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Assessment of children's exposure to carbonaceous matter and to PM major and trace elements

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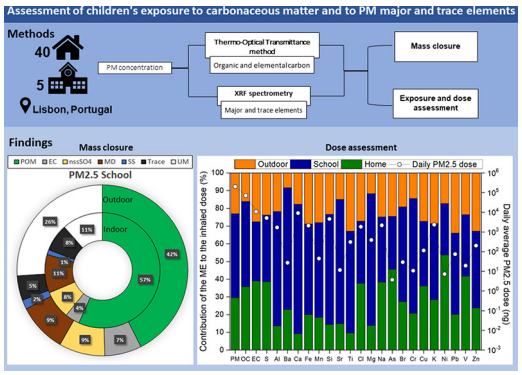
HIGHLIGHTS

- Schools displayed the highest concentrations of PM2.5 and PM10 chemical components.
- Indoor/outdoor ratios are higher in schools than in homes.
- Organic matter was the main contributor to the PM mass in all measurement locations.
- Indoor environments are the main contributors to the exposure and inhaled dose.

GRAPHICAL ABSTRACT



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ABSTRACT

Particulate matter (PM) pollution is one of the major environmental concerns due to its harmful effects on human health. As children are particularly vulnerable to particle exposure, this study integrates the concentration of PM chemical compounds measured in the micro-environments (MEs) where children spend most of their time to assess the daily exposure and inhaled dose. PM samples were analysed for organic and elemental carbon and for major and trace elements. Results showed that the MEs that contribute most to the children's daily exposure (80%) and inhaled dose (65%) were homes and schools. Results indicated that the high contribution of particulate organic matter (POM) indoors indicate high contributions of indoor sources to the organic fraction of the particles. The highest concentrations of PM chemical compounds and the highest Indoor/Outdoor ratios were measured in schools, where the contribution of mineral elements stands out due to the resuspension of dust caused by the students and to the chalk used in blackboards. The contribution of the outdoor particles to inhaled dose (24%) was higher than to the exposure (12%), due to the highest inhalation rates associated with the activities performed outdoor. This study indicates the importance of indoor air quality for the children's exposure and health.

1. Introduction

Particulate Matter (PM) is a complex mixture of small diameter particles whose components have different physical and chemical characteristics (Calvo et al., 2013; EPA, 2017; Seinfeld and Pandis, 2006). Several studies have shown that PM exposure is strongly linked to increased respiratory and heart disease (Brunekreef and Forsberg, 2005;

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Davidson et al., 2005; Hauck et al., 2004; Sandström et al., 2005) and the European Environment Agency (EEA) 2020 report "Air Quality in Europe" indicates that PM2.5 levels in 2018 were responsible for about 417,000 premature deaths in Europe (EEA, 2020).

The health effects depend on the place where the PM is deposited in the respiratory system. This deposition is influenced by PM physicochemical characteristics and subject's breathing parameters (Yeh et al., 1976). The coarse fraction of the particles is deposited in the upper airways (from the nasal or/and oral cavities to the larynx), while the fine fraction of the particles can be transported to the lower airways (lungs and alveolar region).

The chemical constituents of PM, including organic compounds, heavy metals, acids, among others, define the effect of PM on human health, as their toxicity varies significantly with composition. Previous studies have found links between the exposure to elements such as Zn, Al, Br, V, Si, As, Cr, and Ni (in PM2.5) and the increase of cardiovascular and respiratory hospital admissions (Bell et al., 2009; Zanobetti et al., 2009), the exposure to V, Fe, and Ni and systolic blood pressure (Jacobs et al., 2012), and the exposure to sulphate and respiratory illnesses (Lippmann and Thurston, 1996; Pope et al., 1995).

Therefore, the chemical characterization of PM is crucial for identifying sources and determining health effects (Hama et al., 2018; Lighty et al., 2000). However, little is known about the chemical composition of the PM from the micro-environments (MEs) that mostly affect children's daily exposure.

Children belong to a population group with greater sensitivity to particle exposure. This sensitivity to pollutants is due to the fact that their immune and respiratory systems are still developing and also because they breathe greater volumes of air in relation to their body weight (Burtscher and Schüepp, 2012). On average, a child in the city of Lisbon spends more than 85% of their time in indoor environments, whether at home, school, transportation, or in physical activities (Faria et al., 2020). Therefore, high concentrations of pollutants in these MEs can negatively affect the health, brain development, and learning performance of children (Brumberg and Karr, 2021; Mohai et al., 2011; Sunyer et al., 2015).

To assess children's exposure to the different PM chemical compounds and the respective inhaled dose, it is necessary to consider the time they spent in each ME and outdoors, the concentrations of the pollutants in each ME, and the activity performed by the children.

This study focuses on the assessment of children's exposure to carbonaceous matter and to PM major and trace elements. The carbonaceous matter in particles is assessed in terms of Organic Carbon (OC) and Elemental Carbon (EC). OC refers to the carbon found in the form of organic compounds, which constitute a significant part of atmospheric aerosol, and comprises a complex mixture of different classes of organic compounds. OC can be considered primary if emitted directly into the atmosphere, through fireplaces, dust from paved roads, forest fires, industry, fossil fuels, biogenic material, cooking, among others (Alves et al., 2014; Amato et al., 2014; Medeiros et al., 2006). The secondary OC is formed by the fast condensation of gases after their emission and by photochemical reactions in the atmosphere from gaseous precursors (Gelencsér et al., 2007; Seinfeld and Pandis, 2006). Bertrand et al. (1987), Slezakova et al. (2007) and Lewtas (2007) showed that OC can cause carcinogenic effects on the population's health, due to some organic compounds with toxic capacities such as polycyclic aromatic hydrocarbons (PAH) and organic halogenated compounds like dioxins and furans. EC has a chemical structure similar to impure graphite and is produced mainly by combustion processes. It is efficient at absorbing light in the atmosphere and turns that energy into heat, having a significant impact on climate change, affecting global warming of Earth (Bahadur et al., 2012; Evangeliou et al., 2018; Kuzu et al., 2020). The main sources of EC are the combustion of biomass for heating, the production of energy, the incomplete combustion coming from transports and industrial processes (Jaeckels et al., 2007), and cooking (Cunha-Lopes et al., 2019). Newman et al. (2013) found an association between EC from traffic and higher hyperactivity scores in children. Grahame and Schlesinger (2010) present a summary of different studies that associate EC emitted from diesel engines and other vehicles with mortality from cardiopulmonary and cardiovascular disease.

There is a wide variety of major and trace elements identified in atmospheric aerosol particles. Elements in PM can be of primary origin, related either to anthropogenic or natural sources (such as marine aerosol and mineral components) or they may be of secondary origin, resulting from photochemical reactions (Seinfeld and Pandis, 2006). Toxicological and epidemiological studies established a relationship between chemical components and the toxicity of the particles, referring the metal content as a possible harmful component of PM (Zanobetti et al., 2009). Some metallic trace elements of PM, such as As, Cd, Cr, Pb, and Hg, were associated with carcinogenic effects (Tchounwou et al., 2012).

This work was developed in the framework of the LIFE Index-Air project (www.lifeindexair.net) and aims to estimate the integrated children exposure to PM chemical components; it should be noted that the number of studies on the exposure of children to specific PM components is scarce, while this knowledge is critical for the determination of the daily inhaled dose and for the assessment of the health effects of PM on this sensitive population subgroup.

2. Methodology

2.1. Particulate matter sampling

PM was sampled in 5 primary schools (classrooms), 40 homes (living-rooms), and respective outdoors in the city of Lisbon, Portugal, from September 2017 to October 2018. Lisbon has a Mediterranean climate and is surrounded by the Tagus River (south and east), the forest park of Monsanto (west), and neighbouring municipalities (north and northwest). Lisbon has 24 parishes, and the centre is set on seven hills with the predominance of narrow streets. Due to its geographic position and the fact that it is the highest populated city in Portugal (508,368 inhabitants, with a population density of 5081 people per km^2) (FFMS, 2019), Lisbon is affected by marine aerosol (Almeida et al., 2013), mineral dust from North Africa (Almeida et al., 2008), and road traffic (Almeida et al., 2009).

The sampling at each home and school lasted for 5 days, during the occupancy hours (schools: 9 am–6 pm only during weekdays; homes: 6 pm–9 am, during weekdays, and 24 h during weekends). In each location, four medium volume samplers (MVS6, Leckel, Sven Leckel, Germany) were used to collect PM in parallel, at a flow rate of 2.3 m^3/h. PM2.5–10 and PM2.5 were collected by the same sampler, though a specially designed impactor (Faria et al., 2020). Two samplers were installed indoors and the other two outdoors, in order to simultaneously collect PM at two different filter substrates. Specifically, at each location, one sampler sampled on 25 mm and 47 mm Quartz fibre filters (Pall), for PM2.5–10 and PM2.5, respectively. The other sampler sampled on Nuclepore and polytetrafluoroethylene filters (PTFE). PM2.5–10 were sampled in 25 mm Nuclepore filters (Whatman) with 0.4 μm pore size, and PM2.5 were sampled in PTFE 47 mm filters (Whatman) with 2 μm pore size. PM mass concentrations were determined gravimetrically. More details about sampling and quality assurance and control are described in Faria et al. (2020).

2.2. Chemical characterization

PM2.5–10 and PM2.5 samples collected on Nuclepore and PTFE filters, respectively, were analysed by X-Ray Fluorescence (XRF) to determine the following major and trace elements: Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, and Pb. The analysis was performed using an Energy Dispersive X-ray Spectrometer (ED-XRF) Laboratory Instrument (Epsilon 5, PANalytical, the Netherlands). The instrument was calibrated for aerosol filters by utilizing the NIST 2783

and CRMs 2584 and 2583 standards dispersed on filter media. Analytical uncertainty ranged from 0.3 to 10%. The detection limits for the measured elements are provided in Table S1, in the supplementary material.

PM2.5–10 and PM2.5 samples collected on quartz filters were analysed by the Thermo-Optical Transmittance method (TOT) for the determination of the OC and EC. A punch of 1 × 1.5 cm was cut from all quartz filters for the analysis. The TOT analysis was performed using the Lab OC-EC Aerosol Analyser (Sunset Laboratory Inc., USA) and the EUSAAR2 protocol, following the QA/QC procedures described in EN 16909: 2017. The limit of detection was 0.02 μg/m^3. The analytical uncertainty was in the range of 5–9% for OC and 6–54% for EC. The high uncertainties (above 20%) were related to very low EC concentrations, mostly measured in PM2.5–10 samples. The chemical characterization methodology is detailed in Manousakas et al. (2018) and Popovicheva et al. (2019).

2.3. Mass closure

Chemical mass closure was calculated including the assessment of the contribution of particle organic matter (POM), EC, non-sea salt sulphate (nssSO_4^{2-}), mineral dust (MD), sea salt (SS), and trace elements (Trace) to the total mass, in order to better understand the chemical composition and aerosol type sampled in the different MEs. The sum of the chemical species in the aerosol with values lower than the total mass concentration indicates the existence of unidentified mass (UM).

POM was calculated by multiplying OC by a factor of 1.6. This factor is consensual for outdoor urban background locations (Turpin and Lim, 2001; Viidanoja et al., 2002; Wu et al., 2017; Xing et al., 2013; Zheng et al., 2019). For the indoor the same factor was used because all the spaces are naturally ventilated and are highly influenced by the urban outdoor air. However, in homes and schools, fresh OC is expected due to the emissions from indoor sources, which cause different oxidation states. For this reason, this factor could be less accurate for indoor environments. The contribution of each aerosol type was calculated according the equations presented in Table 1. The mineral dust was determined considering the oxides of Al, Si, Ca, K, Fe, Ti, Mn, Sr, and Ba (Calvo et al., 2013; Kong et al., 2015; Zhang et al., 2013) and the soil fractions of Ca, K and Fe were calculated using their typical crustal ratios (Mason, 1966). Sea salt was calculated through the sum of Na, Mg, Cl, ssK, ssCa, and ssSO_4^{2-} (Calvo et al., 2013; Diapouli et al., 2017). The elements V, Cr, Ni, Cu, Zn, As, Br, and Pb and the anthropogenic fractions of K, Ca, and Fe were associated to the trace elements group (Calvo et al., 2013) (Table 1). EC and nssSO_4^{2-} were considered separately from any group.

2.4. Children's daily exposure and dose assessment

A self-report questionnaire on time-activity patterns was applied in 26 schools and obtained 1189 completed responses, allowing to identify the different MEs frequented by the children and the time spent in each one of them. The microenvironments considered in the calculation of exposure and dose were the home, school, and outdoor. These are the 3 MEs where children spend most of their day, with time spent of 56%, 27%, and 10%, respectively, as described in Faria et al. (2020). The children's daily exposure was estimated by integrating the temporal activity data of each child that answered the questionnaire with the average concentrations of the chemical constituents measured in each MEs, and afterwards by averaging all the individual exposure values.

The potential inhaled dose for each child was estimated by multiplying the exposure in each ME by the inhalation rate (IR, m^3/h), which was defined based on the activities performed by the children (5–10 years old) in that ME. Afterwards, the average of all individual doses was calculated. The different IR used in this work (0.31, 0.42, and 0.91 m^3/h for the activities performed in homes, schools, and outdoor, respectively) were based on the study developed by Buonanno et al. (2011).

Table 2 summarizes the equations used for the calculation of the different parameters.

The outdoor concentrations used in the calculation of exposure and dose were measured outside the schools, to better represent the daytime period.

Table 2
Equations used to calculate the average daily exposure, potentially inhaled dose, and contribution of the different MEs for the daily exposure and dose.

Equations		
Average daily exposure (ng/m^3)	$\frac{\sum_{j=1}^{m} C_j \cdot t_j}{\sum_{j=1}^{m} t_j}$	C_j: concentration measured in the ME (j) t_j: time spent in the ME (j) IR_j: inhalation rate in the ME (j)
Potential inhaled dose (ng)	$\sum_{j=1}^{m} (C_j \cdot t_j \cdot IR_j)$	
Contribution of the ME (a) to the daily exposure (%)	$\frac{C_a \times t_a}{\sum_{j=1}^{m} C_j \times t_j} \times 100$	
Contribution of the ME (a) to the daily inhaled dose (%)	$\frac{C_a \times t_a \times IR_a}{\sum_{j=1}^{m} C_j \times t_j \times IR_j} \times 100$	

2.5. Statistical analysis

Statistical calculations using STATISTICA software were performed. Non-parametric tests were used to compare different populations hence they do not consider any assumptions related to the distribution. The Wilcoxon Matched pairs test was applied when both populations were dependent of each other (differences between pairs of indoor and outdoor levels) and the Mann–Whitney U test was selected when the populations were independent (differences between schools and homes). Statistical significance refers to $p < 0.05$.

Table 1
Equations used in the mass closure assessment.

	Equations	Where
POM	1.6 × [OC]	
Sea salt	[Na] + [Cl] + [Mg] + [ssK] + [ssCa] + [ssSO_4^{2-}]	[ssK] = 0.037 × [ssNa] [ssCa] = 0.038 × [ssNa] [ssSO_4^{2-}] = 0.253 × [ssNa]
Mineral dust	1.89 × [Al] + 2.14 × [Si] + 1.67 × [Ti] + 1.4 × [soilCa] + 1.2 × [soilK] + 1.4 × [soilFe] + 1.58 × Mn + 1.12 × Ba + 1.18 × Sr	[soilCa] = 0.45 × [Al] [soilK] = 0.32 × [Al] [soilFe] = 0.62 × [Al]
Trace elements	[anthropoK] + [anthropoCa] + [anthropoFe] + [V] + [Cr] + [Ni] + [Cu] + [Zn] + [As] + [Br] + [Pb]	[anthropoK] = K - soilK – ssK [anthropoCa] = Ca - soilCa – ssCa [anthropoFe] = Fe - soilFe
nssSO_4^{2-}	SO_4^{2-} − ss$SO4^{2-}$	

3. Results

3.1. Particulate matter mass concentration

Summary statistics of the concentrations of PM and associated chemical components measured at homes, schools, and outdoor are provided in Table S2, in the supplementary material.

The PM2.5 and PM10 average concentrations in the living rooms were 15 and 18 μg/m^3, respectively, and the mean PM2.5 and PM10 indoor/outdoor (I/O) ratio was 1.4 and 0.90, respectively. On average, the PM2.5/PM10 ratios were higher indoors (0.78) than outdoors (0.59), evidencing the important contribution of the indoor sources for the fine fraction and higher penetration rates for outdoor-generated fine particles than for the coarse fraction (Chen and Zhao, 2011; Diapouli et al., 2011; Nadali et al., 2020).

These results were similar to the levels found in homes from Porto (PM2.5: 12 μg/m^3) (Madureira et al., 2016), Athens (PM2.5: 13 μg/m^3; PM10: 21 μg/m^3) (Stamatelopoulou et al., 2019), Antwerp (PM2.5: 15 μg/m^3) (Stranger et al., 2007), and Boston (PM10: 20 μg/m^3) (Abt et al., 2000).

In classrooms, the PM2.5 and PM10 average concentrations were 35 and 65 μg/m^3, respectively, and the mean PM2.5 and PM10 I/O ratio was 2.4 and 2.3, respectively. On average, the PM2.5/PM10 ratio indoor (0.57) was lower than outdoor (0.65). The results were similar to the ones measured in Milan of 33 μg/m^3 (Rovelli et al., 2014) and Barcelona of 37 μg/m^3 (Rivas et al., 2014) for PM2.5 and the ones measured in Munich of 72 μg/m^3 (Fromme et al., 2007) for PM10.

The low PM2.5/PM10 ratios found inside schools indicate an increased contribution from the coarse fraction, due to resuspension of dust and generation of particles (coarse principally), related to the movement and different activities performed by the children (Diapouli et al., 2008). The PM levels measured in this study are discussed in more detail in Faria et al. (2020).

3.2. Mass closure

Mass closure reconstructed the PM mass concentrations by achieving closure between gravimetric PM mass and the sum of the PM chemical compounds, in order to determine the contribution of the different aerosol types in each ME and quantify the percentage of non-identified

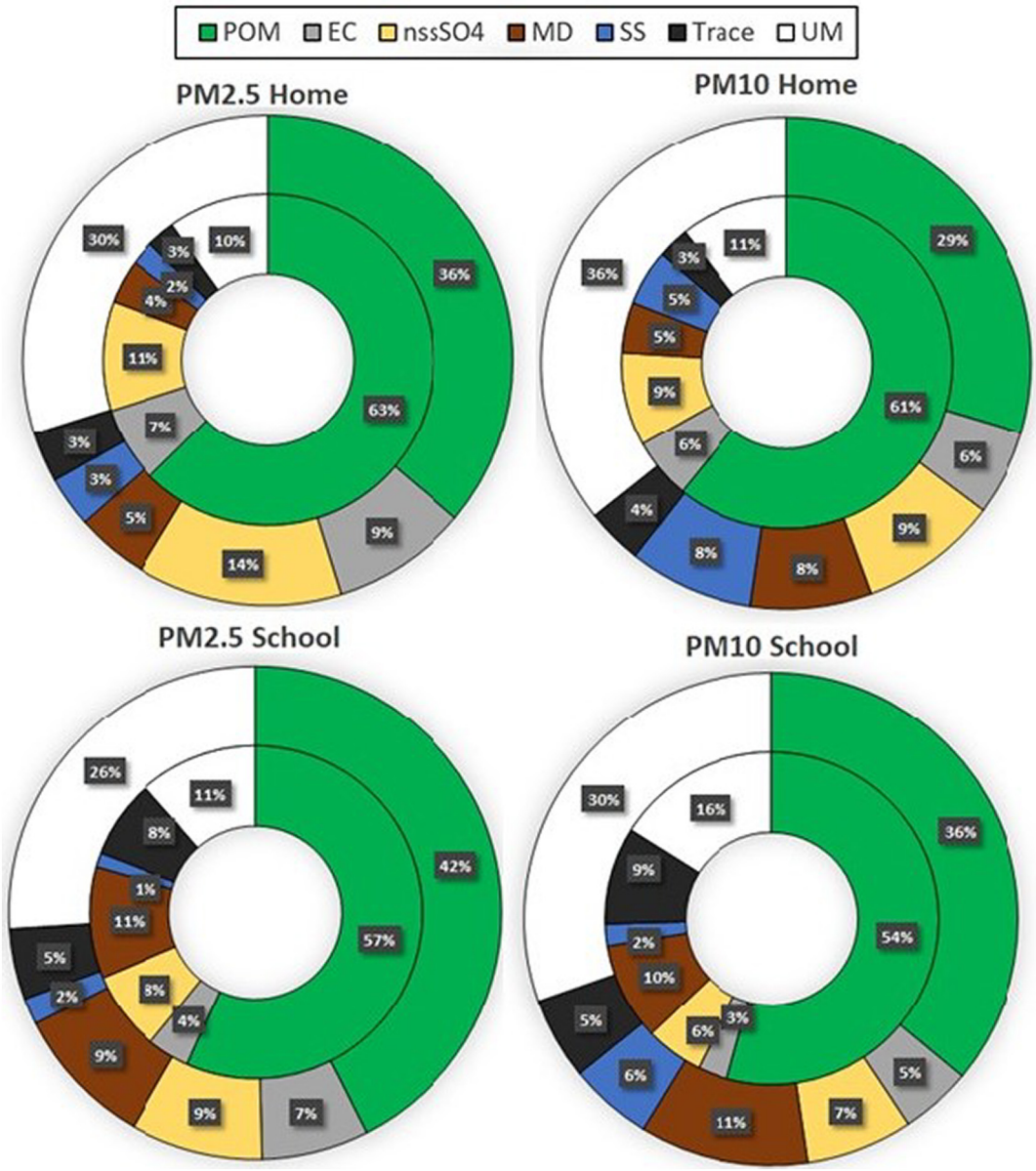

Fig. 1. Average indoor (inner circle) and outdoor (outer circle) PM2.5 and PM10 chemical composition in homes and schools.

compounds in the analysis. Fig. 1 presents the contribution of each chemical compound/aerosol type to the PM mass indoor and outdoor of the homes and schools.

On average, the analysed chemical compounds accounted for 80% of the total PM mass measured in all ME. The remaining fraction can be attributed to nitrates and ammonium, which were not measured in this study besides their importance for the share of the PM mass. Indoors, the contribution of the undefined mass (UM) to the gravimetric mass varied between 10% and 16%. Outdoors the contribution was higher (26% to 36%), which can be attributed to the fact that the contribution of some species like nitrate is higher outdoors than indoors. Sarnat et al. (2006) showed that indoor NH_4NO_3 levels are significantly lower than outdoors since nitrate tends to volatilize at warmer indoor temperatures.

POM was the dominant contributor to the total mass of PM principally inside of homes (63% for PM2.5 and 61% for PM10) and schools (57% for PM2.5 and 54% for PM10). The mineral dust was the second main contributor in schools, accounting for 11% of PM2.5 mass and 10% of PM10 mass followed by trace elements with a contribution of 8–9% and by $nssSO_4^{2-}$ with a contribution of 6–8%. In homes, the sum of $nssSO_4^{2-}$ and the mineral dust accounted for 15% of the PM2.5 and PM10.

3.2.1. Carbonaceous species

The concentration of OC is expressed, in mass balance, as POM with the intention of adding the heteroatoms of the organic matter (H, N, O), also present in organic compounds (Rivas et al., 2014). POM is the dominant contributor in all measured locations. In both fractions, the concentrations of OC inside the homes (PM2.5: 6.2 μg/m^3; PM10: 7.5 μg/m^3) were significantly higher ($p < 0.05$) than the outdoor levels (PM2.5: 3.0 μg/m^3; PM10: 3.8 μg/m^3), with an I/O ratio of 3.2–2.7, respectively. This high contribution of the POM indoors can be related to the infiltration of outdoor particles and the contribution of indoor sources, such as cleaning and hygiene products, cooking, skin debris, sub micrometric fragments of paper, and clothing fibres (Alves et al., 2014).

The highest indoor OC concentrations were registered in a home where two of the residents smoke indoors (OC Range: in PM2.5–26-54 μg/m^3; in PM10: 36–56 μg/m^3). The very high I/O ratios (23 for PM2.5 and 18 for PM10) point towards the importance of cigarette smoke as a primary source of OC (Rogge et al., 1996; Subramanian et al., 2007). Custódio et al. (2014) in residences of Aveiro and São João da Madeira, in Portugal, also measured the highest OC concentrations in smokers' homes (27 ± 18 μg/m^3).

On average, our results were lower than those obtained in other studies conducted in homes, with OC values in PM2.5 of 13 μg/m^3 (Perrino et al., 2016), 15 μg/m^3 (Na and Cocker, 2005), and 17 μg/m^3 (Ho et al., 2004). In all the mentioned studies, the I/O ratio for OC was higher than 1.0.

Regarding schools, the concentrations of OC were higher in the classroom than outdoors for PM2.5 (I/O ratio: 2.7) and PM10 (I/O ratio: 3.4). The OC concentrations in the classrooms (PM2.5: 13 μg/m^3 and PM10: 21 μg/m^3) were significantly higher than in the homes (PM2.5: 6.2 μg/m^3 and PM10: 7.5 μg/m^3) ($p < 0.05$). Levels found in the literature for schools, varied between 10 and 14 μg/m^3 for OC in PM2.5 (Pegas et al., 2012; Rivas et al., 2014; Viana et al., 2014). For OC in coarse particles, Viana et al. (2014) measured values of 22 μg/m^3. These results are within the range of the ones reported in the present study. Pegas et al. (2012) obtained for schools in the centre of Aveiro, Portugal, I/O ratios for OC in PM10 of 3.4 ± 1.4, which were also similar to those found in this study. The high OC I/O ratios suggest that indoor activities/occupancy lead to OC generation. The condensation of semi-volatile organic compounds during the ambient air infiltration indoors and the formation of secondary organic aerosol (SOA) indoors may also contribute to these I/O ratios above 1.0 (Amato et al., 2016; Waring et al., 2011). The study of the Polidori et al. (2006) estimated that 40–75% of the measured organic aerosol is generated indoors and speculated that SOA is an important contributor. The SOA forms due to products of oxidative reactions with reactive organic compounds indoors (Waring, 2014). The higher I/O ratios of OC in PM10 measured in schools, besides a significant contribution from resuspension indoors, due to the presence and movement of a high number of children, could be partly related to the emission of carbonate carbon (CC) indoors, due to the use of chalkboards in some of the schools. On average, the I/O ratio for OC in PM10 in schools that have chalkboards was 3.0, while in schools without chalkboards the I/O ratio was 1.3. The presence of significant amounts of CC in PM samples causes interference with the TOT analysis, leading to overestimation of the OC concentrations mainly (Karanasiou et al., 2011) This is supported by the lower PM2.5/PM10 ratios observed in schools (0.59) compared to homes (0.79) (Figs. 2 and 3).

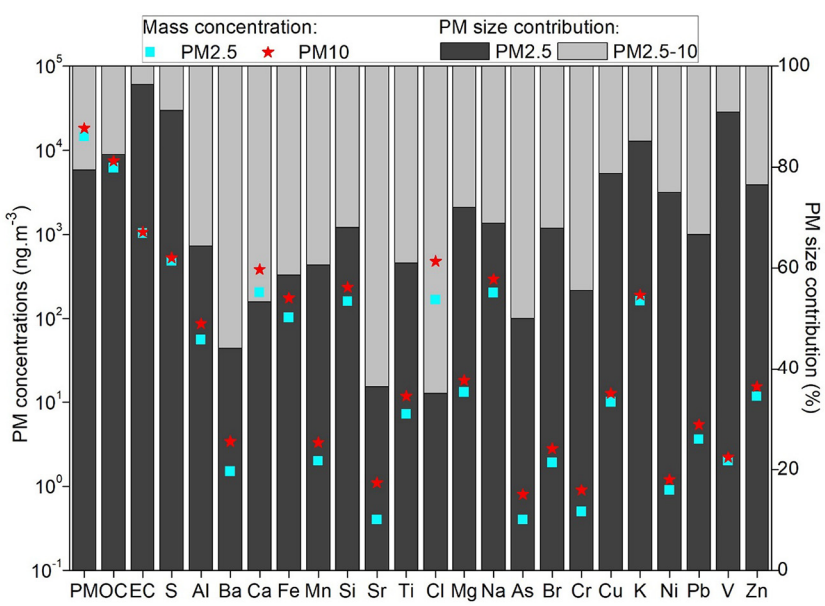

Fig. 2. Mass concentrations in PM2.5 and PM10 measured in homes (values in ng/m^3). Contribution of PM2.5 and PM2.5–10 to PM10 (values in percentage).

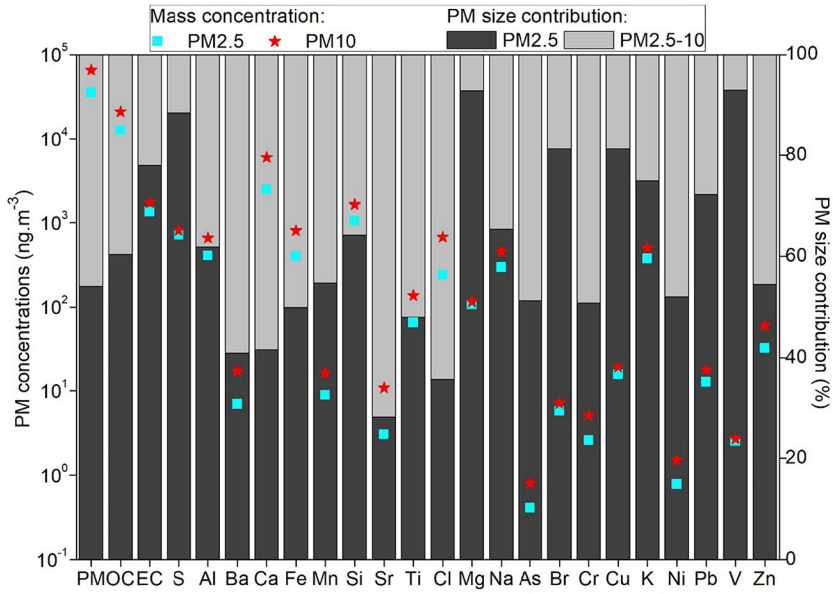

Fig. 3. Mass concentrations in PM2.5 and PM10 measured in schools (values in ng/m^3). Contribution of PM2.5 and PM2.5–10 to PM10 (values in percentage).

For EC, the concentrations were lower in living rooms (PM2.5: 1.0 μg/m^3; PM10: 1.1 μg/m^3) than in the respective outdoor (PM2.5: 1.2 μg/m^3; PM10: 1.3 μg/m^3), representing an I/O ratio of 0.9 and 1.0, respectively, probably due to the fact that the traffic is the main source of EC. These EC concentrations were lower than those obtained in similar studies (Perrino et al., 2016; Na and Cocker, 2005; Ho et al., 2004).

The EC concentrations obtained in schools (PM2.5: 1.3 μg/m^3 and PM10: 1.7 μg/m^3) were similar to the home's levels (PM2.5: 1.0 μg/m^3 and PM10: 1.1 μg/m^3) with an I/O ratio of 1.0 in PM2.5 and of 1.3 in PM10. These results indicate that EC indoors is mainly of ambient origin (Assimakopoulos et al., 2018; Diapouli et al., 2010). Similar concentrations in schools have been found in the literature, with reported values of 1.3 μg/m^3 for EC in PM2.5 (Rivas et al., 2014) and 1.1 μg/m^3 for EC in PM10 (Pegas et al., 2012).

The indoor and outdoor OC and EC concentrations were significantly higher at the school sites because measurements occurred during the occupied periods of the MEs. In schools, the sampling was performed during the period with higher traffic intensity (between 9 am and 6 pm) while in homes occurred mainly during the night-time (from 6 pm to 9 am). The mean ambient OC and EC concentrations were similar to those found in the literature. Other studies measured daily averages between 2.5 and 13 μg/m^3 for ambient OC and between 0.50 and 6.4 μg/m^3 for EC in PM2.5 (Ho et al., 2004; Landis et al., 2001; Na and Cocker, 2005; Olson et al., 2008; Perrino et al., 2016; Viana et al., 2007). Amato et al. (2016) also reported similar OC and EC levels for urban background sites in Southern European cities.

The PM2.5/PM10 ratio has been usually used as an indication in the identification of sources of pollution since different sizes of PM are associated to different sources. Figs. 2 and 3 shows the PM2.5/PM10 ratio for each PM chemical compound and the respective concentrations. The PM2.5/PM10 ratios in the homes (OC: 0.79 and EC: 0.97) were higher than those observed in classroom, pointing towards a significant contribution from coarse particles in schools. In accordance with Martins et al. (2020), OC and EC can adhere to the surface of coarser particles deposited on the surfaces and subsequently resuspended with people's movement. Thus, in the classrooms, the elevated contribution of OC and EC in PM2.5–10 can be related to the higher occupancy and consequent elevated children's activity.

The OC/EC ratio is used to study the differences in the characteristics of carbonaceous aerosol and its sources (Kumar et al., 2016; Pio et al., 2011; Zhao et al., 2019). OC/EC ratios are influenced by emission sources, removal rates by deposition, and SOA formation (Cao et al., 2005). This ratio can vary widely as can be seen in the available literature. In the studies developed by Hueglin et al. (2005); Pio et al. (2011) and Puxbaum et al. (2004) the OC/EC ratio ranged between 1.2 and 3.1, showing an association with vehicle exhaust emissions and fuel burning (Kumar et al., 2016; Zhao et al., 2019). In the studies developed by Long et al. (2000); Na and Cocker (2005); Olson et al. (2008) and Viana et al. (2007) the ratio varied between 4.4 and 9.1 indicating an association with the combustion of coal, burning of biomass (Almeida-Silva et al., 2015; Zhao et al., 2019), formation of SOA or internal sources such as cleaning products, sub-micrometre fragments of paper, and waxes (Almeida-Silva et al., 2015; Alves et al., 2014; Cao et al., 2005). Even though the ratio vary a lot depending on the dominant sources of EC and OC in each region, it has been found that it is rather constant in certain environments, as for example in urban background atmospheres, and it has been used in the past as an effective tool to derive the ratio of OC and EC from fossil fuel combustion and consequently to differentiate OC from primary and secondary sources (Pio et al., 2011).

In this study, the OC/EC ratio was 9.3 and 11 for the living rooms and 3.3 and 4.1 for the respective outdoors in the fraction of PM2.5 and PM10, respectively. In the classrooms, the OC/EC ratio was 12 and 15 for PM2.5 and PM10 and outdoors, the values were 4.9 and 6.1, respectively. These outdoor values of the ratio are typical of urban environments (Lonati et al., 2007).

3.2.2. Sulphate

SO_4^{2-} is a secondary aerosol formed in the atmosphere from precursor gases such as sulphur dioxide (SO_2) (Stockwell et al., 2003), with different sources such as industrial processes, energy production and road traffic (Amato et al., 2014; Calvo et al., 2013). The contribution of SO_4^{2-} to the total mass was higher outdoors (Fig. 1). The I/O ratio was 0.90 in homes and 1.2 in schools for PM2.5 and 0.80 in homes and 1.2 in schools for PM10. The PM2.5/PM10 ratio was 0.90 in homes, 0.82 in schools and 0.79 outdoor, demonstrating that the SO_4^{2-} is principally found in the fine fraction.

3.2.3. Mineral dust

Mineral dust contributed 11% and 10% to the total mass of PM2.5 and PM10, respectively in schools and 4% for PM2.5 and 5% for PM10 in living rooms. Outdoors, the mineral dust contribution varied between 9%

in PM2.5 and 11% in PM10. Mineral dust is generated by the action of wind on the Earth's surface and the main sources are deserts or semi-arid surfaces (Calvo et al., 2013). The dust released into the air depends on several factors intrinsic to the soil and weather conditions (Washington and Todd, 2005). The chemical composition of the dust related particles is dependent on the soil and location where they originate from. Portugal is located in the Iberian Peninsula with semi-arid zones (Artíñano et al., 2001), and frequently affected by Sahara dust events (Almeida et al., 2008). In cities, the road/sidewalk resuspension, construction, and demolition activities and the green spaces can be also sources of mineral dust. Contrary to what happens in homes, in the schools, the I/O ratio for the mineral dust was higher than 1.0. In schools, some elements, such as Si and Ti presented I/O ratios above 2.0, which can be attributed to the transfer of dust from the soil (playground) caused by the students entering in school buildings, and the respective resuspension of dust due to the intense movement of the children.

The PM2.5/PM10 of these mineral elements (such as Al and Si) was slightly higher indoor than in outdoor environments. This result is in accordance with Martins et al. (2020) study, which showed that the mineral elements outdoors are mainly present in the coarse fraction (PM2.5–10), while indoors the fine fraction is more relevant due to the most efficient infiltration rates observed for the fine PM (Nadali et al., 2020).

3.2.4. Sea salt

The contribution of sea salt to the total mass of PM was more evident outdoors than indoors. The Na, Cl, Mg, K and $SO4^{2-}$ are the main elements contributing for the sea salt source (Calvo et al., 2013; Diapouli et al., 2017). In Lisbon city, the main source of sea salt is the ocean (Putaud et al., 2004), due to its geographical position and the dominant regime of western winds, influenced by the presence of semi-permanent air masses over the North Atlantic Ocean (i.e. Azores anticyclone and Icelandic cyclone).

Inside the homes and schools, the PM2.5/PM10 ratio was 0.49 and outside it was 0.24, probably due to the influence of marine air masses that are essentially composed of coarse particles and to higher infiltration rates attributed to the fine particles. The same conclusion is found in the literature (Almeida et al., 2006; Alves et al., 2007).

3.2.5. Trace elements

The trace elements contributed 3% for the total mass of PM2.5 and PM10 in homes. The sum of these elements were significantly higher in the classroom (PM2.5: 2700 ng/m^3; PM10: 6300 ng/m^3) than in living-rooms (PM2.5: 400 ng/m^3; PM10: 620 ng/m^3) and significantly higher indoor than outdoor of schools (PM2.5 and PM10 in playground: 1100 ng/m^3 and 1900 ng/m^3). These results can be explained by the high levels of anthropogenic calcium measured in schools. The average anthropogenic Ca concentrations in schools were 2300 ng/m^3 for PM2.5 and 5600 ng/m^3 for PM10, while in homes, the respective levels were 170 and 490 ng/m^3. These high concentrations of Ca in schools are caused by the use of chalk on blackboards as also observed by Almeida et al. (2011) and Viana et al. (2014). The Ca concentration was from 1.6 to 5.4 times higher in the schools that use chalk than in the ones that use a whiteboard marker.

Outdoors, the concentrations of elements related to the road dust and mechanical abrasion of tyres and brakes, such as Ca, Ti, Si, Al, Ba, Zn, Cu, and Pb (Calvo et al., 2013), were higher in school locations compared to homes, which may indicate a greater contribution from road traffic. According to the time-activity study performed by Faria et al. (2020), the majority of children in Lisbon go to school by private car, which favours traffic congestion on the roads around the school. Moreover, as the sampling was conducted during the normal occupied period, the home samples mostly covered the night-hours. The PM2.5/PM10 ratio shows higher levels of these elements in the fine fraction in homes (0.70) and outdoor (0.60) and the opposite in schools (0.44).

3.3. Exposure and inhaled dose assessment

Figs. 4 and 5 present the contributions of the different MEs to the daily PM2.5 and PM10 exposure. The results show that home and school together have a contribution higher than 80% to the daily exposure of the children to all PM chemical compounds.

Although children spend most of their day at home, the schools displayed the highest contribution for the exposure to the mineral elements. Al, Si, Sr, and Ti concentrations were significantly higher in schools, compensating for the effect of time in calculating the exposure. The contribution of the school ME in the daily exposure to Ca was 78% for PM2.5 and 81% for PM10. The children's exposure to Ca in school was 38,000 ng/m^3·h for PM10, while in the home was 5100 ng/m^3·h (Table S3, in supplementary material). As explained in the previous chapter, this exposure to Ca is related to the use of chalk in the classrooms.

For EC, S, Cl, Na, As, Cu, Ni and V, homes represented the main contributor for the daily exposure of the children, not because their

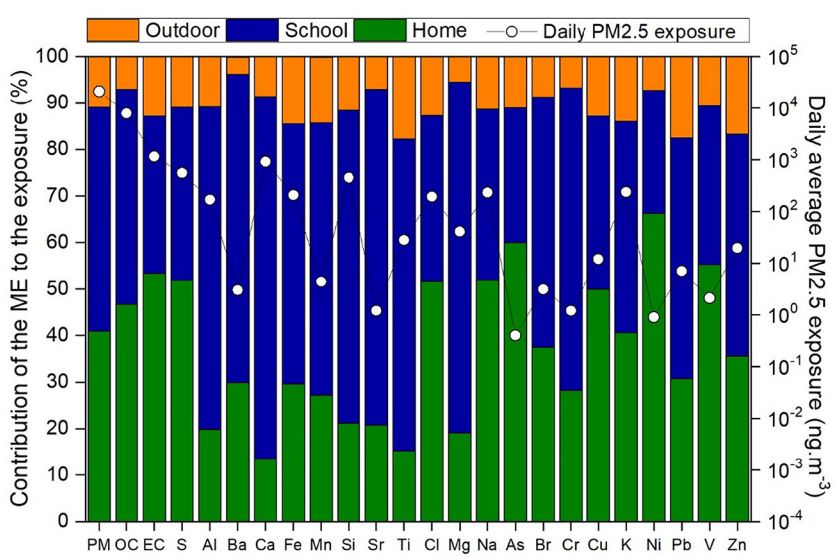

Fig. 4. Contribution of each ME to the daily PM2.5 exposure.

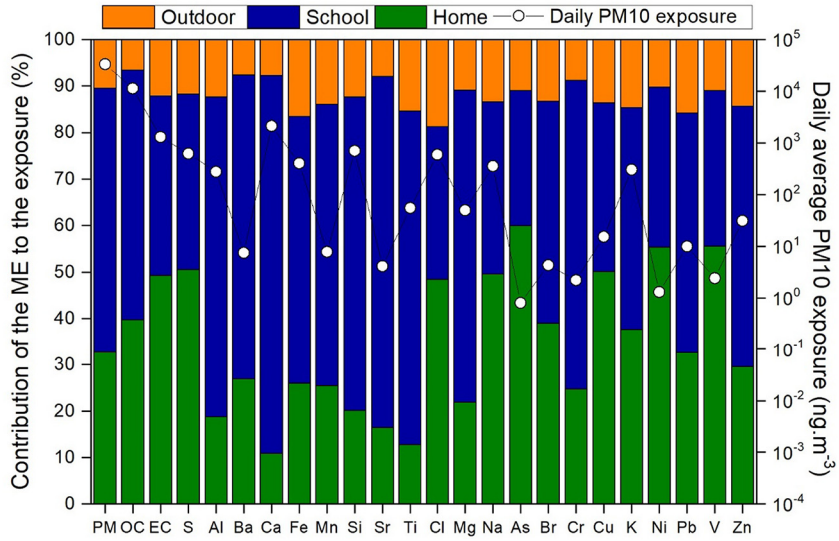

Fig. 5. Contribution of each ME to the daily PM10 exposure.

concentrations were higher in the homes, but because time compensated the effect of the concentration in the calculation of the exposure.

These results agree with other studies about the importance of the assessment and improvement of the air quality indoors. In a study carried out in Denmark, 90% of people's daily exposure to ultrafine particles took place indoors (Bekö et al., 2015). Wu et al. (2005a, 2005b) concluded that indoor locations in Southern California were the most significant MEs for the exposure to the pollutants CO, NO_2, PM10, PM2.5, and EC. In the study performed by Chau et al. (2002), residential homes in Hong Kong were the major contributors for NO_2, PM10, and CO exposures for young, adults, and elderly. Wu et al. (2005a, 2005b) studied the exposure of asthmatic children to PM2.5 and concluded that exposures in MEs with high concentrations of PM, even if occupied for a short period, can still have significant contributions to total exposure. In their study, 45% of the exposure to PM2.5 occurred at home, where they spent more than 60% of their time, and 29% in the school, where they spent only 16% of the time.

Figs. 6 and 7 show that the contribution of each ME to the daily inhaled dose follows the same pattern as the daily exposure, with the home and school together contributing to more than 65%. The main difference is that there is an increase in the contribution of the outdoor atmosphere to the inhaled dose (24%) compared to the contribution to the exposure (12%), due to the higher inhalation rate associated with more intense physical activity during the time spent outdoors by children (outdoor inhalation rate: 0.91). A ventilation rate between 2.2 and 2.9 times higher than when sleeping/resting and studying, respectively. These data reinforce the idea already defended in other studies (Carlisle and Sharp, 2001; Giles and Koehle, 2014; Qin et al., 2019; Ramos et al., 2017, 2016), that physical activity should be carried out away from highly polluted areas, because higher rates of inhalation, potentiates higher inhaled dose of pollutants with effects on health.

4. Conclusions

This work aimed to integrate the concentrations of PM components measured in the MEs where children spend most of their time to assess their exposure, since this is a key determinant of the received dose and thus directly influences the impacts on their health.

The main findings from this work may be summarised as follows:

- Schools displayed the highest concentrations of PM2.5 and PM10 chemical components, which can be attributed to the transfer of

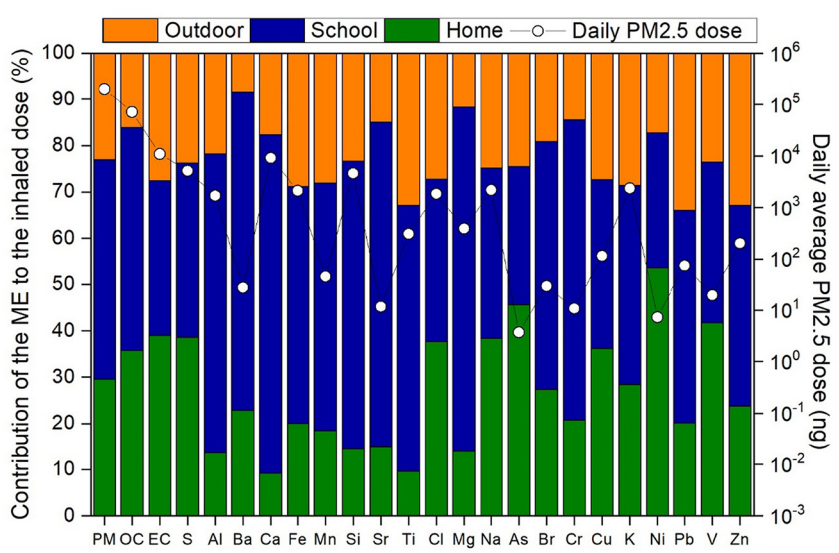

Fig. 6. Contribution of each ME to the PM2.5 inhaled daily dose.

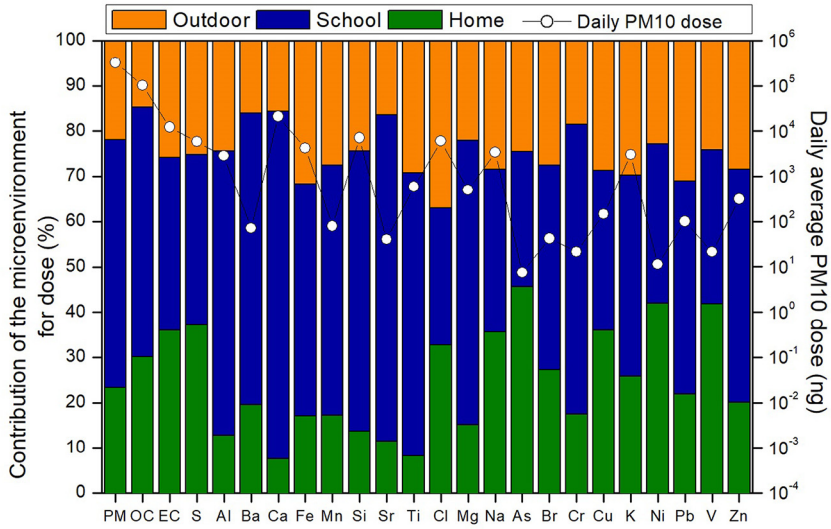

Fig. 7. Contribution of each ME to the PM10 inhaled daily dose.

dust from the soil (playground) to the school buildings and its resuspension due to the intense movement of the children.

- POM was the main contributor to the PM mass in all locations, especially in homes. The mineral dust was the second main contributor in schools and summed with $nssSO_4^{2-}$ accounted for 15% of the PM2.5 and PM10 in homes
- Home and school were the MEs that contribute the most to the children's daily exposure (80%) and to the inhaled dose (65%), highlighting the importance of indoor air quality.
- The contribution from the outdoor was higher in the case of the inhaled dose (24%), in comparison to exposure, due to the higher inhalation rates associated with the activities performed outdoors. This reinforces the importance of developing outdoor activities far away from places with high levels of pollutants.
- As the tools used in this work only provide an indication for possible PM sources, this study should be regarded as a first approach in describing the characteristics of aerosols and children's exposure, and it should be followed by a dedicated work focused on source identification.

CRediT authorship contribution statement

T. Faria: Conceptualization, Methodology, Investigation, Formal analysis, Writing. **V. Martins:** Methodology, Investigation, Validation, Writing - Review & Editing. **N. Canha:** Visualization, Writing - Review & Editing. **E. Diapouli:** Conceptualization, Investigation, Methodology, Writing - Review & Editing, Supervision. **M. Manousakas:** Investigation, Methodology, Writing - Review & Editing. **P. Fetfatzis:** Resources. **M.I. Gini:** Formal analysis. **S.M. Almeida:** Conceptualization, Methodology, Investigation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.151021.

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