentrations were measured using a DustTrak monitor and CO_2 concentrations were monitored by means of an Indoor Air Quality meter (IAQ-Calc) in the middle of the central carriage of the train during a two-way trip along the

whole length of the subway line. The total duration of the trip depended on the length of the line and ranged from 45 to 90 minutes approximately. Both instruments were set at a 5-second time resolution. The instrumentation was transported in a bag with the air uptake inlet placed at shoulder height when sitting. The measurements were carried out after 10:00 h on weekdays, and they were performed twice at each of the selected lines in Athens and Oporto, while they were performed 4 times in Barcelona (twice during each seasonal period), making a total of 32 measurements (Table 2.2). During the colder period of the Barcelona campaign, the measurements were carried out along the whole length of the line with and without air conditioning (not possible during warmer period due to passenger's comfort requirements), so that the effect of it on the air quality could be assessed. A manual record of the time when train doors open and close was performed. The effect of the carriage windows left open in the Athens lines and the differences between underground and aboveground sections in the Oporto lines were also assessed.

Table 2.2 Summary of the sampling and monitoring data.

Subway system		$PM_{2.5}$ samples number [1]		Real-time PM_1, $PM_{2.5}$, PM_{10}		
		Platforms	Outdoor	Platform intensive campaigns [2] (No. of days)	Additional platforms [3] (No. of measurements)	Inside trains [4] (No. of measurements)
Barcelona	W	119	40	119	48	12
	C	109	29	110	60	12
Athens		18	9	21	10	4
Oporto		15	8	18	10	4

[1] $PM_{2.5}$ samples collected daily during the subway operating hours (19 h), except for Barcelona outdoor (24h);
[2] Continuous measurements (24 h day^{-1}) with a 5-minute time resolution;
[3] Measurements performed during 1 h, divided into periods of 15 min at 4 positions equidistant along the platform, with a 5-second time resolution;
[4] Measurements carried out during a two-way trip along the whole length of the subway line with a 5-second time resolution.
W – warmer period; C – colder period.

2.2.3. Outdoor measurements

For comparison purposes, outdoor ambient $PM_{2.5}$ samples were collected concurrently at an urban station in each of the cities. The Barcelona and Athens outdoor measurements were performed using a HVS in the urban background stations of Palau Reial and Demokritos, respectively. The measurements were carried out during 24 h every third day at Palau Reial station and 19 h (subway operating hours) every second

day at Demokritos station. In addition, in the urban background station of Palau Reial, PM_X concentrations were measured by a laser aerosol spectrometer (Environmental Dust Monitor, Model EDM180, Grimm) with a 30-minute time resolution. The Oporto outdoor measurements were conducted in the urban traffic station of Francisco Sá Carneiro – Campanhã with two low-volume Tecora samplers (TCR, Model 2.004.01). $PM_{2.5}$ samples were collected by both TCR samplers simultaneously during 19 h (subway operating hours) every second day. The location of the outdoor sampling stations is shown in Figure 2.1, 2.2 and 2.3, for Barcelona, Athens and Oporto, respectively. In total, 86 outdoor aerosol samples were taken during the sampling campaigns (Table 2.2).

2.3. Instrumentation

2.3.1. Off-line techniques

MCV high volume sampler

$PM_{2.5}$ samples were collected using an automatic sequential high volume sampler (HVS, Model CAV-A/MSb, MCV) equipped with an inlet (PM1025/UNE model, built according to the European Norm: EN 14907) with a specific nozzle plate for $PM_{2.5}$ (Figure 2.4). The sampler operates at a sampling flow rate of 30 $m^3\ h^{-1}$. The air flow passes through the inlet and goes through the nozzles, where the speed increases. Then, the particles larger than 2.5 μm in diameter impact and adhere on a plate impregnated with vaseline and the smaller ones pass through and are collected on quartz fibre filter (150 mm diameter; Pallflex).

Figure 2.4 MCV high volume sampler.

Tisch high volume sampler

The portable high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 67.8 $m^3\ h^{-1}$ were used to collect coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) particles (Figure 2.5), the latter was collected on quartz fibre filters (20.3 x 25.4 cm; Pallflex). The

impaction system for removing PM>10 was designed at the University of Aveiro in accordance with the Marple and Rubow's theory (1986) and constructed in a local metal-mechanic industry. A $PM_{2.5}$ impaction plate (Tisch TE-231 F) was used to separate particles smaller than 2.5 μm. These air sampling units are composed of an aluminium shelter, aluminium blower motor assembly, a mass flow controller and timer, a continuous flow/pressure recorder, a filter holder and a size selective inlet.

Figure 2.5 Tisch high volume samplers.

A comparison of $PM_{2.5}$ concentrations determined in samples simultaneously collected with MCV and Tisch high volume samplers presented a squared Pearson correlation coefficient (R^2) equal to 0.91 and a linear regression with a slope close to unity.

Low-volume Tecora sampler

$PM_{2.5}$ samples were collected on quartz fibre filters (47 mm diameter; Whatman) using a low-volume sampler TCR (TECORA, model 2.004.01) equipped with a $PM_{2.5}$ sampling head in accordance with the EN 14907 norm. The equipment included a specific sampling head ($PM_{2.5}$), a pump operating at a flow of 2.3 $m^3\ h^{-1}$, and a control and data storage unit.

Both MCV and TCR samplers are in compliance with the EN 14907 standards, which assures the comparability between them.

ASAP sampler

The Airborne Sample Analysis Platform system (ASAP; Model 2800 Thermo, USA; Figure 2.6) was used to collect representative, time-resolved samples of aerosols 1 to 10 μm in diameter for subsequent microscope analysis. The device works at a flow rate of 200 L min^{-1}. Particles are collected on the surface of a strip of PUF substrate contained in an iBASS cartridge (Integrated Bio Aerosol Smart Sample).

Figure 2.6 ASAP sampler.

2.3.2. Real-time techniques

Light-scattering laser photometer

Figure 2.7 DustTrak.

The light-scattering laser photometer DustTrak (Model 8533, TSI) is a desktop instrument able to provide real-time measurements of particulate matter on a 90° light scattering sensor (Figure 2.7). It measures size-segregated mass concentrations (PM_1, $PM_{2.5}$, PM_4, PM_{10}, and PM_{Total}) simultaneously over a wide concentration range (0.001 – 150 mg m^{-3}) in real-time. This method combines photometric measurement to cover the mass concentration range and a single particle detection measurement to be able to size discriminate sampled aerosol (TSI, 2012). Prior to each sample cycle the monitor was zero-checked in accordance with manufacturer's guidelines. The time resolution can be chosen and it was set to 5-second for the inside trains and additional platform measurements, and to 5-minute for the intensive campaigns measurements. Logged data was downloaded from the DustTrak to a computer hard drive using TrakPro software version 4.2.0.15 (Trust Science Innovation, TrakPro Version, 2010).

Laser aerosol spectrometer

The laser aerosol spectrometer (Environmental Dust Monitor, Model EDM180, Grimm) is an instrument where the air flow passes through a laser beam and the light scattered by individual particles are collected at a 90° by a mirror and transferred to a photodetector, where it is converted to a proportional voltage pulse. Particle size is determined from the number of single particle counts registered in each channel, by a 15-channel pulse height analyser, and it is converted to mass units using a particle-density based equation thus obtaining size-resolved PM mass concentrations. This instrument measures particles of diameters between 0.3 and 15 μm. In this study only the $PM_{2.5}$ mass concentrations were used.

Optical Particle Sizer

The Optical Particle Sizer (OPS, Model 3330, TSI) is a light, portable unit that provides fast and accurate measurement of particle concentration and particle size distribution

using single particle counting technology in the size range of 0.3 – 10 μm in up to 16 channels (user-adjustable size channels) (Figure 2.8). It uses state-of-the-art optics with 120° light collection and sophisticated electronics processing resulting in precision, high quality data. Rigorous factory calibration standards ensure measurement accuracy. The upper cut-off diameters for each of the channels were adjusted as follows: 0.374, 0.465, 0.579, 0.721, 1, 1.2, 1.4, 1.732, 2.156, 2.5, 3.343, 4.162, 5.182, 6.451, 8.031 and 10 μm. It measures size-segregated number concentrations simultaneously over a wide concentration range from 0 to 3 000 particles cm^{-3} in real-time. The time resolution can be chosen and it was set to 5-minute. The data logged by the OPS instrument was downloaded using the Aerosol Instrument Manager® software.

Figure 2.8 OPS.

Indoor air quality meter

The IAQ-Calc™ indoor air quality meter (Model 7545, TSI) was used to measure CO and CO_2 concentrations, temperature and RH, simultaneously (Figure 2.9). The instrument includes an electrochemical sensor for CO in a range from 0 to 500 ppm with accuracy of ±3.0% of reading or ±3 ppm. The instrument also contains a non-dispersive infrared (NDIR) sensor for CO_2 in a range from 0 to 5000 ppm with accuracy of ±3.0% of reading or ±50 ppm. Temperature and RH were measured continuously by a thermistor (range from 0 to 60°C with an accuracy of ±0.6°C), and a thin-film capacitive sensor (range of 5 to 95%; accuracy ±3.0%), respectively. Data were exported using the LogDat2™ downloading software.

Figure 2.9 IAQ meter.

2.4. Sample treatment and chemical analyses

2.4.1. Filters treatment and weight

Before sampling, quartz microfibre filters were heated in an oven at 200°C during a minimum of 4 h to eliminate the volatile impurities. The filters were equilibrated for at

least 48 h in a conditioned room (20°C and 50% relative humidity) and then weighed before and after sampling by means of a microbalance (Model XP105DR, Mettler Toledo). Filters were preserved individually in aluminium foils inside air sealed boxes and stored at room temperature under dry conditions until sampling or analyses, in case of blank and sampled filters, respectively. The gravimetric $PM_{2.5}$ mass concentrations were determined dividing the weight difference between the blank and sampled filter by the volume of air sampled.

2.4.2. Chemical analyses

Once the gravimetric determination was performed the filters were cut into several sections for subsequent chemical analyses (Figure 2.10).

The final ambient concentrations were calculated after the subtraction of analytical blank values from the corresponding sample concentrations. Detection limits of the analysis techniques were calculated from the standard deviations from the blank filters analyses alongside the analytical uncertainties. The analytical procedures are the same used by Querol et al. (2012).

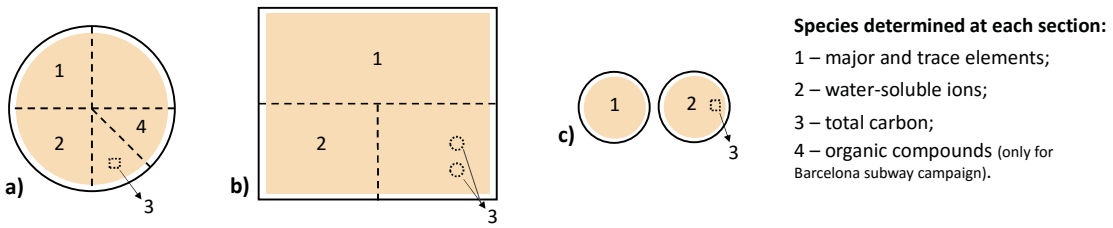


Figure 2.10 Diagram of the filter sections for the different chemical analyses: a) in both subway and outdoor environment in Barcelona and Athens campaigns; b) in Oporto subway system; and c) Oporto outdoor ambient air (two filters collected simultaneously).

Major and trace elements:

A filter section was acid digested using a mix of $HF:HNO_3$ (5:2.5 mL) and then kept into a Teflon reactor at 90°C for at least 6h. After cooling, the Teflon reactor was open and 2.5 mL of $HClO_4$ were added. The acid solutions were then completely evaporated by placing the open reactors on a heating plate at 230 – 240°C. The dry residue was re-

dissolved with 2.5 mL HNO_3 to make up a volume of 50 mL with Milli-Q grade water, resulting a solution of 5% HNO_3. This solution was then chemically analysed by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES: IRIS Advantage TJA Solutions, THERMO) and Mass Spectrometry (ICP-MS: X Series II, THERMO) to determine major (such as Al, Ca, K, Na, Mg, Fe, P, S) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Ba, La, Ce, Pr, Nd, Hf, W, Pb, Bi, Th, U, among others). For every batch of acid digested samples, corresponding blanks and field blanks were digested following the same analytical procedures.

For quality control of the analytical procedure a small amount (approx. 10 mg) of the Standard Reference Material 1633b (Coal Fly Ash) loaded on a similar fraction of a blank quartz microfibre filter was also analysed. The reference material analysis assures the quality of the results permitting the identification of possible analytical or calibration errors. Relative analytical errors were between 3 and 10% for the elements studied.

Water-soluble ions

A second section of each filter was put in a PVC vessel and leached using deionized water (30 g of Milli-Q grade water). For a better extraction of the soluble fraction, the leached solution was placed in an ultrasound bath for 15 – 20 minutes and then heated at 60°C for at least 6h. The solution obtained was filtered and analysed by ion chromatography (IC: WATERS IC-pakTM anion column and WATERS 432 conductivity detector) to determine water-soluble anions (Cl^-, SO_4^{2-} and NO_3^-), and by selective electrode (SE: Electrode Model 710 A+, THERMO Orion) to obtain the ammonium (NH_4^+) concentrations.

Total carbon

A small portion of the filter was used to determine the total carbon (TC) concentrations. The presence of certain minerals in aerosol samples can complicate the optical correction for pyrolysis required in thermal-optical methods for the determination of EC and OC (Karanasiou et al., 2015). Chow et al. (2001) and Fung et

al. (2002) reported that the Fe acts as a catalyser for EC oxidation during the thermal-optical analysis. Therefore, for samples where a high content of Fe is expected the split between OC and EC should be examined carefully (Chow et al., 2004; Karanasiou et al., 2015). The high Fe 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 although some studies have reported EC and OC concentrations in subway environments (Aarnio et al., 2005; Kam et al., 2013; Midander et al., 2012).

- TC concentrations in Barcelona subway samples were determined by a thermal-optical technique using a Lab OC-EC Aerosol Analyser (Sunset Laboratory Inc.) with a simplified protocol for TC (1.5 cm^2 filter punch). The TC concentrations in the outdoor samples from the 3 sampling campaigns (Barcelona, Athens and Oporto) were also determined by this technique.
- TC concentrations in Athens subway samples were determined by an elemental analyser LECO CS-244 in the Centre for Energy, Environment and Technological Research (CIEMAT) (6.2 cm^2 filter punch).
- TC concentrations in Oporto subway samples were determined by a home-made thermal-optical analyser in the University of Aveiro (two 0.6 cm^2 filter punches).

The equivalence between the different methods is guaranteed by a comparison made for a set of samples analysed both by the Sunset instrument and the elemental analyser (R^2=0.988). The TC concentrations obtained by thermal-optical methods using different protocols are equivalent (Karanasiou et al., 2015).

Organic species

The analysed $PM_{2.5}$ organic species were selected based on their representativeness of primary organic aerosol emission sources, and included 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[1,2,3-cd]pyrene, benzo[ghi]perylene and coronene), hopanes (17(H)α-21(H)β-29-norhopane and 17(H)α-21(H)β-hopane), nicotine, levoglucosan, aromatic musk compounds (methyl-dihydrojasmonate and galaxolide), alcohol

saccharides (xylitol and mannitol), phthalate esters (dibuthyl phthalate (DBP) and di(ethylhexyl) phthalate (DHEP)) and primary saccharides (α- and β-glucose).

A filter fraction was ultrasonically extracted with (2:1, v/v) dichloromethane:methanol (3 x 5 mL; Merck, Germany) for 15 minutes. Before extraction, 25 μL of the surrogate standards levoglucosan-d_7, n-$C_{24}d_{50}$ (Cambridge Isotopic Laboratories, UK), succinic acid-d_4 (Sigma Aldrich), anthracene-d_{10}, benz[a]anthrancene-d_{12}, benzo[k]fluoranthene-d_{12} and benzo[ghi]perylene-d_{12} (Dr. Ehrenstorfer) were added. The extracts were filtered over 0.45 μm teflon membrane filters in order to remove insoluble particles. Then, they were concentrated to 1 mL under a gentle N_2-gas stream.

To analyse the levoglucosan, primary and alcohol saccharides, nicotine, musk compounds, and phthalate esters an aliquot of the extract (25 μL) was evaporated under a gentle N_2 stream until dryness. Then, 25 μL of bis(trimethylsilyl)trifluoroacetamide (BSFTA)+trimethylchlorosilane (99:1) (Supelco) and 10 μL of pyridine (Merck) were added for derivatization of the saccharides to their trimethylsilyl esters at 70°C during 1h. Before injection into a Gas Chromatograph coupled to a Mass Spectrometer (GC–MS: Thermo Trace GC Ultra – DSQ II) 25 μL of the internal standard, 1-phenyldodecane were added to the vial.

For the analysis of PAHs and hopanes, the remaining extract was evaporated to almost dryness under a gentle N_2-gas stream and re-dissolved in 0.5 mL hexane + dichloromethane (9:1 v/v) (Merck, Germany). Then, it was cleaned-up by adsorption column chromatography on 1 g of aluminium oxide (Merck, Germany) that was activated overnight at 120°C. The analytes were eluded with 4 mL of (9:1 v/v) hexane:dichloromethane and 4 mL of (1:2 v/v) hexane:dichloromethane, respectively (Merck, Germany). The collected fraction was concentrated under a gentle N_2-gas stream to 50 μL, and the internal standard, 1-phenyldodecane, was added before injection into GC–MS.

2.4.3. Indirect determinations

The concentrations of some components were indirectly estimated by means of empirically obtained factors:

- As silica data were not acquired, SiO_2 was estimated multiplying Al_2O_3 by a factor of 3 (Querol et al., 2001).
- CO_2^{3-} was estimated multiplying Ca by a factor of 1.5 (Querol et al., 2001).
- In the case of Barcelona (Article 2): the carbonaceous aerosol (CA), which includes the elemental carbon (EC) and the organic matter (OM), was calculated from the total carbon (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).

2.4.4. PM mass closure

After the chemical analyses, the components of $PM_{2.5}$ were grouped into seven categories, based on their chemical composition:

1) Fe; expressed as hematite (Fe_2O_3) in Barcelona (Article 2) assuming that all the Fe is in this oxidised form.
2) Crustal matter (CM); corresponding to the sum of components which are typically found in mineral materials, such as Ca, Mg, Al_2O_3, SiO_2, CO_3^{2-}, K_2O, TiO_2 and P_2O_5. In the comparisons among the three subway systems (Article 3 and in section 4.3), CM was calculated as the sum of the elements referred above without considering the oxidation forms of K, Ti and P.
3) Carbonaceous aerosol (CA) in Barcelona (Article 2), or total carbon (TC) in the comparisons among the three subway systems (Article 3 and in section 4.3).
4) Secondary Inorganic Compounds (SIC); the sum of water-soluble SO_4^{2-}, NO_3^- and NH_4^+.
5) Insoluble SO_4^{2-}.
6) Halite; the sum of Na^+ and Cl^-.
7) Trace elements.

2.4.5. Scanning electron microscopy

The morphology and chemical composition of individual PM_{10} particles collected by the ASAP on the Barcelona subway platforms were studied using scanning electron microscopy (SEM) in Cardiff University (UK). The size and shape of individual particles were observed using a JEOL5900LV Scanning Electron Microscope via an energy dispersive X-ray microanalysis system (EDX). PUF substrates were directly "flat-mounted" onto aluminium SEM stubs using epoxy-resin (Araldite) as an adherent between the PUF and the stub. The samples were then gold/palladium-coated using a 208HR Sputter Coater (Cressington, UK) and an MTM20 Thickness Controller (Cressington, UK). The microscope working distance was 10 mm, with an accelerating voltage of 20 kV.

2.5. Data processing

2.5.1. Real-time particle mass concentration correction

$PM_{2.5}$ concentrations provided by DustTrak monitor were corrected against the in-situ and simultaneous gravimetric $PM_{2.5}$ for each station. Concentrations of PM_1 and PM_{10} were corrected using the same correction factors obtained for $PM_{2.5}$. However, previous gravimetric–DustTrak intercomparisons for PM_1 and PM_{10} concentrations carried out by the IDAEA-CSIC group for the ambient outdoor air have shown weak correlations, with PM_1 and PM_{10} concentrations provided for the DustTrak monitor being undervalued and overvalued, respectively. Since the aerosol properties in the subway are different from the outdoor aerosol, the previously determined correlations are not suitable to correct the subway measurements. Therefore, in this study only the $PM_{2.5}$ concentrations are used in absolute terms, whereas the PM_1 and PM_{10} concentrations are only used to assess relative variations.

In the urban background station of Palau Reial, continuous $PM_{2.5}$ concentrations provided by the laser aerosol spectrometer (Grimm) were corrected with in-situ and simultaneous gravimetric $PM_{2.5}$ concentrations determined in samples collected by a high volume sampler (HVS, MCV).

2.5.2. Platform data correction

The $PM_{2.5}$ mass and chemical components concentrations from the intensive campaigns were corrected for spatial variation along the platform and they are reported accordingly in this study. The purpose of this correction is to have $PM_{2.5}$ characterisation representative of the whole platform, based on the measurements described in section 2.2.1., where the $PM_{2.5}$ concentrations were measured at 4 different positions along the platform. On the station platforms selected for the intensive campaigns, one of the 4 measurement positions coincided with the continuous sampling site (devices location). Hence, the concentrations measured during the intensive campaigns at a given location were multiplied by a $PM_{2.5}$ correction factor for spatial variation. These correction factors were obtained by dividing the average $PM_{2.5}$ concentrations across the platform (including the concentrations recorded at the 4 positions) by the average $PM_{2.5}$ concentrations at the selected sampling point for the intensive campaigns. The correction factors very close to 1 showed that the concentrations measured at the continuous sampling site were very similar to the exposure levels of commuters waiting elsewhere along the platform.

2.5.3. Source apportionment

After the complete chemical characterisation of $PM_{2.5}$ a receptor model was applied in order to determine and quantify the sources of atmospheric PM for the Barcelona subway study. The source apportionment was carried out by means of the Positive Matrix Factorization (PMF; Paatero and Tapper, 1994) using the US–EPA PMF 5.0 software. This multivariate receptor model provides estimates of the chemical composition of PM associated with different sources and the mass contribution attributed to each source.

PMF factorizes the chemical composition matrix $\boldsymbol{X}$, containing n samples (rows) with m species (columns), into two submatrices, the chemical profiles $\boldsymbol{F}$ and the time series $\boldsymbol{G}$, so that p different sources of emissions or secondary components are identified and their contribution is quantified. The residual $\boldsymbol{E}$ matrix corresponds to the fraction of $\boldsymbol{X}$ not explained by the solution.

$$\boldsymbol{X = GF + E}$$ **Equation 2.1**

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

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{\sigma_{ij}}\right)^2$$ **Equation 2.2**

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 species uncertainties were calculated according to Escrig et al. (2009). 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).

2.5.4. Deposited dose calculation

Aerosol deposition in human respiratory system was calculated by the dosimetry Exposure Dose Model (ExDoM). A three-months (16th January – 15th April 2015) secondment in Technical University of Crete (Greece) was carried out to this end. A detailed description of this model has been reported by Aleksandropoulou and Lazaridis (2013) and Chalvatzaki and Lazaridis (2015). The dose is the amount of particles deposited in the respiratory tract during breathing, and it can be expressed as:

$$Dose = DF \times C \times t \times Q$$ **Equation 2.3**

where DF is the deposition fraction of aerosol particles in the respiratory system (dimensionless), C is the airborne particle concentration in units of μg m^{-3}, t is the exposure time in hours, and Q is the breathing rate in $m^3\ h^{-1}$. From these parameters, DF is the least accessible factor, because it depends on the exposed subject characteristics, such as age, gender, health status, lungs morphology, respiratory

parameters and activity, as well as on numerous other parameters including particle size, density, shape, and chemical composition (ICRP, 1994; Lazaridis, 2011; Löndahl et al., 2007). Moreover, the DF is different for each region of the respiratory system (extrathoracic, tracheobronchial, and alveolar-interstitial). The breathing rate not only depends on the body size of the subjects, but also on their activity and health status (Bennett and Zeman, 2004; ICRP, 1994). Furthermore, the deposition calculations used in the model are based upon the empirical equations proposed in the ICRP human respiratory tract model (Aleksandropoulou and Lazaridis, 2013).

For the application of the dosimetry model ExDoM the following aspects were considered: i) selection of the exposed subject; ii) identification of the microenvironments where the exposed subject spent time; iii) estimation of the time spent in each microenvironment, iv) determination of the $PM_{2.5}$ exposure concentrations, v) selection of the breathing mode; and vi) selection of breathing rate (volume of air inhaled per unit of time) to be used as a function of the corresponding specific activity levels (classified as sleep, sitting/resting, light exercise and heavy exercise).

Modelling of $PM_{2.5}$ deposition in the HRT was conducted for a healthy Caucasian adult male breathing through the nose living in Barcelona and considering a typical time-activity pattern of a subject who has a sedentary job and commutes by subway. To estimate the overall daily dose some activities were neglected, such as outdoor entertainment or indoor (at home and workplace) activity, and no indoor sources were assumed. Time-activity pattern was based on information from the Spanish national statistical institute (http://www.ine.es/) and previous exposure studies carried out in Barcelona, which included Time-Microenvironment-Activity-Diaries (Schembari et al., 2013). The exposure $PM_{2.5}$ concentrations at home and workplace were estimated using an indoor/outdoor infiltration ratio of 0.91, determined for naturally ventilated buildings in the absence of indoor sources (Morawska and Salthammer, 2003). Therefore these concentrations are underestimated due to the non-consideration of indoor sources, such as e.g. cooking at home or printer emissions in an office. Dosimetry calculations were performed using the aforementioned concentrations during realistic exposure under variant physical activities.

In the case of the subway microenvironment, light exercise was assumed with a breathing rate of 1.5 $m^3\ h^{-1}$ (reference values for adult Caucasian males; ICRP, 1994). Furthermore, the dose was determined for average exposure concentrations from the measurements in the stations and inside the trains in order to represent the overall dose in the subway system. The exposure time assumed was based on the TMB information with an average subway commuting one-way travel of 5 min on the platform and 15 min inside the train. The additional physical activity levels considered were sitting/resting and sleeping with breathing rates of 0.54 and 0.45 $m^3\ h^{-1}$, respectively. Although particles were assumed spherical (shape factor of 1) for the dose calculations it is known from scanning electron microscopy studies that a large fraction of subway PM is laminar (see section 4.3) (e.g. Moreno et al. (2015) and Querol et al. (2012).

Another important factor determining the deposition of particles is their density (Aleksandropoulou and Lazaridis, 2013). The density of the subway particles (ρ_p, g cm^{-3}) was calculated based on the species chemical composition using the following equation (modified from DeCarlo et al., 2004):

$$\rho_p = \frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^+] + [Cl^-] + [CA] + [Fe_2O_3] + [CM]}{\frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^+]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[CA]}{1.5} + \frac{[Fe_2O_3]}{5.26} + \frac{[CM]}{2.7}} \qquad \textbf{Equation 2.4}$$

where $[NO_3^-]$, $[SO_4^{2-}]$, $[NH_4^+]$, $[Cl^-]$, $[CA]$, $[Fe_2O_3]$, and $[CM]$ represent the mass concentration of each species. Equation 2.4 assumes that the densities of ammonium nitrate, ammonium sulphate, and ammonium bisulphate are approximately 1.75 g cm^{-3}; the density of ammonium chloride is 1.52 g cm^{-3}; the density of CA is 1.5 g cm^{-3}; the density of Fe_2O_3 is 5.26 g cm^{-3}; the average density of CM, calculated from the weighted average density of the main oxides, is 2.7 g cm^{-3}. The calculated density of the subway particles ranged from 2.2 to 3.1 g cm^{-3}.

The mass size distribution of the subway $PM_{2.5}$, necessary for ExDoM calculations, was obtained from the OPS data converting the particle number concentration into mass concentration, multiplying the estimated density (ρ_p) by the volume, assuming spherical particles. This resulted in a monodisperse aerosol with a mass mean aerodynamic diameter (MMAD) of 2.1 μm and a geometric standard deviation (GSD)

of 1.7. For outdoor ambient air, the aerosol density was assumed equal to 1.5 g cm^{-3}, which corresponds to the average density of typical ambient aerosols (Zhang et al., 2005). A monodisperse aerosol size distribution was considered with a MMAD of 0.21 μm and a GSD of 1.15 (data from IDAEA-CSIC group).

Chapter 3

Results

Article 1

Exposure to airborne particulate matter in the subway system

Vânia Martins, Teresa Moreno, María Cruz Minguillón, Fulvio Amato, Eladio de Miguel, Marta Capdevila, Xavier Querol

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Overview:

A characterisation of the airborne particulate matter both inside trains and on platforms of the Barcelona subway system was performed, measuring its concentration and investigating its spatial and temporal variability in two seasonal periods (warmer and colder). The influence of outdoor environment and different ventilation settings in the PM concentration within the subway system were assessed. The results of this study were also compared with other studies performed worldwide.

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Exposure to airborne particulate matter in the subway system

Vânia Martins [a,b,*], Teresa Moreno [a], María Cruz Minguillón [a], Fulvio Amato [a], Eladio de Miguel [c], Marta Capdevila [c], Xavier Querol [a]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain
[c] Transports Metropolitans de Barcelona, TMB Santa Eulàlia, Av. Del Metro s/n L'Hospitalet de Llobregat, 08902, Spain

HIGHLIGHTS

- Higher PM concentrations were found on platforms compared to outdoor.
- Air quality was better in the new lines with PSDs.
- PM concentrations were higher in the colder than in the warmer period.
- Ventilation and air conditioning systems improve air quality in the subway system.
- Time commuting in the subway contributes substantially to the personal exposure.

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ABSTRACT

The Barcelona subway system comprises eight subway lines, at different depths, with different tunnel dimensions, station designs and train frequencies. An extensive measurement campaign was performed in this subway system in order to characterise the airborne particulate matter (PM) measuring its concentration and investigating its variability, both inside trains and on platforms, in two different seasonal periods (warmer and colder), to better understand the main factors controlling it, and therefore the way to improve air quality. The majority of PM in the underground stations is generated within the subway system, due to abrasion and wear of rail tracks, wheels and braking pads caused during the motion of the trains. Substantial variation in average PM concentrations between underground stations was observed, which might be associated to different ventilation and air conditioning systems, characteristics/design of each station and variations in the train frequency. Average $PM_{2.5}$ concentrations on the platforms in the subway operating hours ranged from 20 to 51 and from 41 to 91 μg m^{-3} in the warmer and colder period, respectively, mainly related to the seasonal changes in the subway ventilation systems. The new subway lines with platform screen doors showed $PM_{2.5}$ concentrations lower than those in the conventional system, which is probably attributable not only to the more advanced ventilation setup, but also to the lower train frequency and the design of the stations. PM concentrations inside the trains were generally lower than those on the platforms, which is attributable to the air conditioning systems operating inside the trains, which are equipped with air filters. This study allows the analysis and quantification of the impact of different ventilation settings on air quality, which provides an improvement on the knowledge for the general understanding and good management of air quality in the subway system.

1. Introduction

Citizens usually spend a considerable amount of their daily time commuting. Considering that in urban areas road traffic is a major emission source of air particles (Viana et al., 2008), travelling by public transportation saves energy and produces less pollution than travelling in private vehicles. The subway, being an electrical system and one of the cleanest public transport systems in large urban agglomerations, is considered to be the most appropriate public transport since it diverts the burdens of superficial traffic congestion. Its high capacity in terms of number of daily commuters makes it an environmentally friendly alternative. The energy efficiency and reduced urban atmospheric emissions make this kind of public transport a powerful tool to reduce energy demands and improve air quality in urban environments.

However, prior studies in subway systems of several cities worldwide indicate, with few exceptions, that particulate matter (PM)

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

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concentrations are generally higher in these environments than those measured in ambient air (Nieuwenhuijsen et al., 2007). The underground subway system is a confined space that promotes the concentration of contaminants entering from the outside atmosphere in addition to those generated inside. The subway aerosol particles are mainly generated by the abrasion of rail tracks, wheels, catenary and brake pads produced by the motion of the trains, and the movement of passengers which promotes the mixing and suspension of PM (Querol et al., 2012). PM levels have been reported in many subway systems, such as in Milan (Colombi et al., 2013), Barcelona (Querol et al., 2012; Moreno et al., 2014), Taipei (Cheng et al., 2008, 2012; Cheng and Lin, 2010), Seoul (Kim et al., 2008, 2012; Park and Ha, 2008; Jung et al., 2010), Mexico City (Mugica-Álvarez et al., 2012; Gómez-Perales et al., 2004), Los Angeles (Kam et al., 2011a,b), New York (Wang and Gao, 2011; Chillrud et al., 2004, 2005), Shanghai (Ye et al., 2010), Sydney (Knibbs and de Dear, 2010), Buenos Aires (Murruni et al., 2009), Paris (Raut et al., 2009), Budapest (Salma et al., 2007), Beijing (Li et al., 2006, 2007), Prague (Braniš, 2006), Rome (Ripanucci et al., 2006), Helsinki (Aarnio et al., 2005), London (Seaton et al., 2005; Adams et al., 2001), Stockholm (Johansson and Johansson, 2003), Hong Kong (Chan et al., 2002a), Guangzhou (Chan et al., 2002b), Tokyo (Furuya et al., 2001), Boston (Levy et al., 2000), and Berlin (Fromme et al., 1998). However, results are not always directly comparable because of differences in sampling and measurement methods, data analysis, duration of the measurements and the type of environment studied (Nieuwenhuijsen et al., 2007). There are important factors influencing PM concentrations in underground railway systems around the world, which include differences in the length 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, cleaning frequencies, among other factors (Moreno et al., 2014 and references therein).

Despite the number of studies on PM in underground subway systems, the main focus of most of them has been to monitor variations in mass concentration of PM on platforms and in a reduced number of stations. Therefore, there is a need for extensive studies of entire subway systems, covering the vast diversity of lines, trains and stations and providing an overview of the overall exposure to PM in this environment.

With this in mind, this work is the first study that presents a large dataset from an extensive campaign, able to characterise 24 stations in the Barcelona subway system and providing valuable information for human PM exposure studies in such environment, considering its possible adverse health effects (Pope et al., 2004; Seaton et al., 2005; Karlsson et al., 2006, 2008; Gustavsson et al., 2008). For this, continuous PM measurements were carried out in 4 underground subway stations in Barcelona, on a daily basis during two months and supplementary samplings were also performed in a total of 20 additional stations. Measurements inside the trains were also carried out in 6 subway lines.

In order to gather information on the relationship between pollutant levels and the characteristics of the sampling sites, the measurements were obtained in several subway lines, including stations with different characteristics (design and ventilation of the station and tunnels, number and location of connections with the outdoor level, and train frequency). This monitoring scheme was designed to characterise the temporal and spatial variation of particles at each site and to identify their possible sources. Therefore, the four subway stations studied on daily basis have different characteristics; in particular, one of the stations is equipped with platform screen doors (PSDs) for commuters' safety but also resulting in less mixing of air between the platform and tunnels. The influence of the installed PSDs on aerosol characteristics is also investigated in this work.

2. Methodology

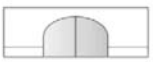
2.1. Field study

The subway system in the city of Barcelona (managed by Transports Metropolitans de Barcelona, TMB) is one of the oldest underground transport systems in Europe, with its first line beginning operation in 1924. By the present decade, the Barcelona subway system comprises 8 lines (3 of them in operation over the last five years) with a total length of 102.6 km and including 140 train stations. The new stations have platforms separated from the tunnel by a wall with mechanical doors (PSDs) that are opened simultaneously with the train doors. Trains run from 5 a.m. until midnight every day, with additional services on Friday nights (finishing at 2 a.m. of Saturday) and Saturday nights (running all night long), with a frequency between 2 and 15 min, depending on the day (weekend or weekday), subway line and time of day. The Barcelona subway absorbs around 50% of the urban commuting load, transporting 1.25 million commuters on weekdays, with the most frequent average journey time being 35 min (Querol et al., 2012).

In all subway systems, two main types of environments are connected: the platform station and the inside of the train. Both types of environments were investigated in this study. Four underground stations with distinct designs belonging to different lines were selected for continuous monitoring in two one-month periods: Joanic on the yellow line (L4), Santa Coloma on the red line (L1), Tetuan on the purple line (L2), and Llefià on the new light blue line (L10). The architecture of the stations and tunnels is different for each station: 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 wall with PSDs in Llefià (Table 1).

The study was conducted in the warmer (2 April–30 July 2013) and colder (28 October 2013–10 March 2014) periods (Table 1), according to TMB ventilation protocols to ascertain seasonal differences. In total, the air quality at each station was measured continuously for 30 days

Table 1
Features of the subway stations and measurement periods.

Subway station (line)	Measurement period		Station	
	Warmer	Colder	Depth	Design
Joanic (L4)	2 Apr–2 May 2013	28 Oct–25 Nov 2013	−7.6 m	
Santa Coloma (L1)	1 Jul–30 Jul 2013	10 Feb–10 Mar 2014	−12.3 m	
Tetuan (L2)	2 May–31 May 2013	25 Nov–20 Dec 2013	−14.8 m	
Llefià (L10)	31 May–1 Jul 2013	13 Jan–10 Feb 2014	−43.6 m	

per season to obtain statistically representative data. Both seasons were analysed using the same analytical methodology and monitoring instruments. For comparison purposes, outdoor ambient PM concentrations were measured concurrently at the urban background station of Palau Reial (41°23′14″ N, 02°06′56″ E) which was used during both campaigns as a reference site.

The platform ventilation conditions in the stations are regulated by introducing outdoor air into the tunnel and/or platform (impulsion) and removing indoor air towards the outdoor environment (extraction). The mechanical ventilation settings (Table 2), with strong or low impulsion and/or extraction of air between the platform stations and tunnels, were adjusted for this study according to different TMB protocols during the sampling periods in order to evaluate the influence in PM concentrations and to determine the best operating conditions for air quality on the platform. Each selected ventilation setting was maintained at least during one week, in order to better evidencing their effects on PM levels.

2.2. Measurements and sampling equipment

Air monitoring equipment included a light-scattering laser photometer (DustTrak, Model 8533, TSI) for PM_1, $PM_{2.5}$ and PM_{10} (particulate matter with aerodynamic diameter less than 1 μm, 2.5 μm and 10 μm, respectively) concentrations, a high volume sampler (HVS, Model CAV-A/MSb, MCV) with a $PM_{2.5}$ head, and an indoor air quality meter (IAQ-Calc, Model 7545, TSI) for CO, CO_2, T and RH values. The instruments were placed at the end of the platform corresponding to the train entry point, far from the passengers' access-to-platform point, and behind a light fence for safety protection. This location was chosen as a compromise between meeting conditions for undisturbed measurement and obstructing commuter's path as little as possible. The aerosol inlets were placed at roughly 1.5 m above the ground level. Two protocols were undertaken concurrently during the study for continuous PM_X measurements: 1) additional measurements of PM_X concentrations on platforms to characterise spatial variations along the platform, and 2) monitoring of air quality inside the trains (see Sections 2.3 and 2.4).

The high volume sampler, which permits the sequential sampling of 15 filters, was equipped with quartz microfiber filters and programmed to sample $PM_{2.5}$ over 19 h (from 5 a.m. to 12 p.m., subway operating hours) at a sampling flow rate of 30 $m^3\ h^{-1}$. A field blank was taken at each station. $PM_{2.5}$ concentrations were determined gravimetrically using a microbalance (Model XP105DR, Mettler Toledo) with a sensitivity of ±10 μg. The sampled filters were pre-equilibrated before weighing for at least 48 h in a conditioned room (20 °C and 50% relative humidity). The quartz filters were used only for gravimetric purpose in this study, however, a detailed chemical analysis will be performed in subsequent studies.

Continuous measurements (24 h day^{-1}) with a 5-minute time resolution were performed using the DustTrak monitor for PM_1, $PM_{2.5}$ and PM_{10} concentrations and the IAQ-Calc for CO_2 and CO concentrations, T and RH. CO concentrations were always below the detection limit (3 ppm) and hence they will not be further mentioned in this study. $PM_{2.5}$ concentrations provided by DustTrak monitor were corrected against the in-situ and simultaneous gravimetric $PM_{2.5}$ for each station. Levels of PM_1 and PM_{10} were corrected using the same correction factors obtained for $PM_{2.5}$. However, previous HVS-DustTrak intercomparisons for PM_1 and PM_{10} concentrations were done for the ambient outdoor air and weak correlations were obtained. The PM_{10} and PM_1 concentrations provided for the DustTrak monitor were undervalued and overvalued, respectively. Since the aerosol properties in the subway are different from the outdoor aerosol, the previously determined correlations are not suitable to correct the measurements. Therefore, in this study only the $PM_{2.5}$ concentrations are used in absolute terms.

In the urban background station of Palau Reial, continuous measurements were performed by a Laser Aerosol Spectrometer (Environmental Dust Monitor, Model EDM180, Grimm), with a 30-minute time resolution, corrected with in-situ and simultaneous measurements obtained with a high volume sampler (HVS, Model CAV-A/MSb, MCV), working for 24 h every third day.

2.3. Additional platform measurements

Measurements at the 4 selected platforms and at 20 additional platforms with wide variety of designs, from 6 subway lines, were carried

Table 2
Operating conditions for tunnel and platform ventilations.

Mode	Stations	Experimental period (week of each month)	Operating conditions			
			Day		Night	
			Platform	Tunnel	Platform	Tunnel
I.W	J, SC, T	1st and 3rd	St. Imp.	St. Ext.	No ventilation	Low Imp.
II.W	J, SC, T	2nd and 4th				Low Ext.
III.W	L	1st and 3rd	St. Imp. + Ext.	St. Imp. + Ext.	St. Imp. + Ext.	St. Imp. + Ext.
IV.W	L	2nd	Low Imp. + Ext.		Low Imp. + Ext.	
V.W	L	4th	St. Imp. + Ext.	Low Imp. + Ext.		Low Imp. + Ext.
I.C	J, SC, T	1st and 4th	Low Imp.	Low Extr.	No ventilation	Low Imp.
II.C	J, SC, T	2nd		No ventilation		
III.C	J, SC, T	3rd		Low Extr.		Low Ext.
IV.C	L	1st and 2nd	St. Imp. + Ext.	St. Imp. + Ext.	St. Imp. + Ext. (*)	St. Imp. + Ext.
V.C	L	3rd	Low Imp. + Ext.		Low Imp. + Ext. (*)	
VI.C	L	4th	St. Imp. + Ext.	Low Imp. + Ext.	St. Imp. + Ext. (*)	Low Imp. + Ext.

W: warmer period; C: colder period; J: Joanic station; SC: Santa Coloma station; T: Tetuan station; L: Llefià station; St: strong; Imp: impulsion; Ext: extraction; and (*): some fans switched off. Normal ventilation conditions marked in shadow.

out using a DustTrak monitor to obtain PM_1, $PM_{2.5}$ and PM_{10} concentrations with 5-second time resolution, enabling us to see the effect of trains and commuters movements. Out of the 24 stations, 4 were new stations (line 10) and the remaining were old stations (lines 1–5). The sampling protocol was as follows: the measurements at each station lasted for 1 h, divided into periods of 15 min in 4 positions approximately equidistant along the platform; the first measurement point was located at the sampling site (placed at the far end of the platform corresponding to the train entry point) for comparison with the average PM_X concentrations measured across the platform; additionally, in the colder period, the sampling in the first point was repeated during 5 min after the 4 positions as a control; a manual record of the exact arrival and departure times of the trains was kept; sampling was performed during weekdays between 9 a.m. and 2 p.m. Sampling was conducted twice in each season campaign (colder and warmer periods), resulting in 96 total sampling studies. In addition, in 12 old stations, in the colder period, measurements were performed once more to study the influence of the piston effect (with the ventilation mode II.C, Table 2) on the air quality of the platforms.

The PM_X concentrations reported in this study for the 4 selected stations are those corrected for spatial variation determined at each platform based on the aforementioned measurements (Table S1). The $PM_{2.5}$ correction factors for spatial variation obtained for the light-scattering laser photometer (DustTrak) data at Joanic, Santa Coloma, Tetuan and Llefià were 1.05, 0.71, 0.92 and 0.71 in the warmer period and 0.96, 1.06, 1.02 and 0.95 in the colder period, respectively. These values were obtained by dividing the average $PM_{2.5}$ concentrations in all station by the average $PM_{2.5}$ concentrations in the first point, located at the sampling site. In general, the factors indicate that levels measured at the sampling sites were very similar to the exposure levels of commuters waiting elsewhere along the platform, as factors were very close to 1, with the exceptions of Santa Coloma and Llefià, in the warmer period, in which exposure levels were around 40% higher in the far end of each platform.

2.4. Measurements inside the trains

Measurements inside the trains from 6 subway lines (L1, L2, L3, L4, L5 and L10) were carried out during a return trip along the whole subway line. PM_1, $PM_{2.5}$ and PM_{10} concentrations were measured using a DustTrak monitor. During the colder period, CO_2 concentrations were also monitored using an Indoor Air Quality meter (IAQ-Calc). The logging interval for all measurements was set at 5 s.

The measurements were performed from 10 a.m. on weekdays in duplicate at each route and were carried out in the middle of the central car of the train, with instrumentation being transported in a bag with the air uptake inlet placed at shoulder height when sitting. A manual record of the time when train doors open and close was performed. During the colder period of the campaign, measurements were carried out along the whole length of the line with and without air conditioning (not possible during warmer period due to passengers comfort requirements).

3. Results and discussion

3.1. PM_X concentrations on platforms

3.1.1. Influence of outdoor environment

The PM_X mass concentrations discussed in this section are those determined by the DustTrak instrument and corrected against gravimetric measurements. Fig. 1 shows a comparison between the average $PM_{2.5}$ concentrations on the subway platforms and outdoor, considering all day data and only operating hours data. Some outliers in the DustTrak time series were identified and associated with occasional, mostly night-time, maintenance or cleaning operations, and were included in the analysis of daily concentrations. In any case the most relevant data are those measured during subway operating hours, due to the commuters' exposure to PM.

$PM_{2.5}$ concentrations on the platforms were significantly higher than those in the outdoor environment. The average concentrations were 1.3–6.1 and 1.3–6.7 times higher on the platforms than outdoors for all day period and in the operating hours period, respectively. The outdoor PM concentrations do not seem to influence significantly the air quality in the subway stations, since most of the PM load in the underground stations is generated within the subway system, due to the abrasion and wear of rail tracks and wheels caused by the motion of the trains as well as to the braking systems (Querol et al., 2012). In Stockholm the exposure levels for $PM_{2.5}$ were 5–10 times higher than the corresponding values measured on the busiest streets in that city (Johansson and Johansson, 2003).

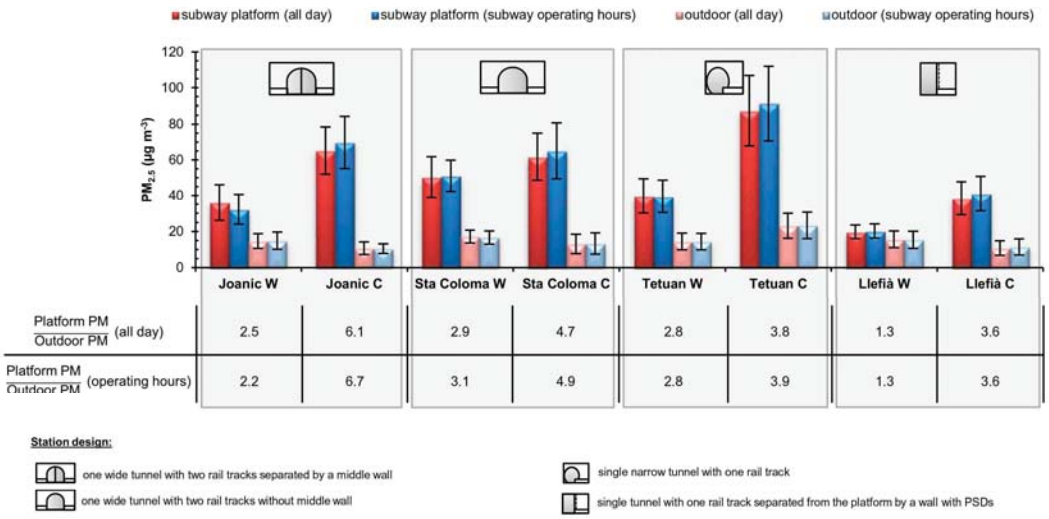


Fig. 1. Average $PM_{2.5}$ concentrations and standard deviations on the subway platforms and outdoor in both periods, and the ratios of $PM_{2.5}$ concentrations with respect to the outdoor levels (W — warmer period; C — colder period).

3.1.2. Comparison at different periods

Average $PM_{2.5}$ concentrations during operating hours were generally higher than those corresponding to the all day, which indicates the importance of $PM_{2.5}$ sources related to the subway operation activities. The opposite trend was only observed during the warmer period in Joanic when night-time maintenance or cleaning operations were more intense, generating larger amounts of $PM_{2.5}$ during non-operating hours (Fig. 1). Average $PM_{2.5}$ concentrations for operating hours on Joanic, Santa Coloma, Tetuan and Llefià subway platforms were 32, 51, 40 and 20 μg m^{-3} in the warmer period, and 70, 65, 91 and 41 μg m^{-3} in the colder period, respectively. Highest concentrations occurred thus during the colder period, mainly due to platform ventilation differences between seasons. The new station (Llefià) showed on average $PM_{2.5}$ concentrations lower (around 50%) than the old stations (Joanic, Santa Coloma and Tetuan), which is probably attributable to the design of the stations, but also due to the less train frequency and more advanced ventilation setup. Nieuwenhuijsen et al. (2007) mentioned that the high levels of PM could be observed in underground environments resulting from the generation or accumulation of PM in a confined space, particularly in old subway systems.

3.1.3. Daily patterns

Average intra-day variations of PM_X and CO_2 concentrations are plotted versus the train traffic frequency separately for weekdays, Saturdays and Sundays on the Joanic and Llefià platforms in Fig. 2, for both warmer and colder periods. Similar daily trends of PM_X and CO_2 concentrations were observed among the conventional stations (Joanic, Santa Coloma and Tetuan), only Joanic is shown as example in Fig. 2.

The PM_X daily pattern during weekdays of the warmer period presents a concentration increase in the morning with the arrival of the first trains until the maximum concentration at around 6 a.m., when the ventilation rate increased. From then the PM_X concentration decreased towards a rather stable concentration throughout the day. With the reduction of the ventilation rate at around 9 p.m. the PM_X levels rise again until midnight (when the trains operation stops) and tends to decrease during the night. In the conventional stations, increases in PM_X concentration up to a factor of 2 were observed around 3 a.m., and they were associated with occasional night-time maintenance or cleaning operations. However, for Joanic W (Fig. 2) there were higher average concentrations during the night than during subway operating hours, mainly due to the intense maintenance works or cleaning operations, as previously discussed. The CO_2 concentrations can also have a slight peak caused by the workers' exhalation and by the use of machinery. The highest peak of CO_2 concentrations on weekdays was found in the morning rush hour between 7 and 9 a.m., due to the higher influx of commuters. The commuters generate CO_2 through exhalation and at the same time they lead to the re-suspension of the PM_X created by walking. On weekends it is possible to observe the same pattern in relation to the ventilation rate. On Saturday, the PM_X levels only decrease after 2 a.m., when the trains stop operating, and on the night of Saturday to Sunday the PM_X concentration decreases gradually as the train frequency also decreases, which shows the train frequency influence in the absence of strong ventilation. Hence, the daily pattern of PM_X and CO_2 concentrations was primarily influenced by the ventilation settings and secondarily by the train frequency. The PM_X concentrations on the platforms are the result of a dynamic system controlled by the train frequency (source) and ventilation settings (removal), however, it is evident that the impact of train frequency on PM_X levels only becomes relevant when lower ventilation rates occur (Fig. 2).

In the colder period it is possible to observe that the stable and relatively low concentration registered in the warmer period (with stronger ventilation) is replaced by higher concentrations that tend to increase during the day, especially during weekend, reflecting the increasing number of trains, and probably enhanced by the accumulation of particles in the station caused by the weaker ventilation during this time of the year. During night-time however the pattern was very similar to the one described above for the warmer period.

The results in Llefià station (equipped with PSDs) for the warmer period showed that its stronger ventilation systems can achieve much lower and stable PM_X concentrations on the platforms, with only a slighter increase of PM levels between 6 and 9 a.m. especially during weekdays. Again, in the colder period, the daily pattern of PM_X concentrations presents higher and less stable values during the whole week due to the lower ventilation rates.

Regarding the three PM_X size fractions, the PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ ratios were lower in the warmer period (Fig. 2), indicating that the ventilation of the subway system was more efficient removing coarser particles. Thus, the PM_1 were the principal size fraction composing the PM in the subway system, especially during the warmer period.

On the platforms, the PM_X concentrations were lower during weekends, probably due to the lower frequency of trains, as Aarnio et al. (2005) and Johansson and Johansson (2003) observed in the Helsinki and Stockholm subway systems, respectively. The average weekday values were between 1.2 and 1.5 times higher than those measured on weekends. Averages, maximum and minimum $PM_{2.5}$ concentrations for operating hours and standard deviations for the four stations are summarized in Table S2 for weekdays and weekends.

3.1.4. Influence of different ventilation settings

Regarding ventilation settings, several protocols (Table 2) were tested during weekly periods to detect PM_X concentration differences and determine the best operating conditions for optimizing the air quality on the platforms. The ventilation modes varying during day/night and platform/tunnel, were the same for the three old stations monitored, being Joanic (old) shown as example in Fig. 3, together with Llefià (new, with PSDs system).

Generally, on the old platforms, when comparing the I.W and II.W modes (Table 2, with different ventilation in tunnel at night) higher PM_X concentrations were recorded in the situation II during night-time hours (see shadow area in Fig. 3a, b), evidencing that the impulsion of outdoor air was more efficient than the extraction of indoor air for air quality purposes. The same effect of ventilation result was obtained during the I.C and III.C modes, also with different ventilation in tunnel at night (only I.C mode shown in Fig. 3c). Note that the general concentrations during the colder period were higher, attributed to the lower daytime ventilation than in the warmer period, as previously discussed. The ventilation mode II.C (Fig. 3d) was tested to observe if the piston effect (with no additional mechanical ventilation in the tunnel) produced by the movement of the trains was enough to reach a good air quality inside the subway system. On average the $PM_{2.5}$ concentrations were around 29% higher during this week compared to the levels observed with the normal ventilation in the colder period (I.C mode).

On Llefià platform, the ventilation III.W and IV.W modes resulted in similar diurnal patterns (only III.W mode shown in Fig. 3e) and the V.W mode resulted in higher PM_X concentrations during all day (Fig. 3f). These results revealed that changes in the ventilation settings on the platform did not influence the air quality in the station, while the opposite was observed for the tunnel ventilation, demonstrating that only the changes in the tunnel ventilation were relevant in the air quality within the new system.

There were no differences among the ventilation modes tested in the colder period (IV.C, V.C and VI.C), but the use of a lower number of fans on the platforms resulted in higher PM_X concentrations.

3.1.5. Spatial and temporal variations along platforms

Some clear spatial and temporal trends were obtained among all measurements, although in some platforms there were day-to-day fluctuations in PM_X concentrations. Representative cases are discussed below (Fig. 4), whereas all the results for $PM_{2.5}$ are displayed in Table S1. As mentioned before, the PM_X concentration on the platforms was generally lower in the warmer period, when compared with the

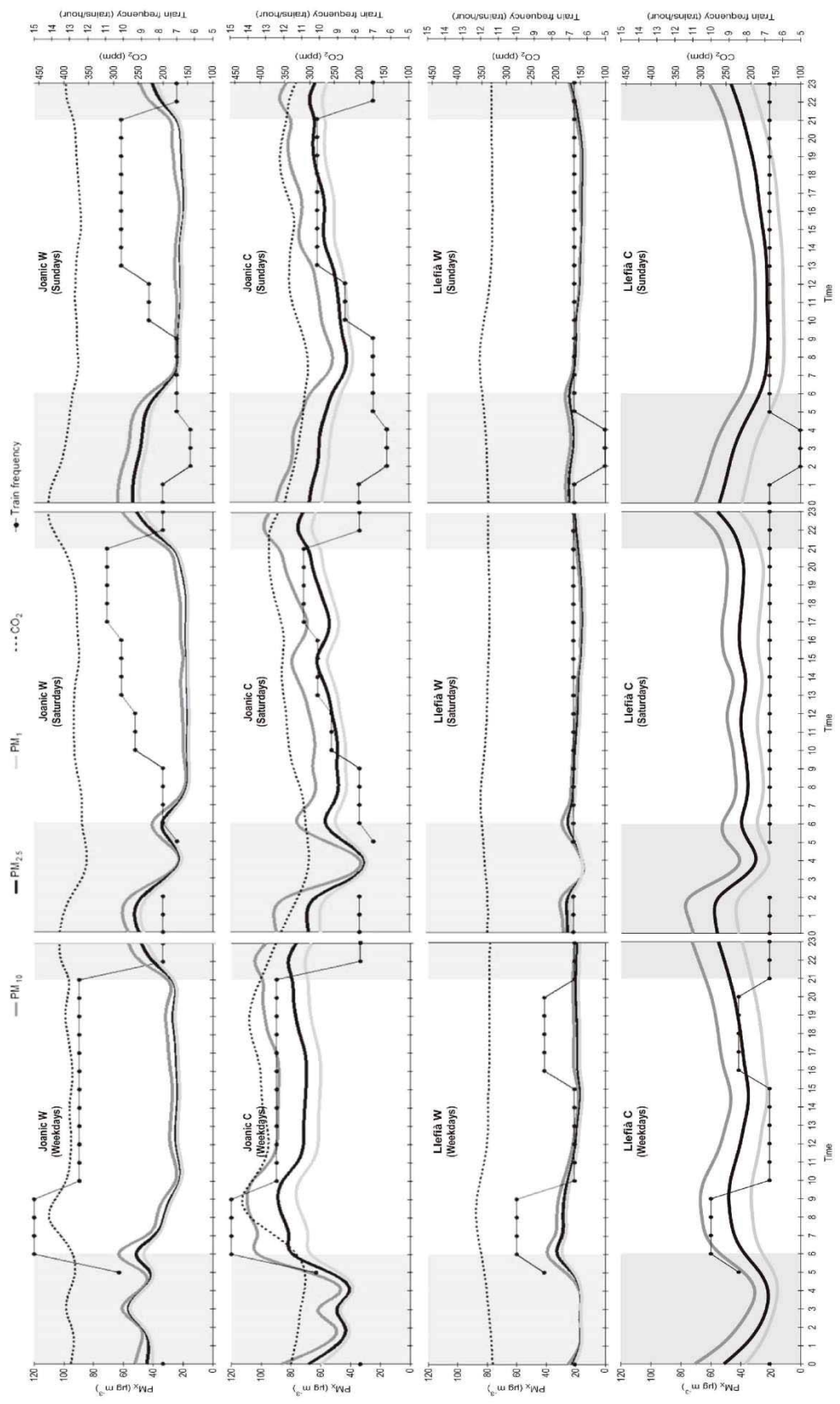


Fig. 2. Relation between the train frequency per hour and the hourly average PM_{10}, $PM_{2.5}$, PM_1 and CO_2 concentrations on the subway platforms of Joanic (old) and Llefià (new) stations, during weekdays, Saturdays and Sundays in both periods (W — warmer period; C — colder period). The (lower) night ventilation is highlighted in grey. See text for details.

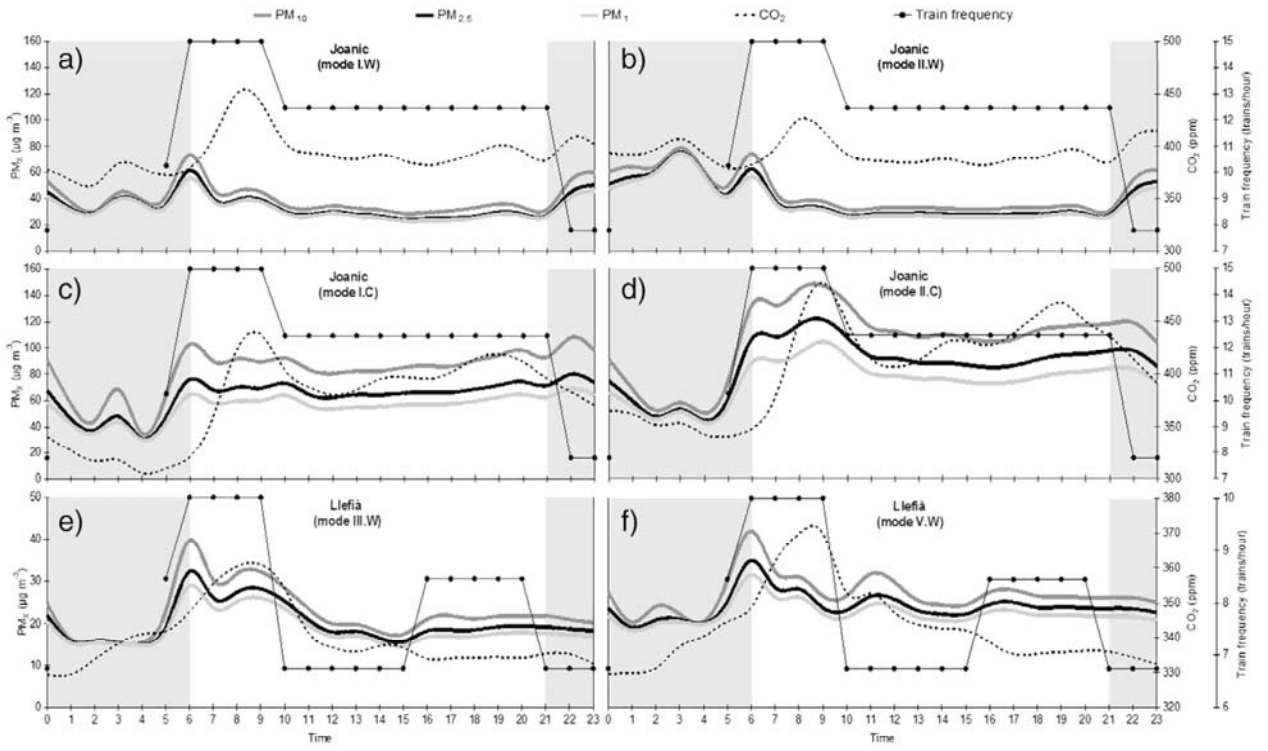


Fig. 3. Hourly average PM_{10}, $PM_{2.5}$, PM_1 and CO_2 concentrations and train frequency on the subway platforms of Joanic and Llefià stations with different ventilation settings. The night ventilation is highlighted in grey (W — warmer period; C — colder period).

colder period, due to the increased use of ventilation throughout the station diluting PM_X (Figs. 4a, b, 5). In addition in colder period, the PM_X concentrations on the platforms were generally more variable in shorter time scales (five second periods) ranging for example from 33 to 133 μg $PM_{2.5}$ m^{-3} in Joanic station.

High time resolution PM_X measurements evidenced that PM_X concentrations on the platform increased when the train entered the platform pushing in polluted air from the tunnel (by piston effect) and decreased when it departed. While the train was stopped in the station the PM_X concentration on the platform was kept stable, due to polluted air introduced by piston effect and PM_X generated by resuspension. The decrease of PM_X concentrations when the train left the station can also be explained by the reverse piston effect as the train moves polluted air from the station, renewing the air of the platform. The same PM_X time patterns were described by Salma et al. (2007) for the Budapest subway, although different patterns were found in other study (Ma et al., 2014). The passage of trains was a very important factor in the PM_X concentrations on some platforms, being especially strong in the new stations (Fig. 4c) and with single rail track (Fig. 4d). In some stations with two rail tracks without middle wall (Fig. 4e, f) this pattern was also observed but in general less frequently.

In some stations, higher PM_X mass concentrations, especially the coarse particles, were recorded at one end of the platform, coinciding with the train entry edge, and a clear decreasing trend for PM_X concentrations was observed along the platform (Fig. 4c). This variation can be attributed to the turbulence generated by the trains entry, due to the wind blasts caused by the trains when they pull into the stations.

The results obtained in the new lines equipped with PSDs showed that this system, despite being an effective security barrier, does not prevent completely air exchange between the railway and the platform. Therefore, the PM_X values were also influenced by the arrival and departure of trains similarly to older platforms.

Gorg station, which is located in the end of one of the new lines and has an uncommon design (directly connected with the street level in the P4 location), also shows high PM_X concentrations at the point of entry and exit of the train (P1, Fig. 4g) caused by the trains' motion. Smaller concentration peaks were observed along the rest of the platform related to the open PSDs while the train was stopped, allowing air exchanges between the tunnel and the platform. In any case the PM_X concentrations in the rest of the platform were lower than those measured in other stations, which can be strongly influenced by outdoor air that may enter the station, influencing the dilution of PM_X.

In the areas closer to the passengers' access to the platforms there is also a high probability of air turbulences, created by the commuters walking and the air flowing in and out of the station. This turbulence can cause PM_X resuspension, which explains the higher mass concentrations measured in these points at Llucmajor and Encants stations (Fig. 4e, f), as it has already been described by Moreno et al. (2014). However, due to the design of both stations (one wide tunnel with two rail tracks without middle wall) it is impossible to assure if the nearest point of entry of the train had also influence in these results. More specific measurements will be required in these cases.

Measurements carried out with normal ventilation used in the colder period (C1) and without ventilation in the tunnel (C2, as the II.C ventilation mode in Table 2), allowed evidencing different spatial variation of PM_X concentrations in some stations (Fig. 4d, h). When the ventilation of the tunnel was turned off (i.e. only piston effect ventilation, Table S1), average PM_X concentrations on the platform were 26% higher than those registered on a fully operational ventilation system, indicating an accumulation of PM_X in the tunnel. This percentage was very similar to the result obtained for the extensive campaigns on the four platforms studied on daily basis (29%).

Overall, a substantial variation in PM_X concentrations between distinct subway stations was observed (averages ranging from 13 to

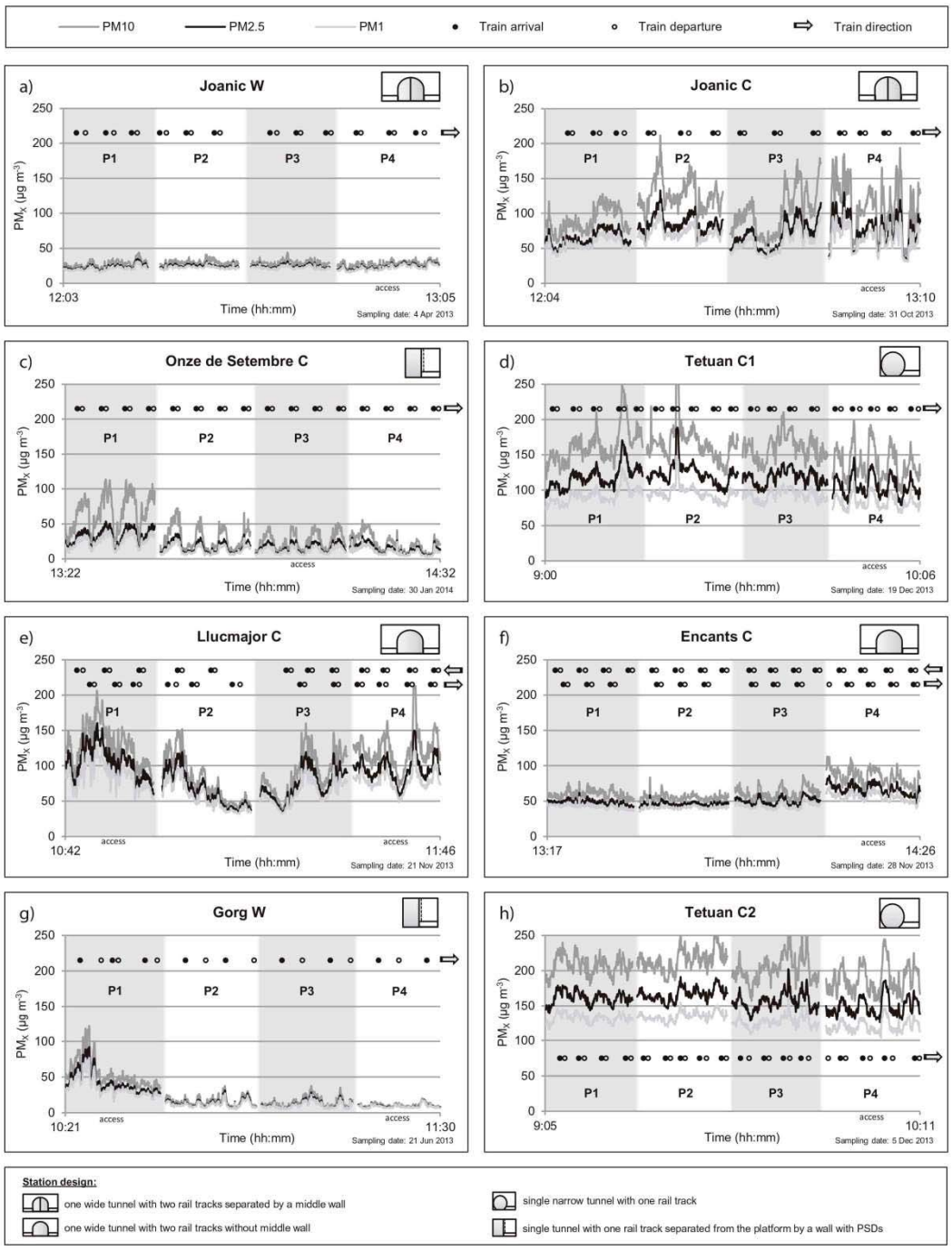


Fig. 4. Concentrations profiles of PM_{10}, $PM_{2.5}$ and PM_1 on selected platforms at 4 different sites (P1, P2, P3 and P4). Locations of accesses to platforms, train arrival/departure and direction are indicated (W — warmer period; C — colder period).

154 μg m^{-3} of $PM_{2.5}$, Table S1. — excluding the piston effect measurements) and this might be related to the differences in the length and design of the stations and tunnels, variations in the train frequency, passenger densities and ventilation systems, among other factors (Moreno et al., 2014 and references therein). In general, the stations composed by a single tunnel with one rail track separated from the platform by a wall with PSDs (new system) showed on average $PM_{2.5}$ concentrations lower (around 50%) than the conventional system (Fig. 5), as previously mentioned (Section 3.1.2). Among the conventional system, the stations with single narrow tunnel and one rail track showed on average $PM_{2.5}$ concentrations higher than those observed in stations with one wide tunnel and two rail tracks separated by a middle wall. The stations with one wide tunnel and two rail tracks without middle wall presented average PM_X concentrations much more variable (Fig. 5).

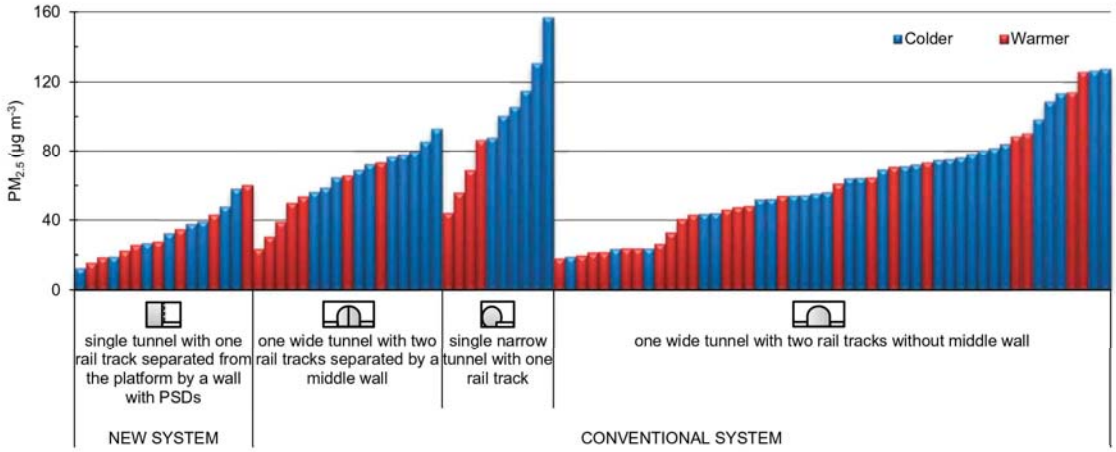


Fig. 5. Average $PM_{2.5}$ concentrations for colder and warmer periods of measurements sorted by subway station design categories.

3.2. PM_X concentrations inside the trains

All measurements carried out inside trains from 6 different lines are shown in Table 3. Lines 1–5 are the oldest ones whereas line 10 is one of the newest, most technologically advanced lines with more efficient mechanical ventilation system. $PM_{2.5}$ concentrations inside the trains in line 10 were on average 2.2 times lower than in the rest of the lines (Table 3). Repetition of measurements showed important variations in some cases (Table 3) indicating a possible dependency on variables such as the number of passengers (not counted in this campaign) although measurements were done at the same hours of the day. Regarding seasonal variations, there was not a regular variability among all results, perhaps influenced by changes of the air filters in the trains (the trains are fitted with air filters coupled to the air conditioning system that are changed monthly). A future study will be performed taking into account the changes of the filters and analysing their influence in the PM_X measurements to obtain a conclusive result.

From the measurements carried out with and without air conditioning, it is possible to conclude that the air conditioning had a clear effect on both concentration and variability of PM_X inside the trains. The results indicate that the ventilation system provides a clear abatement of PM concentrations inside the trains (Fig. 6), resulting in lower PM_X concentrations (by around 47% for $PM_{2.5}$) and finer particles (around 15% finer). Similarly, a study in Hong Kong also reported that the filter in the air-conditioning system was supposed to be capable of removing the larger portion of coarse particles (Chan et al., 2002a).

The PM_X and CO_2 concentration profiles during trips inside trains showed dissimilar behaviours (Fig. 6). Generally, the PM_X concentrations monitored along the lines presented temporary increases after the train doors close in a number of cases, possibly due to turbulence and consequent PM re-suspension produced by the movement of passengers inside the train. The CO_2 concentration profile was most probably proportional to the number of passengers inside the carriages of the trains. Hence the CO_2 concentrations presented always the maximum peak in the central part of each line, coinciding with the maximum influx of people.

3.3. Comparison with other studies

Table 4 shows a comparison of the average $PM_{2.5}$ concentrations on subway platforms worldwide with the results of this study. $PM_{2.5}$ levels measured in the conventional system were in the range of those measured in Budapest (Salma et al., 2007), Helsinki (Aarnio et al., 2005), Los Angeles (Kam et al., 2011a), New York (Wang and Gao, 2011), Mexico (Mugica-Álvarez et al., 2012) and Paris (Raut et al., 2009), and were lower than those from London (Seaton et al., 2005), Buenos Aires (Murruni et al., 2009) and Shanghai (Ye et al., 2010). The average $PM_{2.5}$ value referred by Kim et al. (2012) to the PSDs system present also in Seoul was relatively higher than the result obtained in the current study for a similar system (L10). The PM concentrations found in the present study were lower than those found in a previous study performed in July 2011 in 2 stations of Barcelona subway (Querol et al., 2012) for both conventional and new systems.

Given that the lowest PM_X concentrations were found in the new line both on the platforms and inside the trains, it is possible to conclude that PM_X levels inside the trains were affected by the surrounding

Table 3
Average $PM_{2.5}$ concentrations inside the trains in both periods of measurements.

	Warmer period		Colder period		
	Sampling date	$PM_{2.5}$ (µg m^{-3})	Sampling date	$PM_{2.5}$ (µg m^{-3})	
		With air conditioning		With air conditioning	Without air conditioning
Line 1	05 Jul 2013	74.8	11 Feb 2014	42.1	58.9
Line 1 repetition	19 Jul 2013	59.5	04 Mar 2014	38.9	56.6
Line 2	09 May 2013	34.4	26 Nov 2013	37.5	77.1
Line 2 repetition	16 May 2013	30.2	17 Dec 2013	46.4	98.8
Line 3	24 May 2013	43.8	11 Nov 2013	62.9	75.5
Line 3 repetition	29 May 2013	49.4	09 Dec 2013	71.6	90.9
Line 4	08 Apr 2013	29.3	29 Oct 2013	63.2	87.1
Line 4 repetition	19 Apr 2013	51.1	18 Nov 2013	43.9	72.9
Line 5	12 Jun 2013	43.3	20 Jan 2014	19.2	27.7
Line 5 repetition	28 Jun 2013	41.2	24 Feb 2014	39.1	47.1
Line 10	05 Jun 2013	30.7	14 Jan 2014	23.6	30.1
Line 10 repetition	20 Jun 2013	20.3	27 Jan 2014	18.6	21.2

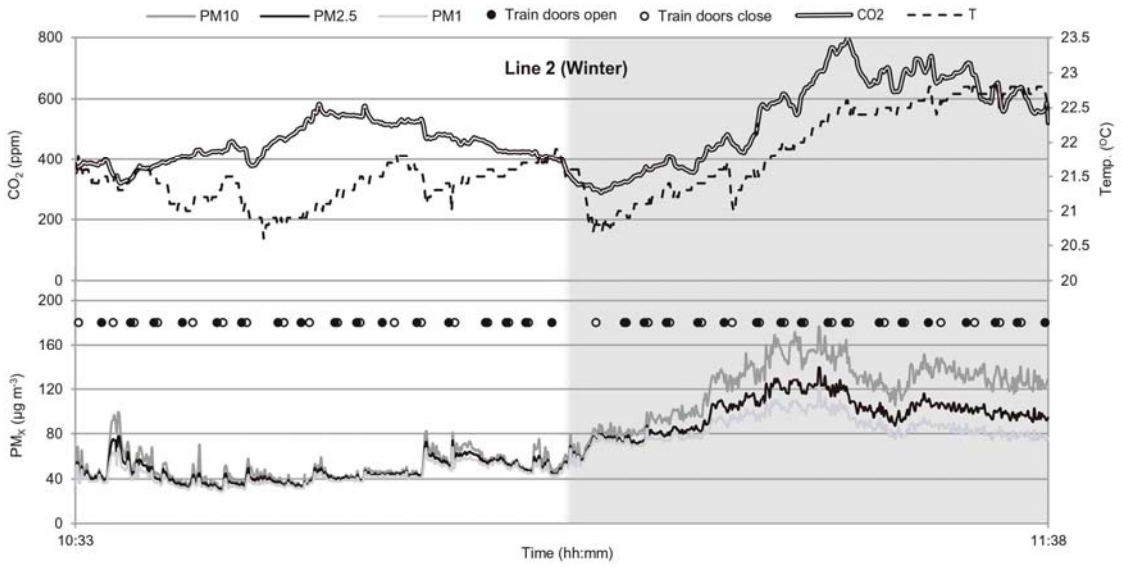


Fig. 6. PM_X, CO_2 concentrations and temperature measured inside the train of line 2, with and without (grey area) air conditioning.

conditions, such as those on the platforms. Hence, air exchange between platforms and the inside of the trains occurred when doors were open with the consequent exchange of air pollutants. Table 4 presents the $PM_{2.5}$ levels inside the trains for different subway systems worldwide. $PM_{2.5}$ levels inside the trains in the conventional Barcelona subway system are lower than those measured in Seoul (Kim et al., 2008; Park and Ha, 2008), Beijing (Li et al., 2007) and London (Seaton et al., 2005), and similar to those measured in Mexico (Gómez-Perales et al., 2004) and New York (Chillrud et al., 2004). The average $PM_{2.5}$ levels of the remaining subway systems referred in Table 4 are more similar to the value obtained for the new system. Both in the conventional and new systems the average concentrations inside the trains found in the present study were higher than those from the previous study in Barcelona (Querol et al., 2012).

Comparing the results with previous worldwide studies measuring the concentrations of PM_X on subway platforms and inside the trains, there is a remarkable variation among respective results. This could be explained by differences in the monitoring conditions such as the time, place, or season of the measurements, the differences in the length and design of the stations and tunnels, the system age, the wheels and rail-track materials, the type of brake mechanism, the train speed and frequency, the measurement equipment used, the ventilation systems, the passenger density, among other factors (Moreno et al., 2014 and references therein). Therefore, the results are not always directly comparable because of differences in sampling methods, data analysis, duration of the measurements and the type of environment studied (Nieuwenhuijsen et al., 2007).

The $PM_{2.5}$ concentrations inside the trains were lower (around 15%) than those on station platforms (Table 4). These measurements results can be explained by PM that was re-suspended on platforms due to train or commuter movement. Moreover, PM concentrations can also be diluted rapidly via the air conditioners inside the trains as the space is confined during operation. Nieuwenhuijsen et al. (2007) implicated the air conditioning in trains as a possible factor favouring low PM levels inside the trains.

3.4. $PM_{2.5}$ exposure during subway commuting

The $PM_{2.5}$ exposure was calculated taking into account all data obtained during both the intensive campaign on the 4 selected stations and the additional 20 platform measurements. Regarding the measurements inside the trains, the data used were obtained in the commuters normal conditions during the warmer period (with air conditioning) and without air conditioning in the colder period for the exposure calculations.

For a subway commuting travel of 30 min in the train and 5 min on the platform, the average $PM_{2.5}$ exposure would reach 53 µg m^{-3}. This value was reduced to 27 µg m^{-3} in the case of line 10, whereas for L1, L2, L3, L4 and L5 lines the exposures were 66, 62, 67, 59 and 40 µg m^{-3}, respectively. The average commuter exposure levels for the warmer and colder periods among all lines were 43 and 63 µg m^{-3} of $PM_{2.5}$, respectively, emphasizing that in the colder period the commuters are exposed to worse air quality when commuting. When air conditioning was switched on, a decrease of 32% of $PM_{2.5}$ exposure levels was reached, being an effective approach to reduce exposure levels.

It has been recognized in several studies that concentrations inside the trains are lower than in subway stations (Chillrud et al., 2004; Aarnio et al., 2005; Seaton et al., 2005; Braniš, 2006), suggesting that time spent in stations may be a better predictor of personal exposure than total time spent underground. The exposure is repeated almost every day for most commuters, which may cause cumulative or chronic health effects over time. Nevertheless, higher health risks for sensitive groups, such as children, the elderly, and individuals with pre-existing health conditions exacerbated by air pollution (many respiratory and cardiovascular diseases) may be significant, even for short periods spent in underground environment (Salma et al., 2007). Train drivers and other workers, who spend several hours a day within the underground subway are subject to higher exposure to PM_X levels than the commuting public and thus possibly greater health risks. In a study of PM exposure of pregnant women in Barcelona, a train/subway source contribution was identified, and its contribution was found not related to the time spent during commuting but only to the fact of using the subway, pointing to a maximum exposure on the platform, as opposed to inside the train (Minguillón et al., 2012).

The average $PM_{2.5}$ exposure during subway commuting in Barcelona obtained in the current study is higher than that reported (26 µg m^{-3}) by Querol et al. (2012), which might be related to the higher amount of measurements carried out in this study. Comparing to subway systems worldwide, the $PM_{2.5}$ exposure obtained in the current study was also higher than that reported in Mexico (33 µg m^{-3}; Gómez-Perales et al., 2007), Taipei (35 µg m^{-3}; Tsai et al., 2008), Hong Kong (33 µg m^{-3}; Chan et al., 2002a) and Guanzhou (44 µg m^{-3}; Chan et al., 2002b),

Table 4
Comparison of $PM_{2.5}$ concentrations measured on platforms and inside the trains at different subway systems worldwide.

Measurement environment	City	$PM_{2.5}$ (μg m^{-3})		Reference
		Range (min–max)	Average	
On the platform	Budapest	–	51	Salma et al. (2007)
	Helsinki	23–103	60	Aarnio et al. (2005)
	London	–	270–480	Seaton et al. (2005)
	Los Angeles	9–130	57	Kam et al. (2011a)
	New York	60–77	68	Wang and Gao (2011)
	New York	–	62	Chillrud et al. (2004)
	Buenos Aires	–	152–270	Murruni et al. (2009)
	Mexico	41–67	48	Mugica-Álvarez et al. (2012)
	Paris	–	61–93	Raut et al. (2009)
	Seoul	82–176	129	Kim et al. (2008)
	Seoul	–	105	Park and Ha (2008)
	Seoul	39–129	66	Kim et al. (2012)
	Seoul PSDs[a]	20–166	58	
	Shanghai	–	287	Ye et al. (2010)
	Stockholm WD[b]	105–388	258	Johansson and Johansson (2003)
	Stockholm WE[c]	24–334	185	
	Taipei	7–100	35	Cheng et al. (2008)
	Barcelona L3[d]	110–186	125	Querol et al. (2012)
	Barcelona L9[e]	12–99	46	
	Barcelona L1, L2, L3, L4 and L5[d]	18–154	66	Current study
	Barcelona L10[e]	13–61	32	
Inside the train	Beijing	–	113	Li et al. (2007)
	Beijing	13–111	37	Li et al. (2006)
	Guangzhou	–	44	Chan et al. (2002b)
	Helsinki	17–26	21	Aarnio et al. (2005)
	Hong Kong	21–48	33	Chan et al. (2002a)
	London	–	130–200	Seaton et al. (2005)
	Los Angeles	11–62	24	Kam et al. (2011b)
	Mexico	31–99	57	Gómez-Perales et al. (2004)
	Mexico	8–68	–	Gómez-Perales et al. (2007)
	New York	34–44	40	Wang and Gao (2011)
	New York	–	62	Chillrud et al. (2004)
	Seoul	115–136	126	Kim et al. (2008)
	Seoul	–	117	Park and Ha (2008)
	Sydney	–	36	Knibbs and de Dear (2010)
	Taipei	8–68	32	Cheng et al. (2008)
	Taipei	3–48	24	Cheng et al. (2012)
	Barcelona L3 and L5[d]	17–32	25	Querol et al. (2012)
	Barcelona L9[e]	11–18	15	
	Barcelona L1, L2, L3, L4 and L5[d]	28–99	57	Current study
	Barcelona L10[e]	20–31	26	

[a] PSDs—platform screen doors.
[b] WD—weekdays.
[c] WE—weekends.
[d] Conventional system.
[e] New system.

and lower than that referred for London (202 μg m^{-3}; Adams et al., 2001) and New York (62 μg m^{-3}; Chillrud et al., 2004).

In addition, an assessment on $PM_{2.5}$ exposure for different commuting modes reported in several studies worldwide (Querol et al., 2012 and references therein) was done to compare the data obtained in the present study. The $PM_{2.5}$ exposure while commuting by bus and passenger car reached values in the range of 33–75 μg m^{-3} and 22–83 μg m^{-3}, respectively, comparable to those reported for subway commuting in Barcelona during this study (27–67 μg m^{-3}). Cycling/motorbike and pedestrian commuting were reported with $PM_{2.5}$ exposure levels of 68–88 and 63 μg m^{-3}, respectively, being markedly higher than in the Barcelona subway.

4. Conclusions

Subway aerosol particles have been monitored in Barcelona on diverse platform stations and inside the trains, focusing on particulate matter mass concentration. The following main conclusions were drawn:

- PM_X concentrations on the platforms were higher than those in outdoor environment approximately 1.3–6.7 times, revealing the prevalence of PM sources on the platform and tunnel level.
- The new system (L10) with PSDs showed on average PM_X concentrations lower (around 50%) than the conventional system (L1–L5).
- The measured $PM_{2.5}$ concentrations on all types of platforms were lower or in the range of other reported subway systems worldwide.
- The measurements in the warmer period (strong ventilation) showed lower concentrations than in the colder period (weak ventilation). Variations in PM_X levels in different seasons were thus clearly influenced by the ventilation system. This suggests that an appropriate ventilation mode should be applied to the subway system to obtain both PM reduction and energy saving.
- The piston effect alone (with no additional mechanical ventilation in the tunnel) produced by the movement of the trains was not an effective approach to obtain a good air quality in the subway system.

- PM_X concentrations displayed a typical diurnal cycle during the weekdays, driven by the ventilation settings and secondarily by the train frequency.
- Both lower PM_X concentrations and less marked cycles were observed on Saturdays and Sundays.
- Real-time measurements of PM_X showed temporal and spatial variations along the platforms, related to the differences in the time, place, or season of the measurements, design of the stations and tunnels, variations in the train frequency, passenger densities and ventilation systems, among other factors.
- The use of air conditioning inside the trains was an effective approach to reduce exposure levels. The PM_X concentrations inside the trains were lower (around 15%) than those on station platforms.
- The ventilation and air conditioning systems were more efficient removing coarse particles, resulting in a relatively fine-dominated PM in the subway system.
- This study shows that the time spent commuting in the subway system can contribute substantially to total daily exposure to $PM_{2.5}$ and be associated with adverse health effects.

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Appendix A. Supplementary data

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References

Aarnio, P., Yli-Tuomi, T., Kousa, A., Mäkelä, T., Hirsikko, A., Hämeri, K., et al., 2005. The concentrations and composition of and exposure to fine particles ($PM_{2.5}$) in the Helsinki subway system. Atmos. Environ. 39 (28), 5059–5066.

Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., McMullen, M.A.S., Khandelwal, P., 2001. Fine particle ($PM_{2.5}$) personal exposure levels in transport microenvironments, London, UK. Sci. Total Environ. 279 (1–3), 29–44.

Braniš, M., 2006. The contribution of ambient sources to particulate pollution in spaces and trains of the Prague underground transport system. Atmos. Environ. 40 (2), 348–356.

Chan, L.Y., Lau, W.L., Lee, S.C., Chan, C.Y., 2002a. Commuter exposure to particulate matter in public transportation modes in Hong Kong. Atmos. Environ. 36 (21), 3363–3373.

Chan, L.Y., Lau, W.L., Zou, S.C., Cao, Z.X., Lai, S.C., 2002b. Exposure level of carbon monoxide and respirable suspended particulate in public transportation modes while commuting in urban area of Guangzhou, China. Atmos. Environ. 36 (38), 5831–5840.

Cheng, Y.-H., Lin, Y.-L., 2010. Measurement of particle mass concentrations and size distributions in an underground station. Aerosol Air Qual. Res. 22–9.

Cheng, Y.-H., Lin, Y.-L., Liu, C.-C., 2008. Levels of PM_{10} and $PM_{2.5}$ in Taipei Rapid Transit System. Atmos. Environ. 42 (31), 7242–7249.

Cheng, Y.-H., Liu, Z.-S., Yan, J.-W., 2012. Comparisons of PM_{10}, $PM_{2.5}$, particle number, and CO_2 levels inside metro trains between traveling in underground tunnels and on elevated tracks. Aerosol Air Qual. Res. 879–891.

Chillrud, S.N., Epstein, D., Ross, J.M., Sax, S.N., 2004. Elevated airborne exposures to manganese, chromium and iron of teenagers from steel dust and New York City's subway system. Environ. Sci. Technol. 38 (3), 732–737.

Chillrud, S.N., Grass, D., Ross, J.M., Coulibaly, D., Slavkovich, V., Epstein, D., et al., 2005. Steel dust in the New York City subway system as a source of manganese, chromium, and iron exposures for transit workers. J. Urban Health 82 (1), 33–42.

Colombi, C., Angius, S., Gianelle, V., Lazzarini, M., 2013. Particulate matter concentrations, physical characteristics and elemental composition in the Milan underground transport system. Atmos. Environ. 70, 166–178.

Fromme, H., Oddoy, A., Piloty, M., Krause, M., Lahrz, T., 1998. Polycyclic aromatic hydrocarbons (PAH) and diesel engine emission (elemental carbon) inside a car and a subway train. Sci. Total Environ. 217 (1–2), 165–173.

Furuya, K., Kudo, Y., Okinaga, K., Yamuki, M., Takahashi, S., Araki, Y., et al., 2001. Seasonal variation and their characterization of suspended particulate matter in the air of subway stations. J. Trace Microprobe Tech. 19 (4), 469–485.

Gómez-Perales, J.E., Colvile, R.N., Nieuwenhuijsen, M.J., Fernández-Bremauntz, A., Gutiérrez-Avedoy, V.J., Páramo-Figueroa, V.H., et al., 2004. Commuters' exposure to $PM_{2.5}$, CO, and benzene in public transport in the metropolitan area of Mexico City. Atmos. Environ. 38 (8), 1219–1229.

Gómez-Perales, J.E., Colvile, R.N., Fernández-Bremauntz, A.A., Gutiérrez-Avedoy, V., Páramo-Figueroa, V.H., Blanco-Jiménez, S., et al., 2007. Bus, minibus, metro inter-comparison of commuters' exposure to air pollution in Mexico City. Atmos. Environ. 41 (4), 890–901.

Gustavsson, P., Bigert, C., Pollán, M., 2008. Incidence of lung cancer among subway drivers in Stockholm. Am. J. Ind. Med. 547 (51), 545–547.

Johansson, C., Johansson, P.-A., 2003. Particulate matter in the underground of Stockholm. Atmos. Environ. 37, 3–9.

Jung, H.-J., Kim, B., Ryu, J., Maskey, S., Kim, J.-C., Sohn, J., et al., 2010. Source identification of particulate matter collected at underground subway stations in Seoul, Korea using quantitative single-particle analysis. Atmos. Environ. 44 (19), 2287–2293.

Kam, W., Cheung, K., Daher, N., Sioutas, C., 2011a. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. Atmos. Environ. 45 (8), 1506–1516.

Kam, W., Ning, Z., Shafer, M.M., Schauer, J.J., Sioutas, C., 2011b. Chemical characterization and redox potential of coarse and fine particulate matter (PM) in underground and ground-level rail systems of the Los Angeles Metro. Environ. Sci. Technol. 45 (16), 6769–6776.

Karlsson, H.L., Ljungman, A.G., Lindbom, J., Möller, L., 2006. Comparison of genotoxic and inflammatory effects of particles generated by wood combustion, a road simulator and collected from street and subway. Toxicol. Lett. 165 (3), 203–211.

Karlsson, H.L., Holgersson, A., Möller, L., 2008. Mechanisms related to the genotoxicity of particles in the subway and from other sources. Chem. Res. Toxicol. 21 (3), 726–731.

Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM_{10} and $PM_{2.5}$) in Seoul Metropolitan Subway stations. J. Hazard. Mater. 154 (1–3), 440–443.

Kim, K.-H., Ho, D.X., Jeon, J.-S., Kim, J.-C., 2012. A noticeable shift in particulate matter levels after platform screen door installation in a Korean subway station. Atmos. Environ. 49, 219–223.

Knibbs, L.D., de Dear, R.J., 2010. Exposure to ultrafine particles and $PM_{2.5}$ in four Sydney transport modes. Atmos. Environ. 44 (26), 3224–3227.

Levy, J.I., Houseman, E. a, Ryan, L., Richardson, D., Spengler, J.D., 2000. Particle concentrations in urban microenvironments. Environ. Health Perspect. 108 (11), 1051–1057.

Li, T.-T., Bai, Y.-H., Liu, Z.-R., Liu, J.-F., Zhang, G.-S., Li, J.-L., 2006. Air quality in passenger cars of the ground railway transit system in Beijing, China. Sci. Total Environ. 367 (1), 89–95.

Li, T.-T., Bai, Y.-H., Liu, Z.-R., Li, J.-L., 2007. In-train air quality assessment of the railway transit system in Beijing: a note. Transp. Res. Part D: Transp. Environ. 12 (1), 64–67.

Ma, H., Shen, H., Liang, Z., Zhang, L., Xia, C., 2014. Passengers' exposure to $PM_{2.5}$, PM_{10}, and CO_2 in typical underground subway platforms in Shanghai. Lect. Notes Electr. Eng. 237–245.

Minguillón, M.C., Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Figueras, F., et al., 2012. Source apportionment of indoor, outdoor and personal $PM_{2.5}$ exposure of pregnant women in Barcelona, Spain. Atmos. Environ. 59, 426–436.

Moreno, T., Pérez, N., Reche, C., Martins, V., de Miguel, E., Capdevila, M., et al., 2014. Subway platform air quality: assessing the influences of tunnel ventilation, train piston effect and station design. Atmos. Environ. 92, 461–468.

Mugica-Álvarez, V., Figueroa-Lara, J., Romero-Romo, M., Sepúlveda-Sánchez, J., López-Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. Atmos. Environ. 49, 284–293.

Murruni, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., et al., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. Atmos. Environ. 43 (30), 4577–4583.

Nieuwenhuijsen, M.J., Gómez-Perales, J.E., Colvile, R.N., 2007. Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. Atmos. Environ. 41 (37), 7995–8006.

Park, D.-U., Ha, K.-C., 2008. Characteristics of PM_{10}, $PM_{2.5}$, CO_2 and CO monitored in interiors and platforms of subway train in Seoul, Korea. Environ. Int. 34 (5), 629–634.

Pope III, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., et al., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease. Circulation 109 (1), 71–77.

Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., et al., 2012. Variability of levels and composition of PM_{10} and $PM_{2.5}$ in the Barcelona metro system. Atmos. Chem. Phys. 12 (11), 5055–5076.

Raut, J.-C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. Atmos. Environ. 43 (4), 860–868.

Ripanucci, G., Grana, M., Vicentini, L., Magrini, A., Bergamaschi, A., 2006. Dust in the underground railway tunnels of an Italian town. J. Occup. Environ. Hyg. 3 (1), 16–25.

Salma, I., Weidinger, T., Maenhaut, W., 2007. Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. Atmos. Environ. 41 (37), 8391–8405.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London Underground: dust and hazards to health. Occup. Environ. Med. 62 (6), 355–362.

Tsai, D.-H., Wu, Y.-H., Chan, C.-C., 2008. Comparisons of commuter's exposure to particulate matters while using different transportation modes. Sci. Total Environ. 405 (1–3), 71–77.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., et al., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. J. Aerosol Sci. 39 (10), 827–849.

Wang, X. (Richard), Gao, H.O., 2011. Exposure to fine particle mass and number concentrations in urban transportation environments of New York City. Transp. Res. Part D: Transp. Environ. 16 (5), 384–391.

Ye, X., Lian, Z., Jiang, C., Zhou, Z., Chen, H., 2010. Investigation of indoor environmental quality in Shanghai metro stations, China. Environ. Monit. Assess. 167 (1–4), 643–651.

Supplementary data

Article 1

Exposure to airborne particulate matter in the subway system

Appendix A. Supplementary data

Table S1
Average $PM_{2.5}$ concentrations and standard deviations (μg m^{-3}) on the subway platforms for the different points of measurements (P1 train entrance – P4) in both periods. Locations of accesses to platforms are highlighted in grey. Platform measurements with the ventilation mode II.C (piston effect only) are underlined.

				Measurements											
Sampling			Stations	P1		P2		P3		P4		P1 repetition		all station	
Subway line	Period	Date		average	sd	average	sd	average	sd	average	sd	average	sd	average	sd
L4	Warmer	4 Apr 2013	Trinitat Nova	27.6	1.6	26.8	1.9	29.6	2.5	37.5	3.9	-		30.6	5.1
			Llucmajor	25.8	3.5	27.1	3.0	28.0	1.7	25.5	4.0	-		26.5	3.4
			Joanic	22.9	3.7	24.5	2.0	24.1	2.4	23.5	3.7	-		23.7	3.2
			Verdaguer	27.9	3.2	31.3	4.3	28.7	2.4	33.9	5.6	-		30.5	4.8
		17 Apr 2013	Trinitat Nova	40.6	1.7	46.9	3.1	55.5	4.2	62.0	4.7	-		51.0	9.0
			Llucmajor	49.3	3.2	40.2	2.3	31.9	2.6	41.3	5.2	-		40.9	7.1
			Joanic	36.6	2.8	40.1	4.6	43.5	4.4	37.0	4.6	-		39.3	5.0
			Verdaguer	65.2	2.8	65.8	3.5	48.2	7.2	37.9	7.3	-		54.0	12.9
	Colder	31 Oct 2013	Trinitat Nova	36.2	5.3	35.7	3.9	34.8	2.5	38.4	2.8	37.1	4.6	36.3	4.1
			Llucmajor	51.4	7.5	43.7	4.2	47.8	8.2	80.0	18.5	43.5	3.7	54.6	17.6
			Joanic	64.3	10.5	84.8	12.9	68.5	19.0	74.0	21.7	84.7	9.0	73.7	18.1
			Verdaguer	62.9	8.9	85.2	8.9	68.9	7.3	102.8	16.1	79.1	10.7	79.8	18.3
		7 Nov 2013	Trinitat Nova	63.7	10.2	62.8	6.7	58.8	4.2	64.6	3.2	64.0	4.4	62.6	6.8
			Llucmajor	54.8	4.5	63.9	17.9	50.7	4.8	48.4	7.6	32.7	3.0	52.5	12.9
			Joanic	84.0	10.2	77.5	7.2	73.2	16.7	76.9	32.5	82.2	9.6	78.3	18.9
			Verdaguer	71.9	12.2	61.3	5.7	70.2	10.2	88.0	13.1	70.7	11.8	72.6	14.1
		21 Nov 2013	Trinitat Nova	33.8	3.7	30.6	2.3	31.4	2.0	40.3	4.2	29.5	2.0	33.6	5.0
			Llucmajor	103.2	23.2	63.8	23.6	72.0	20.9	95.0	17.1	50.2	7.4	80.7	27.3
			Joanic	65.9	8.8	61.7	11.1	63.3	12.5	65.3	22.4	72.7	8.8	65.1	14.2
			Verdaguer	55.7	8.1	55.3	5.4	51.3	5.6	71.0	10.5	66.2	8.5	59.1	10.8
L1	Warmer	3 Jul 2013	Sta Coloma	121.0	27.6	96.4	23.3	80.8	16.3	53.3	7.3	-		88.9	32.4
			Catalunya	146.4	11.7	156.5	14.3	152.0	20.7	139.8	11.6	-		148.6	16.2
			Rocafort	70.3	11.9	70.9	5.5	76.7	10.5	66.1	5.7	-		71.0	9.6
			Torrassa	164.3	25.2	121.0	39.1	79.9	22.4	92.6	18.0	-		114.2	42.3
		17 Jul 2013	Sta Coloma	131.0	27.4	101.2	21.0	68.1	14.7	60.4	12.7	-		90.4	34.7
			Catalunya	142.9	10.2	151.0	18.8	134.7	10.4	123.4	7.4	-		138.1	16.0
			Rocafort	68.6	7.4	73.8	6.8	76.1	7.2	76.6	5.3	-		73.7	7.5
			Torrassa	139.6	34.8	134.0	43.8	117.6	26.6	112.7	21.5	-		125.9	34.4
	Colder	13 Feb 2014	Sta Coloma	63.3	13.7	54.2	8.5	60.8	8.7	46.4	6.3	50.6	6.2	55.6	11.3
			Catalunya	104.2	6.3	102.2	8.6	101.1	5.6	97.4	4.5	102.8	4.3	101.4	6.7
			Rocafort	64.4	5.3	63.3	6.0	51.5	6.2	71.0	17.1	83.7	6.8	64.4	13.2
			Torrassa	111.3	63.0	184.8	76.1	135.5	43.4	96.3	26.7	75.7	6.0	127.6	64.2
		20 Feb 2014	Sta Coloma	72.5	8.0	70.8	9.2	77.2	6.6	111.3	17.0	71.8	7.9	82.1	19.5
			Catalunya	111.6	6.5	113.6	8.7	108.6	5.0	110.2	5.0	107.6	5.8	110.7	6.8
			Rocafort	53.5	6.5	54.3	3.7	76.5	19.5	89.4	18.1	77.7	9.5	69.6	20.0
			Torrassa	88.8	11.7	70.5	10.8	80.3	9.6	76.7	19.9	73.5	13.8	78.7	15.1
		6 Mar 2014	Sta Coloma	76.2	6.4	68.6	6.1	85.5	10.2	82.0	11.0	65.8	4.2	76.6	11.0
			Catalunya	104.8	10.6	97.0	6.9	94.7	6.3	96.7	6.0	97.9	4.3	98.2	8.2
			Rocafort	47.6	10.3	44.1	5.5	46.2	4.5	39.2	6.2	45.3	7.6	44.3	7.7
			Torrassa	97.9	41.0	62.0	35.9	70.9	24.0	45.8	7.0	95.0	31.7	71.4	35.7

				Measurements											
Sampling			Stations	P1		P2		P3		P4		P1 repetition		all station	
Subway line	Period	Date		average	sd	average	sd	average	sd	average	sd	average	sd	average	sd
L2	Warmer	6 May 2013	Tetuan	96.1	9.8	91.2	10.6	88.8	13.2	72.1	4.8	-		86.7	13.5
			Passeig de Gràcia	76.1	10.9	69.0	10.2	66.8	6.1	64.6	10.3	-		69.1	10.5
			Bac de Roda	47.3	2.2	47.8	1.7	47.5	1.2	48.6	2.2	-		47.8	1.9
			Encants	47.7	1.6	49.5	2.4	49.6	2.9	47.1	3.9	-		48.5	3.0
		17 May 2013	Tetuan	59.5	7.2	62.8	10.3	55.8	6.4	46.4	6.6	-		56.2	9.8
			Passeig de Gràcia	51.9	7.1	40.2	6.0	45.6	11.9	39.9	5.9	-		44.4	9.5
			Bac de Roda	21.4	2.8	21.9	2.7	20.7	1.2	22.3	4.6	-		21.6	3.1
			Encants	24.5	2.8	21.4	1.5	21.1	1.3	20.2	1.9	-		21.8	2.5
	Colder	28 Nov 2013	Tetuan	107.2	10.8	114.8	17.7	99.2	9.5	101.3	13.9	103.8	9.3	105.6	14.2
			Passeig de Gràcia	114.0	12.9	105.1	13.9	94.8	9.8	92.2	7.5	93.7	9.2	100.6	14.0
			Bac de Roda	49.8	8.5	57.8	5.2	53.8	6.3	57.9	6.9	48.6	9.3	54.4	7.9
			Encants	48.1	3.5	45.9	2.4	49.9	5.3	66.4	7.6	44.6	2.5	52.2	9.6
		5 Dec 2013	Tetuan	161.6	9.3	166.7	9.1	156.3	12.1	148.7	13.2	143.9	10.9	156.9	13.4
			Passeig de Gràcia	132.9	9.9	132.1	8.8	128.1	5.7	130.3	24.1	132.9	9.8	130.9	13.9
			Bac de Roda	127.5	43.2	91.5	4.5	85.4	2.6	88.8	3.9	97.6	12.9	98.4	27.0
			Encants	95.6	8.6	77.8	4.5	76.4	3.8	82.2	3.7	95.7	4.9	84.5	9.9
		19 Dec 2013	Tetuan	118.2	15.6	122.9	15.1	118.1	10.7	105.0	14.3	106.3	8.4	115.0	15.3
			Passeig de Gràcia	112.4	21.0	84.2	12.0	80.7	7.8	75.5	6.9	84.1	9.1	88.0	18.9
			Bac de Roda	62.8	7.6	74.0	3.5	71.1	2.1	75.6	4.1	89.1	5.7	72.5	8.7
			Encants	70.2	3.0	74.9	2.6	78.1	2.9	78.6	6.1	76.7	3.2	75.6	5.0
L10 (PSDs)	Warmer	3 Jun 2013	Llefià	60.4	9.7	47.0	9.2	34.5	6.5	33.1	5.3	-		43.3	13.4
			Gorg	49.5	10.2	22.8	5.6	23.4	9.5	17.0	9.4	-		27.8	15.2
			La Sagrera	47.4	17.0	50.9	17.2	60.7	15.0	83.4	12.8	-		60.6	21.0
			Onze de Setembre	41.9	2.9	23.1	8.0	15.9	4.4	22.6	3.4	-		25.9	10.9
		21 Jun 2013	Llefià	32.0	8.6	23.1	7.3	16.6	6.9	19.3	6.8	-		22.5	9.4
			Gorg	41.2	15.1	12.6	4.9	11.1	5.0	9.1	2.4	-		19.0	15.9
			La Sagrera	11.5	2.1	15.0	1.9	14.7	1.8	22.6	10.6	-		16.0	7.0
			Onze de Setembre	49.8	5.8	39.0	14.0	24.2	6.0	26.7	3.9	-		34.9	13.2
	Colder	16 Jan 2014	Llefià	57.1	10.5	50.5	12.8	38.7	8.6	41.6	7.8	55.7	7.5	48.1	12.3
			Gorg	51.1	7.8	32.9	2.8	33.5	2.9	35.2	3.9	59.8	5.6	39.5	10.2
			La Sagrera	48.1	5.5	54.3	13.4	61.7	16.5	79.3	8.7	33.3	2.9	58.5	17.5
			Onze de Setembre	33.6	5.2	28.1	4.0	24.0	2.5	22.0	3.1	26.9	5.5	27.0	5.9
		30 Jan 2014	Llefià	33.7	4.8	34.0	7.1	38.0	12.6	27.6	2.5	26.7	2.3	32.7	8.4
			Gorg	25.2	11.2	9.0	1.5	6.4	1.5	8.3	4.0	15.7	4.0	12.8	9.5
			La Sagrera	10.2	6.0	13.8	7.9	37.0	24.6	91.1	39.7	52.1	18.5	38.1	37.9
			Onze de Setembre	32.5	11.2	16.1	7.9	15.5	6.4	13.5	6.9	20.6	9.2	19.5	11.1

Sampling			Stations	Measurements											
				P1		P2		P3		P4		P1 repetition		all station	
Subway line	Period	Date		average	sd	average	sd	average	sd	average	sd	average	sd	average	sd
L3	Warmer	22 May 2013	Liceu	50.0	7.8	57.1	9.1	55.6	10.4	55.4	7.3	-		54.2	9.4
			Poble Sec	63.3	10.5	69.3	8.7	69.7	5.8	75.4	3.5	-		69.4	9.2
			Sants Estació	58.9	7.6	61.2	6.6	50.3	5.8	55.0	4.3	-		56.6	7.6
			Lesseps	23.4	3.5	24.2	7.8	26.0	5.6	18.0	2.8	-		23.8	6.3
		27 May 2013	Liceu	56.9	10.4	54.4	4.2	75.8	16.7	63.4	16.7	-		61.4	15.0
			Poble Sec	84.7	12.6	74.1	11.4	77.6	11.6	69.8	5.3	-		77.0	12.2
			Sants Estació	52.5	5.4	51.4	5.9	47.7	5.5	50.0	4.0	-		50.3	5.6
			Lesseps	47.2	8.4	42.8	5.2	82.5	11.5	97.8	7.1	-		64.9	23.2
	Colder	14 Nov 2013	Liceu	78.8	8.1	70.7	6.5	63.3	5.2	88.1	21.3	74.5	14.0	75.2	15.1
			Poble Sec	86.6	11.2	92.8	16.1	88.4	18.1	77.0	5.7	81.2	15.1	85.8	14.9
			Sants Estació	62.9	9.3	71.8	6.1	63.6	6.6	60.4	6.8	79.1	13.4	66.0	10.0
			Lesseps	83.6	9.9	101.9	18.1	115.6	16.0	142.6	13.6	95.6	10.5	108.8	25.3
		12 Dec 2013	Liceu	103.3	31.0	109.8	4.0	153.9	142.6	134.0	16.2	139.0	7.6	126.5	73.1
			Poble Sec	144.9	15.5	156.8	15.3	164.7	10.9	151.7	8.1	143.5	13.4	153.6	14.9
			Sants Estació	102.9	11.5	97.5	8.8	94.0	7.7	83.7	8.5	79.6	9.2	93.2	12.1
			Lesseps	101.8	27.0	133.2	17.4	108.5	21.5	121.2	14.3	87.8	22.3	113.6	25.2
L5	Warmer	10 Jun 2013	El Coll La Teixonera	51.1	6.5	27.0	7.2	39.6	10.5	82.0	22.2	-		50.7	24.8
			Vilapicina	16.8	3.1	17.4	1.6	16.9	2.9	23.3	6.8	-		18.5	4.8
			Sagrada Família	35.8	7.9	24.7	5.4	19.0	4.2	15.8	3.1	-		23.8	9.3
			Cornellà Centre	22.3	4.9	18.1	3.1	18.6	3.5	21.6	3.3	-		20.2	4.2
		26 Jun 2013	El Coll La Teixonera	49.5	8.9	41.0	6.8	68.9	12.0	81.4	12.6	-		60.6	19.1
			Vilapicina	37.1	7.8	42.2	5.6	43.0	3.0	50.4	5.2	-		43.3	7.3
			Sagrada Família	54.7	20.3	47.3	20.6	43.3	7.0	39.9	3.9	-		46.3	15.9
			Cornellà Centre	36.3	3.5	29.9	4.0	29.6	3.5	36.6	14.3	-		33.1	8.4
	Colder	23 Jan 2014	El Coll La Teixonera	80.3	7.0	54.1	9.4	70.5	12.2	85.8	13.6	89.1	8.3	74.2	16.1
			Vilapicina	48.5	6.3	39.2	3.5	42.2	3.1	46.5	4.3	40.8	3.1	43.9	5.7
			Sagrada Família	65.5	5.4	63.6	11.5	49.7	5.8	47.4	8.8	54.4	6.9	56.4	11.3
			Cornellà Centre	23.1	2.9	19.2	2.6	17.5	1.3	18.6	2.2	18.3	2.0	19.5	3.1
		27 Feb 2014	El Coll La Teixonera	61.4	5.9	36.2	9.6	56.8	8.4	74.0	12.9	54.6	3.2	56.9	16.0
			Vilapicina	23.2	3.0	21.8	1.9	21.8	2.4	28.1	5.5	24.3	1.8	23.8	4.2
			Sagrada Família	99.8	21.9	85.7	18.6	41.2	3.7	35.7	4.5	53.2	3.3	64.6	30.0
			Cornellà Centre	26.2	3.0	21.9	2.8	21.0	1.2	23.1	2.3	27.7	2.7	23.5	3.4

Table S2
Average, standard deviation (sd) and range (min-max) of $PM_{2.5}$ mass concentrations (µg m^{-3}) for weekdays and weekends in the four selected stations in both periods (warmer and colder).

		Weekdays			Weekends		
Subway station	**Period**	**Average**	**Range (min-max)**	**sd**	**Average**	**Range (min-max)**	**sd**
Joanic	Warmer	35.1	21.7-50.3	7.5	24.0	21.3-31.1	3.6
	Colder	75.2	59.5-108.7	13.3	55.9	46.5-63.0	6.2
Santa Coloma	Warmer	54.3	41.4-68.8	7.4	42.8	34.6-55.7	6.6
	Colder	70.7	49.8-91.0	12.2	50.7	35.5-80.9	14.4
Tetuan	Warmer	42.9	30.7-58.7	7.7	30.8	23.1-40.1	5.9
	Colder	96.7	62.4-137.2	19.2	74.1	49.8-94.2	16.7
Llefià	Warmer	21.5	14.5-26.9	3.7	17.8	13.5-24.3	3.3
	Colder	42.9	33.3-67.0	7.9	34.7	27.2-54.2	10.2

Article 2

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

Vânia Martins, Teresa Moreno, María Cruz Minguillón, Barend L. van Drooge, Cristina Reche, Fulvio Amato, Eladio de Miguel, Marta Capdevila, Sonia Centelles, Xavier Querol

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Overview:

The present work assesses indoor air quality in stations of Barcelona subway system, characterising the $PM_{2.5}$ in terms of concentrations and their inorganic and organic chemical composition. The source apportionment of the $PM_{2.5}$ in the subway stations was carried by means of the Positive Matrix Factorization model.

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Invited paper

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

Vânia Martins [a, b, *], Teresa Moreno [a], María Cruz Minguillón [a], Barend L. van Drooge [a], Cristina Reche [a], Fulvio Amato [a], Eladio de Miguel [c], Marta Capdevila [c], Sonia Centelles [c], Xavier Querol [a]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain
[c] Transports Metropolitans de Barcelona, TMB Santa Eulàlia, Av. Del Metro s/n L'Hospitalet de Llobregat, 08902, Spain

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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.

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

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

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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 m^3 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 deionized water to extract the soluble fraction and analysed by ion chromatography for determination of soluble anions (Cl^-, SO_4^{2-}, and NO_3^-), and by specific electrode for ammonium (NH_4^+). A third portion of filter (1.5 cm^2) 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, dibuthyl 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-derivated 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 $\boldsymbol{X}$, containing n samples (rows) with m species (columns), into two submatrices, the chemical profiles $\boldsymbol{F}$ and the time series $\boldsymbol{G}$, so that p different sources of emissions or secondary components are identified and their contribution is quantified. The residual $\boldsymbol{E}$ matrix corresponds to the fraction of $\boldsymbol{X}$ not explained by the solution.

$$\boldsymbol{X} = \boldsymbol{GF} + \boldsymbol{E} \quad (1)$$

The $\boldsymbol{G}$ and $\boldsymbol{F}$ 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 jth species concentration measured in the ith sample, and σ_{ij} is the user defined uncertainty for the jth species in the ith 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 μg m^{-3}, for Joanic, Santa Coloma, Tetuan and Llefià stations, respectively (Fig. 1).

The lower $PM_{2.5}$ concentrations in Llefià 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 (Braniš, 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.

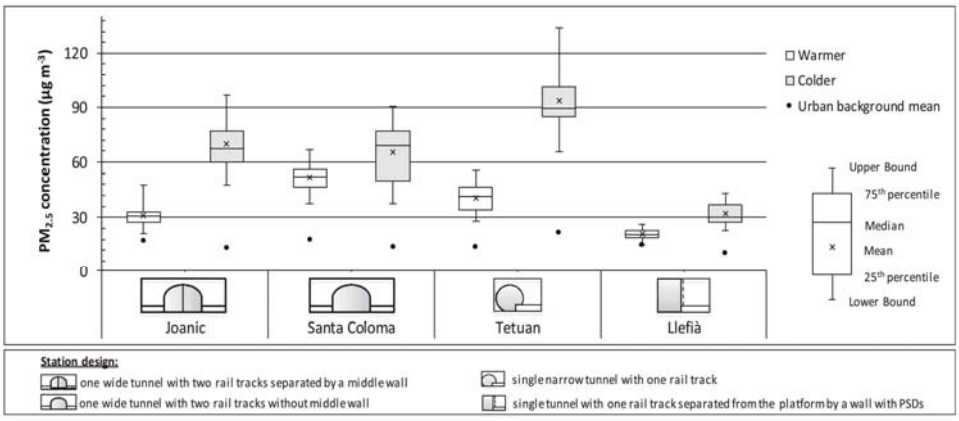

Fig. 1. $PM_{2.5}$ concentrations in the four subway platforms and at the urban background station during the warmer and colder periods.

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 SiO_2 was estimated by multiplying Al_2O_3 by a factor of 3. The CO_3^{2-} 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_2O_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_2O_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_2O	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_2O_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_2O_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 Fe_2O_3, 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 (Fe_2O_3); crustal matter (CM, the sum of Ca, Mg, Al_2O_3, SiO_2, CO_3^{2-}, K_2O, TiO_2 and P_2O_5); 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 $PM_{2.5}$ 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 $PM_{2.5}$, 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; Murruni 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 Llefià 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 μg m^{-3}, representing the second largest component of $PM_{2.5}$. 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 μg m^{-3} in the warmer period and from 2.9 to 8.2 μg m^{-3} in the colder period.

The SIC account for 2.0–10.2% of the total $PM_{2.5}$ 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 $PM_{2.5}$ 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 μg m^{-3} (Table 1). Higher relative amounts of insoluble SO_4^{2-} in the total $PM_{2.5}$ were observed in the warmer period (Table S2). The halite reached similar levels among the stations (0.2–0.8 μg 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 Llefià 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 Llefià 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 $PM_{2.5}$ 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 ∑PAH was 11 ng m^{-3}, in contrast to the moderated values found in other conventional stations (Joanic: $\sum PAH_{colder} = 4$ ng m^{-3}, Santa Coloma: $\sum PAH_{colder} = 6$ ng m^{-3}). The lowest colder time levels were observed in the station of the modern subway system, Llefià, where $\sum PAH_{colder} = 3$ ng m^{-3} and benzo[a]pyrene = 0.2 ng m^{-3}. The low cold-period PAHs concentrations found in Llefià are similar to those observed in the other stations during the warmer time (Table 2), while the levels in Llefià station in the warmer period were lower; $PAH_{warmer} = 1$ 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 Llefià station is probably a direct effect

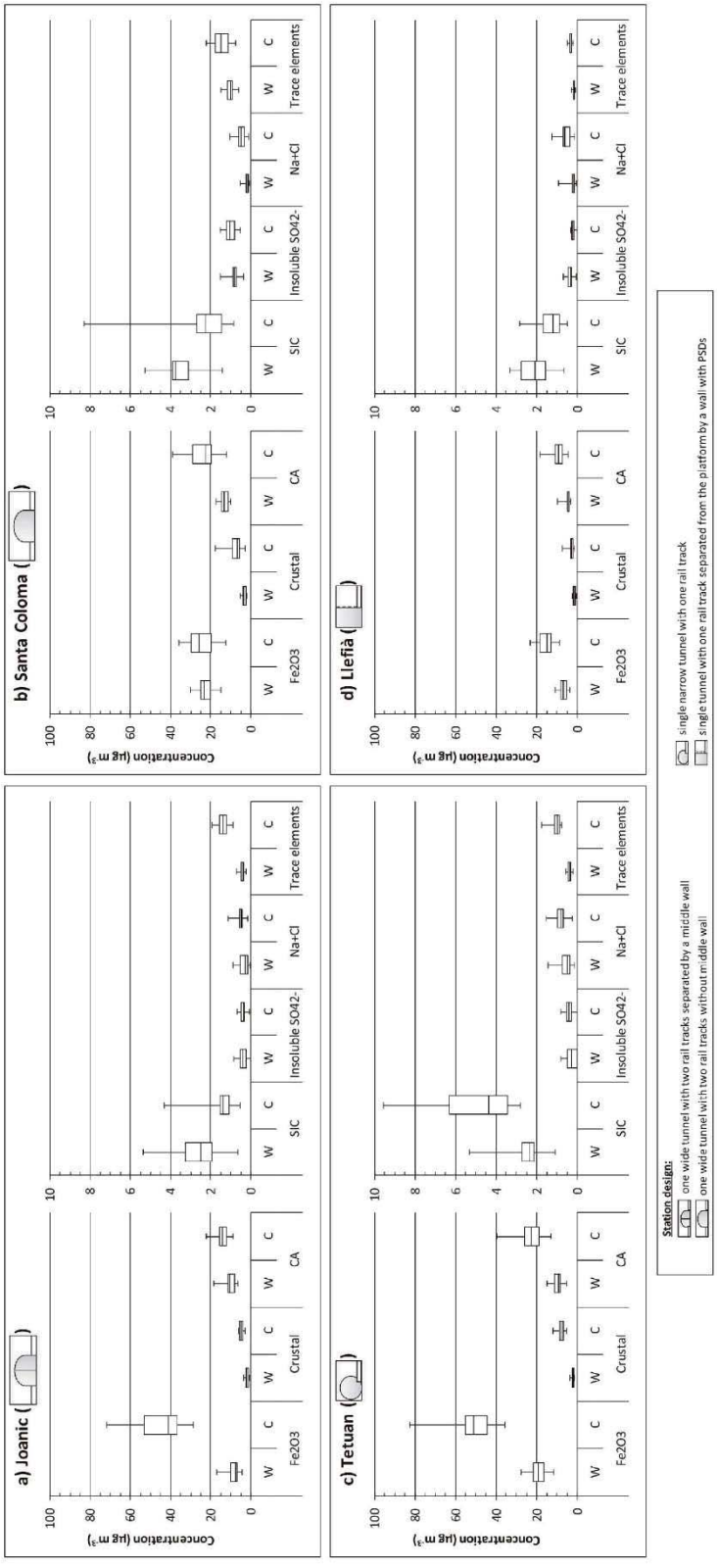

Fig. 2. $PM_{2.5}$ chemical components concentrations during the warmer and colder periods in the subway stations: a) Joanic; b) Santa Coloma; c) Tetuan; d) Llefià (W — warmer period; C — colder period). The line within the box shows the median, while the box bottom and top represent the 25th and 75th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

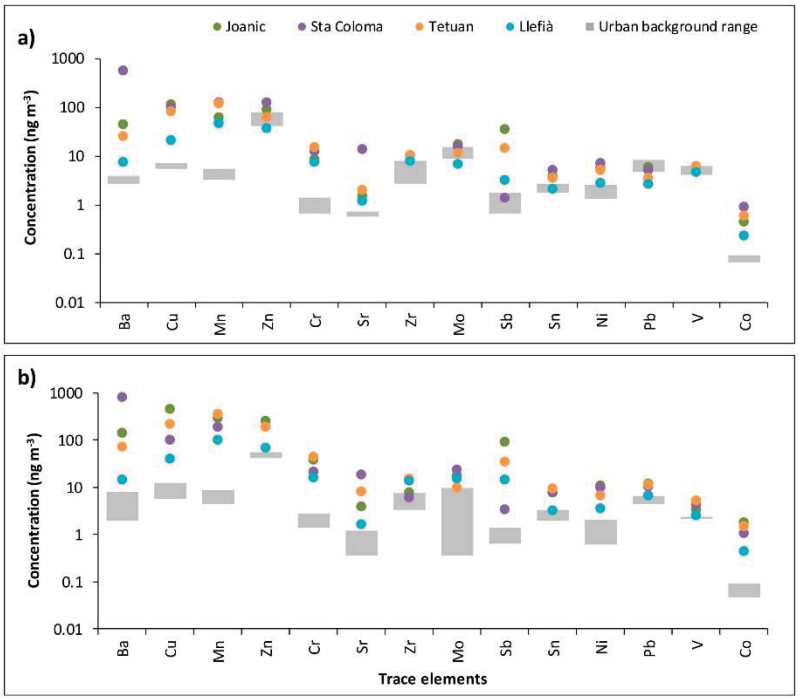

Fig. 3. Mean concentrations of trace elements (ng m^{-3}) for the four subway stations and the simultaneous urban background range (ambient site) a) in the warmer and b) in the colder periods.

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 Llefià 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		Llefià		Joanic		Santa Coloma		Tetuan		Llefià	
	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
Levoglucosan	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.

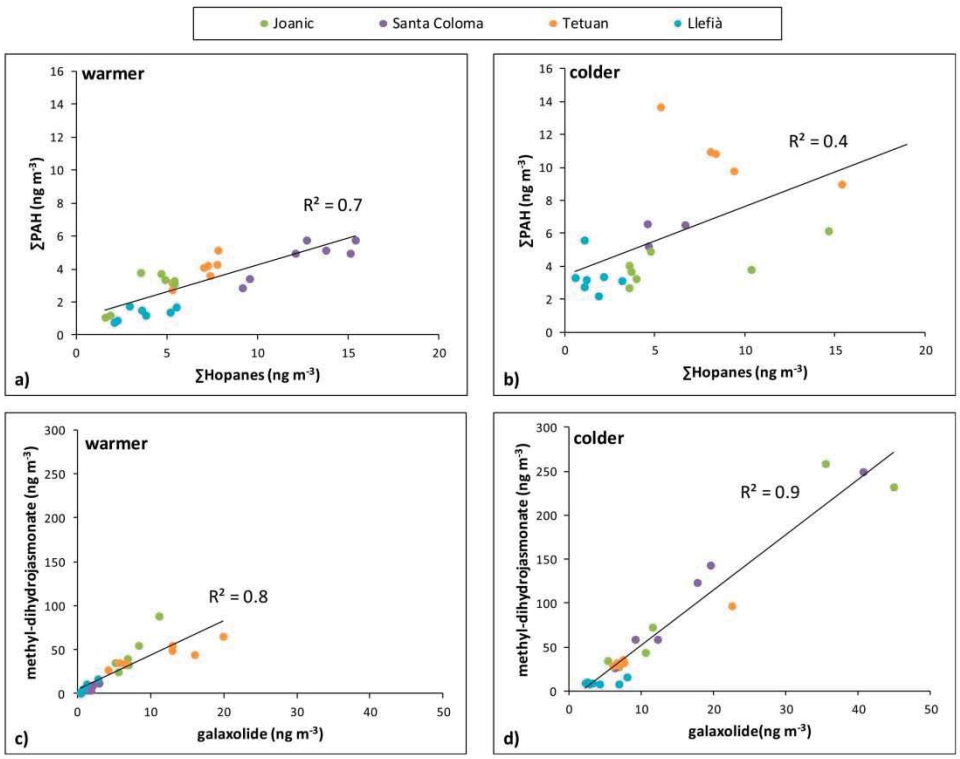

Fig. 4. Comparison of the analysed PAHs and Hopanes concentrations in the a) warmer and b) colder periods, and the methyl-dihydrojasmonate and galaxolide concentrations in the c) warmer and d) colder periods.

(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.

Levoglucosan 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: $R^2_{warmer} = 0.5$; $R^2_{colder} = 0.6$ for data of all stations). In the colder period there was a substantial correlation of PAHs with the outdoor tracer for biomass burning (levoglucosan: $R^2_{colder} = 0.5$). 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 ($R^2_{warmer} = 0.8$; $R^2_{colder} = 0.9$ 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 3
Contribution (μg m^{-3}) of the different sources found in the $PM_{2.5}$ 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 funghi (Simoneit et al., 2004). These compounds were detected in moderate concentrations, compared to typical outdoor concentrations, with the lowest concentrations in Llefià station (∑saccharides = 7 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.

Dibuthyl 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 $PM_{2.5}$ 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

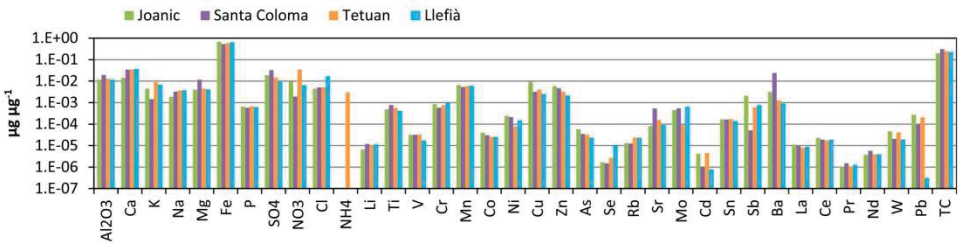

Fig. 5. Source profile of the subway source in Joanic, Santa Coloma, Tetuan and Llefià stations.

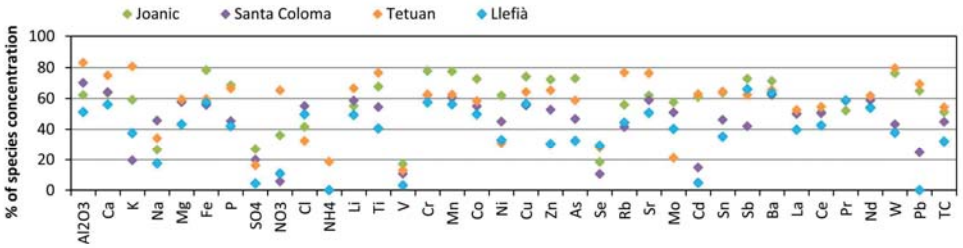

Fig. 6. Percent of species concentration apportioned by the subway source in Joanic, Santa Coloma, Tetuan and Llefià stations.

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 Llefià. 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, panthographs, etc) may result in an improvement of the particle ambient concentrations in the subway environment.

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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.

References

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

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

Agrawal, H., Malloy, Q.G.J., Welch, W.A., Wayne Miller, J., Cocker, D.R., 2008. In-use gaseous and particulate matter emissions from a modern ocean going container vessel. Atmos. Environ. 42, 5504–5510. http://dx.doi.org/10.1016/j.atmosenv.2008.02.053.

Alier, M., van Drooge, B.L., Dall'Osto, M., Querol, X., Grimalt, J.O., Tauler, R., 2013.

Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona (Spain) during SAPUSS. Atmos. Chem. Phys. 13, 10353–10371. http://dx.doi.org/10.5194/acp-13-10353-2013.

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

Bi, X., Sheng, G., Feng, Y., Fu, J., Xie, J., 2005. Gas- and particulate-phase specific tracer and toxic organic compounds in environmental tobacco smoke. Chemosphere 61, 1512–1522. http://dx.doi.org/10.1016/j.chemosphere.2005.04.057.

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

Braniš, M., 2006. The contribution of ambient sources to particulate pollution in spaces and trains of the Prague underground transport system. Atmos. Environ. 40, 348–356. http://dx.doi.org/10.1016/j.atmosenv.2005.09.060.

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

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

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merri, T., 2001. Comparison of IMPROVE and NIOSH carbon measurements. Aerosol Sci. Technol. 34, 23–34. http://dx.doi.org/10.1080/02786820119073.

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

Escrig, A., Monfort, E., Celades, I., Querol, X., Amato, F., Minguillón, M.C., Hopke, P.K., 2009. Application of optimally scaled target factor analysis for assessing source contribution of ambient PM10. J. Air Waste Manage. Assoc. 59, 1296–1307. http://dx.doi.org/10.3155/1047-3289.59.11.1296.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environ. Eng. Sci. 21, 387–409. http://dx.doi.org/10.1089/109287504323067021.

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

Grass, D.S., Ross, J.M., Family, F., Barbour, J., James Simpson, H., Coulibaly, D., Hernandez, J., Chen, Y., Slavkovich, V., Li, Y., Graziano, J., Santella, R.M., Brandt-Rauf, P., Chillrud, S.N., 2010. Airborne particulate metals in the New York City subway: a pilot study to assess the potential for health impacts. Environ. Res. 110, 1–11. http://dx.doi.org/10.1016/j.envres.2009.10.006.

Gustavsson, P., Bigert, C., Pollán, M., 2008. Incidence of lung cancer among subway drivers in Stockholm. Am. J. Ind. Med. 547, 545–547. http://dx.doi.org/10.1002/ajim.20584.

Johansson, C., Johansson, P.-A., 2003. Particulate matter in the underground of Stockholm. Atmos. Environ. 37, 3–9. http://dx.doi.org/10.1016/S1352-2310(02)00833-6.

Jung, H.-J., Kim, B., Malek, M.A., Koo, Y.S., Jung, J.H., Son, Y.-S., Kim, J.-C., Kim, H., Ro, C.-U., 2012. Chemical speciation of size-segregated floor dusts and airborne magnetic particles collected at underground subway stations in Seoul, Korea. J. Hazard. Mater. 213–214, 331–340. http://dx.doi.org/10.1016/j.jhazmat.2012.02.006.

Jung, H.-J., Kim, B., Ryu, J., Maskey, S., Kim, J.-C., Sohn, J., Ro, C.-U., 2010. Source identification of particulate matter collected at underground subway stations in Seoul, Korea using quantitative single-particle analysis. Atmos. Environ. 44, 2287–2293. http://dx.doi.org/10.1016/j.atmosenv.2010.04.003.

Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2013. A comparative assessment of PM2.5 exposures in light-rail, subway, freeway, and surface street environments in Los Angeles and estimated lung cancer risk. Environ. Sci. Process. Impacts 15, 234–243. http://dx.doi.org/10.1039/c2em30495c.

Kam, W., Ning, Z., Shafer, M.M., Schauer, J.J., Sioutas, C., 2011. Chemical characterization and redox potential of coarse and fine particulate matter (PM) in underground and ground-level rail systems of the Los Angeles Metro. Environ. Sci. Technol. 45, 6769–6776. http://dx.doi.org/10.1021/es201195e.

Kamani, H., Hoseini, M., Seyedsalehi, M., Mahdavi, Y., Jaafari, J., Safari, G.H., 2014. Concentration and characterization of airborne particles in Tehran's subway system. Environ. Sci. Pollut. Res. 21, 7319–7328. http://dx.doi.org/10.1007/s11356-014-2659-4.

Karlsson, H.L., Nilsson, L., Möller, L., 2005. Subway particles are more genotoxic than street particles and induce oxidative stress in cultured human lung cells. Chem. Res. Toxicol. 18, 19–23. http://dx.doi.org/10.1021/tx049723c.

Kim, K.-H., Ho, D.X., Jeon, J.-S., Kim, J.-C., 2012. A noticeable shift in particulate matter levels after platform screen door installation in a Korean subway station. Atmos. Environ. 49, 219–223. http://dx.doi.org/10.1016/j.atmosenv.2011.11.058.

Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM10 and PM2.5) in Seoul Metropolitan Subway stations. J. Hazard. Mater. 154, 440–443. http://dx.doi.org/10.1016/j.jhazmat.2007.10.042.

Loxham, M., Cooper, M.J., Gerlofs-Nijland, M.E., Cassee, F.R., Davies, D.E., Palmer, M.R., Teagle, D. a H., 2013. Physicochemical characterization of airborne particulate matter at a mainline underground railway station. Environ. Sci. Technol. 47, 3614–3622. http://dx.doi.org/10.1021/es304481m.

Lu, S., Liu, D., Zhang, W., Liu, P., Fei, Y., Gu, Y., Wu, M., Yu, S., Yonemochi, S., Wang, X., Wang, Q., 2015. Physico-chemical characterization of PM2.5 in the microenvironment of Shanghai subway. Atmos. Res. 153, 543–552. http://dx.doi.org/10.1016/j.atmosres.2014.10.006.

Martins, V., Moreno, T., Minguillón, M.C., Amato, F., de Miguel, E., Capdevila, M., Querol, X., 2015. Exposure to airborne particulate matter in the subway system. Sci. Total Environ. 511, 711–722. http://dx.doi.org/10.1016/j.scitotenv.2014.12.013.

Matamoros, V., Bayona, J.M., 2006. Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. Environ. Sci. Technol. 40, 5811–5816. http://dx.doi.org/10.1021/es0607741.

Midander, K., Elihn, K., Wallén, A., Belova, L., Karlsson, A.-K.B., Wallinder, I.O., 2012. Characterisation of nano- and micron-sized airborne and collected subway particles, a multi-analytical approach. Sci. Total Environ. 427–428, 390–400. http://dx.doi.org/10.1016/j.scitotenv.2012.04.014.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fahrni, S.M., Alastuey, A., Jimenez, J.L., Mohr, C., Ortega, a. M., Day, D. a., Lanz, V. a., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J.F., Baltensperger, U., Prévôt, a. S.H., 2011. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. Atmos. Chem. Phys. 11, 12067–12084. http://dx.doi.org/10.5194/acp-11-12067-2011.

Minguillón, M.C., Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Figueras, F., Salvado, J.A., Grimalt, J.O., Nieuwenhuijsen, M., Querol, X., 2012. Source apportionment of indoor, outdoor and personal PM2.5 exposure of pregnant women in Barcelona, Spain. Atmos. Environ. 59, 426–436. http://dx.doi.org/10.1016/j.atmosenv.2012.04.052.

Moreno, T., Martins, V., Querol, X., Jones, T., BéruBé, K., Minguillón, M.C., Amato, F., Capdevila, M., de Miguel, E., Centelles, S., Gibbons, W., 2015. A new look at inhalable metalliferous airborne particles on rail subway platforms. Sci. Total Environ. 505, 367–375. http://dx.doi.org/10.1016/j.scitotenv.2014.10.013.

Moreno, T., Pérez, N., Reche, C., Martins, V., de Miguel, E., Capdevila, M., Centelles, S., Minguillón, M.C., Amato, F., Alastuey, A., Querol, X., Gibbons, W., 2014. Subway platform air quality: assessing the influences of tunnel ventilation, train piston effect and station design. Atmos. Environ. 92, 461–468. http://dx.doi.org/10.1016/j.atmosenv.2014.04.043.

Mugica-Álvarez, V., Figueroa-Lara, J., Romero-Romo, M., Sepúlveda-Sánchez, J., López-Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. Atmos. Environ. 49, 284–293. http://dx.doi.org/10.1016/j.atmosenv.2011.11.038.

Murruni, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., Vázquez, M., Ozafrán, M., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. Atmos. Environ. 43, 4577–4583. http://dx.doi.org/10.1016/j.atmosenv.2009.06.025.

Nieuwenhuijsen, M.J., Gómez-Perales, J.E., Colvile, R.N., 2007. Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. Atmos. Environ. 41, 7995–8006. http://dx.doi.org/10.1016/j.atmosenv.2007.08.002.

Otake, T., Yoshinaga, J., Yanagisawa, Y., 2001. Analysis of organic esters of plasticizer in indoor air by GC–MS and GC–FPD. Environ. Sci. Technol. 35, 3099–3102. http://dx.doi.org/10.1021/es001914o.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126. http://dx.doi.org/10.1002/env.3170050203.

Park, D., Oh, M., Yoon, Y., Park, E., Lee, K., 2012. Source identification of PM10 pollution in subway passenger cabins using positive matrix factorization. Atmos. Environ. 49, 180–185. http://dx.doi.org/10.1016/j.atmosenv.2011.11.064.

Park, D.-U., Ha, K.-C., 2008. Characteristics of PM10, PM2.5, CO2 and CO monitored in interiors and platforms of subway train in Seoul, Korea. Environ. Int. 34, 629–634. http://dx.doi.org/10.1016/j.envint.2007.12.007.

Pope, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease. Circulation 109, 71–77. http://dx.doi.org/10.1161/01.CIR.0000108927.80044.7F.

Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M.C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., de la Rosa, J., Sánchez de la Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández Patier, R., 2013. Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy. Atmos. Chem. Phys. 13, 6185–6206. http://dx.doi.org/10.5194/acp-13-6185-2013.

Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., Capdevila, M., 2012. Variability of levels and composition of PM10 and PM2.5 in the Barcelona metro system. Atmos. Chem. Phys. 12, 5055–5076. http://dx.doi.org/10.5194/acp-12-5055-2012.

Raut, J.-C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. Atmos. Environ. 43, 860–868. http://dx.doi.org/10.1016/j.atmosenv.2008.10.038.

Reche, C., Moreno, T., Amato, F., Viana, M., van Drooge, B.L., Chuang, H.-C., Bérubé, K., Jones, T., Alastuey, A., Querol, X., 2012. A multidisciplinary approach to characterise exposure risk and toxicological effects of PM10 and PM2.5 samples in urban environments. Ecotoxicol. Environ. Saf. 78, 327–335. http://dx.doi.org/10.1016/j.ecoenv.2011.11.043.

Ripanucci, G., Grana, M., Vicentini, L., Magrini, A., Bergamaschi, A., 2006. Dust in the underground railway tunnels of an Italian town. J. Occup. Environ. Hyg. 3, 16–25. http://dx.doi.org/10.1080/15459620500444004.

Rivas, I., Viana, M., Moreno, T., Pandolfi, M., Amato, F., Reche, C., Bouso, L., Àlvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X., 2014. Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain. Environ. Int. 69, 200–212. http://dx.doi.org/10.1016/j.envint.2014.04.009.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636–651. http://dx.doi.org/10.1021/es00041a007.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1994. Sources of fine organic aerosol. 6. Cigaret smoke in the urban atmosphere. Environ. Sci. Technol. 28, 1375–1388. http://dx.doi.org/10.1021/es00056a030.

Salma, I., Weidinger, T., Maenhaut, W., 2007. Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. Atmos. Environ. 41, 8391–8405. http://dx.doi.org/10.1016/j.atmosenv.2007.06.017.

Schauer, J., Rogge, W., Hildemann, L., Mazurek, M., Cass, G., Simoneit, B., 2007. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos. Environ. 41, 241–259. http://dx.doi.org/10.1016/j.atmosenv.2007.10.069.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London underground: dust and hazards to health. Occup. Environ. Med. 62, 355–362. http://dx.doi.org/10.1136/oem.2004.014332.

Simoneit, B.R., 2002. Biomass burning — a review of organic tracers for smoke from incomplete combustion. Appl. Geochemistry 17, 129–162. http://dx.doi.org/10.1016/S0883-2927(01)00061-0.

Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004. Sugars dominant water-soluble organic compounds in Soils and characterization as tracers in atmospheric particulate matter. Environ. Sci. Technol. 38, 5939–5949. http://dx.doi.org/10.1021/es0403099.

van Drooge, B.L., Fontal, M., Bravo, N., Fernández, P., Fernández, M.A., Muñoz-Arnanz, J., Jiménez, B., Grimalt, J.O., 2014. Seasonal and spatial variation of organic tracers for biomass burning in PM1 aerosols from highly insolated urban areas. Environ. Sci. Pollut. Res. 21, 11661–11670. http://dx.doi.org/10.1007/s11356-014-2545-0.

Supplementary data

Article 2

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

Supplementary data

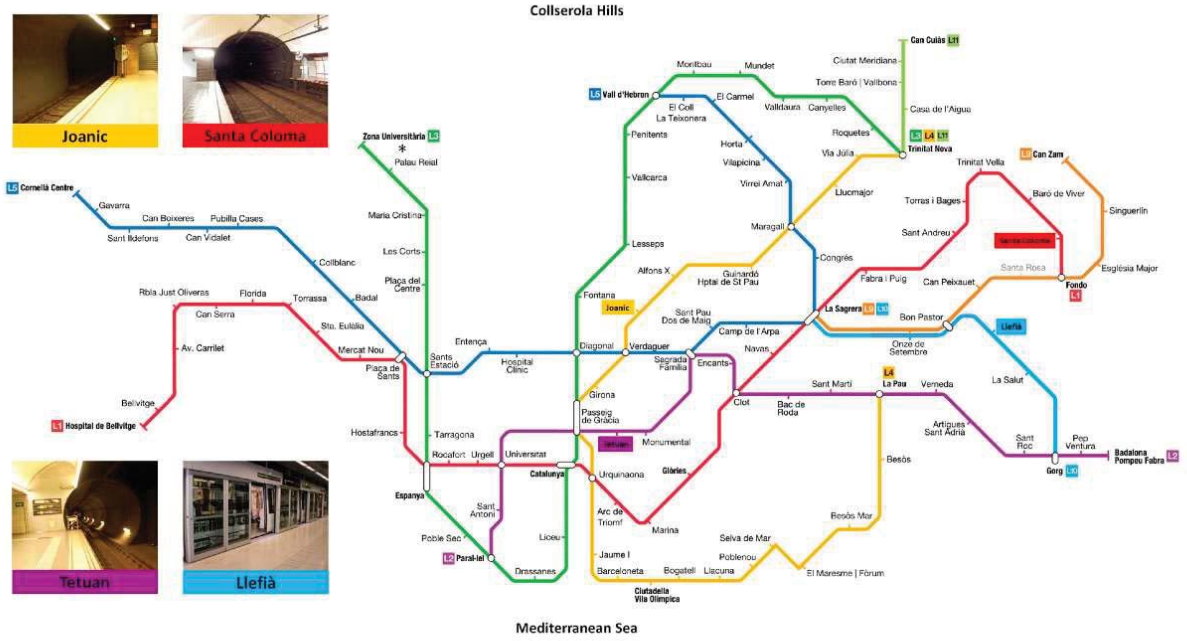


Fig. S1. Map of the Barcelona's subway system indicating the location of the four sampling stations. The location of the Palau Reial urban background station is represented by an asterisk.

Table S1. Features of the subway stations and measurement periods.

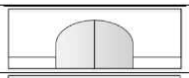
Subway station (line)	Measurements				Station			Mean train frequency (trains/hour)
	Warmer		Colder		Building year	Depth (m)	Design	
	Period	Temp. (ºC)	Period	Temp. (ºC)				
Joanic (L4)	2 Apr – 2 May 2013	21.9	28 Oct – 25 Nov 2013	25.9	1973	-7.6		12
Santa Coloma (L1)	1 Jul – 30 Jul 2013	30.3	10 Feb – 10 Mar 2014	19.6	1983	-12.3		29 (considering both rail tracks)
Tetuan (L2)	2 May – 31 May 2013	21.8	25 Nov – 20 Dec 2013	19.6	1995	-14.8		14
Llefià (L10)	31 May – 1 Jul 2013	25.9	13 Jan – 10 Feb 2014	21.0	2010	-43.6		8

Table S2. Relative abundances (in %) of the chemical components of $PM_{2.5}$ on four subway platforms during the warmer and colder periods. (CM – crustal matter; CA – carbonaceous aerosol; SIC – secondary inorganic compounds)

	Warmer period				Colder period			
	Joanic	Santa Coloma	Tetuan	Llefià	Joanic	Santa Coloma	Tetuan	Llefià
Fe_2O_3	27.9	44.2	47.1	33.3	65.3	38.1	56.2	48.4
CM	6.2	6.6	5.2	6.7	6.8	11.7	8.8	9.1
CA	33.8	25.8	23.6	21.9	20.6	36.6	24.7	30.1
Insoluble SO_4^{2-}	1.3	1.6	0.5	1.7	0.5	1.6	0.4	0.7
SIC	8.6	6.9	6.5	10.2	2.0	3.6	5.3	4.2
Halite	1.0	0.4	1.3	1.1	0.7	0.8	0.9	1.8
Trace elements	1.3	2.0	0.9	0.7	2.0	2.2	1.1	1.0
unaccounted	19.9	12.6	14.9	24.4	1.9	5.4	2.6	4.7

Article 3

Factors controlling air quality in different European subway systems

Vânia Martins, Teresa Moreno, Luís Mendes, Konstantinos Eleftheriadis, Evangelia Diapouli, Célia A. Alves, Márcio Duarte, Eladio de Miguel, Marta Capdevila, Xavier Querol, María Cruz Minguillón

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Overview:

Air quality in subway systems of three South European cities, including Barcelona (Spain), Athens (Greece) and Oporto (Portugal), was assessed and compared, focusing on exposure concentrations and chemical composition of $PM_{2.5}$ on subway stations, as well as $PM_{2.5}$ and CO_2 concentrations inside trains. The main factors controlling air quality in this environment were determined, with special focus on the particles resulting from subway sources.

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Factors controlling air quality in different European subway systems

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

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

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ABSTRACT

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

1. Introduction

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

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

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

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

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

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

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

2. Experimental section

2.1. Sampling methodology

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

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

2.1.1. Subway platforms

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

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

Table 1
Sampling subway systems information.

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

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

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

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

2.1.2. Additional platform measurements

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

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

2.1.3. Inside the trains

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

2.1.4. Outdoor environment

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

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

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

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

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

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

3. Results and discussion

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

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

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

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

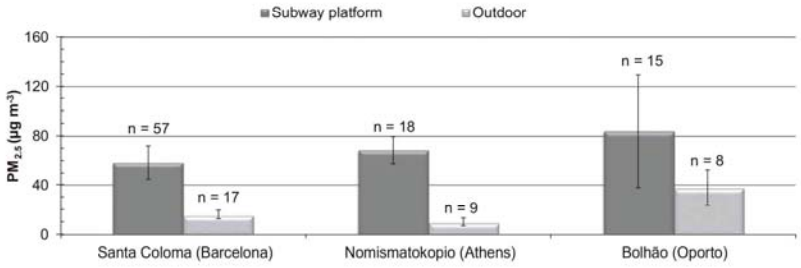

Fig. 1. Mean $PM_{2.5}$ gravimetric concentrations and standard deviations on the subway platforms and outdoor. (n – number of samples).

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

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

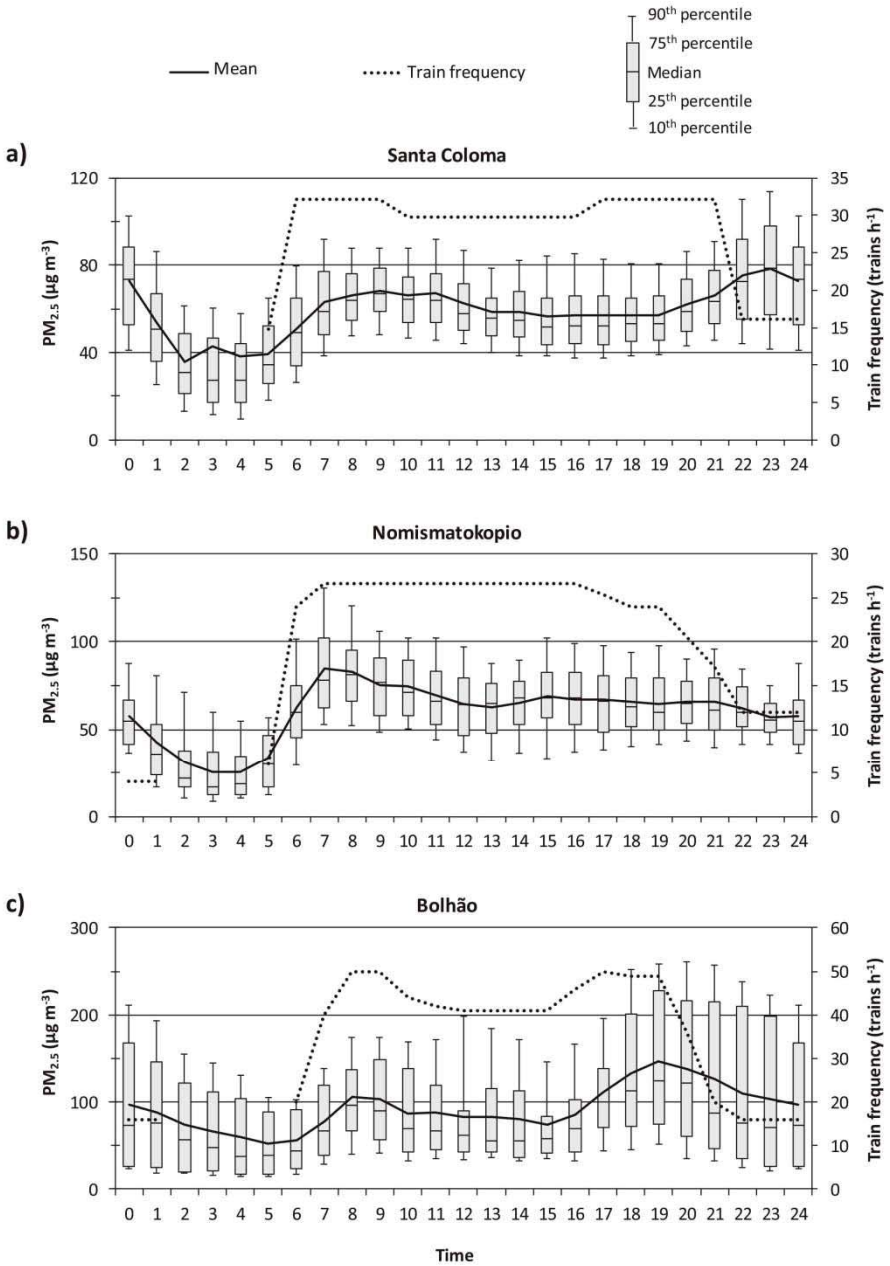

Fig. 2. Temporal variation of mean 1 h $PM_{2.5}$ mass concentrations and train frequency on the weekdays in the Santa Coloma (a), Nomismatokopio (b) and Bolhão (c) subway stations. The grey box represents the median, and the 25th and 75th percentile of hourly $PM_{2.5}$ concentrations. The whiskers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

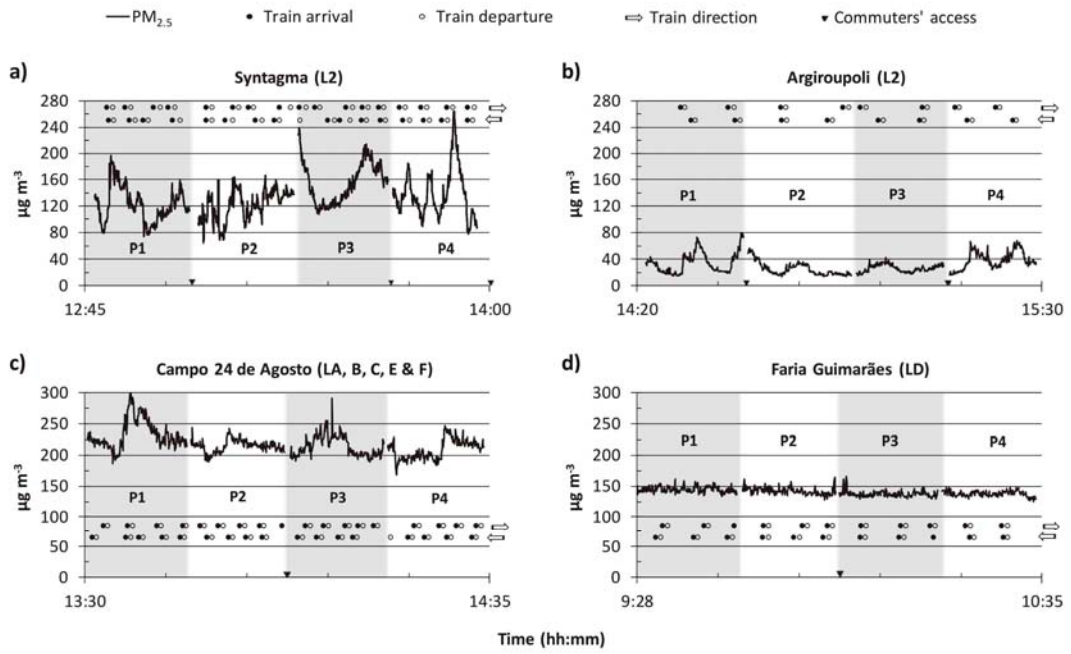

Fig. 3. Profiles of $PM_{2.5}$ concentrations ($\mu g\ m^{-3}$) on platforms from Athens subway (a and b) and Oporto subway (c and d) at 4 different positions (P1, P2, P3 and P4). Train arrival/departure and direction are indicated. Locations of commuters' accesses to platforms are represented either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

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

3.1.1. Daily pattern

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

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

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

3.1.2. Temporal–spatial variations

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

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

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

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

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

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

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

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

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

3.1.3. $PM_{2.5}$ chemical composition

Table 2 summarizes the mean chemical composition of $PM_{2.5}$ on the subway platforms and outdoors. The elemental species were grouped into seven different categories: (1) Elemental iron (Fe), (2) Total carbon (TC), (3) Crustal matter (CM, the sum of Ca, Mg, Al_2O_3, SiO_2, CO_3^{2-}, Ti, K and P), (4) Secondary inorganic compounds (SIC), the sum of water-soluble nitrate (ws-NO_3^-), sulphate (ws-SO_4^{2-}) and ammonium (ws-NH_4^+), (5) Halite (NaCl), (6) Insoluble sulphate and (7) Trace elements. As the oxidation state cannot be determined from the analysis performed, only elemental concentrations are shown in Table 2, but for the chemical mass balance, the oxide concentrations were calculated for Al_2O_3. Because silicon data were not acquired, SiO_2 was estimated by multiplying Al_2O_3 with a factor of 3, and CO_2^{3-} by multiplying Ca by a factor of 1.5 (Querol et al., 2001).

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

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

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

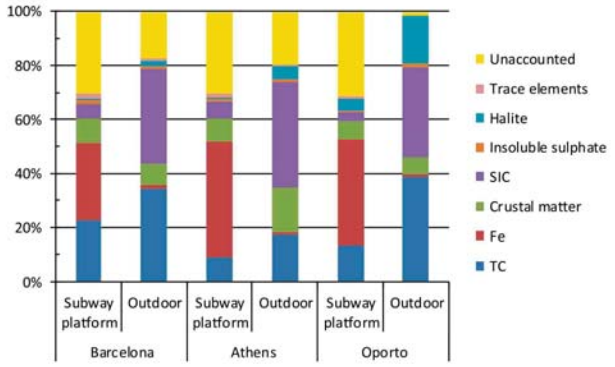

Fig. 4. Relative abundance of chemical components of $PM_{2.5}$ in the subway platforms and outdoor air. (SIC – secondary inorganic compounds; TC – total carbon).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

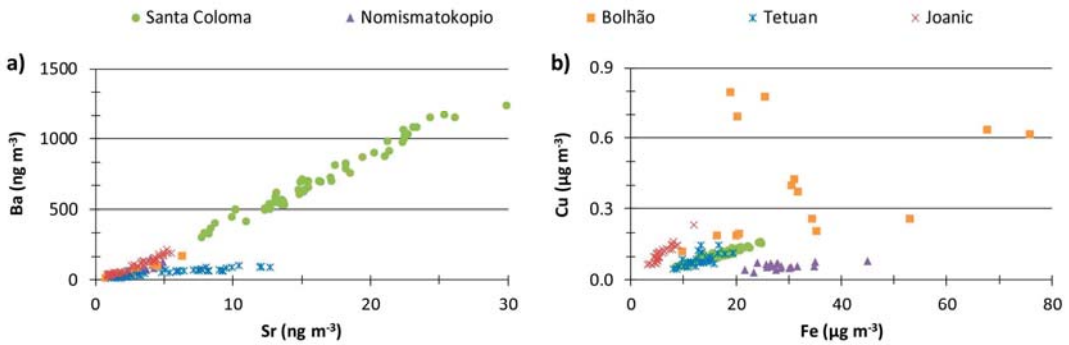

Fig. 5. Scatter plots of the concentrations of Ba vs. Sr (a) and Cu vs. Fe (b) in several subway stations. The results of Tetuan and Joanic stations have been reported by Martins et al. (2016).

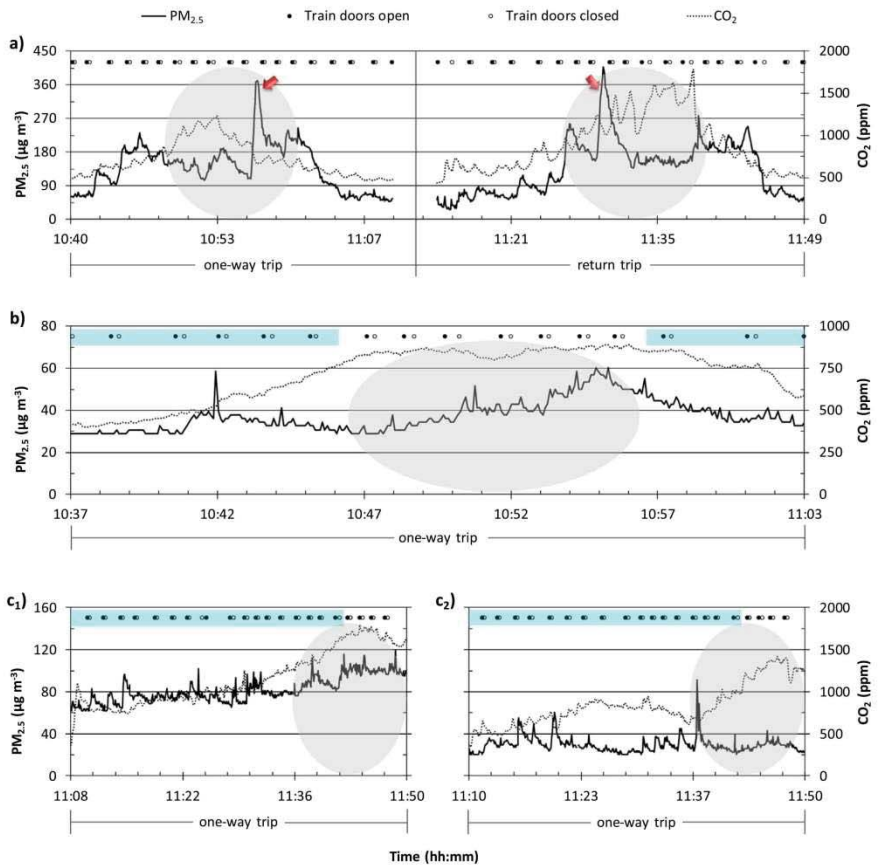

Fig. 6. $PM_{2.5}$ and CO_2 concentrations measured inside the train of Line 2 in the Athens subway system (a) and of Line D (b) and A in two different days (c_1 and c_2) in the Oporto subway system. The times of train doors open and closed are indicated. The central area of the city is grey shadowed.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

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

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

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

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

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

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

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

4. Conclusions

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

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

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Appendix A. Supplementary material

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

References

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

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

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

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

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

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

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

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

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

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

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

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

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

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

chemical compositions of particulate matter collected at the selected metro stations of Shanghai, China. Sci. Total Environ. 496, 443–452. http://dx.doi.org/10.1016/j.scitotenv.2014.07.055.

Gustafsson, M., Blomqvist, G., Swietlicki, E., Dahl, A., Gudmundsson, A., 2012. Inhalable railroad particles at ground level and subterranean stations – physical and chemical properties and relation to train traffic. Transp. Res. D: Transp. Environ. 17, 277–285. http://dx.doi.org/10.1016/j.trd.2011.12.006.

Johansson, C., Johansson, P.-A., 2003. Particulate matter in the underground of Stockholm. Atmos. Environ. 37, 3–9. http://dx.doi.org/10.1016/S1352-2310(02)00833-6.

Jung, H.-J., Kim, B., Ryu, J., Maskey, S., Kim, J.-C., Sohn, J., Ro, C.-U., 2010. Source identification of particulate matter collected at underground subway stations in Seoul, Korea using quantitative single-particle analysis. Atmos. Environ. 44, 2287–2293. http://dx.doi.org/10.1016/j.atmosenv.2010.04.003.

Kam, W., Cheung, K., Daher, N., Sioutas, C., 2011. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. Atmos. Environ. 45, 1506–1516. http://dx.doi.org/10.1016/j.atmosenv.2010.12.049.

Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2013. A comparative assessment of PM2.5 exposures in light-rail, subway, freeway, and surface street environments in Los Angeles and estimated lung cancer risk. Environ. Sci. Process. Impacts 15, 234–243. http://dx.doi.org/10.1039/c2em30495c.

Kamani, H., Hoseini, M., Seyedsalehi, M., Mahdavi, Y., Jaafari, J., Safari, G.H., 2014. Concentration and characterization of airborne particles in Tehran's subway system. Environ. Sci. Pollut. Res. 21, 7319–7328. http://dx.doi.org/10.1007/s11356-014-2659-4.

Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM10 and PM2.5) in Seoul Metropolitan Subway stations. J. Hazard. Mater. 154, 440–443. http://dx.doi.org/10.1016/j.jhazmat.2007.10.042.

Kwon, S.-B., Jeong, W., Park, D., Kim, K.-T., Cho, K.H., 2015. A multivariate study for characterizing particulate matter (PM10, PM2.5, and PM1) in Seoul metropolitan subway stations, Korea. J. Hazard. Mater. 297, 295–303. http://dx.doi.org/10.1016/j.jhazmat.2015.05.015.

Lim, J.-M., Lee, J.-H., Moon, J.-H., Chung, Y.-S., Kim, K.-H., 2010. Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization. Atmos. Res. 95, 88–100. http://dx.doi.org/10.1016/j.atmosres.2009.08.009.

Loxham, M., Cooper, M.J., Gerlofs-Nijland, M.E., Cassee, F.R., Davies, D.E., Palmer, M. R., Teagle, D. a H., 2013. Physicochemical characterization of airborne particulate matter at a mainline underground railway station. Environ. Sci. Technol. 47, 3614–3622. http://dx.doi.org/10.1021/es304481m.

Martins, V., Minguillón, M.C., Moreno, T., Querol, X., de Miguel, E., Capdevila, M., Centelles, S., Lazaridis, M., 2015a. Deposition of aerosol particles from a subway microenvironment in the human respiratory tract. J. Aerosol Sci. 90, 103–113. http://dx.doi.org/10.1016/j.jaerosci.2015.08.008.

Martins, V., Moreno, T., Minguillón, M.C., Amato, F., de Miguel, E., Capdevila, M., Querol, X., 2015b. Exposure to airborne particulate matter in the subway system. Sci. Total Environ. 511, 711–722. http://dx.doi.org/10.1016/j.scitotenv.2014.12.013.

Martins, V., Moreno, T., Minguillón, M.C., van Drooge, B.L., Amato, F., de Miguel, E., Capdevila, M., Centelles, S., Querol, X., 2016. Origin of inorganic and organic components of PM2.5 in subway stations of Barcelona, Spain. Environ. Pollut. 208, 125–136. http://dx.doi.org/10.1016/j.envpol.2015.07.004.

Moreno, T., Martins, V., Querol, X., Jones, T., BéruBé, K., Minguillón, M.C., Amato, F., Capdevila, M., de Miguel, E., Centelles, S., Gibbons, W., 2015a. A new look at inhalable metalliferous airborne particles on rail subway platforms. Sci. Total Environ. 505, 367–375. http://dx.doi.org/10.1016/j.scitotenv.2014.10.013.

Moreno, T., Pérez, N., Reche, C., Martins, V., de Miguel, E., Capdevila, M., Centelles, S., Minguillón, M.C., Amato, F., Alastuey, A., Querol, X., Gibbons, W., 2014. Subway platform air quality: assessing the influences of tunnel ventilation, train piston effect and station design. Atmos. Environ. 92, 461–468. http://dx.doi.org/10.1016/j.atmosenv.2014.04.043.

Moreno, T., Reche, C., Rivas, I., Minguillón, M.C., Martins, V., Vargas, C., Buonanno, G., Parga, J., Pandolfi, M., Brines, M., Ealo, M., Fonseca, A.S., Amato, F., Sosa, G., Capdevila, M., de Miguel, E., Querol, X., Gibbons, W., 2015b. Urban air quality comparison for bus, tram, subway and pedestrian commutes in Barcelona. Environ. Res. 142, 495–510. http://dx.doi.org/10.1016/j.envres.2015.07.022.

Mugica-Álvarez, V., Figueroa-Lara, J., Romero-Romo, M., Sepúlveda-Sánchez, J., López-Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. Atmos. Environ. 49, 284–293. http://dx.doi.org/10.1016/j.atmosenv.2011.11.038.

Murruni, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., Vázquez, M., Ozafrán, M., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. Atmos. Environ. 43, 4577–4583. http://dx.doi.org/10.1016/j.atmosenv.2009.06.025.

Nieuwenhuijsen, M.J., Gómez-Perales, J.E., Colvile, R.N., 2007. Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. Atmos. Environ. 41, 7995–8006. http://dx.doi.org/10.1016/j.atmosenv.2007.08.002.

Park, D., Lee, T., Hwang, D., Jung, W., Lee, Y., Cho, K., Kim, D., Lee, K., 2014. Identification of the sources of PM10 in a subway tunnel using positive matrix factorization. J. Air Waste Manag. Assoc. 64, 1361–1368. http://dx.doi.org/10.1080/10962247.2014.950766.

Park, D.-U., Ha, K.-C., 2008. Characteristics of PM10, PM2.5, CO2 and CO monitored in interiors and platforms of subway train in Seoul, Korea. Environ. Int. 34, 629–634. http://dx.doi.org/10.1016/j.envint.2007.12.007.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Mantilla, E., Ruiz, C.R., 2001. Monitoring of PM10 and PM2.5 around primary particulate anthropogenic emission sources. Atmos. Environ. 35, 845–858. http://dx.doi.org/10.1016/S1352-2310(00)00387-3.

Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., Capdevila, M., 2012. Variability of levels and composition of PM10 and PM2.5 in the Barcelona metro system. Atmos. Chem. Phys. 12, 5055–5076. http://dx.doi.org/10.5194/acp-12-5055-2012.

Raut, J.-C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. Atmos. Environ. 43, 860–868. http://dx.doi.org/10.1016/j.atmosenv.2008.10.038.

Ripanucci, G., Grana, M., Vicentini, L., Magrini, A., Bergamaschi, A., 2006. Dust in the underground railway tunnels of an italian town. J. Occup. Environ. Hyg. 3, 16–25. http://dx.doi.org/10.1080/15459620500444004.

Rivas, I., Viana, M., Moreno, T., Pandolfi, M., Amato, F., Reche, C., Bouso, L., Àlvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X., 2014. Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain. Environ. Int. 69, 200–212. http://dx.doi.org/10.1016/j.envint.2014.04.009.

Salma, I., Pósfai, M., Kovács, K., Kuzmann, E., Homonnay, Z., Posta, J., 2009. Properties and sources of individual particles and some chemical species in the aerosol of a metropolitan underground railway station. Atmos. Environ. 43, 3460–3466. http://dx.doi.org/10.1016/j.atmosenv.2009.04.042.

Salma, I., Weidinger, T., Maenhaut, W., 2007. Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. Atmos. Environ. 41, 8391–8405. http://dx.doi.org/10.1016/j.atmosenv.2007.06.017.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London Underground: dust and hazards to health. Occup. Environ. Med. 62, 355–362. http://dx.doi.org/10.1136/oem.2004.014332.

Sundh, J., Olofsson, U., Olander, L., Jansson, A., 2009. Wear rate testing in relation to airborne particles generated in a wheel – rail contact ‡. Lubr. Sci. 21, 135–150. http://dx.doi.org/10.1002/ls.80.

Supplementary data

Article 3

Factors controlling air quality in different European subway systems

Appendix A. Supplementary material

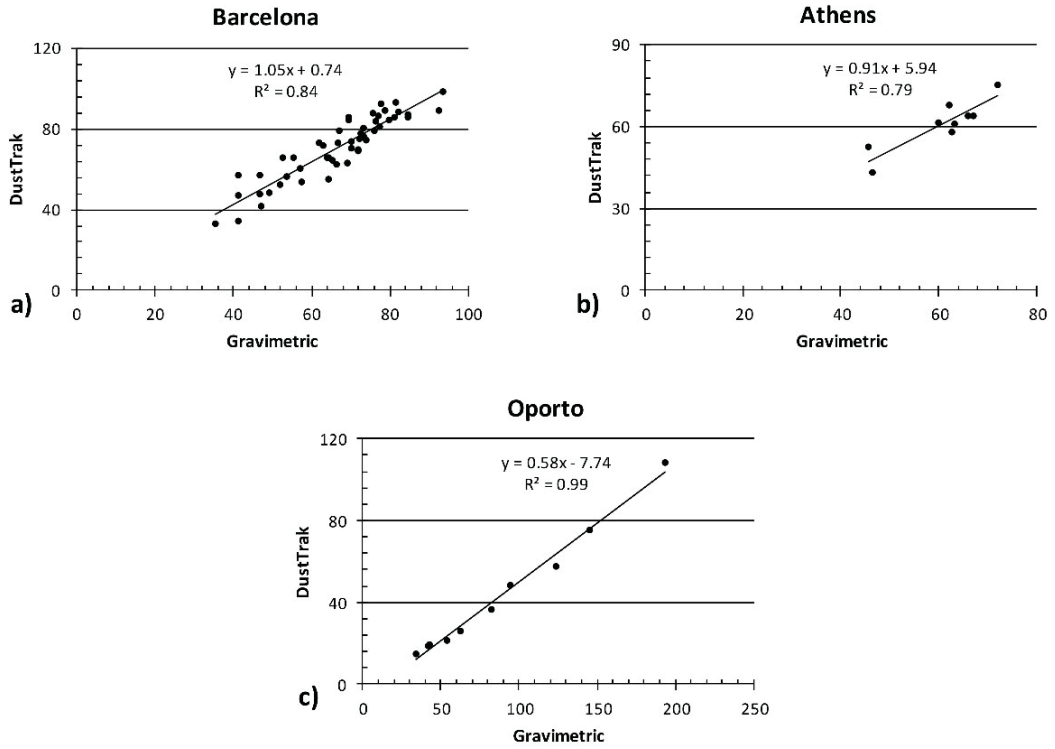

Fig. S1. $PM_{2.5}$ concentrations (μg m^{-3}) measured with the DustTrak vs. those determined gravimetrically from samples collected with high volume samplers in the selected platform of the subway system of a) Barcelona, b) Athens and c) Oporto. Lines and equations correspond to linear regression fits. Squared Pearson correlations (R^2) shown.

Fig. S2. Location of the sampled subway stations and the outdoor sampling stations in a) Oporto, b) Barcelona and c) Athens.

2

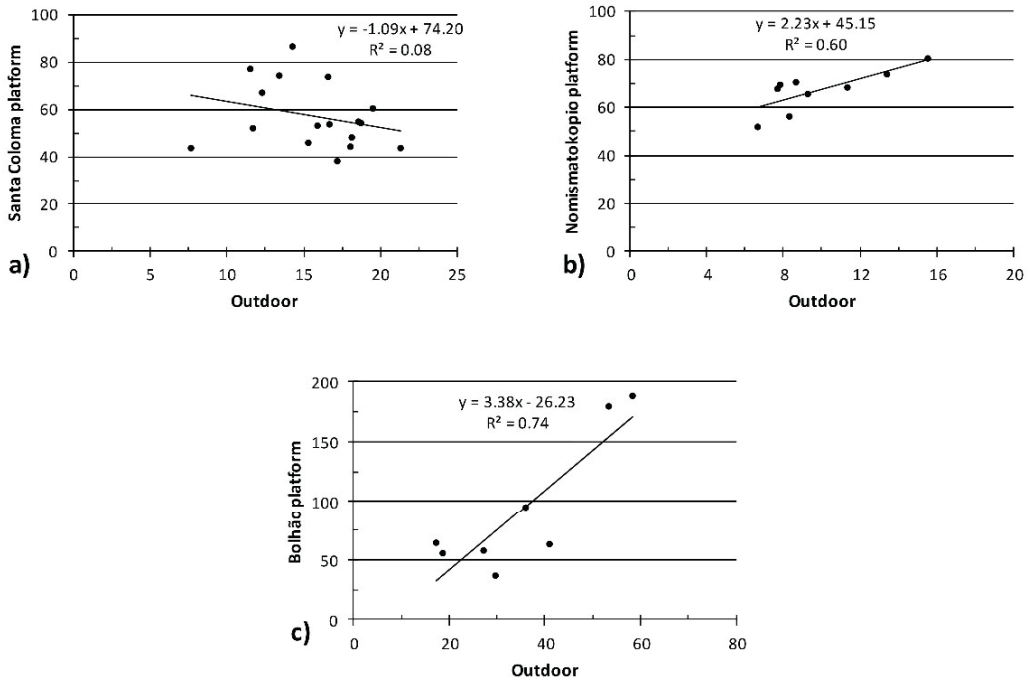

Fig. S3. Scatter plots of $PM_{2.5}$ concentrations (μg m^{-3}) in the indoor subway platform vs. outdoor ambient air in a) Barcelona, b) Athens and c) Oporto. The correlations were obtained using the concentrations indoor and outdoor for the same day.

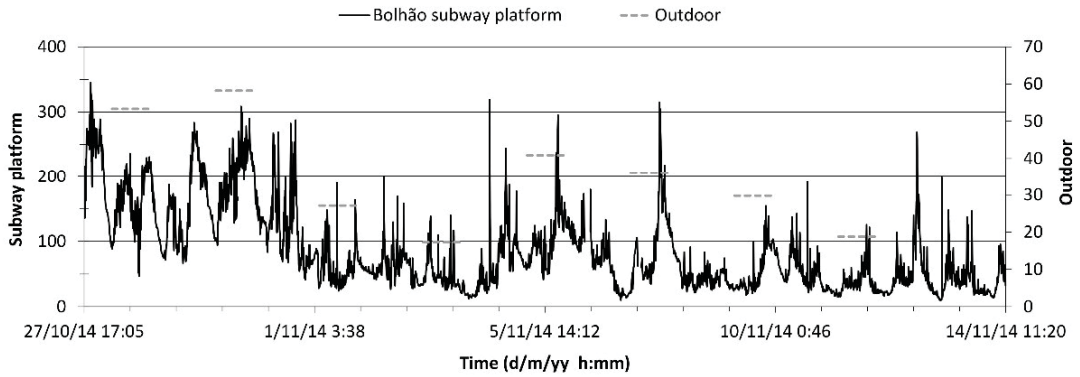

Fig. S4. $PM_{2.5}$ concentrations (μg m^{-3}) in the Bolhão subway platform in Oporto along the sampling campaign and in the outdoor 19 h gravimetric measurements.

Table S1. Daily mean, standard deviation (sd), minimum and maximum of $PM_{2.5}$ concentrations (μg m^{-3}) for weekdays and weekends in the subway stations during the subway operating hours.

	Subway		Weekdays		Weekends	
System	**Operating hours**	**Station**	**Mean ± sd**	**Min – Max**	**Mean ± sd**	**Min – Max**
Barcelona	5:00 to 00:00	Santa Coloma	63.4 ± 12.4	46.6 – 90.3	45.2 ± 6.1	37.5 – 59.0
Athens	5:30 to 00:30	Nomismatokopio	68.7 ± 11.5	51.9 – 99.1	67.0 ± 12.1	51.0 – 80.5
Oporto	6:00 to 01:00	Bolhão	94.5 ± 48.8	46.6 – 188.8	53.9 ± 13.8	37.1 – 70.2

Table S2. Mean $PM_{2.5}$ concentrations and standard deviation (μg m^{-3}) at each studied subway station in Athens and Oporto subway systems, along the 4 different positions (P1, P2, P3 and P4). P1 and P4 are the ends of the platforms with train entrance and exit. Locations of accesses to platforms are indicated with arrows (⇨ and ⇦ – access in the end of the platform; ⇔ – access in the middle of two sampling points). Results from measurements performed in two days are shown for each station.

			Measurements											
Subway system	**Stations**	**Line(s)**	**P1**			**P2**			**P3**			**P4**			**Entire station**	
			mean	**sd**		**mean**	**sd**		**mean**	**sd**		**mean**	**sd**		**mean**	**sd**
Athens	Nomismatokopio	3	134.1	33.7	⇔	79.9	20.8		63.4	15.4	⇔	62.3	19.1		85.9	36.2
			81.2	20.3		54.3	19.2		72.9	21.8		43.0	12.5		62.9	23.3
	Syntagma	3	120.3	14.0		99.0	8.9	⇔	80.3	14.9	⇔	101.7	17.3	⇦	100.8	19.2
			124.9	15.5		104.5	13.8		136.0	24.4		99.0	29.7		114.9	26.1
	Syntagma	2	114.5	16.6	⇔	136.8	18.2		154.5	29.0	⇔	229.8	34.0	⇦	157.7	47.9
			122.1	26.7		121.3	23.2		155.4	31.0		138.0	36.5		128.3	36.3
	Monastiraki	3	58.4	16.5	⇔	64.0	12.6		80.9	16.6	⇔	87.1	22.6		71.4	21.0
			35.4	8.5		44.7	7.5		50.1	8.1		57.2	15.0		46.0	12.9
	Argiroupoli	2	11.3	3.2	⇔	18.3	3.9		20.7	20.7	⇔	37.0	16.9		22.3	13.2
			34.3	15.6		25.1	10.0		26.3	5.6		38.9	13.3		31.4	14.1
Oporto	Bolhão	A, B, C, E & F	270.9	14.0		269.6	10.6	⇔	257.5	14.6		259.1	27.3		264.9	19.4
		⇨	66.2	7.9		63.8	3.7		62.0	3.1		64.5	7.6		64.7	6.6
	Campo 24 de Agosto	A, B, C, E & F	233.4	23.5		214.9	10.0	⇔	214.2	16.5		208.7	16.0		215.6	20.7
			162.4	14.3		156.0	29.0		160.5	13.7		200.6	39.4		171.8	31.8
	Faria Guimarães	D	144.3	5.0		141.7	5.6	⇔	136.9	4.8		137.3	4.4		139.3	6.4
			143.3	10.2		121.0	6.0		125.1	7.0		120.7	5.4		128.0	11.7
	Trindade	D	133.4	10.4		151.6	6.1	⇔	156.8	5.6		148.8	6.6	⇦	148.0	11.2
		⇨	114.6	7.2		116.6	6.9		138.0	8.0		120.9	7.3		122.0	11.6
	Aliados	D	138.4	9.1		140.0	5.6	⇔	135.3	5.6		143.2	5.2		140.1	7.9
			122.2	20.3		118.1	4.5		100.0	5.9		96.3	9.8		108.1	16.3

Table S3. Mean $PM_{2.5}$ concentrations and standard deviation (μg m^{-3}) inside the trains in the different subway systems and lines.

System	Barcelona					Athens		Oporto	
Line	L1	L2	L3	L4	L5	L2	L3	LA	LD
mean	58.3	35.7	53.4	46.0	37.9	124.8	83.4	54.1	44.8
sd	20.9	8.5	15.5	15.0	10.9	70.7	32.3	28.1	22.5

Table S4. Mean $PM_{2.5}$ concentrations and standard deviation (μg m^{-3}) inside the trains of underground and aboveground sections in Oporto subway system.

System	Oporto			
Line	LA		LD	
Section	Underground	Aboveground	Underground	Aboveground
mean	65.7	51.1	46.1	43.7
sd	39.4	23.4	16.2	26.9

Article 4

Deposition of aerosol particles from a subway microenvironment in the human respiratory tract

Vânia Martins, María Cruz Minguillón, Teresa Moreno, Xavier Querol, Eladio de Miguel, Marta Capdevila, Sonia Centelles, Mihalis Lazaridis

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Overview:

Total and regional doses of particles in the human respiratory tract of a healthy Caucasian adult male using the dosimetry model ExDoM were estimated. The overall dose was determined using the mean exposure $PM_{2.5}$ concentrations obtained on platforms and inside trains in the Barcelona subway system. Individual's daily exposure to $PM_{2.5}$ and dose were estimated, considering a typical time-activity pattern of an adult male who lives in Barcelona and commutes by subway.

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Deposition of aerosol particles from a subway microenvironment in the human respiratory tract

Vânia Martins [a,b,*], María Cruz Minguillón [a], Teresa Moreno [a], Xavier Querol [a], Eladio de Miguel [c], Marta Capdevila [c], Sonia Centelles [c], Mihalis Lazaridis [d]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain
[c] Transports Metropolitans de Barcelona, TMB Santa Eulàlia, Av. Del Metro s/n L'Hospitalet de Llobregat, 08902, Spain
[d] Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, 73100 Chania, Greece

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ABSTRACT

Conventional subway systems are characterized by high particulate matter (PM) concentrations. To relate PM exposure to adverse health effects it is important to determine the dose of the inhaled particles in the human respiratory tract (HRT). Therefore, the total and regional doses of particles for a healthy adult male using the dosimetry model ExDoM in the subway system were estimated. The overall dose was determined using the average exposure $PM_{2.5}$ concentrations obtained from an extensive campaign in the Barcelona subway system, including measurements on the platforms and inside the trains. Despite the lower $PM_{2.5}$ concentrations inside the trains with respect to those on station platforms, the highest dose was observed inside the trains due to longer exposure time, evidencing the importance of the exposure period in the estimation of the particle dose. Overall, during a subway commuting travel, roughly 80% of the inhaled mass of subway $PM_{2.5}$ was deposited in the HRT. The highest amount of the inhaled particles was deposited in the extrathoracic region (68%), whereas the deposition was much smaller in the tracheobronchial tree (4%) and alveolar–interstitial region (10%). Individual's daily exposure to $PM_{2.5}$ and dose were estimated, considering a typical time-activity pattern of an adult male who lives in Barcelona and commutes by subway. While a subject typically spends approx. 3% of the day in the subway system, this microenvironment may account for up to 47% of the total $PM_{2.5}$ daily dose. These results might be similarly high for other commuting modes due to the reported high PM exposure levels. The dose is mainly dependent on the particle size and exposure concentrations.

1. Introduction

Urban population is daily exposed to air particulate pollution from a range of sources, including the ambient environment and three main microenvironments: home, workplace and commuting. In fact, the exposure to airborne particles depends on the lifestyle of each individual and the different microenvironments frequented (Buonanno, Fuoco & Stabile, 2011; Buonanno, Marks & Morawska, 2013). Epidemiological and toxicological studies have shown associations between

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

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particulate matter (PM) and adverse health effects (e.g. Dominici et al., 2006; Katsouyanni et al., 2001; Pope & Dockery, 2006; Russell & Brunekreef, 2009; Schikowski et al., 2007; Valavanidis, Fiotakis & Vlachogianni, 2008). Although the large majority of these studies relate health effects to PM exposure (the inhaled concentration), the negative outcomes are mainly caused by the subsequent deposition of PM in the respiratory tract during breathing (Salma, Balásházy, Winkler-Heil, Hofmann & Záray, 2002). Hence, in order to understand the mechanisms behind the health responses, it is crucial to determine the respiratory tract deposition fraction (DF) of aerosol particles, which is their probability to deposit, and the dose (amount of inhaled particles deposited) (Löndahl et al., 2009). For aerosols this dose can be given as number, surface area or mass of the deposited particles. The dose of particles in the human respiratory tract (HRT) depends on a number of factors, including PM exposure concentrations, physicochemical characteristics of PM, exposure duration, and exposed subject characteristics, such as age, gender, state of health, lung morphology, and breathing parameters (Broday & Agnon, 2007; Glytsos, Ondráček, Džumbová, Kopanakis & Lazaridis, 2010; Heyder, 2004; Hofmann, 2011; Lazaridis, Broday, Hov & Georgopoulos, 2001; Patterson, Zhang, Zheng & Zhu, 2014). However, most of the studies on the health impact of aerosol inhalation link the observed health effects with day-averaged concentrations from fixed ambient air quality monitoring stations, rather than personal exposure to particles at the indoor and outdoor places where the individual may be active (Aleksandropoulou, Mitsakou, Housiadas & Lazaridis, 2008).

Inhaled particles are carried with the tidal air through the respiratory system. However, when travelling along an airway, particles will be exposed to different physical mechanisms forcing them to displace off the streamlines of the inhaled air volume and eventually depositing on the surrounding airway surfaces. The most important mechanisms acting upon the inhaled particles are diffusion (Brownian motion), inertial impaction, electrostatic charging, and sedimentation (gravitational settling) (Hofmann, 2011; Hussain, Madl & Khan, 2011; Löndahl et al., 2014).

The deposited dose of atmospheric aerosols in the human respiratory tract is measured by monitoring the inhaled and exhaled particle concentrations (e.g. Löndahl et al., 2008; Montoya et al., 2004; Morawska, Hofmann, Hitchins-Loveday, Swanson & Mengersen, 2005). This provides an empirical estimation for the total deposition pattern of aerosol particles in the respiratory system. Due to experimental limitations, the regional dose in the respiratory system (extrathoracic, tracheobronchial, and alveolar–interstitial regions) cannot be determined experimentally and is typically estimated by means of mathematical models. Several dosimetry models have been developed over the years (Aleksandropoulou & Lazaridis, 2013; Asgharian, 2004; Georgopoulos & Lioy, 2006; Heyder & Rudolf, 1984; ICRP, 1994; Klepeis, 2006; Koblinger & Hofmann, 1990; Lazaridis et al., 2001; Mitsakou, Mitrakos, Neofytou & Housiadas, 2007; Rudolf, Köbrich & Stahlhofen, 1990; Sturm, 2007; Yeh & Schum, 1980). These models for both total and regional deposition have been compared to experimental studies, with a reasonable correlation being obtained between model predictions and experimental measurements (Asgharian & Price, 2007; Löndahl et al., 2008; Stuart, 1984).

Several studies on PM exposure in different commuting modes along complementary routes have stated that all commuting modes (passenger cars, bus, subway, motorbike, cycling and pedestrian) are characterized by high PM exposure levels due to the fact that commuters are close to mobile emission sources. Moreover, in this assessment studies it is very important to account for the breathing rates and journey times (e.g. de Nazelle et al., 2012; Gulliver & Briggs, 2004). Many people living in metropolitan areas worldwide commute using underground subway transportation. Several studies have investigated the air quality in underground subway systems (see Martins et al., 2015a and references therein), and most of them reported elevated pollution levels in terms of PM in comparison to the outdoor ambient air. The PM in this microenvironment is mostly generated internally by the motion of the trains and movement of passengers, but can also origin from the inflow of outside air through the ventilation system, which promotes the mixing and resuspension of PM (e.g. Querol et al., 2012). Despite the relatively short amount of time spent in the subway on a daily basis, or commuting in a general way, PM exposure levels in such microenvironment are of concern given the relatively high PM concentrations. Michaels and Kleinman (2000) reported that peak exposures of 1 h or less, just over the typical time spent in a transport environment, may be extremely relevant in terms of health effects. In addition, the exposure to PM in the subway system has been associated with adverse health effects (Bachoual et al., 2007; Bigert et al., 2008; Seaton et al., 2005). However there is an uncertain and limited nature of the evidence for subway metalliferous PM toxicity (Moreno et al., 2015 and references therein), as for example part of subway particles bioreactivity has been associated to the glass fibre filters in the extracted samples (Karlsson, Ljungman, Lindbom & Möller, 2006), and no increased lung cancer risk has been found amongst subway train drivers (Gustavsson, Bigert & Pollán, 2008).

To the authors' knowledge, there are no studies on the deposition of subway PM in the human respiratory tract. Therefore, the main objectives of this study were to (i) determine the $PM_{2.5}$ exposure of subway commuters, (ii) calculate the total and regional doses in the respiratory tract based on the $PM_{2.5}$ exposure during subway commutes, as a function of the time spent on the platforms and inside the trains, and (iii) estimate the overall daily $PM_{2.5}$ dose, considering a typical time-activity pattern. The exposure and dose assessment was performed using aerosol measurements in the Barcelona subway system and in the urban background of Barcelona (Spain), with limitations for the remaining indoor microenvironments considered, as explained later in results and conclusions. In this study, the $PM_{2.5}$ dose in the HRT was estimated applying the dosimetry model Exposure Dose Model (ExDoM) (Aleksandropoulou & Lazaridis, 2013).

2. Experimental method

2.1. Monitoring sites and measurements

The subway system of Barcelona is managed by the Transports Metropolitans de Barcelona (TMB) and it is one of the oldest underground transport systems in Europe, with its first line beginning operation in 1924. The measurement campaign was conducted in this subway system during two seasonal periods: warmer (2 April–30 July 2013) and colder (28 October 2013–10 March 2014). Different types of subway stations were considered in the experimental campaign in terms of architectural design, in order to investigate the effects on the exposure concentration levels and dose. Particle aerosol measurements were performed on the four stations described hereinafter:

- Joanic on the yellow line (L4): two platforms in the same tunnel with the two rail tracks in the centre, one for each direction, separated by a middle wall.
- Santa Coloma on the red line (L1): one wide tunnel with two rail tracks without middle wall.
- Tetuan on the purple line (L2): one platform in a single narrow tunnel with one rail track.
- Llefià on the new light blue line (L10): a single narrow tunnel with the platform separated from the rail track by a glass wall with mechanical doors that are opened simultaneously with the train doors (known as platform screen doors system – PSDs). The system is automatic, with computer controlled driving system that optimises speed, braking and stopping processes.

The techniques and procedures of the experimental study are described in detail elsewhere (Martins et al., 2015a), and will be only briefly summarised here. $PM_{2.5}$ samples were collected daily on quartz microfibre filters using a high volume sampler (HVS, Model CAV-A/MSb, MCV) over 19 h (from 5 a.m. to midnight, subway operating hours). The filters were gravimetrically analysed to determine the $PM_{2.5}$ mass concentrations. $PM_{2.5}$ mass concentrations ($\mu g\, m^{-3}$) were determined continuously by a light-scattering laser photometer (DustTrak, Model 8533, TSI) with a 5-minutes time resolution. These measurements were performed for each seasonal period during a month at each station. Furthermore, $PM_{2.5}$ mass concentrations were also determined inside the trains, from 6 subway lines (L1, L2, L3, L4, L5 and L10), with 5-seconds time resolution using a DustTrak. $PM_{2.5}$ concentrations provided by DustTrak monitor were corrected against the gravimetric $PM_{2.5}$. Additionally, in the current study the exposure concentrations represent the mean value of the measurements performed at each station and inside the trains of the different lines, in order to simulate the overall PM exposure and dose of a subway commuter. Air quality measurements were performed simultaneously at the urban background station of Palau Reial to obtain mean concentrations of the outdoor environment.

2.2. Respiratory tract deposition model

Aerosol deposition in human respiratory system was calculated by the dosimetry model ExDoM. A detailed description of this model has been reported by Aleksandropoulou and Lazaridis (2013) and Chalvatzaki and Lazaridis (2015). For modelling purposes, the respiratory tract is divided into different anatomical regions: an extrathoracic (ET) region – anterior nasal passages (ET1) and the posterior nasal passages, larynx, pharynx and mouth (ET2); a tracheobronchial (TB) tree – the bronchial region, including trachea and bronchi (BB) and the bronchiolar region consisting of bronchioles and terminal bronchioles (bb); and an alveolar–interstitial (AI) region, consisting of respiratory bronchioles, and alveolar ducts and sacs surrounded by alveoli. The exposure is adjusted by the inhalability, which is the fraction of aerosol particles that enters in the HRT during breathing. The PM deposition fractions for each region of the respiratory tract are calculated after accounting for the filtering effect of the preceding airways (Aleksandropoulou & Lazaridis, 2013).

In particular, the dose depends on the exposure concentration and physicochemical characteristics of the PM, time-activity pattern and the exposed subject characteristics, as the respiratory physiology parameters, physical activity level, breathing pattern, gender and age, among others (Aleksandropoulou & Lazaridis, 2013; ICRP, 1994).

2.3. Exposure scenario and dose calculation

For the application of the dosimetry model ExDoM the following aspects were considered: (i) selection of the exposed subject; (ii) identification of the microenvironments where the exposed subject spent time; (iii) estimation of the time spent in each microenvironment, (iv) determination of the $PM_{2.5}$ exposure concentrations, (v) election of the breathing mode; and (vi) selection of breathing rate (volume of air inhaled per unit of time) to be used as a function of the corresponding specific activity levels (classified as sleep, sitting/resting and light exercise).

Modelling of $PM_{2.5}$ deposition in the HRT was conducted for a healthy Caucasian adult male breathing through the nose. Lippmann, Yeates and Albert (1980) reported that the nasal passages are a more efficient particle filter than the oral ones, thus, persistent mouth breathers deposit more particles in their respiratory system than those breathing entirely through the nose. Additionally, Löndahl et al. (2007) conducted an intensive study determining the dose of particles in the HRT by gender (male and female) and they found that the amount of deposited particles varied remarkably between genders, increasing substantially for the male subjects, because of their higher breathing rate values. The lung of a child differs

significantly from that of adults in terms of airway dimensions and breathing rate (Ménache, Hofmann, Ashgarian & Miller, 2008). Due to the combination of smaller airway sizes, smaller tidal volumes, but higher breathing frequencies, the total deposition fraction in children is generally higher than in adults (Asgharian, Ménache & Miller, 2004). It is also worth noticing that the dose is, in general, higher in subjects with lung problems (such as asthma, obstructive lung diseases, etc.) than healthy subjects (e.g. Anderson, Wilson & Hiller, 1990; Kim & Kang, 1997; Chalupa, Morrow, Oberdörster, Utell & Frampton, 2004).

The size distribution of the subway $PM_{2.5}$ was considered monodisperse with a mass mean aerodynamic diameter (MMAD) of 2.1 μm and a geometric standard deviation (GSD) of 1.7. Although particles were assumed spherical (shape factor of 1) for the dose calculations it is known from scanning electron microscopy studies that a large fraction of subway PM is laminar (Moreno et al., 2015; Querol et al., 2012). Another important factor determining the deposition of particles is their density (Aleksandropoulou & Lazaridis, 2013). The density of the subway particles ranged from 2.2 to 3.1 g cm^{-3}, based on their chemical composition at each subway station and seasonal period (Martins et al., 2015b).

In the case of the subway microenvironment, the estimations were based on the assumption that the subject is under light exercise and consequently the breathing rate equals to 1.5 $m^3\ h^{-1}$ (reference values for adult Caucasian males; ICRP, 1994). Furthermore, the dose was determined for average exposure concentrations from the measurements on the platforms and inside the trains in order to represent the overall dose in the subway system. The exposure time assumed was based on the TMB information with an average subway commuting one-way travel of 5 min on the platform and 15 min inside the train.

The dose is the amount of particles deposited in the respiratory tract during breathing, and it can be expressed as

$$\text{Dose} = \text{DF} \times C \times t \times Q$$

where DF is the deposition fraction of aerosol particles in the respiratory system (dimensionless), C is the airborne particle concentration in units of μg m^{-3} (amount of particle inhaled per volume air), t is the exposure time in hours, and Q is the breathing rate in $m^3\ h^{-1}$. From these parameters, DF is the least accessible factor, because it depends on the exposed subject characteristics, such as age, gender, health status, lungs morphology, respiratory parameters and activity, as well as on numerous other parameters including particle size, density, shape, and chemical composition (ICRP, 1994; Löndahl et al., 2007). DF increases with larger particle size leading to higher dose. Moreover, the DF is different for each region of the respiratory system (extrathoracic, tracheobronchial, and alveolar–interstitial). The breathing rate not only depends on the body size of the subject, but also of their activity and health status (Bennett & Zeman, 2004; ICRP, 1994). Furthermore, the deposition calculations used in the model are based upon the empirical equations proposed in the ICRP human respiratory tract model (Aleksandropoulou & Lazaridis, 2013).

To estimate the overall daily dose some activities were neglected, such as outdoor entertainment or indoor (at home and workplace) activity, therefore, assuming no indoor sources. The daily dose was determined for a healthy adult male living in Barcelona considering a typical time-activity pattern of a subject who has a sedentary job and commutes by subway. Time-activity pattern was based on information from the Spanish national statistical institute (http://www.ine.es/) and previous exposure studies carried out in Barcelona, which included Time-Microenvironment-Activity-Diaries (Schembari et al., 2013). The exposure concentrations at home and workplace were estimated just taking into account the infiltration of $PM_{2.5}$ from outdoor, for naturally ventilated buildings (Morawska & Salthammer, 2003). Therefore, these concentrations are underestimated due to the non-consideration of indoor sources, such as e.g. cooking at home or printer emissions in an office. Dosimetry calculations were performed using the aforementioned concentrations during exposure under variant physical activities. The additional physical activity levels considered were sitting/resting and sleeping with breathing rates of 0.54 and 0.45 $m^3\ h^{-1}$, respectively. The aerosol density outside the subway system was assumed equal to 1.5 g cm^{-3}, which corresponds to the average density of typical ambient aerosols (Zhang, Canagaratna, Jayne, Worsnop & Jimenez, 2005). A monodispersed aerosol size distribution was considered with a MMAD of 0.21 μm and a GSD of 1.15.

Table 1
Average $PM_{2.5}$ mass concentrations (μg m^{-3}) on the subway platforms and at the urban background site (outdoor) for both measurement periods.

Warmer period			Colder period		
Measurement period	Subway station	Outdoor	Measurement period	Subway station	Outdoor
2 Apr–2 May 2013	32.3 (Joanic)	14.9	28 Oct–25 Nov 2013	69.7 (Joanic)	10.5
1 Jul–30 Jul 2013	51.1 (Santa Coloma)	16.6	10 Feb–10 Mar 2014	65.0 (Santa Coloma)	13.2
2 May–31 May 2013	39.6 (Tetuan)	14.3	25 Nov–20 Dec 2013	91.3 (Tetuan)	23.3
31 May–1 Jul 2013	20.2 (Llefià)	15.4	13 Jan–10 Feb 2014	40.5 (Llefià)	11.4

3. Results and discussion

3.1. Exposure concentrations

$PM_{2.5}$ concentrations in the Barcelona subway obtained from this experimental study have been reported by Martins et al. (2015a), and will only be summarised here.

Table 1 displays the average $PM_{2.5}$ concentrations measured at each subway station and in the outdoor environment. The outdoor concentrations were lower than those in the subway stations. Thus, the outdoor $PM_{2.5}$ concentrations do not seem to influence significantly the air quality in the subway stations, since most of the $PM_{2.5}$ load in the underground stations is generated within the subway system by the motion of the trains and the movement of the commuters (e.g. Querol et al., 2012). These results are in agreement with Nieuwenhuijsen, Gómez-Perale and Colvile (2007), who also found high PM concentrations in underground environments resulting from the generation or accumulation of PM in a confined space, particularly in old subway systems. In Barcelona subway, higher $PM_{2.5}$ concentrations were found in the stations during the colder period, mainly due to platform ventilation differences between seasons, being stronger during the warmer period. The new Llefià station showed on average lower $PM_{2.5}$ concentrations (around 50%) in comparison with old conventional stations (Joanic, Santa Coloma and Tetuan), which might be related to the design of the stations (with PSDs), but also due to the lower train frequency and more advanced ventilation setup.

Regarding the measurements inside the trains no seasonal pattern was found, thereby, in the current study average $PM_{2.5}$ concentrations under normal conditions inside the trains (with air conditioning) obtained in both measurement periods were used. These concentrations were 53.8, 37.1, 56.9, 46.9, 35.7 and 23.3 $\mu g\, m^{-3}$ in the lines L1, L2, L3, L4, L5 and L10, respectively. Again $PM_{2.5}$ concentrations inside the trains of older lines (L1-5) were higher than those in the trains of the new PSDs line (L10). On average, the $PM_{2.5}$ concentrations inside the trains were lower (around 15%) than those on station platforms.

Table 2 displays a typical time-activity pattern and the exposure concentrations for a 24-h period, including both indoor and outdoor environments considered for this study. The reported concentrations are the average values of all measurements during both seasonal periods to obtain overall exposure concentrations. For a subway commuting travel of 15 min inside the train and 5 min on the platform, the average $PM_{2.5}$ exposure would reach 44.5 $\mu g\, m^{-3}$ (Table 2), based on the exposure concentrations of 42.3 and 51.2 $\mu g\, m^{-3}$ inside trains and on platforms, respectively. Exposure concentrations at home and workplace were estimated taking into account the mean value of the indoor/outdoor ratio of 0.91 for $PM_{2.5}$, for naturally ventilated buildings in the absence of indoor sources (Morawska & Salthammer, 2003). Thus, the exposure concentrations at home and workplace were obtained based on the average $PM_{2.5}$ outdoor concentration of 15.0 $\mu g\, m^{-3}$ (Table 2). However, in addition to the particles from outdoor origin, aerosols are also generated in the presence of indoor activities (e.g. Abt, Suh, Allen & Koutrakis, 2000a; Abt, Suh, Allen, Catalano & Koutrakis, 2000b; Morawska & Salthammer, 2003; Afshari, Matson & Ekberg, 2005; Hussein, Hämeri, Heikkinen & Kulmala, 2005; Hussein et al., 2006; Lazaridis et al., 2006; Glytsos et al., 2010; Abdullahi, Delgado-Saborit & Harrison, 2013), and this should be taken into account when interpreting the dose results. Moreover, the natural ventilation does not provide a constant indoor/outdoor ratio (Hussein et al., 2006, 2005; Minguillón et al., 2012).

3.2. Particle dose in the subway system

The deposited $PM_{2.5}$ mass in the different regions of the HRT (ET, TB and AI) for a subway commuting travel, assuming the typical exposure time of 5 min on the platforms and 15 min inside the trains, is shown in Fig. 1. Particle dose in the HRT

Table 2
Daily time-activity pattern and $PM_{2.5}$ exposure concentrations.

Time		Duration	Microenvironment	Activity level	$PM_{2.5}$ exposure
Start	End	(h)			($\mu g\, m^{-3}$)
00:00	07:00	7.0	Home	Sleeping	13.6
07:00	08:10	1.2	Home	Light exercise	13.6
08:10	08:20	0.2	Outdoor	Light exercise	15.0
08:20	08:40	0.3	Subway system	Light exercise	44.5
08:40	09:00	0.3	Outdoor	Light exercise	15.0
09:00	18:00	9.0	Workplace	Sitting	13.6
18:00	18:20	0.3	Outdoor	Light exercise	15.0
18:20	18:40	0.3	Subway system	Light exercise	44.5
18:40	18:50	0.2	Outdoor	Light exercise	15.0
18:50	21:00	2.2	Home	Light exercise	13.6
21:00	23:00	2.0	Home	Sitting/resting	13.6
23:00	00:00	1.0	Home	Sleeping	13.6

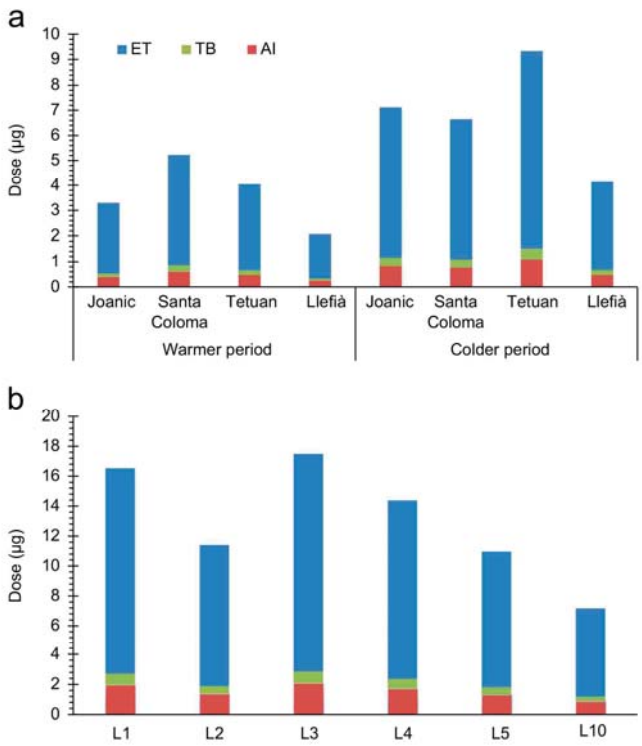

Fig. 1. $PM_{2.5}$ dose (μg) in the HRT for a subway commuting travel during (a) 5 min on the platforms and (b) 15 min inside the trains (regions of the HRT: ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial).

was proportional to the exposure concentrations. Thus, higher $PM_{2.5}$ dose occurred during the colder period in the subway stations (Fig. 1a), mainly due to platform ventilation differences between seasonal periods, as previously discussed.

Based on the intensive study performed in several subway stations of Barcelona by Martins et al. (2015a), different $PM_{2.5}$ concentrations were found among stations depending on the architectural design. The $PM_{2.5}$ dose for commuters in the new stations with PSDs (e.g. Llefià) was lower than in the older conventional stations. Among the latter, the stations with single narrow tunnel and one rail track (e.g. Tetuan) showed higher $PM_{2.5}$ doses than those observed in the rest of stations, taking into account that in the stations with one wide tunnel and two rail tracks without middle wall (e.g. Santa Coloma) a much more variable particle dose is expected, related to the large variability of $PM_{2.5}$ concentrations. Furthermore, the particle dose when a subject is in the subway stations may be affected by several influential parameters (Martins et al., 2015a). Experimentally, $PM_{2.5}$ concentrations showed clear differences during distinct times of the day and location on the platform, reflecting the influence of the ventilation settings, design of the stations and tunnels, train frequency and commuter density. Concentrations were lower during weekends, probably due to the lower frequency of trains. When travelling inside the trains in the oldest lines (L1-5), the $PM_{2.5}$ dose in the HRT was also higher than that in the new line 10 (Fig. 1b), as expected due to higher $PM_{2.5}$ concentrations.

During the subway commuting travel the highest dose was observed inside the trains as a result of the longer exposure time, evidencing that the exposure period is an important factor in the estimation of the particle dose, since the concentrations inside the trains were lower (around 15%) than those on station platforms. However, it is worth observing that the particle dose inside the trains was more than double (averagely 2.5 times higher) of those on the platforms.

Salma et al. (2002) reported that the biological response to airborne particles is assumed to be related to the amount of PM deposited in the different compartments of the HRT. With respect to deposition efficiencies, a large percentage (81.7%) of the inhaled mass of $PM_{2.5}$ was deposited in the whole human respiratory system and the remaining was exhaled. These total deposition follows the tendencies derived from the superposition of the regional depositions ($D_{total}=D_{ET}+D_{TB}+D_{AI}$). As shown in Fig. 1(a) and (b), the deposition fraction over the total inhaled mass showed substantial differences among the regions of the human respiratory tract (ET, TB and AI). The extrathoracic airways received the highest amount of the inhaled $PM_{2.5}$ mass deposited in the HRT (68.5%). This fraction reflects that the deposition of particles occurred mainly in the upper region of the respiratory tract, which does not penetrate into the lung, and is removed much more rapidly than the particles deposited in deeper regions of the respiratory system (e.g. Carvalho, Peters & Williams, 2011; Löndahl et al., 2014). In contrast, the lowest amount of inhaled $PM_{2.5}$ mass was deposited in the tracheobronchial region (3.7%) and the remaining mass in the alveolar–interstitial region (9.6%).

3.3. Estimated personal $PM_{2.5}$ daily dose

The current study deals with the individual's exposure to $PM_{2.5}$, in order to identify the activities and microenvironments that contribute most to an average daily dose. Given that short-term exposure may contribute significantly to average daily exposure to $PM_{2.5}$ mass concentration, the daily doses of total and regional deposited mass were calculated, considering a typical time-activity pattern (Table 2). Figure 2 shows the effect of $PM_{2.5}$ exposure concentrations on dose for total and regional respiratory tract. The deposition increases by increasing the exposure concentration.

In Table 3, dose, deposition rate and the contribution of the different activities/microenvironments for total $PM_{2.5}$ deposited mass are reported for a typical time-activity pattern (Table 2), considering no indoor sources at home and workplace. The minimum 24-h total dose of $PM_{2.5}$ in an adult male was around 78 μg. This value presents the lowest estimate of the particle dose and it is expected to be higher in real-life conditions after considering indoor sources of aerosol particles and spatial variability of outdoor aerosols. Abt et al. (2000a, 2000b) conducted an intensive study characterizing sources of indoor particles and they found that cooking activities, cleaning and the movement of people has a significant impact on indoor particle concentrations. Moreover, the difference in the absolute value is expected to yield higher personal exposure and dose depending on the residence and workplace of the subject being close to a road, in commute traffic, background environment, etc. (e.g. Buonanno et al., 2011; Knibbs, Cole-Hunter & Morawska, 2011; Minguillón et al., 2012; Salma et al., 2015; Wang, Morawska, Jayaratne, Mengersen & Heuff, 2011). In the current study, the outdoor concentrations were measured at a background station located in the urban area of Barcelona, despite the exposure and dose for people living and working nearby major roads and road junctions can be significantly higher, due to very high $PM_{2.5}$ concentrations recorded close to road traffic (Minguillón et al., 2014). Furthermore, as previously mentioned the particle dose is expected to increase while breathing through the mouth.

Regarding the total deposition fraction, 29.4% of the daily inhaled $PM_{2.5}$ was deposited in the HRT and the remaining was exhaled. The dose in the tracheobronchial and in the extrathoracic regions represented from 3.9% to 14.0% of the inhaled particles. The remaining particles were deposited in the alveolar–interstitial region (11.5%). Comparing the daily particle deposition with the particle deposition taking place only at the subway micro environment, the deposition fraction of the inhaled particles in the extrathoracic region and consequently the total deposition fraction were much lower for the daily deposition, due to the smaller particle size of the aerosol outside the subway system (see size distribution in Section 2.3). The decrease in deposition with decreasing particle size is in agreement with predictions of the ICRP model (ICRP, 1994). The deposition fraction in the alveolar–interstitial region was higher in the daily results since the smaller particles can penetrate into deep lung regions and can deposit there. Thus, these results showed that the regional distribution of deposited particles (i.e. the mass of particles that are deposited in each of the respiratory tract regions) is strongly dependent on particle size. However, for health effect purposes, the smaller particles depositing deeper in the lungs are less efficiently cleared compared to the larger particles that deposit preferentially in the upper airways where they are more easily cleared (Carvalho et al., 2011). The clearance mechanisms are a natural defence of the human body and operate in different regions of the lungs to eliminate the trapped foreign material (Hussain et al., 2011). Furthermore, comparing same mass deposits of large and small particles, the latter contains a much higher number of particles that need to be cleared (Carvalho et al., 2011).

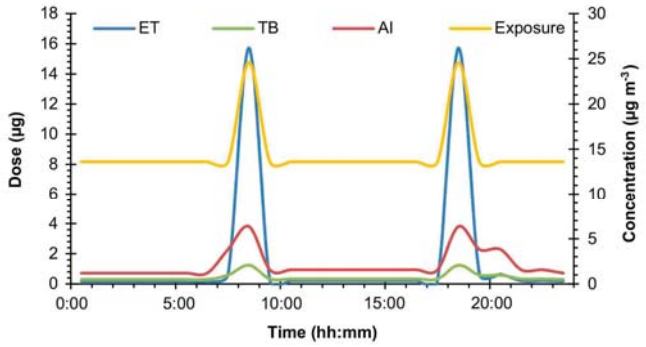

Fig. 2. Daily $PM_{2.5}$ exposure concentration and dose in the different regions of the HRT (ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial).

Table 3
Summary of $PM_{2.5}$ dose and time spend for each microenvironment.

Microenvironment	Dose (μg)	Daily dose fraction (%)	Time exposure (h)	Daily time fraction (%)	Deposition rate (μg h^{-1})
Home	24.4	31.2	13.3	55.6	1.8
Outdoor	3.9	5.0	1.0	4.2	3.9
Subway system	36.4	46.7	0.7	2.8	54.6
Workplace	13.3	17.1	9.0	37.5	1.5

There are considerable differences in the distribution of particle dose in the regions of the HRT along the day (Fig. 2) which are attributed to the different exposure concentrations and size distribution of $PM_{2.5}$ but also to the different physical activity levels. Brand et al. (1999) reported that for all particle sizes, the particle dose for each region of the HRT increases with increasing breathing rate. Increasing the breathing rate demonstrate the effect of inertial impaction in larger particle size, by increasing deposition in the upper respiratory tract and consequently increases the deposition fraction in the extrathoracic region. For smaller particle size, increasing the amount of aerosol inhaled due to high air velocity promotes an increase of particle deposition in the deeper lung.

An increase of physical activity from rest to exercise led to an increase of the dose, as also reported by Löndahl et al. (2007) and Daigle et al. (2003), because of the combined increase in deposition fraction and breathing rate. However, the effect of changing the breathing rate on the distribution of the daily particle dose in the HRT is lower compared to the particle size and the exposure concentrations.

Table 3 shows the contributions of the different microenvironments to the total particle daily dose. An important contribution arises from the commuting time spent in the subway ($\approx 3\%$), which accounted for a maximum of approximately 47% of the overall daily dose, corresponding to more than 36 μg per day. Therefore, commuting in the subway system represents the activity with the highest dose received per time unit (54.6 $\mu g\, h^{-1}$), due to the high particle concentrations and large particle size that contribute disproportionally to dose. Therefore, the high contribution of the subway exposure to the daily dose, despite the low time exposure, is mainly due to the higher PM concentrations and the larger particle size. Moreover, in relative terms, it becomes more relevant due to an underestimation of the dose received by people living/residing in microenvironments where higher particle concentrations are usually experienced, namely considering the indoor sources, as explained before.

Dose at home becomes less important (1.8 $\mu g\, h^{-1}$), partly because it includes night hours with lower PM concentrations and the exposed subject is under low activity level. However, this deposition rate was lower at home and workplace compared to background levels (outdoor), which is typical of an indoor microenvironment without any relevant particle mass sources as considered for this study (Table 3). It should be noted that a high PM dose is expected for all types of commuting means of transport due to the high PM exposure levels, as mentioned previously. Moreover, the particle size of the subway $PM_{2.5}$ is larger than the remaining means of transport, thus for a given concentration lead to a higher dose.

4. Conclusions

PM dosimetry models substantially improve personal dose assessment in replacing experimental investigations because they save time, efforts, and money in assessing the health effects arising from exposure to aerosol particles. However, modelling of the deposited dose require: a detailed description of the exposed subject characteristics and the time-activity pattern, a good estimate of the indoor and outdoor exposure levels to aerosol particle, physicochemical properties of inhaled particles, and a precise deposition fraction of aerosol particles in the different regions of the respiratory system. In this study, the above mentioned factors were taken into account and the dosimetry model ExDoM was applied for the estimation of the respiratory tract dose received by a healthy adult male exposed to $PM_{2.5}$ in the Barcelona environment, especially on subway system. Note that a monodispersed aerosol was considered for the dosimetry model, whereas it is possible that a finer mode is also present, and hence the reported results may underestimate the amount of particle mass that is deposited in the deeper regions of the respiratory system.

The dose of $PM_{2.5}$ during a subway commuting travel was calculated assuming the typical exposure time of 5 min on the platforms and 15 min inside the trains. Particle dose was proportional to the exposure concentrations both on the platforms and inside the trains. The highest dose was observed inside the trains due to the longer exposure time, evidencing that the exposure period is an important factor in the estimation of the particles deposited dose, despite concentrations inside the trains were lower than those on station platforms. Concerning the deposition fractions, a large percentage (82%) of the inhaled mass of $PM_{2.5}$ was deposited in the whole human respiratory system. The separation made for regional dose in the HRT for health effect purposes, shows that the highest amount of the inhaled particles deposited in the extrathoracic airways. However, the particles deposited in this region is removed much more rapidly than the ones in the deeper regions of the respiratory system.

Individual's typical daily exposure to $PM_{2.5}$ and dose were estimated for an adult male who lives in Barcelona and commutes by subway, considering no indoor sources at home and workplace. The distribution of deposited particles in the HRT showed considerable differences along the day, most dependent on the particle size and exposure concentrations. Changing the breathing rate had a minor effect on the distribution of deposited particles in the HRT.

The daily $PM_{2.5}$ dose obtained in this study represents the lowest estimate and it is expected to be higher in real-life conditions where aerosols are generated by indoor activities and outdoor exposure may take place at more polluted locations than the urban background environment, for example considering a traffic or a city-centre environment. Commuting by subway represented the highest dose received per time unit during the day, contributing to around 50% of the total particle dose, although the amount of time spent in the subway system accounts for only 3% of a day, owing mainly to the higher concentration and the larger particle size. However, the relative contribution to the total daily dose of $PM_{2.5}$ due to subway commuting is overestimated, and it should be interpreted as the maximum daily dose of particles received by a subject in this microenvironment. Given the relevance of the commuting dose with respect to the total daily dose, it is

important to mention that a high impact on $PM_{2.5}$ dose is expected regardless of the mean of transport, as reported in several studies, revealing that this result is not exclusive for subway commuting.

The results of this work show the importance of individual exposure and dose assessment, in order to provide information for the protection of public health. Personal exposure studies are an essential tool to identify health risks, set, and review air quality standards and evaluate effective policy interventions.

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References

Abdullahi, K. L., Delgado-Saborit, J. M., & Harrison, R. M. (2013). Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: a review. *Atmospheric Environment*, *71*, 260–294, http://dx.doi.org/10.1016/j.atmosenv.2013.01.061.

Abt, E., Suh, H. H., Allen, G., & Koutrakis, P. (2000a). Characterization of indoor particle sources: a study conducted in the metropolitan Boston area. *Environmental Health Perspectives*, *108*, 35–44.

Abt, E., Suh, H. H., Catalano, P., & Koutrakis, P. (2000b). Relative contribution of outdoor and indoor particle sources to indoor concentrations. *Environmental Science and Technology*, *34*, 3579–3587, http://dx.doi.org/10.1021/es990348y.

Afshari, A., Matson, U., & Ekberg, L. E. (2005). Characterization of indoor sources of fine and ultrafine particles: a study conducted in a full-scale chamber. *Indoor Air*, *15*, 141–150, http://dx.doi.org/10.1111/j.1600-0668.2005.00332.x.

Aleksandropoulou, V., & Lazaridis, M. (2013). Development and application of a model (ExDoM) for calculating the respiratory tract dose and retention of particles under variable exposure conditions. *Air Quality Atmosphere & Health*, *6*, 13–26, http://dx.doi.org/10.1007/s11869-010-0126-z.

Aleksandropoulou, V., Mitsakou, C., Housiadas, C., & Lazaridis, M. (2008). Particulate matter exposure and dose relationships derived from realistic exposure scenarios. *Indoor and Built Environment*, *17*, 237–246, http://dx.doi.org/10.1177/1420326 × 08091201.

Anderson, P. J., Wilson, J. D., & Hiller, F. C. (1990). Respiratory tract deposition of ultrafine particles in subjects with obstructive or restrictive lung disease. *Chest*, *97*, 1115–1120, http://dx.doi.org/10.1378/chest.97.5.1115.

Asgharian, B. (2004). A model of deposition of hygroscopic particles in the human lung. *Aerosol Science and Technology*, *38*, 938–947, http://dx.doi.org/10.1080/027868290511236.

Asgharian, B., Ménache, M. G., & Miller, F. J. (2004). Modeling age-related particle deposition in humans. *Journal of Aerosol Medicine*, *17*, 213–224, http://dx.doi.org/10.1089/jam.2004.17.213.

Asgharian, B., & Price, O. T. (2007). Deposition of ultrafine (nano) particles in the human lung. *Inhalation Toxicology*, *19*, 1045–1054, http://dx.doi.org/10.1080/08958370701626501.

Bachoual, R., Boczkowski, J., Goven, D., Amara, N., Tabet, L., On, D., Leçon-malas, V., Aubier, M., & Lanone, S. (2007). Biological effects of particles from the Paris subway system. *Chemical Research in Toxicology*, *20*, 1426–1433, http://dx.doi.org/10.1021/tx700093j.

Bennett, W. D., & Zeman, K. L. (2004). Effect of body size on breathing pattern and fine-particle deposition in children. *Journal of Applied Physiology*, *97*, 821–826, http://dx.doi.org/10.1152/japplphysiol.01403.2003.

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

Brand, P., Häußinger, K., Meyer, T., Scheuch, G., Schulz, H., Selzer, T., & Heyder, J. (1999). Intrapulmonary distribution of deposited particles. *Journal of Aerosol Medicine*, *12*, 275–284, http://dx.doi.org/10.1089/jam.1999.12.275.

Broday, D. M., & Agnon, Y. (2007). Asymmetric human lung morphology induce particle deposition variation. *Journal of Aerosol Science*, *38*, 701–718, http://dx.doi.org/10.1016/j.jaerosci.2007.06.001.

Buonanno, G., Fuoco, F. C., & Stabile, L. (2011). Influential parameters on particle exposure of pedestrians in urban microenvironments. *Atmospheric Environment*, *45*, 1434–1443, http://dx.doi.org/10.1016/j.atmosenv.2010.12.015.

Buonanno, G., Marks, G. B., & Morawska, L. (2013). Health effects of daily airborne particle dose in children: direct association between personal dose and respiratory health effects. *Environmental Pollution*, *180*, 246–250, http://dx.doi.org/10.1016/j.envpol.2013.05.039.

Carvalho, T. C., Peters, J. I., & Williams, R. O., III (2011). Influence of particle size on regional lung deposition – what evidence is there?. *International Journal of Pharmaceutics*, *406*, 1–10, http://dx.doi.org/10.1016/j.ijpharm.2010.12.040.

Chalupa, D. C., Morrow, P. E., Oberdörster, G., Utell, M. J., & Frampton, M. W. (2004). Ultrafine particle deposition in subjects with asthma. *Environmental Health Perspectives*, *112*, 879–882.

Chalvatzaki, E., & Lazaridis, M. (2015). Development and application of a dosimetry model (ExDoM2) for calculating internal dose of specific particle-bound metals in the human body. *Inhalation Toxicology*http://dx.doi.org/10.3109/08958378.2015.1046201.

Daigle, C. C., Chalupa, D. C., Gibb, F. R., Morrow, P. E., Oberdörster, G., Utell, M. J., & Frampton, M. W. (2003). Ultrafine particle deposition in humans during rest and exercise. *Inhalation Toxicology*, *15*, 539–552, http://dx.doi.org/10.1080/08958370304468.

De Nazelle, A., Fruin, S., Westerdahl, D., Martinez, D., Ripoll, A., Kubesch, N., & Nieuwenhuijsen, M. (2012). A travel mode comparison of commuters' exposures to air pollutants in Barcelona. *Atmospheric Environment*, *59*, 151–159, http://dx.doi.org/10.1016/j.atmosenv.2012.05.013.

Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., & Samet, J. M. (2006). Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *JAMA*, *295*, 1127–1134, http://dx.doi.org/10.1001/jama.295.10.1127.

Georgopoulos, P. G., & Lioy, P. J. (2006). From a theoretical framework of human exposure and dose assessment to computational system implementation: the Modeling ENvironment for TOtal Risk Studies (MENTOR). *Journal of Toxicology and Environmental Health, Part B*, *9*, 457–483, http://dx.doi.org/10.1080/10937400600755929.

Glytsos, T., Ondráček, J., Džumbová, L., Kopanakis, I., & Lazaridis, M. (2010). Characterization of particulate matter concentrations during controlled indoor activities. *Atmospheric Environment*, *44*, 1539–1549, http://dx.doi.org/10.1016/j.atmosenv.2010.01.009.

Gulliver, J., & Briggs, D. J. (2004). Personal exposure to particulate air pollution in transport microenvironments. *Atmospheric Environment*, *38*, 1–8, http://dx.doi.org/10.1016/j.atmosenv.2003.09.036.

Gustavsson, P., Bigert, C., & Pollán, M. (2008). Incidence of lung cancer among subway drivers in Stockholm. *American Journal of Industrial Medicine*, *547*, 545–547, http://dx.doi.org/10.1002/ajim.20584.

Heyder, J. (2004). Deposition of inhaled particles in the human respiratory tract and consequences for regional targeting in respiratory drug delivery. *Proceedings of the American Thoracic Society*, *1*, 315–320, http://dx.doi.org/10.1513/pats.200409-046TA.
Heyder, J., & Rudolf, G. (1984). Mathematical models of particle deposition in the human respiratory tract. *Journal of Aerosol Science*, *15*, 697–707, http://dx.doi.org/10.1016/0021-8502(84)90007-7.
Hofmann, W. (2011). Modelling inhaled particle deposition in the human lung-A review. *Journal of Aerosol Science*, *42*, 693–724, http://dx.doi.org/10.1016/j.jaerosci.2011.05.007.
Hussain, M., Madl, P., & Khan, A. (2011). Lung deposition predictions of airborne particles and the emergence of contemporary diseases Part-I. *theHealth*, *2*, 51–59.
Hussein, T., Glytsos, T., Ondráček, J., Dohányosová, P., Ždímal, V., Hämeri, K., Lazaridis, M., Smolík, J., & Kulmala, M. (2006). Particle size characterization and emission rates during indoor activities in a house. *Atmospheric Environment*, *40*, 4285–4307, http://dx.doi.org/10.1016/j.atmosenv.2006.03.053.
Hussein, T., Hämeri, K., Heikkinen, M. S. A., & Kulmala, M. (2005). Indoor and outdoor particle size characterization at a family house in Espoo–Finland. *Atmospheric Environment*, *39*, 3697–3709, http://dx.doi.org/10.1016/j.atmosenv.2005.03.011.
ICRP, 1994. Human Respiratory Tract Model for Radiological Protection. ICRP Publication 66. Ann. ICRP 24 (1-3).
Karlsson, H. L., Ljungman, A. G., Lindbom, J., & Möller, L. (2006). Comparison of genotoxic and inflammatory effects of particles generated by wood combustion, a road simulator and collected from street and subway. *Toxicology Letters*, *165*, 203–211, http://dx.doi.org/10.1016/j.toxlet.2006.04.003.
Katsouyanni, K., Touloumi, G., Samoli, E., Gryparis, a, Le Tertre, a, Monopolis, Y., Rossi, G., Zmirou, D., Ballester, F., Boumghar, a, Anderson, H. R., Wojtyniak, B., Paldy, a, Braunstein, R., Pekkanen, J., Schindler, C., & Schwartz, J. (2001). Confounding and effect modification in the short-term effects of ambient particles on total mortality: results from 29 European cities within the APHEA2 project. *Epidemiology*, *12*, 521–531, http://dx.doi.org/10.1097/00001648-200109000-00011.
Kim, C. S., & Kang, T. C. (1997). Comparative measurement of lung deposition of inhaled fine particles in normal subjects and patients with obstructive airway disease. *American Journal of Respiratory and Critical Care Medicine*, *155*, 899–905, http://dx.doi.org/10.1164/ajrccm.155.3.9117024.
Klepeis, N. E. (2006). Modeling human exposure to air pollution. In W. Ott, L. Wallace, & A. Steinemann (Eds.), *Human exposure analysis*. Boca Raton: CRC Press.
Knibbs, L. D., Cole-Hunter, T., & Morawska, L. (2011). A review of commuter exposure to ultrafine particles and its health effects. *Atmospheric Environment*, *45*, 2611–2622, http://dx.doi.org/10.1016/j.atmosenv.2011.02.065.
Koblinger, L., & Hofmann, W. (1990). Monte Carlo modeling of aerosol deposition in human lungs. Part I: simulation of particle transport in a stochastic lung structure. *Journal of Aerosol Science*, *21*, 661–674, http://dx.doi.org/10.1016/0021-8502(90)90121-D.
Lazaridis, M., Aleksandropoulou, V., Smolík, J., Hansen, J. E., Glytsos, T., Kalogerakis, N., & Dahlin, E. (2006). Physico-chemical characterization of indoor/outdoor particulate matter in two residential houses in Oslo, Norway: measurements overview and physical properties – URBAN-AEROSOL Project. *Indoor Air*, *16*, 282–295, http://dx.doi.org/10.1111/j.1600-0668.2006.00425.x.
Lazaridis, M., Broday, D. M., Hov, Ø., & Georgopoulos, P. G. (2001). Integrated exposure and dose modeling and analysis system. 3. Deposition of inhaled particles in the human respiratory tract. *Environmental Science & Technology*, *35*, 3727–3734, http://dx.doi.org/10.1021/es001545w.
Lippmann, M., Yeates, D. B., & Albert, R. E. (1980). Deposition, retention, and clearance of inhaled particles. *British Journal of Industrial Medicine*, *37*, 337–362.
Löndahl, J., Massling, A., Pagels, J., Swietlicki, E., Vaclavik, E., & Loft, S. (2007). Size-resolved respiratory-tract deposition of fine and ultrafine hydrophobic and hygroscopic aerosol particles during rest and exercise. *Inhalation Toxicology*, *19*, 109–116, http://dx.doi.org/10.1080/08958370601051677.
Löndahl, J., Massling, A., Swietlicki, E., Bräuner, E. V., Ketzel, M., Pagels, J., & Loft, S. (2009). Experimentally determined human respiratory tract deposition of airborne particles at a busy street. *Environmental Science & Technology*, *43*, 4659–4664, http://dx.doi.org/10.1021/es803029b.
Löndahl, J., Möller, W., Pagels, J. H., Kreyling, W. G., Swietlicki, E., & Schmid, O. (2014). Measurement techniques for respiratory tract deposition of airborne nanoparticles: a critical review. *Journal of Aerosol Medicine and Pulmonary Drug Delivery*, *27*, 229–254, http://dx.doi.org/10.1089/jamp.2013.1044.
Löndahl, J., Pagels, J., Boman, C., Swietlicki, E., Massling, A., Rissler, J., Blomberg, A., Bohgard, M., & Sandström, T. (2008). Deposition of biomass combustion aerosol particles in the human respiratory tract. *Inhalation Toxicology*, *20*, 923–933, http://dx.doi.org/10.1080/08958370802087124.
Martins, V., Moreno, T., Minguillón, M. C., Amato, F., de Miguel, E., Capdevila, M., & Querol, X. (2015a). Exposure to airborne particulate matter in the subway system. *Science of The Total Environment*, *511*, 711–722, http://dx.doi.org/10.1016/j.scitotenv.2014.12.013.
Martins V., Moreno T., Minguillón M.C., van Drooge B.L., Amato F., de Miguel E., Capdevila M., Centelles S. & Querol X. (2015b). Origin of inorganic and organic components of PM2.5 in subway stations of Barcelona, Spain. Environmental pollution (in press), http://dx.doi.org/10.1016/j.envpol.2015.07.004.
Ménache, M. G., Hofmann, W., Ashgarian, B., & Miller, F. J. (2008). Airway geometry models of children's lungs for use in dosimetry modeling. *Inhalation Toxicology*, *20*, 101–126, http://dx.doi.org/10.1080/08958370701821433.
Michaels, R. A., & Kleinman, M. T. (2000). Incidence and apparent health significance of brief airborne particle excursions. *Aerosol Science & Technology*, *32*, 93–105, http://dx.doi.org/10.1080/027868200303803.
Minguillón, M. C., Cirach, M., Hoek, G., Brunekreef, B., Tsai, M., de Hoogh, K., Jedynska, A., Kooter, I. M., Nieuwenhuijsen, M., & Querol, X. (2014). Spatial variability of trace elements and sources for improved exposure assessment in Barcelona. *Atmospheric Environment*. *89*. 268–281. http://dx.doi.org/10.1016/j.atmosenv.2014.02.047.
Minguillón, M. C., Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Figueras, F., Salvado, J. A., Grimalt, J. O., Nieuwenhuijsen, M., & Querol, X. (2012). Source apportionment of indoor, outdoor and personal PM2.5 exposure of pregnant women in Barcelona, Spain. *Atmospheric Environment*, *59*, 426–436, http://dx.doi.org/10.1016/j.atmosenv.2012.04.052.
Mitsakou, C., Mitrakos, D., Neofytou, P., & Housiadas, C. (2007). A simple mechanistic model of deposition of water-soluble aerosol particles in the mouth and throat. *Journal of Aerosol Medicine*, *20*, 519–529, http://dx.doi.org/10.1089/jam.2007.0625.
Montoya, L. D., Lawrence, J., Murthy, G. G. K., Sarnat, J. a, Godleski, J. J., & Koutrakis, P. (2004). Continuous measurements of ambient particle deposition in human subjects. *Aerosol Science & Technology*, *38*, 980–990, http://dx.doi.org/10.1080/027868290519049.
Morawska, L., He, C., Hitchins, J., Mengersen, K., & Gilbert, D. (2003). Characteristics of particle number and mass concentrations in residential houses in Brisbane, Australia. *Atmospheric Environment*, *37*, 4195–4203, http://dx.doi.org/10.1016/S1352-2310(03)00566-1.
Morawska, L., Hofmann, W., Hitchins-Loveday, J., Swanson, C., & Mengersen, K. (2005). Experimental study of the deposition of combustion aerosols in the human respiratory tract. *Journal of Aerosol Science*, *36*, 939–957, http://dx.doi.org/10.1016/j.jaerosci.2005.03.015.
Morawska, L., & Salthammer, T. (2003). *Indoor Environment-Airborne Particles and Settled Dust*. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.
Moreno, T., Martins, V., Querol, X., Jones, T., BéruBé, K., Minguillón, M. C., Amato, F., Capdevila, M., de Miguel, E., Centelles, S., & Gibbons, W. (2015). A new look at inhalable metalliferous airborne particles on rail subway platforms. *Science of The Total Environment*, *505*, 367–375, http://dx.doi.org/10.1016/j.scitotenv.2014.10.013.
Nieuwenhuijsen, M. J., Gómez-Perales, J. E., & Colvile, R. N. (2007). Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. *Atmospheric Environment*, *41*, 7995–8006, http://dx.doi.org/10.1016/j.atmosenv.2007.08.002.
Patterson, R. F., Zhang, Q., Zheng, M., & Zhu, Y. (2014). Particle deposition in respiratory tracts of school-aged children. *Aerosol and Air Quality Research*, *14*, 64–73, http://dx.doi.org/10.4209/aaqr.2013.04.0113.
Pope, C. A., & Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of Air & Waste Management Association*, *56*, 709–742, http://dx.doi.org/10.1080/10473289.2006.10464485.
Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., & Capdevila, M. (2012). Variability of levels and composition of PM10 and PM2.5 in the Barcelona metro system. *Atmospheric Chemistry and Physics*, *12*, 5055–5076, http://dx.doi.org/10.5194/acp-12-5055-2012.
Rudolf, G., Köbrich, R., & Stahlhofen, W. (1990). Modelling and algebraic formulation of regional aerosol deposition in man. *Journal of Aerosol Science*, *21* (Suppl), S403–S406, http://dx.doi.org/10.1016/0021-8502(90)90266-Z.

Russell, A. G., & Brunekreef, B. (2009). A focus on particulate matter and health. *Environmental Science & Technology*, *43*, 4620–4625, http://dx.doi.org/10.1021/es9005459.
Salma, I., Balásházy, I., Winkler-Heil, R., Hofmann, W., & Záray, G. (2002). Effect of particle mass size distribution on the deposition of aerosols in the human respiratory system. *Journal of Aerosol Science*, *33*, 119–132, http://dx.doi.org/10.1016/S0021-8502(01)00154-9.
Salma, I., Füri, P., Németh, Z., Balásházy, I., Hofmann, W., & Farkas, Á. (2015). Lung burden and deposition distribution of inhaled atmospheric urban ultrafine particles as the first step in their health risk assessment. *Atmospheric Environment*, *104*, 39–49, http://dx.doi.org/10.1016/j.atmosenv.2014.12.060.
Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Vrijheid, M., Cirach, M., Martinez, D., Figueras, F., Querol, X., Basagaña, X., Eeftens, M., Meliefste, K., & Nieuwenhuijsen, M. J. (2013). Personal, indoor and outdoor air pollution levels among pregnant women. *Atmospheric Environment*, *64*, 287–295, http://dx.doi.org/10.1016/j.atmosenv.2012.09.053.
Schikowski, T., Sugiri, D., Ranft, U., Gehring, U., Heinrich, J., Wichmann, H.-E., & Kramer, U. (2007). Does respiratory health contribute to the effects of long-term air pollution exposure on cardiovascular mortality?. *Respiratory Research*, *8*, 20, http://dx.doi.org/10.1186/1465-9921-8-20.
Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J. F., & Tran, C. L. (2005). The London Underground: dust and hazards to health. *Occupational & Environmental Medicine*, *62*, 355–362, http://dx.doi.org/10.1136/oem.2004.014332.
Stuart, B. O. (1984). Deposition and clearance of inhaled particles. *Environmental Health Perspectives*, *55*, 369–390, http://dx.doi.org/10.1289/ehp.8455369.
Sturm, R. (2007). A computer model for the clearance of insoluble particles from the tracheobronchial tree of the human lung. *Computers in Biology and Medicine*, *37*, 680–690, http://dx.doi.org/10.1016/j.compbiomed.2006.06.004.
Valavanidis, A., Fiotakis, K., & Vlachogianni, T. (2008). Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. *Journal of Environmental Science and Health Part C*, *26*, 339–362, http://dx.doi.org/10.1080/10590500802494538.
Wang, L., Morawska, L., Jayaratne, E. R., Mengersen, K., & Heuff, D. (2011). Characteristics of airborne particles and the factors affecting them at bus stations. *Atmospheric Environment*, *45*, 611–620, http://dx.doi.org/10.1016/j.atmosenv.2010.10.036.
Yeh, H.-C., & Schum, G. M. (1980). Models of human lung airways and their application to inhaled particle deposition. *Bulletin of Mathematical Biology*, *42*, 461–480, http://dx.doi.org/10.1007/BF02460796.
Zhang, Q., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., & Jimenez, J. L. (2005). Time- and size-resolved chemical composition of submicron particles in Pittsburgh: implications for aerosol sources and processes. *Journal of Geophysical Research Atmospheres*, *110*, 1–19, http://dx.doi.org/10.1029/2004JD004649.

Chapter 4

Summarised Results and Discussion

4. SUMMARISED RESULTS AND DISCUSSION

Extensive and intensive sampling campaigns were carried out in the subway environment of platform stations and inside the trains. On the platforms, PM real-time measurements were performed and PM samples were collected to identify possible spatial and temporal variations and to chemically characterise the subway PM, respectively. Inside the trains only real-time measurements were carried out. In this study three European subway systems were studied (Barcelona, Athens and Oporto), with the main focus on Barcelona.

This thesis provides an in-depth assessment of air quality in subway systems and personal exposure and dose, and the results may be useful to help controlling and improving the air quality in the subway systems. The results of this study are reported in 4 scientific publications presented in section 3. Major findings from the aforementioned articles will be summarised and jointly discussed in this section. The discussion will focus on the $PM_{2.5}$ concentrations, chemical composition and sources during subway operating hours, when the commuters' exposure takes place.

4.1. PM mass concentrations

4.1.1. On platforms

From the extensive characterization of 24 stations with distinct designs of the Barcelona subway system a substantial variation in $PM_{2.5}$ concentrations among the stations was observed (hourly averages ranging from 13 to 154 $\mu g\ m^{-3}$, considering normal ventilation conditions – see Table S1 of Article 1). This variation might be related to the differences in the length and design of the stations and tunnels, variations in the train frequency, passenger densities and ventilation systems, among other factors, as discussed below. Large variations were also observed in Athens (22 – 158 $\mu g\ m^{-3}$; 5 stations) and Oporto (65 – 265 $\mu g\ m^{-3}$; 5 stations) subway systems.

In the Barcelona study, the stations composed by a single tunnel with one rail track separated from the platform by a wall with PSDs (new stations) showed on average

lower $PM_{2.5}$ concentrations (around 50%) in comparison with the old conventional stations, which might be related to a combination of factors such as (i) the PSDs preventing the air from the tunnel entering the platform, (ii) the more advanced ventilation setup and (iii) the lower train frequency. Among the conventional system, the stations with single narrow tunnel and one rail track showed on average $PM_{2.5}$ concentrations higher than those observed in stations with one wide tunnel and two rail tracks separated by a middle wall, most probably due to the less efficient dispersion of air pollution, enhancing the accumulation of PM. In the stations with one wide tunnel and two rail tracks without middle wall $PM_{2.5}$ concentrations were much more variable (Article 1). Similarly, Jung et al. (2010) reported that at narrow platforms there is a larger dependence on strong ventilation to maintain relatively low PM concentrations. Regarding Athens subway system, the $PM_{2.5}$ concentrations in Syntagma station were higher than those in Argiroupoli station, even belonging to the same line (L2), which is probably attributable not only to the fact that Argiroupoli is a new station (opened in 2013), but also because it is located in the periphery of the line (out of the central area of the city) and the train frequency is lower (some trains do not run the entire route). Furthermore, measurements in the transfer station of Syntagma (Lines 2 and 3 intersect) showed that the $PM_{2.5}$ concentrations were higher in the Syntagma platform of Line 2 than that of Line 3, which may be related to the age of the lines and consequently the different materials used (Article 3).

To compare the three subway systems among them, three stations with similar platform design were selected, minimizing other factors influencing the variation of $PM_{2.5}$ concentrations (Article 3): Santa Coloma in Barcelona, Nomismatokopio in Athens and Bolhão in Oporto. The lowest mean $PM_{2.5}$ concentration (± standard deviation of daily concentrations) was found in Santa Coloma station (58.3 ± 13.7 μg m^{-3}) while the highest mean $PM_{2.5}$ concentration was recorded in Bolhão station (83.7 ± 45.7 μg m^{-3}). In the Nomismatokopio station a mean $PM_{2.5}$ concentration of 68.3 ± 11.3 μg m^{-3} was obtained. This range of results may be associated to different ventilation systems, since the Barcelona subway is equipped with mechanical forced ventilation in all its length, whereas in both Athens and Oporto subways only natural ventilation occurs, with air exchange with the outdoor air happening mainly through draught

relief outlets ("blast shafts"). The mechanical forced ventilation is a relevant factor to improve the air quality within the subway system (Article 1), as explained below. Moreover, the majority of the underground sections in the Oporto subway system are composed by curved and/or sloping rail tracks, which may imply higher emissions from the rail–wheel–brake interfaces while trains are stopping on the platform resulting on higher particle mass concentration on the platforms. The frequency of train passages in the Oporto subway station is higher than in the stations of Barcelona and Athens, as trains from 5 different lines (LA, LB, LC, LE and LF) pass through Bolhão station using a common platform, whereas in Barcelona and Athens only trains of one line circulate at each studied station. Furthermore, the daily average $PM_{2.5}$ concentrations were much more variable in the Bolhão station than in the other two stations, because the weather conditions and consequently the $PM_{2.5}$ concentrations in the outdoor ambient air were considerably variable during the sampling period in Oporto (see Fig. S4 of Article 3). The PM concentrations in the Bolhão station may be particularly affected by the outdoor conditions, since it is followed by an aboveground station which favours the air exchange with the exterior.

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

In the weekdays the $PM_{2.5}$ concentrations on the station platforms were considerably higher (1.2 – 1.5 times) than those measured during weekends, probably due to the lower number of commuters and frequency of trains. Similar results have been observed in other subway systems (Aarnio et al., 2005; Johansson and Johansson, 2003; Mugica-Álvarez et al., 2012; Raut et al., 2009). However, considering the 3 subway systems this difference between the weekdays and weekends in $PM_{2.5}$ concentrations was more pronounced in Bolhão station (Oporto) and less in Nomismatokopio station (Athens), possibly again favoured by the busy environment of Bolhão station with the passage of trains of 5 lines.

The mean $PM_{2.5}$ concentrations obtained on the platforms of the three subway systems (gravimetric concentrations) are within the low range reported by previous worldwide subway studies (Figure 4.1).

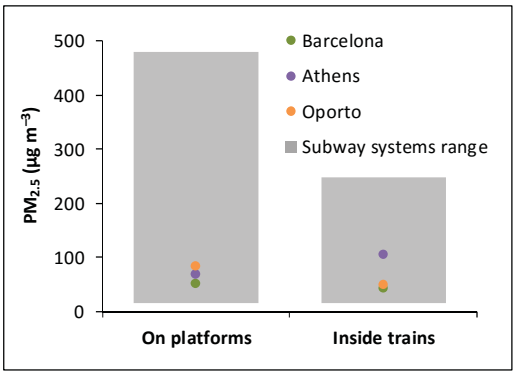

Figure 4.1 Comparison of mean $PM_{2.5}$ concentrations on platforms and inside trains obtained in the three subway systems with the range of reported studies (data and references shown in Table 1.5).

Influence of different ventilation settings

During the extensive campaign in Barcelona mean $PM_{2.5}$ concentrations on Joanic, Santa Coloma, Tetuan and Llefià subway platforms ranged between 21 and 51 µg m^{-3} in the warmer period, and between 32 and 93 µg m^{-3} in the colder period. These seasonal differences among the 4 stations were related mainly to the stronger ventilation in the warmer period that controls the air quality of the subway system, with weaker ventilations enhancing the accumulation of particles in the stations. These results were also observed in the additional platform measurements (Article 1). Regarding the three PM_X size fractions, the PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ ratios were higher in the warmer period, indicating that the ventilation of the subway system was more efficient removing coarser particles. Thus, PM_1 was the major size fraction composing the PM in the subway system, especially during the warmer period. These results are in agreement with Chan et al. (2002), who reported that the ventilation system of the subway system filtered out some coarse particles, but did not remove fine particles.

Moreover, several ventilation protocols were tested to evaluate PM_X concentration differences and determine the best operating conditions for optimizing the air quality

on the platforms. Generally, introducing outdoor air in the conventional system (old stations) was more efficient than the extraction of indoor air, evidencing that the dilution of the subway PM is more adequate for air quality purposes. When the mechanical ventilation of the tunnel was turned off (i.e. only piston effect ventilation produced by the movement of the trains) the $PM_{2.5}$ concentrations were on average around 30% higher than those obtained on a fully operational ventilation system, indicating an accumulation of PM.

In general, PM_X concentrations in the stations with PSDs were not affected by changes in the ventilation intensity on the platforms, however, they were influenced by the number of active fans and ventilation intensity in the tunnel (Article 1).

Daily patterns

Similar daily trends were observed among the subway platforms of the three subway systems (Article 3). The PM_X daily pattern presented a concentration increase in the morning with the arrival of the first trains with a peak in the morning rush hour period, which was attributable not only to the influx of commuters but also to the higher train frequency; the movement of the commuters leads to the PM resuspension, and the train movement promotes the resuspension of PM and its generation due to the abrasion of rail tracks, wheels, brake pads and power supply materials. Afterwards, PM_X concentration decreased towards a stable concentration until late afternoon. An increase in the PM_X concentrations was registered during the evening rush hours, especially in the Bolhão station where the increase in train frequency was higher. In Nomismatokopio there was not an increase in PM_X concentrations in the evening because train frequency decreased during these hours. During the night, there was a continuous decrease in PM_X concentrations due to transport service interruption for several hours, which brought about settlement of a large quantity of PM. Johansson and Johansson (2003) and Salma et al. (2007) reported a similar daily behaviour, evidencing that PM levels in the underground subway stations closely follow the train frequency. However, in the Barcelona subway system some outliers during night-time series were generally identified in the conventional stations (Joanic, Santa Coloma and Tetuan), associated with occasional maintenance or cleaning operations. The CO_2

concentrations also increased during the rush hours, due to the higher influx of commuters and consequently the higher CO_2 generated through exhalation.

In the Barcelona subway system, in addition to the influence of the train frequency, the changes of the ventilation settings had considerable effect in the variations of the PMx concentrations on the platforms along the day, particularly in the warmer period, when the ventilation is more intense (Article 1). Hence, the daily pattern of PMx and CO_2 concentrations in the Barcelona subway systems was primarily influenced by the ventilation settings and secondarily by the train frequency.

In sum, the variations of PMx levels depend largely on the operation and frequency of the trains and the ventilation system, and therefore, the personal exposure to PMx concentrations is dependent on the time of the day used to commute. In the Barcelona subway system, the PMx concentrations on the platforms are the result of a dynamic system controlled by the train frequency (source) and ventilation settings (removal), however, it is evident that the impact of train frequency on PMx levels only becomes relevant in the absence of strong ventilation. In the Athens and Oporto subway systems the PMx daily pattern is predominantly influenced by sources, since only natural ventilation occurs. PMx concentrations decreased gradually when the trains stop operating, and the train frequency also decreases, which indicates the importance of PMx sources related to the subway operation activities.

Temporal and spatial variations

PMx concentrations measurements were performed at 4 different positions along several platforms in the three European subway systems. Although there were generally day-to-day fluctuations in PMx concentrations on the platforms some temporal and spatial trends were observed, probably due to the influence of the ventilation settings, design of the stations and tunnels, location of passengers' access to the platforms, commuter density, as well as to the effect of the passage and frequency of the trains.

The PMx concentrations on some platforms varied significantly in short time scales (e.g. an increase of a factor of 3 in less than 30 seconds), especially in the case of Athens

and Barcelona subways (Article 3). In some cases, the high time resolution measurements evidenced that PMx concentrations on the platform increased when the train entered the platform and decreased when it departed. The train push in polluted air from the tunnel (by the piston effect) and PMx generated by resuspension, and when the train leaves the station the reverse piston effect moves polluted air out of the station, renewing the air on the platform. This effect of passage of trains was especially strong in the new stations (with PSDs) and old stations with single rail track (Article 1), although in some stations with two rail tracks without middle wall this pattern was also observed (Article 1 and 3). The results obtained in the new lines equipped with PSDs showed that this system, despite being an effective security barrier, does not prevent completely PM exchange between the railway and the platform. In general, the time scale for large variations was small, showing that commuters may be exposed to very high concentrations during very short time periods, which may have implications on health effects.

In some subway stations in Barcelona, higher PMx mass concentrations, especially of coarse particles, were recorded in the train entry edges and in the areas closer to the commuters' access to the platforms, in comparison with other points on the platform. However, in the Athens and Oporto cases this spatial variation was not clearly observed. Such variation can be attributed to the turbulence generated by the trains entry, due to the wind blasts produced when they pull into the stations. In the areas closer to the passengers' access to the platforms there is also a high probability of air turbulence, created by the commuters walking and the air flowing in and out of the station (Article 1). This turbulence may cause PMx resuspension, which explains the higher mass concentrations measured in these points.

PMx concentrations were relatively constant in time and along the platform of some stations. Therefore, in these cases the exposure levels of commuters were very similar when waiting anywhere along the platform.

4.1.2. Inside trains

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

The mean $PM_{2.5}$ concentrations ranges inside the trains were 19 – 75, 78 – 135 and 29 – 79 μg m^{-3} in Barcelona (6 lines), Athens (2 lines) and Oporto (2 lines), respectively. In the Barcelona study, the use of air-conditioning provided a clear abatement of PM concentrations, resulting in lower PM_X concentrations (by around 30% for $PM_{2.5}$) and finer particles (PM_1/PM_{10} was around 15% higher), as well as lower variability of PM_X concentrations (Article 1). Additionally, CO_2 exhaled by commuters accumulated inside the trains when air-conditioning was switched off and was less easily removed by the ventilation system compared to PM_X. The trains of the three subway systems are equipped with air conditioning system, and this can induce the relative constant and low PM_X concentrations registered inside the trains along the lines. Generally, the PM_X concentrations along the lines were relatively constant, while short-term peaks were observed after the train doors closed in a number of cases, probably due to turbulence and consequent PM resuspension produced by the movement of passengers inside the trains. In the Athens subway system, carriage windows were usually open, despite the existence of air-conditioning. This resulted in an increase in PM_X concentrations inside trains when passing through some tunnel sections between stations, due to the entrance of PM from the tunnel into the trains through the windows (Article 3). And thus, the highest PM_X concentrations inside the trains from the three systems were found in the lines belonging to Athens subway system. In the Oporto subway system, the PM_X and CO_2 concentrations inside the trains were generally higher while travelling in the undergrounds sections than in the aboveground section, where clean air entering the trains produced an environmental "cleaning effect" (Article 3). The PM_X concentrations inside the trains of this subway system are greatly dependent on outdoor ambient air quality.

The PM_X concentrations inside the trains were in general lower than those on the corresponding platforms in the Barcelona and Oporto subway systems, which may be attributed to the air conditioning system operating inside the trains, and in Oporto also to the predominance of aboveground stations along the lines (Articles 1 and 3). In contrast, in Athens system, the PM_X concentrations inside the trains were in general higher than those on the platforms since, as stated above, the trains run with most windows open, favouring the entrance of polluted air from tunnels and platforms into the trains (Article 3).

In the Barcelona subway system the $PM_{2.5}$ concentrations inside the trains in the new line (L10) were on average around 50% lower than in the oldest lines (Lines 1–5), because it is a technologically advanced line with more efficient mechanical ventilation system. Thus, the lowest PM_X concentrations were found in the new line both on the platforms and inside the trains. Moreover, comparing the real-time measurements performed on the 24 stations with the measurements inside the trains of the 6 lines, there was the evidence that PM_X levels inside the trains were affected by the surrounding conditions, such as those on the platforms. Figure 4.2 shows that the $PM_{2.5}$ concentrations inside the trains were strongly correlated with the $PM_{2.5}$ concentrations on the corresponding platforms (R^2=0.75). The lines with high PM concentrations were the first lines in operation and are the busiest ones because they run through the downtown area. Nevertheless, regarding seasonal variations (warmer vs. colder), there was not a regular trend among the measurements inside the trains as observed on the platforms, perhaps influenced by changes of the air filters coupled to the air-conditioning systems.

The mean $PM_{2.5}$ concentrations determined inside the trains of the three subway systems studied are within the low range reported by previous worldwide subway studies (Figure 4.1).

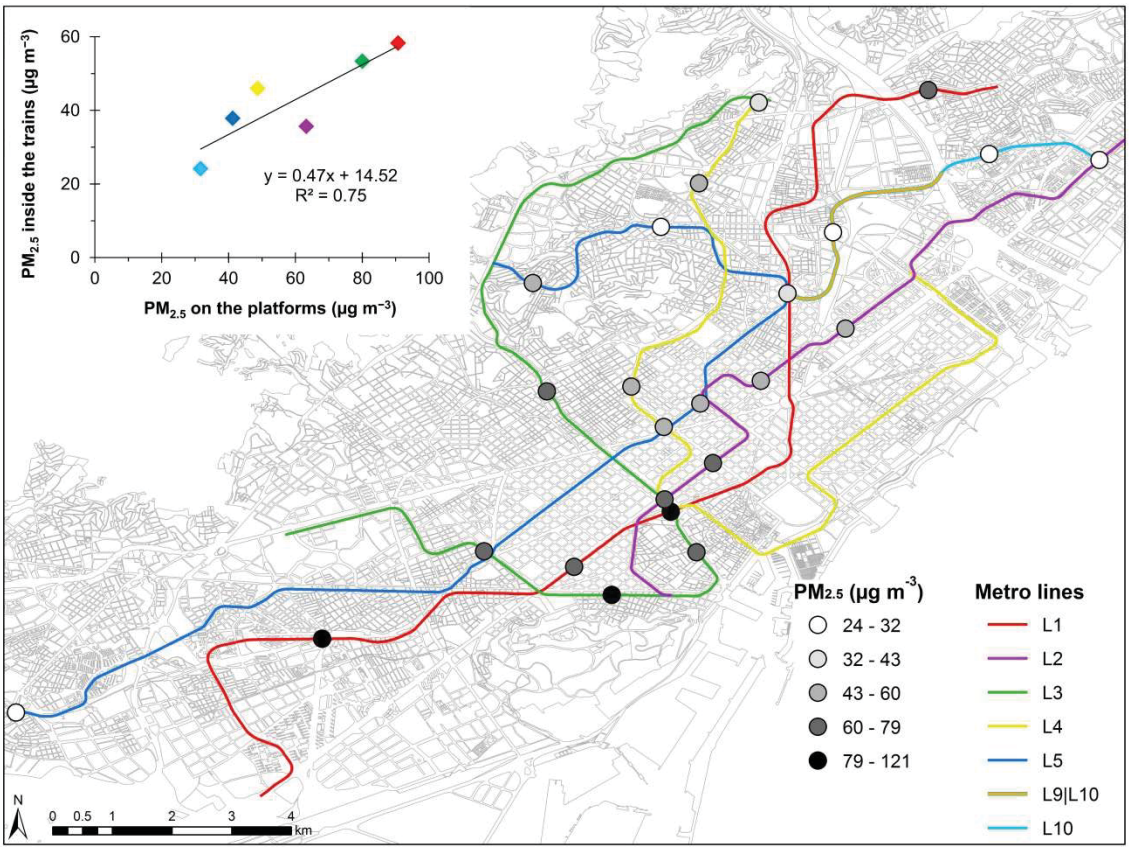

Figure 4.2 Relation between $PM_{2.5}$ concentrations on the platforms and inside the trains in the Barcelona subway system.

4.1.3. Exposure during subway commuting

The $PM_{2.5}$ exposure was calculated taking into account all data obtained during both the intensive campaigns and the additional platform measurements for each of the 3 subway systems. For a subway commuting travel of 15 min inside the train and 5 min on the platform, the average $PM_{2.5}$ exposure would reach 46.7, 98.6 and 78.2 µg m^{-3} for Barcelona, Athens and Oporto subway systems, based on the overall exposure concentrations of all measurements. The highest personal exposure was calculated for Athens, mainly related to the higher $PM_{2.5}$ concentrations observed inside the trains compared with the other subway systems. Nevertheless, the study in the Oporto subway system was only carried out in underground stations and consequently the exposure calculation was performed only considering the data both inside the trains and on platforms in the underground environment. Thus, lower exposure is expected in Oporto subway system when considering the aboveground sections.

4.2. Dose

The deposited $PM_{2.5}$ mass in the different regions (extrathoracic – ET, tracheobronchial – TB and alveolar-interstitial – AI) of the human respiratory tract (HRT) for a subway commuting travel in Barcelona, assuming the typical exposure time of 5 min on the platforms and 15 min inside the trains was calculated. Particle dose in the HRT was proportional to the exposure concentrations (Article 4). Thus, $PM_{2.5}$ dose for commuters in the new stations with PSDs (e.g. Llefià) was lower than in the older conventional stations, with the highest $PM_{2.5}$ dose occurring during the colder period. Furthermore, the particle dose when a subject is in the subway stations may be affected by several influential parameters, such as differences during distinct times of the day and location on the platform, reflecting the influence of the ventilation settings, design of the stations and tunnels, train frequency and commuters density (Article 1). When travelling inside the trains in the oldest lines (L1–5), the $PM_{2.5}$ dose in the HRT was also higher than in the new line 10, as expected due to higher $PM_{2.5}$ concentrations (Article 1).

The dose inside the trains compared with that received on the platforms was more than double (averagely 2.5 times higher) during the subway commuting travel as a result of the longer exposure time, despite the lower $PM_{2.5}$ concentrations registered inside the trains with respect to those on station platforms (Article 1). With respect to deposition efficiencies, a large percentage (81.7%) of the inhaled mass of $PM_{2.5}$ was deposited in the whole human respiratory system and the remaining was exhaled. These total deposition follows the tendencies derived from the superposition of the regional depositions ($D_{total}=D_{ET}+D_{TB}+D_{AI}$). The ET received the highest amount of the inhaled $PM_{2.5}$ mass deposited in the HRT (68.5%). This reflects that the deposition of subway PM occurred mainly in the upper region of the respiratory tract, which does not penetrate into the lung, and is removed much more rapidly than the particles deposited in deeper regions of the respiratory system (e.g. Carvalho et al., 2011; Löndahl et al., 2014).

The daily $PM_{2.5}$ dose in the HRT was estimated for a healthy Caucasian adult male breathing through the nose living in Barcelona and considering a typical time-activity pattern of a subject who has a sedentary job and commutes by subway. The daily total

dose of $PM_{2.5}$ was around 78 μg. This value represents the lowest estimate of the particle dose and it is expected to be higher in real-life conditions after considering indoor sources of PM and spatial variability of outdoor aerosols. Thus, the influence of indoor sources, such as cooking and cleaning activities or the movement of people (e.g. Abt et al., 2000a, 2000b; Buonanno et al., 2011; Minguillón et al., 2012; Wang et al., 2011) on particle concentrations has not been considered. Regarding the total deposition fraction, 29.4% of the daily inhaled $PM_{2.5}$ was deposited in the HRT and the remaining was exhaled. The dose in the TB and ET regions represented from 3.9% to 14.0% of the inhaled particles. The remaining particles were deposited in the AI region. However, these deposition fractions were also calculated considering no indoor sources at home and workplace and no spatial variability of outdoor aerosols.

The deposition fraction of the inhaled particles in the ET region, and consequently the total deposition fraction, was much lower for the daily deposition than the subway, due to the smaller particle size of the aerosol outside the subway system (size distribution in section 2.5.4 of the methodology). The decrease in deposition with decreasing particle size is in agreement with predictions of the ICRP model (ICRP, 1994). The deposition fraction in the AI region was higher in the daily results since the smaller particles can penetrate into deep lung regions and can deposit there. Thus, the regional distribution of deposited particles (i.e. the mass of particles that are deposited in each of the respiratory tract regions) is strongly dependent on particle size. However, for health effect purposes, the smaller particles depositing deeper in the lungs are less efficiently cleared compared to the larger particles that deposit preferentially in the upper airways where they are more easily cleared (Carvalho et al., 2011).

There are considerable differences in the distribution of particle dose in the regions of the HRT along the day which are attributed to the different exposure concentrations and size distribution of $PM_{2.5}$ but also to the different physical activity levels. However, the effect of changing the breathing rate on the particle dose is lower compared to the particle size and the exposure concentrations (Article 4).

An important contribution to the particle daily dose arises from the commuting time spent in the subway (≈3%), which accounted for a maximum of approximately 47% of

the overall daily dose, corresponding to more than 36 μg per day. Therefore, commuting in the subway system represents the activity with the highest dose received per time unit (54.6 μg h^{-1}), due to the high particle concentrations and large particle size that contribute disproportionally to dose. Moreover, in relative terms, it becomes more relevant due to an underestimation of the dose received by people living/residing in microenvironments where higher particle concentrations are usually experienced, namely considering all the indoor sources and the spatial variability of outdoor aerosols, as explained before.

4.3. Chemical composition of $PM_{2.5}$

The species present in $PM_{2.5}$ were grouped into seven different categories: (1) elemental iron (Fe), (2) total carbon (TC), (3) crustal matter (CM), (4) secondary inorganic compounds (SIC), (5) halite (NaCl), (6) insoluble sulphate and (7) trace elements. The analysed chemical species accounted for, on average, 59 – 73% of the total $PM_{2.5}$ on the platforms and 80 – 98% in the outdoor ambient air, respectively. The unaccounted mass can be explained by the presence of oxide species, heteroatoms from the carbonaceous compounds and some water molecules (moisture, formation and crystallisation water) that have not been determined. The relative chemical composition of $PM_{2.5}$ was markedly different between subway platform and outdoor ambient air due to distinct emission source contributions, whereas the distributions of the chemical components were similar in the three subway systems studied.

Iron was the most abundant element in $PM_{2.5}$ found in the subway stations, with relative contribution to the bulk $PM_{2.5}$ ranging from 19 to 46% (28 – 65% if Fe_2O_3 is considered). The considerable amount of Fe in the subway stations is mainly attributed to mechanical friction and wear processes between rails, wheels and brakes (e.g. Kam et al., 2013; Park et al., 2012). However, wear and friction processes initially produce Fe metal particles, and the surface of the primary particles must be reactive enough with oxygen in the air to easily react on the metallic surface, resulting in the formation of iron oxides (Jung et al., 2010). Moreno et al. (2015) reported that the inhalable-sized fraction of ferruginous particles in the Barcelona subway samples displayed the most common morphology in the form of irregular, rough-surfaced flakes (Figure 4.3a), with

the larger examples commonly showing splintery forms (Figure 4.3b). Previous studies have reported Fe as the most abundant species in other subway systems (Aarnio et al., 2005; Chillrud et al., 2004; Furuya et al., 2001; Johansson and Johansson, 2003; Mugica-Álvarez et al., 2012; Salma et al., 2007; Seaton et al., 2005). Furthermore, the relative abundance of Fe in $PM_{2.5}$ on the platforms in the Barcelona subway system during the warmer period (19 – 33%) was lower than that on the platforms in the Nomismatokopio (36 – 46%) and Bolhão (27 – 45%) stations. Considering that all three subway systems have metallic wheels, this lower relative abundance of Fe in $PM_{2.5}$ on the platforms of Barcelona might be attributable to the existence of strong forced ventilation in the subway system in the warmer period, since in the colder period the Fe abundance was similar (27 – 46%) to that in Oporto and Athens subway systems. Outdoor aerosol samples contained less than 1% of Fe particles.

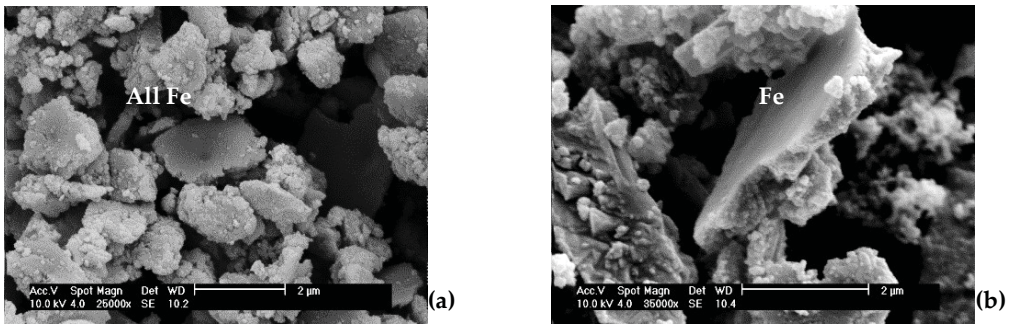

Figure 4.3 SEM images demonstrating the typical morphological aspect of ferruginous particles in subway samples: (a) dominantly ferruginous and flake-like; (b) flake and splintery morphologies.

Total carbon represented the second largest component of the subway $PM_{2.5}$, with mean relative contributions ranging from 9 to 26%. In the ambient urban atmosphere, TC concentrations were generally lower, but their relative contribution to $PM_{2.5}$ was higher, accounting for 17 – 39%, due to the lower bulk $PM_{2.5}$ concentrations. It is important to note that in the three subway systems all trains are powered by electricity, thus, there are no combustion sources of TC, and hence it is somewhat unexpected to find relatively high levels of TC. However, in Barcelona and Athens the TC concentrations on the platforms were around 3 times higher than those in the associated outdoor ambient air. Possible sources of this TC are diesel-powered trains used for maintenance activities running at night, and especially the abrasion of C-

bearing brake pads and catenary power supply materials (Moreno et al., 2015). In contrast, in Oporto the TC concentrations were very similar between the platform and the outdoor air, indicating the clear influence of outdoor air in the Bolhão station which is followed in the line by an aboveground station. Hence the carbonaceous particles on the platform can arise from the outdoor environment in addition to those generated inside (Article 3).

Elements of **crustal** origin were found in higher concentrations in subway $PM_{2.5}$ samples in comparison to outdoor ambient air, with relative contributions of crustal matter in the range of 5 – 12%, representing the third most abundant chemical component on the subway platforms. CM is present in outdoor $PM_{2.5}$ samples, as it derives from soil and urban mineral dust, although in $PM_{2.5}$ a low contribution is expected given the dominant coarse mode of mineral matter. This implies that the crustal particles found in the subway platforms flowed in from the outdoor environment by the commuters and by air-exchange between the indoor and outdoor environments. Moreover, crustal particles on the subway platforms could be originated from the resuspension of particles generated by wind erosion and weathering of construction material in both platform and tunnel, and can also be tracers of occasional construction works in the subway systems.

Secondary inorganic compounds accounted for 2 – 10% of the total $PM_{2.5}$ subway concentrations. In general, SIC (water-soluble nitrate, sulphate and ammonium) are one of the most abundant components in the outdoor atmosphere, accounting for 19 – 39% of the total $PM_{2.5}$, indicating that these particles in the subway environment might arise from the outdoor environment. Moreover, 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 in Barcelona (Article 2), according to the outdoor concentrations, which have a similar seasonal variation (Querol et al., 2008). The relative amount of SIC in the total $PM_{2.5}$ was higher (10%) in the new station, given that the indoor sources for this station were lower. Concentrations of insoluble sulphate were very low and very similar at both subway and outdoor environments, with mean concentrations ranging between 0.1 and 1.0 μg m^{-3}.

The **halite** present in the subway environment is expected to come from outdoors by both air and water infiltration, the latter related to the evaporation of water and subsequent resuspension of halite minerals. Its concentrations were similar at both Barcelona and Athens stations, and comparable to the corresponding outdoor concentrations. In Oporto the halite concentrations were higher both in the subway environment and outdoors, possibly due to the location of the city next to the Atlantic Ocean. Thus, the Cl concentrations in Oporto subway are above the upper limit of the range reported in other studies (Figure 4.4; data and references shown in Table 1.5)

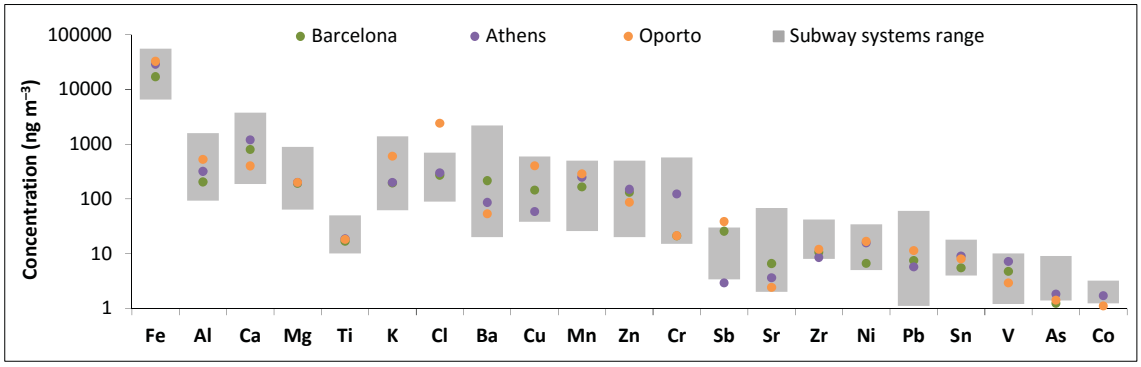

Figure 4.4 Comparison of $PM_{2.5}$ chemical components obtained on the platforms of the three subway systems with the range of reported studies included in Table 1.5.

Higher concentrations of **other metals,** in addition to Fe, such as Ba, Cu, Mn, Zn, Cr, Sb, Sr, Zr, Ni, Sn, As and Co, were found in the subway $PM_{2.5}$ compared to the simultaneous outdoor samples, pointing towards the presence of metal particle sources in the subway stations. As expected, in the Barcelona study the trace elements concentrations in the colder period were higher than those in the warmer period due to the different ventilation programs, as previously stated. Among all the studied stations of the three subway systems, the lowest concentration of trace elements was observed in Llefià station. Although the trace metals represent less than 2% of the total $PM_{2.5}$, they are important for source identification. Differences in the metal concentrations among the stations and subway systems might be associated to the different chemical composition of wheels and rails (Mn, Cr), brakes (Ba, Sb, Cu, Zn, Pb, Ni, Sr), and power supply materials (e.g. Cu-rich catenaries and Cu vs C pantographs) (Moreno et al., 2015). The metals can be originated from mechanical wear and friction processes among these manufactured materials, as reported by other studies in subway systems

(Cheng et al., 2008; Furuya et al., 2001; Gustafsson et al., 2012; Querol et al., 2012). Therefore, a more intense ventilation and a low metal content for any of the above components of the railways and trains would reduce considerably commuters' exposure to metals.

The relative abundance of specific elements of the subway $PM_{2.5}$ varied from station to station among the three subway systems. The Ba/Sr ratio (both elements being present in brake pads) varied from 8 in Tetuan to 45 in Santa Coloma. All stations except Tetuan and Llefià showed close Ba/Sr ratios which can be interpreted as coming from a similar subway source, even when considering different subway systems. This probably reflects the differences in brakes composition used in the different lines of Barcelona subway system. Another relevant difference was the Cu/Fe ratio, which varied from 0.001 in Nomismatokopio to 0.013 in Joanic. In this case Llefià, Santa Coloma and Tetuan showed comparable ratios (0.004 – 0.007). Cu is originated mainly from the wear of the catenaries providing electricity to subway trains. However, in the Bolhão station the Cu/Fe ratio was very variable among sampling days, which is probably attributable to a different subway source not identified, affecting the Cu concentrations. The 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 in Barcelona where pantographs are C-rich (graphite). The relative lower concentrations of Cu in Nomismatokopio are possibly due to the use of a third rail for power supply in the Athens subway system instead of the catenary used in Barcelona and Oporto. 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.

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

In general, the $PM_{2.5}$ chemical components obtained on the platforms of the three subway systems are within the range reported by previous worldwide subway studies (Figure 4.4).

Particulate organic species

Organic compounds were analysed in selected samples from the Barcelona subway platforms (Article 2). Polycyclic aromatic hydrocarbons (PAHs; 13 in total) were detected in all $PM_{2.5}$ 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 system from outdoor air through ventilation. In general the subway PAHs concentrations are in the range of the ones observed in urban road traffic sites of the city (Alier et al., 2013; Reche et al., 2012), although the observed variation among the stations is probably caused by their different designs. The higher levels of PAHs in Tetuan may be caused by the narrow single track structure of the station, whereas the low concentration observed in the new Llefià station is probably a direct effect of the isolation of the platform from the tunnel, and its more advanced ventilation setup.

During 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 4 stations, with the lowest hopane concentrations in Llefià. The presence of hopanes could be attributed to the influence of night-time diesel trains for maintenance activities which can be still measured during daytime and the road traffic emissions infiltration (Rogge et al., 1993; Schauer et al., 2007). In the colder period, hopane concentrations were similar to the ones observed in the warmer period; nevertheless, the correlation with PAHs is weaker, or they are even anti-correlated in Tetuan. This might be probably due to the higher PAHs concentrations in the colder period, due to their enhanced emissions 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 was detected in low concentrations (1.3 − 12 ng m^{-3}) on the subway platforms, which corresponds to the lower range of the outdoor concentrations measured in Barcelona (Alier et al., 2013). 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 cannot be excluded. The levoglucosan concentrations on the subway platforms (5 – 132 ng m^{-3}) are in the order of those observed in the outdoor atmosphere in Barcelona (around 100 ng m^{-3}; van Drooge et al., 2014).

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. Overall, there were strong correlations between these two tracers for fragrances, indicating similar mixtures. However, there were only moderate correlations between these compounds and primary saccharides in the colder period (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) were detected and related to other compounds, such as alcohol saccharides (xylitol and mannitol), all of them constituents of organic matter in dust and attributed to the air movements in the tunnels by the passing trains. Mannitol was detected in moderate concentrations, compared to typical outdoor concentrations. 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.

Dibuthyl phthalate (DBP) and di(ethylhexyl) phthalate (DEHP) were detected in all stations in high concentrations, being interestingly higher in Llefià, which can be attributed to the emissions from new building material in this station, given that these compounds were not correlated with any of the other tracer compounds.

4.4. Source contributions

For the Barcelona subway study, the number of $PM_{2.5}$ sources identified by PMF analysis varied from one station to another, but they can be grouped into outdoor and subway sources, the latter including all emissions generated by the circulation of trains (rail tracks, wheels, brake pads, catenaries and pantographs). Main differences among stations are attributed to: (i) the different characteristics for each station, leading to different influences of the subway emissions on the platform environment, (ii) the different wear of rails, wheels, brakes and power supply materials, and (iii) the different influence of outdoor air, which is affected by the time of the year, among other factors (Article 2).

The outdoor $PM_{2.5}$ sources found in the subway environment included secondary aerosol, sea salt and fuel oil combustion. In the warmer period the secondary source is characterised by a high contribution of sulphate, whereas in the colder it is dominated by nitrate. The sea salt source was mainly characterized by the presence of Na and Cl, with similar contributions in the warmer and the colder periods. The sea salt enters the subway environment from outdoors by both air and water infiltration, the latter related to the evaporation of water and subsequent resuspension of halite minerals. Moreover, a source characterised by V was identified, representing the fuel oil combustion (Agrawal et al., 2008).

The subway source identified has a different chemical profile for each of the stations, although it is dominated by Fe (53 to 68%) at all stations. These Fe-bearing particles are generated mainly from mechanical wear and friction processes at rail-wheel-brake interfaces. This source is also responsible for more than 50% of the Al_2O_3, Ca, Fe, Cr, Mn, Cu, Sr, Ba, Pr, and Nd concentrations at all the stations, and also of Mg, Li, Ti, Co, Zn, and Ce for the old stations (Joanic, Tetuan and Santa Coloma).

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

Chapter 5

Conclusions

5. CONCLUSIONS

This work is the first study that presents a large dataset from intensive and extensive measurement campaigns, able to characterise the air quality in terms of PM in three European subway systems (Barcelona, Athens and Oporto), both on platforms and inside the trains. The sampling campaigns yielded the characterisation of PM concentrations and chemical composition, as well as the identification and quantification of sources. Furthermore, the results provide valuable information for human exposure and dose assessment in such environment. The main conclusions that can be drawn from the work presented in this thesis are listed below.

Variability of PM concentrations on the platforms:

- There are important factors influencing PM concentrations in the subway systems, such as: differences in the design of the stations and tunnels; system age; train frequency; ventilation and air conditioning systems; passenger densities; power system (catenary vs. third rail); composition of wheels, rail tracks, brake pads and power supply materials; rail tracks geometry (curved vs. straight and sloped vs. levelled); and outdoor air quality.
- In the Barcelona subway system, the new stations showed on average lower $PM_{2.5}$ concentrations (around 50%) in comparison with the old conventional stations, mainly related to the design of the stations (with PSDs), but also due to the lower train frequency and more advanced ventilation setup. Furthermore, the higher PM_X concentrations on the platforms were found during the colder period, mainly due to the weaker ventilation during this period. The results also indicated that the ventilation was more efficient removing coarser particles.
- In Athens, the mean PM_X concentrations in a new station located in the periphery of the line (out of the central area of the city) were lower than in a central station, attributed not only to the age and location of the station, but also to the train frequency (some trains do not run the entire line) and lower number of passengers.

- Daily measurements carried out in the three subway systems performed on stations with similar platform design were compared. The highest $PM_{2.5}$ concentrations were observed in the Oporto subway station because the line is composed by curved and/or sloping rail tracks (implicating a higher emission of wear particles) and it has a higher train frequency. Furthermore, mechanical forced ventilation is inexistent in this subway system.
- PM_X concentrations displayed clear diurnal patterns driven by the train frequency and the ventilation settings, with higher concentrations during subway operating hours. Moreover, in some cases the PM_X concentrations showed temporal and spatial variations on the platforms, probably due to the influence of the ventilation settings, design of the stations and tunnels, location of passengers' access to the platforms, commuter densities, as well as to the effect of the passage and frequency of the trains.

Variability of PM concentrations inside the trains:

- PM_X concentrations inside the trains depend on air-conditioning system, windows open/close, travelling above/underground and PM_X concentrations on platforms and tunnels, with short-time variations when doors open. The use of air-conditioning inside the trains was an effective approach to reduce exposure levels, being more efficient removing the coarser particles. Having the carriage windows open promotes the entrance of polluted air from tunnels and platforms into the trains. Nevertheless, even when the carriage windows are closed and the air-conditioning system is switched on, the PM_X concentrations inside the trains continue to be greatly affected by the surrounding air quality conditions, evidenced by the PM concentrations on the platforms. Thus, these results reveal that levels of PM inside the trains are significantly influenced by the traveling environmental conditions despite the use of air-conditioning.

$PM_{2.5}$ dose during subway commuting:

- From the subway dosimetry study carried out for Barcelona, the highest $PM_{2.5}$ dose was observed when travelling inside the trains due to the longer exposure time. A

large percentage of the subway inhaled particles deposit in the human respiratory tract (81.7%), being the highest amount deposited in the upper airways (68.5%). This is a good point in terms of public health, as the particles deposited in this region are removed much more rapidly than the ones in the deeper regions of the respiratory tract.

- In the daily dose study, the distribution of deposited particles in the human respiratory tract showed considerable differences along the day, mostly dependent on the particle size and exposure concentrations. As indoor sources of $PM_{2.5}$ (except in the subway) and spatial variability of outdoor aerosols were not considered, commuting by subway represented the highest $PM_{2.5}$ dose received per time unit during the day, owing mainly to the higher concentration and the larger particle size. Nevertheless, the other environments where the subject is exposed should be further characterised in terms of PM concentrations and size distribution.

Chemical composition and sources of $PM_{2.5}$ on the platforms

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

Subway air quality implications

This extensive study provides a comprehensive assessment of PM characterisation of subway environments. Furthermore, the results reported may be useful to help the control and improve the air quality in the subway systems. This study suggests that an appropriate ventilation mode should be applied to the subway system to obtain both PM reduction and energy saving. It is always worth reducing the concentration of exposure to PM whenever technically possible.

Improvement in the air quality of existing subway systems may be achieved by:

- Upgrading the ventilation system to forced air supply;
- Installing adequate extraction fans at the ventilation ducts along the tunnels;
- Keeping the train windows closed, which is a simple and strongly recommended measure to improve air quality inside the trains.

Future subway systems, or extension of existing ones, should be planned taking also into account air quality, adopting measures like:

- Improved design (with PSDs);
- Avoid curved or/and sloping rail tracks right next to a subway station when possible;
- Selection of advanced construction materials, controlling the composition of the subway components (rails, wheels, brakes and power supply materials) to reduce exposure to trace metals;
- Advanced ventilation settings.

The results exposed above are especially important to understand exposure of commuters to PM, who are subjected to these pollutants and its inherent health effects. This information is of utmost importance to effectively control specific emission sources on platforms, and to establish or improve efficient policies and strategies for an indoor air quality management system in the subway systems. Thus, this work expects to serve as a tool to establish the actions towards an effective reduction of PM levels in subway systems, by identifying and encouraging the application of practical and focused air pollution mitigation strategies, appropriate for subway systems. Some

mitigation strategies are already being applied in the Barcelona subway system, and improvement in air quality is already a real achievement. This work represents a very successful and valuable synergy among scientific research, public and private entities, and the general public, where all parts cooperated and contributed with a joint objective of improving the quality of life of the urban population.

Chapter 6

Future research and outstanding questions

6. FUTURE RESEARCH AND OUTSTANDING QUESTIONS

The research described in this study has helped to strengthen the understanding and the characterisation of PM in subway systems in terms of concentration, chemical composition and source apportionment as well as the personal exposure and dose. Further research in this field is required to fully understand some topics not covered or not completely explored by this study. A brief list of some of the major outstanding questions and suggested future work is described hereinafter:

- The continuation of sampling of PM_x will provide further information on their variability to ascertain the causes for fluctuations in PM_x referred in this study. For example, the spatial variation of PM_x concentrations along the platforms may also be related to the location of the ventilation fans, however, this aspect was not evaluated in this study.

- The present work studied air quality improvement measures based on ventilation settings, using pre-existent infrastructures. The installation of air purification systems within the subway system may also be adopted, but further study is required to evaluate the efficiency and viability of these devices.

- The characterisation of PM in the Oporto subway system should be performed considering seasonal periods to better understand the influence of the outdoor weather conditions within the subway environment.

- The influence of the outdoor environment surrounding the subway stations (e.g. traffic vs. no-traffic location, surface vs. elevated air intakes) may influence the air quality within the subway system in some cases. Further studies are required to assess the magnitude and variability of this influence among locations.

- The effect of the extraction of subway PM through draught relief outlets ("blast shafts") in the outdoor air quality is not clear, and should be addressed in future research.

- Regarding seasonal variation of PM_X inside the trains in the Barcelona subway system, there was no clear trend among all results (warmer vs. colder), perhaps influenced by changes of the air filters in the trains (the trains are fitted with air filters coupled to the air-conditioning system that are changed monthly). A study on the influence of the frequency in the change of the filters on the PM_X concentrations inside the trains is required.

- Results obtained during this work on particle number concentration and size distribution (0.3 – 10 μm) are not included in this thesis, but they represent an opportunity to characterise another parameter hardly studied in the subway systems.

- For comparative purposes the daily dose should be calculated considering all indoor sources of PM (not only when commuting) and spatial variability of outdoor aerosols. Moreover, as the dose study was performed considering the PM mass concentrations, an additional study should be carried out aiming PM number concentrations, since both must be considered in terms of health effects.

- Personal measurements are a suitable methodology in order to accurately assess exposure. More studies in subway systems will verify the results obtained in this thesis and might help to identify the activities, environments and routes, among other parameters that contribute the most to the personal exposure and dose of commuters and, consequently, avoid them or reduce concentrations on these specific sites.

- The accumulative amount of time that commuters spend exposed to high concentrations of metals throughout their lifetime, and the possible adverse health effects associated with such exposure, may be significant and is certainly worthy of further investigation.

- Some trace metals are biologically active, and have documented negative health effects at high concentrations. Information on the chemical forms, oxidation states and speciation, as well as the water solubility (bioavailability), of these metals is of major importance for further investigations.

- Subway sources of air pollutants should be further investigated. Especially the sources related to metals that have been identified in this thesis have an important contribution in the subway environment (Fe, Cu, Ba, Mn, Zn, Cr, among others). Thus, the separate quantification of the contribution of emissions from wheels abrasion, brake wear, rail abrasion, current supply materials, and ballast erosion would be helpful to design mitigation strategies. To this end, longer time series of chemical composition and, even more suitable, chemical composition information at a higher time resolution is required. The identification of the sources considering also the organic compounds would also be very interesting.
- Particles of biological origin or microorganisms can be of special interest for epidemiological considerations, and future studies are needed to cover this subject.

Chapter 7

References

7. REFERENCES

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

Abbasi, S., Jansson, A., Sellgren, U., Olofsson, U., 2013. Particle emissions from rail traffic: a literature review. Crit. Rev. Environ. Sci. Technol. 43, 2511–2544. doi:10.1080/10643389.2012.685348.

Abt, E., Suh, H.H., Allen, G., Koutrakis, P., 2000a. Characterization of indoor particle sources: A study conducted in the metropolitan Boston area. Environ. Health Perspect. 108, 35–44. doi:10.1289/ehp.0010835.

Abt, E., Suh, H.H., Catalano, P., Koutrakis, P., 2000b. Relative contribution of outdoor and indoor particle sources to indoor concentrations. Environ. Sci. Technol. 34, 3579–3587. doi:10.1021/es990348y.

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

Agrawal, H., Malloy, Q.G.J., Welch, W.A., Wayne Miller, J., Cocker, D.R., 2008. In-use gaseous and particulate matter emissions from a modern ocean going container vessel. Atmos. Environ. 42, 5504–5510. doi:10.1016/j.atmosenv.2008.02.053.

Aiken, A., Decarlo, P., Kroll, J., Worsnop, D., Huffman, J., Docherty, K., Ulbrich, I., Mohr, C., Kimmel, J., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P., Canagaratna, M., Onasch, T., Alfarra, M., Prevot, A., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., Jimenez, J., 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. Environ. Sci. Technol. 42, 4478–4485. doi:10.1021/es703009q.

Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P.-M., Exposito, F., García, O., Pedro Diaz, J., Dingenen, R. Van, Putaud, J.P., 2005. Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife

(Canary Islands, Spain) during a Saharan Dust Episode (July 2002). Atmos. Environ. 39, 4715–4728. doi:10.1016/j.atmosenv.2005.04.018.

Aleksandropoulou, V., Lazaridis, M., 2013. Development and application of a model (ExDoM) for calculating the respiratory tract dose and retention of particles under variable exposure conditions. Air Qual. Atmos. Heal. 6, 13–26. doi:10.1007/s11869-010-0126-z.

Alier, M., van Drooge, B.L., Dall'Osto, M., Querol, X., Grimalt, J.O., Tauler, R., 2013. Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona (Spain) during SAPUSS. Atmos. Chem. Phys. 13, 10353–10371. doi:10.5194/acp-13-10353-2013.

Anderson, J.O., Thundiyil, J.G., Stolbach, A., 2012. Clearing the air: A review of the effects of particulate matter air pollution on human health. J. Med. Toxicol. 8, 166–175. doi:10.1007/s13181-011-0203-1.

Anderson, P.J., Wilson, J.D., Hiller, F.C., 1990. Respiratory tract deposition of ultrafine particles in subjects with obstructive or restrictive lung disease. Chest 97, 1115–1120. doi:10.1378/chest.97.5.1115.

Andreae, M.O., Jones, C.D., Cox, P.M., 2005. Strong present-day aerosol cooling implies a hot future. Nature 435, 1187–1190. doi:10.1038/nature03671.

Andreae, M.O., Rosenfeld, D., 2008. Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. Earth-Science Rev. 89, 13–41. doi:10.1016/j.earscirev.2008.03.001.

Asgharian, B., 2004. A model of deposition of hygroscopic particles in the human lung. Aerosol Sci. Technol. 38, 938–947. doi:10.1080/027868290511236.

Asgharian, B., Ménache, M.G., Miller, F.J., 2004. Modeling age-related particle deposition in humans. J. Aerosol Med. 17, 213–224. doi:10.1089/jam.2004.17.213.

Asgharian, B., Price, O.T., 2007. Deposition of ultrafine (nano) particles in the human lung. Inhal. Toxicol. 19, 1045–1054. doi:10.1080/08958370701626501.

Awad, A.H.A., 2002. Environmental study in subway metro stations in Cairo, Egypt. J. Occup. Health 44, 112–118. doi:10.1539/joh.44.112.

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

Baek, B.H., Aneja, V.P., Tong, Q., 2004. Chemical coupling between ammonia, acid gases, and fine particles. Environ. Pollut. 129, 89–98. doi:10.1016/j.envpol.2003.09.022.

Bennett, W.D., Zeman, K.L., 2004. Effect of body size on breathing pattern and fine-particle deposition in children. J. Appl. Physiol. 97, 821–826. doi:10.1152/japplphysiol.01403.2003.

Bentayeb, M., Wagner, V., Stempfelet, M., Zins, M., Goldberg, M., Pascal, M., Larrieu, S., Beaudeau, P., Cassadou, S., Eilstein, D., Filleul, L., Le Tertre, A., Medina, S., Pascal, L., Prouvost, H., Quénel, P., Zeghnoun, A., Lefranc, A., 2015. Association between long-term exposure to air pollution and mortality in France: A 25-year follow-up study. Environ. Int. 85, 5–14. doi:10.1016/j.envint.2015.08.006.

Bernstein, J.A., Alexis, N., Barnes, C., Bernstein, I.L., Nel, A., Peden, D., Diaz-Sanchez, D., Tarlo, S.M., Williams, P.B., 2004. Health effects of air pollution. J. Allergy Clin. Immunol. 114, 1116–1123. doi:10.1016/j.jaci.2004.08.030.

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

Birenzvige, A., Eversole, J., Seaver, M., Francesconi, S., Valdes, E., Kulaga, H., 2003. Aerosol characteristics in a subway environment. Aerosol Sci. Technol. 37, 210–220. doi:10.1080/02786820300941.

Bogomolova, E., Kirtsideli, I., 2009. Airborne fungi in four stations of the St. Petersburg Underground railway system. Int. Biodeterior. Biodegradation 63, 156–160. doi:10.1016/j.ibiod.2008.05.008.

Brand, P., Häußinger, K., Meyer, T., Scheuch, G., Schulz, H., Selzer, T., Heyder, J., 1999. Intrapulmonary distribution of deposited particles. J. Aerosol Med. 12, 275–284. doi:10.1089/jam.1999.12.275.

Braniš, M., 2006. The contribution of ambient sources to particulate pollution in spaces and trains of the Prague underground transport system. Atmos. Environ. 40, 348–356. doi:10.1016/j.atmosenv.2005.09.060.

Broday, D.M., Agnon, Y., 2007. Asymmetric human lung morphology induce particle deposition variation. J. Aerosol Sci. 38, 701–718. doi:10.1016/j.jaerosci.2007.06.001.

Buonanno, G., Fuoco, F.C., Stabile, L., 2011. Influential parameters on particle exposure of pedestrians in urban microenvironments. Atmos. Environ. 45, 1434–1443. doi:10.1016/j.atmosenv.2010.12.015.

Buonanno, G., Marks, G.B., Morawska, L., 2013. Health effects of daily airborne particle dose in children: direct association between personal dose and respiratory health effects. Environ. Pollut. 180, 246–250. doi:10.1016/j.envpol.2013.05.039.

Calvo, A.I., Alves, C., Castro, A., Pont, V., Vicente, A.M., Fraile, R., 2013. Research on aerosol sources and chemical composition: Past, current and emerging issues. Atmos. Res. 120–121, 1–28. doi:10.1016/j.atmosres.2012.09.021.

Cao, J., Wang, Q., Chow, J.C., Watson, J.G., Tie, X., Shen, Z., Wang, P., An, Z., 2012. Impacts of aerosol compositions on visibility impairment in Xi'an, China. Atmos. Environ. 59, 559–566. doi:10.1016/j.atmosenv.2012.05.036.

Cartenì, A., Cascetta, F., Campana, S., 2015. Underground and ground-level particulate matter concentrations in an Italian metro system. Atmos. Environ. 101, 328–337. doi:10.1016/j.atmosenv.2014.11.030.

Carvalho, T.C., Peters, J.I., Williams III, R.O., 2011. Influence of particle size on regional lung deposition – What evidence is there? Int. J. Pharm. 406, 1–10. doi:10.1016/j.ijpharm.2010.12.040.

Castro, A., Alonso-Blanco, E., González-Colino, M., Calvo, A.I., Fernández-Raga, M., Fraile, R., 2010. Aerosol size distribution in precipitation events in León, Spain. Atmos. Res. 96, 421–435. doi:10.1016/j.atmosres.2010.01.014.

Cesaroni, G., Badaloni, C., Gariazzo, C., Stafoggia, M., Sozzi, R., Davoli, M., Forastiere, F., 2013. Long-term exposure to urban air pollution and mortality in a cohort of more than a million adults in Rome. Environ. Health Perspect. 121, 324–331. doi:10.1289/ehp.1205862.

Chalupa, D.C., Morrow, P.E., Oberdörster, G., Utell, M.J., Frampton, M.W., 2004. Ultrafine particle deposition in subjects with asthma. Environ. Health Perspect. 112, 879–882. doi:10.1289/ehp.6851.

Chalvatzaki, E., Lazaridis, M., 2015. Development and application of a dosimetry model (ExDoM2) for calculating internal dose of specific particle-bound metals in the human body. Inhal. Toxicol. doi:10.3109/08958378.2015.1046201.

Chan, C.-C., Spengler, J.D., Özkaynak, H., Lefkopoulou, M., 1991. Commuter exposures to VOCs in Boston, Massachusetts. J. Air Waste Manage. Assoc. 41, 1594–1600. doi:10.1080/10473289.1991.10466955.

Chan, L.Y., Lau, W.L., Lee, S.C., Chan, C.Y., 2002. Commuter exposure to particulate matter in public transportation modes in Hong Kong. Atmos. Environ. 36, 3363–3373. doi:10.1016/S1352-2310(02)00318-7.

Chen, C., Zhao, B., 2011. Review of relationship between indoor and outdoor particles: I/O ratio, infiltration factor and penetration factor. Atmos. Environ. 45, 275–288. doi:10.1016/j.atmosenv.2010.09.048.

Chen, L.C., Lippmann, M., 2009. Effects of metals within ambient air particulate matter (PM) on human health. Inhal. Toxicol. 21, 1–31. doi:10.1080/08958370802105405.

Chen, Y., Xie, S., 2012. Temporal and spatial visibility trends in the Sichuan Basin, China, 1973 to 2010. Atmos. Res. 112, 25–34. doi:10.1016/j.atmosres.2012.04.009.

Cheng, Y.-H., Lin, Y.-L., 2010. Measurement of particle mass concentrations and size distributions in an underground station. Aerosol Air Qual. Res. 22–29. doi:10.4209/aaqr.2009.05.0037.

Cheng, Y.-H., Lin, Y.-L., Liu, C.-C., 2008. Levels of PM10 and PM2.5 in Taipei Rapid Transit System. Atmos. Environ. 42, 7242–7249. doi:10.1016/j.atmosenv.2008.07.011.

Cheng, Y.-H., Liu, Z.-S., Yan, J.-W., 2012. Comparisons of PM10, PM2.5, particle number, and CO2 levels inside metro trains between traveling in underground tunnels and on elevated tracks. Aerosol Air Qual. Res. 12, 879–891. doi:10.4209/aaqr.2012.05.0127.

Cheng, Y.-H., Yan, J.-W., 2011. Comparisons of particulate matter, CO, and CO2 levels in underground and ground-level stations in the Taipei mass rapid transit system. Atmos. Environ. 45, 4882–4891. doi:10.1016/j.atmosenv.2011.06.011.

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

Cho, J.H., Hee Min, K., Paik, N.W., 2006. Temporal variation of airborne fungi concentrations and related factors in subway stations in Seoul, Korea. Int. J. Hyg. Environ. Health 209, 249–255. doi:10.1016/j.ijheh.2005.10.001.

Chow, J.C., Watson, J.G., Chen, L.-W.A., Arnott, W.P., Moosmüller, H., Fung, K., 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environ. Sci. Technol. 38, 4414–4422. doi:10.1021/es034936u.

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merri, T., 2001. Comparison of IMPROVE and NIOSH Carbon Measurements. Aerosol Sci. Technol. 34, 23–34. doi:10.1080/02786820119073.

Claeys, M., Wang, W., Vermeylen, R., Kourtchev, I., Chi, X., Farhat, Y., Surratt, J.D., Gómez-González, Y., Sciare, J., Maenhaut, W., 2010. Chemical characterisation of marine aerosol at Amsterdam Island during the austral summer of 2006–2007. J. Aerosol Sci. 41, 13–22. doi:10.1016/j.jaerosci.2009.08.003.

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

Costa, E.A.L., Campos, V.P., da Silva Filho, L.C.P., Greven, H.A., 2009. Evaluation of the aggressive potential of marine chloride and sulfate salts on mortars applied as renders in the Metropolitan Region of Salvador – Bahia, Brazil. J. Environ. Manage. 90, 1060–1068. doi:10.1016/j.jenvman.2008.04.006.

Coz, E., Gómez-Moreno, F.J., Pujadas, M., Casuccio, G.S., Lersch, T.L., Artíñano, B., 2009. Individual particle characteristics of North African dust under different long-range transport scenarios. Atmos. Environ. 43, 1850–1863. doi:10.1016/j.atmosenv.2008.12.045.

Cusack, M., Talbot, N., Ondráček, J., Minguillón, M.C., Martins, V., Klouda, K., Schwarz, J., Ždímal, V., 2015. Variability of aerosols and chemical composition of PM10, PM2.5 and PM1 on a platform of the Prague underground metr. Atmos. Environ. 118, 176–183. doi:10.1016/j.atmosenv.2015.08.013.

Das, S.K., Jayaraman, A., 2012. Long-range transportation of anthropogenic aerosols over eastern coastal region of India: Investigation of sources and impact on

regional climate change. Atmos. Res. 118, 68–83. doi:10.1016/j.atmosres.2012.05.025.

DeCarlo, P.F., Slowik, J.G., Worsnop, D.R., Davidovits, P., Jimenez, J.L., 2004. Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory. Aerosol Sci. Technol. 38, 1185–1205. doi:10.1080/027868290903907.

Deng, X., Tie, X., Wu, D., Zhou, X., Bi, X., Tan, H., Li, F., Jiang, C., 2008. Long-term trend of visibility and its characterizations in the Pearl River Delta (PRD) region, China. Atmos. Environ. 42, 1424–1435. doi:10.1016/j.atmosenv.2007.11.025.

Dockery, D.W., 2009. Health effects of particulate air pollution. Ann. Epidemiol. 19, 257–263. doi:10.1016/j.annepidem.2009.01.018.

Dominici, F., Peng, R.D., Bell, M.L., Pham, L., McDermott, A., Zeger, S.L., Samet, J.M., 2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. JAMA 295, 1127–34. doi:10.1001/jama.295.10.1127.

Engling, G., Gelencsér, A., 2010. Atmospheric particles: atmospheric brown clouds: From local air pollution to climate change. Elements 6, 223–228. doi:10.2113/gselements.6.4.223.

Eom, H.-J., Jung, H.-J., Sobanska, S., Chung, S.-G., Son, Y.-S., Kim, J.-C., Sunwoo, Y., Ro, C.-U., 2013. Iron speciation of airborne subway particles by the combined use of energy dispersive electron probe X-ray microanalysis and raman microspectrometry. Anal. Chem. 85, 10424–10431. doi:10.1021/ac402406n.

Ervens, B., Turpin, B.J., Weber, R.J., 2011. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. Atmos. Chem. Phys. 11, 11069–11102. doi:10.5194/acp-11-11069-2011.

Escrig, A., Monfort, E., Celades, I., Querol, X., Amato, F., Minguillón, M.C., Hopke, P.K., 2009. Application of optimally scaled target factor analysis for assessing source contribution of ambient PM10. J. Air Waste Manage. Assoc. 59, 1296–1307. doi:10.3155/1047-3289.59.11.1296.

Ferm, M., Watt, J., O'Hanlon, S., De Santis, F., Varotsos, C., 2006. Deposition measurement of particulate matter in connection with corrosion studies. Anal. Bioanal. Chem. 384, 1320–1330. doi:10.1007/s00216-005-0293-1.

Finlayson-Pitts, B.J., Pitts, J.N., 2000. Chemistry of the upper and lower atmosphere: theory, experiments, and applications. Academic Press, San Diego.

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

Fung, K., Chow, J.C., Watson, J.G., 2002. Evaluation of OC/EC speciation by thermal manganese dioxide oxidation and the IMPROVE method. J. Air Waste Manage. Assoc. 52, 1333–1341. doi:10.1080/10473289.2002.10470867.

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

Georgopoulos, P.G., Lioy, P.J., 2006. From a theoretical framework of human exposure and dose assessment to computational system implementation: the Modeling ENvironment for TOtal Risk Studies (MENTOR). J. Toxicol. Environ. Heal. Part B 9, 457–483. doi:10.1080/10937400600755929.

Ghedini, N., Gobbi, G., Sabbioni, C., Zappia, G., 2000. Determination of elemental and organic carbon on damaged stone monuments. Atmos. Environ. 34, 4383–4391. doi:10.1016/S1352-2310(00)00250-8.

Giere, R., Querol, X., 2010. Solid particulate matter in the atmosphere. Elements 6, 215–222. doi:10.2113/gselements.6.4.215.

Ginoux, P., Prospero, J.M., Gill, T.E., Hsu, N.C., Zhao, M., 2012. Global-scale attribution of anthropogenic and natural dust sources and their emission rates based on MODIS Deep Blue aerosol products. Rev. Geophys. 50, RG3005. doi:10.1029/2012RG000388.

Glytsos, T., Ondráček, J., Džumbová, L., Kopanakis, I., Lazaridis, M., 2010. Characterization of particulate matter concentrations during controlled indoor activities. Atmos. Environ. 44, 1539–1549. doi:10.1016/j.atmosenv.2010.01.009.

Gómez-Perales, J.E., Colvile, R.N., Fernández-Bremauntz, A.A., Gutiérrez-Avedoy, V., Páramo-Figueroa, V.H., Blanco-Jiménez, S., Bueno-López, E., Bernabé-Cabanillas, R., Mandujano, F., Hidalgo-Navarro, M., Nieuwenhuijsen, M.J., 2007. Bus,

minibus, metro inter-comparison of commuters' exposure to air pollution in Mexico City. Atmos. Environ. 41, 890–901. doi:10.1016/j.atmosenv.2006.07.049.

Gómez-Perales, J.E., Colvile, R.N., Nieuwenhuijsen, M.J., Fernández-Bremauntz, A., Gutiérrez-Avedoy, V.J., Páramo-Figueroa, V.H., Blanco-Jiménez, S., Bueno-López, E., Mandujano, F., Bernabé-Cabanillas, R., Ortiz-Segovia, E., 2004. Commuters' exposure to PM2.5, CO, and benzene in public transport in the metropolitan area of Mexico City. Atmos. Environ. 38, 1219–1229. doi:10.1016/j.atmosenv.2003.11.008.

Goudie, A., Middleton, N.J., 2006. Desert dust in the global system. Springer.

Grantz, D.A., Garner, J.H.B., Johnson, D.W., 2003. Ecological effects of particulate matter. Environ. Int. 29, 213–239. doi:10.1016/S0160-4120(02)00181-2.

Grass, D.S., Ross, J.M., Family, F., Barbour, J., James Simpson, H., Coulibaly, D., Hernandez, J., Chen, Y., Slavkovich, V., Li, Y., Graziano, J., Santella, R.M., Brandt-Rauf, P., Chillrud, S.N., 2010. Airborne particulate metals in the New York City subway: a pilot study to assess the potential for health impacts. Environ. Res. 110, 1–11. doi:10.1016/j.envres.2009.10.006.

Grobéty, B., Gieré, R., Dietze, V., Stille, P., 2010. Atmospheric particles: airborne particles in the urban environment. Elements 6, 229–234. doi:10.2113/gselements.6.4.229.

Guo, L., Hu, Y., Hu, Q., Lin, J., Li, C., Chen, J., Li, L., Fu, H., 2014. Characteristics and chemical compositions of particulate matter collected at the selected metro stations of Shanghai, China. Sci. Total Environ. 496, 443–452. doi:10.1016/j.scitotenv.2014.07.055.

Gustafsson, M., Blomqvist, G., Swietlicki, E., Dahl, A., Gudmundsson, A., 2012. Inhalable railroad particles at ground level and subterranean stations – Physical and chemical properties and relation to train traffic. Transp. Res. Part D Transp. Environ. 17, 277–285. doi:10.1016/j.trd.2011.12.006.

Hamilton, R.S., Mansfield, T.A., 1993. The soiling of materials in the ambient atmosphere. Atmos. Environ. Part A. Gen. Top. 27, 1369–1374. doi:10.1016/0960-1686(93)90263-X.

Heyder, J., 2004. Deposition of inhaled particles in the human respiratory tract and consequences for regional targeting in respiratory drug delivery. Proc. Am. Thorac. Soc. 1, 315–320. doi:10.1513/pats.200409-046TA.

Heyder, J., Rudolf, G., 1984. Mathematical models of particle deposition in the human respiratory tract. J. Aerosol Sci. 15, 697–707. doi:10.1016/0021-8502(84)90007-7.

Hinds, W.C., 1999. Aerosol technology: properties, behavior, and measurement of airborne particles. John Wiley & Sons, Inc., New York, USA.

Hofmann, W., 2011. Modelling inhaled particle deposition in the human lung-A review. J. Aerosol Sci. 42, 693–724. doi:10.1016/j.jaerosci.2011.05.007.

Holmes, N.S., 2007. A review of particle formation events and growth in the atmosphere in the various environments and discussion of mechanistic implications. Atmos. Environ. 41, 2183–2201. doi:10.1016/j.atmosenv.2006.10.058.

Hussain, M., Madl, P., Khan, A., 2011. Lung deposition predictions of airborne particles and the emergence of contemporary diseases, Part-I. theHealth 2, 51–59.

Hwang, S.H., Park, J.B., 2014. Comparison of culturable airborne bacteria and related environmental factors at underground subway stations between 2006 and 2013. Atmos. Environ. 84, 289–293. doi:10.1016/j.atmosenv.2013.11.064.

Hwang, S.H., Yoon, C.S., Ryu, K.N., Paik, S.Y., Cho, J.H., 2010. Assessment of airborne environmental bacteria and related factors in 25 underground railway stations in Seoul, Korea. Atmos. Environ. 44, 1658–1662. doi:10.1016/j.atmosenv.2010.01.047.

ICRP, 1994. Human Respiratory Tract Model for Radiological Protection. International Commission on Radiological Protection, Pergamon.

IPCC, 2013. Climate change 2013: The physical science basis. Cambridge University Press, Cambridge, United Kingdom.

Jacobson, M.Z., 2005. Fundamentals of Atmospheric Modeling. Cambridge University Press, Cambridge, United Kingdom.

Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M., Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin, C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., E., Dunlea, J., Huffman, J.A., Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel, J.R.,

Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U., Worsnop, D.R., 2009. Evolution of organic aerosols in the atmosphere. Science. 326, 1525–1529. doi:10.1126/science.1180353.

Jimoda, L.A., 2012. Effects of particulate matter on human health, the ecosystem, climate and materials: A review. Work. Living Environ. Prot. 9, 27–44.

Johansson, C., Johansson, P.-A., 2003. Particulate matter in the underground of Stockholm. Atmos. Environ. 37, 3–9. doi:10.1016/S1352-2310(02)00833-6.

Jonsson, L., Karlsson, E., Jönsson, P., 2008. Aspects of particulate dry deposition in the urban environment. J. Hazard. Mater. 153, 229–243. doi:10.1016/j.jhazmat.2007.08.077.

Joos, F., Spahni, R., 2008. Rates of change in natural and anthropogenic radiative forcing over the past 20,000 years. Proc. Natl. Acad. Sci. 105, 1425–1430. doi:10.1073/pnas.0707386105.

Jung, H.-J., Kim, B., Ryu, J., Maskey, S., Kim, J.-C., Sohn, J., Ro, C.-U., 2010. Source identification of particulate matter collected at underground subway stations in Seoul, Korea using quantitative single-particle analysis. Atmos. Environ. 44, 2287–2293. doi:10.1016/j.atmosenv.2010.04.003.

Jung, M.H., Kim, H.R., Park, Y.J., Park, D.S., Chung, K.H., Oh, S.M., 2012. Genotoxic effects and oxidative stress induced by organic extracts of particulate matter (PM10) collected from a subway tunnel in Seoul, Korea. Mutat. Res. Toxicol. Environ. Mutagen. 749, 39–47. doi:10.1016/j.mrgentox.2012.08.002.

Kam, W., Cheung, K., Daher, N., Sioutas, C., 2011a. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. Atmos. Environ. 45, 1506–1516. doi:10.1016/j.atmosenv.2010.12.049.

Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2013. A comparative assessment of PM2.5 exposures in light-rail, subway, freeway, and surface street environments in Los Angeles and estimated lung cancer risk. Environ. Sci. Process. Impacts 15, 234–243. doi:10.1039/c2em30495c.

Kam, W., Ning, Z., Shafer, M.M., Schauer, J.J., Sioutas, C., 2011b. Chemical characterization and redox potential of coarse and fine particulate matter (PM) in underground and ground-level rail systems of the Los Angeles Metro. Environ. Sci. Technol. 45, 6769–76. doi:10.1021/es201195e.

Kampa, M., Castanas, E., 2008. Human health effects of air pollution. Environ. Pollut. 151, 362–367. doi:10.1016/j.envpol.2007.06.012.

Kang, S., Hwang, H., Park, Y., Kim, H., Ro, C.-U., 2008. Chemical compositions of subway particles in Seoul, Korea determined by a quantitative single particle analysis. Environ. Sci. Technol. 42, 9051–9057. doi:10.1021/es802267b.

Karanasiou, A., Minguillón, M.C., Viana, M., Alastuey, A., Putaud, J.-P., Maenhaut, W., Panteliadis, P., Močnik, G., Favez, O., Kuhlbusch, T.A.J., 2015. Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review. Atmos. Meas. Tech. Discuss. 8, 9649–9712. doi:10.5194/amtd-8-9649-2015.

Karlsson, H.L., Holgersson, A., Möller, L., 2008. Mechanisms related to the genotoxicity of particles in the subway and from other sources. Chem. Res. Toxicol. 21, 726–31. doi:10.1021/tx7003568.

Karlsson, H.L., Nilsson, L., Möller, L., 2005. Subway particles are more genotoxic than street particles and induce oxidative stress in cultured human lung cells. Chem. Res. Toxicol. 18, 19–23. doi:10.1021/tx049723c.

Karydis, V.A., Kumar, P., Barahona, D., Sokolik, I.N., Nenes, A., 2011. On the effect of dust particles on global cloud condensation nuclei and cloud droplet number. J. Geophys. Res. Atmos. 116. doi:10.1029/2011JD016283.

Katsouyanni, K., Touloumi, G., Samoli, E., Gryparis, A., Le Tertre, A., Monopolis, Y., Rossi, G., Zmirou, D., Ballester, F., Boumghar, A., Anderson, H.R., Wojtyniak, B., Paldy, A., Braunstein, R., Pekkanen, J., Schindler, C., Schwartz, J., 2001. Confounding and effect modification in the short-term effects of ambient particles on total mortality: results from 29 European cities within the APHEA2 project. Epidemiology 12, 521–531. doi:10.1097/00001648-200109000-00011.

Katul, G.G., Grönholm, T., Launiainen, S., Vesala, T., 2011. The effects of the canopy medium on dry deposition velocities of aerosol particles in the canopy sub-layer above forested ecosystems. Atmos. Environ. 45, 1203–1212. doi:10.1016/j.atmosenv.2010.06.032.

Kim, B.-W., Jung, H.-J., Song, Y.-C., Lee, M.-J., Kim, H.-K., Kim, J.-C., Sohn, J.-R., Ro, C.-U., 2010. Characterization of summertime aerosol particles collected at subway stations in Seoul, Korea using Low-Z Particle Electron Probe X-ray Microanalysis. Asian J. Atmos. Environ. 4, 97–105. doi:10.5572/ajae.2010.4.2.097.

Kim, C.-H., Yoo, D.-C., Kwon, Y.-M., Han, W.-S., Kim, G.-S., Park, M.-J., Kim, Y.S., Choi, D., 2010. A study on characteristics of atmospheric heavy metals in subway station. Toxicol. Res. 26, 157–162. doi:10.5487/TR.2010.26.2.157.

Kim, C.S., Kang, T.C., 1997. Comparative measurement of lung deposition of inhaled fine particles in normal subjects and patients with obstructive airway disease. Am. J. Respir. Crit. Care Med. 155, 899–905. doi:10.1164/ajrccm.155.3.9117024.

Kim, J.-B., Kim, S., Lee, G.-J., Bae, G.-N., Cho, Y., Park, D., Lee, D.-H., Kwon, S.-B., 2014. Status of PM in Seoul metropolitan subway cabins and effectiveness of subway cabin air purifier (SCAP). Clean Technol. Environ. Policy 16, 1193–1200. doi:10.1007/s10098-013-0708-1.

Kim, K.-H., Ho, D.X., Jeon, J.-S., Kim, J.-C., 2012. A noticeable shift in particulate matter levels after platform screen door installation in a Korean subway station. Atmos. Environ. 49, 219–223. doi:10.1016/j.atmosenv.2011.11.058.

Kim, K.-H., Kabir, E., Kabir, S., 2015. A review on the human health impact of airborne particulate matter. Environ. Int. 74, 136–143. doi:10.1016/j.envint.2014.10.005.

Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM10 and PM2.5) in Seoul Metropolitan Subway stations. J. Hazard. Mater. 154, 440–3. doi:10.1016/j.jhazmat.2007.10.042.

Klepczyńska-Nyström, A., Larsson, B.-M., Grunewald, J., Pousette, C., Lundin, A., Eklund, A., Svartengren, M., 2012. Health effects of a subway environment in mild asthmatic volunteers. Respir. Med. 106, 25–33. doi:10.1016/j.rmed.2011.09.008.

Klepeis, N., Nelson, W., Ott, W., Robinson, J., Tsang, A., Switzer, P., Behar, J., Hern, S., Engelmann, W., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. J. Expo. Anal. Environ. Epidemiol. 11, 231–252. doi:10.1038/sj.jea.7500165.

Klepeis, N.E., 2006. Modeling human exposure to air pollution, in: Ott, W., Wallace, L., Steinemann, A. (Eds.), Human Exposure Analysis. CRC Press.

Koblinger, L., Hofmann, W., 1990. Monte Carlo modeling of aerosol deposition in human lungs. Part I: Simulation of particle transport in a stochastic lung structure. J. Aerosol Sci. 21, 661–674. doi:10.1016/0021-8502(90)90121-D.

Kolb, C.E., Worsnop, D.R., 2012. Chemistry and composition of atmospheric aerosol particles. Annu. Rev. Phys. Chem. 63, 471–491. doi:10.1146/annurev-physchem-032511-143706.

Kroll, J.H., Seinfeld, J.H., 2008. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. Atmos. Environ. 42, 3593–3624. doi:10.1016/j.atmosenv.2008.01.003.

Kulkarni, P., Baron, P.A., Willeke, K., 2011. Aerosol measurement: principles, techniques, and applications, 3rd ed. John Wiley & Sons, Inc., Hoboken, New Jersey.

Kulmala, M., 2003. How particles nucleate and grow. Science (80-.). 302, 1000–1001. doi:10.1126/science.1090848.

Kulmala, M., Kerminen, V.-M., 2008. On the formation and growth of atmospheric nanoparticles. Atmos. Res. 90, 132–150. doi:10.1016/j.atmosres.2008.01.005.

Kulmala, M., Laakso, L., Lehtinen, K.E.J., Riipinen, I., Dal Maso, M., Anttila, T., Kerminen, V.-M., Hõrrak, U., Vana, M., Tammet, H., 2004. Initial steps of aerosol growth. Atmos. Chem. Phys. 4, 2553–2560. doi:10.5194/acp-4-2553-2004.

Kwon, S.-B., Jeong, W., Park, D., Kim, K.-T., Cho, K.H., 2015. A multivariate study for characterizing particulate matter (PM10, PM2.5, and PM1) in Seoul metropolitan subway stations, Korea. J. Hazard. Mater. 297, 295–303. doi:10.1016/j.jhazmat.2015.05.015.

Lai, A.C.K., 2004. Particle deposition indoors : a review. Indoor Air 12, 211–214. doi:10.1046/j.0905-6947.2002.1r159a.x.

Lazaridis, M., 2011. First principles of meteorology and air pollution. Springer, Netherlands.

Lazaridis, M., Broday, D.M., Hov, Ø., Georgopoulos, P.G., 2001. Integrated exposure and dose modeling and analysis system 3. Deposition of inhaled particles in the human respiratory tract. Environ. Sci. Technol. 35, 3727–3734. doi:10.1021/es001545w.

Lepeule, J., Laden, F., Dockery, D., Schwartz, J., 2012. Chronic exposure to fine particles and mortality: an extended follow-up of the Harvard six cities study from 1974 to 2009. Environ. Health Perspect. 120, 965–970. doi:10.1289/ehp.1104660.

Levy, J.I., Dumyahn, T., Spengler, J.D., 2002. Particulate matter and polycyclic aromatic hydrocarbon concentrations in indoor and outdoor microenvironments in Boston, Massachusetts. J. Expo. Anal. Environ. Epidemiol. 12, 104–114. doi:10.1038/sj/jea/7500203.

Lim, J.-M., Lee, J.-H., Moon, J.-H., Chung, Y.-S., Kim, K.-H., 2010. Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization. Atmos. Res. 95, 88–100. doi:10.1016/j.atmosres.2009.08.009.

Lippmann, M., Yeates, D.B., Albert, R.E., 1980. Deposition, retention, and clearance of inhaled particles. Br. J. Ind. Med. 37, 337–62.

Lohmann, U., Feichter, J., 2005. Global indirect aerosol effects: a review. Atmos. Chem. Phys. 5, 715–737. doi:10.5194/acp-5-715-2005.

Löndahl, J., Massling, A., Pagels, J., Swietlicki, E., Vaclavik, E., Loft, S., 2007. Size-resolved respiratory-tract deposition of fine and ultrafine hydrophobic and hygroscopic aerosol particles during rest and exercise. Inhal. Toxicol. 19, 109–116. doi:10.1080/08958370601051677.

Löndahl, J., Massling, A., Swietlicki, E., Bräuner, E.V., Ketzel, M., Pagels, J., Loft, S., 2009. Experimentally determined human respiratory tract deposition of airborne particles at a busy street. Environ. Sci. Technol. 43, 4659–4664. doi:10.1021/es803029b.

Löndahl, J., Möller, W., Pagels, J.H., Kreyling, W.G., Swietlicki, E., Schmid, O., 2014. Measurement techniques for respiratory tract deposition of airborne nanoparticles: A critical review. J. Aerosol Med. Pulm. Drug Deliv. 27, 229–254. doi:10.1089/jamp.2013.1044.

Löndahl, J., Pagels, J., Boman, C., Swietlicki, E., Massling, A., Rissler, J., Blomberg, A., Bohgard, M., Sandström, T., 2008. Deposition of biomass combustion aerosol particles in the human respiratory tract. Inhal. Toxicol. 20, 923–933. doi:10.1080/08958370802087124.

Lovett, G.M., Tear, T.H., Evers, D.C., Findlay, S.E.G., Cosby, B.J., Dunscomb, J.K., Driscoll, C.T., Weathers, K.C., 2009. Effects of air pollution on ecosystems and biological diversity in the Eastern United States. Ann. N. Y. Acad. Sci. 1162, 99–135. doi:10.1111/j.1749-6632.2009.04153.x.

Loxham, M., Cooper, M.J., Gerlofs-Nijland, M.E., Cassee, F.R., Davies, D.E., Palmer, M.R., Teagle, D.A.H., 2013. Physicochemical characterization of airborne

particulate matter at a mainline underground railway station. Environ. Sci. Technol. 47, 3614–3622. doi:10.1021/es304481m.

Lu, S., Liu, D., Zhang, W., Liu, P., Fei, Y., Gu, Y., Wu, M., Yu, S., Yonemochi, S., Wang, X., Wang, Q., 2015. Physico-chemical characterization of PM2.5 in the microenvironment of Shanghai subway. Atmos. Res. 153, 543–552. doi:10.1016/j.atmosres.2014.10.006.

Lucas, D.D., Prinn, R.G., 2005. Parametric sensitivity and uncertainty analysis of dimethylsulfide oxidation in the clear-sky remote marine boundary layer. Atmos. Chem. Phys. 5, 1505–1525. doi:1680-7324/acp/2005-5-1505.

Mahowald, N., Ward, D.S., Kloster, S., Flanner, M.G., Heald, C.L., Heavens, N.G., Hess, P.G., Lamarque, J.-F., Chuang, P.Y., 2011. Aerosol Impacts on Climate and Biogeochemistry. Annu. Rev. Environ. Resour. 36, 45–74. doi:10.1146/annurev-environ-042009-094507.

Marple, V.A., Rubow, K.L., 1986. Theory and design guidelines, in: Lodge, J.P., Chan, T.L. (Eds.), Cascade Impactors: Sampling & Data Analysis. Amer Industrial Hygiene Assn, Akron.

Matamoros, V., Bayona, J.M., 2006. Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. Environ. Sci. Technol. 40, 5811–5816. doi:10.1021/es0607741.

Ménache, M.G., Hofmann, W., Ashgarian, B., Miller, F.J., 2008. Airway geometry models of children's lungs for use in dosimetry modeling. Inhal. Toxicol. 20, 101–126. doi:10.1080/08958370701821433.

Meng, Q.Y., Turpin, B.J., Korn, L., Weisel, C.P., Morandi, M., Colome, S., Zhang, J. (Jim), Stock, T., Spektor, D., Winer, A., Zhang, L., Lee, J.H., Giovanetti, R., Cui, W., Kwon, J., Alimokhtari, S., Shendell, D., Jones, J., Farrar, C., Maberti, S., 2005. Influence of ambient (outdoor) sources on residential indoor and personal PM2.5 concentrations: Analyses of RIOPA data. J. Expo. Anal. Environ. Epidemiol. 15, 17–28. doi:10.1038/sj.jea.7500378.

Mészáros, E., 1999. Fundamentals of atmospheric aerosol chemistry. Akademiai Kiadó, Budapest.

Midander, K., Elihn, K., Wallén, A., Belova, L., Karlsson, A.-K.B., Wallinder, I.O., 2012. Characterisation of nano- and micron-sized airborne and collected subway

particles, a multi-analytical approach. Sci. Total Environ. 427-428, 390–400. doi:10.1016/j.scitotenv.2012.04.014.

Mikuška, P., Křůmal, K., Večeřa, Z., 2015. Characterization of organic compounds in the PM2.5 aerosols in winter in an industrial urban area. Atmos. Environ. 105, 97–108. doi:10.1016/j.atmosenv.2015.01.028.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fahrni, S.M., Alastuey, A., Jimenez, J.L., Mohr, C., Ortega, A.M., Day, D.A., Lanz, V.A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J.F., Baltensperger, U., Prévôt, a. S.H., 2011. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. Atmos. Chem. Phys. 11, 12067–12084. doi:10.5194/acp-11-12067-2011.

Minguillón, M.C., Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Figueras, F., Salvado, J.A., Grimalt, J.O., Nieuwenhuijsen, M., Querol, X., 2012. Source apportionment of indoor, outdoor and personal PM2.5 exposure of pregnant women in Barcelona, Spain. Atmos. Environ. 59, 426–436. doi:10.1016/j.atmosenv.2012.04.052.

Mitsakou, C., Mitrakos, D., Neofytou, P., Housiadas, C., 2007. A simple mechanistic model of deposition of water-soluble aerosol particles in the mouth and throat. J. Aerosol Med. 20, 519–529. doi:10.1089/jam.2007.0625.

Montoya, L.D., Lawrence, J., Murthy, G.G.K., Sarnat, J. a, Godleski, J.J., Koutrakis, P., 2004. Continuous measurements of ambient particle deposition in human subjects. Aerosol Sci. Technol. 38, 980–990. doi:10.1080/027868290519049.

Morabia, A., Amstislavski, P.N., Mirer, F.E., Amstislavski, T.M., Eisl, H., Wolff, M.S., Markowitz, S.B., 2009. Air pollution and activity during transportation by car, subway, and walking. Am. J. Prev. Med. 37, 72–7. doi:10.1016/j.amepre.2009.03.014.

Morawska, L., Afshari, A., Bae, G.N., Buonanno, G., Chao, C.Y.H., Hänninen, O., Hofmann, W., Isaxon, C., Jayaratne, E.R., Pasanen, P., Salthammer, T., Waring, M., Wierzbicka, A., 2013. Indoor aerosols: from personal exposure to risk assessment. Indoor Air 23, 462–487. doi:10.1111/ina.12044.

Morawska, L., Hofmann, W., Hitchins-Loveday, J., Swanson, C., Mengersen, K., 2005. Experimental study of the deposition of combustion aerosols in the human respiratory tract. J. Aerosol Sci. 36, 939–957. doi:10.1016/j.jaerosci.2005.03.015.

Morawska, L., Salthammer, T., 2003. Indoor Environment - Airborne Particles and Settled Dust. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Moreno, T., Martins, V., Querol, X., Jones, T., BéruBé, K., Minguillón, M.C., Amato, F., Capdevila, M., de Miguel, E., Centelles, S., Gibbons, W., 2015. A new look at inhalable metalliferous airborne particles on rail subway platforms. Sci. Total Environ. 505, 367–375. doi:10.1016/j.scitotenv.2014.10.013.

Moreno, T., Pérez, N., Reche, C., Martins, V., de Miguel, E., Capdevila, M., Centelles, S., Minguillón, M.C., Amato, F., Alastuey, A., Querol, X., Gibbons, W., 2014. Subway platform air quality: Assessing the influences of tunnel ventilation, train piston effect and station design. Atmos. Environ. 92, 461–468. doi:10.1016/j.atmosenv.2014.04.043.

Mugica-Álvarez, V., Figueroa-Lara, J., Romero-Romo, M., Sepúlveda-Sánchez, J., López-Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. Atmos. Environ. 49, 284–293. doi:10.1016/j.atmosenv.2011.11.038.

Murruni, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., Vázquez, M., Ozafrán, M., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. Atmos. Environ. 43, 4577–4583. doi:10.1016/j.atmosenv.2009.06.025.

Nieuwenhuijsen, M.J., Gómez-Perales, J.E., Colvile, R.N., 2007. Levels of particulate air pollution, its elemental composition, determinants and health effects in metro systems. Atmos. Environ. 41, 7995–8006. doi:10.1016/j.atmosenv.2007.08.002.

Nøjgaard, J.K., Nguyen, Q.T., Glasius, M., Sørensen, L.L., 2012. Nucleation and Aitken mode atmospheric particles in relation to O3 and NOX at semirural background in Denmark. Atmos. Environ. 49, 275–283. doi:10.1016/j.atmosenv.2011.11.040.

Okochi, H., Kameda, H., Hasegawa, S., Saito, N., Kubota, K., Igawa, M., 2000. Deterioration of concrete structures by acid deposition — an assessment of the role of rainwater on deterioration by laboratory and field exposure experiments using mortar specimens. Atmos. Environ. 34, 2937–2945. doi:10.1016/S1352-2310(99)00523-3.

Onat, B., Stakeeva, B., 2013. Personal exposure of commuters in public transport to PM2.5 and fine particle counts. Atmos. Pollut. Res. 4, 329–335. doi:10.5094/APR.2013.037.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126. doi:10.1002/env.3170050203.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269–298. doi:10.1139/er-9-4-269.

Pan, Y.P., Wang, Y.S., 2015. Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. Atmos. Chem. Phys. 15, 951–972. doi:10.5194/acp-15-951-2015.

Park, D., Lee, T., Hwang, D., Jung, W., Lee, Y., Cho, K., Kim, D., Lee, K., 2014. Identification of the sources of PM10 in a subway tunnel using positive matrix factorization. J. Air Waste Manage. Assoc. 64, 1361–1368. doi:10.1080/10962247.2014.950766.

Park, D., Oh, M., Yoon, Y., Park, E., Lee, K., 2012. Source identification of PM10 pollution in subway passenger cabins using positive matrix factorization. Atmos. Environ. 49, 180–185. doi:10.1016/j.atmosenv.2011.11.064.

Park, D.-U., Ha, K.-C., 2008. Characteristics of PM10, PM2.5, CO2 and CO monitored in interiors and platforms of subway train in Seoul, Korea. Environ. Int. 34, 629–34. doi:10.1016/j.envint.2007.12.007.

Park, E.-J., Umh, H., Choi, D.-H., Cho, M., Choi, W., Kim, S.-W., Kim, Y., Kim, J.-H., 2014. Magnetite- and maghemite-induced different toxicity in murine alveolar macrophage cells. Arch. Toxicol. 88, 1607–1618. doi:10.1007/s00204-014-1210-1.

Pathak, R.K., Wu, W.S., Wang, T., 2009. Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. Atmos. Chem. Phys. 9, 1711–1722. doi:10.5194/acp-9-1711-2009.

Patterson, R.F., Zhang, Q., Zheng, M., Zhu, Y., 2014. Particle deposition in respiratory tracts of school-aged children. Aerosol Air Qual. Res. 14, 64–73. doi:10.4209/aaqr.2013.04.0113.

Perrino, C., Marcovecchio, F., Tofful, L., Canepari, S., 2015. Particulate matter concentration and chemical composition in the metro system of Rome, Italy. Environ. Sci. Pollut. Res. 22, 9204–9214. doi:10.1007/s11356-014-4019-9.

Petroff, A., Mailliat, A., Amielh, M., Anselmet, F., 2008. Aerosol dry deposition on vegetative canopies. Part I: Review of present knowledge. Atmos. Environ. 42, 3625–3653. doi:10.1016/j.atmosenv.2007.09.043.

Place Jr., P.F., Ziemba, L.D., Griffin, R.J., 2010. Observations of nucleation-mode particle events and size distributions at a rural New England site. Atmos. Environ. 44, 88–94. doi:10.1016/j.atmosenv.2009.09.030.

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect. J. Air Waste Manage. Assoc. 56, 709–742. doi:10.1080/10473289.2006.10464485.

Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chemie Int. Ed. 44, 7520–7540. doi:10.1002/anie.200501122.

Pósfai, M., Molnár, Á., 2012. Aerosol particles in the troposphere: a mineralogical introduction, in: Vaughan, D.J., Wogelius, R.A. (Eds.), Environmental Mineralogy II. European Mineralogical Union, p. 489.

Prajapati, S.K., 2012. Ecological effect of airborne particulate matter on plants. Environ. Skept. Critics 1, 12–22.

Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S.E., Gill, T.E., 2002. Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product. Rev. Geophys. 40, 2–31. doi:10.1029/2000RG000095.

Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A.M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T.A.J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F., 2010. A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos. Environ. 44, 1308–1320. doi:10.1016/j.atmosenv.2009.12.011.

Querol, X., Alastuey, A., Moreno, T., Viana, M.M., Castillo, S., Pey, J., Rodríguez, S., Artiñano, B., Salvador, P., Sánchez, M., Garcia Dos Santos, S., Herce Garraleta, M.D., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Sanz, M.J., Palomo-Marín, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., Sánchez de la Campa, A., 2008. Spatial and temporal variations in airborne particulate matter (PM10 and PM2.5) across Spain 1999–2005. Atmos. Environ. 42, 3964–3979. doi:10.1016/j.atmosenv.2006.10.071.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Mantilla, E., Ruiz, C.R., 2001. Monitoring of PM10 and PM2.5 around primary particulate anthropogenic emission sources. Atmos. Environ. 35, 845–858. doi:10.1016/S1352-2310(00)00387-3.

Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M.C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., de la Rosa, J., Sánchez de la Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández Patier, R., 2013. Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy. Atmos. Chem. Phys. 13, 6185–6206. doi:10.5194/acp-13-6185-2013.

Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., Capdevila, M., 2012. Variability of levels and composition of PM10 and PM2.5 in the Barcelona metro system. Atmos. Chem. Phys. 12, 5055–5076. doi:10.5194/acp-12-5055-2012.

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos. Environ. 41, 7219–7231. doi:10.1016/j.atmosenv.2007.05.022.

Raut, J.-C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. Atmos. Environ. 43, 860–868. doi:10.1016/j.atmosenv.2008.10.038.

Reche, C., Moreno, T., Amato, F., Viana, M., van Drooge, B.L., Chuang, H.-C., Bérubé, K., Jones, T., Alastuey, A., Querol, X., 2012. A multidisciplinary approach to characterise exposure risk and toxicological effects of PM10 and PM2.5 samples in

urban environments. Ecotoxicol. Environ. Saf. 78, 327–35. doi:10.1016/j.ecoenv.2011.11.043.

Regayre, L.A., Pringle, K.J., Lee, L.A., Rap, A., Browse, J., Mann, G.W., Reddington, C.L., Carslaw, K.S., Booth, B.B.B., Woodhouse, M.T., 2015. The climatic importance of uncertainties in regional aerosol–cloud radiative forcings over recent decades. J. Clim. 28, 6589–6607. doi:10.1175/JCLI-D-15-0127.1.

Ripanucci, G., Grana, M., Vicentini, L., Magrini, A., Bergamaschi, A., 2006. Dust in the Underground Railway Tunnels of an Italian Town. J. Occup. Environ. Hyg. 3, 16–25. doi:10.1080/15459620500444004.

Rodríguez, S., Van Dingenen, R., Putaud, J.-P., Martins-Dos Santos, S., Roselli, D., 2005. Nucleation and growth of new particles in the rural atmosphere of Northern Italy—relationship to air quality monitoring. Atmos. Environ. 39, 6734–6746. doi:10.1016/j.atmosenv.2005.07.036.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636–651. doi:10.1021/es00041a007.

Rohr, A.C., Wyzga, R.E., 2012. Attributing health effects to individual particulate matter constituents. Atmos. Environ. 62, 130–152. doi:10.1016/j.atmosenv.2012.07.036.

Rosati, J.A., Brown, J.S., Peters, T.M., Leith, D., Kim, C.S., 2002. A polydisperse aerosol inhalation system designed for human studies. J. Aerosol Sci. 33, 1433–1446. doi:10.1016/S0021-8502(02)00087-3.

Rückerl, R., Schneider, A., Breitner, S., Cyrys, J., Peters, A., 2011. Health effects of particulate air pollution: A review of epidemiological evidence. Inhal. Toxicol. 23, 555–92. doi:10.3109/08958378.2011.593587.

Rudolf, G., Köbrich, R., Stahlhofen, W., 1990. Modelling and algebraic formulation of regional aerosol deposition in man. J. Aerosol Sci. 21, Supple, S403–S406. doi:10.1016/0021-8502(90)90266-Z.

Ruijgrok, W., Davidson, C.I., Nicholson, K.W., 1995. Dry deposition of particles: Implications and recommendations for mapping of deposition over Europe. Tellus B 47, 587–601. doi:10.1034/j.1600-0889.1996.t01-3-00009.x.

Russell, A.G., Brunekreef, B., 2009. A focus on particulate matter and health. Environ. Sci. Technol. 43, 4620–4625. doi:10.1021/es9005459.

Sacks, J.D., Stanek, L.W., Luben, T.J., Johns, D.O., Buckley, B.J., Brown, J.S., Ross, M., 2011. Particulate matter–induced health effects: who is susceptible? Environ. Health Perspect. 119, 446–454. doi:10.1289/ehp.1002255.

Şahin, Ü.A., Onat, B., Stakeeva, B., Ceran, T., Karim, P., 2012. PM10 concentrations and the size distribution of Cu and Fe-containing particles in Istanbul's subway system. Transp. Res. Part D Transp. Environ. 17, 48–53. doi:10.1016/j.trd.2011.09.003.

Salma, I., 2009. Air pollution in underground railway systems, in: Air Quality in Urban Environments. Royal Society of Chemistry, pp. 65–84.

Salma, I., Balásházy, I., Winkler-Heil, R., Hofmann, W., Záray, G., 2002. Effect of particle mass size distribution on the deposition of aerosols in the human respiratory system. J. Aerosol Sci. 33, 119–132. doi:10.1016/S0021-8502(01)00154-9.

Salma, I., Pósfai, M., Kovács, K., Kuzmann, E., Homonnay, Z., Posta, J., 2009. Properties and sources of individual particles and some chemical species in the aerosol of a metropolitan underground railway station. Atmos. Environ. 43, 3460–3466. doi:10.1016/j.atmosenv.2009.04.042.

Salma, I., Weidinger, T., Maenhaut, W., 2007. Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. Atmos. Environ. 41, 8391–8405. doi:10.1016/j.atmosenv.2007.06.017.

Schauer, J., Rogge, W., Hildemann, L., Mazurek, M., Cass, G., Simoneit, B., 2007. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos. Environ. 41, 241–259. doi:10.1016/j.atmosenv.2007.10.069.

Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., Vrijheid, M., Cirach, M., Martinez, D., Figueras, F., Querol, X., Basagaña, X., Eeftens, M., Meliefste, K., Nieuwenhuijsen, M.J., 2013. Personal, indoor and outdoor air pollution levels among pregnant women. Atmos. Environ. 64, 287–295. doi:10.1016/j.atmosenv.2012.09.053.

Schikowski, T., Sugiri, D., Ranft, U., Gehring, U., Heinrich, J., Wichmann, H.-E., Kramer, U., 2007. Does respiratory health contribute to the effects of long-term air

pollution exposure on cardiovascular mortality? Respir. Res. 8, 20. doi:10.1186/1465-9921-8-20.

Schleicher, N.J., Norra, S., Chai, F., Chen, Y., Wang, S., Cen, K., Yu, Y., Stüben, D., 2011. Temporal variability of trace metal mobility of urban particulate matter from Beijing – A contribution to health impact assessments of aerosols. Atmos. Environ. 45, 7248–7265. doi:10.1016/j.atmosenv.2011.08.067.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London Underground: dust and hazards to health. Occup. Environ. Med. 62, 355–62. doi:10.1136/oem.2004.014332.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change (2nd Ed.). John Wiley & Sons, Inc., New York, USA.

Shaughnessy, W.J., Venigalla, M.M., Trump, D., 2015. Health effects of ambient levels of respirable particulate matter (PM) on healthy, young-adult population. Atmos. Environ. 123, Part, 102–111. doi:10.1016/j.atmosenv.2015.10.039.

Son, Y., Dinh, T., Chung, S., Lee, J., Kim, J., 2014. Removal of particulate matter emitted from a subway tunnel using magnetic filters. Environ. Sci. Technol. 48, 2870−2876. doi:10.1021/es404502x.

Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., Pavoni, B., 2013. Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy). Atmos. Chem. Phys. 13, 1927–1939. doi:10.5194/acp-13-1927-2013.

Stanek, L.W., Sacks, J.D., Dutton, S.J., Dubois, J.-J.B., 2011. Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results. Atmos. Environ. 45, 5655–5663. doi:10.1016/j.atmosenv.2011.07.023.

Steenhof, M., Gosens, I., Strak, M., Godri, K.J., Hoek, G., Cassee, F.R., Mudway, I.S., Kelly, F.J., Harrison, R.M., Lebret, E., Brunekreef, B., Janssen, N.A.H., Pieters, R.H.H., 2011. In vitro toxicity of particulate matter (PM) collected at different sites in the Netherlands is associated with PM composition, size fraction and oxidative potential - the RAPTES project. Part. Fibre Toxicol. 8, 1–15. doi:10.1186/1743-8977-8-26.

Sternbeck, J., Sjödin, Å., Andréasson, K., 2002. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. Atmos. Environ. 36, 4735–4744. doi:10.1016/S1352-2310(02)00561-7.

Stockwell, W.R., Kuhns, H., Etyemezian, V., Green, M.C., Chow, J.C., Watson, J.G., 2003. The Treasure Valley secondary aerosol study II: modeling of the formation of inorganic secondary aerosols and precursors for southwestern Idaho. Atmos. Environ. 37, 525–534. doi:10.1016/S1352-2310(02)00895-6.

Stuart, B.O., 1984. Deposition and clearance of inhaled particles. Environ. Health Perspect. 55, 369–390. doi:10.1289/ehp.8455369.

Sturm, R., 2007. A computer model for the clearance of insoluble particles from the tracheobronchial tree of the human lung. Comput. Biol. Med. 37, 680–690. doi:10.1016/j.compbiomed.2006.06.004.

Sundh, J., Olofsson, U., Olander, L., Jansson, A., 2009. Wear rate testing in relation to airborne particles generated in a wheel – rail contact. Lubr. Sci. 21, 135–150. doi:10.1002/ls.80.

Sysalova, J., Szakova, J., 2006. Mobility assessment and validation of toxic elements in tunnel dust samples—Subway and road using sequential chemical extraction and ICP-OES/GF AAS measurements. Environ. Res. 101, 287–293. doi:10.1016/j.envres.2005.10.001.

Tao, W.-K., Chen, J.-P., Li, Z., Wang, C., Zhang, C., 2012. Impact of aerosols on convective clouds and precipitation. Rev. Geophys. 50, RG2001. doi:10.1029/2011RG000369.

Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: A review. Sci. Total Environ. 400, 270–282. doi:10.1016/j.scitotenv.2008.06.007.

Thurston, G., Lippmann, M., 2015. Ambient particulate matter air pollution and cardiopulmonary diseases. Semin. Respir. Crit. Care Med. 36, 422–432. doi:10.1055/s-0035-1549455.

TSI, 2012. DustTrak™ DRX aerosol monitor theory of operation. U.S.A.

Turpin, B.J., Lim, H.-J., 2001. Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci. Technol. 35, 602–610. doi:10.1080/02786820119445.

Tzanis, C., Varotsos, C., Christodoulakis, J., Tidblad, J., Ferm, M., Ionescu, a., Lefevre, R. -a., Theodorakopoulou, K., Kreislova, K., 2011. On the corrosion and soiling effects on materials by air pollution in Athens, Greece. Atmos. Chem. Phys. 11, 12039–12048. doi:10.5194/acp-11-12039-2011.

Uhde, E., Salthammer, T., 2007. Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry. Atmos. Environ. 41, 3111–3128. doi:10.1016/j.atmosenv.2006.05.082.

Valavanidis, A., Fiotakis, K., Vlachogianni, T., 2008. Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. J. Environ. Sci. Heal. Part C 26, 339–362. doi:10.1080/10590500802494538.

van Drooge, B.L., Cusack, M., Reche, C., Mohr, C., Alastuey, A., Querol, X., Prevot, A., Day, D.A., Jimenez, J.L., Grimalt, J.O., 2012. Molecular marker characterization of the organic composition of submicron aerosols from Mediterranean urban and rural environments under contrasting meteorological conditions. Atmos. Environ. 61, 482–489. doi:10.1016/j.atmosenv.2012.07.039.

van Drooge, B.L., Fontal, M., Bravo, N., Fernández, P., Fernández, M.A., Muñoz-Arnanz, J., Jiménez, B., Grimalt, J.O., 2014. Seasonal and spatial variation of organic tracers for biomass burning in PM1 aerosols from highly insolated urban areas. Environ. Sci. Pollut. Res. 21, 11661–11670. doi:10.1007/s11356-014-2545-0.

Vardaka, E., Cook, C.M., Lanaras, T., Sgardelis, S.P., Pantis, J.D., 1995. Effect of dust from a limestone quarry on the photosynthesis of Quercus coccifera, an evergreen Schlerophyllous shrub. Bull. Environ. Contam. Toxicol. 54, 414–419. doi:10.1007/BF00195114.

Vincent, J.H., 2005. Health-related aerosol measurement: a review of existing sampling criteria and proposals for new ones. J. Environ. Monit. 7, 1037–1053. doi:10.1039/B509617K.

Wallace, L., 2006. Indoor sources of ultrafine and accumulation mode particles: size distributions, size-resolved concentrations, and source strengths. Aerosol Sci. Technol. 40, 348–360. doi:10.1080/02786820600612250.

Wang, J., Cubison, M.J., Aiken, A.C., Jimenez, J.L., Collins, D.R., 2010. The importance of aerosol mixing state and size-resolved composition on CCN concentration and

the variation of the importance with atmospheric aging of aerosols. Atmos. Chem. Phys. 10, 7267–7283. doi:10.5194/acp-10-7267-2010.

Wang, K., Dickinson, R.E., Liang, S., 2009. Clear sky visibility has decreased over land globally from 1973 to 2007. Science (80-.). 323, 1468–1470. doi:10.1126/science.1167549.

Wang, L., Morawska, L., Jayaratne, E.R., Mengersen, K., Heuff, D., 2011. Characteristics of airborne particles and the factors affecting them at bus stations. Atmos. Environ. 45, 611–620. doi:10.1016/j.atmosenv.2010.10.036.

Wang, X.R., Gao, H.O., 2011. Exposure to fine particle mass and number concentrations in urban transportation environments of New York City. Transp. Res. Part D Transp. Environ. 16, 384–391. doi:10.1016/j.trd.2011.03.001.

Warneck, P., 1988. Chemistry of the natural atmosphere, 2nd ed, Chemistry of the Natural Atmosphere. Academic Press, San Diego, California.

Watson, J.G., 2002. Visibility: science and regulation. J. Air Waste Manage. Assoc. 52, 628–713. doi:10.1080/10473289.2002.10470813.

Watt, J., Jarrett, D., Hamilton, R., 2008. Dose–response functions for the soiling of heritage materials due to air pollution exposure. Sci. Total Environ. 400, 415–424. doi:10.1016/j.scitotenv.2008.07.024.

White, W.H., 2008. Chemical markers for sea salt in IMPROVE aerosol data. Atmos. Environ. 42, 261–274. doi:10.1016/j.atmosenv.2007.09.040.

WHO, 2006. Air quality guidelines: Global update 2005. Copenhagen, Denmark.

WHO, 2010. WHO guidelines for indoor air quality: selected pollutants. Copenhagen, Denmark.

WHO, 2013. Review of evidence on health aspects of air pollution – REVIHAAP Project. Copenhagen, Denmark.

Yang, F., Kawamura, K., Chen, J., Ho, K., Lee, S., Gao, Y., Cui, L., Wang, T., Fu, P., 2016. Anthropogenic and biogenic organic compounds in summertime fine aerosols (PM2.5) in Beijing, China. Atmos. Environ. 124, 166–175. doi:10.1016/j.atmosenv.2015.08.095.

Ye, X., Lian, Z., Jiang, C., Zhou, Z., Chen, H., 2010. Investigation of indoor environmental quality in Shanghai metro stations, China. Environ. Monit. Assess. 167, 643–51. doi:10.1007/s10661-009-1080-9.

Yeh, H.-C., Schum, G.M., 1980. Models of human lung airways and their application to inhaled particle deposition. Bull. Math. Biol. 42, 461–480. doi:10.1007/BF02460796.

Yu, F., 2011. A secondary organic aerosol formation model considering successive oxidation aging and kinetic condensation of organic compounds: global scale implications. Atmos. Chem. Phys. 11, 1083–1099. doi:10.5194/acp-11-1083-2011.

Yuan, C.-S., Lee, C.-G., Liu, S.-H., Chang, J., Yuan, C., Yang, H.-Y., 2006. Correlation of atmospheric visibility with chemical composition of Kaohsiung aerosols. Atmos. Res. 82, 663–679. doi:10.1016/j.atmosres.2006.02.027.

Zhang, Q., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., Jimenez, J.L., 2005. Time- and size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes. J. Geophys. Res. Atmos. 110, 1–19. doi:10.1029/2004JD004649.

Zhang, Q.H., Zhang, J.P., Xue, H.W., 2010. The challenge of improving visibility in Beijing. Atmos. Chem. Phys. 10, 7821–7827. doi:10.5194/acp-10-7821-2010.

Zhang, W., Jiang, H., Dong, C., Yan, Q., Yu, L., Yu, Y., 2011. Magnetic and geochemical characterization of iron pollution in subway dusts in Shanghai, China. Geochemistry, Geophys. Geosystems 12. doi:10.1029/2011GC003524.

Zhang, Y., Li, C., Wang, X., Guo, H., Feng, Y., Chen, J., 2012. Rush-hour aromatic and chlorinated hydrocarbons in selected subway stations of Shanghai, China. J. Environ. Sci. 24, 131–141. doi:10.1016/S1001-0742(11)60736-5.

Zhao, H., Che, H., Ma, Y., Xia, X., Wang, Y., Wang, P., Wu, X., 2015. Temporal variability of the visibility, particulate matter mass concentration and aerosol optical properties over an urban site in Northeast China. Atmos. Res. 166, 204–212. doi:10.1016/j.atmosres.2015.07.003.

Zhou, M., He, G., Liu, Y., Yin, P., Li, Y., Kan, H., Fan, M., Xue, A., Fan, M., 2015. The associations between ambient air pollution and adult respiratory mortality in 32 major Chinese cities, 2006–2010. Environ. Res. 137, 278–286. doi:10.1016/j.envres.2014.12.016.

Zhuang, B.L., Li, S., Wang, T.J., Deng, J.J., Xie, M., Yin, C.Q., Zhu, J.L., 2013. Direct radiative forcing and climate effects of anthropogenic aerosols with different mixing states over China. Atmos. Environ. 79, 349–361. doi:10.1016/j.atmosenv.2013.07.004.

Zimmer, A.T., Maynard, A.D., 2002. Investigation of the aerosols produced by a high-speed, hand-held grinder using various substrates. Ann. Occup. Hyg. 46, 663–672. doi:10.1093/annhyg/mef089.

Zufall, M.J., Davidson, C.I., 1998. Dry deposition of particles from the atmosphere, in: Linkov, I., Wilson, R. (Eds.), Air Pollution in the Ural Mountains, NATO ASI Series. Springer Netherlands, pp. 55–73. doi:10.1007/978-94-011-5208-2_5.

List of abbreviations and symbols

LIST OF ABBREVIATIONS AND SYMBOLS

ρ_p	particle density
AI	alveolar-interstitial
ASAP	Airborne Sample Analysis Platform sampler
BC	black carbon
CA	carbonaceous aerosol
CCN	cloud condensation nuclei
CM	crustal matter
D_a	aerodynamic diameter
D_g	geometric diameter
DF	deposition fraction
EC	elemental carbon
ET	extrathoracic
ExDoM	Exposure Dose Model
FePM	ferruginous particulate matter
GSD	geometric standard deviation
HRT	human respiratory tract
HVS	high volume sampler
IN	ice nuclei
k	dynamic shape factor
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
OC	organic carbon
OM	organic matter
OPS	Optical Particle Sizer sampler
PAHs	polycyclic aromatic hydrocarbons
PM	particulate matter
PM_1	particulate matter with aerodynamic diameter less than 1 μm
PM_{10}	particulate matter with aerodynamic diameter less than 10 μm
$PM_{2.5}$	particulate matter with aerodynamic diameter less than 2.5 μm

PMF	Positive Matrix Factorization
PN	particle number
PSDs	platform screen door systems
PUF	polyurethane foam substrate
RH	relative humidity
ROS	reactive oxygen species
RT	respiratory tract
sd	standard deviation
SEM	scanning electron microscopy
SIC	secondary inorganic compounds
SOA	secondary organic aerosol
TB	tracheobronchial
TC	total carbon
TMB	Transports Metropolitans de Barcelona
TSP	total suspended particles
VOCs	volatile organic compounds

Appendix

Appendix. Subway literature review

Exposure studies have assessed the air quality in subway systems of several cities worldwide. A summarised literature review of these studies is presented hereinafter, for each subway system:

Subway system of Amsterdam

In Loxham et al. (2013) the elemental composition of size fractionated underground PM in Amsterdam was compared with that from a woodstove, a road wear generator, and a road tunnel PM. Over the three sampling days at the station, the mean underground PM_{10} mass concentration (± standard deviation) was 287 ± 8 μg m^{-3}, with $PM_{2.5}$ at 75 ± 6 μg m^{-3}, and $PM_{0.18}$ at 38 ± 4 μg m^{-3}. Underground PM was notably rich in Fe, accounting for greater than 40% by mass, and several other transition metals (Cu, Cr, Mn, and Zn). According to these authors, scanning electron microscopy revealed that a component of the coarse fraction of underground PM has a morphology indicative of generation by abrasion, absent for fine and ultrafine particulates, which may be derived from high-temperature processes.

Subway system of Barcelona

The first work on the air quality subway system of Barcelona was published by Querol et al. (2012). In this work PM levels inside the trains in summer were among the lowest reported for worldwide subway systems (11–32 μg m^{-3} $PM_{2.5}$) due to the air conditioning system working in all carriages. Mean levels were considerably higher on the platforms, reaching mean levels of 46 and 125 μg m^{-3} in a new and an old line, respectively. A principal component analysis distinguished three different sources: brake abrasion, outdoor contribution and wheel-rail abrasion. The elements with the highest enrichment were those associated with rail, wheel and brake abrasion products (Ba, Fe, Cu, Man, Cr, Sb, As Mo, Co, Sr, among others), with Fe_2O_3 being the dominant particle type. The implementation of Platform Screen Door systems (PSDs) resulted in reductions of both PM levels and metal concentrations. In addition, an advanced optimised ventilation system gave even a much higher efficiency in reducing exposure to PM of metro commuters. Further study focused on the influence of the train piston

effect concluded that subway platform air quality varies greatly depending on ventilation conditions and station design (Moreno et al., 2014).

Subway system of Boston

During the summer of 2000, measurements of ultrafine particles (0.02–1.0 μm in diameter), $PM_{2.5}$, and particle-bound PAHs were carried out in outdoor and indoor microenvironments in Boston as well as transportation microenvironments, including the subway system (Levy et al., 2002). For the subway, while ultrafine PM concentrations were not especially elevated inside the train or on the subway platform, $PM_{2.5}$ concentrations were higher than in most nontransportation microenvironments (67 $\mu g\ m^{-3}$ on average). PAHs in subway platforms tended to be mostly associated with outdoor urban ambient air emissions.

Subway system of Budapest

PM_{10} mass concentration in the subway of Budapest exhibited two peaks, at 7:00h and 17:00h, corresponding to the morning and afternoon rush hours, when the train frequency is greatest (Salma et al., 2007). Mean PM_{10} concentration for working hours was high (155 ± 55 $\mu g\ m^{-3}$; mean ± sd), with 72% of the mass associated with the $PM_{10\text{-}2.0}$ size fraction. On average, Fe accounted for 40% and 46% of the $PM_{10\text{-}2.0}$ and $PM_{2.0}$ concentration, respectively. PM_{10} concentrations of Fe, Mn, Ni, Cu, and Cr were higher than in outdoor air by factors between 5 and 20. Mechanical wear and friction of electric conducting rails and bow sliding collectors, ordinary rails and wheels, as well as resuspension, were identified as the primary sources. In Salma et al. (2009), the particles were classified into groups of iron oxides and iron, carbonates, silicates, quartz and carbonaceous debris. Fe-rich particles in the $PM_{2.0}$ size fraction typically consisted of aggregates of nano-sized hematite crystals that were randomly oriented, had round shapes and diameters of 5–15 nm, although magnetite was also present. $PM_{2.0}$ fraction particles typically had a rugged surface with layered or granular morphologies. Hematite was a major Fe-bearing species in the $PM_{10\text{-}2.0}$ size fraction. Mean atmospheric concentration of Fe in the $PM_{10\text{–}2.0}$ size fraction was 34 $\mu g\ m^{-3}$ corresponding a relative amount of 36% (in the $PM_{2.0}$ size fraction it was 15.5 $\mu g\ m^{-3}$ (Salma et al., 2007)). It is indicated in this publication that the increased adverse health

effects of aerosol particles in subways with respect to ambient outdoor particles is linked to the differences in the oxidation states, surface properties or morphologies.

Subway system of Buenos Aires

According to Murruni et al. (2009), total suspended particles (TSP) concentrations in stations of the Buenos Aires subway system and outdoors were poorly correlated, indicating that TSP levels in the subway were mainly influenced by internal sources. TSP levels were found to be between 152 and 270 μg m^{-3} on the platforms of the stations, 3 times higher on average than those for outdoor urban ambient air. Regarding metal concentrations, the most enriched element in TSP was Fe, the levels of which ranged from 8 to 86 μg m^{-3}.

Subway system of Cairo

Microbial indicators associated with suspended dust have been studied in detail in the underground system of Cairo (Awad, 2002), where it was observed that higher average concentrations were recorded at the surface than in tunnel stations. Mechanical ventilation in the tunnel station reduces and removes particles >5μm whereas natural ventilation at the surface station possible removes smaller particles and leaves larger ones suspended. High ozone concentrations in the tunnel were attributed to the effects of electrical charge from train daytime lamps, and insufficient ventilation.

Subway system of Helsinki

Fine particulate matter ($PM_{2.5}$) and particle number (PN) concentrations were monitored in the Helsinki subway system (Aarnio et al., 2005). The average EC (4.0 μg m^{-3}), OC (7.4 μg m^{-3}), BC (6.3 μg m^{-3}) concentrations and ultrafine particle number ($3.1x10^4$ # cm^{-3}) daytime concentrations were rather similar to those in outdoor ambient air, while $PM_{2.5}$ concentrations were significantly higher at the subway platform (47–60 μg m^{-3} vs 10 μg m^{-3} at urban background). Average $PM_{2.5}$ concentration in subway cars was 21 μg m^{-3}. The most enriched element in subway $PM_{2.5}$ was Fe (29 μg m^{-3}). Other enriched elements included Mn, Cr, Ni, and Cu. Results concerning passenger exposure showed that a 30 min commuting plus 9 min stay at the stations per day increased the exposure to $PM_{2.5}$ mass by only approximately 3% compared to staying in an urban traffic environment, although the exposure to iron in $PM_{2.5}$ increased nearly 200%, to Mn 60% and to Cu 40%.

Subway system of Hong Kong

Chan et al. (2002) examined the in-vehicle exposure to PM_{10} and $PM_{2.5}$ while commuting in different public transportation modes in Hong Kong. Authors reported that filters in the air-conditioning system are capable of removing the larger portion (2.5–10 μm) of PM_{10}. Mean PM_{10} and $PM_{2.5}$ concentrations were 44 μg m^{-3} (23–85 μg m^{-3}) and 33 μg m^{-3} (21–48 μg m^{-3}), respectively.

Subway system of Istanbul

The indoor air quality in the subway system of Istanbul was characterised in Şahin et al. (2012). Fluctuations in PM_{10} at the stations were slightly higher from 07:00 to 10:00 and from 16:00 to 22:00 (rush hours), when passenger and the traffic density were high. Mean PM_{10} concentrations on the platforms during normal hours ranged between 58 and 213 μg m^{-3}, and between 59 and 201 μg m^{-3} during rush hours. Fe-containing particles in the stations were 3.5–8 times higher than those in the urban air of Istanbul. Approximately 15–30% of the inhalable PM of size >2.1 μm was determined as Fe-containing particles. In of total PM, the average Fe concentrations ranged between 10.3 ± 1.6 μg m^{-3} and 28.2 ± 19.6 μg m^{-3}. A commuting study was carried out by Onat and Stakeeva (2013) using four transport modes: bus, subway–bus, car and walking. Lower $PM_{2.5}$ concentrations were observed inside the subway-bus (45.4 ± 18.6 μg m^{-3} for rush hours and 39.9 ± 16.0 μg m^{-3} for non-rush hours) than inside the bus and walking, probably due to the PM filtering of cabin air by the air-conditioning system.

Subway system of London

Some of the highest average levels of PM were measured in the London subway system. According to Seaton et al. (2005), $PM_{2.5}$ concentrations on station platforms ranged between 270 and 480 μg m^{-3}, and PN concentrations between $1.4x10^4$ and $2.9x10^4$ # cm^{-3}. Train cabins concentrations over a shift averaged 130–200 μg m^{-3} and $1.7x10^4$–$2.3x10^4$ # cm^{-3}. The dust comprised by mass approximately 67% iron oxide, 1–2% quartz, and traces of other metals, the residue being volatile matter. The finest particles are drawn underground from the surface while the coarser dust is generated by interaction of brakes, wheels, and rails. Adams et al. (2001) performed a study on of personal exposure to $PM_{2.5}$ in London transport microenvironments (bicycle, bus, car

and subway) and concluded that the mean exposure levels on the London subway system were 3–8 times higher than the surface transport modes.

Subway system of Los Angeles

Kam et al. (2011a, 2011b) reported data on the physical and chemical characterization of personal exposure to airborne PM in the Los Angeles subway. The average PM_{10} concentrations on station platforms and inside the train were 78.0 μg m^{-3} (56.7 μg m^{-3} for $PM_{2.5}$) and 31.5 μg m^{-3} (24.2 μg m^{-3} for $PM_{2.5}$) in the underground subway line, respectively. In general, the subway's platforms and train have PM levels double those of the aboveground light-rail's platforms and trains, especially for the coarse fraction ($PM_{2.5-10}$). Subway stations have PM_{10}, $PM_{2.5}$, and $PM_{2.5-10}$ levels that are 2.5, 2.8, and 2.0 times greater than those at the urban ambient environment. In coarse PM, the gravimetric mass of the underground, the ground level line, and the urban ambient air contains 27%, 6%, and 2% of Fe; $PM_{2.5}$ in the corresponding sites contains 32%, 3%, and 1% Fe. Mn, Cr, Co, Ni, Cu, Ba, Mo, Cd, Eu were also enriched in the subway, especially in the fine fraction. It was found that elements in the subway system account for a lower solubility than elements in the ground rail line and in ambient air. According to the authors, the piston effect of a subway train provides an explanation for how outdoor air can enter the underground subway environment. A comparative assessment of $PM_{2.5}$ exposures in light-rail, subway, freeway, and surface street environments in Los Angeles was carried out by Kam et al. (2013). The lowest EC and OC levels were found in the subway system. They also observed that metals associated with stainless steel, notably Fe and other steel-associated elements (Mn, Mo, Ba, Cr, Co, Ni, and Cd), were elevated for the subway system, most likely from abrasion processes between the rail and brakes; elements associated with tire and brake wear and oil additives (Ca, Ti, Sn, Sb, and Pb) were elevated on roadways. For water-solubility, metals observed on the subway were the least soluble.

Subway system of Mexico City

Relatively low PM levels have been recorded in the subway system of Mexico City owing to the use of trains equipped with rubber wheels. Commuters' exposure to $PM_{2.5}$, CO, and benzene was evaluated by Gómez-Perales et al. (2004), and their concentrations were 61 μg m^{-3}, 7 ppm and 4 ppb on average, respectively. Total carbon

was identified as the main component of the total composition of $PM_{2.5}$. Mugica-Álvarez et al. (2012) obtained concentrations of PM_{10} and $PM_{2.5}$ on the platform of a subway station in Mexico City and in an outdoor location close to it. The concentration levels in both sizes were similar during all days with the exception of weekends, especially on Sunday when activity decreases due to lower trains' frequency. The largest particles concentrations in the subway were found from 06:00 to 14:00 and the lowest concentrations were registered from 22:00 to 06:00. $PM_{2.5}$ levels ranged between 41 and 67 μg m^{-3} (6% higher than outside), whereas PM_{10} levels ranging from 88 to 145 μg m^{-3} (20% higher than outside). Greater Fe, Cu, Ni, Cr and Mn concentrations were quantified in the subway PM as compared to the outdoor ambient air. Differences indoor-outdoor regarding Fe concentrations were especially significant (60% higher for PM_{10}, and 40% higher for $PM_{2.5}$).

Subway system of Milan

The subway stations of Milan were investigated by Colombi et al. (2013). Mean weekday PM_{10} concentrations between 105 and 283 μg m^{-3} were found on the platform (with higher levels recorded at stations with narrow tunnels, deeper underground, and those where connections with the outside air are limited), while average ambient concentrations of 36 μg m^{-3} were observed. PM_{10} levels are shown to be well correlated with train frequency, and PM was qualitatively different from that found in typical urban ambient air, both in chemical composition and in size distribution. A cluster analysis showed that wheel, brake and track wear (characterised by Fe, Mn, Sb and Ba oxides) contributed 40–73% of total PM_{10} mass, and electric cable wear (characterised by Cu and Zn oxides) 2-3%.

Subway system of Naples

An intensive particulate sampling campaign was carried out for measuring the PM concentrations in the Naples subway system (Cartenì et al., 2015). Mean PM_{10} concentrations measured on the monitored underground station platforms ranged between 172 and 262 μg m^{-3}, while the mean $PM_{2.5}$ concentration ranged between 45 and 58 μg m^{-3}. Furthermore, a direct correlation between trains passage and PM concentrations was observed, with an increase up to 42% above the average value. This correlation was possibly caused by the resuspension of the particles due to the

turbulence induced by trains. The results showed that high concentrations of both PM_{10} (58–138 μg m^{-3}) and $PM_{2.5}$ (18–36 μg m^{-3}) were also measured inside trains. Furthermore, measurements showed that windows left open on trains caused the increase in PM concentrations inside trains in the underground section, while in the ground-level section the clean air entering the trains produced an environmental "washing effect".

Subway system of New York

Workers and commuters' exposure through the subway has been studied in detail in the New York City's subway system. Chillrud et al. (2004) analysed the causes of metal (Fe, Mn and Cr) exposures by high school students for 48 hours and reported that the subway was the most important source. Steel dust in the New York subway system was the dominant source of airborne exposures to Fe (26 μg m^{-3}), Mn (240 ng m^{-3}) and Cr (84 ng m^{-3}). Airborne concentrations of these three metals associated with $PM_{2.5}$ were observed to be more than 100 times higher in the subway environment than in home indoor or outdoor settings. According to Morabia et al. (2009), total $PM_{2.5}$ exposures did not differ much among car, subway, and walking (respectively, 21.4, 30.6, and 26.5 μg m^{-3}) travels in New York City. Grass et al. (2010) calculated that the subway worker's mean time-weighted $PM_{2.5}$ exposure was 52 μg m^{-3} with a median of 27 μg m^{-3}, and a range of 6–469 μg m^{-3}. Fe, Mn, and Cr in subway worker personal $PM_{2.5}$ fell well below occupational standards. The study performed by Wang and Gao (2011) on travellers' exposure to $PM_{2.5}$ mass and number concentrations across various transportation-related microenvironments in New York City (NYC) showed that the highest exposure to $PM_{2.5}$ mass occurring at underground subway stations and onboard subway trains and that the highest mean $PM_{2.5}$ number exposure occurring on urban street sides. It was also found that the day-to-day variation of $PM_{2.5}$ mass tends to be greater than the variation in number.

Subway system of Paris

Raut et al. (2009) reported average daytime PM_{10} and $PM_{2.5}$ concentrations in an underground railway station were approximately 5–30 times higher than those measured in Paris streets. Aerosol concentrations in the subway station displayed a repeatable diurnal cycle during weekdays characterized by two sharp peaks during

traffic condition. Both lower levels of particle concentrations and a less marked cycle were observed during weekends and nights. Particles are mainly brought by the numerous trains travelling in the underground subway system and by passengers in transit. Concentrations are also influenced by ambient air from the nearby streets through tunnel ventilation. Particles were mainly constituted of dust, with high concentrations of iron and other metals, but also composed of black and organic carbon.

Subway system of Prague

Passenger exposure to PM_{10} during subway commuting showed seasonal differences in Prague (Braniš, 2006), being the mass concentrations inside the train, in the underground spaces of stations and outdoor significantly higher in winter compared to summer season. On average, the highest PM_{10} concentration was recorded inside the trains (113.7 μg m^{-3}), the second highest in the underground spaces of stations (102.7 μg m^{-3}), followed by outdoor environment (74.3 μg m^{-3}). The correlation between concentrations from both underground microenvironments was strong indicating a common source of aerosol inside the subway system. This study suggests that in some instances, besides the underground related sources (friction between wheels and rail, wear of brakes, vaporization of metals due to sparking, resuspension due to movement of people and trains), outdoor levels of aerosol may significantly influence air quality in the underground transport system presumably by adding ambient pollution through ventilation systems and/or station escalator tunnels and corridors. Recently, Cusack et al. (2015) performed measurements of PM_{10}, $PM_{2.5}$ and PM_1 and particle number concentration and size distribution during 24 h on a platform of the Prague underground subway. Measurements were performed both when the metro was in operation and when it was inoperative and closed to the public (referred to as background). PM concentrations were elevated during both periods, but were substantially increased in the coarse fraction during hours when the metro was in operation. Average PM concentrations were 214.8, 93.9 and 44.8 μg m^{-3} for PM_{10}, $PM_{2.5}$ and PM_1, respectively. Average particle number concentrations were $8.5x10^3$ # cm^{-3} for background hours and $11.5x10^3$ # cm^{-3} during operational hours. Particle number concentrations were found to not vary as significantly as PM concentrations

throughout the day. Variations in PM were strongly governed by passing trains, with highest concentrations recorded during rush hour. PM was found to be highly enriched with Fe, especially in the coarse fraction, comprising 46% of PM_{10} (98.9 μg m^{-3}). This reduces to 6.7 μg m^{-3} during background hours, proving that the trains themselves were the main source of iron, most probably from wheel-rail mechanical abrasion. Other enriched elements relative to background hours included Ba, Cu, Mn, Cr, Mo, Ni and Co, among others. Many of these elements exhibited a similar size distribution, further indicating their sources were common and were attributed to train operations.

Subway system of Rome

Ripanucci et al. (2006) studied two lines of the subway system of Rome, focusing on the analysis and measurement of dust granulometric classes PM_{10}, respirable fraction, respirable combustible dust, and the organic, metallic, siliceous, and fibrous components. Authors found that dust concentrations in the tunnels and platforms (351 μg m^{-3}) were 3.5 times higher than average value recorded aboveground. Fe and Si were the major components found in the dust. Authors concluded that the commuters spending approximately 1 hour in trains or on station platforms per day, would increase the 24-hour average exposure by 3 μg m^{-3}, and gave recommendations to improve the air quality in the subway system, such as upgrading the ventilation system for the artificial air supply and installing adequate extraction fans at the ventilation ducts opened along the tunnels. Recently, Perrino et al. (2015) characterised the air quality at the main station of the metro system of Rome (Termini hub) by the point of view of PM concentration and chemical composition. PM chemical characterization included ions, elemental carbon, organic carbon, macro-elements, and the bio-accessible and residual fractions of micro- and trace elements. Almost all the considered chemical components showed a significant increase (I/O>10) in the subway microenvironments and particularly on the platform and in train carriages without air conditioning. I/O ratio up to two orders of magnitude were measured for Fe, Ba, Mn, Cu, and Zn. Authors found a noticeable increase of PM components produced by train wheels, train brakes, and rails erosion, by the weathering of construction material and by the presence and movements of the passengers. The relative abundance of these

components decreases as the distance from the tunnel increases, and in carriages equipped with air-conditioning with respect to those without air-conditioning.

Subway system of Seoul

The subway is the main means of public transit in the Seoul metropolitan area. As a response to increasing public concerns regarding indoor air quality in underground environments, several studies have been carried out to characterise the PM in the urban subway system of Seoul. Kim et al. (2008) examined the concentrations of PM_{10} and $PM_{2.5}$ in areas within the Seoul Subway network providing fundamental data in order to protect respiratory health of subway workers and passengers from air pollutants. Levels of PM were measured both subway worker areas (station offices, rest areas, ticket offices and driver compartments) and passenger areas (station precincts, train carriages and platforms). The mean concentrations of PM_{10} and $PM_{2.5}$ were relatively higher on platforms, inside train carriages and in driver compartments than in the other areas monitored. Kang et al. (2008) identified 4 major types of subway particles on an underground platform, based on their chemical compositions: Fe-containing, soil-derived, carbonaceous, and secondary nitrate and/or sulphate particles. Fe-containing particles were associated with wear processes at rail-wheel-brake interfaces, while the others were thought to be introduced mostly from the outdoor urban atmosphere. Fe-containing particles were the most common ones, with relative abundances in the range 61–79%. In Kim C.-H. et al. (2010), air quality was assessed in six selected subway stations, PM was captured on platforms, and 11 types of heavy metals were analysed. The results showed that the mean concentration of Fe was the highest (average 8.7 $\mu g\ m^{-3}$) out of the heavy metals in PM, followed by Cu (2.5 $\mu g\ m^{-3}$), K (1.8 $\mu g\ m^{-3}$), Ca (1.0 $\mu g\ m^{-3}$), Zn (0.6 $\mu g\ m^{-3}$), Ni (0.4 $\mu g\ m^{-3}$), Na (0.3 $\mu g\ m^{-3}$), Mn (0.1 $\mu g\ m^{-3}$), Mg (0.05 $\mu g\ m^{-3}$), Cr (0.03 $\mu g\ m^{-3}$) and Cd (0.008 $\mu g\ m^{-3}$). Jung et al. (2010) analysed airborne particles collected at 4 different locations in underground subway stations, i.e. in tunnels, at platforms, near ticket offices, and outdoors. Four major particle types were encountered: Fe-containing, soil-derived, carbonaceous, and secondary nitrate and/or sulphate particles. For samples collected at the platform, near the ticket office, and outdoors, the relative abundance of Fe-containing particles decreased as the distance of the sampling locations from the tunnel increased. The

results clearly indicated that Fe-containing particles originating in tunnels predominated in the indoor microenvironment of subway stations, with their relative abundances of 75–91%. Soil-derived particles, such as aluminosilicates, SiO_2, and $CaCO_3$, were introduced in the indoor subway from ambient urban atmosphere. The source of the carbonaceous particles and the nitrate and sulphate particles may be also the outdoor environment. Complementarily, Eom et al. (2013) found that the majority of airborne particles collected in the underground subway tunnels were found to be magnetite, hematite, and iron metal. The efficiency of mitigation strategies based on the use of magnetic filters to remove PM was assessed in subway tunnels by Son et al. (2014) Authors obtained a maximum removal efficiency of PM_{10} (52%), $PM_{2.5}$ (46%), and PM_1 (38%) at a 60 Hz fan frequency using double magnetic filters. The effect on PM levels of the installation of PSDs was evaluated by Kim et al. (2012). The installation of PSDs at the subway was more efficient for removing coarse fraction of PM infiltrating from subway railway into the passenger platform, levels before the installation being 116 ± 25.4 μg m^{-3} for PM_{10} and 66.2 ± 22.9 μg m^{-3} for $PM_{2.5}$; reducing to 97.2 ± 44.7 μg m^{-3} for PM_{10} and 58.1 ± 29.2 μg m^{-3} for $PM_{2.5}$ after PSDs installation. Recently, Kwon et al. (2015) monitored the concentration of PM_{10}, $PM_{2.5}$, and PM_1 in six major transfer stations. The average PM concentration observed was approximately 2 or 3 times higher than outdoor PM_{10} concentration, showing similar temporal patterns at concourses and platforms. Outdoor PM_{10} was determined to be the most significant factor in controlling indoor subway PM concentration. In addition, the station depth and number of trains passing through stations were found to be additional influences on PM_X.

To date, only two studies on air quality in subway systems include source apportionment analysis, both in Seoul. The first one focused on subway passenger cabins (Park et al., 2012), and the second on the subway tunnel (Park D. et al., 2014). Park et al. (2012) reported mean PM_{10} concentrations of 65.7 μg m^{-3}, composed of 52.5% inorganic components, 10.2% anions and 37.3% other materials including organic and inorganic cations. Fe was the most abundant element and significantly correlated with Mn, Ti, Cr, Ni, and Cu. The PM_{10} sources characterized by PMF were soil and road dust sources (27.2%), railroad-related sources (47.6%), secondary nitrate sources (16.2%),

and a chlorine factor mixed with a secondary sulphate source (9.1%). Overall, railroad-related sources contributed the most to PM_{10} subway cabin air. On the other hand, Park D. et al. (2014) revealed a similar chemical composition in the subway tunnel. PM_{10} consisted of 40.4% inorganic species, 9.1% anions, 4.9% cations, and 45.6% other materials. The iron fraction was the highest, contributing 36.1% of the PM_{10} levels. According to PMF analysis, major contributors in the subway tunnel were rail, wheel, and brake wear (59.6%), oil combustion (17.0%), secondary aerosols (10.0%), electric cable wear (8.1%), and soil and road dust (5.4%). The internal sources (rail, wheel, brake, and electric cable wear) were the major contributors of PM_{10} in the subway tunnel (67.7%).

Subway system of Shanghai

A field study was carried out in Shanghai subway stations to obtain the PM levels (Ye et al., 2010). The mean levels of PM_1, $PM_{2.5}$, and PM_{10} were 231 ± 152, 287 ± 177, and 366 ± 193 μg m^{-3}, respectively. The contribution of PM_1 to $PM_{2.5}$ and $PM_{2.5}$ to PM_{10} was up to 79% and 76%, respectively. This means that fine particles or ultrafine particles constituted the preponderant part of subway station PM. Guo et al. (2014) measured mean PM_1 and $PM_{2.5}$ concentrations ranging from 59.6 to 122.3 and from 82.5 to 177.7 μg m^{-3}, respectively. Fe, Cr, Ba, Mn, Sr, Cu and Pb concentrations in the subway stations were significantly higher in comparison with urban ambient air, implicating that these trace metals may be associated with the subway system working. The morphology and mineralogy characteristics of airborne dusts revealed that the presence of most individual particles were with no definite shape and most of them were with a large metal content. Fe was the most abundant metal, mainly as hematite, iron-metal and mineral Fe. Magnetite only existed in aboveground subway line. Recently, Lu et al. (2015) also demonstrated that mass levels of $PM_{2.5}$ in the Shanghai subway stations (ranged from 49.2 ± 19.7 to 66.1 ± 25.2 μg m^{-3}) were higher than that in ambient air (ranged from 24.5 ± 3.3 to 65.6 ± 5.6 μg m^{-3}). The $PM_{2.5}$ in the subway stations was mainly composed of iron-containing particles and mineral particles, while the $PM_{2.5}$ in ambient air largely consisted of mineral particles and soot aggregates. Fe was the most abundant element in subway $PM_{2.5}$, followed by a series chemical elements, including Na, Mg, Al, K, Ca, Zn, Mn, Ba, Li, Cr, Ni, Cu, Ga, Sr, Pb, Be, V, As,

Se, Rb, Ag, Cd, Tl, Bi. Mass levels of Ca, Al and Zn in ambient $PM_{2.5}$ were higher than those in subway $PM_{2.5}$. Organic aerosols have been studied in depth in the subway system of Shanghai by Zhang et al. (2012). Mean levels of major aromatic and chlorinated hydrocarbons were higher indoors than outdoors, while BTEX (benzene, toluene, ethylbenzene, xylene) within the stations were predominantly transported from outdoor (vehicle-related emissions).

Subway system of Stockholm

Johansson and Johansson (2003) reported $PM_{2.5}$ and PM_{10} concentrations of 260 and 470 $\mu g\ m^{-3}$, respectively, during weekdays; these levels being a factor 5–10 higher than the corresponding values measured in one of the busiest streets in central Stockholm. The concentrations in the underground followed closely the train traffic intensity and a clear daily pattern. During weekends the levels decreased slightly due to less frequent train passages. Authors reported that the subway cleaning operations decreased the mass concentrations of PM in the subway system. According to Midander et al. (2012), mean $PM_{2.5}$ and PM_{10} levels in the subway system of the city centre were 60 and 160 $\mu g\ m^{-3}$, respectively, with particles predominantly consisting of iron, oxygen and carbon. Mean EC and OC concentrations of 10 and 28 $\mu g\ m^{-3}$, respectively, were reported for total PM. Mean Fe concentration was 4.4 $\mu g\ m^{-3}$ for total PM. On the other hand, mean particle number concentration on the platform of this station ($1.2x10^4$ # cm^{-3}) was 4 times lower than outdoor. A large number of volatile and semi-volatile organic compounds were identified in subway particle size fractions of $PM_{2.5}$ and PM_{10}. In extracts from the subway particles carcinogenic aromatic compounds such as antracene were identified.

Subway system of Taipei

Cheng et al. (2008) observed that PM levels within underground stations and outdoors in Taipei were positively correlated, indicating that PM levels in the subway system were influenced significantly by outdoor ambient PM levels. Mean $PM_{2.5}$ levels inside trains and on station platforms were 8–68 and 7–100 $\mu g\ m^{-3}$, respectively, and mean PM_{10} levels were 10–97 and 11–137 $\mu g\ m^{-3}$, respectively. PM_{10} and $PM_{2.5}$ levels in the subway stations were about 0.65–1.53 times and 0.89–1.75 times, respectively, those for urban ambient air. On the other hand, PN concentrations on the platforms resulted 0.3–

0.6 times lower than those in outdoor environments (Cheng and Yan, 2011). In this study, subway CO concentrations were measured, ranging between 0.30 and 0.48 ppm. Cheng and Lin (2010) also reported that PM levels at the concourse in the Taipei main underground station were significantly influenced by outdoor ambient PM levels. Cheng et al. (2012) demonstrated that $PM_{2.5}$, PM_{10} and CO_2 levels inside subway trains traveling in underground environments were approximately 20–50% higher than those in aboveground environments. However, PN levels inside trains traveling in underground environments were approximately 20% lower than those in aboveground ones. $PM_{2.5}$ inside the trains was transferred from the outside and significantly influenced by the surrounding conditions of the trains. Additionally, a high fraction of PM_{10} was observed inside the metro trains, possibly due to resuspension by the movement of commuters. The measurement results showed that, unlike PM, which is transferred from outside environments, CO_2 inside trains was elevated internally by exhalation from commuters. Clearly, CO_2 exhaled by commuters could accumulate inside metro trains and, compared to PM, is not as easily removed by the ventilation system when air circulation does not provide enough fresh air in the trains, particularly in trains traveling in underground environments.

Subway system of Tokyo

As in Barcelona (Querol et al., 2012) and Prague (Braniš, 2006), seasonal PM variations were obtained in the Tokyo subway stations (Furuya et al., 2001), with lower levels in summer (30–85 $\mu g\ m^{-3}$) than in winter (85–120 $\mu g\ m^{-3}$). PM mass concentration was also higher at the subway stations than in the aboveground throughout the seasons. The elements that were observed at high concentrations in the subway suspended PM were Fe, Ba, Cu, and Ca. Fe showed the highest concentrations, being 30–60 times higher than those aboveground. PAHs collected at the subway stations showed similar concentrations and characteristics to those observed in the outdoor urban atmosphere.